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Full Paper

Copper(II) Complexes of Two New Pyridyl–Aliphatic Amine Ligands: Synthetic, Structural, EPR, and Magnetic Studies*

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Two new polyamine ligands, L^1 and L^2 , incorporating pyridyl and aliphatic amine donor sites have been prepared and their reaction with copper(II) yields the mono- and binuclear complexes $[Cu(L^1)](ClO_4)_2$ (1) and $[Cl_2Cu(L^2)CuCl(H_2O)]ClO_4$ (2), respectively. The X-ray structure of 1 confirms that the five nitrogen donors of L^1 are bound to the central copper ion to give a distorted square pyramidal coordination sphere. In 2, L^2 acts as a bridging ligand with its N₃-donor coordination domains separated by a *m*-xylylene spacer group. An unusual feature of this latter complex is that symmetrical L^2 gives rise to non-equivalent coordination behaviour at the individual copper sites; while both sites display five-coordination with distorted square pyramidal arrangements, they differ in having N₃Cl₂- and N₃ClO-donor atom sets, respectively. The electron paramagnetic resonance (EPR) spectra of both complexes are discussed. Variable temperature magnetic susceptibility data confirmed the absence of magnetic interactions in 1 while a weak antiferromagnetic interaction between copper(II) centres occurs in 2.

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Introduction

The syntheses, crystal structures, and magnetic properties of low-dimensional transition metal complexes continue to receive a great deal of attention, in part motivated by the desire to uncover new functional materials.^[1] In view of this, such studies have typically focussed on elucidating structure/function relationships. We now report the results of a further investigation of this type involving the synthesis of two copper(II) complexes of the new polyamine ligands L^1 and L^2 (see Scheme 1). In this context it is noted that ligands incorporating both aliphatic and heterocyclic nitrogen donor groups (including such 'classic' ligand systems as 2,2'-dipyridylamine, 2-picolylamine, and their derivatives)^[2] have been very well documented to provide versatile ligand systems for a range of transition and post-transition metal ions.

Results and Discussion

Ligand and Complex Synthesis

The syntheses of L^1 and L^2 employed conventional organic procedures and are summarised in Scheme 1 (parts (a) and (b)). Reaction of copper(II) chloride with L^1 in methanol followed by chromatography on SP Sephadex C-25 and addition of perchlorate led to the isolation of blue crystals whose microanalysis and X-ray structure determination (see below) confirmed that they were a 1 : 1 complex of type [Cu(L^1)](ClO₄)₂ (1). A similar

^{*}Dedicated to Allan H. White – a fine crystallographer and solid-state chemist.



Scheme 1. Outline of the synthetic procedure used to prepare (a) L^1 and (b) L^2 .



Fig. 1. View of complex **1**. The displacement ellipsoids are represented at the 30 % probability level. The counterions are omitted.

procedure using copper(II) chloride and L^2 yielded blue crystals that, following microanalysis and X-ray structure determination, were shown to be a complex of type [Cl₂Cu(L²)CuCl (H₂O)]ClO₄ (**2**).

X-Ray Structures

The X-ray structure of 1 (Fig. 1) confirms that the five nitrogen atoms of L¹ coordinate to the central copper to give a distorted square pyramidal environment, with the atoms N2, N3, N4, and N5 defining the basal plane (root mean square (rms) deviation 0.20 Å) and atom N1 in the axial position. According to the definition of the distortion parameter τ [$\tau = (\beta - \alpha)/60$] by



Fig. 2. View of complex **2**. The displacement ellipsoids are represented at the 30 % probability level. The hydrogen atoms of carbons and counterions are omitted.

Addison et al.^[3] where β is the largest and α is the second largest basal angle, respectively, the experimental τ value of **1** is 0.36. It reflects that **1** has a distorted square pyramidal geometry. The Cu atom is displaced by 0.2138(11) Å from the basal plane, on the same side as atom N1. The packing displays an alternation of sheets of complex molecules separated by sheets of counterions parallel to the *ab* plane. The protons bound to N3 and N5 are involved in hydrogen bonds with the perchlorate counterions.

