Synthesis, crystal structure and properties of trigonal bipyramidal
[M(L\(^5\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O complexes [M = cobalt(ii) (S = 3/2) or
copper(ii) (S = 1/2); HL\(^5\) = N-(2-chloro-6-methylphenyl)pyridine-2-
carboxamide]

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Using a bidentate ligand N-(2-chloro-6-methylphenyl)pyridine-2-carboxamide (HL\(^5\)), in its deprotonated form, two
new five-co-ordinate complexes of composition [M(L\(^5\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O (M = Co\(^{II}\) 1 or Cu\(^{II}\) 2) have been prepared and
characterized including X-ray crystallography. The co-ordination geometry at Co\(^{II}\) and Cu\(^{II}\) is approximately
trigonal bipyramidal (two deprotonated amide nitrogens and a water molecule in the equatorial plane and two
pyridines in the axial positions), being more distorted in the case of Cu\(^{II}\). The observed distortion is caused by (i)
a small bite angle of the chelating ligand and (ii) the presence of two ortho substituents, a chloro and a methyl group,
on the phenyl ring (steric effect). To the best of our knowledge, 1 represents the first structurally characterized
mononuclear high-spin cobalt(ii) complex with a pyridine amide ligand. The magnetic moments of 1 and 2 at 300 K
reveal that the compounds are paramagnetic (1 has S = 3/2 and 2 has S = 1/2), both as solids and in dmf solution.
Temperature dependent magnetic susceptibility measurements confirmed their spin state. The stereochemistry of the
cobalt(ii) centre in 1 does not change to any measureable extent on dissolution in dmf (cf. solid and solution state
absorption spectra). The geometry of the cobalt(ii) centre in 2 observed in the solid state is not retained in dmf
solution (absorption spectra), changing to a tetragonal stereochemistry. Cyclic voltammetric measurements (dmf
solution; glassy carbon electrode) on 1 reveal an oxidative response at 0.48 V vs. saturated calomel electrode (SCE).
and a reductive response at ~1.66 V corresponding to Co\(^{III}\)-Co\(^{II}\) and Co\(^{III}\)-Co\(^{II}\) redox couples, respectively. For 2 the
Cu\(^{III}\)-Cu\(^{II}\) process was observed at ~0.53 V vs. SCE.

Introduction

During the past few years we have been investigating the ability of bi-
and tetra-dentate \(^2\) pyridine-2-carboxamide and triden-
tate \(^3\) pyridine-2,6-dicarboxamide ligands, in their deprotonated
form, to modulate the structural and electronic properties of
first-row transition-metal centres. We\(^{1,2}\) and others\(^{3,4}\) have demonstrated that sterically and/or electronically demanding
pyridine amide ligands can dictate the geometry and co-
ordination number of such complexes. For example, whereas
the tetradeptentate ligand L\(^1\) gives rise to a square-pyramidal
structure with copper(ii) in [Cu(L\(^1\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O it
is interesting that the copper(ii) complexes of L\(^2\) and L\(^4\) behaved similarly,
impling that the presence of only one ortho substituent
on the phenyl ring could not affect the metal stereochemistry, to
any measurable extent. In order to observe a measurable change
in metal geometry, a new picolinamide ligand HL\(^5\) has been
designed with a chloro and a methyl substituent in the 2 and
6 positions of the phenyl ring, hoping to enforce distorted
geometries on the metal centre which in turn would give rise to
novel properties. To test this hypothesis we became interested in
probing the co-ordinative behaviour of the deprotonated form
of HL\(^5\), in its bis-chelate complexes toward cobalt(ii) and
copper(ii). Interestingly, the number and type of co-ordinating
sites in these complexes will be analogous to complexes with
dinagative L\(^1\)/L\(^2\). In essence, by designing this ligand, we have introduced (i) flexibility in the N\(_4\) co-ordination unit and (ii) steric crowding near the amide N donor site.

