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[a] Sydney Grammar School, Darlinghurst, NS, Australia [b] Centre for Heavy Metals Research, School of Chemistry, University of Sydney, Sydney, Australia [c] Chemistry M313, The University of Western Australia, Crawley, WA, Australia

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Self-assembly of Hydrogen-bonded Supramolecular Structures Based on the Neutral Pseudo-macrocyclic Complex Bis(dimethylglyoximato)copper(II)

MICHAEL M. BISHOP[a,b], ANDREW H.W. LEE[b], LEONARD F. LINDOY[a,*], PETER TURNER[a], BRIAN W. SKELTON[c] and ALLAN H. WHITE[c]

[a]*Centre for Heavy Metals Research, School of Chemistry, University of Sydney, Sydney NSW 2006, Australia;* [b]*Sydney Grammar School, College Street, Darlinghurst, NSW 2010, Australia;* [c]*Chemistry M313, The University of Western Australia, Crawley, WA 6009, Australia*

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Three new complexes based on the neutral pseudo-macrocyclic complex bis(dimethylglyoximato)copper(II) and the substituted pyridines, 4-phenylpyridine, 3-pyridin-4-ylpropan-1-ol and isonicotinamide, which occupy a fifth coordination site on the copper, are described. The usefulness of such complexes in building supramolecular arrays is examined. The complex containing 3-pyridin-4-ylpropan-1-ol forms hydrogen-bonded chains that, lying across one another, form layers within the crystal. The isonicotinamide-containing complex yields a host–guest assembly that incorporates channels containing guest molecules. The prospect of 'tuning' the size of the channel is discussed.

Keywords: Crystal engineering; Self-assembly; Supramolecular; Copper(II)

INTRODUCTION

In recent times there has been a growing interest in the rational design of crystals containing transition metal complexes, both by the formation of coordination polymers and, more recently, by using hydrogen bonding and other weak interactions between coordinated ligands [1]. Such complexes are often charged and the influence of the counter-ion and the possible incorporation of solvent molecules (both of which have steric requirements that must be met in the crystal and that are often less than innocent bystanders in the formation of hydrogen-bonded networks) become critical issues in the design of such systems [2]. By using neutral complexes, the use of counter-ions can be avoided and the likelihood of incorporation of solvent molecules can be reduced by minimizing the presence of surplus hydrogen-bonding sites in the structural components of the system.

In this article we report the use of the neutral pseudo-macrocyclic complex bis(dimethylglyoximato)copper(II) as a building block to form extended supramolecular structures held together by hydrogen bonds. Such a complex was of interest as the basis for a supramolecular tecton because it is neutral, because of the relative ease of incorporating different pendant R groups and because of the existence of a fifth coordination site on the copper. The parent complex is itself five-coordinate in the solid state with ligand oxygens acting as bridges to a second copper(II) centre resulting in the formation of centrosymmetric dimers. The paucity of hydrogen-bonding sites on the pseudo-macrocycle and the fact that the systems in this study self-assemble from a mixture of the individual ligands and copper ions in basic conditions were both additional attractive features.

A search of the Cambridge Structure Database (CSD) [3] found four structures relevant to the current study and these are summarized in Scheme 1. In these complexes either one or both of the deprotonated glyoximato oxygens act as hydrogen-bond acceptors; the ligands in the other coordination site(s) act as hydrogen-bond donors.

*Corresponding author. Tel.: +61-2-9351-4400. Fax: +61-2-9351-7067. E-mail: l.lindoy@chem.usyd.edu.au

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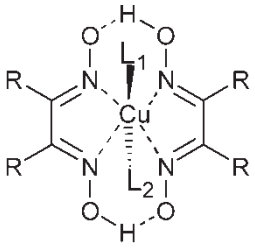

Refcode	R	L_1	L_2	ref.
CAWWUS	Ph	H_2O	-	[4]
GLIMCV	Me	imidazole	-	[6]
JECXEU	Me	thiourea	-	[7]
JETMIE	Et	thiourea	thiourea	[8]

Scheme 1

In crystals of aqua-bis(diphenylglyoximato-*N*,*N*′)copper(II) (CSD refcode: CAWWUS) [4] each complex is linked to two neighbours by centrosymmetric $R_2^2(10)$ rings [5] resulting in chains that run parallel to the *a* axis. The coordinated water molecules are aligned with the deprotonated oxygen atoms of the pseudo-macrocycle with the result that the pendant phenyl groups are arranged along the edges of the chain. Thus the water ligands effectively lie in tubes formed by the pseudo-macrocycles and the pendant groups.

In bis(dimethylglyoximato-*N*,*N*′)-imidazolecopper (II) (GLIMCV) [6] the imidazole is coordinated through the unprotonated nitrogen. The other (protonated) nitrogen acts as a hydrogen-bond donor to one of the deprotonated oxygens of a neighbouring complex, resulting in the formation of chains running quasi-parallel to the *a* axis of the unit cell.

