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Synthesis and spectroscopic characterisation of cobalt(II), nickel(II) and copper(II) complexes with 5-methyl-1-(2'-pyridyl)pyrazole-3-carbohydrazide

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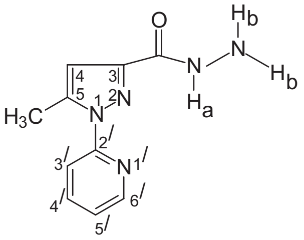
The chelating behaviour of the title pro-ligand, **1** (MPyPzCH), is demonstrated by preparation of a range of its distorted-octahedral Co^{II}, N i^{II} and Cu^{II} complexes with various counter ions, X (X = Cl, Br, NO_3, SCN, BF_4, or ClO_4). The neutral, tetradentate ligand appears to bind through the pyrazolyl 2_N and pyridyl $1'_{N,}$ amidic oxygen (ketonic form) and the terminal N of the hydrazide residue, respectively. The anions (X) in all cases are coordinated. The ESR spectra of some of the Cu^{II} complexes indicate $dx^2–y^2$ as ground state.

Keywords: spectroscopy, electrochemistry, pyridyl-pyrazole carbohydrazide, tetradentate, cobalt(II), nickel(II), copper(II)

The potential complexing ability of substituted hydrazines with transition metal ions is well known.[1] The remarkable anti-tuberculosis activity[-2] of isonicotinoyl hydrazide (Isoniazide) and the fact that the mode of action of isoniazide is dependent on chelation with transition metal ions present in the system, have prompted an exhaustive investigation of the coordination chemistry of pyridine-carboxylic hydrazides.[3] In addition, substituted pyrazoles, long being acclaimed for their medicinal values, have been exhaustively used as coordinating ligands towards transition metals, because of the biological implications of the free ligands in the fight against cancer.[4] It has therefore been our aim to design a pyrazole derivative containing a hydrazide residue that might have potential biological activity and to study its chelation behaviour with transition metal ions.

In continuation of earlier work[5] from our laboratory, we report studies of the chelating behaviour of 5-methyl-1-(2'-pyridyl)pyrazole-3-carbohydrazide (**1**) towards cobalt(II), nickel(II) and copper(II).



Results and discussion

The electron impact mass spectrum of (**1**) gives a molecular ion peak at *m/z* 217 that corresponds to the molecular formula $C_{10}H_{11}N_5O$. Its IR spectrum shows bands at 3480(b,s), 3300(s), 3260(m) and 3200(w) cm$^{–1}$ which are due probably to hydrogen-bonded NH and NH_2 stretching frequencies. The very strong band at 1680 cm^1 can be justifiably assigned as the amide-1 band (*i.e.*$\nu_{C=O}$).The strong band at 1630 cm^{-1} may be attributed to β-NH_2. The $\nu_{C=N}$ frequencies of the pyridine ring appear at 1595 cm^{-1} while those of the pyrazole ring appear at 1585, 1540 and 1480 cm$^{–1}$ respectively. ^{1}H NMR data are also consistent with the assigned formulation of (**1**) (see Experimental).

The cobalt(II) complexes of (**1**) conform to the general composition [Co(MPyPzCH)X_2]as ascertained from analytical data (Table 1). The magnetic moment values fall within the range 4.29–4.87B.M. (Table 1), consistent with 6-coordinate high spin cobalt(II) complexes.[6] The significant lowering of magnetic moment value (4.29 B.M.) for the fluoborato-species indicates that the species has a singlet ground state and distorted octahedral geometry. The molar conductance (Λ_M) values (Table 1) recorded in dry methanol (Λ_M = 65-90 mho cm^{2}mol$^{–1}$) are indicative of 1: 1 electrolytic nature[7] in this solvent, possibly due to partial solvolysis.

