

GROUP 6B METAL-CARBONYL COMPLEXES OF 2-MERCAPTOPYRIMIDINE AND 4-DIMETHYLAMINOPYRIDINE LIGANDS; SYNTHESIS, STRUCTURAL INVESTIGATIONS, AND DFT CALCULATIONS

by

SEDA TANYILDIZI

**THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE ABANT İZZET BAYSAL UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
DEPARTMENT OF CHEMISTRY**

DECEMBER 2012

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Yaşar DÜRÜST
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Çetin BOZKURT
Head of the Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. İzzet MORKAN
Supervisor

Examining Committee Members

1- Prof. Dr. İzzet MORKAN

2- Prof. Dr. Saim ÖZKAR

3- Prof. Dr. Çetin BOZKURT

ABSTRACT

**GROUP 6B METAL-CARBONYL COMPLEXES OF 2-
MERCAPTOPYRIMIDINE AND 4-DIMETHYLAMINOPYRIDINE
LIGANDS; SYNTHESIS, STRUCTURAL INVESTIGATIONS, AND DFT
CALCULATIONS**

Tanyıldızı, Seda
M.Sc., Department of Chemistry
Supervisor: Prof. Dr. İzzet Amour MORKAN
DECEMBER 2012, 127 pages

The number of studies concerning the interaction modes and reactivity of transition metal complexes containing pyridine, pyridinethiolate and pyrimidinethiolate ligands is growing rapidly such ligands are especially interesting because the pyridine group is a constituent of nucleic acids and they have ability to chelate and bridge transition metals.

The photolysis of hexacarbonyl metal(0) (M; Cr, Mo, W) complex in the presence of 2-mercaptopyrimidine ligand at 10 °C yields the corresponding pentacarbonyl-N-pyrimidinethiol metal(0) complex. These organometallic complexes were purified by recrystallization under high vacuum and stored at very low temperatures.

The structure of these complexes have been investigated using IR, ^1H -NMR, ^{13}C -NMR and UV spectroscopic methods. The appearance of three absorption bands in the carbonyl region of these complexes IR spectra is the best indication for the formation $\text{M}(\text{CO})_5$ part of the molecule with C_{4v} local symmetry. The spectroscopic results showed that the 2-mercaptopyrimidine ligand exhibit tautomeric equilibrium between thiol and thione as a consequence of the highly mobile protons that it possess and exhibits a predominant thione form in solid state. However, the IR data obtained from the polar dichloromethane solution implies that both free ligand and coordinated ligand exist in the thiol form. Moreover, 2-mercaptopyrimidine coordinated to the metal ion through its nitrogen atom lone pair of the aromatic ligand.

The thermal behaviour of pentacarbonyl(2-mercaptopyrimidine) metal(0) complexes were also investigated by using DTA/TGA methods. At each temperature corresponding to TG/DTA curve the complex titled has been subjected to X-ray powder diffraction(XRD) and infrared spectroscopic techniques. The results of the analysis showed that the complexes decomposed in four different temperatures.

Disubstituted carbonyl complexes of 4-dmap ligand was done also to produce the unfavored cis-tetracarbonyl(4-dmap)metal(0) (M; W) complexes as the major product from the reaction of metal-hexacarbonyls and excess ligand. The structure of the complex was investigated using IR and NMR spectroscopies.

In addition the theoretical calculations, including bond angles, bond distances and vibrational frequencies have also performed with the calculation of their NMR and UV spectral data using the Gaussian 03 DFT calculation method(Gaussian 03W single, CPU serial number; PC99997441W-5042N) at different basis sets. Finally these theoretical results have been compared with their experimental values. It has been shown that there is a good agreement between the theoretical and experimental results.

Keywords: Pentacarbonyl, Tetracarbonyl, 2-mercaptopyrimidine, 4-(dimethylamino)pyridine Thermal analysis, DFT calculations

ÖZET

2-MERKAPTOPİRİMİDİN VE 4-DİMETİLAMİNOPİRİDİN LİGANDLARININ GRUP 6B METAL-KARBONİL BİLEŞİKLERİNİN SENTEZİ, YAPISAL İNCELENMESİ VE DFT HESAPLAMALARI

TANYILDIZI, SEDA

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. İzzet Amour MORKAN

ARALIK 2012, 127 sayfa

Piridin, piridintiyolat ve pirimidintiyolat ligandlarını içeren geçiş metali komplekslerinin etkileşim ve reaktivitesini inceleyen çalışmalar hızla artmaktadır. Bu ligandların ilgi çekiciliği, içerdiği piridin halkasının nükleik asitlerin bileşeni ve bu ligandların geçiş metalleriyle köprü ve şelat oluşturabilmesinden ileri gelmektedir.

Hekzakarbonil metal(0) (M; Cr, Mo, W) komplekslerinin, 2-merkaptopirimidin varlığında 10 °C' deki fotolizi pentakarbonil(2-merkaptopirimidin) metal (0) komplekslerinin oluşumuna yol açmaktadır.

Bu organometalik kompleksler yüksek vakum altında, geri kristallendirme yöntemiyle saflaştırılır ve düşük sıcaklıklarda saklanırlar. Bu komplekslerin yapısal analizi IR, ^1H -NMR, ^{13}C -NMR ve UV spektroskopik yöntemleri kullanılarak incelenmiştir. IR spektroskopisi sonucunda, karbonil bölgesinde görülen üç soğurma bandı, molekülün C_{4v} yerel simetriye sahip olan $\text{M}(\text{CO})_5$ kısmının oluştuğunu göstermektedir. Spektroskopik analizler sonucunda 2-merkaptopirimidin ligandının yapısında bulunan ve son derece hareketli olan protondan dolayı tiyol-tiyon tautomerik dengede bulunduğu görülmüştür. Katı halde baskın olarak tiyon şeklinde bulunmaktadır. Fakat polar olan diklorometan çözücüsünde alınan IR spektrumundan elde edilen sonuçlar, hem ligandın hem de komplekslerin tiyol halde bulunduğunu ispatlamaktadır. Ayrıca, 2-merkaptopirimidin ligandı metale yapısında bulunan azot atomunun ortaklaşmamış elektron çifti üzerinden bağlanmaktadır.

Pentakarbonil(2-merkaptopirimidin) metal(0) komplekslerinin ısısal davranışları DTA/TGA methodu kullanılarak incelenmiştir. Kompleksler TG/DTA eğrisinde karşılık gelen her bir bozunma sıcaklığında XRD methodu ve IR spektroskopik yöntemiyle incelenmiştir. Bu analizler sonucunda komplekslerin dört farklı sıcaklıkta bozunduğu anlaşılmıştır.

Hekzakarbonil volfram bileşiğinin 4-dimetilaminopiridin ligandı varlığında gerçekleştirilen reaksiyon sonucu asıl ürün olarak cis-tetrakarbonilbis(4-dimetilaminopiridin) bileşiği elde edilmiştir. Bu organometalik bileşiğin yapısı IR ve NMR spektroskopisi kullanılarak incelenmiştir.

Gaussian 03 DFT hesaplama programında farklı temel setler kullanılarak, bağ açıları, bağ uzunlukları ve titreşim frekanslarını içeren teorik hesaplamalarla birlikte NMR ve UV analizi yapılmıştır. Sonuç olarak yapılan bu teorik hesaplamalarla deneysel değerler karşılaştırıldığında teorik hesaplamalarla deneysel bulguların birbiriyle uyum içinde olduğu görülmüştür.

Anahtar Kelimeler; pentakarbonil, tetrakarbonill, 2-merkaptopirimidin, 4-(dimetilamino)piridin, termal analiz, DFT hesaplama

to my family

ACKNOWLEDGMENTS

I am heartily thankful to my supervisor, Prof. Dr. İzzet MORKAN, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. I would like also thank to Prof. Dr. Ayşe UZTETİK MORKAN for her endless moral support and motivation. The technical assistance of Hasan Can YAZICI is gratefully acknowledged. I would like to thank İlker KÖPRÜ, who as a good friend, was always willing to help and give his best suggestions. I would also like to thank to other faculty members especially Asst. Prof. Dr. Erhan BUDAK and Dr. Sevim DEMİRÖZÜ ŞENOL, for their support whenever I need. I offer my regards and blessing to all of those who supported me any respect during completion of the thesis. Last but not the least, I would like to thank my family. The constant inspiration and guidance kept me focused and motivated. I can't express my gratitude for my mom in words, whose unconditional love has been my greatest strength.

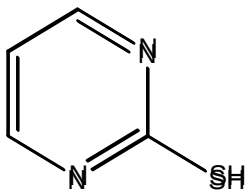
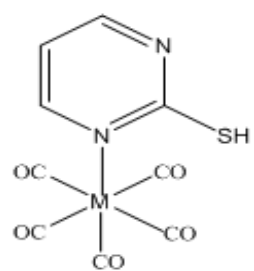
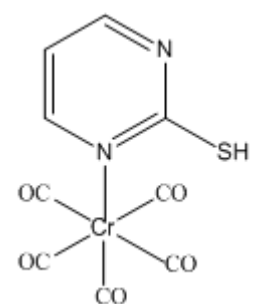
TABLE OF CONTENT

	Page
ABSTRACT	iii
ÖZET	vi
ACKNOWLEDGEMENT	x
TABLE OF CONTENT	xi
TABLE OF ABBREVIATIONS	xiv
LIST OF FIGURES	xvii
LIST OF TABLES	xxi
CHAPTER	
1. INTRODUCTION	1
2. THEORETICAL BACKGROUND	10
2.1. Metal-Carbonyl Bonding	10
2.2. Metal-Olefin Bonding	18
2.3. Metal-Pyrimidine and –Pyridine Bonding	22
3. EXPERIMENTAL STUDIES	28
3.1. Basic Techniques	28
3.1.1. FT-IR (Fourier Transform Infrared)- Spectra	32
3.1.2. UV/VIS Spectra	32
3.1.3. ^1H -NMR Spectra	32
3.1.4. ^{13}C -NMR Spectra	32
3.1.5. TGA/DTA	32

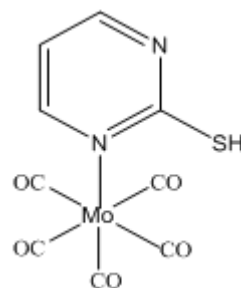
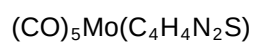
3.2.	The Synthesis of Complexes	33
3.2.1.	Pentacarbonyl(2-mercaptopyrimidine)metal(0), (M(CO) ₅ (2-mpm); M: Cr, Mo, W)	33
3.2.2.	Cis-tetracarbonylbis(4-dimethylaminopyridine) metal(0), (M(CO) ₄ (4-dmap); M: Cr, Mo, W)	34
4.	RESULTS AND DISCUSSION	35
4.1.	Infrared Spectra	35
4.1.1.	Infrared Spectra of 2-mercaptopyrimidine	35
4.1.1.1.	C-H vibrations	38
4.1.1.2.	C-C vibrations	39
4.1.1.3.	C-N, C=N vibrations	40
4.1.1.4.	S-H and C-S vibrations	40
4.1.2.	IR Spectra of M(CO) ₅ L Complexes	41
4.1.2.1.	C-N and C=N Bond Stretching Frequencies	48
4.1.2.2.	S-H, N-H, C-S, C=S Stretching Frequencies	50
4.2.	Thermal Analysis	55
4.3.	SEM Micrograph of the Complexes	63
4.4.	Computational Details	65
4.4.1.	Vibrational Frequencies	68
4.4.2.	Atomic Charges	70
4.4.3.	Molecular Geometry	72
4.4.4.	Thermodynamic Properties	76
4.4.5.	UV-Vis Spectra Analysis	77
4.4.6.	HOMO-LUMO Analysis	81

4.4.7. Magnetic Properties	84
4.5. Cis-tetracarbonylbis(dimethylamino)pyridine tungsten(0) complex	92
4.5.1. IR-spectroscopy	92
4.5.2. NMR Spectroscopy	96
4.5.3. Computational Calculations (DFT)	103
5. CONCLUSION	113

TABLE OF ABBREVIATIONS

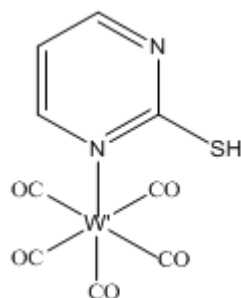
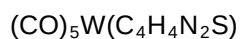
NOMENCLATURE	CHEMICAL FORMULA	STRUCTURE	ABBREVIATION
2-pyrimidinethiol or 2-mercaptopyrimidine	$C_4H_4N_2S$		2-mpm
Pentacarbonyl (2-mercapto- pyrimidine) metal(0)	$(CO)_5M(C_4H_4N_2S)$		$M(CO)_5$ 2-pythiol
Pentacarbonyl (2-mercapto- pyrimidine) Cr(0)	$(CO)_5Cr(C_4H_4N_2S)$		$Cr(CO)_5$ 2-pythiol

Pentacarbonyl (2-mercapto-
pyrimidine) Mo(0)



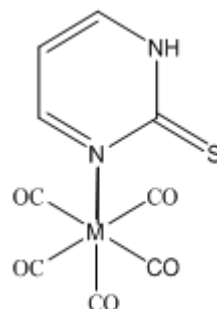
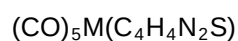
$\text{Mo}(\text{CO})_5$
2-pythiol

Pentacarbonyl (2-mercapto-
pyrimidine) W(0)



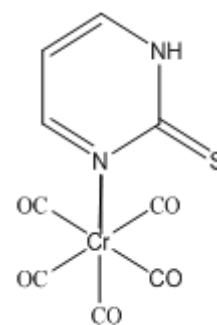
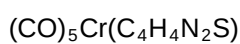
$\text{W}(\text{CO})_5$
2-pythiol

Pentacarbonyl (2-pyrimidine-
thione) metal(0)



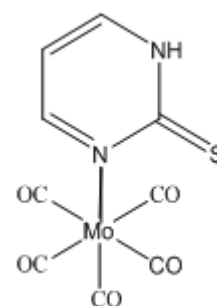
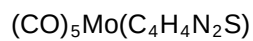
$\text{M}(\text{CO})_5$
(2-pythione)

Pentacarbonyl (2-pyrimidine-
thione) Cr(0)



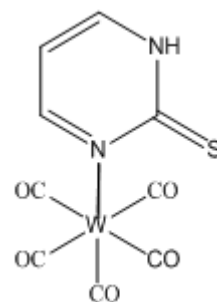
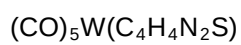
$\text{Cr}(\text{CO})_5$
(2-pythione)

Pentacarbonyl (2-pyrimidine-
thione) Mo(0)



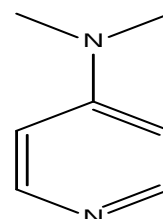
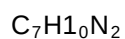
$\text{Mo}(\text{CO})_5$
(2-pythione)

Pentacarbonyl (2-pyrimidine-
thione) W(0)



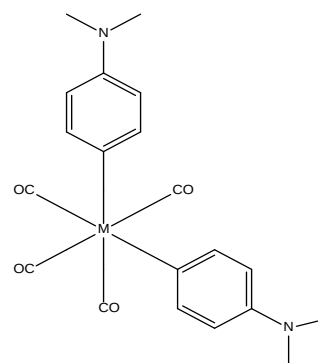
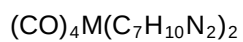
$\text{W}(\text{CO})_5$
(2-pythione)

N,N dimethylpyridine-4-amine
4-(dimethylamino)pyridine



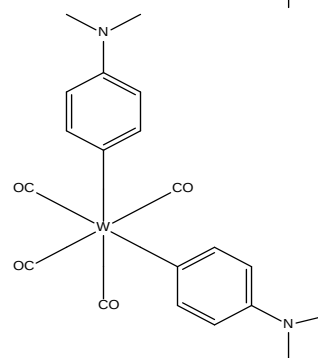
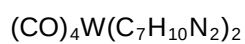
4-dmap

Cis-tetracarbonylbis
(4-dimethylaminopyridine)metal(0)



$\text{M}(\text{CO})_4$
(4-dmap)₂

Cis-tetracarbonylbis
(4-dimethylaminopyridine)tungsten(0)



$\text{W}(\text{CO})_4$
(4-dmap)₂

LIST OF FIGURE	Page
Figure 2.1.1. The molecular orbital diagram of carbon monoxide	11
Figure.2.1.2. Synergic bonding of CO to a transition metal; implications for nucleophilic (Nu-) attack	12
Figure 2.1.3. Electronic structure of the carbonyl ligand ;the three highest occupied and the two lowest unoccupied orbitals	13
Figure.2.1.4.a. Donation of CO lone pair to empty orbital on M	14
Figure.2.1.4.b. Donation of electrons from filled M d-orbital to empty π^* -antibonding orbital on CO	14
Figure.2.1.5. The synergistic effect of metal-carbonyl bonding	15
Figure 2.2.1. The metal olefin bonding	19
Figure 2.2.2.a. Dewar-Chatt-Duncanson model of metal-olefin bonding, σ -interaction	21
Figure 2.2.2.b. Dewar-Chatt-Duncanson model of metal-olefin bonding, π -interaction	21
Figure 2.2.3. The synergistic effect of metal-olefin bonding	22
Figure 2.3.1 The coordination modes of the ligand with metal	24
Figure. 3.1.1 A typical Schlenk line	28
Figure.3.1.2 (a) Standard Schlenk tube and (b) transferring liquid in nitrogen atmosphere	29
Figure.3.1.3. Apparatus used for photochemical reactions	31
Figure 4.1.1.1. The IR spectrum of 2-mercaptopyrimidine dispersed in KBr pellet	36

Figure 4.1.1.2.	The IR spectrum of 2-mercaptopyrimidine in CH_2Cl_2 solution	36
Figure 4.1.1.3	The ^1H -NMR spectrum of 2-mercaptopyrimidine recording from DMSO solution rel. TMS	37
Figure 4.1.1.1.1.	The structure of 2-mercaptopyrimidine	38
Figure 4.1.2.1.	The IR spectrum of $\text{Cr}(\text{CO})_5$ 2-mpm in dichloromethane solution	42
Figure 4.1.2.2.	The IR spectrum of $\text{Mo}(\text{CO})_5$ 2-mpm in dichloromethane solution	42
Figure 4.1.2.3.	The IR spectrum of $\text{W}(\text{CO})_5$ 2-mpm in dichloromethane solution	43
Figure 4.1.2.4	The IR spectrum of $[\text{Cr}(\text{CO})_5$ 2-mpm] dispersed in KBr pellet	45
Figure 4.1.2.5	The IR spectrum of a) 2-mercaptopyrimidine and b) $[\text{Cr}(\text{CO})_5$ 2-mpm] dispersed in KBr pellet	47
Figure 4.1.2.2.1	The full scaled spectrum of $[\text{W}(\text{CO})_5$ 2-mpm] in dichloromethane	50
Figure 4.1.2.2.2	The IR spectrum of a) $[\text{W}(\text{CO})_5$ 2-mpm] dispersed in KBr pellet b) in CH_2Cl_2 solution	52
Figure 4.1.2.2.3	The IR spectrum of $[\text{Mo}(\text{CO})_5$ 2-mpm] a) dispersed in KBr pellet b) in CH_2Cl_2 solution	53
Figure 4.1.2.2.4	The IR spectrum of $[\text{Cr}(\text{CO})_5$ 2-mpm] a) dispersed in KBr pellet b) in CH_2Cl_2 solution	54
Figure 4.2.1.	The TGA/DTA curve of pentacarbonyl(2-mercaptopyrimidine) chromium(0) complex	55
Figure 4.2.2.	The IR spectra of pentacarbonyl(2-mercaptopyrimidine) chromium(0) complex at 25, 135 and 205 ° C	56
Figure 4.2.3.	The IR spectra of pentacarbonyl(2-mercaptopyrimidine) chromium(0) complex at 25, 473 and 631 ° C	57
Figure 4.2.4.	The XRD pattern of the $[\text{Cr}(\text{CO})_5$ 2-mpm] at 25 °C	58
Figure 4.2.5.	The IR spectrum of $[\text{Cr}(\text{CO})_5$ 2-mpm] at 25 °C	58

Figure 4.2.6.	The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 25 °C-135 °C	59
Figure 4.2.7.	The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 25 °C-135 °C	59
Figure 4.2.8.	The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 135°C-205°C	60
Figure 4.2.9.	The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 135°C-205°C	60
Figure 4.2.10.	The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 205°C-473°C	61
Figure 4.2.11.	The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 205°C-473°C	61
Figure 4.2.12.	The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 473°C-631 °C	62
Figure 4.2.13.	The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 473°C-631 °C	62
Figure 4.3.1.	The SEM micrograph of the complexes; (a) $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$, (b) $[\text{Mo}(\text{CO})_5 \text{ 2-mpm}]$, (c) $[\text{W}(\text{CO})_5 \text{ 2-mpm}]$	65
Figure 4.4.3.1.	The molecular structure of pentacarbonyl(2-pyrimidinethiol) metal(0) complex (M; Cr, Mo, W)	74
Figure 4.4.3.2.	The molecular structure of pentacarbonyl(2-pyrimidinethione) metal(0) complex (M; Cr, Mo, W)	75
Figure 4.4.5.1.	UV-Vis spectrum of $\text{Cr}(\text{CO})_5 \text{ 2-mercaptopyrimidine}$ complex in CH_2Cl_2	79
Figure 4.4.6.1.	3D plots of HOMO and LUMO of the $\text{W}(\text{CO})_5 \text{ 2-mercaptopyrimidine}$ complex	83
Figure 4.5.1.1	The IR spectrum of $\text{cis}-(\text{CO})_4\text{W}(\text{4-dmap})_2$ from dichloromethane solution	92

Figure 4.5.1.2	The structure of 4-dimethylaminopyridine	94
Figure 4.5.1.3	The molecular structure of $[\text{W}(\text{CO})_4(4\text{-dmap})_2](1)$	95
Figure 4.5.1.4	The molecular structure of $[\text{W}(\text{CO})_4(4\text{-dmap})_2](2)$	96
Figure 4.5.2.1	The ^1H -NMR spectrum of 4-dmap recording from d- chloroform solution rel. TMS	98
Figure 4.5.2.2	The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of 4-dmap recording from d-chloroform solution rel. TMS	99
Figure 4.5.2.3	The ^1H -NMR spectrum of cis- $[\text{W}(\text{CO})_4(4\text{-dmap})_2]$ recording from d-chloroform solution rel. TMS	100
Figure 4.5.2.4	The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of cis- $[\text{W}(\text{CO})_4(4\text{-dmap})_2]$ recording from d-chloroform solution rel. to TMS	102

LIST OF TABLES		Page
Table 2.1.1.	IR data (cm ⁻¹) ^a for [M(CO)x] ⁿ	17
Table 3.1.1.	Representative Data for the Physical and Structural Properties of M(CO) ₆	30
Table 4.1.1.1.1	Vibrational frequencies and their probable assignments for 2-mercaptopyrimidine	39
Table 4.1.2.1.	The CO-stretching frequencies of [M(CO) ₅ 2-mpm]	43
Table 4.1.2.2.	IR data of 2-mercaptopyrimidine and its complexes with assignments.	46
Table 4.1.2.1.1.	The IR data of free ligand and metal coordinated ligand in dichloromethane solution	49
Table 4.2.1.	Thermal decomposition of Cr(CO) ₅ 2-mercaptopyrimidine complex	63
Table 4.4.1.1.	Selected experimental and calculated vibrational modes of pentacarbonyl(2-mercaptopyrimidine) W(0) complex	70
Table 4.4.2.1.	Atomic charges for optimized geometry of pentacarbonyl(2-mercaptopyrimidine chromium(0) and pentacarbonyl(2-mercaptopyrimidine) tungsten(0) complexes	71
Table 4.4.3.1.	The optimized bond length of pentacarbonyl(2-mercaptopyrimidine) chromium(0) at different basis sets	72
Table 4.4.3.2.	The optimized bond angle of pentacarbonyl(2-mercaptopyrimidine) chromium(0) at different basis sets	73
Table 4.4.4.1.	Thermodynamic data of some prepared complexes	77

Table 4.4.5.1.	Theoretical electronic absorption spectra values of pentacarbonyl(2-pyrimidinethione) W(0) and pentacarbonyl(2-pyrimidinethiol) W(0) complexes	80
Table 4.4.6.1.	Selected energy values of pentacarbonyl(2-mercaptopyrimidine) W(0) complex in its ground state with different basis sets	81
Table 4.4.1.	Special values of tautomeric thiol structure in CH ₂ Cl ₂ solution	86
Table 4.4.2.	Special values of tautomeric thione structure in CH ₂ Cl ₂ solution	86
Table 4.4.3.	Special values of tautomeric thiol structure in vacuum	87
Table 4.4.4.	Special values of tautomeric thione structure in vacuum	87
Table 4.4.5.	Bond Length (Å) of thiol and thione complexes calculated in CH ₂ Cl ₂ solution	88
Table 4.4.6.	Bond Angle of thiol and thione complexes calculated in CH ₂ Cl ₂ solution	89
Table 4.4.7.	Atomic charges for optimized geometry of thiol and thione tautomers	90
Table 4.4.8.	Molecular orbital analysis of thiol and thione forms in CH ₂ Cl ₂ solution	91
Table 4.5.3.1	Selected calculated bond length and bond angle of the free ligand (4-dmap) and complex	104
Table 4.5.3.2	Theoretical ¹ H and ¹³ C NMR chemical shifts (with respect to TMS) of (4-dimethylaminopyridine) and cis-tetracarbonylbis(dimethylaminopyridine) tungsten(0)	105
Table 4.5.3.3	Calculated thermodynamic properties of 4-dimethylaminopyridine and the complex cis-tetracarbonylbis(dimethylaminopyridine) tungsten(0) using the MPW1PW91/SDD/6-311G ¹ method	106
Table 4.5.3.4	NBO Analysis of the free ligand and complex	107

Table 4.5.3.5	MLCT and LCT States of the free ligand and complex	108
Table 4.5.3.6	Calculated vibrational frequencies of 4-(dimethylamino)pyridine	109
Table 4.5.3.7	Calculated vibrational frequencies of $[\text{W}(\text{CO})_4(4\text{-dmap})_2]$	110

CHAPTER 1

INTRODUCTION

Coordination chemistry is a branch of inorganic chemistry that deals with the study of coordination compounds. The modern scientific studies on coordination compounds began with two scientists, Alfred Werner and Sophous Jorgensen [1], both are astute chemists who made great contribution of the elucidation of the structure of the complexes with coordination numbers higher than four.

Organotransition metal chemistry is distinct area in chemistry. The development of transition metal chemistry dates back to 1827 when Zeise reported the first organometallic compound, $K[PtCl_3C_2H_4]$ [2].

Organometallic chemistry is defined as the chemistry of metal carbon bonds. More generally it is a part of coordination chemistry and inorganic chemistry and concerns the transformation of organic compounds using metals from the main groups; transition series, lanthanides and actinides [3].

Organometallic compounds; with their metal-carbon bonds; lie at the interface between classical organic and inorganic chemistry is dealing with the interaction between inorganic metal species and organic molecules [4].

The first organometallic compound, 'cacadyl' tetramethyldiarsine, $[\text{As}_2(\text{CH}_3)_4]$ was synthesized by a French chemist L. C. Cadet in 1760 [5].

The structure of d and f block organometallics are difficult or impossible to deduce by chemical means alone, fundamental advances had to await the development of X-ray diffraction for precise structural data on solid samples and of IR and NMR spectroscopy for structural information about organometallic complexes in solution. Significant interest in this area did not develop until the synthesis of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, has been reported in 1951 [6].

In 1951, in an attempt to synthesize Fulvalene from cyclopentadienyl bromide, Kealy and Pauson reacted the Grignard reagent cyclo- $\text{C}_5\text{H}_5 \text{ MgBr}$ with FeCl_3 , using anhydrous diethyl ether as solvent [7]. This reaction did not yield the desired fulvalene but rather an orange solid, ferrocene. The product was surprisingly stable; it could be sublimed in air without decomposition and was resistant to catalytic hydrogenation and Diels-Alder reactions [8].

The discovery of the prototype sandwich compound ferrocene rapidly led to the discovery of other sandwich compounds, other compounds containing metal atoms bonded to cyclic organic ligands, and a vast array of additional compounds containing other organic ligands [8]. It is often stated, with justification, that the discovery of ferrocene began the era of 'modern' organometallic chemistry, an area that has grown with increasing rapidity in the succeeding decades.

One of the most important and common organometallic compounds type is metal-carbonyl complexes in which carbonyl group acts a two electron donor ligand. The first compound containing carbonmonoxide as a ligand was reported in 1890 by Mond et al as tetracarbonylnickel(0) $[\text{Ni}(\text{CO})_4]$ [9]. Followed the synthesis of $\text{Ni}(\text{CO})_4$, in 1891, the discovery of pentacarbonyliron, $\text{Fe}(\text{CO})_5$, was reported independently by Mond [10] and Berthelot [11].

During the next twenty years, the commonyl known complexes of group VIB metals are synthesized and isolated as a volatile, white, air stable and diamagnetic crystalline compounds with six coordinated octahedral complexes of the type $\text{M}(\text{CO})_6$, M: Cr, Mo, W. Hexacarbonyl Molybdenum (0) has been synthesized by Mond in 1910 [12, 13]. Followed by the synthesis of Hexacarbonylchromium(0) and tungsten(0) which are isolated by John and co-workers [14, 15]. Carbonyl ligand form strong bonds with metals in coordination complexes although it is not a very stong base. The oxidation state of metal in these kind of complexes is usually zero and sometimes appeared as low positive and negative oxidation states. These carbonyl compounds generally obey the 18-electron rule.

The development of organometallic compounds speed up with the application of photochemistry. Study of their photochemical properties and reactions has led to the photochemical syntheses of these materials. The first recorded substance was the result of conversion of $\text{Fe}(\text{CO})_5$ into a new substance with sunlight in 1905 by Dewan and Jones [16].

The correct formula of which was later reported by Speyer and Wolf to be $\text{Fe}_2(\text{CO})_9$ [17]. The syntheses of $\text{Fe}_2(\text{CO})_9$ is described in organometallic synthesis to be the most influential syntheses reference in this area [18]. Photochemical studies began with a series of researches at Strohmeier laboratory in Würzburg at which the application of photochemistry to the substitution of carbonyl ligands in the group VI carbonyls [19] and $\text{CpMn}(\text{CO})_3$ [20] was reported.

The vibrational spectra of metal carbonyls is very informative and a good approximation for specific group frequencies. The CO stretching bonds observed in infrared spectra are sharp, sensitive to environment, and commonly intense [21]. Metal carbonyl complexes with one or more CO bonded to a single metal atom show one or more intense infrared bonds between 2200 and 1800cm^{-1} [22]. Because of polarization of carbonyl on binding metal, the dipole moment during vibration is large therefore intensity is large [23].

Photochemical synthesis has been a route for synthesizing or 'molecular engineering' new and unusual organometallic complexes and a large number of new compounds with novel structures and properties have been obtained [24, 25]. The uniqueness of photochemical synthesis is that it allows the synthesis of organometallic complexes which can not be easily made or can not be made at all by conventional thermochemical synthesis methods.

Photosubstitution is the most commonly used synthesis method for making organometallic complexes [26, 27, 28]. Photochemical substitution of

ligands, most commonly carbonyl groups, has been used as a versatile synthetic method for new coordination compounds [29]. Particularly, numerous numbers of the $M(CO)_5L$ type complexes have been prepared by using the photochemical CO substitution of Group VI metal-carbonyls [30].

The initial photochemical step in photosubstitution is to photochemically detach a ligand of the organometallic compound to create a vacant coordination site on the metal ion center. In this way, the Group 6 metal-carbonyl complexes of substituted pyrimidines have also been isolated a long time ago [31, 32].

A characteristic feature of the d group transition metals is their ability to form complexes with a variety of neutral molecules such as carbonmonoxide, isocyanides, substituted phosphines, various molecules with delocalized π orbitals, such as pyridine, pyrimidine [33].

Pyrimidines are one of the main constituents of nucleic acids and play an important role in many biological systems. Substituted pyrimidines are also biologically important; pyrimidine thiones were found to inhibit the synthesis of t-RNA under certain conditions [34].

Owing to their many fields of application, mercaptopyrimidines have been widely studied over the past years [35]. Thiols, thiones, sulfenyl anions (thiolates, RS^-), sulfenyl radicals (thiyl, RS^0), and disulfides also play important roles in diverse fields such as atmospheric chemistry, biological chemistry, environmental chemistry, industrial chemistry, organic synthesis, and medicine [36]. Ligands of the thiopyrimidines types and their complexes are

currently being investigated as antiviral, antimetabolite and antitumor drugs as well as for their interesting photochemical properties[37]. Pyrimidinethiols (-N=C-SH), pyrimidinethiones (-NH-C=S) and derivatives have been used extensively in surface chemistry and in coordination chemistry because of the binding capabilities of nitrogen and sulfur to metals [38-43].

The chemistry of pyriminethiols (mercaptopyrimidines) that incorporate both S and N atoms in their structure is rich because these compounds can coordinate as monodentate ligands [44] and more frequently as polydentate ligands either to a single metal center, acting as a chelating ligand [45, 46], or to several metal centers as a bridging ligand [44].

The number of studies concerning the interaction modes and reactivity of transition metal complexes containing pyridinethiolate and pyrimidinethiolate ligand is growing rapidly as such ligands are especially interesting because (i) they contain functional groups common in crude oils (thiolate-S and aromatic-N), (ii) the pyrimidine group is a constituent of nucleic acids, and (iii) they have ability to chelate and bridge transition metals, allowing access to both mononuclear and oligonuclear products [46, 47].

Pentacarbonylpyrimidinemetal(0) complexes of the Group VI elements have been known since 1972 [48]. Since pyrimidine is known mainly a σ -donor with a little π acceptor ability ligand, the M-N bond in these low valent metals is not very strong. These heterocyclic ligands exhibit tautomeric equilibrium between the thiol (>C-SH) and thione (>C=S) as a consequence of highly mobile protons that they possess [49-52]. The predominant form

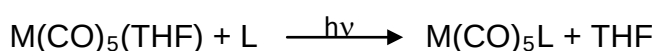
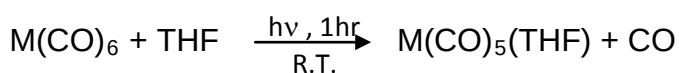
largely depends on the state and conditions of the molecule. As a result, $M(CO)_5(2\text{-pyrimidinethiol})$ complexes are quite labile toward ligand substitution reactions [53].

Pyridine derivatives are an essential class of azoheterocycles found in many natural products, active pharmaceuticals, and functional materials [54].

The coordination chemistry of the pyridine bases has been a subject of interest for many years and has been studied from a variety of perspectives by many different research groups [55,56]. Pyridine is known to act mainly as a σ -donor ligand with little π -accepting ability [57], therefore the M-N bond in such low valent metal complexes is not very strong. In accordance, $M(CO)_5(\text{pyridine})$ complexes are quite labile toward ligand substitution reactions [56]. As electron releasing groups, alkyl substituents are expected to increase the basicity of pyridine. The $M(CO)_5L$ complexes with L ; 4-substituted pyridine such as 4-methylpyridine, 4-phenylpyridine, 4-cyanopyridine, 4-acetylpyridine, and 4-formlypyridine are known [58-60]. Some of them have been identified only by solution IR spectroscopy. Pyridine derivatives having ligated atoms in 2-positions such as 2-phenylpyridine, 2-cyanopyridine as a ligand (L) in the complexes of $M(CO)_5L$ [58,61] indicating that non-bulky groups in the position 2 does not hinder the coordination of pyridine to the transition metal. Therefore, pyridine derivatives with ligated atoms or groups in 2- or 6- positions are expected to show more than one binding possibilities. For example 2,6-diaminopyridine (dap) can bind the transition metal atom through the sp^3 -hybridized nitrogen atom of the ammine

group and/or through the sp²-hybridized nitrogen atom of the aromatic pyridine ring.

In this study we aim to realize the synthesis of 2-pyrimidinethiol complexes of group 6B metals in which the pyrimidinethiol ligand coordinates to the central atom through its N-donor site. The above mentioned complexes can be made by the UV-irradiation of pentacarbonyltetrahydrofuranemetal(0) complexes with the 2-mercaptopyrimidine ligand at room temperature according to the following reactions;

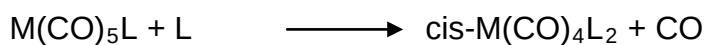
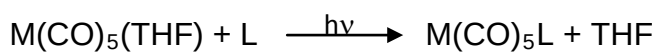
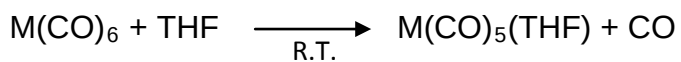


In the above reactions, L: 2-pyrimidinethiol, 2-mercaptopyrimidine (2-mpm) ;
M: Cr, Mo, W.

The resulting complexes have been purified by recrystallization. The structural identification of these complexes was done using IR-, ¹H- and ¹³C-NMR spectroscopies. The thermal analysis of these complexes using TGA/DTA methods followed by the XRD analysis at the designed temperature. Finally, DFT calculations of these complexes were made by using Gaussian Software.

The second part of this study aimed to for the synthesis of the tetracarbonyl complexes of this ligand. But unfortunately we have not succeed to isolate these complexes. Instead we have synthesized the corresponding sterically unfavored cis-tetracarbonyl complexes of 4-dimethylaminopyridine

(4-dmap). These complexes have been synthesized according to the following reactions,



Structural investigations of these complexes have been done using IR and NMR and spectroscopies.

CHAPTER 2

THEORITICAL BACKGROUND

2.1. Metal-Carbonyl Bonding

The diverse chemistry of the transition metal centres on the involvement of partially filled d-orbitals in the bonding to ligands. The majority of the metal phenomena can be accommodated by a molecular orbital or Ligand Field treatment. For the classical ligands, the large electronegativity difference between the donor atom and the metal would be expected to favour largely ionic character. For the bonding of carbon to transition metals the electronegativity difference is modest or negligible. Hence the concept of covalency and electroneutrality become all-important, whilst the concept of oxidation state rapidly loses its usefulness.

Carbon monoxide is the most common π -ligand in organometallic chemistry [6]. The simple classical two-electron dative interaction from the lone pair on carbon, although important, is seldom sufficiently strong to bind CO firmly to a transition metal (Figure 2.1.1.).

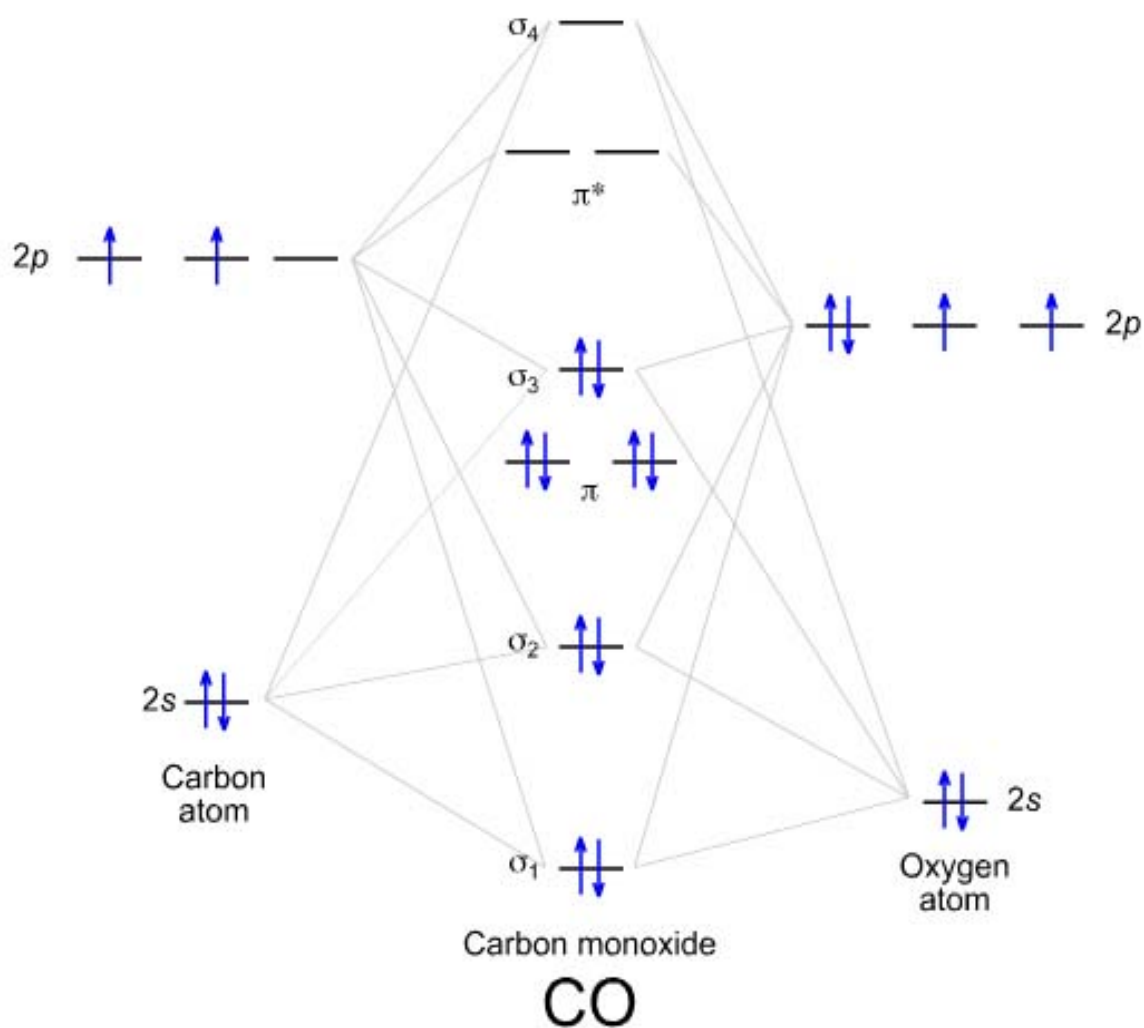


Figure 2.1.1. The molecular orbital diagram of Carbon monoxide.