For the coordinated thiourea in bis(dimethylglyoximato-*N*,*N*′)-(thiourea-*S*)copper(II) (JECXEU) [7] and bis(3,4-hexanedionedioximato-*N*,*N*′)-bis(thiourea-*S*)copper(II) (JETMIE) [8], the N−H groups act as hydrogen-bond donors, while the deprotonated oxygen(s) of the pseudo-macrocycle act as acceptors. In the five-coordinate complex, just one N−H is used (although another makes a short contact with the acceptor giving an $R_2^1(6)$ pattern) and one acceptor, and the complexes are linked in chains running parallel to the *c* axis. The six-coordinate complexes form sheets rather than chains. Each complex is involved in four $R_2^1(6)$ hydrogen-bond patterns and provides the donors for two and the acceptors for the remaining. Centrosymmetric short contact $R_2^2(8)$ patterns formed by unused N−H donors and the coordinated S atoms are also present.

In this article we examine the supramolecular structures formed in crystals in which substituted pyridines occupy the fifth coordination site in square pyramidal complexes based on bis(dimethylglyoximato-*N*,*N*′)copper(II). The ligands chosen for the fifth site, 4-phenylpyridine, 3-pyridin-4-ylpropan-1-ol and isonicotinamide (pyridine-4-carboxamide), have substituents (all in the 4 position) with no, one and two potential hydrogen-bonding sites, respectively.

EXPERIMENTAL

Synthesis

*Bis(dimethylglyoximato-*N,N′*) (4-phenylpyridine)copper(II), 1*

Dimethylglyoxime (0.232 g, 2 mmol) was dissolved in absolute ethanol (20 mL) and to this solution was added 4-phenylpyridine (0.155 g, 1 mmol). Copper(II) chloride dihydrate (0.171 g, 1 mmol) was dissolved in water (10 mL) and excess ammonia solution (30%) added. This solution was added to a solution of the ligands in ethanol and the mixture was allowed to stand uncovered in the fume cupboard. The large black crystals that formed were removed from the mother liquor and dried in a desiccator, yield 0.255 g. Anal. Calcd. for $C_{19}H_{23}CuN_5O_4$(%): C, 50.83; H, 5.16; N 15.60. Found: C, 50.57; H, 5.04; N, 15.48.

*Bis(dimethylglyoximato-*N,N′*) (3-pyridin-4-ylpropanol-N)copper(II), 2*

Dimethylglyoxime (0.232 g, 2 mmol) was dissolved in absolute ethanol (20 mL) and to this solution was added 3-pyridin-4-ylpropan-1-ol (0.411 g, 3 mmol). Copper(II) chloride dihydrate (0.171 g, 1 mmol) was dissolved in water (10 mL) and excess ammonia solution (30%) added. This solution was added to a solution of the ligands in ethanol and the mixture was allowed to stand uncovered in the fume cupboard. The large black crystals that formed were removed from the mother liquor and dried in a desiccator, yield 0.186 g. Anal. Calcd. for $C_{16}H_{25}CuN_5O_5$(%): C, 44.59; H, 5.85; N 16.25. Found: C, 44.89; H, 5.97; N, 16.07.

Bis(dimethylglyoximato-N,N′) (pyridine-4-carboxamide-N)copper(II) $\frac{1}{2}$(pyridine-4-carboxamide) 3H_2O, 3

Dimethylglyoxime (0.232 g, 2 mmol) was dissolved in absolute ethanol (20 mL) and to this solution was added isonicotinamide (0.366 g, 3 mmol). Copper(II) chloride dihydrate (0.171 g, 1 mmol) was dissolved in water (10 mL) and excess ammonia solution (30%) was added. This solution was added to the solution of the ligands in ethanol and the mixture was allowed to stand uncovered in the fume cupboard. The large black crystals that formed were removed from the mother liquor, yield 0.176 g. The sample for analysis was dried at room temperature in a desiccator over silica gel with the loss of water. Anal. Calcd. for $C_{17}H_{23}CuN_7O_{5.5}$ 1/2 H_2O(%): C, 42.01; H, 4.98; N 20.18. Found: C, 42.22; H, 4.82; N, 20.17.

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When 2 mole equivalents of isonicotinamide were used in the synthesis above, two phases, bis[(μ_2-(*O*)-dimethylglyoximato)(dimethylglyoximato)copper(II)], **3** and **4**, formed. A redetermination of the X-ray structure of **4** (originally reported in 1959 and again in 1970) [9, 10] was undertaken.

X-ray Crystal Structure Determination

Data hemispheres (full spheres: **3**, **4**) were collected at approximately 150 K using omega scans on a Bruker SMART 1000 diffractometer using graphite-monochromated Mo Kα radiation generated from a sealed tube ($\lambda = 0.7107_3$ Å). The data integration and reduction were undertaken with SAINT and XPREP [11] and subsequent computations were carried out with the teXsan [12], WinGX [13] and XTAL [14] graphical user interfaces. Multiscan absorption corrections determined with SADABS [15–16] were applied to the data for **1**, **3** and **4**, and a Gaussian [11,17] correction was applied to data for **2**. Structures were solved with direct methods using SIR97 [18] for **1** and **2** and XTAL for **3** and **4**. The structures were extended and refined with full-matrix least-squares using SHELXL97 [19] for **1** and **2**, and XTAL for **3** and **4**. In general, anisotropic thermal parameters were refined for the non-hydrogen model atoms and a riding atom model was used for hydrogen atoms. ORTEP [20] depictions are provided in Figs 1–3, crystallographic details are given below and in Tables I and II, and CIF files for all structures are deposited with the Cambridge Crystallographic Data Centre, CCDC Nos 243236–243239.

