metal-organic papers

[μ-2,8-Dimethyl-5,11-bis(dimethylaminoethyl)-1,4,5,6,7,10,11,12-octahydrodiimidazo-[4,5-*h*;4,5-*c*][1,6]diazecine]bis[aquacopper(II)] diacetate hexahydrate

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In the title compound, $[Cu_2(C_2H_3O_2)_2(C_{20}H_{36}N_8)(H_2O)_2](C_2H_3O_2)_2 \cdot 6H_2O$, the dinuclear cation has inversion symmetry and contains square-pyramidal Cu^{II} ions separated by 7.471 (1) Å. Symmetry-related cations are linked to a framework of rings of five water molecules, where each water molecule acts as both a single hydrogen-bond donor and acceptor, an arrangement very close to that believed to exist in liquid water.

Comment

The preparation and characterization of dinuclear metal complexes with imidazole-derived ligands is of current interest, due to their interesting magnetic behaviour and catalytic activity in biomimetic oxidation reactions (Andrade Alves *et al.*, 2003; Mukherjee *et al.*, 2004; Sosa *et al.*, 2005). We have previously reported a dicopper complex of a related ligand based on a diazecine core, namely 2,8-dimethyl-1,4,5,6,7,10,11,12-octahydroimidazo[4,5-*h*]-imidazo[4,5-*c*]-[1,6]-diazecine-5,11-diethanoic acid (glymeim; see scheme), with perchlorate as the counteranion (Mendoza-Díaz *et al.*, 2002). Bearing in mind the coordination ability of this class of ligands, an interesting modification of glymeim is the substitution of the carboxylic acid functionalities by tertiary amines. Following this idea, we have now synthesized such a ligand, namely 2,8-dimethyl-5,11-di-(dimethylethyleneamine)-1,4,5,-6,7,10,11,12-octahydroimidazo[4,5-*h*]imidazo[4,5-*c*][1,6]diazecine (dimeim; see scheme) and prepared its Cu^{II} complex, (I). We present here the X-ray structure of (I).
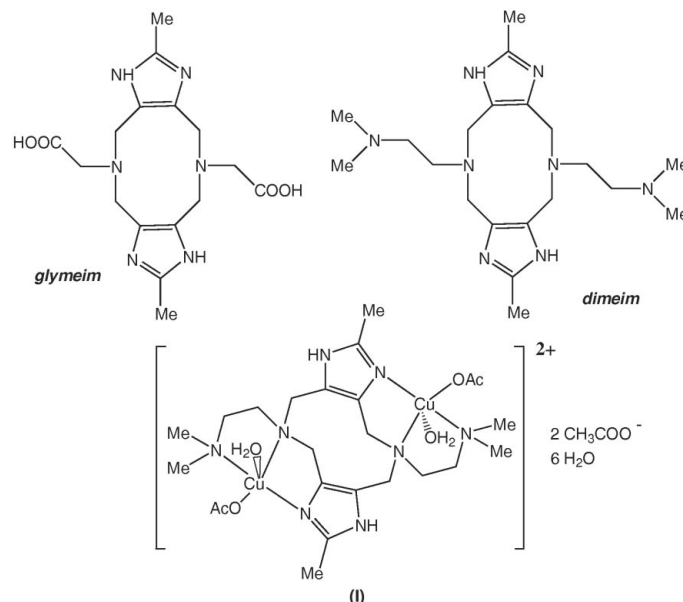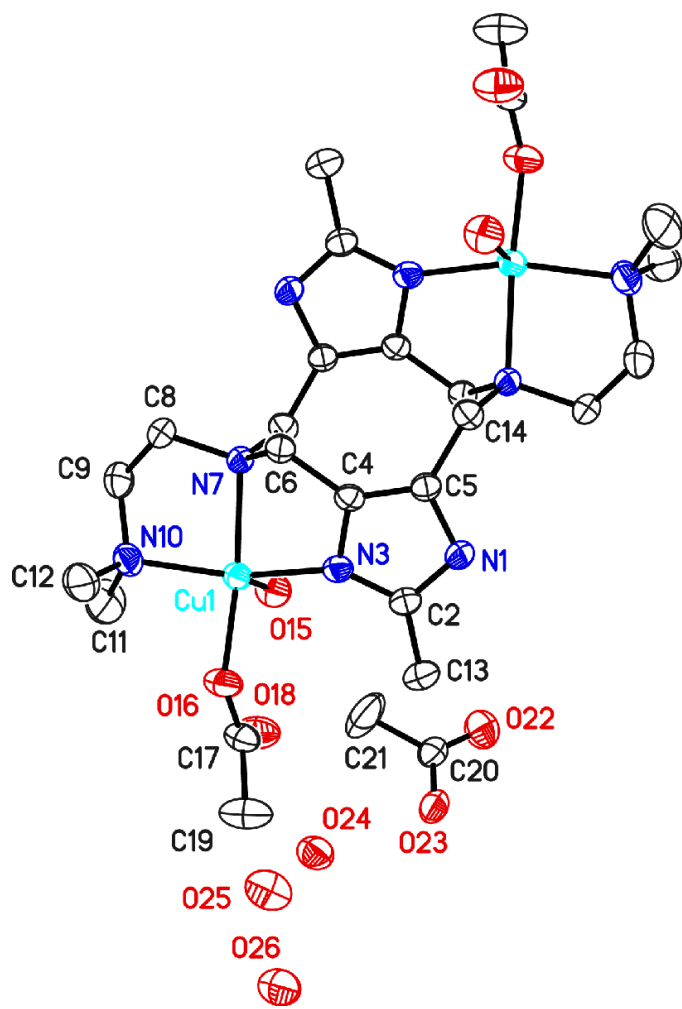
Figure 1
The structure of (I), with displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity and the numbering scheme is given for the asymmetric unit.