The diffuse reflectance spectra (DRS) of the Co^{II} species are also consistent with an overall octahedral environment in the complexes. The principal absorption bands are located in the region 8975–9365 and 19600–20040 cm$^{–1}$ and may be assigned as $\nu_1[^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ and $\nu_3[^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)]$ transitions[8] respectively in an idealised O_h symmetry. Using the two known relationships,[9] it has been possible to deduce the ligand field parameters (Dq = 1008–1054; B = 733–790 cm$^{–1}$ and β = 0.76–0.82) from the assigned positions of ν_1 and ν_3 bands; these are quite consistent with those reported generally[10] for octahedral cobalt(II) species. Using the relationship $\nu_2 = \nu_1 + 10Dq$, the position of ν_2 bands are found to lie in the region 19050–19905 cm$^{–1}$, very close to ν_3 bands as expected. In some cases, shoulders or weak bands appearing in the region (26900–29940 cm^{-1}) are due to LMCT transitions. The electronic spectral data taken in methanolic solutions indicate that no significant change in geometry occurs on dissolutions of the complexes in the said solvent. The low values of molar extinction coefficients ($\varepsilon \geq 28$ dm^3 mol^{-1}cm^{-1}) found for the spectral bands further support octahedral geometry.

Nickel(II) complexes of (**1**) conform to the general composition [Ni(MPyPzCH)X_2]as ascertained from analytical data (Table 1); the effective magnetic moment values (μ_{eff}) (Table 1) of the species fall in the range 3.02–3.20B.M. at RT (30°C), as expected for 6-coordinate nickel(II) complexes.[11] The methanolic solutions of these Ni^{II} species furnish molar conductances (Λ_M = 100–170 mho cm^{2}mol$^{–1}$) indicative of 1:2 electrolytes[7] due to partial and almost complete solvolysis. The DRS of the mono-chelate of Ni^{II} consist of three main bands appearing in the region 9500–10250; 16300–17010 and 25600–27890 cm$^{–1}$ which can be safely assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) respectively in an O_h symmetry. The weak bands or shoulder appearing at 13000 cm^{-1} are probably due to the spin-forbidden transition.[12] An additional band appearing around 32000 cm$^{–1}$ could be due to LMCT transitions. The ligand field parameters (Dq = 954–1024 cm$^{–1}$; B = 860–941 cm$^{–1}$, β = 0.79–0.89 and ν_2/ν_1 = 1.61–1.73) substantiate an overall octahedral geometry for the reported Ni^{II} species.[11,13] All the present mono-chelates of Ni^{II} on dissolution in methanol afford green solutions and suggest

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Table 1 Analytical and physical data of Co^{II}, Ni^{II} and Cu^{II} complexes

Complex (Colour)	Elemental analysis(%): found/(calc.)[a]						
	C	H	N	M	Anion	Λ_M	μ_{eff} at 30°C (B.M.)
1 [Co(MPyPzCH)Cl$_2$] (Reddish brown)	34.7 (34.5)	3.2 (3.1)	20.0 (20.1)	16.8 (17.0)	20.7 (20.4)	90	4.87
2 [Co(MPyPzCH)Br$_2$] (Reddish brown)	27.7 (27.5)	2.6 (2.5)	16.1 (16.0)	13.5 (13.5)	36.8 (36.7)	65	4.69
3 [Co(MPyPzCH) (SCN)$_2$] (Bright pink)	30.8 (30.6)	2.9 (2.8)	25.1 (25.9)[b]	15.1 (15.0)	 –	70	4.75
4. [Co(MPyPzCH)(BF$_4$)$_2$] (Brown)	26.9 (26.6)	2.4 (2.4)	15.4 (15.6)	13.3 (13.1)	–	80	4.29
5 [Ni(MPyPzCH) Cl$_2$] (Greenish blue)	34.8 (34.6)	3.3 (3.1)	20.0 (20.2)	16.9 (16.9)	20.6 (20.8)	130	3.11
6 [Ni(MPyPzCH)Br$_2$] (Deep Blue)	27.7 (27.5)	2.5 (2.5)	15.9 (16.0)	13.3 (13.4)	36.9 (36.8)	170	3.07
7 [Ni(MPyPzCH)(NO$_3$)$_2$] (Greyish blue)	30.2 (30.0)	2.8 (2.7)	24.6 (24.5)[b]	14.8 (14.7)	–	100	3.02
8 [Ni(MPyPzCH)(SCN)$_2$] (Light blue)	30.8 (30.6)	2.9 (2.6)	24.9 (24.8)[b]	15.0 (15.0)		140	3.17
9 [Ni(MPyPzCH) (BF$_4$)$_2$] (Light blue)	26.6 (26.7)	2.5 (2.4)	15.4 (15.4)	13.1 (13.0)		120	3.20
10 [Ni(MPyPzCH) (ClO$_4$)$_2$] (Deep blue)	23.6 (23.4)	2.9 (2.7)	13.6 (13.7)	11.4 (11.5)	–	150	3.14
11 [Cu(MPyPzCH)Cl$_2$] (Green)	34.3 (34.1)	3.2 (3.1)	19.8 (19.9)	18.0 (18.1)	20.3 (20.6)	30	1.72
12 [Cu(MPyPzCH)Br$_2$] (Grey green)	27.4 (27.2)	2.4 (2.5)	15.7 (15.9)	14.5 (14.4)	36.4 (36.8)	40	1.90
13 [Cu(MPyPzCH) (NO$_3$)$_2$] (Deep blue)	29.8 (29.6)	2.8 (2.7)	24.3 (24.2)[b]	15.7 (15.7)	–	50	2.20
14 [Cu(MPyPzCH) (BF$_4$)$_2$] (Light blue)	26.5 (26.4)	2.6 (2.6)	15.2 (15.4)	14.1 (14.0)	 –	60	1.86
15 [Cu(MPyPzCH) (ClO$_4$)$_2$] (Pale blue)	25.1 (25.0)	2.3 (2.3)	14.5 (14.6)	8.7 (8.6)	13.1 (13.2)	90	1.78

