

Laura Gasque,\* Edgar Mijangos  
and Luis Ortiz-FradeDepartamento de Química Inorgánica, Facultad  
de Química, UNAM, Ciudad Universitaria,  
04510 México DF, MexicoCorrespondence e-mail:  
gasquel@servidor.unam.mx

## Key indicators

Single-crystal X-ray study  
 $T = 298\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.061  
 $wR$  factor = 0.148  
Data-to-parameter ratio = 20.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>. **$[\mu\text{-}5,11\text{-Bis}(\text{dimethylethyleneamino})\text{-}2,8\text{-dimethyl-}1,4,5,6,7,10,11,12\text{-octahydroimidazo}[4,5\text{-}h]\text{imidazo}[4,5\text{-}c][1,6]\text{diazecine}] \text{bis}[\text{aquasulfatocopper}(\text{II})] \text{hexahydrate}$ : a dinuclear copper sulfate complex based on a diazecine ligand**

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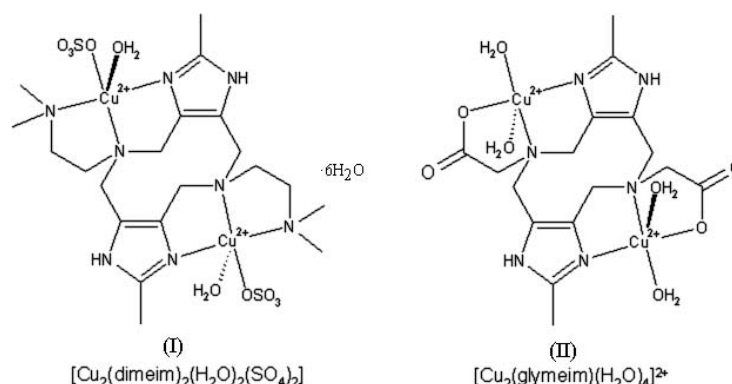
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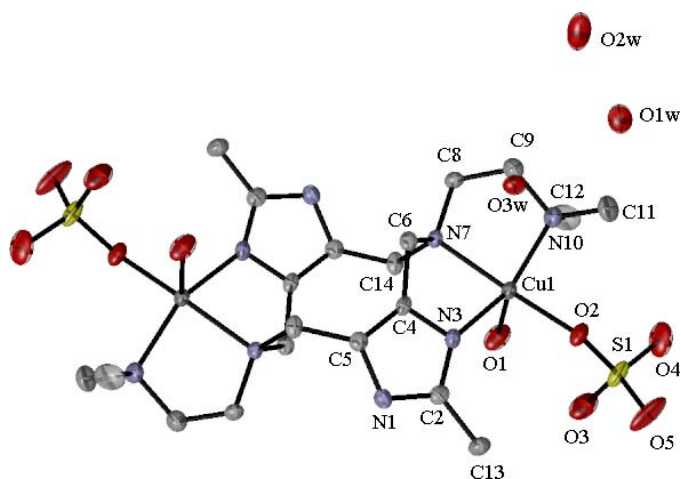
Online 18 March 2005

In the title compound,  $[\text{Cu}_2(\text{SO}_4)_2(\text{C}_{20}\text{H}_{36}\text{N}_8)(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$ , the dinuclear molecule lies across an inversion centre and contains square-pyramidal  $\text{Cu}^{\text{II}}$  ions separated by  $7.5709(18)\text{ \AA}$ . Symmetry-related molecules are linked together by hydrogen bonds between the coordinated water molecules and the sulfate ligands. They are further linked by a framework of fused cyclic water tetrameric and pseudo-hexagonal units in a three-dimensional hydrogen-bonded network involving both coordinated and uncoordinated water molecules, as well as sulfate ligands. While the tetrameric units are purely composed of water molecules, the pseudo-hexagonal units involve O atoms from the sulfate. Further hydrogen bonding also involves the NH group from the imidazole in addition to the above-mentioned units.