To reveal stereochemical changes around the metal centre
caued by ligand structure modification upon changing from
L\(^2\)/L\(^4\) to L\(^5\), we have determined the crystal structures of
[M\(^{II}\)(L\(^1\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O (M = Co 1 and Cu 2). To the best of our
knowledge, the structure of [Co\(^{II}\)(L\(^1\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O represents the
first structural proof of a cobalt(ii) complex with a pyridine
amide ligand. The spin state properties of the cobalt(ii) and
copper(ii) centres in 1 and 2 have been determined from
temperature-dependent magnetic susceptibility measurements.
As the synthesis of [Co(L\(^1\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O has been reported\(^{4,6}\) we have
investigated its redox properties and compared them with those
of [Co(L\(^2\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O, to reveal the effect of structure and spin state on redox thermodynamics. As the crystal structures of
[Cu(L\(^1\)]\(2\)(H\(_2\)O)]\(\cdot\)H\(_2\)O and [Cu(L\(^2\)]\(2\) are already known, the
present investigation gives us an opportunity to pinpoint the
structural effect on the electronic properties (absorption
spectroscopic, EPR and redox) of the copper(ii) centres in these
complexes.
Experimental

Reagents and materials
All chemicals were obtained from commercial sources and used as received. Solvents were purified/dried following standard procedures.1, 3, 12 Tetra-n-butylammonium perchlorate, was prepared/purified as before.26 The complex [Co(L^3)]H_2O was synthesized following a reported procedure.26

Syntheses
N-(2-Chloro-6-methylphenyl)pyridine-2-carboxamide, HL^3.
The ligand was prepared by adding a solution of 2-chloro-6-
methylaniline (5 g, 0.035 mol) in pyridine (5 cm^3) dropwise to a
stirred solution of pyridine-2-carboxylic acid (4.34 g, 0.035 mol) in pyridine (10 cm^3) at room temperature. The resulting
solution was stirred for 20 min and afterwards the temperature
was gradually increased to ≈100 °C using a water-bath. To this
solution, triphenylphosphine (10.9 g, 0.035 mol) was added
dropwise with stirring. Heating and stirring were continued for
10 h. The pyridine was then distilled off under reduced pressure
at ≈100 °C to obtain an oil. It was then dissolved in CHCl_3 (20
cm^3), washed three times with water, four times with saturated sodium hydrogencarbonate solution and again three times with
water. The resulting CHCl_3 solution was evaporated in vacuo to
obtain an oil. It was again washed four times with cold Et_2O (15
cm^3 in each batch) and kept in air. After ≈10 d, a white lump of
the desired ligand which formed, was collected by filtration and
washed three times with cold C_2H_5OH. The solid thus obtained
was recrystallized from CHCl_3–i-hexane to afford a white
crystalline lump of the ligand (3.5 g, 40%), mp 73 °C (IR, KBr,
cm^-1, selected peaks): ν(N–H) 3340 (s), ν(v) 1680. HI NMR
(CDC_13): δ 2.35 (3 H, s, CH_3), 7.0–8.5 (6 H, m, aromatic
protons), 8.71 (1 H, d, pyridine proton adjacent to N atom) and
9.68 (1 H, br, NH).

