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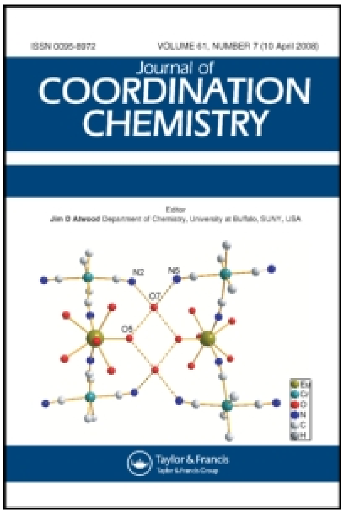

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Studies on oxovanadium(IV), Cr(III), Co(II), Ni(II), and Cu(II) chelates of some bisketimino ligands

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The oxovanadium(IV), Cr(III), Ni(II), Co(II), and Cu(II) chelates of some bisketimino Schiff-base ligands (H_2L) obtained by condensation of 4-butyryl-3-methyl-1-phenyl-(or-1,3-diphenyl)-2-pyrazolin-5-ones with thiourea were synthesized and characterized by elemental analyses and thermogravimetric analyses, molar conductivities, magnetic susceptibility measurements, mass, infrared, and electronic spectroscopies. Ligand field parameters, such as splitting energy, Racah parameter, spin–orbit coupling constant, and covalency parameter of the Cr(III), Ni(II), and Co(II) chelates were calculated by band-fitting methods. Based on these studies, tetragonally distorted octahedral environment around OV(IV) and Cu(II) and octahedral Cr(III), Ni(II), and Co(II) have been proposed.

Keywords: Schiff bases; 4-Acyl-5-pyrazolones; Metal chelates; Bisketimines; Ligand field parameters

1. Introduction

Ligands containing "C=N" linkages with bonding through nitrogen and oxygen or sulfur to metal ions comprise an important class of biologically active compounds providing models for metal–ligand binding sites in several enzymes [1, 2].

Sulfur-containing ligands show pronounced biological potency as antituberculosis [3], antifungal [4], and antitumor [5] agents. These species are also important biochemical, analytical, industrial, and antimicrobial agents [6]; some possess catalytic properties, some have applications as pigment dyes [6], and they are also known for their physiological and pharmaceutical properties [7–9] due to the environment around metal which is key for metalloproteinase to carry out specific physiological functions [10]. Prompted with this and our continuing interest in chelated Schiff-base compounds, we synthesize metal chelates of ligands derived from thiourea [11–14]. In this article, we describe oxovanadium(IV), Cr(III), Ni(II), Co(II), and Cu(II) chelates of bisketimino Schiff bases (H_2L) obtained by condensation of 4-butyryl-3-methyl-1-phenyl/1,3-diphenyl-2-pyrazolin-5-ones with thiourea. A general structural representation and

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abbreviations of the ligands used in the present study are given in figure 1 and the reactions in scheme 1.

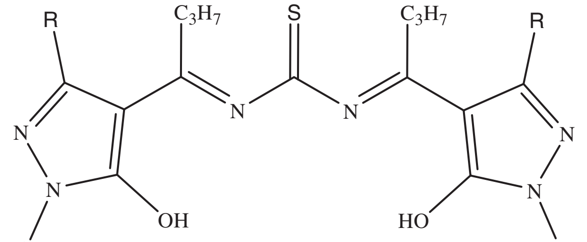
2. Experimental

2.1. *Chemicals*

All the chemicals were of laboratory reagent grade. Ethyl acetoacetate, ethyl benzoylacetate, and dimethyl formamide (DMF) were obtained from Ranbaxy, Fine Chemicals Ltd., New Delhi, India. Butyryl chloride of Fluka was obtained from the General Trading Corporation, Mumbai, India. Absolute alcohol was bought from Alembic Chemical Works Co. Ltd., Baroda, India and used after distillation. Phenyl hydrazine and dioxane were obtained from Bhavin Enterprise, Baroda, India. Pure pyridine was brought from Samir Tech-Chem Pvt. Ltd., Vadodara, India. The hydrated metal nitrates, calcium hydroxide, and thiourea were used to prepare all the metal chelates, except oxovanadium for which the vanadyl sulfate was used.

