

**DOKUZ EYLUL UNIVERSITY  
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**PHOTOCHEMICAL SUBSTITUTION REACTIONS OF  
SOME TRANSITION METAL CARBONYL  
COMPLEXES**

**by**

**Pelin KÖSE**

**June, 2008  
İZMİR**

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SOME TRANSITION METAL CARBONYL  
COMPLEXES**

**A Thesis Submitted to the  
Graduate School of Natural and Applied Sciences of Dokuz Eylül University  
In Partial Fulfillment of the Requirements for the Degree of Master of Science in  
Chemistry**

**by  
Pelin KÖSE**

**June, 2008  
İZMİR**

## M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**PHOTOCHEMICAL SUBSTITUTION REACTIONS OF SOME TRANSITION METAL CARBONYL COMPLEXES**” completed by **PELİN KÖSE** under supervision of **ASSOC. PROF. DR. ELİF SUBAŞI** and we certify that in our opinion it is fully adequate, in scope and in quality , as a thesis for the degree of Master of Science

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**Pelin KÖSE**

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## ABSTRACT

Transition metal carbonyl complexes especially VIB metal carbonyls are the oldest classes of organometallic chemistry. These are among the most well studied organometallic compounds. Metal carbonyls have been proved as reactive species in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation. Carbon monoxide serves simply as a ligand providing the complex with the necessary reactivity and/or stability to allow reaction to ensue. A large number of Schiff bases and their complexes have been studied for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins and complexing ability towards some toxic metals.

We have investigated photochemical reactions of VIB metal carbonyl complexes with salen type [O, N, N, O] Schiff bases in THF. The new **1-6** complexes have been synthesized and characterized by elemental analyses, FTIR, <sup>1</sup>H-NMR and mass spectra. The spectroscopic studies show that first ligand is coordinated to the central metal as a tetradentate ligand coordinating *via* the central azomethine nitrogens (C=N) and phenolic oxygen atoms to the central metal in **1-3**, whereas second ligand is coordinated to the central metal as a tetradentate ligand coordinating *via* aromatic methoxy and phenolic oxygen atoms to the central metal in **4-6**.

**Keywords:** Metal carbonyls; Schiff base; Photochemical reaction

# BAZI GEÇİŞ METAL KARBONİL KOMPLEKSLERİNİN FOTOKİMYASAL SÜBSTİTÜSYON REAKSİYONLARI

## ÖZ

Geçiş metal karbonil kompleksleri özellikle de VIB grubu metal karbonilleri organometalik kimyanın en eski sınıfındandır. Bunlar organometalik bileşiklerin en çok çalışılanları arasındadır. Metal karbonilleri, hidrojenleme, hidroformilleme ve karbonilleme gibi homojen kataliz tepkimelerinde reaktif türler olarak kullanılmaktadır. Karbonmonoksit tepkimenin meydana gelmesini sağlayan gerekli reaktivite ve kararlılıktaki kompleks oluşumunda basit bir ligand olarak hizmet eder. Schiff bazı ve kompleksleri tersinir olarak oksijene bağlanabilen olefinlerin hidrojenlenmesinde katalitik aktivite gösterme ve bazı zehir etkisi olan metallerle kompleksleşebilme gibi önemli ve ilginç özellikleri nedeniyle geniş ölçüde çalışılmaktadır.

Biz VIB metal karbonil kompleksleri ile Salen tipi [O, N, N, O] Schiff bazlarının THF içindeki fotokimyasal tepkimelerini inceledik. **1- 6** kompleksleri sentezlendi ve elemental analiz, FTIR, <sup>1</sup>H-NMR ve kütle spektrumları ile yapıları aydınlatıldı. Spektroskopik çalışmalar ilk ligandın **1- 3** komplekslerinde merkez metale azometin azotu ve fenolik oksijen atomları vasıtasıyla dört dişli olarak koordine olduğunu, buna karşın ikinci ligandın **4- 6** komplekslerinde aromatik metoksi ve fenolik oksijen atomları ile merkez metale dört dişli bağlandığını göstermektedir.

**Anahtar kelimeler:** Metal karbonil; Schiff baz; Fotokimyasal reaksiyon

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## CHAPTER ONE

### INTRODUCTION

The preparation of new transition metal complexes is perhaps the most important step in the development of coordination chemistry which exhibits unique properties and novel reactivity. There is no doubt that changes in the electronic, steric, and geometric properties of the ligand alter the orbitals at the metal center and thus affect its properties. Recently, interest in the chemistry of transition metal compounds that contain Schiff base ligands has increased greatly due mainly to their involvement in many important reactions.

Schiff bases play an important role as chelating ligands in main group and transition metal coordination chemistry. (Temel H., & Şekerci M., 2001; Bermejo M.R, Sousa A., Garcia-Deibe A., Maneiro M., Sanmartin M., & Fondo J., 1999; Temel H., Ilhan S., Şekerci M. & Ziyadanoğullari R., 2002; Temel H., Hoşgören H., 2002; Temel H., Ilhan S., & Şekerci M., 2002). Recently, interest in chemistry of transition metal compounds that contain Schiff-base ligands has increased greatly due mainly to their involvement in many important reactions. Transition metal complexes of Schiff-base ligands find applications as models of certain metal enzymes and in catalysis and materials chemistry. (Garoufis A., Kasselouri S., Mitsopoulou C.A., Sletten J., Papadimitriou C., & Hadjiliadis N., 1999). Schiff-base complexes are known to show antifungal activity, which is increased by the presence of a hydroxy group in the ligand (Chang-Hsien L., 1993).

The Schiff-base metal carbonyl complexes have continued to attract attention in part because of the different possible coordination geometries which the ligand may adopt. (Kirtley S.W., in: G. Wilkinson, F.G.A., Stone E.W. Abel (EDs.), 1982; Lal De R. Samanta (née Bera) K., & Banerjee I., 2001; Kaim W., & Kohlmann S., 1987). Their low energy metal-to-ligand charge transfer (MLCT) transitions make these molecules attractive for luminescence and electron transfer reactions. (Trost B.M., & Lautens M.; 1983). Besides this, several of these complexes have been shown to be effective catalysts in allylic alkylation reactions. (Brisdon B.J., Brown D.W., &

Wills C.R., 1986; Shiu K.B., Chou C.C., Wang S.L., & Wei S.C., 1990) and in the activation of aromatic carbon-hydrogen bonds (orthometallation) *via* intramolecular  $\eta^2$ -bonding of arenes (Kagan H.B., in: G. Wilkinson, F.G.A. Stone, E.W., 1982) Polydentate Schiff bases containing nitrogen and oxygen donor atoms are useful for the synthesis of transition metal complexes which play important role in biological systems. (Frausto da Silva J.J.R., Williams R.J.P, 1991; Kaim W., Schwederski B.,1996). Such classes of ligands were also found to provide catalytic characteristics especially for epoxidation reactions (Katsuki T., 1995; Horwitz C.P., Creager S.E., & Murray R.W., 1990; K.Srinivasan, P.Michaud, J.K. Kochi, 1986; Samsel E.G., Srinivasan K., & Kochi J.K., 1985)

## **1.1 VIB Metal Hexacarbonyls (M = Cr, Mo, W )**

### ***1.1.1 Chromium Hexacarbonyl***

Chromium hexacarbonyls,  $\text{Cr}(\text{CO})_6$ , is the most important organochromium compounds. It is an air stable, volatile complex with few atoms and high symmetry, and as a consequence it has been the subject of numerous studies. Moreover, chromium hexacarbonyls is an octahedral  $d^6$  complex that is kinetically inert, so its reaction kinetics can be conveniently studied. Chromium hexacarbonyls is used as the starting material for virtually all chromium carbonyls compounds and a large number of other chromium (0) species. Chromium carbonyl compounds have several industrial uses, and the potential for many more.

#### *1.1.1.1 Synthesis*

Chromium hexacarbonyl  $\text{Cr}(\text{CO})_6$  was first synthesized by Jop and Cassal in 1926 by the reactions of anhydrous chromium trichloride with carbon monoxide and a large excess of phenylmagnesium bromide at 40°C and atmospheric pressure, followed by acid hydrolysis. This “Grignard Method” has subsequently been modified and improved by a number of workers (Table 1.1), but yields have been

variable and sensitive to solvents and conditions. It is probable that these syntheses proceed via labile arylchromium intermediates (Figure 1.1) (Wilkinson, G., Stone, F.G.A., & Abel, E.W., 1982)

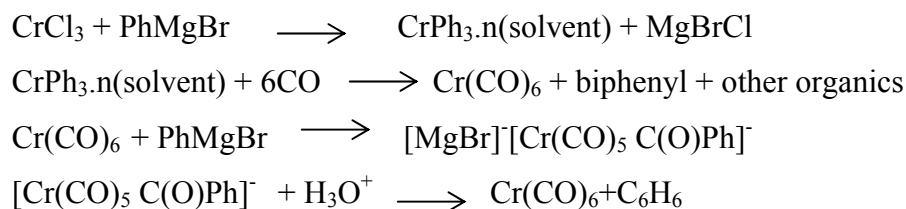


Figure 1.1 Synthesis of  $\text{Cr}(\text{CO})_6$  via labile aryl chromium intermediates

A preferred method for the synthesis of chromium carbonyl involves the reactions of a chromium (III) salt with a suitable reducing agent in the presence of carbon monoxide (Table 1. 1). these reductive carbonylation reactions that use the Grignard method. Most reductive carbonylation reactions produce chromium hexacarbonyl directly, but in the presence of sodium a chromium (2-) species is formed initially (Figure 1. 2). (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982),

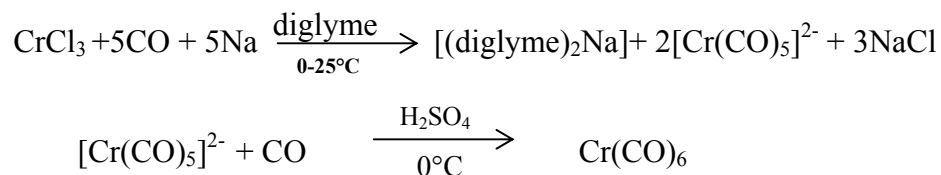


Figure 1.2 Synthesis of  $\text{Cr}(\text{CO})_6$  via “ reductive carbonylation “

Unlike many other transition metals, chromium cannot easily be combined directly with carbon monoxide to produce chromium hexacarbonyl. However, chromium metal specially prepared by the reduction of  $\text{CrCl}_3$ . THF solutions by potassium is sufficiently reactive to combine directly with carbon monoxide Table 1.1. Since chromium hexacarbonyl is available from a number of commercial sources, few workers in the field currently synthesize it. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

Tablo 1.1 Synthesis of  $\text{Cr}(\text{CO})_6$ 

Reactions	Solvent	T(°C)	p <sub>co</sub> (atm)	Comments
<b>A-Grignard method</b>				
$\text{CrCl}_3 + \text{excess} + \text{PhMgBr} + \text{CO}$	Diethyl ether	4	1	Followed by acid hydrolysis
$\text{CrCl}_3 + \text{CO} + 7.5\text{PhMgBr}$	Diethyl ether		50	3h; followed by acid hydrolysis
<b>B-Reductive carbonyllation</b>				
$\text{Cr}(\text{acac})_3 + \text{CO} + \text{Mg} + \text{I}_2$	Pyridine	80-170	100-300	iodine catalyst
$\text{CrCl}_3 + \text{CO} + \text{LiAlH}_4$	Diethyl ether	65	100	
$\text{CrCl}_3\text{py}_3 + \text{e}^-$	Pyridine	85	60	electrochemical reduction
$\text{CrCl}_3 + \text{AlCl}_3 + \text{Al} + \text{CO}$	Benzene	145	150-200	10h
$\text{CrCl}_3 + \text{Et}_3\text{Al} + \text{CO}$	Diethyl ether	115	100-200	7h
$\text{CrCl}_3 + \text{Na} + \text{CO}$	diglyme	-10to25	50	24h; followed by acid hydrolysis under CO
<b>C.Direct combination</b>				
$\text{CrCl}_3 \cdot 3\text{THF} + \text{K} \rightarrow \text{Cr} + 6\text{CO}$	THF	high	280	

(Taken from (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982))

#### 1.1.1.1 Physical Properties

Chromium hexacarbonyl is a colorless, odorless, volatile diamagnetic solid that forms orthorhombic crystals with a density of  $1.77\text{gcm}^{-3}$ . The solid melts in air at  $130^\circ\text{C}$  with decompositions and under vacuum at  $150^\circ\text{C}$  without decomposition, chromium hexacarbonyl is hydrophobic, air stable compound that is very slightly soluble in nonpolar organic solvent (1% w/v), slightly soluble in polar organic solvent such as THF and chloroform (5% w/v maximum), and insoluble in water. Solution of chromium hexacarbonyl decomposes very slowly when exposed to oxygen. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

#### 1.1.1.2 Thermodynamic Data

Chromium hexacarbonyl is extraordinary for a compound with a molecular weight of 220.06. It is easily sublimed, even at  $25^\circ\text{C}$  and 0.1 at  $100^\circ\text{C}$ . The heat of sublimation and other thermodynamic data are collected in Table 1.2.

Table 1.2 Thermodynamic data for Cr(CO)<sub>6</sub> at 298 K

Process	Reactions	Symbol	Best Value	Range
Sublimation	$\text{Cr(CO)}_{6(c)} \rightarrow \text{Cr(CO)}_{6(g)}$	$\Delta H^\circ_s$	71.6	69.3-76.1
Combustion	$\text{Cr(CO)}_{6(c)} + 3.75\text{O}_{2(g)} \rightarrow 0.5\text{Cr}_2\text{O}_{3(c)} + 6\text{CO}_{2(g)}$	$\Delta H^\circ_c$	-1941	-1845 to -1949
Formation	$\text{Cr}_{(c)} + 6\text{C}_{(g)} + 3\text{O}_{2(g)} \rightarrow \text{Cr(CO)}_{6(c)}$	$\Delta H^\circ_f$	-980	-978 to -1077
Ther.decom.	$\text{Cr(CO)}_{6(c)} \rightarrow \text{Cr}_{(c)} + 6\text{CO}_{(g)}$	$\Delta H^\circ$	315	315

(Taken from (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

#### 1.1.1.4 Molecular Structure

The structure of chromium hexacarbonyl (Figure 1.3) results an electron diffraction study of gaseous Cr(CO)<sub>6</sub> and X-ray and neutron diffraction studies of crystalline Cr(CO)<sub>6</sub> at liquid nitrogen temperatures. The studies all indicate that the molecule has virtually perfect octahedral (Oh) molecular symmetry. Bond distances and angles of chromium hexacarbonyl are collected in Table 1.3. the compound crystallizes in the orthorhombic space group *Pnma*, and although the molecule only lies on a minor plane in the crystal (site symmetry C<sub>s</sub>), the octahedral symmetry is retained to an excellent approximation. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982).

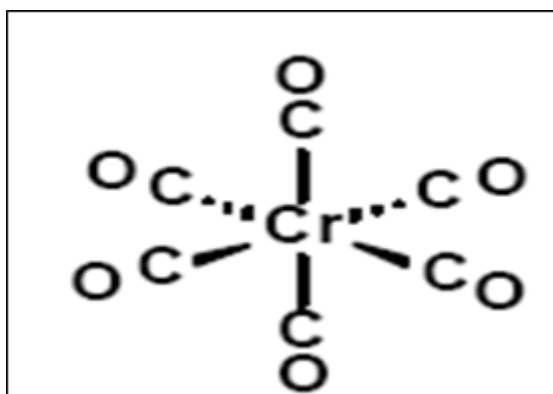


Figure 1.3 The molecular structure of Cr(CO)<sub>6</sub>

Table 1.3 The molecular structure of  $\text{Cr}(\text{CO})_6$ 

Diffraction method	Distance ( $\text{\AA}$ )	Angle
Electron	Cr-C 1.92(4)	
	Cr-O 1.16(5)	
X-Ray	Cr-C 1.915(1)	Cr-C-O 179.4(1)
	Cr-O 1.140(1)	C-Cr-C (cis) 90.02(3)
X-Ray	Cr-C 1.909(3)	
	Cr-O 1.137(4)	
Neutron	Cr-C 1.914(1)	Cr-C-O 179.48(5)
	Cr-O 1.140(1)	C-Cr-C (cis) 90.03(2)
		C-Cr-C (trans) 179.35(7)

(Taken from (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

Molybdenum and Tungsten are VIB group metals, like Chromium. Therefore, the properties of these metals are discussed in the next sections. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

## 1.1.2 Molybdenum Hexacarbonyl

### 1.1.2.1 Synthesis

Molybdenum hexacarbonyl  $\text{Mo}(\text{CO})_6$  was the first of the Group VIB metal carbonyl to be prepared. It was synthesized by Mond in 1910 by reacting pyrophoric molybdenum, obtained from the oxychloride by hydrogen reduction, with carbon monoxide at 250 atm and 200°C. This and other “dry methods” of synthesis are collected in Table 1.4. The “wet methods” used to synthesize  $\text{Cr}(\text{CO})_6$ , reductive carbonylation and Grignard methods, have also been used to synthesize  $\text{Mo}(\text{CO})_6$  and some are also listed in Table 1.4. Since  $\text{Mo}(\text{CO})_6$  is commercially available, few workers currently synthesize the compound. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

Tablo 1.4 Selected Mo(CO)<sub>6</sub> synthesis

Reactions	Conditions	Yield (%)
Mo+CO	dry ;p <sub>CO</sub> =250 atm;200°C	Low
MoCl <sub>5</sub> +PhMgBr+CO	diethyl ether	15-20
MoCl <sub>5</sub> +Zn+CO	ether-benzene;p <sub>CO</sub> =100 atm;0-10°C	46
MoCl <sub>5</sub> +Al+CO	ether;3-16h; p <sub>CO</sub> =70 atm;20-100 °C	60-90
MoCl <sub>5</sub> +Fe+(CO) <sub>5</sub> +CO	ether;HCl present ;p <sub>CO</sub> =100 atm	28
MoCl <sub>5</sub> +Et <sub>3</sub> Al+CO	benzene;3h;p <sub>CO</sub> =70 atm;50-60 °C	76
MoCl <sub>5</sub> +Na+CO follwed by Acid hydrolysis	diglyme;-20 to 25 °C ;p <sub>CO</sub> =65 atm 50-60°C	65
MoO <sub>3</sub> +CO	300°C;p <sub>CO</sub> =200 atm ;12h	89

(Taken from (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

### 1.1.2.2 Physical Properties

Mo(CO)<sub>6</sub> is colorless, odorless, diamagnetic solid that forms orthorhombic crystals with a density of 1.96 gcm<sup>-3</sup>. The crystals are air stable and hydrophobic and decompose without melting at 150°C, but melt reversibly under vacuum at 146(2)°C. Mo(CO)<sub>6</sub> is very slightly soluble of Mo(CO)<sub>6</sub> are quite stable to oxidation and decompose only very slowly in air. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

### 1.1.2.3 Thermodynamic Data

Mo(CO)<sub>6</sub> has a high vapor pressure (0.27 Torr at 30°C, 42.8 Torr at 100°C) and is easily sublimed at room temperature has been calculated to be  $\log p=11.727 - 3561.3/T$  between 55°C and 145°C or  $\log p=11.727-3788.3/T$  between 50.5°C and 129.6 °C. Other thermodynamic data are collected in Table 1.5.