[a]Conductivity in MeOH(mho cm^{2}mol^{-1}). [b]Including nitrogen present in the anions.

that there is no gross departure from the stereochemical environment. The low values of molar extinction co-efficients($\varepsilon \geq 56$) gives additional support to the octahedral geometry.[14]

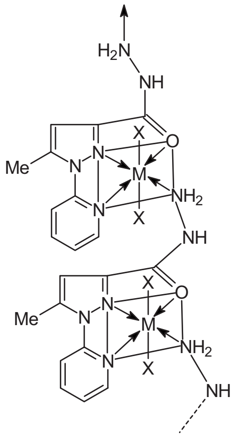
The copper(II) complexes of the title ligand, have the composition [Cu(MPyPzCH)X$_2$] and (μ_{eff}) values in the range 1.75–2.20 B.M. (Table1). It is well authenticated[15] that magnetic moment values for mononuclear Cu^{II} complexes lie in the range 1.72–2.20 B.M. with no major interactions between Cu^{II} ions in the solid state. The molar conductance (Λ_M = 30–90 mho cm^2 mol^{-1}) values of the reported species in dry methanol (Table 1) are indicative of 1:1 electrolytes.[7] The reflectance spectra of these Cu^{II} complexes exhibit a strong broad band in the region 13 300–16 600 cm^{-1}; the nature of the indicates that more transitions are buried under the absorption envelope. Studies[16] on the electronic spectra of Cu^{II} complexes have indicated that the three transitions $^2B_1 \rightarrow {}^2A_1$ (ν_1), $^2B_1 \rightarrow {}^2B_2$ (ν_2) and $^2B_1 \rightarrow {}^2E$ (ν_3) are close in energy, often giving rise to a single broadband envelope. Thus, the present Cu^{II} species are best regarded as having distorted octahedral structures with symmetry lower than O$_h$, though the extent of distortion is not known. An additional band in all these cases appearing in the region 27000–28000 cm^{-1} could be due to LMCT transition. However, electronic spectral data in methanol indicate that there is no stereochemical change on dissolution.