2.2. *Synthesis of Schiff-base ligands*

The procedure for preparation of 4-butyryl-3-methyl-3-phenyl or 1,3-diphenyl-2-pyrazolin-5-ones (HBMPP or HBDPP) and their derivatives with thiourea to get



. R	Ligand
$-CH_3$	H_2L^1
$-C_6H_5$	H_2L^2

Figure 1. Structural representation and abbreviations of H_2L.

$$\mathrm{VOSO_4H_2O} + \mathrm{H_2L} \xrightarrow[\text{Reflux}]{\text{Ethanol/Water}} [\mathrm{VO(L)(H_2O)}] + \mathrm{H_2SO_4} \qquad [\mathrm{I}]$$

$$\mathrm{M(NO_3)_X{\cdot}yH_2O} + \mathrm{H_2L} \xrightarrow[\text{Reflux}]{\text{Ethanol}} [\mathrm{M(L)(H_2O)_2}]\mathrm{X} + 2\mathrm{HNO_3} + (\mathrm{y}-2)\mathrm{H_2O} \qquad [\mathrm{II}]$$

For M = Cr, x = 3, X = NO_3, y = 9; M = Ni or Co, x = 2, X = –, y = 6; M = Cu(II), x = 2, X = –, y = 3.

Scheme 1. General reaction scheme of metal complex formation.

bisketimino Schiff-base ligands (H_2L) were the same as reported previously [13, 14]. A representative ligand [H_2L^2] shows molecular ion peak at $m/z = 653$ (R.I. = 40%, Calcd mol. wt. = 653), which is in good agreement with the molecular weight of the ligand. The suggested general structure of the ligands is shown as figure 1.

2.3. *Synthesis of metal chelates*

A hot solution (50 mL) of respective hydrated metal nitrate (except vanadium) (10 mmol, 4.0 g of $Cr(NO_3)_3 \cdot 9H_2O$ or 2.9 g of $Co(NO_3)_2 \cdot 6H_2O$ or 2.9 g of $Ni(NO_3)_2 \cdot 6H_2O$ or 2.4 g of $Cu(NO_3)_2 \cdot 3H_2O$) in hot ethanol was added dropwise with constant stirring to hot ethanolic solution (100 mL) of Schiff base (10 mmol, 5.3 g of H_2L^1 or 6.5 g of H_2L^2) in slight excess over 1 : 1 metal : ligand ratio. For oxovanadium(IV) chelates, 1.8 g of $VO(IV)SO_4 \cdot H_2O$ dissolved in water was used. To the resulting mixture was added 9.0 mg of sodium acetate, except for copper and oxovanadium(IV) chelates, and the solution was refluxed for 1 h, evaporated to 75.0 mL by boiling over water and cooled. The crystalline products were filtered *in vacuo*, washed several times with hot water, finally with ethanol, and dried in an oven at 45°C.

2.4. *Physico-chemical measurements*

All the measurements were made at room temperature (25 ± 2°C). The gravimetric oxide methods were used for the estimation of metal content for all the chelates. Carbon, hydrogen, and nitrogen were estimated with Perkin-Elmer, 2400 series-II CHN analyzer. The room temperature molar conductivities were measured by ‘‘Systronics 305 Conductivity Bridge’’. The room temperature magnetic susceptibilities of solid chelates were measured on a Model 7304 vibrating sample magnetometer, Lake Shore, USA. Diffuse reflectance spectra (DRS) of solid compounds diluted with MgO (1 : 3) were obtained on a Perkin-Elmer Lamda-19 UV-VIS-NIR spectrophotometer from 350 to 1700 nm with standard reflectance attachment. Infrared (IR) spectra of all the compounds were recorded with a Nicolet-400 D spectrophotometer from 400 to 4000 cm^{-1} using KBr discs. ^1H NMR spectra of the ligands were obtained in $CDCl_3$ on a HITACHI R 1500 FT-NMR spectrometer. Mass spectra were obtained on a Jeol SX-102 (FAB) mass spectrometer at Sophisticated Instrumentation Centre, CDRI, Lucknow, India. The thermograms of all the compounds were obtained at 25–350°C using nitrogen flux with a SDT 2960 TA thermoanalyzer.

3. Results and discussion

3.1. *Analytical data*

Table 1 shows the analytical and physical characteristic data of the Schiff bases and their metal chelates. All metal chelates are stable at room temperature, insoluble in water, benzene, acetonitrile, carbon tetrachloride, etc. However, all the chelates have solubility in strong coordinating solvents, such as DMF and dimethyl sulfoxide (DMSO). The molar conductivities of all the metal chelates are 4–32 $cm^2\,\Omega^{-1}\,mol^{-1}$ in

DMF (table 1), except Cr(III) chelates, suggesting that all the metal chelates are non-electrolytes. The molar conductivities of Cr(III) chelates are 73–77 $cm^2\Omega^{-1}mol^{-1}$ in DMF, suggesting 1 : 1 electrolytes [15]. The analytical data suggest 1 : 1 metal to ligand stoichiometry for all the metal chelates.