The asymmetric unit of (I) contains one-half of the cation, which lies on an inversion centre, one acetate anion and three water molecules on general positions, giving a complex of formula $[Cu_2(OH_2)_2(CH_3COO)_2(dimeim)](CH_3COO)_2 \cdot 6H_2O$ (Fig. 1). The centrosymmetric cation is a dinuclear Cu^{II} complex, with the five-coordinate metal centres displaying square-pyramidal environments. The base of the pyramid is formed by three N atoms of the dimeim ligand and one O atom of an acetate anion, and the metal cation is situated 0.3112 (2) Å above the N3/N7/N10/O16 least-squares plane. The apical position is occupied by a water molecule. Overall, the coordination geometry around the Cu^{II} ions does not present unusual features (Table 1).

The 1,6 diazecine ring C5/C4/C6/N7/C14^i/C5^i/C4^i/C6^i/N7^i/C14 [symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, -z$] adopts a chair conformation, with a total puckering amplitude of 1.4428 (16) Å. The conformation observed for dimeim in (I) is very similar to that observed for the equivalent glymeim atoms in $[Cu_2(OH_2)_4(glymeim)]^{2+}$ (Mendoza-Díaz et al., 2002), suggesting that the diazecine ring has no fluxional character.

This idea is supported by comparing, for instance, the distances between the centroids of the parallel imidazole rings in the glymeim complex and (I), at 4.562 (6) and 4.5730 (4) Å, respectively. A key consequence related to magnetic properties is that the $Cu^{II} \cdots Cu^{II}$ separation is almost the same, regardless of the functionality bonded to the N atoms of the diazecine core, and regardless of the ancillary ligands used for completion of the coordination sphere: the $Cu \cdots Cu$ distance is 7.471 (1) Å in (I), versus 7.445 (3) Å in the glymeim complex (Mendoza-Díaz et al., 2002).

In contrast with the molecular structure, the crystal structure depends on the nature of the counteranions. In the case of (I), a complex three-dimensional hydrogen-bond scheme arises (Table 2), involving water molecules (O15, O24, O25, O26), the acetate anions and the N—H group of the imidazole moiety. The intramolecular O15—H152···O16 hydrogen bond is very long and perhaps of questionable significance.

The most relevant aspect of the hydrogen-bond network concerns the non-coordinated water molecules (O24, O25, O26), which are doubly hydrogen-bonded, forming cyclic pentameric motifs. These rings are fused, sharing O25···O26 edges, and are hydrogen-bonded to the cations by means of atom O18 belonging to the coordinated acetate group (Fig. 2). This pentameric arrangement of water molecules is known to predominate in liquid water at 298 K (Raghuraman et al., 2003) and its characteristic spectroscopic signature has been observed by far-IR laser vibration–rotation tunnelling spectroscopy (Liu et al., 1996). Density functional theory studies (Xantheas, 1995) indicated that the most stable form of the pentamer is a slightly puckered ring, with a mean O···O separation of 2.862 Å. The water molecules in (I) fit this conformation remarkably well: the ring O24/O25/O26^i/O25^{ii}/O26 [symmetry codes: (i) $\frac{5}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{5}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z$] clearly adopts an E_{26} conformation (i.e. an envelope with O26 as the flap atom), with O···O separations in the range 2.776 (3)–2.848 (3) Å. Interestingly, the crystal structure of glymeim·8H₂O (Mendoza-Díaz et al., 2002) includes cyclic water hexamers bridging symmetry-related glymeim molecules. This arrangement of the water molecules is that found in normal ice (I_h ice).

