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# Synthesis, crystal structure and properties of trigonal bipyramidal $[M(L^5)_2(H_2O)]\cdot H_2O$ 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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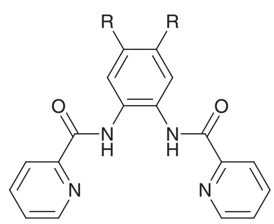
Using a bidentate ligand N-(2-chloro-6-methylphenyl)pyridine-2-carboxamide ($HL^5$), in its deprotonated form, two new five-co-ordinate complexes of composition $[M(L^5)_2(H_2O)]\cdot H_2O$ (M = $Co^{II}$ **1** or $Cu^{II}$ **2**) have been prepared and characterized including X-ray crystallography. 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 copper(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 $Co^{II}$–$Co^{I}$ redox couples, respectively. For **2** the $Cu^{II}$–$Cu^{I}$ process was observed at −0.53 V *vs.* SCE.

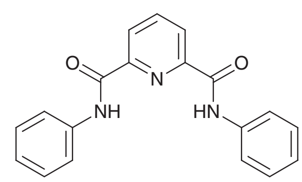
## Introduction

During the past few years we have been investigating the ability of bi-[1] and tetra-dentate[2] pyridine-2-carboxamide and tridentate[3] pyridine-2,6-dicarboxamide ligands, in their deprotonated form, to modulate the structural and electronic properties of first-row transition-metal centres.[1–3] We[1–3] and others[4–10] 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 tetradentate ligand $L^1$ gives rise to a square-pyramidal structure with copper(II) in $[Cu(L^1)(H_2O)]$,[4b] the bidentate ligand $L^4$ exerts a tetrahedral twist (≈40°) between the two co-ordinating planes of four-co-ordinate $[Cu(L^4)_2]$.[1] It is interesting that the copper(II) complexes of $L^4$ and $L^6$ behaved similarly,[1] implying 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 dinegative $L^1/L^2$. 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.

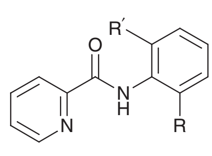
To reveal stereochemical changes around the metal centre caused by ligand structure modification upon changing from $L^4/L^6$ to $L^5$, we have determined the crystal structures of $[M^{II}(L^5)_2(H_2O)]\cdot H_2O$ (M = Co **1** and Cu **2**). To the best of our knowledge, the structure of $[Co^{II}(L^5)_2(H_2O)]\cdot H_2O$ 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 $[Co(L^1)]\cdot H_2O$ has been reported[4a,6c] we have investigated its redox properties and compared them with those of $[Co(L^5)_2(H_2O)]\cdot H_2O$, to reveal the effect of structure and spin state on redox thermodynamics. As the crystal structures of $[Cu(L^1)(H_2O)]$[4b] and $[Cu(L^4)_2]$[1] 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.



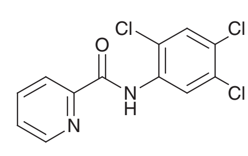

R = H ($H_2L^1$)
R = Cl ($H_2L^2$)




($H_2L^3$)




R = R′ = H ($HL^4$)
R = Me, R′ = Cl ($HL^5$)




($HL^6$)

## Experimental

### Reagents and materials

All chemicals were obtained from commercial sources and used as received. Solvents were purified/dried following standard procedures.[1–3] Tetra-*n*-butylammonium perchlorate, was prepared/purified as before.[2a] The complex $[Co(L^1)]\cdot H_2O$ was synthesized following a reported procedure.[6c]

### Syntheses

***N*-(2-Chloro-6-methylphenyl)pyridine-2-carboxamide, HL$^5$.** 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, triphenyl phosphite (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 two times with cold $C_2H_5OH$. The solid thus obtained was recrystallized from $CHCl_3$–*n*-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, ν(amide I) 1680. $^1$H NMR ($CDCl_3$): 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).

**$[Co(L^5)_2(H_2O)]\cdot H_2O$ 1.** To a vigorously stirred solution of $Co(MeCO_2)_2\cdot 4H_2O$ (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, *ca*. 68%). Found: C, 56.62; H, 4.68; N, 10.16. Calc. for $C_{26}H_{24}Cl_2CoN_4O_4$: 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, $\Lambda_M$ (dmf, 298 K) = 10 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. $\mu_{eff}$ (in dmf, 298 K) 4.04 $\mu_B$. Variable-temperature magnetic susceptibility data ($T$/K, $\mu_{eff}/\mu_B$): 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.

