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FULL PAPER

A comparative investigation of supramolecular structures involving copper(II) complexes of imidazolinylalkanimidamides

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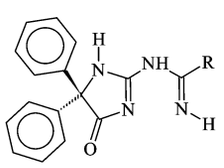
Received 18th July 2002, Accepted 18th September 2002
First published as an Advance Article on the web 24th October 2002

The syntheses of three new copper(II) complexes based on the bidentate ligand *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)ethanimidamide are reported. In the solid state these products assemble into elaborate supramolecular structures featuring hydrogen bonds within, and between, complexes as well as weak aryl–aryl and alkyl–aryl interactions between complexes; different coordination geometries and tautomeric forms are also observed. Dimethyl sulfoxide molecules show a variety of interactions within the structures, including coordination to the copper, hydrogen bonding, as well as weak alkyl–aryl interactions with the ligands.

Introduction

In earlier papers we have described the incorporation of a number of transition metal complexes into supramolecular arrays using complementary hydrogen bonding motifs.[1–3] In these arrays the complexes occur in three-component subunits, or in chains, which then interact further by hydrogen bonding to form more elaborate structures.

In this paper we report an extension of these studies involving the synthesis and crystallographic analysis of solids incorporating complexes of the bidentate ligands *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)ethanimidamide, **1**, and *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)propanimidamide, **2**.



1 R = Me,
2 R = Et

Our interest in the above alkanimidamido ligands stems from the fact that they possess a self-complementary doublet hydrogen bonding motif, which gives them the potential to form chains in the solid state. They differ from the 2-guanidinobenzimidazole ligand previously used by us[1,2] in two important respects. Namely, once chains of bis(ligand) complexes form there is no longer the possibility of other hydrogen bonds occurring between neighbouring complexes since all other hydrogen bond donor or acceptor groups have either been removed or are utilised in forming intra-complex hydrogen bonds. In addition, the presence of pendant phenyl groups adds a three-dimensional character to the ligands, which opens up the possibility of forming local environments within the crystal that involve weakly polar interactions. Although such interactions may be weak, experience shows that they should not be ignored in crystal engineering since, they may be responsible for the difference between two otherwise similar structures. Further, they may control molecular aggregation (and thus, which of the possible multiple polymorphic forms will be observed) or they may even be the only stabilising interactions apart from van der Waals' forces.[4]

Weakly polar interactions have long been of interest in biochemistry and their occurrence in the interior of globular proteins has received a good deal of attention. One reason for this interest is that, even though they are weak, they may contribute from around −4 to −10.5 kJ mol^{-1} to the corresponding free energy of stabilisation and they can frequently determine the adoption of a particular structure. For example, a change in the stabilisation energy of just −4 to −8 kJ mol^{-1} is enough to convert a mesophilic protein into a thermophilic one.[5] Aromatic interactions, offset face-to-face stacking and edge-to-face interactions, also fall into the category of weak interactions and have been investigated over many years;[6–8] π–π interactions may vary considerably in geometry and the clustering of aromatic rings may make a significant contribution to overall stability.[9] Their role in molecular recognition, and more generally in supramolecular chemistry, has now been widely examined.[10,11] An electrostatic model for such interactions has been described.[12]

Aromatic rings have now been well documented to act as hydrogen bond acceptors.[10] This was predicted on the basis of a simple electrostatic model[12] and the possibility that aromatic rings might interact with alkyl groups in a similar way was raised by Levitt and Perutz[13] who estimated a likely interaction energy of about 4 kJ mol^{-1}.

The strengths of aromatic–alkyl (and aromatic–aryl) interactions in particular small molecules have been investigated experimentally by means of a 'molecular torsion balance'; in these studies it was demonstrated that cyclohexyl, phenyl and *tert*-butyl groups all showed similar affinities for the face of an aromatic ring, affecting conformational energies by about 2 kJ mol^{-1} at 298 K.[14]

Experimental

2-Amino-5,5-diphenylimidazolin-4-one, 3

To sodium hydroxide (0.834 g, 21 mmol) in absolute ethanol (50 mL) was added guanidine hydrochloride (2.097 g, 22 mmol) in absolute ethanol (50 mL) and the mixture was heated under reflux. After 2 h a white precipitate of NaCl was filtered from the hot solution. The filtrate was reheated to boiling and a solution of benzil (2.190 g, 10.4 mmol) in absolute ethanol (50 mL) was added dropwise over a period of 2 h. Heating was continued for 1 h after which the microcrystalline product that formed was filtered off, washed with cold ethanol (2 × 5 mL)

 DOI: 10.1039/b207031f

followed by diethyl ether (2 × 5 mL), and air dried. The white product was recrystallised from ethanol. Yield 1.539g (30%), mp 360–363 °C. IR 3353, 1659, 1495, 1268, 754, 698 cm^{-1} (Found: C, 71.93; H, 5.27; N, 16.91. Calc. for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72%).

