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Reaction of group 6 metal carbonyls with salicylaldehyde *p*-hydroxybenzoylhydrazone

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ABSTRACT

Thermal reaction of salicylaldehyde-*p*-hydroxybenzoylhydrazone ($sbhH_2$) with $Cr(CO)_6$ in absolute EtOH under reduced pressure gave the oxodicarbonylchromium complex, $CrO(CO)_2(sbhH_2)$. When the reaction was carried out in MeOH in day sunlight, the oxochromium complex $CrO(sbhH_2)_2$ was isolated. Reflux of $sbhH_2$ with molybdenum hexacarbonyl in absolute EtOH in either air or under reduced pressure yielded the bis-derivative $Mo(sbhH)_2$. However, When the reaction proceeded in sunlight in methanol, the dioxomolybdenum complex $MoO_2(sbh)$ was isolated. $W(CO)_6$ reacted with $sbhH_2$ in ethanol to give a dinuclear complex with a molecular formula $W_2O_4(sbh)_2$. The molecular structures of the complexes were determined based on elemental analysis, vibrational (infrared and Raman), ^{1}HNMR and mass spectra. It was proved that the hydrazone coordinates via the hydrazone or the azine forms.

INTRODUCTION

Hydrazones were extensively investigated due to their potential applications as antiviral or anti-inflammatory agents either in the free or metal complexed states[1,2]. Hydrazones are also interesting chelating agents[3] and their derivatives are used as fungicides and in the treatment of diseases such as tuberculosis and mental disorder[4]. Aroylhydrazones constitute important classes of organic compounds. The interest for these compounds may arise owing to their biological activities, strong tendency to chelate transition metals[5], lanthanide[6] and main group metals, forming complexes with the aroylhydrazone acting as a neutral or mononegative bidentate ligand, or even as a dianionic ligand depending on the aroyl substituents and the reaction conditions[7].

The metal hexacarbonyls of group VI are extremely useful intermediates for the preparation of organometallic compounds of chromium, molybdenum and tungsten. Most of the reactions involve nucleophilic substitution of one or more CO groups with other ligands[8].

Various metal carbonyl derivatives play an important role in homogenous catalysis involving hydrogenation, hydroformylation, carbonylation and oxo transfer reactions[9]. Reactions of metal carbonyls with hydrazones are relatively less studied[10]. So in this work, the results obtained from the reactions of $M(CO)_6$ (M = Cr, Mo and W) with salicylaldehyde *p*-hydroxybenzoyl hydrazone ($sbhH_2$) are given.

EXPERIMENTAL

Reagents

The metal carbonyls $Mo(CO)_6$, $Cr(CO)_6$ and $W(CO)_6$ were purchased from Aldrich. They were of high purity and were used without further purification. Salicylaldehyde and *p*-hydroxybenzoylhydrazine were supplied from Fluka. All solvents were of analytical reagent grade and were purified by distillation before use. TABLE 1 gives both the elemental analysis and mass spectroscopic data of the studied complexes.

TABLE 1 : Microanalytical, mass and ^{1}HNMR data of the complexes

Compound	% calculated (found)			Mass data		^{1}HNMR (ppm)a
	C	H	N	MW	m/z	
sbhH$_2$	65.63 (65.20)	4.69 (4.38)	10.94 (10.71)	256	[L]$^+$	6.86-7.84m, 8.59 s,10.05s, 11.37s,b,11.80s
CrO(CO)$_2$(sbhH$_2$)	44.40 (44.03)	3.16 (3.05)	7.37 (7.27)	380	336 [P-(CO+O]$^+$	-----------
CrO(sbhH$_2$)$_2$	57.94 (57.72)	4.13 4.05	9.65 (9.56)	580	576 [P-4H]$^+$	------------
Mo(sbhH)$_2$	55.0 55.3	3.63 3.49	9.24 9.18	606	353 [P-L]	6.76-7.86m, 8.59 s,8.83s, 11.8 b
MoO$_2$(sbh)	43.48 43.64	2.62 2.51	7.33 7.27	382	382 [P]$^+$	6.85-7.86m, 8.85 s,10.20 s,
W$_2$O$_4$(sbh)$_2$	35.85 35.65	2.13 2.10	5.97 5.92	940	469 [1/2P]$^+$	6.86-7.90m, 8.84 s,10.26s,

