Pergamon

PII: S0277-5387(97)00115-0

Polyhedron Vol. 16, No. 20, pp. 3577–3583, 1997
© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0277–5387/97 $17.00+0.00

New cobalt(II) and nickel(II) complexes with 2-(pyrazol-1-ylmethyl)pyridine. Stereochemical variations in cobalt(II) complexes and X-ray crystal structure of bis[2-(pyrazol-1-ylmethyl) pyridine]dichlorocobalt(II) tetrahydrate

Tapan Kumar Lal and Rabindranath Mukherjee*

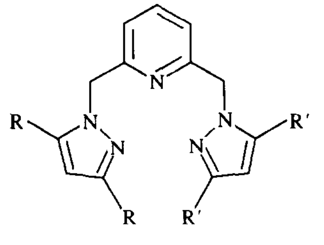
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

(Received 31 January 1997; accepted 19 March 1997)

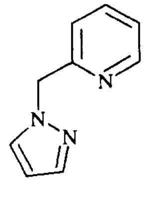
Abstract—Using a non-planar bidentate ligand 2-(pyrazol-1-ylmethyl)pyridine (L^4) a group of three high-spin cobalt(II) ($S = 3/2$) and two paramagnetic nickel(II) ($S = 1$) complexes of compositions [CoL^{4}Cl$_2$] **1**, [ML$^4_2$Cl$_2$]·4H$_2$O (M = Co, **2**; M = Ni, **4**) and [ML$^4_3$] (ClO$_4$)$_2$·H$_2$O (M = Co, **3**; M = Ni, **5**) have been prepared and their stereochemical properties investigated. Characterizations of the new complexes have been done be elemental analysis, conductivity measurements, solution-state magnetic moment, infrared and absorption spectral data. A representative six-co-ordinate complex of cobalt(II), **2** has been structurally characterized. The pertinent bond lengths (Å) are: Co—Cl, 2.413(4) Å; Co—N (pyridine), 2.198(6) Å; Co—N (pyrazole), 2.106(7) Å. Variable-temperature (80–300 K) magnetic susceptibility measurements on solid samples of **2** and **3** confirm their high spin character ($S = 3/2$). The blue or pink cobalt(II) and light green or violet nickel(II) complexes display ligand field transitions. For **3** and **5**, analyses of their *d–d* transition energies reveal that L^4 is a weak field ligand, comparable to that of L^3 [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine]. For cobalt(II) complexes in the solution state stereochemical interconversions have been neatly demonstrated. © 1997 Elsevier Science Ltd

Keywords: 2-(pyrazol-1-ylmethyl)pyridine; cobalt(II) and nickel(II) complexes; stereochemical variations in cobalt(II) complexes; absorption spectral studies; temperature-dependent magnetism for cobalt(II) complexes; crystal structure of a cobalt(II) complex.

During the past few years we have investigated the co-ordination chemistry of a group of three non-planar bis(pyrazol-1-ylmethyl)pyridine ligands L^1–L^3 with manganese(II), iron(II), cobalt(II), nickel(II) and ruthenium(II) [1,2]. We demonstrated (i) decrease in ligand field and increase in M^{III}–M^{II} reduction potential in going from L^1 to L^3 (predominance of steric over electronic effect) [1], (ii) temperature-dependent spin state transition in [FeL$^1_2$] (ClO$_4$)$_2$·H$_2$O [2a], and longest Fe—N (pyridine) bond in [FeL$^2_2$] (ClO$_4$)$_2$ [2b]. Interestingly, these ligands provide six-membered boat conformations [2b,3a], when chelating a transition metal atom and exert a relatively weak field around the metal ion [1a,d,e]. In continuation of our involvement with this class of relatively unexplored ligands [1–7], we became interested in probing the co-ordinative behaviour of a closely similar bidentate



R, R' = H ; L^1
R, H , R' = Me ; L^2
R , R' = Me ; L^3



L^4

---

* Author to whom correspondence should be addressed.

ligand L^4 [4,7] towards cobalt(II) and nickel(II). An additional impetus derives from the current interest in studying cobalt(II)–pyrazole ligated complexes [5,8–10]. We present here the results of our investigation along with structural characterization of a representative bis-ligand complex, [CoL$^4_2$Cl$_2$]·4H$_2$O.