Experimental

The dimeim ligand was prepared by dissolving 2-methylimidazole (1.6 g, 20 mmol) in water (ca 40 ml) and mixing this solution with N,N-dimethylethylenediamine (2.25 ml, 20 mmol) previously dissolved in water (10 ml). To this mixture, a 37% solution (3.2 ml) of formaldehyde (40 mmol) was added dropwise with constant stirring. After stirring for 24 h at 343 K, a white precipitate of dimeim was collected. Analysis found: C 48.47, H 9.64, N 22.37%; calculated for $C_{20}H_{36}N_8 \cdot 6H_2O$: C 48.37, H 9.74, N 22.56%. Complex (I) was then prepared in the following manner. Cu(AcO)₂·H₂O (2 mmol, 0.399 g) was dissolved in distilled water (20 ml). To this solution, the solid dimeim ligand (1 mmol, 0.496 g) was added in small portions, allowing for complete dissolution after each addition. The resulting deep-blue solution was filtered and allowed to stand. Single crystals of (I) were collected after two weeks. Analysis, found: C 37.72, H 7.13, N 12.41%; calculated for $Cu_2C_{28}H_{64}N_8O_8$: C 37.54, H 7.15, N 12.51%.
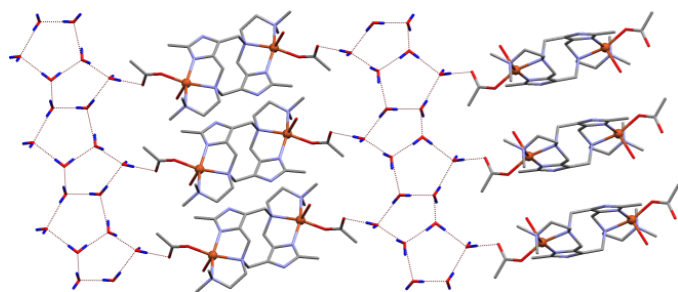
Figure 2
Part of the crystal structure of (I), showing the rings of five water molecules (hydrogen bonds indicated by dashed lines) joining the cations. For the sake of clarity, non-coordinated acetate anions and H atoms of the cations have been omitted.

Crystal data

$[Cu_2(C_2H_3O_2)_2(C_{20}H_{36}N_8)(H_2O_2)]\cdot$
$\quad (C_2H_3O_2)_2\cdot 6H_2O$
$M_r = 895.95$
Monoclinic, $C2/c$
$a = 23.562\ (3)$ Å
$b = 6.5271\ (5)$ Å
$c = 28.881\ (4)$ Å
$\beta = 108.863\ (10)°$
$V = 4203.1\ (8)$ Å^3
$Z = 4$

$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 75
$\quad$ reflections
$\theta = 4.1–13.8°$
$\mu = 1.09$ mm^{-1}
$T = 296\ (1)$ K
Irregular lump, blue
$0.50 \times 0.48 \times 0.40$ mm

Data collection

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan
$\quad$ (*XSCANS*; Siemens, 1996)
$\quad T_{min} = 0.597$, $T_{max} = 0.646$
11 427 measured reflections
5582 independent reflections
4720 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$
$\theta_{max} = 29.0°$
$h = -32 \rightarrow 1$
$k = -8 \rightarrow 8$
$l = -37 \rightarrow 39$
3 standard reflections
$\quad$ every 97 reflections
$\quad$ intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.093$
$S = 1.02$
5582 reflections
269 parameters
H atoms treated by a mixture of
$\quad$ independent and constrained
$\quad$ refinement

$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2$
$\quad + 2.3286P]$
$\quad$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXTL-Plus* (Sheldrick, 1998)
Extinction coefficient: 0.0045 (2)

Table 1
Selected geometric parameters (Å, °).

Cu1—O16	1.9657 (13)	Cu1—N7	2.0992 (13)
Cu1—N3	2.0026 (14)	Cu1—O15	2.2186 (14)
Cu1—N10	2.0417 (15)		
O16—Cu1—N3	94.44 (6)	N10—Cu1—N7	84.64 (6)
O16—Cu1—N10	93.69 (6)	O16—Cu1—O15	97.20 (6)
N3—Cu1—N10	161.07 (6)	N3—Cu1—O15	99.44 (6)
O16—Cu1—N7	159.97 (5)	N10—Cu1—O15	96.46 (6)
N3—Cu1—N7	81.87 (5)	N7—Cu1—O15	102.83 (5)

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O15—H152···O16	0.91 (3)	2.78 (3)	3.1430 (19)	105 (2)
O15—H152···O18	0.91 (3)	1.86 (3)	2.726 (2)	158 (3)
O24—H241···O23	0.68 (3)	2.03 (3)	2.708 (2)	171 (4)
N1—H1A···O23^i	0.86	1.85	2.6866 (19)	165
O15—H151···O22^{ii}	0.77 (3)	1.95 (3)	2.711 (3)	168 (3)
O24—H242···O18	0.85 (3)	1.95 (3)	2.802 (2)	177 (3)
O25—H251···O24	0.78 (4)	2.05 (4)	2.820 (3)	172 (4)
O25—H252···O26^{iii}	0.83 (4)	1.95 (4)	2.776 (3)	173 (4)
O26—H261···O24	0.71 (4)	2.15 (4)	2.848 (3)	168 (5)
O26—H262···O25^{iv}	0.82 (4)	2.01 (5)	2.806 (3)	164 (4)

Symmetry codes: (i) $2-x, 1-y, -z$; (ii) $2-x, -y, -z$; (iii) $\frac{5}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, 1+y, z$.

H atoms bonded to C and N atoms were placed in idealized positions and refined as riding, with N—H = 0.86 Å and C—H = 0.96–0.97 Å. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) or $1.5U_{eq}$(methyl carrier) was applied, as appropriate. Water H atoms were located in difference maps. Their positions were freely refined with the constraint $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL-Plus*.

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