**$[Cu(L^5)_2(H_2O)]\cdot H_2O$ 2.** A solution of the ligand HL$^5$ (0.134 g, 0.543 mmol) in MeOH (5 cm$^3$) was slowly added to a stirred light blue solution of $Cu(MeCO_2)_2\cdot H_2O$ (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, *ca*. 75%). Found: C, 53.24; H, 4.15; N, 9.63. Calc. for $C_{26}H_{24}Cl_2CuN_4O_4$: 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 1610 (ν(amide I)). Molar conductance, $\Lambda_M$ (dmf, 298 K) = 8 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. $\mu_{eff}$ (in dmf, 298 K) 1.89 $\mu_B$. Variable-temperature magnetic susceptibility data ($T$/K, $\mu_{eff}/\mu_B$): 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 Microanalysis 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[2d,3a] comprising an electromagnet with constant gradient pole caps (Polytronic Corporation, Mumbai, India), an ultravacuum Sartorius M25-D/S Balance (Germany), a closed-cycle refrigerator and a Lake Shore temperature controller (Cryo Industries, USA). All measurements were made at a fixed main field strength of ≈10 kG. Solution state magnetic susceptibility was obtained by the NMR technique of Evans[11] in dmf with a PMX-60 JEOL (60 MHz) NMR spectrometer. 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 $\mu_{eff} = 2.828[\chi_m T]^{1/2}$, where $\chi_m$ 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.[2a,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 Enraf 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 XTAL 3.2 crystallographic software package.[14] 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 not locate the hydrogen atoms of the water molecules.

For $[Co(L^5)_2(H_2O)]\cdot H_2O$ the Cl atom and the methyl group C atom of the phenyl ring were found to be statistically disordered. This disorder was such that Cl(1) and C(131) are bonded to C(8) with site occupancy factors of 0.7 and 0.3, respectively; Cl(11) and C(132) are bonded to C(12) with site occupancy factors of 0.3 and 0.7, respectively in one of the ligands. The multiplicity factors for each set of Cl atoms [Cl(1) and Cl(11)] and C atoms [C(131) and C(132)] 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 C(25) with site occupancy factors of 0.5 each and Cl(21) and C(262) are bonded to C(21) with site occupancy factors of 0.5 each. A similar disorder situation was encountered for $[Cu(L^5)_2(H_2O)]\cdot H_2O$. 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 $^1H$ 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 $\nu$(amide I) vibration[4a] 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 $\nu$(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 $[M^{II}(L^5)_2(H_2O)]\cdot H_2O$ (M = Co **1** 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 $[Co(L^5)_2(H_2O)]\cdot H_2O$ **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 $CoN_4O$ 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 $[Cu(L^5)_2(H_2O)]$ 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