## 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, (II), 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), with perchlorate as the counter-anion (Mendoza-Díaz *et al.*, 2002). Bearing in mind the coordination ability of this class of ligands, an interesting modification of glymeim consists in the substitution of the carboxylic acid functionalities by tertiary amines. This variation in the coordination sphere of the Cu atoms is expected to induce variations in their solution behaviour, such as their solubility and their catalytic activity.



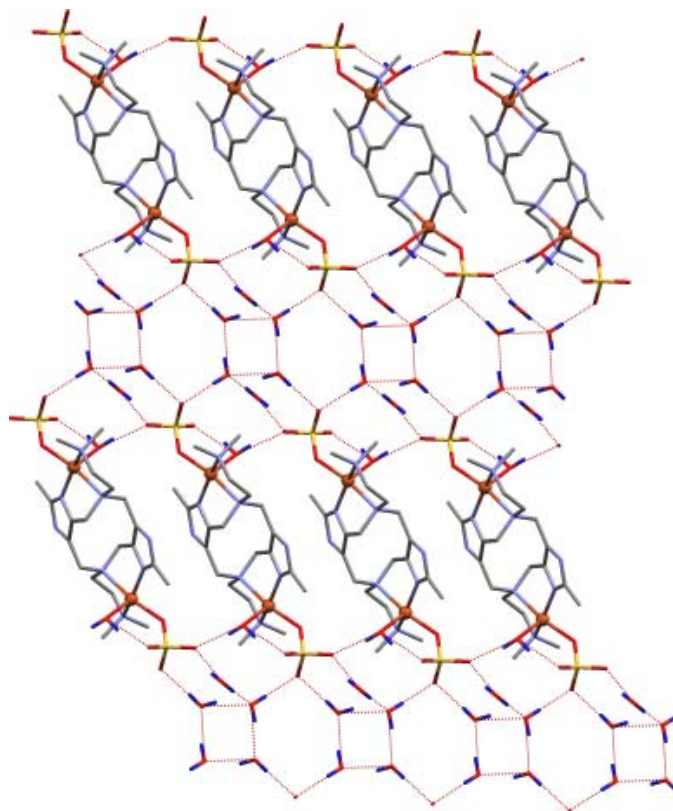

**Figure 1**

The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. Unlabelled atoms are related to labelled atoms by  $2 - x$ ,  $1 - y$ ,  $1 - z$ .

Following this idea, we have now synthesized such a ligand, 2,8-dimethyl-5,11-bis(dimethylethylamine)-1,4,5,6,7,10,11,12-octahydroimidazo[4,5-*h*]imidazo[4,5-*c*][1,6]diazecine (dimeim), and prepared some of its  $\text{Cu}^{\text{II}}$  complexes. The structure of the acetate derivative has been described recently (Gasque *et al.*, 2005). We present here the X-ray structure of the title sulfate complex, (I).

The asymmetric unit of (I) contains one-half of the dinuclear complex molecule and three water molecules in general positions. Inversion symmetry generates the full molecule, giving a complex of formula  $[\text{Cu}_2(\text{OH}_2)_2(\text{SO}_4)_2(\text{dimeim})]_2 \cdot 6\text{H}_2\text{O}$ . The molecule is a dinuclear  $\text{Cu}^{\text{II}}$  complex consisting of five-coordinated metallic centers in a square-pyramidal environment (Fig. 1). The base of the pyramid is formed by three N atoms of the dimeim ligand and one O atom of a sulfate, with the metal ion situated 0.2963 (6) Å above the N3/N7/N10/O2 least-squares plane. The apical position is occupied by a water molecule. The coordination geometry around the  $\text{Cu}^{\text{II}}$  ions does not present unusual geometrical features (Table 1).