*Bis(dimethylglyoximato-*N,N′*)(4-phenylpyridine)copper(II), 1*

Crystal Data

$[(4\text{-}C_6H_5 \cdot C_4H_4N)Cu(dmg)_2] \equiv C_{19}H_{23}CuN_5O_4$, $M = 448.96$. Monoclinic, space group $P2_1/c$ (#14),

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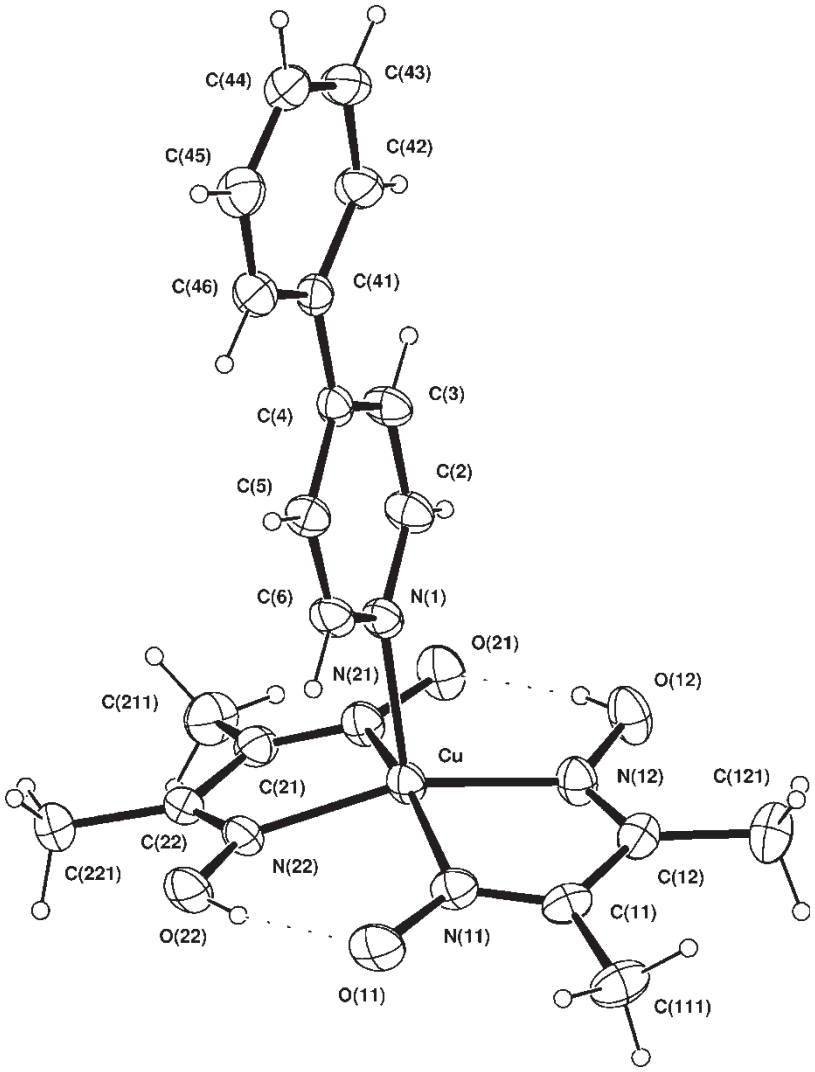

FIGURE 1 An ORTEP [20] depiction of a molecule of complex **1** with thermal ellipsoids displayed at the 20% level.

