SYNTHESIS AND STRUCTURAL STUDIES OF OXO-VANADIUM (IV), CHROMIUM(III), MANGANESE(II), IRON(II), COBALT(II), NICKEL(II), AND COPPER(II) COMPLEXES WITH A NEW TETRA DENTATE SCHIFF BASE HAVING O: N: O DONOR SYSTEM

Mahmoud N. Al-Jibouri
Chemistry Department, College of science, Al-Mustansiriya University, Iraq, Baghdad.

Abstract
The complexes of a new quadridentate Schiff base derived from ethylene diamine and 4-hydroxy-2-methyl-3-acetyl-pyrane-2-on (dehydroacetic acid) with oxovanadium(IV), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) have been synthesized and characterized on the bases of their elemental analysis, conductivity, magnetic moments in addition to spectral data of I.R. and U.V.-Visible.

Metal to ligand ratio in all complexes has been found to be 1:1. The Schiff base behaves as neutral tetradentate ligand with O:N:N:O system. Cr(III), Mn(II), Fe(II), Co(II), and Cu(II) complexes have been assigned octahedral stereo chemistry, Ni(II) complex has been assigned as square planer geometry, while V(IV) complex was square pyramid.

Introduction
The coordination complexes of the Schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological processes (1-3). The coordination compounds quadridentate Schiff bases have been reported to act as inhibitors for enzymes (4). Considerable interest has been shown in the synthesis of transition metal complexes of quadridentate Schiff bases (5-6). Pyran-2-one derivatives containing hydroxyl, acetyl and phenylazo substitutes have been employed as complexing agents (7-10).

Literatures survey reveals that very little work has, however, been reported on Schiff bases of pyran-2-one. Keeping this in view, we report here the synthesis and characterization of a new quadridentate Schiff base (L) derived from 3-acetyl 4-hydroxy-6-methyl-2-one (I) and ethylene diamine and its complexes with oxo-vanadium(IV), Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

Experimental
Physical measurements and analysis:
Melting points were recorded on Gallen Kamp melting point apparatus and were uncorrected. FTIR spectra were recorded using FTIR–8300 Shimadzo in the range (4000-200)cm\(^{-1}\). Samples were measured as CsI–disc. The U.V.-visible spectra of compounds were recorded on UV–1650 PC shimadzu spectrophotometer. Magnetic susceptibility measurements were done at room temperature by Gouy method using mercury tetrathiocyanato cobalt (II) as calibrante. Metal estimations were carried out spectrophotometrically using atomic absorption Shimadzo AA-670 spectrophotometer.

Conductivity measurements were obtained using Corning conductivity meter 220. The elemental analysis data of the ligand and complexes were obtained on a Carlo Erba Model EA 1108 (C.H.N.) Elemental analyzer.

Materials and preparations:
3-acetyl-4-hydroxy-6-methyl-pyrane-2-one (I) was prepared by the reported procedure (9). All the other chemicals used were of AR grade.

Synthesis of the Schiff base (L):
An ethanolic solution (I) (1.56 gm, 0.01 mol in 25 ml) was added to an ethanolic solution of 1,2-diaminoethane (0.3g, 0.005mol in 10 ml), the mixture was refluxed on a water-bath for 2hr. The excess of solvent was partially evaporated under vacuum, and the separated yellow precipitate was filtered under reduced pressure, washed with ethanol and crystallized from ethanol. The compound was dried in vacuum at room temperature over silica gel as can be described in Scheme (1).
The physical properties of ligand can be shown in Table (1).

![Scheme (1)](image)

- **Preparation of the complex:**
  The metal complexes were prepared by refluxing hot ethanolic solutions of metal chloride (0.01 mol) [except in case of Fe(II) and oxovanadium (IV) complexes where aqueous ethanolic solutions were used] and the ligand (0.01 mol) for 3hr, on a water bath. The complexes separated on adjusting the pH to 7.5. Were filtered, washed with cyclohexanol, followed by petroleum ether (60–80°C) and dried in air.

- **Study of complex formation in solution:**
  The complexes of the ligand (L) with the selected metal ions [Cr(III), V(IV), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)], were studied in solution using ethanol as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method(10).

A series of solutions were prepared having a constant concentration (C) $10^{-3}$ M of the hydrated metal chlorides or vandyl sulfate VOSO$_4$•5H$_2$O, and the ligand (L).

The [M:L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:L]. The result of complexes formation in solution were listed in Table (2).

- **Stability constant of the complexes (Ks):**
  The stability constant of the (1:1) [M:L] complex, was evaluated using the following equation:

$$K_s = 1 - \alpha/\alpha^2 c \quad \text{........................................(1)}$$

Where $\alpha$ is the degree of the dissociation, and $c$ is the concentration of the complex.