a: m multiplet, s singlet, b broad

Instruments

The infrared measurements were performed on a Bruker FT-IR spectrometer with the use of KBr. The Raman measurements for the solid samples were performed on a Nicolet FT-Raman spectrometer equipped with a YAG laser of wavelength 1064 nm using a laser power of *ca.* 200 mW. The nuclear magnetic resonance measurements were carried out on a Spectrospin–Varian Hg 300 MHz NMR spectrometer. The samples were dissolved in $(CD_3)_2SO$ using tetra-methylsilane (TMS) as an internal reference. The mass spectroscopic measurements were performed on a Finnigan MAT SSQ 7000 spectrometer. Elemental analyses were carried out on a Perkin Elmer 2400 CHN elemental analyzer. The Magnetic susceptibilities of the paramagnetic complexes in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. Diamagnetic corrections were made by Pascal's constant and $Hg[Co(SCN)_4]$ was used as a calibrant.

Synthesis of salicylaldehyde-p-hydroxybenzoylhydrazone (sbhH$_2$)

A mixture of salicylaldehyde (6.0 cm^3, 0.05 mol) and *p*-hydroxybenzoylhydrazine (7.0 g, 0.05 mol) in 50 ml absolute EtOH was heated to reflux on a water bath for 3 hrs. The product was filtered off as yellow solid, washed with EtOH, recrystallized from absolute EtOH to give faint yellow crystals (yield; 82.0 %, m.p. 235°C).

Synthesis of the complexes

Synthesis of CrO(CO)$_2$(sbhH$_2$)

$Cr(CO)_6$ (0.10 g, 0.45 mmol) and sbhH$_2$ (0.12 g, 0.45 mmol) were mixed together in a sealed tube containing *ca*. 20 mL absolute ethanol. The mixture was degassed and then heated for 48 hrs. The colour of the reaction mixture was turned from colourless to brown colour. The reaction mixture was then cooled and the solvent was removed on a vacuum line. The brown residue was washed several times with boiling petroleum ether and then recrystallized from hot ethanol to give very fine brown crystals. The complex was left to dry under vacuum (yield: 64 %, m. p. >300ºC).

Synthesis of CrO(sbhH$_2$)$_2$complex

$Cr(CO)_6$ (0.10 g, 0.45 mmol) and sbhH$_2$ (0.12 g, 0.45 mmol) were dissolved in *ca*. 100 mL methanol. The solution was irradiated by sunlight for 4 days in winter. During the irradiation, the colour of the reaction mixture changed from colourless to dark yellow. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a brown solid. The brown residue was washed several times by methanol and petroleum ether and then recrystallized from hot ethanol to give brown crystals. The complex was left to dry under vacuum (yield: 72 %, m. p. >300ºC).

Synthesis of Mo(sbhH)$_2$

$Mo(CO)_6$ (0.05 g, 0.19 mol) and sbhH$_2$ (0.089 g, 0.38 mol) were mixed together in *ca*. 20 mL absolute ethanol. The mixture was degassed and heated to reflux for 30 minutes, at which a dark brown solution was obtained. The solvent was removed and the dark brown residue was washed several times by boiling petroleum ether. The compound was then recrystallized from ethanol to give dark brown solid (yield: 78 %, m. p.

>300ºC). The same product was obtained when the reaction was carried out in benzene solvent.

Synthesis of MoO_2(sbh)

$Mo(CO)_6$ (0.05 g, 0.19 mmol) and $sbhH_2$ (0.049 g, 0.19 mmol) were dissolved in *ca*. 100 mL methanol. The solution was irradiated by sunlight for 5 days in winter. During the irradiation, the colour of the reaction mixture was turned from colourless to dark yellow colour. After the irradiation, the reaction mixture was evaporated under vacuum, yielding red crystals. The product was recrystallized from hot ethanol to give deep red crystals. The complex was left to dry under vacuum (yield: 76 %, m. p. >300ºC).

Synthesis of $W_2O_4(sbh)_2$

A mixture of $W(CO)_6$ (0.05 g, 0.14 mmol), $sbhH_2$ (0.036 g, 0.14 mmol) were dissolved in *ca*. 100 mL methanol. The solution was irradiated by sunlight for 6 days in winter, at which a dark yellow solution was obtained. After the irradiation, the reaction mixture was evaporated under vacuum, yielding a brown solid. The brown solid was washed several times by methanol and petroleum ether and then recrystallized from hot ethanol to give dark brown solid. The complex was left to dry under vacuum (yield: 58 %, m. p. >300ºC).

