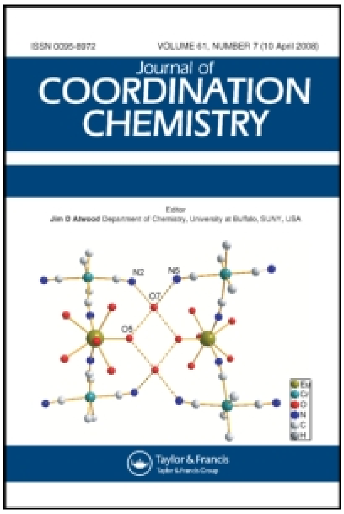

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Cobalt(II) and nickel(II) chelates of some 5-pyrazolone-based, Schiff-base ligands

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To cite this Article Parmar, N. J. and Teraiya, S. B.(2009) 'Cobalt(II) and nickel(II) chelates of some 5-pyrazolone-based, Schiff-base ligands', Journal of Coordination Chemistry, 62: 14, 2388 — 2398

To link to this Article: DOI: 10.1080/00958970902833058

URL: http://dx.doi.org/10.1080/00958970902833058

Journal of Coordination Chemistry
Vol. 62, No. 14, 20 July 2009, 2388–2398

Cobalt(II) and nickel(II) chelates of some 5-pyrazolone-based, Schiff-base ligands

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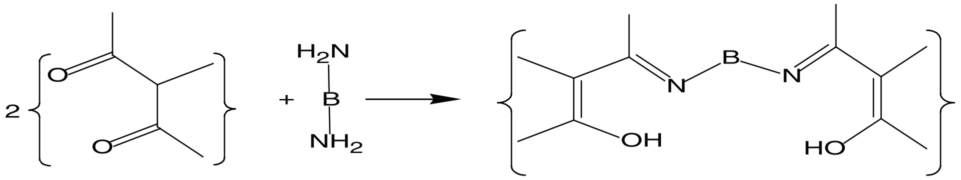
(*Received 19 June 2008; in final form 19 November 2008*)

The cobalt(II) and nickel(II) chelates of Schiff bases, derived by condensing 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPP) with *o*-, *m*-, *p*-phenylenediamine, benzidine, and ethylenediamine have been synthesized and characterized by elemental analyses, thermogravimetric analyses (TGA), conductance data, magnetic measurements, IR, ^{1}H NMR, ^{13}C NMR, mass, and electronic spectroscopies. Each of the Schiff bases was an ONNO donor to metal forming chelates formulated as $[M(L)(H_2O)_2]_n$ with $M = Ni(II)$ and Co(II) and L is the di-anion of the Schiff base. The monomeric ($n = 1$) and dimeric ($n = 2$) species of these metal chelates, based on available evidence, are suggested.

Keywords: Cobalt(II); Nickel(II); Schiff base; 5-Pyrazolones; ONNO donor ligands

1. Introduction

Schiff bases derived from β-diketone and primary amine provide imino or ketimino with hydroxyl for coordination [1–7]. There are many reports on metal chelates of this class of compounds but very little on the bisketimino compound derived from heterocyclic β-diketone [1–5], which give ONNO donor array towards metal ions.



We have previously reported Cr(III) and Ni(II) chelates of Schiff bases derived from 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one [1, 3] and report here the cobalt(II) and nickel(II) chelates of Schiff bases derived from 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one with *o*-, *m*-, *p*-phenylenediamine, benzedine, and ethylenediamine. A general structural representation and abbreviations of the ligands used are given in figure 1.