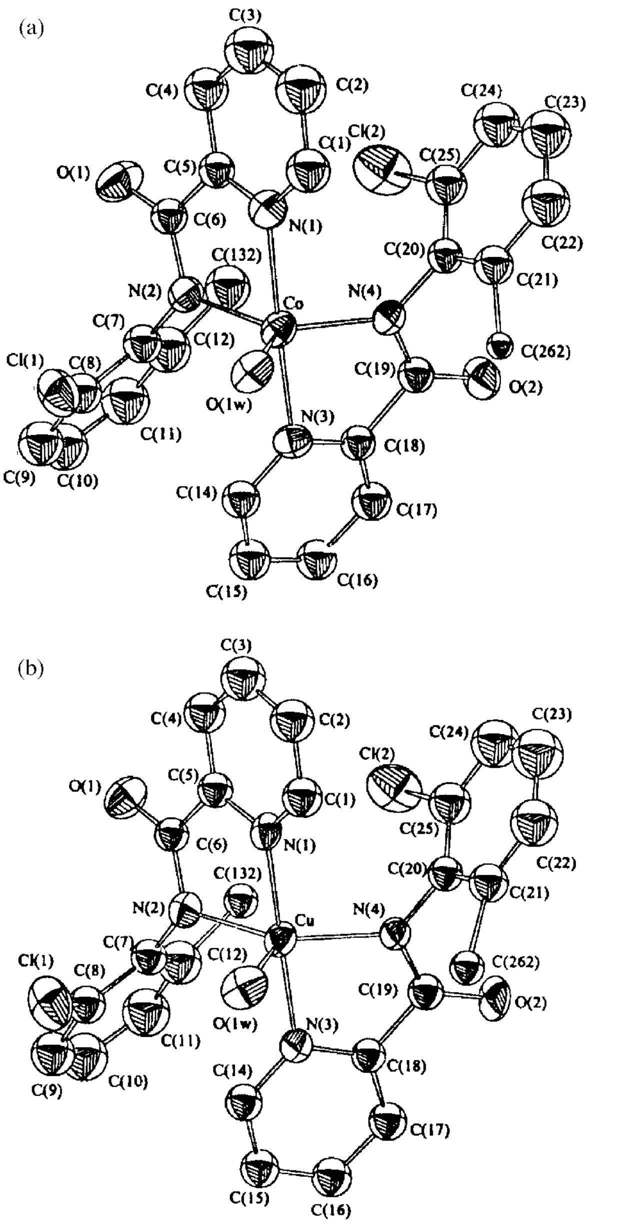



**Fig. 1** Molecular structures of (*a*) $[Co(L^5)_2(H_2O)]$ in complex **1** and (*b*) $[Cu(L^5)_2(H_2O)]$ in complex **2**. The thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted.

is best described as distorted trigonal bipyramidal with a square pyramidal component of structural index $\tau = 0.69$ [$= (\beta - \alpha)/60$, where $\beta$ = N(1)–Cu–N(3) 177.8° and $\alpha$ = N(2)–Cu–N(4) 136.5°]; for perfect square pyramidal and trigonal bipyramidal geometries the value of $\tau$ 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 $[Cu(L^5)_2(H_2O)]\cdot H_2O$ is in sharp contrast to that in $[Cu(L^4)_2]$. 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 equatotrial 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

**Table 1** Data collection and structure refinement parameters for $[Co(L^5)_2(H_2O)]\cdot H_2O$ **1** and $[Co(L^5)_2(H_2O)]\cdot H_2O$ **2**

| | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{26}H_{24}Cl_2CoN_4O_4$ | $C_{26}H_{24}Cl_2CuN_4O_4$ |
| *M* | 585.93 | 590.5 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Pbca* (no. 61) | *Pcba* (no. 61) |
| *a*/Å | 21.039(9) | 21.139(7) |
| *b*/Å | 15.841(3) | 15.858(6) |
| *c*/Å | 15.678(5) | 15.665(6) |
| $U$/Å$^3$ | 5225.15(3) | 5251.26(3) |
| *T*/K | 293 | 293 |
| *Z* | 8 | 8 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.90 | 1.08 |
| No. unique reflections | 4594 | 4618 |
| No. observed data ($I > 3\sigma(I)$) | 1978 | 2771 |
| *R* | 0.058 | 0.056 |
| *R′* | 0.046 | 0.054 |

**Table 2** Selected bond lengths (Å) and angles (°) for $[Co(L^5)_2(H_2O)]\cdot H_2O$ **1** and $[Co(L^5)_2(H_2O)]\cdot H_2O$ **2**

| **1** | | **2** | |
|---|---|---|---|
| Co–N(1) | 2.115(7) | Cu–N(1) | 1.993(5) |
| Co–N(2) | 2.012(7) | Cu–N(2) | 2.022(5) |
| Co–N(3) | 2.104(7) | Cu–N(3) | 1.994(5) |
| Co–N(4) | 2.008(7) | Cu–N(4) | 1.989(5) |
| Co–O(1w) | 2.039(6) | Cu–O(1w) | 2.266(4) |
| N(1)–Co–N(2) | 80.1(3) | N(1)–Cu–N(2) | 81.5(2) |
| N(1)–Co–N(3) | 171.7(3) | N(1)–Cu–N(3) | 177.8(2) |
| N(1)–Co–N(4) | 95.5(3) | N(1)–Cu–N(4) | 96.5(2) |
| N(1)–Co–O(1w) | 92.4(2) | N(1)–Cu–O(1w) | 90.8(2) |
| N(2)–Co–N(3) | 95.9(3) | N(2)–Cu–N(3) | 97.8(2) |
| N(2)–Co–N(4) | 118.8(3) | N(2)–Cu–N(4) | 136.5(2) |
| N(2)–Co–O(1w) | 116.3(3) | N(2)–Cu–O(1w) | 110.3(2) |
| N(3)–Co–N(4) | 80.0(3) | N(3)–Cu–N(4) | 82.6(2) |
| N(3)–Co–O(1w) | 96.0(2) | N(3)–Cu–O(1w) | 91.5(2) |
| N(4)–Co–O(1w) | 124.9(3) | N(4)–Cu–O(1w) | 113.2(2) |