Table 1.5 Thermodynamic data for Mo(CO)<sub>6</sub> at 298K

Process	Reactions	Symbol	Range
Sublimation	Mo(CO) <sub>6(c)</sub> → Mo(CO) <sub>6(g)</sub>	ΔH <sup>°</sup> <sub>s</sub>	68.3-73.6
Combustion	Mo(CO) <sub>6(c)</sub> + 4.5O <sub>2(g)</sub> → MoO <sub>3(c)</sub> + 6CO <sub>2(g)</sub>	ΔH <sup>°</sup> <sub>c</sub>	-2116 to -2123
Formation	Mo <sub>(c)</sub> + 6C <sub>(g)</sub> + 3O <sub>2(g)</sub> → Mo(CO) <sub>6(c)</sub>	ΔH <sup>°</sup> <sub>f</sub>	-919
Ther.decom.	Mo(CO) <sub>6(c)</sub> → Mo <sub>(c)</sub> + 6CO <sub>(g)</sub>	ΔH <sup>°</sup>	297-326

(Taken from (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982)

### 1.1.2.4 Molecular Structure

The structure of Mo(CO)<sub>6</sub> (Figure 1.4) results from electron diffraction studies and an early X-Ray diffraction study. They indicate that Mo(CO)<sub>6</sub> has octahedral (Oh) symmetry in both gaseous and solid states. Values of the Mo-C distance from electron diffraction studies are 2.08(4), 2.06(2) and 2.063(3) Å and the corresponding C-O distances are 1.15(5), 1.15 and 1.145(2) Å. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

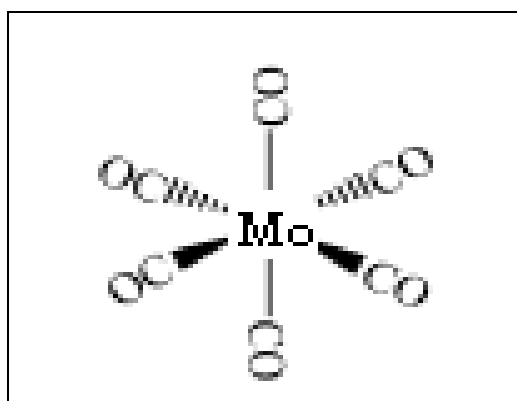


Figure 1.4 The molecular structure of Mo(CO)<sub>6</sub>



### 1.1.3 Tungsten Hexacarbonyl

#### 1.1.3.1 Synthesis

Tungsten hexacarbonyl  $W(CO)_6$  was first prepared by Jop and Rouvillois in 1928 via the reaction of  $WCl_6$  with  $PhMgBr$  and carbonmonoxide. Later, improved syntheses of  $W(CO)_6$  used reductive carbonylation and synthetic details of both methods are listed in Table 1.6.  $W(CO)_6$  can be formed by direct combination of the metal with CO at high pressure and temperature. Since  $W(CO)_6$  is commercially available from many sources, few workers in the field currently synthesize the compound. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982).

Tablo 1.6 Selected  $W(CO)_6$  syntheses

Reactions	Conditions	Yield (%)
$WCl_6+PhMgBr+CO$ Followed by acid hydrolysis	diethyl ether	Low
$WCl_6+Zn+CO$	$p_{CO}=100$ atm; ether/benzene;0-10°C	70
$WCl_6+Al+CO$	$p_{CO}=70$ atm ;3-16h;;20-100 °C	60-90
$WCl_6+Et_3Al+CO$	benzene; $p_{CO}=70$ atm;50-95 °C; 3h	92
$WCl_6+Fe(CO)_5$	$H_2$ ; pressure ;diethyl ether	85
$WCl_6+Na+CO$	diglyme; $p_{CO}=60$ atm ;20-25 °C ;20h	75
$W+CO$	$p_{CO}=200$ atm ; 200-300°C; dry	-
$WO_3+CO$	24h; 300°C; $p_{CO}=2000$ atm ; dry	85

(Taken from (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982)

#### 1.1.3.2 Physical Properties

$W(CO)_6$  is a colorless, odorless, diamagnetic solid that forms orthorhombic crystals of density  $2.65 \text{ g cm}^{-3}$ . The crystals are air stable, hydrophobic and melt with decompositon at  $150^\circ\text{C}$ , but under vacuum melt reversibly at  $166(2)^\circ\text{C}$ .  $W(CO)_6$  is very slightly soluble in non-polar organic solvent such as hexane (1% by weight), slightly soluble in polar organic solvents such as THF (to a maximum 5% by weight) and insoluble in water. Solutions of  $W(CO)_6$  are quite stable to oxidation and decompose very slowly when exposed to air. (Wilkinson, G., Stone, F.G.A.& Abel, E.W., 1982).

### 1.1.3.3 Thermodynamic Data

In spite of a molecular weight of 351.91,  $\text{W}(\text{CO})_6$  has a vapor pressure of 0.35 Torr at  $50^\circ\text{C}$  and 14.1 Torr at  $100^\circ\text{C}$  and therefore sublimes quite readily under vacuum. The variation of vapor pressure with temperature, along with other thermodynamic data is collected in Table 1.7. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

Table 1.7 Thermodynamic data for  $\text{W}(\text{CO})_6$  at 298K

Process	Reactions	Symbol	Range
Sublimation	$\text{W}(\text{CO})_{6(\text{c})} \rightarrow \text{W}(\text{CO})_{6(\text{g})}$	$\Delta H^\circ_s$	69.7-76.6
Combustion	$\text{W}(\text{CO})_{6(\text{c})} + 4.5\text{O}_{2(\text{g})} \rightarrow \text{WO}_{3(\text{c})} + 6\text{CO}_{2(\text{g})}$	$\Delta H^\circ_c$	-2243 to -2258
Formation	$\text{W}_{(\text{c})} + 6\text{C}_{(\text{g})} + 3\text{O}_{2(\text{g})} \rightarrow \text{W}(\text{CO})_{6(\text{c})}$	$\Delta H^\circ_f$	-946 to -961
Ther.decom.	$\text{W}(\text{CO})_{6(\text{c})} \rightarrow \text{W}_{(\text{c})} + 6\text{CO}_{(\text{g})}$	$\Delta H^\circ$	296

(Taken from (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982))

### 1.1.3.4 Molecular Structure

The structure of  $\text{W}(\text{CO})_6$  (Figure 1.5) results from electron diffraction studies. They indicate that  $[\text{W}(\text{CO})_6]$  has octahedral (Oh) symmetry, with values of the W-C distances 2.06(4), 2.07(2) and 2.058(3) Å, and the corresponding C-O distances 1.13(5), 1.15 and 1.148(3) Å. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

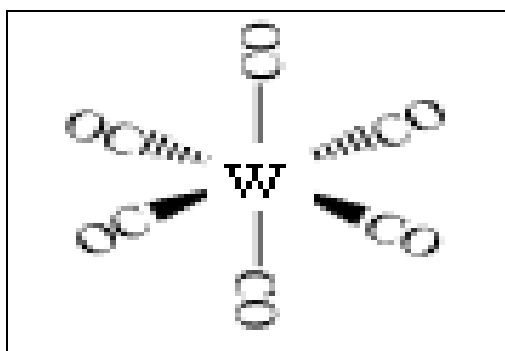


Figure 1.5 The molecular structure of  $\text{W}(\text{CO})_6$

### 1.1.4 Bonding

The bonding of  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  are qualitatively identical to that of  $\text{Cr}(\text{CO})_6$ . The valence bond picture is depicted in Figure 1.6. In Figure 1.6a the lone pair of electrons in a  $\sigma$ -orbital on the carbon atom of CO interacts with an empty 3d  $\sigma$ -orbital on the chromium atom by forming a “coordinate covalent”  $\sigma$ -bond between C-Cr. This is called the forward interaction, and is a typical donor-acceptor interaction. In Figure 1.6b, the second component of the bonding is shown, and consists of the interaction of a filled 3d  $\pi$ -orbital on the chromium with an empty  $\pi^*$ -orbital of the carbonmonoxide. This “back donation” strengthens the chromium–carbon bond while decreasing the C-O bond order. The canonical forms are shown at the right of Figure 1.6, but it should be stressed neither interaction results in a full bond. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982)

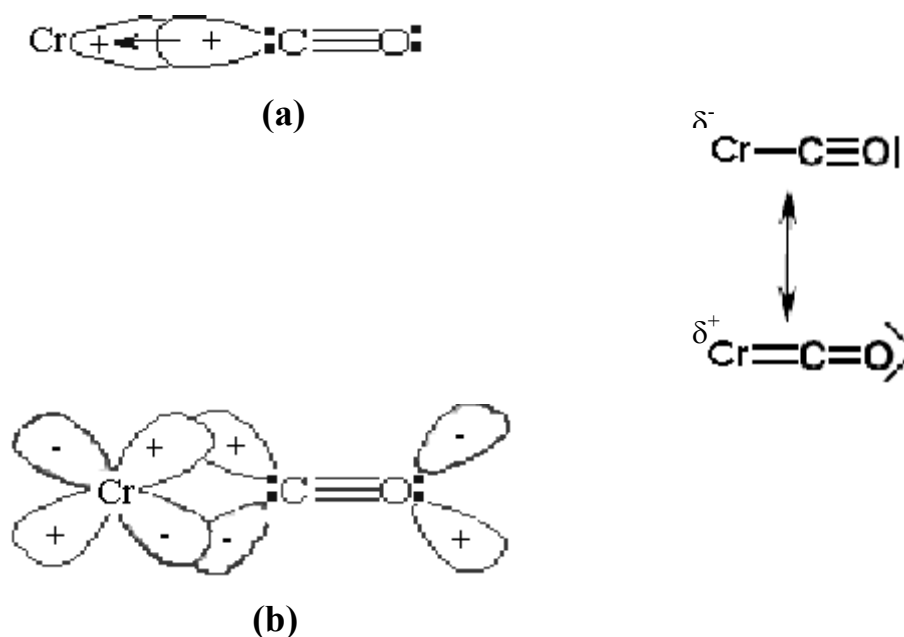


Figure 1.6 The valence bond description of chromium –carbonmonoxide bonding

### 1.1.5 Spectroscopic Properties

Spectroscopic properties of  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  are as appropriate to  $\text{Cr}(\text{CO})_6$ . Quantitative spectroscopic data for  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ) are collected in Table 1.8. (Wilkinson, G., Stone, F.G.A. & Abel, E.W.,

Table 1.8 Selected spectroscopic data for (M=Cr, Mo, W)

Method	Adsorption			Assignment	Phase
	Cr(CO) <sub>6</sub>	Mo(CO) <sub>6</sub>	W(CO) <sub>6</sub>		
IR	2000.4cm <sup>-1</sup>	2004 cm <sup>-1</sup>	1998 cm <sup>-1</sup>	T <sub>1u</sub> (νCO)	Gas
	668.1 cm <sup>-1</sup>	593 cm <sup>-1</sup>	585 cm <sup>-1</sup>	T <sub>1u</sub> (δMCO)	„
	440.5 cm <sup>-1</sup>	368 cm <sup>-1</sup>	374 cm <sup>-1</sup>	T <sub>1u</sub> (νM-C)	„
	97.8 cm <sup>-1</sup>	81 cm <sup>-1</sup>	81 cm <sup>-1</sup>	T <sub>1u</sub> (δCMC)	„
	1984.4 cm <sup>-1</sup>			T <sub>1u</sub> (νCO)	CCl <sub>4</sub> solution
	664.6 cm <sup>-1</sup>			T <sub>1u</sub> (δCrCO)	„
	443.8 cm <sup>-1</sup>			T <sub>1u</sub> (νCr-C)	„
	103 cm <sup>-1</sup>			T <sub>1u</sub> (δCCrC)	CH <sub>2</sub> Cl <sub>2</sub> solution
Raman sol.	2114 cm <sup>-1</sup>	2116 cm <sup>-1</sup>	2119 cm <sup>-1</sup>	A <sub>1g</sub> (νCO)	„
	2017 cm <sup>-1</sup>	2019 cm <sup>-1</sup>	2014 cm <sup>-1</sup>	E <sub>g</sub> (νCO)	„
	535 cm <sup>-1</sup>	476 cm <sup>-1</sup>	487 cm <sup>-1</sup>	T <sub>2g</sub> (δMCO)	„
	399 cm <sup>-1</sup>	394 cm <sup>-1</sup>	415 cm <sup>-1</sup>	E <sub>g</sub> (νM-C)	„
	379 cm <sup>-1</sup>	401 cm <sup>-1</sup>	427 cm <sup>-1</sup>	A <sub>1g</sub> (νM-C)	„
	100 cm <sup>-1</sup>	94 cm <sup>-1</sup>	94 cm <sup>-1</sup>	T <sub>2g</sub> (δCMC)	Solid
	2109.9 cm <sup>-1</sup>			A <sub>1g</sub> (νCO)	„
	2006.1 cm <sup>-1</sup>			E <sub>g</sub> (νCO)	„
	533.1 cm <sup>-1</sup>			T <sub>2g</sub> (δCrCO)	„
	397.7 cm <sup>-1</sup>			E <sub>g</sub> (νCr-C)	„
	388.0 cm <sup>-1</sup>			A <sub>1g</sub> (νCr-C)	„
	114.2 cm <sup>-1</sup>			T <sub>2g</sub> (δCCrC)	CHCl <sub>3</sub> solution
	212.3 ppm	202.0 ppm	192.1 ppm	M- <sup>13</sup> CO	CH <sub>2</sub> Cl <sub>2</sub> solution
	212.5 ppm	204.1 ppm	193.7 ppm	M- <sup>13</sup> CO	C <sub>6</sub> F <sub>6</sub> solution
214.6 ppm	202.0 ppm	191.6 ppm	M- <sup>13</sup> CO	CDCl <sub>3</sub> /C <sub>6</sub> F <sub>6</sub> sol.	
212.1 ppm		192.1 ppm	M- <sup>13</sup> CO	THF slolution	
Cr NMR (CrO <sub>4</sub> <sup>2-</sup> =0ppm) Electronic	-1795(3)ppm			<sup>53</sup> Cr-CO	
	44 200 cm <sup>-1</sup>	43.950 cm <sup>-1</sup>	44 600 cm <sup>-1</sup>	t <sub>2g</sub> → t <sub>2u</sub>	Gas
	35800 cm <sup>-1</sup>	34.900 cm <sup>-1</sup>	34 700 cm <sup>-1</sup>	t <sub>2g</sub> → t <sub>1u</sub>	Gas
	43600 cm <sup>-1</sup>			t <sub>2g</sub> → t <sub>2u</sub>	CCl <sub>4</sub> solution
			t <sub>2g</sub> → t <sub>1u</sub>	CCl <sub>4</sub> solution	
Mass spectra	8.15(17) ev	8.23(12) ev	8.47(10) ev		Gas
	8.18(17) ev	8.30(3) ev	8.48(5) ev		„
	8.48(17) ev	8.46(8) ev	8.56(13) ev	ionization	„
	8.44(5) ev	8.43(5) ev	8.46(2) ev	pot.(appearance	„
	8.42(3) ev	8.46(1) ev		potential for	„
				M(CO) <sub>6</sub>	„
Photoionazation Uvphoteelectron ESCA	9.17(4)	9.80(15) ev	9.80(17) ev	apperance	„
	9.95(10)	9.64(5) ev		potential for	„
		9.43(10) ev		M(CO) <sub>5</sub> <sup>+</sup>	„
	9.32 ev	9.14 ev	9.97(4) ev		„
	9.85 ev	10.02(2) ev	9.86(10) ev	ioanization pot.	„
	8.38(2) ev	8.35(7) ev	8.60(3) ev		„
	8.40(2)ev	8.50(2) ev	8.56(2) ev	„	„
	8.4 ev	8.5 ev	8.6 ev	„	„
					„
					„

(Taken from (Wilkinson, G., Stone, F.G.A.&amp; Abel, E.W., 1982)

The earliest studies of  $\text{Cr}(\text{CO})_6$  utilized i.r spectroscopy to examine the carbonyl stretch vibrations. The CO stretching frequency of gaseous  $\text{Cr}(\text{CO})_6$  is located at  $2000 \text{ cm}^{-1}$ , significantly lower than the value for free gaseous CO ( $2143 \text{ cm}^{-1}$ ). The lowering of the frequency corresponds to a lowering of the C-O bond order due to the occupancy of antibonding  $\pi$ -orbitals in CO by chromium 3d electron density. The lower bond order is accompanied by an increase in the C-O bond distance, from  $1.128 \text{ \AA}$  in free CO to  $1.140 \text{ \AA}$  in  $\text{Cr}(\text{CO})_6$ .

A quantitative measure of the bond order of the Cr-C and C-O bonds in  $\text{Cr}(\text{CO})_6$  can be obtained from force constant calculations. The calculations utilize IR and Raman spectroscopy, and if the simple and useful approximation that the carbonyl vibrations may be treated as if they were completely decoupled from the rest of the molecule is used, a value of  $16.49 \text{ mdyne \AA}^{-1}$  for the force constant for the C-O bond in  $\text{Cr}(\text{CO})_6$  is obtained. Since the value of the force constant of free CO is  $18.4 \text{ mdyne \AA}^{-1}$ , a decrease in the C-O bond strength is again indicated. More sophisticated calculations of force constant can be made by correcting for anharmonicity and/or using a general quadratic valence force field that does not assume that the carbonyl vibrations are decoupled. Values for the force constant of both the M-C and C-O bonds for  $\text{M}(\text{CO})_6$  (M= Cr, Mo, W ) are collected in Table 1.9, along with bond energies for the M-C bond. Both methods, however, agree that the W-CO bond is significantly stronger than the Mo-CO or Cr-CO bond, and three compounds are comparable. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

Table 1.9 the M-C and C-O bond strengths in  $\text{M}(\text{CO})_6$  (M=Cr, Mo, W )

Compound	M-C Bond energy( $\text{kJmol}^{-1}$ )	$F_{\text{M-C}}$ ( $\text{mdyne \AA}^{-1}$ ) Gen.quadratic harmonic	$F_{\text{C-O}}$ ( $\text{mdyne \AA}^{-1}$ ) Gen.quadratic harmonic	$F_{\text{C-O}}$ ( $\text{mdyne \AA}^{-1}$ ) CO factored field harmonic
$\text{Cr}(\text{CO})_6$	107	2.08	17.24	17.16
$\text{Mo}(\text{CO})_6$	151	1.96	17.33	17.15
$\text{W}(\text{CO})_6$	179	2.36	17.22	17.10

(Taken from (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982)

### ***1.1.6 Photochemistry***

The photosensitivity of metal carbonyls has been known almost as long as the class of coordination compounds itself. Among no other group of inorganic compounds may one find so many light-sensitive materials. Hence photochemical reactions of metal carbonyls have found wide applications for synthetic purposes. However, whereas much research has been done to understand the thermal reactions, the mechanism leading to photochemical reactions of metal carbonyls is not yet well investigated.

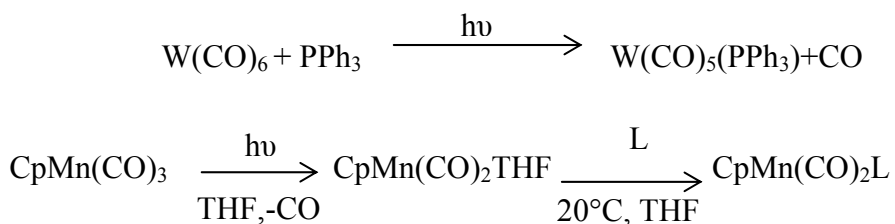
Since the metal in most carbonyl complexes, such as  $\text{Cr}(\text{CO})_6$ , has the formal oxidation state zero, a simple electrostatic picture can not account for the stability of these compounds. Only MO theory provides a model that is in agreement with the chemical and physical properties of metal carbonyls. The necessary condition to form a stable complex with a metal in low oxidation state is that the ligands be able to form  $\pi$  acceptor bonds in addition to  $\sigma$  donor bonds. The ligands must provide empty  $\pi$  orbitals that are low enough to interact with lower lying filled  $d\pi$  orbitals are thus lowered in energy to give  $\pi$ -bonding MOs that contribute very much to the stability of the complex. The metal character of this  $\pi$ -bonding MO may still predominate, but some electron density of the metal is shifted toward the ligands. The extension of the metal d orbitals toward the ligands thus introduces an appreciable covalent character into the metal-ligand bond. This delocalization of d-electron density into the ligands induces an electrostatic attraction between ligands and metal. It follows that the formation of  $\pi$  acceptor bonds (“back donations” of charge), in turn, facilitates increased  $\sigma$ -bonding, which again contributes to the stability of the complex. Both effects  $\pi$ -and  $\sigma$ -bonding are responsible for the very large d orbital splitting that occur in metal carbonyls.

It is generally accepted that this picture describes the bonding situation of metal carbonyls qualitatively. However, the quantitative description is still controversial among investigators in this field. Although different semiempirical MO calculations seem to agree with the experimental data obtained for a certain metal carbonyl, the

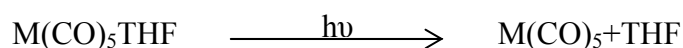
detailed interpretation of the nature of the bonding varies with the calculational procedure used. For a critical survey of different methods and their limitations the reader is referred to a paper by Fenske. ( Adomson, A.W., & Fleischauer, D.P.,1984)

### 1.1.6.1 Photochemical Substitution at Metal Carbonyl

This is the best known and the most frequently executed photoreaction in organometallic chemistry. Example :



In the carbonyl complexes  $\text{M(CO)}_m\text{L}_n$  with a mixed coordination sphere, photochemical excitation causes dissociation of that ligand which is most weakly bonded in the ground state as well. This will be the ligand at the lowest position respectively in the spectrochemical series,

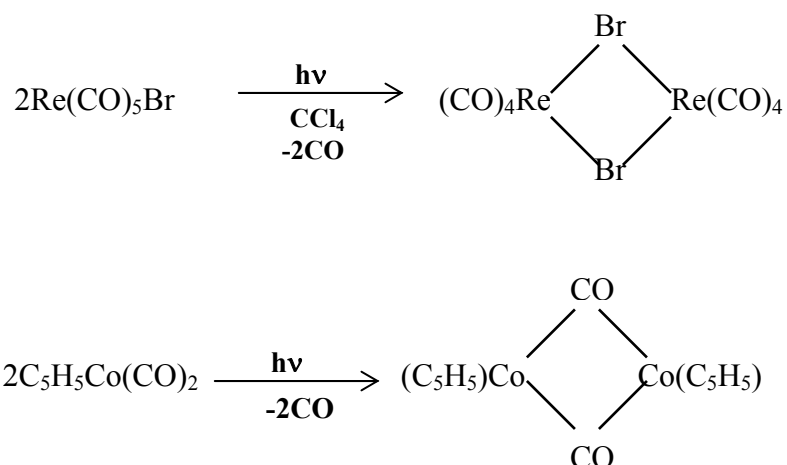


For this reason, the weakly bonded ligand THF can only be introduced once. Among ligands which form bonds of comparable strength, competitive reactions are observed.

