

**Synthesis ,Characterization and Kinetic Study of Metal
Complexes with new acyclic Legend N_2O_2
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Abstract

The complexes of a new tetra dentate acyclic ligand derived from 1,2-diamino propane and 3-acetyl-4-hydroxy-6-methyl-pyran-2-one ,with vanadium(IV), Cr(III), F(II), Fe(III), Mn(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 H^1 NMR ,I.R. and U.V.-Visible. Spectra. Metal to ligand ratio in all complexes has been found to be 1:1. The Schiff base behaves as neutral tetra dentate legend with N_2O_2 system. Cr(III), Fe(III), Mn(II), Co(II), and Cu(II) complexes have been assigned octahedral stereo chemistry, Ni(II) complex has been suggested as square planer geometry, while V(IV) complex was square pyramid. The thermodynamic parameters such as ΔG^* , ΔH^* and ΔS^* are calculated from the curve of $\log K_s$ verse temperature. It is found that Ni(II) and Cu(II) are the most stable complexes, from the data of formation constant and Gibbs free energy.

Key words: kinetic study, metal complexes, acyclic legends, thermodynamic stability and stability constants.

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تحضير, تشخيص ودراسة حركية لمعقدات فلزية مع ليكاند جديد شبه حلقي نوع N_2O_2

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الخلاصة

تم تحضير ليكاند متعدد السن ذات النظام المفتوح رباعية السن من ذرات واهبة ذات نوع N_2O_2 الواهب بواسطة التفاعل ألتكثيفي لمركب 3-استيل-4-هيدروكسي-6-مethyl-بايران-2-أون (I) مع 1,2-ثنائي امينو بروبان كليكاند استخدم في تخليق معقدات جديدة للفناديوم الرباعي و الكروم والحديد الثلاثية, المنغيز , 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, وطيف الرنين النووي المغناطيسي (H^1NMR) إضافة لإثبات الصيغة التركيبية المقترحة بواسطة تحاليل C.H.N والنسبة المئوية للفلز (M%), قياس الحساسية المغناطيسية للمعقدات بالحالة الصلبة, التوصيل المولاري في محلول DMF, وفضلا عن تحديد النسبة المولية للفلز : ليكاند, وحساب استقرارية المعقدات في المحلول من خلال حساب ثابت تكوين المعقدات طيفيا وبنسب مولية 1:1 في جميع المعقدات, واثبت أن المشتق الجديد N_2O_2 يسلك سلوك رباعي السن مكونا معقدات كلينية مستقرة حركيا وثرموديناميكيا. تم تعيين الشكل ثنائي السطوح لمعقدات الكروم والحديد الثلاثية, المنغيز, الكوبلت, والنحاس الثنائية فيما تم اقتراح الشكل المربع – مستوي لمعقد النيكل والشكل الهرم المربعي لمعقد الفناديوم الرباعي. تم حساب الدوال الثرموديناميكية ΔG^* و ΔH^* و ΔS^* ومن خلالها تم استخراج ثابت تكوين المعقدات الموصلة الكتروليتيا ووجد ان معقدي النيكل والنحاس الثنائية هي الاكثر استقرارا.

الكلمات المفتاحية: دراسات حركية, معقدات فلزية, ليكاندات شبه حلقيه, استقرارية ثرموديناميكية وثوابت الاستقرار.

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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 properties⁽¹⁻³⁾. The coordination compounds tetra dentate 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 tetra dentate Schiff bases⁽⁵⁻⁶⁾. Pyran-2-one derivatives containing hydroxyl, acetyl and phenyl azo substitutes have been employed as complexing agents⁽⁷⁻¹⁰⁾. Literature 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 tetra dentate Schiff base (L) derived from 3-acetyl 4-hydroxy-6-methyl -2- one (I) and ethylene diamine and its complexes with vanadium(IV), Cr(III), Fe(III), Mn(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. The FTIR spectra were recorded using FTIR – 8300 Shimadzo in the range (4000-400)cm⁻¹ and ν Samples of metal complexes were measured as CsI – disc, while the free ligand was done in KBr – disk. The U.V.- visible spectra of compounds were recorded on Shimadzu model spectrophotometer. Magnetic susceptibility χ_g of the solid complexes were done at room temperature using magnetic balance – model MS-Bmkl at AL-Nahrain University by Gouy method using $Co[Hg(SCN)_4]$ as calibrate. Metal estimations were carried out spectrophotometrically using atomic absorption Shimadzo AA-670 spectrophotometer. The proton NMR spectra of the prepared compounds were done on Varian 300 MHz in Jordan university using $Si(CH_3)_4$ as internal reference.

Molar conductance of the solutions of the complexes in DMF ($10^{-3}M$) were measured on PW9526 digital conductivity meter. The elemental analysis data of the ligand and complexes were obtained on a Carlo Erba Model EA 1108 (C.H.N.) Elemental analyzer. The presents of

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metals in complexes (C_1 - C_6) were estimated in Ibn-Cina center via Shimdzu AA680 G atomic absorption spectrophotometer.

Materials and preparations

Dehydroacetic acid(I) starting material for synthesis of N_2O_2 ligand (L) was prepared by the reported procedure⁽⁹⁾. All the other chemicals used were of AR grade. The metal salt solutions were normalized by the recommended procedure⁽¹¹⁾. Dilute solutions of the metal ions and tetra dentate ligand (N_2O_2) under study of $2.5 \times 10^{-6}M$, $1 \times 10^{-6}M$, $2.5 \times 10^{-5}M$, $1 \times 10^{-5}M$ and $1 \times 10^{-4}M$ were prepared with accurate dilution.

▪ Synthesis of the Schiff base (L):

An ethanolic solution (I) (1.56gm, 0.01 mol in 25ml) was added to an ethanolic solution of 1,2-diamino propane (0.43, 0.005mol in 10ml), 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 described in scheme(1). The physical properties of ligand shown in table (1).