override this effect the metal atom has increased its co-ordination number with an additional water ligation. This is a manifestation of the predominance of the ligand steric effect over the electronic effect.

It is interesting to make comparison with complexes of similar ligands. While the average Cu–N (amide) distance in complex **2** (2.006 Å) is longer than that observed in $[Cu(L^4)_2]$ (1.931 Å), the average Cu–N (pyridyl) distance (1.993 Å) in **2** is shorter than that in $[Cu(L^4)_2]$ (2.006 Å).[1] A similar bonding situation was observed before, with sterically demanding pyridine amide ligands.[3,18]

## Absorption spectra

The electronic spectra of complexes **1** and **2**, measured (280–1100 nm) both in the solid state (dispersed in mineral oil mull) and in dmf solution, are reported in Table 3. It is to be noted that the diffuse reflectance spectrum of dark brown $[Co(L^1)]\cdot H_2O$ displays[6c] a band at 735 nm with a shoulder at 505 nm. The stereochemistry of $[Co(L^1)]\cdot H_2O$ is expected to be square pyramidal. It is worth noting here that for $[Co(L^5)_2(H_2O)]\cdot H_2O$ 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[19–21] 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 below) 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[a]

| Complex | $\lambda_{max}$/nm ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) |
|---|---|
| **1** $[Co(L^5)_2(H_2O)]\cdot H_2O$ | 656 (15), 520 (sh) (50), 470 (sh) (85), 305 (sh) (5500) |
| | reflectance 650 (sh), 520 (sh), 470 (sh) |
| **2** $[Cu(L^5)_2(H_2O)]\cdot H_2O$ | 800 (sh) (75), 595 (170), 407 (1550), 310 (sh) (5950) |
| | reflectance 793 and 600 (sh) |

[a] In dmf solutions (or solid reflectance, where stated).