The X-ray structure of **2** (Fig. 2) shows that this dinuclear complex displays an unusual unsymmetrical structure in which the two copper centres are non-equivalent. While both metal cations are characterised by 5-coordination, they are associated with different donor atom sets, N₃Cl₂ and N₃ClO for Cu1 and Cu2, respectively. Both cations are in distorted square pyramidal environments, with the basal planes defined by the three nitrogen atoms and Cl1 for Cu1 (rms deviation 0.21 Å) or Cl3 for Cu2 (rms deviation 0.13 Å). The experimental τ values by



Fig. 3. Electron paramagnetic resonance spectra (solid lines) obtained for the frozen solution state of (a) **1** and (b) **2** in frozen 0.5 mM DMF at 110 K, along with the numerical simulation (dotted line) for the spectrum of **1**.

Addison et al.^[3] for Cu1 and Cu2 are 0.35 and 0.24, respectively, and indicate that both geometries are best described as disordered square pyramidal. The metal atoms are at 0.3267(9) and 0.2445(8) Å, respectively, from the planes, and they are on the same side as the axial donor atoms (Cl2 and O1, respectively). The two basal planes make a dihedral angle of $48.66(3)^\circ$. The molecule assumes an S shape which brings the three aromatic rings in a suitable position for the formation of intramolecular π -stacking interactions, with centroid...centroid distances of 3.6955(13) and 3.7572(13) Å, and dihedral angles of 30.70(11) and 31.44(11)°. Moreover, two N-H…Cl hydrogen bonds join the two halves of the molecule, while the water ligand is hydrogen bonded to the Cl2 atom pertaining to a neighbouring molecule, and to the perchlorate anion. The complex molecules are stacked so as to form columns parallel to the a axis, between which the counterions are located.

EPR Studies

The EPR spectrum of **1** in a frozen DMF solution at 110 K and its numerical simulation is given in Fig. 3a. The spectrum displays the axial characteristics of the *g*-tensor and the copper nuclear hyperfine couplings; typical for a copper(II) ion with a d_{x2-y2} ground state.^[4] The spectrum is well simulated with the axial *g*-tensor (S = 1/2, $g_{\parallel} = 2.215$, $g_{\perp} = 2.050$) and the axial copper nuclear hyperfine tensor (I = 3/2, $A_{\parallel} = 170$ G). These values fall in the range of those for the EPR of type 2 copper centres or model complexes with square planar or square pyramidal coordination geometries, in good agreement with the crystal structure of $\mathbf{1}$.^[5a-d] The observed *g*-values also preclude the possibility that complex $\mathbf{1}$ has the electronic structure of a trigonal bipyramid where g_{\perp} is generally larger than g_{\parallel} .^[5e] The ¹⁴N_{eq}(I = 1) nuclear super-hyperfine couplings between

The ¹⁴N_{eq} (I = 1) nuclear super-hyperfine couplings between copper(II) and the equatorial nitrogen atoms, which are often observed in copper(II) complexes with square-plane-based geometries, are not resolved in **1**. This may be due to the



Fig. 4. The $\chi_m T$ versus temperature curve for **2**.

Temperature [K]

presence of longer $Cu^{II}-N_{eq}$ bond lengths than is usual for related systems.

The EPR spectrum of **2** exhibits a broad band from 2690 to 3420 G, in accord with the presence of a dipolar interaction between the two copper(π) centres (Fig. 3b). The width of this feature is close to the overall EPR spectroscopic width for **1**, perhaps suggesting that both **1** and **2** have similar electronic structures.

Magnetic Studies

 $\chi_m T$ [cm³ K mol⁻¹]

The temperature-dependent magnetic susceptibilities of both 1 and 2 were measured in the temperature range from 2 to 300 K in the form of the $\chi_m T$ versus T curve, where χ_m is the molar magnetic susceptibility and T the temperature. The mononuclear complex 1 exhibits a $\chi_m T$ value of 0.5 cm³ K mol⁻¹, which is close to the spin-only value for the copper(II) ion over the whole temperature range; no long-range (internuclear) interactions were detected in this case.