▪ Preparation of the complexes:

The metal complexes were prepared by refluxing hot ethanolic solutions of metal chloride (0.01 mol) [except in case of Fe(II) and vanadium(IV) complexes where aqueous ethanolic solutions were used] and the ligand (0.01mol) for 3hr, on a water bath. The complexes separated on adjusting the PH to 7.5 . were filtered, washed with ethanol, chloroform and then left overnight to afford 0.67g(79% yield)of deep yellow crystals of polydentate ligand.

• Study of complex formation in solution :

The complexes of the ligand (L) with the selected metal ions [Cr(III), Fe(III),V(IV),Mn(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

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method⁽¹⁰⁾ . A series of solutions were prepared having a constant concentration (C) $10^{-3}M$ of the hydrated metal chlorides or vanadyl sulfate $VOSO_4 \cdot 5H_2O$, 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 (K_s):

The stability constant of the (1:1) [M:L] complex, was evaluated using the following equation⁽¹⁰⁾ :

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

Where α is the degree of the dissociation of ionization of (C₁-C₇) were determined by the equation (2):

$$\alpha = (A_s - A_m) / A_m \quad \text{----(2)}$$

or conduct metrically by the equation (3):

$$\alpha = \Lambda_m / \Lambda^\circ \quad \text{----(3)}$$

Λ_m : molar conductance of the complex solution in $10^{-3}M$ (DMF).

Λ° : molar conductance in infinite dilution⁽¹²⁾.

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(4)

:-

$$A_m = \epsilon_{max} \cdot b \cdot C \quad \text{----(4)}$$

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 1cm .

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Λ_m = molar conductance were measured in units of $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$.

SD = standard deviation which is estimated after carrying out three data of experiments.

An evident in table (4) that stability constant K_s for Ni(II) complex in ($2.3 \cdot 10^6$) , compared with Cr(III) complex in ($4 \cdot 10^5$) $\text{L} \cdot \text{mol}^{-1}$ which investigates the presence of d^8 configuration and agrees with Irving Willimson⁽¹³⁾ .

a = molar absorptivity have been measured in $\text{L}^{-1} \cdot \text{mole}^{-1} \cdot \text{cm}$

b = formation constant of complexes were determined by spectroscopic method

The stability constant (K_s) was evaluated using the following equations:

$$K_s = (1 - \alpha) / \alpha^2 c \quad \text{----(5)}$$

$$A = A_m - A_s / A_m \quad \text{----(6)}$$

(α) is the degree of the dissociation (c)

is the concentration of the complex in (mole/L) units, (A_s and A_m) are the absorbance values of the solution were measured at (λ_{max}) of the maximum absorption. The molar absorptivity (ϵ_{max}) (eq.7) has been calculated using equation :

$$A = \epsilon_{\text{max}} \cdot b \cdot C \quad \text{----(7)}$$

(A) Is the average of three measurements of the absorption containing the same amount of metalion and three fold excess of ligand, (b) is the depth of the quartz cell usually equal 1 cm⁽¹⁰⁾.

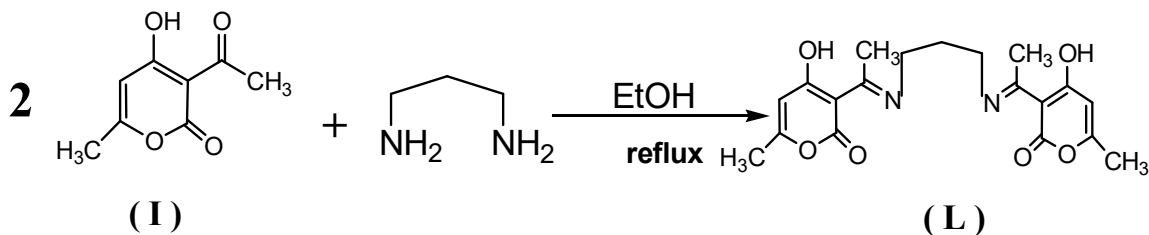
Results and Discussion:

The free tetra dentate ligand (L) has been prepared by condensation reaction of two moles of dehydroacetic acid and one mole of 1,2-diamino propane scheme (1). The ligand was stable in atmosphere , and insoluble in common organic solvents except DMF and DMS.

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Scheme (1)

Elemental analysis

The physical and analytical data of the tetra dentate legend (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 DMF. 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⁽¹⁴⁾.

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	78	120–122	60.83(59.99)	6.02(5.77)	7.43(6.66)	-
$[VO(L)]SO_4$	C_1	Olive	88	203–205	56.93(55.1)	4.26(3.66)	4.97(5.00)	11.33(10.00)
$[Cr(L)Cl_2]Cl$	C_2	Pale green	79	250 ^d	51.02(51.53)	5.06(56.71)	5.68(6.71)	12.01(13.87)
$[Mn(L)Cl_2]$	C_3	pink	70	245–247	53.92(52.36)	54. (3.66)	5.11(7.00)	10.43(11.31)
$[Fe(L)Cl_2]$	C_4	Dark brown	79	258–260	54.83(55.33)	3. (3.00)	4.10(6.50)	12.20(11.79)
$[Co(L)Cl_2]$	C_5	Dirty green	93	245–247	58.73(56.09)	4.4 (3.99)	6.08(7.51)	15.39(14.66)
$[Ni(L)Cl_2]$	C_6	Orange	73	233–235	52.1(53.1)	6.2(5.8)	6.5(7.1)	13.91(13.99)
$[Cu(L)Cl_2]$	C_7	Pale blue	77	266 ^d	41.15(39.99)	5.00(5.31)	36.00(6.11)	13.61(12.89)

Where : d = decomposed

* = analysis of metal content via flame atomic absorption

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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 complication for $\nu_{(C=N)}$ and $\nu_{(C=O)}$ and are constant with coordination carbonyl oxygen and azomethine nitrogen atoms, moreover the presence of bands at range. 415 – 610 and 395 – 415cm⁻¹ are assigned to $\nu_{(M-N)}$ (15-16) and $\nu_{(M-O)}$ respectively. The infrared spectra of chloro complexes show one new band at 295 – 350cm⁻¹ as assigned to $\nu_{(M-Cl)}$ of trans - isomer (17). A strong band in the vanadium(IV) complex was observed at 790cm⁻¹ which is assigned to $\nu_{(V=O)}$ (18).figures (1,2 and 3).