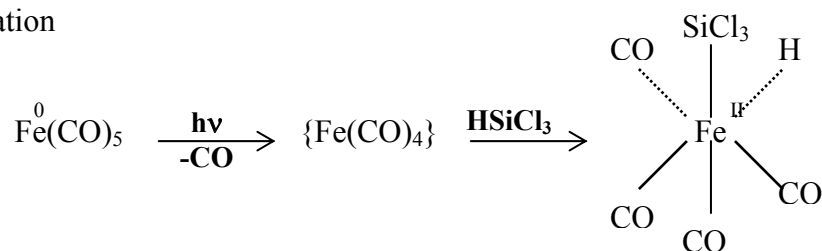


Thus, in the presence of an excess of trimethylphosphine, quantitative photochemical conversion of  $\text{Mo(CO)}_6$  into  $\text{Mo[P(OMe)}_3\text{]}_6$  can be achieved

If suitable free ligands are absent, the gap in the coordination sphere, generated through photochemical dissociation of CO, may be closed by dimerization.



Another possibility of coordinative saturation is oxidative addition, as exemplified by hydrosilation



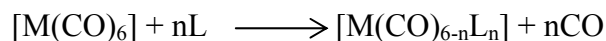
Whereas the previous examples of carbonyl substitution featured dissociative activation, the electronic peculiarities of the ligand NO permit an associative mechanism which is initiated by a preceding photochemical conversion of  $\text{NO}^+$  (linear coordination) into  $\text{NO}^-$  (bent coordination). (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982)

### 1.1.7 Substitution Reactions

By far most important property of  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ) is its use as the starting material for a vast number of substitution reactions where the metal does not change oxidation state and  $\text{L}=\text{monodentate}$  ligand. The ligand need not to be



monodentate, as a large number of similar reactions with bi- and tri-dentate ligands, are also known.



Since many products of these substitution reactions are important in their own right. Heat and/or UV radiation is often used to assist in the evolution of CO. In some cases substitution can be complete and the resultant complex will not contain CO. Because the number of potential ligands is so large, they will be divided here into three classes based on bonding modes : (1)  $\sigma$ -donor only ligands such as hydride, halide, hydroxide, ammonia, etc. (2)  $\sigma$ -donor ligands with high energy vacant  $t_{2g}$  orbitals capable of  $\pi$ -back bonding, such as phosphines, phosphites, arsine, NO, etc. and (3)  $\pi$ -donor/  $\pi$ -acceptor ligands where the electrons donated from the ligand to the metal are of the  $\pi$  type, such as alkenes and arenes. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

#### 1.1.7.1 With $\sigma$ -Donor Ligands

Table 1.10 lists some representative substitution reactions of  $\sigma$ -donor only ligands with  $\text{M}(\text{CO})_6$  ( $\text{M}=\text{Cr}, \text{Mo}, \text{W}$ ). The reactions typically are run in an ether solvent such as diethyl ether, THF, DME or diglyme, with elevated temperatures and/or UV light used to assist in CO removal. Included are monodentate, bidentate and bridging ligands. Because of zero oxidation state of chromium and the fact that the  $\sigma$ -donor ligands cannot help dissipate the electron build up on the metal, it appears that a minimum of three carbonyls must remain to accept electron density from the metal. This can be seen in the IR spectra of  $[\text{Cr}(\text{CO})_{6-x}\text{L}_x]$  complexes, for as  $x$  increases the electron population in the CO  $\pi^*$ -orbitals, which in turn decreases the bond order and the C-O stretching frequencies. For the series  $[\text{Cr}(\text{CO})_6]$ ,  $[\text{Cr}(\text{CO})_5\text{NH}_2\text{C}_y]$ ,  $[\text{Cr}(\text{CO})_4(\text{en})]$ ,  $[\text{Cr}(\text{CO})_3(\text{dien})]$ , the most intense CO stretching absorption decreases in the order 1985, 1935, 1855, 1735  $\text{cm}^{-1}$  respectively. Anionic ligands are often introduced as the salt of a large cation such as  $\text{R}_4\text{N}^+$ ,  $\text{PPN}^+$  or  $\text{R}_4\text{AS}^+$ . (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

Tablo 1.10 Representative substitution reactions of  $M(\text{CO})_6$  ( $M=\text{Cr, Mo, W}$ ) with  $\sigma$ -donor ligands

Ligand	Product	Conditions , Comment
<b>A. Hydrogen</b> $\text{H}^-$	$[\text{M}_2(\text{CO})_{10}(\mu\text{-H})]^-$	$\text{NaBH}_4$ , THF, $\Delta$
<b>B. Nitrogen</b> $\text{NEt}_3$ Dien En $\text{NCS}^-$	$[\text{M}(\text{CO})_{6-x}(\text{NEt}_3)_x]^-$ $[\text{M}(\text{CO})_3(\text{dien})]$ $[\text{M}(\text{CO})_4(\text{en})]$ $[\text{M}_2(\text{CO})_{10}(\mu\text{-NCS})]^-$	$x=1.2$  $\text{R}_4\text{N}^+\text{SCN}^-$
<b>C. Oxygen</b> $\text{OH}^-$ THF $\text{RCO}_2^-$	$[\text{M}(\text{CO})_5\text{OH}]^-$ $[\text{M}(\text{CO})_5\text{THF}]$ $[(\text{OC})_5\text{MOC}(\text{OR})]^-$	crown ether  $\text{R}=\text{Ph, Et, Bu}^n$
<b>D. Sulfur</b> $\text{R}_2\text{S}$ $\text{R}_3\text{PS}$	$[\text{M}(\text{CO})_5\text{SR}_2]$ $[\text{M}(\text{CO})_5(\text{SPR}_3)]$	$\text{R}=\text{Me, Ph, UV}$ $\text{R}=\text{Ph, Me, UV}$
<b>E. Selenium</b> $\text{R}_3\text{PSe}$ $(\text{Me}_3\text{M})_2\text{Te}$	$[\text{M}(\text{CO})_5\text{SePR}_3]$ $[\text{M}(\text{CO})_5\text{Se}(\text{MMe}_3)_2]$	$\text{R}=\text{Ph}$ $\text{M}=\text{Ge, Sn, Pb}$
<b>F. Tellurium</b> $(\text{Me}_3\text{M})_2\text{Te}$	$[\text{M}(\text{CO})_5\text{Te}(\text{MMe}_3)_2]$	$\text{M}=\text{Ge, Sn, Pb}$
<b>G. Halogen</b> $\text{X}^-$ $\text{X}^-$	$[\text{M}(\text{CO})_5\text{X}]^-$ $[\text{M}_2(\text{CO})_{10}\text{X}]^-$	$\text{X}=\text{F, Cl, Br}$ $\text{X}=\text{Cl, Br, I}$

(Taken from Wilkinson, G., Stone, F.G.A. &amp; Abel, E.W., 1982)

*1.1.7.2 With  $\sigma$ -Donor/ $\pi$ -Acceptor ligands*

The  $\sigma$ -donor/ $\pi$ -acceptor ligands, like CO, have the capability to donate electrons to the chromium and accept electrons back from the chromium into  $t_{2g}(\pi)$  orbitals of energy. Substitution reactions of such ligands with  $M(\text{CO})_6$  ( $M=\text{Cr, Mo, W}$ ) are listed Table 1.11. These synthesis employ routes and conditions similar to these used to make substituted  $\sigma$ -complexes, the  $\sigma/\pi$  complexes are sometimes capable of substituting for more than three carbonyls. Thus, can equal 1-6 for the  $\sigma/\pi$  ligands, but only 1-3 for  $\sigma$  ligands. The more complete substitutions, where  $n=4-6$ , occur only for small, excellent  $\pi$ -acceptor ligands such as  $\text{PF}_3$ . (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

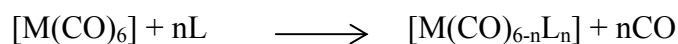


Table 1.11 Substitution reactions of  $M(\text{CO})_6$  ( $M=\text{Cr, Mo, W}$ ) with  $\sigma$ -donor/ $\pi$ -acceptor ligands

Ligand	Product	Metal	Conditions , Comment
<b>A. Carbon</b>			
CN <sup>-</sup>	$[\text{M}(\text{CO})_{6-x}(\text{CN})_x]^{x-}$	Cr, Mo, W	x=1-3
CNR	$[\text{M}(\text{CO})_{6-x}(\text{CNR})_x]^{x-}$	Cr, Mo, W	x= 1
CCR <sup>-</sup>	$[\text{M}(\text{CO})_5(\text{CCR})]^{-}$	Cr, Mo, W	R=Me, Ph
<b>B. Nitrogen</b>			
Py	$[\text{M}(\text{CO})_{6-x}(\text{py})_x]$	Cr, Mo, W	x= 1-3
Bipy	$[\text{M}(\text{CO})_{6-2x}(\text{bipy})_x]$	Cr, Mo, W	x= 1-2
Phen	$[\text{M}(\text{CO})_{6-2x}(\text{phen})_x]$	Cr, Mo, W	x= 1-3
NO	$[\text{M}(\text{NO})_4]$	Cr	
<b>C. Sulfur, Selenium</b>			
$\text{S}_2\text{C}_2(\text{CR}_3)_2$	$\text{M}\{\text{S}_2\text{C}_2(\text{CR}_3)_2\}$	Cr, Mo, W	dithiolene
$\text{S}_2\text{C}_2(\text{CF}_3)_2$	$\text{M}\{\text{S}_2\text{C}_2(\text{CF}_3)_2\}$	Mo, W	diselenoline
<b>D. Phosphorous</b>			
$\text{PH}_3$	$[\text{M}(\text{CO})_{6-x}(\text{PH}_3)_x]$	Cr, Mo, W	x=1-2
$\text{PR}_3$	$[\text{M}(\text{CO})_{6-x}(\text{PR}_3)_x]$	Cr, Mo, W	x=1-3; R=Et, Ph
$\text{PCl}_3$	$[\text{M}(\text{CO})_{6-x}(\text{PCl}_3)_x]$	Cr, Mo, W	x=1-3
Diphos	$[\text{M}(\text{CO})_{6-2x}(\text{diphos})_x]$	Cr, Mo, W	x=1-2
Triphos	$[\text{M}(\text{CO})_{6-3x}(\text{triphos})_x]$	Cr, Mo, W	x=1
$\text{R}_4\text{P}_2$	$[\text{M}_2(\text{CO})_8(\mu\text{-PR}_2)_2]$	Mo	
<b>E. Arsenic</b>			
$\text{AsH}_3$	$[\text{M}(\text{CO})_5(\text{AsH}_3)]$	Cr, Mo, W	
$\text{AsBu}_3^1$	$[\text{M}(\text{CO})_5(\text{AsBu}_3)]$	Cr, Mo, W	
Diars	$[\text{M}(\text{CO})_{6-2x}(\text{diars})_x]$	Cr, Mo, W	x=1-2
Triars	$[\text{M}(\text{CO})_3(\text{triars})]$		
$\text{AsMe}_2$	$[\text{M}_2(\text{CO})_8(\mu\text{-AsMe}_2)]$	Cr, Mo, W	

(Taken from Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982)

### 1.1.7.3 With $\pi$ -Donor/ $\pi$ Acceptor Ligands

Unsaturated organic molecules such as alkenes and arenes can donate  $\pi$ -electron density to accept metal 3d electrons into empty  $\pi^*$ -orbitals of appropriate symmetry.

The reaction of  $M(\text{CO})_6$  ( $M=\text{Cr, Mo, W}$ ) with either conjugated or non-conjugated cyclic alkenes typically results in the displacement of a maximum of three carbonyls, i.e. <3 in. Arenes, which are better  $\pi$ -acceptor ligands, can displace more than three carbonyls, however. Three of the most important classes of this type of substitution reaction are represented in Figure 1.7. A number of typical products are collected in Table 1.12. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

Table 1.12 substitution reactions of  $M(\text{CO})_6$  ( $M=\text{Cr, Mo, W}$ ) with  $\pi$ -donor/ $\pi$ -acceptor ligands

Ligand	Formula	Name	Product
Arene	$\text{C}_6\text{H}_6$	Benzene	$[\text{M}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)]$
Arene	$\text{C}_6\text{H}_6\text{Me}_3$	Mesitylene	$[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_6\text{Me}_3)]$
Anionic arene	$\text{C}_5\text{H}_5$	Cyclopentadienil	$[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$
Conjugated triene	$\text{C}_7\text{H}_8$	Cycloheptatriene	$[\text{M}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$
Conjugated triene	$\text{C}_8\text{H}_{10}$	1,3,5- cyclooctatriene	$[\text{M}(\text{CO})_3(\eta^6\text{-C}_8\text{H}_{10})]$
Non-conjugated diene	$\text{C}_8\text{H}_{12}$	cycloocta-1,5-diene	$[\text{M}(\text{CO})_4(\eta^4\text{-C}_8\text{H}_{12})]$
Non-conjugated diene	$\text{C}_7\text{H}_8$	norbornadien	$[\text{M}(\text{CO})_4(\eta^4\text{-C}_7\text{H}_8)]$
heterocycle	$\text{C}_4\text{H}_4\text{S}$	thiophene	$[\text{M}(\text{CO})_4(\eta^5\text{-C}_4\text{SH}_4)]$

(Taken from Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982)

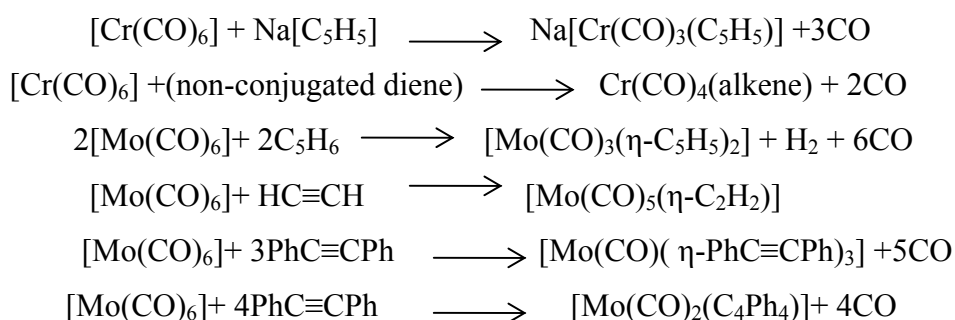
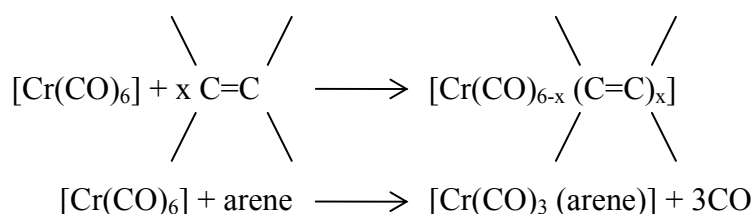


Figure 1.7 Substitution Reaction

### 1.1.8 Kinetics and Mechanisms of $M(\text{CO})_6$ ( $M=\text{Cr, Mo, W}$ ) Substitution Reactions

The substitution reactions of metal VIB hexacarbonyl are promoted by heat and/or UV light. The primary photoreaction of  $M(\text{CO})_6$  ( $M=\text{Cr, Mo, W}$ ) is the dissociation of CO, and it is quite likely that  $M(\text{CO})_5$  is the primary product of thermal reactions as well.

If the reaction takes place in a solvent with donor properties, such as pyridine, THF or acetonitrile, the 16-electron, coordinatively unsaturated pentacoordinate species forms a solvent stabilized complex (Figure 1.8) (S=solvent). In solvents with poor donor ability, experiments indicate that the  $M(CO)_5$  intermediate is quite reactive; flash photolysis studies show that in CO saturated hexane, the recombination rate constant is approximately  $3 \times 10^6 \text{ mol dm}^{-3} \text{ s}^{-1}$ . Competition ratio studies show the  $M(CO)_5$  species to have a low discriminatory ability. The solvent-metal atom interaction is usually quite weak, and the solvent can be easily displaced by a better incoming ligand L (Figure 1.8). Subsequent reactions can displace another CO or the ligand L. (Wilkinson, G., Stone, F.G.A. & Abel, E.W., 1982).

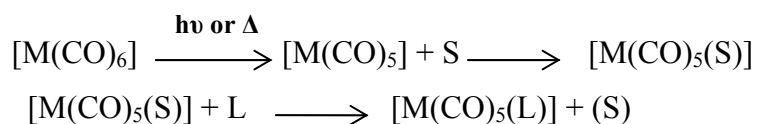


Figure 1.8 Substitution of metal hexacarbonyls by heat and/or UV light

## CHAPTER TWO

### SCHIFF BASE COMPLEXES

#### 2.1 Schiff Bases Properties as a Ligand

Metallo-organic coordination networks with varied complex molecular and crystalline architectures have been extensively studied for their interesting chemical and physical properties. Schiff base ligands have played an integral and important role in this area since the late 19th century. That metal complexes with this type of ligands are ubiquitous is a clear reflection of their facile synthesis, easily tunable steric and electronic properties, good solubility in common organic solvents, wide application and overall accessibility of diverse structural modifications. So, extensive research on these Schiff base metal complexes has expanded enormously nowadays, and has embraced very wide and diversified subjects comprising vast areas of organometallic compounds and various aspects of bioinorganic chemistry. (Chakraborty J., Thakurta S., Samanta B., Ray A., Pilet G., Batten S. R., Jensen P., Mitra S., 2007)

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864. (Schiff H., 1864) Schiff base ligands are able to coordinate metals through imine Nitrogen and another group, usually linked to the aldehyde. Modern chemists still prepare Schiff bases, and nowadays active and well-designed Schiff base ligands are considered “privileged ligands”. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations.