The 1,6 diazecine ring, C5/C4/C6/N7/C14<sup>i</sup>/C5<sup>j</sup>/C4<sup>i</sup>/C6<sup>j</sup>/N7<sup>j</sup>/C14 [symmetry code: (i)  $2 - x$ ,  $1 - y$ ,  $1 - z$ ], adopts a chair conformation, with a total puckering amplitude (Cremer & Pople, 1975) of 1.2372 (1) Å. The conformation observed for dimeim in (I) is very similar to that observed for glymeim in the related cation,  $[\text{Cu}_2(\text{OH}_2)_4(\text{glymeim})]^{2+}$  (Mendoza-Díaz *et al.*, 2002). This similarity is further illustrated by comparing, for instance, the distances between the centroids of the coplanar imidazole rings in the glymeim complex and (I), 4.562 (6) and 4.564 (2) Å, respectively. A key consequence concerning their magnetic properties is that in these two complexes, the intramolecular  $\text{Cu}^{\text{II}} \cdots \text{Cu}^{\text{II}}$  separation is almost the same: the metal  $\cdots$  metal distance is 7.5709 (18) Å in (I) versus 7.445 (3) Å in the glymeim complex (Mendoza-Díaz *et al.*, 2002). In the recently described analogue of (I) with


**Figure 2**

Part of the crystal structure of (I), showing the cyclic water tetramers and pseudo-hexagonal units.

acetate instead of sulfate (Gasque *et al.* 2005), which also displays a very similar conformation, there is a 7.471 (1) Å intramolecular  $\text{Cu} \cdots \text{Cu}$  distance.

In contrast with the molecular structure, the crystal structure changes when the coordinated anion is changed. In the case of (I), a complex three-dimensional hydrogen-bond scheme is built, involving non-coordinated water molecules (O1W, O2W and O3W), sulfate ligands (O4) and the N—H group of the imidazole (Table 2). The complexes are linked by hydrogen bonds between the coordinated  $\text{H}_2\text{O}$  molecules and sulfate ligands, to form a ladder structure which runs parallel to the *a* axis. A chain of tetrameric and pseudo-hexagonal units also runs parallel to the crystallographic *a* axis. Tetrameric units are formed by two of the non-coordinated water molecules (O1W and O2W) and their symmetry equivalents, and they share edges with the pseudo-hexagonal units (12-membered rings containing six non-H atoms), which are completed by two equivalent O4 atoms from the sulfate ligand (Table 2, Fig. 2).

There are two other sets of rings worth describing, which contribute to link the above-mentioned tetrameric–hexagonal chain to the coordination centres. The first set are ten-membered rings defined by the O atom from a third non-coordinated water molecule, O3W, O5—S1—O4 from the sulfate, and finally O2W and O1W, which make up one of the edges of the tetrameric units described above. This ring is linked to the imidazole NH through O3W.

Another observable ring is 12-membered, involving the O atom from the coordinated water molecule, O1, O3—S1—O4 from the sulfate, two O atoms from non-coordinated water molecules O1W and O3W, and O5 from a neighbouring sulfate.

Interestingly, the crystal structure of glymeim·8H<sub>2</sub>O (Mendoza-Díaz *et al.*, 2002) includes cyclic water hexamers bridging symmetry-related glymeim molecules. This arrangement for water molecules is that found in normal ice (Ih ice). It is also relevant to point out that the acetate analogue of (I) (Gasque *et al.*, 2005) contains a pentameric arrangement of water molecules, similar to the predominant arrangement in liquid water.