The IR spectral data of all the metal ion complexes reveals a negative shift of $\nu_{C=O}$ (*i.e.* Amide-1) ($\Delta\nu$ = 20–35 cm^{-1}) of (**1**) upon ligation; this result is quite consistent with the participation[17] of the amide oxygen (ketonic form of the hydrazide residue) in complexation. The $\nu_{C=N}$ (pyrazole) in all the species suffers a positive shift ($\Delta\nu$ = 5–40 cm^{-1}), ν_{N-N} (pyrazole) attains negative shift ($\Delta\nu$ = 5–25 cm^{-1}) and $\nu_{C=N}$ (pyridine) also gains positive shift ($\Delta\nu$ = 5–25 cm^{-1}) in the IR spectra of the metal ion complexes. These observations clearly indicate that the tertiary N atoms *i.e.* pyrazolyl 2_N and pyridyl $1'_N$ are the points of attachment[18] to the central metal ions respectively. The IR spectra of the metal ion complexes show a broad diffuse band in the 3μ region (3460–3200 cm^{-1}), which is significantly lowered when compared to the free ligand. This clearly suggests the involvement[19] of the terminal N atom (amino nitrogen) of the hydrazide residue in complexation. Other assignments of IR spectra of these complexes are: ν_{M-O} (amidic) (415 –460 cm^{-1})[20], ν_{M-N} (270–300 cm^{-1}; pyrazolyl 2_N)[21], ν_{M-N} (250–270 cm^{-1}; pyridyl $1'_N$)[22] respectively.

The mode of attachment of the anions (X) [X = Cl, Br, NO$_3$, SCN, BF$_4$, ClO$_4$] in the reported metal ion species can be qualitatively inferred from the IR spectra. The halide complexes show a single metal–halogen stretching frequency at around 300 cm^{-1} [differentiable from ν_{M-N} (ring)] assigned to ν_{M-X} stretch.[23a] The IR spectra of Co^{II}, Ni^{II} and Cu^{II} nitrate species exhibit three bands of which two (1280–1390 cm^{-1}) could be components of ν_3 and the third (~800 cm^{-1}) be the ν_2 vibration of a monodentate nitrate group in C$_{2v}$ symmetry.[24] The spectra of thiocyanato-complexes Co^{II}, Ni^{II} and Cu^{II} exhibit strong bands at around 2100 and 800 cm^{-1} respectively, which could be assigned to the $\nu_{C=N}$ vibration[25] and ν_{C-S} stretch of N-bonded[26] NCS. A band around 500 cm^{-1} can be assigned to δ_{N-C-S} mode of vibration of an N-bonded thiocyanate group.[27] The spectra of the fluoborato complexes of Co^{II}, Ni^{II} and Cu^{II} exhibit three bands in the region 1100–1200,1080–1090 and 1040–1070 cm^{-1} which can be assigned to the split components of ν_3 of a monodentate fluoborate group in C$_{3v}$ symmetry.[28] The components of ν_{Cl-O} in C$_{3V}$ symmetry have been found at ~1200, ~1080 and ~1060 cm^{-1} in the perchlorato-complexes of Ni^{II} and Cu^{II},[1] respectively; these indicate clearly the monodentate nature of the perchlorate ion[29] in these species.

Thus in it appears that the central metal ion in these complexes has an overall octahedral geometry. The stereochemistry of the ligands about the metal atom is interesting and is best described as follows.

Inspection of models suggest that it is difficult to fit the proposed donor atoms of pyridine-N, pyrazole-N(tertiary), ketonic-O and β-N into a plane, leaving the two X ligands *trans* to one another. The three bonds from the carbon atom next to the two nitrogens on the pyrazole ring must be coplanar, which means that the pyridine-N, pyrazole-N(tertiary), and ketonic-O atoms are coplanar since they are binding the same metal atom. The two X ligands are monodentately coordinated to the central metal atom *trans* to one another since for *cis* coordination C_{2V} symmetry is not indicated from the IR data. It is therefore suggested that the central metal atom attains six coordination by binding the terminal N atom (β-N) of the adjacent hydrazide moiety of the second chelate. This kind of framework is geometrically easier and there is no metal-metal interaction as evident from magnetic data (Table 1). This noteworthy framework establishes uniformly magnetically dilute species.