[Co(L^3)(H_2O)]H_2O 1. To a vigorously stirred solution of Co(MeCO_2)_2·H_2O (0.025 g, 0.100 mmol) in 1:1 (v/v) C_2H_5OH–water (5 cm^3) a solution of the ligand (0.05 g, 0.202 mmol) in C_2H_5OH (5 cm^3) was added dropwise. The resulting light brown solution was then stirred for 1 h and the clear
solution thus obtained was kept in air for 3 d. The yellow crystalline precipitate thus formed was filtered off, washed with C_2H_5OH and dried in vacuo. Recrystallization from 1:1 (v/v) MeOH–
water (10 cm^3) afforded golden yellow crystals of 1 (yield 0.04 g,
cas. 68%). Found: C, 56.62; H, 4.68; N, 10.16. Calc. for
C_2H_5Cl_2CoNO_2C_7H_9O_2: C, 56.43; H, 4.43; N, 9.56%. IR (KBr, cm^-1, selected peaks): 3640 (ν(OH) of co-ordinated water molecule); 3300, 3200 and 1620 (ν(OH) of water of crystallization) and 1600 (ν(amide I)). Molar conductance, λ_m (dmf, 298 K) = 10 Ω^-1 cm^2 mol^-1, ρ_ε (in dmf, 298 K) 4.04 μεF/cm. Variable-temperature magnetic susceptibility data (T/K, μ_ε/μ_B): 300, 4.22; 280, 4.16; 260, 4.18; 240, 4.15; 220, 4.12; 200, 4.10; 180, 4.07; 160, 4.02; 140, 3.93; 120, 3.87; 100, 3.82; 81, 3.79.

[Co(L^3)(H_2O)]·H_2O 2. A solution of the ligand HL^3 (0.134 g, 0.543 mmol) in MeOH (5 cm^3) was slowly added to a stirred
light blue solution of Cu(MeCO_2)_2·H_2O (0.054 g, 0.027 mmol)
in MeOH (5 cm^3). The resulting deep green solution was stirred for 8 h. To this reaction mixture, water (20 cm^3) was added and kept for two days in air. The deep green crystals thus formed were washed with 1:1 (v/v) MeOH–water and dried in vacuo (yield, 0.12 g, cas. 75%). Found: C, 53.24; H, 4.15; N, 9.63. Calc. for
C_2H_5Cl_2CuNO_2C_7H_9O_2: C, 52.83; H, 4.06; N, 9.48%. IR (KBr, cm^-1, selected peaks): 3640 (ν(OH) of co-ordinated water molecule); 3400 (br) and 1630 (ν(OH) of water of crystallization) and 1600 (ν(amide I)). Molar conductance, λ_m (dmf, 298 K) = 8 Ω^-1 cm^2 mol^-1, ρ_ε (in dmf, 298 K) 1.89 μεF/cm. Variable-temperature magnetic susceptibility data (T/K, μ_ε/μ_B): 300, 2.01; 280, 2.01; 260, 2.00; 240, 2.00; 220, 1.99; 200, 1.99; 180, 1.98; 160, 1.95; 140, 1.93; 120, 1.91; 100, 1.87; 81, 1.82.

Physical measurements
Elemental analyses (C, H, N) were obtained at the Micro-
analysis Service Centre of the Department of Inorganic
Chemistry, Indian Association for the Cultivation of Science,
Calcutta. Infrared spectra were recorded on a Perkin-Elmer
M-1320 spectrophotometer using KBr discs or Nujol mulls,
electronic spectra using a Perkin-Elmer Lambda 2 spectrophotometer. Solution electrical conductivity measurements (25 °C) were carried out at a concentration of ≈1 × 10^{-3} mol dm^-3 with an Elico (Hyderabad, India) Type CM-82 T conductivity bridge. X-Band EPR spectra were recorded with a Varian E-109 C spectrometer.

Magnetism
Variable temperature (81–300 K) magnetic susceptibility
measurements in the solid state were performed using a locally
built Faraday balance comprising an electromagnet with constant gradient pole caps (Polytron Corporation, Mumbai,
India), an ultracavum Sartorius M25-D/S Balance (Germany), a closed-cycle refrigerator and a Lake Shore
temperature controller (Cryo Industries, USA). All measure-
ments were made at a fixed main field strength of ±10 kG. Solution state magnetic susceptibility was obtained by the
NMR technique of Evans and Haneef.10 1610 (ν(OH) of water of crystallization) and 1554 (ν(C=O)) dropwise to a
stirred solution of the ligand (0.05 g, 0.202 mmol) in C_2H_5OH (10 cm^3) and 4H NMR spectrum. Susceptibilities were corrected
for the diamagnetic contribution, which was calculated to be
–231.34 × 10^{-6} cm^3 mol^{-1} for both the complexes, by using
literature values.12 Effective magnetic moments were calculated
from μ_eff = 2.828ζ_m T^1/2, where ζ_m is the corrected molar
susceptibility.