RESULTS AND DISCUSSION

Spectroscopic studies of salicylaldehyde-*p*-hydroxybenzoyl hydrazone ($sbhH_2$)

The IR spectrum of salicylaldehyde *p*-hydroxybenzoyl hydrazone, showed bands at 3320, 3159 and 1448 cm^{-1} due to, ν(NH), ν(OH) and δ(OH) modes, respectively, (TABLE 2). Also, it exhibited a strong bands at 1644, 1610, 1542, 1280 and 1238 cm^{-1} which can be, respectively, assigned to ν(C=O, amide I), ν(C=N) and δ(N-H, amide II), ν(C-O), ν(C-N, amide III) vibrations[11,12]. These modes are observed at comparable wavenumbers in the Raman spectra of the ($sbhH_2$), Figure 1 and (TABLE 2). The ^{1}H NMR spectrum of ($sbhH_2$) in DMSO, d_6, displayed two signals at 11.80 and 11.37 ppm, attributed to the OH and NH protons, respectively, (TABLE 1). The signal for OH was obtained downfield due to the possibility of the formation of intramolecular hydrogen bonding with the adjacent nitrogen atom of the azomethine group. On the other hand, the ^{1}H NMR spectrum displayed two sharp signals at 8.59 and 10.05 ppm. can be assigned to the CH=N group and the p- OH proton. Also, the aromatic protons of both rings appeared as a multisignals within the 6.86–7.84 ppm range[13]. The mass spectrum of the complex showed a molecular ion peak at *m/z* 353, corresponding to the ion [P – L]$^+$, where P is the parent and L is the ligand.

TABLE 2 : Important IR and Raman data of $sbhH_2$ ligand and its complexes[a] (Raman frequencies are given between parentheses).

$sbhH_2$	$CrO(CO)_2(sbhH_2)$	$CrO(sbhH_2)_2$	$Mo(sbhH)_2$	MoO_2(sbh)	$W_2O_4(sbh)_2$	Assignment
3159m,b	3203m,b	3425m,b	3327m,b	3320m	3360m,b	νOH
3320w	3322m,b		3235m,b	--------	---------	νNH
1644s (1645w)	1650m	-------------	1648s	--------	---------	νC=O amideI
1610s (1614s)	1604s	1605s (1608s)	1608s	1600s (1526s)	1614s	νC=N
1542m (1545w)	1547m	-------------	1550m	--------	--------	δNH amideII
1280 s (1286m)	1260s	1279s (1285m,1327m)	1270s	1327m (1322m,1344m)	1255m,1273m	νC-O[b]
1238s (1230m)	1230m	-------------	1230s	---------	---------	ν C –N amideIII

[a] s, strong; m, medium; w, weak; b, broad.[b] s, singlet; m, multiplet; and b, broad.