3.2. *Infrared spectra*

Important IR spectral data and assignments are given in table 2. Bands at ~1270, ~1320, ~1387, ~1595, and ~1630 cm^{-1} are attributed to δ(O–H), ν(C–O), ν(C=S) (thioureas), ν(C=N)(azomethine), and ν(C=N)(cyclic), respectively [6]. A broad band at 3500–2800 cm^{-1} indicates strongly hydrogen-bonded OH [16]. The bathochromic shift of the band at 1630 cm^{-1} and disappearance of the band at 1240 cm^{-1} of the ligands on chelation indicate coordination through ketimine nitrogen and oxygen of 5-OH of the 5-pyrazolone ring [6]. Positions of bands at 1595 and 1387 cm^{-1} remain practically unaltered, suggesting non-coordination of $>$C=N(cyclic) and $>$C=S(thiourea) during chelation [12].

The presence of water is also inferred from thermogravimetric analyses (TGA) of respective metal chelates [17]. Thus, IR spectral data suggest tetradentate ONNO bonding of each Schiff base toward metal ions, two N from ketimine, and two from OH of the 5-pyrazolone ring (figure 1).

The oxovanadium(IV) chelates show a band at 930–970 cm^{-1}, due to ν(V=O) [18]. The frequency spread may be due to coordination of water [19]. The Cr(III) chelates show bands at ~1420, 720, and 998 cm^{-1}, which may be assigned to ν_1, ν_2, and ν_3 of (NO_3^-).

3.3. *^{1}H NMR spectra*

The ^{1}H NMR spectra of the Schiff bases show phenyl multiplets at δ ~7.38. Multiplet and triplet signals between δ 0.6 and 2.5 are assigned to butylidene group on pyrazoline. The signal due to enolic proton is observed at δ 11–12.

3.4. *Diffuse reflectance spectra*

3.4.1. Oxovanadium(IV) chelates. The DRS of oxovanadium(IV) chelates gave three bands at 11,000–25,000 cm^{-1} assigned to $d_{xy} \rightarrow d_{xz}, d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$, expected in the 10,000–30,000 cm^{-1} range (table 3) [18–20]. In addition, it also shows a band at 33,000 cm^{-1} with a multiple structure assignable to the first-spin-forbidden charge transfer transition [20, 21].

To support these assignments, each complex was dissolved in a mixture of ether : toluene : ethanol (2 : 1 : 1) and allowed to stand to bring about air oxidation. The color of solution changes rapidly from green or blue to brown or yellow, suggesting change in oxidation from IV to V. The solution spectra show the absence of bands in the region 11,000–25,000 cm^{-1} with one band observed at ~33,000 cm^{-1}, assigned to charge transfer [22].

Each complex was dissolved in pyridine and spectra were taken, showing no major change in bands compared to the DRS. Thus, there is no change in the stereochemistry

Table 1. Analytical data of Schiff bases and their metal chelates.

						Elemental analysis Found (Calcd)%					
Compound Empirical formula	F.W. (g mol^{-1}) Found (Calcd)	Yield (%)	Color	Melting point (°C)	Λ_M^a (DMF)	Metal	C	H	N	S	μ_{eff} (B.M.)
H_2L^1	528.10	72	Pale	185	–	–	65.91	6.12	15.92	6.19	–
$C_{29}H_{32}N_6O_2S$	(528.23)		yellow				(65.88)	(6.10)	(15.89)	(6.05)	
$[OV(L^1)(H_2O)]$	612.01	78	Light	183	4.2	8.38	57.01	5.30	13.81	5.28	1.76
$C_{29}H_{32}N_6O_4SV$	(611.61)		green			(8.33)	(56.95)	(5.27)	(13.74)	(5.23)	
$[Cr(L^1)(H_2O)_2]NO_3$	676.33	68	Green	>250^b	77.2	7.90	51.55	5.15	14.81	4.80	3.81
$C_{29}H_{34}CrN_7O_7S$	(676.16)					(7.68)	(51.47)	(5.06)	(14.49)	(4.73)	
$[Co(L^1)(H_2O)_2]$	621.23	65	Light	240	8.2	9.50	56.10	5.62	13.62	5.05	4.81
$C_{29}H_{34}CoN_6O_4S$	(621.62)		pink			(9.48)	(56.03)	(5.51)	(13.52)	(5.15)	
$[Ni(L^1)(H_2O)_2]$	621.33	70	Pale	205	4.2	9.47	56.10	5.62	13.64	5.08	3.30
$C_{29}H_{34}N_6NiO_4S$	(620.17)		green			(9.45)	(56.06)	(5.52)	(13.53)	(5.15)	
$[Cu(L^1)(H_2O)_2]$	626.12	79	Pale	200	3.9	9.98	55.68	5.52	13.48	5.02	1.91
$C_{29}H_{34}CuN_6O_4S$	(626.23)		green			(10.10)	(55.62)	(5.47)	(13.42)	(5.11)	
H_2L^2	652.22	75	Pale	184	–	–	62.80	5.40	13.01	4.95	–
$C_{39}H_{36}N_6O_2S$	(652.81)		yellow				(62.43)	(5.55)	(12.87)	(4.91)	
$[OV(L^2)(H_2O)]$	736.40	69	Buff	230	21.8	6.14	63.30	5.15	11.22	4.40	1.74
$C_{39}H_{36}N_6O_4SV$	(735.75)		white			(6.09)	(62.87)	(5.13)	(11.20)	(4.35)	
$[Cr(L^2)(H_2O)_2]NO_3$	801.01	55	Green	250	73.64	6.28	58.28	4.88	12.3	4.02	3.71
$C_{39}H_{38}CrN_7O_7S$	(800.82)					(6.50)	(58.49)	(4.77)	(12.24)	(3.99)	
$[Co(L^2)(H_2O)_2]$	746.06	56	Pink	245	9.81	6.50	58.55	4.80	12.20	4.30	4.75
$C_{39}H_{38}CoN_6O_4S$	(745.76)					(6.90)	(58.21)	(4.75)	(12.18)	(4.29)	
$[Ni(L^2)(H_2O)_2]$	746.03	54	Light	230	31.9	7.87	63.50	5.14	11.30	4.29	3.20
$C_{39}H_{38}N_6NiO_4S$	(745.52)		green			(7.90)	(62.83)	(5.13)	(11.27)	(4.23)	
$[Cu(L^2)(H_2O)_2]$	750.24	07	green	290	18.22	8.50	62.62	5.12	11.40	4.11	1.90
$C_{39}H_{38}CuN_6O_4S$	(750.37)					(8.50)	(62.49)	(5.10)	(11.20)	(4.26)	

