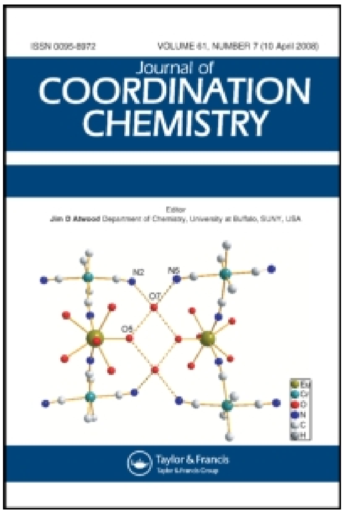

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Synthesis and X-ray crystal structures of three copper(II) complexes of 1,4-<i>bis</i>(di-2-pyridylmethyl)phthalazine

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Synthesis and X-ray crystal structures of three copper(II) complexes of 1,4-*bis*(di-2-pyridylmethyl)phthalazine

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The synthesis and X-ray crystal structures of three discrete copper(II) complexes of 1,4-*bis*(di-2-pyridylmethyl)phthalazine (**L**) are reported. The complexes **1**–**3** have Cu_2L, Cu_3L and Cu_2L_2 composition and display interesting relationships to previously reported complexes of this ligand.

Keywords: Copper; N ligands; Phthalazine; Dinucleating ligands

1. Introduction

1,4-*Bis*(di-2-pyridylmethyl)phthalazine (**L**) is a binucleating ligand that has been much studied in recent years for the preparation of models for the active sites of several metalloproteins [1, 2]. For example, dinuclear nickel complexes of this ligand have proved effective models for urease [3–5] and have been the subject of recent high-level theoretical studies [6, 7]. In 2004 the preparation and characterization of a number of dinuclear copper complexes of this ligand were reported as models for dioxygen-binding, copper-containing enzymes [8]. These included Cu_2(I,I), Cu_2(II,II) and mixed-valence Cu_2(I,II) complexes. We now report the syntheses and X-ray crystal structures of three new copper(II) complexes, **1**–**3**, of this ligand, including a novel trinuclear example (scheme 1).

2. Experimental

2.1. *General experimental*

Reagents were obtained from commercial sources and used as received. Ligand L was prepared by a literature procedure [5] and isolated as a hydrochloride salt.

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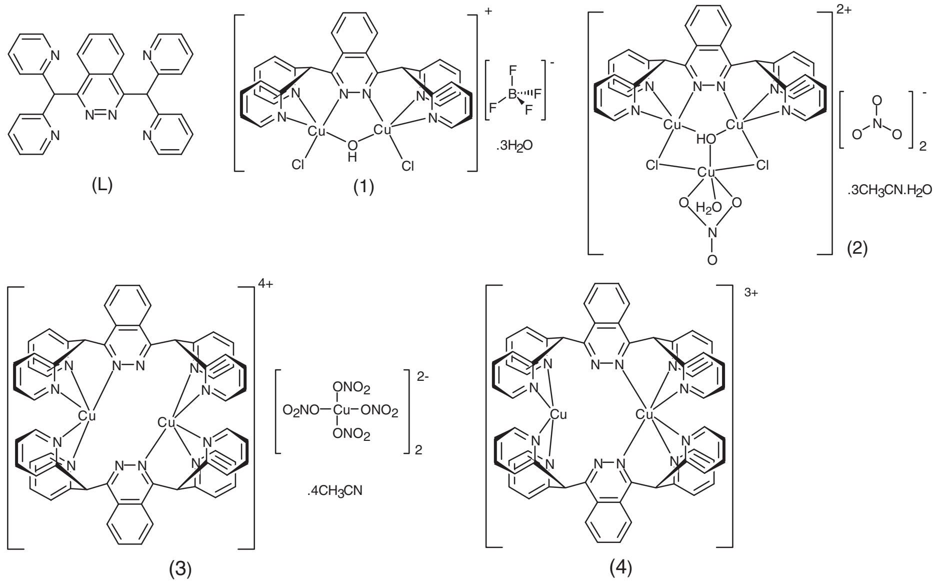

Scheme 1. Structures of **L** and **1**–**4**.

Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were carried out at the Campbell microanalytical laboratory at the University of Otago.

2.2. *Preparation of the complexes*

2.2.1. $[Cu_2(L)Cl_2(OH)](BF_4)\cdot 3H_2O$ (1). Copper tetrafluoroborate (15.1 mg, 0.044 mmol) and L (19.8 mg, 0.043 mmol) were both dissolved in hot methanol and the solutions combined. On cooling a blue crystalline precipitate formed containing crystals suitable for X-ray crystallography. Yield 9.1 mg (26%), m.p. 284–287°C (dec.). (Found: C, 43.51; H, 2.96; N, 10.02. $C_{30}H_{23}BN_6OF_4Cl_2Cu_2\cdot 3H_2O$ requires: C, 43.81; H, 3.55; N, 10.22).

2.2.2. $[Cu_3(L)Cl_2(OH)(NO_3)(H_2O)](NO_3)_2\cdot 3CH_3CN\cdot H_2O$ (2) and $[Cu_2(L)_2][Cu(NO_3)_4]_2\cdot 4CH_3CN$ (3). Reaction of L (20.0 mg, 0.043 mmol) with copper nitrate (22.0 mg, 0.091 mmol) in methanol gave a blue precipitate. Recrystallization by vapor diffusion of pentane into an acetonitrile solution of the precipitate gave green (**2**) and blue (**3**) crystals, both of which were suitable for X-ray crystallography. **2**: Yield 7.5 mg (16%), m.p. 198°C (dec.). **3**: Yield 17.6 mg (48%), m.p. >330°C. (Found: C, 42.09; H, 2.78; N, 15.94. $C_{60}H_{44}N_{20}O_{24}Cu_4$ requires: C, 41.91; H, 2.81; N, 16.29).

2.3. *X-ray crystallography*

The crystal data, data collection and refinement parameters for **1**–**3** are listed below. The measurements were made with a Siemens CCD area detector using graphite monochromatized Mo-Kα ($\lambda = 0.71073$ Å) radiation. The intensities were corrected for Lorentz and polarization effects and for absorption [9]. The structures were solved by direct methods using SHELXS [10] and refined on F^2 using all data by full-matrix least-squares procedures using SHELXL-97 [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 (aromatic) or 1.5 (aliphatic) times the isotropic equivalent of their carrier carbon atoms.

2.3.1. Crystallographic data for 1. $C_{60}H_{58}B_2Cl_4Cu_4F_8N_{12}O_8$, *Fw* 1644.76, monoclinic, $C2/c$, $a = 30.426(7)$, $b = 11.904(3)$, $c = 38.968(9)$ Å, $\beta = 110.010(3)^\circ$, $V = 13262(5)$ Å^3, $Z = 8$, $F(000) = 6656$, Bruker CCD area detector, $T = 168(2)$ K, blue plate, $0.39 \times 0.33 \times 0.09$ mm, $\mu = 1.513$ mm^{-1}, $D_x = 1.648$ g cm^{-3}, 2θ-range 3–53°, 13532 unique reflections, 6804 with $I > 2\sigma(I)$, 898 parameters, wR_2 (all data) 0.060, R_1 [$I > 2\sigma(I)$] 0.039.

2.3.2. Crystallographic data for 2. $C_{36}H_{36}Cl_2Cu_3N_{12}O_{12}$, Fw 1090.29, orthorhombic, $Pnma$, $a = 22.397(5)$, $b = 12.393(3)$, $c = 15.984(4)$ Å, $V = 4436.5(17)$ Å^3, $Z = 4$, $F(000) = 2212$, Bruker CCD area detector, $T = 168(2)$ K, green block, $0.60 \times 0.33 \times 0.20$ mm, $\mu = 1.619$ mm^{-1}, $D_x = 1.632$ g cm^{-3}, 2θ-range 4–50°, 3986 unique reflections, 3014 with $I > 2\sigma(I)$, 320 parameters, wR_2 (all data) 0.090, R_1 [$I > 2\sigma(I)$] 0.038.