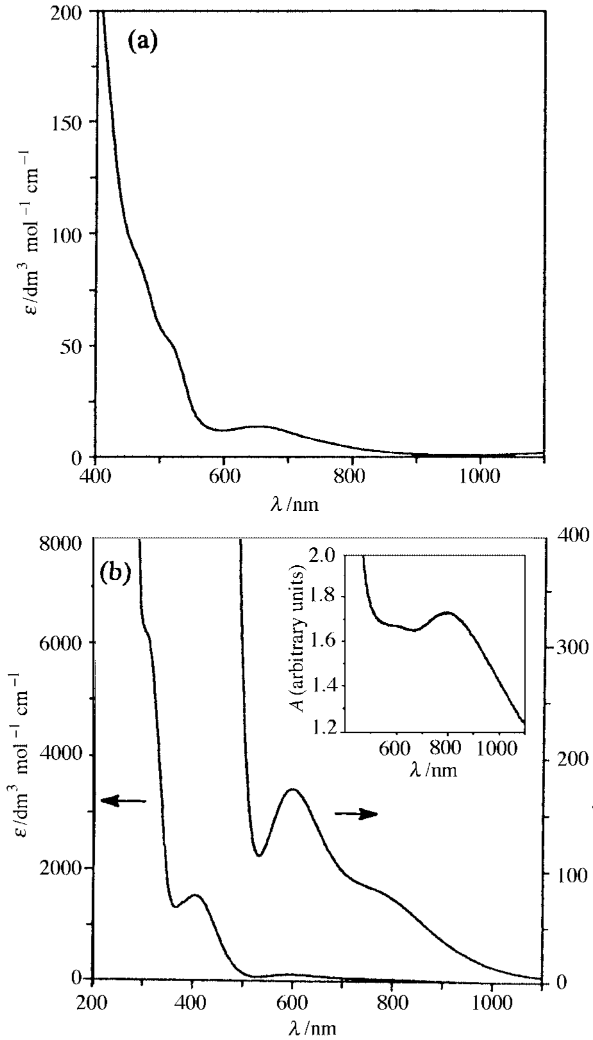



**Fig. 2** Electronic absorption spectra of (a) $[Co(L^5)_2(H_2O)]\cdot H_2O$ **1** ($3.6 \times 10^{-3}$ mol dm$^{-3}$ in dmf) and (b) $[Cu(L^5)_2(H_2O)]\cdot H_2O$ **2** ($1 \times 10^{-3}$ mol dm$^{-3}$ in dmf). The solid reflectance spectrum of **2** is shown as an inset.

The solid state reflectance spectrum of $[Cu(L^5)_2(H_2O)]\cdot H_2O$ 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).[22] 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 $[Cu(L^5)_2(H_2O)]\cdot H_2O$ 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 $\mu_{eff}$ 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–Weiss law ($\chi_m = C/(T - \theta)$) in the temperature range 81–300 K.

In fact, for trigonal bipyramidal cobalt(II) complexes the $\mu_{eff}$ values lie in the range 4.26–5.03 $\mu_B$, owing to the orbital contribution of the excited E levels.[19] The large spread of $\mu_{eff}$ 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[20g] high-spin cobalt(II) complexes with tetrahedrally 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) $\mu_{eff}$ 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(III) impurity. The $\mu_{eff}$ 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 $[Co(L^1)]\cdot H_2O$ is 2.26 $\mu_B$, implying its low-spin character.[4a] The reason behind the presence of a decreased ligand field of $L^5$ 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 ($g_{\parallel} = 2.24$, $g_{\perp} = 2.02$, $A_{\parallel} = 175$ G) characteristic of a $d_{x^2-y^2}$ ground state.[22] In fact, the spectrum is closely similar to that of $[Cu(L^4)_2]$.[1] We can therefore infer that the copper(II) centre in $[Cu(L^5)_2(H_2O)]\cdot H_2O$ assumes a tetragonal geometry in dmf solution (*cf.* absorption spectral result),[22] implying a structural change in going from solid to solution.

### Redox properties

The redox behaviour of $[Co^{II}(L^5)_2(H_2O)]\cdot H_2O$ **1** and $[Cu^{II}(L^5)_2(H_2O)]\cdot H_2O$ **2** was examined by cyclic voltammetry in dmf solutions at a glassy carbon working electrode. In order to identify the effect of geometry on the $Co^{III}$–$Co^{II}$ and $Cu^{II}$–$Cu^{I}$ redox potentials, the results were compared to those of the reported complexes $[Co^{II}(L^1)]\cdot H_2O$,[4a,6c] $[Cu^{II}(L^1)(H_2O)]$[4b] and $[Cu^{II}(L^4)_2]$.[1] It is to be noted that the redox behaviour of $[Co^{II}(L^1)]\cdot H_2O$ has not been reported; however, it has for the last two complexes.[1]

Under identical experimental conditions, $[Co^{II}(L^5)_2(H_2O)]\cdot H_2O$ and $[Co^{II}(L^1)]\cdot H_2O$ exhibit an oxidative redox process due to the $Co^{III}$–$Co^{II}$ 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, $\Delta E_p = 200$ mV; $[Co(L^1)]\cdot H_2O$, 0.06 V, $\Delta E_p = 80$ mV) in the $Co^{III}$–$Co^{II}$ potential between the two cobalt(II) complexes, caused by differing stereochemistry and spin state. The stereochemical flexibility provided by two bidentate $L^5$ ligands in **1** is expected to stabilize the cobalt(II) state more than in $[Co(L^1)]\cdot H_2O$, where the cobalt(II) centre is co-ordinated by a rigid tetradentate ligand $L^1$. However, it should be noted here that while the cobalt(II) centre in **1** is high spin, it is low spin for $[Co(L^1)]\cdot H_2O$.[4a] The low-spin state of the resulting cobalt(III) species, generated at the electrode surface, is expected to be attained more easily in the case of low-spin $[Co(L^1)]\cdot H_2O$ 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 $[Co(L^1)]\cdot H_2O$ (*cf.* $\Delta E_p$ values).[13]