M = Co / Ni / Cu X= Cl, Br, NO_3, SCN, BF_4, ClO_4

The ESR spectra of some of the Cu^{II} complexes, [Cu(MPyPzCH)X_2] (X = Cl, Br,NO_3) in polycrystalline form at *RT* (~30°C) do not show any hyperfine splitting. The chloride species shows two g values with $g_{\|} > g_{\perp} > 2$ (Table 2) which is characteristic of a tetragonally distorted geometry with a $d_{X^2-Y^2}$ ground state and the species may contain some sort of exchange interaction[30] since it has G<4 (G = 3.09).The bromide species gives an isotropic spectrum with g = 2.13. The nitrate species has three g values with G = 5.07, indicating negligible interactions.[31]

Electrochemistry of some Cu^{II} species of the series, [Cu(MPyPzCH)X_2] (X = Cl, ClO_4) in dry MeOH in the potential range + 1.20 to –1.20 V *vs* SCE shows that in each case, Cu^{II} is reduced to Cu^{I} irreversibly at around –0.35 V *vs* SCE. The well-defined redox couple formed in the positive potential area is due to the Cu^{III}/Cu^{II} system;[32] the anodic peak potential corresponds to the oxidation of Cu^{II} ($3d^9$) to Cu^{III} ($3d^8$) and the cathodic counterpart is due to a quasi-reversible one-electron change process, since the ratio I_p^{red}/I_p^{ox} is very close to one and is expressed as $Cu^{II} \rightarrow Cu^{III} + e$. The $E_{½}$ values (Table 3) are dependent on the nature of the coordinated ions.. The metallic copper deposited in the electrode surface is irreversibly oxidised in the potential range –0.05 to + 0.05 V *vs* SCE in each run.

Experimental

All the materials used at different stages for the preparation of the ligand and complexes reported were of GR/AR quality and were used without further purification. Spectrograde solvents were used for spectral, conductance and electrochemical measurements. D_6-DMSO (Aldrich) was used for recording ^{1}H NMR data.

Synthesis of (**1**): 5-methyl-1-(2'-pyridyl)pyrazole-3-carbohydrazide was prepared from ethyl-5-methyl-1-(2'-pyridyl)pyrazole-3-carboxylate (EMPyPzC)[5e] following a method similar to that reported by Dewar *et al.*[4b,5a] An ethanolic solution of EMPyPzC (9.3 g, 0.004 mol, dissolved in minimum volume of dry ethanol) and hydrazine hydrate (100%) (3 ml, 3 g, 0.06 mol) was heated under reflux for 1 h at water bath temperature. The solution was then concentrated at water bath temperature to half its original volume and cooled in ice; the product separated out immediately. This was filtered off, washed with ethanol and water. The product on recrystallisation from hot water yielded the pure hydrazide (m.p. 140°C). ^{1}H NMR: δ = 6.61(s, 1H, H4), 2.56 (s, 3H, CH_3), 9.50 (s, 1H, Ha), 4.39 (d, 2H, Hb, b; *J* = 2.4 Hz), 7.92 (m, 1H, H3'), 7.99 (m, 1H, H4'), 7.37 (m, 1H, H5'), 8.46 (d, 1H, H6'); *J* = 2.8 Hz). Anal. Calcd. for $C_{10}H_{11}N_5O$: C, 55.2; H, 5.0; N, 32.2; found: C, 55.4; H, 5.1; N, 32.0%.

Synthesis of metal ion complexes of MPyPzCH: [M(MPyPzCH)X_2] (M = Co^{II}/Ni^{II}/Cu^{II}; X = Cl, Br, NO_3, SCN, BF_4, ClO_4)

An ethanolic solution of $MX_2.nH_2O$ (0.002 mol dissolved in 20 ml dry ethanol) was added to solution of the ligand, MPyPzCH (0.45 g, 0.002 mol dissolved in 20 ml dry ethanol) in the same solvent. The resultant solution (pH ~5) was concentrated at water bath temperature and cooled to room temperature (~30°C), when a microcrystalline compound separated out in each case. The compound was filtered off, washed with cold ethanol and dried over silica gel at RT (~30° C).

Table 2 ESR spectral parameters of some of the representative Cu^{II} complexes

Complex	$g_{\|}$	$g_{\perp}$	g_{iso}	g_{av}	G	G
1 [Cu(MPyPzCH)Cl_2]	2.19	2.06	–	2.10	3.07	2.91
2 [Cu(MPyPzCH)Br_2]	–	–	2.13	–	–	3.17
3 [Cu(MPyPzCH)$(NO_3)_2$]	2·32 2·36 2·28	2.06	–	2.15	5.07	3.18

Table 3 Cyclic voltammetric results of some of the representative Cu^{II} complexes of MPyPzCH