Table (2): 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 (DMF)
L	293	$\Pi \rightarrow \Pi^*$	1705 3400 1615	C = O OH C = N	-	-
Cr(III)	220 285 541 392 388	$\Pi \rightarrow \Pi^*$ $n \rightarrow \Pi^*$ $A_2g^4 \rightarrow T_2g^4$ $A_2g^4 \rightarrow T_1g^4$ $A_2g^4 \rightarrow T_1g^4(p)$	1677 1578 350 415 515	C = O C = N Cr - Cl Cr - N Cr - O	3.04	75
VO	276 606 720	$\Pi \rightarrow \Pi^*$ $B_2 \rightarrow E_2$ $B_2g^2 \rightarrow E_g^2$	1660 1588 400-600 797	C=O C=N V-N V=O	1.5	82.0
Mn(II)	265 362 415	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$ $A_1g^6 \rightarrow E_g^4$	1685 1585 400,470	C = O C = N Mn-Cl,Mn-N,Mn-O	4.4	15
Fe(III)	426 417	$n \rightarrow \Pi^*$ $A_2g^6 \rightarrow T_2g^4$	1644,1600 340, 415	C = O , C = N Fe-Cl,Fe-N,Fe-O	2.35	10
Co(II)	475 500	$T_1g^4 \rightarrow T_2g^4(b)$ $T_1g^4 \rightarrow T_1g^4(p)$	1710,1600 295,415,480	C = O,C=N Co-Cl,Co-O Co-N	4.2	55
Ni(II)	306 540	$L \rightarrow M.CT$ $A_1g^1 \rightarrow B_1g^1$	1660,1564 450,543	C = O , C = N Ni - O , Ni - N	0.33	160
Cu(II)	250 525	$\Pi \rightarrow \Pi^*$ $E_g^2 \rightarrow T_2g^2$	1675,1580 323 , 400,490	C = O , C = N Cu-Cl ,Cu-O ,Cu-N	1.35	22

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H¹NMR Spectra

A review of the literature revealed that NMR spectroscopy has been proven to be useful in establishing that nature and structure of acyclic tetra dentate N₂O₂ as well as their complex in solutions. The NMR spectra of ligand and Ni^(II) complex were recorded in d₆-DMSO. solvent using Si(CH₃)₄ as internal standard up on examination the figures (4 and 5) table(3), it is found –OH signal at δ 14.0 ppm that appeared in the spectrum of free ligand has subjected to down load due to complication through – OH and C=O of pyran ring as well as the signal in the range 6-8.0 ppm revealed the presence of C=C-H of pyran-2-one ring. Moreover the signal observed at 3.35ppm and 4.5 ppm indicates the propyl group of(CH₂)₃ and 2CH₃ methyl groups on pyran ring⁽¹⁹⁾. The signals δppm of Ni^(II) complex revealed the diamagnetic properties of d⁸- complex and suggests the square planner symmetry around Ni^(II) ion⁽²⁰⁾.

Table (3): Absorption (chemical shifts) δppn for ligand and Ni(II) complex in d₆-DMSO solvent

Complex	Δppm	Assignment
L	13.10	(O-H)-position2
	8.50	(O-H)-position4
	(6-8)	(H-) of pyran.)and propyl group(6H)
	1.9	
Ni ^(II) –L	14.05	O-H (2H,singlet)-2-position
	8.5	O-H (2H,singlet)4-position
	7-7.5	C-H (multiplet)-pyran-ring
	2-3	CH ₂ -(triplet)

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 Fig. (3and4). The vanadyl complex (C₁) show a weak peak in the visible region 365, 560 and 750nm which are assigned to ²B₂ → ²E, ²B₂ → ²B₁ and ²B₂ → ²A₁ transitions respectively⁽¹⁷⁾ which are consistent with octahedral environment of V(IV) complexes. The

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magnetic moment of 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 ${}^4A_{2g} \longrightarrow {}^4T_{2g}(\nu_1)$ and ${}^4A_{2g} \longrightarrow {}^4T_{1g}(f)\nu_1$ transitions. The (ν_2/ν_1) ratio is 1.35 which is very close the value of 1.42 obtained for pure octahedral Cr(III) complexes⁽²¹⁾. The Mn(II) complexes shows a slightly low value when compared to spin-only value (5.92BM). The low values may be due to the presence of Mn(III) species or spin – exchange in the solid phase⁽²²⁾. The electronic spectrum of copper(II) complex shows a broad band at 525nm, which is assigned to $E^2g \longrightarrow {}^2T_{2g}$ in distorted octahedral geometry⁽²⁰⁾. The observed magnetic value of Cu(II) complex exhibits μ_eH value well in the range to be expected for distorted octahedral geometry. In the case of other complexes, the assignments agree with the proposed stereo chemistry. The results shown in table(2), indicate that the molar ratio of(1:1) for complexes yielded high stability. Furthermore the molar extinction coefficients for all complexes is rather high, this probably was investigated on the presence of tetra dentate ligand of N_2O_2 system which was stable kinetically from the formation of six-membered ring with the central metal ion⁽²³⁾. On the bases of magnetic data and spectral studies ,vanadium(IV), Cr(III), Mn(II), Co(III), and Cu(II) complexes According to previous data reported by Fengetal have been assigned octahedral geometries (structures I and IV) while square – planer geometry is proposed for the Ni(II) complex (structure III)⁽²⁴⁾.