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902833058

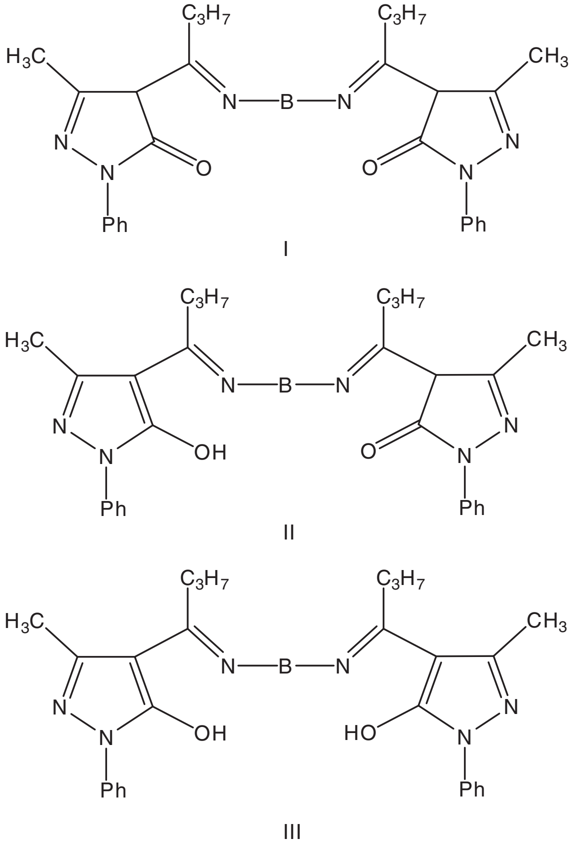

Figure 1. Suggested tautomeric forms of Schiff-base ligands. B = 1,2-C_6H_4 (*ortho*), H_2BMPPOPD; B = 1,3-C_6H_4 (*meta*), H_2BMPPMPD; B = 1,4-C_6H_4 (*para*), H_2BMPPPPD; B = 4,4′-$C_{12}H_8$, H_2BMPPBD; B = CH_2CH_2, H_2BMPPEN.

2. Experimental

2.1. *Chemicals*

Ethylenediamine, *o*-, *m*-, *p*-phenylenediamine, and ethyl acetoacetate were purchased from Chiti-Chem. Corporation, Baroda, India. Benzidine was bought from S.D. Fine Chem. Ltd, Boiser, India. Phenylhydrazine and dioxane were obtained from Bhavin Enterprise, Baroda, India and used after purification [8, 9]. DMF was obtained from RANBAXY, Fine Chemicals Ltd, New Delhi, India. Butyryl chloride was obtained from Lancaster Pvt. Ltd, England. Absolute alcohol was obtained from Alembic Chemical Works Co. Ltd, Baroda, India and used after distillation. For preparation of all the metal chelates, hydrated metal nitrates were used.

2.2. *Synthesis*

2.2.1. Preparation of Schiff bases. The Schiff bases (H_2L) were synthesized in three steps: (i) 3-methyl-1-phenyl-2-pyrazolin-5-one [10], (ii) 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPP) [11, 12], and (iii) Schiff bases (condensation of BMPP with respective diamines). An identical procedure has been used in the syntheses of all the Schiff bases. One millimole of BMPP (2.44 g) and 0.5 mmol of *o*-, *m*-, or *p*-phenylenediamine (0.54 g), benzidine (0.92 g), and/or ethylenediamine (0.30 g) in 150 cm^3 of ethanol were refluxed for 2 h. The colored products obtained were kept overnight, filtered, washed several times with water, and recrystallized from ethanol. The elemental analyses and physical properties of the Schiff bases are listed in table 1.

2.2.2. Preparation of metal chelates. To 150 cm^3 hot ethanolic solution of Schiff base (5 mmol) a slight excess over the required metal : ligand ratio of 1 : 1, 50 cm^3 of ethanolic solution containing 5 mmol of cobalt(II) nitrate (1.40 g) or nickel(II) nitrate (1.40 g) was added dropwise with constant stirring. To the resulting mixture 2 g of sodium acetate was added and then refluxed for 1 h, concentrated to half the original volume, and cooled. The colored crystalline product was filtered *in vacuo*, washed several times with hot water, and finally with hot ethanol. The product was dried at 45°C in air.

2.2.3. Measurements. All the measurements were carried out at room temperature ($25 \pm 2°C$). Carbon, hydrogen, and nitrogen were estimated on a PERKIN ELMER 2400 SERIES-II. Mass spectra of the ligands were obtained on a JEOL SX-102 (FAB) Mass Spectrometer at the Sophisticated Instrumentation Centre, CDRI, Lucknow, India. The gravimetric oxide method for estimation of metals was employed. Conductivity measurements were made with "SYSTRONICS 305 Conductivity Bridge" at room temperature. The molecular weights of the ligands were determined using a K-7000 KNAUER vapor pressure osmometer in DMF. The magnetic susceptibility measurements were made on a 7304 Vibrating Sample magnetometer, Lake Shore, USA. Diffuse reflectance spectra of solid compounds suitably diluted with MgO were obtained on a BECKMAN-DK-2A Recording Spectrophotometer from 350–1700 nm with standard reflectance attachment. IR spectra of all the compounds were recorded with a NICOLET-400D Spectrophotometer in the 400–4000 cm^{-1} range using KBr discs. Thermograms were obtained in the temperature range 25–350°C, using nitrogen flux with a SDT 2960 TA Thermoanalyzer. ^{1}H NMR and ^{13}C NMR were recorded on an AVANCE-400, BRUKER.

