Reaction of group 6 metal carbonyls with salicylaldehyde
p-hydroxybenzoylhydrazone

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ABSTRACT

Thermal reaction of salicylaldehyde-p-hydroxybenzoylhydrazone (sbhH2) with Cr(CO)6 in absolute EtOH under reduced pressure gave the oxodicarbonylchromium complex, CrO(CO)2(sbhH2). When the reaction was carried out in MeOH in day sunlight, the oxochromium complex CrO(sbhH2) was isolated. Reflux of sbhH2 with molybdenum hexacarbonyl in absolute EtOH in either air or under reduced pressure yielded the bis-derivative Mo(sbhH2). However, when the reaction proceeded in sunlight in methanol, the dioxomolybdenum complex MoO2(sbh) was isolated. W(CO)6 reacted with sbhH2 in ethanol to give a dinuclear complex with a molecular formula W2O4(sbh). The molecular structures of the complexes were determined based on elemental analysis, vibrational (infrared and Raman), 1HNMR 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 states1,2. Hydrazones are also interesting chelating agents3 and their derivatives are used as fungicides and in the treatment of diseases such as tuberculosis and mental disorder4. Aroylhydrazones constitute important classes of organic compounds. The interest for these compounds may arise owing to their biological activities, strong tendency to chelate transition metals5, lanthanide6 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 conditions7.

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 ligands8. Various metal carbonyl derivatives play an important role in homogenous catalysis involving hydrogenation, hydroformylation, carbonylation and oxo transfer reactions9. Reactions of metal carbonyls with hydrazones are relatively less studied10. So in this work, the results obtained from the reactions of M(CO)6 (M = Cr, Mo and W) with salicylaldehyde p-hydroxybenzoyl hydrazone (sbhH2) 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 ¹H NMR data of the complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>% calculated (found)</th>
<th>Mass data</th>
<th>¹H NMR (ppm)a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>sbhH₂</td>
<td>65.63</td>
<td>4.69</td>
<td>10.94</td>
</tr>
<tr>
<td>CrO(CO)₂(sbhH₂)</td>
<td>44.40</td>
<td>3.16</td>
<td>7.37</td>
</tr>
<tr>
<td>Cr(sbhH₂)₂</td>
<td>57.94</td>
<td>4.13</td>
<td>9.65</td>
</tr>
<tr>
<td>Mo(sbhH)₂</td>
<td>55.0</td>
<td>55.2</td>
<td>3.63</td>
</tr>
<tr>
<td>MoO₂(sbh)</td>
<td>43.48</td>
<td>43.64</td>
<td>2.62</td>
</tr>
<tr>
<td>W₂O₄(sbh)₂</td>
<td>35.85</td>
<td>35.65</td>
<td>2.13</td>
</tr>
</tbody>
</table>

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 (CD₃)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 analyser. 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 (sbhH₂)**

A mixture of salicylaldehyde (6.0 cm³, 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(sbhH₂)**

Cr(CO)₆ (0.10 g, 0.45 mmol) and sbhH₂ (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. >300°C).

**Synthesis of CrO(sbhH₂)₂ complex**

Cr(CO)₆ (0.10 g, 0.45 mmol) and sbhH₂ (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. >300°C).

**Synthesis of Mo(sbhH)₂**

Mo(CO)₆ (0.05 g, 0.19 mol) and sbhH₂ (0.089 g, 0.38 mol) were mixed together in ca. 20 mL absolute ethanol. The mixture was degassed and heated to reflux for 3 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.
>300°C). 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 sbH$_2$ (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. >300°C).

**Synthesis of W$_2$O$_4$(sbh)$_2$**

A mixture of W(CO)$_6$ (0.05 g, 0.14 mmol), sbH$_2$ (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. >300°C).