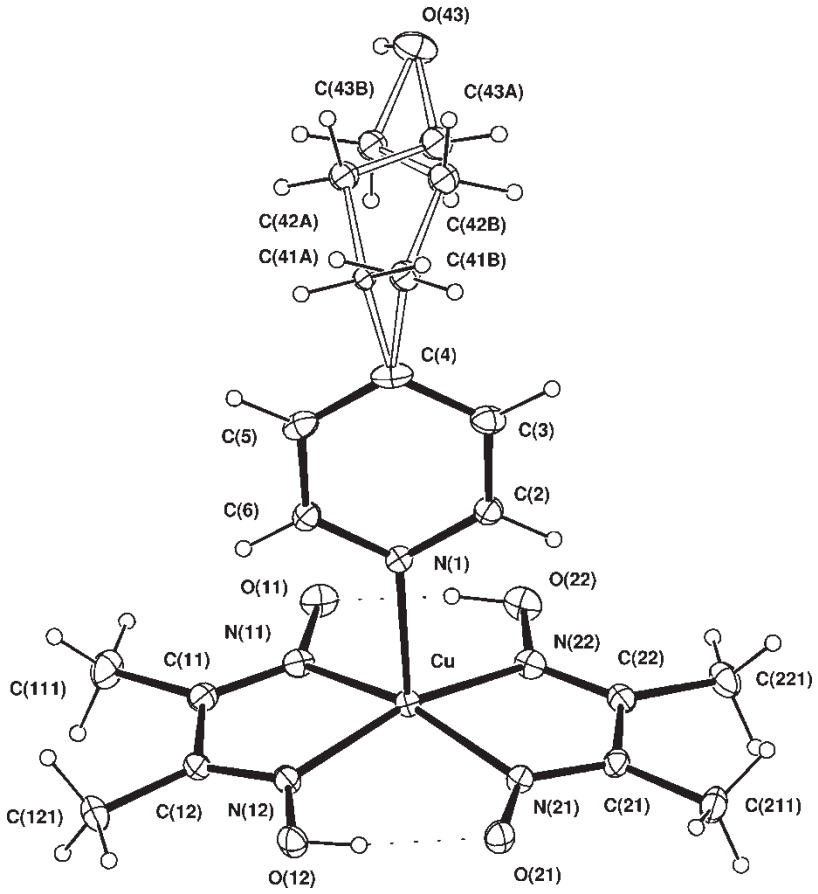

FIGURE 2 An ORTEP [20] depiction of a molecule of complex **2** with thermal ellipsoids displayed at the 20% level.

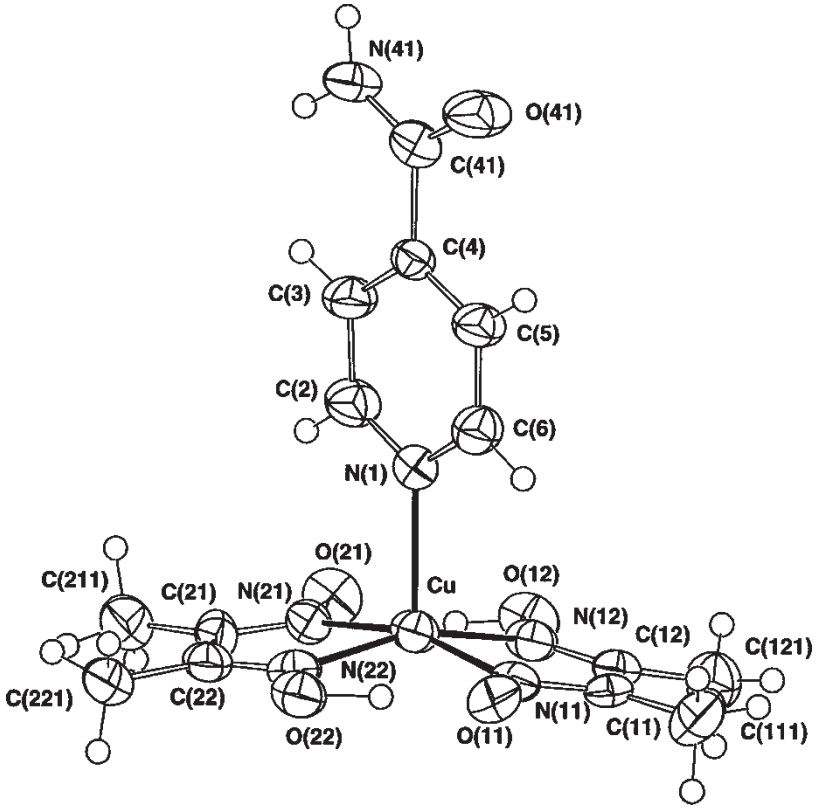

FIGURE 3 An ORTEP [20] depiction of a molecule of complex **3** with thermal ellipsoids displayed at the 20% level.

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TABLE I Pertinent bond lengths (Å) for **1–4**

	1	**2**	**3**	**4**
Cu–N(1)	2.1961(16)	2.1877(11)	2.200(6)	a
Cu–N(11)	1.9493(15)	1.9611(12)	1.916(6)	1.9701(14)
Cu–N(12)	1.9528(16)	1.9455(15)	1.933(7)	1.9485(14)
Cu–N(21)	1.9545(15)	1.9622(12)	1.961(6)	1.9569(16)
Cu–N(22)	1.9464(15)	1.9462(15)	1.947(7)	1.9539(13)

[a] Cu–O(22)* = 2.2861(12)Å. *Symmetry operator: $-x, -y, -z+1$.