[a] Ω^{-1} cm^2 mol^{-1}.

[b] Decomposition point.

Table 2. Some IR frequencies (cm^{-1}) for the ligands and their metal complexes.

Compound Empirical formula	ν(O–H) (H_2O)	ν(C=N)[c]	ν(C=N)[d]	ν(C–O)	δ(O–H)
H_2L^1 [a]	–	1629 s	1595 s	1320 s	1270 s
$[OV(L^1)(H_2O)]$	3390 m	1625 m	1595 m	1330 w	–
$[Cr(L^1)(H_2O)_2]NO_3$	3408 m	1622 m	1595 s	1330 sh	1270 sh
$[Co(L^1)(H_2O)_2]$	3400 m	1626 w	1595 s	1324 s	–
$[Ni(L^1)(H_2O)_2]$	3450 m	1602 w	1595 s	1322 m	1270 sh
$[Cu(L^1)(H_2O)_2]$	3401 m	1615 w	1595 s	1322 sh	–
H_2L^2 [b]	–	1635 s	1595 s	1370 s	1266 s
$[OV(L^2)(H_2O)]$	3408 w	1608 s	1595 s	1394 sh	–
$[Cr(L^2)(H_2O)_2]NO_3$	3350 br	1602 s	1595 sh	1400 w	–
$[Co(L^2)(H_2O)_2]$	3388 br	1622 s	1595 sh	1394 w	–
$[Ni(L^2)(H_2O)_2]$	3422 br	1635 s	1595 sh	1400 sh	–
$[Cu(L^2)(H_2O)_2]$	3380 br	1622 s	1595 s	1380 sh	–

[a] νO–H(H-bonded): 2800–3350 cm^{-1}.
[b] C=S(thiourea): 1387 cm^{-1} s.
[c] ν(C=N)ketimine.
[d] ν(C=N)cyclic.

Table 3. The electronic spectral data of OV(IV) complexes (cm^{-1}).

Complex empirical formula	Spectra	$d_{xy} \rightarrow d_{xz}, d_{yz}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{z^2}$	CT[a]
$[OVL^1(H_2O)]$	Solid	12,820	18,867	23,809	33,333
	Oxidation	–	–	–	33,222
	Pyridine	12,820	18,691	23,923	33,333
$[OVL^2(H_2O)]$	Solid	12,738	19,047	24,096	33,670
	Oxidation	–	–	–	34,602
	Pyridine	12,758	18,975	24,038	33,898

[a] CT: charge transfer.

in a donor solvent [23], ruling out coordination of pyridine suggesting tetragonally distorted octahedral structure for these complexes [24].

3.4.2. Chromium(III) chelates. The DRS of $[Cr(L^1)(H_2O)_2]NO_3$ exhibit three bands at 16,538, 24,390, and 37,907 cm^{-1} (table 4), assigned to $^4A_{2g} \rightarrow {}^4T_{2g}(F)(\nu_1)$, $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)(\nu_2)$, and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ expected at ~17,000, ~25,000, and 37,000 cm^{-1}, respectively, for six coordinated sphere [25]. The shoulder type nature of "ν_2" band suggest the probable mixing of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of ligand with charge transfer spectra [26, 27].

