DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL CARBONYL COMPLEXES CONTAINING NITROGEN AND SULPHUR DONOR LIGANDS

by
Senem KARAHAN

May, 2009
İZMİR

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL CARBONYL COMPLEXES CONTAINING NITROGEN AND SULPHUR DONOR LIGANDS"** completed by **SENEM KARAHAN** 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 Doctor of Philosophy.

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ABSTRACT

The hitherto unknown Schiff base-metal carbonyl complexes were synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with four Schiff base ligands, *N,N′* - bis (2 - aminothiophenol) - 1,4 - bis (2 - carboxaldehydephenoxy) butane**,** *N,N′* - bis (2 - aminothiophenol) - 1,7 - bis (2-formylphenyl) - 1,4,7 - trioxaheptane**,** *N,N′* - bis (2 - hydroxynaphthalin - 1 - carbaldehydene) - 1,2 - bis (*p*- aminophenoxy) ethane and *N,N′* - bis (2-hydroxynaphthalin - 1 - carbaldehydene) - 1,4 - bis (*p*- aminophenoxy) butane.

The complexes were characterized by elemental analysis, LC- mass spectrometry, magnetic studies, FTIR and ^{1}H NMR spectroscopy.

The spectroscopic studies show that *N,N′* - bis (2 - aminothiophenol) - 1,4 - bis (2-carboxaldehydephenoxy) butane and *N,N′* - bis (2 - aminothiophenol) - 1,7 - bis (2-formylphenyl) - 1,4,7 - trioxaheptane ligands are converted to benzothiazole derivatives after UV irradiation and coordinated to the central metal as bridging tetradentate ligands in addition to *N,N′* - bis (2 - hydroxynaphthalin - 1 - carbaldehydene) - 1,2 - bis (*p*-aminophenoxy) ethane and *N,N′* - bis (2-hydroxynaphthalin - 1 - carbaldehydene) - 1,4 - bis (*p*-aminophenoxy) butane ligands are coordinated to the central metal as tetradentate ligands.

Keywords: *N,N′*-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy) butane, *N,N′* - bis (2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane, *N,N′*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy) ethane, *N,N′*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy) butane, metal carbonyls, Schiff base.

AZOT VE SÜLFÜR DONOR LİGANLAR İÇEREN BAZI GEÇİŞ METAL KARBONİL KOMPLEKSLERİNİN SENTEZİ VE KARAKTERİZASYONU

ÖZ

Şimdiye kadar bilinmeyen Schiff bazı-metal karbonil kompeksleri ışınlanma ara ürünü olan $M(CO)_5THF$ (M = Cr, Mo, W) ile dört Schiff baz ligandı *N,N′* - bis (2-aminotiyofenol) - 1,4 - bis (2 - karboksaldehidfenoksibütan), *N,N′* - bis (2-aminotiyofenol) - 1,7 - bis (2 - formilfenil) - 1,4,7 - trioksaheptan, *N,N′* - bis (2-hidroksinaftalin - 1 - karbaldehiden) - 1,2 - bis (*p*-aminofenoksi) etan ve *N,N′* - bis (2- hidroksinaftalin - 1 - karbaldehiden) - 1,4 - bis (*p*-aminofenoksi) bütan arasındaki fotokimyasal tepkime ile sentezlendi.

Sentezlenen komplekslerin yapıları elementel analiz, LC- kütle spektrometrisi, manyetik çalışmalar, FTIR ve ^1H NMR spektroskopisi ile aydınlatılmaya çalışıldı.

Spektroskopik çalışmalar *N,N′* - bis (2 - hidroksinaftalin - 1 - karbaldehiden) - 1,2-bis (*p*-aminofenoksi) etan ve *N,N′* - bis (2 - hidroksinaftalin - 1 - karbaldehiden)-1,4-bis (*p*-aminofenoksi) bütan ligandlarının merkez atomuna dört dişli ligandlar olarak koordine olmasına ek olarak *N,N′* - bis (2-aminotiyofenol) - 1,4 – bis (2-karboksaldehidfenoksibütan) ve *N,N′* - bis (2-aminotiyofenol) -1,7-bis(2-formilfenil)-1,4,7-trioksaheptan ligandlarının UV ışınlanma sonrasında benzotiyazol türevlerine dönüştüğünü ve merkez atomuna köprü konumunda dört dişli ligandlar olarak bağlandığını göstermiştir.

Anahtar sözcükler: *N,N′* - bis (2-aminotiyofenol) - 1,4 - bis (2 - karboksaldehidfenoksibütan), *N,N′* - bis (2 - aminotiyofenol) - 1,7 - bis (2 - formilfenil) - 1,4,7 - trioksaheptan, *N,N′* - bis (2 - hidroksinaftalin - 1 -karbaldehiden) - 1,2 - bis (*p*-aminofenoksi) etan, *N,N′* - bis (2 - hidroksinaftalin - 1 - karbaldehiden) - 1,4 – bis (*p*-aminofenoksi) bütan, metal karboniller, Schiff bazı.

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CHAPTER ONE

INTRODUCTION

1.1 Metal Carbonyls

Carbon monoxide is one of the most important and versatile ligands in transition metal chemistry (Cotton, Wilkinson, Murillo, & Bochmann, 1999). Since the discovery of the first metal carbonyl complexes, $Pt(CO)_2Cl_2$, $Pt_2(CO)_4Cl_4$ and $Pt_2(CO)_3Cl_4$ by Schützenberger in 1868 (Schützenberger & Hebd, 1870; Schützenberger, 1868, 1870) and the discovery of the first homoleptic metal carbonyl, $Ni(CO)_4$ by Mond in 1890 and its immediate industrial application for the preparation of ultrapure nickel (Mond, Langer, & Quincke, 1890), metal carbonyls have played a very important role in chemistry and the chemical industry (Colquhoun, Thompson, & Twigg, 1991; Falbe J., 1980). Many industrial processes employ CO as a reagent and transition metal compounds as heterogeneous or homogeneous catalysts and involve the intermediates of metal carbonyls (Henrici-Olive´ & Olive´, 1983; Sen, 1993).

VIB metal hexacarbonyls $M(CO)_6$, (M= Cr, Mo, W) are also considered important. Some properties of these metal carbonyls have been given in the following.

1.2 Chromium Hexacarbonyl

1.2.1 Physical Properties

Chromium hexacarbonyl is a colorless, odorless, volatile diamagnetic solid that forms orthorhombic crystals with a density of 1.77 g cm^{-3}. The solid melts in air at 130 °C with decomposition and under vacuum at 150(2) °C without decomposition. Chromium hexacarbonyl is a hydrophobic, air stable compound that is very slightly soluble in non-polar organic solvents (1% w/v), slightly soluble in polar organic solvents 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, Gordon, Stone, & Abel, 1982).

1.2.2 Thermodynamic Data

Chromium hexacarbonyl is extraordinarily volatile for a compound with a molecular weight of 220.6. It is easily sublimed, even at 25 °C and 0.1 Torr. (Wilkinson & et al., 1982).

1.2.3 Molecular Structure

The structure of chromium hexacarbonyl (Figure 1.1) results from an electron diffraction study of gaseous $Cr(CO)_6$ and X-Ray and neutron diffraction studies of crystalline $Cr(CO)_6$ at liquid nitrogen temperatures. The studies all indicate that the molecule has virtually perfect octahedral (O_h) molecular symmetry. The compound crystallizes in the orthorhombic space group and although the molecule only lies on mirror plane in the crystal (site symmetry C_s), the octahedral symmetry is retained to an excellent approximation (Wilkinson & et al., 1982).

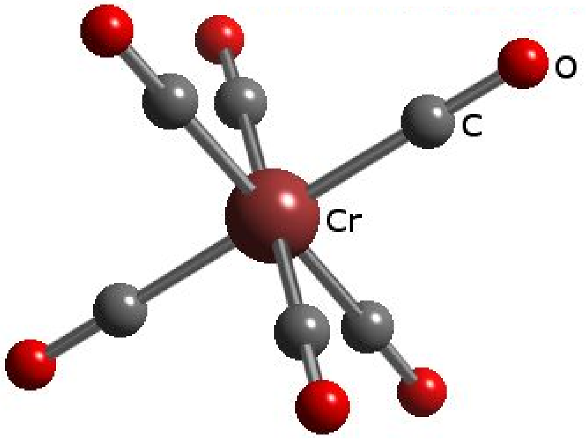


Figure 1.1 The molecular structure of $Cr(CO)_6$

1.3 Molybdenum Hexacarbonyl

Molybdenum hexacarbonyl $Mo(CO)_6$ was the first of the Group VIB metal carbonyls to be prepared.

1.3.1 Physical Properties

$Mo(CO)_6$ is a colorless, odorless, diamagnetic solid that forms orthorhombic crystals with a density of 1.96 g cm^{-3}. The crystals are air stable and hydrophobic and decompose without melting at 150 °C, but melt reversibly under vacuum at 146(2) °C. $Mo(CO)_6$ is very slightly soluble in non-polar organic solvents, slightly soluble in polar organic solvents and insoluble in water. Solutions of $Mo(CO)_6$ are quite stable to oxidation and decompose only very slowly in air (Wilkinson & et al., 1982).

1.3.2 Thermodynamic Data

$Mo(CO)_6$ has a high vapor pressure (0.27 Torr at 30 °C, 42.8 Torr at 100 °C) and is easily sublimed at room temperature under a good vacuum (Wilkinson & et al., 1982).

1.3.3 Molecular Structure

The structure of $Mo(CO)_6$ (Figure 1.2) results from electron diffraction studies and an early X-Ray diffraction study. They indicate that $Mo(CO)_6$ has octahedral (O_h) symmety 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 & et al., 1982).

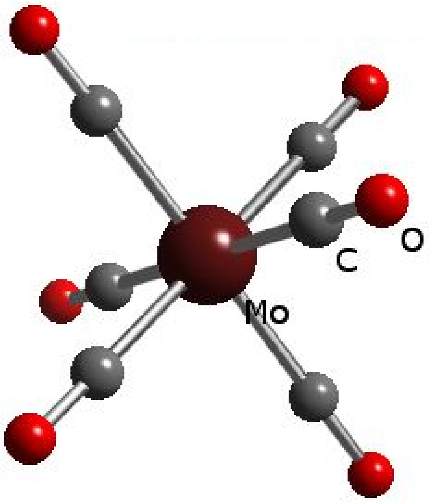


Figure 1.2 The molecular structure of $Mo(CO)_6$

1.4 Tungsten Hexacarbonyl

1.4.1 Physical Properties

$W(CO)_6$ is a colorless, odorless, diamagnetic solid that forms orthorhombic crystals with a density of 2.65 g cm^{-3}. The crystals are air stable, hydrophobic and melt with decomposition at 150 °C, but under vacuum melt revesibly at 166(2) °C. $W(CO)_6$ is very slightly soluble in non-polar organic solvents such as hexane (1% by weight), slightly soluble in polar organic solvents such as THF (to a maximum of 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 & et al., 1982).

1.4.2 Thermodynamic Data

In spite of a molecular weight of 351.91, $W(CO)_6$ has a vapor pressure of 0.35 Torr at 50 °C and 14.1 Torr at 100 °C and therefore sublimes quite readily under vacuum (Wilkinson & et al., 1982).

1.4.3 Molecular Structure

The structure of $W(CO)_6$ (Figure 1.3) results from electron diffraction studies. They indicate that $[W(CO)_6]$ has octahedral (O_h) symmery, with values of the W-C distance 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 & et al., 1982).

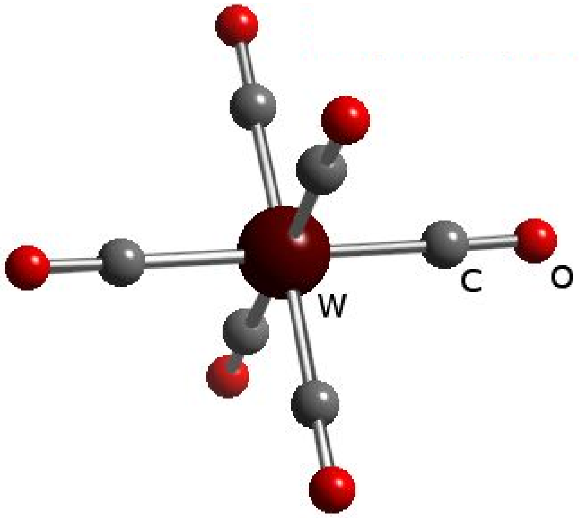


Figure 1.3 The molecular structure of $W(CO)_6$

1.5 Bonding

The bonding of $Mo(CO)_6$ and $W(CO)_6$ are quialitatively identical to that of $Cr(CO)_6$. The valance bond picture is depicted in Figure 1.4. In figure 1.4a, the lone pair of electrons in a σ-orbital on the carbon atom of CO interacts with an empty 3d σ-orbital on the chromium atom to form a "coordinate covalent" σ-bond between C and Cr. This is called the forward interaction and is a typical donor-acceptor interaction. In Figure 1.4b, the second component of the bonding is shown and consists of the interaction of a filled 3d π-orbital on the chromium with an empty π*-orbital of the carbon monooxide. 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 1.4, but it should be stressed that neither interaction results in a full bond (Wilkinson & et al., 1982).

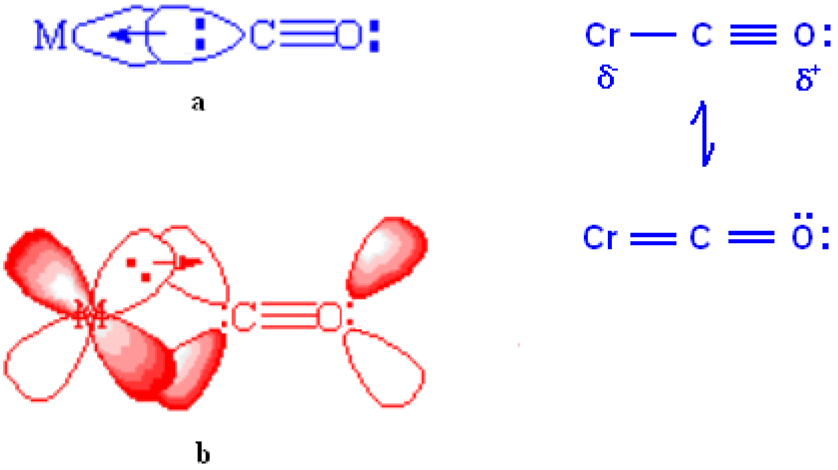


Figure 1.4 The valance bond description of chromium-carbon monoxide bonding

1.6 Infrared Spectroscopy Properties

Infrared properties of $Mo(CO)_6$ and $W(CO)_6$ are as appropriate to $Cr(CO)_6$. IR spectroscopy data for $M(CO)_6$ (M= Cr, Mo, W) are collected in Table 1.1 (Jones, McDowell, & Goldblatt, 1969).

Table 1.1 Infrared spectroscopy data for $M(CO)_6$

Method	**Absorption**			**Assignment**	**Phase**
	$Cr(CO)_6$	**$Mo(CO)_6$**	**$W(CO)_6$**		
IR	2000.4 cm^{-1}	2004 cm^{-1}	1998 cm^{-1}	T_{1u} ν(CO)	Gas
	668.1 cm^{-1}	593 cm^{-1}	585 cm^{-1}	T_{1u} δ(MCO)	,,
	440.5 cm^{-1}	368 cm^{-1}	374 cm^{-1}	T_{1u} ν(MC)	,,
	97.8 cm^{-1}	81 cm^{-1}	81 cm^{-1}	T_{1u} δ(CMC)	,,
	1984.4 cm^{-1}			T_{1u} ν(CO)	CCl_4 solution
	664.6 cm^{-1}			T_{1u} δ(CrCO)	,,
	443.8 cm^{-1}			T_{1u} ν(CrC)	,,
	103 cm^{-1}			T_{1u} δ(CCrC)	,,

The earliest studies of $Cr(CO)_6$ utilized IR spectroscopy to examine the carbonyl stretch vibrations. The CO stretching frequency of gaseous $Cr(CO)_6$ is located at 2000 cm^{-1}, significantly lower than the value for free gaseous carbon monoxide (2143 cm^{-1}). The lowering of the frequency corresponds to a lowering of the C-O bond order due to the occupancy of antibonding π-orbitals in carbon monoxide by chromium 3d electron density. The lower bond order is accompanied by an increase in the C-O bond distance, from 1.128 Å in free CO to 1.140 Å in $Cr(CO)_6$. A quantitative measure of the bond order of the M-C and C-O bonds in $M(CO)_6$ (M= Cr, Mo, W) can be obtained from force constant calculations. W-CO bond is significantly stronger than the Mo-CO or Cr-CO bond (Wilkinson & et al., 1982).

1.7 Photochemistry

The photosensivity 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 (Adamson, & Fleischauer, 1984).

Metal carbonyls are among the most photoreactive metal complexes known in general. The dominant photoreaction for $M(CO)_6$ (M=Cr, Mo, W) is the dissociation of CO (equation 1). The unsaturated $M(CO)_5$ is generated quite efficiently, and has a substantial lifetime. The pentacarbonyl intermediate either recombine with CO (equation 2) or combine with another ligand L, as in equation 3. Thus, photochemical substitution is a common reaction of $M(CO)_6$ (Wilkinson & et al., 1982).

$$[M(CO)_6] \xrightarrow{h\upsilon} [M(CO)_5] + CO$$

$$[M(CO)_5] + CO \rightarrow [M(CO)_6]$$

$$[M(CO)_5] + L \rightarrow [M(CO)_5L]$$

1.8 Substitution Reactions

By far the most important property of $M(CO)_6$ (M= Cr, Mo, W) is its use as the starting material for a vast number of substitution recations where the metal does not change oxidation state and L (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.

$$[M(CO)_6] + nL \rightarrow [M(CO)_{6-n}L_n] + nCO$$

Many products of these substitution reactions are important. 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) σ-donor only ligands such as hydride, halide, hydroxide, ammonia, etc. (2) σ-donor ligands with high energy vacant t_{2g} orbitals cabaple of π-back bonding, such as phosphines, arsines, NO, etc. and (3) π-donor/π-acceptor ligands where the electrons donated from the ligand to the metal are of the π type, such as alkenes and arenes.

1.8.1 With σ-Donor Ligands

Table 1.2 lists some representative substitution reactions of σ-donor only ligands with $M(CO)_6$ (M=Cr, Mo, 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 the zero oxidation state of chromium and the fact that the σ-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 $[M(CO)_{6-x}L_x]$ complexes, for as x increases more electron density must be accepted by the remaining carbonyls, which increases the electron population in the CO π*-orbitals, which in turn decreases the bond order and the C-O stretching frequencies.

Table 1.2 Some representative substitution reactions of $M(CO)_6$ (M=Cr, Mo, W) with σ-donor ligands

Ligand	Product	Conditions , Comment
nitrogen		
NEt_3	$[M(CO)_{6-x}(NEt_3)_x]$	x=1.2 (Ref. 1)
en	$[M(CO)_4(en)]$	(Ref. 2)
oxygen		
THF	$[M(CO)_5THF]$	(Ref. 3)
sulfur		
R_2S	$[M(CO)_5SR_2]$	R=Me, Ph ;UV (Ref. 4)

1. (Strohmeier, Gerlach & von Hobe, 1961)
2. (Kraihanzel & Cotton, 1963)
3. (Strohmeier &Gerlach, 1961)
4. (Herberhold & Süss, 1977)

1.8.2 With σ-Donor/π-Acceptor Ligands

The σ-donor/π-acceptor ligands, like CO, have the capability to donate electrons to the metal and accept electrons back from the metal into $t_{2g}(\pi)$ orbitals of energy. Substitution reactions of such ligands with $M(CO)_6$ (M=Cr, Mo,W) are listed Table 1.3. These syntheses employ routes and conditions similar to those used to make substituted σ-donor complexes, the σ/π complexes are sometimes capable of substituting for more than three carbonyls. Thus, n can equal 1-6 for the σ/π ligands, but only 1-3 for σ ligands. The more complete substitutions, where n= 4-6, occur only for small, excellent π-acceptor ligands such as PF_3.

$$[M(CO)_6] + nL \rightarrow [M(CO)_{6-n}L_n] + nCO$$

Tablo 1.3 Some substitution reactions of $M(CO)_6$ with σ-donor/π-acceptor ligands

Ligand	Product	Metal	Conditions , Comment
nitrogen			
py	$[M(CO)_{6-x}(py)_x]$	Cr, Mo, W	x=1-3 (Ref. 1)
NO	$[M(NO)_4]$	Cr	(Ref. 2)
phosphorous			
PH_3	$[M(CO)_{6-x}(PH_3)_x]$	Cr, Mo, W	x= 1,2 (Ref. 3)
PR_3	$[M(CO)_{6-x}(PR_3)_x]$	Cr, Mo, W	x= 1-3;R=Et, Ph (Ref. 4)
arsenic			
AsH_3	$[M(CO)_5(AsH_3)]$	Cr, Mo, W	(Ref. 5)

1. (Abel, Bennett, & Wilkinson, 1959; Behrens & Vogl, 1963; Hieber & Floss, 1957; Kraihanzel & Cotton, 1963; Strohmeier & Gerlach, 1961)
2. (Satija & Swanson, 1976)
3. (Fischer, Louis, Bathelt, Moser, & Müller, 1969)
4. (Mathieu & Poilblanc, 1972; Poilblanc & Bigorgne, 1962)
5. (Dobson & Houk, 1967)

1.8.3 With π-Donor/π-Acceptor Ligands

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

The reaction of $M(CO)_6$ (M=Cr, Mo, W) with either conjugated or non-conjugated cyclic alkenes typically results in the displacement of a maximum of three carbonyls. Arenes, which are better π-acceptor ligands, can displace more than three carbonyls, however (Wilkinson & et al., 1982). Three of the most important classes of this type of substitution reaction are represented in Table 1.4.

Tablo 1.4 Some substitution reactions of $M(CO)_6$ (M=Cr, Mo, W) with π-donor/π-acceptor ligands

Ligand	**Formula**	**Name**	**Product**
arene	C_6H_6	benzene	$[M(CO)_3(\eta\text{-}C_6H_6)]$ (Ref. 1)
conjugated triene	C_7H_8	cycloheptatriene	$[M(CO)_3(\eta^6\text{-}C_7H_8)]$ (Ref. 2)
non-conjugated diene	C_7H_8	norbornadien	$[M(CO)_4(\eta^4\text{-}C_7H_8)]$ (Ref. 2b)

1. (Nicholls & Whiting, 1959)
2. a (Abel, Bennett, Burton, & Wilkinson, 1958) b (Bennett, Pratt, & Wilkinson, 1961)

1.9 Photochemical Substitution at Metal Carbonyls

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

$$W(CO)_6 + PPh_3 \xrightarrow{h\nu} W(CO)_5(PPh_3) + CO$$

$$CpMn(CO)_3 \xrightarrow[\text{THF, -CO}]{h\nu} CpMn(CO)_2THF \xrightarrow[\text{20°C, -THF}]{L} CpMn(CO)_2L$$

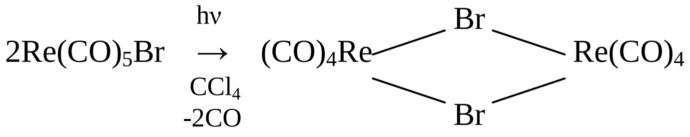
In metal carbonyl complexes $M(CO)_mL_n$ with a mixed coordination sphere, photochemical excitation causes dissociation of that ligand which is most weakly bonded in the ground state as well. This will be the ligand at the lowest position respectively in the spectrochemical series.

$$M(CO)_5THF \xrightarrow{h\nu} M(CO)_5 + THF$$

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.

$$CO + M(CO)_4L \xleftarrow{h\nu} M(CO)_5L \xrightarrow{h\nu} M(CO)_5 + L$$

If suitable free ligands are absent, the gap in the coordination sphere, generated through photochemical dissociation of CO, may be closed by dimerization (Elschenbroich & Salzer, 1992).



1.10 Kinetics And Mechanisms of $M(CO)_6$ Substitution Reactions

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

Interest in the photoactivation of transition-metal carbonyls stems in part from their potential use as photocatalysts (Borowczak, Szymanska-Buzar, & Ziolkowski, 1984; Hennig, Rehorek, & Archer, 1985). Metal carbonyl complexes are among the most photoreactive transition metal complexes known. The photochemistry of group 6 metal hexacarbonyls, $M(CO)_6$ (M= Cr, Mo, W) has been studied extensively during the past three decades (Geoffroy & Wrighton, 1979; Nasielski & Colas, 1975; Simon & Xie, 1987; Wrighton, 1974). The primary event upon irradiation of these complexes in solution, is the efficient loss of CO to give coordinatively unsaturated species, $M(CO)_5$. This product is typically very short-lived in solution at ambient temperatures; in perfluoromethylcyclohexane solution flushed with CO at room temperature, the half-life of $Cr(CO)_5$ is only 13 ns (Bonneau & Kelly, 1980) and in the same condition the half-life of $W(CO)_5$ is 20ps (Kelly, Long, & Bonneau, 1983).

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 (S=solvent). In solvents with poor donor ability, experiments indicate that the $M(CO)_5$ intermadiate is quite reactive; flash photolysis studies show that in carbon monoxide saturated hexane, the recombination rate constant is approximately $3x10^6$ mol $dm^{-3}s^{-1}$. 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 . Subsequent reactions can displace another CO or the ligand L.

$$[M(CO)_6] \xrightarrow[\text{or } \Delta]{h\upsilon} [M(CO)_5] \xrightarrow{S} [M(CO)_5(S)]$$

$$[M(CO)_5(S)] + L \rightarrow [M(CO)_5(L)] + S$$

1.11 Applications of Photochemistry

The application of photochemistry to organometallic compounds has its roots deep in the history of the field. The first recorded instance appears to have been the recognition by Dewar and Jones in 1905 that sunlight resulted in the conversion of the very newly discovered $Fe(CO)_5$ into a new substance (Dewar & Jones, 1905; 1907 a; 1907 b) the correct formula of which was later reported by Speyer and Wolf to be $Fe_2(CO)_9$ (Speyer & Wolf, 1927).

Photochemical studies began in earnest with a series of papers from the Strohmeier laboratory in Würtzburg. These papers examined the application of photochemistry to the substitution of carbonyl ligands in the Group VI carbonyls (Strohmeier & Gerlach 1960 a) and $CpMn(CO)_3$ (Strohmeier & Gerlach, 1960 b).

As described above, the first applications of photochemistry involved photolysis of metal carbonyl compounds leading to the loss of a carbon monoxide ligand to form an intermediate that can undergo subsequent reaction with other ligands Fleckner, Grevels, & Hess, 1984).

Photochemical reactions are particularly useful when the incoming ligand is weakly bound by the metal such as the nitrogen ligand derivatives reported by Strohmeier, the synthesis of reactive intermediates such as $CpM(CO)_2THF$, where M, Mn or Re, or the formation of weakly bound chelated species as reported by Johnson and coworkers (Pang, Johnson, & VanDerveer, 1996).

Recent papers appearing in the Journal of Organometallic Chemistry have described the photochemical reaction of the Group VI carbonyls with terminal alkynes (Abd-Elzaher, Weibert, & Fischer, 2003) and vinyl ferrocenes (Özkar, Kayran, & Demir, 2003) to yield $M(CO)_5L$ derivatives. In an article in press as of this writing, Özkar and coworkers have described the synthesis and molecular structure of $Cr(CO)_5$(2,5-diaminopyridine) (Morkan, Güven, & Özkar, 2004). Tilset and coworkers have recast the King and Wojiciki acyl decarbonylation reactions in a new light with the photochemical synthesis of $TpFe(CO)(PMe_3)Me$ from $TpFe(CO)(PMe_3)(C(=O)Me)$ (Grazani, Toupet, Hamon, & Tilset, 2003).

One of the more broadly utilized organometallic photochemical reactions is the photolysis of Fischer carbenes in the presence of doubly bonded substrates to yield cycloaddition products in which the metal complex is a de facto ketene source. For example, reactions with immines yield b-lactams (McGuire & Hegedus, 1982) aldehydes yield lactones (Colson & Hegedus, 1994) alkenes yield cyclobutanones (Brown & Hegedus, 1998; Koebbing, Mattay, & Raabe, 1993) and alcohols and amines yield substituted acids and amides, respectively (Hegedus, 1995; Zhu, Deur, & Hegedus, 1997).

CHAPTER TWO

SCHIFF BASE COMPLEXES

2.1 Schiff Base

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864 (Schiff, 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’’ (Cozzi, 2004).

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. The resultant functional group, $R^1HC{=}N{-}R^2$, is called an imine and is particularly for binding metal ions via the N atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocycles. Ketones, of course, will also form imines of the type $R^1R^2C{=}N{-}R^3$, but the reactions tend to occur less readily than with aldehydes. Examples of a few compounds of interest are given below.

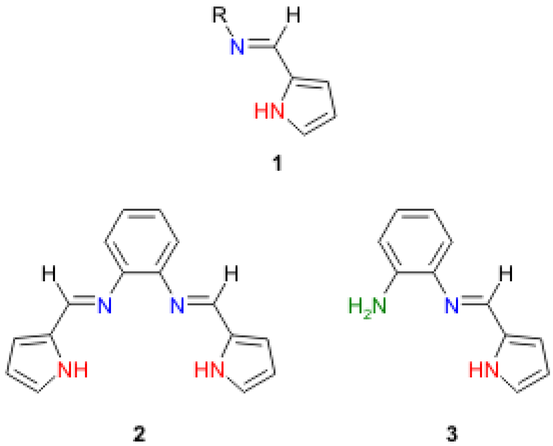


Figure 2.1 Some of Schiff base ligands

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 (Figure 2.2) (Cozzi, 2004).

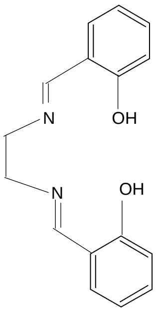


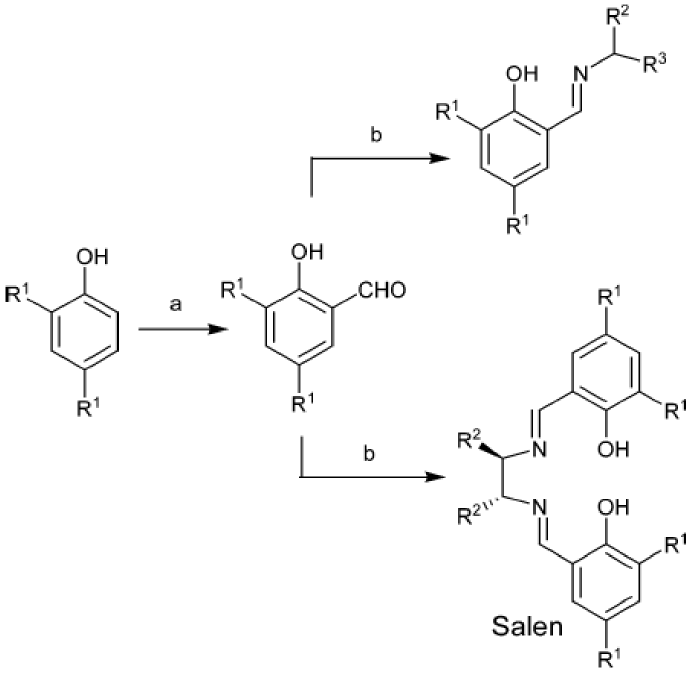
Figure 2.2 Salen

The salen ligand has been known for some time and is well established in the area of metal coordination chemistry (Hobdy & Smith, 1972; Calligaris & Randaccio, 1987). Made via a [2 + 1] condensation reaction from salicylaldehyde and a diamine, this ligand forms a tetradentate cleft with two nitrogen and two oxygen atoms (N_2O_2, also H_2L). Functionalization of either precursor is generally straightforward, and for this reason there are a number of salen analogues reported in the literature. (Sesler, Melfi, & Patnos, 2005).

2.2 Preparation of Schiff Bases

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. $MgSO_4$ 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 (Et_2O, CH_2Cl_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’’ (Figure 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 (Scheme 2.1 a) (Cozzi, 2004).



Scheme 2.1 Preparation of Schiff Bases

2.3 Importance of Schiff Base and Schiff Base Complexes

The preparation of new transition metal complexes is perhaps the most important step in the development of coordination chemistry that 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 (Bermejo, Sousa, Garcia-Deibe, Maneiro, Sanmartin, & Fondo, 1999; Temel & Şekerci, 2001).

The metal complexes with Schiff bases as ligands have been playing an important part in the development of coordination chemistry as a whole. However, it was not until the 1950s that concrete and rapid advances in this field became evident. In the early days the main efforts were directed toward synthesis and characterization of rather fundamental complexes, which do not looking striking nowadays but were strongly needed in those days. (Herzfeld & Nagy, 1999; Temel, Çakır, Otludil, & Uğraş, 2001).

Monodentate Schiff bases are not known to form stable complexes probably due to the insufficient basic strength of the imino nitrogen of the C=N group. Multidentate Schiff bases with at least one donor atom, suitably near to the nitrogen atom, may stabilize the metal-nitrogen bond through formation of chelate rings. In spite of the facile ligating capability, these donors have not been used to an appreciable extent in the CO displacement reactions of group VI metal carbonyls. Since the first publication, which appeared in 1972, the reactions of only a few ligands, viz. RCH=NR have been investigated mainly with molybdenum hexacarbonyl and for a few exceptional cases with chromium hexacarbonyl (Srivastava, Shrimal, & Tiwari, 1992).

Schiff bases are suitable ligands for the preparation of libraries due to the easy reaction conditions and the variety of amines and aldehydes used as precursors. They possess many interesting characteristics. Schiff bases 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 (Cozzi, 2004).

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties; their ability to reversibly bind oxygen (Jones, Summerville, & Basolo, 1979), catalytic activity in hydrogenation of olefins (Henrici-Olive & Olive, 1983) and transfer of an amino group (Dugas & Penney, 1981), photochromic properties (Margerum & Miller, 1971) and complexing ability towards toxic metals (Sawodny & Riederer, 1977).