[(Dimethyl sulfoxide)bis(*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)ethanimidamido)copper(II)], 4

Anhydrous copper(II) chloride (0.048 g, 0.36 mmol) was dissolved in acetonitrile (50 mL) and **1** (0.208 g, 0.83 mmol) was added. The mixture was refluxed for 2 h after which the solution had become light green; a few drops of a saturated KOH solution in ethanol were added until a pink precipitate began to form. When precipitation was complete the solid was filtered off, washed with acetonitrile (2 × 5 mL) followed by diethyl ether (2 × 5 mL), and air-dried. The product was obtained as a pink powder (0.028 g). This pink solid was dissolved in DMSO, a little ethanol was added and the mixture set aside until crystals formed. IR 3245, 3064, 1702, 1597, 1215, 695 cm^{-1} (Found: C, 59.25; H, 5.03; N 15.35. Calc. for $C_{36}H_{36}CuN_8O_3S$: C, 59.68; H, 5.02; N, 15.47%).

[Bis(*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)propanimidamido)copper(II)]·0.5H_2O, 5·0.5H_2O

Anhydrous copper(II) bromide (0.269 g, 1.2 mmol) was dissolved in propionitrile (70 mL) and solid **1** (0.564 g, 2.1 mmol) was added slowly to the solution. The resulting mixture was refluxed for an hour and left to stand at room temperature overnight after which a solution of KOH (0.135 g, 2.4 mmol) in methanol (5 mL) was added. The mixture was filtered and allowed to stand. The product formed as red crystals; yield 0.120 g (Found: C, 63.10; H, 5.06; N, 16.49. Calc. for $C_{36}H_{35}CuN_8O_{2.5}$: C, 63.29; H, 5.13; N, 16.41%).

[Bis(*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)propanimidamido)copper(II)]·1.75DMSO, 6·1.75DMSO

The copper complex **5** (0.020 g) was dissolved in dimethyl sulfoxide (3 mL) and the solution was warmed to 50 °C. Dark purple crystals containing solvent formed on allowing the solution to stand. The crystals turned to powder immediately if washed with alcohol and lost solvent slowly on removal from the growth solution (Found: C, 58.61; H, 5.55; N, 13.80. Calc. for $C_{39.5}H_{44.5}CuN_8O_{3.75}S_{1.75}$: C, 58.50; H, 5.49; N, 13.82%).

X-Ray structure determinations

Single crystal diffraction data were collected using ω scans to 56° 2θ, with a Bruker SMART 1000 CCD diffractometer employing graphite monochromated MoKα radiation generated from a sealed tube. Crystals were cooled with an Oxford Cryosystems Cryostream. In each case there was no significant change in the intensities of a set of reflections recollected at the end of the data collection. The data integration and reduction were undertaken with SAINT and XPREP,[15] and subsequent computations were carried out with the teXsan,[16] WinGX[17] and XTAL[18] graphical user interfaces. A Gaussian absorption correction[15,19] was applied to the data, and a subsequent empirical correction determined with SADABS[20] was also applied to the data for **4**. The structure for **4** was obtained using SHELXS97[21] and the structures of **5** and **6** were determined with SIR97.[22] The structures were extended and refined with SHELXL97.[21] ORTEP[23] depictions of the molecules with 20% displacement ellipsoids are provided in Figs. 1, 4 and 6; pertinent geometry details are given in Tables 1, 3 and 4.

[(Dimethyl sulfoxide)bis(*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)ethanimidamido)copper(II)], 4. The asymmetric unit contains the complex molecule with a weakly coordinated and slightly disordered DMSO molecule. The

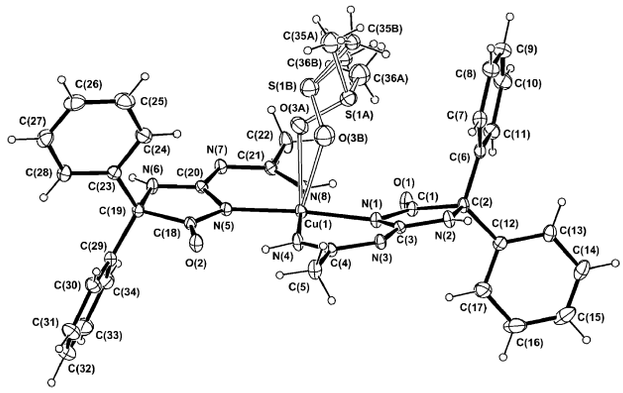


Fig. 1 An ORTEP[23] depiction of complex **4** with 20% displacement ellipsoids.

Table 1 Pertinent geometry details for **4**

Cu(1)–N(4)	1.919(2)	Cu(1)–N(8)	1.928(2)
Cu(1)–N(5)	2.034(2)	Cu(1)–N(1)	2.049(2)
Cu(1)–O(3B)	2.342(18)	Cu(1)–O(3A)	2.409(3)
O(1)–C(1)	1.225(3)	O(2)–C(18)	1.225(3)
N(1)–C(1)	1.367(3)	N(1)–C(3)	1.376(3)
N(2)–C(3)	1.349(3)	N(2)–C(2)	1.459(3)
N(3)–C(3)	1.330(3)	N(3)–C(4)	1.366(3)
N(4)–C(4)	1.283(3)	N(5)–C(18)	1.375(3)
N(5)–C(20)	1.379(3)	N(6)–C(20)	1.339(3)
N(6)–C(19)	1.454(3)	N(7)–C(20)	1.335(3)
N(7)–C(21)	1.368(3)	N(8)–C(21)	1.283(3)
N(4)–Cu(1)–N(8)	173.37(10)	N(5)–Cu(1)–N(1)	175.07(8)
N(4)–Cu(1)–N(5)	93.18(9)	N(4)–Cu(1)–O(3A)	98.44(12)
N(8)–Cu(1)–N(5)	86.35(9)	N(8)–Cu(1)–O(3A)	88.16(11)
N(4)–Cu(1)–N(1)	85.76(9)	N(5)–Cu(1)–O(3A)	88.87(10)
N(8)–Cu(1)–N(1)	94.14(9)	N(1)–Cu(1)–O(3A)	96.06(11)