EXPERIMENTAL

Materials

All reagents were purchased from commercial sources and used as received. The ligand 2-(pyrazol-1-ylmethyl)pyridine (L^4) was prepared as described [4a]. Acetonitrile (MeCN), benzene, dichloromethane, ethanol, methanol and diethyl ether were purified as reported previously [1,2]. Chloroform was dried following an analogous method as that followed for dichloromethane. Acetone was dried over CaSO$_4$.

Synthesis of cobalt(II) complexes

[CoL^{4}Cl$_2$] **1**. To an ethanolic solution (5 cm^3) of CoCl$_2$·6H$_2$O (0.100 g, 0.77 mmol) was added an ethanolic solution (8 cm^3) of L^4 (0.122 g, 0.77 mmol) dropwise while stirring. After 15 min the resulting blue solution was rotary evaporated. The blue solid obtained was collected, washed several times with benzene and dried *in vacuo* (yield *ca* 82%). Found: C, 37.3; H, 3.0; N, 14.6. Calc. for C$_9$H$_9$N$_3$Cl$_2$Co: C, 37.4; H, 3.1; N, 14.5%.

[CoL$^4_2$Cl$_2$]·4H$_2$O **2**. An ethanolic solution (3 cm^3) of L^4 (0.150 g, 0.94 mmol) was added to an ethanolic solution (3 cm^3) of CoCl$_2$·6H$_2$O (0.100 g, 0.42 mmol). The solution was then refluxed for 2 h. When it was cooled to room temperature pink crystalline solid separated out. The solid was collected and washed thoroughly with ethanol and dried *in vacuo* (yield *ca* 50%). X-ray quality crystals were obtained by slow evaporation from EtOH–H$_2$O mixture. Found: C, 41.4; H, 5.0; N, 16.0. Calc. for C$_{18}$H$_{26}$N$_6$O$_4$Cl$_2$Co: C, 41.5; H, 5.0; N, 16.2%. IR/cm^{-1}: ν(OH) 3250 and 3150 (split band). Variable-temperature magnetic moment (T/K, $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$): 300, 5.20; 280, 5.21; 260, 5.21; 240, 5.17; 220, 5.10; 200, 5.15; 180, 5.14; 160, 5.15; 140, 5.08; 120, 5.04; 100, 4.96; 81, 4.89.

[CoL$^4_3$] (ClO$_4$)$_2$·H$_2$O **3**. To an ethanolic solution (6 cm^3) of L^4 (0.520 g, 3.28 mmol) was added an ethanolic solution (6 cm^3) of [Co(H$_2$O)$_6$] (ClO$_4$)$_2$ (0.300 g, 0.82 mmol). The reaction mixture was stirred for 3 h and then the solvent was removed. Recrystallization was achieved by slow diffusion of diethyl ether to an acetonitrile solution of the resulting solid (yield *ca* 45%). Found: C, 42.9; H, 3.8; N, 16.6. Calc. for C$_{27}$H$_{29}$N$_9$O$_9$Cl$_2$Co: C, 43.0; H, 3.9; N, 16.7%. IR/cm^{-1}: ν(ClO$_4^-$) 1110, 620; ν(OH) 3400 and 3230. Variable-temperature magnetic moment data (T/K, $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$): 300, 5.19; 280, 5.19; 260, 5.20; 240, 5.17; 220, 5.12; 200, 5.11; 180, 5.08; 160, 5.07; 140, 5.00; 120, 4.85; 100, 4.79; 81, 4.73.

Synthesis of nickel(II) complexes

[NiL$^4_2$Cl$_2$]·4H$_2$O **4**. To an ethanolic solution (5 cm^3) of L^4 (0.134 g, 0.843 mmol) was added dropwise an ethanolic solution (5 cm^3) of NiCl$_2$·6H$_2$O (0.100 g, 0.421 mmol). The mixture was initially stirred at room temperature for 30 min and then refluxed for 2 h. After cooling the solvent was removed *in vacuo*. The light green solid thus obtained was washed 2–3 times with chloroform and once with acetone and finally dried in air (yield *ca* 77%). Found: C, 41.7; H, 5.1; N, 16.3. Calc. for C$_{18}$H$_{26}$N$_6$O$_4$Cl$_2$Ni: C, 41.6; H, 5.0; N, 16.2%. IR/cm^{-1}: ν(OH) 3400 and 3230 (split band).