Bonding of metal and carbonyl ligand can be described with molecular orbital terms. Molecular orbital calculations allow to derive a molecular orbital diagram resulting from the interaction of metal orbitals with the ligands orbitals of corresponding symmetry. The molecular orbital diagram of the complex contains bonding and antibonding molecular orbitals resulting from these interactions and non-bonding metal orbitals that do not interact with ligand orbitals.

In carbon monoxide the highest occupied molecular orbital (3σ) is primarily based on carbon, and the degenerate set of antibonding π^* orbitals (2π) Lowest unoccupied molecular orbital also have their greatest contribution from carbon p-orbitals. The most important component of the bonding involves the combination of occupied metal t_{2g} orbitals with the empty π^* antibonding (2π) orbitals of CO.

The interaction of the 3σ and 2π orbitals of CO with those of a transition metal is illustrated in Figure 2.1.2.

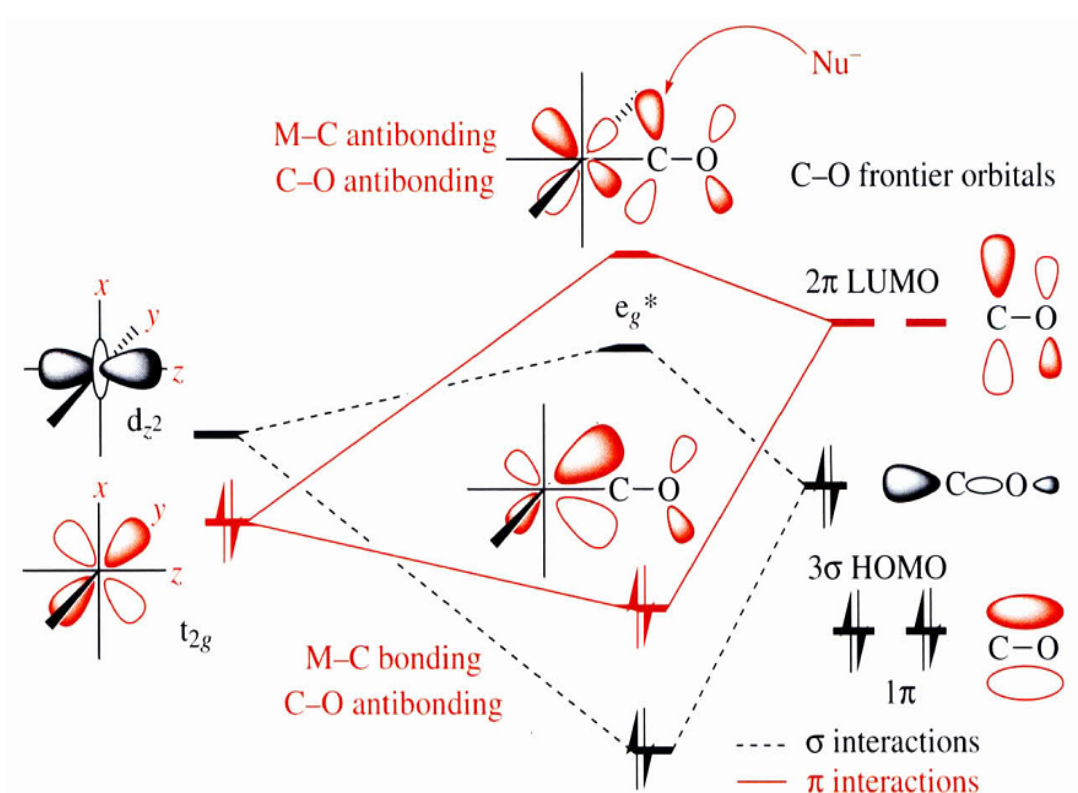


Figure.2.1.2. Synergic bonding of CO to a transition metal; implications for nucleophilic (Nu^-) attack.

In this figure, the formation of σ -bond by overlap of the metal d-orbitals with the filled carbon orbitals of σ -symmetry is shown. The flow of electrons from carbon monoxide to the metal would lead to an enhanced electron

accumulation on the metal, which attempts to reduce the charge by pushing electrons back to the ligand. The metal d-orbitals have the suitable symmetry to overlap with the antibonding π^* orbitals of the carbonyl ligand.

Salient features may be summarized as follows;

- (i) The conventional two- electron dative metal-ligand σ -bond ($3\sigma + sp^3d^2$ hybrid, or dz^2).
- (ii) Two orthogonal bonds of π - symmetry (e.g. $dxz + 2\pi_x$, $d_{yz} + 2\pi_y$; only one is shown).

The electrons in these bonds originated from pure metals t_{2g} orbitals but now reside in molecular orbitals with considerable ligand character. The σ -bond between the carbonyl ligand and the metal centre is formed by the σ_C orbital that characterizes the lone pair on the carbon atom (Figure 2.1.3.) and by a d orbital on the metal.

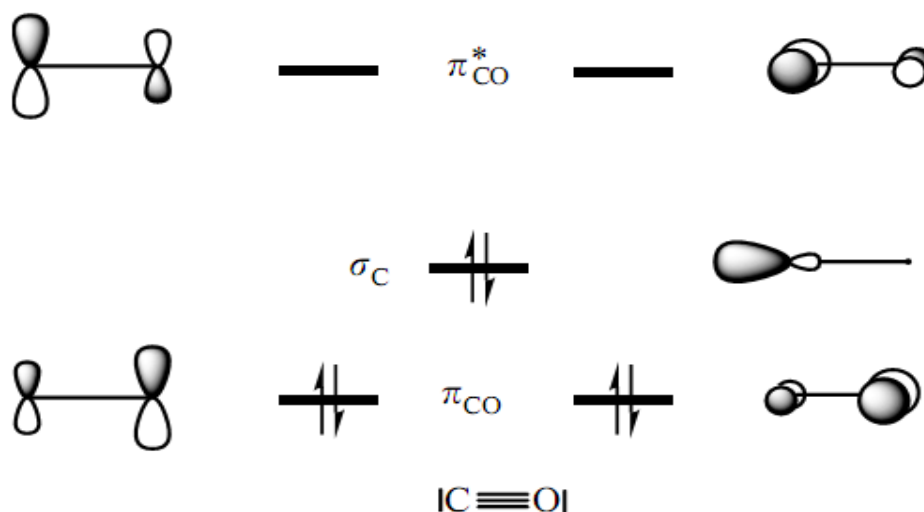
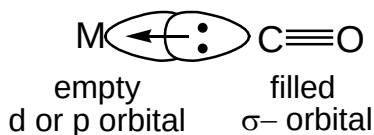


Figure 2.1.3. Electronic structure of the carbonyl ligand ;the three highest occupied and the two lowest unoccupied orbitals.

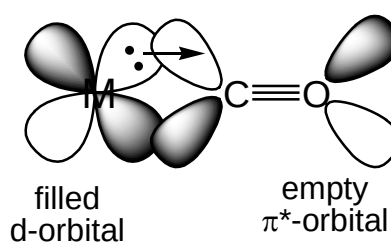
This interaction, which leads to a transfer of electrons from the ligand to metal, is called donation interaction (Figure 2.1.4.a). The π interactions produce a transfer of electrons in the opposite direction, from the metal to ligand. These are back-donation interactions (Figure 2.1.4.b). The carbonyl ligand is therefore simultaneously a σ -donor and a π -acceptor [61].

Ligand to metal σ -bond:



(a)

Metal to ligands π -backbond:



(b)

Figure.2.1.4.a. Donation of CO lone pair to empty orbital on M.

Figure.2.1.4.b. Donation of electrons from filled M d-orbital to empty π^* -antibonding orbital on CO.

This phenomenon has a number of names including π -acceptance, retrodonation or back-bonding, and is in essence similar to the C-N multiple bonding found in organic amides, in which the lone pair of an sp^2 hybridized nitrogen mixes with the empty π^* orbital of the CO bond.

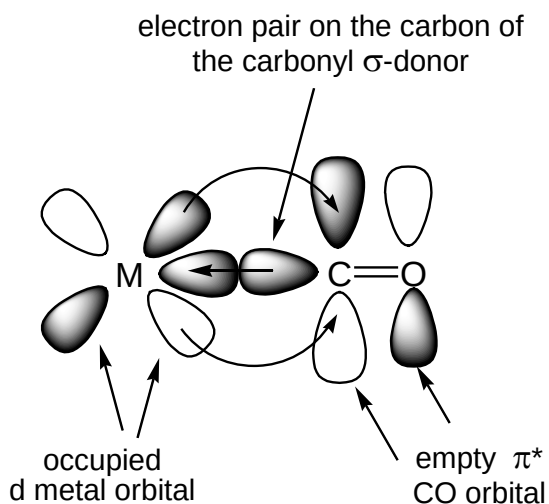
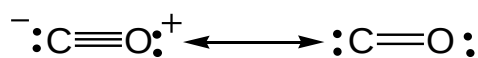


Figure.2.1.5. The synergistic effect of metal-carbonyl bonding.

The π interactions reinforce the metal-carbon bond but weaken the CO bond. This electronic reorganization can be represented by the resonance structures.



As a result, the carbonyl ligand usually binds to a transition metal in the η^1 mode, with a linear M-CO arrangement that maximizes the σ overlap. The π interactions, that involve both the π CO bonding MO and the π^* CO antibonding MO, are added to this σ interaction. This example illustrates a problem posed by all the ligands with a double or triple bond that are coordinated to the metal in the η^1 mode; using their occupied π orbital(s), they can act as a π donor, whereas their empty π^* orbital can allow them to act as a π acceptor. Depending on the relative strength of these two interactions, the ligand can act overall either as a π donor or as a π acceptor.

For carbonyl complexes, a combination of IR and ^{13}C -NMR spectroscopy will often reveal the molecular symmetry and also provide further information about the nature of the metal centre to which the CO ligand is bonded.

Infrared spectroscopy (IR) provides a far better probe, from the value of the IR absorption frequency associated with the stretching of the CO bond $\nu(\text{CO})$. This frequency is related to the strength of the bond and is very sensitive to the electronic population on the π^* CO orbitals.

Effective backdonation is most readily apparent as a decrease in the stretching frequency ($\nu(\text{CO})$) of the CO ligand observed using vibrational spectroscopy. Free CO absorbs at 2143 cm^{-1} , but in transition metal complexes the $\nu(\text{CO})$ frequency is typically in the range $1840\text{--}2120\text{ cm}^{-1}$ [62].

Table 2.1.1. IR data (cm^{-1})^a for $[\text{M}(\text{CO})_x]^n$

$\text{Oh}^- [\text{M}(\text{CO})_6]^n$			$\text{Td}^- [\text{M}(\text{CO})_4]^n$		
M	n	$\nu(\text{CO})$	M	n	$\nu(\text{CO})$
V	-1	1859	Cr	-4	1460
V	0	1973	Mn	-3	1670
Cr	0	2000	Os	-2	1787
Mo	0	2004			
W	0	1998			
Mn	+1	2096			
Fe	+2	2203			

^aFor $(\text{CO})_g$, $\nu(\text{CO}) = 2143 \text{ cm}^{-1}$; for $[\text{CO}]_g^+$, $\nu(\text{CO}) = 2214 \text{ cm}^{-1}$

Table 2.1.1. illustrates the affect of the π -basicity of the metal centre on $\nu(\text{CO})$ for various metal carbonyls. Increasing the negative charge on the metal centre raises the energy of the metal t_{2g} orbitals, making the transfer of electron density to the 2π orbitals of CO more effective and resulting in a decrease in the CO bond strength accompanied by an increase in the strength of metal-carbon bond .

Conversely, metal centres with low π -basicity (low energy t_{2g} orbitals, positive charge, other strong and therefore competitive π -acidic co-ligands)

will have labile CO ligands. The value of $\nu(\text{CO})$ may therefore be used as an indicator of the lability of CO coordination towards nucleophilic attack; the higher the $\nu(\text{CO})$ frequency, the more labile the carbonyl ligand.

Photosubstitution is the most commonly used synthesis method for making organometallic complexes [26, 27, 28]. Photochemical substitution of ligands, most commonly carbonyl groups, has been used as a versatile synthetic method for new coordination compounds [29]. It is often more selective, but less conveniently applicable to large-scale syntheses. For example, photolysis of the $(t_{2g})^6 (e_g^*)^0$ complex $\text{Cr}(\text{CO})_6$ will promote electrons into the previously empty e_g^* orbitals, which are antibonding with respect to the Cr-CO bonds. Thus the photoexcited molecule can relax by ejection of one CO ligand. Typically this is carried out in a weakly coordinating solvent, e.g., tetrahydrofuran (continuously purged with nitrogen to remove liberated CO) to provide a labile deep red solvato complex $\text{Cr}(\text{CO})_5(\text{THF})$.

Once photolysis is complete (typically monitored by solution IR spectroscopy and color change of the solution), this may then be used in situ for subsequent facile substitution of the THF ligand by more strongly coordinating ligands, including those which might be photo sensitive to survive direct photolysis.

2.2. Metal-Olefin Bonding

The ligand that possesses a π -system are bonded to the metal centre by a single atom (coordination mode η^1). The situation is different when several

ligand atoms are bond in an equivalent way to the metal centre. In particular, this is the case for π complexes in which the π system of the ligand 'points' in the direction of the metal, rather than being perpendicular to the metal-ligand bond.

Although the first known organometallic complex is Zeisse Salt [2], it was not known how ethylene bonded to platinum metal. In 1950, X-ray analyse results showed that molecular plane of ethylene is perpendicular to interaction axis of metal. Ethylene molecule bonded to metal in a way that the molecular plane is perpendicular to this bonding axis and metal is the center of two carbon atoms of ethylene. The distance between metal and carbon atoms of ethylene is short enough to make a chemical bond between them. It was said that the two carbon atoms of ethylene bonded to the metal. Upon this, three scientists Dewar, Chatt and Duncanson developed a model which is known as their names which explains metal-olefin bonding with molecular orbital theory [61-63].

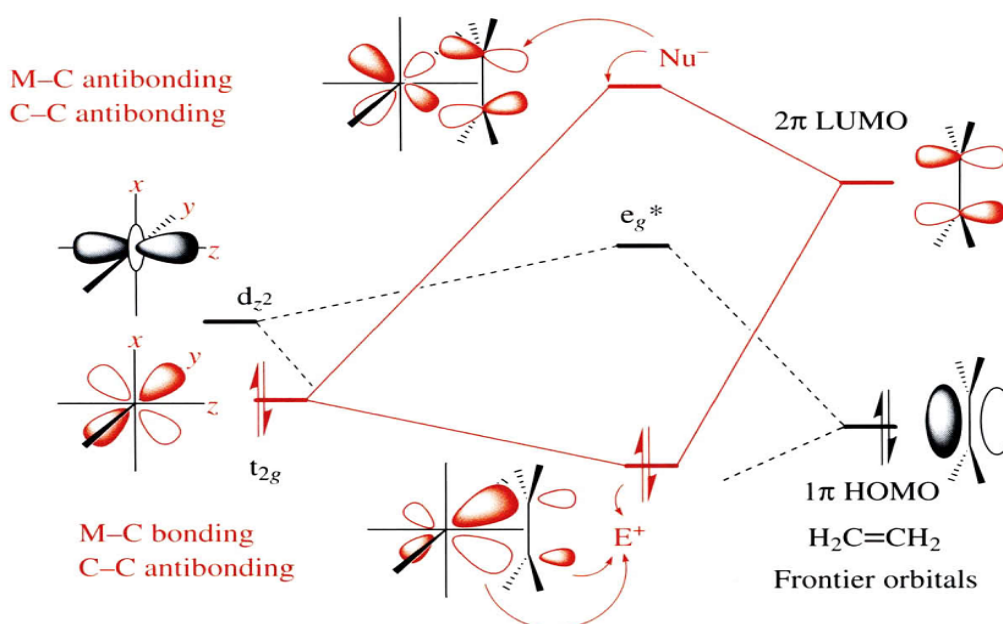


Figure 2.2.1. The metal olefin bonding.

Bonding of ethene to a transition metal centre; implications for electrophilic (E+) and nucleophilic (Nu-) attack

As carbon monoxide (CO) and olefin (C_2H_4) is one of the most important ligands in organometallic chemistry. The ligand, L, olefin coaxially give a pair of electrons to the metal π orbital of C_2H_4 towards a vacant d metal orbital. According to the Dewar-Chatt-Duncanson model the metal-olefin bond, like metal-carbonyl bond, consists of two parts; σ - and π -bond. First one is interaction between filled π molecular orbital of olefin and σ orbital of metal. Here, olefin acts as σ -donor because there is an electron flow through filled orbital of ethylene to empty orbital of metal. In other words, olefin gives π -electron density to the metal (Fig.2.2.2.a). The resulting overlap is intermediate between an axial overlap, normally associated with a σ interaction, and a lateral overlap which corresponds to a π interaction.

Secondly, antibonding π^* orbital of olefin is in π symmetry to metal-olefin bonding axis and make a π -interaction with the d orbital of metal which is in the appropriate symmetry. There is an electron flow through filled d orbital of metal to empty antibonding π^* orbital of olefin(Fig.2.2.2.b). The interaction that involves the π^* orbital can therefore be described as a π -interaction.

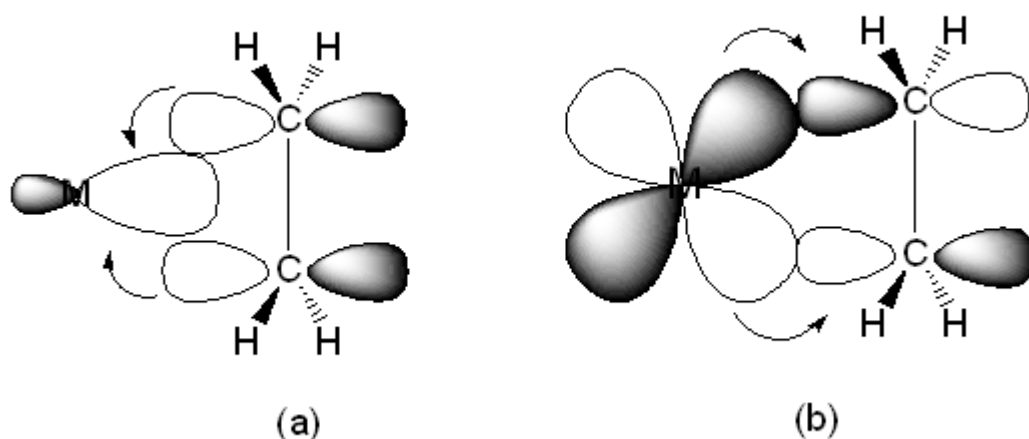


Figure 2.2.2.a. Dewar-Chatt-Duncanson model of metal-olefin bonding, σ -interaction.

Figure 2.2.2.b. Dewar-Chatt-Duncanson model of metal-olefin bonding, π -interaction.

This is therefore a back-donation interaction, where ethylene plays the role of a π acceptor, using its empty π^* orbital. The doubly occupied orbital, mainly concentrated on the metal, is part of the d block of the complex; it can be described as a metal d orbital that is stabilized by a bonding interaction with the π^* orbital on ethylene. As a result, these two interactions fortify each other so there is a very strong bond formed between olefin and metal [63].

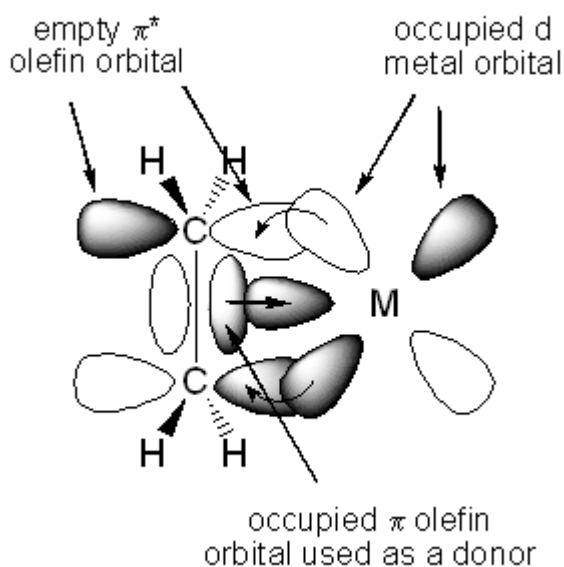


Figure 2.2.3. The synergistic effect of metal-olefin bonding.

2.3.Metal-Pyrimidine and –Pyridine Bonding

In modern coordination chemistry, many different inorganic and organic compounds are used as ligands [63-66]. In spite of the tremendous variety of these ligand systems, typical structures are defined as a basis for the study of their coordination chemistry.

Among the interesting features of modern science the persistent increase in the rate of appearance of new journals and the concomitant rate of publication of papers are the most noticeable. The field of study of the coordination potential of heterocyclic thiones especially those possessing an α - N- heteroatom as well as their corresponding anions, referred to as thionates, could not be exception [67].

The coordination chemistry of the pyridine and pyrimidine bases has been a subject of interest for many years and has been studied from a variety of perspectives by many different research groups [68,69]. Pyrimidine is known to act mainly as a σ -donor ligand with little π -accepting ability [7], therefore the M-N bond in such low valent metal complexes is not very strong.

Thiols are important antioxidants and are easily converted to their anions, radicals, and disulfides. Thiols, thiones, sulfenyl anions (thiolate, RS⁻), sulfenyl radicals (thiyl, RS⁰), and disulfides also play important roles in diverse fields such as atmospheric chemistry, biological chemistry, organic synthesis and medicine [36].

The interest in thio derivatives of pyrimidine is related to their use as inert substituents [70,71] and to the possibility of readily replacing the substituted groups [72]. The synthesis of pyrimidine and condensed pyrimidines has attracted the attention of medicinal chemists because of their pharmacodynamic properties.

2-pyrimidinethiol nucleotides have been detected in Escherichia Coli sRNA and yeast tRNA ; it has been found that they inhibit the synthesis of tRNA, thus acting as antitumor and antithyroid agents. It is shown that 2-mercaptopyrimidine (HSpym) and 2-mercapto 4-amino pyrimidine (HSapym), similar to 2-mercaptopyrimidine in nucleotides, are able to inhibit the synthesis of tRNA. Thus they may act as valuable substrates for synthesizing antitumor-active compounds [73].

These ligands and their derivatives have been used in coordination chemistry because of binding capabilities of nitrogen and sulfur to metals [38-43]. Such ligands possess at least one soft donor site (thionato sulfur) and one hard site (thioamido nitrogen) and hence are capable of coordination to a great variety of main-group and transition metals and in diverse bonding modes [44]. They can coordinate with metals as a neutral species (-NH-C=S) or as a conjugate base (-N=C-S^-).

There is indeed a considerable versatility in the coordination modes of these molecules which may include monodentate binding through S(I) or through N(II), bridging through a single S(III), bridging through both S and N (IV) or chelating via the S to N backbone (VI) (Figure 2.3.1).

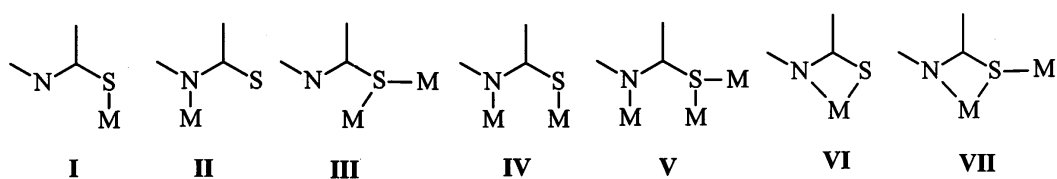


Figure 2.3.1. The coordination modes of the ligand with metal

All these modes either alone or in combinations (V, VII) have been observed and assigned on the basis of congruent evidence of spectroscopic characterizations or crystal structure determination of both homo- and heteroleptic metal complexes [74].

The relative energies of tautomers and the mechanism of the tautomerism of the heterocyclic thiols and thiones also play significant roles in many areas of science. Tautomerism is an essential ingredient in several chemical and biochemical processes understanding tautomeric reactions is

very important in biological mechanisms and is a strong motivation for theoretical studies [75]. The heterocyclic compounds exhibit tautomeric equilibrium between the thiol ($>\text{C-SH}$) and thione ($>\text{C=S}$) as a consequence of the highly mobile protons that they possess [49-52]. The predominant form largely depends on the state and conditions of the molecule. Thus from X-ray diffraction, it has been demonstrated that 2-mercaptopyrimidine exhibits a predominant thione form in the solid state, although it can also develop dimeric structures through hydrogen hydrogen bridges [76,77].

However, in liquid phase, there are several additional factors involved in the shift of tautomeric equilibrium. Among these, the solvent, temperature, pH and concentration remain prominent [78]. Thus, it has been demonstrated by means of UV spectroscopy that the thione predominates over the thiol form and dimer formation can be shifted toward the thiol form by increasing temperature or by decreasing the concentration in polar solvent [51]. NMR studies also provide evidence concerning the predominance of the thione structure; inclusively, the prototropic interconversion between the tautomers has been reported [79].

Infrared is another valuable instrument to investigate the chemical structure of these compounds and derivatives and has allowed several experiments to be performed the results of which allow full interpretation of their vibrational spectra [80,81].

Indeed, the coordination and structural diversity of metal complexes with 2-mercaptopyridine and 2-mercaptopyrimidine, for instance, is an established field of study [44]. The first complete treatment of this body of

information appeared about 15 years ago [82] and considered the sum of the relevant literature.

The author of that work was the late Eric Raper, who was a major contribution in the expansion and exploitation of the field and he continued by publishing three more reviews concerning the advances in the thione [83] and thionate [84] coordination chemistry, respectively. This is an attempt to carry on his coverage of the thione-thiolate coordination versatility, including the studies published in main stream literature since 1996 when Eric's last review as well as a extensive one describing thione complexes of group 11 metals appeared [44] until about the middle of 1999, just a year after his transition to eternity.

Pyridine is capable of acting as either a π or σ ligand. However, only randomly does it donate its π -electron system to the electronic shell of a metal atom. The higher affinity of pyridine toward donation of a σ electrons is due to its inherent structure. Pyridine forms a dipole with the electron density localized on the nitrogen atom. Moreover, the lone pair of N-electrons has a geometry that makes it easily accessible for donation to a central metal atom in the resultant complex.

It is practically impossible to determine the strength of the pyridine ligand by means of any universal parameters. It varies from one metal to another and depends also on steric interactions in the inner coordination sphere. Substituents, which reside on the ring, are also important.

Substituents located in the α -positions of the pyridine can affect the site of coordination. It should be noted that some substituents on pyridine prohibit the N-coordination on the metal. This is quite common in the case of 2-pyridone. This compound always become a ligand through the oxygen atom, and the possibility of the chelation involving the ring nitrogen atom is rejected independently of the higher affinity of a given metal to oxygen or nitrogen [85-90].

CHAPTER 3

EXPERIMENTAL STUDIES

3.1 Basic Techniques

Most of the organometallic compounds are thermodynamically unstable to oxidation, the driving force being provided by the negative free energies of formation of metal oxide, carbondioxide and water [91].

Because of the air sensitivity of organometallic compounds, all reactions and purification of synthesized organometallic compounds were carried out under dry and deoxygenated nitrogen gas atmosphere under vacuum as shown in Figure 3.1.1

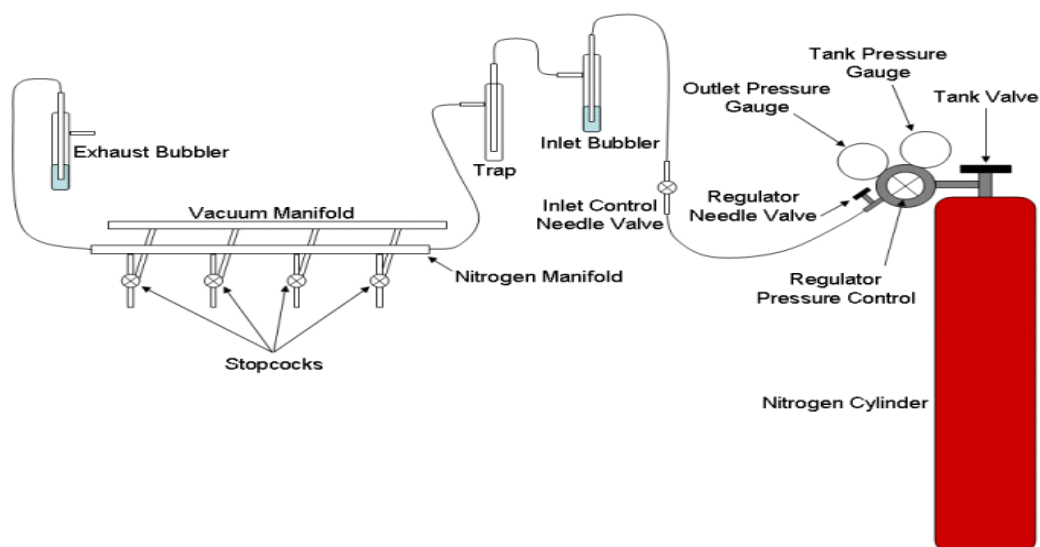


Figure. 3.1.1 A typical Schlenk line

In order to overcome this difficulty, all experiments of this work were carried out by using the vacuum line and schlenk glassware. The simplest and best known techniques is the 'Schlenk' technique. A schlenk tube is a flask that has at least one arm where inert gas can be introduced. Usually a three or two-way stopcock is fitted at the end of the arm. Some typical schlenk flasks are shown in Figure 3.1.2.

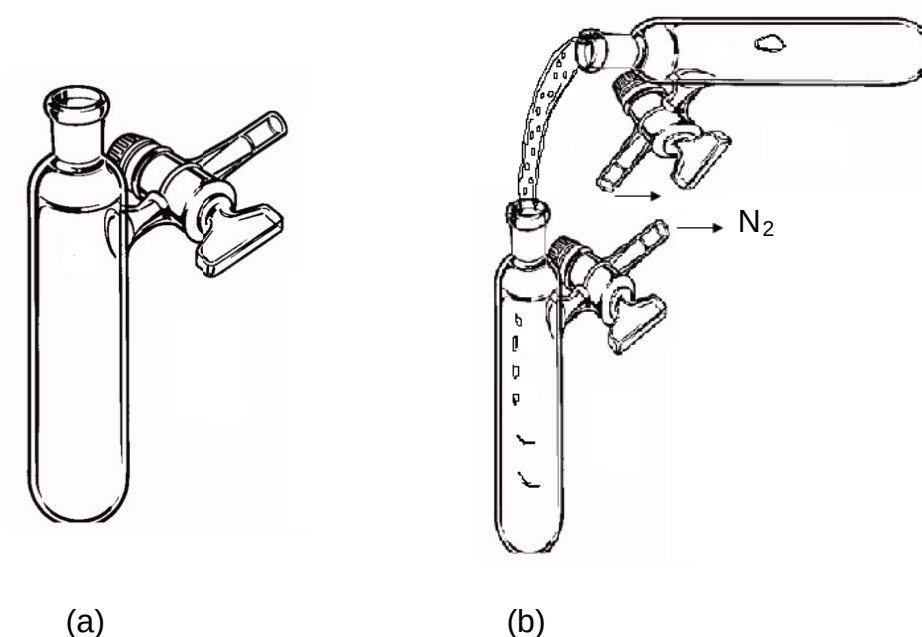


Figure.3.1.2 (a) Standard Schlenk tube and (b) transferring liquid in nitrogen atmosphere.

In use, the air in a schlenk flask should be replaced at least three times by inert gas using a pump and all subsequent handling should be carried out under nitrogen flow. Transfer of a liquid sample under nitrogen gas atmosphere can be carried out by connecting two schlenk tubes by using an adaptor (Figure 3.1.2.b).

Solvents were purified by refluxing over metallic sodium or anhydrous phosphorous pentoxide under an inert atmosphere of nitrogen or argon for three or four days before using. Hexacarbonyl metals and organic compounds that used as ligand were purchased from the Merck and Aldrich, and used without further purification.

The octahedral complexes of the type $M(CO)_6$ (M: Cr, Mo, W) are air-stable, hydrophobic white crystalline solids which are readily sublimable under vacuum. They are very slightly soluble in non-polar solvents and are slightly soluble in polar solvents such as THF and $CHCl_3$. Some physical and structural properties of $M(CO)_6$ are summarized in Table 3.1.1 [92].

Table 3.1.1. Representative Data for the Physical and Structural Properties of $M(CO)_6$.

	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
Molecular Weight	220.06	264.00	351.91
Vapor pressure (Torr/ °C)	1.63/ 50	0.27/30	0.35/50
Melting Point, °C	130	150	150
(under vacuum)	150	146	166
M-C bond energy, kJ/mol	107	151	179
B. length, °A (M-C)	1.915	2.063	2.058
(C-O)	1.140	1.145	1.148
IR (gas) $\nu(CO)$, cm^{-1}	2000.4	2004	1998

For the photochemical reactions, a special apparatus (Figure 3.1.3) was used. The apparatus consists of three coaxial glass tubings. Into the inner part (a) a mercury lamp, (b) (Hg- Tauclampe TQ 150 high pressure mercury lamp (Quartzlampe GmbH, Hereaus, Germany, Solidex glass, $\lambda < 280\text{nm}$) is immersed. To carry out photochemical reactions, the prepared solution mixtures (consist of $\text{M}(\text{CO})_6$, (M: Cr, Mo, W) and the ligands dissolved into the THF) is filled into the outer part (c) and cooled to room temperature by circulating tap water through the space and third tubings.

Figure.3.1.3 Apparatus used for
photochemical reactions

(a) Inner part

(b) Mercury lamp

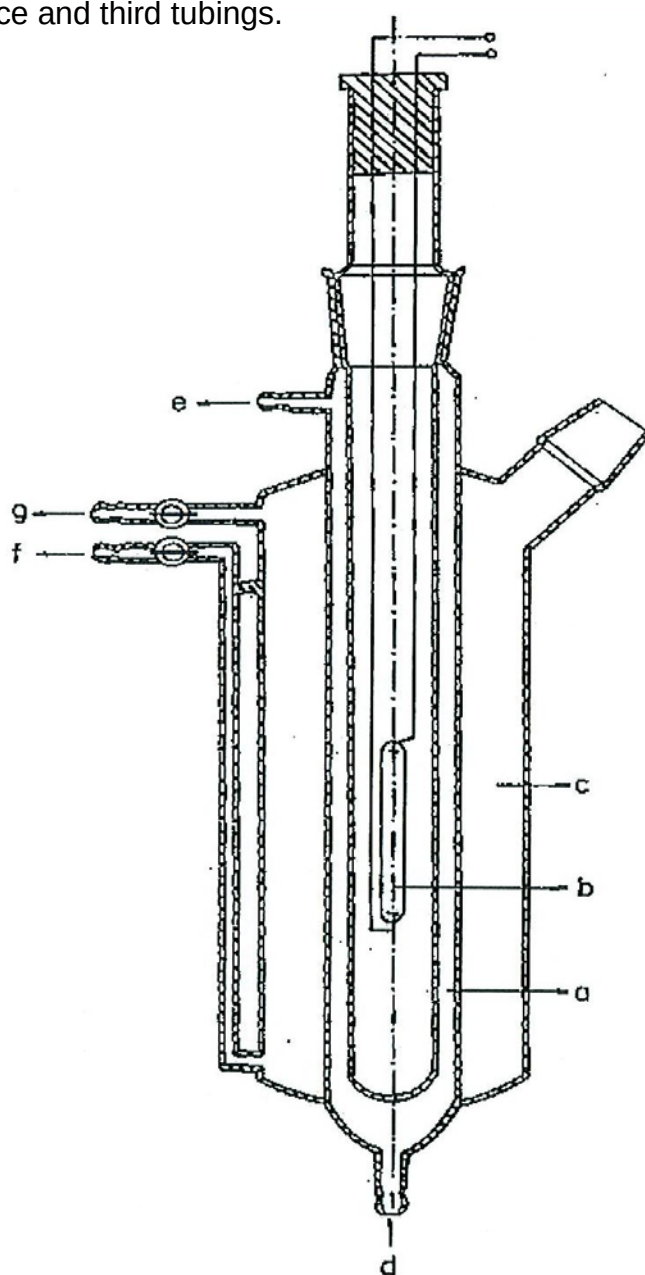
(c) Outer part

(d) Tap water inlet

(e) Tap water outlet

(f) Nitrogen gas inlet

(g) Nitrogen gas outlet



3.1.1. FT-IR (Fourier Transform Infrared)- Spectra

The synthesis of complexes and substitution reactions were followed by taking IR-spectra at intervals during the reactions. The IR spectra were recorded using Schmadzu FTIR- 8400S spectroscopy.

3.1.2. UV/VIS Spectra

The UV/Vis spectra of these complexes were recorded from their dichloromethane solutions using JASCO V-530 UV/VIS spectrophotometer in quartz cell.

3.1.3. ^1H -NMR Spectra

The ^1H -NMR spectra of these complexes were recorded from their d-chloroform and d-dimethylsulfoxide solutions using Bruker-Spectroscopin DPX 400 MHz spectrometer.

3.1.4. ^{13}C -NMR Spectra

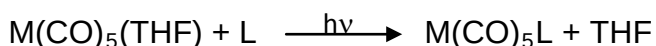
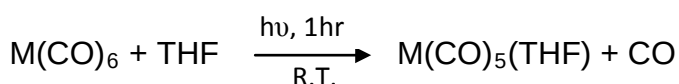
The ^{13}C -NMR spectra of these complexes were recorded from their d-chloroform solutions using Bruker-Spectroscopin DPX 400 MHz spectrometer. All chemical shift values are given relative to TMS signal which has been used as an internal reference.

3.1.5 TGA/DTA

The thermal analysis of the complexes $M(CO)_5L$; (M: Cr, Mo, W ; L: 2-mercaptopyrimidine) was measured by using SII EXSTAR 6000 TGA/DTA 6300.

3.2 The Synthesis of Complexes

The proposed complexes have been synthesized by the UV-irradiation of pentacarbonyltetrahydrofuranemetal(0) complexes with the 2-mercaptopyrimidine ligand at room temperature according to the following reaction;



In the above reactions, L: 2-pyrimidinethiol, 2-mercaptopyrimidine (2-mpm) ;
M: Cr, Mo, W.

3.2.1 Pentacarbonyl(2-mercaptopyrimidine)metal(0), ($M(CO)_5(2-mpm)$; M: Cr, Mo, W).

0.5 gram $M(CO)_6$ [M; Cr(2.27 mmol), Mo(1.89 mmol), W(1.42 mmol)] was dissolved in excess amount of THF and irradiated for one hour at room temperature. A stoichiometric amounts of 2-mercaptopyrimidine (0.26g, 0.21g, 0.16g) was added to the reaction mixture and the irradiation continued until no starting compounds exist. The reaction process was

followed by IR spectra taken at 20 minutes intervals, during the reaction nitrogen gas passed through the reaction vessel.

At the end of reaction, the color of solutions were bright red for $\text{Cr}(\text{CO})_5(2\text{-mpm})$, dark red for $\text{Mo}(\text{CO})_5(2\text{-mpm})$ and red for $\text{W}(\text{CO})_5(2\text{-mpm})$.

Each solution was filtered to an evacuated schlenk storage tubes under nitrogen gas atmosphere. The resulting solutions was evaporated under high vacuum.

3.2.2Cis-tetracarbonylbis(4-dimethyaminopyridine)tungsten(0), [W(CO)₄(4-dmap)₂]

1g $\text{W}(\text{CO})_6$ (2.84 mmol) was dissolved in 200 ml THF solution and irradiated for 1hr using a high pressure mercury lamp which was housed in a water-cooled glass jacket at room temperature. A stoichiometric amounts of 4-(dimethylamino)pyridine (0.35 g) was added to the reaction mixture and irradiation continued until no more starting materials are exist in the reaction mixture. At the end of the reaction, evaporating the excess solvents and strating materials under high vacuum leaving a dark yellow residue. The residue was washed with n-hexane solution. The n-hexane insoluble part of the solution was then dissolved in CH_2Cl_2 and recrystallized from dichloromethane solution. Before the recrystallization the solution was purified double solvent (1:5 n-hexane; dichloromethane mixture). The resulting pyridine complex was dried under high vaccum for one day then storred under pure inert gas for the routine analysis.