## 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 of formaldehyde (3.2 ml, 40 mmol) was added dropwise with constant stirring. After 24 h of stirring at 343 K, a white precipitate was collected. Analysis found: C 48.47, H 9.64, N 22.37%; calculated for C<sub>20</sub>H<sub>36</sub>N<sub>8</sub>·6H<sub>2</sub>O: C 48.37, H 9.74, N 22.56%; yield: 65%. Complex (I) was prepared in the following manner. CuSO<sub>4</sub>·5H<sub>2</sub>O (0.499 g, 2 mmol) was dissolved in water (20 ml). To this solution, (0.496 g, 1 mmol) of solid dimeim ligand was added slowly and with constant stirring. A deep blue solution was obtained and left to stand. Green crystals of (I) were collected after 3 d. Analysis found: C 28.42, H 6.19, N 13.68%; calculated for Cu<sub>2</sub>C<sub>20</sub>H<sub>52</sub>N<sub>8</sub>O<sub>16</sub>S<sub>2</sub>: C 28.20, H 6.15, N 13.15%.

### Crystal data

[Cu <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (C <sub>20</sub> H <sub>36</sub> N <sub>8</sub> )(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> ·6H <sub>2</sub> O	Z = 1
<i>M<sub>r</sub></i> = 851.9	<i>D<sub>x</sub></i> = 1.643 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 6.902 (2) Å	Cell parameters from 51 reflections
<i>b</i> = 9.036 (2) Å	$\theta$ = 5.0–22.6°
<i>c</i> = 15.164 (4) Å	$\mu$ = 1.44 mm <sup>-1</sup>
$\alpha$ = 103.600 (10)°	<i>T</i> = 298 (2) K
$\beta$ = 93.360 (10)°	Prism, green
$\gamma$ = 108.750 (10)°	0.25 × 0.1 × 0.1 mm
<i>V</i> = 861.1 (4) Å <sup>3</sup>	

### Data collection

Siemens P4 diffractometer	$\theta_{\max}$ = 30°
2 $\theta/\omega$ scans	<i>h</i> = -1 → 9
Absorption correction: none	<i>k</i> = -12 → 11
6105 measured reflections	<i>l</i> = -21 → 21
4960 independent reflections	3 standard reflections
2931 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	every 97 reflections
<i>R</i> <sub>int</sub> = 0.050	intensity decay: 6.3%

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )] = 0.061	<i>w</i> = 1/[ $\sigma^2(F_o^2) + (0.0626P)^2$ ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.148	where <i>P</i> = ( <i>F<sub>o</sub></i> <sup>2</sup> + 2 <i>F<sub>c</sub></i> <sup>2</sup> )/3
<i>S</i> = 0.98	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
4960 reflections	$\Delta\rho_{\max}$ = 0.66 e Å <sup>-3</sup>
244 parameters	$\Delta\rho_{\min}$ = -0.57 e Å <sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O2	1.977 (3)	C11—N10	1.491 (7)
Cu1—N3	2.027 (4)	C14—N7	1.511 (6)
Cu1—N10	2.039 (4)	O1—H1O	0.84 (4)
Cu1—N7	2.113 (3)	O1—H2O	0.85 (4)
Cu1—O1	2.179 (4)	O2—S1	1.502 (3)
C2—N3	1.329 (6)	O1W—H1W	0.78 (4)
C2—N1	1.343 (5)	O1W—H2W	0.83 (2)
C4—N3	1.375 (5)	O3—S1	1.471 (4)
C4—C6	1.503 (6)	O2W—H3W	0.83 (4)
C5—N1	1.396 (6)	O2W—H4W	0.81 (4)
C6—N7	1.501 (5)	O4—S1	1.469 (4)
C8—N7	1.494 (5)	O3W—H5W	0.85 (4)
C9—N10	1.493 (6)	O3W—H6W	0.82 (4)
C12—N10	1.486 (7)	O5—S1	1.461 (4)
O2—Cu1—N3	93.79 (14)	C14—N7—Cu1	113.2 (3)
O2—Cu1—N10	95.13 (15)	C12—N10—C9	110.8 (4)
N3—Cu1—N10	152.59 (17)	C11—N10—C9	107.4 (4)
O2—Cu1—N7	168.72 (13)	C12—N10—Cu1	109.8 (3)
N3—Cu1—N7	81.75 (14)	C11—N10—Cu1	113.7 (3)
N10—Cu1—N7	84.53 (15)	C9—N10—Cu1	105.5 (3)
O2—Cu1—O1	95.41 (14)	Cu1—O1—H1O	103 (4)
N3—Cu1—O1	96.43 (15)	Cu1—O1—H2O	123 (4)
N10—Cu1—O1	108.43 (17)	H1O—O1—H2O	104 (4)
N7—Cu1—O1	95.38 (14)	S1—O2—Cu1	131.3 (2)
C2—N3—C4	106.7 (3)	H1W—O1W—H2W	104 (5)
C2—N3—Cu1	140.7 (3)	H3W—O2W—H4W	107 (4)
C4—N3—Cu1	110.3 (3)	H5W—O3W—H6W	104 (4)
C8—N7—C6	111.8 (3)	O5—S1—O4	110.0 (3)
C8—N7—C14	112.8 (3)	O5—S1—O3	110.3 (3)
C6—N7—C14	110.2 (3)	O4—S1—O3	110.2 (3)
C8—N7—Cu1	108.4 (2)	O5—S1—O2	107.0 (2)
C6—N7—Cu1	99.8 (2)		