The DRS of $[Cr(L^2)(H_2O)_2]NO_3$ show bands at 14,903, 19,608, and 36,363 cm^{-1} as expected corresponding to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$, respectively for six coordinated sphere [25, 28]. It was possible to calculate the ν_3, B_{35}, and β_{35} for each complex using observed ν_1 and ν_2 bands following band-fitting methods [29]. The low value of β_{35} of 0.920 and 0.816 cm^{-1} indicates the presence of π as well as σ-type delocalization [30]. The spin–orbit coupling constant, λ, was calculated using the empirical expression $\lambda = 0.0110(B_{35} + 1.08)^3 + 0.0062$ (table 4) [31]. The values of covalency parameter, γ, calculated using the relation $\lambda/90$, were found to be 0.93 and 0.81 for the complexes of H_2L^1 and H_2L^2, respectively. The γ is analogous to the nephelauxetic parameter β_{35}. The ligands used in this study give the order of γ

Table 4. Electronic spectral data of Cr(III) and Ni(II) complexes.

		Observed and calculated transition energies (cm^{-1})							
Complex empirical formula	Article I Method	ν_1	ν_2	ν_3	B_{35} (cm^{-1})	β_{35} (cm^{-1})	$\delta\nu$ (cm^{-1})	ν_2/ν_1	λ[a] (cm^{-1})
$[Cr(L^1)(H_2O)_2]NO_3$	Observed	16,538	24,390	37,901	–	–	–	1.47	= 84.7
	(a)	10Dq	Fitted	37,905	845	0.920	−0004		$\gamma = 0.93$[b]
	(b)	10Dq	24,387	Fitted	845	0.920	+0003		
	(c)	10Dq	24,388	37,903	845	0.920	+0002		
	(d)	10Dq	24,382	37,893	844	0.919	+0008		
$[Cr(L^2)(H_2O)_2]NO_3$	Observed	14,903	19,608	36,363	–	–	–	1.30	73.61
	(a)	10Dq	Fitted	31,749	443	0.48	−4614		$\gamma = 0.81$[b]
	(b)	10Dq	23,091	Fitted	983	1.071	−3483		
	(c)	10Dq	21,912	34,059	750	0.816	−2304		
	(d)	10Dq	24,334	41,089	1380	1.5032	−4726		
$[Ni(L^1)(H_2O)_2]$	Observed	9800	16,000	25,310	–	–	–	1.63	−174
	(a)	10Dq	Fitted	27,009	907	0.872	−1,699		$\mu = 3.19$[c]
	(b)	10Dq	15,636	Fitted	770	0.740	+364		
	(c)	10Dq	15,709	25,600	794	0.763	+291		
	(d)	10Dq	15,496	24,805	727	0.698	+504		
$[Ni(L^2)(H_2O)_2]$	Observed	9804	16,129	25,000	–	–	–	1.65	−168
	(a)	10Dq	Fitted	27,777	966	0.928	−2,777		$\mu = 3.20$[c]
	(b)	10Dq	15,556	Fitted	743	0.714	+573		
	(c)	10Dq	15,677	25,452	781	0.750	+452		
	(d)	10Dq	15,284	24,155	668	0.642	+845		

[a] Spin–orbit coupling.
[b] Covalency parameter.
[c] Calculated μ_{eff} (B.M.).

to be $H_2L^2 < H_2L^1$. The low value of λ compared to free ion value of 90 cm^{-1} indicates covalent character of metal–ligand bond [32].

3.4.3. Cobalt(II) chelates. The DRS of the Co(II) complexes are consistent with octahedral stereochemistry (table 5). Three spin-allowed transitions for octahedral geometry may be expected [33]:

$$\nu_1 : {}^4T_{1g}(F) \rightarrow {}^4\, T_{2g}(F) \;\; \sim 8000\,\mathrm{cm}^{-1},$$

$$\nu_2 : {}^4T_{1g}(F) \rightarrow {}^4\, T_{1g}(P) \;\; \sim 16,000\,\mathrm{cm}^{-1},$$

$$\nu_3 : {}^4T_{1g}(F) \rightarrow {}^4\, TA_{2g}(F) \;\; \sim 20,000\,\mathrm{cm}^{-1},$$

Generally, two rather than three are observed because the transition to $^4A_{2g}$(F) level is a "two electron" transition and is usually very weak [34]. In the present work, the band 16,949 cm^{-1} (ν_2) in DRS of $[Co(L^2)(H_2O)_2]$ is seen along with 8368 (ν_1) and 19,607 cm^{-1} (ν_3). The DRS of $[Co(L^1)(H_2O)_2]$ show only two bands 8403 (ν_1) and 18,867 cm^{-1} (ν_3).

According to the weak field approximation for octahedral ligand field, ^{4}F splits into $^4T_{1g}$, $^4T_{2g}$ and $^4A_{2g}$, which are mixed by term interaction giving rise to the following equation:

$$E_{1,2}({}^4T_{1g}) = 7.5B - 3D_q \pm (225B^2 + 10D_q^2 + 180D_qB)$$

Table 5. Electronic spectral data of Co(II) and Cu(II) complexes.