3. Results and discussion

3.1. *Analytical data*

Analytical data of the Schiff bases and their complexes are listed in table 1. The three tautomeric forms of the Schiff bases are shown in figure 1. The complexes possess 1 : 1 metal : ligand stoichiometry, however, the vapor pressure osmometry (VPO) measurements show complexes based on *m*- or *p*-phenylenediamine and benzidine to be dimers. Thus, the formation of the metal chelates can be represented by the general equation,

$$n\mathrm{M(NO_3)_2} \cdot 6\mathrm{H_2O} + n\mathrm{H_2L} \xrightarrow[\text{Reflux}]{\text{Ethanol}} [\mathrm{ML(H_2O)_2}]_n + 2n\mathrm{HNO_3} + 4n\mathrm{H_2O}$$

where $\mathrm{M} = \mathrm{Co(II)}$ or Ni(II), and $n = 1$ for monomeric and 2 for dimeric complexes.

Table 1. Analytical data of the Schiff bases and their metal complexes.

Compound	F.W. ($g\,mol^{-1}$) Found (Calcd)	Yield (%)	Color	Melting point (°C)	Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$)	Elemental analysis found (Calcd) % Metal	C	H	N	μ_{eff} (B.M.)
H_2BMPPOPD	5602 (560.7)	65	Yellow	189	–	–	72.12 (72.83)	5.28 (5.47)	13.92 (13.98)	–
[Co(BMPPOPD)(H_2O)$_2$]	– (653.5)	60	Wooden yellow	265[a]	37.0	8.90 (9.02)	62.52 (62.58)	5.92 (5.86)	12.89 (12.86)	4.92
[Ni(BMPPOPD)(H_2O)$_2$]	– (653.4)	72	Yellowish green	215	31.3	8.88 (8.98)	62.57 (62.50)	5.90 (5.86)	12.88 (12.86)	3.30
H_2BMPPMPD	560.3 (560.7)	70	Light almond	164	–	–	71.42 (72.83)	7.67 (7.47)	14.71 (14.98)	–
[Co(BMPPMPD)(H_2O)$_2$]$_2$	1297.1 (1306.8)	65	Pink	279[a]	40.8	8.92 (9.02)	62.53 (62.48)	5.93 (5.86)	13.01 (13.86)	4.88
[Ni(BMPPMPD)(H_2O)$_2$]$_2$	1320.6 (1306.8)	68	Light grey	250[a]	35.4	9.68 (8.98)	62.58 (62.50)	5.91 (5.86)	12.89 (12.86)	3.27
H_2BMPPPPD	561.0 (560.7)	72	Dark almond	160	–	–	72.01 (72.83)	6.39 (6.47)	14.82 (14.98)	–
[Co(BMPPPPD)(H_2O)$_2$]$_2$	1318.0 (1306.8)	78	Wooden yellow	279[a]	25.8	9.10 (9.02)	62.50 (62.48)	5.95 (5.86)	13.02 (12.86)	4.86
[Ni(BMPPPPD)(H_2O)$_2$]$_2$	1319.7 (1306.8)	70	Light green	219	38.0	8.62 (8.98)	62.59 (62.50)	5.92 (5.86)	12.99 (12.86)	2.78
H_2BMPPBD	– (634.8)	68	Light green	255[a]	–	–	74.46 (75.44)	6.19 (6.33)	13.54 (13.20)	–
[Co(BMPPBD)(H_2O)$_2$]$_2$	1465.8 (1455.4)	60	Yellow	270[a]	12.1	8.02 (8.02)	65.88 (65.84)	5.90 (5.80)	11.57 (11.52)	4.70
[Ni(BMPPBD)(H_2O)$_2$]$_2$	1469.1 (1454.8)	72	Greenish yellow	215	27.1	8.07 (8.05)	65.88 (65.86)	5.82 (5.80)	11.75 (11.52)	2.77
H_2BMPPEN	– (512.6)	69	Crème	226	–	–	69.25 (70.29)	7.09 (7.08)	16.51 (16.39)	–
[Co(BMPPEN)(H_2O)$_2$]	– (605.5)	62	Orange	268[a]	5.0	9.62 (9.73)	59.57 (59.50)	6.38 (6.32)	13.89 (13.88)	4.81
[Ni(BMPPEN)(H_2O)$_2$]	– (605.4)	69	Green	260[a]	49.8	9.52 (9.70)	59.55 (59.52)	6.39 (6.33)	13.89 (13.88)	3.12

[a] Decomposition point.