The interest of studying Schiff bases containing ONS donors arose from their significant antifungal, antibacterial, and anticancer activities (Saxena, Koacher, & Tandon, 1981). 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 (Abd El-Gaber, Hassaan, El-Shabasy, & El-Roudi, 1991; Dixit & Mehta, 1986; Kushekar & Khanolkar, 1983). The salicyaldehyde-thio-Schiff bases have recently acquired a considerable importance due to their chemical and especially their promising biological properties (Padhye & Kauffman, 1985; West, Padhye, & Sonawane, 1991). Antibacterial (Dobek, Klayman, Dickson, Scovill, & Oster, 1983), antineoplastic (Klayman & et al., 1983), antimalarial (Klayman, Scovill, Bartosevich, & Mason, 1979) and antiviral (Shipman, Smith, Darch, & Klayman, 1986) behaviour has been found. Relationships are evident between chelate formation in the complexes and the in vivo activity (Miertus & Filipovic, 1982; Scovill, Klayman, Lambrose, Childs, & Notsch, 1984). In the area of bioinorganic chemistry interest in Schiff base complexes has centred on the role such complexes may have in providing synthetic models for the metal containing sites in metalloproteins and metalloenzymes (Soliman & Linert, 2007).

Schiff bases play an important role as chelating ligands in main group and transition metal coordination chemistry. It is noteworthy that chiral Schiff base complexes of transition metals are very effective catalysts for asymmetric cyclopropanation and epoxidation of alkenes, and they are used in allylic alkylation reactions and in the activation of aromatic carbonhydrogen bonds (orthometallation) via intramolecular η^2-bonding of arenes (Brisdon, Brown, & Wills, 1986; Lopez, Liang, & Bu, 1998; Shiu, Chou, Wang, & Wei, 1990).

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 (Kaim & Kohlmann, 1987; Lal De, Samanta, & Banerjee, 2001). Their low energy metal-to-ligand charge transfer (MLCT) transitions make these molecules attractive for luminescence and electron transfer reactions (Trost & Lautens, 1983). Polydentate Schiff bases containing nitrogen and oxygen donor atoms are useful for the synthesis of transition metal complexes which play important roles in biological systems (Frausto da Silva & Williams, 1991; Kaim & Schwederski, 1996).

Recently, the introduction of lateral polar hydroxyl groups was reported to enhance the molecular polarizability of liquid crystalline compounds as well as stabilizing them. A typical example is the effect of lateral hydroxyl groups on the mesomorphism of azobenzene derivatives. Schiff bases have found extensive applications in analytical chemistry, used in the determination of some transition metals (Chang-Hsien, 1993).

The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural lability and are sensitive to molecular environment. The environment around the metal center ‘as co-ordination geometry, number of coordinated ligands and their donor group’ is the key factor for metalloprotein to carry out specific physiological function (Chakraborty & Patel, 1996; Klement & et al., 1999). Further, Schiff bases offer opportunities for inducing substrate chirality, tuning metal centered electronic factor, enhancing solubility and stability of either homogeneous or heterogeneous catalyst (Clercq & Verpoort, 2002; Opstal & Verpoort, 2002). In the use of transition metal carbonyls as reactive species in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation, carbon monoxide serves simply as ligand providing the complex with the necessary reactivity and stability to allow reaction (Collman & Hegedus, 1980).

Transition metal complexes of heterocyclic compounds containing nitrogen, such as pyridine, di- and polypyridine, azines and their derivatives, are also of great interest because of their facile electrochemical processes (Abdel-Shafi, Khalil, Abdella, & Ramadan, 2002; Molnar, Neville, Jensen, & Brewer, 1993). Their ability to absorb visible light and act as electron reservoirs also make them promising for applications as photosensitizers (Balzani, Juris, Venturi, Campagna, & Serroni, 1996; Flamigni & et al., 1999). For example, ruthenium and osmium complexes of nitrogen donor ligands, especially azine derivatives, absorb or emit visible light and reversibly exchange electrons. These compounds could thus find application as components in molecular electronics and as photochemical molecular devices for solar energy conversion and information storage (Borje, Kothe, & Juris, 2001). Metal carbonyl derivatives of nitrogen donor ligands are important in the preparation metal carbonyl complexes (van Slageren & Stufkens, 2001).

2.4 Objectives of This Work

Polydentate Schiff bases containing oxygen, nitrogen and sulphur donor atoms are useful for the synthesis of transition metal complexes which play an important role in biological systems. Such classes of ligands are also found to provide catalytic characteristics.

The role of transition-metal carbonyls, particularly those of group 6 metals, in homogeneous photocatalytic and catalytic processes is a matter of considerable interest. UV irradiation of metal carbonyls is the method of choice for the generation of catalitically active species or for the synthesis of substituted derivatives in the presence of potential ligands. UV irradiation provides a simple and convenient method for the generation of thermally active coordinately unsaturated catalysts for alkenes or alkynes transformation. By using tungsten and molybdenum carbonyl compounds as catalysts, alkynes and alkenes can be polymerized, isomerized or metathesized. Therefore we will direct efforts toward the synthesis of group 6 metal carbonyl complexes containing nitrogen and sulphur donor Schiff base ligands.

The aim of this study is synthesis of different group 6 metal carbonyl complexes by use of different Schiff base ligands. For this purpose, photochemical reactions will be used. Because, since photochemical reactions are frequently very selective they are used to prepare derivatives when thermal reactions either do not proceed or produce unwanted side-products. Photochemical reactions are particularly useful when the incoming ligand is weakly bound by the metal such as the nitrogen ligand derivatives.

After the synthetic pathway, synthesized complexes will be characterized by spectroscopic and spectrometric methods. Original ligands will also be characterized. For characterizations, spectroscopic techniques like ^{1}H NMR, FTIR and Mass will be used. Furthermore, elemental analyses and magnetic studies will be performed.

Synthesized complexes will try to be crystallized and in the light of the X-Ray spectroscopic techniques their detailed structures are most likely to be investigated.

CHAPTER THREE

MATERIAL AND METHOD

3.1 Instruments

Elemental Analysis: Leco 932 CHNS elemental analyser (TÜBİTAK)

Magnetic Susceptibility: Sherwood Scientific Magnetic Susceptibility Balance (Ege University, Science Faculty, Chemistry Department)

Infrared Spectroscopy: Varian 1000 FT spectrophotometer (Dokuz Eylül University, Faculty of Science and Arts, Chemistry Department)

^{1}H NMR: 500 MHz High Performance Digital FT-NMR instrument (Ege University, Science Faculty, Chemistry Department)

LC-Mass Spectroscopy: Agilent 1100 MSD device (TÜBİTAK)

UV-Lamp: 125 W Medium Pressure Mercury Lamp through quartz-walled immersion well reactor (Dokuz Eylül University, Faculty of Science and Arts, Chemistry Department)

3.2 Chemicals

Solvents: Tetrahydrofuran, dichloromethane, petroleum ether (Merck)

Metal Carbonyls: $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ (Aldrich)

Vacuum Grease: High vacuum grease (Merck)

3.2.1 Purification of Solvents

The solvents used were dried and degassed using standard techniques and stored under nitrogen until used. For this purpose, all solvents were refluxed over the special drying agents under the nitrogen atmosphere (Perrin, Armerago, & Perrin, 1980).

3.3 Preparation of Ligands

N,N′-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)butane (H_2L^1)

A solution of 2-aminothiophenol (2.5 g, 20 mmol) in 50 mL absolute ethanol is added dropwise over 2 h to a stirred solution of 1,4-bis(2-carboxyaldehydephenoxy)butane (2.98 g, 10 mmol) dissolved in 50 mL warm absolute ethanol. A solid separated on cooling and is kept in a refrigerator for better crystallization. It is then filtered, washed with ether and recrystallized from absolute ethanol–DMF (Temel, Alp, İlhan, & Ziyadanoğulları, 2008) (Figure 3.1).

The aldehyde used in the synthesis is prepared from salicylaldehyde, 1,4-dibromobutane and K_2CO_3 as reported in the literature of (Adam et al., 1983; Lindy & Armstrong, 1975).

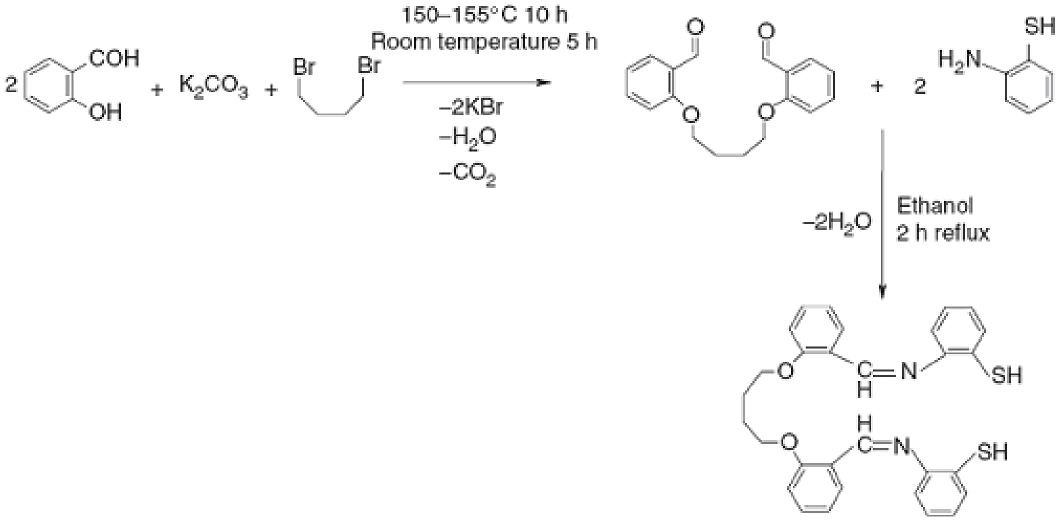


Figure 3.1 Synthesis of *N,N′*-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)butane, (H_2L^1)

N,N′-bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane (H_2L^2)

A solution of 2-aminothiophenol (2.5 g, 20 mmol) in 50 mL absolute ethanol is added dropwise over 2 h to a stirred solution of 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane (3.14 g, 10 mmol) dissolved in 50 mL warm absolute ethanol. A solid mass separated out on cooling, which is kept in a refrigerator for better crystallization. It is then filtered off and recrystallized from a mixture of absolute ethanol-DMF (Temel, Alp, İlhan, Ziyadanoğulları, & Yılmaz, 2007) (Figure 3.2).

1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane is prepared by the literature method (Adam et al., 1983; Lindy & Armstrong, 1975).

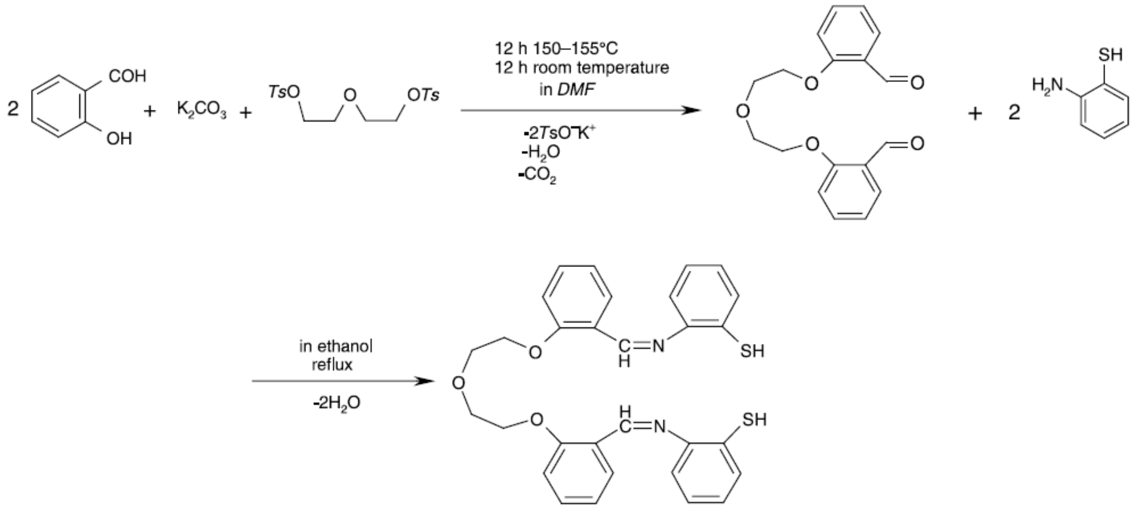


Figure 3.2 Synthesis of *N,N′*-bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane, (H_2L^2)

N,N′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane (H_2L^3)

N,N′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane **(H_2L^3)** is prepared by amounts of 1,2-bis(aminophenoxy)ethane (2.44 g, 10 mmol) and 2-hydroxynaphthalin-1-carbaldehyde (3.44 g, 20 mmol) in 100 mL absolute ethanol under reflux for 2 h. The crystals of the Schiff base that separated on cooling are recrystallized from DMF (Temel, İlhan, Şekerci, & Ziyadanoğulları, 2002).

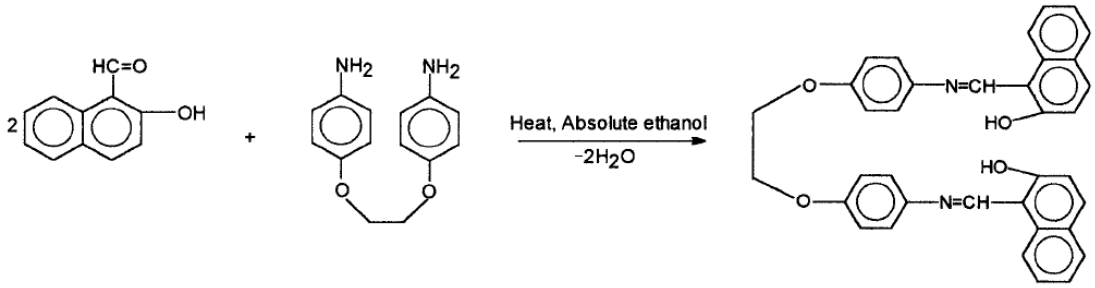


Figure 3.3 Synthesis of *N,N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane, (H_2L^3)

N,N'-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy)butane (H_2L^4)

N,N'-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy)butane **(H_2L^4)** is prepared using the same method thats of *N,N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane. But only 1,4-bis(aminophenoxy)butane is used instead of 1,2-bis(aminophenoxy)ethane (Figure 3.4).

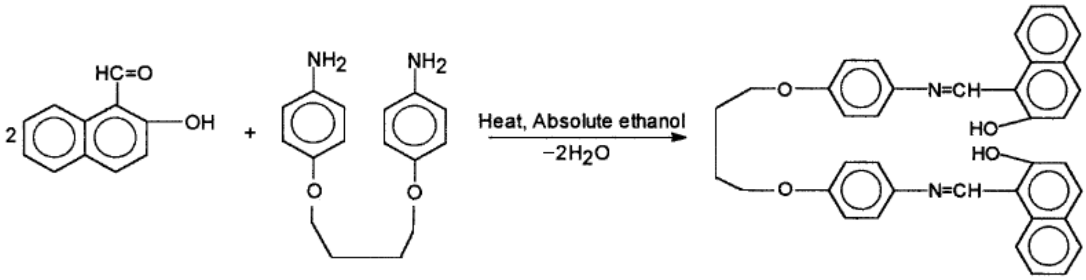


Figure 3.4 Synthesis of *N,N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy)butane, (H_2L^4)

3.4 Preparation of Complexes

All complexes given in this thesis study were synthesized under an oxygen free nitrogen atmosphere using Schlenk techniques. The nitrogen-vacuum line used in the syntheses is given in Figure 3.9. UV irradiations were performed with a medium-pressure 125 W mercury lamp through a quartz-walled immersion well reactor, which was cooled by circulating water (Figure 3.10).

3.4.1 Preparation of [$M_2(CO)_6(\mu$-CO)(μ-L^1)], [M= Cr; 1, Mo; 2, W; 3]

The complexes, [$M_2(CO)_6$(µ-CO)(µ-L^1)], [M= Cr; **1**, Mo; **2**, W; **3**] were prepared by the photochemical reactions of $M(CO)_5$THF (M= Cr, Mo, W) with *N*,*N'*-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)butane **(H_2L^1)** and obtained in 63-70% yield by similar methods; the following is typical (Figure 3.5).

A solution of $Cr(CO)_6$ (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 h at room temperature. A solution of **H_2L^1** (0.15 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the $Cr(CO)_5$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_2Cl_2 (10 mL). Addition of petroleum ether (50 mL) resulted in precipitation of a dark yellow solid which was washed with petroleum ether and dried under vacuum, and shown to be [$Cr_2(CO)_6$(µ-CO)(µ-L^1)], **1,** (66% yield). Traces of unreacted $Cr(CO)_6$ was sublimed out in vacuum on a cold finger at –20˚C.

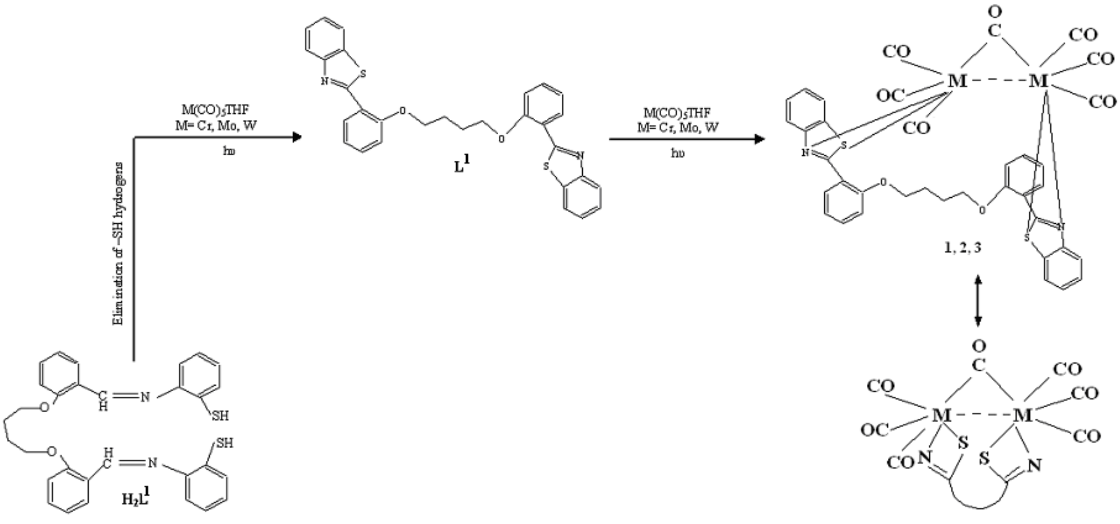


Figure 3.5 Photogeneration of [$M_2(CO)_6$(µ-CO)(µ-L^1)], [M= Cr; 1, Mo; 2, W; 3]

3.4.2 Preparation of [$M_2(CO)_6(\mu$-$CO)(\mu$-$L^2)$], [M= Cr; 4, Mo; 5, W; 6]

The complexes, [$M_2(CO)_6(\mu$-$CO)(\mu$-$L^2)$], [M= Cr; **4**, Mo; **5**, W; **6**] were prepared by the photochemical reactions of $M(CO)_5THF$ (M= Cr, Mo, W) with *N*,*N'*-bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane **(H_2L^2)** and obtained in 64-72% yield by similar methods; the following is typical (Figure 3.6).

A solution of $Cr(CO)_6$ (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 h at room temperature. A solution of **H_2L^2** (0.16 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the $Cr(CO)_5THF$ 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_2Cl_2 (10mL). Addition of petroleum ether (50 mL) resulted in precipitation of a dark yellow solid which was washed with petroleum ether and dried under vacuum, and shown to be [$Cr_2(CO)_6(\mu$-$CO)(\mu$-$L^2)$], **4,** (72 % yield). Traces of unreacted $Cr(CO)_6$ was sublimed out in vacuum on a cold finger at –20˚C.

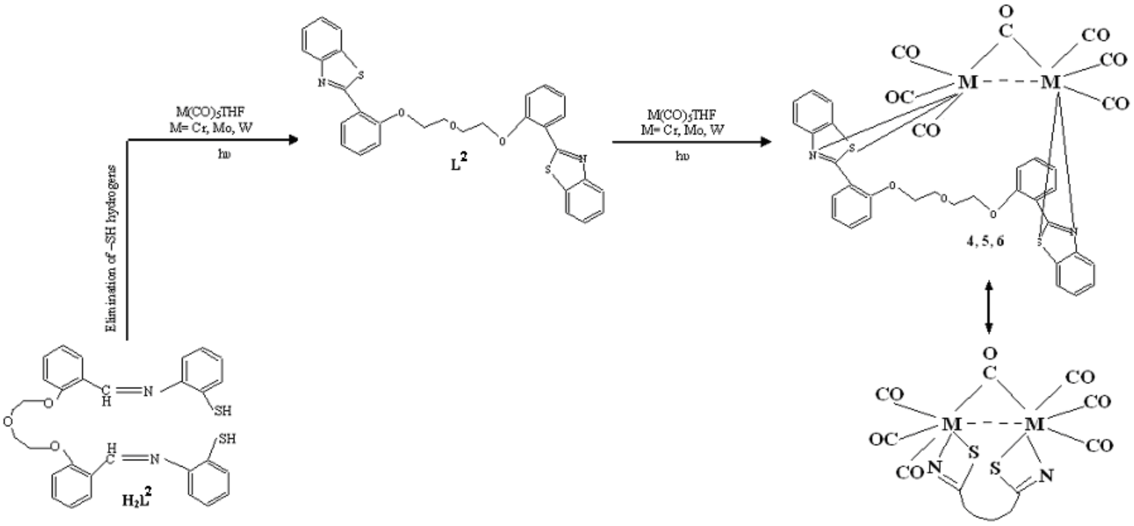


Figure 3.6 Photogeneration of [$M_2(CO)_6(\mu$-$CO)(\mu$-$L^2)$], [M= Cr; 4, Mo; 5, W; 6]

3.4.3 Preparation of [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^3)$_2$], 7; [(μ-CO)M$_2$(CO)$_2$(η^4- H$_2$L^3)$_2$], [M= Mo; 8, W; 9]

The complexes, [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^3)$_2$], **7**; [(μ-CO)M$_2$(CO)$_2$(η^4-H$_2$L^3)$_2$], [M= Mo; **8**, W; **9**] were prepared by the photochemical reactions of M(CO)$_5$THF (M= Cr, Mo, W) with *N*,*N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane **(H$_2$L^3)** and obtained in 61-67% yield by similar methods; the following is typical (Figure 3.7).

A solution of Cr(CO)$_6$ (0.11 g, 0.50 mmol) in 60 mL of THF was irradiated to obtain Cr(CO)$_5$THF with UV light in a quartz vessel under a stream of nitrogen for 1 h at room temperature. A solution of **H$_2$L^3** (0.16 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the Cr(CO)$_5$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 brown. The solvent was removed under vacuum afford a brown solid which was shown to be [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^3)$_2$], **7** (61% yield). Traces of unreacted Cr(CO)$_6$ was sublimed out in vacuum on a cold finger at –20˚C.

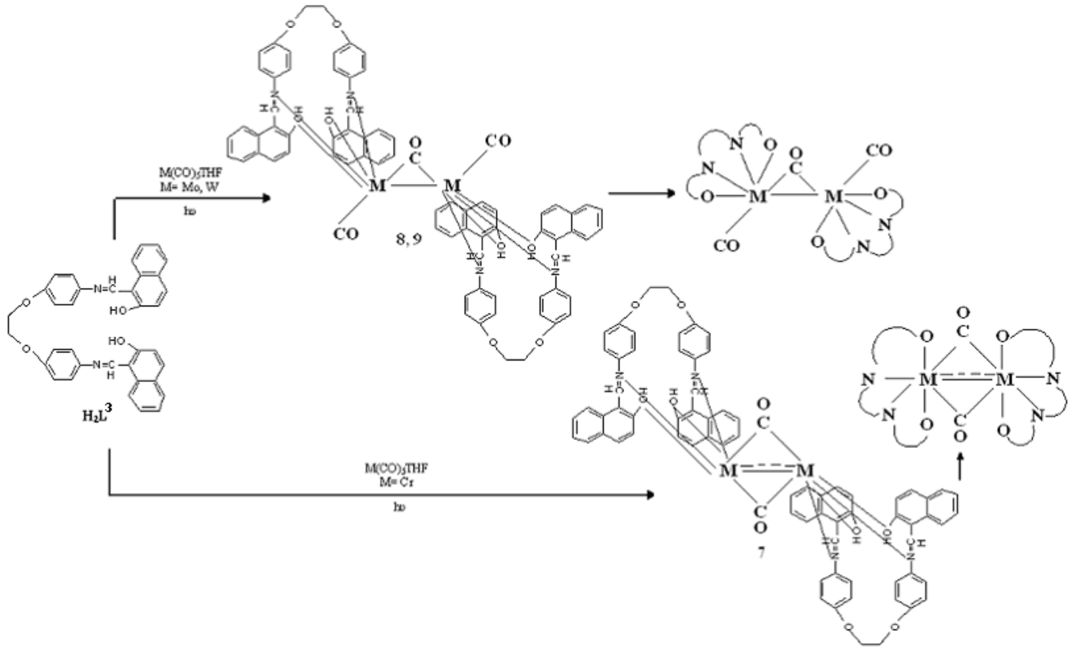


Figure 3.7 Photogeneration of [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^3)$_2$], 7; [(μ-CO)M$_2$(CO)$_2$(η^4- H$_2$L^3)$_2$], [M= Mo; 8, W; 9]

3.4.4 Preparation of [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^4)$_2$], 10; [(μ-CO)M$_2$(CO)$_2$(η^4- H$_2$L^4)$_2$], [M= Mo; 11, W; 12]

The complexes, [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^4)$_2$], **10**; [(μ-CO)M$_2$(CO)$_2$(η^4- H$_2$L^4)$_2$], [M= Mo; **11**, W; **12**] were prepared by the photochemical reactions of M(CO)$_5$THF (M= Cr, Mo, W) with *N,N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy)butane **(H$_2$L^4)** and obtained in 64-70% yield by similar methods; the following is typical (Figure 3.8).

A solution of Cr(CO)$_6$ (0.11 g, 0.50 mmol) in 60 mL of THF was irradiated to obtain Cr(CO)$_5$THF with UV light in a quartz vessel under a stream of nitrogen for 1 h at room temperature. A solution of **H$_2$L^4** (0.17 g, 0.30 mmol) in 20 mL of THF was added to the resulting solution of the Cr(CO)$_5$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 brown. The solvent was removed under vacuum afford a brown solid which was shown to be [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L$_4$)$_2$], **10** (64% yield). Traces of unreacted Cr(CO)$_6$ was sublimed out in vacuum on a cold finger at –20˚C.

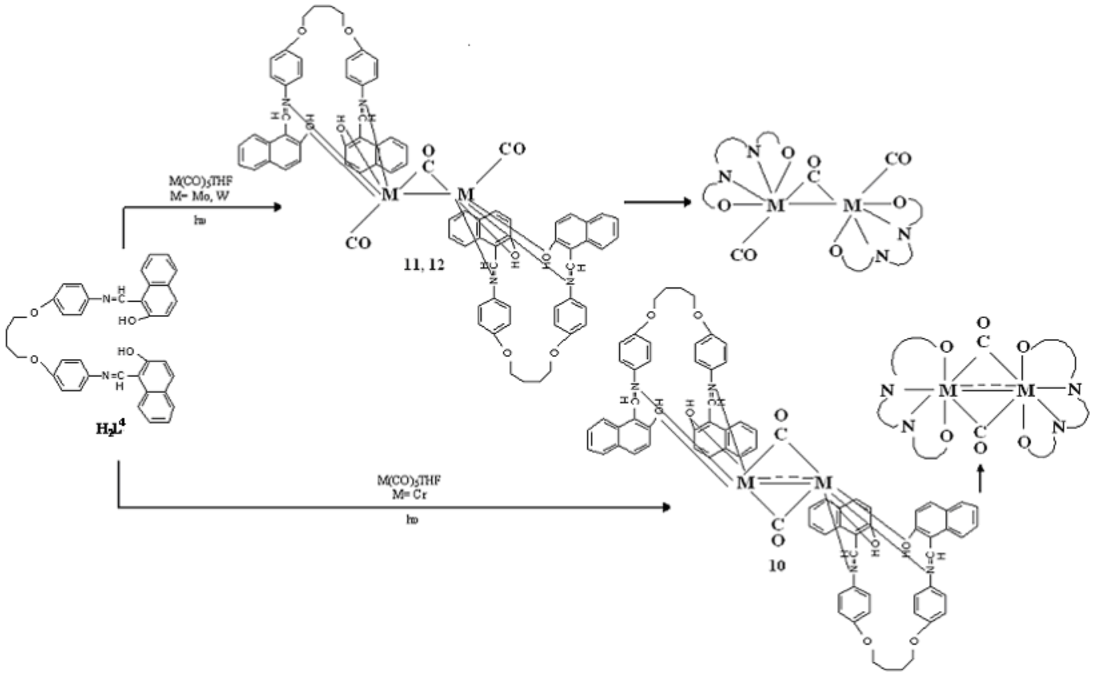


Figure 3.8 Photogeneration of [(μ-CO)$_2$Cr$_2$(η^4-H$_2$L^4)$_2$], 10; [(μ-CO)M$_2$(CO)$_2$(η^4- H$_2$L^4)$_2$], [M= Mo; 11, W; 12]

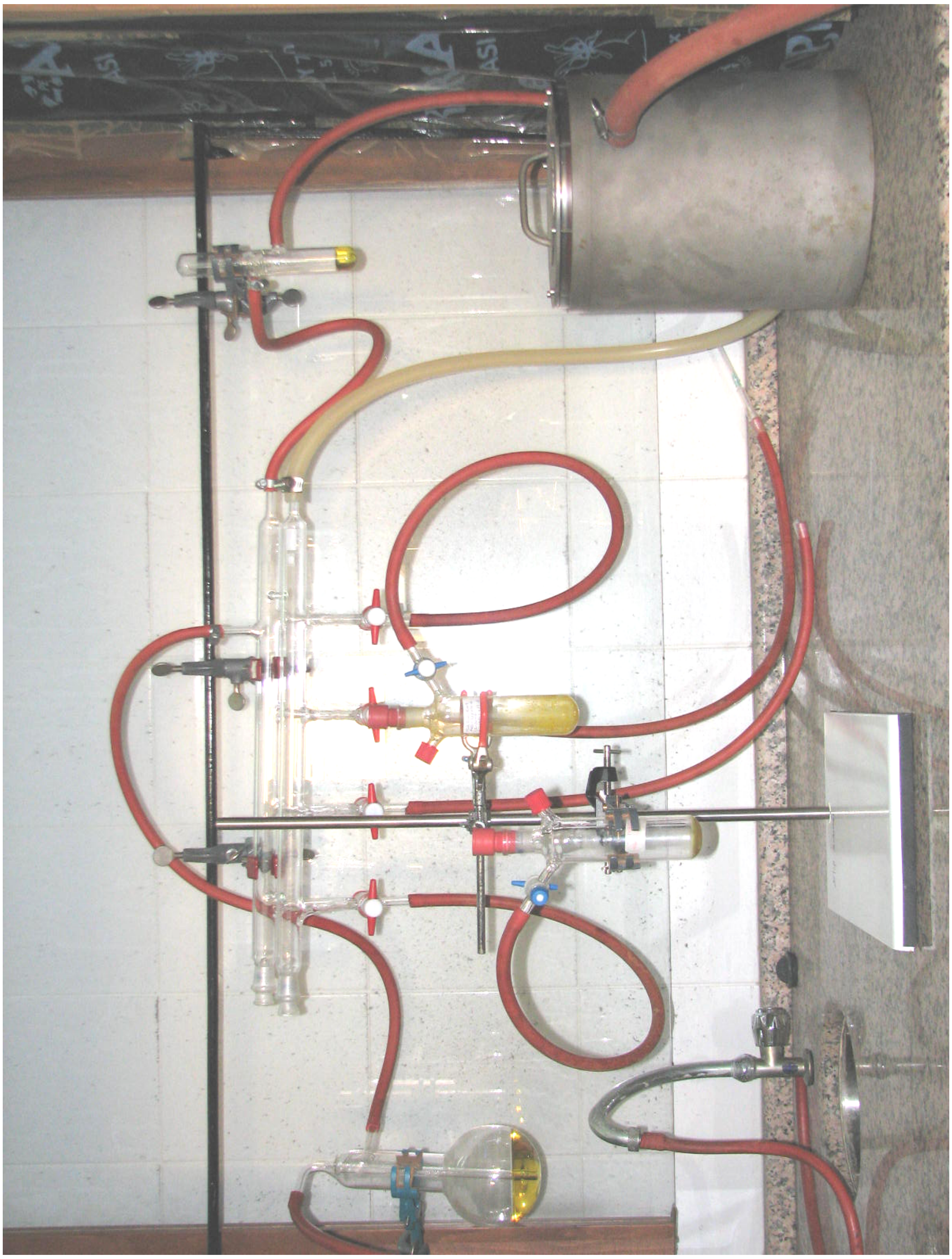


Figure 3.9 The nitrogen vacuum line

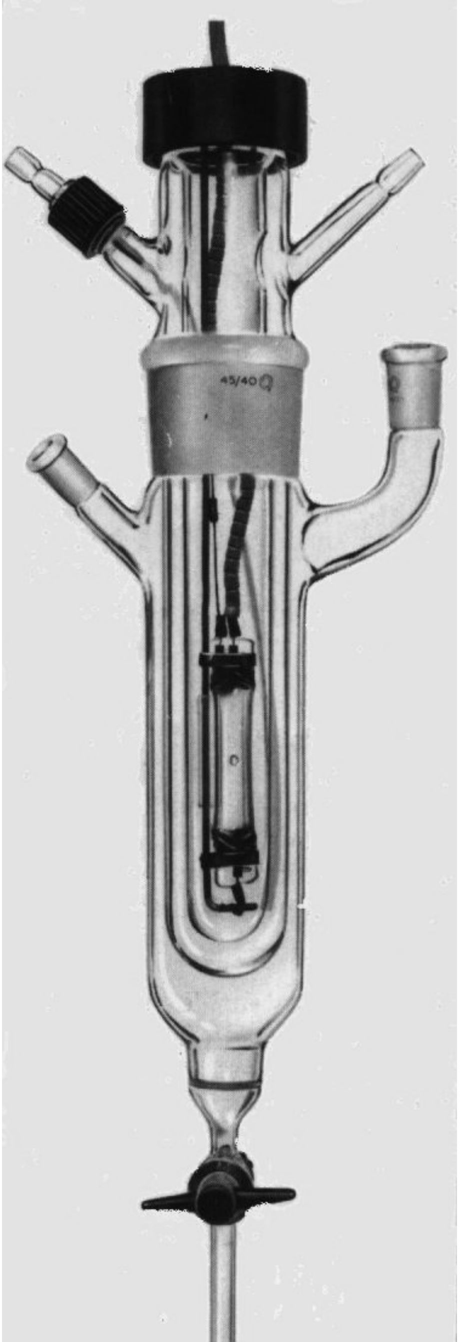


Figure 3.10 125 W lamp, quartz-walled immersion well reactor

CHAPTER FOUR

RESULTS

4.1 Analytical Data of Schiff Bases

Some analytical results of the novel Schiff bases are summarized in Table 4.1. **H_2L^1** and **H_2L^2** are light yellow solids, stable at room temperature. They are insoluble in all common organic solvents, viz., acetone, alcohol, benzene, etc. and soluble in polar organic solvents (Temel, Alp, İlhan, & Ziyadanoğulları, 2008; Temel, Alp, İlhan, Ziyadanoğulları, & Yılmaz, 2007). **H_2L^3** and **H_2L^4** are yellow solids and also stable at room temperature (Temel, İlhan, Şekerci, & Ziyadanoğulları, 2002).