[NiL$^4_3$] (ClO$_4$)$_2$·H$_2$O **5**. To a stirred ethanolic solution (3 cm^3) of L^4 (0.600 g, 3.774 mmol) was added solid [Ni(H$_2$O)$_6$] (ClO$_4$)$_2$ (0.400 g, 1.094 mmol) in portions. The mixture was stirred for 2 h at room temperature and then the solvent was removed. Violet crystalline compound with bluish tinge was obtained following petroleum ether diffusion to an MeCN solution of the resulting solid product (yield *ca* 22%). Found: C, 42.9; H, 3.8; N, 16.7. Calc. for C$_{27}$N$_{29}$N$_9$O$_9$Cl$_2$Ni: C, 43.1; H, 3.9; N, 16.7%. IR/cm^{-1}: ν(ClO$_4^-$) 1110, 620; ν(OH) 3400 and 3230.

CAUTION! Perchlorate salts are potentially explosive. Although no detonation tendencies have been observed, caution is advised and handling of only small quantities is recommended.

Measurements

Infrared spectra were recorded on a Perkin–Elmer 1320 spectrophotometer as KBr pellets. Electronic spectra were recorded on a Perkin–Elmer Lambda-2 spectrophotometer. Solution electrical conductivity measurements were done with an Elico type CM-82 T conductivity bridge (Hyderabad, India) with solute concentrations of *ca* 10^{-3} mol dm^{-3}. Solution state magnetic susceptibility measurements were done by the NMR method [11] with a PMX-60 JEOL (60 MHz) spectrometer. Magnetic susceptibility measurements in the solid state were performed using a locally built Faraday type magnetic balance comprising an electromagnet (Polytronic Corporation, Bombay, India), an ultravacuum Sartorius Balance Model M25D-S (Sartorius, Germany) and a closed cycle refrigerator (Cryo Industries, U.S.A.). Details of measurements and set up are already described in the literature [12]. In the present study measurements were done at a main field strength of ~6 kG. Appropriate diamagnetic corrections were made using literature values [13].

Structure determination and refinement

Details of crystal data and refinement parameters for [CoL$^4_2$Cl$_2$]·4H$_2$O **2** are given in Table 1. Intensity

Table 1. Crystallographic data for [CoL$^4_2$Cl$_2$]·4H$_2$O **2**

Chemical formula	$C_{18}H_{26}Cl_2O_4N_6Co$
M$_r$	519.93
a (Å)	7.124(1)
b (Å)	8.854(2)
c (Å)	10.144(9)
α ( )	106.92(4)
β ( )	93.74(4)
γ ( )	111.29(2)
U (Å^3)	559.79(0.54)
D_{calc} (g cm^{-3})	1.543
Z	1
Crystal system	Triclinic
Space group	$P\bar{1}$
λ	(Mo-K$_\alpha$) (0.71073)
μ (mm^{-1})	1.03
Crystal size (mm)	0.3 × 0.2 × 0.2
F (000)	268.9
Max., min. transmission factors	0.8242, 0.8235
2θ, range ( )	2–50
No. of reflections measured	2187
No. of observed reflections ($I > 3\sigma$)	1896
R	0.079
R_w	0.099
Largest and mean Δ/σ	0.3165×10^{-4} and 0.3280×10^{-5}
Largest difference peak (e Å^{-3})	1.39
Largest difference hole (e Å^{-3})	−1.54

data were measured at 293 K on an Enraf Nonius CAD-4 Mach four-circle diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Three standard reflections monitored every 97 showed no significant variation in intensity over the data collection period. Intensity data (θ–2θ scan technique) were corrected for Lorentz and polarization effects and for absorption employing an empirical method. Anomalous dispersion was applied for all non-hydrogen atoms. Scattering factors and anomalous dispersion correction terms used were those incorporated in the program package. Crystallographic calculations were carried out with the XTAL3.2 package [14] installed on a PC 486 computer. The structure was solved by direct methods and successive difference Fourier techniques (see Fig. 1). All refinements were performed