Table(4): Stability constants, and molar absorptivities of the complexes (C₁-C₇).

Complex	A_s	A_m	A	λ_{max}	$K_s(L.mol^{-1})$	ϵ_{max}
C1	0.33	0.30	0.212	381	$4 \cdot 10^5$	5730
C2	0.56	0.371	0.155	521	$4.6 \cdot 10^5$	150
C3	0.678	0.366	0.265	265	$2.5 \cdot 10^5$	5990
C4	0.345	0.379	0.143	298	$3.9 \cdot 10^5$	6770
C5	0.381	0.451	0.53	475	$4.8 \cdot 10^5$	1500
C6	0.234	0.521	0.166	474	$2.3 \cdot 10^6$	380
C7	0.451	0.461	0.123	600	$5.3 \cdot 10^6$	250

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

Molar Conductance of complex

By using the relation $\Lambda_m = K/C$ the molar conductance of the complex (Λ_m) can be calculated where C is the molar concentration of 10^{-3} molar of their solutions at $25 \pm 2^\circ C$ were measured. It is calculated from the results that $Cr^{(III)}$, $V^{(IV)}$, $Ni^{(II)}$ are electrolytes in 1:1 and 1:2 ratio respectively⁽¹⁴⁾. The thermodynamic of new metal complex have been measured conductometrically that $\Delta G = -1150$ KJ/mole for $V(IV)$ complex. In addition the stability constant of $VO(IV)$ complex in DMF various temperature, was obtained from variation of molar conduction as a function of ligand/metal cation mole ratios using a Genplot computer program⁽²⁵⁾. Sufficiently, large value of ΔG^* for $VO(IV)$ complex showed that spontaneous formation of the complexes⁽²⁶⁾.

Table (5): Thermodynamic parameters for $VO(IV)$, $Cr(III)$ and $Ni(II)$ complexes in DMF solutions

complex	Λ_m $Ohm^{-1}.cm^2.mol^{-1}$	$-\Delta G^* \pm SD$ KJ/mole	$\Delta H^* \pm SD$ KJ/mole	$\Delta S^* \pm SD$ KJ/mole
$Cr^{III}-L$	85	15.85 ± 2.80 (13.263)	-83.5 ± 6.4	-195 ± 18.9
$VO^{IV}-L$	91	18.95 ± 0.44 (14.50)	35.06 ± 8.00	148.5 ± 30.1
$Ni^{II}-L$	135	20.51 ± 0.56 (25.3×10^3)	49.71 ± 7.3	149.5 ± 2.500

The thermodynamic parameters, free energy ΔG^* , enthalpy change ΔH^* and entropy change ΔS^* were calculated by the following relationships⁽²⁷⁾

$$\Delta G^* = -RT \ln K_{eq} \quad \text{----(8)}$$

And from changing the values K_{eq} with $1/T$

$$\left(\frac{d \log K_{eq}}{dt} \right) = \left(\frac{\Delta H^*}{2.303RT^2} \right) \quad \text{----(9)}$$

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The value of ΔH^* were estimated.

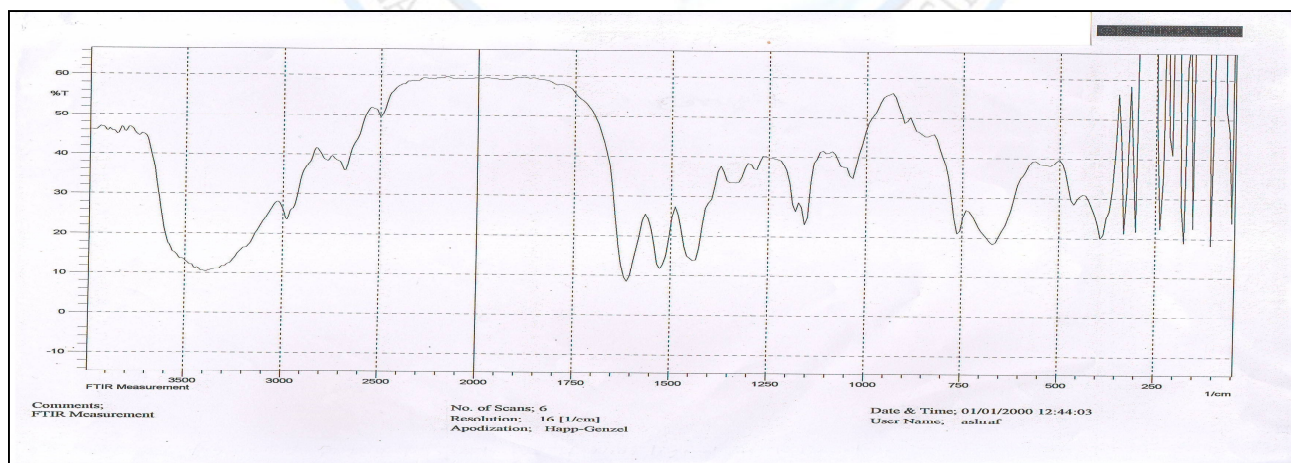
Finally ΔS^* value was calculated from Gibbs equation:

$$\Delta G^* = \Delta H^* - T\Delta S^* \text{ ----(10)}$$

Table (6): Parameters for evaluation of K_s of Cr^{II}, Co^{II}, Ni^{II} and Cu^{II} complex

Complex	A _s	A _m	A	K _s ^b	ε _{max} ^a	λ _{max} nm
Cr ^{III} -L	0.93	0.85	0.039	5.9*10 ⁴	4590	380
Co ^{II} -L	0.93	0.98	0.05	4.3*10 ⁴	1450	395
Ni ^{II} -L	1.05	0.95	0.070	6.1*10 ⁴	3570	480
Cu ^{II} -L	0.85	0.95	0.049	9.1*10 ⁵	520	600