Table 4.1 Elemental analysis results of Schiff bases

Schiff Base	F.W (g/mole)	Elemental analyses %, Calculated (Found)			
		C	H	N	S
H_2L^1	512	70.28 (70.53)	5.50 (5.44)	5.46 (5.42)	12.51 (12.56)
H_2L^2	528	68.46 (68.09)	5.28(5.33)	5.32 (5.29)	12.19 (12.12)
H_2L^3	552	78.26 (78.08)	5.07 (5.16)	5.07 (5.13)	-
H_2L^4	580	78.62 (78.40)	5.51 (5.65)	4.82 (4.90)	-

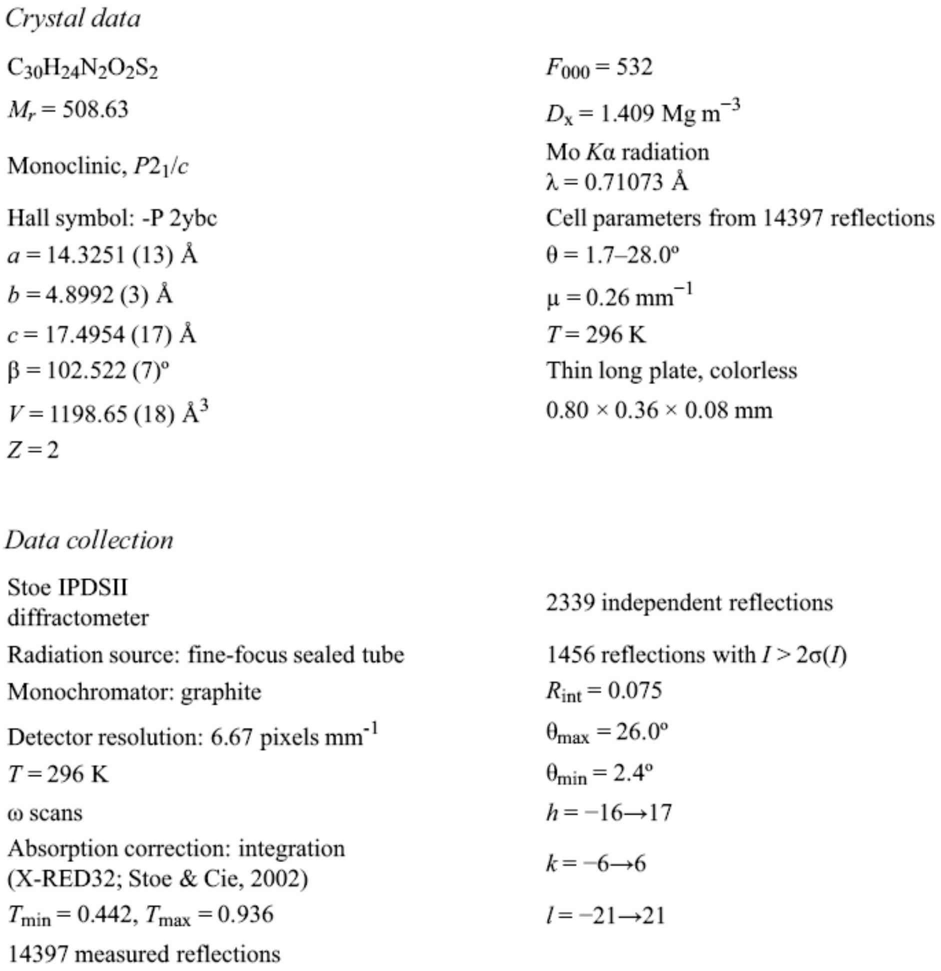
4.2 Benzothiazole Structures of H_2L^1 and H_2L^2

We have reported that *N,N'*-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)butane **(H_2L^1)** is converted to 1,4-bis[2-(1,3-benzothiazol-2-yl)phenoxy]butane **(L^1)** as a benzothiazole derivative after UV irradiation (Büyükgüngör, Özek, Karahan, & Subasi, 2008).

According to this reference; L^1 displays an inversion centre with a half molecule in the asymmetric unit. The benzene ring and its fused thiazole ring are nearly coplanar, with the maximum deviation from the least-squares plane through

S1/N1/C1-C7 occuring at S1 [0.033 (9) Å]. However, the molecule itself is nonplanar; the dihedral angle between the coplanar benzothiazole ring system and benzene ring is 11.06 (7)°. The N1-C7 [1.299 (2) Å] bond indicates double-bond character, wheares the S-C bond lengths are indicative of significant single-bond character. The S1-C1 [1.7231 (19) Å] bond is shorter than S1-C7 [1.7552 (18) Å], due to the fact that C7 is sp^2 hybridized, whereas C1 is part of the aromatic ring. Crystal data and structure refinement for 1,4-bis[2-(1,3-benzothiazol-2-yl)phenoxy]butane **(L^1)** is in Table 4.2.

Table 4.2 Crystal data and structure refinement for L^1

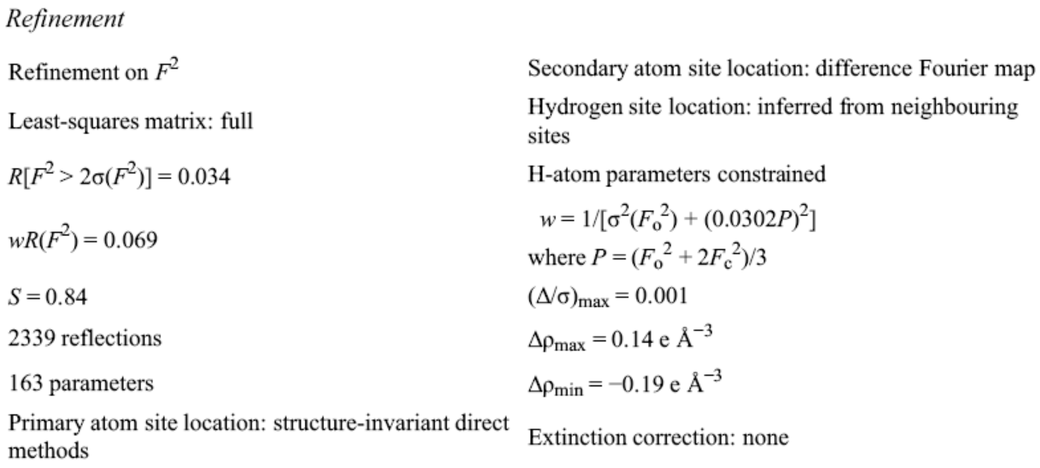


Crystal data

$C_{30}H_{24}N_2O_2S_2$	F_{000} = 532
M_r = 508.63	D_x = 1.409 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 14397 reflections
a = 14.3251 (13) Å	θ = 1.7–28.0°
b = 4.8992 (3) Å	μ = 0.26 mm^{-1}
c = 17.4954 (17) Å	T = 296 K
β = 102.522 (7)°	Thin long plate, colorless
V = 1198.65 (18) Å^3	0.80 × 0.36 × 0.08 mm
Z = 2	

Data collection

Stoe IPDSII diffractometer	2339 independent reflections
Radiation source: fine-focus sealed tube	1456 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.075
Detector resolution: 6.67 pixels mm^{-1}	θ_{max} = 26.0°
T = 296 K	θ_{min} = 2.4°
ω scans	$h = -16 \rightarrow 17$
Absorption correction: integration (X-RED32; Stoe & Cie, 2002)	$k = -6 \rightarrow 6$
T_{min} = 0.442, T_{max} = 0.936	$l = -21 \rightarrow 21$
14397 measured reflections	



Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.069$

$S = 0.84$

2339 reflections

163 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.14$ e Å^{-3}

$\Delta\rho_{min} = -0.19$ e Å^{-3}

Extinction correction: none

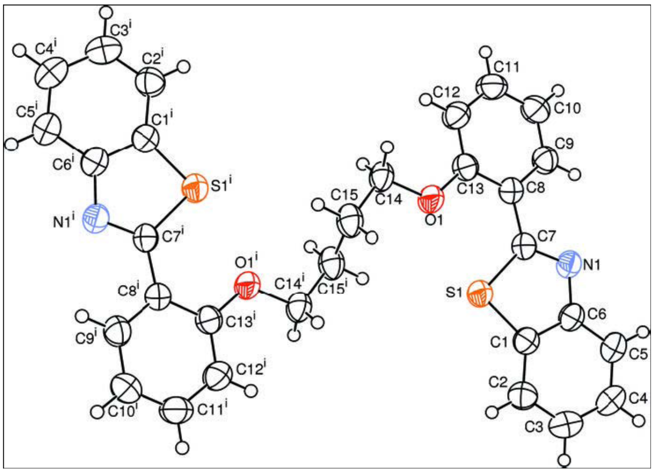


Figure 4.1 A view of L^1 with the atom-numbering scheme

Although we couldn’t obtained the single crystal of benzothiazole $\mathbf{L^2}$, spectroscopic data of the synthesized complexes confirm that $\mathbf{H_2L^2}$ converts to benzothiazole $\mathbf{L^2}$ under the photolysis and coordinates to metal as benzothiazole derivative as observed for $\mathbf{H_2L^1}$.

4.3 The Molecular Structure of VIB Metal Carbonyl Complexes of Schiff Bases

The photogeneration reaction of $M(CO)_5$ from $M(CO)_6$ has been extensively studied. These 16-electron $M(CO)_5$ fragments react avidly with any available donor atom (Cotton & Wilkinson, 1988). The photochemical reactions of $M(CO)_5THF$ (M=

Cr, Mo, W) with tetradentate Schiff-bases, proceed in this expected manner to yield the hitherto unknown series of complexes **1-12**.

4.3.1 The Structures of [$M_2(CO)_6$(μ-CO)(μ-L^1)], [M= Cr; 1, Mo; 2, W; 3] and [$M_2(CO)_6$(μ-CO)(μ-L^2)], [M= Cr; 4, Mo; 5, W; 6]

Six new complexes, [$M_2(CO)_6$(μ-CO)(μ-L^1)], [M= Cr; **1**, Mo; **2**, W; **3**] and [$M_2(CO)_6$(μ-CO)(μ-L^2)], [M= Cr; **4**, Mo; **5**, W; **6**] have been synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with thio Schiff base ligands, *N,N'*-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)butane **(H_2L^1)** and *N,N'*-bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane **(H_2L^2)**. The spectroscopic studies show that **H_2L^1** and **H_2L^2** ligands are converted to benzothiazole derivatives **L^1** and **L^2**, after UV irradiation and coordinated to the central metal as bridging ligands *via* the central azomethine nitrogen and sulphur atoms in **1-6**.

4.3.1.1 Analytical Data

The analytical data for novel complexes **1-6** are summarized in Table 4.3. The stochiometry of the ligands and their complexes have been confirmed by their elemental analyses. The spectroscopic data confirm that **H_2L^1** and **H_2L^2** coordinate to metal as benzothizole derivatives (Karahan, Köse, Subasi, Alp, & Temel, 2008).

Table 4.3 Elemental analysis results and physical properties for the complexes (1-6)

Complex	Yield (%)	Colour	Found (Calcd.) (%) C	H	N	S
1	66	dark yellow	54.75 (54.95)	2.86 (2.97)	3.38 (3.46)	7.76 (7.92)
2	63	dark yellow	49.46 (49.55)	2.51 (2.67)	2.97 (3.12)	7.00 (7.14)
3	70	orange-yellow	41.23 (41.41)	2.17 (2.23)	2.41 (2.61)	5.79 (5.97)
4	72	dark yellow	53.73 (53.88)	2.71 (2.91)	3.26(3.39)	7.65 (7.76)
5	64	orange-yellow	48.56 (48.68)	2.46 (2.63)	2.88 (3.07)	6.92 (7.01)
6	71	orange-yellow	40.63 (40.80)	2.08 (2.20)	2.33 (2.57)	5.70 (5.88)

4.3.1.2 Infrared Spectra

Characteristic infrared data are listed in Table 4.4 (Karahan, Köse, Subasi, Alp, & Temel, 2008). The infrared spectra of the complexes have been compared with those of ligands. The IR spectrum of complex **1** (Figure 4.4) exhibits three prominent bands at 1943, 1906 and 1717 cm^{-1} in the CO stretching vibrational region. First two bands belong to terminal and the third belongs to bridging CO group. This is similar to the spectrum of the $Fe_2(CO)_9$ which has two terminal (2030 and 2034 cm^{-1}) and one bridging (1828 cm^{-1}) CO stretching bands (Sheline & Pitzer, 1950). The CO modes in the complexes **1-6** are at lower wave numbers as compared to $Cr(CO)_6$ and $Cr(CO)_5THF$ (Table 4.4). IR spectra of the other five complexes exhibit essentially the same ν(CO) absorption pattern as observed for **1**. The IR spectra of $\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$ (Figure 4.3 and Figure 4.7) show characteristic bands due to the functional groups C=N, N-H and C–S. The IR spectra of all complexes display the ligand characteristic bands with appropriate shifts due to complex formation.

Table 4.4 Characteristic infrared bands (cm^{-1}) of H_2L^1, H_2L^2 and the complexes

Complex	$\nu_{(CO)}$	$\nu_{(C=N)}$	$\nu_{(N-H)}$ [b]	$\nu_{(C-S)}$
$Cr(CO)_6$	1999s	-	-	-
$Mo(CO)_6$	2001s	-	-	-
$W(CO)_6$	1996s	-	-	-
$Cr(CO)_5THF$	2059s, 1933m, 1877m	-	-	-
$Mo(CO)_5THF$	2080s, 1982m, 1959m	-	-	-
$W(CO)_5THF$	2069s, 1972m, 1941m	-	-	-
H_2L^1 [a]	-	1673m, 1592s	3423m	750s, 724w, 687w
H_2L^2 [a]	-	1669s, 1591s	3401m	753s, 726w, 694m
1	1943w, 1906w, 1717w	1653w, 1595s	-	753s, 726m, 695m
2	1938w, 1904w, 1720m	1655w, 1595s	-	749s, 726w, 694m
3	1968w, 1923m, 1732m	1648m, 1592m	-	751s, 724w, 690w
4	1975w, 1933w, 1717w	1655w, 1595s	-	754m, 726w, 694w
5	1934m, 1859w, 1720m	1646m, 1595m	-	752s, 724w, 694w
6	1960w, 1938w,1724w	1653w, 1595m	-	754s, 729w, 693m

[a] Taken from (Temel, Alp, İlhan, & Ziyadanoğulları, 2008; Temel, Alp, İlhan, Ziyadanoğulları, & Yılmaz, 2007)

[b] Intramolecular hydrogen bonded N---HS

The bands at 1673, 1592 cm^{-1} and 1669, 1591 cm^{-1} in the IR spectrum of free **H_2L^1** and **H_2L^2** respectively belong to the C=N stretching vibration. First band shifts towards lower frequency considerably in compounds **1-6** showing that the **H_2L^1** and **H_2L^2** ligands 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. The bands at 3423 cm^{-1} and 3401 cm^{-1} in the IR spectrum of the free Schiff base ligands are assigned to the stretching of the intramolecular hydrogen bonded N-HS (Temel, Alp, İlhan, & Ziyadanoğulları, 2008; Temel, Alp, İlhan, Ziyadanoğulları, & Yılmaz, 2007). This band is absent in the IR spectra of the complexes **1-6**. The elimination of hydrogen from the SH group, which is also confirmed by the disappearance of the SH signal in the ^{1}H NMR spectrum (Table 4.5), indicate that **H_2L^1** and **H_2L^2** coordinate to the metal as benzothiazole derivatives **L^1** and **L^2**.

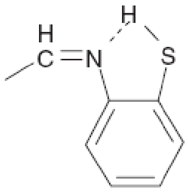


Figure 4.2 The intramolecular hydrogen bonded N---HS

C-S stretching vibrations at *ca.* 754, 726 and 694 cm^{-1} in the IR spectra of the complexes **1-6** show shifts and intensity changes upon complex formation.

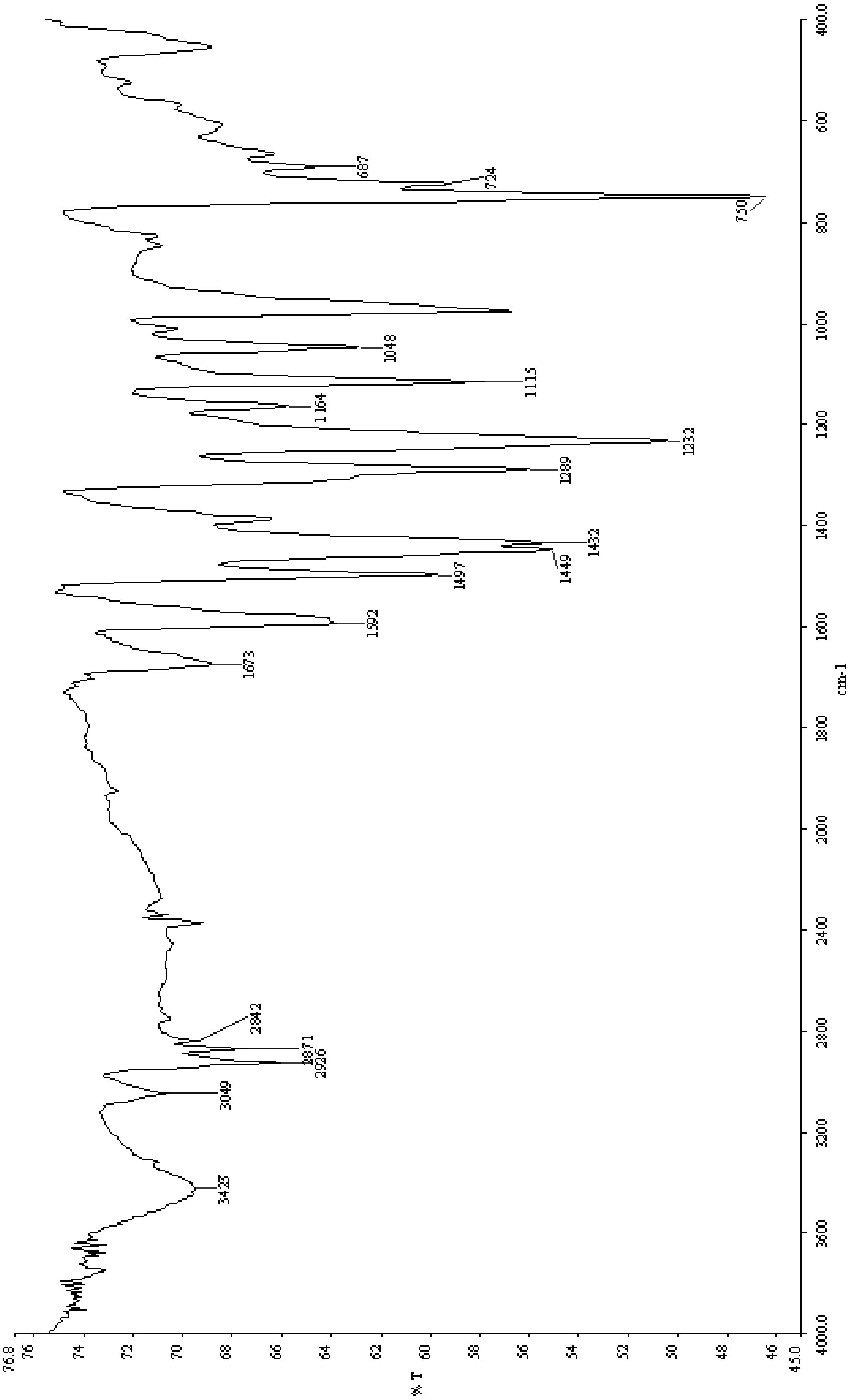


Figure 4.3 The infrared spectrum of H_2L^1

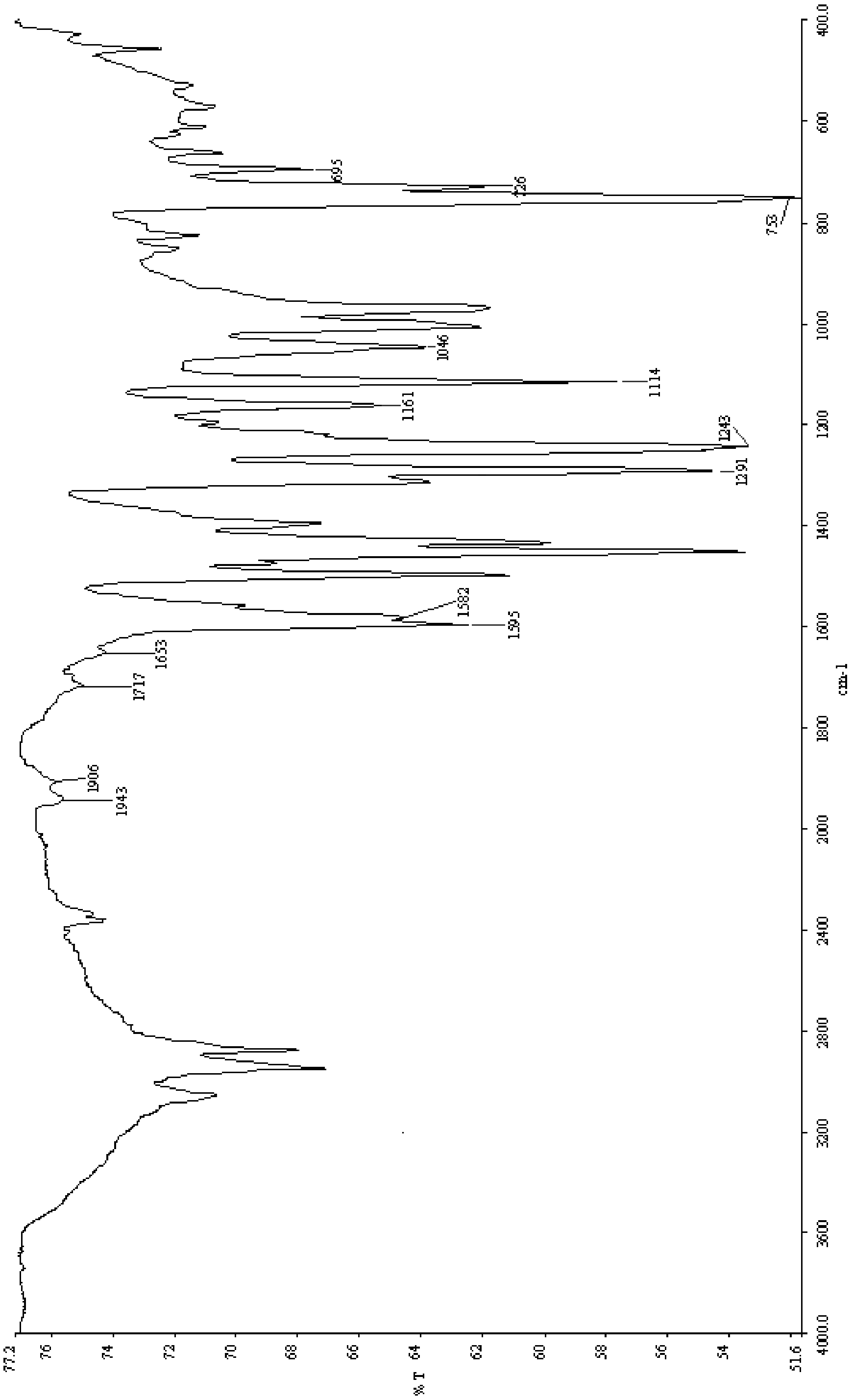


Figure 4.4 The infrared spectrum of 1, $[Cr_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

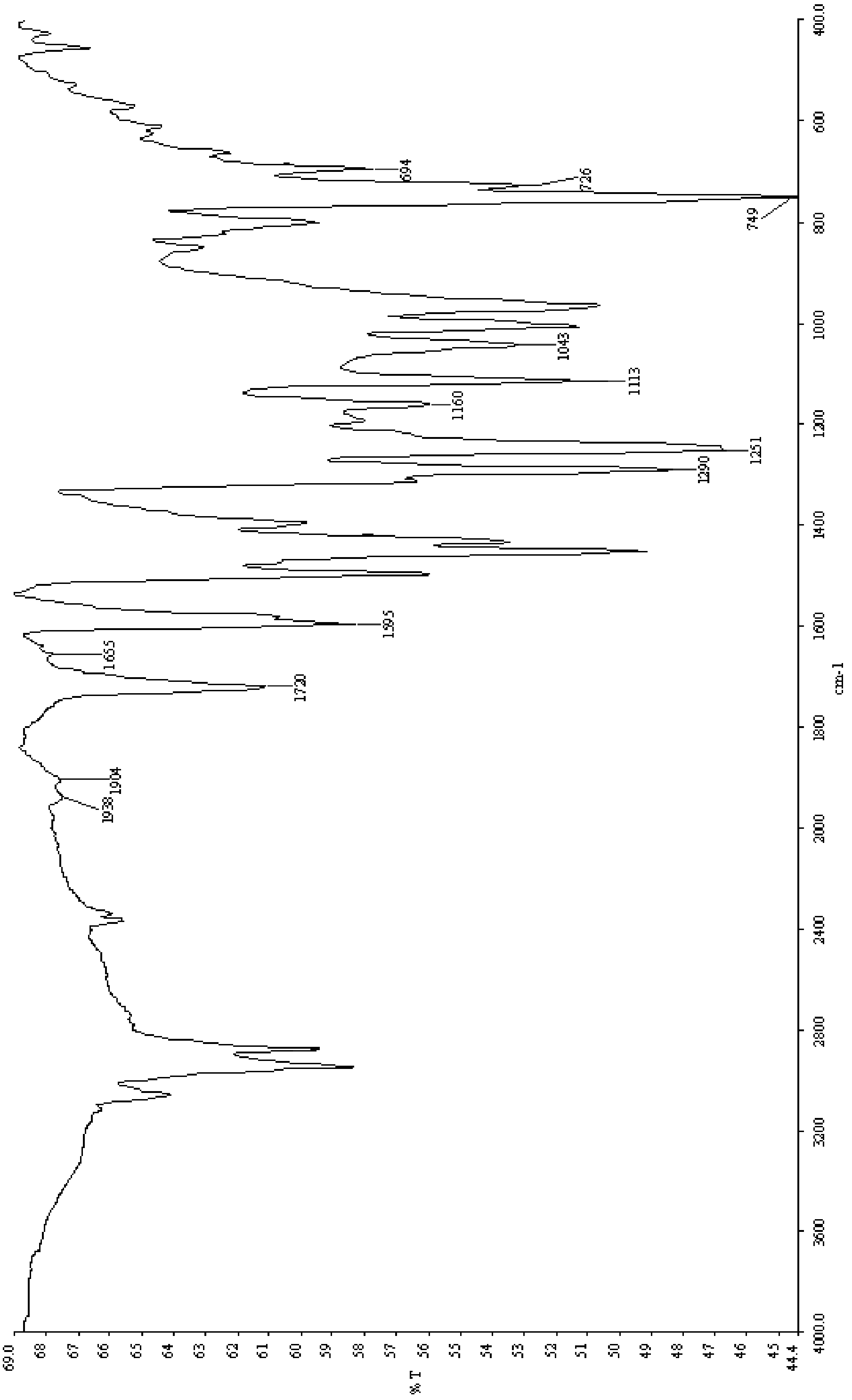


Figure 4.5 The infrared spectrum of 2, $[Mo_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

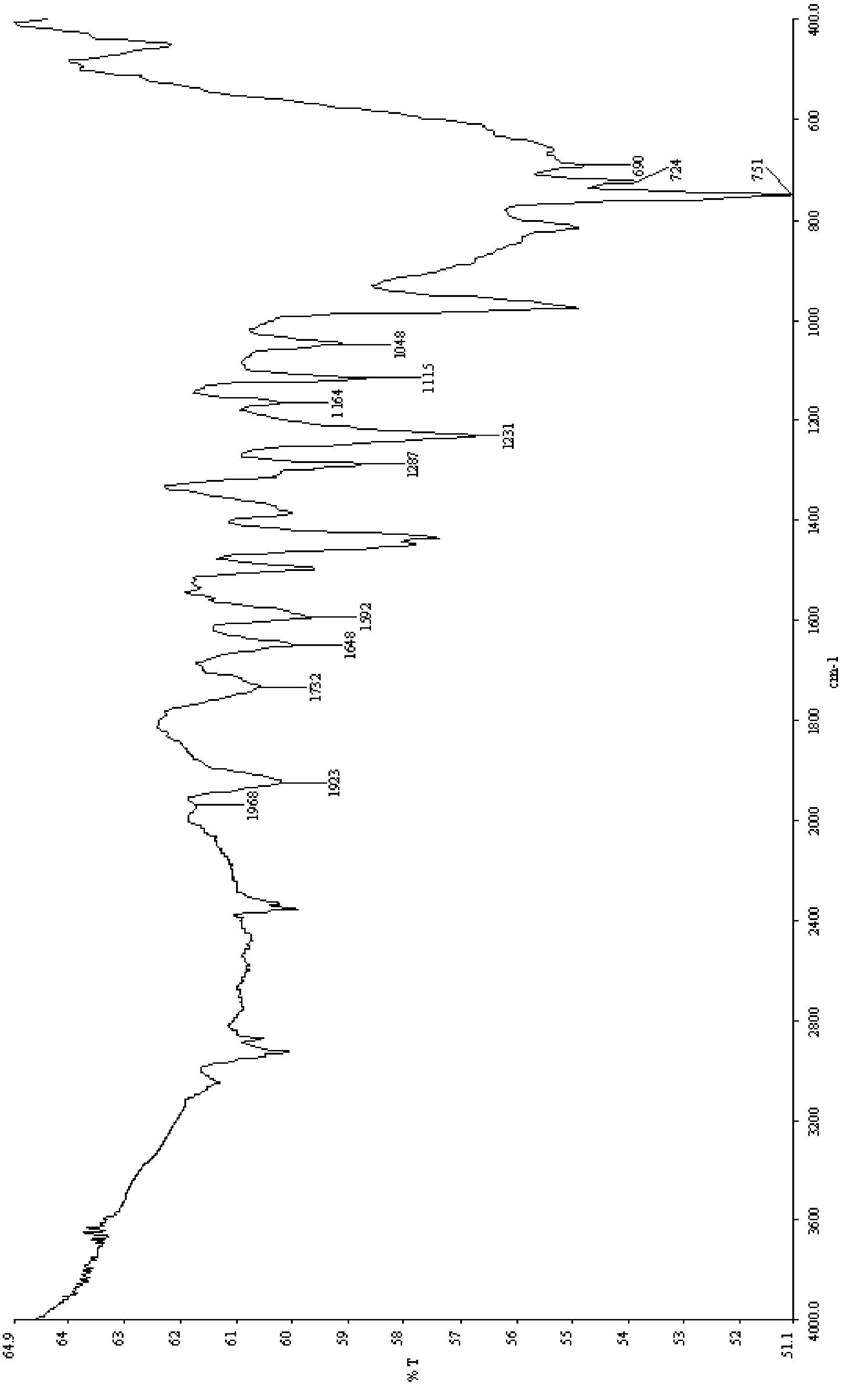


Figure 4.6 The infrared spectrum of 3, $[W_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