Active catalytic Schiff base metal complexes are obtained in situ, and are not well characterized. However, the appropriate choice of metal precursor and the reaction conditions are crucial for catalytic properties. Finally, a particular class of Schiff bases will also be discussed. When two equivalents of salicylaldehyde are combined

with a diamine, a particular chelating Schiff base is produced. The so-called Salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins, but more easily prepared. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in the literature to describe the class of [O,N,N,O] tetradentate bis-Schiff base ligands (Fig.2.1). Basic guidelines for the design, synthesis and application of metal Schiff base complexes in catalysis will thus be surveyed with the emphasis on the relevant problems in producing active and useful complexes. (Cozzi P., 2004)

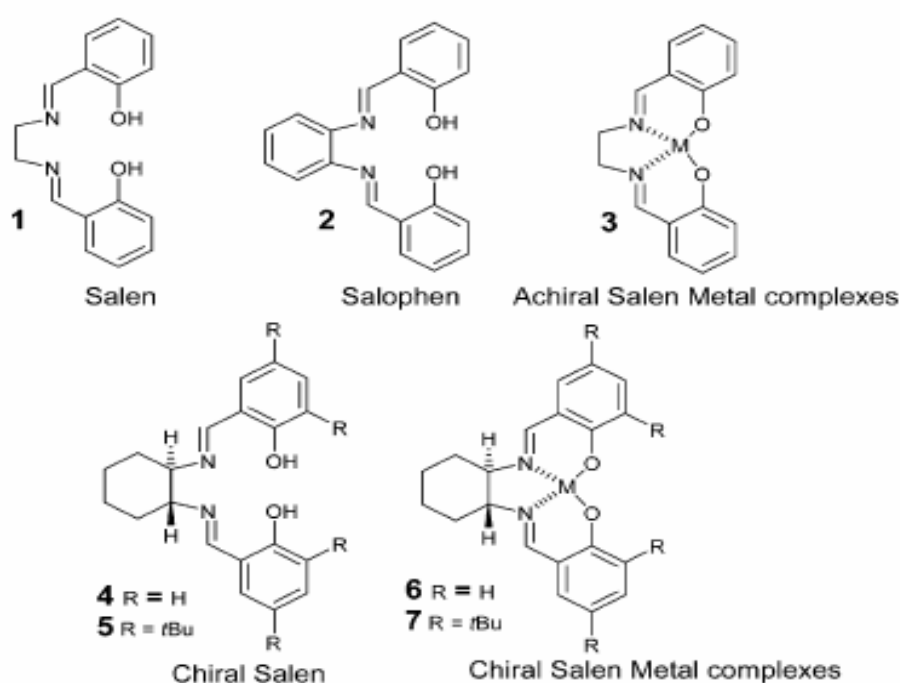


Figure 2.1 Different Salen ligands and M(Salen) complexes (Taken from Cozzi P., 2004)

In fact, Schiff bases possess many interesting characteristics. They are moderate electron donors, with a chelating structure and a low electron counting number. In addition, a large library of Schiff bases can easily be generated, with structural diversity, both sterically and electronically. Schiff base complexes of early transition metals are active catalysts for polymerization, provided that some simple criteria in the synthetic design are met. (Makio H., Kashiwa N., & T. Fujita, 2002),

In addition, the presence of both a hard and a soft donor group in one ligand increases the coordination ability towards hard as well as soft acidic metals. Metal complexes of Schiff bases derived from salicylaldehyde and various amines have been widely investigated. The salicylaldehyde-thio-Schiff bases have recently acquired a considerable importance due to their chemical and especially their promising biological properties. Antibacterial, antineoplastic, antimalarial, antiviral behaviour has been found. Relationships are evident between chelate formation in the complexes and the *in vivo* activity. In the area of bioinorganic chemistry interest in Schiff base complexes has centred on the role such complexes have in providing synthetic models for the metal containing sites in metalloproteins and metalloenzymes. (Soliman A.A.& Linert W. 2006)

### ***2.1.1 Preparation of Schiff Base Complexes***

Condensation between aldehydes and amines is realized in different reaction conditions, and in different solvents. The presence of dehydrating agents normally favours the formation of Schiff bases.  $\text{MgSO}_4$  is commonly employed as a dehydrating agent. The water produced in the reaction can also be removed from the equilibrium using a Dean Stark apparatus, when conducting the synthesis in toluene or benzene. Finally, ethanol, at room temperature or in refluxing conditions, is also a valuable solvent for the preparation of Schiff bases. Degradation of the Schiff bases can occur during the purification step. Chromatography of Schiff bases on silica gel can cause some degree of decomposition of the Schiff bases, through hydrolysis. In this case, it is better to purify the Schiff base by crystallization. If the Schiff bases are insoluble in hexane or cyclohexane, they can be purified by stirring the crude reaction mixture in these solvents, sometimes adding a small portion of a more polar solvent ( $\text{Et}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ ), in order to eliminate impurities.

In general, Schiff bases are stable solids and can be stored without precautions. Condensation of salicylaldehydes or salicylaldehyde derivatives with 1,2- diamines



leads to the formation of one extremely important class of ligands, generally known as “Salens” ( Fig. 2.2). Salicylaldehydes bearing different substituents are obtained by the introduction of a formyl group, using a simple and well established reaction, into the corresponding phenol derivatives. The combinatorial approach to the discovery of new catalysts is an innovative and exciting area of research.

(Gennari C., &Piarulli U. 2003). Schiff bases are suitable ligands for the preparation of libraries due to the easy reaction conditions and the variety of chiral amines and aldehydes used as precursors. Aminoacids and peptides are particularly suitable for the creation of effective catalysts, as indicated in the research of Hoveyda and Snapper. (1996). The condensation of aldehyde-bearing coordinating groups with amino acids and peptides provides interesting Schiff bases, used to make a combinatorial library of ligands. (Cozzi P. 2004).

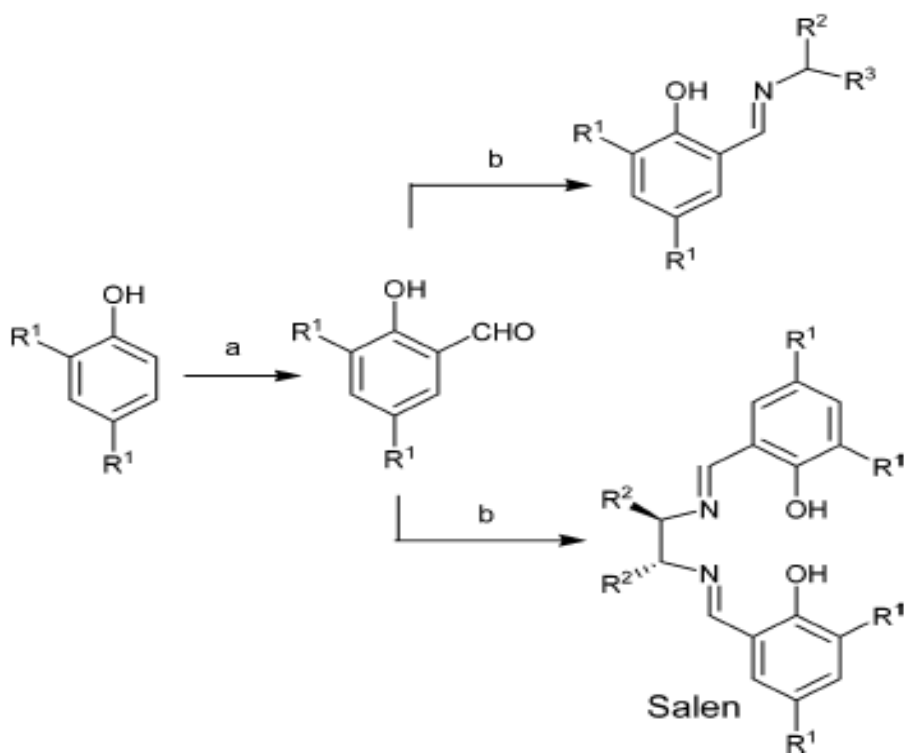


Figure 2.2 Preparation of Schiff bases (Taken from Cozzi P., 2004)

## CHAPTER THREE

### MATERIAL AND METHOD

#### 3.1 Instrument

**Elemental Analysis:** Leco 932 instrument at Technical and Scientific Research Council of Turkey, TUBITAK.

**Infrared Spectroscopy:** FTIR spectra of samples were recorded (KBr pellets) on a Varian 1000 FT spectrophotometer.

**<sup>1</sup>H-NMR:** <sup>1</sup>H NMR spectra were recorded in DMSO-d<sub>6</sub> on 500 MHz High Performance Digital FT-NMR and chemical shifts were referenced to tetramethylsilane (TMS).

**LC- Mass Spectroscopy:** LC- Mass spectra analyses were performed on Agilent 1100 MSD device at TUBITAK.

#### 3.2 Chemicals

**Solvents:** THF, dichloromethane, petroleum ether (Merck)

**Metal Carbonyl:** Cr(CO)<sub>6</sub>, Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub> (Aldrich)

**Vacuum Grease:** High vacuum Grease (Merck)

**Auxiliary Equipment:** KBr (Potassium Bromide), Nitrogen tube (N<sub>2</sub>), Vacuum-nitrogen line (Figure 3.1), Base bath.



Figure 3.1 Vacuum- nitrogen line

### 3.3 Preparations of the Ligands

#### 3.3.1 Preparations of *N,N'*-bis(salicylidene)-1,4-diaminobutane, ( $H_2L'$ )

*N,N'*-bis(salicylidene)-1,4-diaminobutane ( $H_2L'$ ) ligand was prepared as previously reported. (Pillai M.R.A.; John J.M.; Schlemper E.O.&Troutner D.E.; 1990).

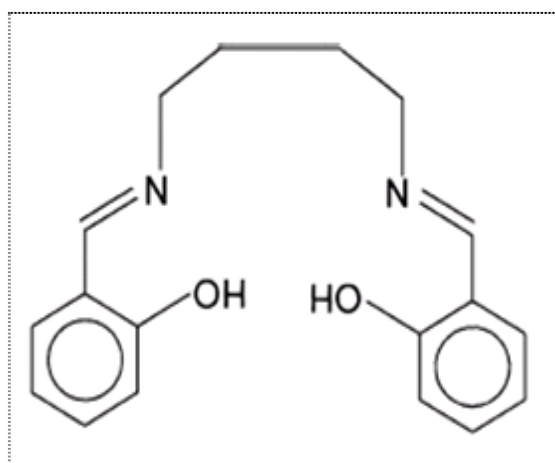


Figure 3.2 *N,N'*-bis(salicylidene)-1,4-diaminobutane ( $H_2L'$ )

### 3.3.2 Preparations of *N,N'*-bis(2-hydroxy-3-methoxybenzylidene)ethylenediamine, ( $H_2L''$ )

*N,N'*-bis(3-methoxy-2-hydroxybenzylidene)ethylenediamine was prepared as previously reported. The  $H_2L''$  ligand was prepared by reaction of ethylenediamine (1mmol) and 2-hydroxy-3-methoxybenzaldehyde (2 mmol) in hot ethanol (70 ml). The yellow compound precipitated from solution on cooling. (Elmali A.& Elerman Y. 2005)

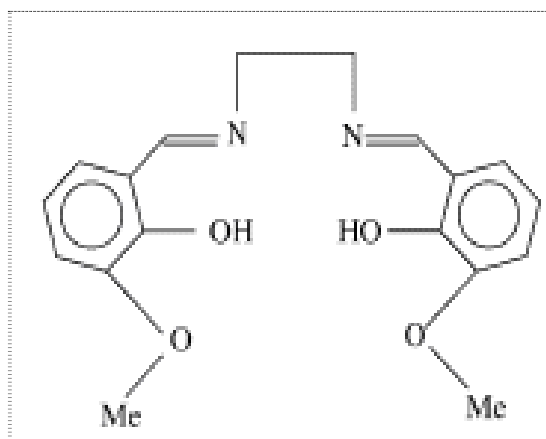


Figure 3.3 *N,N'*-bis(2-hydroxy-3-methoxy-benzylidene)ethylenediamine, ( $H_2L''$ )

## 3.4 Syntheses of the Complexes

### 3.4.1 Synthesis of the *cis*-[Cr(CO)<sub>2</sub>( $\eta^4$ - $H_2L'$ )]

A solution of Cr(CO)<sub>6</sub> (0.11 g, 0.50 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.15 h at room temperature. A solution of  $H_2L'$  (0.09 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the Cr(CO)<sub>5</sub>THF intermediate. The reaction mixture was irradiated again at room temperature for 1.5 h at same conditions. During this irradiation, the solution changed from yellow to light brown. After this irradiation the solvent was removed under vacuum afford a solid which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of an light brown solid which was washed with petroleum ether and dried under vacuum, and

shown to be *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L')], **1**, (60 % yield). Traces of unreacted Cr(CO)<sub>6</sub> was sublimed out in vacuum on a cold finger at -20°C.

### 3.4.2 Synthesis of *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L')]

A solution of Mo(CO)<sub>6</sub> (0.13 g, 0.50 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1 h at room temperature. A solution of H<sub>2</sub>L' (0.09 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the Mo(CO)<sub>5</sub>THF intermediate. The reaction mixture was irradiated again at room temperature for 2 h at same conditions. During this irradiation, the solution changed from yellow to light brown. After this irradiation the solvent was removed under vacuum afford a solid which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of an light brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L')], **2**, (65 % yield). Traces of unreacted Mo(CO)<sub>6</sub> was sublimed out in vacuum on a cold finger at -20°C.

### 3.4.3 Synthesis of *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L')]

A solution of W(CO)<sub>6</sub> (0.18 g, 0.50 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.15 h at room temperature. A solution of H<sub>2</sub>L' (0.09 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the W(CO)<sub>5</sub>THF intermediate. The reaction mixture was irradiated again at room temperature for 2 h at same conditions. During this irradiation, the solution changed from yellow to dark brown. After this irradiation the solvent was removed under vacuum afford a solid which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Addition of petroleum ether (50 cm<sup>3</sup>) resulted in precipitation of an dark brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L')], **3**, (72 % yield). Traces of unreacted W(CO)<sub>6</sub> was sublimed out in vacuum on a cold finger at -20°C.

#### 3.4.4 Synthesis of *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L'')] ]

A solution of Cr(CO)<sub>6</sub> (0.11 g, 0.50 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.5 h at room temperature. A solution of H<sub>2</sub>L'' (0.098 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the Cr(CO)<sub>5</sub>THF intermediate. The reaction mixture was irradiated again at room temperature for 2 h at same conditions. During this irradiation, the solution changed from yellow to orange. After this irradiation the solvent was removed under vacuum afford a solid which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Addition of petroleum ether (50 cm<sup>3</sup>) resulted in precipitation of a dark brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L'')] ], **4**, (75 % yield). Traces of unreacted Cr(CO)<sub>6</sub> was sublimed out in vacuum on a cold finger at -20°C.

#### 3.4.5 Synthesis of *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L'')] ]

A solution of Mo(CO)<sub>6</sub> (0.13 g, 0.50 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.5 h at room temperature. A solution of H<sub>2</sub>L'' (0.098 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the Mo(CO)<sub>5</sub>THF intermediate. The reaction mixture was irradiated again at room temperature for 2 h at same conditions. During this irradiation, the solution changed from yellow to dark brown. After this irradiation the solvent was removed under vacuum afford a solid which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a dark brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L'')] ], **5**, (73 % yield). Traces of unreacted Mo(CO)<sub>6</sub> was sublimed out in vacuum on a cold finger at -20°C.

#### 3.4.6 Synthesis of *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L'')] ]

A solution of W(CO)<sub>6</sub> (0.18 g, 0.50 mmol) in 60 mL of THF was irradiated with UV light in a quartz vessel under a stream of nitrogen for 1.5 h at room temperature.

A solution of  $\mathbf{H}_2\mathbf{L}''$  (0.098 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the  $\text{W}(\text{CO})_5\text{THF}$  intermediate. The reaction mixture was irradiated again at room temperature for 2 h at same conditions. During this irradiation, the solution changed from yellow to dark orange. After this irradiation the solvent was removed under vacuum afford a solid which was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of an dark brown solid which was washed with petroleum ether and dried under vacuum, and shown to be *cis*- $[\text{W}(\text{CO})_2(\eta^4\text{-H}_2\mathbf{L}'')]_2$ , **6**, (68 % yield). Traces of unreacted  $\text{W}(\text{CO})_6$  was sublimed out in vacuum on a cold finger at  $-20^\circ\text{C}$ .





The analytical data for novel complexes **1-6** are summarized in Table 4.1. The stoichiometry of the ligands and their complexes were confirmed by their elemental analyses. The complexes (**1-6**) are all air-stable and soluble in chlorinated solvents.

Table 4.1. Elemental analyses results and physical properties for the complexes.

Complex	Yield (%)	Colour	Found (Calcd.) (%)			
			C	H	N	O
<b>1</b>	60	light brown	60.45 (60.85)	3.35 (3.46)	4.01 (4.04)	9.53(9.66)
<b>2</b>	65	light brown	56.94 (57.04)	3.24(3.30)	3.58(3.70)	8.94(8.96)
<b>3</b>	72	dark brown	50.32 (50.42)	2.79(2.87)	3.37(3.41)	7.86(7.95)
<b>4</b>	75	dark orange	54.91(55.04)	4.41(4.58)	6.40(6.42)	21.98(22.01)
<b>5</b>	73	dark brown	49.25 (50.00)	4.03(4.16)	5.79(5.83)	19.97(20.00)
<b>6</b>	68	dark red	42.13(42.25)	3.47(3.52)	4.83(4.92)	16.88(16.90)

Characteristic IR data are listed in Table 4.2. The IR spectra of all complexes (**1-6**) exhibit two prominent bands between 1980 and 1918  $\text{cm}^{-1}$  in the CO stretching vibrational region. These two bands belong to terminal CO group. This is similar to the spectrum of the *cis*-[Cr(CO)<sub>2</sub>(salenH<sub>2</sub>)] which has two terminal (1945 and 1857  $\text{cm}^{-1}$ ) CO stretching bands (Sabry D.Y., Youssef T.A., El-Medani S.M., & Ramadan R.M. 2003). The CO modes in the complexes **1-6** are at lower wave numbers as compared to M(CO)<sub>6</sub> (M: Cr, Mo and W). The presence of two CO bands in the IR spectra suggested that they were bound to the metal in *cis* positions. (Sabry D.Y., Youssef T.A., El-Medani S.M., & Ramadan R.M. 2003) The two band  $\nu(\text{CO})$  pattern indicates that the local C<sub>2v</sub> symmetry of M(CO)<sub>2</sub> unit in 1-6. (Nakamoto K.,1986).

The IR spectra of **H<sub>2</sub>L'** and **H<sub>2</sub>L''** showed characteristic bands due to the functional groups C=N, O-H, N-H and C-O also Ar-OCH<sub>3</sub> only for **H<sub>2</sub>L''**. The IR spectra of all complexes displayed the ligand characteristic bands with appropriate shifts due to complex formation.

The bands at 1632  $\text{cm}^{-1}$  and 1631  $\text{cm}^{-1}$  in the IR spectrum of free **H<sub>2</sub>L'** and **H<sub>2</sub>L''** respectively belong to the C=N stretching vibration. First band shifts towards lower frequency and there is a considerable decrease in the intensity of the peaks in compounds **1-3** showing that the **H<sub>2</sub>L'** ligand coordinate to the metal *via* the imine

(C=N) nitrogen donor atoms. This shift has been assessed as a weakening of the C=N bond resulting from the transfer of electron density from the nitrogen to the metal atom. However, alteration of the C=N imine stretching bands were not observed for the complexes of **H<sub>2</sub>L''** (**4-6**). As seen from the spectra, Ar-OCH<sub>3</sub> stretching vibration observed at 1081 cm<sup>-1</sup> of **H<sub>2</sub>L''** ligand shifts to lower frequency region. It shows that **H<sub>2</sub>L''** ligand coordinate to the metal via the methoxy (Ar-OCH<sub>3</sub>) oxygen donor atoms, in compounds (**4-6**).

And also the bands at 3446cm<sup>-1</sup> and 3425 cm<sup>-1</sup> in the IR spectrum of the free Schiff base ligands are assigned to the stretching of the intramolecular hydrogen bonded (OH) (Temel H.,Cakır U., Otludil B. & Ugras H. İ.; 2001)

High intensity bands around 1284 and 1252 cm<sup>-1</sup> in the free Schiff-bases **H<sub>2</sub>L'** and **H<sub>2</sub>L''** is due to the phenolic C-O stretching frequency, respectively. The C-O stretching vibration appears at a slightly lower frequency at 1280-1277 cm<sup>-1</sup> in complexes **1-3** and 1249-1250 cm<sup>-1</sup> in complexes **4-6** confirming the coordination through the phenolic oxygen atom. (Frausto da Silva J.J.R., & Williams R.J.P., 1991; Kaim W., & Schwederski B., 1996)

Table4. 2. Characteristic FTIR bands (cm<sup>-1</sup>) of H<sub>2</sub>L', H<sub>2</sub>L'' and complexes (1-6)

Complex	$\nu_{(\text{CO})}$	$\nu_{(\text{C}=\text{N})}$	$\nu_{(\text{O}-\text{H})}^{\text{a}}$	$\nu_{(\text{C}-\text{OCH}_3)}$	$\nu_{(\text{C}-\text{O})}$
<b>Cr(CO)<sub>6</sub></b>	1999s	-	-	-	-
<b>Mo(CO)<sub>6</sub></b>	2001s	-	-	-	-
<b>W(CO)<sub>6</sub></b>	1996s	-	-	-	-
<b>H<sub>2</sub>L'</b>	-	1632s	3446m	-	1284s
<b>1</b>	1975w, 1918w	1630s	3428m	-	1280m
<b>2</b>	1977s, 1926m	1628s	3426m	-	1277m
<b>3</b>	1971w, 1918w	1629m	3425m	-	1278w
<b>H<sub>2</sub>L''</b>	-	1631s	3425m	1081m	1252s
<b>4</b>	1977w, 1920m	1631s	3389m	1062w	1250m
<b>5</b>	1975m, 1922w	1631s	3400m	1070m	1249s
<b>6</b>	1980w, 1918m	1630m	3391m	1072m	1250m

<sup>a</sup> Intramolecular hydrogen bonded OH---M (M=Cr, Mo, W) (Temel H.,Cakır U., Otludil B. & Ugras H. İ.; 2001)

$^1\text{H}$  NMR data in  $\text{DMSO-d}_6$  solutions of complexes **2,3** and **5,6** are collected in Table 4.3. The  $^1\text{H}$  NMR spectrum of the chromium complexes of  $\text{H}_2\text{L}'$  and  $\text{H}_2\text{L}''$  could not be obtained since these complexes were not dissolved in  $\text{DMSO-d}_6$  completely. Except that  $\text{HC=N}$  imine and  $\text{Ar-OH}$  protons chemical shift, all of the other chemical shifts of the coordinated  $\text{H}_2\text{L}'$  ligand of the compounds **1,3** have almost similar values to those of the free ligand. In  $^1\text{H}$  NMR spectra of the complexes **1,3** imine  $\text{HC=N}$  and aryl  $\text{OH}$  proton signals have been observed in lower field. This situation supports the coordination of ligands to the metal center as imine derivatives. The down-field shift of the  $\text{HC=N}$  imine proton may be related to a decrease in  $\pi$ -electron density in the  $\text{C=N}$  bond with complex formation in **1, 3**.