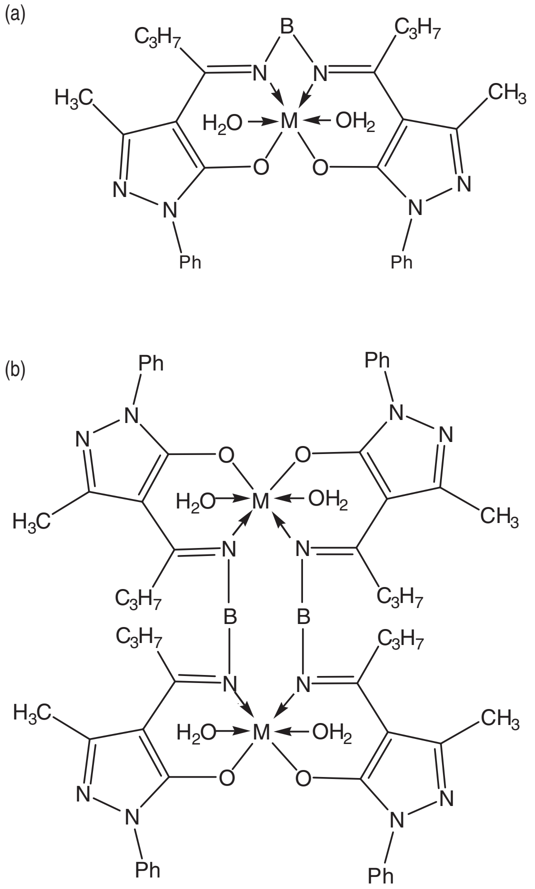

Figure 2. Suggested general structure of chelates of (a) 1 : 1 metal : ligand and (b) 2 : 2 metal : ligand stoichiometry.

Table 1 also lists the colors, yields, melting points, conductivities, and magnetic moments (μ_{eff}). All the complexes are stable in air and insoluble in common organic solvents. The conductance in DMF show values from 5 to 49 $\Omega^{-1}\text{cm}^2\,\text{mol}^{-1}$ indicating non-electrolytic nature [13].

3.2. *Mass spectral characterization*

The mass fragmentation pattern of a representative Schiff base [H_2BMPPPPD], along with possible molecular ion peaks is given in "Supplementary material". The molecular weights of Schiff bases are in good agreement with suggested structures (figure 2).

3.3. *Spectroscopic characterization*

3.3.1. IR spectra. IR spectra of the free ligands and their metal complexes are given in table 2. The OH stretching frequency of the free ligands is displaced to the 3350–2800 cm^{-1} region due to the internal hydrogen bonding of OH with N=C [14, 15].

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

Compound formula	ν(O-H) coordinated (H_2O)	ν(C=N)[b]	ν(C=N)[c]	ν(C–O)	δ(O–H) free ligand
H_2BMPPOPD[a]	–	1629 s	1595 s	1320 s	1240 s
[Co(BMPPOPD)(H_2O)$_2$]	3300 br	1625 m	1595 m	1330 m	–
[Ni(BMPPOPD)(H_2O)$_2$]	3300 br	1615 m	1595 s	1330 sh	–
H_2BMPPMPD[a]	–	1635 s	1595 s	1310 m	1240 s
[Co(BMPPOPD)(H_2O)$_2$]	3350 br	1630 m	1595 s	1320 sh	–
[Ni(BMPPMPD)(H_2O)$_2$]	3300 br	1630 sh	1595 s	1320 sh	–
H_2BMPPPPD[a]	–	1630 s	1595 m	1305 s	1240 s
[Co(BMPPPPD)(H_2O)$_2$]	3350 br	1626 s	1595 m	1320 sh	–
[Ni(BMPPPPD)(H_2O)$_2$]	3300 br	1622 s	1595 s	1320 w	–
H_2BMPPBD[a]	–	1630 m	1595 s	1305 w	1246 s
[Co(BMPPBD)(H_2O)$_2$]	3300 br	1623 s	1595 s	1320 sh	–
[Ni(BMPPBD)(H_2O)$_2$]	3300 br	1622 m	1595 s	1310 sh	–
H_2BMPPEN[a]	–	1629 s	1595 s	1310 s	1240 s
[Co(BMPPEN)(H_2O)$_2$]	3300 br	1610 s	1595 s	1320 sh	–
[Ni(BMPPEN)(H_2O)$_2$]	3300 br	1620 w	1595 s	1320 sh	–