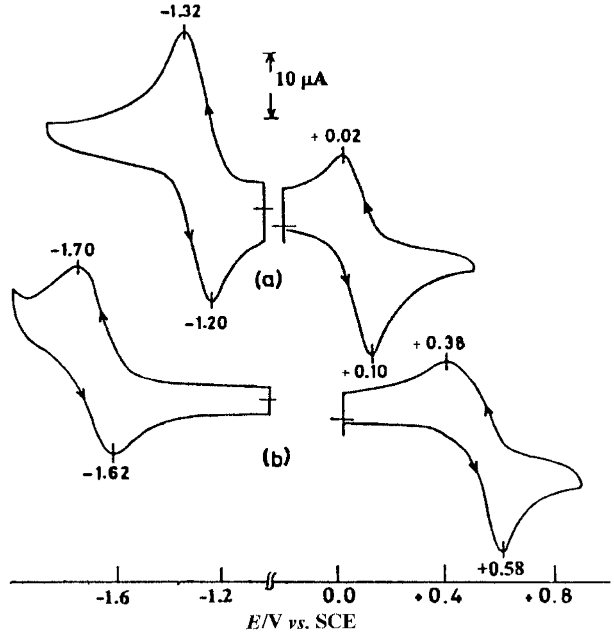



**Fig. 3** Cyclic voltammograms of (*a*) $[Co(L^1)]\cdot H_2O$ in dmf–0.1 mol $dm^{-3}$ $[NBu^n_4][ClO_4]$, $c = 1.4 \times 10^{-3}$ mol $dm^{-3}$, scan rate = 100 mV $s^{-1}$ and (*b*) $[Co(L^5)_2(H_2O)]\cdot H_2O$ in dmf–0.1 mol $dm^{-3}$ $[NBu^n_4][ClO_4]$, $c = 2 \times 10^{-3}$ mol $dm^{-3}$, scan rate = 100 mV $s^{-1}$.

Both the complexes display an additional reduction process (Fig. 3): **1**, −1.66 V, $\Delta E_p = 80$ mV; $[Co(L^1)]\cdot H_2O$, −1.26 V, $\Delta E_p = 120$ mV. We assign this as due to the $Co^{II}$–$Co^{I}$ couple, based on our previous experience[2b] on the redox behaviour of *trans*-$[Co(L^1/L^2)X_2]^-$ systems ($X = Cl^-$, $N_3^-$ or $MeCO_2^-$). Here the redox potential values clearly indicate that the cobalt(I) state is better stabilized in the complex $[Co(L^1)]\cdot H_2O$ than in **1**. This is understandable given the $d^8$ configuration of $Co^I$, which would prefer a planar co-ordination. It should be mentioned here that the generation of cobalt(I) species from $[Co(L^1)]\cdot H_2O$ and $[Co(L^2)]\cdot H_2O$ by sodium tetrahydroborate has been reported.[6c]

Complex **2** displays a quasireversible[13] reductive response due to the $Cu^{II}$–$Cu^{I}$ process. In going from $[Cu(L^1)(H_2O)]$ to $[Cu(L^5)_2(H_2O)]\cdot H_2O$ the redox potential shifts anodically by 570 mV [**2**, −0.53 V, $\Delta E_p = 100$ mV; $[Cu(L^1)]\cdot H_2O$, −1.10 V, $\Delta E_p = 80$ mV]. This can be rationalized given the differing copper(II) geometry in these two complexes {the $Cu^{II}$ in $[Cu(L^1)(H_2O)]$ is square pyramidal[4b] and in dmf solution that in **2** is tetragonal}. Interestingly, the $Cu^{II}$–$Cu^{I}$ redox potential values for **2** and $[Cu^{II}(L^4)_2]$ [$E_{1/2} = -0.47$ V, $\Delta E_p = 90$ mV][1] 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 $[Co(L^5)_2(H_2O)]\cdot H_2O$ 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 $L^5$. It has been shown that for the $Cu^{II}$–$Cu^{I}$ redox process $L^4$, $L^5$ 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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