$a = 13.8774(17)$, $b = 9.7820$ (12), $c = 15.9250(19)$ Å, $\beta = 111.001(2)^\circ$ $V = 2018.2(4)$ Å^3, $D_c = 1.478\,g\,cm^{-3}$, $Z = 4$; crystal size: $0.39 \times 0.38 \times 0.29$mm, colour: black, habit: prismatic, $\mu_{Mo} = 1.118\,mm^{-1}$, $T(SADABS)_{min/max} = 0.73$, $2\theta_{max} = 56^\circ$, $N = 73911$, $N_{ind} = 4641(R_{merge} = 0.0261)$, $N_{obs} = 3926$ $(I > 2\sigma(I))$, ($N_{var} = 269$, $R1(F) = 0.032$, $wR2(F^2) = 0.10_5$, $w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 0.4210P]$, where $P = (F_o^2 + 2F_c^2)/3)$. GoF(all) = 0.929, $\Delta\rho_{min,max} = -0.36$, $0.30\,eÅ^{-3}$.

The hydroxy hydrogen sites were located and modelled with isotropic displacement parameters.

Bis(dimethylglyoximato-N,N′) (3-pyridin-4-ylpropanol-N)copper(II), 2

Crystal Data

Formula $C_{16}H_{25}CuN_5O_5$, $M = 430.95$. Monoclinic, space group $C2/c$ (#15), $a = 19.048(3)$, $b = 9.5410(14)$, $c = 21.043(3)$Å, $\beta = 91.927(3)^\circ$, $V = 3822.1(10)$ Å^3, $D_c = 1.498\,g\,cm^{-3}$, Z = 8, crystal size: $0.529 \times 0.484 \times 0.445$ mm, colour: black, habit: prismatic, $\mu_{Mo} = 1.18\,mm^{-1}$, $T(Gaussian)_{min/max} = 0.595,\ 0.675$. $2\theta_{max} = 64^\circ$, $N = 27445$, $N_{ind} = 6655(R_{merge} = 0.036)$, $N_{obs} = 5603(I > 2\sigma(I))$, $N_{var} = 258$, $R1(F) = 0.030$, $wR2(F^2) = 0.085$ $(w = 1/[\sigma 2F_o^2) + (0.04P)^2 + 1.5P]$, where $P = (F_0^2 + 2F_c^2)/3)$, GoF(all) = 1.14, $\Delta\rho_{min/max} = -0.43, 0.72\,eÅ^{-3}$.

The pendant propyl residue exhibits two orientations and the site occupancies were refined and then fixed at the first decimal place. The partially occupied sites were modelled with isotropic displacement parameters. The hydroxy hydrogen sites were located and modelled with isotropic displacement parameters.

Bis(dimethylglyoximato-N,N′) (pyridine-4-carboxamide-N)copper(II), 3

Crystal Data

$[(H_2N\ CO\ C_5H_4N)Cu(dmg)_2]\ (H_2NCO\ C_5H_4N)_{0.5}\ 3H_2O \equiv C_{17}H_{29}CuN_7O_{8.5}$, $M = 531.0$. Orthorhombic, space group $Pnna$, (D_{2h}^6,No.52), $a = 16.798(1)$, $b = 26.606(2)$, $c = 10.455(3)$ Å, $V = 4673(1)$ Å^3. $D_c = 1.509\,g\,cm^{-3}$, $Z = 8$, $\mu_{Mo} = 0.99\,mm^{-1}$; crystal size: $0.42 \times 0.38 \times 0.28$ mm; $'T''_{min/max} = 0.44$. $2\theta_{max} = 50^\circ$; $N_t = 12732$, $N_{ind} = 4105(R_{merge} = 0.047)$, $N_{obs}(F > 4\sigma(F)) = 2859$; $R = 0.087$, $R_w = 0.098$ (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$), $N_{var} = 313$,$\Delta\rho_{min/max} = -0.82$, $1.25\,eÅ^{-3}$.

The relatively good merging statistics for the data are a foil for 'difficult' material with respect to both data acquisition and, subsequently, the modelling and refinement of the structure. The complex molecules pack in layers, with the $(dmg)_2$ bases of the square pyramidal arrays comprising planes quasi-normal to b, which confront similar layers across $y = 0.25$. The pendants interleave about $y = 0$; despite a considerable presumed propensity for hydrogen bonding, they mesh with a disorderly uncoordinated ligand/solvent water array, the ligand modelled in terms of a pair of superimposed components disordered about a crystallographic inversion centre (isotropic displacement parameter forms).

Bis[(μ_2-(O)-dimethylglyoximato) (dimethylglyoximato)copper(II)], 4

Crystal Data

$[Cu_2(dmg)_4] \equiv C_{16}H_{28}Cu_2N_8O_8$, $M = 587.5$. Monoclinic, space group $P2_1/n$ (#14), $a = 9.7352(9)$, $b = 16.978(2)$, $c = 7.0921(6)$ Å, $\beta = 108.552(1)^\circ$, $V = 1111.3(3)$Å^3. $D_c = 1.756\,g\,cm^{-3}$, $Z = 2$ dimers, $\mu_{Mo} = 1.98\,mm^{-1}$; crystal size: $0.65 \times 0.24 \times 0.10$ mm; $'T''_{min/max} = 0.68$. $2\theta_{max} = 58^\circ$; $N = 10834$, $N_{ind} = 2795(R_{merge} = 0.026)$, $N_{obs}(F > 4\sigma(F)) = 2571$; $R = 0.025$, $R_w = 0.034$ (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$), $N_{var} = 210$, $\Delta\rho_{min/max} = -0.41, 0.46\,eÅ^{-3}$.