Complex	E_a (V)	E_c (V)	ΔE (V)	$E_{½}$ (V)
1 [Cu(MPyPzCH)Cl_2]	0.45	0.28	0.17	0.37
2 [Cu(MPyPzCH)$(ClO_4)_2$]	0.47	0.22	0.25	0.34

E_a and E_c are the anodic and cathodic peak potentials respectively; $\Delta E = E_a - E_c$; $E_{½} = ½(E_a + E_c)$

Physical measurements

C, H, N of the ligand and its complexes with Co^{II}, Ni^{II} and Cu^{II} were analysed at IACS, Calcutta, with a Perkin-Elmer CHNS/O analyser 2400. The mass spectrum of the ligand was recorded at RSIC, Chennai, with a Finnigan Mat 8230 GC–MS instrument. ^{1}H NMR spectra were recorded in D_6-DMSO with a Bruker AM 300L (300 MHz) super-conducting FT NMR. The cobalt content of the complexes was determined gravimetrically as anhydrous $CoSO_4$, except for the perchlorate species, where the metal was determined as the $CoHg(SCN)_4$ after decomposing the complex with conc. HNO_3 and H_2SO_4 mixture. The nickel content of the species was estimated gravimetrically as nickel dimethyl glyoximate, after decomposing the metal complex with an acid mixture. The copper content of the complexes were determined iodometrically after decomposing the complex with HNO_3 and HCl mixture. The halogen content of the complexes was determined as silver halide following the standard procedure. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer at IACS, Calcutta. The molar conductance values of the complexes in methanolic solution were obtained with a Systronics model 304 digital conductivity metre. The diffused reflectance spectra and the solution spectra of the complexes were recorded on U-3501 spectrophotometer. IR spectra were recorded on a Perkin-Elmer model 883 infrared spectrophotometer in the solid state (KBr pellets). EPR spectra were taken on a Varian E112 spectrometer at RSIC, Calcutta. Cyclic voltammograms were recorded with the PAR model 270/250 Research Electrochemistry Software (version 4.23) at Burdwan University, in methanolic solution of the species (1×10^{-3} M) using tetrabutyl ammonium perchlorate (NBu_4ClO_4, 0.1M) as supporting electrolyte, a Pt-electrode as working electrode and a standard calomel electrode (SCE) as reference electrode; the scan rate employed was 50 mV s^{-1}.