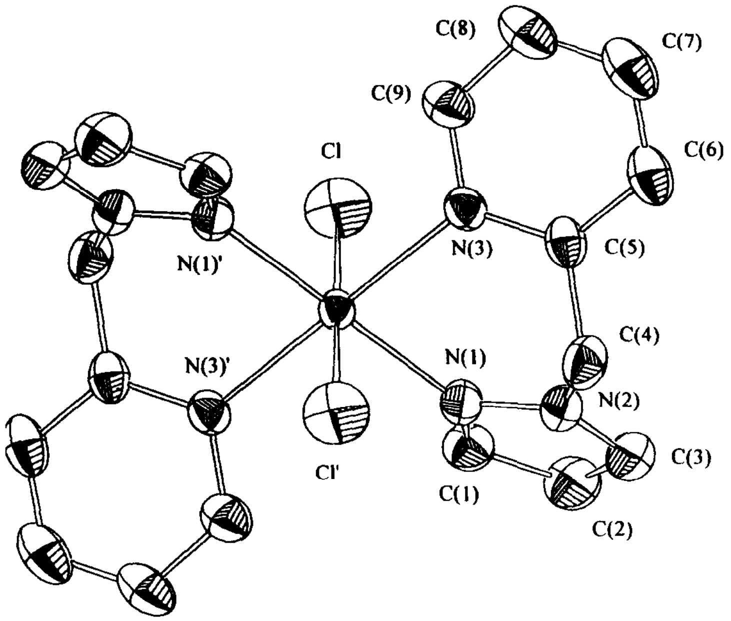


Fig. 1. Structure of [CoL$^4_2$Cl$_2$]·4H$_2$O (water molecules are not shown).

Table 2. Selected bond lengths (Å) and angles (°) for $[CoL^4_2Cl_2]\cdot 4H_2O$ 3

Co—Cl	2.413(4)	Co—N(1)	2.106(7)
Co—N(3)	2.198(6)		
Cl—Co—Cl′	180.00	Cl—Co—N(1)	92.9(2)
Cl—Co—N(3)	89.9(2)	Cl′—Co—N(1)	87.1(2)
Cl′—Co—N(3)	90.1(2)	N(1)—Co—N(3)	94.3(2)
N(1)′—Co—Cl	87.1(2)	N(1)—Co—N(1)′	180.0(3)
N(1)′—Co—N(3)	85.7(2)	N(3)′—Co—Cl	90.1(2)
N(3)′—Co—N(1)	85.7(2)	N(3)—Co—N(3)′	180.0(3)
Cl′—Co—N(1)′	92.9(2)	Cl′—Co—N(3)′	89.9(2)
N(1)′—Co—N(3)′	94.3(2)		

by full-matrix least-squares procedure on F where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$. All non-H atoms were refined anisotropically and H atoms were located from the difference Fourier maps and included in the refinements with fixed isotropic thermal parameters. Two water molecules were located from the difference Fourier maps. However, for one water molecule (O(1w)) hydrogens could not be located. Unit weights were applied and the refinement based on 142 parameters converged with R and R' values of 0.079 and 0.099, respectively. The relatively high R values are most likely caused by the poor crystal quality and the high residual density 1.39 e/Å^3 located near one of the water molecules (O1w). The goodness of fit value $\{[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}\}$ was 1.538. Selected bond lengths and angles for 2 are given in Table 2. Additional material deposited comprises structure factors, atomic co-ordinates, anisotropic thermal parameters, hydrogen atom co-ordinates and a full list of bond lengths and angles.

RESULTS AND DISCUSSION

The cobalt(II) and nickel(II) complexes and their selected properties

The mono-ligand and bis-ligand cobalt(II) and bis-ligand nickel(II) complexes were prepared by the straightforward stoichiometric reactions in ethanol between $MCl_2\cdot 6H_2O$ (M = Co or Ni) and the ligand L^4. The tris-ligand complexes were isolated from stoichiometric reactions between $[M(H_2O)_6]$ $(ClO_4)_2$ (M = Co or Ni) and L^4. The complexes are air-stable solids, except $[CoL^4Cl_2]$ which is moisture sensitive. The four-co-ordinate cobalt(II) complex $[CoL^4Cl_2]$ **1** is blue, the six-co-ordinate dichloro complex $[CoL^4_2Cl_2]\cdot 4H_2O$ **2** is pink and the tris-chelate $[CoL^4_3]$ $(ClO_4)_2\cdot H_2O$ **3** is pink. The dichloro nickel(II) complex $[NiL^4_2Cl_2]\cdot 4H_2O$ **4** is light green in colour and the tris-ligand complex $[NiL^4_3]$ $(ClO_4)_2\cdot H_2O$ **5** is bluish violet. Understandably, the colour of these complexes are signatures of their identity.