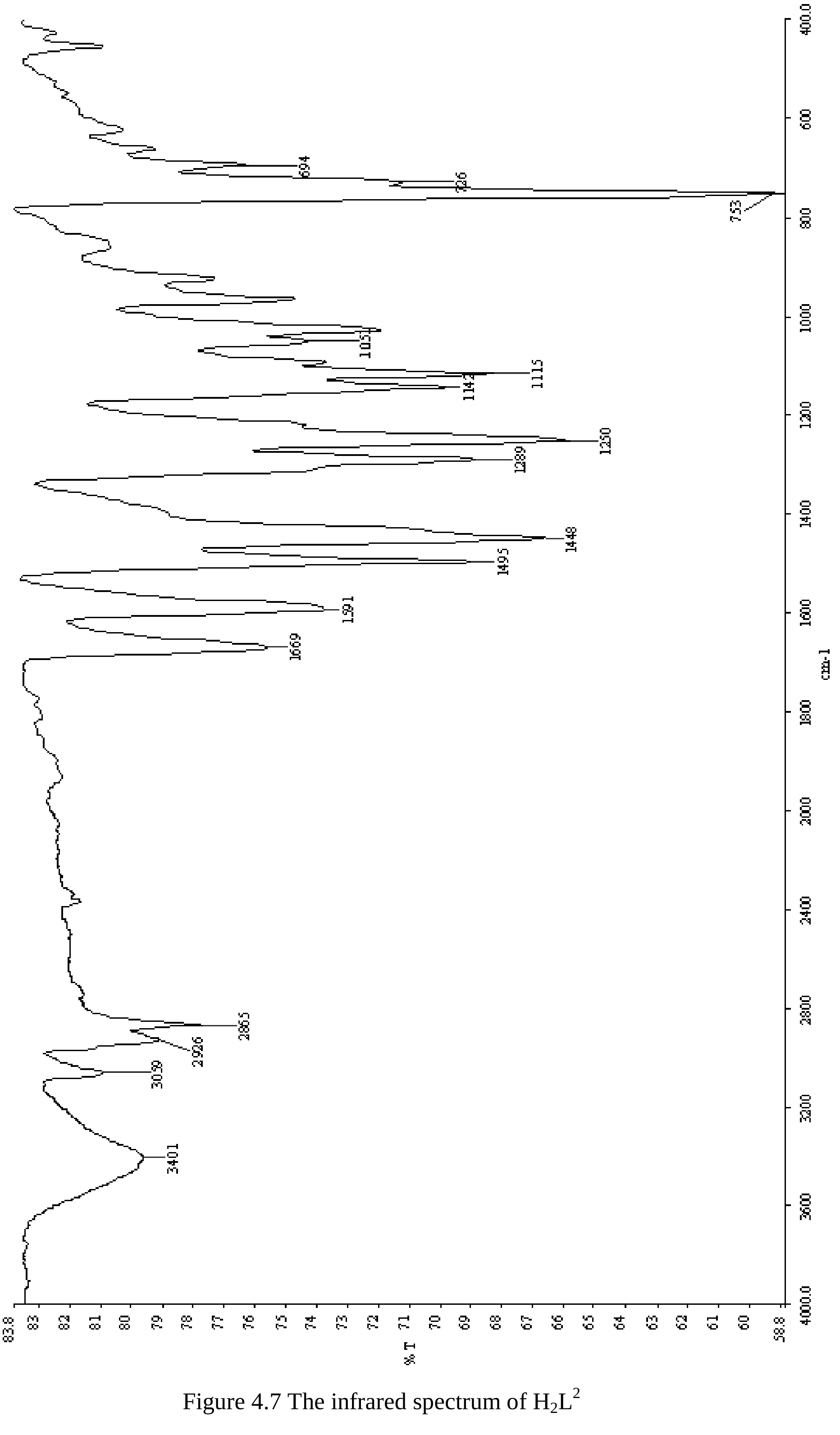


Figure 4.7 The infrared spectrum of H_2L^2

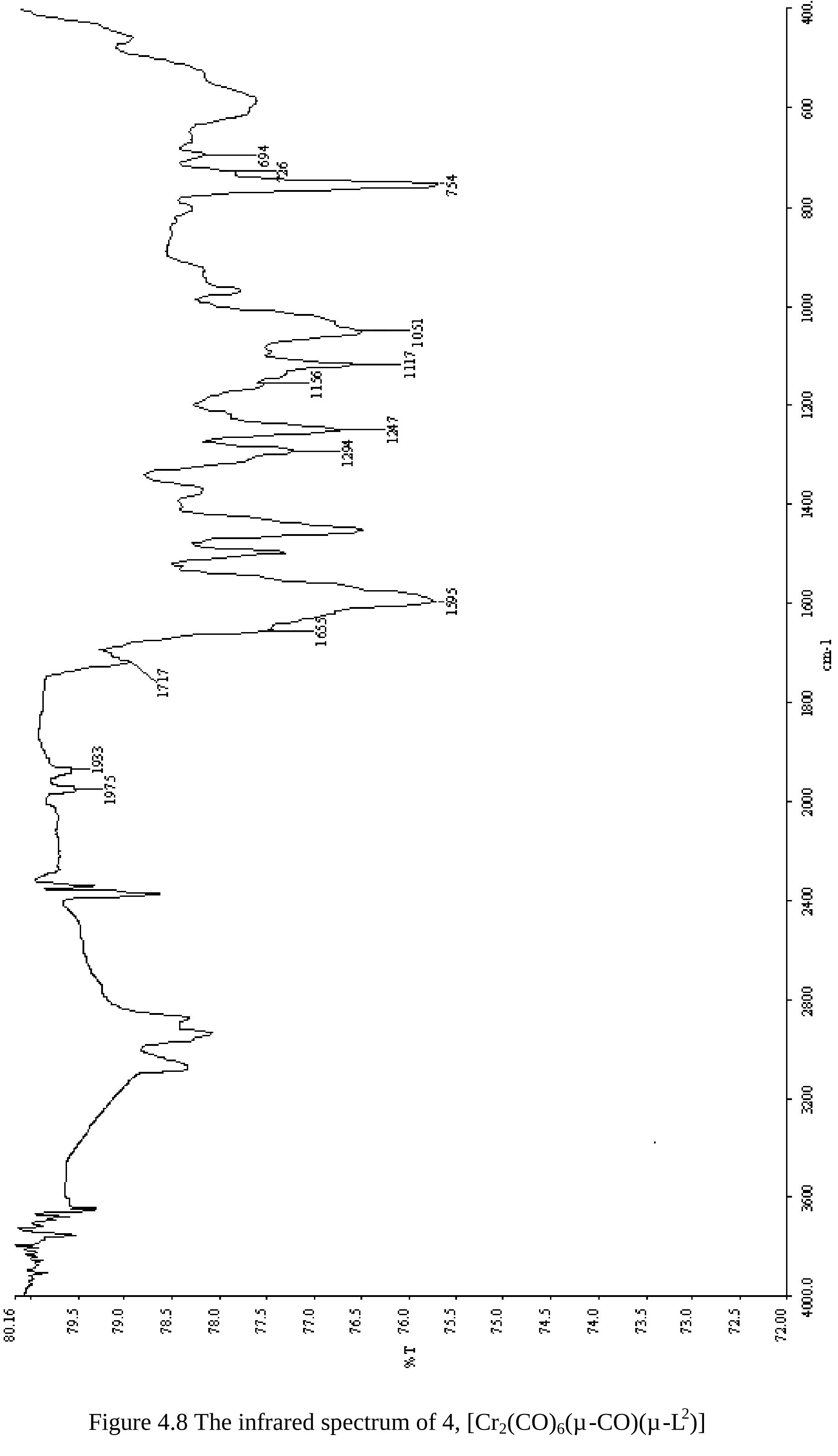


Figure 4.8 The infrared spectrum of 4, $[Cr_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

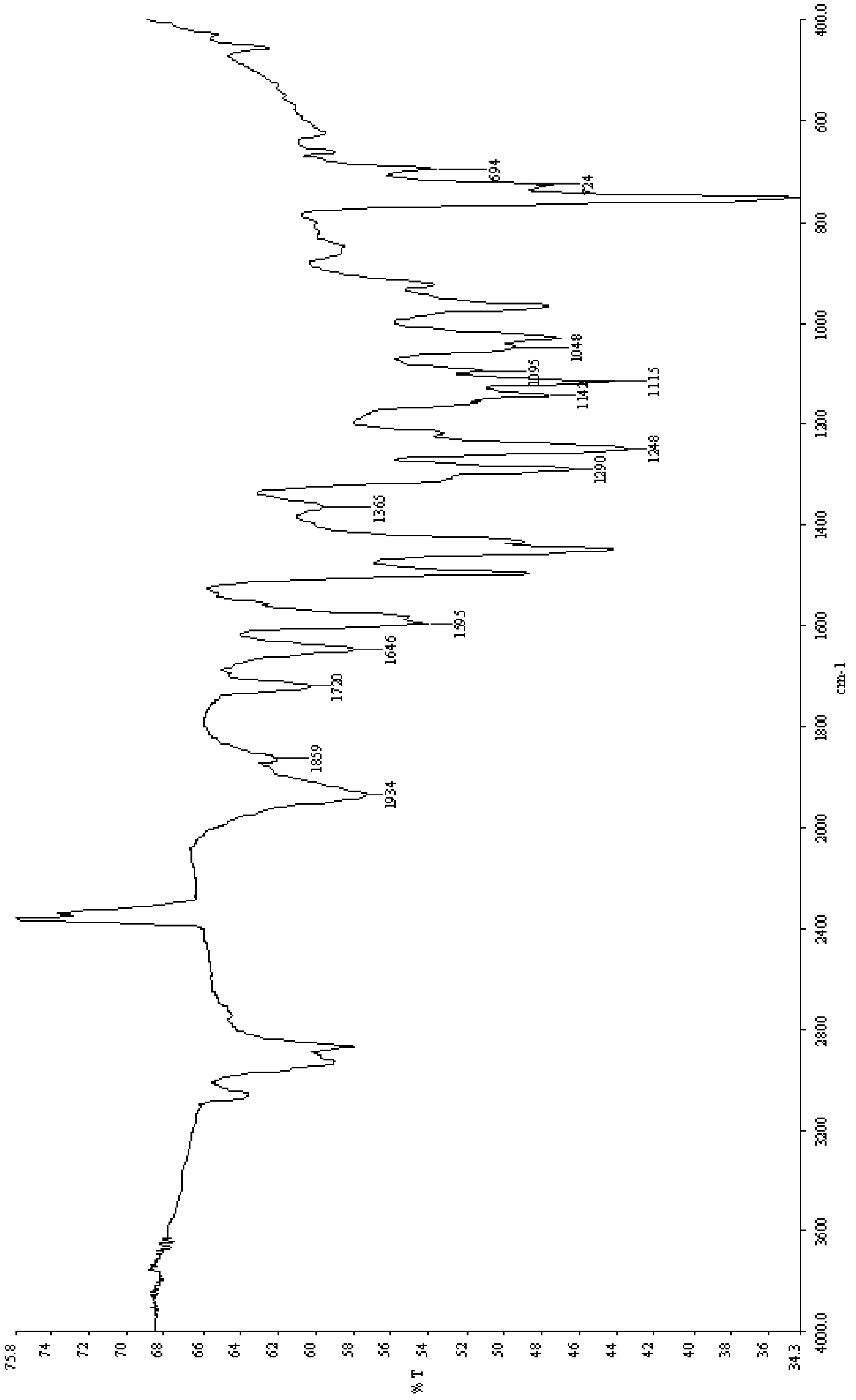


Figure 4.9 The infrared spectrum of 5, $[Mo_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

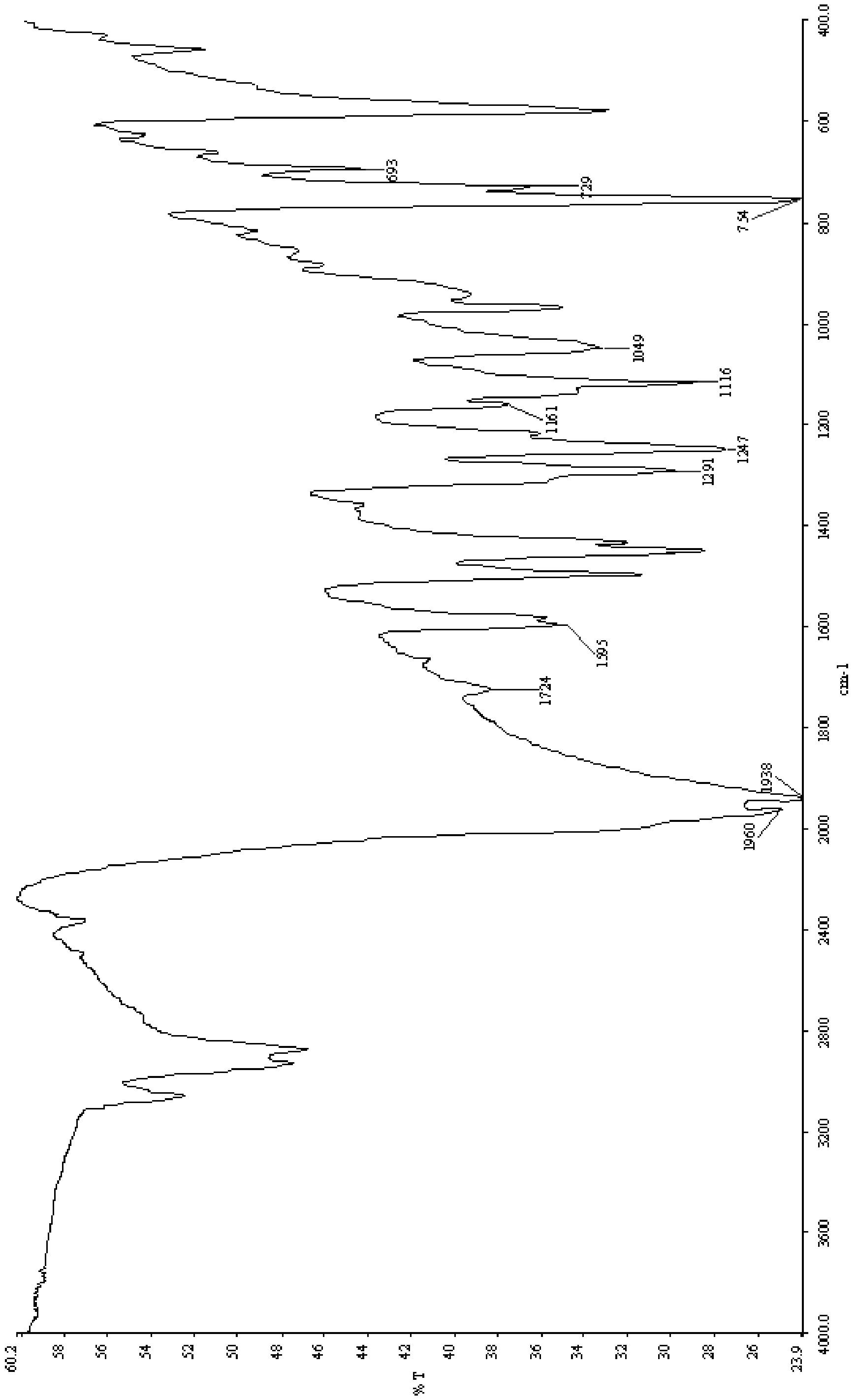


Figure 4.10 The infrared spectrum of 6, $[W_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

4.3.1.3 ^{1}H NMR Spectra

^{1}H NMR spectra data in DMSO-d_6 solutions of complexes **1-6** are collected in Table 4.5 (Karahan, Köse, Subasi, Alp, & Temel, 2008). The NMR spectra are given in Figures 4.11-4.17. The ^{1}H NMR spectrum of the chromium complex of **H_2L^2** could not be obtained since this complex was not dissolved in DMSO-d_6 completely. The ^{1}H NMR spectra of the other metal complexes of **H_2L^1** and **H_2L^2** were obtained.

Except for the HC=N imine and Ar-SH protons all other chemical shifts of coordinated **H_2L^1** and **H_2L^2** have little changes compared with those of the free ligands. While imine CH and aryl SH proton signals in ^{1}H NMR spectra of the ligands can be observed at nearly 8.40 and 3.30 ppm, these signals in ^{1}H NMR spectra of the complexes have not been observed. This situation supports the coordination of ligands to the metal center as benzothiazole derivatives **L^1** and **L^2** after changing the Schiff base structures via the UV irradiations.

Table 4.5 ^{1}H NMR data for the ligands and metal complexes in DMSO-d_6 solution [a]

Complex	CH_2-CH_2O	CH_2- OCH_2	Ar-SH	CH_2-O	Ar-H	HC=N
H_2L^1 [b]	2.28, s, 4H	-	3.30, s, 2H	4.43, s, 4H	7.11-8.00, m, 16 H	8.43, s, 2H
1	2.50, s, 4H	-	-	4.40, s, 4H	7.00-8.10, m, 16 H	-
2	2.27 s, 4H	-	-	4.36, s, 4H	7.13-8.18, m, 16 H	-
3	2.28, s, 4H	-	-	4.43, s, 4H	7.10-8.01, m, 16 H	-
H_2L^2 [c]	-	4.13, t, 4H	3.32, s,2H	4.44, d, 4H	7.09-8.00, m, 16 H	8.40,s, 2H
5	-	4.13, t, 4H	-	4.36, d, 4H	7.01-7.93, m, 16 H	-
6	-	4.13, t, 4H	-	4.37, d, 4H	6.99-7.91, m, 16 H	-

[a] δ in ppm
[b] Taken from (Temel, Alp, İlhan, & Ziyadanoğulları, 2008)
[c] Taken from (Temel, Alp, İlhan, Ziyadanoğulları, & Yılmaz, 2007)

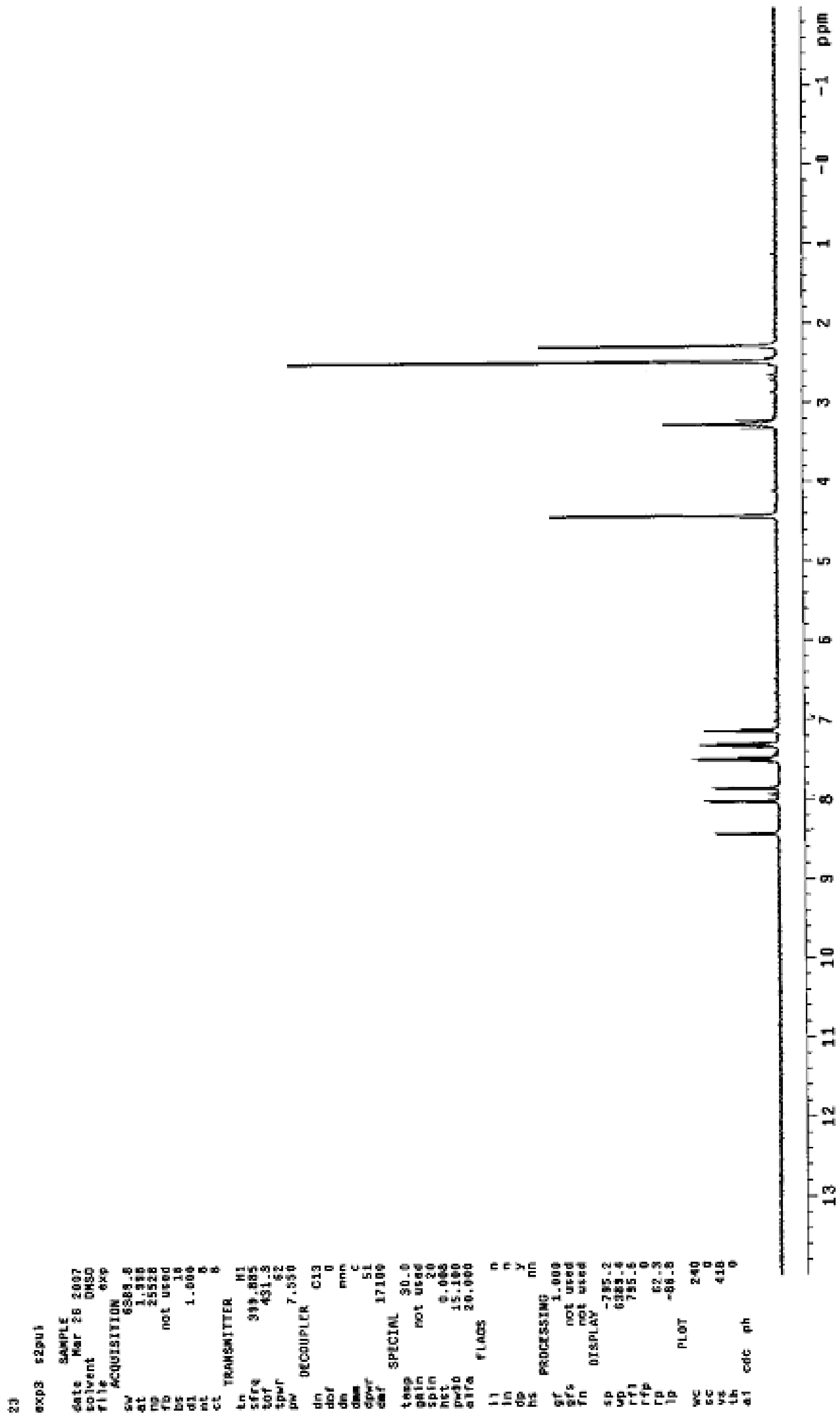


Figure 4.11 The ^{1}H NMR spectrum of H_2L^1

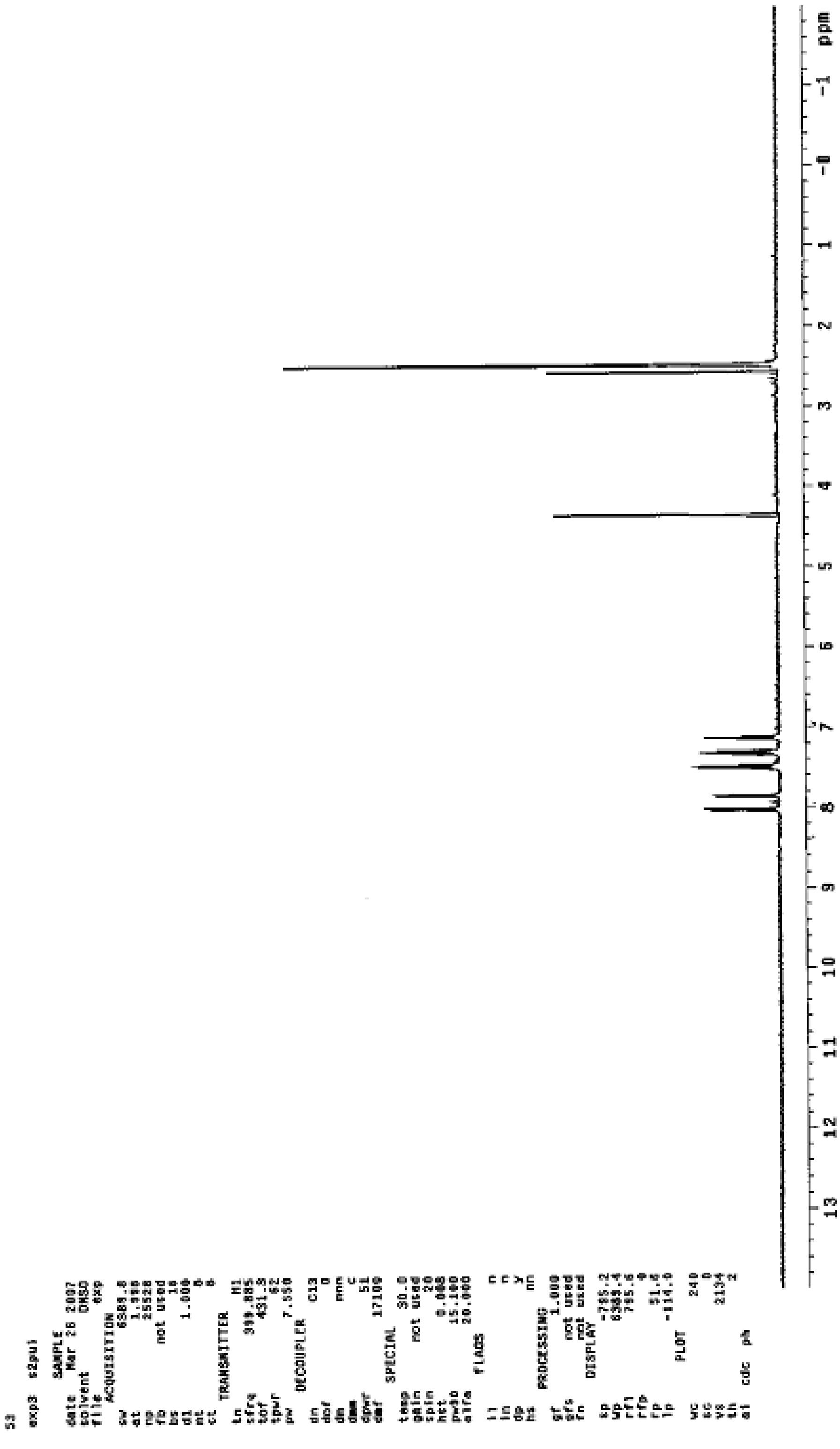
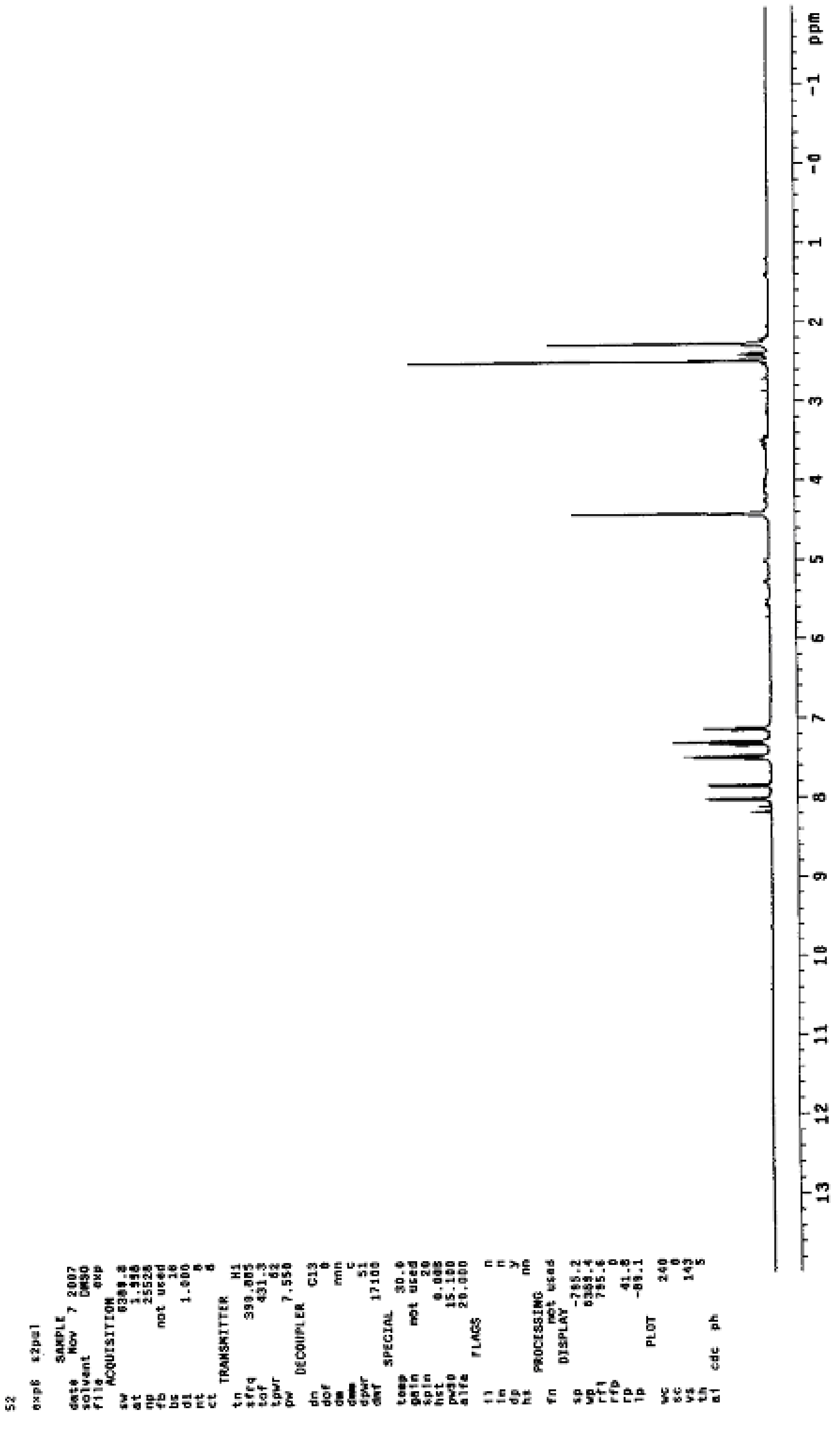