[b] ν C-O attached to the phenyl ring and of the enol group

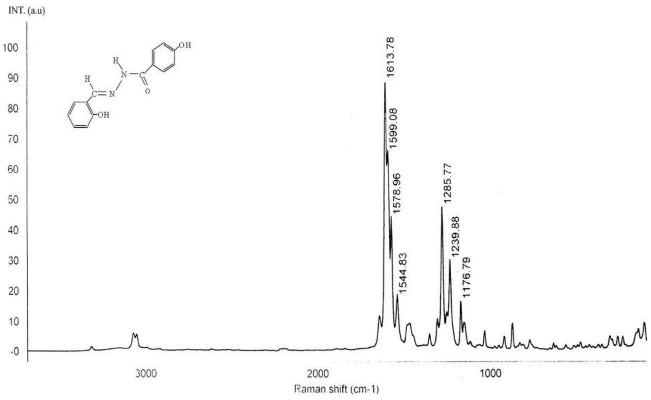
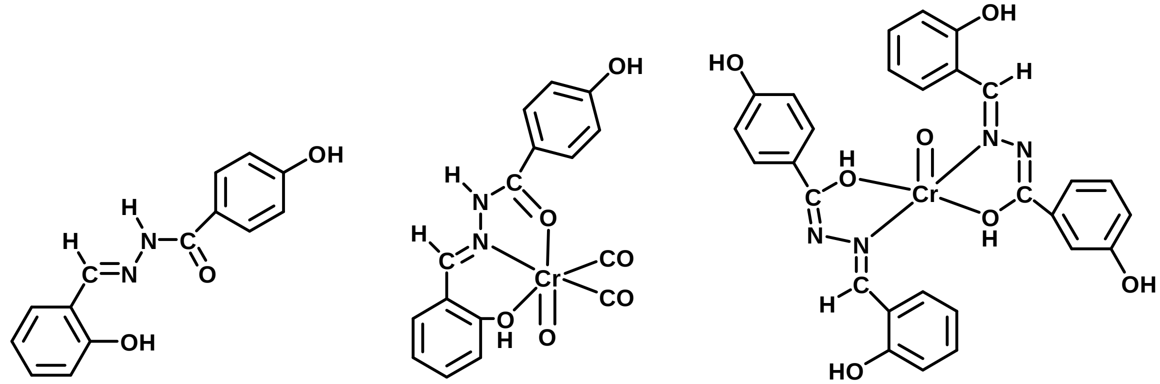


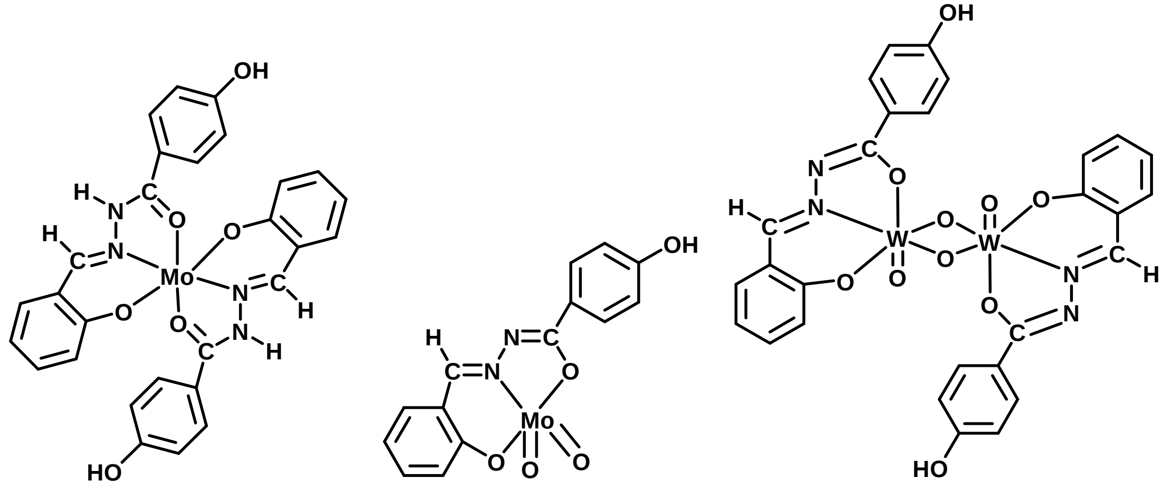
Figure 1 : The Raman spectrum of $sbhH_2$

Reactions of $Cr(CO)_6$ with ($sbhH_2$)

Thermal reaction of $Cr(CO)_6$ with $sbhH_2$ in absolute ethanol under reduced pressure resulted in the formation of the dicarbonylchromium complex with the molecular formula $CrO(CO)_2(sbhH_2)$. The mass spectrum of the complex showed a molecular ion peak at m/z = 336, which was corresponding to the molecular ion $[P - (CO + O)]^+$. The IR spectrum of the dicarbonyl complex showed significant shifts of the characteristic bands of the ligand due to complex formation (TABLE 2). Interestingly, the IR spectrum also displayed two strong bands in the terminal metal carbonyl range at 1948 and 1866 cm^{-1}, which assigned to the symmetric and asymmetric stretching frequencies of two CO groups[14], which was also confirmed by the observation of two new bands at 1925 and 1887 cm^{-1} in the Raman spectrum of the complex (TABLE 2), indicated that the complex contains two terminal CO groups of *cis*-configuration[14]. On the other hand, the C-O stretching band of the C-OH group of the salicyl moiety was shifted to 1260 cm^{-1} in the IR spectrum of the complex (TABLE 2). Furthermore, the presence of ν(OH) and δ(OH) bands in the spectrum showed that the OH group of the salicyl moiety coordinates to the chromium atom without proton displacement. Also, the ν(C=O) band was shifted to higher frequency while the ν(C=N) was shifted to lower frequency confirming the coordination of the metal occurred from these two sites. In addition, the IR spectrum exhibited a weak band at 895 cm^{-1}, which is due to Cr=O bond. Also, a weak band appeared at 592 cm^{-1}, due to the Cr-O bond[10,13]. Measurements of the magnetic susceptibility of the solid $CrO(CO)_2(sbhH_2)$ complex was investigated at 304°K using the Gouy method suggested the paramagnetic character of the complex with an effective magnetic moment of 3.23 BM. This value is less than the spin-