CHAPTER 4

RESULT AND DISCUSSION

4.1. Infrared Spectra

4.1.1. Infrared Spectra of 2-mercaptopyrimidine

It is well known that aromatic heterocyclic molecules bearing a mobile H atom undergo rapid and facile tautomeric transformations in solution. The predominant form largely depends on the state and conditions of the molecule. 2-mercaptopyrimidine exhibits a predominant thione form in solid state. However, in liquid phase, there are several additional factors involved in the shift of tautomeric equilibrium.

FT- IR spectra of 2-mercaptopyrimidine recorded from its KBr pellet and dichloromethane solution are shown in Figure 4.1.1.1 and 4.1.1.2. In addition the observed frequencies of 2-mercaptopyrimidine together with the relative intensities, assignments, calculated frequencies and force constants are presented in Table 4.1.1.1.1.

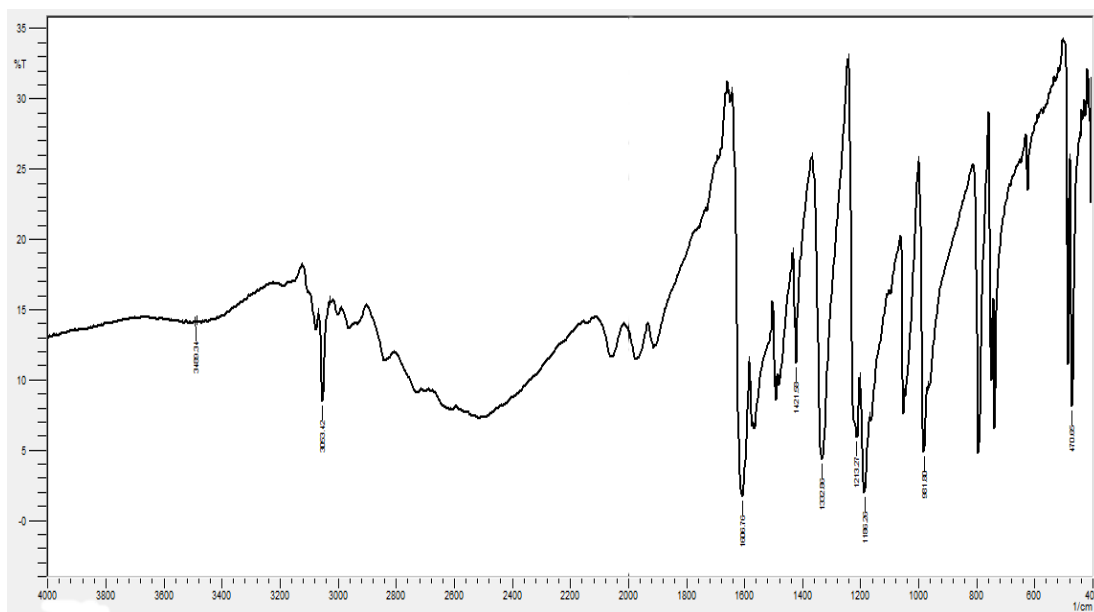


Figure 4.1.1.1. The IR spectrum of 2-mercaptopyrimidine dispersed in KBr pellet.

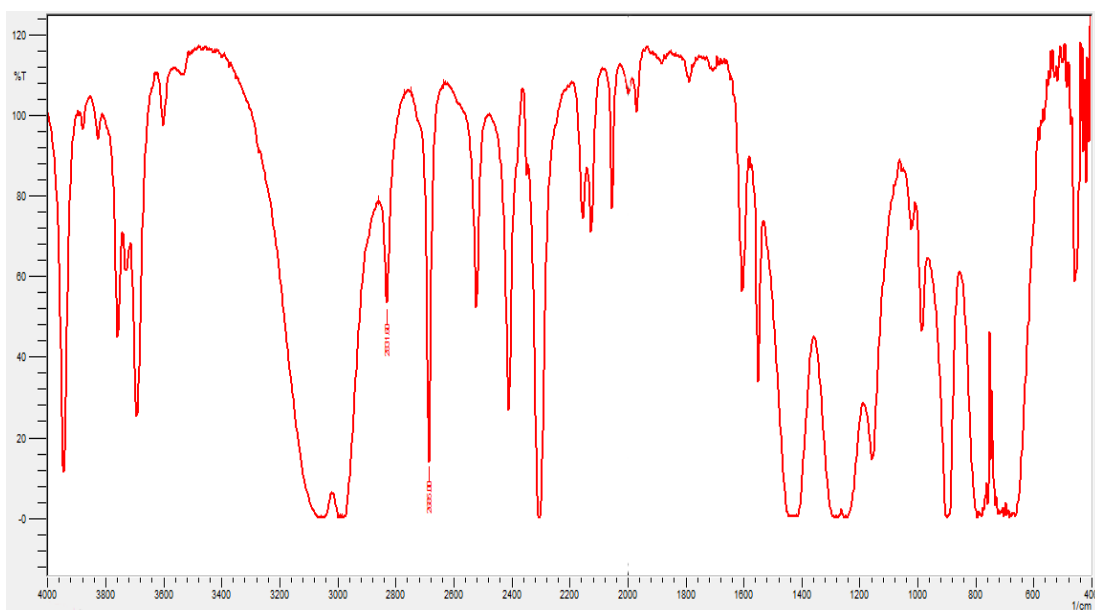


Figure 4.1.1.2. The IR spectrum of 2-mercaptopyrimidine in CH_2Cl_2 solution.

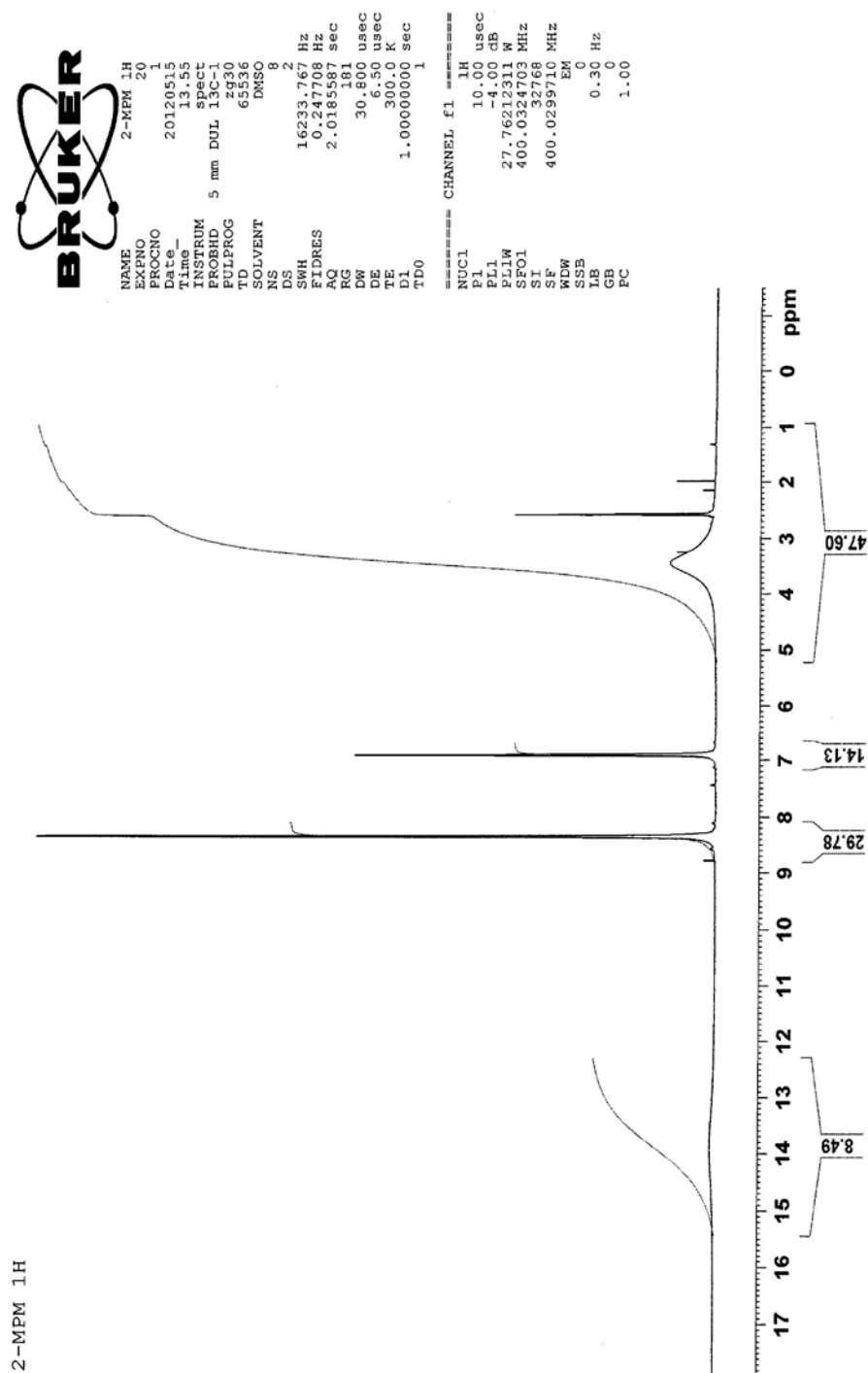


Figure 4.1.1.3 The ^1H -NMR spectrum of 2-mercaptopyrimidine recording from DMSO solution rel. TMS

4.1.1.1 C-H vibrations

The carbon- hydrogen stretching vibrations give rise to bands in the region $3000\text{--}3100\text{ cm}^{-1}$ in all aromatic compounds. The expected three stretching vibrations (Table 4.1.1.1.1.) corresponds to stretching modes of C3-H, C5-H, C6-H units.

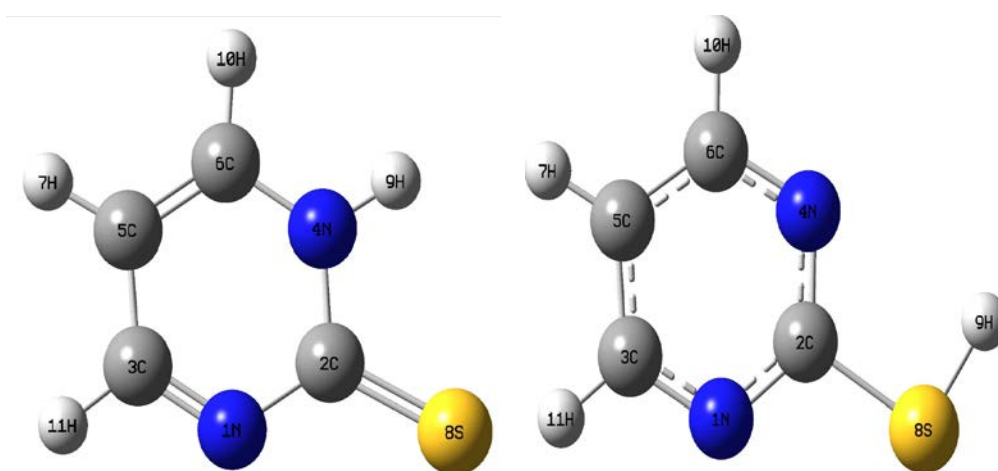


Figure 4.1.1.1.1. The structure of 2-mercaptopyrimidine

The vibrations assigned to aromatic C-H stretch in the region $3129\text{--}3244\text{ cm}^{-1}$ by B3PW91 method are in agreement with experimental result $3079\text{--}3191\text{ cm}^{-1}$. The bands corresponding to both out-of plane and in-plane C-H deformations are observed in the region $1050\text{--}1330\text{ cm}^{-1}$.

Table 4.1.1.1.1 Vibrational frequencies and their probable assignments for 2-mercaptopyrimidine.

vibrational modes	Solid	Dichloromethane	Vacuum			Dichloromethane			Cyclohexane		
	Exp	Exp	IR	I	FC	IR	I	FC	IR	I	FC
$\nu(\text{C}=\text{S})$	468.71	451.35	461.27	25.87	0.3211	469.99	29.75	0.3436	465.67	27.46	0.3321
$\delta(\text{N-H})$	750.28		755.46	30.47	0.5596	753.45	123.09	0.5555	752.46	82.49	0.7163
$\nu(\text{C-H}) + \delta(\text{C-H})$	792.71		774.55	0.42	0.4711	806.89	0.00	0.4866	789.67	0.00	0.4720
Ring	981.71	985.57	987.70	48.73	3.8703	995.42	111.52	4.0184	980.26	0.58	0.7480
$\nu(\text{C-N}) + \nu(\text{C-C}) + \nu(\text{C-H})$	1053.17		1049.02	7.70	1.6547	1069.81	13.62	1.6459	1058.46	9.65	1.6450
$\nu(\text{C-N}) + \nu(\text{C-H}) + \delta(\text{C}=\text{C})$	1186.14	1157.33	1169.27	46.96	1.7203	1187.54	303.32	2.7569	1179.30	93.61	1.9648
$\nu(\text{C}=\text{S})$ in SCNH	1213.14	1247.85	1221.12	209.91	1.7354	1215.63	304.57	1.8942	1219.14	309.97	2.0257
$\nu(\text{N-H}) + \nu(\text{C-H})$	1332.71		1384.94	20.91	1.7209	1371.70	112.99	1.8523	1380.59	51.46	1.7878
$\delta(\text{C-H}) + \delta(\text{C-C}) + \delta(\text{C-N})$	1421.43	1433.20	1468.28	80.51	2.6638	1467.18	106.12	2.4622	1467.87	93.64	2.6111
$\nu(\text{N-H}) + \nu(\text{C-H})$	1492.78		1495.44	43.64	3.3705	1505.56	178.70	2.9942	1499.34	90.34	3.1322
$\nu(\text{N-H}) + \nu(\text{C}=\text{C}) + \nu(\text{C-C})$	1571.86	1550.82	1601.14	439.41	4.7117	1602.97	756.68	4.7722	1602.04	584.26	4.6504
$\delta(\text{C}=\text{C}) + \delta(\text{C}=\text{N})$	1606.57	1604.83	1677.34	181.38	9.0057	1666.97	223.13	7.8045	1672.53	209.00	8.4969
$\nu(\text{C-H}) + \delta(\text{C-H})$	3056.14	2831.60	3129.87	24.45	6.2951	3151.99	30.01	6.3883	3139.93	27.22	6.3374
$\nu(\text{C-H}) + \delta(\text{C-H})$	3079.27	2987.84	3213.66	3.68	6.6460	3239.92	1.41	6.7544	3225.45	2.38	6.6951
$\nu(\text{C-H}) + \delta(\text{C-H})$	3191.05	3070.78	3244.36	1.83	6.8085	3256.98	0.58	6.8735	3249.57	1.25	6.8350
$\nu(\text{N-H})$	3534.10		3611.96	49.96	8.2913	3602.12	100.05	8.2522	3610.25	68.62	8.2850
vibrational modes	Solid	Dichloromethane	Vacuum			Dichloromethane			Cyclohexane		
	Exp	Exp	IR	I	FC	IR	I	FC	IR	I	FC
Transition		896.85	940.19	12.18	0.6335	922.25	18.15	0.6120	933.45	14.39	1.9171
Transition		2854.74	2823.88	11.62	2.1063	2803.05	30.34	2.0825	2814.46	17.97	2.0949

4.1.1.2. C-C vibrations

C=C stretching vibrations appear in the region $1425\text{--}1625\text{ cm}^{-1}$. In this work, the frequencies observed in IR spectrum at 1421 and 1571 cm^{-1} have been assigned to C-C stretching vibrations. The theoretically calculated values show good agreement with experimental data. The frequencies observed in IR spectrum at 981 cm^{-1} have been assigned to ring stretching. The theoretically calculated values of 987 shows excellent agreement with experimental data.

4.1.1.3. C-N, C=N vibrations

The identification of C-N stretching frequencies is a very difficult task, since mixing of bands are possible in this region [93,94]. In this work, the bands observed at 1606 cm^{-1} in IR spectrum are assigned to $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ vibrations. $\nu(\text{C}=\text{N})$ vibration gives rise to a band at 1421 cm^{-1} , which also contains the $\delta(\text{C}-\text{H}) + \delta(\text{C}-\text{C})$ deformation. The observed result are good agreement with the theoretical value.

4.1.1.4. S-H and C-S vibrations

The sulfur atoms give rise to bending vibrations along with the neighbouring atoms. However, there has been considerable discussion and conflicting reports concerning the locations of C-S and C=S stretching frequencies [95-98]. In compounds containing a C=S group adjacent to a C-N or C-O group, there may be interactions between the stretching vibrations of the groups that may produce new frequencies in unexpected regions of the spectrum.

The absence of an IR band at $\sim 2600\text{ cm}^{-1}$ in the spectrum of 2-mercaptopyrimidine suggests that the ligand exist in its thione form in solid state. This is corroborated by the appearance of the medium $\nu(\text{C}=\text{S})$ band at 1213 cm^{-1} and IR $\nu(\text{N}-\text{H})$ band at 3489.34 cm^{-1} . In the presence of a solvent, tautomeric equilibrium is shown. The band in the 2685 cm^{-1} region and the

band in the 3534 cm^{-1} region are sufficiently different and can be used to differentiate between the tautomeric species of 2-mercaptopyrimidine.

4.1.2. IR Spectra of $\text{M}(\text{CO})_5\text{L}$ Complexes

Discussion of the IR spectra of the prepared complexes $[\text{M}(\text{CO})_5\text{ 2-mpm}]$ (M; Cr, Mo, W , 2-mpm; 2-mercaptopyrimidine) will done in two regions, in the carbonyl region and as full IR region.

In the first part of this discussion we would like to discuss the IR spectra of the prepared coordination complexes in the carbonyl region ($1700\text{--}2300\text{ cm}^{-1}$) that are recorded from their dichloromethane solutions. This discussion will lead to the result to what type of complexes are formed. The IR spectra of the complexes in this region show three stretching bands at different intensities indicating C_{4v} local symmetry of the $\text{M}(\text{CO})_5$ part of the octahedral structure [99-101]. The IR spectra of $[\text{Cr}(\text{CO})_5\text{ 2-mpm}]$, $[\text{Mo}(\text{CO})_5\text{ 2-mpm}]$, $[\text{W}(\text{CO})_5\text{ 2-mpm}]$ are given seperately in Figure 4.1.2.1, 4.1.2.2, 4.1.2.3 respectively.

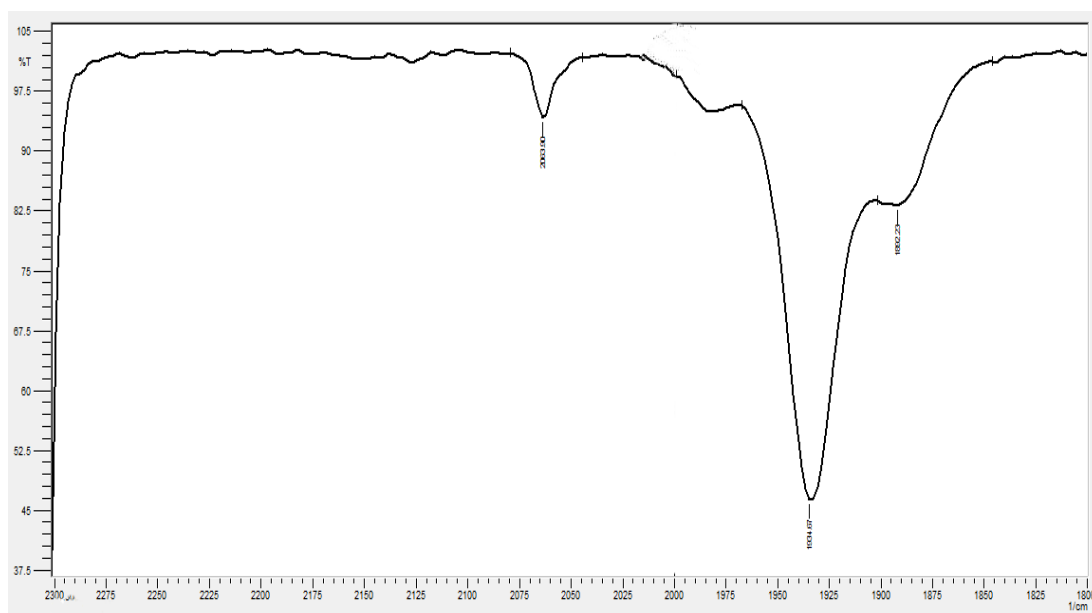


Figure 4.1.2.1. The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ in dichloromethane solution.

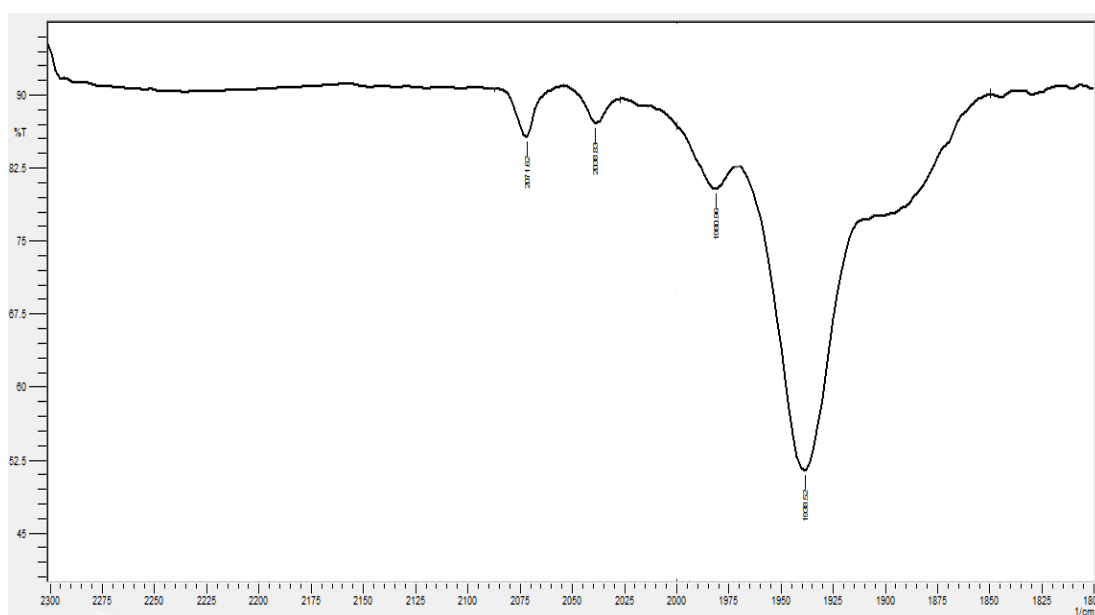


Figure 4.1.2.2. The IR spectrum of $[\text{Mo}(\text{CO})_5 \text{ 2-mpm}]$ in dichloromethane solution.

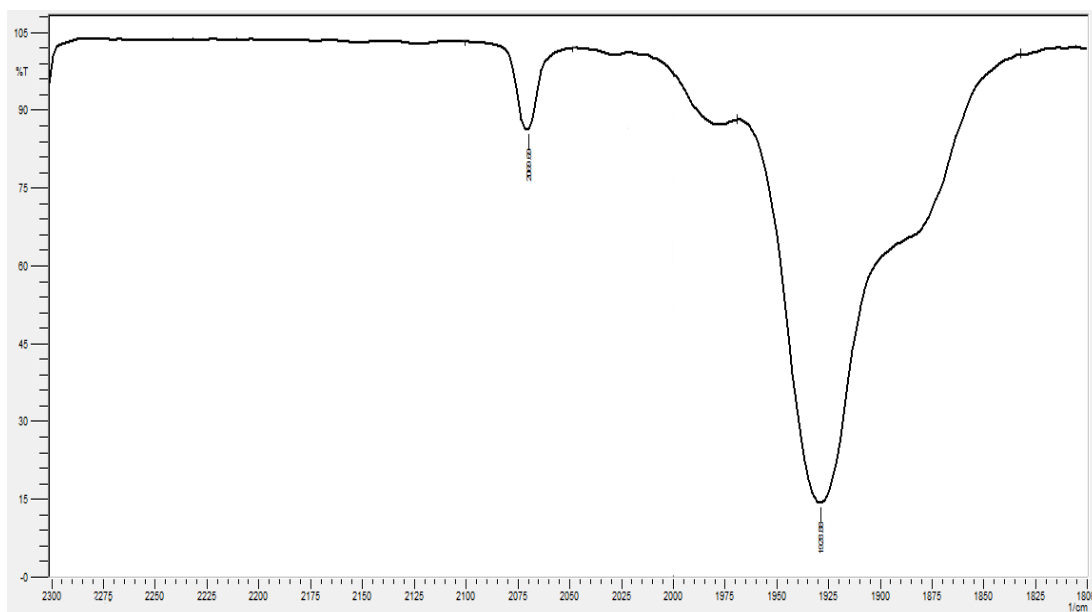


Figure 4.1.2.3. The IR spectrum of $[\text{W}(\text{CO})_5 \text{ 2-mpm}]$ in dichloromethane solution.

Assignments of the carbonyl absorption bands in the IR-spectra of the complexes to the expected modes are presented in table 4.1.2

Table 4.1.2.1 : The CO-stretching frequencies of $[\text{M}(\text{CO})_5 \text{ 2-mpm}]$.

Complex	$\nu(\text{CO}) (\text{cm}^{-1})$		
	$A_1(1)$	$A_1(2)$	E
$\text{Cr}(\text{CO})_5 \text{ 2-mpm}$	2063.90	1896.09	1934.67
$\text{Mo}(\text{CO})_5 \text{ 2-mpm}$	2071.62	1903.80	1938.52
$\text{W}(\text{CO})_5 \text{ 2-mpm}$	2069.69	1878.00	1928.88

The $A_1(1)$ mode is lower in energy than the E mode which is symptomatic of the 2-mercaptopyrimidine ligand which is lower π -bonding ability than the CO group. The result of the IR discussion in this part would indicate the formation of the pentacarbonyl complexes, eliminating the

existence of the di-substituted tetracarbonyl complexes at which different IR patterns would appear.

The second part of this discussion will focus on the type of the bonding between the metal atoms and the pyrimidine ligand either through its nitrogen or sulfur lone pairs. The tautomeric ability of the pyrimidinethiol ligands could make the IR spectra of these complexes in the region for 400-4000 cm^{-1} more complicated.

In the infrared spectra of 2-mercaptopyrimidine distinction between the vibrational characteristics of the thiol and thione forms is lost due to intermolecular N---HS or NH---S bonding. For same reasons, it is difficult to associate the vibrational spectra in aqueous solution with a particular tautomeric form, unless obtained in very dilute solutions free from intermolecular association, which is not feasible in this case [51,52].

To discuss and assign the IR peaks of these possible tautomers one can propose the assignments of S-H, C-S, N-H, C=S stretching modes.. Although the presence or absence of a S-H or N-H stretching band in the 2600- 3400 cm^{-1} region would help to discriminate between thiol and thione species by the IR and SERS (Surface-enhanced Raman) spectra, these bands are often too weak to be observed..

The IR data analysis of the complexes in the region of 400-4000 cm^{-1} will be done in both solid and aqueous forms. Starting with the IR spectra of

the prepared complexes in the region of 400-4000 cm^{-1} in their solid form as KBr pellets, the appearance or disappearance of the some typical stretching modes implies which tautomer is favour in solid form. As example of these spectra the full scaled IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ is given in Figure 4.1.2.4.

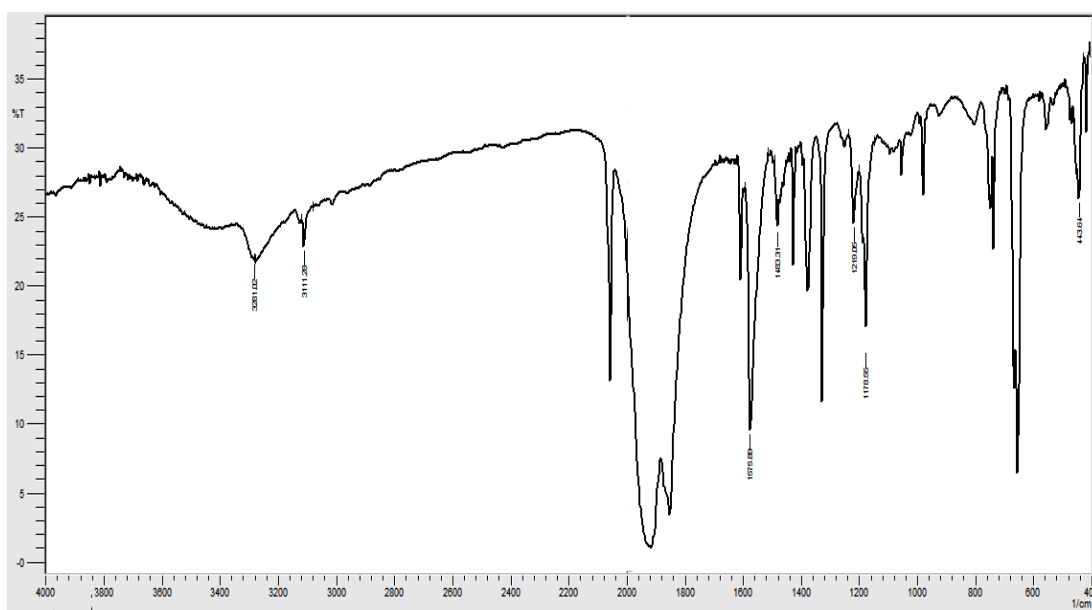


Figure 4.1.2.4 The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ disperses in KBr pellet.

As it is shown from the IR spectra one can observe a strong stretching band at 1219.05, 1178.55 and 443.64 cm^{-1} area, this indicate the appearance of the C=S bond from which we can decide the thione tautomer rather than the thiol one. The IR stretching modes results are given in Table 4.1.2.1.

Table 4.1.2.2. IR data of 2-mercaptopyrimidine and its complexes with assignments.

	2-mercaptopyrimidine	Cr 2-mpm	Mo 2-mpm	W 2-mpm
Vibrations	Experimental (solid)	Experimental (solid)	Experimental (solid)	Experimental (solid)
Modes	Band, cm^{-1}	Band, cm^{-1}	Band, cm^{-1}	Band, cm^{-1}
$\nu(\text{N-H})$	3481.63	3458.48	3452.70	3458.48
$\nu(\text{C-H})$ asym	3201.94 m	3277.17	3288.74 m	3244.38
$\nu(\text{C-H})$ sym	3053.42-2951.19	3111.28	3126.71-2872.10	3111.28
$\nu(\text{CO})$		2058.11	2071.62	2069.69
$\nu(\text{CO})$		1925.02	1925.06	1919.24
$\nu(\text{CO})$		1853.65	1863.02	1878.73
$\nu(\text{C}=\text{C})$	1606.76	1608.69	1587.47	1604.83
$\nu(\text{C}=\text{N})$	1566.25	1575.89	1425.44	1554.68
$\nu(\text{C}=\text{N})+\delta(\text{C-H})+\delta(\text{N-H})$	1421.58	1427.37	1379.15	1421.58
$\nu(\text{C-N})$	1332.86	1327.07	1329.00	1311.64
$\nu(\text{C}=\text{S})$	1186.26, 1213.27	1178.55, 1219.05	1176.62, 1255.70	1165.04, 1236.41
ring stretching	981.80	979.87	985.66	981.80
$\delta(\text{N-H})$	792.77	748.41	800.49	731.05
$\nu(\text{C}=\text{S}), \beta(\text{C}=\text{S})$	470.65	443.64	418.57	412.78

On the other hand the N-H stretching modes are another typical modes for the existence of the thione tautomer. In the IR spectra one can easily observe a broad N-H bending vibrations at 1053.17, 1483.31 and 1575.89 cm^{-1} are belong to the out of deformation of N-H bond.

But it should not be forgotten that the stretching bands of the C-N and C=N bond are also seen at that region. The double bond character of the C=S bond increases with loss of H^+ and H from the SH group of the molecule, resulting in a greater contribution of the CS stretching motion to the higher frequency modes (700 cm^{-1}).

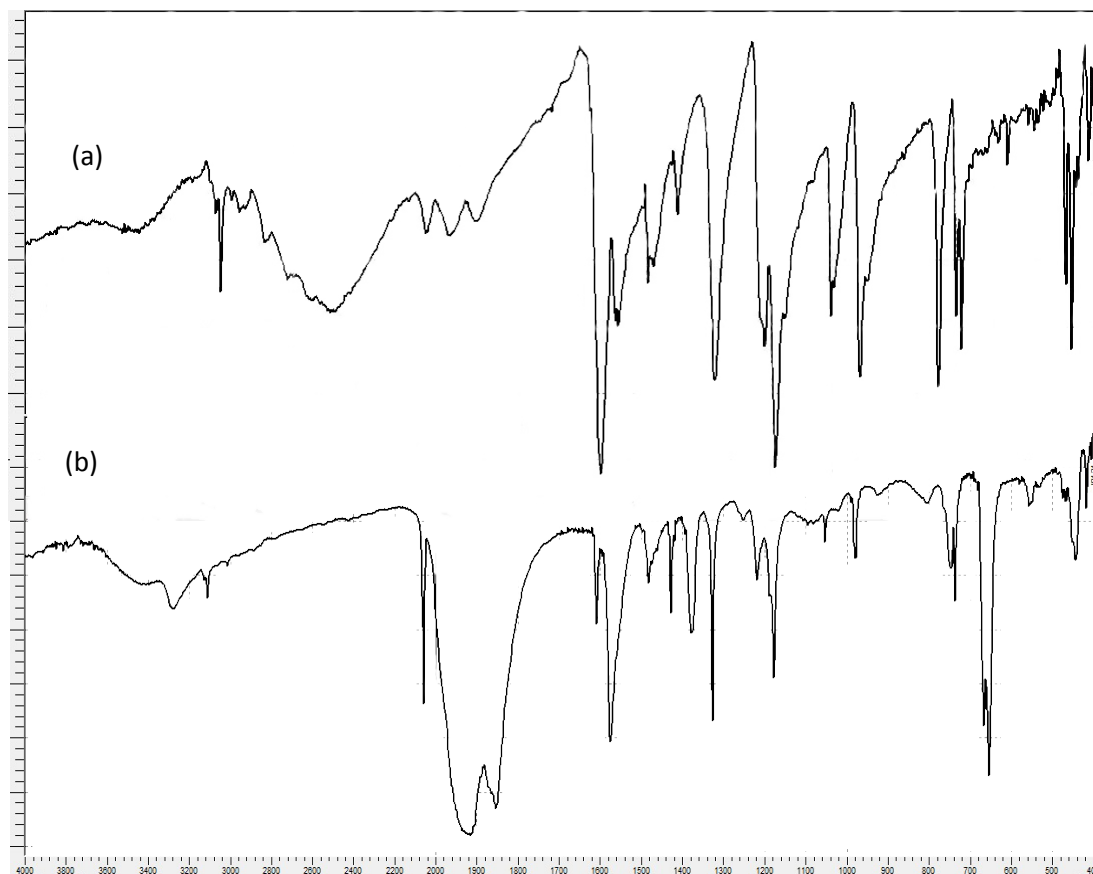


Figure 4.1.2.5 : The IR spectrum of a) 2-mercaptopyrimidine and b) $[\text{Cr}(\text{CO})_5$ 2-mpm] dispersed in KBr pellet.

The appearance of the C=S and N-H stretching modes would indicate the existence of the thione tautomer of these complexes in solid state. Furthermore, the absence of the S-H stretching and bending bands in the $850\text{--}900\text{ cm}^{-1}$ region would help to discriminate between the thiol and thione species.

Moreover if the IR spectral data of free 2-mercaptopyrimidine ligand and the metal bonded ligand, the none significant shift the C=S bands (

1213.14 for free ligand , 1219.05 for complex) and N-H modes (3489.34 for free ligand, 3458.48 for complex) would rule out any metal-sulfur coordination.

The IR data analysis of the complexes in aqueous form will be based on first the shift of the stretching frequencies values of the C-N, C=N and the C-S bonds, second on the appearance or disappearance of the stretching frequencies of S-H, N-H, C-S and C=S bonds. Therefore we would like to discuss each bond frequency separately as will be given down.

4.1.2.1. C-N and C=N Bond Stretching Frequencies

Assignments of C-N stretching frequencies depends on the difference in their positions from those for free ligand and metal coordinated ligand. C-N and C=N stretching frequencies of the free ligand are shown at 1433.20 cm^{-1} and 1550.82 cm^{-1} respectively (Table 4.1.2.1.1.)

If we compare the stretching frequencies of these bonds of the free ligand to those of the coordinated ligand (C-N at 1427.37 cm^{-1} , C=N at 1550.82 cm^{-1}) one can easily observe a very small shift of these stretching frequencies indicating a weak metal-nitrogen bond through one of the nitrogen lone pairs at the pyrimidine ring.

Table 4.1.2.1.1. The IR data of free ligand and metal coordinated ligand in dichloromethane solution.

	2-mercaptopyrimidine	Cr 2-mpm	Mo 2-mpm	W 2-mpm
Vibration Modes	Experimental (CH ₂ Cl ₂)	Experimental (CH ₂ Cl ₂)	Experimental (CH ₂ Cl ₂)	Experimental (CH ₂ Cl ₂)
	Band, cm ⁻¹	Band, cm ⁻¹	Band, cm ⁻¹	Band, cm ⁻¹
v(N-H)	-----	-----	-----	-----
v(C-H) asym	3070.78	3055.35	3051.49	3070.78
v(C-H) sym	2987.84	2982.05	2980.12	2991.69
v(N-H-S)transition	2831.60	2831.60	2831.60	2829.67
v(CO)	-----	2054.26	2054.26	2054.26
v(CO)	-----	1969.39	1969.39	1932.74
v(CO)	-----	1932.74	1938.52	-----
v(C=C)	1604.83	1604.83	1604.83	1600.97
v(C=N)	1550.82	1550.82	1550.82	1550.82
v(C-N)+δ(C-H)+δ(N-H)	1433.20	1427.37	1427.37	1431.23
v(C=S)	1157.33 w	1155.40, 1243.16 w	1157.40, 1244.13 w	1157.33 w
ring stretching	985.66 s	987.59	985.66	987.59
v(S-H)	895.00	895.00	895.00	898.86
v(C=S), β(C=S)	457.14	455.22	453.29	457.14

From the previous discussion in section 4.1.2.1. one can conclude easily that the metal atoms coordinated to the 2-mercaptopyrimidine ligand through one of the sp² nitrogen lone pairs of the pyrimidine ring.

4.1.2.2 S-H, N-H, C-S, C=S Stretching Frequencies

As it is mentioned before, in the infrared spectra of prepared complexes characteristic vibrational frequency of the thiol and thione forms more complicated to understand due to intermolecular N---HS or NH---S bonding. The full scaled spectrum of $[\text{W}(\text{CO})_5 \text{ 2-mpm}]$ in dichloromethane is given as example in Figure 4.1.2.3.1.

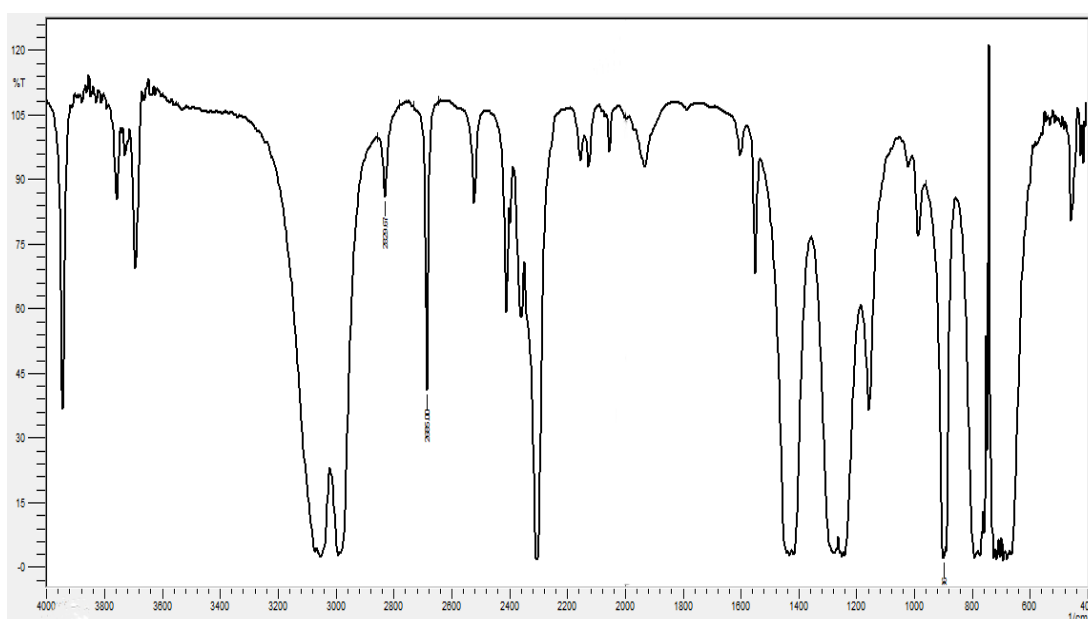


Figure 4.1.2.2.1. The full scaled spectrum of $[\text{W}(\text{CO})_5 \text{ 2-mpm}]$ in dichloromethane.