Cyclic voltammetry
Cyclic voltammograms were recorded at 298 K on PAR model
370 electrochemistry system consisting of a model 174A
polarographic analyzer and a model 175 universal programmer. A standard three-electrode cell was employed with a PAR
model G0021 glassy carbon working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode (SCE) as
reference; no corrections were made for junction potentials.
Details of cell configuration and criterion for reversibility are as
reported previously.26,13

Crystallography
A yellow crystal of complex 1 and a green crystal of 2 were
used for data collection (θ/2θ scan technique) on an Elnar
Nonius CAD-4 Mach four-circle diffractometer using graphite-
monochromated Mo-Kα radiation. Data were corrected for Lorentz-polarization effects; analytical absorption corrections
were also applied. Anomalous dispersion was applied for all non-hydrogen atoms. All calculations were performed using
the X-TAL 3.2 crystallographic software package.24 The structures were solved by direct methods and successive Fourier-difference
syntheses. All refinements were performed by full-matrix least-
squares procedure on F, with anisotropic thermal parameters
for all non-hydrogen atoms except C. The positions of the
hydrogen atoms were calculated assuming ideal geometries, and
their positions and thermal parameters not refined. We could
determine the hydrogen atoms of the water molecules.

For [Co(L^3)(H_2O)]·H_2O the Cl atom and the methyl group
C atom of the phenyl ring were found to be statistically
disordered. This disorder was such that C1(C1) and C131 are
bonded to C8 with site occupancy factors of 0.7 and 0.3,
respectively; Cl(C1) and C132 are bonded to C12 with site
occupancy factors of 0.3 and 0.7, respectively. The positions of
the ligands. The multiplicity factors for each set of Cl atoms [Cl(C1)
and Cl(11)] and C atoms [C131 and C132] were chosen such
that the total multiplicity for each site was unity. In the case of the
other ligand Cl(2) and C(261) are bonded to C25 with site

occupancy factors of 0.5 each and Cl(21) and Cl(262) are bonded to C(21) with site occupancy factors of 0.5 each. A similar disorder situation was encountered for [Cu(L\(^5\)](H\(_2\)O))\(\cdot\)H\(_2\)O. For atom sites Cl(1), Cl(11), Cl(2), Cl(21), C(131), C(132), C(261) and C(262) the occupancy factors are 0.55, 0.45, 0.65, 0.35, 0.45, 0.55, 0.35 and 0.65, respectively and the sets of atoms Cl(1) and C(131), Cl(11) and C(132), Cl(2) and C(261), Cl(21) and C(262) are bonded to C(8), C(12), C(25) and C(21), respectively. Pertinent crystallographic parameters are summarized in Table 1.

CCDC reference number 186/1501.

See http://www.rsc.org/suppdata/dt/1999/2461/ for crystallographic files in.cif format.

**Results and discussion**

**Syntheses**

The ligand HL\(^5\) was synthesized in high yield by condensation of pyridine-2-carboxylic acid and 2-chloro-6-methylaniline in pyridine using triphenyl phosphite as water scavenger. The ligand was characterized by \(^1\)H NMR and IR spectra. The cobalt(ii) and copper(ii) complexes were synthesized from the reaction between metal acetate and ligand in 1:2 mole ratio, in an aqueous alcoholic medium. The acetate ion of the metal salt acts as a base to deprotonate the NH group of the ligand.