[a] νO–H(H–bonded): 2800–3350 cm^{-1}.
[b] ν(C=N)azomethine.
[c] Cyclic.
Abbreviations: br = broad, s = strong, sh = shoulder, m = medium, w = weak.

The ligands are relatively planar with intramolecular distance favoring hydrogen bond formation [16]. The presence of electron donating groups on the nitrogen also favors intramolecular/intermolecular hydrogen bonding [16], suggesting that ligands exist in the enolic form (figure 1). The wavenumber of C=N (1629–1635 cm^{-1}) of the ligands is shifted to a lower value (1610–1630 cm^{-1}) in all the complexes, suggesting coordination through the azomethine nitrogen [17–19].

The wavenumber of C=N (1595 cm^{-1}) of cyclic group of the ligands does not change in the metal complexes, indicating no coordination via C=N(cyclic) [20]. Similarly, the displacement of the C–O stretch (1305–1320 cm^{-1}) of the ligands to a higher value (1310–1330 cm^{-1}) in their complexes indicates the participation of 5–OH of pyrazoline in chelation [14]. Evidence for such bonding in a few of our chelates is also inferred from a very weak shoulder appeared in this region [21, 22]. The far-infrared spectra of all the metal chelates show bands at 490–500 and 400–415 cm^{-1} assigned to Co–N and Ni–N vibrations of azomethine nitrogen, consistent with octahedral geometry [22]. All the complexes show a band from 3500–3100 cm^{-1}, due to the presence of water [23].

3.3.2. The ^{1}H NMR spectra. ^{1}H NMR spectra of the Schiff bases show the phenyl multiplets in the range 7.0–7.6 δ ppm. Three signals (triplet, multiplet, and triplet) between 0.6 and 2.5 ppm are assigned to propyl group on pyrazoline. Enolic proton is observed in the range 12–14 δ ppm. The ^{13}C NMR confirms aliphatic and aromatic carbon with peaks between in the ranges of 9–46 and 100–150 δ ppm, respectively.

3.3.3. Diffuse reflectance spectra. Diffuse reflection spectra (drs) of all the Co(II) complexes are consistent with octahedral stereochemistry (table 3) [24, 25]. Generally two rather than three spin-allowed bands are observed, since the transition to $^4A_2g(F)$ level is very weak [26]. In [Co(BMPPPPD)(H_2O)$_2$]$_2$ and [Co(BMPPOPD)(H_2O)$_2$], this band is observed, while in [Co(BMPPMPD)(H_2O)$_2$]$_2$, [Co(BMPPBD)(H_2O)$_2$]$_2$, and [Co(BMPPEN)(H_2O)$_2$] this band is not observed.

Table 3. Electronic spectral data of Co(II) complexes (cm^{-1}).

Complex formula	Method	Observed and calculated transition energy			$10D_q$ (cm^{-1})	B_{35} (cm^{-1})	β_{35}	$\delta\nu$ (cm^{-1})	ν_2/ν_1
		ν_1	ν_2	ν_3					
$[Co(BMPPPPD)(H_2O)_2]_2$	Observed	8,695	16,528	19,230	–	–	–	–	1.9
	(a)	Fitted	18,515	Fitted	9,815	777	0.800	+1,987	
	(b)	7,710	Fitted	Fitted	8,803	840	0.865	−985	
	(c)	6,919	16,666	Fitted	7,833	645	0.664	−1,776	
$[Co(BMPPOPD)(H_2O)_2]$	Observed	9,217	16,666	20,000	–	–	–	–	1.8
	(a)	Fitted	19,607	Fitted	10,389	797	0.821	+2,941	
	(b)	7,769	Fitted	Fitted	8,894	890	0.922	−1,448	
	(c)	6,948	14,037	Fitted	7,833	601	0.619	−2,269	
$[Co(BMPPMPD)(H_2O)_2]_2$	(a)	8,333	17,823[a]	20,202	9,484	868	0.891	–	2.1
$[Co(BMPPBD)(H_2O)_2]_2$	(a)	8,849	18,807[a]	18,867	9,946	741	0.761	–	2.1
$[Co(BMPPEN)(H_2O)_2]$	(a)	9,259	19,713[a]	20,408	10,455	823	0.847	–	2.1

[a] Calculated.