There is an uncertainty about the band observed at 2685 cm^{-1} to be belonging to S-H stretching or not. Because the $2400\text{--}2700 \text{ cm}^{-1}$ region was searched over a wide concentration range, but in none of the solvent system was it possible to identify as assignable S-H band above background noise.

In compounds containing a C=S group adjacent to a C-N or C-O group, there may be interactions between the stretching vibrations of the groups that may produce new frequencies in unexpected regions of the spectrum.

The discussion of N-H vibrational frequency in the IR spectra of the prepared complexes is another important point to decide which tautomer is favoured in aqueous solution. This state depends on the appearance of the stretching frequency that is expected to appear as a broad band at 3450-3490 cm^{-1} .

This tautomerization mechanism is unknown but it is thought to arise from hydrogen migration. The hydrogen migration is more susceptible to form tautomers. Usually the nitrogen atoms with larger value of net charges accept proton shifts more easily. The proton transfer site of 2-mercaptopyrimidine is predicted to be the main basic centre in accordance with the negative charge distribution on heteroatoms. The appearance of the peak at around 2830 cm^{-1} could show the formation of the unfavoured N---H---S transition complex.

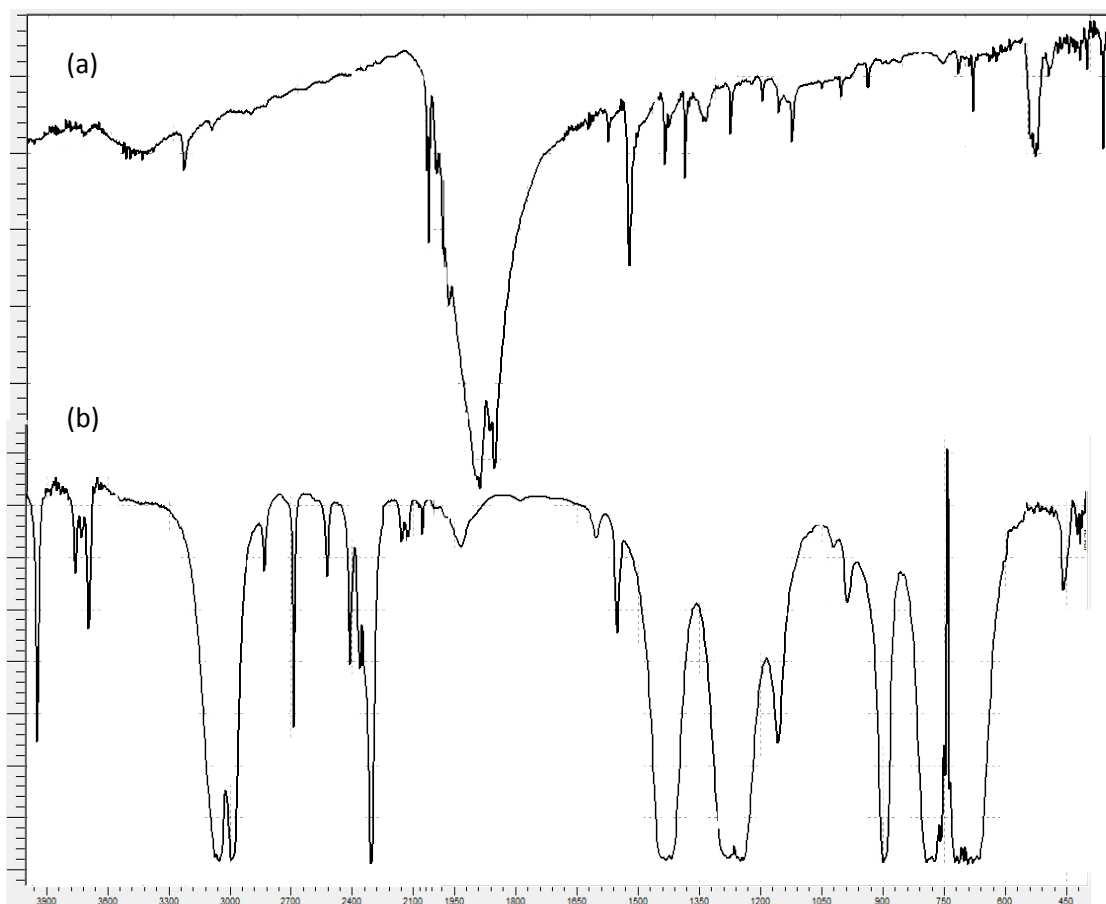


Figure 4.1.2.2.2: The IR spectrum of a) $[\text{W}(\text{CO})_5 \text{ 2-mpm}]$ dispersed in KBr pellet b) in CH_2Cl_2 solution.

If we compare the IR spectra of the $\text{W}(\text{CO})_5 \text{ 2-mpm}$ and $\text{Mo}(\text{CO})_5 \text{ 2-mpm}$ complexes solid and aqueous forms it can easily notice that stretching and bending bands of the N-H bond disappear in the IR spectra of the complexes obtained from their dichloromethane solution.

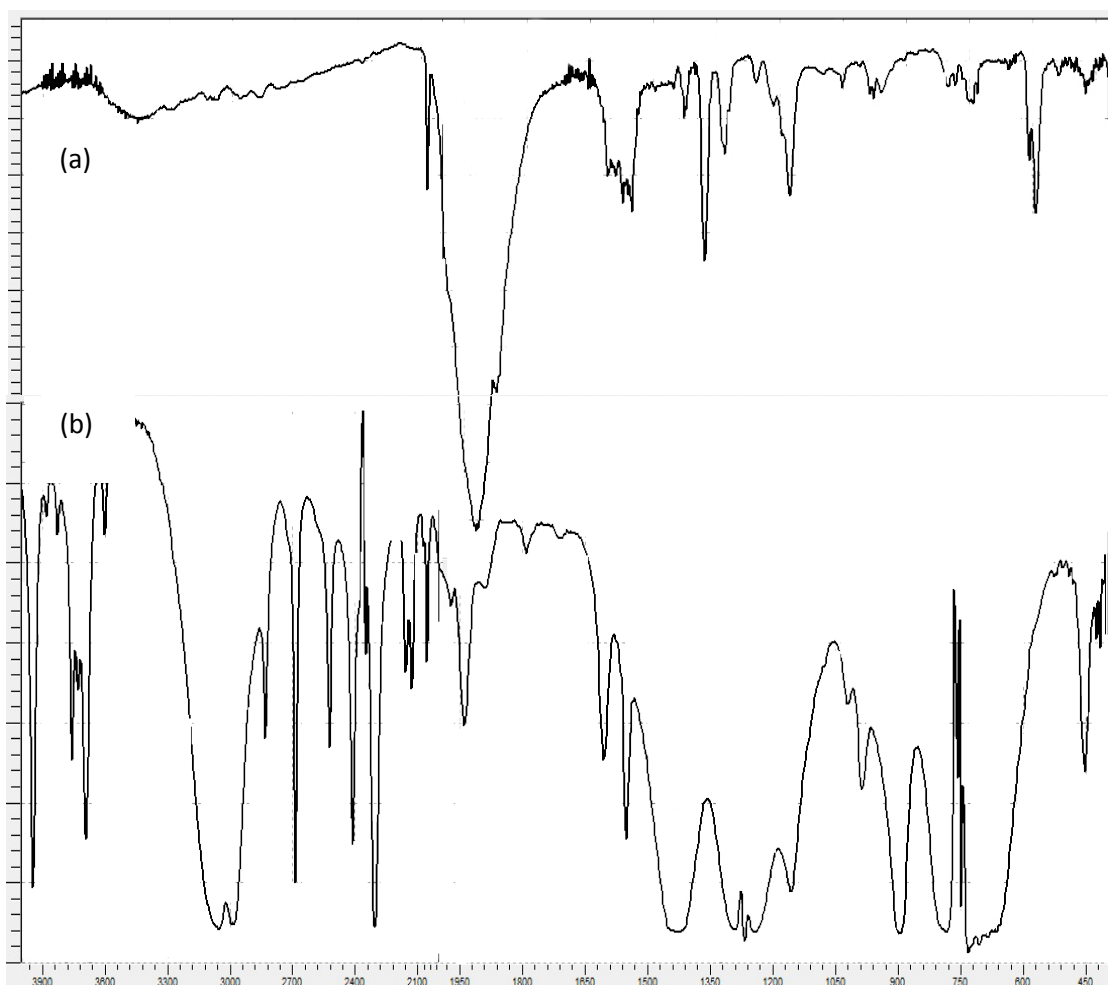


Figure 4.1.2.2.3 : The IR spectrum of $[\text{Mo}(\text{CO})_5 \text{ 2-mpm}]$ a) disperses in KBr pellet b) in CH_2Cl_2 solution.

And this discussion can be supported by the appearance of the S-H band vibration mode that is appeared as strong mode at $895\text{-}900 \text{ cm}^{-1}$. The discussion of the IR data in this section could easily implies that both free ligand and coordinated ligand are exist in the thiol form.

On the other hand, the IR spectrum of pentacarbonyl chromium(0) complex, $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$, recorded from its dichloromethane solution show the appearance of the typical stretching vibration mode of the N-H bond at 3465.55 cm^{-1} as a broad band (Figure 4.1.2.2.4).

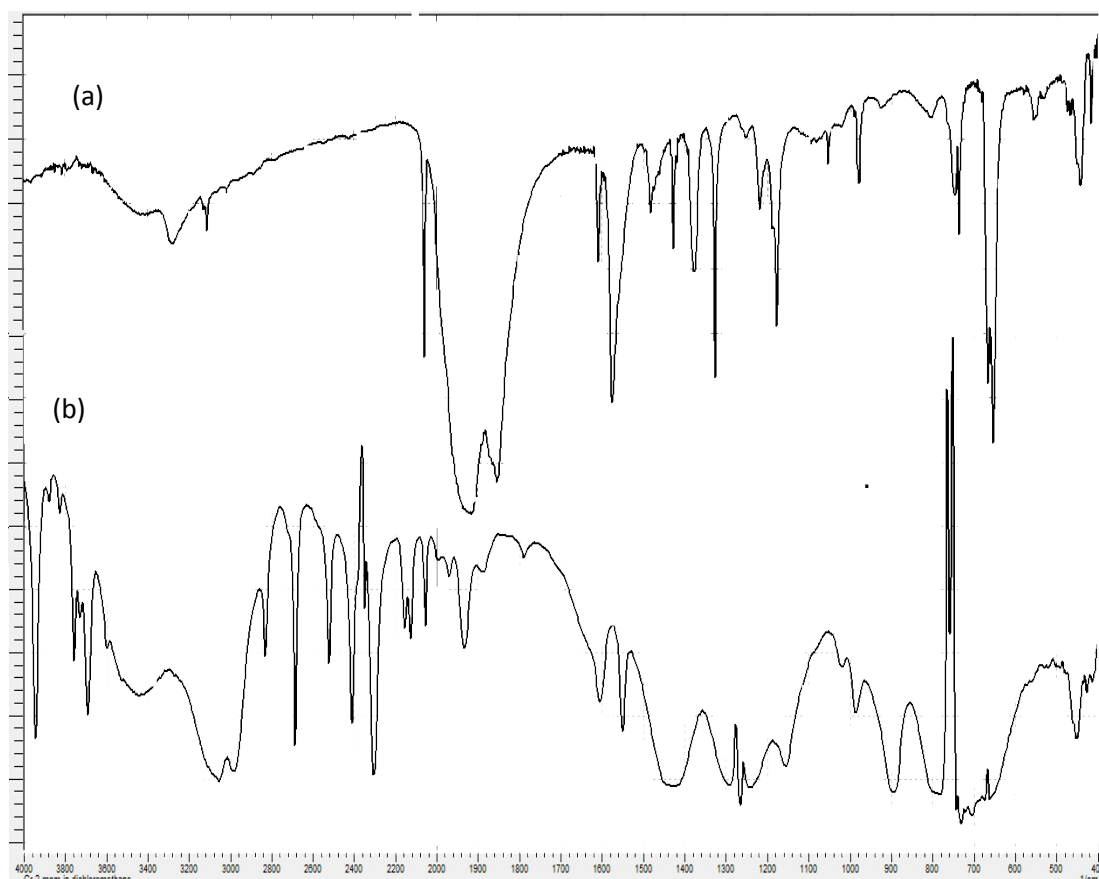


Figure 4.1.2.2.4 : The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ a) disperses in KBr pellet b) in CH_2Cl_2 solution.

The appearance of the N-H stretching vibration at 3465.55 cm^{-1} and also the S-H bending vibration mode that is appeared as strong mode at 895.00 cm^{-1} implies that both the thiol and thione tautomeric forms are exist at the same time in dichloromethane solution. As a consequence, It has

been confirmed that the thione form dominates in the solid state, together with the importance of the solvent in shifting the tautomeric equilibrium, the thiol tautomeric formation in liquid phases rather than thione tautomer.

4.2. Thermal Analysis

Thermal analysis of the prepared complexes were performed using SII EXSTAR 600 TG/DTA 6300 thermogravimetric analyser. As example for these complexes the TGA/DTA curve of pentacarbonyl(2-mercaptopyrimidine) chromium(0) is given Figure 4.2.1.

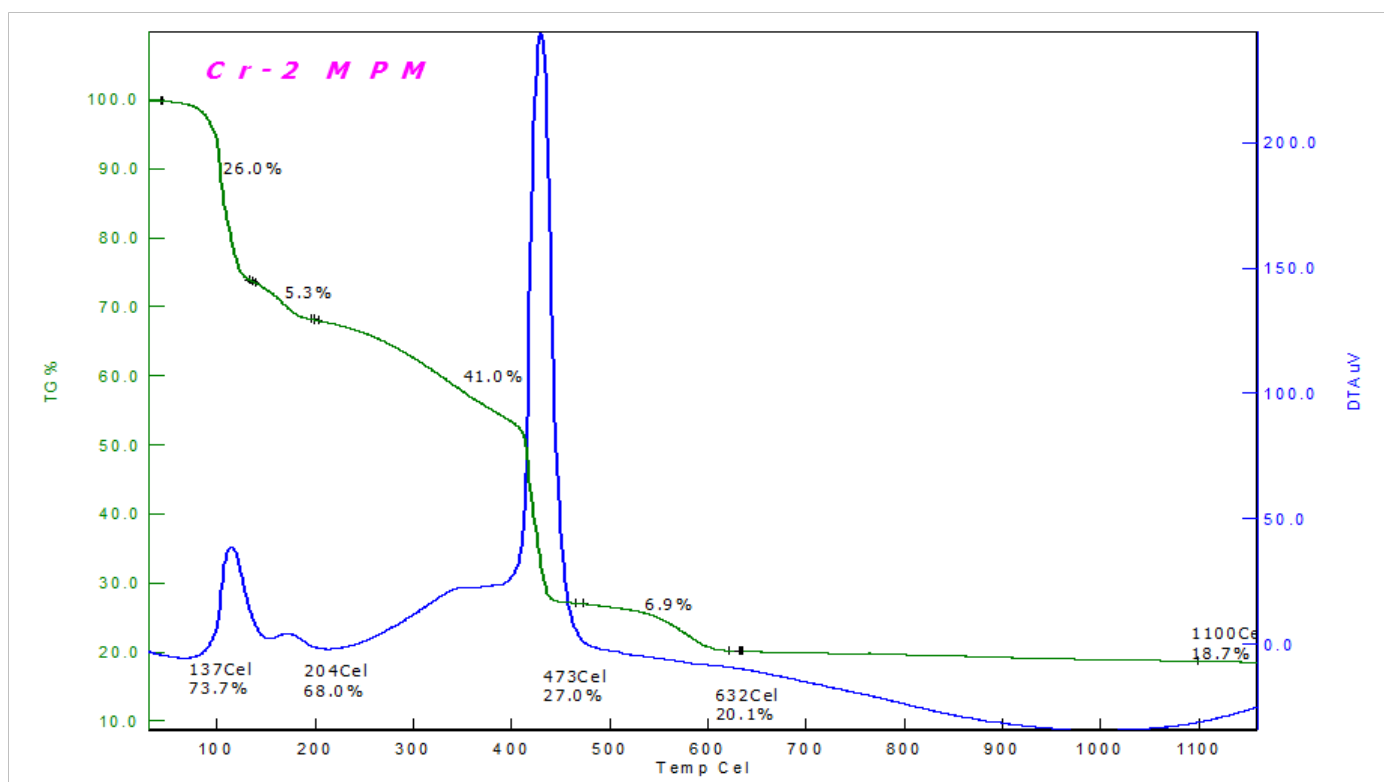


Figure 4.2.1. The TGA/DTA curve of pentacarbonyl(2-mercaptopyrimidine) chromium(0) complex.

Analysis of the given spectrum based on percentages of the decompose groups from the molecule at different temperature intervals. Moreover, the IR spectra of the complex at these temperature are also given in Figure 4.2.2. and Figure 4.2.3.

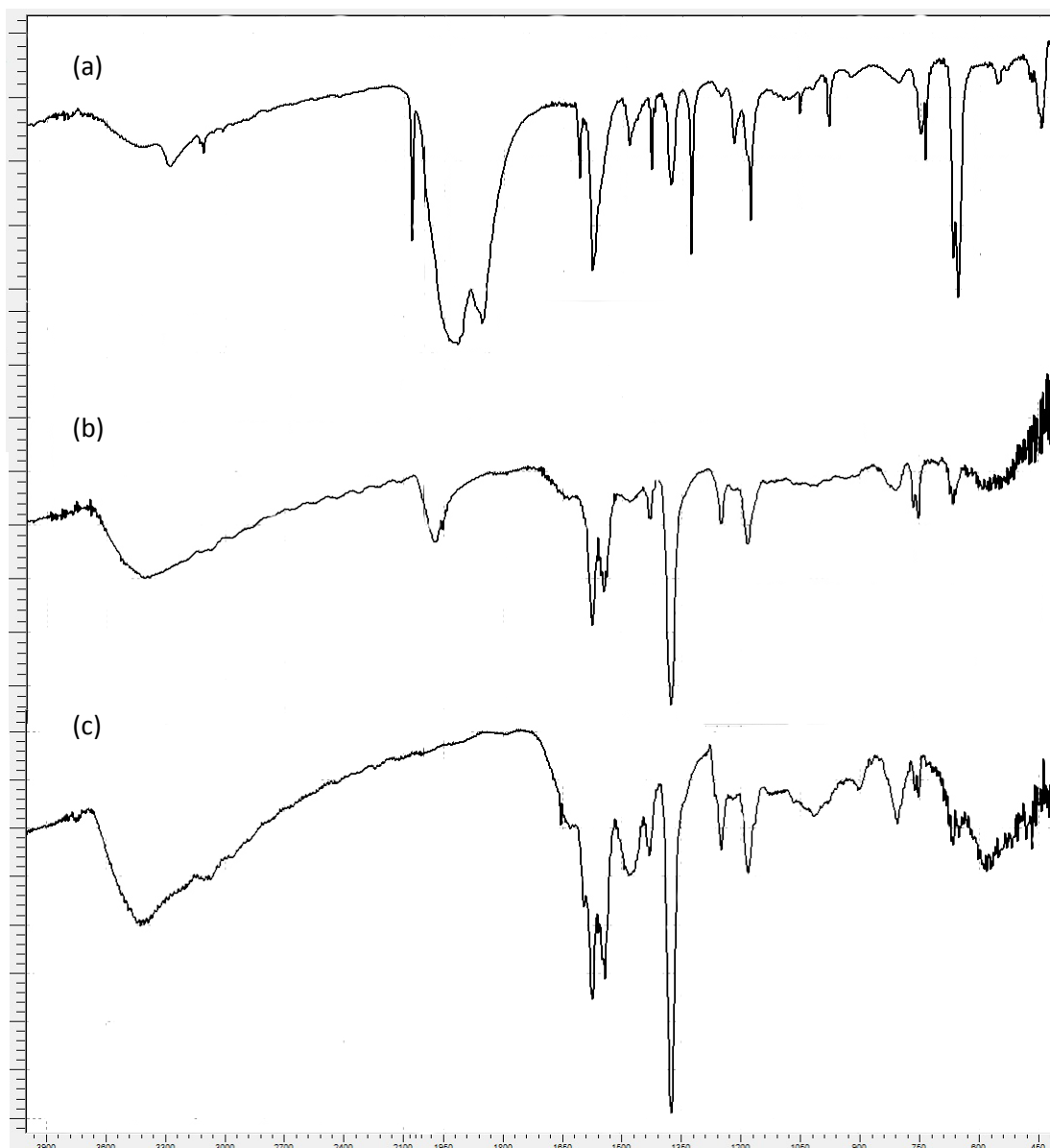


Figure 4.2.2. The IR spectra of pentacarbonyl(2-mercaptopyrimidine) chromium(0) complex (a) at 25, (b) at 135 and (c) at 205 ° C.

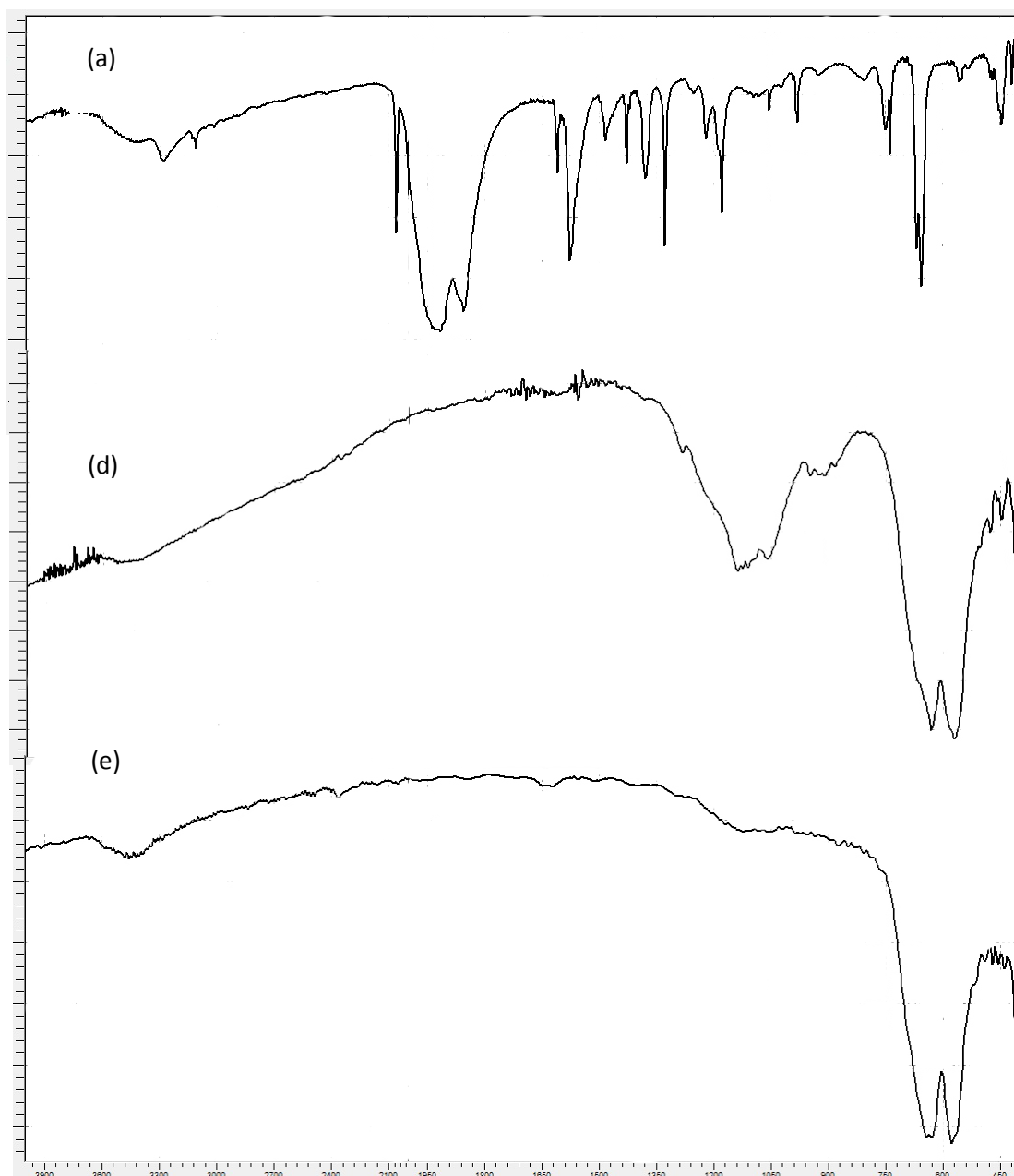


Figure 4.2.3. The IR spectra of pentacarbonyl(2-mercaptopyrimidine) chromium(0) complex (a) at 25, (d) at 473 and (e) at 631 ° C.

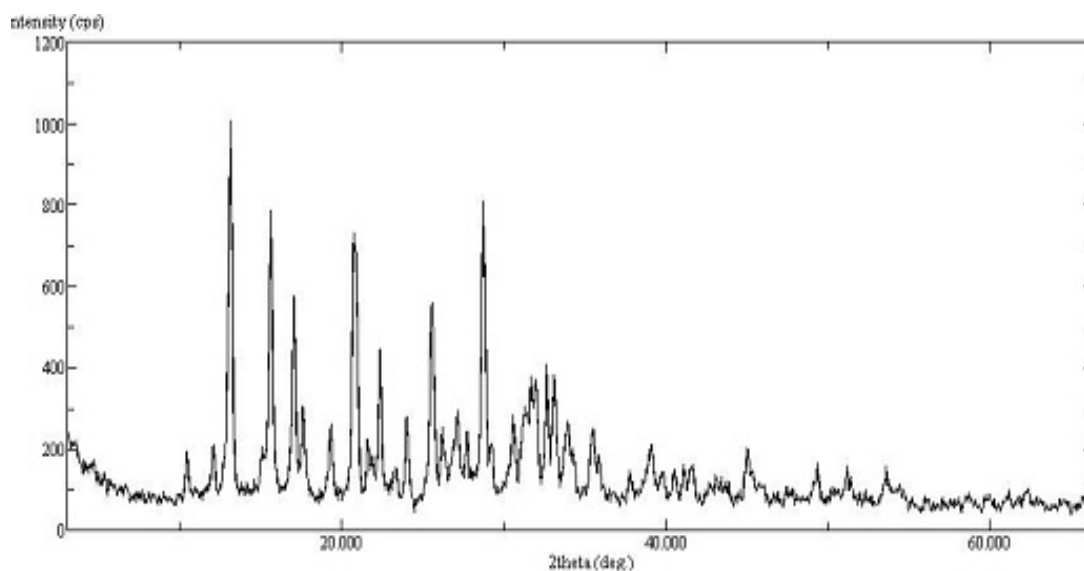


Figure 4.2.4 : The XRD pattern of the $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ at 25 °C.

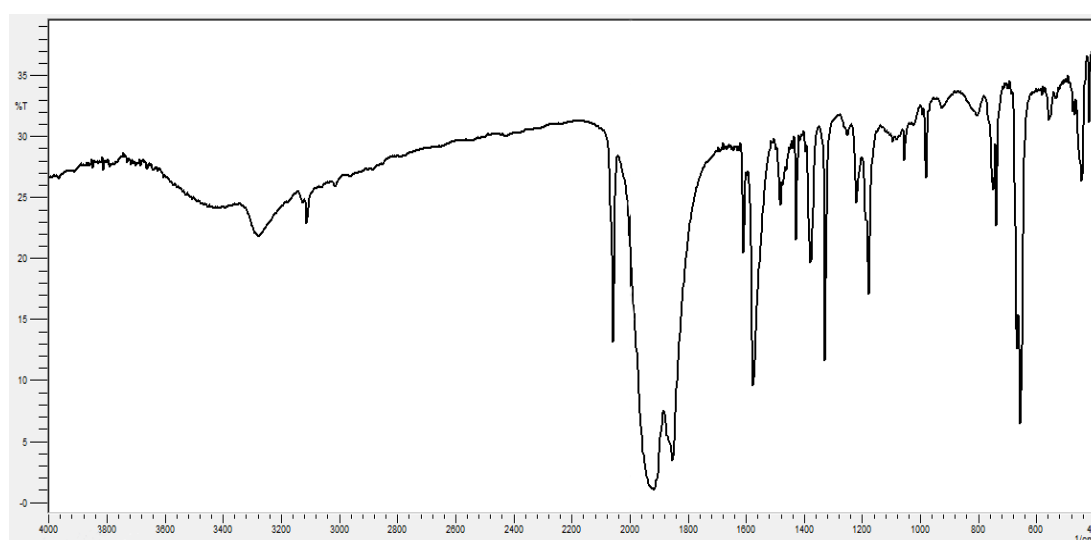


Figure 4.2.5 : The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ at 25 °C.

The first decomposition step occurs in the temperature range 25-135 °C with a net weight loss of 26 %. This step could be attributed to the decomposition of aromatic ligand and some of the CO groups from the molecule. The XRD pattern at 25 °C indicates the formation of crystalline form of the molecule meanwhile the XRD pattern at 135 and 205 °C amorphous pattern are observed.

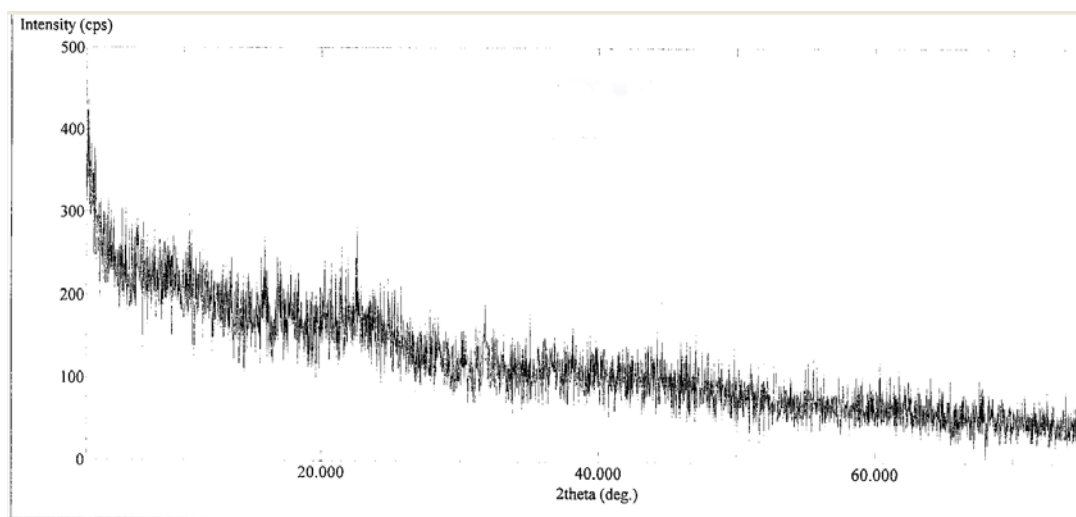


Figure 4.2.6 : The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of $25\text{ }^{\circ}\text{C}$ - $135\text{ }^{\circ}\text{C}$.

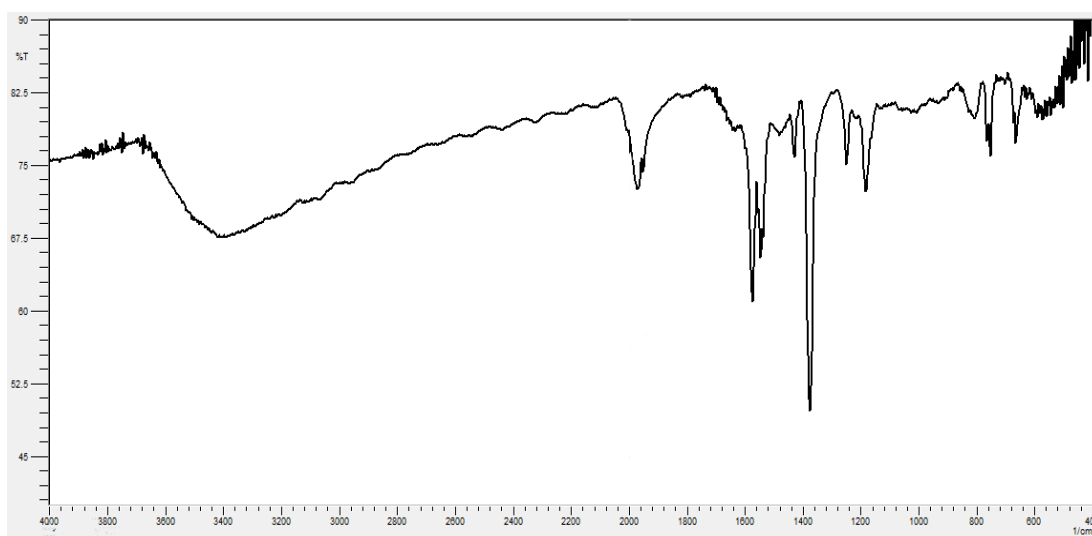


Figure 4.2.7 : The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of $25\text{ }^{\circ}\text{C}$ - $135\text{ }^{\circ}\text{C}$.

The second weight loss could be best confirm by comparing the IR spectrum at room temperature with at $135\text{ }^{\circ}\text{C}$. One can easily show the disappearance of 2CO peaks at 1932.74 and 2054.26 and C=C bond peak at 1604.83 . In addition, the C-H stretching band at 2982.05 cm^{-1} has also

disappear from the spectrum confirming the 26 % weight loss assigned to from TG/DTA data.

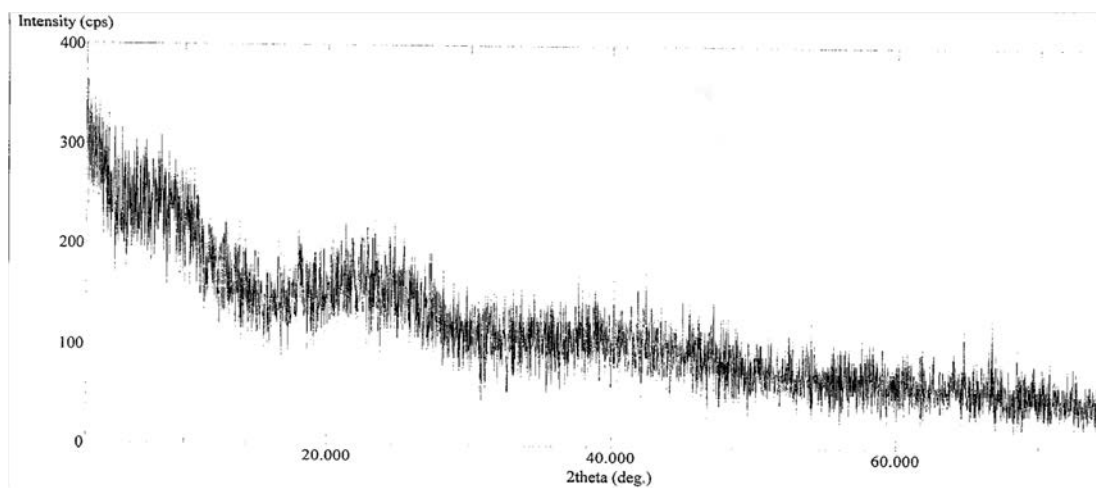


Figure 4.2.8 : The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 135°C - 205°C .

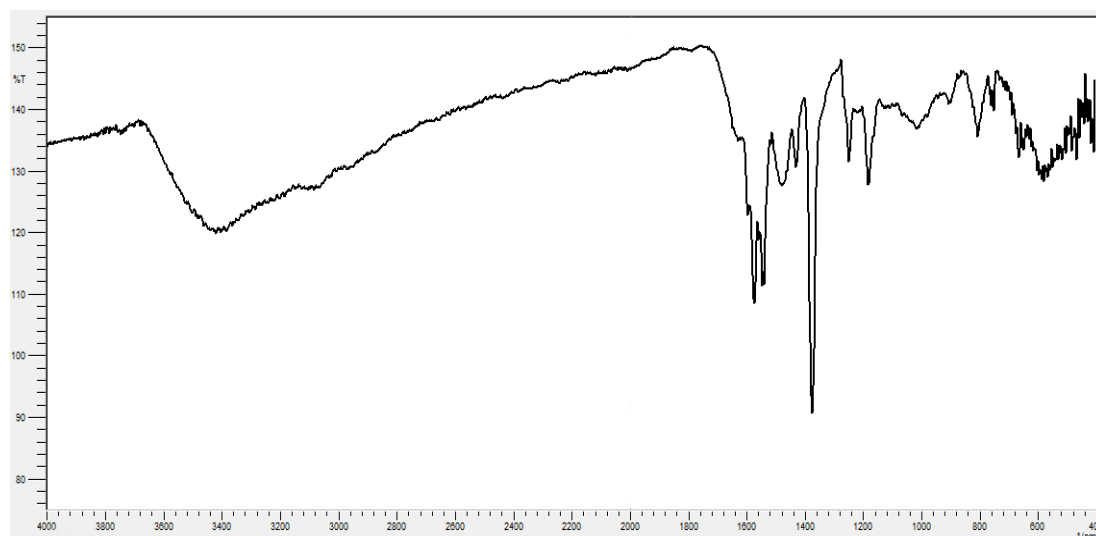


Figure 4.2.9 : The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 135°C - 205°C .

The second decomposition step at 205-473 °C is attributed to the weight loss 41 % of the molecule which indicate the decomposition of all CO, C=C, C-C, C-H, S-H, C-S groups at this temperature.

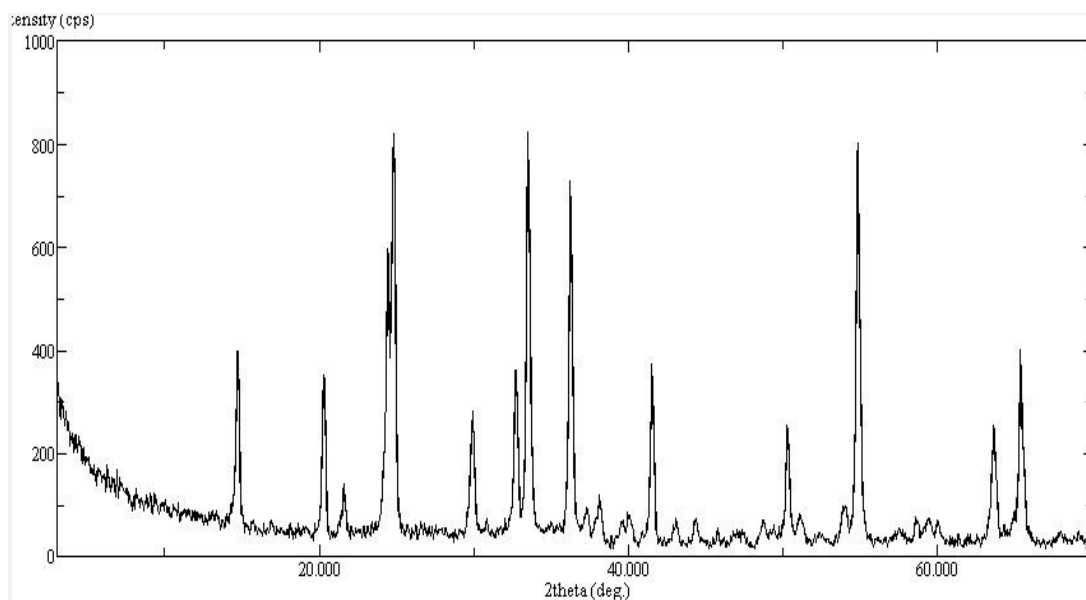


Figure 4.2.10 : The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 205°C-473°C.