The cell and coordinate settings follow those of a previous film determination [10], and $(x, y, z, U_{iso})_H$ were refined.

TABLE II Hydrogen-bond geometries for complexes **1–3**

Complex	Donor	Hydrogen	Acceptor	D–H (Å)	H–A (Å)	D–A (Å)	∠DHA (°)
1	O(12)	H(12O)	O(21)	0.82	1.79	2.574(2)	160
	O(22)	H(22O)	O(11)	0.82	1.76	2.542(2)	160
2	O(12)	H(12O)	O(21)	0.84	1.77	2.6045(16)	172
	O(22)	H(22O)	O(11)	0.90	1.66	2.5554(19)	170
	O(43)	H(43O)	O(21)[a]	0.78	1.95	2.7262(17)	175
3	O(12)	H(12)	O(21)	0.96	1.64	2.576(9)	172
	O(22)	H(22)	O(11)	1.06	1.48	2.545(8)	174
	N(41)	H(41a)	O(22)[b]	0.86	2.31	3.080(8)	149

[a] $x - 1/2, y - 1/2, z$ [b] $-x, -y, -z$.

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RESULTS AND DISCUSSION

It was not expected that **1** would show an extended supramolecular structure. And indeed, the individual complex molecules, in which the copper environments are square pyramidal with the copper lying 0.3287(9)Å out of the ligand nitrogen plane, are essentially discrete in the crystal, the only intermolecular interaction being a short contact between the aromatic hydrogens of the phenylpyridine ligand on one complex and the pseudo-macrocyclic oxygens on two neighbouring complexes (Fig. 4). With respect to this interaction it is also interesting that the C(5)–C(4)–C(41)–C(46) torsion angle is just −7.00(26)°, which is very low compared with those found for 4-phenyl pyridine in the CSD, the large majority of which lie in the range 20–40°; in fact, only two examples have a smaller torsion angle (QIJVEK and ZUHVEF) [21, 22].

The complexes in **2** are also square pyramidal with the copper lying 0.2837(6)Å out of the plane of the four dimethylglyoximato nitrogen atoms, N(11), N(12), N(21), N(22). The complexes are linked into chains by OH…O hydrogen bonds between the alcohol functional group, O(43) and O(21), the latter being one of the deprotonated oxygen atoms of the pseudo-macrocycle. The OH group lies on the same side of the acceptor pseudo-macrocyclic ring as the fifth ligand. Each square pyramid in one chain is paired with another square pyramid, base-to-base, rotated through approximately 90°and slightly offset (Fig. 5). (This pairing is not possible in GLIMCV [6] because the hydrogen-bond donor is on the opposite side of the acceptor pseudo-macrocyclic ring to the imidazole of the acceptor complex.) Each of these paired complexes forms part of another hydrogen-bonded chain running across the first, forming a 'cross-hatched' layer, which lies quasi-normal to *c* (Fig. 6).

A number of supramolecular structures incorporating complexes of isonicotinamide have been reported, with the complexes differing in the metal ion present, the number of isonicotinamide ligands used, and the arrangement of the isonicotinamide ligands around the metal ion [23–27]. Several hydrogen-bond patterns in which carboxamide donors and acceptors have been directly linked have also been observed: C(4), $R_2^2(8)$, $R_4^4(16)$ and $R_2^2(28)$. In other cases, intervening solvent molecules and/or anions have linked the carboxamide groups and more than one pattern may be observed in a single crystal. Only in one case has a neutral complex been reported to form such an arrangement, and in this case the crystals contain carboxamide groups linked into C(4) chains [23]. One example of a 3D network containing guest isonicotinamide molecules in large square channels has been observed [26]; however, in no case has the structure of a complex incorporating just one isonicotinamide ligand been reported.

The individual complexes in structure **3** are square pyramidal with the copper lying 0.3058(22)Å out of the least-squares N(11), N(12), N(21), N(22) plane.