The absorbance of the solutions were measured at ($\lambda_{max}$) of the maximum absorption, furthermore the molar absorptivity ($\epsilon_{max}$) for the complexes were calculated from equation (2):

$$A_m = \epsilon_{max} \cdot b \cdot C \quad \text{........................................(2)}$$

Where $A_m$ is the average of three measurements of the absorption containing the same amount of metal ion and five fold excess of ligand, and $b$ is the depth of the quartz cell, usually equal to 1 cm.

**Table (1)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symbol</th>
<th>Color</th>
<th>Yield (%)</th>
<th>M.P. C$^\circ$</th>
<th>Elemental analysis</th>
<th>Calc.(found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand</td>
<td>L</td>
<td>Yellow</td>
<td>80</td>
<td>180 - 182</td>
<td>C% 57.83(56.99)</td>
<td>H% 6.02(5.81)</td>
</tr>
<tr>
<td>[ VO (L) ]SO$_4$</td>
<td>C$_1$</td>
<td>Green</td>
<td>72</td>
<td>220 - 222</td>
<td>C% 49.03(40.1)</td>
<td>H% 4.26(3.66)</td>
</tr>
<tr>
<td>[Cr(L) Cl$_2$]Cl</td>
<td>C$_2$</td>
<td>Green</td>
<td>79</td>
<td>250$^\circ$</td>
<td>C% 34.02(38.53)</td>
<td>H% 4.06(3.71)</td>
</tr>
<tr>
<td>[Mn(L) Cl$_2$]</td>
<td>C$_3$</td>
<td>Brown</td>
<td>65</td>
<td>245 - 247</td>
<td>C% 41.92(40.36)</td>
<td>H% 4.36(3.66)</td>
</tr>
<tr>
<td>[Fe(L) Cl$_2$]</td>
<td>C$_4$</td>
<td>Dark red</td>
<td>79</td>
<td>258 - 260</td>
<td>C% 41.83(40.33)</td>
<td>H% 4.35(4.00)</td>
</tr>
<tr>
<td>[Co(L) Cl$_3$]</td>
<td>C$_5$</td>
<td>Light pink</td>
<td>90</td>
<td>270 - 272</td>
<td>C% 41.73(40.09)</td>
<td>H% 4.34(3.99)</td>
</tr>
<tr>
<td>[Ni(L)Cl]</td>
<td>C$_6$</td>
<td>Red</td>
<td>95</td>
<td>298 - 300</td>
<td>C% 43.1(40.1)</td>
<td>H% 6.9(5.8)</td>
</tr>
<tr>
<td>[Cu(L) Cl$_2$]</td>
<td>C$_7$</td>
<td>Green</td>
<td>92</td>
<td>280 - 282</td>
<td>C% 41.15(39.99)</td>
<td>H% 6.00(5.31)</td>
</tr>
</tbody>
</table>

Where : $d$ = decomposed


### Table 2
Stability constants, and molar absorptivities of the complexes (C1-C7).

<table>
<thead>
<tr>
<th>Complex</th>
<th>As</th>
<th>Am</th>
<th>α</th>
<th>λ_{max}</th>
<th>K_s (L.mol^{-1})</th>
<th>C_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.31</td>
<td>0.30</td>
<td>0.166</td>
<td>365</td>
<td>3 \times 10^{5}</td>
<td>5730</td>
</tr>
<tr>
<td>C2</td>
<td>0.361</td>
<td>0.371</td>
<td>0.155</td>
<td>455</td>
<td>4.5 \times 10^{5}</td>
<td>150</td>
</tr>
<tr>
<td>C3</td>
<td>0.325</td>
<td>0.366</td>
<td>0.149</td>
<td>265</td>
<td>2.5 \times 10^{5}</td>
<td>5990</td>
</tr>
<tr>
<td>C4</td>
<td>0.371</td>
<td>0.379</td>
<td>0.15</td>
<td>280</td>
<td>3.9 \times 10^{5}</td>
<td>6770</td>
</tr>
<tr>
<td>C5</td>
<td>0.381</td>
<td>0.44</td>
<td>0.53</td>
<td>475</td>
<td>4.8 \times 10^{5}</td>
<td>1500</td>
</tr>
<tr>
<td>C6</td>
<td>0.391</td>
<td>0.401</td>
<td>0.163</td>
<td>550</td>
<td>2.3 \times 10^{6}</td>
<td>380</td>
</tr>
<tr>
<td>C7</td>
<td>0.401</td>
<td>0.461</td>
<td>0.181</td>
<td>525</td>
<td>5.3 \times 10^{6}</td>
<td>250</td>
</tr>
</tbody>
</table>

Where As is the average of three measurements of the absorption of solution containing astoichiometric amount of ligand and metal ion.