The vales of K_{eq} of the electrolytic complexes VO(IV),Cr(III) and Ni(II), were determined by using Ostwald dilution equation⁽²⁸⁾,after estimation the infinite conductance



Figure(1):F.T.I.R spectrum of ligand in KBr disk

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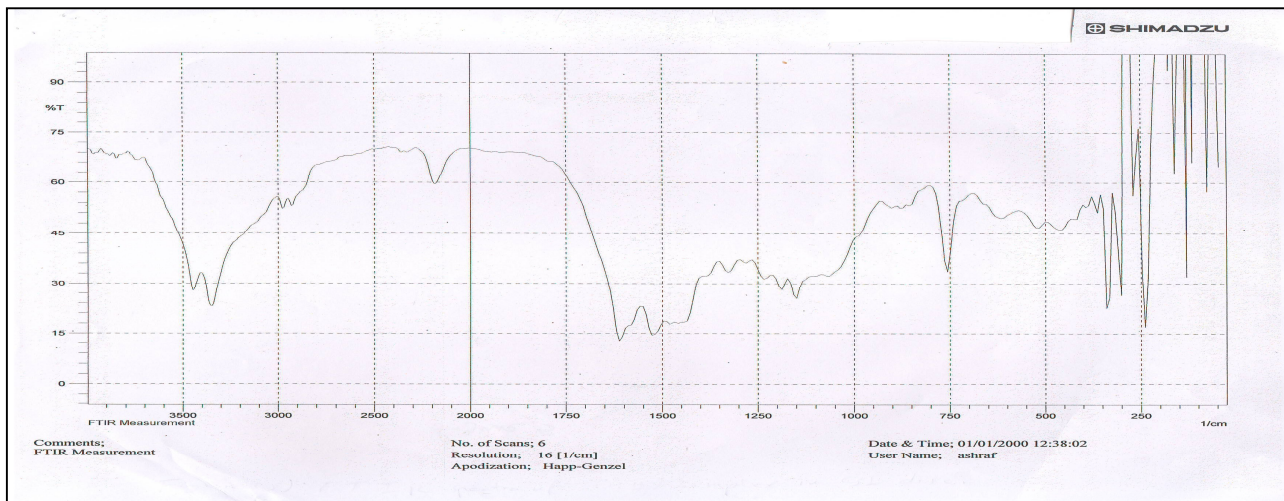


Figure (2):F.T.I.R spectrum of Cr(III) complex in CsI disk

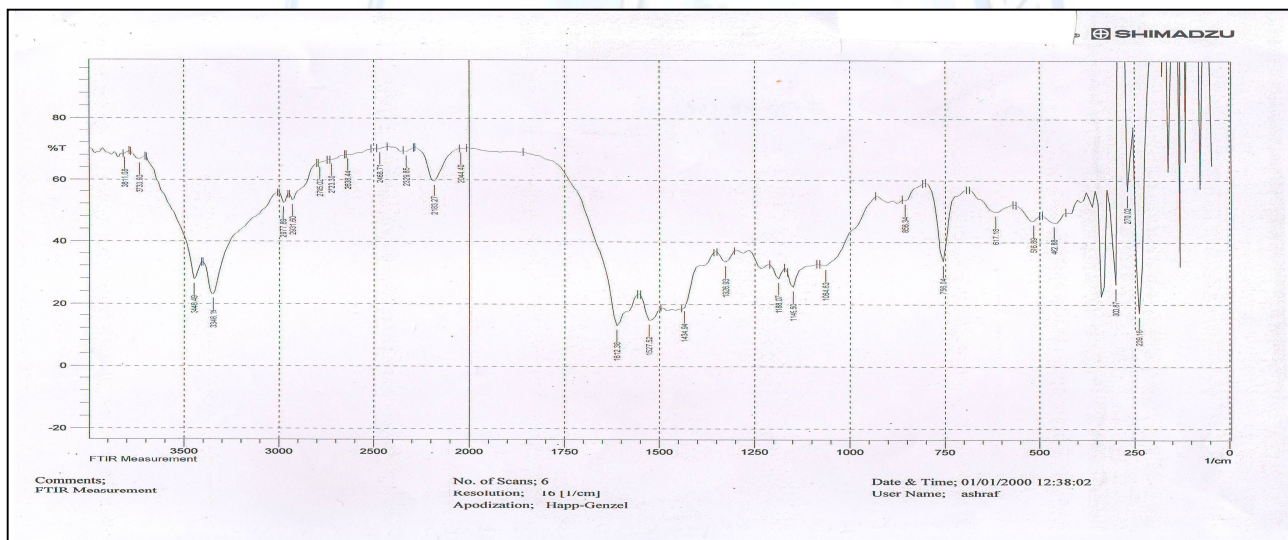
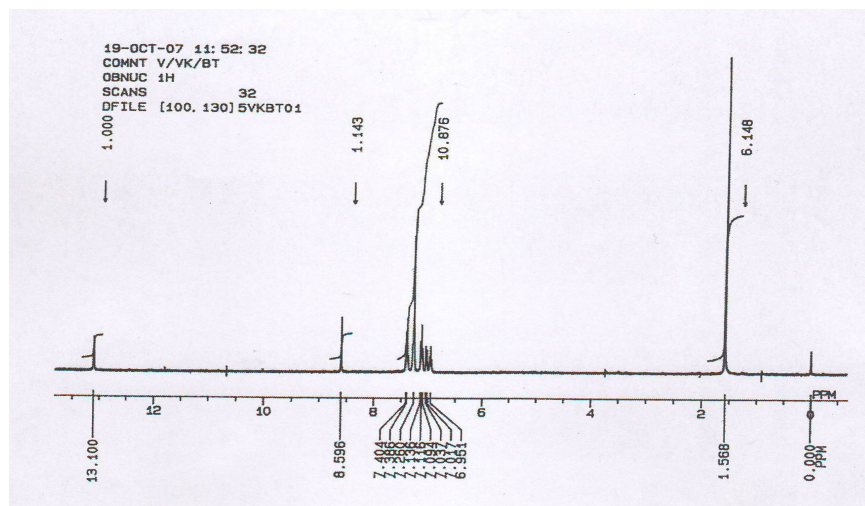
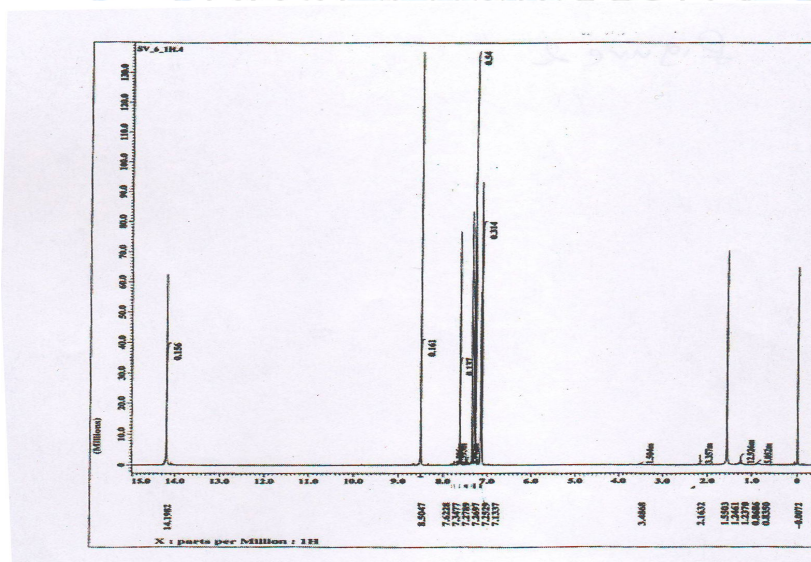