Compared to the “free” ligand a low-energy shift in the ν(amide I) vibration\(^14\) and absence of the N–H vibration in the IR spectra of these complexes indicate co-ordination by the deprotonated ligand. Identical IR spectra of cobalt(ii) and copper(ii) complexes reveal that they are isostructural. For both complexes a sharp band at 3640 cm\(^{-1}\), due to ν(OH) of the co-ordinated water, is observed. Furthermore, an additional broad band in the range 3200–3400 cm\(^{-1}\) is observed which is due to the presence of a water molecule, as solvent of crystallization.\(^15\) The molar conductivities of both complexes in dmf are well below that expected for a 1:1 electrolyte,\(^16\) consistent with their formulation as neutral species. Based on the above facts and microanalytical data, we propose the composition of these two new complexes as [M\(^{2+}\)(L\(^5\)](H\(_2\)O))\(\cdot\)H\(_2\)O (M = Co or Cu 2), which were finally confirmed by their crystal structure determination.

**Crystal structures**

Complexes 1 and 2 were found to be isostructural (cf. IR spectra). A perspective view of the metal co-ordination environment of [Co(L\(^5\)](H\(_2\)O))\(\cdot\)H\(_2\)O 1 with the atomic numbering scheme is shown in Fig. 1. The complex is a monomer and from each L\(^5\) ligand the pyridine and the amide nitrogen provide an axial and an equatorial co-ordination, respectively. The fifth co-ordination site in the equatorial position is occupied by a water molecule [Co–O distance, 2.039(6) Å], which is hydrogen bonded to the water molecule present as solvent of crystallization [O(1w)···O(2w) 2.723(9) Å]. The structure therefore contains a CoN\(_5\)O co-ordination unit in an approximate trigonal bipyramidal geometry (Table 2). The axial Co–N distances are longer than the equatorial distances by ∼0.1 Å. The ligand bite angles of N (pyridyl)-Co–N (amide) are ∼80°. The Co atom is only 0.015 Å out of trigonal plane, containing two amide nitrogen atoms and the co-ordinated water molecule, towards the axially co-ordinated pyridine nitrogen atom N(3). The angle between the planes defined by the two CoN\(_2\) units Co, N(1), C(5), C(6), N(2) and Co, N(3), C(18), C(19), N(4) is 114.79°. To our knowledge, compound 1 represents the first structurally characterized cobalt(ii) complex with a pyridine amide ligand.

A perspective drawing of the co-ordination sphere of the complex [Cu(L\(^5\)](H\(_2\)O)] in 2 is also shown in Fig. 1. Compared to 1, the metal co-ordination sphere in 2 is more distorted (Table 2). The co-ordination environment around the Cu atom is best described as distorted trigonal bipyramidal with a square pyramidal component of structural index τ = 0.69 [ = (β − α) / 60, where β = N(1)–Cu–N(3) 177.8° and α = N(2)–Cu–N(4) 136.5°]; for perfect square pyramidal and trigonal bipyramidal geometries the value of τ is zero and unity, respectively.\(^17\) The Cu–O(1w) distance of 2.266(4) Å is 0.23 Å longer than that of Co–O(1w) in 1. As in 1, the co-ordinated water molecule is hydrogen bonded to the water molecule present as solvent of crystallization [O(1w)···O(2w) 2.838(7) Å]. The ligand bite angles are similar to those observed in 1. The Cu atom is 0.018 Å out of the trigonal plane, towards the pyridine nitrogen atom N(3). The angle between the planes defined by the two CuN\(_2\) units Cu, N(1), C(5), C(6), N(2) and Cu, N(3), C(18), C(19), N(4) is 130.88°. The distorted trigonal bipyramidal geometry observed in [Cu(L\(^5\)](H\(_2\)O)]\(\cdot\)H\(_2\)O is in sharp contrast to that in [Cu(L\(^5\)])\(_2\)\]. It is to be noted that for one ligand the axial and equatorial Cu–N distances are comparable, however, for the other ligand the axial Cu–N distance is shorter than the equatorial distance by ∼0.03 Å. We strongly believe that the presence of a chloro and a methyl substituent near the donor site (amide nitrogen) has caused reduced overlap between the metal and the amide nitrogen (at least for one ligand) and to

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**Fig. 1** Molecular structures of (a) [Co(L\(^5\)](H\(_2\)O)] in complex 1 and (b) [Cu(L\(^5\)](H\(_2\)O)] in complex 2. The thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted.
from that in dmf solution. It is well documented is to be noted that the spectrum in the solid is not at all di

nm. The spectrum of

in the solid state the main absorption band is blue shifted by 85

distortion. As the absorption spectral behaviour of high-spin cobalt(ii) complexes (see above) with amide ligands has not

been reported, we are not in a position to compare the feature of 1 with related systems.