We have used these bands to compute ligand field and repulsion parameters from equations [27, 28]:

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

The following methods were used to determine $10D_q$ and B for the chelates [27]:

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

By fitting first and third observed bands, second and third observed bands, and all three observed bands using a, b, and c respectively, the values of B_{35}, $10D_q$, and β_{35} were calculated (table 3). Transition energies calculated by method (b) give the smallest $\delta\nu$, however, in method (b) the use of the ν_2 is required.

In $[Co(BMPPMPD)(H_2O)_2]_2$, $[Co(BMPPBD)(H_2O)_2]_2$, and $[Co(BMPPEN)(H_2O)_2]$, ν_2 band is obscured; (a) was used to calculate ν_2, $10D_q$, and B_{35} [27, 28]. The magnitude of B determined for all complexes may be compared with that for free Co(II) ion ($971\,cm^{-1}$).

Decrease in B_{35} is considered as an indication of covalent character in M–L. 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 following nephelauxetic series order:

$H_2BMPPOPD > H_2BMPPMPD > H_2BMPPPPD > H_2BMPPEN > H_2BMPPBD$

The diffuse reflectance spectra (table 4) of the Ni(II) complexes studied in the present work are typical octahedral Ni(II) spectra consisting of three bands [22], ν_1: $^3A_{2g} \rightarrow {}^3T_{2g}$, ν_2: $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ν_3: $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The observed d–d transitions have energies which agree perfectly with octahedral nickel(II) and $\nu_2 : \nu_1$ ratio is in the normal range expected for octahedral Ni(II) [29, 30]. 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 interactions and their energies can be determined from the following secular determinant [27]:

$$\begin{array}{ccc} & {}^3T_{1g}(F) & {}^3T_{1g}(P) \\ {}^3T_{1g}(F) & \left| \begin{array}{l} 6D_q - E \\ 4D_q \end{array} \right. & \left. \begin{array}{l} 4D_q \\ 15B - E \end{array} \right| = 0 \\ {}^3T_{1g}(P) & & \end{array}$$

which results in $E_{1,2}(^3T_{1g}) = (7.5B + 3D_q) \pm ½(225B^2 + 100D_q^2 - 180D_q\ B)^{1/2}$, leading to [27]:

$$\nu_1 = 10D_q$$
$$\nu_2 = ½(15B + 30D_q) - ½[(15B - 10D_q)^2 + 12B \cdot 10D_q]^{1/2}$$

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

Complex formula	Method	Observed and calculated transition energies (cm^{-1})			B_{35} (cm^{-1})	β_{35} (cm^{-1})	$\delta\nu$ (cm^{-1})	ν_2/ν_1	$-\lambda$ (cm^{-1})	$\mu_{eff}{}^{a}$ (B.M.)
		ν_1	ν_2	ν_3						
[NiBMPPOPD(H_2O)$_2$]	Observed	9,090	14,740	24,515	–	–	–			
	(a)	10D_q	Fitted	24,513^{a}	799	0.767	−2			
	(b)	10D_q	14,740^{a}	Fitted	799	0.780	0	1.62	190	3.22
	(c)	10D_q	14,740^{a}	24,515^{a}	799	0.768	0			
	(d)	10D_q	14,741^{a}	24,516^{a}	799	0.780	+1			
[NiBMPPMPD(H_2O)$_2$]$_2$	Observed	9,804	15,900	25,650	–	–	–			
	(a)	10D_q	Fitted	26,449^{a}	862	0.829	+799			
	(b)	10D_q	15,726^{a}	Fitted	798	0.779	−174	1.62	180	3.19
	(c)	10D_q	15,759^{a}	25,791^{a}	809	0.777	+141			
	(d)	10D_q	15,668^{a}	25,418^{a}	778	0.760	−232			
[NiBMPPPPD(H_2O)$_2$]$_2$	Observed	9,095	14,925	25,695	–	–	–			
	(a)	10D_q	Fitted	25,524^{a}	878	0.843	−171			
	(b)	10D_q	14,952^{a}	Fitted	891	0.870	+27	1.64	235	3.22
	(c)	10D_q	14,948^{a}	25,672^{a}	889	0.854	±23			
	(d)	10D_q	14,956^{a}	25,726^{a}	893	0.872	+31			
[NiBMPPBD(H_2O)$_2$]$_2$	Observed	8,990	14,430	22,845	–	–	–			
	(a)	10D_q	Fitted	23,563^{a}	735	0.706	+718			
	(b)	10D_q	14,241^{a}	Fitted	674	0.658	−189	1.61	142	3.23
	(c)	10D_q	14,283^{a}	22,992^{a}	687	0.660	±147			
	(d)	10D_q	14,159^{a}	22,574^{a}	651	0.636	−271			
[NiBMPPEN(H_2O)$_2$]	Observed	9,490	16,110	23,800	–	–	–			
	(a)	10D_q	Fitted	31,309^{a}	1303	1.252	+7509			
	(b)	10D_q	14,937^{a}	Fitted	684	0.668	−1173	1.69	166	3.21
	(c)	10D_q	15,194^{a}	24,716^{a}	763	0.733	±916			
	(d)	10D_q	13,849^{a}	21,539^{a}	461	0.450	−2261			

