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: N: O DONOR SYSTEM

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Abstract

The complexes of a new quodridentate Schiff base derived from ethylene diamine and 4-hydroxy-2-mehyl -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 $(4000\text{-}200)cm^{-1}$. Samples were measured as CsI–disc. The U.V.-visible spectra of compounds were recorded on UV–1650 PC shimdzu 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 spectro-photometer.

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).
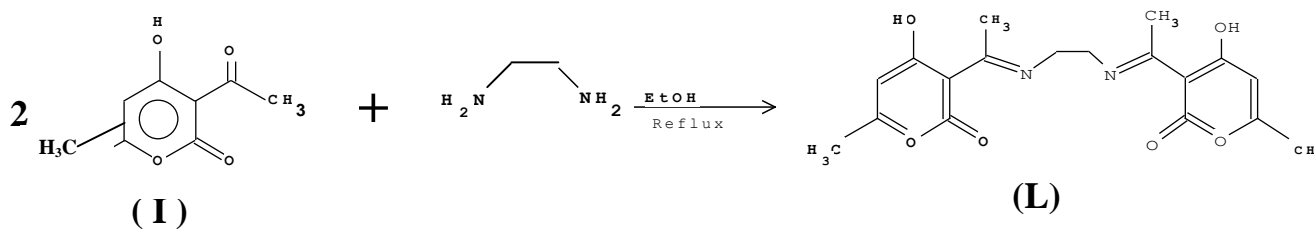
Scheme (1)

▪ **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] . Aseries of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrated metal chlorides or vandyl sulfate $VOSO_4.5H_2O$, 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 :

$$Ks = 1-\alpha/\alpha^2 c \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where α is the degree of the dissociation, and c is the concentration of the complex..

The absorbance of the solutions were measured at (λ_{max}) of the maximum absorption, furthermore the molar absorptivity (ϵ_{max}) for the complexes were calculated from equation (2) :-

$$A_m = \epsilon_{max} . b.C \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

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)
Physical and analytical data for the ligand and their complexes.

Compound	Symbol	Color	Yield (%)	M.P. C°	Elemental analysis Calc.(found)			
					C%	H%	N%	%M
Ligand	L	Yellow	80	180 - 182	57.83(56.99)	6.02(5.81)	8.43	-
[VO (L)]SO$_4$	C$_1$	Green	72	220 - 222	40.93(40.1)	4.26(3.66)	5.97(5.00)	10.66(9.69)
[Cr(L) Cl$_2$]Cl	C$_2$	Green	79	250^d	34.02(38.53)	4.06(3.71)	5.68(5.71)	10.96(10.01)
[Mn(L) Cl$_2$]	C$_3$	Brown	65	245 - 247	41.92(40.36)	4.366(3.66)	6.11)7.00)	12.00(11.31)
[Fe(L) Cl$_2$]	C$_4$	Dark red	79	258 – 260	41.83(40.33)	4.35(4.00)	6.10(6.50)	12.20(11.79)
[Co(L) Cl$_2$]	C$_5$	Light pink	90	270 – 272	41.73(40.09)	4.34(3.99)	6.08(6.51)	12.39(12.00)
[NiL]Cl$_2$	C$_6$	Red	95	298 – 300	43.1(40.1)	6.9(5.8)	7.5(8.1)	14.91(13.99)
[Cu(L) Cl$_2$]	C$_7$	Green	92	280 – 282	41.15(39.99)	6.00(5.31)	36.00(6.11)	13.61(12.89)

Where : d = decomposed

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

Complex	As	Am	α	λ_{max}	Ks(L.mol^{-1})	ϵ_{max}
C$_1$	0.31	0.30	0.166	365	$3*10^5$	5730
C$_2$	0.361	0.371	0.155	455	$4.5*10^5$	150
C$_3$	0.325	0.366	0.149	265	$2.5*10^5$	5990
C$_4$	0.371	0.379	0.15	280	$3.9*10^5$	6770
C$_5$	0.381	0.44	0.53	475	$4.8*10^5$	1500
C$_6$	0.391	0.401	0.163	550	$2.3*10^6$	380
C$_7$	0.401	0.461	0.181	525	$5.3*10^6$	250

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.