In the  $^1\text{H-NMR}$  spectra of the compounds (**5,6**)  $\text{HC=N}$  imine protons of the free ligand at 8,54 ppm remains approximately unchanged in the complexes and show that the imine group does not participate in coordination. Furthermore, the complexes of  $\text{H}_2\text{L}''$  (**5,6**)  $\text{Ar-OCH}_3$  and  $\text{Ar-OH}$  protons signal alteration have been found.  $\text{C-OCH}_3$  and  $\text{Ar-OH}$  signals of  $\text{H}_2\text{L}''$  have been observed at 3.31 and 13.50 ppm.. These values have been shifted to 3.32-3.34 ppm and 13.51-13.53 ppm (lower field) for complexes **5-6** respectively as such in the spectra of **1-3**. Thus, it can be concluded that the coordination through the  $\text{Ar-OCH}_3$  and  $\text{Ar-OH}$  oxygen atoms have been existed.

Table 4.3 <sup>1</sup>H NMR data for **H<sub>2</sub>L'**, **H<sub>2</sub>L''** and (2-3; 5-6) in DMSO-d<sub>6</sub> solution<sup>a</sup>.

Complex	-CH <sub>2</sub> -	-CH <sub>2</sub> -	Ar-OH	Ar-OCH <sub>3</sub>	Ar-H	HC=N
<b>H<sub>2</sub>L'</b>	2.48, m, 4H	3.61, m, 4H	13.56, s, 2H	-	7.31-7.38,m,8H	8.53,s,2H
<b>2</b>	2.49, m, 4H	3.62, m, 4H	13.57, s, 2H	-	7.35-7.40,m,8H	8.55,s,2H
<b>3</b>	2.50, m, 4H	3.62, m, 4H	13.57, s, 2H	-	7.76-7.59,m,8H	8.58,s,2H
<b>H<sub>2</sub>L''</b>	2.48, m, 4H	-	13.50, s, 2H	3.31,s, 6H	6.98-6.76,m,8H	8.54,s,2H
<b>5</b>	2.50, m, 4H	-	13.53, s, 2H	3.34, s, 6H	6.84-6.70,m, 8H	8.54,s, 2H
<b>6</b>	2.48, m, 4H	-	13.51, s, 2H	3.32, s, 6H	6.82-6.74,m,8H	8.54,s, 2H

<sup>a</sup>δ in ppm

Data for mass spectra of **1-6** are given in Table 4.4, and show fragmentation *via* successive loss of CO groups and organic ligands. Proposed **1-6** structures are consistent with the obtained mass fragments containing nitrogen, oxygen and central metal atom. In homoleptic mononuclear metal carbonyls, metal atom provides fewer electrons for bonding, so that additional ligands are required for metal atom to achieve the favored 18-electron noble gas configuration. According to the 18 electron rule two metal atoms must interact to each other to stabilize the complexes (**1-6**).

Table 4.4. Mass spectroscopy data for (1-6).

Complex	M.W.	Relative intensities of the ions $m/z$ <sup>a</sup>
<b>1</b>	404	346 (35), [CrC <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> ]; 297 (75), [C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> ]; 193 (8), [CrC <sub>4</sub> HN <sub>2</sub> O <sub>4</sub> ]; 176 (100), [CrC <sub>4</sub> N <sub>2</sub> O <sub>3</sub> - (OH)]; 163 (14), [CrC <sub>4</sub> N <sub>2</sub> O <sub>2</sub> -(O)]; 135 (2), [CrC <sub>3</sub> N <sub>2</sub> O-(CO)]; 107 (17), [CrC <sub>2</sub> N <sub>2</sub> -(CO)].
<b>2</b>	448	295 (1), [MoC <sub>8</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> ]; 282 (1), [MoC <sub>7</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> -(C-H)]; 265 (2), [MoC <sub>7</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> -(OH)]; 221 (1), [MoC <sub>5</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> -(OH)-(C-H)-(CH <sub>2</sub> )]; 193 (30), [MoC <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O-(CO)]; 178 (1), [MoC <sub>4</sub> H <sub>6</sub> NO-(N)]; 122 (4), [MoCO-(N)-3(CH <sub>2</sub> )].
<b>3</b>	535	299 (78), [WC <sub>2</sub> N <sub>2</sub> O <sub>4</sub> ]; 285 (79), [WC <sub>2</sub> NO <sub>4</sub> -(N)]; 271 (74), [WC <sub>2</sub> O <sub>4</sub> -(N)]; 243 (10), [WCO <sub>3</sub> -(CO)]; 227 (79), [WCO <sub>2</sub> -(O)]; 200 (50), [WO-(CO)]; 184 (2), [W-(O)]
<b>4</b>	436	269(17), [CrC <sub>8</sub> H <sub>11</sub> O <sub>6</sub> N]; 241 (4), [CrC <sub>7</sub> H <sub>11</sub> O <sub>5</sub> N-(CO)]; 213(4), [CrC <sub>6</sub> H <sub>11</sub> O <sub>4</sub> N -(CO)]; 199 (9), [CrC <sub>6</sub> H <sub>11</sub> O <sub>4</sub> -(N)]; 157 (4), [CrC <sub>4</sub> H <sub>9</sub> O <sub>3</sub> -(CH)-(C)-(OH)]; 99 (5), [CrCH <sub>3</sub> O <sub>2</sub> -(OH)-2(CH)-(CH <sub>3</sub> )]
<b>5</b>	480	286 (8), [MoC <sub>6</sub> H <sub>9</sub> O <sub>6</sub> N]; 258(4) [MoC <sub>5</sub> H <sub>9</sub> O <sub>5</sub> N -(CO)]; 243 (4), [MoC <sub>4</sub> H <sub>6</sub> O <sub>5</sub> N-(CH <sub>3</sub> )]; 196 (8), [MoC <sub>3</sub> H <sub>3</sub> O <sub>3</sub> -(OCH <sub>3</sub> )-(O)]; 152 (13.3), [MoCHO <sub>2</sub> -(CH)-(N)-(C)-(OH)]; 135 (3), [MoCO- (OH)]; 107 (3)[Mo- (CO)].
<b>6</b>	568	335 (87), [WC <sub>4</sub> H <sub>8</sub> O <sub>6</sub> ]; 307 (14), [WC <sub>3</sub> H <sub>8</sub> O <sub>5</sub> -(CO)]; 279 (8), [WC <sub>2</sub> H <sub>8</sub> O <sub>4</sub> -(CO)]; 262 (8), [WC <sub>2</sub> H <sub>7</sub> O <sub>3</sub> -(OH)]; 245 (18), [WC <sub>2</sub> H <sub>6</sub> O <sub>2</sub> -(OH)]; 230 (28), [WCH <sub>3</sub> O <sub>2</sub> -(CH <sub>3</sub> )]

<sup>a</sup>Relative intensities are given in parentheses and assignments in square

## CHAPTER FIVE

### CONCLUSIONS

#### 5.1 Conclusions

In this thesis study we have investigated photochemical reactions of VIB metal carbonyl complexes  $[M(CO)_6]$   $[M= Cr, Mo, W]$  with Schiff bases; *N,N'*-bis(salicylidene)-1,4-diaminobutane, (**H<sub>2</sub>L'**) and *N,N'*-bis(2-hydroxy-3-methoxybenzylidene)ethylenediamine, (**H<sub>2</sub>L''**) in THF. The new complexes *cis*- $[M(CO)_2(\eta^4- \mathbf{H}_2\mathbf{L}')] ]$  and *cis*- $[M(CO)_2(\eta^4- \mathbf{H}_2\mathbf{L}'')] ]$  (M: Cr, Mo, W) have been synthesized and characterized by elemental analyses, FTIR, <sup>1</sup>H-NMR and mass spectra. C=N/Ar-OH and Ar-OH/Ar-OCH<sub>3</sub> vibrations have been shifted to lower wave number in the IR spectra of the complexes (**1-3**) and (**4-6**) respectively. The observation of two carbonyl bands in the CO stretching region is consistent with the formulation of the complexes **1-6**. <sup>1</sup>H NMR data exhibited expected integrals and shifts. Mass spectra fragmentation patterns are in line with the proposed structures of **1-6**.

In summary, **H<sub>2</sub>L'** ligand is coordinated to the central metal as a tetradentate ligand coordinating *via* the central azomethine nitrogens (C=N) and phenolic oxygen atoms to the central metal in **1-3**, whereas **H<sub>2</sub>L''** ligand is coordinated to the central metal as a tetradentate ligand coordinating *via* aromatic methoxy and phenolic oxygen atoms to the central metal in **4-6**. Coordination of **H<sub>2</sub>L''** ligand via its oxygen donor atoms instead of imine nitrogen as obtained for the 1-3 complexes might arise from steric cavity of the ligand.

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## APPENDICEX

Figure 4.1.1. FTIR spectrum of *N,N'*-bis(salicylidene)-1,4-diaminobutane, ( $H_2L'$ )

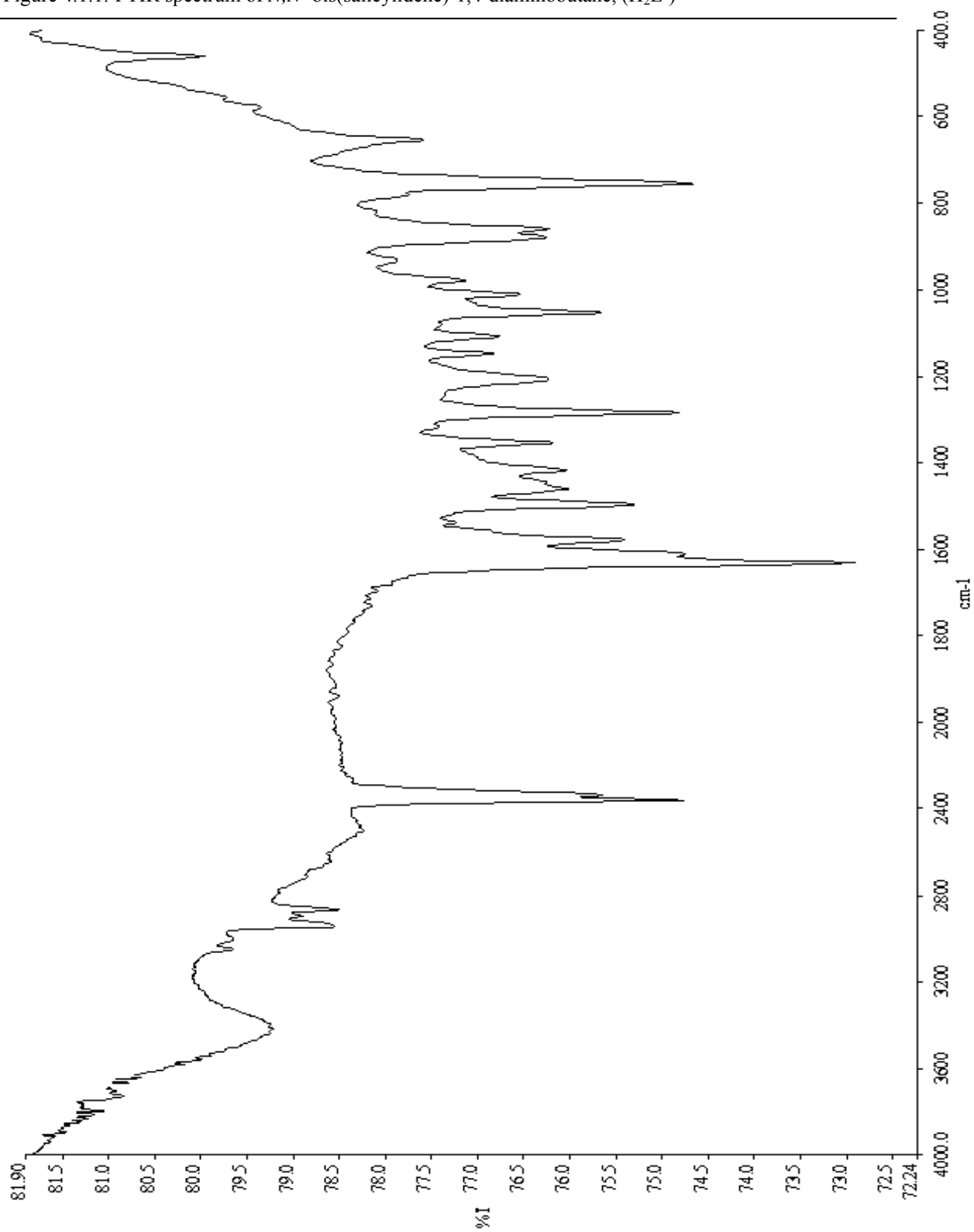


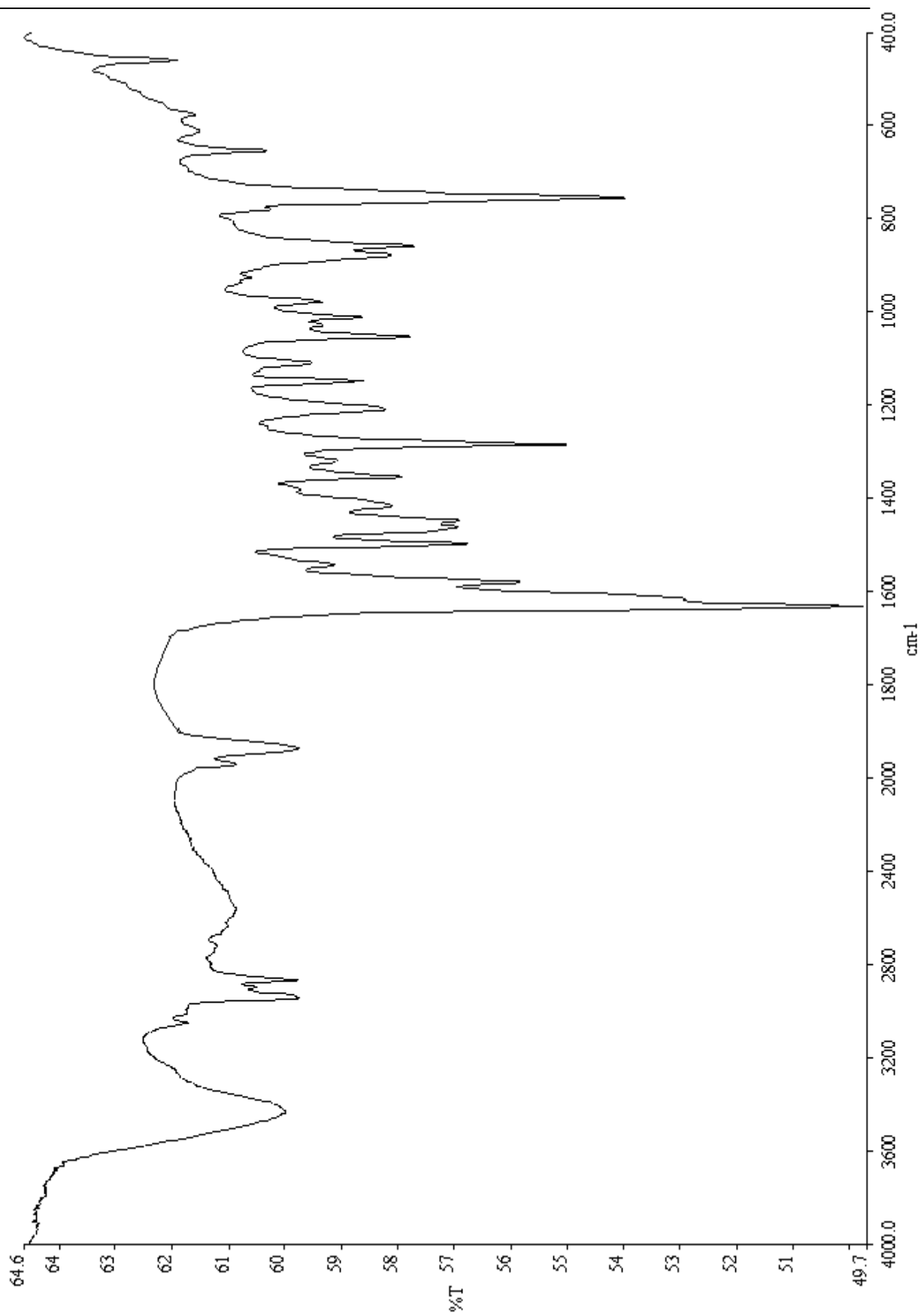
Figure 4.1.2 FTIR spektrum of *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

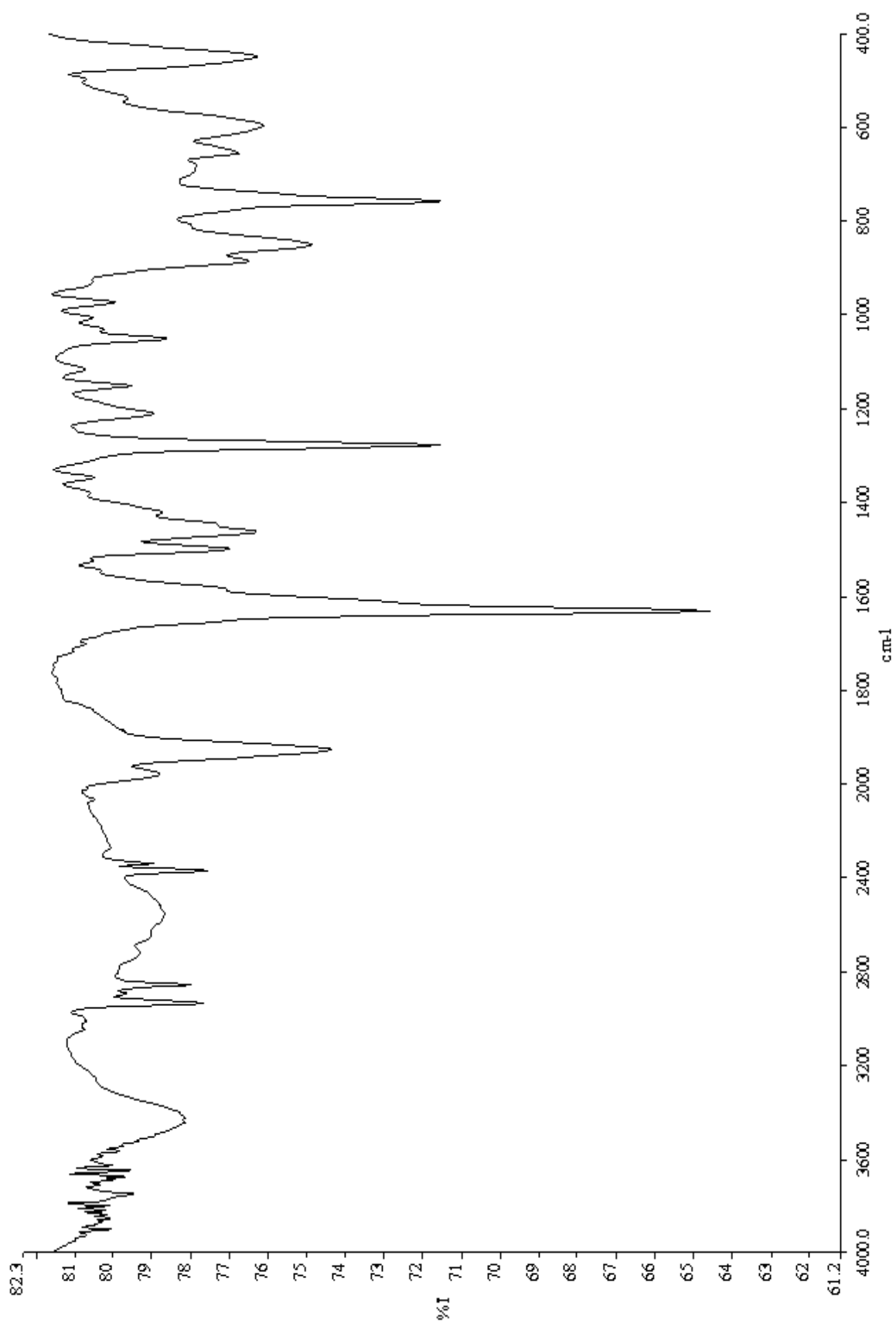
Figure 4.1.3 FTIR spektrum of *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