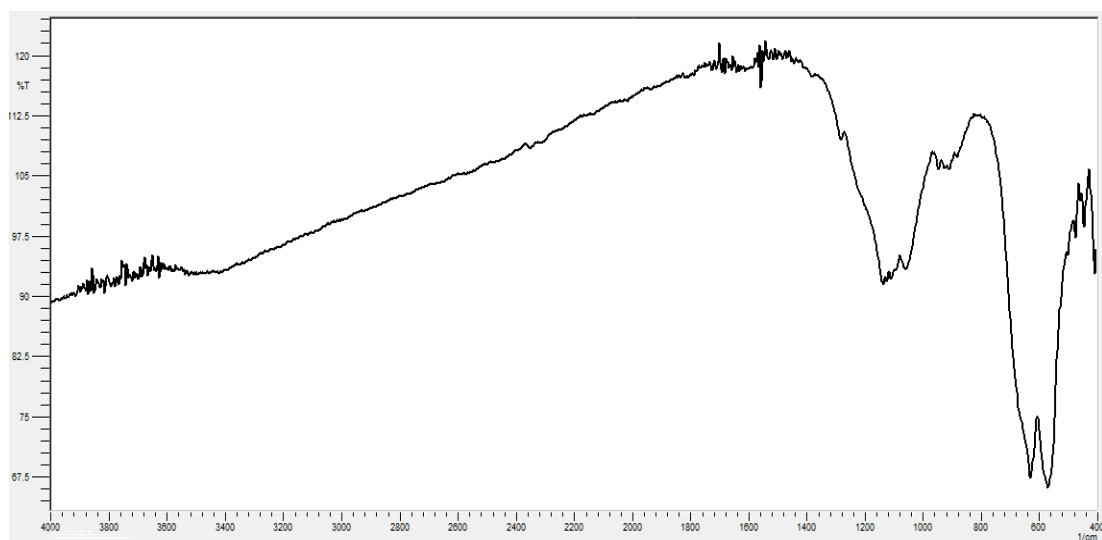


Figure 4.2.11 : The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 205°C-473°C.

If we examine the IR spectrum taken at 473 °C we could easily observe the disappearance of the IR bands of these groups.

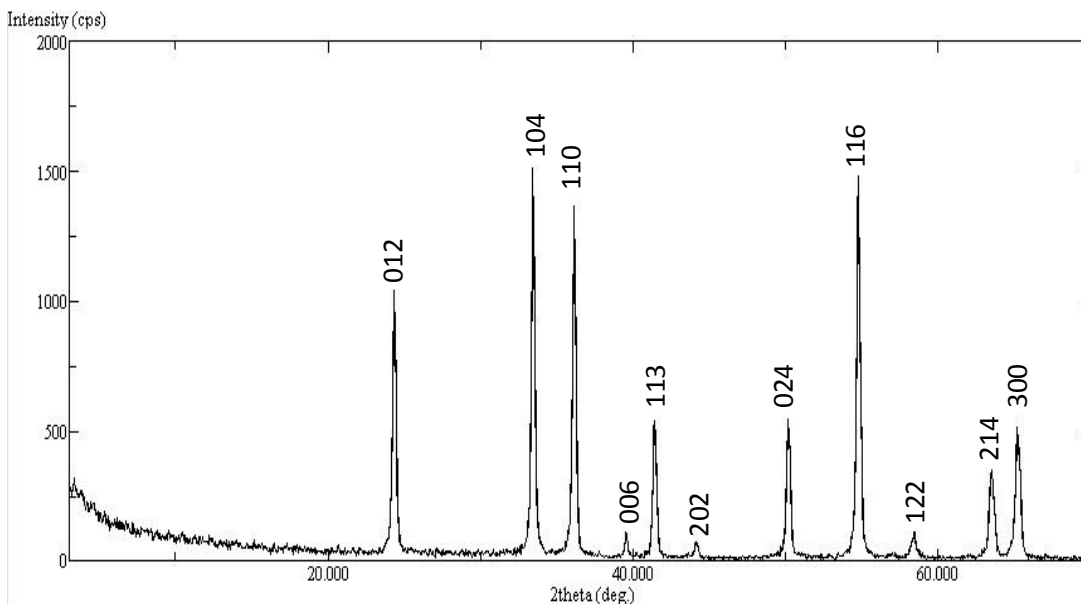


Figure 4.2.12 : The XRD pattern of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 473°C-631 °C.

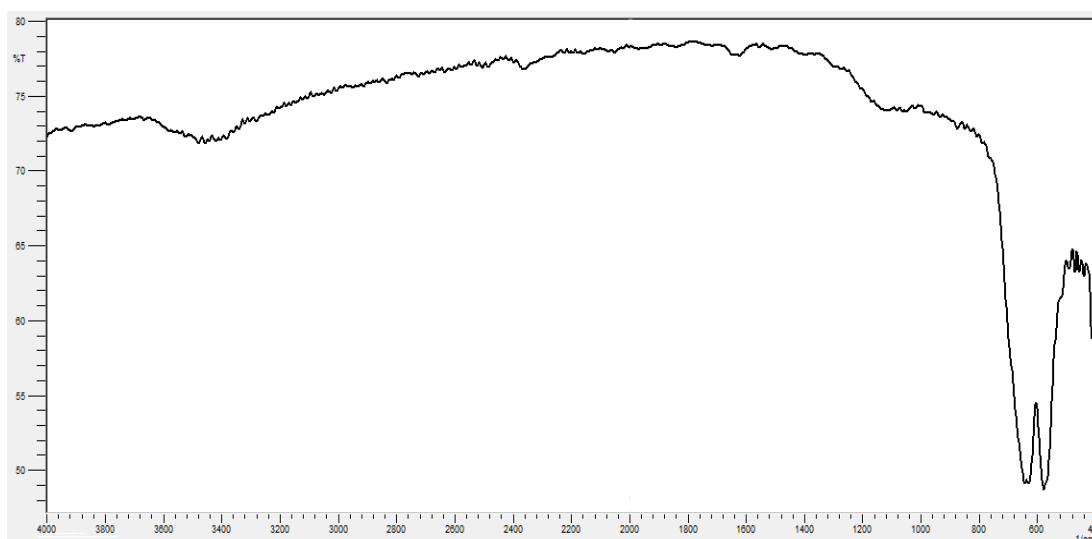


Figure 4.2.13 : The IR spectrum of $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$ after heating in the range of 473°C-631 °C.

The last the decomposition step at 473-631 °C indicate the formation of Cr_2O_3 only. This could be also confirms by examining the IR spectrum at

631 °C as shown in Figure I. The XRD of the molecule recorded at 631 °C can also implies the formation Cr_2O_3 crystalline pattern.(ICDD No: 38-1479)

Table 4.2.1. Thermal decomposition of $[\text{Cr}(\text{CO})_5$ 2-mercaptopyrimidine] complex.

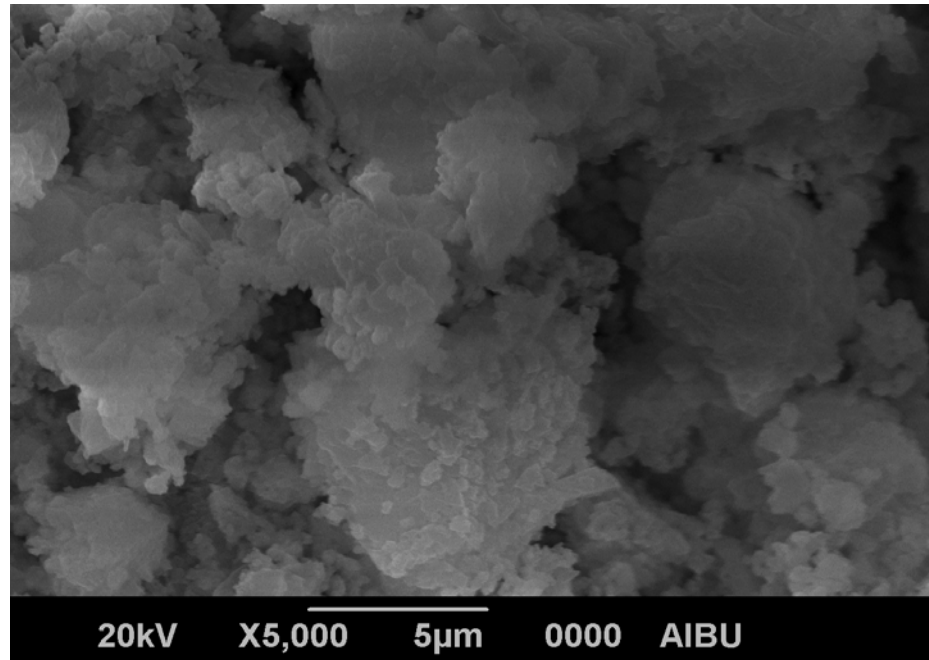
Decomposition Temperature	Lost Amount (%)	Sample Amount (%)	Lost Molecular Weight (g/mol)
0-136	26.1	0.834	79.39
136-205	5.7	0.182	17.34
205-473	41.0	1.311	124.73
473-631	6.9	0.221	20.99

4.3. SEM Micrograph of the Complexes

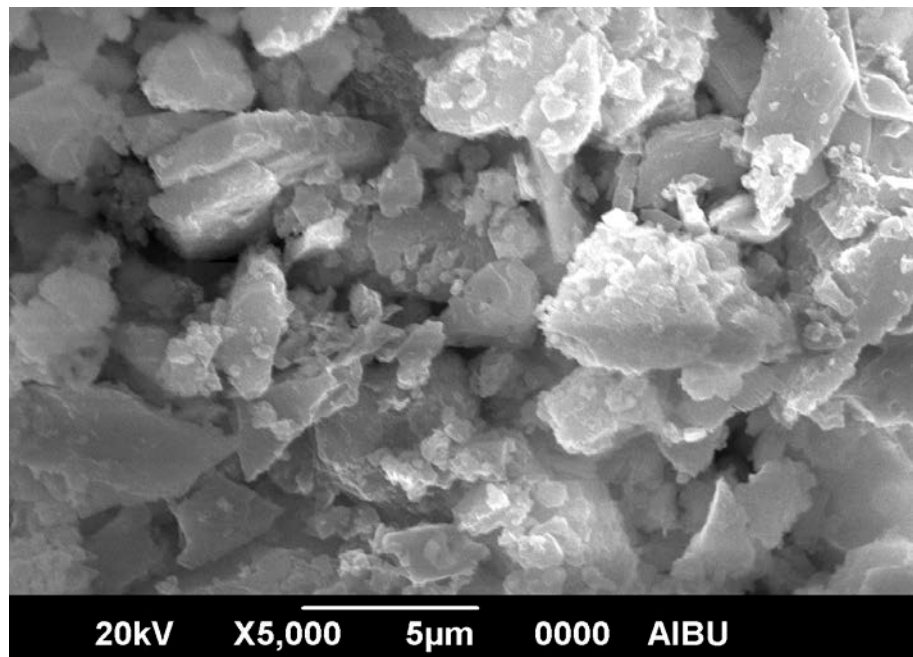
The surface morphology and grain connectivity of the freshly fractured surface of the complexes are studied by using scanning electron microscope (SEM) JEOL 6390-LV, operated at 20kV in the secondary electron image (SEI) mode with a resolution power of 3 nm.

The surfaces of the films are imaged by Scanning Electron Microscopy (SEM) technique. Figure 4.3.1 indicates the SEM pictures (taken in the secondary electron image mode) of the fractured surface of all the complexes. The texturing of the Cr sample are found to be better compared to the other samples and the surface of the sample is more uniform with better alignment of grains. Additionally, SEM image of the Cr complex exhibits a broad grain size distribution and the best crystallinity in comparison with the others.

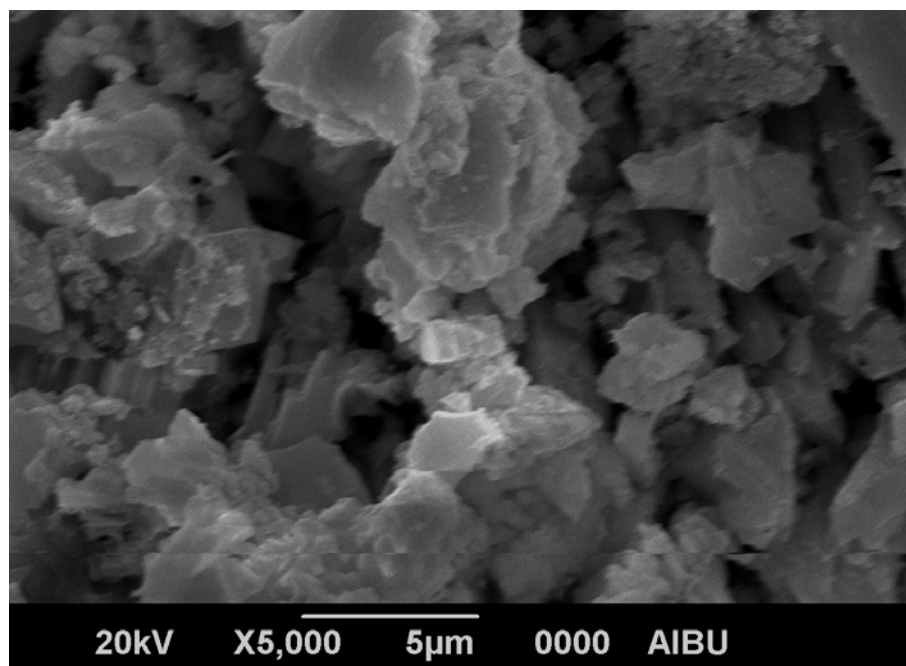
According to the results of the SEM measurements, the Cr sample has the largest average crystallite size, lowest porosity, best crystallinity (densest and smoothest) and grain connectivity, supported by the XRD patterns.



(a)



(b)



(c)

Figure 4.3.1 : The SEM micrograph of the complexes; (a) $[\text{Cr}(\text{CO})_5 \text{ 2-mpm}]$, (b) $[\text{Mo}(\text{CO})_5 \text{ 2-mpm}]$, (c) $[\text{W}(\text{CO})_5 \text{ 2-mpm}]$.

On the other hand, there are voids and signs of partial melting on the SEM micrographs of the other samples (Mo and W).

4.4. Computational Details

Density functional theory (DFT) is a theory of electronic structure, based on the electron density distribution $n(r)$, instead of the many-electron wavefunction $\Psi(r_1, r_2, r_3, \dots)$. Having been widely used for over 30 years by physicists working on the electronic structure of solids, surfaces, defects, etc. , it has more recently also become popular with theoretical and computational chemists.

Density functional theory (DFT) is primarily a theory of electronic ground state structure, couched in terms of the electronic density distribution $n(r)$. Since its birth, about three decades ago, it has become increasingly useful for the understanding and calculation of the ground state density, $n(r)$ and Energy, E , of molecules, clusters, and solids any system consisting of nuclei and electrons with or without applied static perturbations. It is an alternative, and complementary, approach to the traditional methods of quantum chemistry which are couched in terms of the many electron wavefunction $\Psi(r_1, \dots, r_N)$. Both Thomas- Fermi and Hatree- Fock- Slater methods can be regarded as ancestors of modern DFT. But whereas those theories are intrinsically approximate, modern DFT is in principle exact [102].

Quantum chemical calculations which utilize density functional theory are now perhaps amongst the most frequently performed because of their relatively low cost and accuracy, especially as result obtained from DFT based methods are often as good as those derived from MP2 calculations [103-107].

Recent development in density functional theory has shown that DFT may become a powerful computational alternative to the conventional quantum chemical methods [108]. The computational efficiency and accuracy of the DFT methods have been very well documented by their applications to variety of chemical problems and chemical system including transition-metal complexes [109]. Success of ECP (effective core potentials) in the calculation of geometries and energies of molecules containing transition metal

complexes is well documented [110,111] and their use in conjunction with density functional theory is also found to be adequate [112-114].

In this work, we examine the general applicability of DFT methods to the prediction of vibrational frequencies, transition states, NMR shift values of the 2-mercaptopyrimidine ligand and pentacarbonyl(2-mpm) metal(0) , M; Cr, Mo, W complexes using readily available DFT methods and basis sets. For the optimization of the molecules B3PW91[115-118] , B3LYP [119-121] and MPW1PW91 methods were used at 6-311G(d,p), 6-31G(2d), 6-31(d,p) [122-126] basis set levels to obtain more accurate results.

All the computational calculations were performed using Gauss-View(Gauss-view serial number; GV52967189W-5042N) molecular visualization program [127] and Gaussian 03(Gaussian 03 Single CPU serial number; PC99997441W-5042N) program package [128] on the personal computer.

It is known that computational studies of sulfur-containing compounds often show large basis set effects [129-132]. In this study the DFT hybrid functionals B3LYP, B3PW91 give similar predictions of molecular parameters and relative energies and the results from B3PW91 is the most consistent and efficacious. The usefulness of B3PW91 to describe the tautomeric equilibrium of 2-mercaptopyrimidine in solution has been reported [98] and it has also been observed that B3PW91 performs much better than BLYP and

B3LYP in a study of the interaction energies of Van der Waals and hydrogen bonded systems [133].

The DFT model was treated according to Becke's three parameters gradient corrected Exchange potential and the Lee-Yang-Parr gradient corrected correlation potential (B3LYP), Perdew and Wang's 1991 gradient-corrected correlation functional (Perdew/ Wang 91, B3PW91) and computations have been done by adding polarization function d and diffuse function on heavy atoms [134]. Gaussian visualization program were also used for the simulating the HOMO and LUMO figures of the molecule.

4.4.1. Vibrational Frequencies

Vibrational spectroscopy is of utmost importance in many areas of chemical research and the application of electronic structure methods for the calculation of harmonic frequencies has been of great value for the interpretation of complex experimental spectra. Numerous unusual molecules have been identified by comparison of computed and observed frequencies.

The computational prediction of vibrational spectra is among the important areas of application for modern quantum chemical methods because it allows the interpretation of experimental spectra and can be very instrumental for the identification of unknown species. The pioneering comprehensive study of monometal carbonyls by Jonas and Thiel, 1995, was

probably the first devoted to the computation of vibrational spectra for such compounds using density functional theory.

A vibrational spectrum could be consist of two characteristics, the frequency of the incident light at which the absorption occurs and how much of the radiation is observed. The first quantity can be obtained computationally by calculating the harmonic vibrational frequencies of a molecule [135]. To obtain spectroscopic signature of pentacarbonyl(2-mercaptopyrimidine) metal(0) complexes a frequency calculation analysis have been performed. B3PW91/ 6-311G, B3PW91/6-31G, B3PW91/SDD, and 6-311G^a methods were used for vibrational ferquencies. Then all scaled frequencies have been compared with experimantal values.

All compared data have been shown to have in a good agreement with each other [Table 4.4.1.1.]. Moreover, the correlation coefficients (R^2) between experimental data and computational data have been shown to be in good agreement to each other, eventhough the best calculated results were determined for the B3PW91/6-311G^a method and basis set.

Table 4.4.1.1. Selected experimental and calculated vibrational modes of pentacarbonyl(2-mercaptopyrimidine) W(0) complex.

Vibrations Modes	Pentacarbonyl(2-mercaptopyrimidine W(0))			
	Experimental	B3WP91/6-311G ^a	B3WP91/ 6-311G	B3PW91/6-311G
Band, cm ⁻¹	Solid	Vacuum	Vacuum	Vacuum
$\nu(\text{N-H})$	3489.34	3612,43	3609.36	3601,72
$\nu(\text{C-H})$ asym	3244.38	3257,15	3298.61	3239,49
$\nu(\text{C-H})$ sym	3111.28	3215,25	3273.03	3235,14
$\nu(\text{CO})$	2069.69	2076,48	2042.69	2012,39
$\nu(\text{CO})$	1919.24	2027,03	1965.67	1931,29
$\nu(\text{CO})$	1878.73	2022,42	1931.42	1893,04
$\nu(\text{C}=\text{C})$	1604.83	1604,35	1604.87	1639,35
$\nu(\text{C}=\text{N})$	1566.25	1458,92	1515.79	1508,06
$\nu(\text{C}=\text{N})+\delta(\text{C-H})+\delta(\text{N-H})$	1421.58	1353,71	1472.45	1465,99
$\nu(\text{C-N})$	1311.64	1259,71	1362.94	1351,63
$\nu(\text{C}=\text{S})$	1165.04-1236.41	1221,64	1217.15	1206,54
ring stretching	981.80	1006,00	1002.79	1006,61
$\delta(\text{N-H})$	731.05	729,04	754.73	790,90
$\nu(\text{C}=\text{S}), \beta(\text{C}=\text{S})$	412.78	439,87	413.50	403,23

4.4.2. Atomic Charges

Atomic charges of pentacarbonyl(2-mercaptopyrimidine) metal(0) complexes calculated by Mulliken method [136,137] at the B3LYP/6-31G, B3PW91/SDD and B3PW91/6-311G^a levels of calculation. All obtained magnitudes are in good agreement with each other. The magnitudes of the carbon atomic charges are found to be either positive or negative at the basis set. Moreover, carbon atoms connected to metal atom have the maximum charge magnitudes at calculation levels. Atomic charges for optimized geometry of pentacarbonyl(2-pyrimidinethiol) W(0) and pentacarbonyl(2-pyrimidinethiol) Cr(0) complexes are shown Table 4.4.2.1.

Table 4.4.2.1. Atomic charges for optimized geometry of pentacarbonyl(2-mercaptopyrimidine chromium(0) and pentacarbonyl(2-mercaptopyrimidine) tungsten(0) complexes.

Atom	Cr(CO) ₅ 2pythiol		W(CO) ₅ 2-pythiol	
	Muliken	NBO	Muliken	NBO
M12	0.0671	-2.3353	0.6061	-1.7907
C13	0.1799	0.8819	0.0814	0.7625
O14	-0.2159	-0.4674	-0.2101	-0.4528
C20	0.1799	0.8819	0.0814	0.7625
O21	-0.2159	-0.4674	-0.2101	-0.4528
C17	0.2338	0.8915	0.0668	0.7561
O18	-0.2532	-0.4977	-0.2511	-0.4930
C19	0.1720	0.8695	0.0786	0.7551
O22	-0.2133	-0.4692	-0.2080	-0.4548
C15	0.1720	0.8695	0.0786	0.7551
O16	-0.2133	-0.4692	-0.2080	-0.4548
N1	-0.4521	-0.4135	-0.5213	-0.4540
C2	0.4558	0.3374	0.4754	0.3410
C6	0.0279	0.1349	0.0506	0.1421
N3	-0.3786	-0.5109	-0.3710	-0.5079
C5	-0.3227	-0.2775	-0.3145	-0.2778
C4	0.0103	0.1303	0.0098	0.1338
S10	-0.2971	0.0866	-0.3107	0.0979
H11	0.2824	0.1669	0.2917	0.1668
H8	0.2514	0.2392	0.2533	0.2411
H9	0.2755	0.2122	0.2745	0.2172
H7	0.2541	0.2064	0.2565	0.2075

4.4.3. Molecular Geometry

The molecular structure of pentacarbonyl(2-mercaptopyrimidine) metal(0) is shown in Figure 4.4.3.1. and Figure 4.4.3.2. along with labeling. The calculated bond length and bond angle of thiol form of the pentacarbonyl(2-mercaptopyrimidine) Cr(0) complexes are given in Table 4.4.3.1. and Table 4.4.3.2. at different basis set levels.

Table 4.4.3.1. The optimized bond length of pentacarbonyl(2-mercaptopyrimidine) chromium(0) at different basis sets.

<i>Bond Length</i>	B3PW91	B3PW91	B3PW91
	6-311G ^a	6-311G	SDD
Cr12-C13	1.8987	1.8909	1.8707
Cr12-C20	1.8987	1.8909	1.8707
Cr12-C17	1.8426	1.8479	1.8259
Cr12-C19	1.9066	1.9021	1.8817
Cr12-C15	1.9067	1.9021	1.8817
Cr12-N1	2.2280	2.1865	2.1753
C13-O14	1.1454	1.1696	1.1795
C20-O21	1.1454	1.1697	1.1795
C17-O18	1.1526	1.1769	1.1868
C19-O22	1.1451	1.1685	1.1784
C15-O16	1.1451	1.1685	1.1784
N1-C2	1.3496	1.3578	1.3662
N1-C6	1.3468	1.3637	1.3696
C2-N3	1.3330	1.3413	1.3503
C2-S10	1.7545	1.8068	1.7987
C6-C5	1.3797	1.3834	1.3930
C6-H9	1.0825	1.0767	1.0810
N3-C4	1.3273	1.3435	1.3487
C5-C4	1.3887	1.3911	1.4029
C5-H8	1.0822	1.0782	1.0818
C4-H7	1.0865	1.0798	1.0843
S10-H11	1.3485	1.3805	1.3716

Table 4.4.3.2. The optimized bond angle of pentacarbonyl(2-mercaptopyrimidine) chromium(0) at different basis sets.

Bond Angle	B3PW91	B3PW91	B3PW91
	6-311G ^a	6-311G	SDD
C13-Cr12-C20	90.773	91.077	90.873
C13-Cr12-C17	88.215	88.237	88.257
C13-Cr12-C15	87.960	87.806	88.027
C13-Cr12-N1	89.819	89.909	90.132
C20-Cr12-C17	88.203	88.233	88.258
C20-Cr12-C19	87.958	87.806	88.025
C20-Cr12-N1	89.829	89.913	90.134
C17-Cr12-C19	87.095	87.305	87.479
C17-Cr12-C15	87.086	87.299	87.478
C19-Cr12-C15	92.921	92.962	92.756
C19-Cr12-N1	94.829	94.514	94.102
C15-Cr12-N1	94.840	94.520	94.100
Cr12-N1-C2	127.151	127.248	127.139
Cr12-N1-C6	117.619	117.155	117.459
C2-N1-C6	115.230	115.597	115.402
N1-C2-N3	125.783	124.969	125.172
N1-C2-S10	117.673	118.978	118.873
N3-C2-S10	116.544	116.053	115.955
N1-C6-C5	123.153	122.697	122.916
N1-C6-H9	116.334	116.272	116.691
C5-C6-H9	120.513	121.031	120.394
C2-N3-C4	117.492	118.426	118.339
C6-C5-C4	116.399	117.319	117.116
C6-C5-H8	121.191	120.766	120.847
C4-C5-H8	122.410	121.916	122.037
N3-C4-C5	121.943	120.992	121.056
N3-C4-H7	116.339	116.445	116.755
C5-C4-H7	121.718	122.563	122.189
C2-S10-H11	92.904	93.228	94.197
Cr12-C13-O14	176.632	176.770	176.593
Cr12-C20-O21	176.624	176.770	176.594
Cr12-C17-O18	179.877	179.814	179.902
Cr12-C19-O22	173.099	173.020	172.869
Cr12-C15-O16	173.091	173.014	172.867
C17-Cr12-N1	177.199	177.352	177.706
C20-Cr12-C15	175.157	175.426	175.626
C13-Cr12-C19	175.177	175.436	175.626

Figure 4.4.3.1. The molecular structure of pentacarbonyl(2-pyrimidinethiol) metal(0) complex (M; Cr, Mo, W).

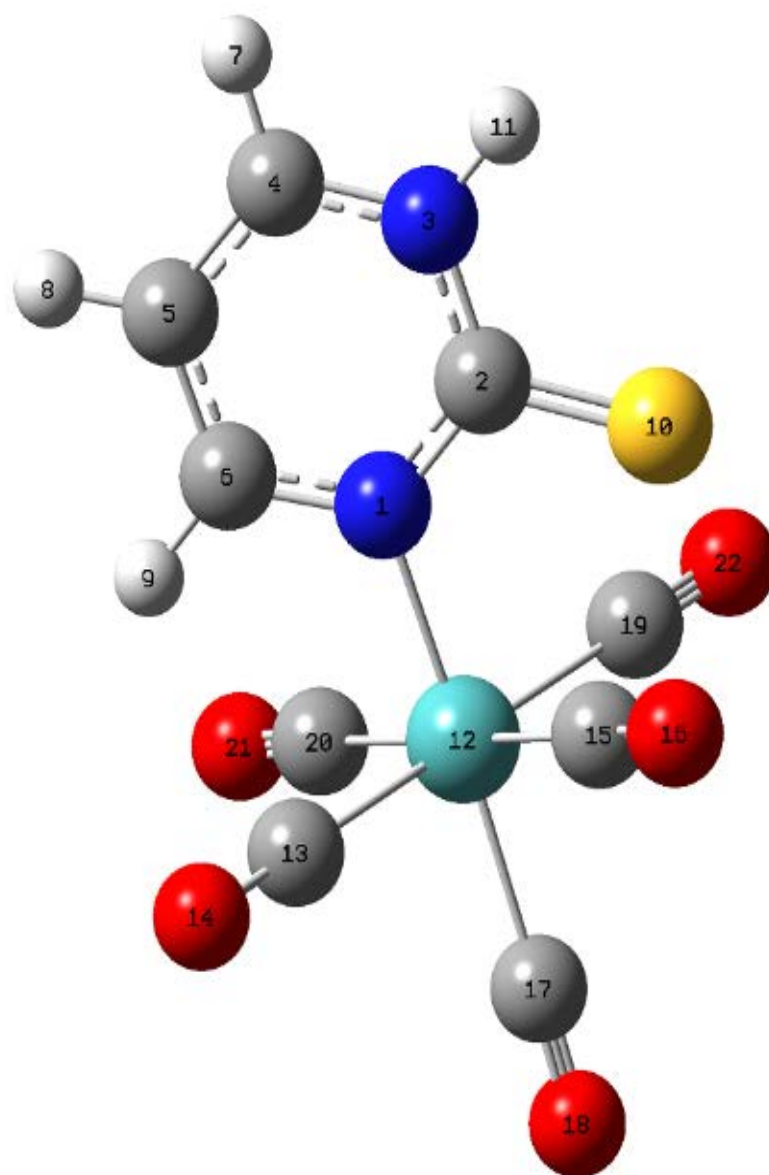


Figure 4.4.3.2. The molecular structure of pentacarbonyl(2-pyrimidinethione) metal(0) complex (M; Cr, Mo, W).

The metal-carbon bond distance for CO in trans position(axial) to the 2-mercaptopyrimidine [M12-C17 = 1.8426 Å] (Table 6) is slightly shorter than that of the other four cis-CO ligands [M12-C13 = 1.8987 Å] in the equatorial positions.

The difference in M-CO bond distances between CO ligands in cis and trans positions in the complex is due to the metal ($d\pi$) $\rightarrow$ carbonyl (π^*) back-donation arising from the fact that the π accepting ability of nitrogen atom is much less than that of CO.

It is shown also that the four equatorial CO groups in the complex, with the M12-C19 distance of 1.9066, are slightly bent away from the 2-mercaptopyrimidine ligand with the N1-Cr12-C19 angle of 94.829°, while the angle C19-Cr12-C17 is 87.095° (Table 4.4.3.2.).

4.4.4. Thermodynamic Properties

To obtain thermodynamic parameters of complexes different methods and basis sets were used. Table 4.4.4.1. demonstrates thermodynamic parameters of some of the complexes without experimental data at B3PW91/6-311G^a basis set.

Calculation of energy parameters of the thione form of complexes are smaller than the thiol form. The maximum dipole moment has been found to be 10.9612 Debye for W(CO)₅ 2-pyrimidinethione complex at B3PW91/6-311G^a calculation level.

Table 4.4.4.1. Thermodynamic data of some prepared complexes.

	Cr(CO) ₅ 2-pythiol	W(CO) ₅ 2-pythiol	Mo(CO) ₅ 2-pythione	W(CO) ₅ 2-pythione
<i>E_{Electronic}</i> (Hartrees)	-1315.324	-1296.803	-1296.669	-1296.789
<i>E_{ZPVE}</i> (Hartrees)	-1315.203	-1296.683	-1296.546	-1296.666
<i>E</i> (Hartrees)	-1315.185	-1296.664	-1296.527	-1296.647
<i>H</i> (Hartrees)	-1315.184	-1296.663	-1296.526	-1296.646
<i>G</i> (Hartrees)	-1315.252	-1296.733	-1296.596	-1296.716
<i>ΔE_{ZPVE}</i> (Kcal/Mol)	75.823	75.024	77.101	77.534
<i>ΔH</i> (Kcal/Mol)	88.097	87.476	89.644	89.859
<i>ΔG</i> (Kcal/Mol)	45.198	43.660	45.444	46.106
<i>ΔE</i> (Kcal/Mol)				
<i>Total</i>	87.504	86.883	89.051	89.266
<i>Translational</i>	0.890	0.890	0.890	0.890
<i>Rotational</i>	0.890	0.890	0.890	0.890
<i>Vibrational</i>	85.727	85.106	87.273	87.489
<i>ΔS</i> (Cal/Mol-Kelvin)				
<i>Total</i>	143.883	146.960	148.244	146.750
<i>Translational</i>	43.032	44.299	43.451	44.107
<i>Rotational</i>	33.370	33.661	33.670	33.685
<i>Vibrational</i>	67.481	69.000	71.123	68.958
<i>C_v</i> (Cal/Mol-Kelvin)				
<i>Total</i>	64.421	65.126	64.808	64.191
<i>Translational</i>	2.981	2.981	2.981	2.981
<i>Rotational</i>	2.981	2.981	2.981	2.981
<i>Vibrational</i>	58.459	59.165	58.846	58.229
<i>HOMO Energy (a.u.)</i>	-0.14445	-0.14004	-0.13216	-0.12584
<i>LUMO Energy (a.u.)</i>	-0.03716	-0.05268	-0.09214	-0.09463
<i>ΔE_{LUMO-HOMO}</i> (a.u.)	0.10729	0.08736	0.04002	0.03121
<i>RMS Gradient (a.u.)</i>	0.00000701	0.00001123	0.00000982	0.00001625
<i>Dipole Moment (Debye)</i>	6.2705	8.9577	10.6808	10.9612

4.4.5. UV-Vis Spectra Analysis

TD-DFT methods was used for the electronic transitions of the complexes in dichloromethane solution. TD-DFT generalizes density-functional theory to a time-dependent situation in which a system is subjected to a time-dependent perturbation, which modifies its external potential. In Khon-Sham formalism, time-dependent Khon-Sham equations can be derived by assuming the existence of an effective potential for an

independent particle model of which the orbital gives the same density as that of the interacting system.

In response theory, transition energies and oscillator strengths can be determined from the response of the charge density to a perturbation [138].

UV-Vis spectra of complexes dissolved in dichloromethane solution are shown Figure 4.4.5.1. The electronic spectra of the complexes in dichloromethane exhibit one band at 244 nm and 238 nm for Cr and Mo and two bands for W.

TD-DFT calculations aimed at studying electronic structure and possible UV-Vis transitions of complexes in different methods and basis sets. The DFT calculations again indicated good agreement with the experimentally detected wavelength of the electronic transitions of pentacarbonyl 2-mercaptopyrimidine metal(0) complexes in dichloromethane solvent. The orbitals involved in these transitions are shown in Figure 4.4.6.1.

In the case of thiol, only a single band corresponding to a $\pi \rightarrow \pi^*$ type transition is present, HOMO and LUMO+1 being the only orbitals involved in such a transition.

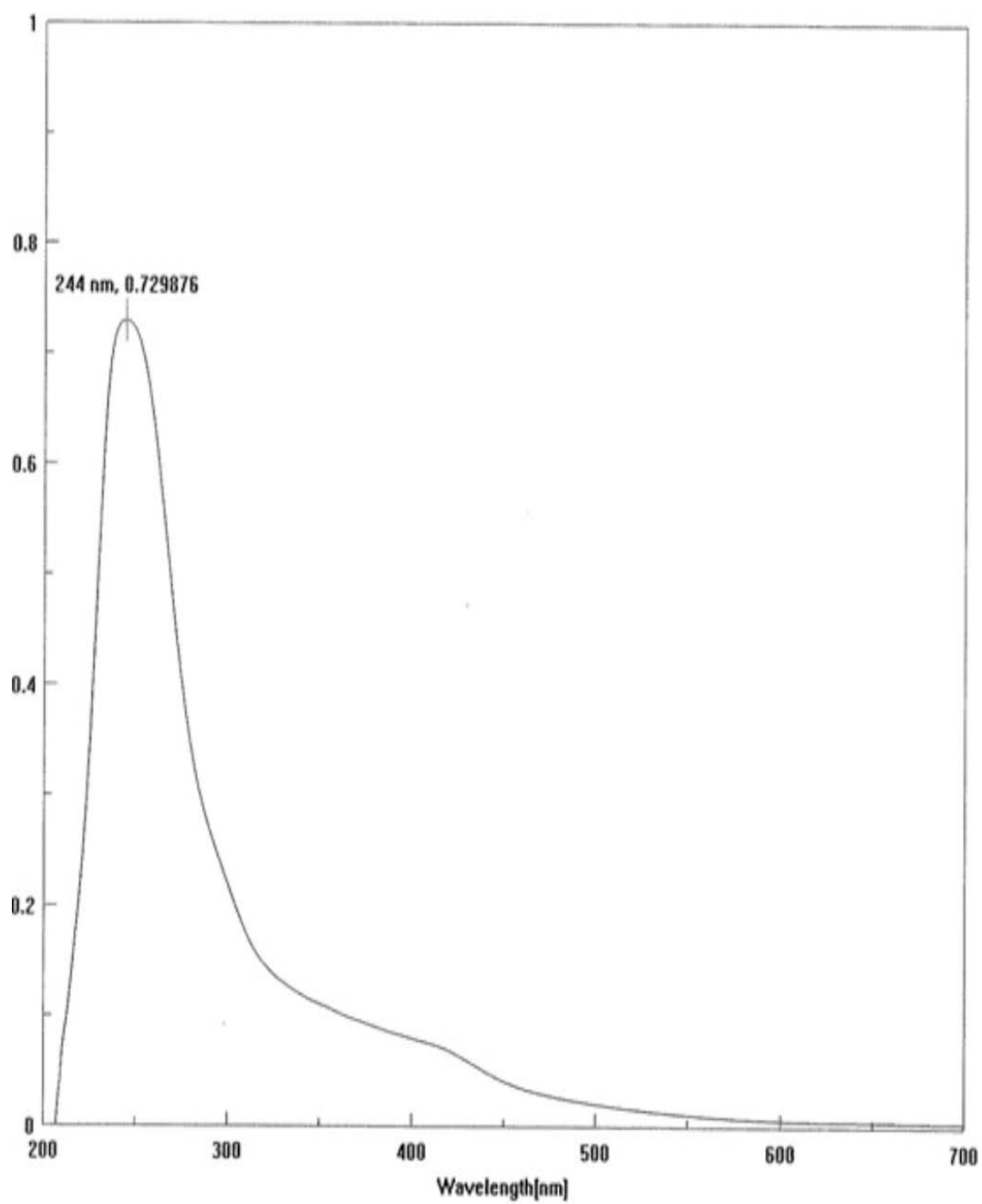


Figure 4.4.5.1. UV-Vis spectrum of $\text{Cr}(\text{CO})_5$ 2-mercaptopyrimidine complex in CH_2Cl_2 .

Table 4.4.5.1. Theoretical electronic absorption spectra values of pentacarbonyl(2-pyrimidinethione) W(0) and pentacarbonyl(2-pyrimidinethiol) W(0) complexes.

Transition	E.E (eV)	W.L (nm)	O.S
68 -> 74	4.8009	258.25	0.1293
67 -> 73	5.3131	233.35	0.1754
71 -> 78			
67 -> 77	6.0667	204.37	0.3886
68 -> 76			
68 -> 78			
69 -> 76			
69 -> 79			
69 -> 80			
70 -> 77			
70 -> 84			
71 -> 74			
71 -> 85			
67 -> 78	6.1377	202.01	0.3290
68 -> 75			
68 -> 77			
69 -> 75			
69 -> 81			
70 -> 74			
70 -> 83			
70 -> 85			
71 -> 77			

Transition	E.E (eV)	W.L (nm)	O.S
68 -> 74	5.3893	230.06	0.3440
68 -> 75			
71 -> 81			
69 -> 76	5.9601	208.00	0.5440
69 -> 78			
69 -> 82			
70 -> 73			
70 -> 78			
70 -> 82			
71 -> 77			
69 -> 75	5.9708	207.60	0.4780
69 -> 80			
70 -> 77			
71 -> 73			
71 -> 78			
71 -> 82			
65 -> 74	6.4053	193.50	0.2330
66 -> 72			
70 -> 83			
70 -> 84			
70 -> 86			
71 -> 80			

E.E., excitation energy; W.L., wave length; O.S., oscillator strength.

4.4.6. HOMO-LUMO Analysis

Highest occupied molecular (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. We can determine how the molecule interacts with other species; hence, they are called the frontier orbitals. Owing to the interaction between HOMO and LUMO orbital of a structure, transition state of $\pi \rightarrow \pi^*$ type is observed with regarding to the molecular orbital theory [63]. Therefore, while the energy of the HOMO is directly related to the ionization potential. LUMO energy is directly related to the electron affinity. Energy gap between HOMO and LUMO that is an important stability for structures [61] has been calculated using three different basis sets as shown in Table 4.4.6.1.

Table 4.4.6.1. Selected energy values of pentacarbonyl(2-mercaptopyrimidine) W(0) complex in its ground state with different basis sets.

Energy Level	B3PW91/6-311G	B3PW91/SDD	B3PW91/6-311G ^a
HOMO Energy (eV)	-0.15293	0.15098	-0.14004
LUMO Energy (eV)	-0.07743	-0.07257	-0.05268
$\Delta E_{\text{LUMO-HOMO}}$ (eV)	0.0755	0.07841	0.08736

According to the DFT-B3PW91 method at 6-311G and SDD calculation levels, the energy band gap, ΔE , between HOMO and LUMO of the molecule was found in order of 0.07550, 0.07841, 0.08736 AU. The molecule behaves as a conductor because of the small energy band gap. 3D plots of highest occupied molecular orbitals (HOMO) and lowest unoccupied

molecular orbitals (LUMO) are shown in Figure 4.4.6.1. In addition, the highest occupied molecular orbitals are mainly localized on the complex part of the molecule; moreover, no transition appears on the pyrimidine ring. On the other hand, the lowest unoccupied molecular orbitals are mainly localized on the pyrimidine part.