Figure 4.12 The ^1H NMR spectrum of 1, $[Cr_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$



```
52
exp6  s2pul
        SAMPLE
date    Nov  7 2007
solvent        DMSO
file            exp
      ACQUISITION
sw           6389.8
at            1.998
np            25528
fb         not used
bs               16
d1            1.000
nt                8
ct                8
      TRANSMITTER
tn               H1
sfrq        399.865
tof           431.3
tpwr             62
pw            7.550
      DECOUPLER
dn              C13
dof               0
dm              nnn
dmm               c
dpwr             51
dmf           17100
      SPECIAL
temp           30.0
gain       not used
spin             20
hst           0.008
pw90         15.100
alfa         20.000
      FLAGS
il                n
in                n
dp                y
hs               nn
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fn         not used
      DISPLAY
sp           -785.2
wp           6389.4
rfl           795.6
rfp               0
rp             41.8
lp            -89.1
      PLOT
wc              240
sc                0
vs              143
th                5
ai   cdc  ph
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Figure 4.13 The ^{1}H NMR spectrum of 2, [$Mo_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)$]

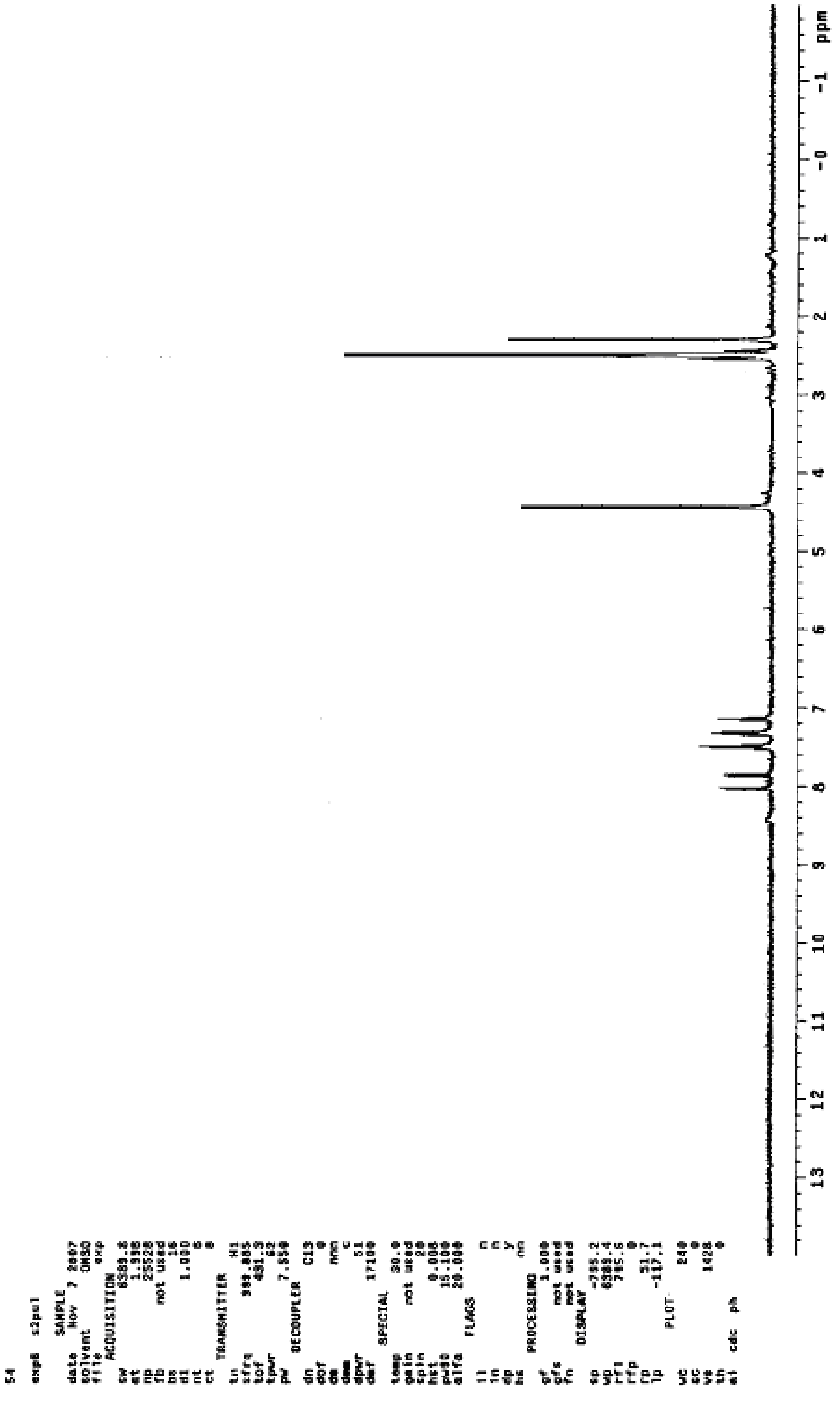

Figure 4.14 The ^{1}H NMR spectrum of 3, $[W_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

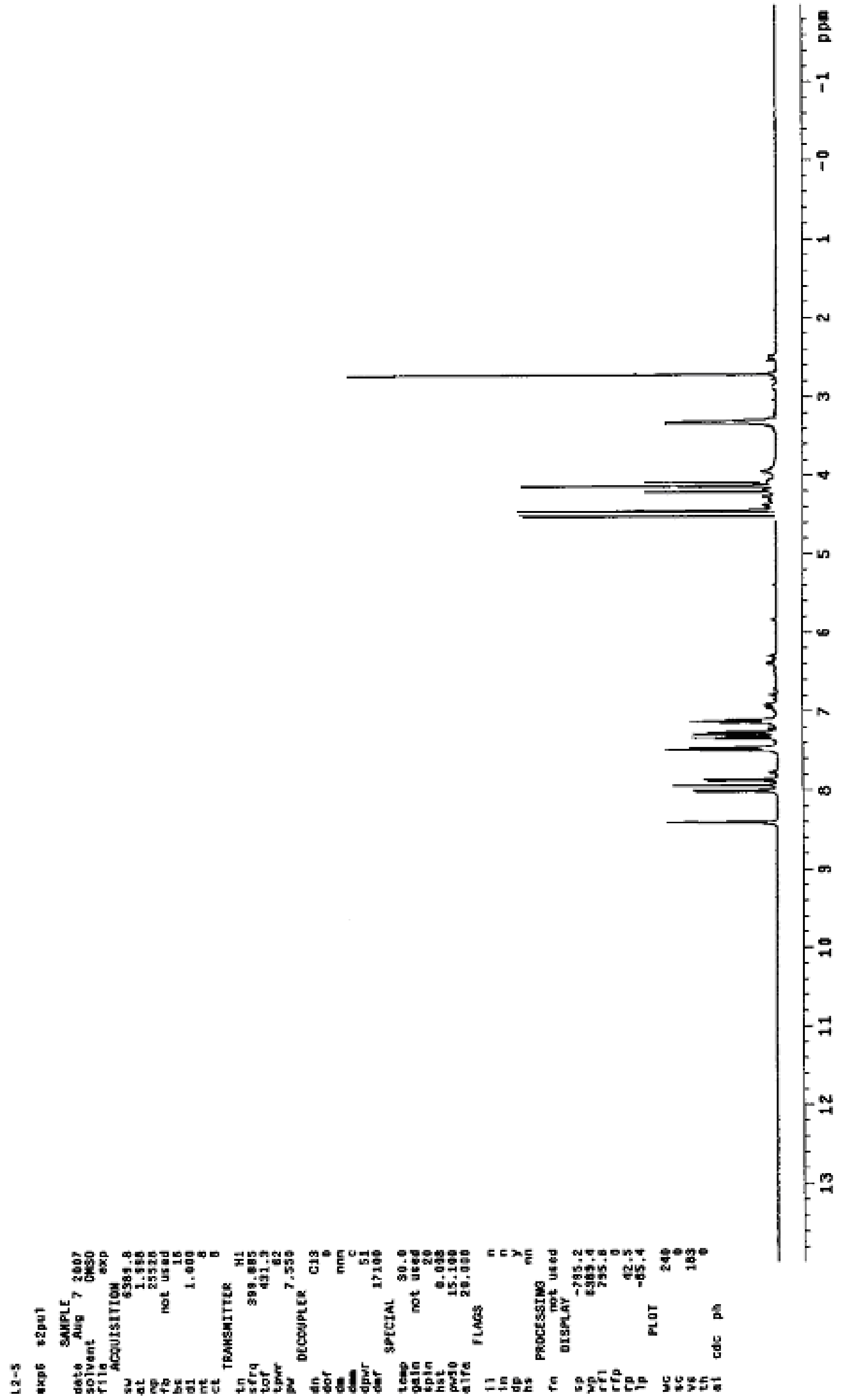

Figure 4.15 The ^1H NMR spectrum of H_2L^2

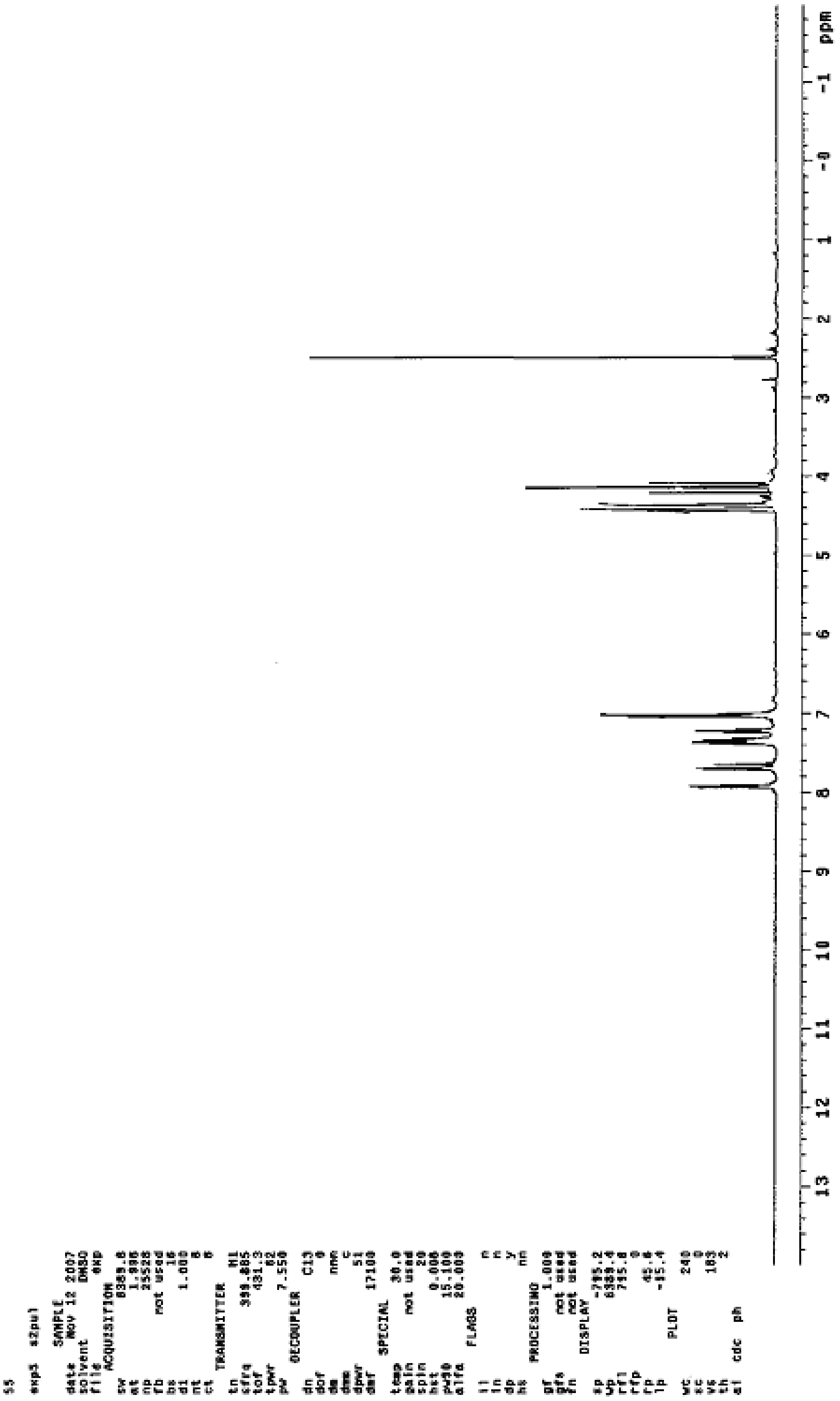

Figure 4.16 The ^{1}H NMR spectrum of 5, $[Mo_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

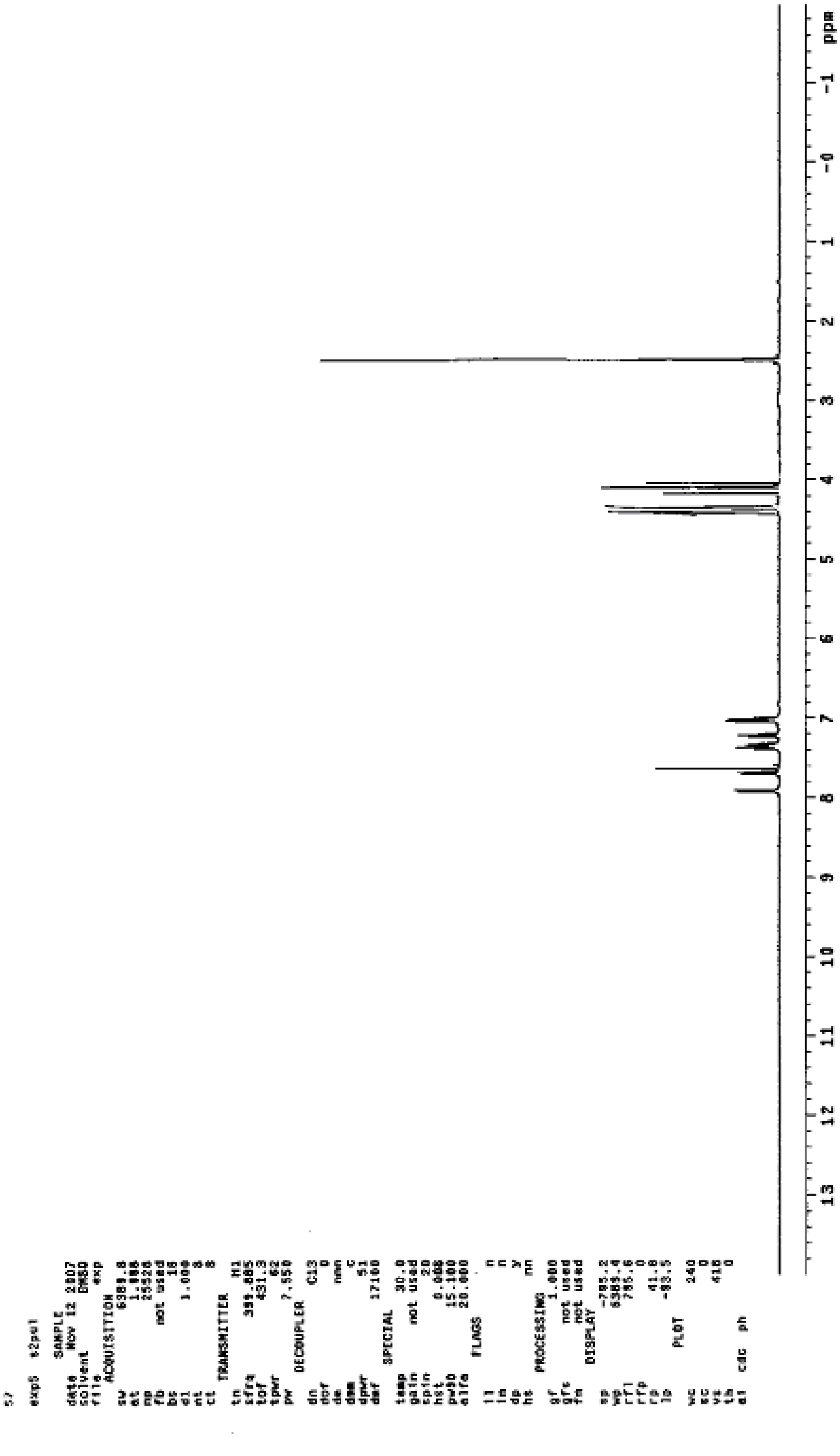

Figure 4.17 The ^{1}H NMR spectrum of 6, $[W_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

4.3.1.4 Mass Spectra

LC-Mass spectra data for complexes **1-6** are listed in Table 4.6 (Karahan, Köse, Subasi, Alp, & Temel, 2008) and show fragmentation *via* successive loss of CO groups and organic ligands. Relative intensities of the fragments are given in parantheses. Proposed **1-6** structures are consistent with the obtained mass fragments containing nitrogen, sulphur and two central metal atoms. The LC-Mass studies of the complexes are entirely in accord with their IR and ^{1}H NMR spectroscopic studies. The spectra of complexes **1-6** are shown in Figures 4.18-4.23.

Table 4.6 LC-Mass spectra data for the complexes

Complex	M.W.	Relative intensities of the ions m/z
1	808	510 (34), [$Cr_2C_{16}H_{10}N_2O_7S_2$]; 404 (1), [$Cr_2C_{16}H_{10}N_2O_7S_2$-3(CO)-(C)-10(H)]; 356 (2), [$Cr_2C_{12}N_2O_4S_2$-4(C)]; 314 (5), [$Cr_2C_8N_2O_4S_2$-(CO)-(N)]; 286 (6), [$Cr_2C_7NO_3S_2$-(CO)]; 258 (5), [$Cr_2C_6NO_2S_2$-(CO)]; 230 (2), [$Cr_2C_5NOS_2$-(CO)].
2	896	547 (3), [$Mo_2C_{12}H_7N_2O_7S_2$]; 418 (3), [$Mo_2C_{12}H_7N_2O_7S_2$-4(CO)-(C)-5(H)]; 388 (3), [$Mo_2C_7H_2N_2O_3S_2$-(CO)-2(H)]; 282 (15), [$Mo_2C_6N_2O_2S_2$-2(CO)-3(C)-(N)].
3	1072	656 (1), [$W_2C_7N_2O_7S_2$]; 544 (2), [$W_2C_7N_2O_7S_2$-4(CO)]; 516 (3), [$W_2C_3N_2O_3S_2$-CO)]; 286 (36), [$W_2C_2N_2O_2S_2$-(W)-(S)-(N)]; 258 (34), [WC_2NO_2S-(CO)]; 230 (6), [WCNOS-(CO)].
4	824	434 (7), [$Cr_2C_{10}H_6N_2O_7S_2$]; 404 (12), [$Cr_2C_{10}H_6N_2O_7S_2$-2(H)-(CO)]; 314 (8), [$Cr_2C_9H_4N_2O_6S_2$-2(CO)-(S)-2(H)]; 202 (1), [$Cr_2C_7H_2N_2O_4S$-4(CO)] 149 (1), [$Cr_2C_3H_2N_2S$-2(C)-2(N)-(H)].
5	912	567 (3), [$Mo_2C_{14}H_3N_2O_7S_2$]; 527 (13), [$Mo_2C_{14}H_3N_2O_7S_2$-(CO)-(C)]; 404 (6), [$Mo_2C_{12}H_3N_2O_6S_2$-3(CO)-3(C)-3(H)]; 298 (10), [$Mo_2C_6N_2O_3S_2$-2(CO)-3(C)-(N)]; 270 (17), [Mo_2CNOS_2-(CO)]; 224 (1), [Mo_2NS_2-(N)-(S)].
6	1088	657 (2), [$W_2C_7HN_2O_7S_2$]; 526 (36), [$W_2C_7HN_2O_7S_2$-3(CO)-(S)-(N)-(H)]; 314 (14), [$W_2C_4NO_4S$-(CO)-(W)]; 286 (21), [WC_3NO_3S-(CO)]; 258 (21), [WC_2NO_2S-(CO)]; 230 (8), [WCNOS-(CO)].

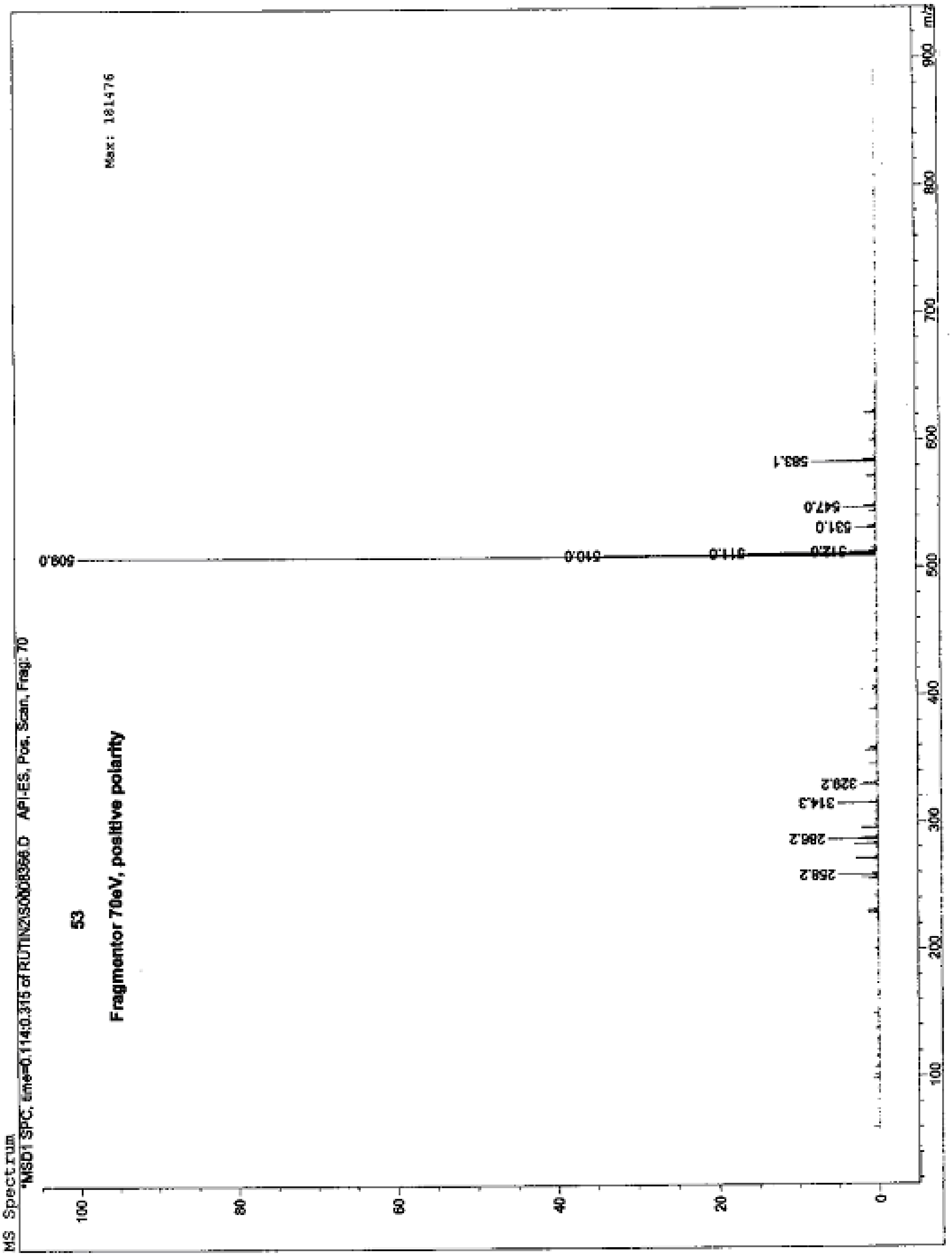

Figure 4.18 The LC-Mass spectrum of 1, $[Cr_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

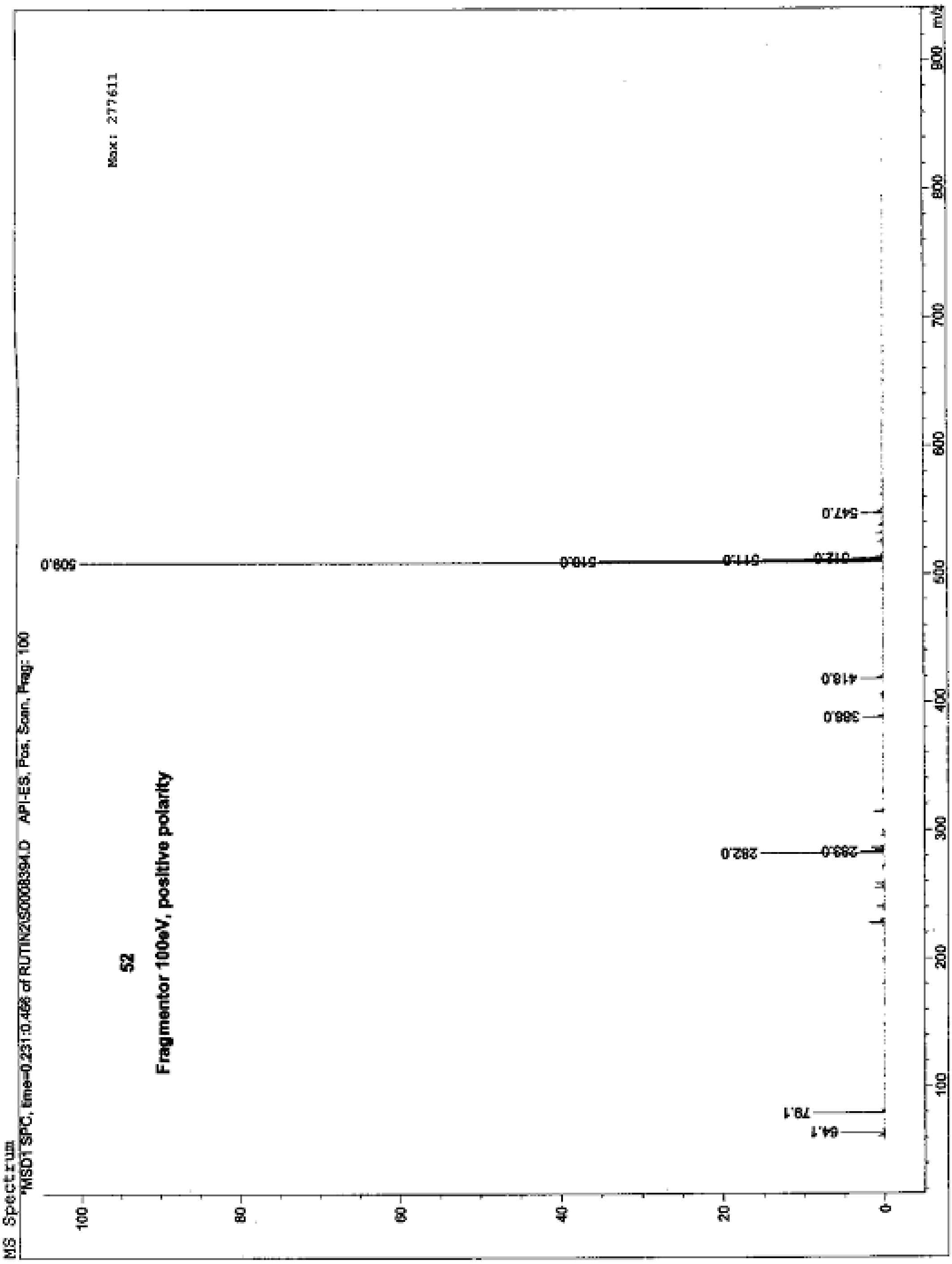

Figure 4.19 The LC-Mass spectrum of 2, $[Mo_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

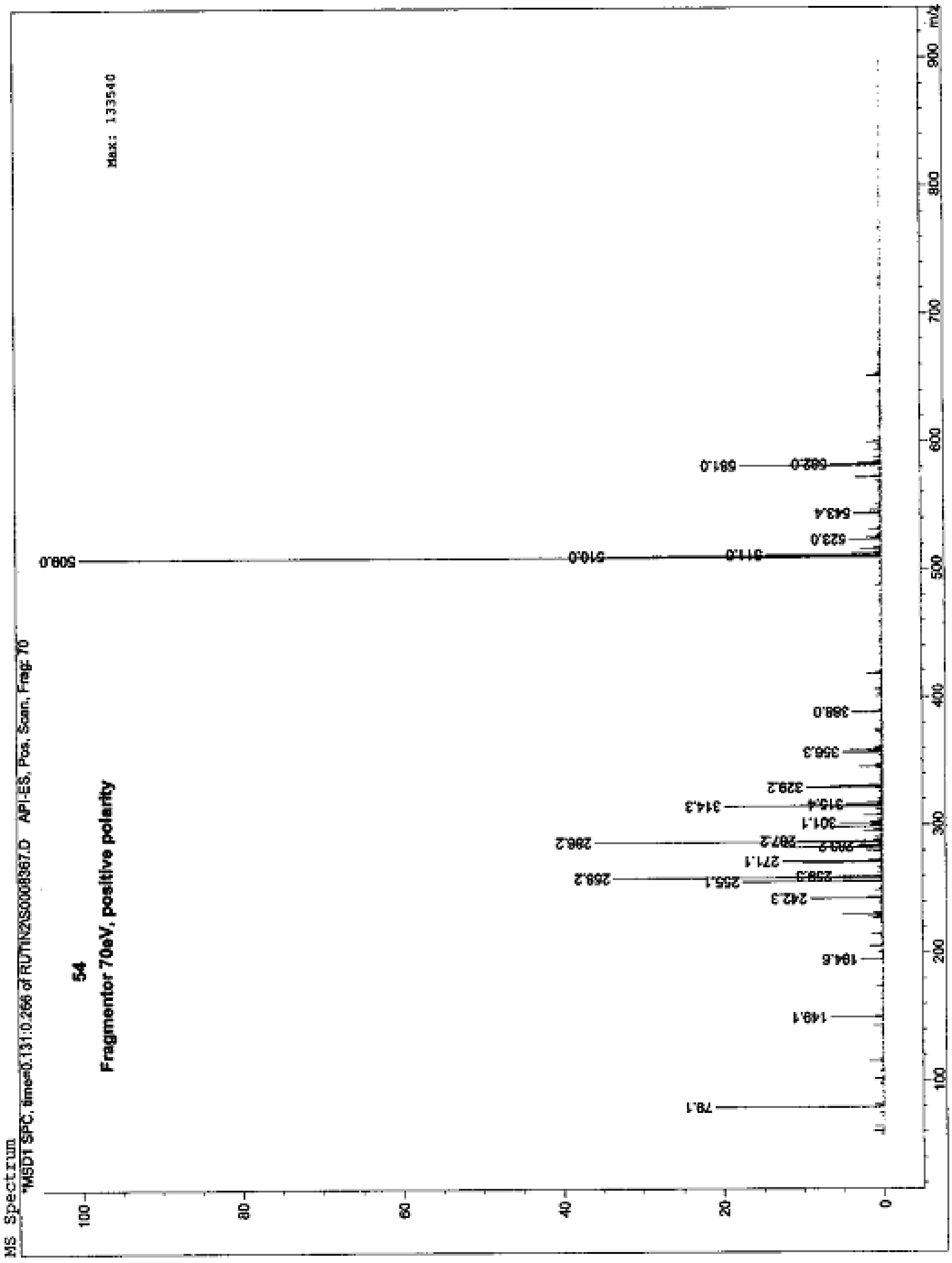

Figure 4.20 The LC-Mass spectrum of 3, $[W_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$

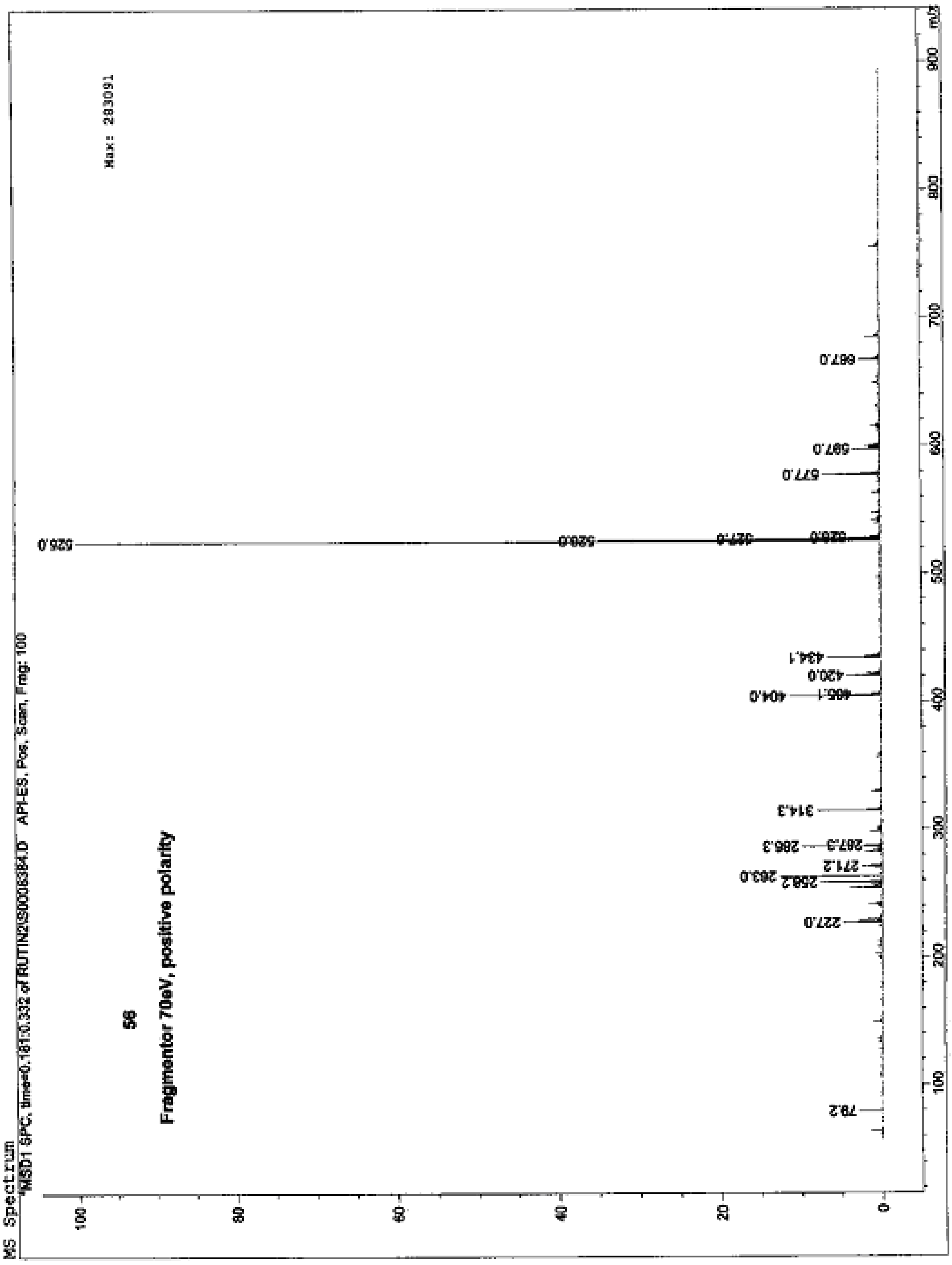

Figure 4.21 The LC-Mass spectrum of 4, $[Cr_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

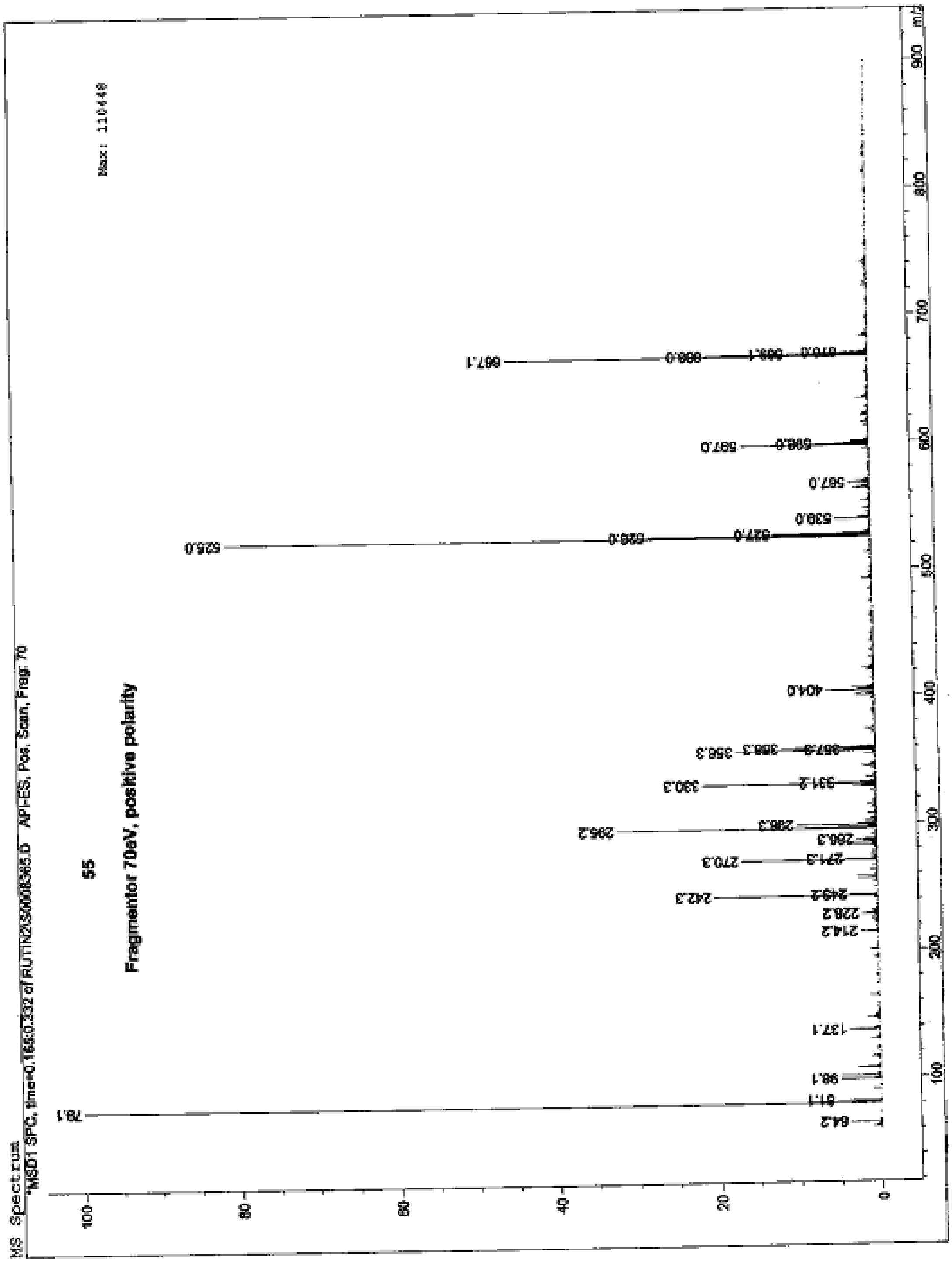

Figure 4.22 The LC-Mass spectrum of 5, $[Mo_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

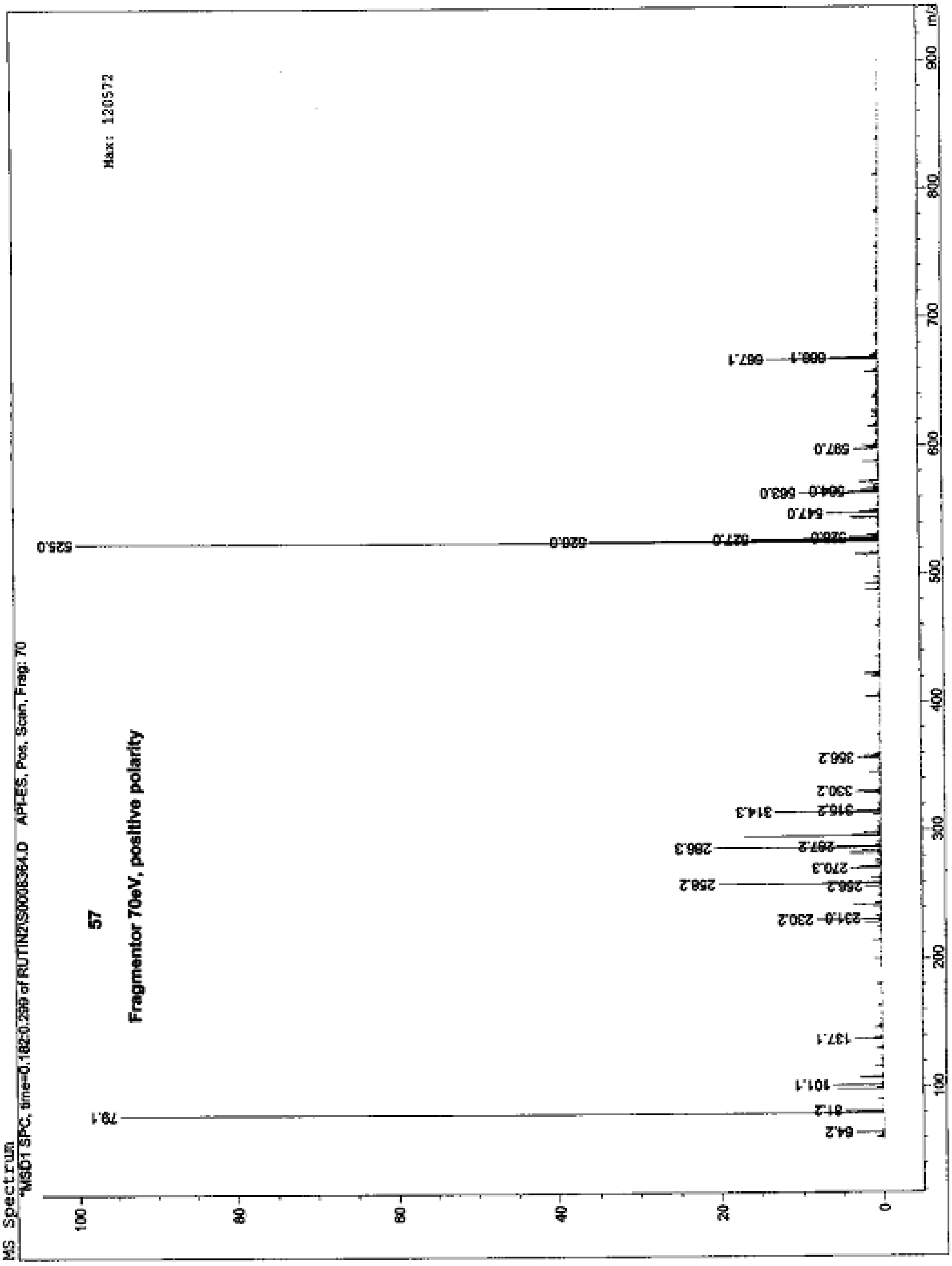

Figure 4.23 The LC-Mass spectrum of 6, $[W_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$

4.3.1.5 Magnetic Susceptibility Studies

Magnetic susceptibility measurements show that **1-6** complexes were diamagnetic. These complexes have M(0) [M= Cr, Mo, W] with a low-spin d^6 configuration. Such diamagnetism might arise from further splitting of the d orbitals in the low symmetry complexes, i.e., $d^2_{xy}\ d^2_{xz}\ d^2_{yz}\ d^0_{x2\text{-}y2}\ d^0_{z2}$.

Also, in homoleptic binuclear metal carbonyls, the pair of metal atoms provides two fewer electrons for bonding, so that additional ligands are required for each metal atom to achieve the favored 18-electron noble gas configuration (Li, Richardson, King, & Schaefer, 2003). According to the 18 electron rule two metal atoms must interact to each other to stabilize the complexes **1-6**.