Table 1 Data collection and structure refinement parameters for [Co(L)\(_2\)](H\(_2\)O)\(_3\)H\(_2\)O 1 and [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O 2

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<td>C(<em>{26})H(</em>{36})Cl(_2)CoN(_6)O(_4)</td>
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<td>(M)</td>
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<td>(c) Å</td>
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Table 2 Selected bond lengths (Å) and angles (°) for [Co(L)\(_2\)](H\(_2\)O)\(_3\)H\(_2\)O 1 and [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O 2

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<tr>
<td>N(4)–Co–O(1w)</td>
<td>124.9(3)</td>
<td>113.2(2)</td>
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Absorption spectra

The electronic spectra of complexes 1 and 2, measured (280–1100 nm) both in the solid state (dispersed in mineral oil) and in dmf solution, are reported in Table 3. It is to be noted that the diffuse reflectance spectrum of dark brown [Co(L)\(_2\)](H\(_2\)O) displays\(^4\) a band at 735 nm with a shoulder at 505 nm. The stereochemistry of [Co(L)\(_2\)](H\(_2\)O) is expected to be square pyramidal. It is worth noting here that for [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O in the solid state the main absorption band is blue shifted by 85 nm. The spectrum of 1 in dmf solution is displayed in Fig. 2. It is to be noted that the spectrum in the solid is not at all different from that in dmf solution. It is well documented\(^20\) that five-co-ordinate high-spin cobalt(ii) complexes exhibit a wide variety of spectral features depending on the nature of the distortion. As the absorption spectral behaviour of high-spin cobalt(ii) complexes (see above) with amide ligands has not been reported, we are not in a position to compare the feature of 1 with related systems.

Table 3 Electronic spectroscopic data for the complexes\(^*\)

<table>
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<tr>
<th>Complex</th>
<th>(\lambda_{\text{max}}) (nm) ((\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="H(_2)O">Co(L)(_2)</a>(_2)H(_2)O 1</td>
<td>656 (15), 520 (sh) (50), 470 (sh) (85), 305 (sh) (5500) reflectance 650, 520, 470 (sh)</td>
</tr>
<tr>
<td><a href="H(_2)O">Co(L)(_2)</a>(_2)H(_2)O 2</td>
<td>800 (sh) (75), 595 (170), 407 (1550), 310 (sh) (5950) reflectance 793 and 600 (sh)</td>
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*In dmf solutions (or solid reflectance, where stated).

Fig. 2 Electronic absorption spectra of (a) [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O 1 (3.6 × 10\(^{-3}\) mol dm\(^{-3}\) in dmf) and (b) [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O 2 (1 × 10\(^{-3}\) mol dm\(^{-3}\) in dmf). The solid reflectance spectrum of 2 is shown as an inset.

The solid state reflectance spectrum of [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O displays (Fig. 2) a broad band at 793 nm with a shoulder at relatively higher energy (600 nm). This feature is characteristic of a trigonal bipyramidal geometry around copper(ii).\(^21\) However, in dmf solution it displays a shoulder at 800 nm followed by a band due to a d–d transition at 595 nm (Fig. 2), indicating square pyramidal geometry\(^22\) around Cu\(^{II}\). Therefore, it is interesting that for [Co(L)\(_2\)](H\(_2\)O)\(_2\)H\(_2\)O in going from the solid to the solution phase a stereochemical change around Cu\(^{II}\) from trigonal bipyramidal to square pyramidal has occurred.