Compound	Electronic absorption bands	Assignment	IR frequency peaks (cm^{-1})	Assignment (stretching)	μ_e ff (BM)	Λ_m Ohm^{-1}.cm^2.mol^{-1} (DMSO)
L	205 293	$\Pi \to \Pi^*$ $n \to \Pi^*$	1720 3400 1615	C = O OH C = N	-	-
C$_1$	220 285 750 560 365	$\Pi \to \Pi^*$ $n \to \Pi^*$ $B_2g^2 \to E_2g^2$ $B_2g^2 \to B_1g^2$ $B_2g^2 \to A_1g^2$	1705 1590 390 400-600 797	C = O C = N V – N V = O	1.68	80.5
C$_2$	240 625 455	$\Pi \to \Pi^*$ $A_2g^4 \to T_2g$ $A_2g^4 \to T_1g^4$	1715 1605 350 415 515	C = O C = N Cr – Cl Cr – N Cr – O	3.94	75.0
C$_3$	265 225 715	$n \to \Pi^*$ $\Pi \to \Pi^*$ $Eg^2 \to T_1g^2$	1705 1585 355,400,470	C = O C = N Mn-Cl,Mn-N,Mn-O	2.5	18
C$_4$	280 570	$n \to \Pi^*$ $A_2g^1 \to T_2g^1$	1700,1600 340,395,415	C = O ,C = N Fe-Cl,Fe-N,Fe-O	2.35	20
C$_5$	475 500	$T_1g^4 \to T_2g^4$ $T_1g^4 \to$ $T_1g^4(p)$	1695,1600 295,415,480	C = O,F=N Co-Cl,Co-O Co-N	3.9 4.2	43
C$_6$	306 540	$n \to \Pi^*$ $A_1g \to A_2g^2$	1710,1605 450,610	C = O ,C = N Ni – O , Ni - N	0.0	145
C$_7$	250 525	$\Pi \to \Pi^*$ $Eg^2 \to T_2g^2$	1690,1580 250 , 400,490	C = O ,C = N Cu-Cl ,Cu-O ,Cu-N	1.6	25

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 ratio, as well as magnetic moment and molar conductivity in 10^{-3}M solution of DMSO. The Values of Λ_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 $\upsilon_{(C=N)}$ and $\upsilon_{(c=o)}$ and are constant with coordination carbonyl oxygen and azomethan nitrogen atoms, moreover the presence of bands at range. 415–610 and 395–415cm^{-1} are assigned to $\upsilon_{(M-N)}$ [12-14] and $\upsilon_{(M-O)}$ respectively. The infrared spectra of chloro complexes show one new band at 295–350 cm^{-1} as assigned to $\upsilon_{(M-Cl)}$ of trans - isomer [15]. A strong band in the oxo-vanadium (IV) complex was observed at 790cm^{-1} which is assigned to $\upsilon_{(V=O)}$ [16].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 750nm which are assigned to $^2B_2 \rightarrow ^2E$, $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2A_1$ transitions respectively[17] 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[18]. The ligand field spectra of Cr(III) complex exhibits two bands in the region 624 and 455 nm which are assignable to $^4A_2g \rightarrow ^4T_2g$ (υ_1) and $^4A_2g \rightarrow ^4T_1g$ (f)υ_1 transitions. The (υ_2/υ_1) ratio is 1.35 which is very close the value of 1.42 obtained for pure octahedral Cr(III)

complexes[19]. 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[20]. The electronic spectrum of copper (II) complex shows a broad band at 525nm, which is assigned to $E^2g \rightarrow ^2T_2g$ in distorted octahedral geometry[17]. The observed magnetic value of Cu (II) complex exhibits μ_{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[22]. 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:
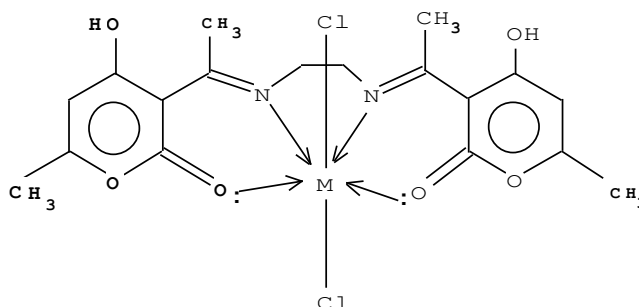

Where M = Mn(II), Fe(II), Co(II) or Cu(II)