4.3.2 The Structures of $[(\mu\text{-}CO)_2Cr_2(\eta^4\text{-}H_2L^3)_2]$, 7; $[(\mu\text{-}CO)M_2(CO)_2(\eta^4\text{-}H_2L^3)_2]$, [M= Mo; 8, W; 9]; $[(\mu\text{-}CO)_2Cr_2(\eta^4\text{-}H_2L^4)_2]$, 10 and $[(\mu\text{-}CO)M_2(CO)_2(\eta^4\text{-}H_2L^4)_2]$, [M= Mo; 11, W; 12]

The new complexes, $[(\mu\text{-}CO)_2Cr_2(\eta^4\text{-}H_2L^3)_2]$, **7**; $[(\mu\text{-}CO)M_2(CO)_2(\eta^4\text{-}H_2L^3)_2]$, [M= Mo; **8**, W; **9**]; $[(\mu\text{-}CO)_2Cr_2(\eta^4\text{-}H_2L^4)_2]$, **10** and $[(\mu\text{-}CO)M_2(CO)_2(\eta^4\text{-}H_2L^4)_2]$, [M= Mo; **11**, W; **12**] have been synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with two oxygen and nitrogen donor Schiff base ligands, *N,N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane **(H_2L^3)** and *N,N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy)butane **(H_2L^4)**. The spectroscopic studies show that **H_2L^3** and **H_2L^4** ligands are coordinated to the central metal as tetradentate ligands coordinating via their imine N and O donor atoms in complexes **7-12**.

4.3.2.1 Analytical Data

The analytical data and some physical properties of complexes **7-12** are summarized in Table 4.7 (Karahan, Köse, Subasi, & Temel, 2008). The stochiometry of the ligands and their complexes have been confirmed by their elemental analyses.

Table 4.7 Elemental analysis results and physical properties for the complexes (7-12)

Complex[a]	Yield (%)	Found (Calcd.) (%) C	H	N
7	61	69.96 (70.25)	4.22 (4.43)	4.24 (4.43)
8	67	65.02 (65.21)	3.80 (4.05)	3.89 (4.05)
9	65	57.32 (57.84)	3.40 (3.59)	3.12 (3.59)
10	64	70.45 (70.90)	4.70 (4.84)	4.11 (4.24)
11	70	65.68 (66.01)	4.21 (4.45)	3.78 (3.89)
12	67	58.62 (58.80)	3.60 (3.97)	3.32 (3.47)

[a]All complexes are brown

4.3.2.2 Infrared Spectra

Characteristic infrared data of complexes **7-12** are listed in Table 4.8 (Karahan, Köse, Subasi, & Temel, 2008). IR spectra are presented in Figures 4.24-4.31. The infrared spectra of the complexes have been compared with those of ligands. The IR spectra of **7** and **10** exhibit one prominent band at 1722 and 1718 cm^{-1} respectively in the CO stretching vibrational region. One band ν(CO) pattern at this region indicates the presence of two bridging CO groups which are at similar positions. The IR spectrum of **8** contains two bands at 1973 cm^{-1} and 1717 cm^{-1} in the CO stretching vibrational region. While the band at 1717 cm^{-1} indicates the presence of a bridging CO group between the metal atoms, the band at 1973 cm^{-1} belongs to two terminal CO groups. Terminal CO groups and Schiff base ligands in **8** are at trans positions each others. As indicated in (Wang, Xie, King, & Schaefer, 2006) trans-[$(\mu\text{-CO})_2Fe_2(CO)_2Cp_2$] which has similar structure with **8** has been contained two CO bands at 1962 cm^{-1} and 1794 cm^{-1} like **8**. In addition, same literature explains that [$(\mu\text{-CO})Fe_2(CO)_2Cp_2$] which has one bridging CO group and two terminal CO groups at cis positions indicates three bands in the CO stretching vibrational region. This situation supports that the coordination of CO and Schiff base ligands to the metal centers is at trans positions rather than cis positions. IR spectra of **9, 11** and **12** exhibit essentially the same ν(CO) absorption pattern as observed for **8**. These modes shift to lower wave numbers when compared with those of $M(CO)_6$ and $M(CO)_5THF$ (M=Cr, Mo, W).

Table 4.8 Characteristic infrared bands (cm^{-1}) of H_2L^3, H_2L^4 and the complexes

Complex	$\nu_{(CO)}$	$\nu_{(C=N)}$	$\nu_{(O-H)}$[a]	$\nu_{(OH)}$	$\nu_{(phen\ C-O)}$
H_2L^3[b]	-	1617s	2881w	3418m	1289m
H_2L^4[b]	-	1618s	2871w	3443m	1299w
7	1722s	1620s	2886w	3410s	1294w
8	1973s, 1717m	1620s	2886w	3384w	1304w
9	1968s, 1717w	1623s	2876w	3423s	1311w
10	1718s	1619s	2876w	3420s	1301w
11	1968s, 1721m	1619s	2872w	3433m	1291m
12	1975m, 1719m	1620s	2876m	3418s	1297w

[a] Intramolecular hydrogen bonded –OH,
[b] Taken from (Temel, İlhan, Şekerci, & Ziyadanoğulları, 2002).

The infrared spectra of the complexes **7-12** display the characteristic bands of **H_2L^3** and **H_2L^4** with the appropriate shifts due to complex formation. The strong bands at nearly 1617 cm^{-1} in the IR spectra of free **H_2L^3** and **H_2L^4** belong to the C=N stretching vibration (Temel, İlhan, Şekerci, & Ziyadanoğulları, 2002). This band contain shifts in compounds **7-12** showing that the **H_2L^3** and **H_2L^4** ligands coordinate to the metal *via* the imine (HC=N) nitrogen donor atom. The bands in the IR spectra of the Schiff bases **H_2L^3** and **H_2L^4** at 2881 cm^{-1} and 2871 cm^{-1} respectively are assigned to the stretch of the intramolecular hydrogen bonded –OH (Temel, İlhan, Şekerci, & Ziyadanoğulları, 2002). These bands have appeared and showed shifts considerably in the IR spectra of the complexes **7-12**. However appearence of the intramolecular hydrogen bonded –OH bands, the broad and medium ν(OH) bands occuring 3418 cm^{-1} and 3443 cm^{-1} in the IR spectra of **H_2L^3** and **H_2L^4** respectively exhibit shifts considerably in the IR spectra of complexes. The bands at 1289 cm^{-1}

and 1299 cm^{-1} concerning phenolic C-O stretching vibrations in the IR spectra of $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ are found in the region 1294-1311 cm^{-1} and 1291-1301 cm^{-1} in the IR spectra of complexes. These changes suggest that the o-OH groups of $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ moieties have taken part in complex formation without elimination of hydrogen atoms from the OH groups, which were also confirmed by the appearance of the OH signals in the ^{1}H-NMR spectra (Table 4.9). Conclusive evidence of the bonding have been also seen by the observation that the new bands in the spectra of the metal complexes is appeared at 527-590 cm^{-1} and 412-451 cm^{-1} ascribed to the M-O and M-N vibrations which are not observed in the spectra of the ligands.