Structure of $sbhH_2$ $CrO(CO)_2(sbhH_2)$ $CrO(sbhH_2)_2$



$Mo(sbh)_2$ $MoO_2(sbh)$ $W_2O_4(sbh)_2$

Scheme 1

only value for four unpaired electrons, which is expected for a d^4 high-spin Cr(II) species (4.90 BM). Thus, from the elemental analysis and the spectroscopic data, it can be concluded that the chromium atom existed in an octahedral environment and was bonded to the $sbhH_2$ ligand, acting as a tridentate ligand, coordinating *via* the nitrogen atom of the azomethine C=N, carbonyl group in the keto form and the protonated OH group of the salicyl moiety. Also, the Cr atom has two CO groups in *cis*-configuration and coordinated to a terminal oxygen atom to form an octahedral species, Scheme 1.

The reaction of $Cr(CO)_6$ with $sbhH_2$ in methanol in the sunlight yielded an oxochromium complex with the molecular formula $CrO(sbhH_2)_2$. The mass spectrum of the complex showed a molecular ion peak at *m/z* = 576, due to the molecular ion $[P - 4H]^+$. The IR spectrum of the complex showed the characteristic bands of the ligand with the corresponding shifts due to complex formation (TABLE 2**)**. In addition, the disappearance of the band at 1644 cm^{-1} due to ν(C=O), which was also confirmed by the absence of its Raman line in the Raman spectra of the complex, Figure 2. Furthermore, the absence of ν C=O (amide I), ν NH and δ N-H (amide II) and ν C-N (amide III) bands in the IR and in the Raman spectra and also a new medium band appeared at 1519 cm^{-1} in the Raman spectra, (Figure 2, TABLE 2) which could be assigned to the symmetric ν_s(C=N) stretching frequency[15,16] indicated that the elimination of the N-H proton and the coordination of the ligand *via* the enol oxygen. On the other hand, the IR spectrum of the complex displayed no shift for the band at 1280 cm^{-1} which is corresponding to a stretching of a C-OH bond of the o-OH group does not change in the Raman spectrum, indicated that the OH group of the salicyl moiety was not involved in coordination. The IR spectrum also showed a medium band at 895 cm^{-1}, which was assigned to Cr=O bond. Also, a new band was appeared at 598 cm^{-1} due to ν(Cr-O). Investigation of the magnetic properties of the oxochromium complex showed that it was a paramagnetic. The magnetic susceptibility measurements of the oxochromium paramagnetic complex $CrO(sbhH_2)_2$.The effective magnetic moment (μ_{eff}) of the complex gave a value of 3.67 BM. The μ_{eff} value is smaller than the spin-only moment for the four unpaired electrons as expected for Cr(II),d^4 species. Based on the above and according to the spectroscopic studies and elemental analysis, it can be concluded that the chromium atom bonded to two $sbhH_2$ ligands, each ligand acting as a bidentate ligand coordinating *via* the azomethine C=N group and the carbonyl oxygen in its enol form to produce a chelate of 5-membered ring, and the complex also contains the Cr=O bond, Scheme 1.