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References

1 J.R. Dilworth, *Coord. Chem. Rev*., 1976, **21**, 29.
2 Coleman, *Amer. Rev. Tuberc*., 1954, **69**, 1862.
3 (a) K. Nagano, H. Kinoshita and H. Kirakawa, *Chem. Pharm. Bull. Japan*, 1964, **12**, 1198; (b) K. Nagano, H. Kinoshita and Tamura, *Chem. Pharm. Bull. Japan,* 1963**, 11**, 999*;* (c) Z. Tamura and K. Nagano*, Chem. Pharm. Bull. Japan,* 1963, **11**, 793; (d) R.C. Aggarwal, T. Prasad and B.N. Yadav, *J. Inorg. Nucl. Chem*., 1975, **37**, 899.
4 (a) A.N. Kost and I.I. Grandberg, Advances in Heterocyclic Chemistry, vol. 6, A.R. Katrizky and A.J. Boulton, (eds) Academic Press, N.Y., 1966, pp348-349; (b) M.J.S. Dewar and F.E. Kind, *J. Chem. Soc*., 1945, 114.
5 (a) N. Saha and K.M. Dutta, *Inorg. Nucl. Chem*., 1981, **43**, 1405; (b) N. Saha and K.M. Dutta, *Ind. J. Chem*., 1982, **21A**, 180; (c) N. Adhikari, S. Chowdhury, R.J. Butcher and N. Saha, *Polyhedron*; 1999, **18**, 1323; (d) N. Adhikari and N. Saha, *J. Indian Chem. Soc.,* 2006, **83**, 426*;* (e) N. Adhikariand N. Saha, *J. Indian Chem. Soc*., in press.
6 (a) B.N. Figgis and J. Lewis, *Prog. Inorg. Chem*.; 1964, **6**, 37; (b) L. Knorr and J. Macdonald, *Ann. Chim*., 1894, **279**, 217.
7 W.J. Geary, *Coord. Chem. Rev*., 1971, **7**, 81.
8 (a) A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968, p. 318; (b) I.J. Sallomi and A.J. Shaheen, *Polyhedron,* 1998, **17,** 142.
9 (b) C.J. Ballhausen, Introduction to ligand field theory, McGraw Hill Series, N.Y., 1962, p.256.
10 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsivier, Amsterdam, 1964, p.324.
11 K.C. Patel and Goldberg, *J. Inorg. Nucl. Chem*.; 1972, **34**, 637.
12 C.J. Jorgensen, *Acta. Chem. Scad*., 1955, **9**, 1362.
13 A.B.P. Lever, *Coord. Chem. Rev*., 968, **3**, 119.
14 W. Manch W.C. Fernelius, *J. Chem. Edu*., 1961, **38**, 192.
15 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Eastern Pvt. Ltd., New Delhi, 1969, pp. 901-902.
16 (a) D.E. Billing and A.E. Underhill, *J. Inorg. Nucl. Chem*., 1968, **30**, 2147; (b) Y. Nishida and S. Kida., *Coord. Chem. Rev*., 1979, **27**, 275.
17 (a) L. Sacconi, *J. Am. Chem. Soc*., 1952, **74**, 4503; (b) R.M. Issa, M.F.E. Shazly, M.F. Iskander, *Z. Anorg. Allg. Chem*., 1967, **354**, 90.
18 (a) J.P. Ferraro, *Appl. Spectros*.; 1969, **23**, 160; (b) N.N. Greenwood and Wade, *J. Chem. Soc*.; 1960, 1130.
19 (a) H. Ohta, *Bull. Chem. Soc*., Japan, 1958, **31**, 1056; (b) H.H. Fox, J.T. Gibas and A. Motchane, *J. Org. Chem*., 1956, **21**, 349.
20 R.C. Agarwal and T.R. Rao, *J. Inorg. Nucl. Chem*, 1978**, 40**, 171.
21 R.C. Paul, R.S. Chopra and G. Sing., *Inorg. Chim. Acta*., 1975, **14**, 105.
22 J.G. Vos and W.L. Groeneveld, *Inorg. Chim. Acta*; 1977, **36**, 123.
23 (a)D.M. Adams, *Metal-ligand and related vibrations*, E. Arnold, London, 1967, p. 308; (b) W. Levason and C.A. McAuliffe, *Inog. Chim. Acta*., 1976, **16**, 167.
24 (a) N.F. Curtis and Y.M. Curtis, *Inorg. Chem*.; 1965, **4**, 804; (b) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd. edn, 1977, pp.244-247.
25 (a) K.C. Patel and Goldberg, *J. Inorg, Nucl. Chem*.; 1972, **34**, 648; (b) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn, 1977, p.271.
26 M.F. Farago and J.M. James, *Inorg. Chem*.; 1965, **4**, 1706.
27 (a) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Cordination Compounds, 3rd edn, 1977, p.271; (b) I. Berlini and A. Sabatini, *Inorg. Chem.*, 1966, 1025.
28 S. Chanda, K.B. Pandeya and R.P. Singh, *J. Indian. Chem. Soc*.; 1981, **58**, 1097.
29 B.J. Hathaway and A.E. Underhill, *J. Chem. Soc*., 1961, 3091.
30 C.J. Ballhausen, *An Introduction to Ligand Field Theory*, McGraw Hill, New York, 1962, p.134.
31 A.A.G. Tomilinson and B.J. Hathaway, *J. Chem. Soc*. (*A*), 1968, 1685.
32 (a)S.K. Mandal, L.K. Thompson, K. Nag, J.P. Charland and J.E. Gaba, *Inorg. Chem*.; 1987, **26**, 9; (b) T.A. Newbecker, S.T. Kriskey, T.K.L. Chellappa and D.W. Margerum, *Inorg. Chem*., 1983, **22**, 1611; (c) D.C. Olson and J. Vasilevkis, *Inorg. Chem*., 1971, **70**, 463; (d) S. Djebbar-sid, O. Benali-Baitich and J.P. Deloume, *Polyhedron*; 1997, **16**, 2175.