Magnetism

In order to determine the spin-state properties of the metal ions we performed temperature-dependent magnetic susceptibility
measurements on the powdered samples of complexes 1 and 2 using the Faraday method. At 300 K the \( \mu_{\text{eff}} \) values are 4.22 \( \mu_B \) \((S = 3/2)\) for 1 and 2.01 \( \mu_B \) \((S = 1/2)\) for 2. The complexes follow the Curie-\( \text{Weiss} \) law \((C = (T - 0))\) in the temperature range 81–300 K.

In fact, for trigonal bipyramidal cobalt(II) complexes the \( \mu_{\text{eff}} \) values lie in the range 4.26–5.03 \( \mu_B \), owing to the orbital contribution of the excited \( \epsilon \) levels. The large spread of \( \mu_{\text{eff}} \) values is attributed to distortion that influences the magnitude of the ligand field splitting. The effective magnetic moment of 1 is low as in some of the reported high-spin cobalt(II) complexes with tetradeptally distorted trigonal bipyramidal geometry. The observed behaviour of 1 implies that the orbital contribution to the spin-only value (3.87 \( \mu_B \)) is fairly small. This can be rationalized if we invoke that the excited levels are less populated even at 300 K, possibly due to the presence of a low symmetry ligand field component, as revealed in the crystal structure of 1 (Table 2).

At 300 K the solution-state (Evans’ method) \( \mu_{\text{eff}} \) value of complex 1 (4.04 \( \mu_B \)) is reduced compared to that obtained in the solid state. Given the results at hand we are not in a position to provide any explanation for this behaviour and also why the magnetic moment decreases with temperature (cf. solid state behaviour). However, based on the redox stability of the cobalt(II) state (see below) we rule out the possibility of any cobalt(II) impurity. The \( \mu_{\text{eff}} \) value of 2 in dmf solution is in agreement with the solid state value.

It is to be noted here that the room temperature effective magnetic moment of \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) is 2.26 \( \mu_B \), implying its low-spin character. The reason behind the presence of a decreased ligand field of \( \ell \) in 1 (high-spin compound) must be associated with the ortho substituent-induced steric effect.

EPR Spectra

To extract complementary information about the stereochemistry at the copper(II) centre in complex 2, EPR spectral studies in the solid state as well as in the solution phase were carried out. The complex displays an isotropic signal at \( g = 2.11 \) in the solid state at 300 K as well as at 77 K. However, in dmf solution at 300 K as well as at 77 K, it shows a well resolved four-line tetragonal spectrum (\( g_{bb} = 2.24, g_{aa} = 2.02, A_1 = 175 \text{ G} \)) characteristic of a d\( 4\) - \( \gamma \) ground state. In fact, the spectrum is closely similar to that of \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\). We can therefore infer that the copper(II) centre in \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) assumes a tetragonal geometry in dmf solution (cf. absorption spectral result), implying a structural change in going from solid to solution.

Redox properties

The redox behaviour of \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) and \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) was examined by cyclic voltammetry in dmf solutions at a glassy carbon working electrode. In order to identify the effect of geometry on the \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) and \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) redox potentials, the results were compared to those of the reported complexes \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\), \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\), and \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\). It is to be noted that the redox behaviour of \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) has not been reported; however, it has for the last two complexes.