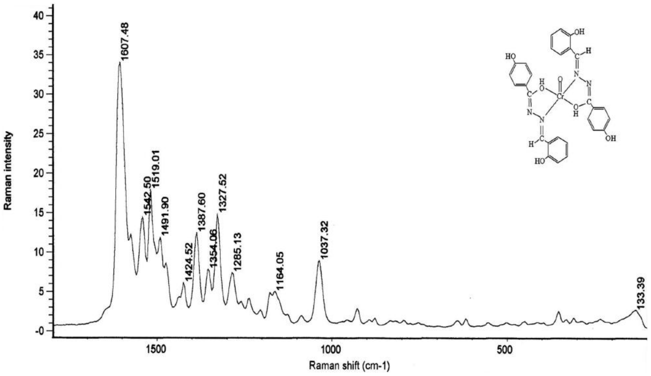


Figure 2 : The Raman spectrum of $CrO(sbhH_2)_2$

Reactions of $Mo(CO)_6$ with ($sbhH_2$)

The reaction of $Mo(CO)_6$ with $sbhH_2$ in absolute Ethanol in air or under reduced pressure resulted in the formation of the bis-derivative $Mo(sbhH)_2$. The mass spectrum of the complex showed a molecular ion peak at *m/z* 353, corresponding to the ion $[M – L]^+$. The IR spectrum of the complex showed a pattern closely related to that of salicylaldehyde *p*-hydroxybenzoyl hydrazone with a slight shifts in the ν(C=O), ν(C=N) stretching frequencies due to the complex formation (TABLE 2). In addition, the absence of ν(OH) band in the spectrum showed that the OH group of the salicyl moiety coordinates to the molybdenum atom with proton displacement. Investigation of the magnetic properties of the bis derivative complex showed that it was a diamagnetic. The ^{1}HNMR spectrum of $Mo(sbhH)_2$ complex in DMSO, d_6, (TABLE 1), showed a pattern similar to that of the ligand $sbhH_2$ with the disappearance of the signal of OH group of the salicyl moiety, indicated that ligand coordinated oxidatively to the metal[14]. Also, a broad signal for the NH proton appeared around 11.8 ppm. The p-OH appeared 8.82 ppm. Thus, it can be concluded that the molybdenum was bonded oxidatively to two sbhH ligands, each acting as a tridentate ligand, coordinating *via* the azomethine C=N group, the carbonyl group in the keto form and the deprotonated OH group of the salicyl moiety to form an octahedral species, Scheme 1.

When the reaction proceeded in day sunlight in methanol, the dioxomolybdenum complex MoO_2(sbh) was isolated. The mass spectrum of the complex showed a molecular ion peak at *m/z* 384 due to the parent ion (M^+) ion peak. The IR spectrum of the complex showed the characteristic bands of the ligand with the corresponding shifts due to complex formation (TABLE 2). However, the bands due to NH and C=O groups of the ligand were disappeared from the spectrum of the complex indicating the deprotonation of the N-H proton and coordination *via* the enol oxygen and the formation of the azine skeleton. In the Raman spectrum of the complex, Figure 3, the two bands appearing at 1322 and 1344 cm^{-1} represent the C-O of the enol form and the C-O attached to the phenyl ring, respectively which were shifted to higher wave-numbers relative to the ligand vibrations due to complex formation. These two bands are shifted to approximate frequencies in the infrared spectrum of the complex. In addition, the IR spectrum of the complex also showed a medium band at 932 cm^{-1} and a strong band at 895 cm^{-1} due to symmetric and asymmetric Mo=O stretching frequencies for *cis*-dioxo coordination. The Raman spectrum of this complex (Figure 3, TABLE 2) confirmed this assignment since two new Raman bands were observed at 934 cm^{-1} (strong) and 892 cm^{-1} (weak) which could be assigned to the symmetric $\nu_s(MoO_2)$ and asymmetric $\nu_{as}(MoO_2)$ stretching modes. Also, the azine skeleton was confirmed by the appearance of a new ν(C=N) mode at 1526 cm^{-1} as a strong Raman line and also the ν(N-N) mode as a new band in the Raman spectra at 1035 cm^{-1} with medium intensity[15,16]. In the far IR spectrum of the complex, two bands observed at 589 and 440 cm^{-1} which are, respectively, due to the Mo-O and Mo-N bonds. Magnetic susceptibility measurements of the solid MoO_2(sbh) complex at 298 °K showed that the complex was diamagnetic. The ^1H NMR spectrum of MoO_2(sbh) complex in DMSO, d_6, (TABLE 1), showed a pattern similar to that of the ligand $sbhH_2$ with the disappearance of the signal of OH group of the salicyl moiety, indicated that ligand coordinated oxidatively to the metal[10]. Also, the ^1H NMR spectrum of the dioxomolybdenum complex revealed the absence of the signal of the NH proton, confirming the coordination *via* the enol oxygen. The p-OH appeared at 10.1 ppm. Thus, the molybdenum in the MoO_2(sbh) complex may exist in a trigonal bipyramid environment and was bonded oxidatively to sbh ligand, in a tridentate fashion in the azine form, coordinating *via* the carbonyl oxygen in its enol form, the nitrogen atom of the C=N group and the oxygen atom of the deprotonated OH group of the salicyl moiety and the complex also contains two Mo=O bonds as shown below.