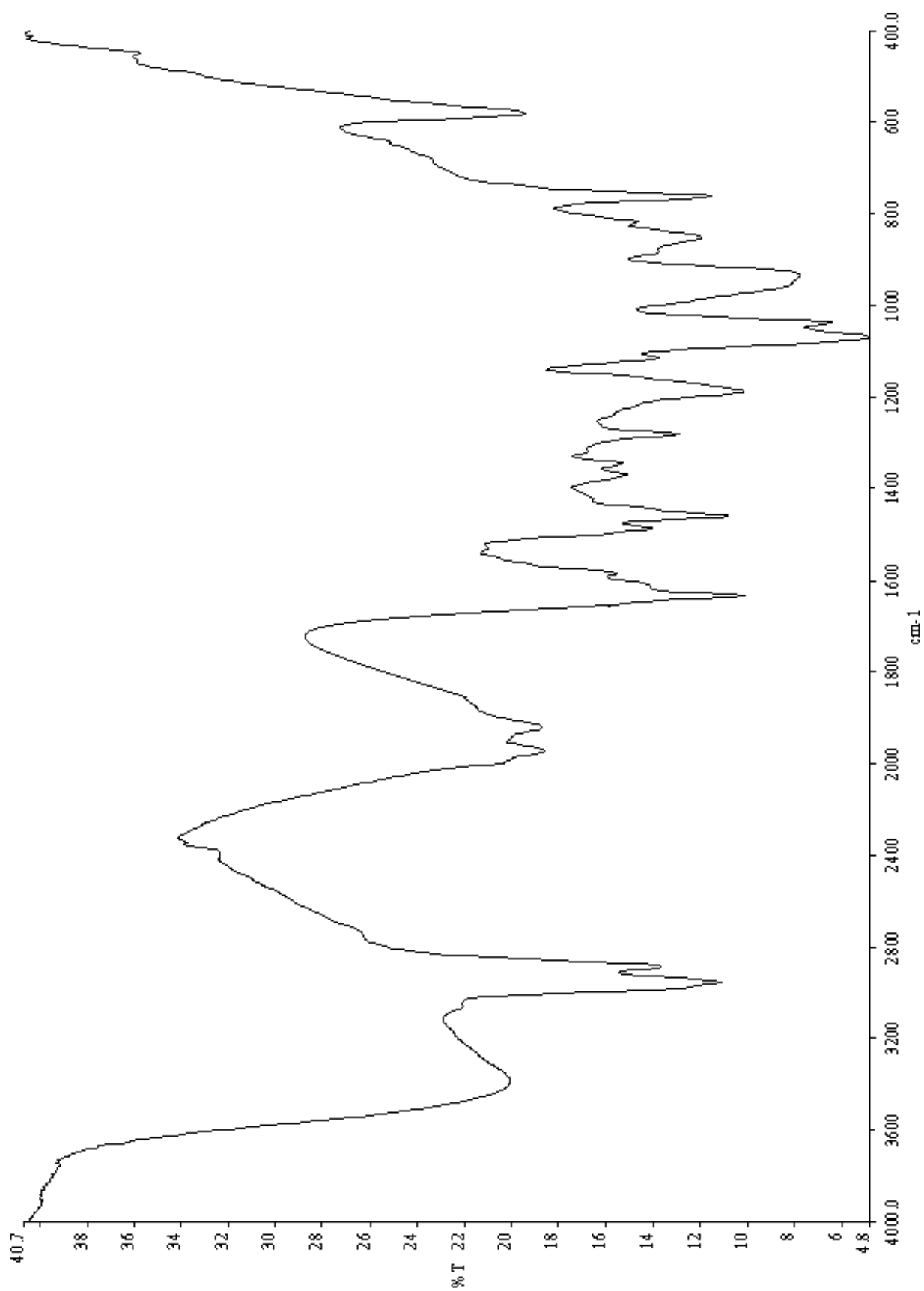
Figure 4.1.4 FTIR spektrum of *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

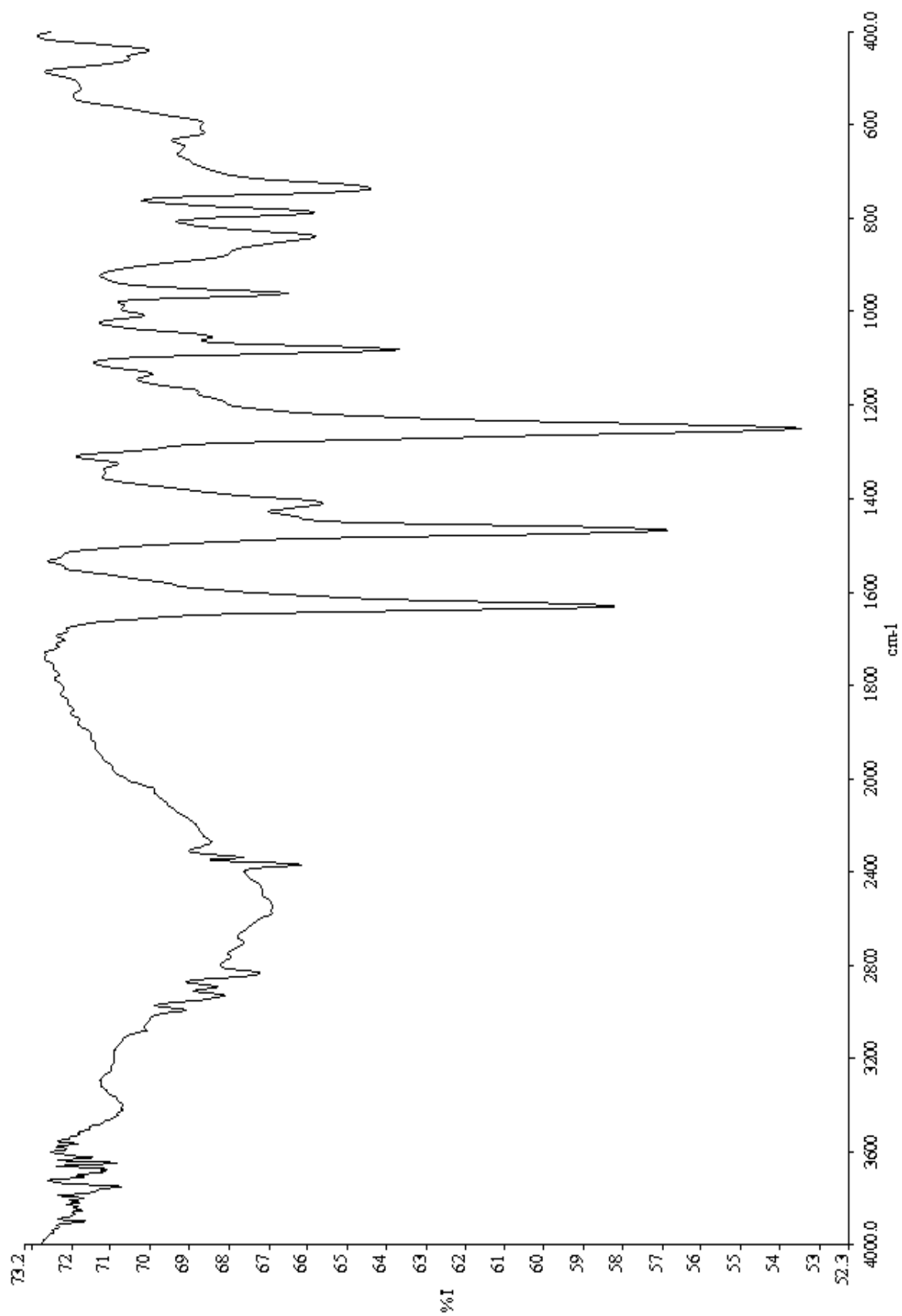
Figure 4.1.5 FTIR spektrum of *N,N'*-bis(2-hydroxy-3-methoxybenzylidene)ethylenediamine, ( $H_2L''$ )



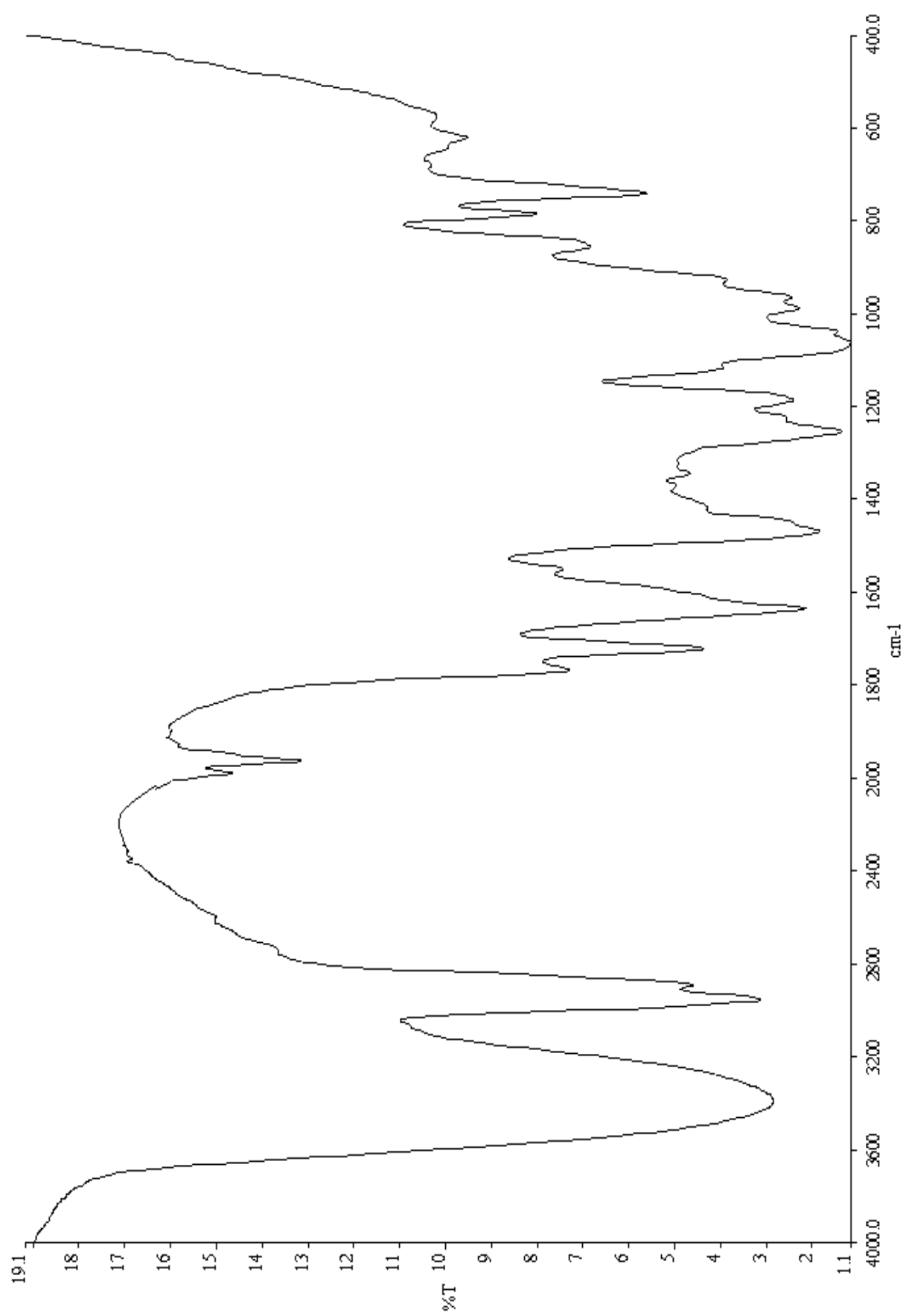
Figure 4.1.6 FTIR spektrum of *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L<sup>n</sup>)

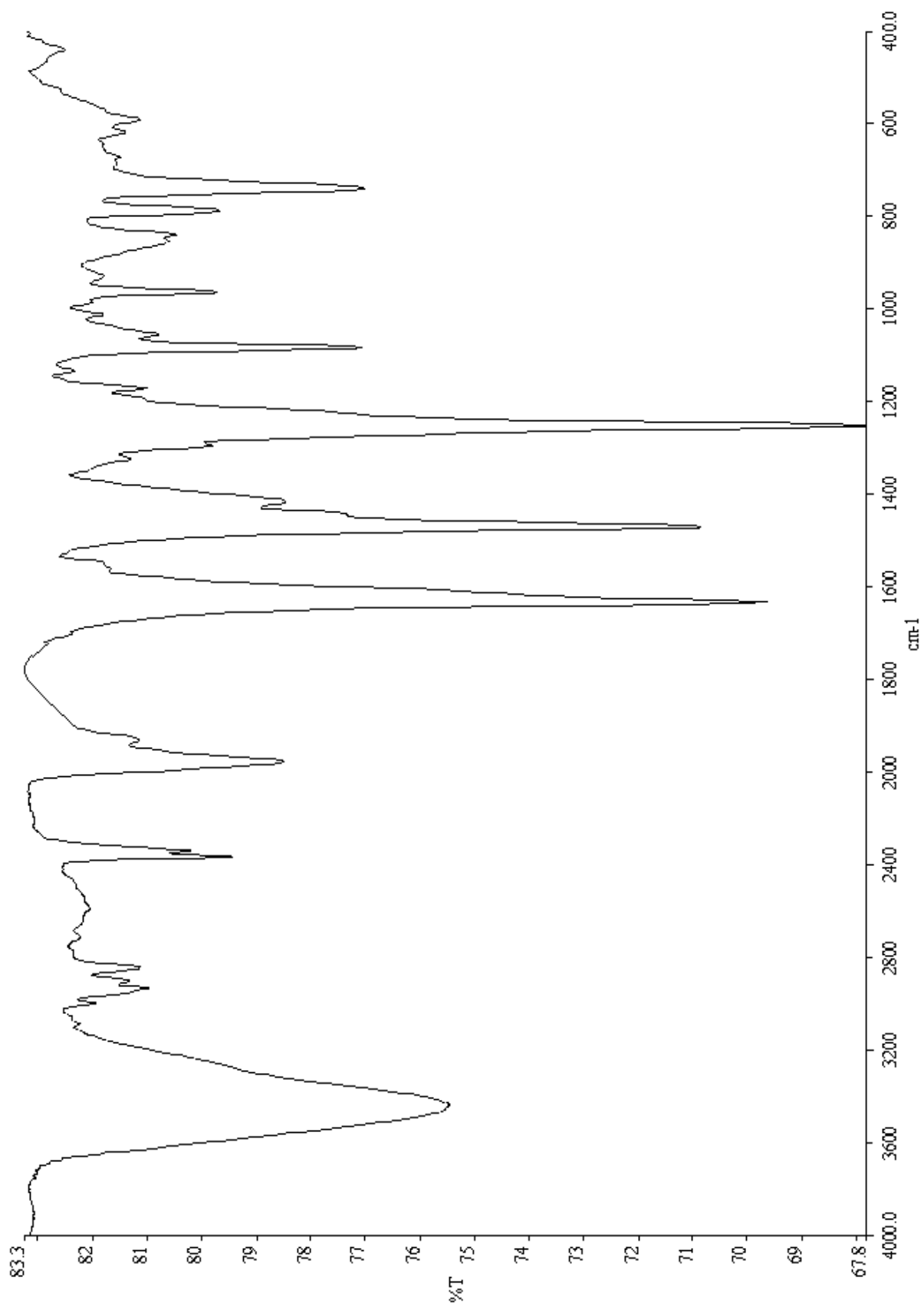
Figure 4.1.7 FTIR spektrum of *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

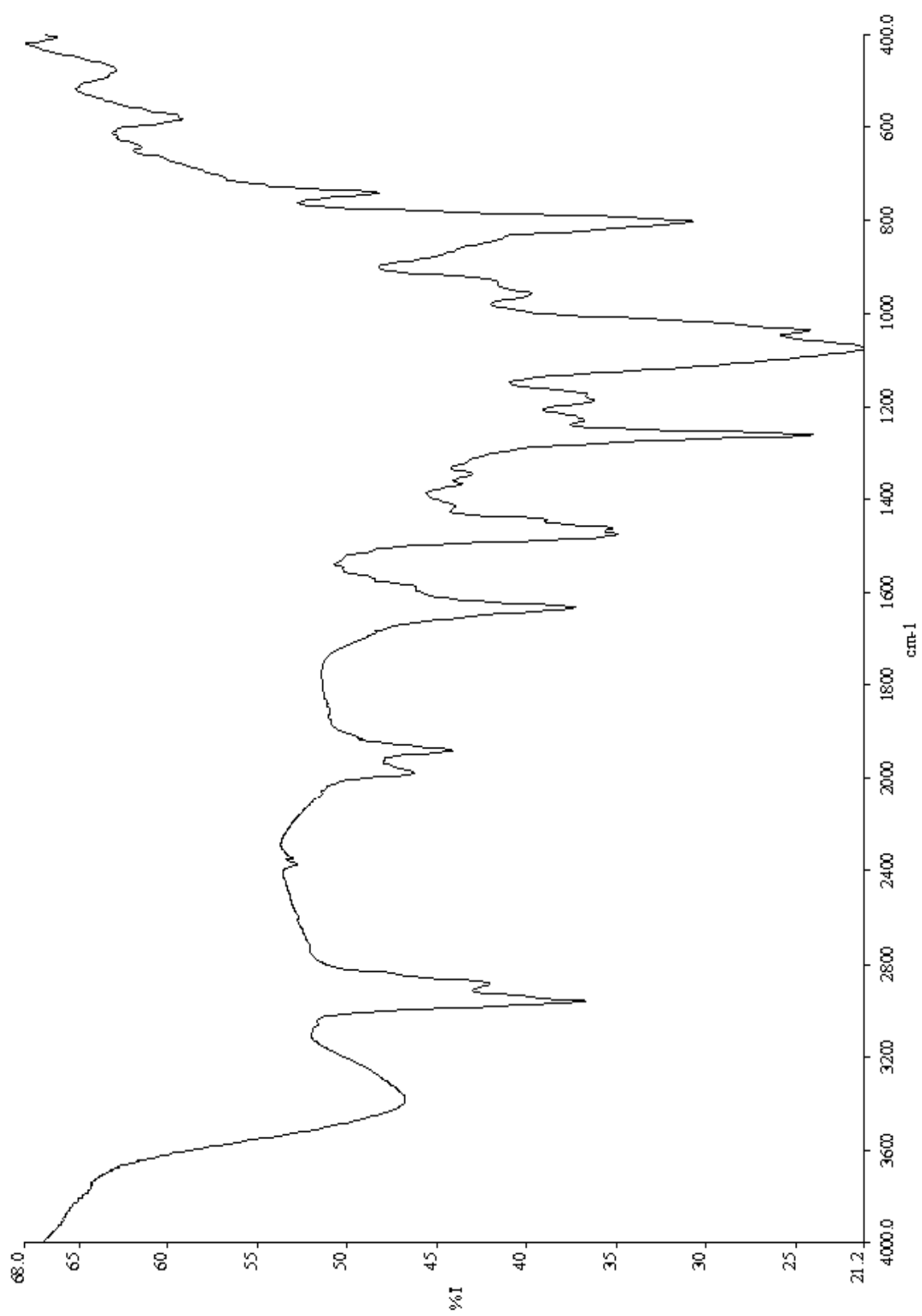
Figure 4.1.8 FTIR spektrum of *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