The $\chi_m T$ value of the binuclear complex **2** at 300 K is $1.02 \text{ cm}^3 \text{ K mol}^{-1}$, which is consistent with the spin-only value for two copper(II) ions. However, on cooling, the value decreases gradually, and the $\chi_m T$ versus *T* profile indicates antiferromagnetic coupling (Fig. 4). The χ_m versus *T* data were fitted to the Bleaney–Bowers equation^[6] ($H = -2J\hat{S}_1\cdot\hat{S}_2$) where 2J is the singlet–triplet splitting, and the solid line in Fig. 4 represents the best-fit situation with g = 2.18 and $2J = -1.23 \text{ cm}^{-1}$. The Cu…Cu distance is 4.9529(5) Å. This result indicates that a weak antiferromagnetic interaction is operative in the intramolecular Cu…Cu core of this complex.

Conclusion

The synthesis of the copper(II) complexes of two new mixed pyridyl–aliphatic amine ligands is reported along with their X-ray structures and variable temperature magnetic behaviour. Unusual non-symmetric coordination behaviour was observed for the dinuclear species, $[Cl_2Cu(L^2)CuCl(H_2O)]ClO_4$ (2), which also shows weak antiferromagnetic coupling between its copper(II) centres.

Experimental

All reagents were purchased from Aldrich and used as received. Chromatography was conducted using a glass column under gravity flow employing SP-Sephadex C25 (Na⁺ form) ion exchange resin. Electronic absorption spectra were measured with a SCINCO S-2100 diode array spectrophotometer and elemental analysis on a Chemtronics TEA-3000 analyser. Crystals used for X-ray diffraction were stored under the corresponding reaction solution before mounting on the diffractometer. Samples for microanalysis were dried at 60°C in air. An X-Band (9 GHz) EPR spectrum was recorded on a Jeol (Japan) JES-TE300 ESR spectrometer using a 100 kHz field modulation and a Jeol ES-DVT3 variable temperature controller. The spectroscopic simulation was performed using the program Simfonia (v. 1.25, Bruker Instruments Inc.). Magnetic susceptibilities of ground samples were measured on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) under an external field of 5000 Oe. The EPR spectra were measured using the following conditions: microwave frequency, 9.133 GHz; microwave power, 1.0 mW; modulation amplitude, 10 G; time constant, 0.3 s; scan speed, 1250 G min⁻¹. Simulation parameters for EPR of 1: $g = [2.050 \ 2.050 \ 2.215]; A^{Cu} = [0 \ 0 \ 170] \text{ G};$ linewidth = [45 45 45] G along the g-tensor frame.

$[CuL^{1}](ClO_{4})_{2}$ (1) (where $L^{1} = N^{1}$ -(2-aminoethyl)-2,2dimethyl- N^{1} , N^{3} -bis(pyridin-2-ylmethyl)- propane-1,3-diamine))

2,2-Dimethylpropane-1,3-diamine (5.1 g) and 2-pyridinecarboxaldehyde (10.7 g) were reacted in methanol (100 mL) and treated with NaBH₄ (8.0 g) in an analogous manner to that described for the initial step in the above procedure to give the crude product (yield: 11.1 g). The product (8.0 g) was dissolved in acetonitrile (150 mL), tosylaziridine (11.2 g) was added, and then the mixture was heated at the reflux for 6 h. The dark red solution was evaporated under reduced pressure to give a dark red oil. Concentrated H₂SO₄ (100 mL) was slowly added and the mixture was heated with continuous stirring at 130°C for 72 h. The solution was cooled in an ice bath and ethanol/diethyl ether (1:1, 1500 mL) was slowly added to give a hygroscopic dark brown precipitate that was separated by filtration and then immediately dissolved in $5 \text{ mol } \text{L}^{-1}$ NaOH (150 mL) and extracted with chloroform $(3 \times 100 \text{ mL})$. The combined extracts were evaporated under reduced pressure to give a red oil. This was dissolved in methanol (150 mL) and CuCl₂·2H₂O (4.8 g) was added with stirring and stirring was continued for 30 min. The mixture was evaporated to dryness under reduced pressure. The blue residue was dissolved in water (500 mL) and chromatographed on an SP Sephadex column with 0.3 mol L^{-1} NaCl as per the method above. The blue major band was collected, the solution was evaporated to dryness under reduced pressure, and the residue was extracted with ethanol to separate NaCl. The ethanol solution was then evaporated under reduced pressure to give a blue powder (yield: 4.3 g). This was dissolved in a minimum volume of warm water containing an excess of LiClO₄. Slow evaporation of the solution at ambient temperature yielded blue crystals suitable for a structure determination. (Anal. Calc. for C₁₉H₂₉Cl₂CuN₅O₈: C 38.68, H 4.96, N 11.87. Found: C 38.8, H 5.01, N 11.6 %.) λ_{max} (water)/nm (ϵ/M^{-1} cm⁻¹) 633 (1265).