[a] Calculated.

and

$$\nu_3 = \tfrac{1}{2}(15B + 30D_q) + \tfrac{1}{2}[(15B - 10D_q)^2 + 12B \cdot 10D_q]^{1/2}$$

The equations used to calculate B_{35} are [27]:

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

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 [27]. In all the complexes, the best fit is according to the method (c). The magnitude of B_{35} determined by method (c) may be compared with that for the free Ni(II) ion, $1041\,\mathrm{cm}^{-1}$ [27, 31]. The decrease in B_{35} is considered as an indication of the amount of covalent character in the bonds [31]. The ratio B_{35}(found): B_{35}(free ion) $= \beta_{35}$ depends on the position of the ligand in the nephelauxetic series. The ligands give the following nephelauxetic series order based on the method (c):

$$\mathrm{H_2BPMP\text{-}PPD > H_2BPMP\text{-}MPD > H_2BPMP\text{-}OPD > H_2BPMP}\nu\mathrm{EN} \\ \mathrm{> H_2BPMP\text{-}BD}$$

An attempt has been made to obtain approximate value of λ, the spin-orbit coupling constant, using $\lambda = 2.7\,B_{35}^2/10D_q$ [30, 32]. To seek correlation between spectral and magnetic data of Ni(II) complexes, μ_{eff} was calculated using $10D_q$ by ${}^{\mathrm{Calcd.}}\mu_{\mathrm{eff}} = {}^{\mathrm{S.O.}}\mu_{\mathrm{eff}}$ $[1\text{–}4\lambda_0/10D_q]$ [28]. The free ion value of nickel(II), $\lambda_0 = -315\,\mathrm{cm}^{-1}$ is used in the calculations. These values are also shown in table 4 [S.O. = 2.8284].

3.4. *Magnetic properties*

All Co(II) complexes exhibit magnetic moments from 4.70 to 4.92 B.M., close to the value required for octahedral geometry [33, 34]. All Ni(II) complexes show magnetic moments in the range 2.77–3.30 B.M. as required for octahedral complexes [34–37]. Calculated values (table 4) are in good agreement with observed values.

3.5. *Thermogravimetric analysis (TGA)*

The TGA data provide evidence regarding the number and types of the water molecules present in the compound. The complexes show weight loss of 5.2% in the range 130–200°C, corresponding to two coordinated water molecules [23].

4. Conclusion

Based on the data obtained from elemental analyses, conductivity, magnetic measurememts, thermal analyses, mass, IR, NMR, and electronic spectra, the divalent cobalt and nickel complexes are $[\mathrm{M(L)(H_2O)_2}]_n$, L is di-anion of ligand. The complexes based on benzidine or *p*-/*m*-phenylinediamine are dimeric and those based on *o*-phenylene/ethylene are monomeric. Weight loss of 2.5% in the temperature range 130–200°C may be assigned to two coordinated water molecules. The proposed structure suggests octahedral geometry with two bisketimino groups and two 5OH groups of pyrazoline of the Schiff base (ONNO donor). The remaining coordination sites are occupied by water.

Acknowledgments

We are thankful to Dr J.S. Parmar, Head, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar – 388120, Gujarat, India for providing us required facilities for this work.

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