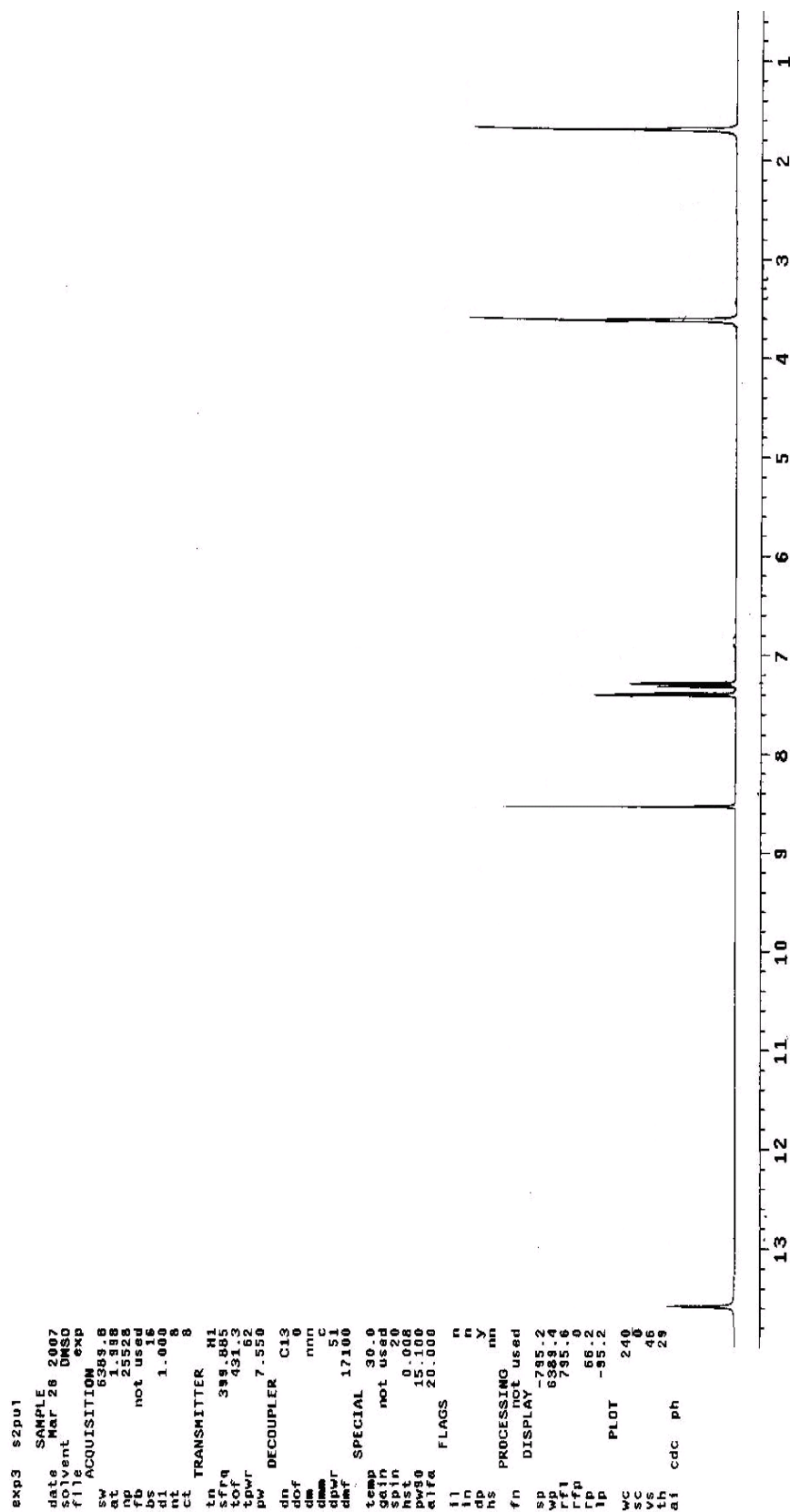
Figure 4.2.1.  $^1\text{H}$  NMR spectrum of [*N,N'*-bis(salicylidene)-1,4-diaminobutane( $\text{H}_2\text{L}$ )]

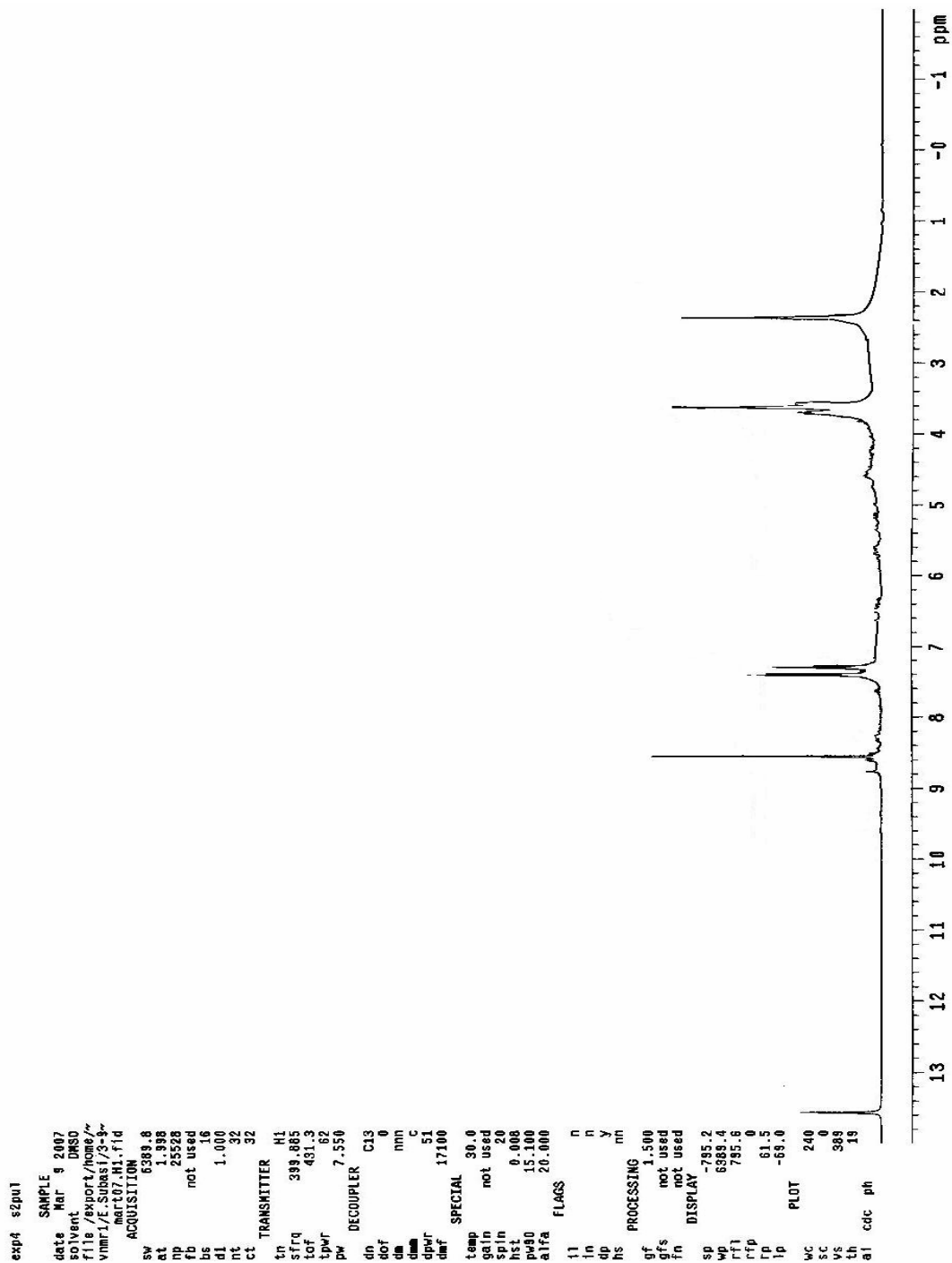
Figure 4.2.2.  $^1\text{H}$  NMR spectrum of *cis*- $[\text{Mo}(\text{CO})_2(\eta^4\text{-H}_2\text{L})]$ 

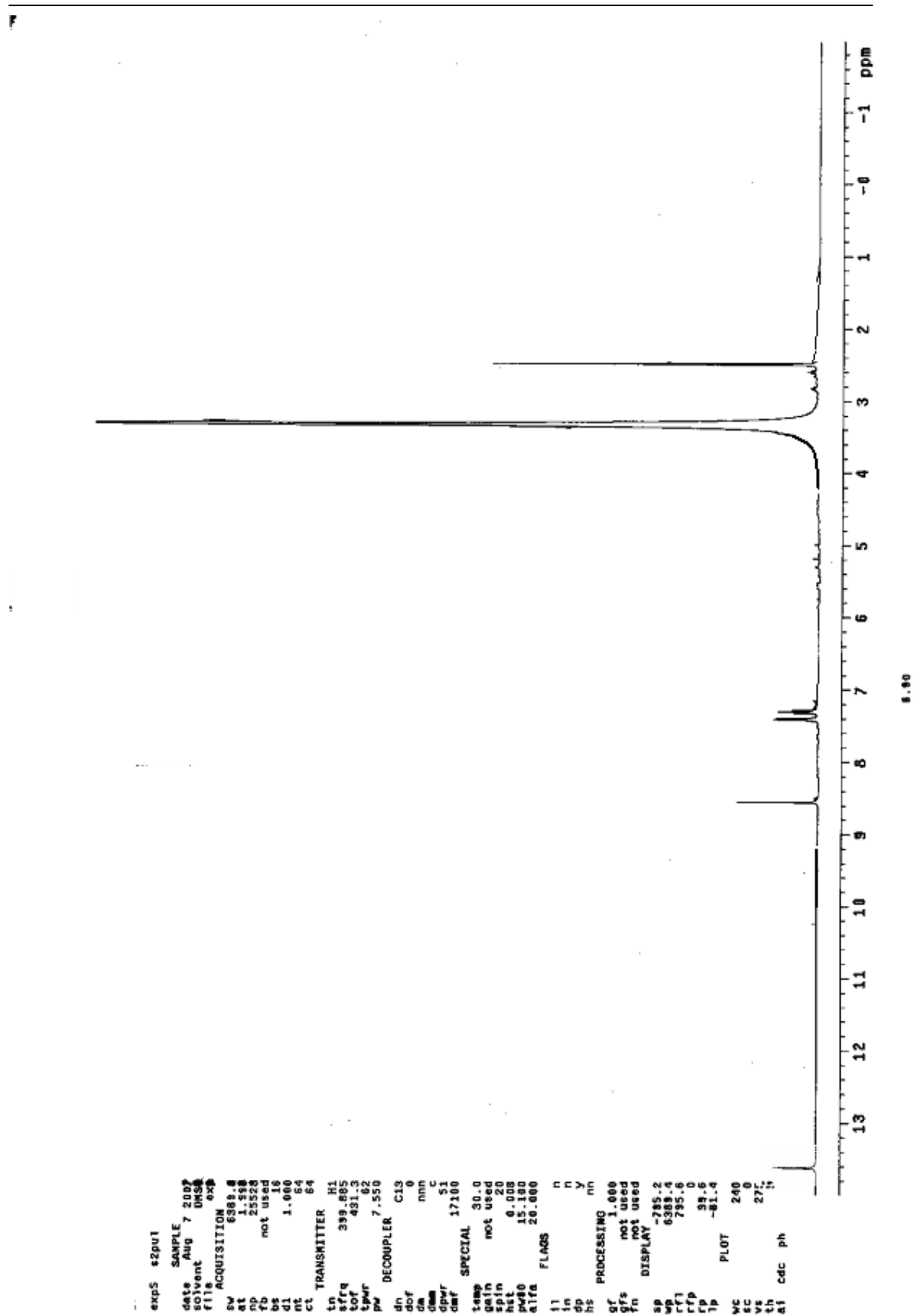
Figure 4.2.3.  $^1\text{H}$  NMR spectrum of *cis*- $[\text{W}(\text{CO})_2(\eta^4\text{-H}_2\text{L})]$ 

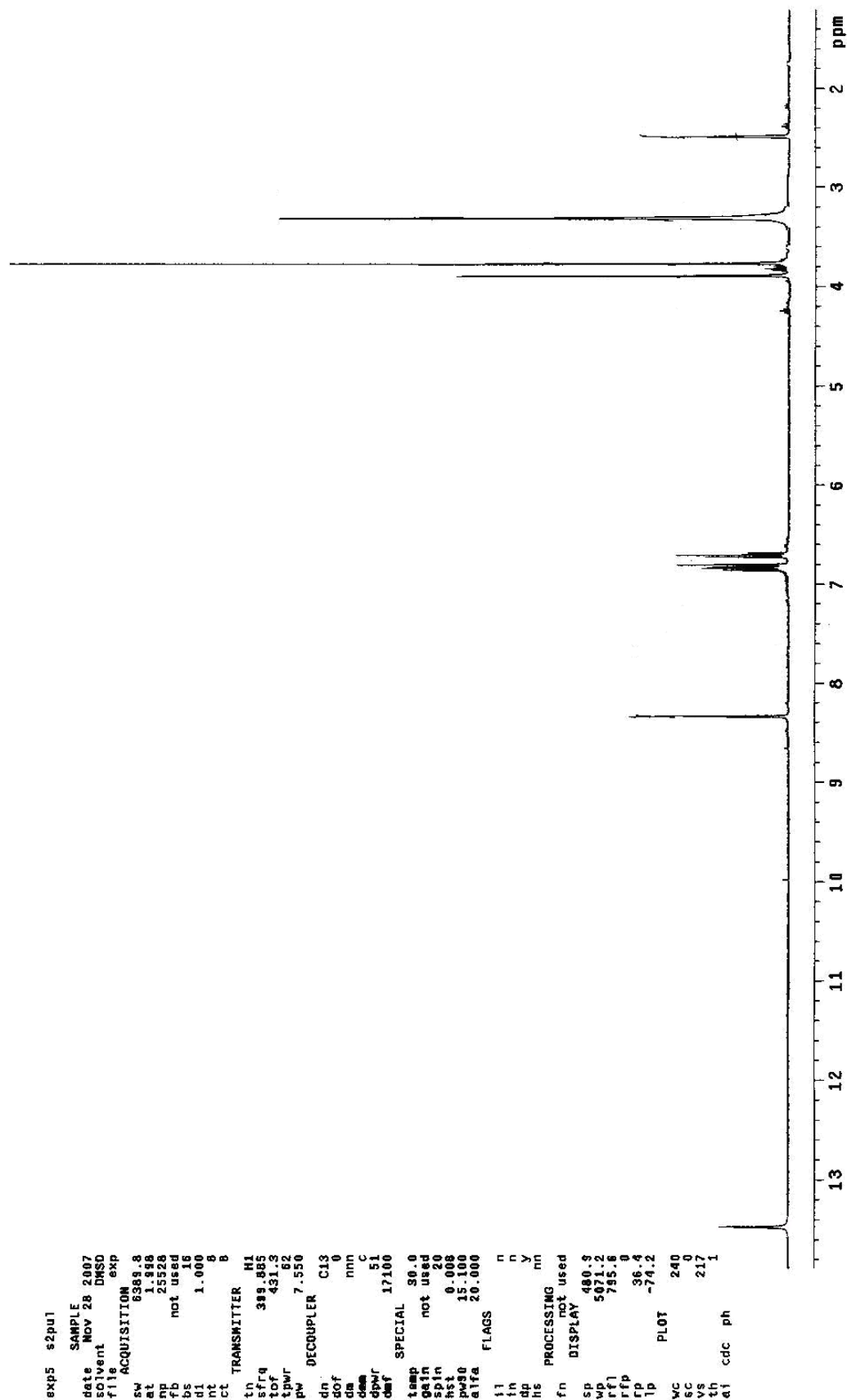
Figure 4.2.4  $^1\text{H}$  NMR spectrum of [*N,N'*-bis(2-hydroxy-3-methoxybenzylidene)ethylenediamine, ( $\text{H}_2\text{L}^{\text{H}}$ )]

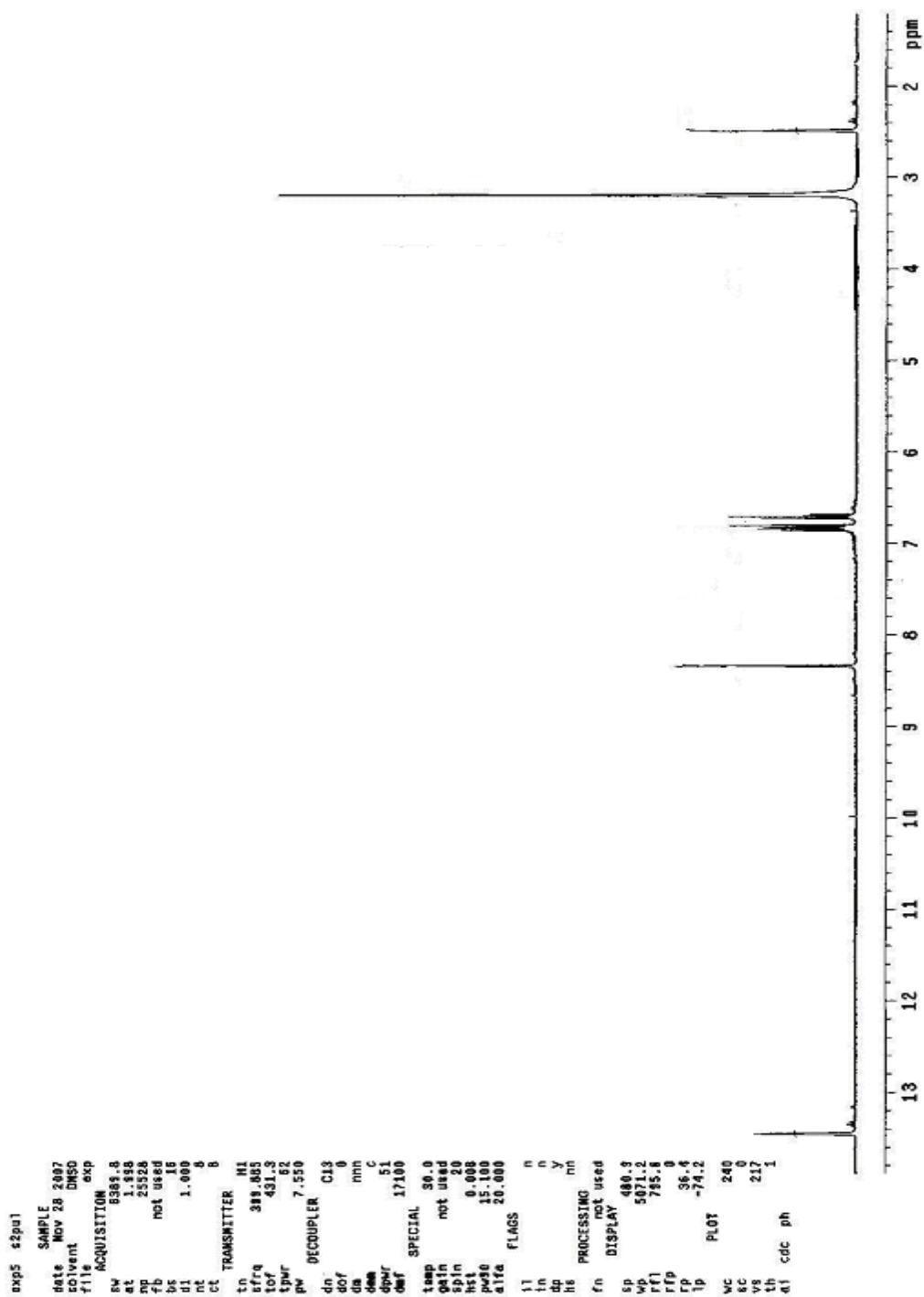
Figure 4.2.5.  $^1\text{H}$  NMR spectrum of *cis*- $[\text{Mo}(\text{CO})_2(\eta^4\text{-H}_2\text{L})]$ 



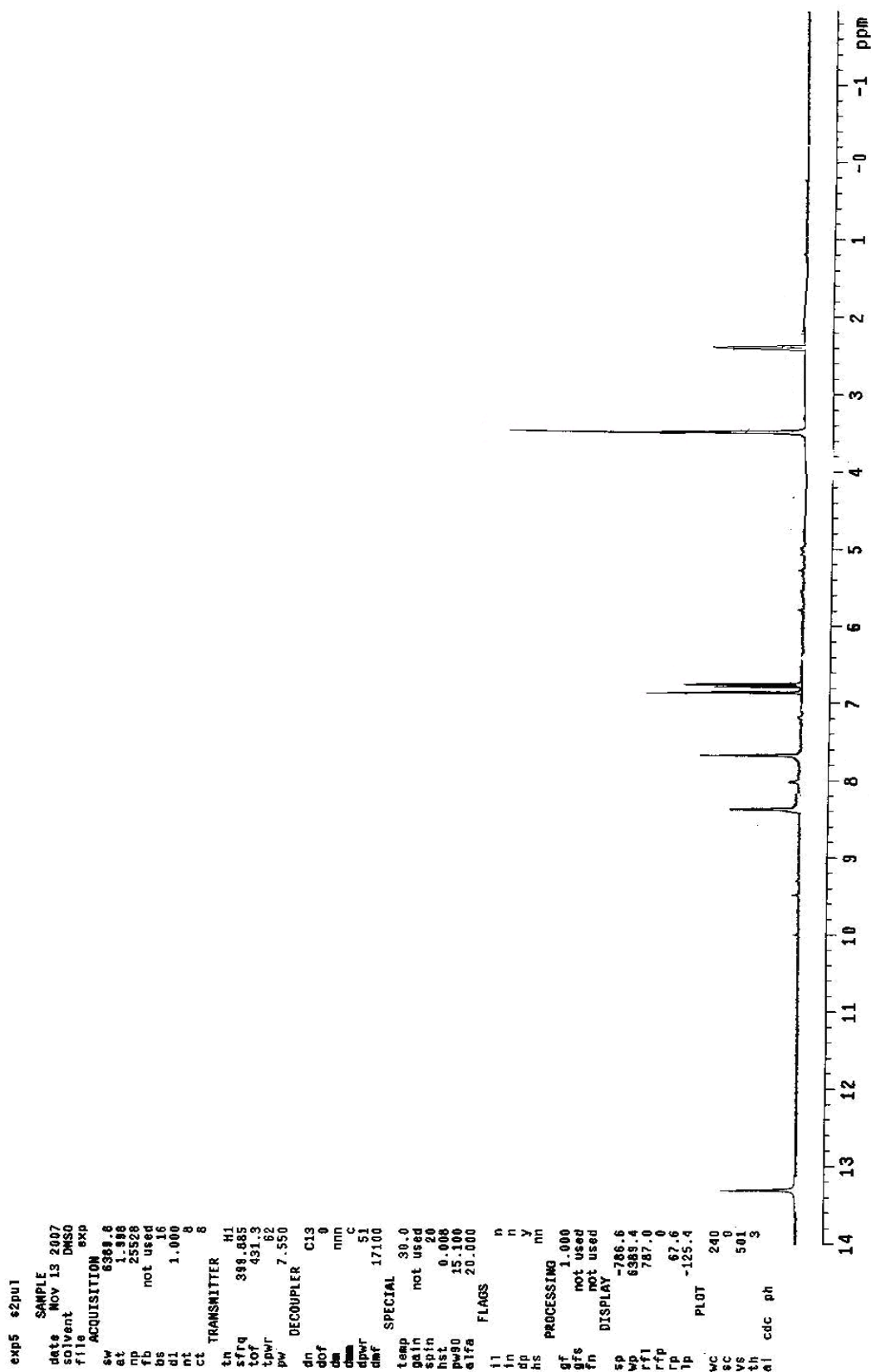
Figure 4.2.6.  $^1\text{H}$  NMR spectrum of *cis*- $[\text{W}(\text{CO})_2(\eta^4\text{-H}_2\text{L})]$ 