$[Cl_2Cu(\mathbf{L}^2)CuCl(H_2O)]ClO_4$ (**2**) (where $\mathbf{L}^2 = N^1, N^{1'}$ -(1,3-phenylenebis(methylene))bis(N^1 -(pyridin-2-ylmethyl) propane-1,3-diamine))

m-Xylylenediamine (5.1 g) was dissolved in dry ethanol (100 mL), 2-pyridine-carboxaldehyde (8.1 g) was added, and the

mixture was heated at 80°C for 12 h under nitrogen. The pale yellow solution was cooled to room temperature and NaBH₄ (12.0 g) was slowly added. The mixture was stirred overnight and then 1.0 mol L⁻¹ HCl (5 mL) followed by 1.0 mol L⁻¹ NaOH (5 mL) were added and the solution was evaporated to dryness under reduced pressure and the residue dissolved in water (100 mL). The solution was extracted with dichloromethane (50 mL × 5), the combined extracts were washed with water (50 mL × 3) and then dried over Na₂SO₄. This solution was evaporated under reduced pressure to give the product as a brown oil which was used for complex formation without further purification (yield: 11.7 g).

The above product (7.7 g) was dissolved in acrylonitrile (38.0 g) and glacial acetic acid (2.9 g) was added. The mixture was heated at reflux for 72 h under a nitrogen atmosphere. The resulting deep brown solution was evaporated to dryness under reduced pressure. Dichloromethane (100 mL) was added and the solution was washed with 0.88 mol L^{-1} NH₃ (100 mL) and then water $(3 \times 100 \text{ mL})$ and the organic phase was dried over Na₂SO₄. The solution then was evaporated to dryness under reduced pressure to give a yellow oil which was dissolved in methanol (50 mL). Raney-Ni (4.0 g) in water (20 mL) was added followed by slow addition of NaBH₄ (18.9 g) in 4% NaOH (200 mL) with vigorous stirring at 60°C. The mixture was stirred overnight and then filtered through Celite and evaporated to dryness under reduced pressure. The residue was dissolved in $8 \text{ mol } \text{L}^{-1}$ NaOH (50 mL) and extracted with dichloromethane $(5 \times 50 \text{ mL})$. The combined extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give L^2 as a brown oil that was used for complex formation without further purification (yield: 6.8 g).

The above product (5.4 g) was dissolved in methanol (100 mL) and CuCl₂·2H₂O (4.3 g) in methanol (100 mL) was added with stirring. The blue mixture was evaporated to dryness under reduced pressure and the residue was dissolved in water (1 L) and the solution was filtered. The filtrate was applied to a SP-Sephadex C-25 (Na⁺ form) in a column which was initially washed with water (300 mL) and then eluted with 0.3 mol L NaCl. The (major) blue band was separated and the eluent evaporated to dryness under reduced pressure. The complex product was then extracted several times into ethanol to remove NaCl. The extracts were evaporated to dryness under reduced pressure (yield: 5.2 g). The residue was dissolved in a minimum volume of water and slow evaporation of the solution at ambient temperature after addition of LiClO₄ provided blue crystals suitable for a structure determination. (Anal. Calc. for C₂₆H₃₈Cl₄Cu₂N₆O₅: C 39.86, H 4.89, N 10.73. Found: C 39.2, H 4.87, N 10.5 %.) λ_{max} (water)/nm (ϵ/M^{-1} cm⁻¹) 625 (2105).

Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer^[7] using graphite-monochromated $Mo_{K\alpha}$ radiation (λ 0.71073 Å). The crystals were introduced into glass capillaries with a protecting 'Paratone-N' oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, and then refined on all data. The data (combinations of φ - and ω -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with *HKL2000*.^[8] Absorption effects were corrected empirically with the program *SCALEPACK*.^[8] The structures were solved by direct methods with *SHELXS-97*, expanded by subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with

 Table 1. Crystal data and structure refinement details

	1	2
Empirical formula	C19H29Cl2CuN5O8	C26H38Cl4Cu2N6O5
$M[\text{g}\text{mol}^{-1}]$	589.91	783.50
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
<i>a</i> [Å]	18.1096(9)	11.4897(2)
<i>b</i> [Å]	8.9447(5)	16.0924(2)
<i>c</i> [Å]	15.8658(4)	17.5316(3)
β [deg.]	110.935(3)	98.8066(6)
V[Å ³]	2400.4(2)	3203.32(9)
Ζ	4	4
$D_{\rm calc} [{\rm gcm^{-3}}]$	1.632	1.625
<i>F</i> (000)	1220	1608
$\mu(Mo_{K\alpha}) [mm^{-1}]$	1.188	1.708
Measured reflections	90603	107701
Independent reflections	4533	8278
Observed reflections	3973	6960
$[I > 2\sigma(I)]$		
R _{int}	0.023	0.030
Parameters refined	318	388
R_1	0.036	0.033
wR_2	0.098	0.087
S	1.045	1.040
$\Delta \rho_{\rm min} [{\rm e} {\rm \AA}^{-3}]$	-0.57	-0.68
$\Delta \rho_{\rm max} [{\rm e} {\rm \AA}^{-3}]$	0.79	0.64

 Table 2.
 Selected bond lengths [Å] and angles [deg.] for 1 and 2

1	2			
Cu–N(1)	2.158(2)	Cu(1)–N(1)	2.1209(18)	
Cu-N(2)	2.086(2)	Cu(1)–N(2)	2.0085(16)	
Cu-N(3)	2.035(2)	Cu(1)–N(3)	1.9909(19)	
Cu-N(4)	2.016(2)	Cu(2)–N(4)	2.0757(17)	
Cu-N(5)	2.030(2)	Cu(2)–N(5)	2.0086(17)	
		Cu(2)–N(6)	1.9891(17)	
N(4)-Cu-N(5)	95.64(9)	Cu(1)– $Cl(1)$	2.3291(7)	
N(4)-Cu-N(3)	81.23(9)	Cu(1)-Cl(2)	2.4992(6)	
N(5)-Cu-N(3)	156.57(10)	Cu(2)–Cl(3)	2.3000(6)	
N(4)-Cu-N(2)	178.10(8)	Cu(2)–O(1)	2.2101(17)	
N(5)-Cu-N(2)	85.72(8)			
N(3)-Cu-N(2)	96.99(8)	N(3)-Cu(1)-N(2)	172.01(8)	
N(4)-Cu-N(1)	98.84(8)	N(3)-Cu(1)-N(1)	92.26(8)	
N(5)-Cu-N(1)	100.22(8)	N(2)-Cu(1)-N(1)	81.54(7)	
N(3)-Cu-N(1)	103.21(9)	N(3)-Cu(1)-Cl(1)	88.80(7)	
N(2)-Cu-N(1)	82.20(8)	N(2)-Cu(1)-Cl(1)	94.27(5)	
		N(1)-Cu(1)-Cl(1)	151.65(5)	
		N(3)-Cu(1)-Cl(2)	93.17(7)	
		N(2)-Cu(1)-Cl(2)	93.33(5)	
		N(1)-Cu(1)-Cl(2)	105.37(5)	
		Cl(1)-Cu(1)-Cl(2)	102.86(2)	
		N(6)-Cu(2)-N(5)	172.75(7)	
		N(6)-Cu(2)-N(4)	92.28(7)	
		N(5)-Cu(2)-N(4)	83.09(7)	
		N(6)-Cu(2)-O(1)	98.20(7)	
		N(5)-Cu(2)-O(1)	87.98(7)	
		N(4)-Cu(2)-O(1)	97.97(7)	
		N(6)-Cu(2)-Cl(3)	88.04(5)	
		N(5)-Cu(2)-Cl(3)	94.41(5)	
		N(4)-Cu(2)-Cl(3)	159.93(5)	
		O(1)-Cu(2)-Cl(3)	101.85(5)	

SHELXL-97.^[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen and nitrogen atoms were found on Fourier-difference maps, and the carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH₃).

Crystal data and structure refinement parameters are given in Table 1 and selected bond lengths and angles in Table 2. The molecular plots were drawn with *SHELXTL*.^[9] Full crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif under CCDC numbers 870461 and 870462.

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