Under identical experimental conditions, \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) and \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) exhibit an oxidative redox process due to the \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) couple (Fig. 3). In these two closely related complexes the type and number of donor atoms provided by the chelating ligands and also the charge of the complexes are invariant. Therefore, the present investigation gave us a unique opportunity to pinpoint the structural and spin state effect on the redox chemistry. Fig. 3 reveals a substantial shift of 420 mV (1, 0.48 V; \( \Delta E_p = 200 \text{ mV} \); [Co(III)]H₂O, 0.06 V; \( \Delta E_p = 80 \text{ mV} \)) in the Co⁷⁺–Co⁷⁺ potential between the two cobalt(II) complexes, caused by differing stereochemistry and spin state. The stereochemical flexibility provided by two bidentate \( \ell \) ligands in 1 is expected to stabilize the cobalt(II) state more than in \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\), where the cobalt(II) centre is co-ordinated by a rigid tetradenate ligand \( \ell \). However, it should be noted here that while the cobalt(II) centre in 1 is high spin, it is low spin for \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\). The low-spin state of the resulting cobalt(II) species, generated at the electrode surface, is expected to be attained more easily in the case of low-spin \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) than in the case of high-spin 1. It is understandable that for 1 additional energy is necessary to bring about spin reorganization. To extract information about the nature of the oxidative redox process of 1 we examined its scan rate dependence (20–200 mV s⁻¹). The anodic peak current and peak-to-peak separation (\( \Delta E_p \)) increase as a function of scan rate, as expected for a quasireversible system. The shape of the cyclic response, however, remains unaffected. Thus while the redox process is quasireversible for 1, it is reversible for \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) (cf. \( \Delta E_p \) values).

Both the complexes display an additional reduction process (Fig. 3): 1, \(-1.66 \text{ V}, \Delta E_p = 80 \text{ mV} \); [Co(III)]H₂O, \(-1.26 \text{ V}, \Delta E_p = 120 \text{ mV} \). We assign this as due to the Co⁷⁺–Co⁷⁺ couple, based on our previous experience in the redox behaviour of \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) systems (X = Cl⁻, Br⁻ or MeCO₂⁻). Here the redox potential values clearly indicate that the cobalt(II) state is better stabilized in the complex \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) than in 1. This is understandable given the \( \delta \) configuration of Co¹, which would prefer a planar co-ordination. It should be mentioned here that the generation of cobalt(II) species from \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) and \([\text{Co}^{111}\text{L}]\text{H}_2\text{O}\) by sodium tetrahydroborate has been reported.

Complex 2 displays a quasireversible reductive response due to the Cu⁷⁺–Cu⁷⁺ couple. In going from \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) to \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) the redox potential shifts anodically by 570 mV (2, \(-0.53 \text{ V}, \Delta E_p = 100 \text{ mV} \); [Cu(II)]H₂O, \(-1.10 \text{ V}, \Delta E_p = 80 \text{ mV} \)). This can be rationalized given the differing copper(II) geometry in these two complexes (the Cu⁷⁺ in \([\text{Cu}^{111}\text{L}]\text{H}_2\text{O}\) is square pyramidal and in dmf solution that in 2 is tetragonal). Interestingly, the Cu⁷⁺–Cu⁷⁺ redox potential values for 2 and \([\text{Cu}^{111}\text{L}]\) \( E_{\text{Cu}^{111}\text{L}} = -0.47 \text{ V} \), \( \Delta E_p = 90 \text{ mV} \) are closely similar, implying similar stereochemistry.
Conclusion

Although many trigonal bipyramidal complexes of cobalt(II) are known, neutral tridentate/tetradentate ligands appear to be more common in providing five-co-ordinate geometry of this type. In this investigation we provide examples of distorted trigonal bipyramidal geometry of cobalt(II) ($S = 3/2$) and copper(II) ($S = 1/2$) complexes using a bidentate monoanionic amide ligand. The compound $[\text{CoL}_2(H_2O)]_2H_2O$ represents the first structurally characterized cobalt(II) complex with a pyridine amide ligand. The properties in the solid state have been systematically compared with those in dmf solution. The effects of stereochemistry and spin state have been neatly demonstrated in the redox chemistry of cobalt(II) complexes of $L^1$ and $L^6$. It has been shown that for the Cu$^{II/III}$ redox process $L^2$, $L^3$ and $L^6$ behave similarly; however, compared to $L^1$ these ligands considerably stabilize the copper(I) state over Cu$^{II}$, due to geometrical flexibility.

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References