Complex **1** is soluble in dichloromethane, MeCN and acetone resulting in dark blue solutions. However, it gives rise to pink solutions in MeOH and EtOH, implying change in stereochemistry. Complex **2** is moderately soluble in MeOH and sparingly soluble in EtOH, giving rise to pink solutions. Interestingly, complex **2** is sparingly soluble in dichloromethane, MeCN and acetone, generating blue solutions, again implying change in geometry. Complex **4** is soluble in MeOH and EtOH generating light green colour. The tris-complexes **3** and **5** are highly soluble in polar organic solvents, giving rise to orange and violet colours respectively.

In the IR spectrum, complexes **2** and **4** exhibit split ν(OH) bands at 3290 and 3150 cm^{-1}, suggesting presence of hydrogen-bonded water of crystallization (*vide* X-ray structure of **2**). Complexes as **3** and **5** display broad ν(OH) absorption at 3400 cm^{-1} and ionic perchlorate bands at 1100 and 620 cm^{-1}. In MeCN solution, complex **1** behaves as a non-electrolyte and complexes **3** and **5** behave as 1 : 2 electrolytes (Table 3) [15]. Complexes **2** and **4** are 1 : 1 electrolytes in methanol solutions, implying partial chloride dissociation. The elemental analyses, IR spectra and solution electrical conductivity data are in good agreement with the proposed formulations. The co-ordination geometry of a representative bis-ligand complex $[CoL^4_2Cl_2]\cdot 4H_2O$ **2** has been confirmed by single-crystal X-ray structural analysis (see below).

Description of the structure of **2**

Figure 2 illustrates the immediate co-ordination environment about cobalt, with atom labelling scheme. The cobalt atom sits on a crystallographically imposed inversion centre and hence the co-ordination polyhedron around cobalt is *trans* octahedral. The four positions are occupied by the nitrogen atoms of the two L^4 ligands and two chloride ions complete the co-ordination sphere around cobalt. From their theoretical value of 90°, the co-ordinating angles are ranging from 85.7(2) to 94.3(3)° (Table 2), implying a distorted structure. An interesting feature to note is that the Co—N(pyridine) and Co—N(pyrazole) bond distances (Table 2) are on the longer end of that reported for similar complexes [5,8–10]. Additionally,

Table 3. Solution electrical conductivity, [a–c] magnetic moment, [a,b,d] and electronic spectral data [a,b,e] of the complexes at 298 K

Complex	Δ_M (Ω^{-1} cm^2 mol^{-1})	μ_{eff}/μ_B	λ (nm) (ε/dm^3 mol^{-1} cm^{-1})
$[CoL^4Cl_2]$[a]	12	4.65 (4.53)	1100 (10), 656 (260), 630 (sh) (190), 590 (170), 575 (sh) (150), 535 (sh) (35), 515 (sh) (15), 268 (sh) (2990), 261 (sh) (4290), 255 (4610) [980 (sh), 550 (sh), 520 (sh), 490, 314 (sh), 266]
$[CoL^4_2Cl_2]\cdot 4H_2O$[b]	140	4.91	> 1100 (broad), 510 (20) and 90 (sh) (18) [980 (sh), 550 (sh), 520 (sh), 490, 314 (sh), 266]
$[CoL^4_3](ClO_4)_2\cdot H_2O$[a]	296	5.25 (5.28)	1038 (6), 530 (sh) (10), 504 (sh) (15), 478 (22), 301 (sh) (840), 260 (6660)
$[NiL^4_2Cl_2]\cdot 4H_2O$[b]	70	2.98 (3.02)	972 (12), 589 (sh) (13), 362 (30)
$[NiL^4_3](ClO_4)_2\cdot H_2O$[b]	290	2.92	974 (12), 591 (9), 366 (16)

[a] In MeCN.

[b] In MeOH.

[c] Expected range for 1:1 and 1:2 electrolytes are: (in MeCN) 120–160 and 220–300 Ω^{-1} cm^2 mol^{-1}, respectively; (in MeOH) 80–115 and 160–220 Ω^{-1} cm^2 mol^{-1}, respectively.