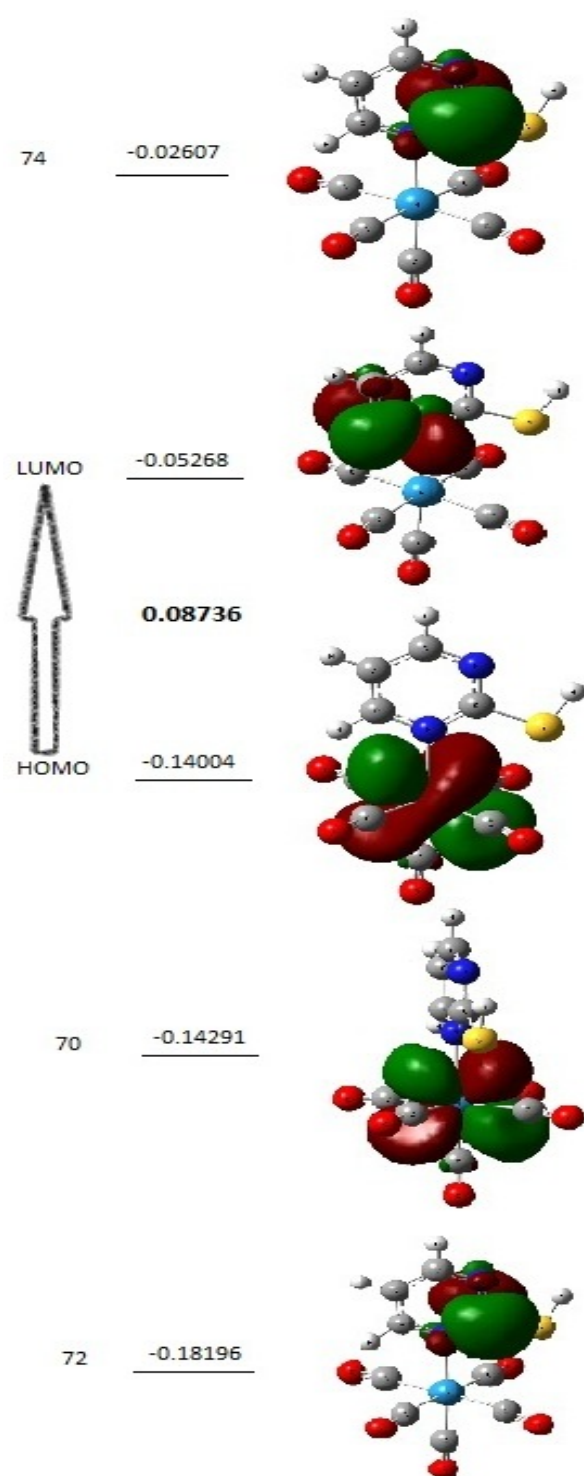


Figure 4.4.6.1. 3D plots of HOMO and LUMO of the W(CO)_5 2-mercaptopyrimidine complex.

4.4.7. Magnetic Properties

When a molecule is under the influence of an external magnetic field, this perturbation gives rise to some very important effects, which all involve the interaction of a nuclear or electron spin with the local electronic currents induced by the externally applied magnetic field. The earliest DFT calculations of NMR chemical shifts were done 20 years ago. These calculations were not at the point of practical applicability mainly due to the use of very small basis sets and of an inappropriate approximation to the Exchange-correlation (XC) Functional [139-143].

Modern applications of DFT to the calculation of NMR chemical shifts have been pioneered by Malkin et al. [144-147] with their DFT-IGLO (individual gauge for localized orbitals) method and by Schreckenbach and Ziegler [148-152] who used the gauge including atomic orbitals (GIAO) approach. DFT-NMR calculations on metal complexes include the work of Kaupp et al [153]. They have reviewed computational NMR studies on transition metal complexes.

The most important magnetic property by far is the chemical shift of NMR spectroscopy. Computational studies in ^1H chemical shifts are less frequent than for other nuclei because proton shifts span only some ten ppm and rovibrational and solvent effects might be comparable to the range of chemical shifts itself [135].

In summary the tautomeric forms of pentacarbonyl(2-mercaptopyrimidine) complexes were revealed by infrared (FTIR), ultraviolet (UV) and nuclear magnetic resonance (NMR) techniques. Density functional theory (DFT) calculations allowed us to elucidate these molecular structures. DFT calculations aimed at describing the vibrational structure of the two tautomeric species fit fairly well with the experimental infrared spectra, as shown in Table 4. A band at 1236 cm^{-1} associated with the stretching vibration of C=S bond did not appear in the IR spectra taken with dichloromethane solution. It appears that the accuracy of DFT is uniformly good for geometries, vibrational frequencies and probably good for total energies. It can be stated that DFT indeed is a very useful tool in organometallic and bioinorganic chemistry.

Table 4.4.1. Special values of tautomeric thiol structure in CH₂Cl₂ solution.

	Cr(CO) ₅ 2-pythiol				Mo(CO) ₅ 2-pythiol				W(CO) ₅ 2-pythiol			
<i>Method</i>	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91
<i>Metal Basis Set</i>	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD
<i>Metal (ECP)</i>	LANL2	LANL2	MDF	LANL2	LANL2	LANL2	MWB	LANL2	LANL2	LANL2	MWB	LANL2
<i>Basis Set</i>	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a
<i>M-N Bond</i>	V	X	V	V	X	X	X	X	V	X	V	V
<i>C2 - S10</i>	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
<i>N1 - C2</i>	Single	Double	Single	Single	Double	Double	Double	Double	Single	Double	Single	Single
<i>N1 - C6</i>	Double	Single	Double	Single	Single	Single	Single	Single	Double	Single	Double	Double
<i>C6 - C5</i>	Single	Double	Single	Double	Double	Double	Double	Double	Single	Double	Single	Single
<i>C5 - C4</i>	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
<i>N3 - C4</i>	Single	Double	Single	Double	Double	Double	Double	Double	Single	Double	Single	Double
<i>C2 - N3</i>	Double	Single	Double	Single	Single	Single	Single	Single	Double	Single	Double	Single
<i>Ligand Delocalization</i>	X	V	X	X	V	V	V	V	X	V	X	X
<i>M-N Bond Abundant</i>	1,90935	X	1,90807	1,59469	X	X	X	X	1,91672	X	1,91219	1,91449
<i>Medium</i>	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂
<i>Structure</i>	V	X	V	V	X	X	X	X	V	X	V	V
<i>M-N Bond Enegy</i>	-0,50080	X	-0,50747	-0,21235	X	X	X	X	-0,52480	X	-0,51223	-0,51658
<i>Basis</i>	272	187	222	469	272	187	222	469	272	187	222	469
<i>Primitive</i>	544	466	501	789	538	463	501	789	534	457	501	789

Table 4.4.2. Special values of tautomeric thione structure in CH₂Cl₂ solution.

	Cr(CO) ₅ 2-pythione				Mo(CO) ₅ 2-pythione				W(CO) ₅ 2-pythione			
<i>Method</i>	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91
<i>Metal Basis Set</i>	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD
<i>Metal (ECP)</i>	LANL2	LANL2	MDF	LANL2	LANL2	LANL2	MWB	LANL2	LANL2	LANL2	MWB	LANL2
<i>Basis Set</i>	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a
<i>M-N Bond</i>	X	X	X	X	V	X	X	X	V	V	V	V
<i>C2 - S10</i>	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double
<i>N1 - C2</i>	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
<i>N1 - C6</i>	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double
<i>C6 - C5</i>	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
<i>C5 - C4</i>	Double	Double	Double	Double	Single	Double	Double	Double	Single	Single	Single	Single
<i>N3 - C4</i>	Single	Single	Single	Single	Double	Single	Single	Single	Double	Double	Double	Double
<i>C2 - N3</i>	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
<i>Ligand Delocalization</i>	V	V	V	V	X	V	V	V	X	X	X	X
<i>M-N Bond Abundant</i>	X	X	X	X	1,91695	X	X	X	1,91604	1,91962	1,91051	1,91349
<i>Medium</i>	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂
<i>Structure</i>	X	X	X	X	V	X	X	X	V	V	V	V
<i>M-N Bond Enegy</i>	X	X	X	X	-0,50172	X	X	X	-0,51634	-0,53321	-0,50412	-0,50859
<i>Basis</i>	272	187	222	469	272	187	222	469	272	187	222	469
<i>Primitive</i>	544	466	501	789	538	463	501	789	534	457	501	789

Table 4.4.3. Special values of tautomeric thiol structure in vacuum.

	Cr(CO) ₅ 2-pythhiol				Mo(CO) ₅ 2-pythhiol				W(CO) ₅ 2-pythhiol			
Method	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91
Metal Basis Set	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD
Metal (ECP)	LANL2	LANL2	MDF	LANL2	LANL2	LANL2	MWB	LANL2	LANL2	LANL2	MWB	LANL2
Basis Set	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a
M-N Bond	V	X	V	V	X	X	X	X	V	V	V	X
C2 - S10	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
N1 - C2	Single	Double	Single	Single	Double	Double	Double	Double	Single	Single	Single	Double
N1 - C6	Single	Single	Single	Single	Single	Single	Single	Single	Double	Double	Double	Single
C6 - C5	Double	Double	Double	Double	Double	Double	Double	Double	Single	Single	Single	Double
C5 - C4	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
N3 - C4	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double
C2 - N3	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
Ligand Delocalization	X	V	X	X	V	V	V	V	X	X	X	V
M-N Bond Abundant	1,60232	X	1,59341	1,60860	X	X	X	X	1,91738	1,92025	1,91314	X
Medium	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum
Structure	V	X	V	V	X	X	X	X	V	V	V	X
M-N Bond Energy	-0,23178	X	-0,24449	-0,21575	X	X	X	X	-0,53810	-0,55309	-0,52567	X
Basis	272	187	222	469	272	187	222	469	272	187	222	469
Primitive	544	466	501	789	538	463	501	789	534	457	501	789

Table 4.4.4. Special values of tautomeric thione structure in vacuum.

	Cr(CO) ₅ 2-pythhone				Mo(CO) ₅ 2-pythhone				W(CO) ₅ 2-pythhone			
Method	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91	B3PW91
Metal Basis Set	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD	CEP-121G	LANL2DZ	SDD	SDD
Metal (ECP)	LANL2	LANL2	MDF	LANL2	LANL2	LANL2	MWB	LANL2	LANL2	LANL2	MWB	LANL2
Basis Set	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a	6-311G	6-31G	SDD	6-311G ^a
M-N Bond	X	V	X	X	V	X	X	V	V	V	X	V
C2 - S10	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double
N1 - C2	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
N1 - C6	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double	Double
C6 - C5	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
C5 - C4	Double	Double	Double	Double	Double	Double	Double	Double	Single	Single	Double	Double
N3 - C4	Single	Single	Single	Single	Single	Single	Single	Single	Double	Double	Single	Single
C2 - N3	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single	Single
Ligand Delocalization	V	V	V	V	V	V	V	V	X	X	V	V
M-N Bond Abundant	X	1,89788	X	X	1,91691	X	X	1,90871	1,91627	1,91975	X	1,91325
Medium	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum
Structure	X	V	X	X	V	X	X	V	V	V	X	V
M-N Bond Energy	X	-0,48901	X	X	0,51480	X	X	-0,48380	-0,53068	-0,54717	X	-0,52039
Basis	272	187	222	469	272	187	222	469	272	187	222	469
Primitive	544	466	501	789	538	463	501	789	534	457	501	789

Table 4.4.5 Bond Length (Å) of thiol and thione complexes calculated in CH₂Cl₂ solution.

<i>Bond Length</i>	Cr(CO)₅ 2pythiol	W(CO)₅ 2-pythiol
M12-C13	1.8987	2.0428
M12-C20	1.8987	2.0428
M12-C17	1.8426	1.9790
M12-C19	1.9066	2.0477
M12-C15	1.9067	2.0477
M12-N1	2.2280	2.3210
C13-O14	1.1454	1.1471
C20-O21	1.1454	1.1471
C17-O18	1.1526	1.1557
C19-O22	1.1451	1.1468
C15-O16	1.1451	1.1468
N1-C2	1.3496	1.3529
N1-C6	1.3468	1.3497
C2-N3	1.3330	1.3318
C2-S10	1.7545	1.7520
C6-C5	1.3797	1.3780
C6-H9	1.0825	1.0824
N3-C4	1.3273	1.3269
C5-C4	1.3887	1.3896
C5-H8	1.0822	1.0821
C4-H7	1.0865	1.0864
S10-H11	1.3485	1.3495

<i>Bond Length</i>	Mo(CO)₅ 2pythione	W(CO)₅ 2-pythione
M12 - C13	2.0421	2.0323
M12 - C20	2.0421	2.0323
M12 - C17	1.9803	1.9848
M12 - C19	2.0731	2.0591
M12 - C15	2.0731	2.0592
M12- N1	2.3705	2.3185
C13 - O14	1.1476	1.1497
C20 - O21	1.1476	1.1497
C17 - O18	1.1512	1.1525
C19- O22	1.1420	1.1440
C15 - O16	1.1420	1.1440
N1 - C2	1.3887	1.3937
N1 - C6	1.3234	1.3278
C2 - N3	1.3948	1.3935
C2 - S10	1.6465	1.6451
C6 - C5	1.4047	1.4018
C6- H9	1.0847	1.0840
N3 - C4	1.3421	1.3416
N3 - H11	1.0111	1.0111
C5 - C4	1.3651	1.3658
C5 - H8	1.0806	1.0805
C4 - H7	1.0837	1.0835

Table 4.4.6. Bond Angle of thiol and thione complexes calculated in CH₂Cl₂ solution.

<i>Bond Angle</i>	Cr(CO) ₅ 2pythiol	W(CO) ₅ 2-pythiol
C13-M12-C20	90.773	90.753
C13-M12-C17	88.215	88.111
C13-M12-C15	87.960	88.109
C13-M12-N1	89.819	89.836
C20-M12-C17	88.203	88.109
C20-M12-C19	87.958	88.109
C20-M12-N1	89.829	89.838
C17-M12-C19	87.095	87.075
C17-M12-C15	87.086	87.072
C19-M12-C15	92.921	92.623
C19-M12-N1	94.829	94.940
C15-M12-N1	94.840	94.942
M12-N1-C2	127.151	126.731
M12-N1-C6	117.619	117.884
C2-N1-C6	115.230	115.385
N1-C2-N3	125.783	125.523
N1-C2-S10	117.673	117.583
N3-C2-S10	116.544	116.894
N1-C6-C5	123.153	122.993
N1-C6-H9	116.334	116.118
C5-C6-H9	120.513	120.889
C2-N3-C4	117.492	117.648
C6-C5-C4	116.399	116.469
C6-C5-H8	121.191	121.113
C4-C5-H8	122.410	122.418
N3-C4-C5	121.943	121.981
N3-C4-H7	116.339	116.339
C5-C4-H7	121.718	121.680
C2-S10-H11	92.904	92.730
M12-C13-O14	176.632	176.631
M12-C20-O21	176.624	176.617
M12-C17-O18	179.877	179.762
M12-C19-O22	173.099	174.387
M12-C15-O16	173.091	174.383
C17-M12-N1	177.199	177.077
C20-M12-C15	175.157	175.082
C13-M12-C19	175.177	175.086

<i>Bond Angle</i>	Mo(CO) ₅ 2pythione	W(CO) ₅ 2-pythione
C13 - M12 - C20	90.430	90.213
C13 - M12 - C17	88.250	88.412
C13 - M12 - C15	89.295	89.244
C13 - M12 - N1	89.654	89.558
C20- M12 - C17	88.254	88.414
C20 - M12 - C19	89.296	89.244
C20- M12 - N1	89.632	89.537
C17 - M12 - C19	87.870	87.811
C17- M12 - C15	87.875	87.812
C19 - M12 - C15	90.717	91.049
C19- M12 - N1	94.218	94.201
C15 - M12 - N1	94.230	94.219
M12 - N1 - C2	123.451	123.286
M12- N1 - C6	117.854	118.314
C2 - N1 - C6	118.696	118.400
N1 - C2 - N3	115.667	115.618
N1 - C2 - S10	125.715	125.815
N3 - C2 - S10	118.618	118.567
N1 - C6 - C5	125.385	125.473
N1 - C6 - H9	115.383	115.308
C5 - C6 - H9	119.232	119.220
C2 - N3 - C4	125.402	125.664
C2 - N3 - H11	114.042	113.824
C4 - N3 - H11	120.556	120.512
C6 - C5 - C4	116.230	116.397
C6 - C5 - H8	121.529	121.343
C4 - C5 - H8	122.242	122.260
N3 - C4 - C5	118.620	118.449
N3 - C4 - H7	116.766	116.831
C5 - C4 - H7	124.614	124.720
M12- C13 - O14	177.533	177.832
M12- C20- O21	177.545	177.846
M12 - C17- O18	179.707	179.655
M12- C19- O22	174.709	174.872
M12- C15- O16	174.708	174.865
C17- M12- N1	177.011	177.110
C20- M12 - C15	176.126	176.200
C13- M12 - C19	176.117	176.198

Table 4.4.7. Atomic charges for optimized geometry of thiol and thione tautomers.

Atom	Cr(CO) ₅ 2pythiol		W(CO) ₅ 2-pythiol		Atom	Mo(CO) ₅ 2pythione		W(CO) ₅ 2-pythione	
	Muliken	NBO	Muliken	NBO		Muliken	NBO	Muliken	NBO
M12	0.0671	-2.3353	0.6061	-1.7907	M12	0.5451	-1.9269	0.6187	-1.7864
C13	0.1799	0.8819	0.0814	0.7625	C13	0.0695	0.7747	0.0556	0.7415
O14	-0.2159	-0.4674	-0.2101	-0.4528	O14	-0.2025	-0.4582	-0.2106	-0.4561
C20	0.1799	0.8819	0.0814	0.7625	C20	0.0695	0.7748	0.0557	0.7415
O21	-0.2159	-0.4674	-0.2101	-0.4528	O21	-0.2026	-0.4582	-0.2106	-0.4562
C17	0.2338	0.8915	0.0668	0.7561	C17	0.0715	0.7968	0.0672	0.7573
O18	-0.2532	-0.4977	-0.2511	-0.4930	O18	-0.2184	-0.4701	-0.2257	-0.4688
C19	0.1720	0.8695	0.0786	0.7551	C19	0.1092	0.7932	0.0931	0.7635
O22	-0.2133	-0.4692	-0.2080	-0.4548	O22	-0.1835	-0.4439	-0.1914	-0.4408
C15	0.1720	0.8695	0.0786	0.7551	C15	0.1093	0.7932	0.0932	0.7635
O16	-0.2133	-0.4692	-0.2080	-0.4548	O16	-0.1835	-0.4439	-0.1914	-0.4408
N1	-0.4521	-0.4135	-0.5213	-0.4540	N1	-0.5075	-0.4335	-0.5406	-0.4399
C2	0.4558	0.3374	0.4754	0.3410	C2	0.4925	0.2379	0.5134	0.2391
C6	0.0279	0.1349	0.0506	0.1421	C6	0.0559	0.1753	0.0731	0.1764
N3	-0.3786	-0.5109	-0.3710	-0.5079	N3	-0.5993	-0.5143	-0.6012	-0.5128
C5	-0.3227	-0.2775	-0.3145	-0.2778	C5	-0.3742	-0.3245	-0.3720	-0.3228
C4	0.0103	0.1303	0.0098	0.1338	C4	0.1384	0.1270	0.1371	0.1257
S10	-0.2971	0.0866	-0.3107	0.0979	S10	-0.3711	-0.0963	-0.3589	-0.0865
H11	0.2824	0.1669	0.2917	0.1668	H11	0.4176	0.4291	0.4191	0.4300
H8	0.2514	0.2392	0.2533	0.2411	H8	0.2444	0.2371	0.2456	0.2382
H9	0.2755	0.2122	0.2745	0.2172	H9	0.2588	0.2132	0.2687	0.2161
H7	0.2541	0.2064	0.2565	0.2075	H7	0.2609	0.2176	0.2620	0.2183

Table 4.4.8. Molecular orbital analysis of thiol and thione forms in CH₂Cl₂ solution.

Cr (CO) ₅ 2-pyrimidinethiol						W (CO) ₅ 2-pyrimidinethiol				
O	OT	A1	A2	Fullness	OE	OT	A1	A2	Fullness	OE
64	LP1	N1	---	1.6552	-0.36827	LP1	N3	---	1.9062	-0.37543
65	BD2	N3	C4	1.7174	-0.33826	BD2	N1	C6	1.7440	-0.35751
66	BD2	C6	C5	1.6328	-0.29609	BD2	N3	C4	1.7159	-0.34078
67	LP2	S10	---	1.8169	-0.27473	LP2	S10	---	1.8114	-0.27701
68	BD1	Cr12	N1	1.5947	-0.21235	LP*1	C2	---	0.9300	-0.18196
72	BD*1	Cr12	N1	1.2451	-0.20905	LP1	W12	---	1.4362	-0.15446
69	LP1	Cr12	---	1.5347	-0.18563	LP1	C5	---	1.0212	-0.14981
70	LP1	C2	---	0.9320	-0.17841	LP3	W12	---	1.4135	-0.14291
71	LP2	Cr12	---	1.4670	-0.14162	LP2	W12	---	1.4209	-0.14004
73	BD*2	N3	C4	0.3414	-0.02391	BD*2	N1	C6	0.4338	-0.05268
74	BD*2	C6	C5	0.2543	-0.00493	BD*2	N3	C4	0.3378	-0.02607
75	BD*3	C15	O16	0.1463	0.02854	BD*2	C13	O14	0.1547	0.02180
76	BD*3	C19	O22	0.1463	0.02855	BD*2	C20	O21	0.1547	0.02180
77	BD*3	C21	O21	0.1355	0.02995	BD*3	C13	O14	0.1730	0.02222
78	BD*3	C13	O14	0.1354	0.02996	BD*3	C20	O21	0.1730	0.02223
79	BD*2	C15	O16	0.1310	0.03091	BD*2	C15	O16	0.1503	0.02421
80	BD*2	C19	O22	0.1310	0.03092	BD*2	C19	O22	0.1503	0.02421
81	BD*2	C17	O18	0.1793	0.03267	BD*3	C15	O16	0.1810	0.02579
82	BD*1	C17	O18	0.1813	0.03476	BD*3	C19	O22	0.1810	0.02580
83	BD*2	C13	O14	0.1327	0.05262	BD*3	C17	O18	0.2198	0.03074
84	BD*2	C20	O20	0.1327	0.05272	BD*2	C17	O18	0.2224	0.03370
85	BD*1	S10	H11	0.0127	0.16892	BD*1	S10	H11	0.0141	0.16620
86	BD*1	C2	S10	0.0416	0.18424	BD*1	C2	S10	0.0404	0.17239

Mo(CO) ₅ 2pythione						W(CO) ₅ 2-pythione				
O	OT	A1	A2	Fullness	OE	OT	A1	A2	Fullness	OE
65	BD2	C5	C17	1.7116	-0.33706	BD2	C5	C4	1.7056	-0.33851
66	BD2	N3	---	1.5306	-0.33390	LP1	N3	---	1.5292	-0.33634
67	BD2	C2	S18	1.9710	-0.32154	BD2	C2	S10	1.9709	-0.32473
68	LP2	S10	---	1.8435	-0.22419	LP2	S10	---	1.8388	-0.22651
69	LP1	Mo12	---	1.5110	-0.16047	LP1	W12	---	1.4360	-0.14316
70	LP2	Mo12	---	1.4826	-0.14558	LP3	W12	---	1.4100	-0.13279
71	LP3	Mo12	---	1.4798	-0.13216	LP2	W12	---	1.4249	-0.12584
72	BD*2	C2	S18	0.4311	-0.09214	BD*2	C2	S10	0.4293	-0.09463
73	BD*2	N1	C14	0.2979	-0.05624	BD*2	N1	C6	0.3186	-0.06241
74	BD*2	C5	C17	0.2627	-0.04284	BD*2	C5	C4	0.2698	-0.04489
75	BD*3	C13	O3	0.1595	0.03098	BD*3	C13	O14	0.1863	0.03062
76	BD*3	C20	O5	0.1595	0.03098	BD*3	C20	O21	0.1863	0.03062
77	BD*2	C20	O5	0.1491	0.03204	BD*2	C20	O21	0.1702	0.03151
78	BD*2	C13	O3	0.1491	0.14906	BD*2	C13	O14	0.1702	0.03151
79	BD*3	C19	O9	0.1385	0.03878	BD*2	C19	O22	0.1384	0.03807
80	BD*3	C15	O11	0.1384	0.03879	BD*2	C15	O16	0.1383	0.03809
81	BD*2	C19	O9	0.1189	0.03909	BD*3	C19	O22	0.1654	0.03863
82	BD*2	C15	O11	0.1189	0.03910	BD*3	C15	O16	0.1654	0.03866
83	BD*3	C17	O7	0.1851	0.04599	BD*2	C17	O18	0.2162	0.04622
84	BD*1	C17	O7	0.1882	0.06922	BD*3	C17	O18	0.2024	0.04631
85	BD*1	C2	S18	0.0117	0.29346	BD*1	C2	S10	0.0110	0.29197

4.5. Cis-tetracarbonylbis(4-dimethylaminopyridine) tungsten(0) complex

4.5.1. IR-spectroscopy

The IR spectrum of the given complexes was recorded from its dichloromethane solution. Analysis of the spectrum in the CO-stretching region show the appearance of four strong CO absorption bands in the region of $1800 - 2300\text{ cm}^{-1}$ as shown in Figure 4.5.1.1.

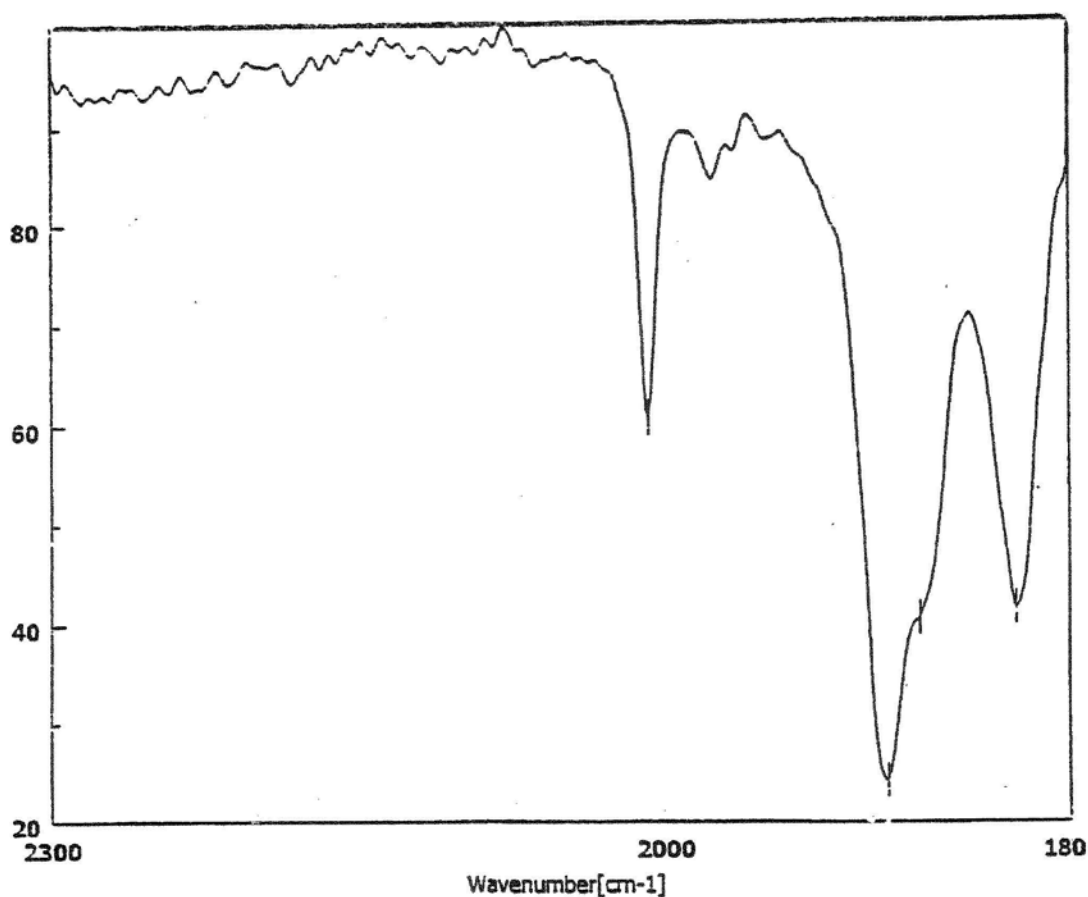


Figure 4.5.1.1 The IR spectrum of $\text{cis}-(\text{CO})_4\text{W}(\text{4-dmap})_2$ from dichloromethane solution

The observation of these strong bands in this region is considered as the best proof to the formation of the cis-W(CO)₄ group of the molecule with its C_{2v} local symmetry. The strong absorption band at approximately 2006 cm⁻¹ is considered to be specific for the existence of the cis-M(CO)₄ group. This could also rule out any thought about the formation of the trans-tetracarbonyl isomer at which only one strong CO-absorption band at approximately 1930 cm⁻¹ will appear. Analysis of these bands could be done depending on the group theoretical data as A₁(1) (IR active), A₁(2) (IR active), B₁(IR active), and B₁(IR active).

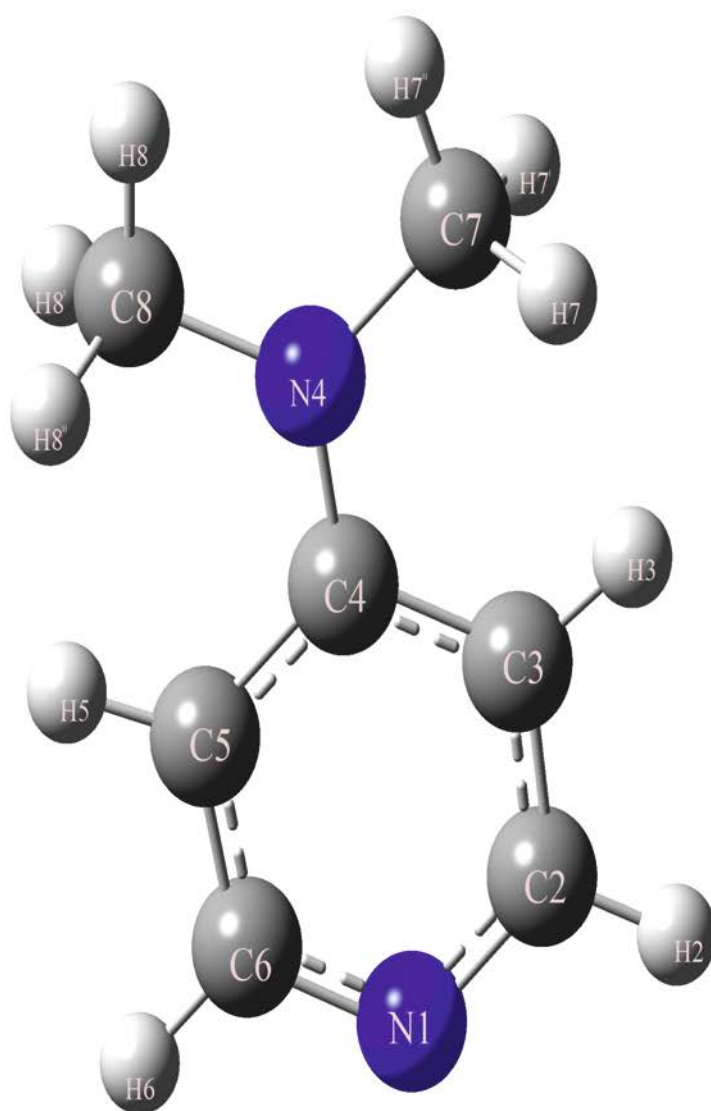


Figure 4.5.1.2. The molecular structure of 4-dimethylaminopyridine

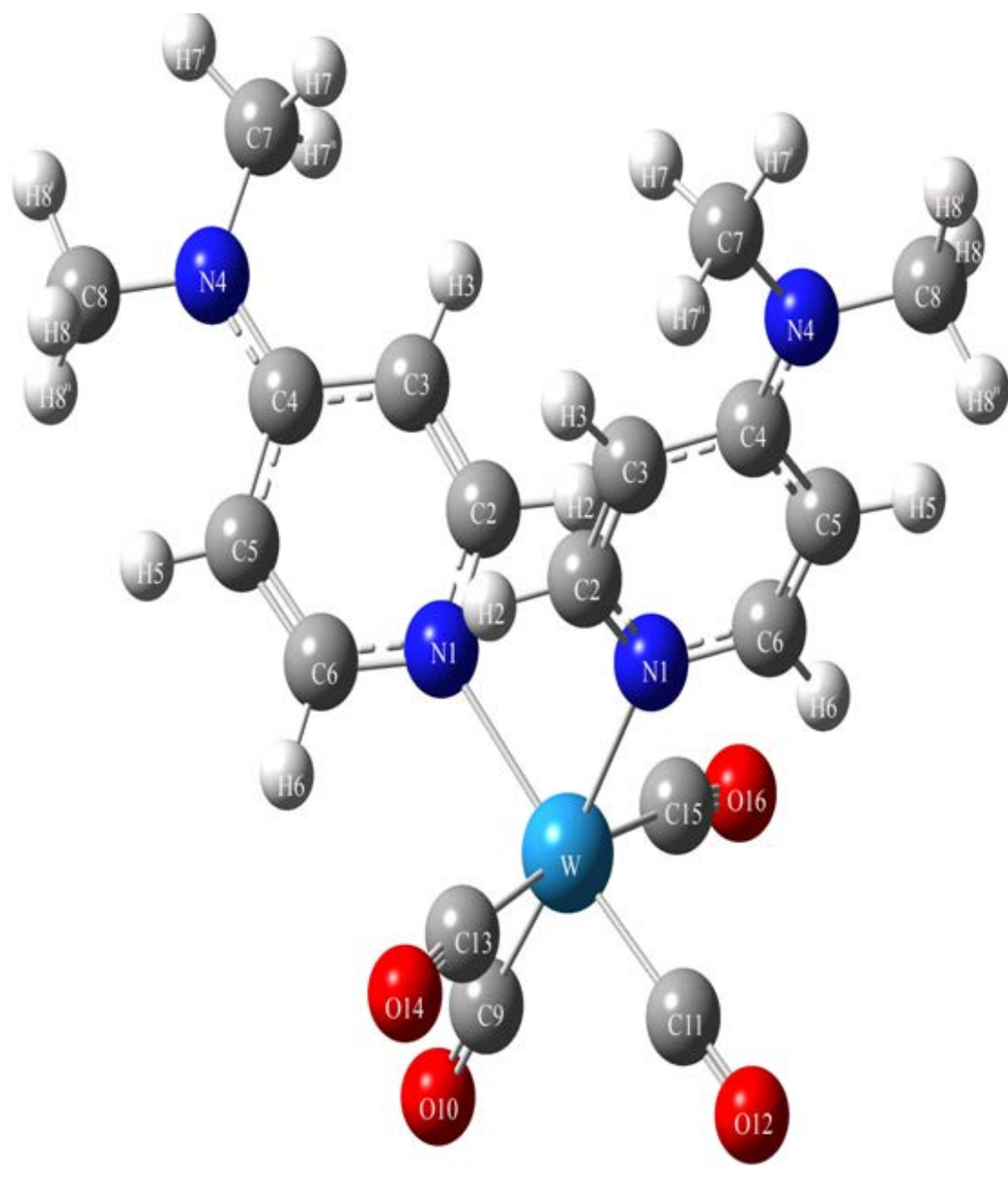


Figure 4.5.1.3 The molecular structure of $[\text{W}(\text{CO})_4(4\text{-dmap})_2](1)$

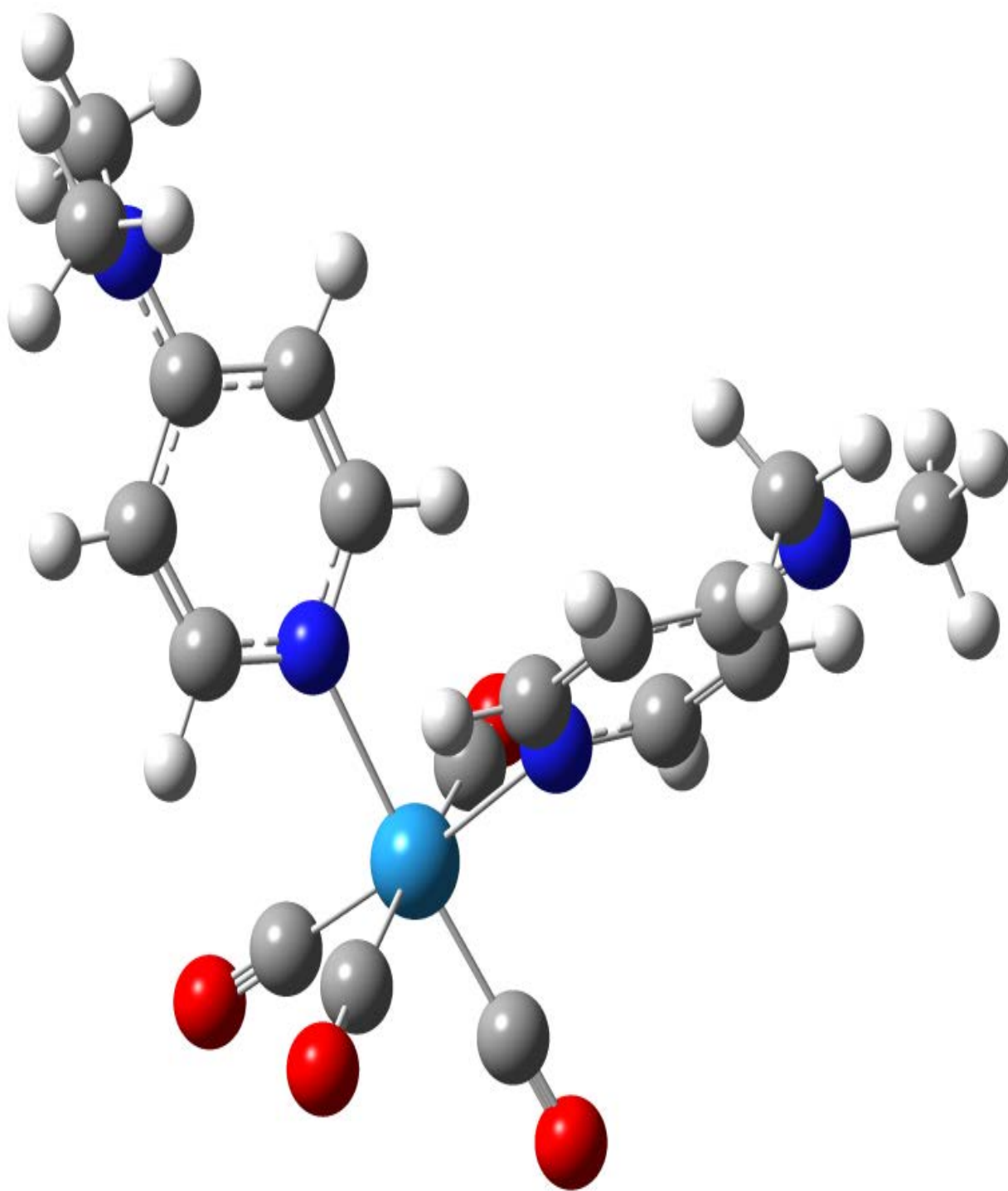


Figure 4.5.1.4 The molecular structure of $[W(CO)_4(4\text{-dmap})_2]$ (2)

4.5.2. NMR spectroscopy

¹H-NMR spectroscopy

The ¹H-NMR spectrum of the free 4-dimethylaminopyridine ligand recorded from its d-chloroform solution show the appearance of a doublet at 6.462 ppm belonging to H-3,5 and a doublet at 8.192 ppm belonging to H-2,6 of the pyridine ring. One singlet was also observed at 2.969 ppm belonging to the substituted methyl groups (Figure 4.5.2.1.).

Analysis of the signals in the ¹H-NMR spectrum of the complex $\text{cis}(\text{CO})_4(4\text{-dmap})_2$ could depend on the chemical shifts of the pyridine ring protons and its methyl group substituents, and also could depend on the appearance of a new signals in these regions (Figure 4.5.2.3). Its important to imply that the discussion of the ¹H-NMR spectrum of the synthesised complex will not give any information about the formation of the appraciate isomers cis or trans or even to the formation of the penta- or tetra-carbonyl complexes. The ¹H-NMR spectrum of the $\text{cis}(\text{CO})_4\text{W}(4\text{-dmap})_2$ complex recording from its d-chloroform solution show the appearance of two doublet of doublets at 6.301 ppm and at 8.192 ppm for the aromatic protons H3,5 and H2,6 of approximate equal intensities respectively. One can also observe additional doublets at 6.350 ppm and 8.240 ppm with a very very intensities. In addition one singlet is also observed at 2.995 ppm belonging to the methyl groups of the dimethylamino substituted group. The discussion of these signals would depend on their chemical shifts upon metal coordination comparing to those of the free 4-dimethylaminopyridine ligand.