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.
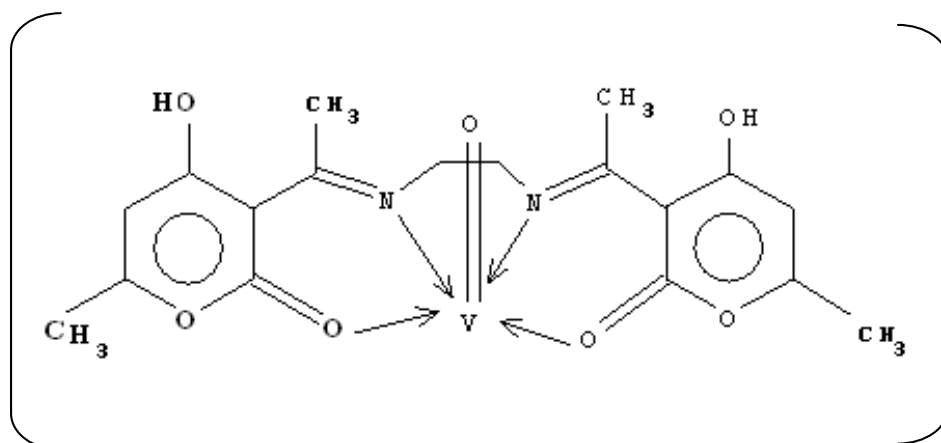
**Oxo-1,2-(3-acetimino-4-hydroxy – 6- methyl- pyran-2-one) ethane- Vanadium(IV)Sulfate.
Square pyramid geometry of V(IV) complex.**
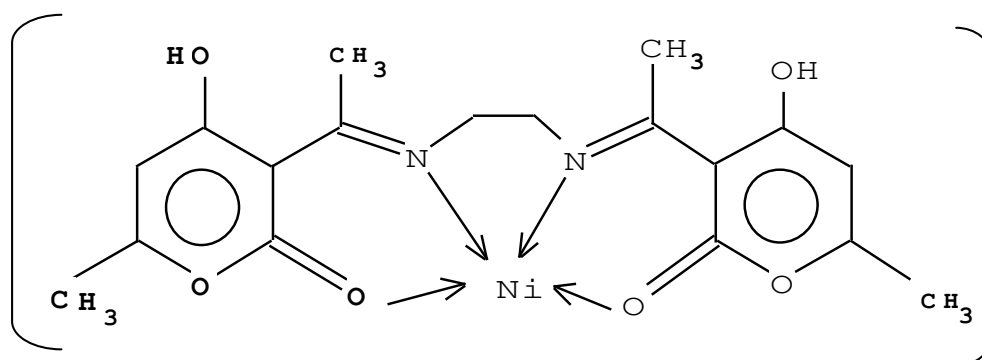
**1,2-(3-acetimino-4-hydroxy – 6- methyl- pyran-2-one) ethane- Nickel(II) chloride.
square planer geometry of Nickel complex.**
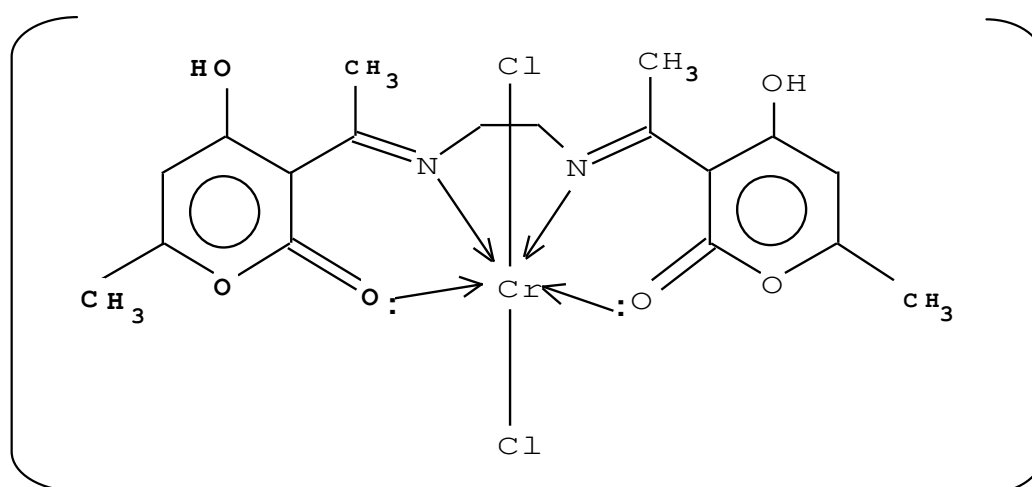
**Dichloro-1,2-(3-acetimino-4-hydroxy-6-methyl-pyran-2-one) ethane- Chromium(III)
Octahedral geometry of Cr(III) complex.**

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الخلاصة

تم تحضير قاعدة شيف جديدة رباعية السن ذات نظام O: N: N: O الواهب بواسطة التفاعل ألتكثيفي لمركب 3–استيل–4–هيدروكسي–6–مثيل–بايران–2–أون (I) مع الاثيلين ثنائي الأمين.تم تحضير معقدات الفناديوم الرباعي و الكروم الثلاثي, المنغنيز ,الحديد ,الكوبلت , النيكل, والنحاس الثنائية مع الليكاند الرباعي السن وعزلها وتم تشخيصها طيفيا بواسطة طيف الأشعة تحت الحمراء المعززة بتحويلات فورير, طيف الأشعة فوق البنفسجية والأشعة المرئية, إضافة لإثبات الصيغة التركيبية المقترحة بواسطة تحاليل C.H.N والنسبة المئوي ة للفلز (M%) , قياس الحساسية المغناطيسية للمعقدات بالحالة الصلبة, التوصيل المولاري في محلول DMSO. , وفضلا عن تحديد النسبة المولية للفلز : ليكاند ,وحساب استقرارية المعقدات في المحلول من خلال حساب ثابت تكوين المعقدتا طيفيا وأعطت نتائج 1:1 في جميع المعقدات, واثبت أن الليكاند الجديد يسلك سلوك رباعي السن المتعادل.

تم تعيين الشكل ثماني السطوح لمعقدات الكروم الثلاثي,المنغنيز, الحديد, الكوبلت, والنحاس الثنائية فيما تم اقتراح الشكل المربع–مستوي لمعقد النيكل والشكل الهرم المربعي لمعقد الفناديوم الرباعي.