2.3.3. Crystallographic data for 3. $C_{68}H_{56}Cu_4N_{24}O_{24}$, Fw 1847.53, monoclinic, $P2_1/c$, $a = 23.714(8)$, $b = 15.856(5)$, $c = 20.682(7)$ Å, $\beta = 90.582(5)^\circ$, $V = 7776(4)$ Å^3, $Z = 4$, $F(000) = 3760$, Bruker CCD area detector, $T = 168(2)$ K, blue plate, $0.58 \times 0.52 \times 0.08$ mm, $\mu = 1.172$ mm^{-1}, $D_x = 1.578$ g cm^{-3}, 2θ-range 4–53°, 15695 unique reflections, 7225 with $I > 2\sigma(I)$, 1085 parameters, wR_2 (all data) 0.111, R_1 [$I > 2\sigma(I)$] 0.048.

3. Results and discussion

Complex **1** was prepared by reaction of L with one equivalent of copper tetrafluoroborate in methanol. It crystallizes in the monoclinic space group $C2/c$, with an asymmetric unit containing two discrete molecules of the complex, two tetrafluoroborate anions and six lattice water molecules, two of which are disordered. A perspective view of one molecule of the complex is shown in figure 1, which shows that the ligand L acts as a ditopic tripodal bridge between two copper atoms, which are also bridged by a hydroxide. The other sites of the five-coordinate coppers are occupied by chlorides. The coppers have a slightly distorted square-pyramidal geometry (τ values between 0.02 and 0.15 for the four copper atoms in the asymmetric unit), with a pyridine ring occupying the apical positions. The Cu–Cu distances in the two complexes within the asymmetric unit are identical [3.250(2) and 3.251(2) Å]. This value is typical of metal-metal separations in similar complexes involving pyridazine and phthalazine ligands [2, 5, 8, 12, 13].

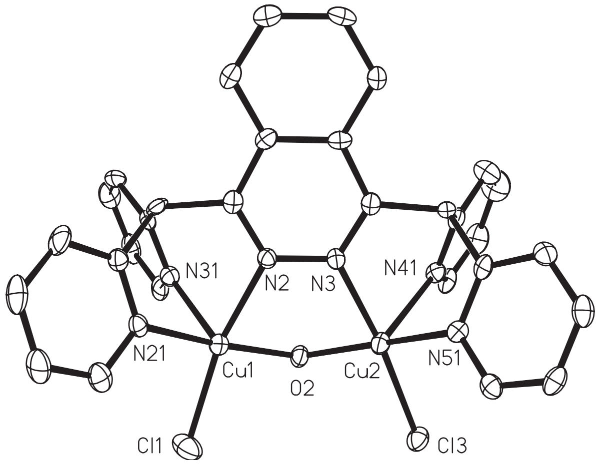

Figure 1. A perspective view of **1** with hydrogen atoms, non-coordinated anions and lattice water molecules omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–O(2) 1.904(2), Cu(1)–N(21) 2.010(3), Cu(1)–N(2) 2.078(3), Cu(1)–N(31) 2.229(3), Cu(1)–Cl(1) 2.270(1), Cu(2)–O(2) 1.883(2), Cu(2)–N(51) 1.985(3), Cu(2)–N(3) 2.050(3), Cu(2)–N(41) 2.286(3), Cu(2)–Cl(3) 2.309(1), Cu(2)–O(2)–Cu(1) 118.34(10).

The packing of the cationic **1** is generated through weak C–H···acceptor hydrogen bonds to coordinated chloride anions and non-coordinated tetrafluoroborate anions in the structure. A cluster of four water molecules lying in the cleft of the cationic complex are hydrogen bonded through the disordered water molecules in the structure to a symmetry related cluster associated with a second cation. This results in discrete pockets of hydrogen-bonded water molecules throughout the extended structure.