[d] Measured using Evans' method. Solid-state values are in parentheses.

[e] Solid-state values are in square brackets.

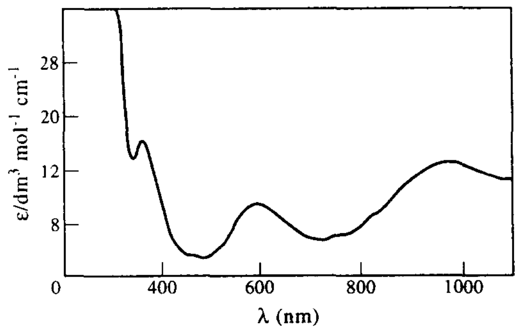


Fig. 2. Absorption spectrum of $[NiL^4_3](ClO_4)_2\cdot H_2O$ in MeOH.

it is worth noting that the Co—N(pyridine) bond is appreciably longer than the Co—N(pyrazole) bond and the difference is ~0.1 Å. To the best of our knowledge, the Co—N(pyridine) bond length could be the longest compared to that reported for complexes with similar ligands [5]. Thus the metric parameters observed for **2** deserve special attention.

The pyridine and pyrazole rings are each planar with the pyrazole mean plane inclined to the pyridine mean plane at an angle of 120.58°. Thus, as is the case for related structures with this class of ligands [2b,3a,4a], the six-membered chelate rings adopted by L^4 exist in boat conformations.

Two water protons are involved in hydrogen bonding interactions: H(21w) is bonded to Cl since their bond distance (2.395 Å) is shorter than 3.00 Å, the sum of their van der Waals radii and the O—H(21w)···Cl angle at H(21w) is 125.31°; similarly H(22w) is bonded to O1w [O(1w)—H(22w) bond distance is 2.155 Å and the sum of their van de Waals radii is 2.60 Å] and the angle at O—H(22w)···Cl is 147.84°. These observations are consistent with similar kinds of hydrogen bonding interactions [6b].

Absorption spectra

The visible and ultraviolet spectra of the cobalt(II) complexes in MeCN (**1** and **3**) and MeOH (**2**) solutions along with solid state values of **1** and **2** and six-co-ordinate nickel(II) complexes **4** and **5** measured in MeOH are reported in Table 3. In addition to their extinction coefficients, the blue colour of **1** and pink/orange colour of **2** and **3** indicate a tetrahedral stereochemistry for the former and octahedral stereochemistry for the latter two, based on the observation that octahedral cobalt(II) complexes are typically pale red to orange, whereas many common tetrahedral cobalt(II) complexes are an intense blue. The electronic spectral feature of two types of cobalt(II) complexes and nickel(II) complexes are characteristic of grossly tetrahedral (**1**) and octahedral (**2**–**5**), respectively [1e,16,17].

The visible spectrum of **3** has been assigned [1c, 16,17] and analysed in order to compare the co-ordinating behaviour of L^1–L^3 and L^4 toward six-co-ordinate cobalt(II). The spectral feature of **3** is closely similar to $[CoL^1_2]^{2+}$ species [1e]. Following the equations of Dou [18], the Dq and B' values for **3** were calculated as 1087 and 835 cm^{-1}, respectively. The spectral parameters obtained here closely match with that observed for $[CoL^3_2]^{2+}$ ($Dq = 1080$ cm^{-1} and $B' = 830$ cm^{-1}) [1e]. Thus the ligand field created around cobalt(II) ion in **3** is very weak and the behaviour of L^4 is closely similar to that of L^3.

The absorption spectral feature of six-co-ordinate nickel(II) complexes **4** and **5** is characteristic of grossly octahedral geometry [1d,16,17]. The observed three bands for the nickel(II) tris-chelate **5** (Fig. 2) have been assigned [1d,16,17] in order of increasing energy (cm^{-1} as follows: ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$), 10,266; ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$ (F)), 16,920; ν_3 ($^3A_{2g} \rightarrow {}^3T_{1g}$ (P)), 27,322. The parameters calculated [18] are worth mentioning. The Dq and B values are 1027 and 896 cm^{-1}, respectively. The corresponding values for $[NiL^3_2]^{2+}$ are 1073 and 853 cm^{-1}, respectively [1d]. As is the case for the cobalt(II) complex once again we observe that the ligand field strength of L^4 is comparable to that of L^3.