DMSO solvate molecule exhibits sp^3 inversion disorder, with an occupancy of 0.8 for the S(1A) containing conformer, and a complementary occupancy of 0.2 for the S(1B) conformer. The occupancies were refined and then fixed. In general the non-hydrogen atoms were modelled with anisotropic thermal parameters and a riding atom model was used for the hydrogen atoms. The partially occupied non-hydrogen sites were modelled with isotropic displacement parameters, except for S(1A) and O(3A) which were treated anisotropically. The nitrogen bound hydrogen atoms were located and modelled with isotropic displacement parameters; distance restraints were required for the N(3) and N(7) hydrogens. Formula $C_{36}H_{36}CuN_8O_3S$, M 724.33, monoclinic, space group $C2/c$ (no. 15), a 11.3898(15), b 14.843(2), c 40.196(5) Å, β 95.298(2)°, V 6766.4(16) Å^3, D_c 1.422 g cm^{-3}, Z 8, crystal size 0.213 by 0.137 by 0.022 mm, colour purple, habit plate, temperature 294(2) K, λ(MoKα) 0.71073 Å, μ(MoKα) 0.757 mm^{-1}, T(Gaussian and SADABS)$_{min,max}$ 0.896, 0.983, $2\theta_{max}$ 56.62, hkl range −15 15, 0 19, −51 52, N 35758, N_{ind} 8107(R_{merge} 0.0590), N_{obs} 5341($I > 2\sigma(I)$), N_{var} 470, residuals $R1(F)$ 0.0492, $wR2(F^2)$ 0.1201, GoF(all) 1.261, $\Delta\rho_{min,max}$ −0.389, 0.537 e Å^{-3}. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections, $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 2.0P]$ and $P = (F_o^2 + 2F_c^2)/3$.

[Bis(*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-propanimidamido)copper(II)], 5. The asymmetric unit contains three crystallographically independent complex molecules, two of which are centred on inversion sites. The non-hydrogen atoms were modelled with anisotropic displacement parameters, and in general a riding atom model was used for the hydrogen atoms. The H(3N), H(4N), H(6N), H(8N), H(10N) and H(14N) hydrogen sites were located and modelled with isotropic displacement parameters. Formula $C_{36}H_{34}CuN_8O_2$,

M 674.25, monoclinic, space group $P2_1/n$ (no. 14), *a* 13.184(3), *b* 27.498(7), *c* 19.121(5) Å, *β* 108.662(4)°, *V* 6567(3) Å^3, D_c 1.364 g cm^{-3}, *Z* 8, crystal size 0.366 by 0.333 by 0.149 mm, colour purple, habit prism, temperature 150(2) K, *λ*(MoKα) 0.71073 Å, *μ*(MoKα) 0.711 mm^{-1}, T(Gaussian)$_{min,max}$ 0.788, 0.905, $2\theta_{max}$ 56.60, *hkl* range −16 16, −36 36, −25 25, *N* 57558, N_{ind} 15233(R_{merge} 0.0368), N_{obs} 10799($I > 2\sigma(I)$), N_{var} 878, residuals *R*1(*F*) 0.0375, *wR*2(F^2) 0.0869, GoF(all) 1.270, $\Delta\rho_{min,\ max}$ −0.434, 0.665 e Å^{-3}. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2)^{1/2}$ all reflections, $w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 7.2571P]$ where $P = (F_o^2 + 2F_c^2)/3$.