Figure (3):F.T.I.R spectrum of Cu(II) complex in CsI disk

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Figure(4): H^1 NMR spectrum of ligand in d_6 -DMSO solvent



Figure(5): H^1 NMR spectrum of Ni(II) complex in d_6 -DMSO solvent

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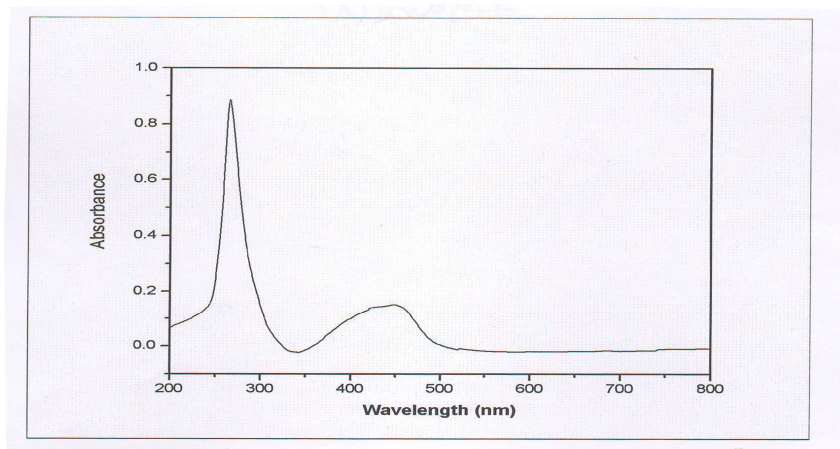


Figure (6):UV-Visibe of ligand in ethanol ($10^{-3}M$)

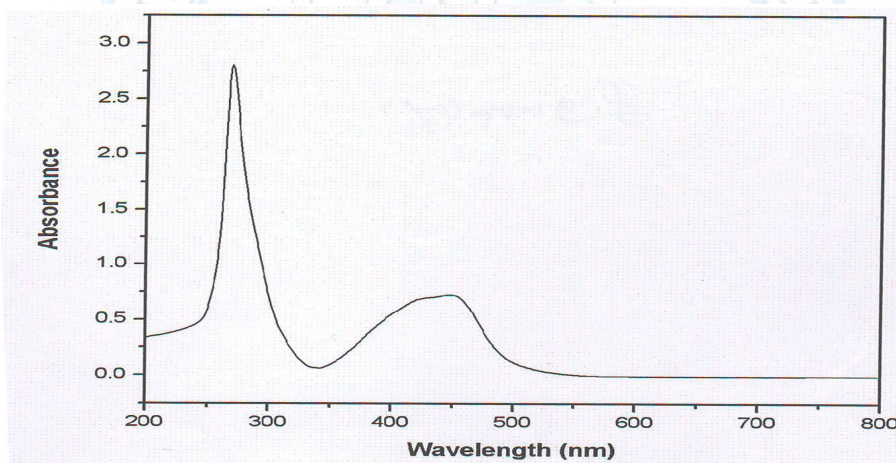


Figure (7):UV-Visible of Co(II) complex in DMF solution($10^{-3}M$)

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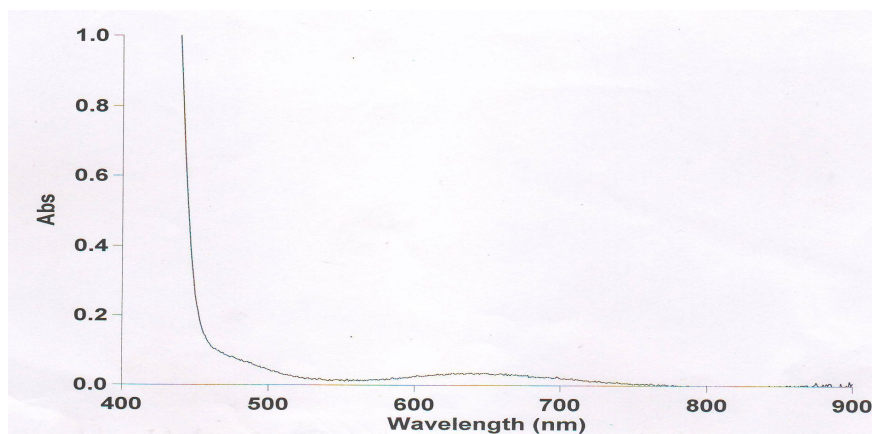