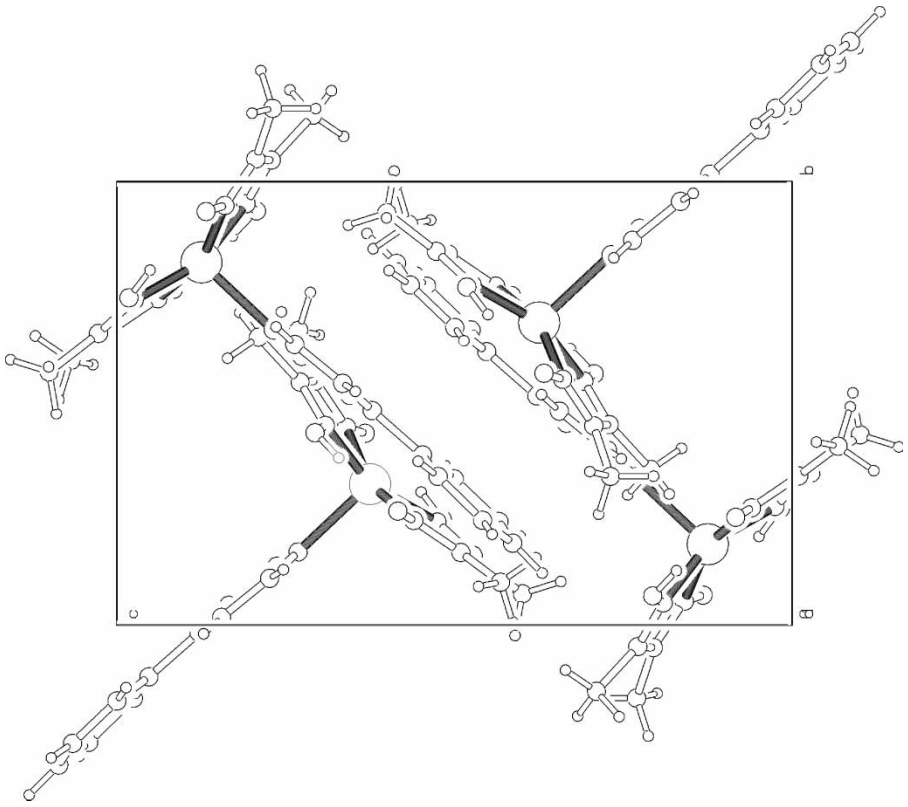

FIGURE 4 Unit cell of **1** viewed down the *a* axis of the unit cell.

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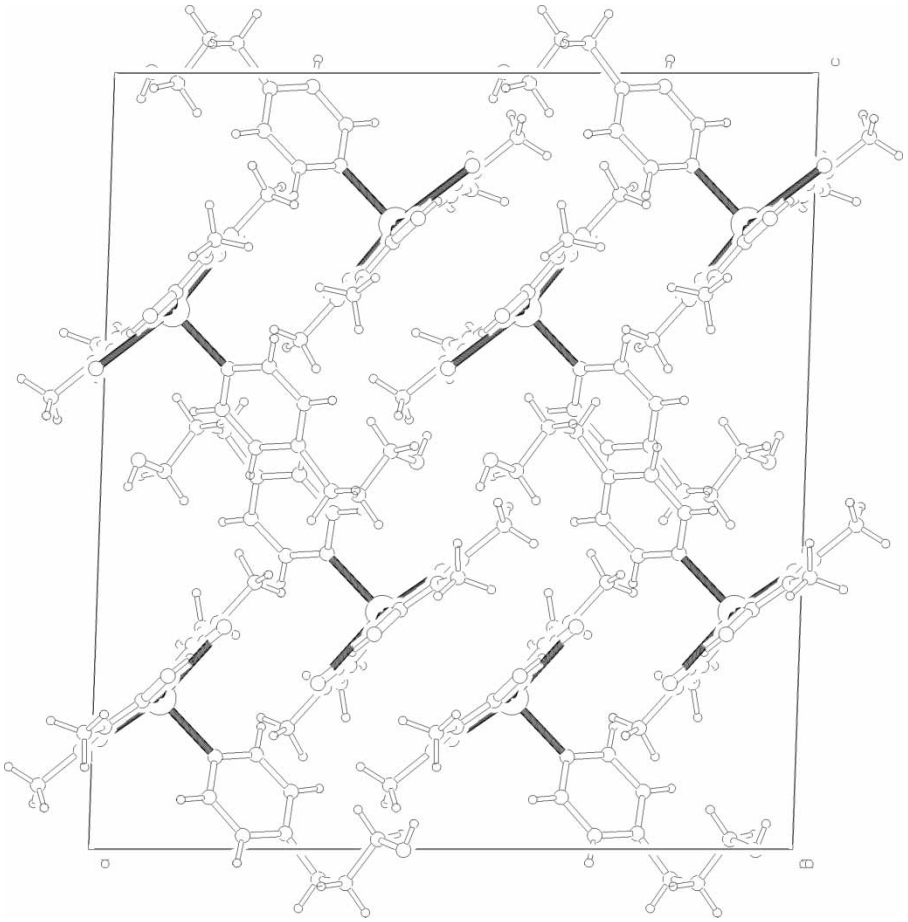

FIGURE 5 Unit cell of **2** viewed down the *b* axis of the unit cell.