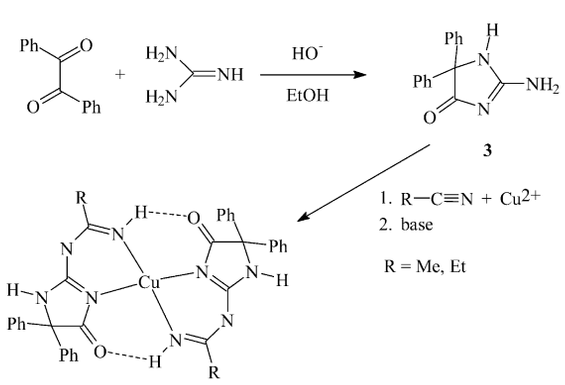
[Bis(*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)-propanimidamidocopper(II)]·2DMSO, 6·2DMSO. The asymmetric unit contains a complex molecule together with two dimethyl sulfoxide solvate molecules. One of the DMSO molecules is disordered about two sites, and on one of those sites the molecule has two partially occupied sulfur sites related by sp^3 inversion. The disordered DMSO site populations were refined and then fixed. The disordered DMSO molecule has hydrogen bond interactions with hydrogens bound to N(2) and N(3), and these hydrogen sites have corresponding occupancies of 0.25 and 0.75, respectively. The existence of the hydrogen at N(2) is inferred from the location of the DMSO oxygen O(5). The ordered DMSO molecule forms a hydrogen bond with H(6N). In general, the non-hydrogen atoms were modelled with anisotropic displacement parameters, and a riding atom model was used for the hydrogen atoms. Isotropic displacement parameters were used for the disordered S(3) sites, and the disordered carbon and oxygen sites. The N(3), N(4) N(6) and N(8) hydrogen atoms were located and modelled with isotropic displacement parameters. Formula $C_{40}H_{46}CuN_8O_4S_2$, *M* 830.51, triclinic, space group $P\bar{1}$ (no. 2), *a* 11.592(5), *b* 16.662(5), *c* 10.435(5) Å, *α* 93.233(5), *β* 94.704(5), *γ* 99.777(5)°, *V* 1974.4(14) Å^3, D_c 1.397 g cm^{-3}, *Z* 2, crystal size 0.290 by 0.058 by 0.058 mm, colour red, habit columnar, temperature 150(2) K, *λ*(MoKα) 0.71069 Å, *μ*(MoKα) 0.711 mm^{-1}, T(Gaussian)$_{min,\ max}$ 0.829, 0.965, $2\theta_{max}$ 56.58, *hkl* range −14 14, −21 21, −13 13, *N* 19578, N_{ind} 9136(R_{merge} 0.0446), N_{obs} 5806($I > 2\sigma(I)$), N_{var} 539, residuals *R*1(*F*) 0.0467, *wR*2(F^2) 0.0600, GoF(all) 1.192, $\Delta\rho_{min,\ max}$ −0.613, 0.943 e Å^{-3}. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2)^{1/2}$ all reflections, $w = 1/[\sigma^2(F_o^2)]$.

CCDC reference numbers 190103–190105.

See http://www.rsc.org/suppdata/dt/b2/b207031f/ for crystallographic data in CIF or other electronic format.

Results and discussion

The synthesis of **3** and the subsequent template synthesis of **4** are outlined in Scheme 1. The formation of **3** involves a benzilic acid rearrangement[24] that parallels the well-known rearrangement of this type that occurs when urea reacts with benzil.[25,26] Our result corresponds to that reported elsewhere,[27] and follows another closely related condensation,[28] but it is noted that it differs from further reports of the same condensation.[29] The template synthesis of **4** involved the addition of the amine functionality across a nitrile triple bond. Although vigorous conditions are often employed for such reactions, they have also been reported to occur under mild conditions in the presence of a copper(I) catalyst.[30] Given the present reaction conditions, the assistance of copper(I) in catalysing the reaction cannot be ruled out.



Scheme 1

The crystal structure of **4** is depicted in Figs. 1–3, and selected geometry details are provided in Table 1. The copper(II) ion has a square pyramidal coordination geometry, with minor disorder associated with sp^3 inversion at the sulfur atom. The axial ligand Cu(1)–O(3A) bond length (2.409(3) Å) is similar to that found in $[Cu(NH_3)_4(OH_2)]SO_4$.[31] The base of the pyramid is formed by the donor nitrogen atoms of the two bidentate ligands of type **1**. These bidentate ligands are connected *via* two N–H ··· O hydrogen bonds resulting in the formation of a 16-membered pseudo-macrocyclic ring (Fig. 2 and Table 2(a)).

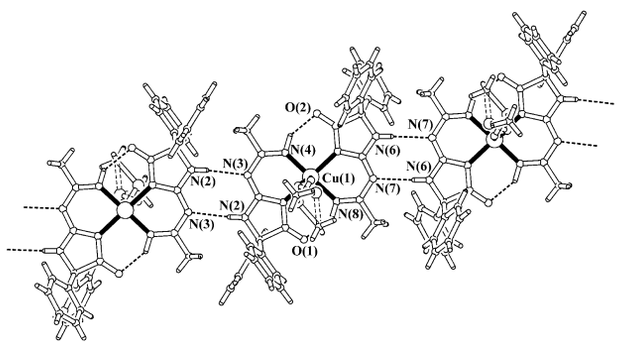


Fig. 2 A PLATON[37] depiction of the hydrogen bond linked chains in complex **4**.

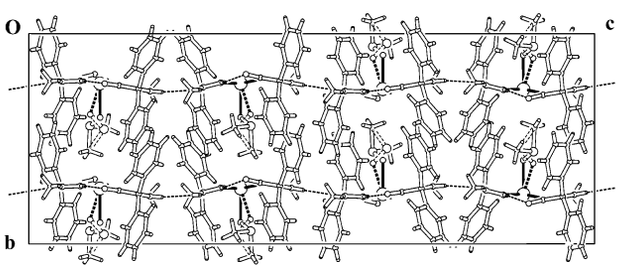


Fig. 3 A PLATON[37] view of the unit cell of **4** projected down the *a*-axis. Slightly undulating chains or ribbons of hydrogen bond linked complexes run across the (0,4,0) planes at an angle of approximately 30° to the *c*-axis. The amplitude of the undulation is approximately 0.03 Å.