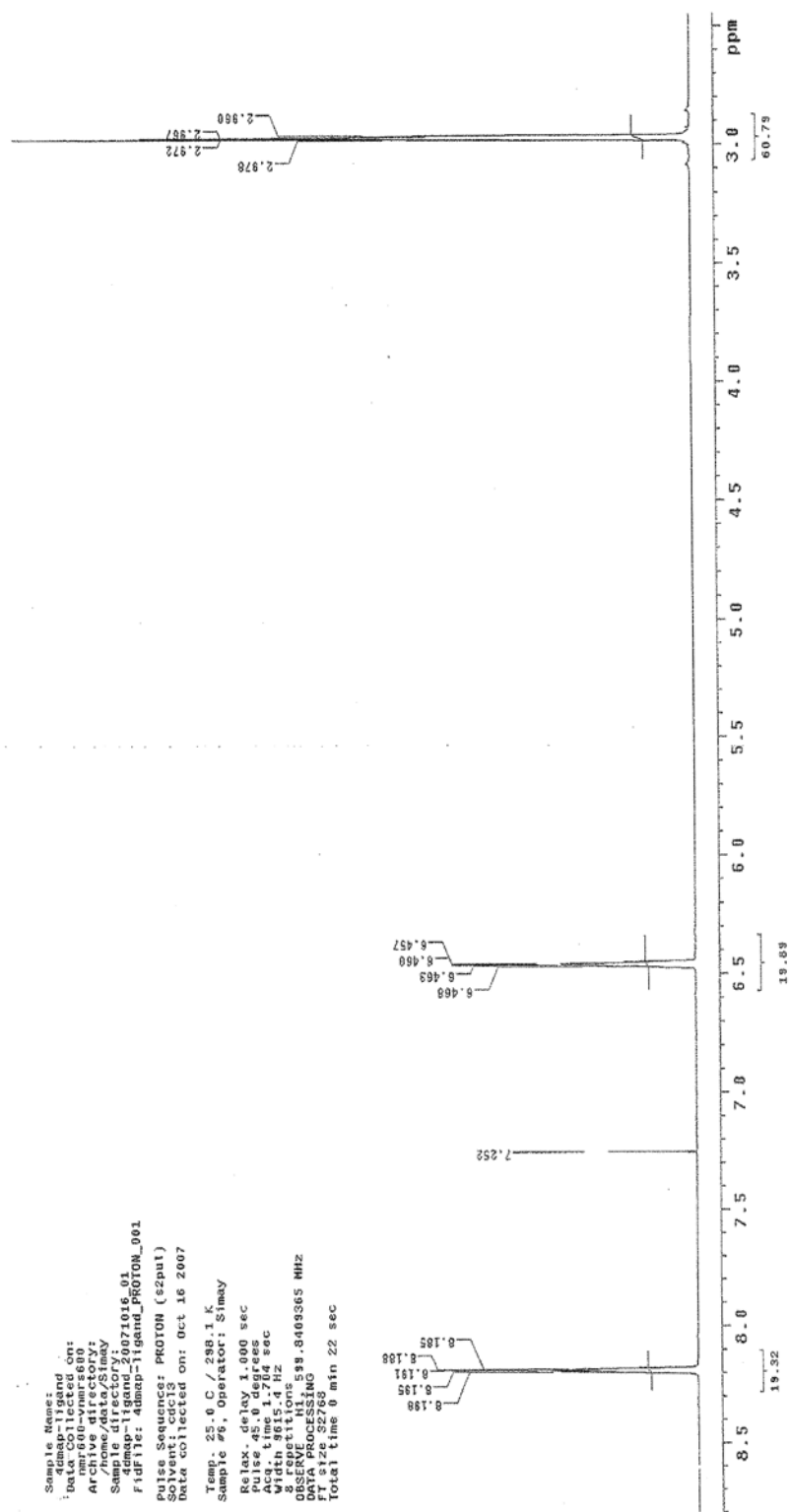


Figure 4.5.2.1 : The ^1H -NMR spectrum of 4-dmap recording from d-chloroform solution rel. TMS

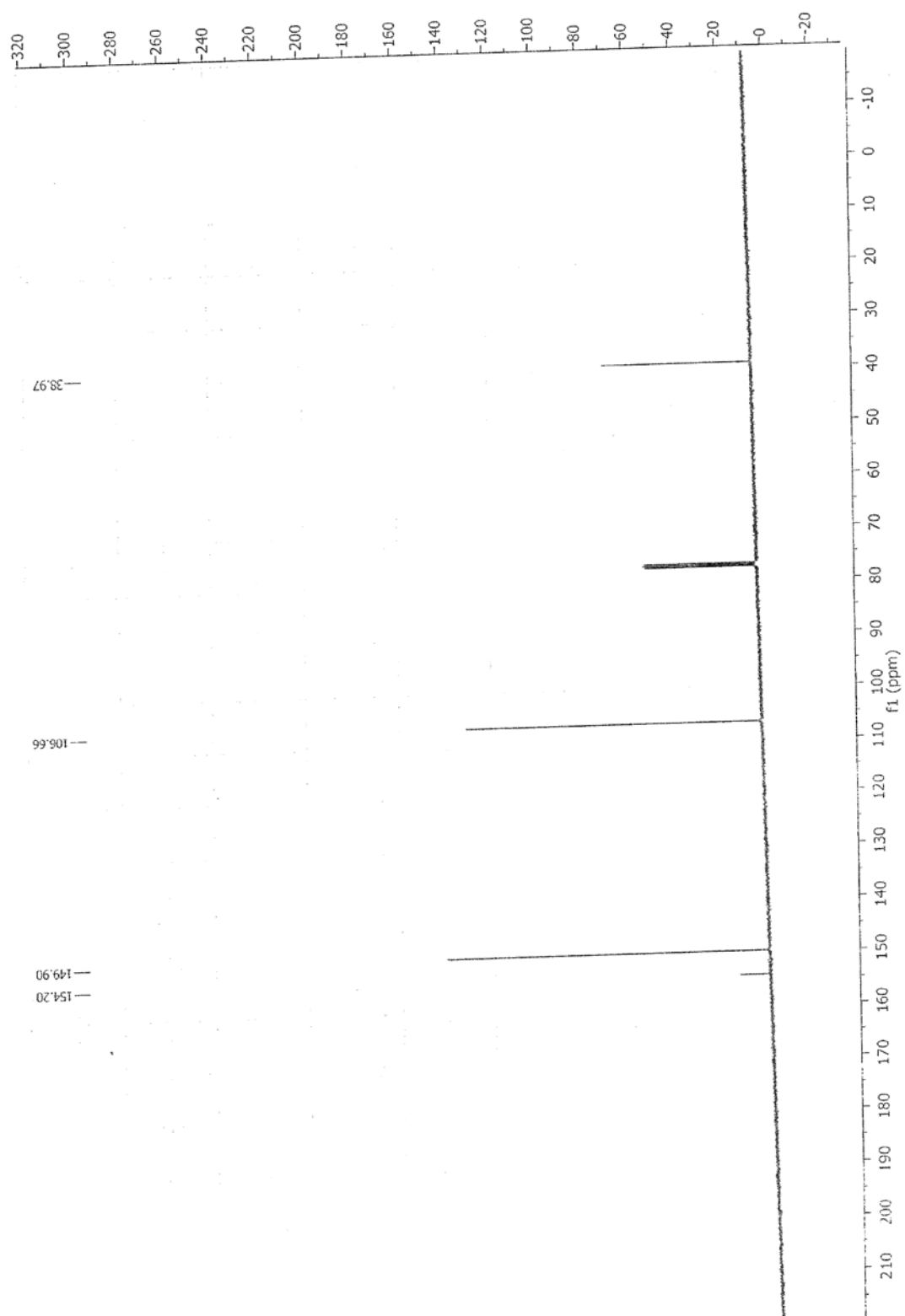


Figure 4.5.2.2 : The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of 4-dmap recording from d-chloroform solution rel. TMS

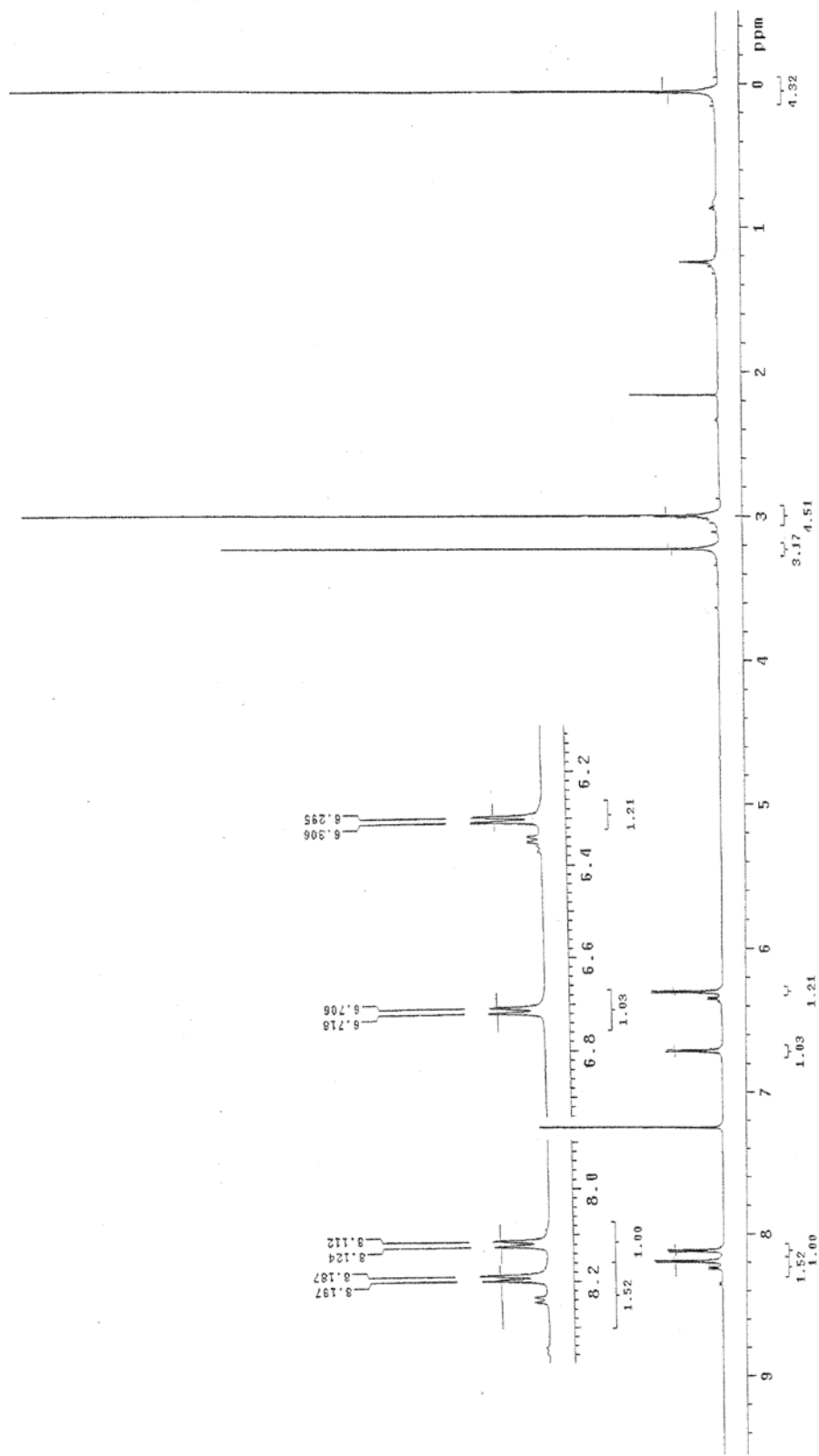


Figure 4.5.2.3 : The ^1H -NMR spectrum of $\text{cis-}[\text{W}(\text{CO})_4(4\text{-dmap})_2]$ recording from d-chloroform solution rel. TMS

One can easily observe no significant shift of the aromatic protons and of the methyl groups of the substituted group from those of the free ligand upon metal coordination of the free ligand (free ligand show the appearance of two doublets at 6.462 ppm and at 8.192 ppm for H_{3,5} and H_{2,6} respectively and one singlet at 2.969 ppm for the methyl groups protons). The spectrum show also the appearance of an additional two low intensity doublets at 6.712 ppm and at 8.118 ppm and a singlet at 3.120 ppm beside the complex signals. We can easily say that the splitting of the signals belonging to H_{3,5} and H_{2,6} arises from the stereoisomerization of the 4-dimethylamino pyridine ligand.

¹³C-{¹H}-NMR spectroscopy

The ¹³C-{¹H}-NMR spectrum of the prepared complex, cis-[W(CO)₄(4-dmap)₂], based mainly on the appearance of the signals of the carbon atoms of the ligand upon metal coordination and the appearance of a new signals in the region of 30-170 ppm. Moreover, the appearance of a new signals on the carbonyl region, 190-220 ppm of the spectrum would be very useful to predict the formation of the M(CO)₄ part of the complex.

The ¹³C-{¹H}-NMR spectrum of free 4-dimethylamino pyridine ligand recorded from its d-chloroform solution relatively to TMS shows the appearance of a signal for the methyl groups of the N(CH₃)₂ substituent group at 38.97 ppm, asignal for C_{3,5} at 106.66 ppm, a signal for C_{2,6} at 149.90 ppm and as signal for C₄ at 154.20 ppm.

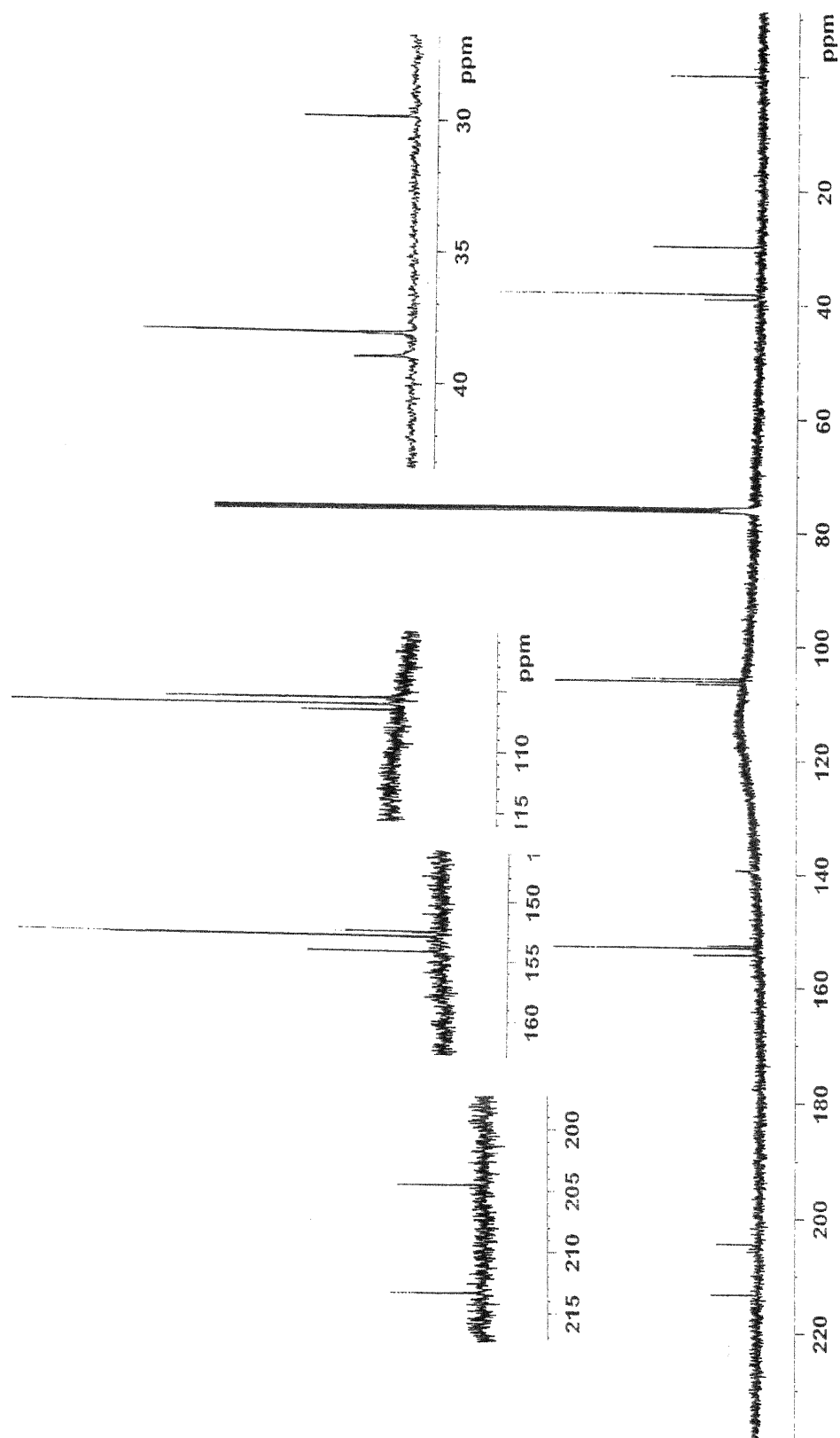


Figure 4.5.2.4 : The ^{13}C - $\{^1\text{H}\}$ -NMR spectrum of $\text{cis-[W(CO)}_4(4\text{-dmap})_2]$ recording from d-chloroform solution rel. to TMS

Upon coordination of the pyridine ligand to the W- central atom, the $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum of the $\text{cis-W(CO)}_4(4\text{-dmap})_2$ complex recording from its d-chloroform solution (Figure 4.5.2.4) shows the appearance of signals for the methyl group, C3,5 , C2,6 and C4 at 38.15, 105.96, 152.74 and 153.34 ppm respectively. This unremarkable shift of these signals would easily imply the weak metal ligand coordination through the nitrogen lone pair of the pyridine ligand. One could easily observe the appearance additional signals very closed to those of the free ligand. Additional signals at 39.03 ppm for methyl groups, at 106.35 and 106.80 ppm for C3,5 and at 152.74, 153.05,154.34 ppm for C2,6. This splitting of the signals belonging to CH_3 , C3,5 and C2,6 could be best explain by the stereogenic nitrogen. However, pyramidal nitrogen is normally not configurationally stable. It rapidly inverts its configuration (equilibrium arrows) by passing through a planar, sp^2 -hybridized transition state, leading to a mixture of interconverting R and S configurations. In addition the spectrum of the complex show the appearance of two signals at 204.42 and 213.10 ppm for the carbonyl groups of the M(CO)_4 part of the complex. The appearance of these two signals with relative intensities 1:1 for the carbonyl groups is the best indication to the formation of the cis-W(CO)_4 part instead of trans group at which onyl signal is expected.

4.5.3. COMPUTATIONAL CALCULATIONS (DFT)

Computational calculations of the free ligand (4-dmap) and $W(CO)_4(4\text{-dmap})_2$ complex were performed by using Gauss-view molecular visualization program and Gaussian 03 program package. To compare the results, the geometry of the complex was optimized using MPW1PW91/SDD/6-311G¹ method.

The molecular structure of tetracarbonylbis(4-dimethylaminopyridine) tungsten(0) is shown in Figure 4.5.1.3 along with labeling and symbolizing. The calculated selected bond length and bond angle of the free ligand and complex are given in Table 4.5.3.1 at SDD/6-311G¹ basis set level. Carbonyl ligand (CO) are known to act as σ -donor and π -acceptor species. The M-CO σ -bond is formed by donation of electron pair of carbon atom(HOMO) to the empty d-orbital of the transition element (CO-M bond). The result is called π -back bonding. In the case of the N atom pyridine ligands, the σ -donating component occurs as it takes place in pyridine, pyrimidine ligands. Also, presence of the substituent group in position on the pyridine ring would affect the π component of the W-N bond.

From the results of the calculation one can say that the metal –carbon bond distance for CO in trans-position (axial) to the 4-dmap (W-C11=1.9585 Å) is slightly shorter than that of other cis-CO ligands (W-C13/W-C15 = 2.025 Å) in the equatorial positions. The reason of that is coming from the π -accepting ability of nitrogen atom is much less than that of CO. In other words, CO ligand is a strong σ -donor/ π -acceptor ligand than pyridine.

Also, from the DFT calculations of the free ligand the N1-C2 bond in the pyridine ring is found to be 1.3340 Å. After bonding with metal small change of the bond length is improve that forming a weak metal-pyridine bond.

Table 4.5.3.1 Selected calculated bond length and bond angle of the free ligand (4-dmap) and complex

ATOM	Bond Length (Å)	
	Ligand	Complex
N1-C2	1.3340	1.3435
N1-C6	1.3340	1.3439
C2-C3	1.3801	1.3724
C5-C6	1.3801	1.3728
C4-N4	1.3572	1.3495
N4-C7	1.4465	1.4489
C2-H2	1.0868	-----
C6-H6	1.0868	-----
C3-C4	1.4093	-----
C3-H3	1.0804	-----
C5-C4	1.4094	-----
C5-H5	1.0804	-----
N4-C8	1.4466	-----
N1-W	-----	2.2840
W-C13	-----	2.0254
C13-O14	-----	1.5446
W-C11	-----	1.9585
C11-O12	-----	1.1656
W-C15	-----	2.0255
C15-O16	-----	1.5446

ATOM	BOND ANGLE	
	Ligand	Complex
C3-C4-N4	122.16	122.22
C4-N4-C8	120.06	120.18
C2-N1-C6	115.26	-----
N1-C2-C3	125.12	-----
C3-C4-C5	115.65	-----
C5-C4-N4	122.19	-----
C4-N4-C7	120.04	-----
C7-N4-C8	119.88	-----
N4-C7-H7	109.27	-----
W-N1-C2	-----	121.61
N1-W-C11	-----	175.7
N1-W-C15	-----	93.98
N1-W-C13	-----	93.98
C6-N1-W	-----	122.66
N1-W-C9	-----	94.43
W-C13-O14	-----	173.91

Table 4.5.3.2 Theoretical ^1H and ^{13}C NMR chemical shifts (with respect to TMS) of (4-dimethylaminopyridine) and cis-tetracarbonylbis (dimethylaminopyridine) tungsten(0)

^1H -NMR (Chem. Shift (ppm))			^{13}C -NMR (Chem. Shift (ppm))		
ATOM	Ligand	Complex	ATOM	Ligand	Complex
H2	8.1771	7.3222	C2	147.12	150.34
H6	8.1771	8.2174	C6	147.12	150.77
H5	6.2119	6.1136	C3	101.93	102.71
H3	6.2119	5.8799	C5	101.93	102.38
H7	2.4888	2.4562	C4	149.26	149.54
H7 ^I	2.7435	2.6072	C7	33.68	33.76
H7 ^{II}	2.7435	2.6072	C8	33.68	33.76
H8	2.4888	2.4562	C13,15	-----	199.74
H8 ^I	2.7435	2.7534	C9,11	-----	217.73
H8 ^{II}	2.7435	2.7534			

Table 4.5.3.3 Calculated thermodynamic properties of 4-dimethylaminopyridine and the complex cis-tetracarbonylbis(dimethylaminopyridine) tungsten(0) using the MPW1PW91/SDD/6-311G¹ method

Parametre	Molecule
E_{Electronic} (Hartrees)	-382.259
E_{ZPVE} (Hartrees)	-382.096
E (Hartrees)	-382.087
H (Hartrees)	-382.086
G (Hartrees)	-382.130
ΔE_{ZPVE} (Kcal/Mol)	102.413
ΔH (Kcal/Mol)	108.468
ΔG (Kcal/Mol)	80.692
ΔE (KCal/Mol)	
Total	107.876
Translational	0.890
Rotational	0.890
Vibrational	106.098
ΔS (Cal/Mol-Kelvin)	
Total	93.162
Translational	40.313
Rotational	28.732
Vibrational	24.118
C_v (Cal/Mol-Kelvin)	
Total	31.403
Translational	2.981
Rotational	2.981
Vibrational	25.441
HOMO Energy (a.u.)	-0.25233
LUMO Energy (a.u.)	0.02054
ΔE_{LUMO-HOMO} (a.u.)	0.27287
RMS Gradient (a.u.)	0.00000000
Dipole Moment (Debye)	6.0721

Parameter	Molecule
E_{Electronic} (Hartrees)	-1285.604
E_{ZPVE} (Hartrees)	-1285.239
E (Hartrees)	-1285.210
H (Hartrees)	-1285.209
G (Hartrees)	-1285.304
ΔE_{ZPVE} (Kcal/Mol)	229.011
ΔH (Kcal/Mol)	248.051
ΔG (Kcal/Mol)	188.470
ΔE (KCal/Mol)	
Total	247.459
Translational	0.890
Rotational	0.890
Vibrational	245.681
ΔS (Cal/Mol-Kelvin)	
Total	199.833
Translational	44.745
Rotational	36.495
Vibrational	118.593
C_v (Cal/Mol-Kelvin)	
Total	103.406
Translational	2.981
Rotational	2.981
Vibrational	97.445
HOMO Energy (a.u.)	0.01063
LUMO Energy (a.u.)	-0.02184
ΔE_{LUMO-HOMO} (a.u.)	0.03247
RMS Gradient (a.u.)	0.00001527
Dipole Moment (Debye)	21.8051

Table 4.5.3.4 : NBO Analysis of the free ligand and complex

State	Orbital	Character	Bond	Occupancy	Energy
29	H-4	LP1	N1	1.92093	-0.34780
30	H-3	BD2	N1 - C6	1.73622	-0.30130
31	H-2	BD2	C2 - C3	1.72202	-0.26827
32	H-1	BD2	C5 - C4	1.59579	-0.26022
33	H	LP1	N4	1.68901	-0.25233
34	L	BD*2	N1 - C6	0.43588	0.02054
35	L+1	BD*2	C5 - C4	0.44079	0.02827
36	L+2	BD*2	C2 - C3	0.30737	0.03824
37	L+3	BD*2	N4 - C8	0.01670	0.37263
38	L+4	BD*2	N4 - C7	0.01670	0.37265

State	Orbital	Character	Bond	Occupancy	Energy
95	H-6	BD2	C5-C6	1.73047	-0.28379
96	H-5	BD2	C5-C6	1.73041	-0.28371
97	H-4	LP1	N1	1.34990	-0.22481
98	H-3	LP1	N1	1.34978	-0.22467
99	H-2	LP1	W	1.40270	-0.11692
100	H-1	LP2	W	1.37626	-0.10626
101	H	LP3	W	1.15072	0.01063
102	L	BD*2	C4-N4	0.64500	-0.02184
103	L+1	BD*2	C4-N4	0.64507	-0.02180
104	L+2	BD*2	C5-C6	0.27130	0.02791
105	L+3	BD*2	C5-C6	0.27133	0.02797
106	L+4	BD*2	C2-C3	0.27410	0.02805
107	L+5	BD*2	C2-C3	0.27421	0.02810

Table 4.5.3.5: MLCT and LCT States of the free ligand and complex

State	Transition	Composition (%)	Wavelength (nm)	Oscillator	Energy (eV)
3	32 -> 34	100	226.49	0	5.4742
4	32 -> 35	100	218.52	0.0044	5.6737
5	33 -> 36	100	193.22	0.0343	6.4169
6	33 -> 34	15.64	191.69	0.1501	6.4679
7	30 -> 35	15.85	182.48	0.5366	6.7944
	31 -> 34	69.51			
	33 -> 35	14.64			
9	33 -> 38	87.13	171.31	0	7.2376
10	33 -> 37	14.47	164.4	0.0174	7.5414
12	32 -> 36	74.31	155.97	0.0089	7.9492
13	30 -> 34	74.15	155.76	0.3027	7.9598
	31 -> 35	25.85			
14	31 -> 36	30.14	154.69	0.0003	8.0148
15	29 -> 34	100	154.08	0.0059	8.0466
16	29 -> 35	100	151.8	0	8.1675
19	31 -> 38	80.54	143.93	0.0154	8.6141
21	31 -> 37	60.08	143.56	0.0001	8.6365
22	32 -> 37	13.34	143.28	0.0118	8.6533
23	32 -> 38	17.15	142.48	0.1762	8.702

State	Transition	Composition (%)	Wavelength (nm)	Oscillator	Energy (eV)
1	101 ->102	81.50	414.43	0.0351	2.9917
3	100 ->102	72.24	393.35	0.0005	3.1520
7	101 ->104	11.64	341.03	0.0953	3.6356
	101 ->105	62.05			
	101 ->106	11.15			
9	101 ->107	67.23	318.16	0.0230	3.8970
10	100 ->104	83.66	313.69	0.0524	3.9525
12	100 ->105	47.15	308.22	0.0359	4.0226
13	99 ->104	49.73	306.80	0.1284	4.0412
15	100 ->106	85.41	294.46	0.0109	4.2106
16	99 ->106	70.92	288.54	0.0132	4.2970
	99 ->107	17.57			
20	99 ->105	6.81	269.65	0.0533	4.5980
28	98 ->102	32.58	250.32	0.0590	4.9530
30	97 ->102	12.56	243.41	0.1686	5.0936
36	97 ->104	33.50	234.64	0.2948	5.2839
	98 ->105	42.32			
	98 ->106	13.72			
37	97 ->105	30.07	234.46	0.1917	5.2880
	97 ->106	15.27			
	98 ->104	19.72			
	98 ->107	19.16			
44	97 ->107	69.19	219.78	0.0211	5.6412
53	99 ->102	5.96	206.90	0.1855	5.9925
	100 ->107	5.24			
55	96 ->102	83.73	204.13	0.0373	6.0738
56	96 ->104	11.85	203.81	0.1794	6.0832
60	95 ->102	23.80	199.91	0.1699	6.2019
61	95 ->104	14.02	199.89	0.0186	6.2027
	96 ->105	12.37			
	96 ->106	9.87			

Table 4.5.3.6 Calculated vibrational frequencies of 4-(dimethylamino)pyridine

PEAK STATES	IR	RM	FC	I	VIBRATION MODES
$\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{C}) + \nu(\text{C}-\text{H})$	415.59	2.7377	0.2786	0.00	$\nu_{2,4} (4,0) + \nu_{2,5} (4,6) + \nu_{3,6} (4,4)$
$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{H})$	485.60	3.6696	0.5098	4.72	$\nu_{4,9} (2,5) + \nu_{8,11} (3,0) + \nu_{11,12} (3,0) + \nu_{12,13} (2,7) +$
$\nu(\text{C}-\text{H})$	550.76	2.5634	0.4581	24.52	$\nu_{2,5} (3,8) + \nu_{6,10} (4,4)$
$\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{N})$	555.03	3.6542	0.6632	3.03	$\nu_{1,2} (2,5) + \nu_{6,8} (3,0) + \nu_{11,12} (4,0)$
Ring	679.68	6.9597	1.8943	0.22	Ring
$\nu(\text{C}=\text{N}) + \delta(\text{C}=\text{C})$	762.66	2.9405	1.0077	0.01	$\nu_{1,3} (2,5) + \nu_{6,10} (3,0) + \text{Dihedral (C}=\text{C Bond)}$
$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{H})$	774.20	4.8350	1.7075	9.91	$\nu_{1,2} (6,2) + \nu_{3,7} (5,3)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	837.28	1.8795	0.7763	99.58	$\nu_{6,10} (6,0) + \nu_{2,5} (3,8) + \delta_{2,4,9} (3,1) + \delta_{4,8,9} (3,2) + \text{Dihedral (C-H Bonds)}$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	851.09	1.2426	0.5303	0.00	$\nu_{6,10} (10,0) + \nu_{2,5} (4,1) + \delta_{2,4,9} (5,2) + \delta_{4,8,9} (5,1) + \text{Dihedral (C-H Bonds)}$
$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{H})$	984.74	3.0130	1.7214	6.77	$\nu_{11,12} (3,0) + \nu_{11,16} (2,8) + \nu_{12,13} (4,0) + \nu_{16,19} (3,1)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	989.05	1.3298	0.7664	0.16	$\nu_{2,5} (3,0) + \nu_{6,10} (2,8) + \delta_{6,3,7} (5,2) + \delta_{1,3,7} (5,1) + \text{Dihedral (C-H Bonds)}$
Ring	1012.00	6.6679	4.0235	85.90	Ring
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1016.51	1.4299	0.8705	0.00	$\nu_{2,5} (9,4) + \nu_{6,10} (3,6) + \delta_{1,3,7} (4,8) + \delta_{6,3,7} (5,2) + \text{Dihedral (C-H Bonds)}$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1093.80	1.4617	1.0303	34.60	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1101.08	1.9775	1.4125	2.09	$\nu_{3,7} (4,0) + \nu_{4,9} (11,3) + \delta_{3,6,10} (5,7) + \delta_{8,6,10} (5,3)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1139.16	1.5658	1.1972	2.79	$\nu_{3,7} (6,4) + \nu_{4,9} (9,7) + \delta_{3,6,10} (4,0) + \delta_{8,6,10} (5,3)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1152.62	1.2469	0.9760	0.02	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1152.73	1.3233	1.0360	0.31	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1214.48	1.6760	1.4565	3.87	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1261.85	1.2417	1.1648	45.20	$\nu_{3,7} (12,3) + \nu_{4,9} (8,9) + \delta_{1,2,5} (5,5) + \delta_{4,2,5} (6,1) + \delta_{3,6,10} (3,5) + \delta_{8,6,10} (4,4)$
$\nu(\text{C}-\text{H})$	1284.94	3.2741	3.1850	67.42	$\nu_{4,9} (5,4)$
$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C}) + \nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1355.49	4.2462	4.5966	8.46	$\nu_{1,3} (2,7) + \nu_{2,4} (2,1) + \nu_{3,7} (2,9) + \nu_{4,9} (3,4) + \delta_{3,6,10} (2,5) + \delta_{8,6,10} (2,2)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1388.87	1.5590	1.7718	15.80	$\nu_{3,7} (7,4) + \nu_{4,9} (5,0) + \delta_{1,2,5} (3,8) + \delta_{4,2,5} (3,7)$
$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{H})$	1428.15	2.7041	3.2496	147.43	$\nu_{3,7} (3,9) + \nu_{4,9} (3,8) + \nu_{8,11} (3,1) + \nu_{11,12} (3,7) + \nu_{16,19} (3,3)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1461.25	1.2553	1.5792	1.54	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1480.22	2.0594	2.6585	0.93	$\nu_{3,7} (4,5) + \nu_{4,9} (4,7) + \delta_{3,6,10} (3,2) + \delta_{4,2,5} (3,2)$
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1498.92	1.0334	1.3679	0.04	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1501.50	1.2406	1.6479	69.64	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{H})$, asym	1507.62	1.0401	1.3928	24.32	$\nu_{12,13} (9,0) + \nu_{16,17} (6,4) + \nu_{16,19} (6,9)$
$\nu(\text{C}-\text{H})$, asym	1525.16	1.1136	1.5262	4.33	$\nu_{12,14} (5,7) + \nu_{12,15} (6,8) + \nu_{16,18} (8,9)$
$\nu(\text{C}-\text{H})$	1541.87	1.1509	1.6121	24.34	All C-H Bonds In CH_4 Molecules
$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{H}) + \delta(\text{C}-\text{H})$	1577.99	2.4198	3.5501	264.54	$\nu_{1,2} (2,2) + \nu_{3,7} (5,0) + \nu_{4,9} (3,1) + \nu_{8,11} (3,0) + \delta_{1,2,5} (2,9) + \delta_{4,2,5} (2,6)$
$\nu(\text{C}=\text{N}) + \nu(\text{C}-\text{C})$	1603.80	6.7078	10.1655	73.81	$\nu_{1,3} (2,2) + \nu_{4,8} (2,9) + \text{Dihedral (C}=\text{N \& C-C)}$
$\nu(\text{C}-\text{N}) + \nu(\text{C}=\text{C}) + \nu(\text{C}-\text{H})$	1667.21	5.3353	8.7376	549.62	$\nu_{1,2} (3,2) + \nu_{2,4} (3,7) + \nu_{3,6} (3,1) + \nu_{3,7} (4,9) + \nu_{4,9} (5,4) + \nu_{6,8} (4,8)$
$\nu(\text{C}-\text{H})$, asym	3031.97	1.0378	5.6209	130.01	$\nu_{12,14} (7,8) + \nu_{12,15} (8,0) + \nu_{16,19} (7,5)$
$\nu(\text{C}-\text{H})$, sym	3040.61	1.0412	5.6717	51.41	$\nu_{12,14} (7,0) + \nu_{12,15} (8,0) + \nu_{16,19} (7,5)$
$\nu(\text{C}-\text{H})$, asym	3087.37	1.1033	6.1961	0.23	$\nu_{12,14} (8,0) + \nu_{12,15} (8,0) + \nu_{16,19} (6,3)$
$\nu(\text{C}-\text{H})$, asym	3087.74	1.1064	6.2153	107.50	$\nu_{12,14} (7,8) + \nu_{12,15} (7,8) + \nu_{16,19} (6,3)$
$\nu(\text{C}-\text{H})$, asym	3170.03	1.0971	6.4955	27.66	$\nu_{16,17} (12,3) + \nu_{12,13} (5,5)$
$\nu(\text{C}-\text{H})$, asym	3171.08	1.0893	6.4540	52.34	$\nu_{2,5} (9,4) + \nu_{3,7} (6,3)$
$\nu(\text{C}-\text{H})$, sym	3175.06	1.0909	6.4796	36.18	$\nu_{2,5} (11,6) + \nu_{3,7} (7,7)$
$\nu(\text{C}-\text{H})$, sym	3183.94	1.0959	6.5455	40.57	$\nu_{16,17} (17,9) + \nu_{12,13} (8,0)$
$\nu(\text{C}-\text{H})$, sym	3248.34	1.0916	6.7862	14.30	$\nu_{4,9} (8,0)$
$\nu(\text{C}-\text{H})$, sym	3248.59	1.0918	6.7888	8.70	$\nu_{6,10} (18,9)$

Table 4.5.3.7 Calculated vibrational frequencies of [W(CO)₄(4-dmap)₂]