		Observed and calculated transition energies (cm^{-1})								
Complex empirical formula	Method	ν_1	ν_2	ν_3	$10D_q$ (cm^{-1})	B_{35} (cm^{-1})	β_{35} (cm^{-1})	$\delta\nu$ (cm^{-1})	ν_2/ν_1	ν_2–ν_1
$[Co(L^1)(H_2O)_2]$	Observed	8403	17,907[a]	18,867	9503	771	0.794	–	2.13	9604
$[Co(L^2)(H_2O)_2]$	Observed	8368	16,949	19,607	–	–	–	–	2.03	8581
	(a)	Fitted	Fitted	9341	8581	079	0.081	+10,266		
	(b)	Fitted	17,869	Fitted	9501	825	0.850	−920		
	(c)	7916	Fitted	Fitted	9032	854	0.880	+452		
	(d)	7547	16,127	Fitted	0763	764	0.787	+821		
$[Cu(L^1)(H_2O)_2]$	Observed	–	15,384[c]	23,529[b]	7692	–	–	–	–	–
$[Cu(L^2)(H_2O)_2]$	Observed	–	17,094[c]	23,530[b]	8547[d]	–	–	–	–	–

[a] Calculated.
[b] Charge transfer spectra.
[c] Enveloped.
[d] Calculated.

leading to the following equations [29]:

$$\nu_1 = 1/2(10D_q - 15B) + 1/2[(10D_q + 15B)^2 - 120D_qB]^{1/2},$$
$$\nu_2 = 1/2(30D_q - 15B) + 1/2[(10D_q + 15B)^2 - 120D_qB]^{1/2},$$
$$\nu_3 = [(10D_q + 15B)^2 - 120D_qB]^{1/2}.$$

The following methods were used to determine $10D_q$ and B [26]:

(a) $10D_q = \nu_2 - \nu_1$; $B = (2\nu_1^2 - \nu_1\nu_2)/(12\nu_2 - 27\nu_1)$,
(b) $10D_q = 2\nu_1 - \nu_3 + 15B$; $B = 1/30[-(2\nu_1 - \nu_3) + \{-\nu_2 + \nu_3^2 + \nu_1\nu_3\}^{1/2}]$,
(c) $10D_q = 1/3(2\nu_1 - \nu_3) + 5B$; $B = 1/510[7(\nu_3 - 2\nu_2) \pm 3\{81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)\}^{1/2}]$,
(d) $10D_q = \nu_2 - \nu_1$, $B = (\nu_2 + \nu_3 - 3\nu_1)/15$.

By fitting the first and second observed bands (a), first and third observed bands (b), second and third band (c), and difference between first and second band (d), one can calculate B_{35}, $10D_q$, β_{35}, $\delta(\nu_{cal} - \nu_{obsd})$, and ν_2/ν_1 (table 5). The data show that the transition energies calculated by the method (c) gives the smallest $\delta\nu$. Thus, the method (c) is the best fitted method with the lowest value of $\delta\nu = +452\,cm^{-1}$. By considering this method the calculated values of B_{35}, $10D_q$, β_{35}, and ν_2/ν_1 are 854, 9032, 0.880, and $2.03\,cm^{-1}$, respectively (table 5).

In complexes of H_2L^1, ν_2 band is obscured. Employing method (a), it was possible to calculate ν_2 (17,907), $10D_q$ (9503), and B_{35} (771) cm^{-1} [29]. The experimental accuracy of ν_2 for octahedral Co(II) is expected to be lower than that of ν_1 and ν_3. However, in the method (c) the use of the ν_2 is required. Therefore, the superior performance of this method is surprising. The magnitude of B determined for all the chelates may be compared with that for free ion ($971\,cm^{-1}$). Reduction in the electron–electron repulsion parameter B, $771\,cm^{-1}$ for $[Co(L^1)(H_2O)_2]$ and $854\,cm^{-1}$ for $[Co(L^2)(H_2O)_2]$, is in the range 12–20% of the free value. The decrease in B_{35} is considered an indication of covalent character in the M–L bond. The ratio B_{35}(found)/B_{35}(free ion) depends on the position of the ligand in the nephelauxetic series. The ligands used in the present study give the nephelauxetic series order: $H_2L^1 < H_2L^2$.