Magnetism

Solution state magnetic moment values for the cobalt(II) and nickel(II) complexes (Table 3) reveal that they are paramagnetic with respect to three and two unpaired electrons, respectively [16]. Thus cobalt(II) complexes have high spin d^7 electronic configuration. The temperature-dependence (80–300 K) of the magnetic susceptibility of solid samples of **2** and **3** have been measured by the Faraday method and were found to adhere closely to the Curie–Weiss law [$\chi_M = C/(T+\theta)$]. The room temperature values were found to be ~ 5.2 μ_B, which is within the accepted range of 4.7–5.2 for high-spin octahedral cobalt(II) complexes [17]. The behaviour of **3** is displayed in Fig. 3.

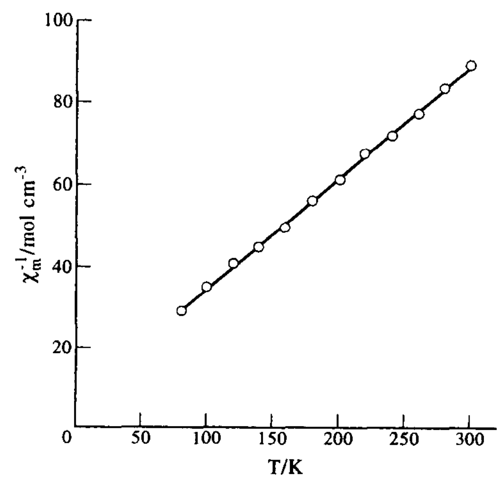


Fig. 3. Reciprocal molar susceptibility versus temperature plot for $[CoL^4_3](ClO_4)_2 \cdot H_2O$.

Stereochemical interconversion studies in cobalt(II) complexes

Experiments were performed to address the question of possible stereochemical interconversions within the cobalt(II) complexes **1**–**3**. In fact, four set of experiments were done. We would like to mention here that the quantitative measurements of the equilibria described below could not be made due to very fast rate of these reactions. In fact, the reactions are instantaneous.

(1) When complex **1** was reacted with 1.25 molar equiv. of L^4 (slightly more than the stoichiometric requirement), in an appreciably polar solvent like ethanol, complex **2** was formed. This was monitored by absorption spectroscopy. This neatly demonstrates stereochemical conversion from tetrahedral to octahedral stereochemistry. (2) In dichloromethane, MeCN and acetone, the complex **2** gave rise to blue solutions, exhibiting electronic spectra characteristic of the tetrahedral co-ordination, as indicated by the strict similarity of the electronic spectrum of **1**. It reflects demonstrated preference of cobalt(II) for tetrahedral geometry [16]. (3) When complex **2** was reacted with 3 equiv. of L^4 in ethanol–water mixture or in methanol in the presence of 2 equiv. of $NaClO_4 \cdot H_2O$, tris-ligand complex **3** was formed. This corroborates the conductivity behaviour of **2** in methanol (*vide supra*). (4) Interestingly, when reacted with 2 equiv. of $Et_4NCl \cdot H_2O$ in EtOH–MeCN mixture, complex **3** transforms to **2**. This could be due to released steric strain in going from a tris-ligand to a bis-ligand complex. These reactions neatly demonstrate the attainment of stereochemical variations within cobalt(II) complexes of L^4.

Conclusions

The present study underscores the co-ordination behaviour of non-planar flexible ligand L^4 toward cobalt(II) and nickel(II). With cobalt(II), L^4 allows formation of three types of products (mono-, bis- and tris-ligand) and their interconversions can be neatly followed using absorption spectroscopy. In the case of nickel(II) only six-co-ordinate complexes have been isolated, as expected. A representative complex **2** has been structurally characterized, revealing trans (octahedral) geometry with appreciably longer Co—N (pyridine) and Co—N(pyrazole) distances. Absorption spectroscopic studies reveal weak field nature of ligand L^4. Variable-temperature magnetic studies on six-co-ordinate cobalt(II) complexes reveal their high spin nature.

Acknowledgements—Financial assistance from the Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), Government of India, New Delhi is gratefully acknowledged. The support of DST for establishing the National X-ray Diffractometer facility at this Department is gratefully acknowledged. We thank Mr A. K. Patra and Mr R. Gupta for their help in magnetic susceptibility measurements.