Figure (8): Visible of Cu(II) complex in DMF solution ($10^{-2}M$)

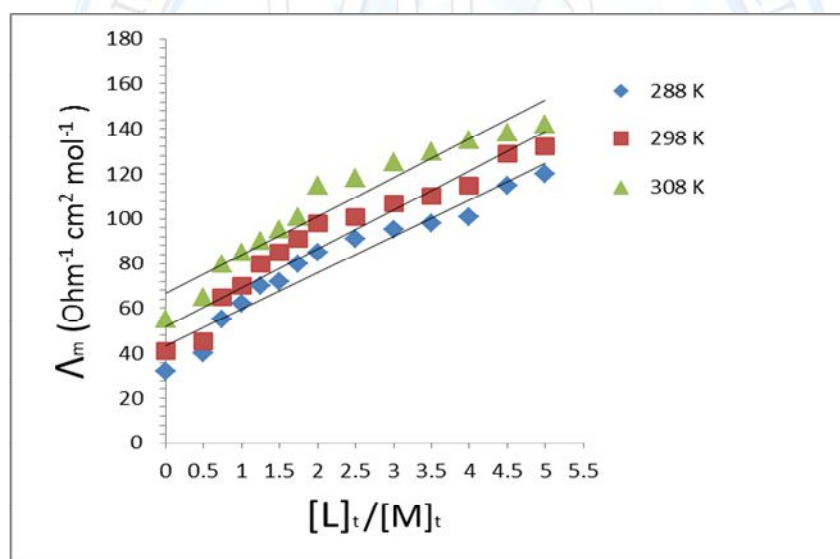
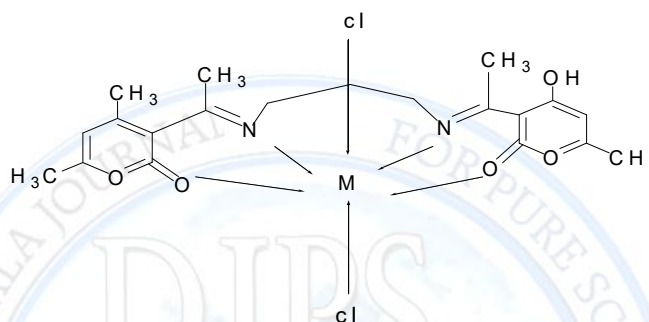


Figure (9): Molar conductance mole-ratio for VO(IV) complex in pure DMF at different temperature

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General suggested stereo chemistry structures of complexes (C₁ – C₇)

According to the results obtained from the elemental and spectral analysis, the general structures of the above mentioned complexes can be illustrated as follow:

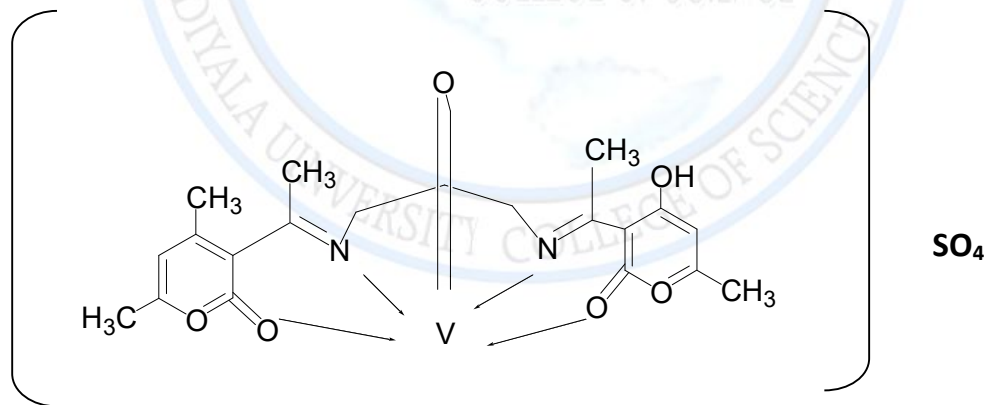


Where M = Mn(II), Fe(III),

Co(II) or Cu(II)

Dichloro-1,2-(3-acetimino-4-hydroxy-6-methyl-pyran-2-one) propane- Metal(II)

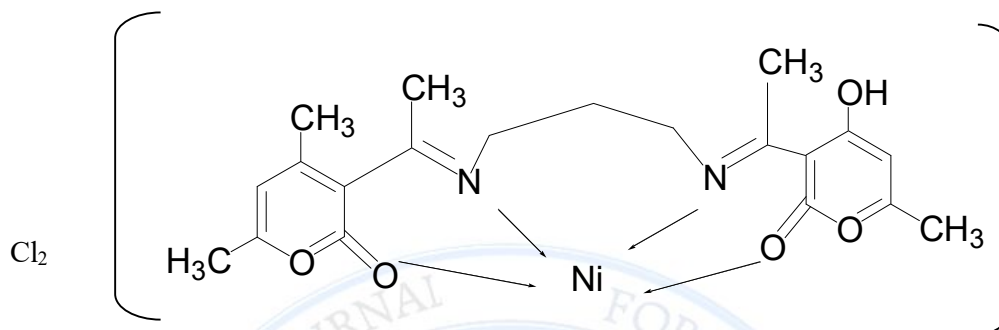
Octahedral geometry of Mn, , Co, Cu(II) and Fe(III) complexes



Oxo—1,2-(3-acetimino-4-hydroxy – 6- methyl- pyran-2-one) propane- Vanadium(IV) Sulfate.