Adjacent complexes are linked by hydrogen bonds between opposing amine acceptor and imidazole nitrogen donor atoms to form centrosymmetric planar $R_2^2(8)$ hydrogen bonded rings (Fig. 2); the graph set notation[32] describes an eight membered ring, with two donors (subscript) and two acceptors (superscript). There are then slightly undulating chains or ribbons of complexes running across the (0,4,0) planes at an angle of approximately 30° to the *c*-axis (Fig. 3); there is no hydrogen bonding between the chains. The axial ligand of a complex in the (0,0.25,0) plane is accommodated in pockets defined by the phenyl residues of the complex and the phenyl residues of two complexes in the (0,0.75,0) plane. The disposition of the axial ligand is such that one dimethyl sulfoxide (DMSO) methyl group (C36) is approximately 3.74 Å from the centroid of the C(6)–C(11) residue within the same complex, while the other (C(35)) is approximately 3.38 Å from the centroid of the C(12)–C(17) phenyl ring of a complex in a neighbouring chain. The simple electrostatic model[13] for the methyl–phenyl interaction predicts that the interaction energy lies below room temperature thermal energy (*RT*) when the carbon atom of the methyl

Table 2 Hydrogen bond geometries within the structures of **4**–**6**

D–H ··· A	D–H/Å	H ··· A/Å	D ··· A/Å	DHA D–H ··· A/°
(a) **4**				
N(4)–H(4N) ··· O(2)	0.95(3)	1.89(3)	2.378(3)	146(3)
N(2)–H(2N) ··· N(3[a])	0.834(17)	2.279(18)	3.110(3)	175(3)
N(8)–H(8N) ··· O(1)	0.85(3)	2.07(3)	2.803(3)	145(2)
N(6)–H(6N) ··· N(7[b])	0.822(17)	2.221(18)	3.039(3)	173(3)
(b) **5**				
N(4)–H(4N) ··· O(2)	0.79(2)	2.12(2)	2.800(2)	144(2)
N(2)–H(3N) ··· N(7[c])	0.83(2)	2.14(2)	2.971(2)	178(2)
N(8)–H(8N) ··· O(1)	0.801(14)	2.306(19)	2.866(2)	127.6(19)
N(6)–H(6N) ··· N(3[d])	0.83(2)	2.09(2)	2.908(2)	170.6(19)
N(10)–H(10N) ··· N(15)	0.789(18)	2.141(19)	2.927(2)	174.5(18)
N(12)–H(12N) ··· O(3[e])	0.88	2.01	2.787(2)	146.1
N(14)–H(14N) ··· N(11)	0.800(18)	2.122(19)	2.916(2)	171.7(19)
N(16)–H(16N) ··· O(4[f])	0.88	2.04	2.807(2)	145.4
(c) **6**				
N(2)–H(2N) ··· O(5)	0.88	2.02	2.794(9)	146.8
N(3)–H(3N) ··· O(4)	0.88(3)	1.93(3)	2.803(3)	172(3)
N(4)–H(4N) ··· O(2)	0.81(2)	2.01(2)	2.757(3)	153(2)
N(6)–H(6N) ··· O(3)	0.881(18)	1.940(19)	2.807(3)	167.6(19)
N(8)–H(8N) ··· O(1)	0.82(2)	2.05(2)	2.807(3)	152(2)

Symmetry codes: [a] $-x + 1/2, -y + 1/2, -z$. [b] $1 - x, y, -z + 1/2$. [c] $x - 1/2, 1/2 - y, z - 1/2$. [d] $1/2 + x, 1/2 - y, 1/2 + z$. [e] $-x, 1 - y, -z$. [f] $1 - x, 1 - y, 1 - z$.

group lies between 3.6 and 4.4 Å from the centroid of the aromatic ring (methyl C to aromatic C distances 3.9 and 4.6 Å).

A search of the Cambridge Structure Database[33] for DMSO methyl to phenyl contacts yielded 48 examples of such intermolecular contacts from 79 structures that contain both DMSO and phenyl groups. (The search was restricted to C(methyl) to aromatic centroid distances that lie between 3.0 and 4.5 Å, with the angle between the C(methyl) to centroid vector and the normal to the aromatic plane being restricted to lie between 0 and 30°.) Forty of the forty-eight examples had distances in the range 3.5–4.0 Å with the shortest contact being 3.47 Å.[34]

The phenyl groups project above and below the plane of the macrocycle and form a herringbone offset edge-to-face pattern. The angles between the rings and the offsets between centroids are consistent with attractive interactions in this crystal.[6,9]

Complexes **5** and **6** utilise the bidentate ligand **2**. The crystal structure of **5** contains three crystallographically independent complexes for which numbered depictions are provided in Fig. 4(a–c) and geometric details are listed in Table 3. The ligand ethyl groups lie approximately in the plane of each ligand and the terminal methyl groups of these residues have a *syn* conformation with respect to the coordinated imino groups.