PEAK STATES	FREQUENCY	REDUCED MASS	FORCE CONSTANTS	INTENSITY	VIBRATION MODES
$\nu(\text{C-H})$, sym	3262.36	1.0938	6.8586	4.19	$\nu_{17,21}$ (30,4) + $\nu_{15,20}$ (23,9)
$\nu(\text{C-H})$, sym	3262.23	1.0939	6.8588	4.02	$\nu_{5,10}$ (32,0) + $\nu_{7,11}$ (22,2)
$\nu(\text{C-H})$, asym	3261.77	1.0926	6.8491	8.43	$\nu_{15,20}$ (34,3) + $\nu_{17,21}$ (27,2)
$\nu(\text{C-H})$, asym	3261.63	1.0925	6.8479	8.21	$\nu_{5,10}$ (25,7) + $\nu_{7,11}$ (36,5)
$\nu(\text{C-H})$, sym	3233.81	1.0907	6.7205	3.76	$\nu_{13,16}$ (25,1) + $\nu_{14,18}$ (16,9)
$\nu(\text{C-H})$, sym	3233.50	1.0908	6.7192	6.03	$\nu_{3,6}$ (24,7) + $\nu_{4,8}$ (17,7)
$\nu(\text{C-H})$, asym	3231.75	1.0887	6.6991	2.33	$\nu_{3,6}$ (9,8) + $\nu_{4,8}$ (14,7) + $\nu_{13,16}$ (14,9) + $\nu_{14,18}$ (23,1)
$\nu(\text{C-H})$, asym	3231.40	1.0887	6.6979	17.73	$\nu_{3,6}$ (16,6) + $\nu_{4,8}$ (21,5) + $\nu_{13,16}$ (10,2) + $\nu_{14,18}$ (14,2)
$\nu(\text{C-H})$, sym	3192.56	1.0966	6.5854	40.68	$\nu_{36,37}$ (23,8) + $\nu_{40,41}$ (15,7)
$\nu(\text{C-H})$, sym	3192.43	1.0967	6.5851	39.27	$\nu_{32,33}$ (25,6) + $\nu_{44,45}$ (23,9)
$\nu(\text{C-H})$, asym	3184.45	1.0983	6.5620	3.30	$\nu_{36,37}$ (23,8) + $\nu_{40,41}$ (25,7)
$\nu(\text{C-H})$, asym	3184.00	1.0984	6.5607	3.33	$\nu_{32,33}$ (25,7) + $\nu_{44,45}$ (27,6)
$\nu(\text{C-H})$, asym	3102.13	1.1062	6.2719	57.98	$\nu_{36,38}$ (22,0) + $\nu_{36,39}$ (22,6)
$\nu(\text{C-H})$, asym	3102.00	1.1067	6.2744	98.49	$\nu_{44,46}$ (16,6) + $\nu_{44,47}$ (16,6)
$\nu(\text{C-H})$, asym	3101.55	1.1039	6.2563	0.36	$\nu_{32,34}$ (19,7) + $\nu_{32,35}$ (20,4) + $\nu_{44,46}$ (16,6) + $\nu_{44,47}$ (16,6)
$\nu(\text{C-H})$, asym	3101.41	1.1044	6.2590	15.67	$\nu_{36,38}$ (9,6) + $\nu_{36,39}$ (9,9) + $\nu_{40,42}$ (27,0) + $\nu_{40,43}$ (27,9)
$\nu(\text{C-H})$, sym	3050.09	1.0406	5.7039	80.47	All C-H Bonds In CH ₄
$\nu(\text{C-H})$, sym	3049.96	1.0406	5.7033	64.74	All C-H Bonds In CH ₄
$\nu(\text{C-H})$, asym	3043.02	1.0380	5.6629	156.90	All C-H Bonds In CH ₄
$\nu(\text{C-H})$, asym	3043.01	1.0379	5.6625	51.88	All C-H Bonds In CH ₄
$\nu(\text{C}\equiv\text{O})$, sym	2093.77	13.2546	34.2353	598.62	All C≡O Bonds In CO
$\nu(\text{C}\equiv\text{O})$, asym	1946.51	13.3100	29.7127	1431.31	All C≡O Bonds In CO
$\nu(\text{C}\equiv\text{O})$, asym	1938.15	13.4259	29.7145	4875.51	$\nu_{26,27}$ (26,3) + $\nu_{28,29}$ (26,2)
$\nu(\text{C}\equiv\text{O})$, asym	1896.02	13.3340	28.2421	2923.35	$\nu_{22,23}$ (28,2) + $\nu_{24,25}$ (28,1)
$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$	1687.64	5.5313	9.2820	779.67	$\nu_{3,5}$ (3,3) + $\nu_{4,7}$ (3,3) + $\nu_{13,15}$ (3,3) + $\nu_{14,17}$ (3,4)
$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$	1685.57	5.3655	8.9816	678.77	$\nu_{3,5}$ (3,3) + $\nu_{4,7}$ (3,4) + $\nu_{13,15}$ (3,3) + $\nu_{14,17}$ (3,3)
$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$	1593.61	5.9965	8.9725	33.44	$\nu_{15,19}$ (5,0) + $\nu_{17,19}$ (6,2) + $\nu_{12,14}$ (4,6)
$\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$	1593.21	5.7859	8.6531	85.04	$\nu_{7,9}$ (6,2) + $\nu_{5,9}$ (4,7) + $\nu_{12,14}$ (4,6)
$\nu(\text{C}=\text{N})$	1590.35	2.8034	4.1775	546.86	$\nu_{19,31}$ (4,0)
$\nu(\text{C}=\text{N})$	1589.83	2.8804	4.2894	362.48	$\nu_{9,30}$ (4,0)
$\delta(\text{C-H})$	1543.46	1.1478	1.6110	23.39	At All CH ₄ In L2
$\delta(\text{C-H})$	1543.00	1.1460	1.6075	25.25	At All CH ₄ In L1
$\delta(\text{C-H})$	1528.34	1.2549	1.7270	2.79	At All CH ₄ In L2
$\delta(\text{C-H})$	1527.99	1.2511	1.7209	2.75	At All CH ₄ In L1
$\delta(\text{C-H})$	1511.02	1.0395	1.3984	25.55	At All CH ₄ In L2
$\delta(\text{C-H})$	1510.73	1.0396	1.3979	27.85	At All CH ₄ In L1
$\delta(\text{C-H})$	1502.90	1.0341	1.3761	1.02	At All CH ₄ In L2
$\delta(\text{C-H})$	1502.47	1.0340	1.3752	0.69	At All CH ₄ In L1
$\delta(\text{C-H})$	1499.53	1.2350	1.6362	106.63	At All CH ₄ In L2
$\delta(\text{C-H})$	1498.74	1.2533	1.6586	92.90	At All CH ₄ In L1
$\nu(\text{C}=\text{C}) + \delta(\text{C-H})$	1498.14	2.0759	2.7452	6.37	$\nu_{13,15}$ (3,5) + $\nu_{14,17}$ (3,5) + All C-H Bonds In L2
$\nu(\text{C}=\text{C}) + \delta(\text{C-H})$	1498.04	2.0382	2.6949	8.72	$\nu_{3,5}$ (3,4) + $\nu_{4,7}$ (3,5) + All C-H Bonds In L1
$\delta(\text{C-H})$	1464.33	1.1722	1.4809	0.24	At All CH ₄ In L2
$\delta(\text{C-H})$	1463.25	1.1704	1.4764	0.32	At All CH ₄ In L1
$\nu(\text{C}=\text{N})$	1438.16	2.3918	2.9147	216.00	$\nu_{19,31}$ (4,2)
$\nu(\text{C}=\text{N})$	1437.63	2.3847	2.9039	227.75	$\nu_{9,30}$ (4,1)
$\delta(\text{C-H})$	1388.12	1.5370	1.7449	9.44	In L1 And L2 Rings
$\delta(\text{C-H})$	1387.79	1.5383	1.7456	43.98	In L1 And L2 Rings

$\nu(\text{C-N})$	1358.94	3.8173	4.1534	4.94	$\nu_{12,13} (2,9) + \nu_{12,14} (3,0) + \nu_{2,3} (3,6) + \nu_{2,4} (3,8)$
$\nu(\text{C-N})$	1357.85	3.7827	4.1092	11.07	$\nu_{12,13} (3,6) + \nu_{12,14} (3,8) + \nu_{2,3} (2,9) + \nu_{2,4} (3,0)$
$\nu(\text{C-N}) + \nu(\text{C-C}) + \delta(\text{C-H})$	1289.10	2.6770	2.6210	36.33	In L2 Ring
$\nu(\text{C-N}) + \nu(\text{C-C}) + \delta(\text{C-H})$	1288.46	2.6794	2.6207	52.69	In L1 Ring
$\delta(\text{C-H})$	1269.49	1.2001	1.1395	103.94	In L1 And L2 Rings
$\delta(\text{C-H})$	1264.50	1.2026	1.1329	151.45	In L1 And L2 Rings
$\delta(\text{C-H})$	1218.86	1.6468	1.4414	4.47	At All CH ₄ In L2
$\delta(\text{C-H})$	1218.19	1.6498	1.4425	5.10	At All CH ₄ In L1
$\delta(\text{C-H})$	1157.99	1.6625	1.3135	0.79	In L2 Ring
$\delta(\text{C-H})$	1156.90	1.6661	1.3138	0.98	In L1 Ring
$\delta(\text{C-N}) + \delta(\text{C-H})$	1154.37	1.3318	1.0456	0.08	At All N-CH ₄ In L2
$\delta(\text{C-N}) + \delta(\text{C-H})$	1154.21	1.3318	1.0454	0.16	At All N-CH ₄ In L2
$\delta(\text{C-H})$	1149.25	1.2436	0.9677	0.02	At All CH ₄ In L2
$\delta(\text{C-H})$	1148.89	1.2446	0.9679	0.01	At All CH ₄ In L1
$\nu(\text{W-N}) + \nu(\text{C-N})$	1106.48	2.2534	1.6255	20.28	$\nu_{1,2} (2,5) + \nu_{1,12} (3,1) + \nu_{2,3} (3,1) + \nu_{2,4} (3,2) + \nu_{12,13} (3,9) + \nu_{12,14} (4,0)$
$\nu(\text{C=N}) + \nu(\text{C=C})$	1104.27	2.2459	1.6136	28.81	$\nu_{1,2} (3,0) + \nu_{1,12} (2,4) + \nu_{2,3} (3,9) + \nu_{2,4} (3,9) + \nu_{12,13} (3,2) + \nu_{12,14} (3,1)$
$\nu(\text{C-N}) + \delta(\text{C-N}) + \delta(\text{C-H})$	1096.92	1.4848	1.0526	35.79	At All N-CH ₄ In L2
$\nu(\text{C-N}) + \delta(\text{C-N}) + \delta(\text{C-H})$	1095.90	1.4846	1.0505	36.36	At All N-CH ₄ In L1
Ring	1038.97	6.1473	3.9097	68.60	L1 And L2 Rings
Ring	1037.14	6.2569	3.9654	79.84	L1 And L2 Rings
$\delta(\text{C-H})$	1018.96	1.3907	0.8507	1.19	In L1 Ring
$\delta(\text{C-H})$	1018.71	1.3914	0.8507	1.65	In L2 Ring
$\delta(\text{C-H})$	1001.50	1.3293	0.7855	0.51	In L1 And L2 Rings
$\delta(\text{C-H})$	1000.00	1.3266	0.7816	0.57	In L1 And L2 Rings
$\nu(\text{C-N}) + \nu(\text{C-C})$	987.08	2.9831	1.7125	7.61	$\nu_{15,19} (4,7) + \nu_{17,19} (4,9) + \nu_{31,36} (6,8) + \nu_{31,40} (6,8)$
$\nu(\text{C-N}) + \nu(\text{C-C})$	986.42	2.9767	1.7065	7.54	$\nu_{15,19} (4,7) + \nu_{7,9} (4,6) + \nu_{30,32} (6,7) + \nu_{30,44} (6,7)$
$\nu(\text{C-C}) + \nu(\text{C=N}) + \nu(\text{W-N})$	786.21	5.0618	1.8435	0.18	$\nu_{1,12} (4,7) + \nu_{15,19} (4,1) + \nu_{17,19} (4,1) + \nu_{19,31} (4,3) + \nu_{31,36} (5,7) + \nu_{31,40} (5,8)$
$\nu(\text{C-C}) + \nu(\text{C=N}) + \nu(\text{W-N})$	786.15	5.0679	1.8454	0.21	$\nu_{1,2} (4,7) + \nu_{5,9} (4,1) + \nu_{7,9} (4,1) + \nu_{9,30} (4,3) + \nu_{30,32} (5,8) + \nu_{30,44} (5,7)$
Ring	762.41	3.2839	1.1247	0.91	L1 Ring (Dihedral)
Ring	762.37	3.2879	1.1259	0.84	L2 Ring (Dihedral)
Ring	680.12	7.0713	1.9272	0.40	L2 Ring (Angle)
Ring	679.71	7.0529	1.9198	1.25	L1 Ring (Angle)
$\delta(\text{W-C}) + \delta(\text{C=O})$	624.50	12.1030	2.7810	44.03	W-C-O (Dihedral)
$\delta(\text{W-C}) + \delta(\text{C=O})$	614.56	12.7103	2.8283	42.99	W-C-O (Dihedral)
$\delta(\text{W-C}) + \delta(\text{C=O})$	604.31	12.2531	2.6364	9.95	W-C-O (Dihedral)
$\delta(\text{W-C}) + \delta(\text{C=O})$	602.04	11.9772	2.5578	3.82	W-C-O (Dihedral)
$\delta(\text{W-C}) + \delta(\text{C=O})$	552.69	2.6708	0.4807	32.12	W-C-O (Dihedral)
Ring	550.87	2.4909	0.4454	12.06	L1 And L2 Rings
$\delta(\text{W-C}) + \delta(\text{C=O})$	523.55	9.0954	1.4689	6.98	C26-O27 C28-O29 DIHEDRAL
$\nu(\text{W-C})$	504.67	14.7692	2.2163	0.11	$\nu_{1,22} (15,4) + \nu_{1,24} (14,4)$
$\delta(\text{W-C}) + \delta(\text{C=O})$	496.33	5.7662	0.8369	21.58	W-C-O (Dihedral)
$\delta(\text{W-C}) + \delta(\text{C=O})$	495.34	3.7567	0.5431	2.17	W-C-O (Dihedral)
$\delta(\text{W-C}) + \delta(\text{C=O})$	492.98	5.9423	0.8509	10.73	W-C-O (Dihedral)
$\nu(\text{W-C})$	451.91	14.0737	1.6934	2.67	$\nu_{1,26} (10,9) + \nu_{1,28} (10,9)$
$\delta(\text{W-C})$	435.52	12.4222	1.3882	1.62	$\delta_{1,26,27} (7,1) + \delta_{1,28,29} (7,1)$
$\delta(\text{C=C})$	432.08	2.9100	0.3201	0.28	$\tau_{12,14,17,19} (3,7) + \tau_{12,13,15,19} (3,4)$
$\delta(\text{C=C})$	431.14	2.9136	0.3191	0.24	$\tau_{2,3,5,9} (3,7) + \tau_{2,4,7,9} (3,6)$
$\delta(\text{W-C}) + \delta(\text{C=O})$	422.90	12.1544	1.2807	0.00	W-C-O (Dihedral)
$\nu(\text{W-N}) + \delta(\text{C-N})$	413.32	3.4306	0.3453	0.41	$\nu_{1,12} (6,4) + \nu_{1,2} (3,9) + \delta_{36,31,40} (5,9)$
$\nu(\text{W-N}) + \delta(\text{C-N})$	411.34	3.4289	0.3418	0.23	$\nu_{1,12} (4,0) + \nu_{1,2} (6,6) + \delta_{32,30,44} (6,1)$

CHAPTER 5

CONCLUSION

In this work, the aim was the synthesis of some organometallic compounds of 2-mercaptopyrimidine and 4-dimethylaminopyridine. The cause behind choosing these ligands was their multi bonding possibility to the central atom. In the first part of the work, 2-mercaptopyrimidine ligand was used and the result was the pentacarbonyl copmplexes of the N-bonded(thione) and the S-bonded (thiol) tautomeric forms in the solid and liquid phases respectively. We can easily conclude from the IR spectra of these complexes the formation of the N-bonded tautomer (thione) in solid phase and the S-bonded tautomer (thiol) in liquid phase.

In the second part of this work we aimed to the synthesis and charactarization of the sterically hindered $\text{cis-W(CO)}_4(4\text{-dmap})_2$ complex. The multibonding ability of the 4-substituted pyridine ligand was the main cause behind choosing it to metal coordination. The formation of the cis-W(CO)_4 part of the complex was first assigned by the appearance of four IR absorption bands in the CO-region of the spectrum. Besides the unremarkable shifts of the pyridine ring hydrogens and carbons in the NMR (^1H , ^{13}C) spectra would indicate the metal ligand coordination through the N1 donor site more than N4 site at which the chemical shifts of these protons will be very large. In the ^1H -NMR spectrum, one could easily observe the

splitting of these doublets to doublet of doublets. On the other hands the ^{13}C -NMR spectrum shows the appearance of a new signals in beside those assigned to the aromatic carbons. These results could be best explain by the stereogenic nitrogen in $\text{N}(\text{CH}_3)_2$ substituent on the pyridine ring causes the additional signals in the ^1H and ^{13}C NMR spectra. Unstable configuration of the pyrimidal nitrogen rise to splitting of the signal for each proton and carbon atom in the ring and the methyl groups in dimethylamine sustituent.

In addition the appearance of two signals of the relative intensity 1:1 in the carbonyl reagon (190 – 230 ppm) was the best indication to the formation of the cis-tetracarbonyl part of the complex.

At the end of this work we aimed also to the DFT calculations of all the synthysised complexes at different bases sets and we have concluded that there were a good agreement between the experimental results we have measured and the theoretical results we have calculated using the Density Functional Theory calculation methods in our personal computer.

REFERENCES

- [1] Werner, A. Z. , 1893, Inorganic Chem. 3, 267 .
- [2] Zeise, W. C. , 1831, Annalen der Physic. and Chemic, 21, 497-541.
- [3] Astruc, D; 2000, Organometallic Chemistry and Catalysis, Springer Verlag Berlin Heidelberg.
- [4] Crabtree, R. H. , 2005 The Organometallic Chemistry of the Transition Metals Fourth Edition, John Wiley & Sons Inc, N. J.
- [5] Methora, R. C; Singh, A. ; 2000, Organometallic Chemistry A Unified Approach, Second Edition, New Age International Ltd, Press, NewDelhi.
- [6] Wilkinson G. , Rosenblum M. , Witting M.C. , Woodward R. H. , J. Amer. Chem. Soc. 74, 2125 (1952).
- [7] Kealy J. J. and Pauson P. L. ,1951, Nature, 168, 1039.
- [8] Spessard G. O. , Miessler G. L, 2000, Organometallic Chemistry.
- [9] Mord L. , Hirtz H. ,Cowap M. D. 1910, J.Chem. Soc. ,62, 789.
- [10] Malatesta L. , Angoletta M. ,1957, J. Chem. Soc. ,1186.
- [11] Malatesta L. ,Cariello C. ,1958, J. Chem. Soc. ,2323.
- [12] Store F. G. A. ,West R. , 1975, 'Advanced in Organometallic Chemistry'.

- [13] Mord L. , Hirtz Z. ,1910, All gem. Chem. , 68, 789.
- [14] Job A. , Cassel A. , 1927, Bull. Chem. Soc. , France, 41, 1041.
- [15] Job A. ,Rauvilous J. ,1928, Compt. Rend. ,187,564.
- [16] Dewar J. , Jones H. O. ,1907, Chem, News, J. Indust. Sci. 95, 129.
- [17] Speyer E. , Wolf M. ,1927, Chem. Ber. 60,1424-1425.
- [18] King R. B. , Eisch J.J. , King(Eds.) R. B. ,Organometallic Synthesis, Vol.1 Academic Press.
- [19] (a) $\text{Cr}(\text{CO})_6$:Strohmeier W. ,Gerlach K. ,Natuforsch Z. ,1960, 15b, 413; (b) Strohmeier W. ,Gerlach K. ,Natuforsch Z. ,1960, 15b, 622; (c) Strohmeier W. ,Gerlach K. ,Natuforsch Z., 1960, 15b,1346-1349; $\text{Mo}(\text{CO})_6$: Strohmeier W. ,Gerlach K. , Matthias G., Natuforsch Z. ,1960, 15b, 621-622.
- [20] Strohmeier W. ,Gerlach K. ,Natuforsch Z. , 1960, 15b, 675-676.
- [21] Jones L. H. ,1961, Advanced in the Chemistry of Coordination Compounds, Kirschner, S.Edition, Macmillon, New York.
- [22] Brateman P. S. ,1975, Metal Carbonyl Spectra, Academic Press,Lond.
- [23] Crabtree R. H. , 1998, The Organometallic Chemistry of the Transition Metals, John Wiley and Sons Inc. ,New York.
- [24] Yorbrough W. A. , 1989, MRS Fall Meeting, Boston, Nov. 28, Paper Fl.3.
- [25] Bar-Yam Y. , Maustakes T. D. , 1989, Nature 342, 786.
- [26] Matsumato S. , Sato Y. , Tsutsumi M. ,1982, et al. ,J. Matter, Sci. 17, 3106.

- [27] Spear K. E. , 1987, Earth Miner . Sci. 56-53.
- [28] Zhang Y. F. , Zhang F.G. ,1994, Chem. J. Matter. Res. 9,2845.
- [29] Bifferwolf T.E. , 2004, J. Organometal. Chem. ,689 (24), 3939.
- [30] Wrighton M. , Hammond G. S. ,Gray H. B. , 1970, J. Am. Chem .Soc. , 92,6068; Wrighton M. , Hammond G. S. ,Gray H. B. ,1971, J. Am. Chem .Soc. ,93, 3285; Wrighton M. , Hammond G. S. ,Gray H. B. , 1974, J.Organometal. Chem .Soc. ,70, 283; Wrighton M. S. , Hammond G. S. ,Gray H. B. , 1971, J. Am. Chem .Soc. ,93, 4336; Inorg. Chem. ,1972, 11, 3122, Mol. Photochem. , 1973, 5, 179.
- [31] Weiner M. A. , Gin A. And Lattman M. ,1977, Inorg. Chim. Acta, 24, 235.
- [32] Nasielski J. and Colos A. , 1975, J. Organometal. Chem. ,101,215 ; Nasielski J. and Colos A. ,1978, Inorg. Chem. ,17, 237.
- [33] Cotton F.A., Wilkinson G. 1962, 1966, 1972, Advanced Inorganic Chemistry, Third Edition, John Wiley&Sons Inc.
- [34] Khan, T. ; Zkeeruddin, S.U. ,1986, Inorg. Chim. Acta, 24, 5-11.
- [35] Senge, M.O. , 1996, Angew. Chem. , Int. Ed. Engl. 35,1923.
- [36] (a) S-centered Radicals ; Alfassi, Z. B. , Ed. ; Wiley; Chichester, U. K. 1999. (b) Sulfur-centered Reactive Intermediates in Chemistry and Biology; Chatgililoglu, C. , Asmus, K. –D. , Ed. ; NATO ASI Series; Plenum Press; New York, 1990. (c) Gonzalez, V. M. ; Fuertes, M. A. ; Perez-Alvarez, M.J. ; Cervantez, G. ; Morem , V. ; Alonso, C. ; Perez , J. M. Biochem. Pharm. 2000, 60, 371-379. (d) Toda, F. ; Tanaka, K. ; Sato, J. Tetrahedron; Asymmetry 1993, 4, 1771-1774.
- [37] Von Poelhsitz, G. ; Batista, A. A. ; Ellena, J. ; Castellano, E.E. ; Schulz Lang, E. , 2005, Inorg. Chem. Comm. , 8, 805-808.
- [38] (a) Contretras, J.G. ; Seguel, G.V. ; Alderete, J. B. Spectrachim. Acta, 1994, 50A, 371-374. (b) Contretras, J.G. ; Alderete, J. B. Bol. Soc. Chil.

Quim. 1994, 39, 17-21. (c) Contretras, J.G. ; Alderete, J. B. Folia Chim. Theor. Lat. 1991, 19, 211-223.

[39] (a) Zhang, H. –L. ; Evans, S. D. ; Henderson, J. R. ; Miles, R. L. ; Shen, T. J. Phys. Chem. B 2003, 107, 6087-6095. (b) Zhang, H. –L. ; Chen, M. ; Li, H. –L. J. Phys. Chem. B 2000, 104, 28-36.

[40] (a) Calvente, R. M. ; Campos- Martin, J. M. ; Fierro, J. L. G. Catal. Commun. 2002, 3, 247-251. (b) Taqui Khan, M . M. ; Chartteerjee, D. ; Hussain, A. ; Moiz, A. Polyhedron 1990, 22, 2681-2687. (c) Fernandez- Gala, R. ; Manzano, B. R. ; Otero, A. ; Poujaud, N. ; Kubicki, M. J. Organomet. Chem. 1999, 576, 321-327. (d) Romero, J. ; Duran, M. L. ; Rodriguez, A. ; Garcia- Vazquez, J. A. ; Sousa, A. ; Rose, D.J. ; Zubieta, J. Inorg. Chim. Acta 1998, 274, 131-136.

[41] Tripathi, G. N. R. ; Clements, M. J. Phys. Chem. B 2003, 107, 11125-11132.

[42] (a) Pinheiro, L. S. ; Temperini, M. L. A. Surf. Sci, 1999, 441, 45-52. (b) Pinheiro, L. S. ; Temperini, M. L. A. Surf. Sci, 1999, 441, 53-64, (c) Pinheiro, L. S. ; Temperini, M. L. ; A. Appl. Surf. Sci, 2001, 171, 89-100. (d) Davis, J. J. ; Hill, H. A. ; Yamada, R. ; Naohara, H. ; Mosaki, K. J. Chem. Soc. , Faraday Trans. 1988, 94, 1315-1319, (e) Pang, Y. S. ; Hwang, H. J. ; Kim, M. S. J. Mol. Struct. 1998, 441, 63-76.

[43] (a) Huber, F. ; Schmiedgen, R. ; Schurmann, M. ; Barbieri, R. ; Ruisi, G. ; Silvestri, A. Appl. Organomet. Chem. 1997, 11, 869-888. (b) Schmiedgen, R. ; Huber, F. ; Schurmann, M. ; Silvestri, A. ; Ruisi, G. ; Rossi, M. ; Barbieri, R. Appl. Organomet. Chem. 1998, 12, 861-871.

[44] Raper, E. S. , Coord. Chem. Rev. 1996, 153, 199.

[45] Fandos, R. ; Lfranchi, A. ; Otero A. ; Pellinghelli, M. A. ; Ruiz, M. J. ; Terreros, P. ,1996, Organometallics, 15, 4725.

[46] Brandt, K. ; Sheldrick, W. S. Inorg. Chim. Acta, 1998, 267, 39.

[47] Antiolo, A. ; Carrilo Hermosilla, F. ; Corrocharo, A. E. ; Fandos, R. ; Fernandet Baeza, J. ; Rodriguez, A. M. ; Ruiz, M. J. ; Otero, A. ,1999, Organometallics, 18, 5219-5224.

- [48] Dennenberg, R. J. ,Darensbourg, D. J. ,1972, Inorg. Chem, 11, 72.
- [49] Spinner, E. J. , 1960, Chem. Soc., 1237.
- [50] Jones, R. A. ; Katrinzky, A. R. ,1958, J. Chem. Soc, 3610.
- [51] Stoyanov, S. ; Petrov, L. ; Antorov, L. ; Stoyanov, T. ; Karagianniais, P. ; Aslanidis, P. Can. J. Chem. , 1990, 68, 1482.
- [52] Stoyanov, S. ; Stoyanov, T. ; Akrivos, P. D. , 1998, Trends, Appl. Spectrosc, 2, 89.
- [53] Aroney, M. J. ; Clarkson, R. M. ; Hambley, T. W. ; Pierens, R. K. , 1992, J. Organomet. Chem. 426, 331.
- [54] Banarjee S. , Voit B. , Heinrich G. , Böhme F. , 2012, Germany.
- [55] Denneberg R. J. , Darensbourg D. J. , 1972, Inorg. Chem. , 11, 72.
- [56] Annoney M. J. , Clarkson R. M. , Hambley T. W. , Pierens R. K. , 1992, J. Organometal. Chem. , 426, 331.
- [57] Van Dam H. , Boxhoorn G. , Stufkens D. J. , 1981, Oskam Ad. Inorg. Chim. Acta, 53, 235.
- [58] Kolodziej R. M. , Lees A. J. , 1986, Organometallics, 5, 450.
- [59] Creaven B. S. , Howie R. A. , Long C, 2001, Acta Crystallogr. C, 57, 385.
- [60] Boxhoorn G. S. , Stufkens D. J. , Coolwijk P. J. M. , Hezemans A. M. F. , 1981, Inorg. Chem. , 20, 2778.
- [61] Hill, A. F. , 2002, Organotransition Metal Chemistry.

- [62] Jean. Y. , 2005, Molecular Orbitals of Transition Metal Complexes.
- [63] Wilkinson, G. , 1987, (Ed.), Comprehensive Coordination Chemistry, Vols. 1-7, Pergamon Press, Oxford.
- [64] Kawaguchi, S. , 1988, Variety in Coordination Modes of Ligands in Metal Complexes, Springer, Berlin.
- [65] Garnovskii, A. D. , 1988, Coord. Chem. (USSR), 14, 579.
- [66] Garnovskii, A. D. , Nivorozhkin, A. L. , Minkin, V. I. , 1993, Coord. Chem. Rev. 126.
- [67] Akrivos, P. D. , 2001, Coord. Chem. Rev. 213, 181-210.
- [68] Denneberg, R. J. , Darensbourg, D. J. ,1972, Inorg. Chem. 11, 72.
- [69] Anoney, M. J. ,Clarkson, R. M. , Hambley, T.W. , Pierens, R. K. ,1992, J. Organomet. Chem. 420, 331.
- [70] Koppel, H. C. , Springer, R. H. , Chong, C. C. , Robins, R. K. ,1962, J. Org. Chem . ,27, 181-184.
- [71] Anoyan, A. A. , Kaldrikyan, M. A. , Grigoryan, L. A. ,1973, Arm. Khim. Zh. ,22(5), 401-405; 32(12), 1020-1025.
- [72] Hull, R. , Lovell, B. J. , Openshaw, H. T. , Todd, A. R. ,1947, J. Chem. Soc. , 41-44; Curd, F. H. S. , Rose, F. L. , 1946, J. Chem. , 343-345; Swiss Patent No. 345, 426, (1962)
- .
- [73] Hadjikakou, S. K. , Demertzis, M. A. ,Kubicki, M. , Kovala-Demertzi, D. ,2000, Organotin adducts with pyrimidinethione; crystal structure of dimethyldi(pyrimidine-2-thiolato)tin IV and diphenyldi(pyrimidine-2-thiolato)tin (IV), Applied Organometallic Chemistry, vol. , 14, no.11, pp.727.

- [74] Akrivos, P.D. ,2001, Coord. Chem. Rev. ,213, 181-210.
- [75] Lima, M. C. , Coutinho, K. , Canuto, S. , Rocha, W.R. ,2006, J. Chem. A, 110, 7253-7261.
- [76] Penfold, B. R. , 1953, Acta Crystallogr., 6, 707.
- [77] Beak, P. , Fry, I. S. ; Lee, J. ; Steela, F. ,1976, J. Am. Chem. Soc. , 98, 171.
- [78] Perrin, D. D. , 1956, Dissociation contents of organic bases in aqueous solution ; Butterworths ;London, p 164.
- [79] Kashima, C. ; Katoh, A. ; Shimiuzu, M.; Omote, Y., 1984, Heterocycles, 22(11), 2591.
- [80] Grupta, S. P. ,Sharma, S. ; Goel , R. K.,1986, Spectrachim. Acta, 42 A(10), 1171.
- [81] Guo-Sheng, H. ; Yong-Hong, L. ; Bao- Hua, C. ,Yong-Xiang, M. Chem. Pap.1999, 53(1), 65.
- [82] Raper, E. S. ,1985, Coord. Chem . , Rev. ,61, 115.
- [83] Raper, E. S. ,1994 , Coord. Chem . , Rev., 129, 91.
- [84] Raper, E. S. ,1997, Coord. Chem . , Rev. , 165, 475.
- [85] Reedjik J. , Smit J. A. , 1972, Recl. Trav. Chim. Pays-Bays 91, 681.
- [86] Reedjik R. , 1969, Recl. Trav. Chim. Pays-Bays. ,88, 1139.

- [87] Cook D. , 1963, Can. J. Chem. ,41, 515.
- [88] Houk C. C. , Emerson K. , 1968, J. Inorg. Nucl. Chem. , 30, 1493.
- [89] Kennedy B. P. , Lever A. B. P. , 1972, Can. J. Chem. , 50, 3488.
- [90] Evans P. I. , Wilkinson G. , 1974, J. Chem. Soc. Dalton Trans. ,946.
- [91] Coates G. E. , Green M. L. H. ,Powell P. , Wade K. , 1968, Principles of Organometallic Chemistry.
- [92] Wilkinson G. , Stone F. G. A. , Abel E. W. , 1982, Ed. , Comprehensive Organometallic Chemistry, Vol.3, Sections 26.1, 27.1, 28.1, Pergamon Press, Oxford.
- [93] Sundaraganesan N. , Saleem H. , Mohan S. ,2003, Spectrochim. Acta (Part A) 59, 1113.
- [94] Peek P. S. , Mcdermatt D. P. , 1988, Spectrochim. Acta 44, 371.
- [95] (a) Zhang H. –L. ; Evans, S. D. ; Henderson, J. R. ; Miles, R. L. ; Shen, T. J. Phys. Chem. B 2003, 107, 6087-60. (b) Zhang, H. –L. ; Chen, M. ; Li, H.-L. J. Phys. Chem, B 2000, 104, 28-36.
- [96] Nowak, M. J. ; Rostkowska, H. ; Lapinski, L. ; Leszczynski, J. ; Kwiatkowski, J. S. Spectrochim. Acta 1991, 47A, 339-353.
- [97] (a) Sathyanarayana, D. N. ; Roja, S. V. K. Spectrachim Acta 1985. 41 A, 809-813. (b) Shinmugam, R. ; Sathyanarayana, D. N. Bull Soc. Chim. Belg. 1984, 93, 121-127. (c) Shunmugam, R. ; Sathyanarayana, D. N. Spectrachim Acta, 1954, 40A, 757-761. (d) Goel, R. K. ; Gupta, C. ; Gupta, S. P. ; Indian J. Pure Appl. Chem. 1985, 23, 344-348. (e) Spinner, E. J. Chem Soc. 1960, 1237. (f) Spinner, E. J. Org. Chem. 1958, 23, 2037-2308.

[98] (a) Martos-Calvente, R. ; de la Pena O'Shea, V. A. ; Campos-Martin, J. M. ; Fierro, J. L. G. J. Phys. Chem . A 2003, 107, 7490-7495.

[99] Poilbac R. , and Beyergne, M. 1962, Bull. Soc. Chim. France, 1301.

[100] Orgel, L. E. , 1962, Inorg. Chem, 1, 25.

[101] Kaesz, H. D. , El- Sayed, M. A. , 1962, J. Mol. Spectry. , 9, 310.

[102] Kohn, W. , Becke, A. D. , Parr, R. G. ,1996, Density Functional Theory of Electronic Structure.

[103] Andzelm, J. , Wimmer, E. ,1992, J. Chem. Phys. 96, 1280.

[104] Johson, B. G. , Gill, P.M.W. ,Pople, J. A. , 1993, J. Chem. Phys.98, 5612.

[105] Handy, N. C. , Murray, C. W. , Amos, R. D. ,1993, J. Phys. Chem. 97, 4392.

[106] Scott, A. P. , Radom, L. ,1996, J. Phys. Chem.100, 16502.

[107] Wong, M. W. , 1996, Chem. Phys. Lett. 256, 391.

[108] (a) Hohenberg, P. ; Kohn , W. ,1964, Phys. Rev. 136, 864. (b) Kohn, W. , Sham, L. ,1965, J. Phys. Rev. ,140, 1133. (c) Parr, R. G. , Yang, W. ,1989, Density Functional Theory of Atoms and Molecules, Oxford University Press; Oxford.

[109] (a) Ziegler, T. , 1991, Chem. Rev. 91, 651. (b) Johnson, B. G. , Gill, P.M.W. ,Pople, J. A. ,1993, J. Chem. Phys. ,98, 5612. (c) Siegbahn, P. E. , 1996, M. Adv. Chem. Phys. , 93. 333.

- [110] Gordon, M. S. , Cundari, T. R. ,1996, Coord. Chem. Rev. ,147. 87.
- [111] Lin, Z. , Hall, H. B. , 1993, Coord. Chem. Rev. ,123, 149.
- [112] Russo, T. V. , Martin, R. L. , Hay, P. J. , 1995, J. Phys. Chem. 99, 17085.
- [113] Van Wüllen, C. , 1996, Int. J. Quantum Chem. 58, 147.
- [114] Bytheway, I. , Bacskay, G. B. , Hush, N. S. , 1996, J. Phys. Chem. 100, 6023.
- [115] Burke, K. , Perdew, J. P. , Wang, Y. , in: Dobson, J. F. , Vignale, G. , das, M. P.(Eds.), 1998, Electronic Density Functional Theory; recent Progress and New directions, Plenum, New York, pp. 81-121.
- [116] Perdew, J. P. , in: Ziesche, P. , Eschring, H (Eds.), 1991, Electronic Structure of Solids 91, Akademie Verlag, Berlin, pp. 11-20.
- [117] Perdew, J. P. , Chevary, A. J. , Vosko, S. H. , Jackson, K. A. , Pederson, M. R. , Singh, D. J. , Fiolhais, C. ,1992, Phys. Rev. B46, 6671-6687.
- [118] Perdew, J. P. , Chevary, A. J. , Vosko, S. H. , Jackson, K. A. , Pederson, M. R. , Singh, D. J. , Fiolhais, C. ,1992, Phys. Rev. B48, 4978-14978.
- [119] (a) Becke, A. D. , 1992, J.Chem. Phys. 97, 9173-9177. (b) Becke, A. D., 1993, J.Chem. Phys. 98, 5648-5652.
- [120] Lee, C. T. , Yang, W. T. , Parr, R.G. , 1988, Phys. Rev. , 785-789.

[121] Stephens, P. J. ,Devlin , F. J. , Chabalowski, C. F. , Frisch, M. J. , 1994, J. Phys. Chem. 98, 11623-11627.

[122] Ditchfie, R. Hehre, W. J. , Pople, J. A. , 1971, J. Chem. Phys.54, 724.

[123] Hehre, W. J. , Pople, J. A. ,1972, J. Chem. Phys.56, 4233.

[124] Binkley, J. S. , Pople, J. A. , 1977, J. Chem. Phys.60, 879-880.

[125] Hehre, W. J. , Ditchfie, R. , Pople, J. A. , 1972, J. Chem. Phys.56, 2257.

[126] Francl, M. M. , Pietro, W. J. , Hehre, W. J. , Binkley, J. S. , Gordon, M. S. , 1982, J. Chem. Phys.77, 3654-3665.

[127] Frish, A. , Nielsen, A. B. , Holder, A. J. , 2001, Gauss View User Manual, Gaussian Inc. ,Pittsburgh.

[128] Frish, M.J. , et al, 2003, Gaussian 03, Revision B4, Gaussian Inc., Pittsburgh,PA.

[129] Moran, D. , Sukchroenphon, K. , puchta, R. , Schaefer, H. F. , III.; Schleyer , P.v. R. ; Hoff, C. D., 2002, J. Org. Chem. , 9061-9069 and references therein.

[130] (a) Xantheas, S. , Dunning, T. H. , 1993, J. Phys. Chem.97, 6616. (b) Smart, B. A. , Schiesser, C. H. ,1995, J. Comput. Chem. , 16, 1055. (c) Ruttink, P. J. A. , Burgers, P.C. , Francis, J. T. , Terlouw, J. K. , 1996, J. Phys. Chem. 100, 9694. (d) Frank, A. J. , Sadilek, M. , Ferrier, J. G. , Turecek, F. , 1997, J. Am. Chem. Soc. 119, 12343. (f) Turecek, F. , 1998, J. Phys. Chem.A 102, 4703.

[131] Freeman, F. , Cha, C. , 2004, J. Phys. Org. Chem. 17, 32-41.

- [132] Freeman, F. , 2004, J.Phys. Chem. 96, 443-455.
- [133] Tsuzuki, S. , Lüthi, H. P. , 2001, J. Chem. Phys.,114, 3949-3957.
- [134] Clark, T. , Chandrasekhar, J. , Spitznagel, G. W. ,Schleyer, P.v.R. ,1983, J. Comp. Chem., 294.
- [135] Koch, W. , Holthausen, M. C. , 2001, A Chemist's Guide to Density Functional Theory , second Edition.
- [136] Olsen, J. , Jargensen, P. J. 1985, J. Chem .Phys. 82, 3235-3264.
- [137] Helgaker, T. U. , Jensen ,H.J.A. , Jorgensen, P. J. , 1986, J. Chem. Phys.84, 6280-6284.
- [138] Chang, D.P. ; Casida, M. E. , 1995, Recent advances in density functional methods, World Scientific; Singapore, part1.
- [139] Fukui, K. , 1975, Theory of Orientation and Stereoselection, Springer-Verlag, Berlin.
- [140] Lewis, D. F. V. , Loannide, C. , Parke, D. V. , 1994, Xenobiotica 24, 401-408.
- [141] Bieger, W. , Seifert, G. , Eschrig, H. , Großmann, G. 1985, Chem. Phys. Lett. 115, 275.
- [142] Friedrich, K. , Seifert, G., Großmann, G. 1990, Phys.D,17,45.
- [143] Friedrich, K. 1990, PhD thesis, Technische Universität Dresden, Dresden, Germany (in German).

[144] Malkin, VG. , Malkina OL. , Salahub, DR, 1993, Chem. Phys. Lett, 204, 80.

[145] Malkin VG. , Malkina OL. , Salahub, DR, 1993, Chem. Phys. Lett, 204, 87.

[146] Malkin VG. , Malkina OL, Casida ME, Salahub DR, 1994, J. Am. Chem. Soc. 116, 5898.

[147] Malkin VG., Malkina OL, Erikson LA, Salahub DR, 1995. In; Politzer P, Seminario, JM (eds) Modern density functional theory; a tool for chemistry; Elsevier, Amsterdam, p 273.

[148] Schreckenbach, G. , Ziegler, T. , 1995, J. Phys. Chem. 99, 606.

[149] Schreckenbach, G. , Ziegler, T. , 1996, Int. J. Quantum. Chem. 60, 753.

[150] Schreckenbach, G. Dickson, RM. , Ruiz-Morales, Y. , Ziegler, T., 1996, In; Laird BB, Ross RB, Ziegler T, (eds) chemical applications of density functional theory. ACS Symposium Series 629. American Chemical Society, Washington DC. , p 328.

[151] Schreckenbach, G. Ziegler T, 1997, Int. J. Quantum Chem, 61, 899.

[152] Schreckenbach, G. ,1996, PhD thesis , University of Calgary, Alberta, Canada.

[153] Kaupp, M., Malkina OL, Malkin VG, 1998, In ; Schleyer PRv (ed) Encyclopedia of computational chemistry, Wiley, New York.