REFERENCES

1. (a) Mahapatra, S., Gupta, N. and Mukherjee, R. N., *J. Chem. Soc., Dalton Trans.*, 1991, 2911; (b) Mahapatra, S., Bhuniya, D. and Mukherjee, R. N., *Polyhedron*, 1992, **11,** 2045; (c) Mahapatra, S. and Mukherjee, R. N., *J. Chem. Soc., Dalton Trans.*, 1992, 2337; (d) Mahapatra, S. and Mukherjee, R. N., *Ind. J. Chem.*, 1993, **32A,** 64, 428; (e) Mahapatra, S., Lal, T. K. and Mukherjee, R. N., *Polyhedron*, 1993, **12,** 1477.
2. (a) Mahapatra, S. and Mukherjee, R. N., *Polyhedron*, 1993, **12,** 1603; (b) Mahapatra, S., Butcher, R. J. and Mukherjee, R. N., *J. Chem. Soc., Dalton Trans.*, 1993, 3723.
3. (a) Watson, A. A., House, D. A. and Steel, P. J., *Inorg. Chim. Acta*, 1987, **130,** 167; (b) Downard, A. J., Honey, G. E. and Steel, P. J., *Inorg. Chem.*, 1991, **30,** 3733.
4. (a) House, D. A., Steel, P. J. and Watson, A. A., *Aust J. Chem.*, 1986, **39,** 1525; (b) Byers, P. K., Canty, A. J., Honeyman, R. T. and Watson, A. A., *J. Organomet. Chem.*, 1990, **385,** 429.
5. Astley, T., Canty, A. J., Hitchman, M. A., Rowbottom, G. L., Skelton, B. W. and White, A. H., *J. Chem. Soc., Dalton Trans.*, 1991, 1981.
6. (a) Masood, Md. A. and Hodgson, D. J., *Inorg. Chem.*, 1993, **32,** 4839; (b) Masood, Md. A. and Hodgson, D. J., *Inorg. Chem.*, 1994, **33,** 3038.
7. Shirin, Z., Mukherjee, R. N., Richardson, J. F. and Buchanan, R. M., *J. Chem. Soc., Dalton Trans.*, 1994, 465.
8. (a) Driessen, W. L., de Graaff, R. A. G., Parlevliet, F. J., Reedijk, J. and de Vos, R. M., *Inorg. Chim. Acta*, 1994, **216,** 43; (b) van Berkel, P. M., Driessen, W. L., Hämäläinen, R., Reedijk, J. and Turpeinen, U., *Inorg. Chem.*, 1994, **33,** 5920; (c) Dowling, C., Murphy, V. J. and Parkin, G., *Inorg. Chem.*, 1996, **35,** 2415.
9. (a) Chang, W.-K., Lee, G.-H., Wang, Y., Ho, T.-I., Su, Y. O. and Lin, Y.-C., *Inorg. Chim. Acta*, 1994, **223,** 139; (b) Sheu, S.-C., Tien, M.-J., Cheng, M.-C, Ho, T.-I, Peng, S.-M. and Lin, Y.-C., *J. Chem. Soc., Dalton Trans.*, 1995, 3503.
10. Huang, J., Lee, L., Haggerty, B. S., Rheingold, A. L. and Walters, M. A., *Inorg. Chem.*, 1995, **34,** 4268.
11. Evans, D. F., *J. Chem. Soc.*, 1959, 2003.
12. Ray, M., Ghosh, D., Shirin, Z. and Mukherjee, R. N., *Inorg. Chem.*, 1997, **36,** in press.
13. O'Connor, C. J., *Prog. Inorg. Chem.*, 1982, **29,** 203.
14. Hall, S. R., Flack, H. D. and Stewart, J. M., University of Western Australia, Geneva and Maryland, 1992.
15. Geary, W. J., *Coord. Chem. Rev.*, 1971, **7,** 81.
16. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 5th ed., pp. 729–732 and pp. 744–745, John Wiley, New York (1986).
17. Figgis, B. N., *Introduction to Ligand Fields*, Wiley Eastern, New Delhi, 1976.
18. Dou, Y.-S., *J. Chem. Educ.*, 1990, **67,** 134.