The two complexes incorporating Cu(2) and Cu(3) are square planar, with the metal ions residing on crystallographic inversion centres. The complex containing Cu(1) has a significant tetrahedral distortion from square planar geometry, and the two ligand planes (the least squares planes of the five ligand atoms in the metallarings) form a dihedral angle of 26.21(7)°. The copper ion in this complex is essentially located in the ligand least squares plane defined by N(5), C(21), N(7), C(22), and N(6), but is 0.375(2) Å from the least squares plane defined by N(1), C(3), N(3), C(4) and N(4).

The distortion from square planar coordination does not prevent the formation of the hydrogen-bonded, pseudo-macrocycle in **5**. As in **4**, complementary $R_2^2(8)$ hydrogen bond patterns are present between neighbouring complexes; however the rings are considerably twisted in **5** (Fig. 5). Although the two hydrogen bonds are linear, they are far from being co-planar. It is interesting to note that if the methyl group had an *anti* disposition (pointing towards the neighbouring complex instead of away from it), then steric hindrance would prevent the hydrogen bond interaction. A related example of a twisted hydrogen-bonded ring, perhaps reflecting steric interactions, occurs in the dimeric structure of *N,N′*-bis(2,6-diisopropylphenyl)acetamidine.[35]

Table 3 Pertinent geometry details for **5**

Cu(1)–(4)	1.9257(18)	Cu(1)–N(8)	1.9323(18)
Cu(1)–(1)	1.9804(16)	Cu(1)–N(5)	1.9835(15)
N(1)–C(3)	1.372(2)	N(1)–C(1)	1.378(2)
N(2)–C(3)	1.346(2)	N(2)–C(2)	1.460(2)
N(3)–C(3)	1.325(2)	N(3)–C(4)	1.367(2)
N(4)–C(4)	1.290(2)	N(5)–C(21)	1.378(2)
N(5)–C(19)	1.378(2)	N(6)–C(21)	1.337(2)
N(6)–C(20)	1.449(2)	N(7)–C(21)	1.330(2)
N(7)–C(22)	1.362(2)	N(8)–C(22)	1.291(2)
Cu(2)–N(12)	1.9163(16)	Cu(2)–N(9)	2.0279(15)
N(9)–C(37)	1.388(2)	N(9)–C(39)	1.378(2)
N(10)–C(38)	1.454(2)	N(10)–C(39)	1.343(2)
N(11)–C(39)	1.327(2)	N(11)–C(40)	1.362(2)
N(12)–C(40)	1.292(2)		
Cu(3)–N(16)	1.9247(16)	Cu(3)–N(13)	2.0447(15)
N(13)–C(55)	1.378(2)	N(13)–C(57)	1.378(2)
N(14)–C(57)	1.341(2)	N(14)–C(56)	1.451(2)
N(15)–C(57)	1.325(2)	N(15)–C(58)	1.362(2)
N(16)–C(58)	1.293(2)		
N(4)–Cu(1)–N(8)	160.72(8)	N(8)–Cu(1)–N(5)	87.84(7)
N(4)–Cu(1)–N(1)	87.18(7)	N(1)–Cu(1)–N(5)	169.37(6)
N(8)–Cu(1)–N(1)	93.59(7)	N(9)–Cu(2)–N(12)	87.66(6)
N(4)–Cu(1)–N(5)	94.95(7)	N(13)–Cu(3)–N(16)	87.64(6)

As in the structure of **4**, the hydrogen bonds link the complexes in **5** into chains, however this time there are two distinct chains present (Fig. 5). Linked complexes incorporating Cu(1) comprise one chain, while the second chain has alternating Cu(2)- and Cu(3)-containing complexes. The two twisted crystallographically independent chains are quasi-parallel to one another, and the pendant phenyl groups that project from the chains are tightly interlocked.

Red crystals of **5** dissolve in DMSO and the dark purple crystals of **6** isolated from this solution contain two DMSO molecules per complex molecule (Fig. 6, Table 4). In contrast to **4**, there is no axial DMSO coordinated to the copper, which has essentially square planar coordination geometry, with the *trans* N–Cu–N angles being 179.27(10) and 178.89(9)° respectively.