### Table 3
U.V.-visible, I.R. spectra and other physical properties of the prepared compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electronic absorption bands</th>
<th>Assignment</th>
<th>IR frequency peaks (cm^{-1})</th>
<th>Assignment (stretching)</th>
<th>\mu_e (BM)</th>
<th>\Lambda_{m} (\Omega^{-1}.cm^{2}.mol^{-1}) (DMSO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>205, 293</td>
<td>\Pi \rightarrow \Pi^* \ n \rightarrow \Pi^* n</td>
<td>1720, 3400, 1615</td>
<td>C = O, OH, C = N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>220, 285, 750, 560, 365</td>
<td>\Pi \rightarrow \Pi^* \ n \rightarrow \Pi^* B_{2g}^2 \rightarrow E_{2g}^2 B_{g}^2 \rightarrow B_{1g}^2 B_{2g}^2 \rightarrow A_{1g}^2</td>
<td>1705, 1590, 797</td>
<td>C = O, C = N</td>
<td>1.68</td>
<td>80.5</td>
</tr>
<tr>
<td>C2</td>
<td>240, 625, 455</td>
<td>\Pi \rightarrow \Pi^* A_{2g}^4 \rightarrow T_{2g}^4 A_{2g}^4 \rightarrow T_{1g}^4 \ Eg^2 \rightarrow T_{1g}^2</td>
<td>1715, 1605, 415, 515</td>
<td>C = O, C = N, Cr – Cl, Cr – N, Cr – O</td>
<td>3.94</td>
<td>75.0</td>
</tr>
<tr>
<td>C3</td>
<td>265, 225, 715</td>
<td>\Pi \rightarrow \Pi^* \ n \rightarrow \Pi^* \ Eg^2 \rightarrow T_{1g}^2</td>
<td>1705, 1585, 355,400,470</td>
<td>C = O, C = N, Mn-Cl,Mn-N,Mn-O</td>
<td>2.5</td>
<td>18</td>
</tr>
<tr>
<td>C4</td>
<td>280, 570</td>
<td>\Pi \rightarrow \Pi^* \ n \rightarrow \Pi^* A_{2g}^1 \rightarrow T_{2g}^1</td>
<td>1700,1600,340,395,415</td>
<td>C = O, C = N, Fe-Cl,Fe-N,Fe-O</td>
<td>2.35</td>
<td>20</td>
</tr>
<tr>
<td>C5</td>
<td>475, 500</td>
<td>T_{1g}^4 \rightarrow T_{2g}^4 T_{1g}^4 \rightarrow T_{1g}^4(p)</td>
<td>1695,1600,295,415,480</td>
<td>C = O,F=N, Co-Cl,Co-O,Co-N</td>
<td>3.9</td>
<td>43</td>
</tr>
<tr>
<td>C6</td>
<td>306, 540</td>
<td>\Pi \rightarrow \Pi^* \ n \rightarrow \Pi^* \ A_{1g} \rightarrow A_{2g}^2</td>
<td>1710,1605,450,610</td>
<td>C = O, C = N, Ni – O , Ni - N</td>
<td>0.0</td>
<td>145</td>
</tr>
<tr>
<td>C7</td>
<td>250, 525</td>
<td>\Pi \rightarrow \Pi^* \ Eg^2 \rightarrow T_{2g}^2</td>
<td>1690,1580,250,400,490</td>
<td>C = O,C = N, Cu-Cl,Cu-O,Cu-N</td>
<td>1.6</td>
<td>25</td>
</tr>
</tbody>
</table>

Where \Pi is the average of three measurements of the absorption of solution containing astoichiometric amount of ligand and metal ion.
Results and Discussion

Elemental analysis:
The physical and analytical data of the quadridentate ligand (L), and its metal complexes are given in Table (1), which are in a satisfactory agreement with the calculated values. The suggested molecular formulas are supported by the subsequent spectral, and molar conductivity in $10^{-3}$M solution of DMSO. The Values of $\Lambda_m$ Table (2) show that $C_1$ and $C_2$ complexes are electrolytes in ratio 1:1, whereas $C_6$ complex is conductive in 2:1.

Infra-red spectra:
Table (2) lists the most useful infrared assignments for those bands most diagnostic of the mode of coordination of ligand (L). The infrared spectra of all metal complexes a decrease in the frequency by (15-20) cm$^{-1}$ on complexation for $\nu$(C=N) and $\nu$(C=O) and are constant with coordination carbonyl oxygen and azomethan nitrogen atoms, moreover the presence of bands at range. 415–610 and 395–415 cm$^{-1}$ are assigned to $\nu$(MNi) (12-14) and $\nu$(M-O) respectively. The infrared spectra of chloro complexes show one new band at 295–350 cm$^{-1}$ as assigned to $\nu$(M-Cl) of trans -isomer. A strong band in the oxo–vanadium (IV) complex was observed at 790 cm$^{-1}$ which is assigned to $\nu$(V=O) (15). Figs. (1) and (2).