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1O...O2 <sup>i</sup>	0.84 (4)	2.80 (5)	3.077 (5)	102 (4)
O1—H1O...O3 <sup>i</sup>	0.84 (4)	1.89 (4)	2.688 (5)	159 (5)
O1—H1O...S1 <sup>i</sup>	0.84 (4)	2.75 (5)	3.368 (4)	132 (5)
O2W—H3W...O1W <sup>i</sup>	0.83 (4)	2.06 (4)	2.864 (6)	163 (5)
O3W—H5W...O1W <sup>i</sup>	0.85 (4)	1.94 (4)	2.783 (5)	170 (5)
O2W—H4W...O4 <sup>ii</sup>	0.81 (4)	2.05 (4)	2.859 (6)	174 (6)
O2W—H4W...O5 <sup>ii</sup>	0.81 (4)	2.98 (5)	3.566 (7)	131 (4)
O3W—H6W...O5 <sup>ii</sup>	0.82 (4)	1.91 (4)	2.713 (5)	167 (6)
O1—H2O...O5 <sup>iii</sup>	0.85 (4)	1.92 (4)	2.728 (5)	158 (6)
O1W—H1W...O2W <sup>iv</sup>	0.78 (4)	2.02 (4)	2.773 (6)	162 (6)
N1—H1...O3W <sup>v</sup>	0.86	1.93	2.788 (5)	171
O1—H2O...O3W <sup>vi</sup>	0.85 (4)	3.00 (5)	3.420 (5)	113 (4)
O1W—H2W...S1 <sup>vii</sup>	0.83 (2)	2.98 (4)	3.688 (4)	145 (5)
O1W—H2W...O3 <sup>vii</sup>	0.83 (2)	2.95 (5)	3.391 (6)	116 (5)
O1W—H2W...O4 <sup>vii</sup>	0.83 (2)	2.00 (2)	2.815 (6)	170 (6)

Symmetry codes: (i) *x*, *y*, *z*; (ii) *x*, *y* - 1, *z*; (iii) *x* + 1, *y*, *z*; (iv) -*x* + 1, -*y* + 1, -*z* + 2; (v) -*x* + 1, -*y* + 1, -*z* + 1; (vi) *x* + 1, *y* + 1, *z*; (vii) *x* - 1, *y* - 1, *z*.

Water H atoms were located in difference Fourier maps and subsequently refined, with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). All other H atoms were placed geometrically, with N—H = 0.86, C—H = 0.96–0.97 Å, and included in the refinement using a riding model, with *U*<sub>iso</sub>(H) = 1.2 or 1.5*U*<sub>eq</sub>(parent atom).

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

ORTEP3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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