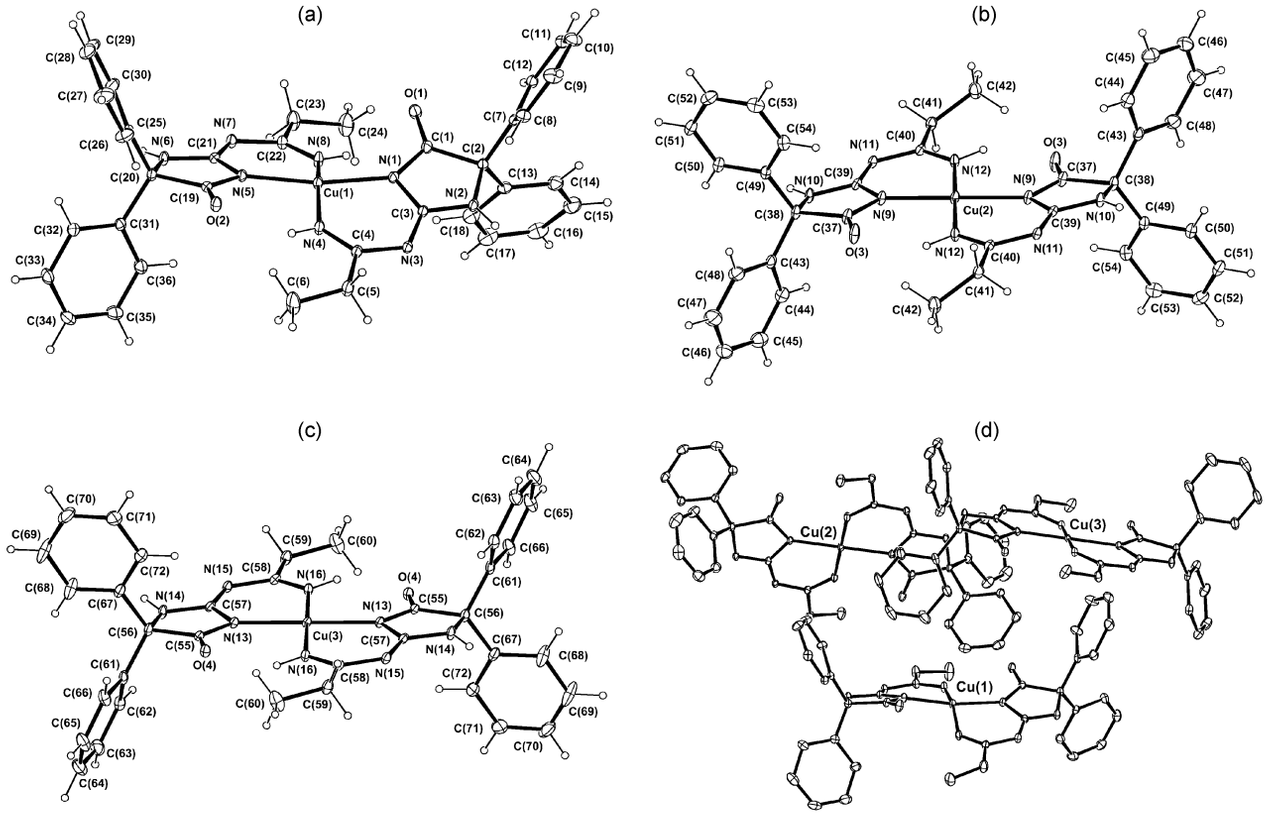


Fig. 4 ORTEP[23] depictions with 20% displacement ellipsoids of the three crystallographically independent complexes in **5**; individually (a–c) and their positions with respect to one another (d).

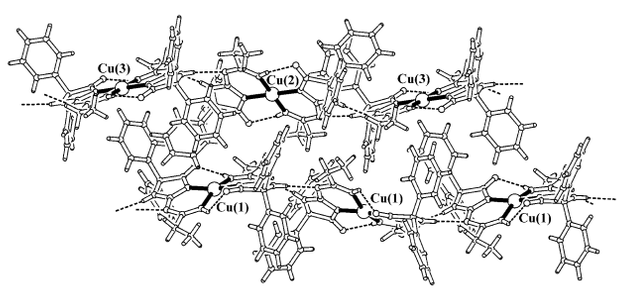


Fig. 5 A PLATON[37] depiction of the two independent chains of complexes in the crystal structure of **5**. The twisted chains have 'interlocking' pendant phenyl groups.

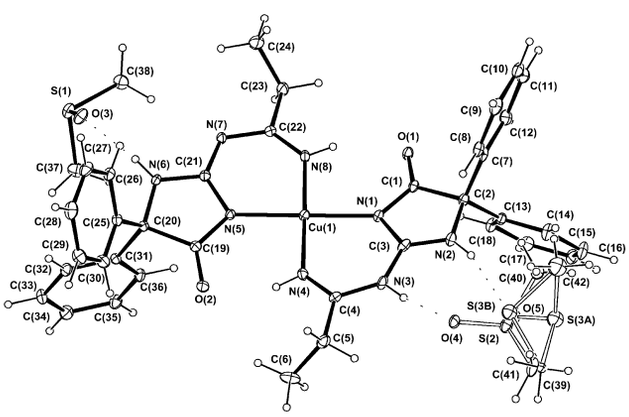


Fig. 6 An ORTEP[23] depiction of complex **6** with 20% displacement ellipsoids.