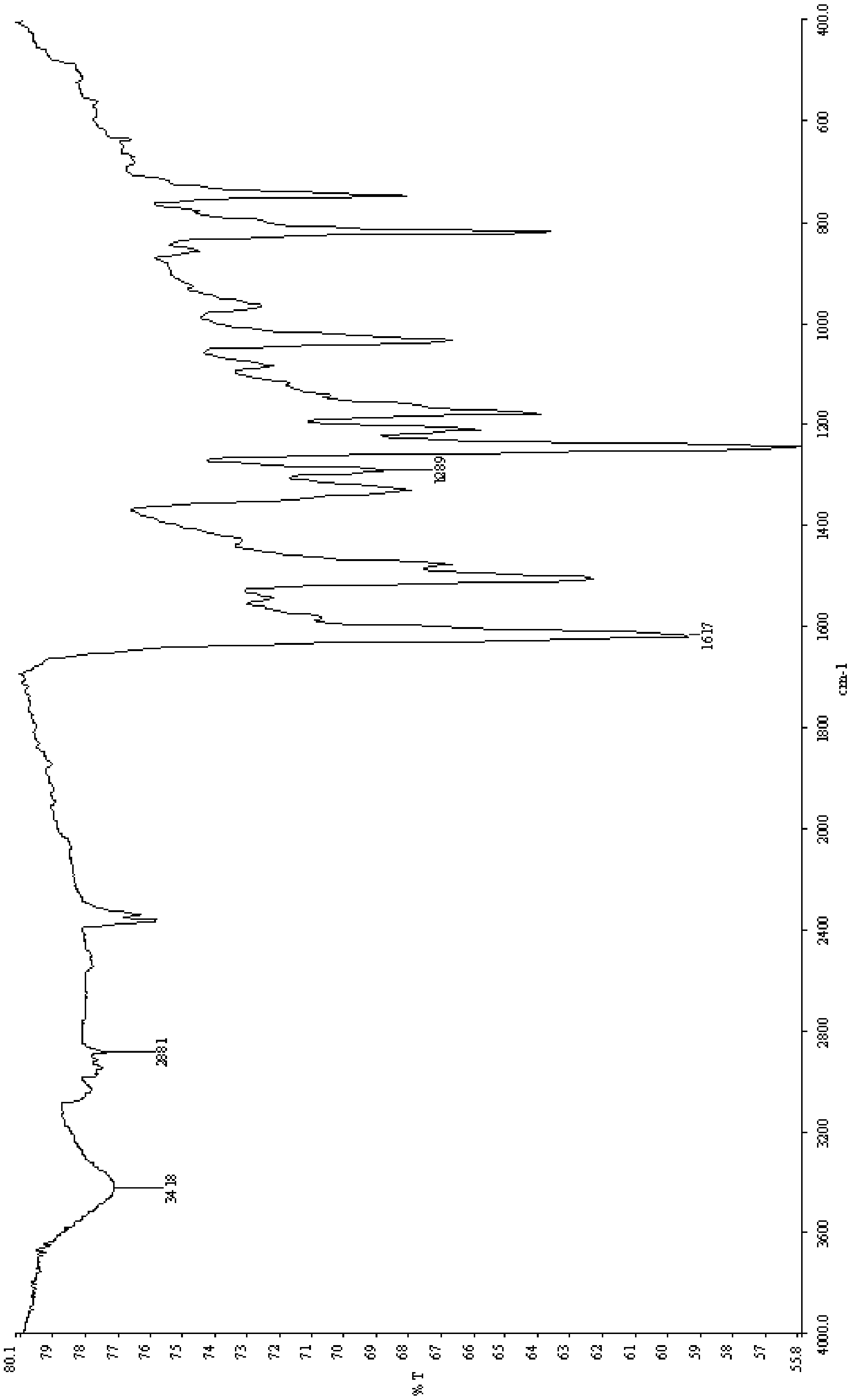

Figure 4.24 The infrared spectrum of H_2L^3

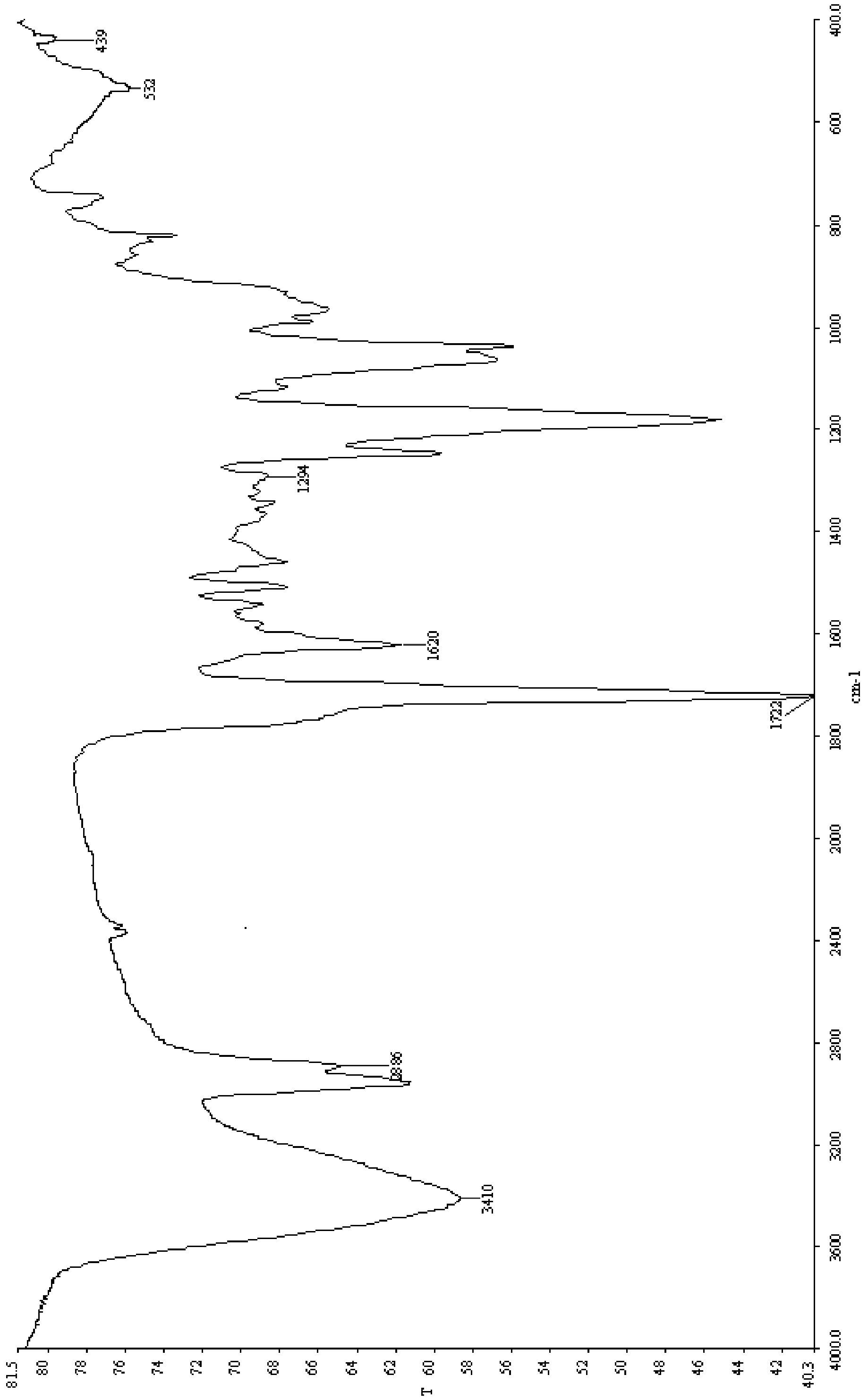

Figure 4.25 The infrared spectrum of 7, $[(\mu\text{-CO})_2\mathrm{Cr}_2(\eta^4\text{-H}_2\mathrm{L}^3)_2]$

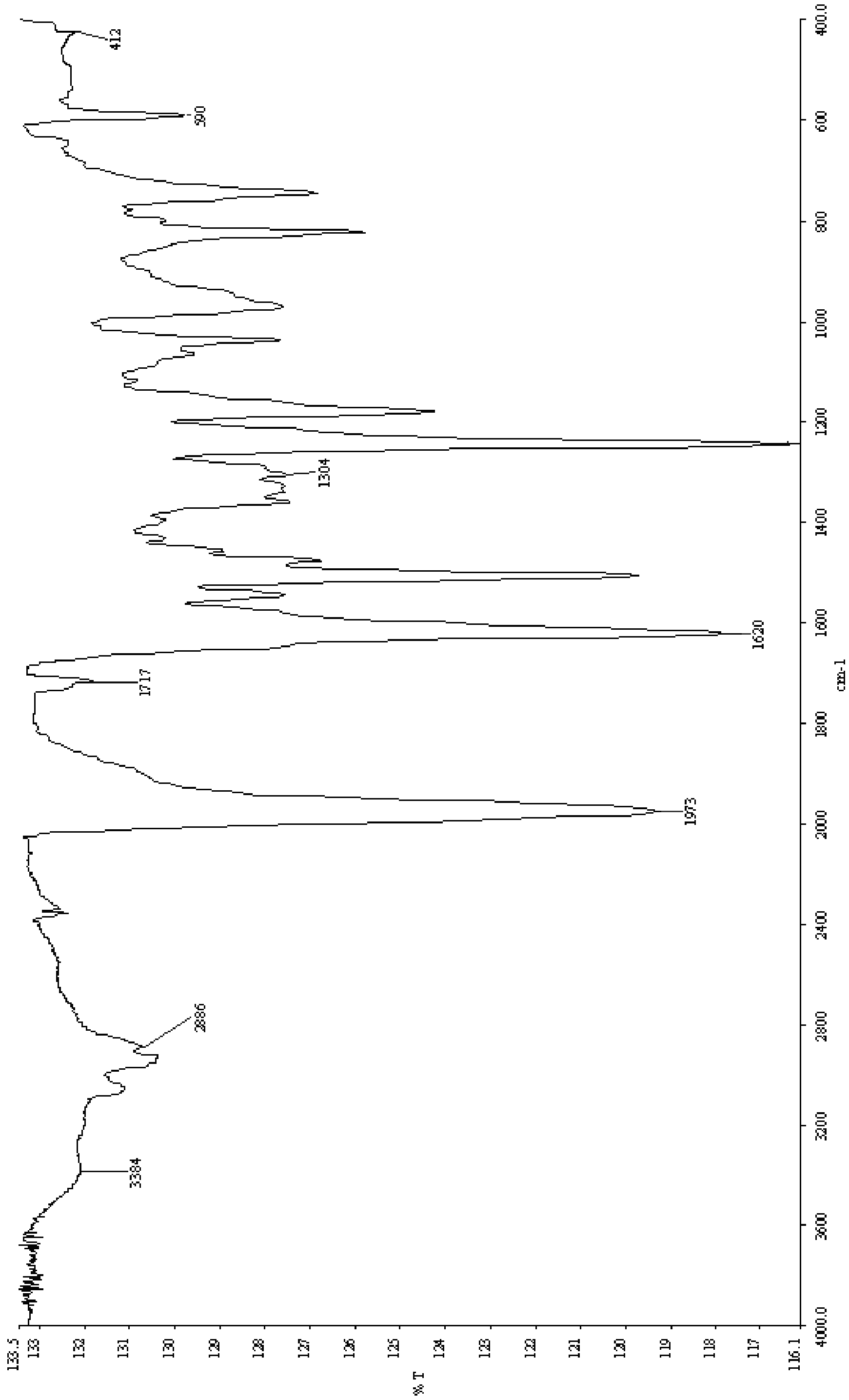

Figure 4.26 The infrared spectrum of 8, [(μ-CO)$Mo_2(CO)_2(\eta^4$- $H_2L^3)_2$]

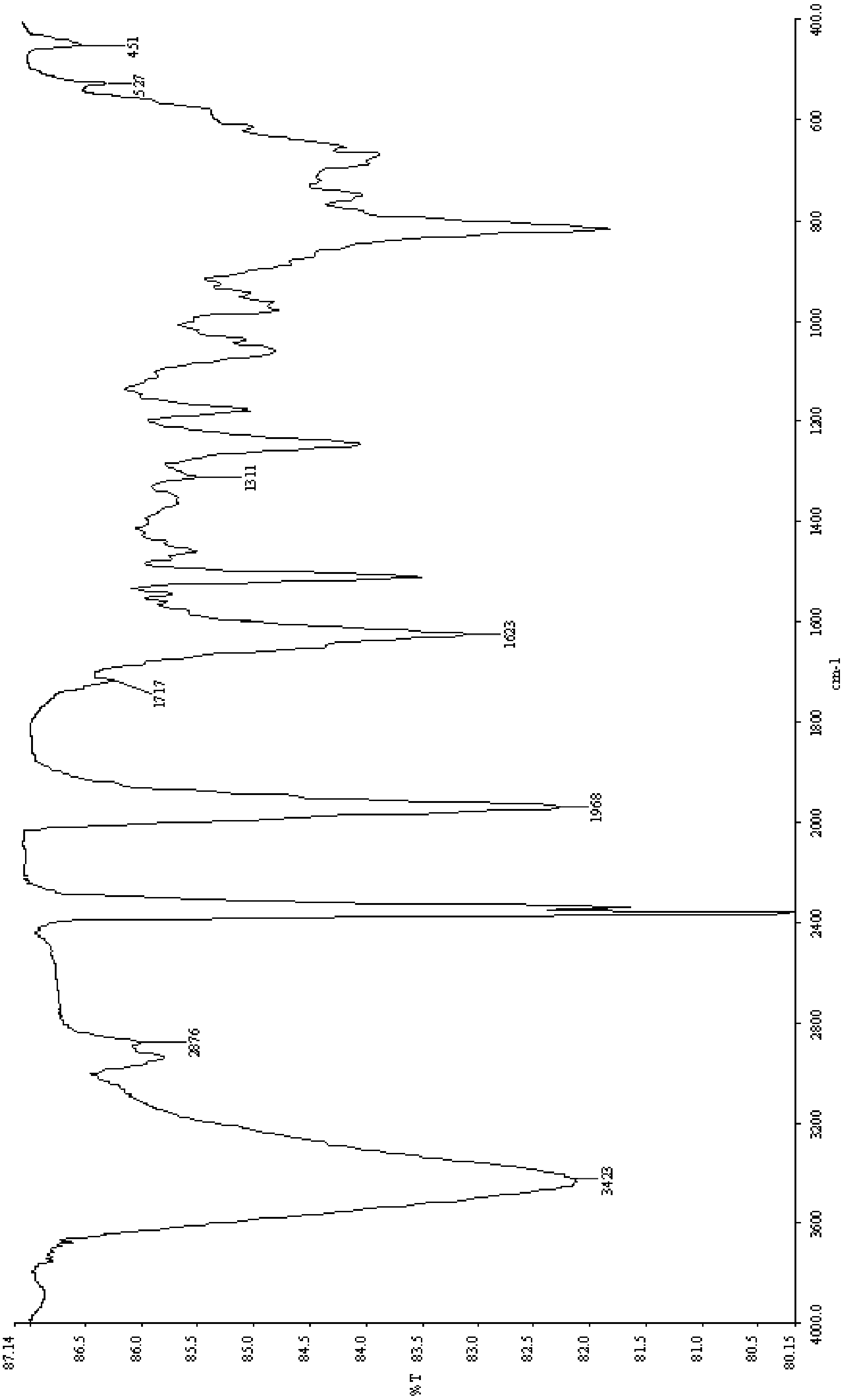

Figure 4.27 The infrared spectrum of 9, $[(\mu\text{-CO})W_2(CO)_2(\eta^4\text{- }H_2L^3)_2]$

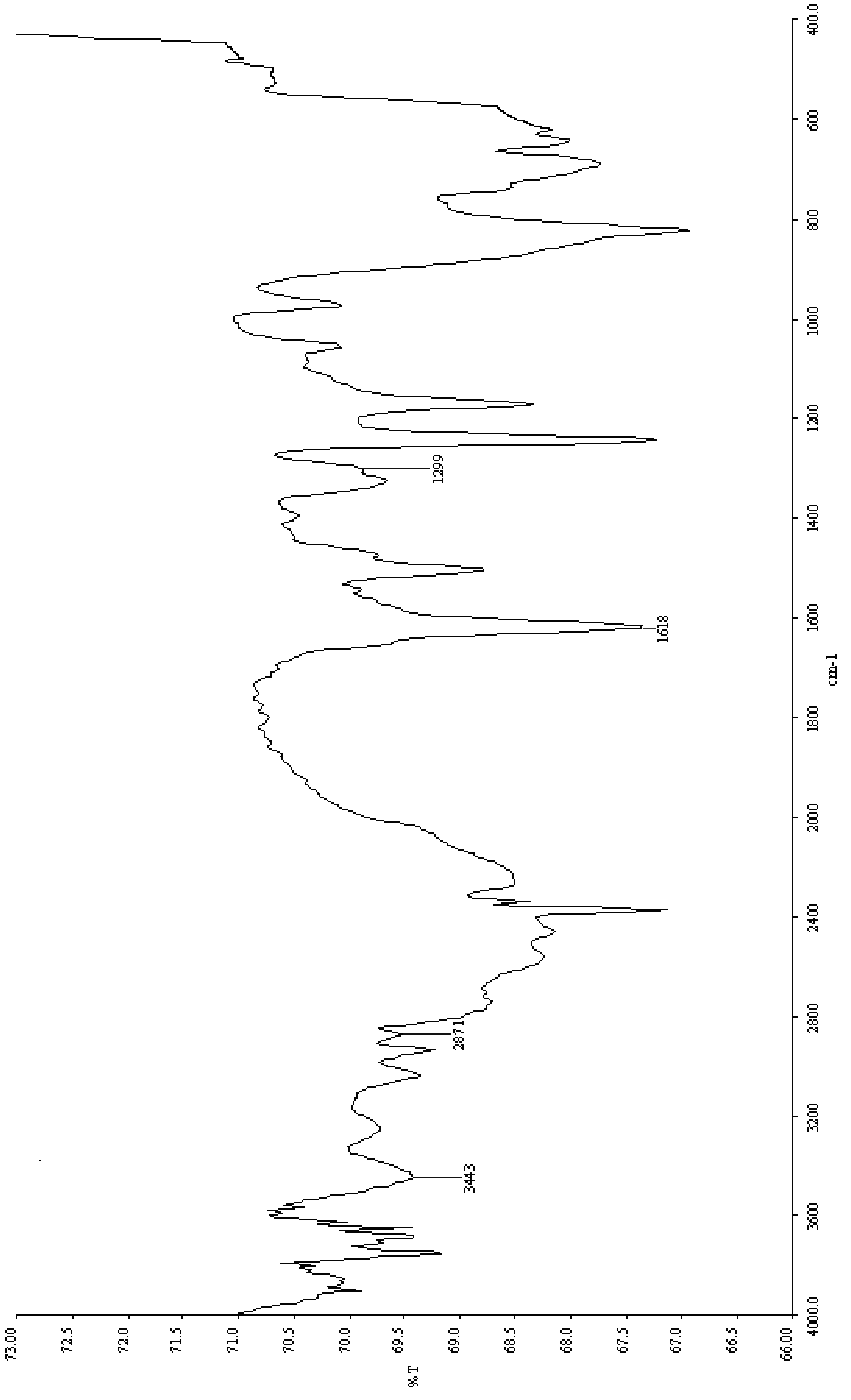

Figure 4.28 The infrared spectrum of H_2L^4

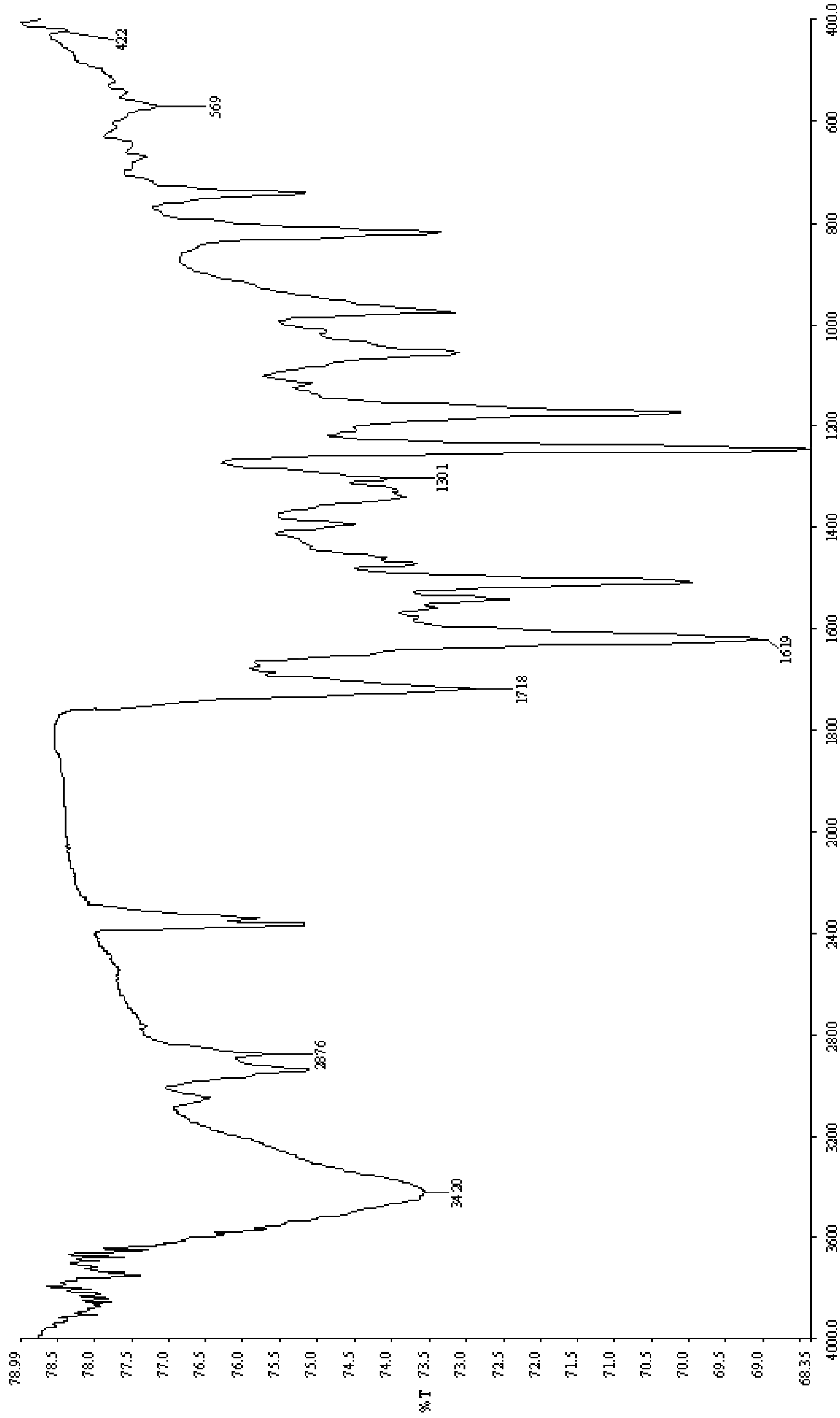

Figure 4.29 The infrared spectrum of 10, $[(\mu\text{-CO})_2Cr_2(\eta^4\text{-}H_2L^4)_2]$

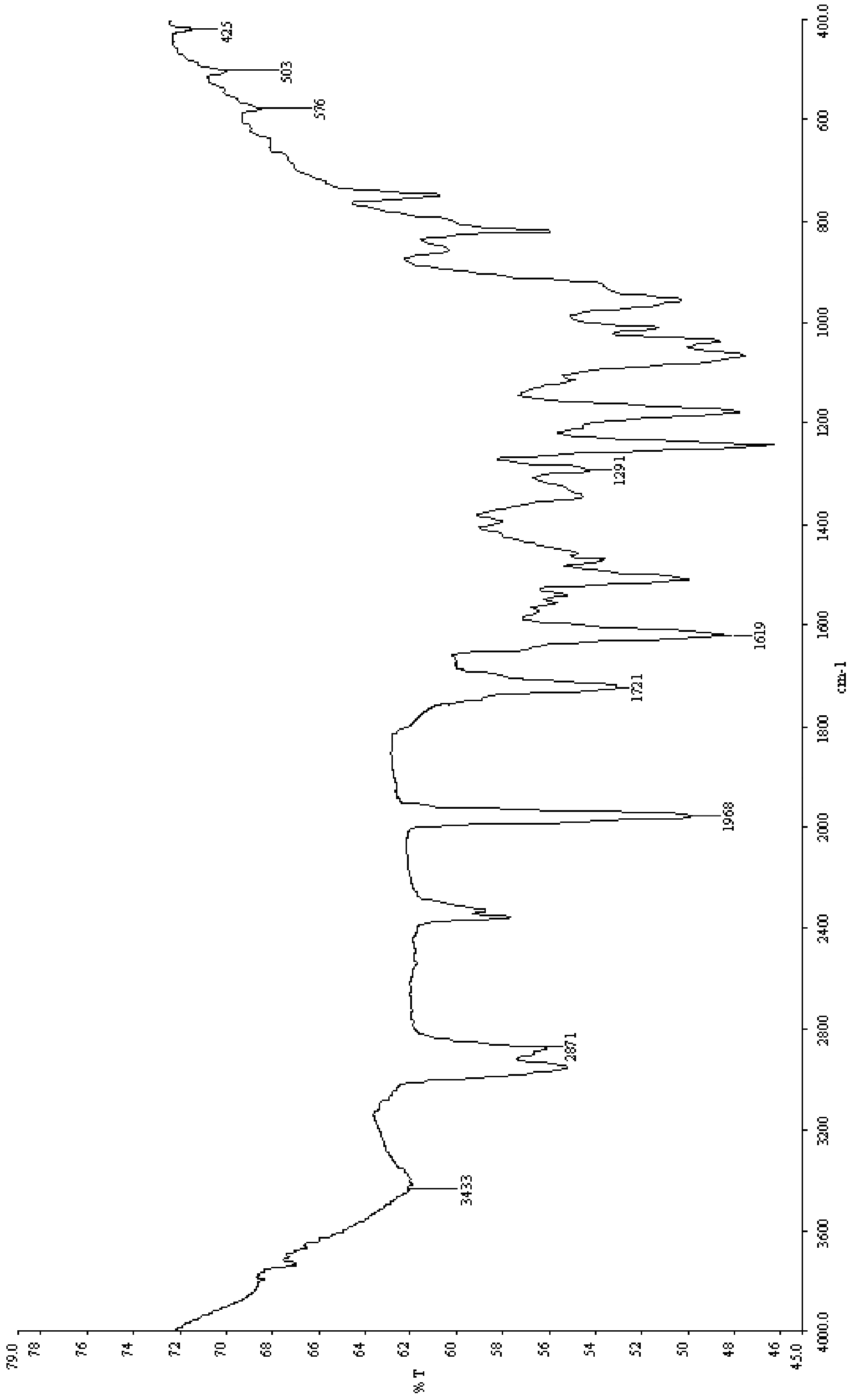

Figure 4.30 The infrared spectrum of 11, $[(\mu\text{-CO})Mo_2(CO)_2(\eta^4\text{- }H_2L^4)_2]$

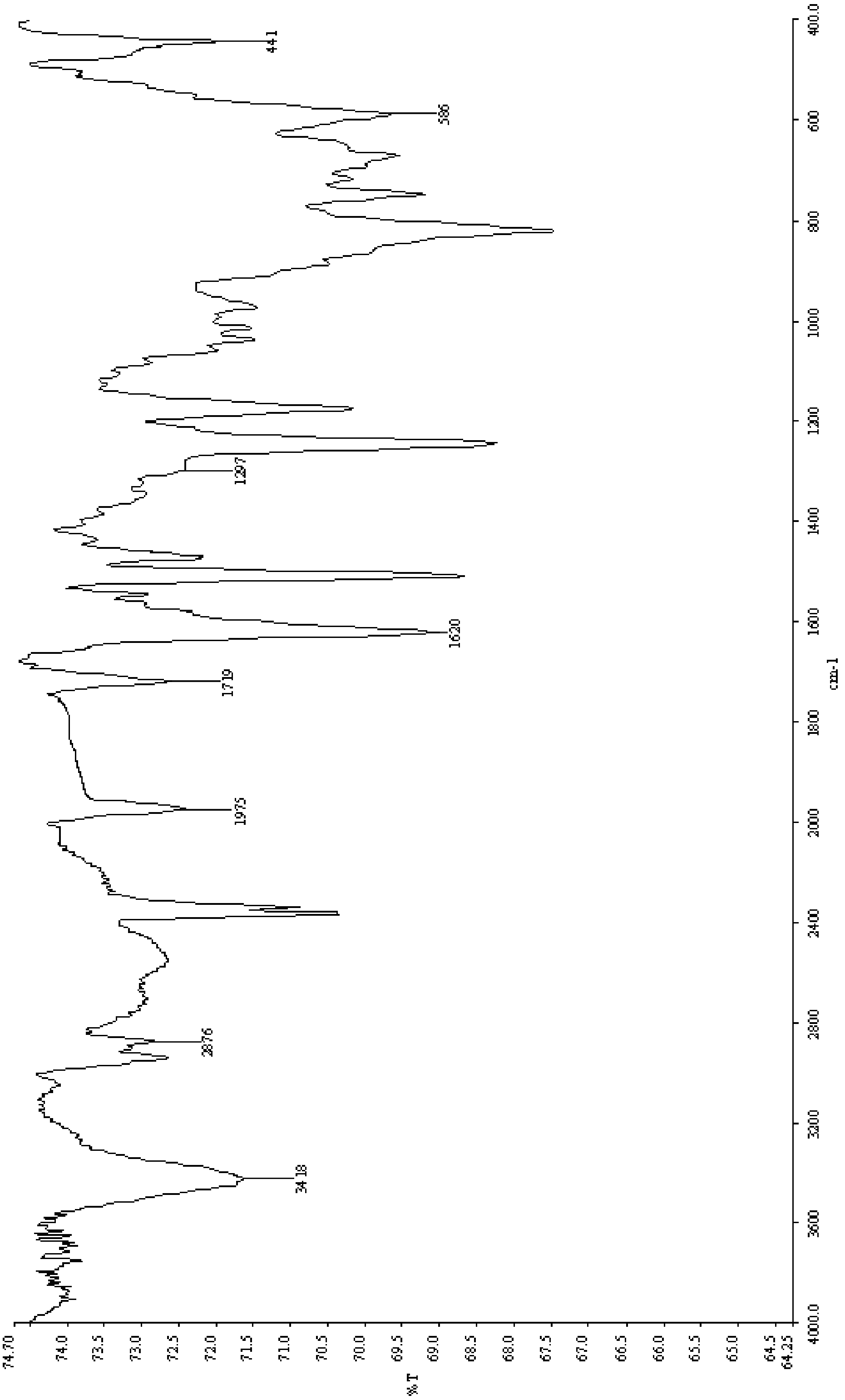

Figure 4.31 The infrared spectrum of 12, $[(\mu\text{-CO})W_2(CO)_2(\eta^4\text{- } H_2L^4)_2]$

4.3.2.3 ^{1}H NMR Spectra

^{1}H NMR spectra data in DMSO-d_6 solutions of complexes **8-12** are collected in Table 4.9 (Karahan, Köse, Subasi, & Temel, 2008). The NMR spectra are given in Figures 4.32-4.38. The ^{1}H NMR spectrum of the chromium complex of $\mathbf{H_2L^3}$ could not be obtained since this complex was not dissolved in DMSO-d_6 completely. The ^{1}H NMR spectra of the other metal complexes of $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ were obtained.

Generally the ^{1}H NMR values of the complexes exhibit shifts to down-field compare with that of ligands. HC=N imine proton signals of $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ are at 9.63 and 9.62 ppm respectively. In the ^{1}H NMR spectra of complexes **8-12** imine proton signals are at 9.61-9.67 ppm. The down-field shift of the HC=N imine proton may be related to a decrease in the π-electron density in the C=N bond with complex formation in **7-12**. Also Ar-OH and O-CH_2 signals in the complexes have been observed at 3.27-3.42 ppm and 4.12-4.43 ppm respectively while the signals of $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ are at 3.29, 3.27 ppm and 4.40, 4.10 ppm for Ar-OH and O-CH_2. These changes of Ar-OH and O-CH_2 signals in the complexes have indicated that $\mathbf{H_2L^3}$ and $\mathbf{H_2L^4}$ ligands coordinate to the metal atoms *via* both azomethines' nitrogen and oxygen donor atoms, behaving like tetradentate neutral ligand.

Table 4.9 ^{1}H NMR data for the ligands and metal complexes in DMSO-d_6 solution [a]

Complex	Ar-OH	O-CH_2	Ar-H	HC=N
$\mathbf{H_2L^3}$ [b]	3.29, s, 2H	4.40, s, 4H	7.02-8.49, m, 20H	9.63, s, 2H
$\mathbf{H_2L^4}$ [b]	3.27, s, 2H	4.10, s, 4H	7.00-8.48, m, 20H	9.62, s, 2H
8	3.33, s, 2H	4.43, s, 4H	7.05-8.52, m, 20H	9.67, s, 2H
9	3.42, s, 2H	4.40, s, 4H	7.01-8.47, m, 20H	9.61, s, 2H
10	3.28, s, 2H	4.12, s, 4H	7.01-8.47, m, 20H	9.62, s, 2H
11	3.27, s, 2H	4.14, s, 4H	7.00-8.50, m, 20H	9.67, s, 2H
12	3.39, s, 2H	4.30, s, 4H	7.06-8.52, m, 20H	9.67, s, 2H

[a] δ in ppm [b] Taken from (Temel, İlhan, Şekerci, & Ziyadanoğulları, 2002)

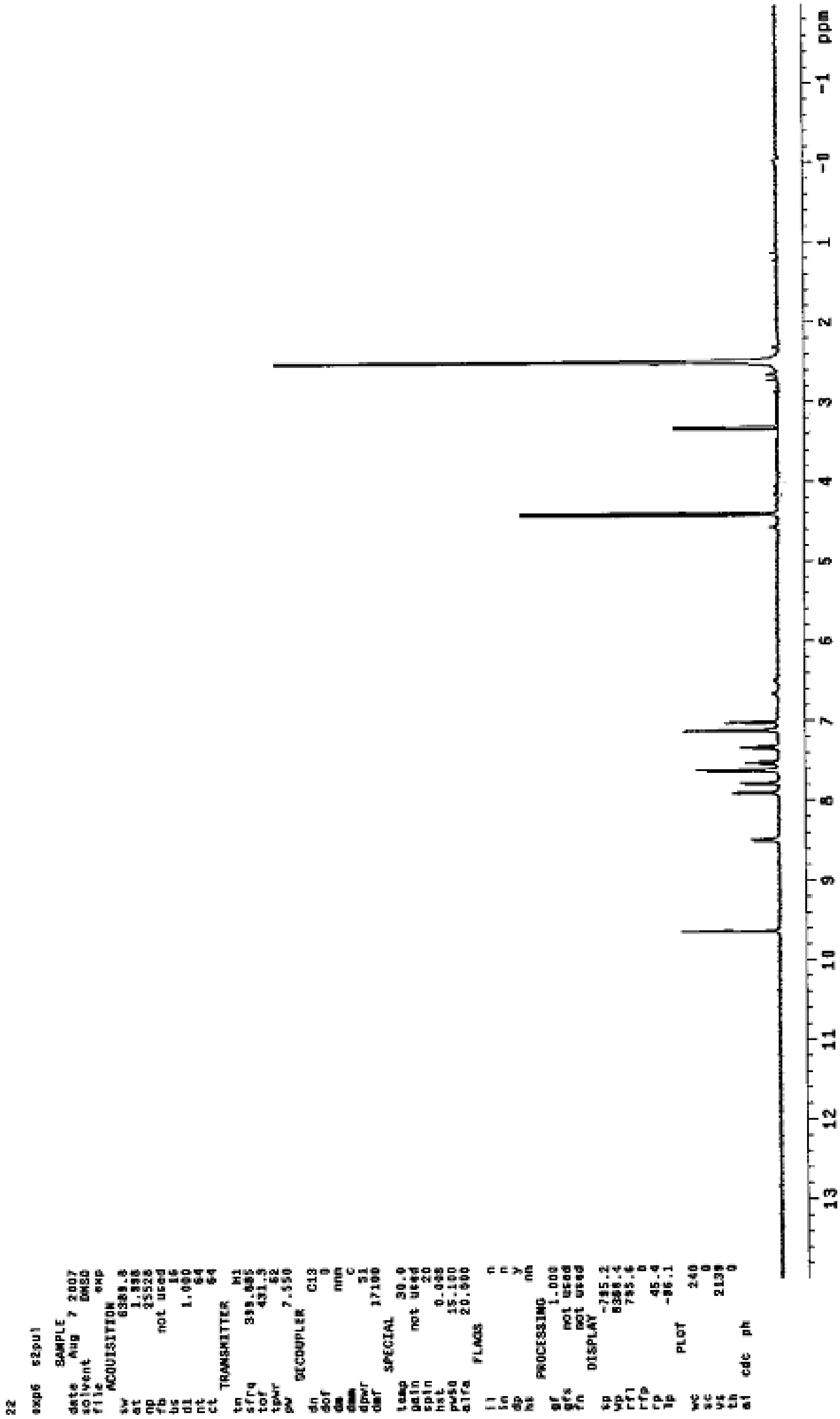

Figure 4.32 The ^1H NMR spectrum of H_2L^3

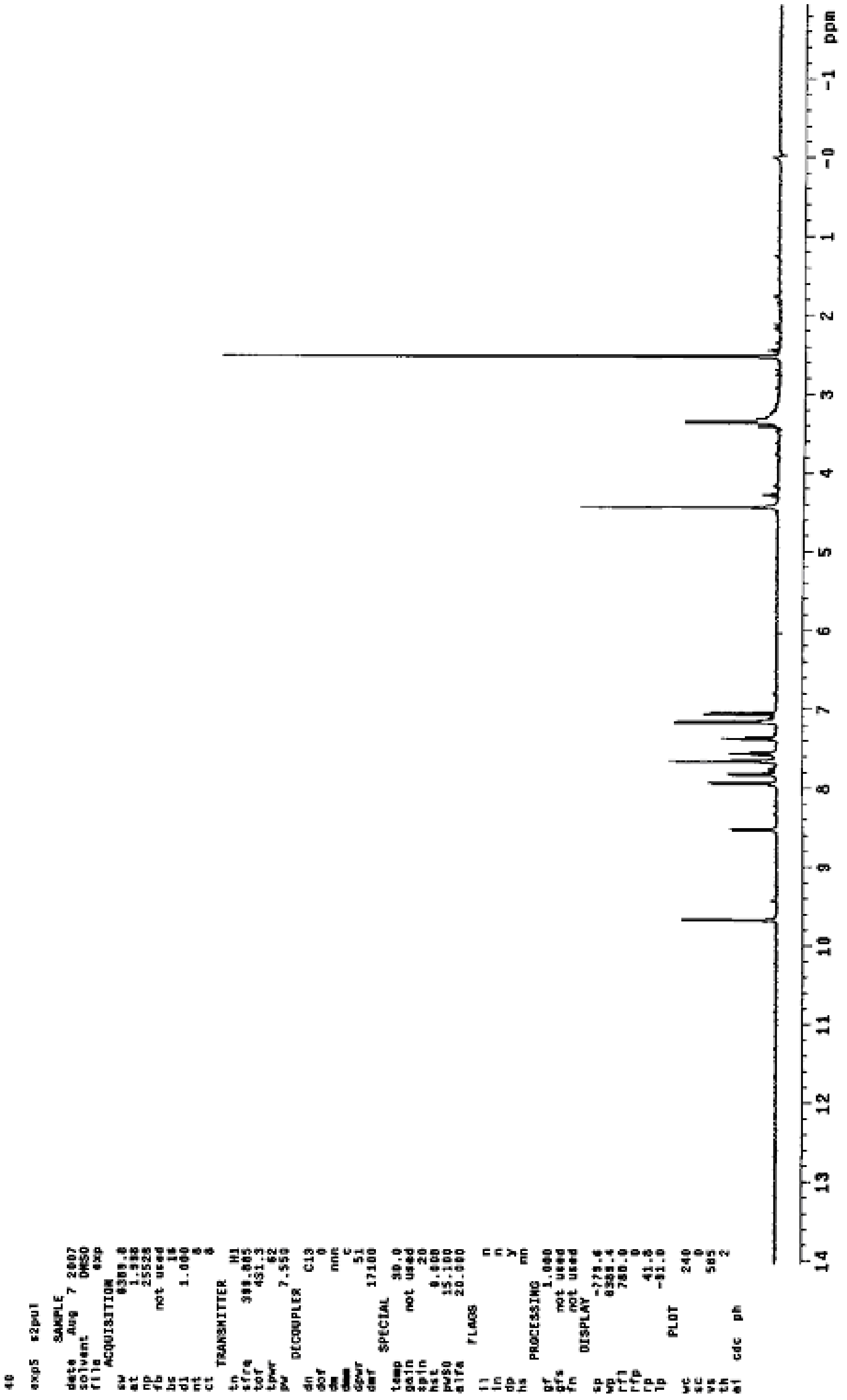

Figure 4.33 The ^1H NMR spectrum of 8, $[(\mu\text{-CO})Mo_2(CO)_2(\eta^4\text{- }H_2L^3)_2]$

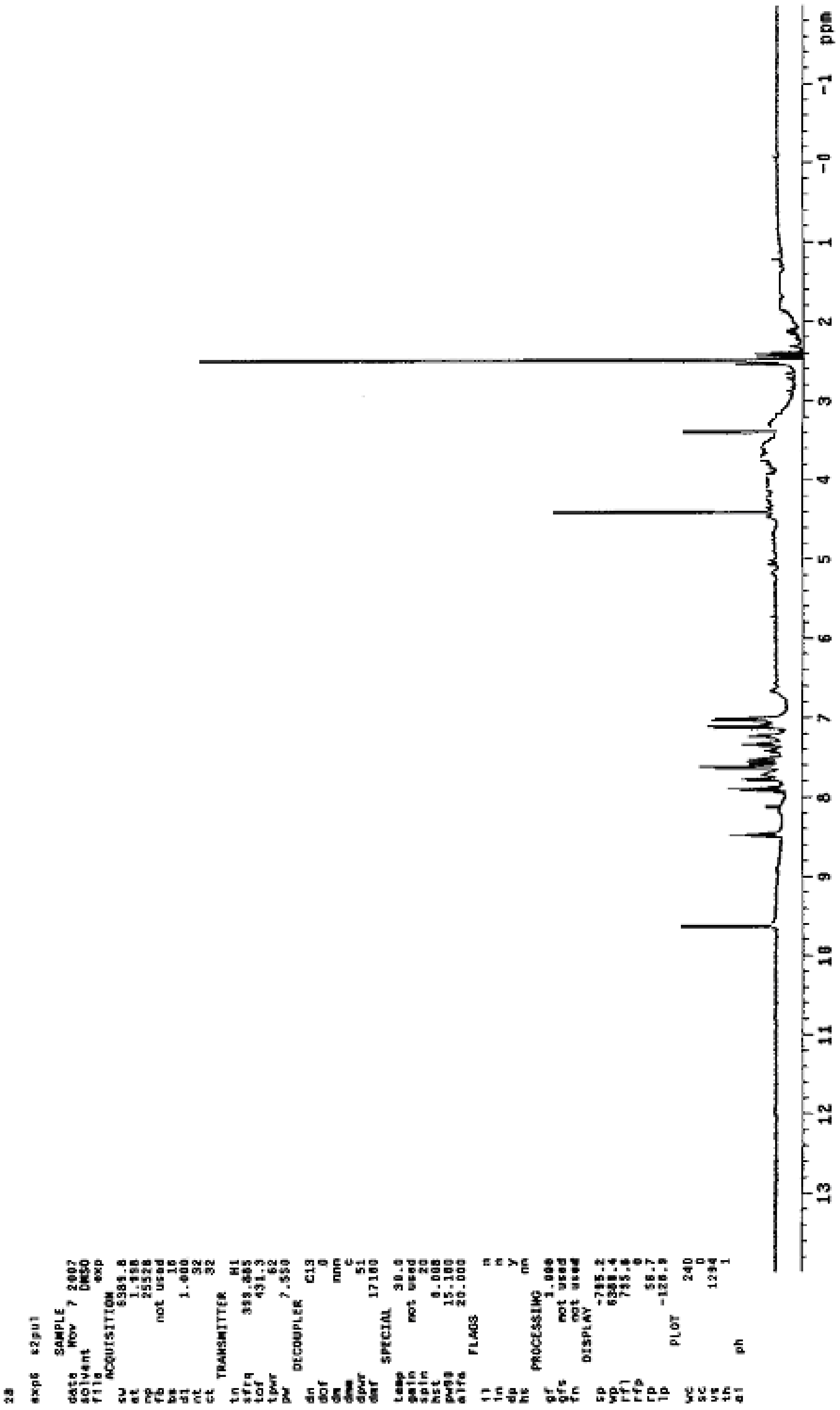

Figure 4.34 The ^{1}H NMR spectrum of 9, $[(\mu\text{-CO})W_2(CO)_2(\eta^4\text{- }H_2L^3)_2]$

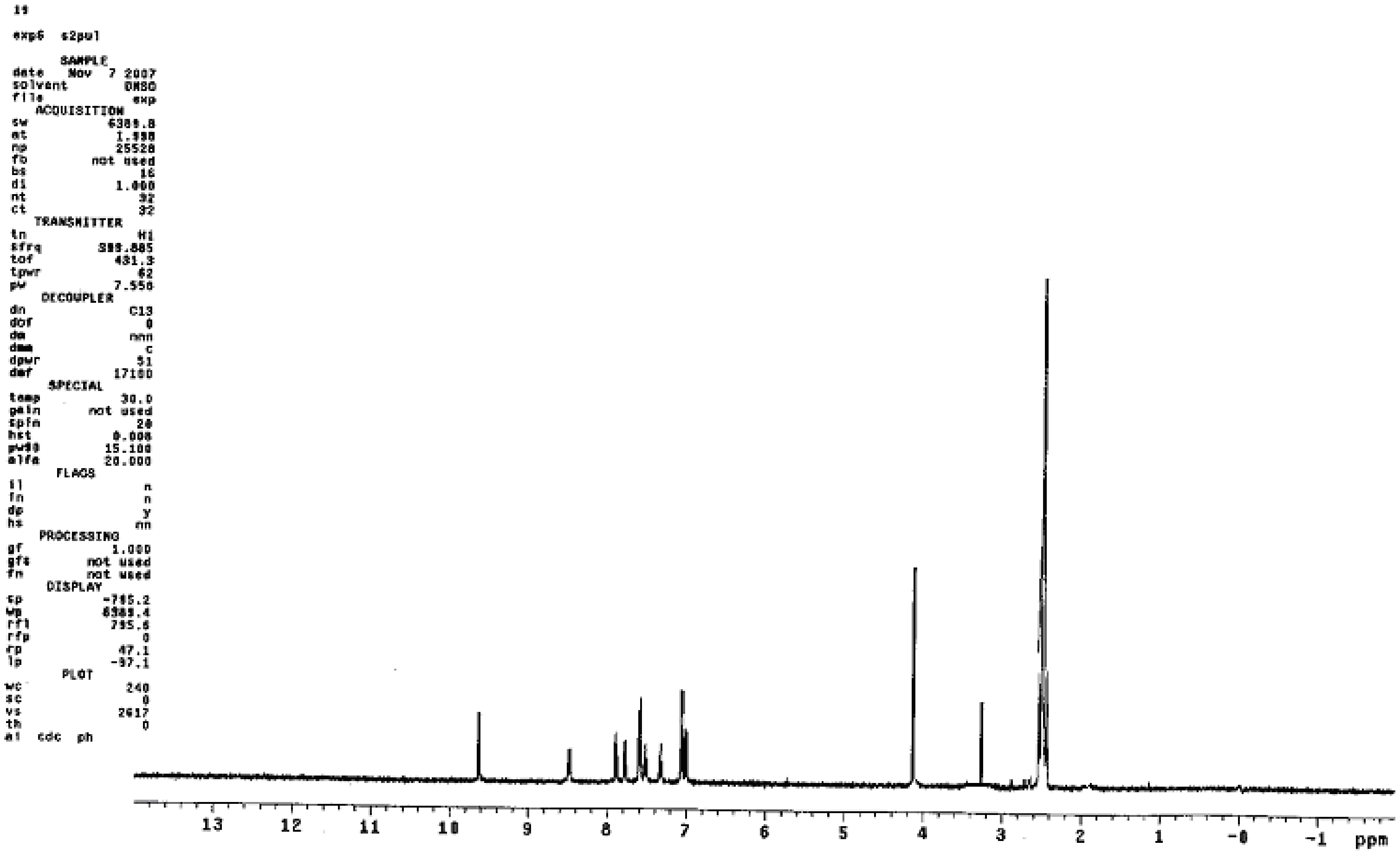

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Figure 4.35 The ^1H NMR spectrum of H_2L^4

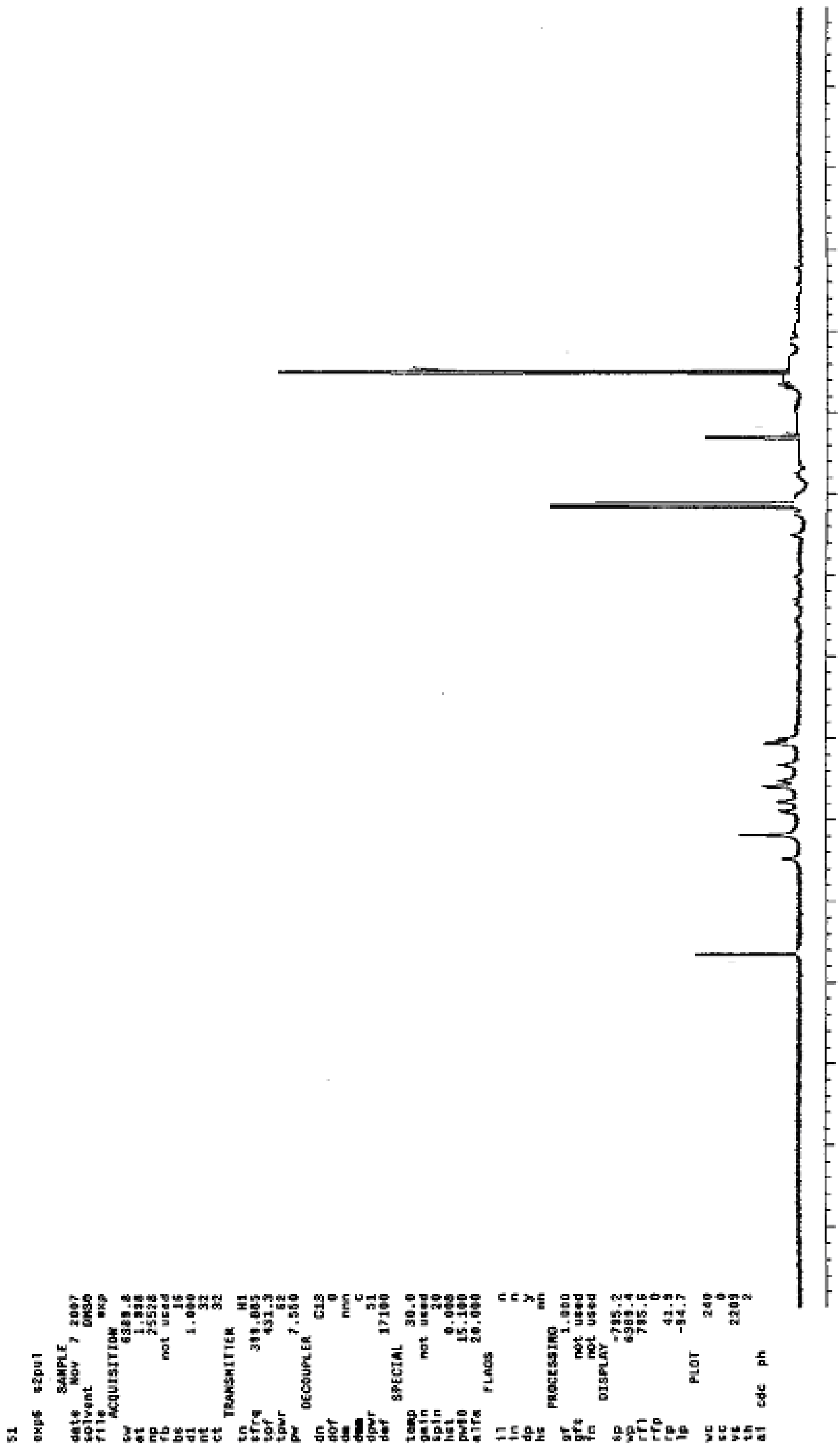

Figure 4.36 The ^{1}H NMR spectrum of 10, $[(\mu\text{-CO})_2Cr_2(\eta^4\text{-}H_2L^4)_2]$

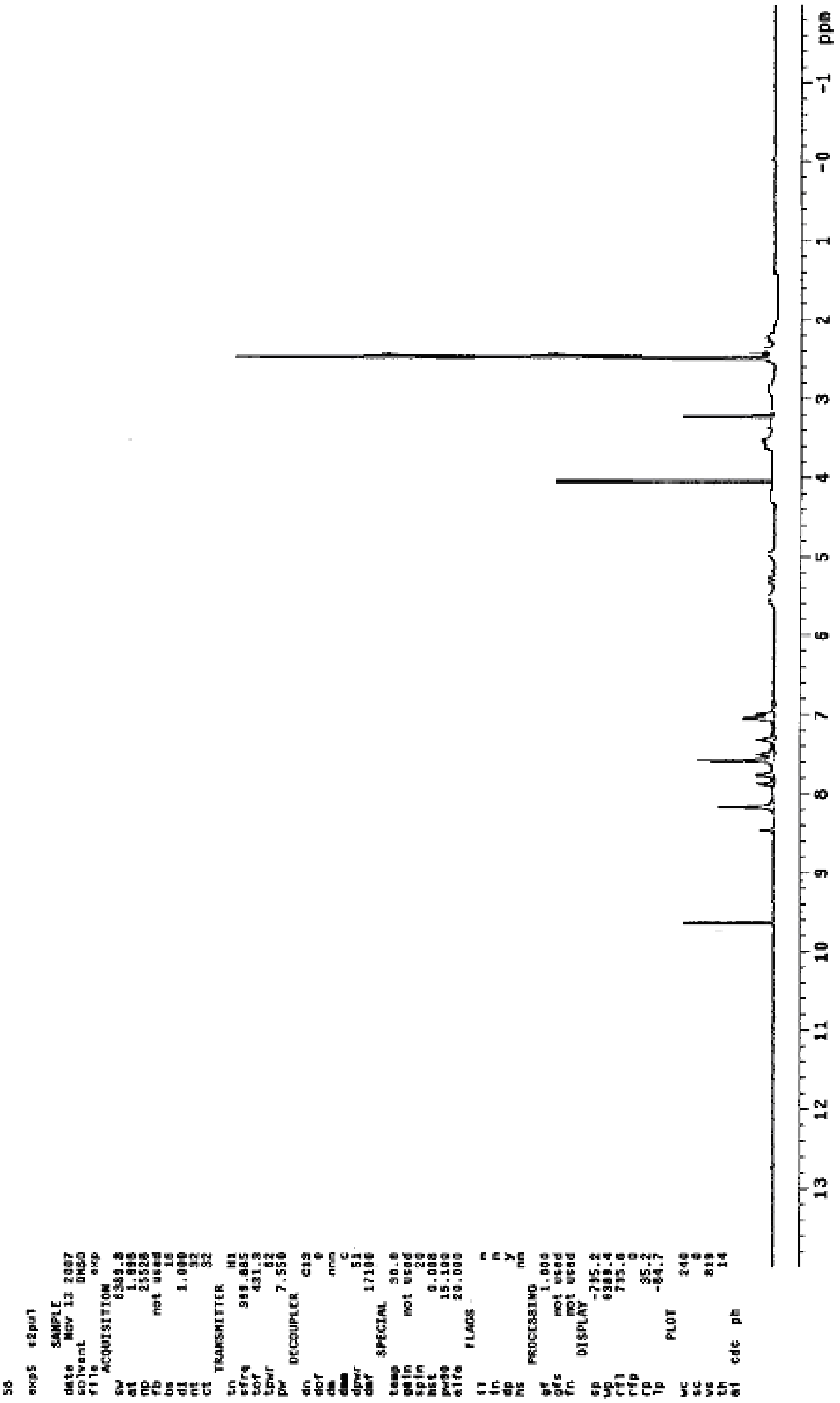

Figure 4.37 The ^{1}H NMR spectrum of 11, [(μ-CO)$Mo_2(CO)_2(\eta^4$- $H_2L^4)_2$]

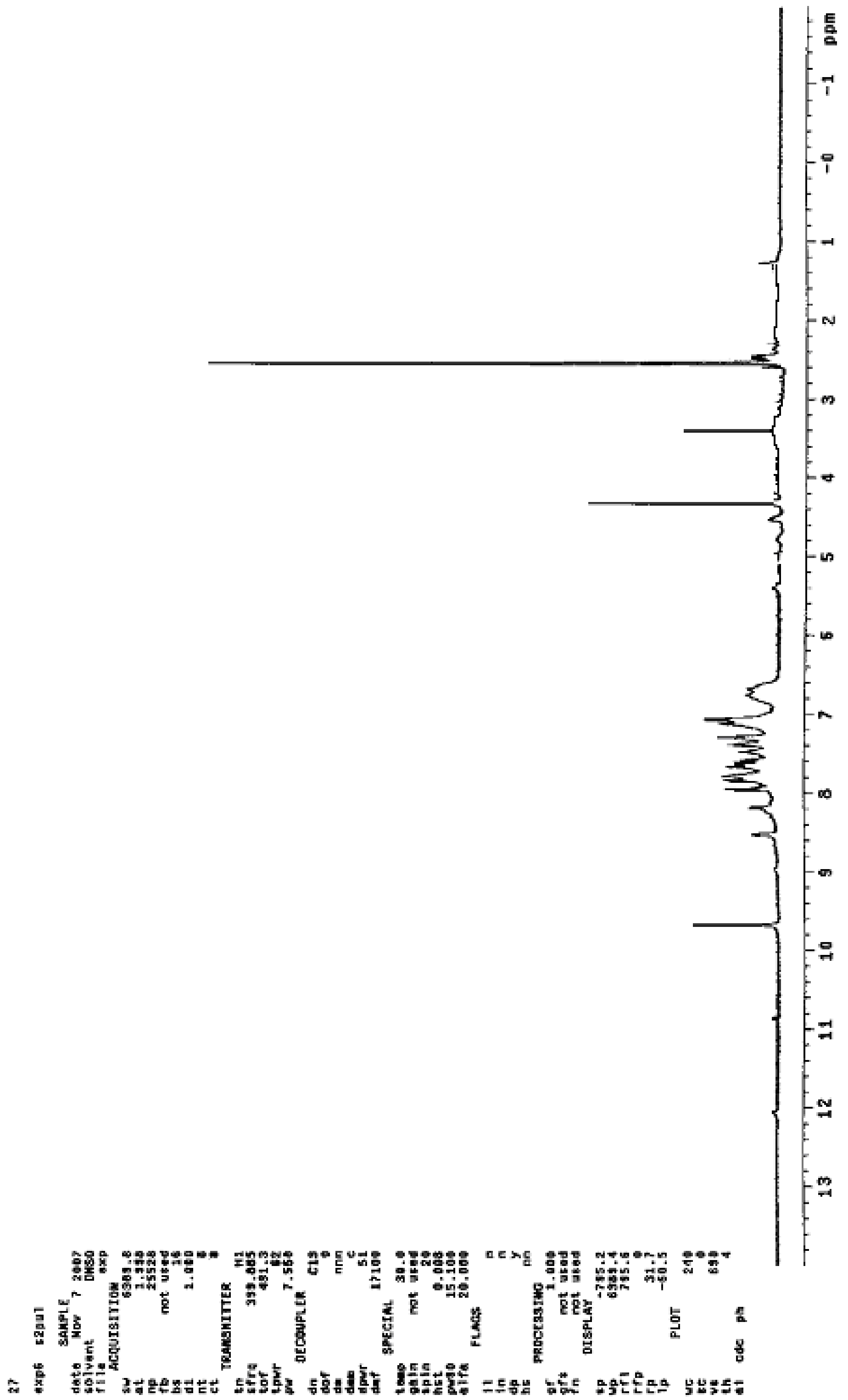

Figure 4.38 The ^{1}H NMR spectrum of 12, [(μ-CO)W_2(CO)$_2$(η^4- H_2L^4)$_2$]

4.3.2.4 Mass Spectra

LC-Mass spectra data for complexes **7-12** are listed in Table 4.10 (Karahan, Köse, Subasi, & Temel, 2008) and show fragmentation *via* successive loss of CO groups and organic ligands. The structures of complexes **7-12** are consistent with the obtained mass fragments containing nitrogen, oxygen and two central metal atoms. The LC-Mass studies of the complexes are entirely in accord with their IR and ^1H NMR spectroscopic studies. The spectra of complexes **7-12** are given in Figures 4.39-4.44.

Table 4.10 LC-Mass spectra data for the complexes

Complex	M.W.	Relative intensities of the ions m/z
7	1264	284 (13), [$Cr_2C_2H_4N_4O_6$]; 256 (19) [$Cr_2C_2H_4N_4O_6$-(CO)]; 228 (4), [$Cr_2CH_4N_4O_5$-(CO)]; 200 (8), [$Cr_2H_4N_4O_4$-2(N)]; 114 (1), [$Cr_2H_4N_2O_4$-2(OH)-(Cr)]; 80 (2), [$CrH_2N_2O_2$-2(OH)].
8	1380	399 (50), [$Mo_2C_3H_3N_4O_7$]; 356 (6), [$Mo_2C_3H_3N_4O_7$-(CO)-(N)-(H)]; 298 (3), [$Mo_2C_2H_2N_3O_6$-2(CO)-2(H)]; 270 (4), [$Mo_2N_3O_4$-2(N)]; 256 (1), [Mo_2NO_4-(N)]; 224 (1), [Mo_2O_4-2(O)].
9	1556	572 (2), [$W_2C_3N_4O_7$]; 544 (2), [$W_2C_3N_4O_7$-(CO)]; 498 (1), [$W_2C_2N_4O_6$-(N)-2(O)]; 400 (30), [$W_2C_2N_3O_4$-2(CO)-3(N)]; 200 (3), [W_2O_2-(W)-(O)].