**RESULTS AND DISCUSSION**

Spectroscopic studies of salicylaldehyde-$_p$-hydroxybenzoyl hydrazone (sbH$_2$)

The IR spectrum of salicylaldehyde-$_p$-hydroxybenzoyl hydrazone, showed bands at 3320, 3159 and 1448 cm$^{-1}$ due to, $\nu$(NH), $\nu$(OH) and $\delta$(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 $\nu$(C=O, amide I), $\nu$(C=N) and $\delta$(N-H, amide II), $\nu$(C-O), $\delta$(C-N, amide III) vibrations$^{[11,12]}$. These modes are observed at comparable wavenumbers in the Raman spectra of (sbH$_2$), Figure 1 and (TABLE 2). The $^1$H NMR spectrum of (sbH$_2$) 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 sbH$_2$ ligand and its complexes$^a$(Raman frequencies are given between parentheses).**

<table>
<thead>
<tr>
<th>sbH$_2$</th>
<th>CrO(CO)$_2$(sbH$_2$)</th>
<th>CrO(sbH$_2$)$_2$</th>
<th>Mo(sbH)$_2$</th>
<th>MoO$_2$(sbH)</th>
<th>W$_2$O$_4$(sbH)$_2$</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>3159m,b</td>
<td>3203m,b</td>
<td>3425m,b</td>
<td>3327m,b</td>
<td>3320m</td>
<td>3360m,b</td>
<td>$\nu$(OH)</td>
</tr>
<tr>
<td>3320w</td>
<td>3322m,b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\nu$(NH)</td>
</tr>
<tr>
<td>1644s (1645w)</td>
<td>1650m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\nu$(C=O, amide I)</td>
</tr>
<tr>
<td>1610s (1614s)</td>
<td>1604s</td>
<td>1605s (1608s)</td>
<td>1608s</td>
<td>1600s (1526s)</td>
<td>1614s</td>
<td>$\nu$(C=N)</td>
</tr>
<tr>
<td>1542m (1545w)</td>
<td>1547m</td>
<td></td>
<td>1550m</td>
<td></td>
<td></td>
<td>$\delta$(N-H, amide II)</td>
</tr>
<tr>
<td>1280s (1286m)</td>
<td>1260s</td>
<td>1279s (1285m,1327m)</td>
<td>1270s</td>
<td>1272m (1322m,1344m)</td>
<td>1255m,1273m</td>
<td>$\nu$(C=O)</td>
</tr>
<tr>
<td>1238s (1230m)</td>
<td>1230m</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\nu$ C–N amide III</td>
</tr>
</tbody>
</table>

$^a$s, strong; m, medium; w, weak; b, broad. $^b$s, singlet; m, multiplet; and b, broad.

$^b$ $\nu$ C-O attached to the phenyl ring and of the enol group.

Figure 1 : The Raman spectrum of sbH$_2$
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 $\nu$(OH) and $\delta$(OH) bands in the spectrum showed that the OH group of the salicyl moiety coordinates to the chromium atom without proton displacement. Also, the $\nu$(C=O) band was shifted to higher frequency while the $\nu$(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-
only value for four unpaired electrons, which is expected for a d⁴ 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 sbhH₂ 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 sbhH₂ in methanol in the sunlight yielded an oxochromium complex with the molecular formula CrO(sbhH₂)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 ν₃ (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(sbhH₂)₂.The effective magnetic moment (μₑffective) of the complex gave a value of 3.67 BM. The μₑffective value is smaller than the spin-only moment for the four unpaired electrons as expected for Cr(II), d⁴ 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 sbhH₂ 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.