Reaction of L with two equivalents of copper nitrate gave a product which, after recrystallization from acetonitrile, gave a mixture of green and blue crystals. The green complex **2** crystallizes in the orthorhombic space group *Pnma*. The asymmetric unit comprises half the ligand, one and a half copper atoms (one on a mirror plane), three half nitrates (all on the mirror plane), a μ_2-chloride, a μ_3-bridging hydroxide (also located on the mirror plane), two water molecules (on the mirror plane) and one and a half acetonitrile solvate molecules. A perspective view of the structure is shown in figure 2 with hydrogen atoms, non-coordinated anions and solvate molecules omitted for clarity.

Within the structure of **2** L adopts the same bridging coordination mode as in **1**. However, the complex is very different to other complexes of L because of the additional bridging by anions to a third copper atom. Thus, **2** is related to **1** by the addition of a $[Cu(NO_3)(H_2O)]^+$ unit through attachment to the chloride and hydroxide ligands of **1**. This third copper atom [Cu(2)] has a very unusual donor set with a chelating nitrate, two μ_2-chlorides, a μ_3-hydroxide and a water molecule forming a highly distorted octahedral coordination geometry. The copper [Cu(1)] in the binding sites normally provided by the ligand has a square-pyramidal geometry and the two symmetry-related copper atoms are bridged by one molecule of L and the μ_3-hydroxide. The water solvate, which is not shown in the figure, is weakly associated with these two copper atoms [Cu–O distance 2.466(3) Å]. Thus, the geometry could alternatively be described as pseudo-octahedral.

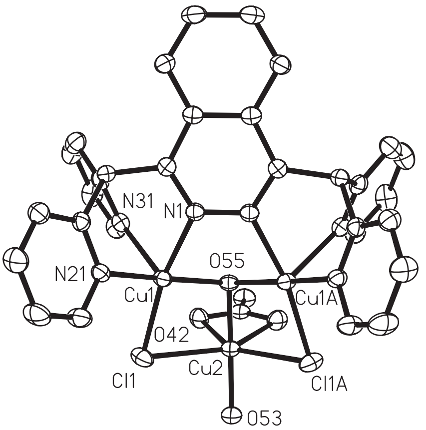

Figure 2. A perspective view of the trimetallic copper complex **2**. Non-coordinated nitrate anions, solvate molecules and hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Cu(1)–O(55) 1.978(2), Cu(1)–N(21) 1.979(3), Cu(1)–N(1) 2.062(2), Cu(1)–N(31) 2.229(3), Cu(1)–Cl(1) 2.3406(9), Cu(2)–O(55) 1.924(3), Cu(2)–O(53) 1.942(3), Cu(2)–O(42) 2.309(2), Cu(2)–Cl(1) 2.4476(10).

The μ_3-hydroxide oxygen atom has tetrahedral geometry with Cu–O bond lengths of 1.978(2) Å [Cu(1)] and 1.924(3) Å [Cu(2)]. Cu(1) and Cu(2) are bridged by a μ_2-chloride with Cu–Cl bond lengths of 2.3406(9) and 2.4476(10) Å to Cu(1) and Cu(2), respectively. The Cu–Cu distance between the symmetry-related Cu(1) atoms is 3.127(1) Å and the Cu(1)–Cu(2) distance is 3.141(1) Å. The trinuclear copper coordination unit with a μ_3-hydroxide is not an uncommon motif, with many higher nuclearity clusters having the same connectivity within a larger structure. However, to our knowledge, there are no examples of discrete trinuclear copper centers with the donor atoms described here.

In the packing of **2** the bridging water and hydroxide ligands on the trinuclear copper cation are hydrogen bonded to the non-coordinated nitrate anions that lie in the clefts formed by L, with O–H $\cdots$ O distances in the range 1.90–2.39 Å ($D = 2.70$–3.04 Å). These nitrate anions are in turn weakly hydrogen bonded to other cations and acetonitrile solvate molecules through C–H $\cdots$ O bonds. This leads to an intricate hydrogen bonding network throughout the crystal lattice. Two acetonitrile solvate molecules hydrogen bond to the coordinated water attached to Cu(2) with distances typical for such an interaction.