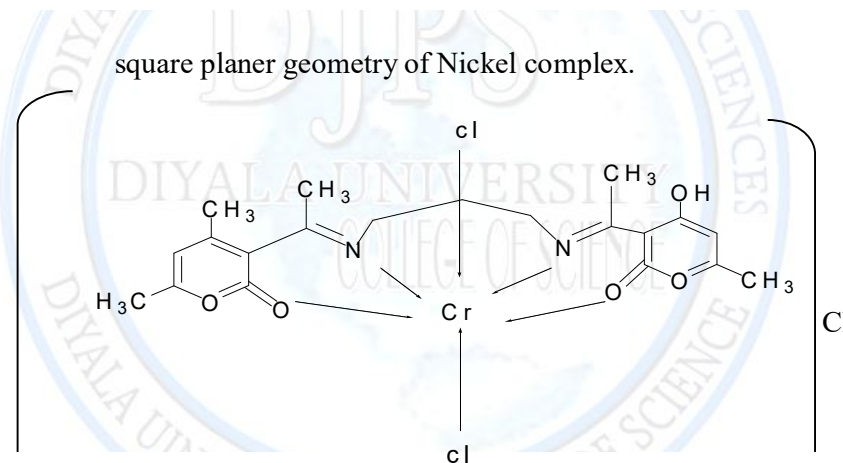
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Octahedral geometry of V(IV) complex.



**1,2-(3-acetimino-4-hydroxy – 6- methyl- pyran-2-one) propane- Nickel(II)
chloride.**

square planer geometry of Nickel complex.



Dichloro-1,2-(3-acetimino-4-hydroxy-6-methyl-pyran-2-one) propane- Chromium(III)

Octahedral geometry of Cr(III) complex.

References

1. S.Tuba ,T.Serap and Cigdem I.J.*Chem and Eng.*(2011),54(4),pp.978-983.
2. S.D.Poonam,AmitR.Yaud,J.Bohjan,and,S.A.Aswar,*WorldJ.of Chem.*,(2010),5(1),pp.57-61.
3. A.S.Munde, V.A.Shelke, S.M.Jadhav, A.S.KirdantandT.K. Chondhekar, *Appl.Sci.J.* (2012),3(1),pp.157-182.

Synthesis, Characterization and Kinetic Study of Metal
Complexes with new acyclic Legend N_2O_2
Wael Mohammed Hamud

4. K.Popov,P.Igor,W.Hams,and,V.Andrey,Internationalprof.Test.J.,(2007),9(2),pp.13-17.
5. Smith,R.M,Martel,A.E."The selection of critical stability constants in chemicalequilibrium and reaction models" *American J.Chem.*,(1995),soc.42.
6. Tubas,chin.Chem.Letters,(2003),14,No.11,pp.1207-1210.
7. B.M.Kalshetty,S.S.Surarkandin,P.S.Hiremath and M.B.Kalashetti"*International J. of Appl.Tech*",(2011),2,Issu2.
8. Majia.R.,A.Kassim,S.Ahmed Zaher,Nor.Azah Y.and HossR in A.,Int J.Electrochem.,(2011),sci.6.pp.4378-4387.
9. R.Marie,V.Peter and V.K.Krizovn"*Inorg.Chem.J*",(2009),3,pp.26-32.
10. "Fundamentals of Analyticalchemistry",Intrtscience,Skoog, and,D.A.,NewYourk,(1998),p.536.
11. "*Textbook of Quautitative aInorganic Analysis*",A.I.Vogel,Longmous Green London,(1961).
12. W.H.Brock,K.A.Jensem,C.K.Jorgensem,and,G.B.Kaufmam,*Polyhedron*,(1983),2,pp.1-7.
13. "*Priniple of Inorganic Chem.5thed.*",Cotton and Wikons,(1981).
14. Conductivity of coordiration comounds in oraganic solvent,W.Geary,(1970).
15. Hetrocyclicchemistry,YamanakaH.Obba S. and Sokamoto,(1975),31,pp.1115-1127.
16. Ain seough A.W.,and Plowmam R.A.Aust.J.Chem,(1970),699,p.23.
17. A.K.Rama and ShahJ.R.,Indian J.Chem.,(1981),soc.58.
18. "Infrared and Ramam spectra of Inorganic coordination compounds", K.Nakamoto,John Wiely and Sous,(1986).
19. "Determination of chemical structure",Pasto DJ and UK.,Prentcehall,(1969).
20. H.C.Zahid,M.A.AKhter and T.Scloud in bioinorg chem. And application,article,(2006),ID83131,pp.1-13.
21. Pandeya,K.B,ompraksh and Singh R.P.Indian J.Chem.,(1983),soc.531.
22. "Elementes of magneto chemistery,2nded".,Data R.L and Symal A., west east press NewDelhi,(1993),p.101.

**Synthesis ,Characterization and Kinetic Study of Metal
Complexes with new acyclic Legend N_2O_2
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23. Satish,M.Annigeri,M.P.Suthish and V.K.Revankar"Spectroscopic studies of bridge binuclear complexes of Co(II),Ni(II),Cu(II) and Zn(II) transition metal Chem."springer,(2007),32,pp.81-87.
24. *An introduction to ligand field*,Figgis B.N,NewDelhi,(1976).
25. Genplot,graphic service,USA,(1989).
26. T.Atalay,E.G.Akgemic,*Turk.J.Chem.*(2000),24,p.89.
27. F.Kham,J.Chin.*Chem.*(2007),soc.673.
28. A.Malovikova,K.Hayakawa and C.T Kwak,*J.phys.Chem.*,(1984),88,pp.1930-1933.