3.4.4. Ni(II) chelates. DRS of the Ni(II) complexes have typical octahedral Ni(II) spectra consisting of three bands [35]: ν_1: $^3A_{2g}\rightarrow{}^3T_{2g}$ ($\sim$9000 cm^{-1}), ν_2: $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ $\sim$15,000 cm^{-1}, ν_3: $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ ($\sim$25,000 cm^{-1}) (table 4). The observed d–d transitions have energies which agree perfectly with the secular equations for octahedral nickel(II). The observed ν_2/ν_1 ratio is in the normal 1.63–1.65 range expected for octahedral Ni(II) [36, 37]. According to Russell–Saunders coupling scheme, Ni(II) gives two triplet terms, ^3F and ^3P. The ^3F term is the ground term and ^3P is $15B$ higher in energy. According to the weak field approximation, the transition energies can be obtained from the equations $E(^3A_{2g}) = -12D_q$ and $E(^3T_{2g}) = -2D_q$. The two $^3T_{1g}$ states are mixed by term interaction and their energies have to be determined from the following secular determinant [29]:

$$\begin{array}{c|cc|c} & ^3T_{1g}(F) & ^3T_{1g}(P) & \\ ^3T_{1g}(F) & 6D_q\text{-E} & 4D_q & \\ & & & = 0 \\ ^3T_{1g}(P) & 4D_q & 15\text{B-E} & \end{array}$$

which results in $E_{1,2}(^3T_{1g}) = 7.5B + 3D_q \pm ½\ (225B^2 + 100D_q{}^2 - 180D_q \cdot B)^{1/2}$ and the following equations [29]:

$$\nu_1 = 10D_q;\ \nu_2 = 1/2\,(15B + 30D_q) - 1/2[(15B - 10D_q)^2 + 12B \cdot 10D_q]^{1/2} \quad \text{and}$$
$$\nu_3 = 1/2(15B + 30D_q) + 1/2[(15B - 10D_q)^2 + 12B \cdot 10D_q]^{1/2}.$$

The equations used to calculate B_{35} are [26]:

(a) $10D_q = \nu_1;\ B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1)$,
(b) $10D_q = \nu_1;\ B = (2\nu_1^2 + \nu_3^2 - 3\nu_1\nu_3)/(15\nu_3 - 27\nu_1)$,
(c) $10D_q = \nu_1;\ B = (\nu_2 + \nu_3 - 3\nu_1)/15$,
(d) $10D_q = \nu_1;\ B = 1/75\ [3\nu_1 + \{25(\nu_3 - \nu_2)^2 - 16\nu_1^2\}^{1/2}]$.

The above expressions correspond to the method of fitting; (a) the second band, (b) the third band, (c) the sum of the second and third band, and (d) the difference between the second and third band [29]. The results are listed in table 4 along with the values of β_{35} and δ_ν. In all the complexes, the best fit is according to the method (c). The magnitude of B_{35} (794 for $[Ni(L^1)(H_2O)_2]$ and 781 cm^{-1} for $[Ni(L^2)(H_2O)_2]$) determined by the method (c) may be compared with that for free Ni(II) (1041 cm^{-1}) [28, 29]. The reduction in the electron repulsion parameter B_{35}, in the Ni(II) complexes under investigation is $\sim$24% of the free ion value. The size of reduction in B_{35} indicates the covalent character in the bonds [38]. The ratio B_{35}(found)/B_{35}(free ion) $= \beta_{35}$ depends on the position of the ligand in the nephelauxetic series. The ligands used in the present study give nephelauxetic series order $H_2L^2 < H_2L^1$. An attempt has been made to obtain approximate value of λ, the spin–orbit coupling constant, using $\lambda = 2.7\ B_{35}^2/10D_q$ [37, 39]. The values of B_{35}, 794 and 781 cm^{-1} for

$[Ni(L^1)(H_2O)_2]$ and $[Ni(L^2)(H_2O)_2]$, calculated according to the method (c) were used in the calculations. These values are shown in table 4.

In an attempt to seek correlation between spectral and magnetic data of Ni(II) complexes, μ_{eff} has been calculated by $\mu_{eff} = \mu_{eff\cdot(S.O.)}$ $[1–4\lambda_o/10D_q]$ [29]. The free ion value of nickel(II), $\lambda_o = -315\,cm^{-1}$, is used in the calculations. These values are 3.19 and 3.20, respectively, for $[Ni(L^1)(H_2O)_2]$ and $[Ni(L^2)(H_2O)_2]$ which are in good agreement with observed 3.30 and 3.20 B.M.