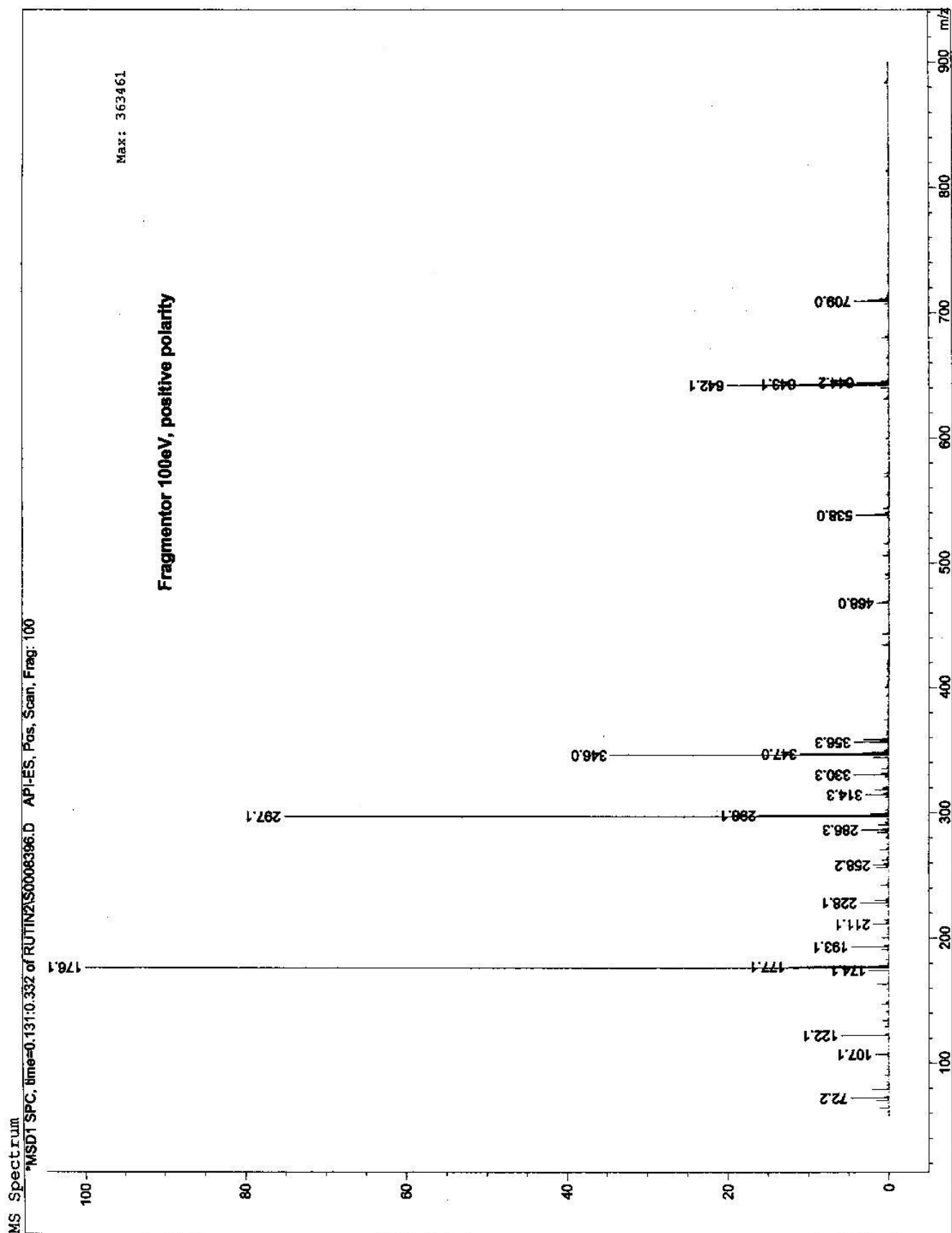
Figure 4.3.1. LC-Mass spectrum of *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

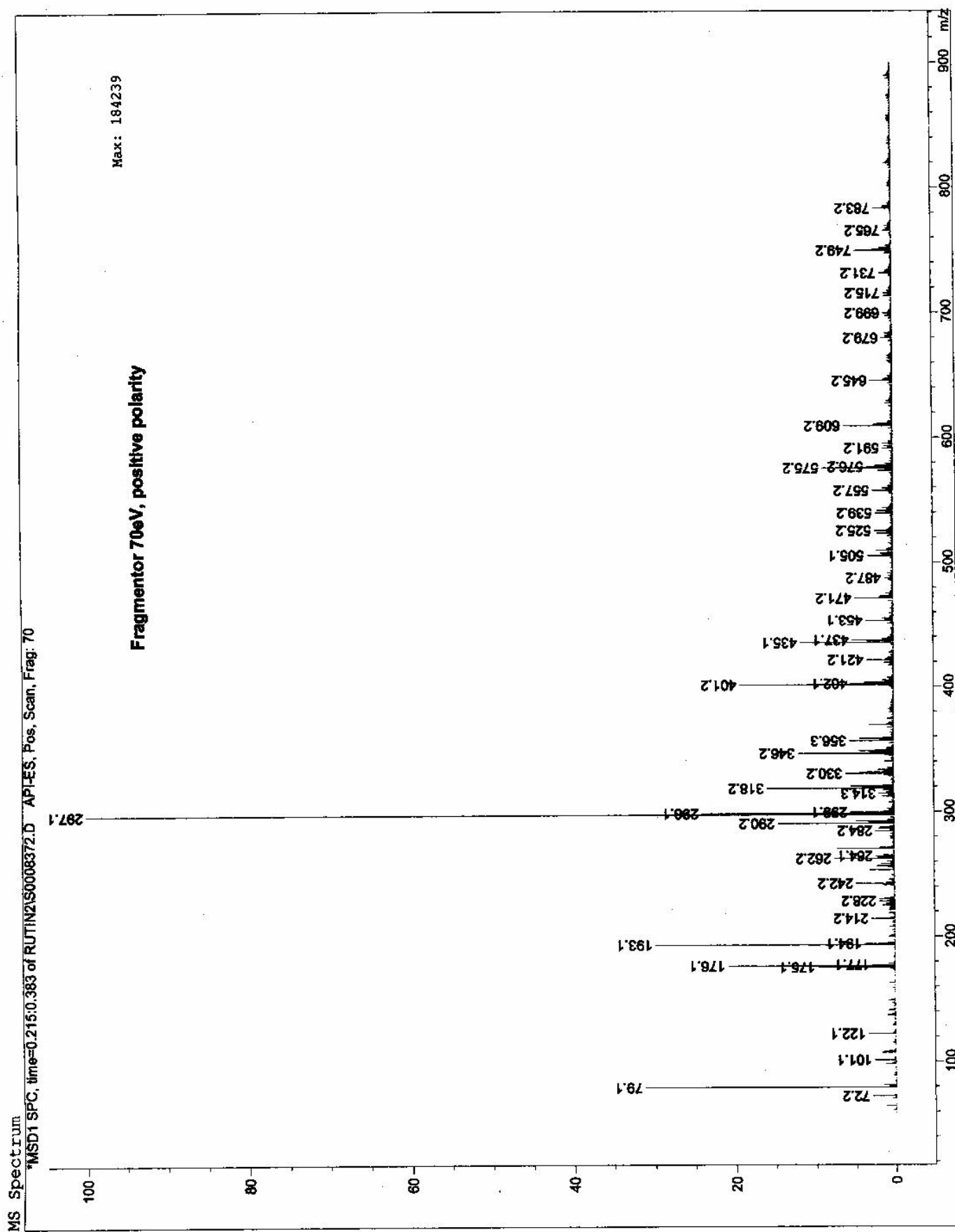
Figure 4.3.2. LC-Mass spectrum of *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

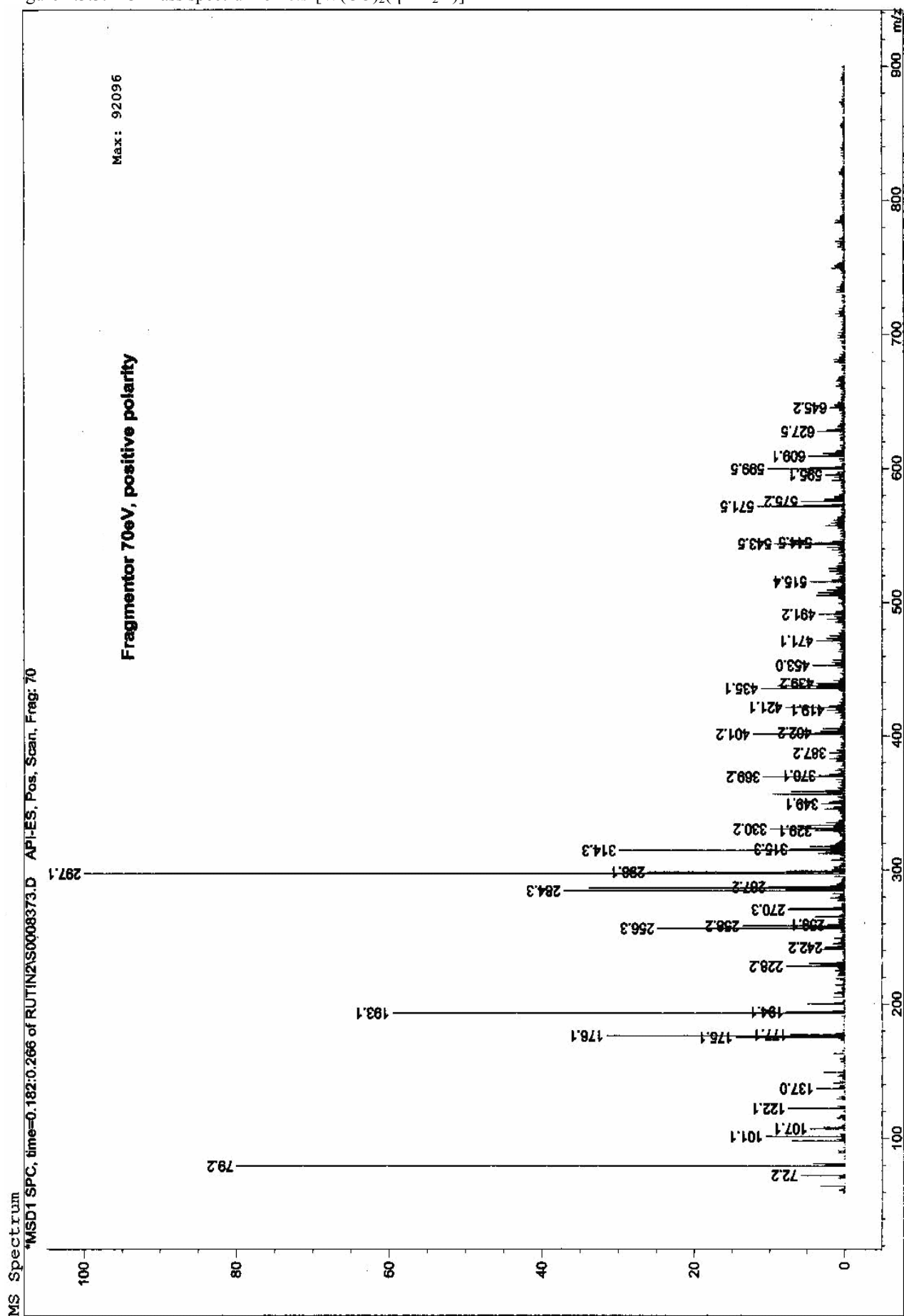
Figure 4.3.3. LC-Mass spectrum of *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L)]

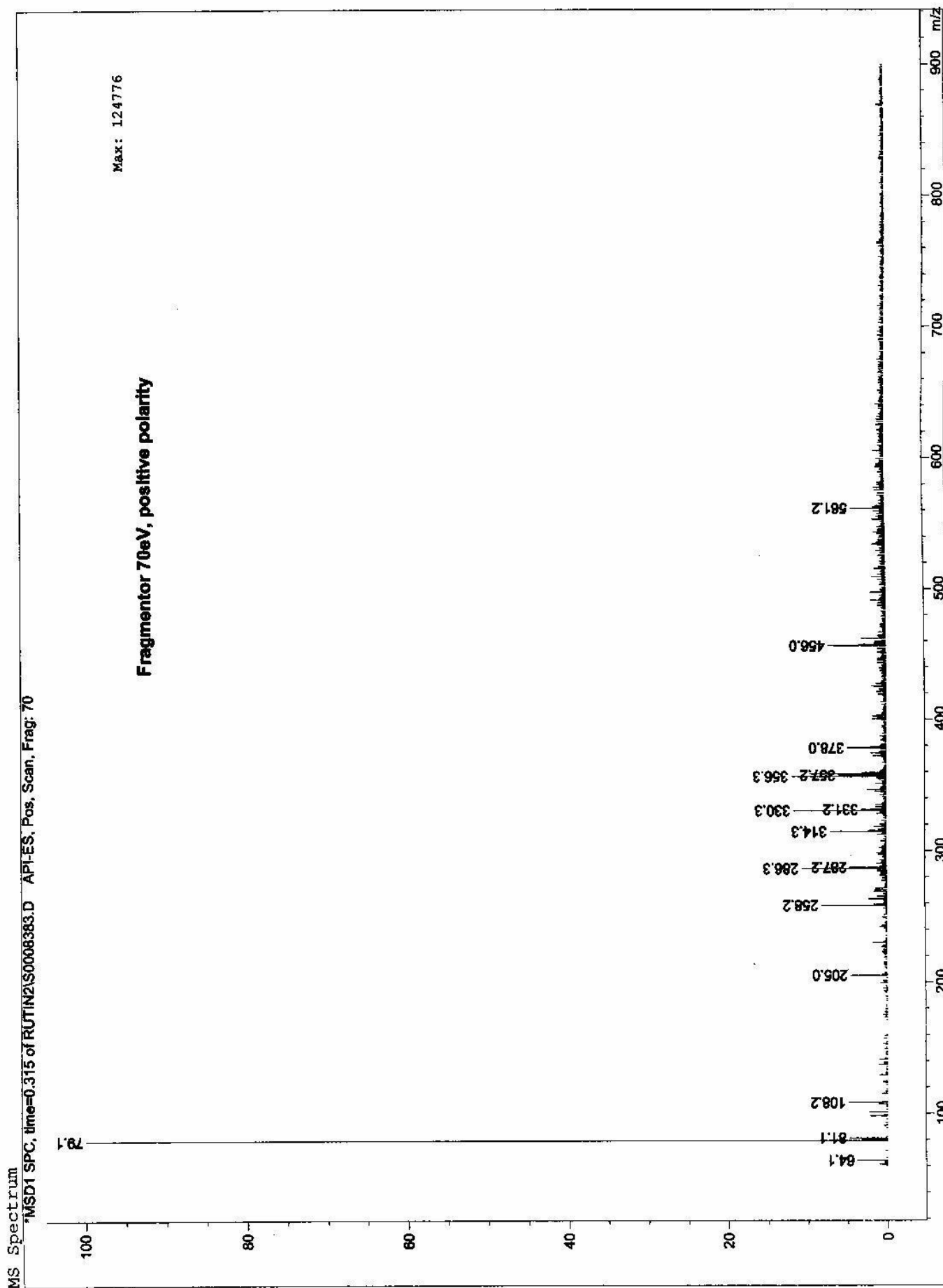
Figure 4.3.4. LC-Mass spectrum of *cis*-[Cr(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L<sup>+</sup>)]

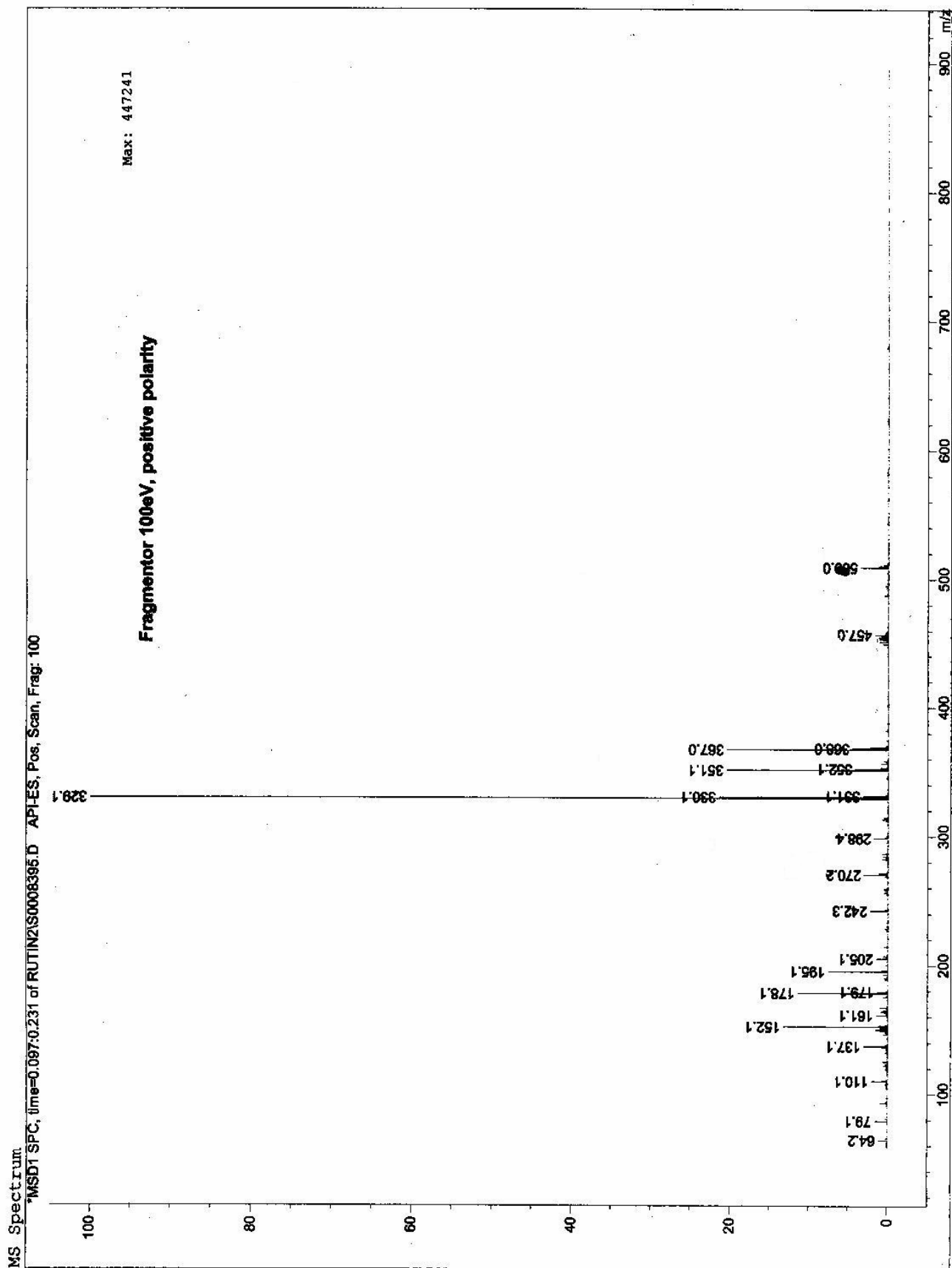
Figure 4.3.5. LC-Mass spectrum of *cis*-[Mo(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L<sup>+</sup>)]

Figure 4.3.6. LC-Mass spectrum of *cis*-[W(CO)<sub>2</sub>(η<sup>4</sup>-H<sub>2</sub>L<sup>+</sup>)]