Reactions of Mo(CO)₆ with (sbhH₂)

The reaction of Mo(CO)₆ with sbhH₂ 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 ¹HNMR spectrum of Mo(sbhH₂) complex in DMSO, d₆, (TABLE 1), showed a pattern similar to that of the ligand sbhH₂ 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 \(\text{MoO}_2(\text{sbh})\) was isolated. The mass spectrum of the complex showed a molecular ion peak at \(m/z\) 384 due to the parent ion (\(\text{M}^+\)) 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 \(\text{NH}\) and \(\text{C}=\text{O}\) groups of the ligand were disappeared from the spectrum of the complex indicating the deprotonation of the \(\text{N-H}\) proton and coordination \(\text{via}\) 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 \(\text{C}=\text{O}\) of the enol form and the \(\text{C}=\text{O}\) 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 \(\text{Mo}=\text{O}\) stretching frequencies for \(\text{cis}\)-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 \(\nu_{\text{s}}\) (\(\text{MoO}_2\)) and asymmetric \(\nu_{\text{as}}\) (\(\text{MoO}_2\)) stretching modes. Also, the azine skeleton was confirmed by the appearance of a new \(\nu(\text{C=N})\) mode at 1526 cm\(^{-1}\) as a strong Raman line and also the \(\nu(\text{N-N})\) 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 \(\text{Mo-O}\) and \(\text{Mo-N}\) bonds. Magnetic susceptibility measurements of the solid \(\text{MoO}_2(\text{sbh})\) complex at 298 °K showed that the complex was diamagnetic. The \(^1\text{H NMR spectrum of MoO}_2(\text{sbh})\) complex in DMSO, \(d_6\) (TABLE 1), showed a pattern similar to that of the ligand sbh\(\text{H}_2\) with the disappearance of the signal of \(\text{OH}\) group of the salicyl moiety, indicated that ligand coordinated oxidatively to the metal\(^{[10]}\). Also, the \(^1\text{H 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 \(\text{MoO}_2(\text{sbh})\) complex may exist in a trigonal bipyramid environment and was bonded oxidatively to sbh ligand, in a tridentate fashion in the azine form, coordinating \(\text{via}\) the carbonyl oxygen in its enol form, the nitrogen atom of the \(\text{C=N}\) group and the oxygen atom of the deprotonated \(\text{OH}\) group of the salicyl moiety and the complex also contains two \(\text{Mo}=\text{O}\) bonds as shown below.

Reactions of \(\text{W(CO)}_6\) with \((\text{sbhH}_2)\)

\(\text{W(CO)}_6\), reacted with sbh\(\text{H}_2\) in methanol in sunlight (reaction time period 6 days) resulted in the formation of the dinuclear tungsten complex, \(\text{W}_2\text{O}_4(\text{sbh})_2\). The mass spectrum of the complex, showed a molecular ion peak at \(m/z = 469\), which was corresponding to the ion \([1/2 \text{P}]^+\). 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 \(\nu(\text{NH})\) and \(\nu(\text{C}=\text{O})\) were absent from the complex spectrum indicating the deprotonation of the \(\text{N-H}\) and the coordination \(\text{via}\) the enol oxygen. Also, the absence of \(\delta(\text{OH})\) and \(\nu(\text{OH})\) bands in the spectrum showed that ligand was added to the metal oxidatively. In addition, the \(\text{C}=\text{O}\) stretching band was also shifted to lower frequency while the \(\nu(\text{C}=\text{N})\) was shifted to higher frequency with respect to those of the ligand itself confirming the coordination of the metal occurred \(\text{via}\) these two sites (TABLE 2). A new weak band at 598 cm\(^{-1}\) was assignable for the \(\nu(\text{W-N})\) for the complex. Also the IR spectrum exhibited only one strong band at 936 cm\(^{-1}\), which was assigned to \(\text{W}=\text{O}\) bonds indicating that the complex contains two terminal \(\text{W}=\text{O}\) groups of \(\text{trans}\)-configuration and a \(\text{C}_{2\text{h}}\) 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$_2$O$_4$(sbh)$_2$ complex at 298 °K showed that the complex was diamagnetic. The $^1$H NMR spectrum of W$_2$O$_4$(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$_2$O$_4$(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 hydrazine 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].

REFERENCES