Again the two bidentate ligands are connected by hydrogen bonds to form a sixteen-membered pseudo-macrocycle, with the DMSO molecules being hydrogen bonded to the ligand

Table 4 Pertinent geometry details for **6**

Cu(1)–N(8)	1.921(2)	Cu(1)–N(4)	1.928(2)
Cu(1)–N(5)	2.0275(19)	Cu(1)–N(1)	2.0303(19)
N(1)–C(1)	1.364(3)	N(1)–C(3)	1.393(3)
N(2)–C(3)	1.296(3)	N(2)–C(2)	1.464(3)
N(3)–C(4)	1.349(3)	N(3)–C(3)	1.370(3)
N(4)–C(4)	1.287(3)	N(5)–C(19)	1.367(3)
N(5)–C(21)	1.388(3)	N(6)–C(21)	1.342(3)
N(6)–C(20)	1.447(3)	N(7)–C(21)	1.321(3)
N(7)–C(22)	1.357(3)	N(8)–C(22)	1.293(3)
N(1)–Cu(1)–N(8)	93.23(9)	N(4)–Cu(1)–N(8)	179.27(10)
N(1)–Cu(1)–N(4)	87.43(9)	N(4)–Cu(1)–N(5)	92.12(9)
N(1)–Cu(1)–N(5)	178.89(9)	N(5)–Cu(1)–N(8)	87.21(9)

N–H donors (Fig. 6 and Table 2(c)). The DMSO hydrogen bond interaction with the ligands prevents the formation of the R_2^2 (8) synthon[36] and thus the concatenation observed in **4** (which was also crystallised from DMSO) and in **5** does not occur in **6**.

Perhaps surprisingly, one of the two ligands in complex **6** exists in two different tautomeric forms within the crystal, and there is associated DMSO disorder. The predominant ligand tautomer is protonated at the metallaring amine nitrogen N(3) (75% occupancy), whereas the second form of this ligand is protonated at the imidazole nitrogen N(2) (25% occupancy). The second ligand in the complex is protonated only at the imidazole nitrogen N(6). That is, the two otherwise identical ligands in the predominant form of the complex have different tautomeric forms. The presence of the low population tautomer was indicated by both residual electron density in the final crystallographic difference maps, and by the disorder present in the DMSO on that side of the complex; O(5) would be too close to N(2) if it were not protonated. It seems not possible to determine if the tautomerism is responsible for the DMSO disorder, or if the DMSO disorder is responsible for the tautomerism.

Unlike the ordered DMSO molecule, the disordered DMSO molecule is close to an equivalent symmetry related site and it may be the proximity of another DMSO molecule that drives the DMSO disorder and perhaps then the tautomerism. The presence of the nearby DMSO molecule prevents the disordered molecule from having a similar orientation, with respect to the complex, to that of the ordered DMSO molecule. The phenyl groups in complex **6** are involved in either C–H to π-facial or in methyl–phenyl interactions (Fig. 7), and the

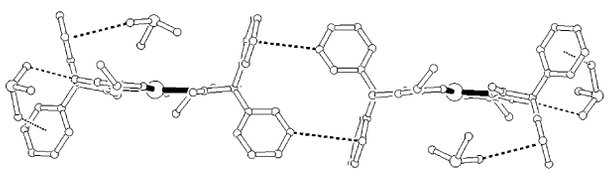


Fig. 7 A PLATON[37] illustration of the principal intermolecular hydrogen bonding and weak interactions in **6**; the disorder and the hydrogen atoms have been omitted for clarity. Each phenyl ring is involved in a C–H to π-facial interaction or in an interaction with a DMSO methyl group.

ordered DMSO molecule, participates in a methyl–phenyl interaction with the complex to which it is hydrogen bonded. The methyl groups of the disordered DMSO molecule, however, are oriented so that they do not interact with the phenyl residues of the ligand to which it is hydrogen bonded. Instead they show methyl–phenyl interactions with the phenyl group of a neighbouring complex. Additionally, the two ethyl groups have different orientations; the terminal methyl group C(24) lies in an approximately *anti* conformation, while the C(6) methyl group, approximates a *syn* orientation. A nearby neighbouring phenyl residue prevents C(6) from having an *anti*-conformation and the consequential position of C(6) prevents C(24) having a *syn*-conformation. A simple calculation suggests that if the C(5)–C(6) ethyl residue orientation was similar to that of the C(23)–C(24) residue, then it would be approximately 2.7 Å from the phenyl C(11) on the neighbouring complex. It would also be approximately 3.0 Å from O(4) of the disordered DMSO molecule and so prevent the observed tautomerism.

Conclusions

The new ligands reported here possess a number of features that are capable of being altered synthetically in such a way that the changes might be expected to affect the supramolecular assembly of their complexes and, as a consequence, contribute to a better understanding of rational crystal design.

First, the anionic form of the ligand has self-complementary doublet hydrogen bonding motifs and the potential for hydrogen bonding between neighbouring complexes is restricted to these motifs because the other hydrogen bond donor and acceptor in the ligand are used in the formation of the pseudo-macrocyclic rings. Steric or electronic inhibition of the above hydrogen bonding will clearly likely result in changes in the supramolecular structure adopted.

In addition, there is a structural feature that provides an alternative means of assembling the complexes into chains (though in this work only dimers have been observed); namely, the complementary CH to π-facial interactions between the pairs of aromatic rings on each ligand. Such an assembly, based as it is on weak interactions, would not be expected to occur unless the formation of the self-complementary hydrogen bonded rings mentioned above did not form, whether for steric reasons or, for example, because the ligand was in its neutral form.

Finally, the R groups, Me or Et in the current work, might be changed, for example, to –OMe, $–NMe_2$ or –NHPh, which have different steric requirements that may preclude the formation of the hydrogen bonded rings and which would also change the electronic properties of the ligand.

Acknowledgements

We thank the Australian Research Council for support.

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