Electronic spectra and magnetic moment studies:
The UV-visible spectra of the ligand and their metal complexes were recorded for their solutions in ethanol and DMSO as solvents in the range (200–1000) nm Figs. (6) and (7). The vanadyl complex ($C_1$) show a weak peak in the visible region 365, 560 and 750 nm which are assigned to $^2B_2 \rightarrow ^2E$, $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2A_1$ transitions respectively which are consistent with square pyramid environment of V(IV) complexes. The magnetic moment of oxo vanadium complex is consistent with presence of one unpaired electron. The ligand field spectra of Cr(III) complex exhibits two bands in the region 624 and 455 nm which are assignable to $^4A_2g \rightarrow ^4T_2g$ ($\nu_1$) and $^4A_2g \rightarrow ^4T_1g$ ($\nu_2$) transitions. The ($\nu_2/\nu_1$) ratio is 1.35 which is very close the value of 1.42 obtained for pure octahedral Cr(III) complexes. The Mn (II) complexes shows a slightly low value when compared to spin-only value (5.92 BM). The low values may be due to the presence of Mn (III) species or spin-exchange in the solid phase. The electronic spectrum of copper (II) complex shows a broad band at 525 nm, which is assigned to $E^2g \rightarrow ^2T_2g$ in distorted octahedral geometry. The observed magnetic value of Cu (II) complex exhibits $\mu_{eff}$ value well in the range to be expected for distorted octahedral geometry. In the case of other complexes, the assignments agree with the proposed stereochemistry. The results shown in Table (2), indicate that the molar ratio of (1:1) for complexes yielded high stability. Furthermore the molar absorptivities for all complexes is rather high, this probably was investigated on the presence of quadridentate ligand of O:N:O system which was stable kinetically from the formation of six-membered ring with the central metal ion. On the bases of magnetic data and spectral studies, oxo vanadium (IV), Cr (III), Mn (II), Co (III), and Cu (II) complexes have been assigned octahedral geometries (structures I and IV) while square–planer geometry is proposed for the Ni (II) complex (structure III).

General suggested stereo chemistry structures of complexes ($C_1$-C$_7$):
According to the results obtained from the elemental and spectral analysis, the general structures of the above mentioned complexes can be illustrated as follow:

Dichloro-1,2-(3-acetimino-4-hydroxy-6-methyl-pyran-2-one) ethane- Metal(II) Octahedral geometry of Mn, Fe, Co, and Cu(II) complexes.
Oxo-1,2-(3-acetimino-4-hydroxy – 6- methyl- pyran-2-one) ethane- Vanadium(IV)Sulfate.
Square pyramid geometry of V(IV) complex.

1,2-(3-acetimino-4-hydroxy – 6- methyl- pyran-2-one) ethane- Nickel(II) chloride.
square planer geometry of Nickel complex.

Dichloro-1,2-(3-acetimino-4-hydroxy-6-methyl-pyran-2-one) ethane- Chromium(III)
Octahedral geometry of Cr(III) complex.
References:

الخلاصة

تم تحضير قائمة شفف جلدية ربعية السن ذات نظام الواهب بواسطة التفاعل التكنولوجي لمركب O: N: N: O
-أ- استيل-4-هيدروكس-6-ستيل-پر-2-أون (I) مع الأثيلين ثنائي الأمين. تم تحضير معدقات الفناديو الروباعي و الكروم الثلاثي، المنغنيز، الحديد، الكوبالت، النينك، والنحاس الثنائية مع الليكينات الروباعي السن وعزلها وتم تشخيصها  طيفيا بواسطة طيف الأشعة تحت الحمراء المعززة بتحولات فورير، طيف الأشعة فوق البنفسجية والأشعة المرئية. إضافة إلى إنتاج الصيغة التركيبية المفترضة بواسطة تحايل (M%)، قياس الحساسية المغناطيسية للمعدقات مع الحالة الصلبة، التوصيل الموالي في محلول DMSO، وفضاء عن تحديد النسبة المولارية لللفاز، حساب استقرار المعدقات في محلول من خلال حساب ثابت تكون المعداتا طيفيا وأعطت نتائج 1:1 في جميع المعدقات، وثبت أن الليكينات الحديد سلوك ربعي السن المتعدد.

تم تعليق الشكل ثنائي السطوح لمعدقات الكروم الثلاثي، المنغنيز، الحديد، الكوبالت، والنحاس الثنائية فيما تم اقتراح الشكل المرعبي-مستوي لمعدقات النينك، والشكل الهرمي المرعبي لمعدقات الفناديو الروباعي.