10	1320	330 (9), [$Cr_2C_6H_2N_4O_6$]; 314 (18) [$Cr_2C_6H_2N_4O_6$-(O)]; 286 (30), [$Cr_2C_6H_2N_4O_5$-(CO)]; 258 (30), [$Cr_2C_5H_2N_4O_4$-(CO)]; 230 (10), [$Cr_2C_4H_2N_4O_3$-(C)-(N)-2(H)]; 146 (2), [$Cr_2C_3N_3O_3$-3(O)-3(C)]; 80 (2), [Cr_2N_3-(N)-(Cr)].
11	1436	428 (11), [$Mo_2C_5H_8N_4O_7$]; 388 (6), [$Mo_2C_5H_8N_4O_7$-2(OH)-6(H)]; 314 (28), [$Mo_2C_5N_4O_5$-(CO)-2(O)-(N)]; 286 (41), [$Mo_2C_4N_3O_2$-(CO)]; 258 (39), [$Mo_2C_3N_3O$-(CO)]; 149 (5), [$Mo_2C_3N_3$-(N)-(Mo)]; 125 (1), [MoC_2N_2-2(C)].
12	1612	572 (4), [$W_2C_3N_4O_7$]; 516 (2), [$W_2C_3N_4O_7$-2(CO)]; 428 (14) [$W_2CN_4O_5$-2(O)-2(N)-(CO)]; 414 (2), [$W_2N_2O_2$-(N)]; 214 (23), [W_2NO_2-(W)-(O)]; 200 (2), [WNO-(N)].

For the mass spectral data relative intensities are given in parentheses; probable assignments in square brackets.

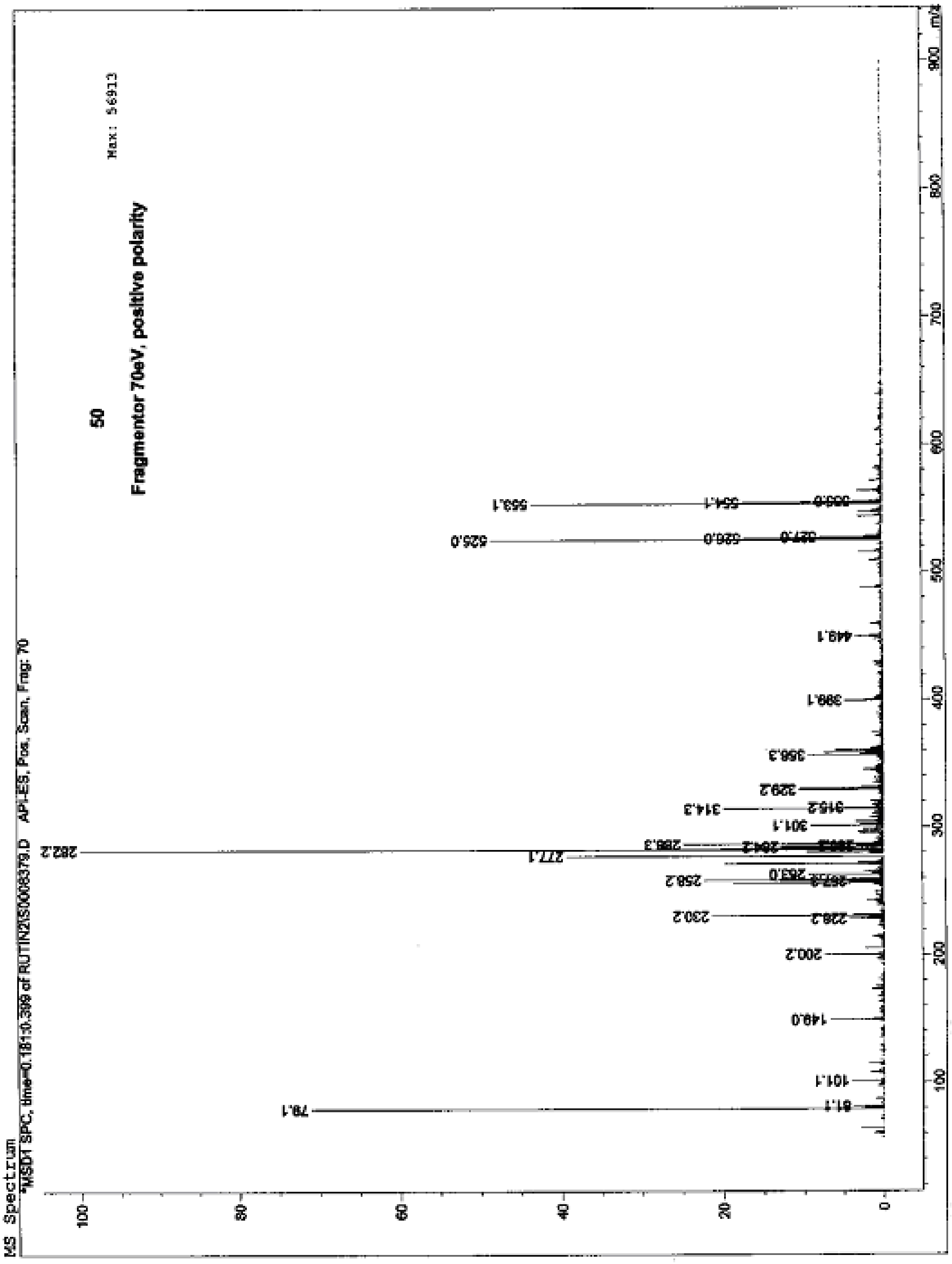

Figure 4.39 The LC-Mass spectrum of 7, $[(\mu\text{-CO})_2Cr_2(\eta^4\text{-}H_2L^3)_2]$

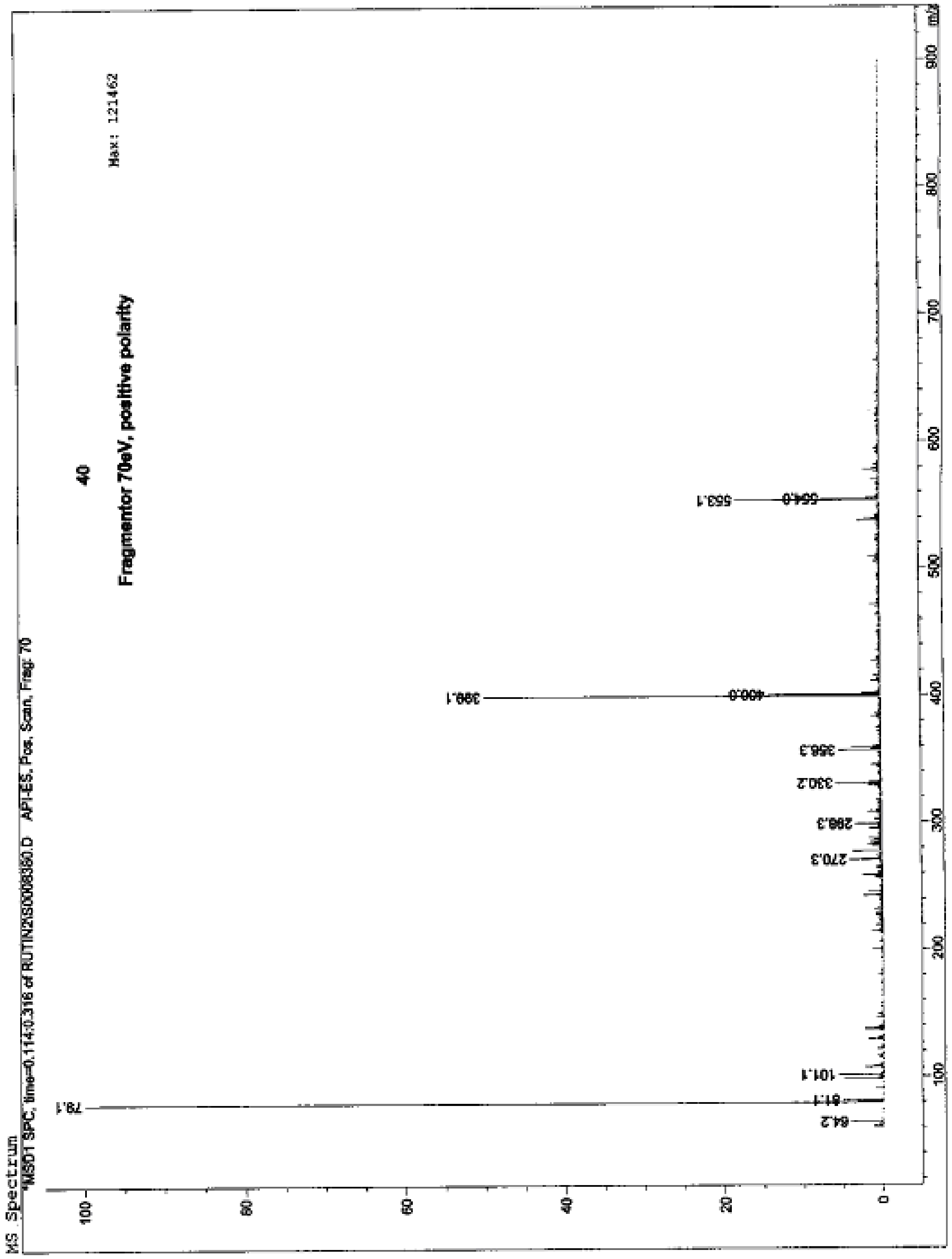

Figure 4.40 The LC-Mass spectrum of 8, $[(\mu\text{-CO})Mo_2(CO)_2(\eta^4\text{-} H_2L^3)_2]$

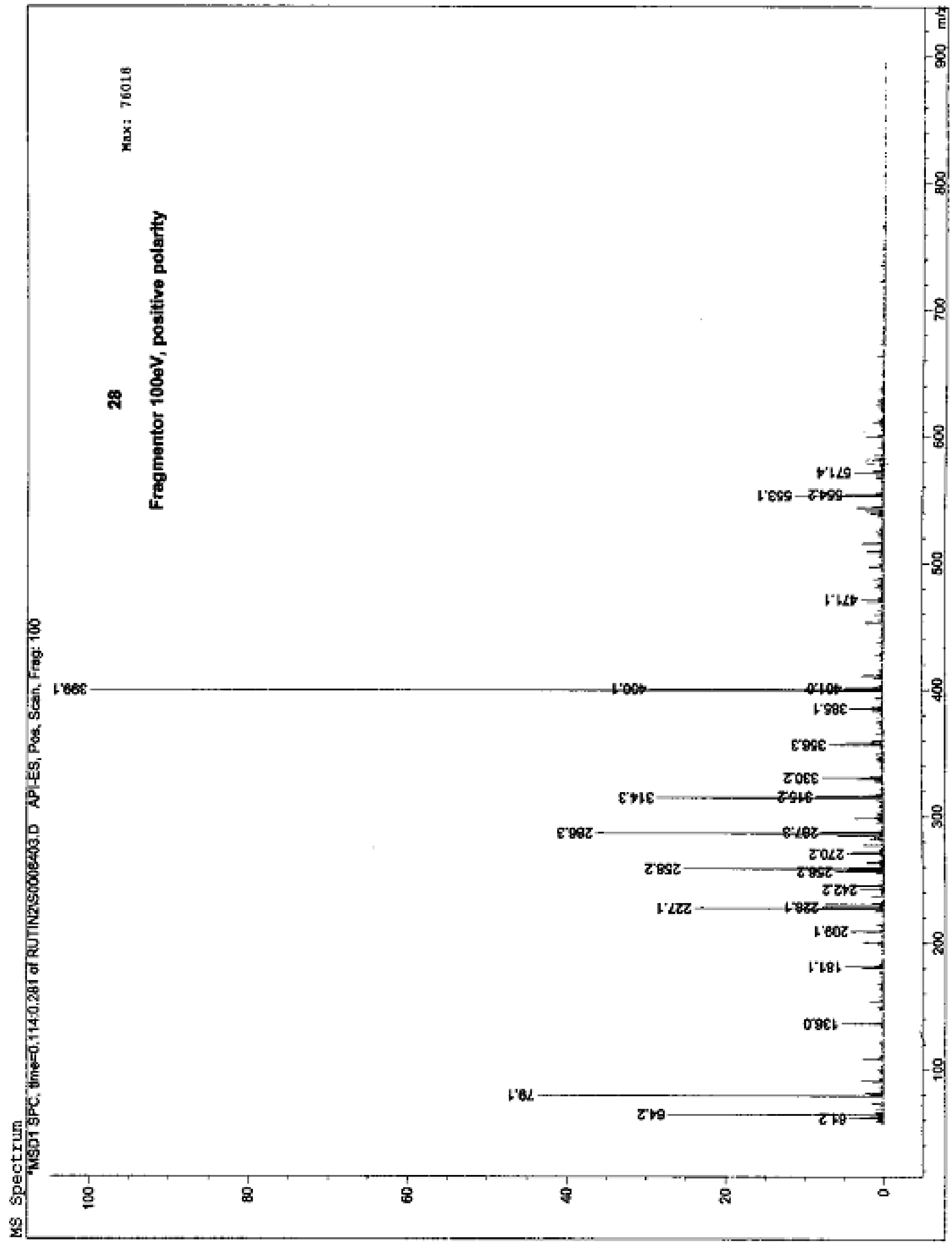

Figure 4.41 The LC-Mass spectrum of 9, $[(\mu\text{-CO})W_2(CO)_2(\eta^4\text{- }H_2L^3)_2]$

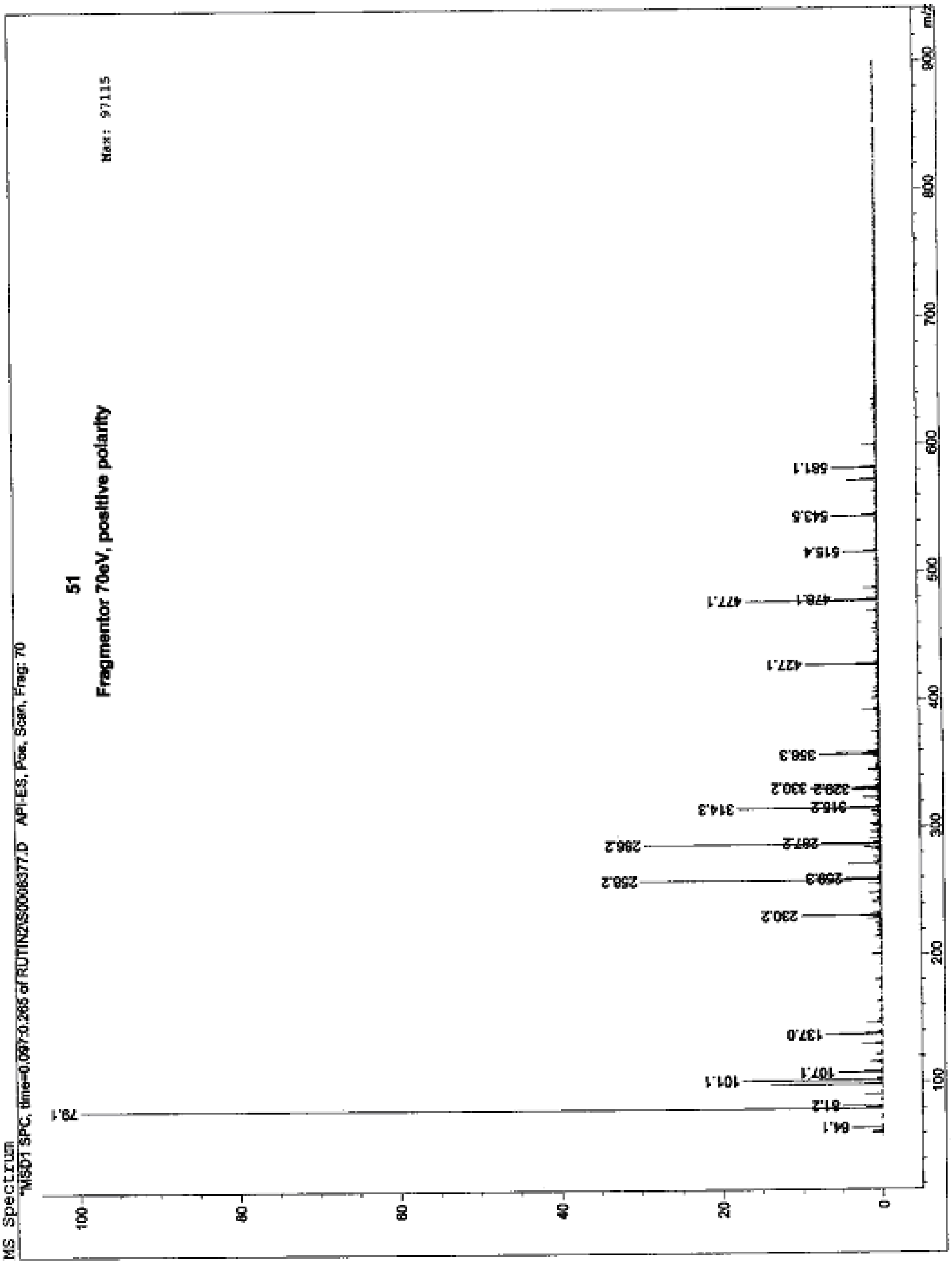

Figure 4.42 The LC-Mass spectrum of 10, $[(\mu\text{-CO})_2Cr_2(\eta^4\text{-}H_2L^4)_2]$

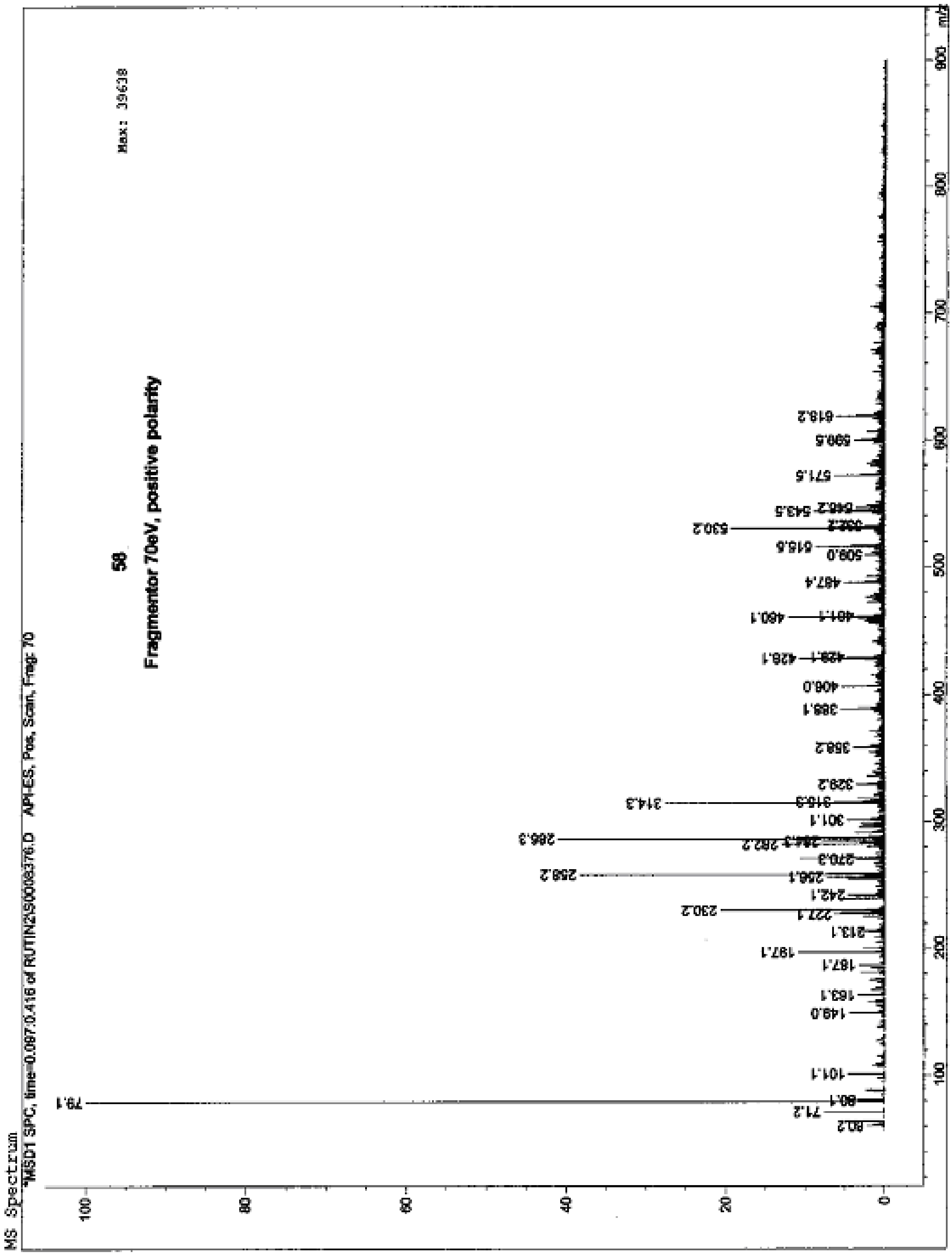

Figure 4.43 The LC-Mass spectrum of 11, $[(\mu\text{-CO})Mo_2(CO)_2(\eta^4\text{- }H_2L^4)_2]$

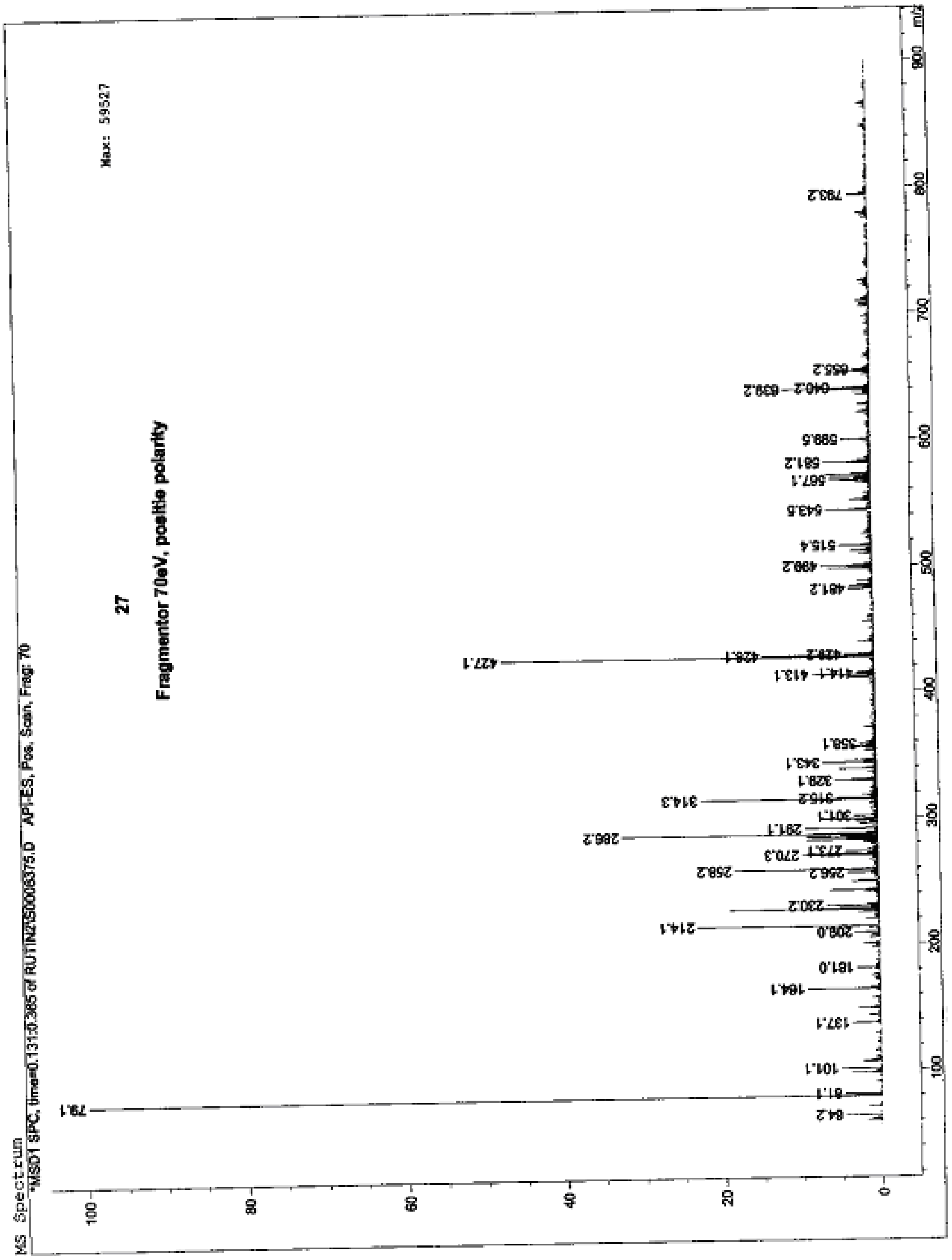

Figure 4.44 The LC-Mass spectrum of 12, [(μ-CO)$W_2(CO)_2(\eta^4$- $H_2L^4)_2$]

4.3.2.5 Magnetic Susceptibility Studies

Magnetic susceptibility measurements show that **7-12** complexes were diamagnetic. These complexes have M(0) [M= Cr, Mo, W] with a low-spin d^6 configuration. Such diamagnetism might arise from further splitting of the d orbitals in the low symmetry complexes, i.e., $d^2_{xy}\ d^2_{xz}\ d^2_{yz}\ d^0_{x2-y2}\ d^0_{z2}$.

According to the 18 electron rule two metal atoms must interact to each other to stabilize the complexes **7-12**. Cr = Cr double bond is required to give each Cr atom the favored 18-electron rare gas configuration if the single terminal CO group is a normal two-electron donor and bridging CO group is a one-electron donor in **7** and **10**. In **8**, **9**, **11**, **12** complexes a single bond between M atoms (M= Mo, W) is enough to reach 18-electron rare gas configuration.

CHAPTER FIVE

CONCLUSIONS

Polydentate Schiff bases containing oxygen, nitrogen and sulphur donor atoms are useful for the synthesis of transition metal complexes which play an important role in biological systems. Such classes of ligands are also found to provide catalytic characteristics.

The main aim of this study was synthesis of different group 6 metal carbonyl complexes by use of different oxygen, nitrogen and sulphur donor Schiff base ligands. For this purpose, photochemical reactions were used since they are frequently very selective when thermal reactions either do not proceed or produce unwanted side-products. After the synthetic pathway, synthesized complexes were characterized by spectroscopic and spectrometric methods. All complexes given in this thesis study were synthesized under an oxygen free nitrogen atmosphere using Schlenk techniques. UV irradiations were performed with a medium-pressure 125 W mercury lamp through a quartz-walled immersion well reactor, which was cooled by circulating water.

We investigated twelve new complexes **1–12** which were prepared for the first time, by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with tetradentate Schiff base ligands containing [O,N,N,O] and [S,N,N,S] donor atoms. The complexes were characterized by elemental analysis, LC- mass spectrometry, magnetic studies, FTIR and ^1H NMR spectroscopy.

Six complexes, $[M_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^1)]$, [M= Cr; **1**, Mo; **2**, W; **3**] and $[M_2(CO)_6(\mu\text{-}CO)(\mu\text{-}L^2)]$, [M= Cr; **4**, Mo; **5**, W; **6**] were synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with thio Schiff base ligands, *N,N′*-bis(2-aminothiophenol)-1,4-bis(2-carboxaldehydephenoxy)butane **(H_2L^1)** and *N,N′*-bis(2-aminothiophenol)-1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane **(H_2L^2)**.

Other new complexes **7-12**, $[(\mu\text{-CO})_2Cr_2(\eta^4\text{-}H_2L^3)_2]$, **7**; $[(\mu\text{-CO})M_2(CO)_2(\eta^4\text{-}H_2L^3)_2]$, [M= Mo; **8**, W; **9**]; $[(\mu\text{-CO})_2Cr_2(\eta^4\text{-}H_2L^4)_2]$, **10** and $[(\mu\text{-CO})M_2(CO)_2(\eta^4\text{-}H_2L^4)_2]$, [M= Mo; **11**, W; **12**] were synthesized by the photochemical reactions of photogenerated intermediate, $M(CO)_5THF$ (M = Cr, Mo, W) with two oxygen and nitrogen donor Schiff base ligands, *N*,*N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*p*-aminophenoxy)ethane **(H_2L^3)** and *N*,*N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,4-bis(*p*-aminophenoxy)butane **(H_2L^4)**.

The spectroscopic studies showed that **H_2L^1** and **H_2L^2** ligands were converted to benzothiazole derivatives **L^1** and **L^2**, after UV irradiation and coordinated to the central metal as bridging ligands *via* the central azomethine nitrogen and sulphur atoms in **1-6**. Also **H_2L^3** and **H_2L^4** ligands were coordinated to the metal as tetradentate ligands coordinating via their imine N and O donor atoms in complexes **7-12**.

One of the aims of this work was to carry out cyrstallization studies. In view of this, the benzothiazole derivative **L^1** of **H_2L^1** was obtained as a crystal and crystallographically characterized.

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