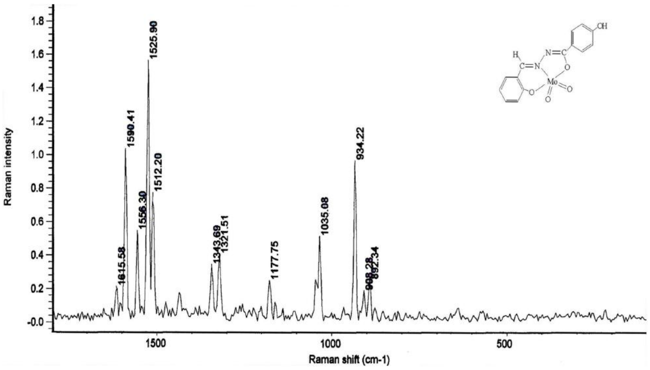


Figure 3 : The Raman spectrum of MoO_2(sbh)

Reactions of $W(CO)_6$ with ($sbhH_2$)

$W(CO)_6$, reacted with $sbhH_2$ in methanol in sunlight (reaction time period 6 days) resulted in the formation of the dinuclear tungsten complex, $W_2O_4(sbh)_2$. The mass spectrum of the complex, showed a molecular ion peak at *m/z* = 469, which was corresponding to the ion $[1/2\ P]^+$. The IR spectrum of the complex showed the characteristic bands of the ligand with appropriate shifts due to the complex formation (TABLE 2). However, the spectral bands due to ν(NH) and ν(C=O) were absent from the complex spectrum indicating the deprotonation of the N-H and the coordination *via* the enol oxygen. Also, the absence of ν(OH) and δ(OH) bands in the spectrum showed that ligand was added to the metal oxidatively. In addition, the C-O stretching band was also shifted to lower frequency while the ν(C=N) was shifted to higher frequency with respect to those of the ligand itself confirming the coordination of the metal occurred *via* these two sites (TABLE 2). A new weak band at 598 cm^{-1} was assignable for the ν(W-N) for the complex. Also the IR spectrum exhibited only one strong band at 936 cm^{-1}, which was assigned to W=O bonds indicating that the complex contains two terminal W=O groups of *trans*-configuration and a C_{2h} point group. Also, a new strong band was appeared at 796 cm^{-1}, which could be due to the W-O-W bonds[17]. Magnetic susceptibility measurements of the solid $W_2O_4(sbh)_2$ complex at 298 °K showed that the complex was diamagnetic. The ^1H NMR spectrum of $W_2O_4(sbh)_2$ complex in DMSO showed that the signals due to OH proton of the salicyl moiety and also, the signal due to the NH proton are absent in the spectrum which indicates that the ligand reacted with metal via its enol form (TABLE 1). Thus, according to spectroscopic evidences, the dinuclear complex might has the formula $W_2O_4(sbh)_2$, where each tungsten atom in the dinuclear complex existed in an octahedral environment with two bridged oxygen atoms and was bonded to the salicylaldehyde-*p*-hydroxybenzoylhydrazone, in a tridentate manner, coordinating *via* the azomethine C=N, the C-O group in the enol form and the deprotonated OH group of the salicyl moiety. Each tungsten was also coordinated to a terminal oxygen atom to form an octahedral species.

The coordinating atoms of the ligand in these complexes can also be confirmed by calculating the structures of minimum energies in both of the azine and hydrazone forms and partial charges of the ligand which indicated that the two coordinating oxygen sites have residual negative charges as indicating by extended HMO calculations, IR and x-ray structure analysis of similar complexes[18].

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