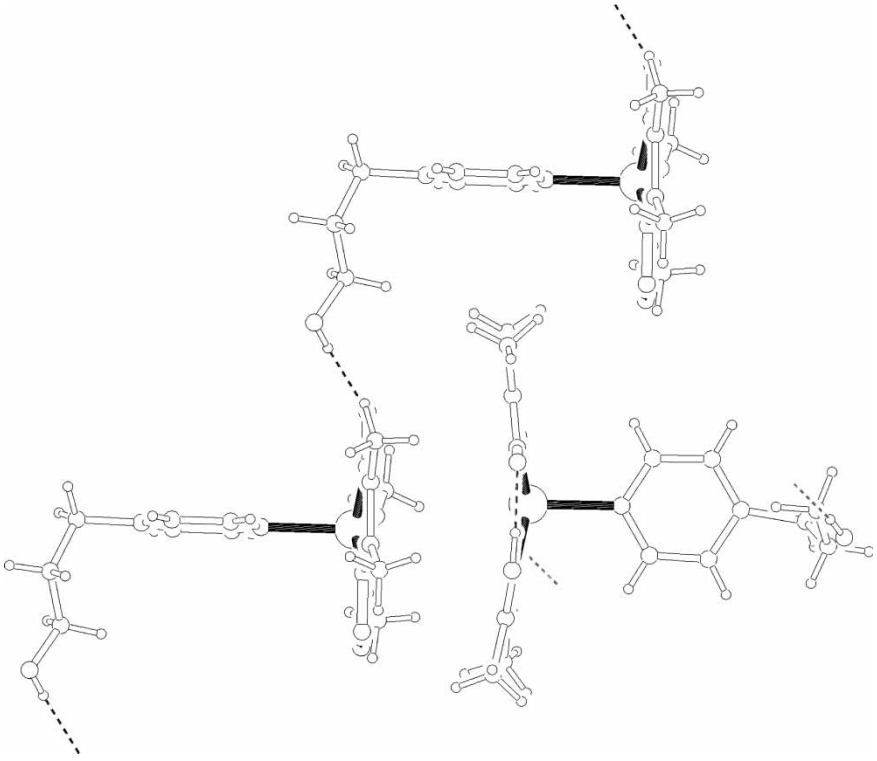

FIGURE 6 A Platon depiction of the hydrogen bonding in **2** (disorder is not shown).

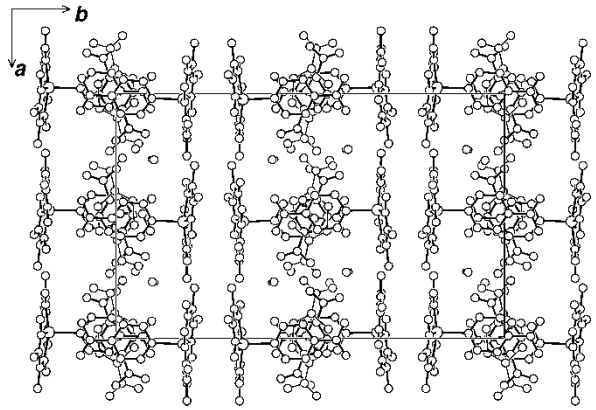

FIGURE 7 View of the hydrogen-bonded network of **3** showing the zigzag chains lined by square pyramidal complex molecules running quasi-parallel to the *a* axis and giving rise to adjacent channels.

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The isonicotinamide ligands in **3** are not linked directly by hydrogen bonding, but the complexes are linked in centrosymmetric pairs by hydrogen bonds between a carboxamide NH and O(22), a protonated oxygen in the pseudo-macrocycle. This hydrogen bond is rather long, with the donor to acceptor distance being 3.080(8)Å. The two deprotonated oxygens, O(11) and O(21), act as hydrogen-bond acceptors from water molecules, forming a complex hydrogen-bonded network that both links the two parts of the dimer and joins it to neighbouring dimers. Two water molecules form a chain connecting the two parts of each dimer. The result of this hydrogen-bond network is that zigzag chains are formed that run quasi-parallel to the *a* axis (Fig. 7). The bases of the adjacent square pyramids are rotated by approximately 90° with respect to one another. The chains lie side by side in planes quasi-normal to the *b* axis, and between adjacent chains in these planes lie channels lined with water molecules and isonicotinamide ligands. Within these channels lie disordered isonicotinamide guest molecules, the pyridine rings of which are positioned between the aromatic rings of the ligand isonicotinamide in an offset π-facial arrangement. The layers are stacked in the direction of the *b* axis, with the chains offset from one layer to the next so that the square planar copper complexes are arranged base-to-base in a manner similar to **2**.

There are clearly no direct interactions between neighbouring chains (although the guest molecules may provide them within an intermediate layer) and the size of the channel appears to depend on the size of the pendant groups on the pseudo-macrocyclic rings, which may provide an opportunity for 'tuning' the size of the channel.

CONCLUSIONS

We have reported here the incorporation of a pseudo-macrocyclic copper(II) complex into supramolecular arrays in crystals. The complexes are five-coordinate and the arrays are formed not by hydrogen bonding between donor and acceptor groups on the pseudo-macrocycles but by hydrogen bonding between a donor on the ligand in the fifth coordination site and an acceptor on the pseudo-macrocycle. The complex molecules pack with the bis-dimethylgloximato ligands of the square pyramidal arrays stacked face to face but rotated approximately 90° with respect to one another. In one case layers are formed by hydrogen-bonded chains. In another, a complicated structure formed, with the complexes arranged in layers. The crystals were found to contain hydrogen-bonded water molecules and channels in which disordered molecules of the uncoordinated heterocyclic base were trapped.

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