3.4.5. Cu(II) chelates. Only one spin allowed d–d transition, $^2E_g \rightarrow {}^2T_{2g}$, is expected in the visible spectra of copper(II) complexes [40]. However, the d^9 configuration is highly Jahn–Teller unstable and the resulting tetragonal distortion (D_4h) leads to further splitting of ^2E_g and $^2T_{2g}$ levels into $^2B_{1g}$, $^2A_{1g}$ and $^2B_{2g}$, ^2E_g levels [41] giving three-spin-allowed transitions: $\nu_1 : {}^2B_{1g} \rightarrow {}^2A_{1g}$, $\nu_2 : {}^2B_{1g} \rightarrow {}^2B_{2g}$, and $\nu_3 : {}^2B_{1g} \rightarrow {}^2E_g$. The splitting of the states increases with tetragonal component of crystal field. As the energy of $^2A_{1g}$ state increases, this state may be sufficiently close to the ^2E_g and $^2B_{2g}$ states for the three transitions not to be resolved. The complexes of this study show a strong charge transfer band at $23{,}530\,cm^{-1}$ (table 5) and three transitions within one envelope. This is in agreement with general observation that the d–d transitions for Cu(II) complexes are normally close in energy [42]. If the tetragonal field follows barycenter rule then the approximate value of $10D_q$ may be obtained from $10D_q = \nu_3 - 1/2\nu_1 - 1/3(\nu_3 - \nu_2)$, where $\nu_1 = \nu_2 = \nu_3$ [43]. The calculated values $10D_q$ are shown in table 5.

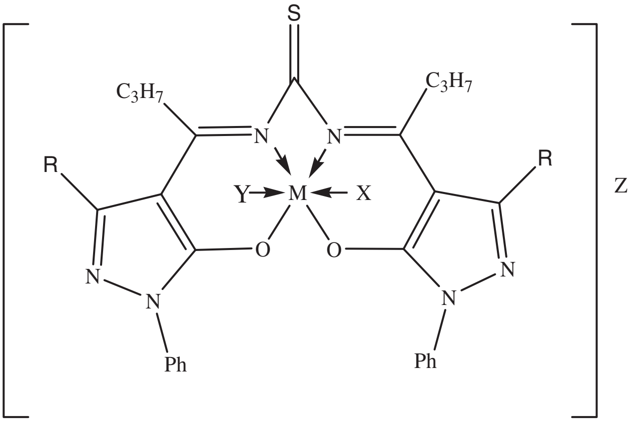
3.5. *Magnetic measurements*

The vibrating sample magnetometer gives slope "*m*(emu)/H(Oe.)" from the plot of *m*(emu) *versus* applied magnetic field, *H*(Oe.). Taking the slope as the volume susceptibility $[\chi(cm^3)]$, the gram susceptibility (χ_g), and the molar susceptibility (χ_M) were calculated by equations: (i) $\chi_g = \chi$ (cm^3)/mass and (ii) $\chi_M = \chi_g \times$ molecular weight [44, 45]. The μ_{eff} (B.M.) was then calculated by $\mu_{eff} = 2.84\ (\chi'_M \cdot T)^{1/2}$ (table 1), where T is the temperature (Kelvin) and χ'_M = corrected molar susceptibility.

The room temperature magnetic moments (μ_{eff}) of the Cr(III) complexes fall within the 3.71–3.81 B.M. range expected for octahedral structure [46]. Magnetic moments in 1.74–1.76 B.M. range of all OV(IV) complexes are very close to the spin-only value (1.73 B.M.) corresponding to one unpaired electron. The Co(II) complexes exhibit magnetic moments of 4.70–4.92 B.M., close to the value required for octahedral geometry. The Ni(II) complexes show magnetic moments from 2.77 to 3.30 B.M. expected for six-coordinate octahedral complex [47]. The magnetic moments of Cu(II) are ~1.90 B.M. corresponding to one unpaired electron [47].

3.6. *Thermogravimetric analyses*

TGA data provide evidence for determining the number and type of water present in the complexes. Thermal studies on $[Ni(L^1)(H_2O)_2]$ indicate weight loss of 5.2% at ~200°C due to the removal of two water molecules. Then weight loss is due to decomposition of organic ligand. From DTA, further decomposition occurs exothermically at ~297°C; weight loss continues at ~350°C. Similar behavior is observed for



M	X	Y	Z
OV(IV)	H_2O	--	--
Cr(III)	H_2O	H_2O	NO_3
Ni(II) or Co(II) or Cu(II)	H_2O	H_2O	--

Figure 2. Suggested structures of complexes.

other complexes at 130–200°C, except OV(IV) complexes which show a weight loss of one water molecule at ~140°C [17].

4. Conclusion

From elemental analyses, conductivity and magnetic measurements, TGA, mass, IR, NMR, and electronic spectra, the suggested structures are $[M(L^n)(H_2O)X)]Z$, where $X = Z = -$ for $M = OV$; $X = H_2O$, $Z = NO_3$ for $M = Cr$; $X = H_2O$, $Z = -$ for $M = Co$, Ni, and Cu. L is a dianion of the ligand and $n = 1$ or 2 for corresponding ligands (figure 2). The thermograms show weight loss of two coordinated water molecules from 130 to 200°C, except for OV chelates which show loss of one water molecule at ~140°C. The structures for all the metal complexes suggest octahedral geometry in which two bisketimino groups and two 5OH groups of pyrazoline of the Schiff base are ONNO donors to metal. The remaining coordination sites are occupied by coordinated water.

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