The blue complex **3** is a binuclear double-stranded helicate, crystallizing in the monoclinic space group $P2_1/c$, with an asymmetric unit containing one molecule of the helicate, four acetonitrile solvate molecules and two tetranitrocuprate counteranions. A perspective view of the complex is shown in figure 3 with anions, solvate molecules and hydrogen atoms omitted for clarity. The copper atoms lie in a square-pyramidal environment (τ values of 0.07 and 0.00) with tripodal coordination by one ligand and bidentate coordination by the other L. Thus, the bridging ligand uses only five of the six available nitrogen donors, with one of the central phthalazine nitrogens being non-coordinated. This arrangement is very similar to that in a related helicate containing a central pyridazine ring [14]. The Cu–N distances are 2.015(3)–2.042(3) Å for the equatorial bonds, while the axial Cu–N distances

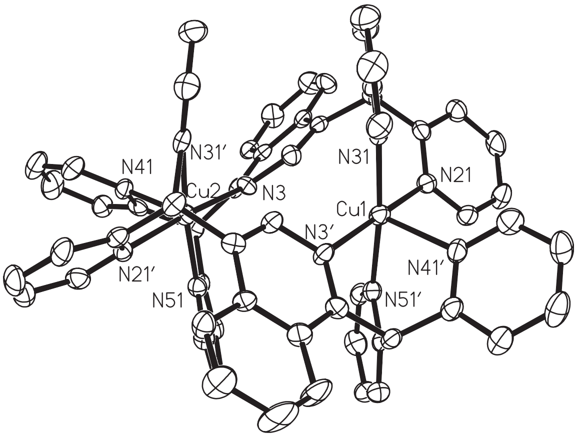

Figure 3. A perspective view of **3** with anions, solvate molecules and hydrogen atoms omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Cu(1)–N(21) 2.028(3), Cu(1)–N(31) 2.028(3), Cu(1)–N(51′) 2.031(3), Cu(1)–N(3′) 2.036(3), Cu(1)–N(41′) 2.243(4), Cu(2)–N(51) 2.015(3), Cu(2)–N(31′) 2.022(3), Cu(2)–N(21′) 2.026(3), Cu(2)–N(3) 2.042(3), Cu(2)–N(41) 2.255(3).

are longer at 2.243(4) and 2.255(3) Å. These are slightly longer than the corresponding distances in the previously reported dinuclear copper helicate [14]. The metal–metal distance in this complex is 4.506(1) Å, which is shorter than that reported for the pyridazine analogue [14]. The tetranitrocuprate anions contain copper atoms with a square planar geometry with monodentate coordination by four nitrate groups with Cu–O distances ranging from 1.982(3) to 2.020(3) Å, although the nitrate groups also make weaker contacts to the copper through a second oxygen atom (ca 2.59 Å). This is similar to other structures that contain this anion [15, 16].

Crystal packing of the double-stranded helicate **3** is again unremarkable. Despite the structure containing a significant number of hydrogen bond acceptors there are no strong donors; consequently the extended structure represents close-packing of the cationic helicate, the anions and non-coordinated solvate molecules with weak C–H···O or C–H···N interactions apparent.

Complex **3** bears an intriguing resemblance to an isomeric but not isoelectronic complex **4**, reported by the Lippard group. This also contains two copper centers bridged by two molecules of L [8]. However, their mixed-valence Cu_2(I,II) complex has one octahedral Cu(II) center and one tetrahedral Cu(I) center and has the two phthalazine rings bound to the same metal. In contrast, our Cu_2(II,II) complex has two pentacoordinate copper atoms. Thus, the one electron reduction of **3** to **4** appears to induce a switching process wherein one of the central phthalazine rings is transferred from one metal to the other. As such, this represents a new example of redox-driven molecular movement.

In summary, we have synthesized three new copper(II) complexes of the title ligand which have different metal : ligand stoichiometries. The structures of all three compounds were determined by single crystal X-ray crystallography.

Supplementary material

Crystallographic data for **1–3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 641991–641993). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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