

{ μ -*N,N'*-Bis[3-(dimethylamino)propyl]-oxamidato(2-)- κ^6 *N,N',O':N'',N''',O*}-bis[(1*H*-imidazole- κ *N*³)(methanol- κ *O*)-copper(II)] bis(perchlorate)}

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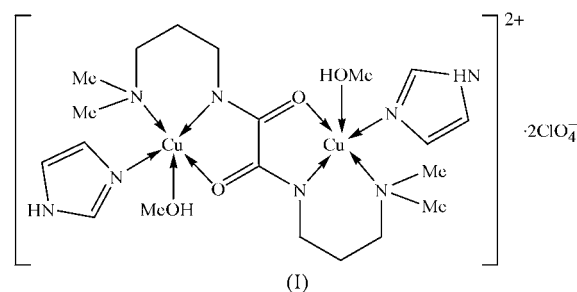
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The structure of the title compound, $[\text{Cu}_2(\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_2)(\text{C}_3\text{H}_4\text{N}_2)_2(\text{CH}_3\text{O})_2](\text{ClO}_4)_2$ or $[\text{Cu}_2(\text{dmoxpn})(\text{HIm})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$, where dmoxpn is the dianion of *N,N'*-bis[3-(dimethylamino)propyl]oxamide and HIm is imidazole, consists of a centrosymmetric *trans*-oxamidate-bridged copper(II) binuclear cation, having an inversion centre at the mid-point of the central C—C bond, and two perchlorate anions. The Cu^{II} atom has square-pyramidal coordination geometry involving two N atoms and an O atom from the dmoxpn ligand, an N atom from an imidazole ring, and an O atom from a methanol molecule. The crystal structure is stabilized by O—H...O, N—H...O and C—H...O hydrogen bonds and imidazole π — π stacking interactions to form a three-dimensional supramolecular array.

Comment

Many studies have been devoted to the development of synthetic strategies for the architecture of coordination metal supramolecules (Hoskins & Robson, 1990; Black *et al.*, 1996; Funeriu *et al.*, 1997). A successful strategy leading to three-dimensional supramolecular systems is to utilize the π — π stacking of aromatic groups and/or the hydrogen bonding of coordinated ligands in addition to their coordination capability to interlink zero-, one- or two-dimensional coordination molecules (Chen *et al.*, 1998; Yi *et al.*, 2004). As is well known, *N,N'*-disubstituted oxamidate has proven to give rise to three-dimensional supramolecular structures because of its easy *cis*—*trans* conformational change, its flexible binding mode, and its ability to form hydrogen bonds (Chen *et al.*, 1998). On the other hand, imidazole (HIm) is a suitable ligand in the construction of supramolecular frameworks owing to the strong tendency to form π — π stacking interactions and hydrogen bonds (Chen *et al.*, 1994; Zhang *et al.*, 1999). To our knowledge, only three crystal structures of oxamidate-bridged

binuclear metal complexes containing an imidazole ligand have been characterized, *viz.* $[\text{Cu}_2(\text{oxpn})(\text{NO}_3)_2(\text{HIm})_2]$, denoted **A** (Zhang *et al.*, 1999), $[\text{Cu}_2(\text{oxpn})(\text{HIm})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, denoted **B** (Chen *et al.*, 1994), and $[\text{Cu}_2(\text{oxen})(\text{HIm})_2](\text{ClO}_4)_2$, denoted **C** (Li *et al.*, 2004), where oxpn is deprotonated *N,N'*-bis(3-aminopropyl)oxamide and oxen is deprotonated *N,N'*-bis(3-aminoethyl)oxamide. However, the hydrogen bonds in these complexes were not discussed in detail and the π — π stacking of the imidazole groups was not studied at all. In order to obtain more information on supramolecular architecture constructed by hydrogen bonds and π — π stacking interactions in this kind of complex, we chose *N,N'*-bis[3-(dimethylamino)propyl]oxamide (H_2dmoxpn) as the bridging ligand and imidazole as a terminal ligand to synthesize a binuclear copper(II) complex formulated as $[\text{Cu}_2(\text{dmoxpn})(\text{HIm})_2(\text{CH}_3\text{OH})_2](\text{ClO}_4)_2$ (**I**).



The molecular structure of (**I**), as shown in Fig. 1, consists of a centrosymmetric dinuclear copper(II) cation, in which the Cu^{II} atoms are bridged by a dmoxpn^{2-} anion and coordinated by two imidazole and two methanol molecules, and two perchlorate counter-anions. The $\text{Cu} \cdots \text{Cu}$ separation through the oxamide bridge is 5.2824 (13) Å. The cation has a *transoid* conformation and occupies a special inversion centre at the mid-point of the C6—C6ⁱ bond [symmetry code: (i) $-x, -y, -z$], as in the other three examples of oxamide complexes **A**—

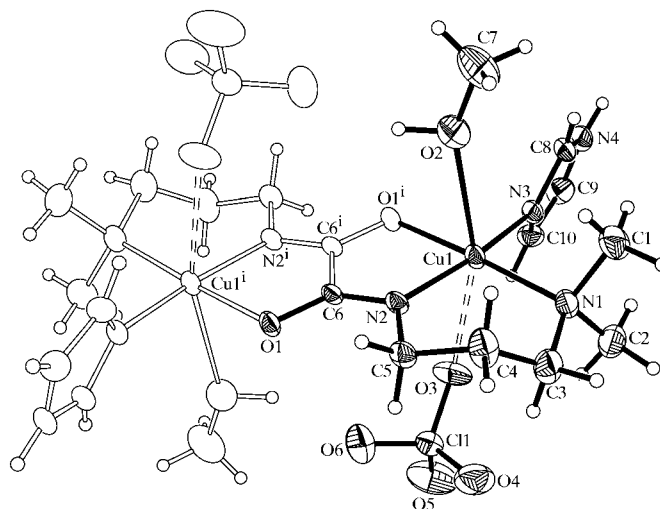


Figure 1
The molecular structure of (**I**), shown with 30% probability displacement ellipsoids. [Symmetry code: (i) $-x, -y, -z$.]

C. In contrast to the ligands oxpn and oxen, the dmoxp ligand can only adopt a *trans* conformation when it coordinates to metal ions owing to the steric hindrance induced by the presence of methyl substituents on the amine groups (Ruiz *et al.*, 1999; Lloret *et al.*, 1992). The coordination environment of the Cu^{II} atom in (**I**) is square pyramidal, with the coordinated methanol molecule and perchlorate ion in axial sites to form a [4+2] quasi-octahedral geometry. The Cu^{II} atom is displaced by 0.0751 (17) Å out of the basal plane. The axial Cu⋯O distances of 2.616 (4) (Cu1—O2) and 2.851 (4) Å (Cu1⋯O3) are significantly longer than those in the equatorial plane (Table 1). The imidazole ring is nearly perpendicular to the

coordination plane, with a dihedral angle of 75.67 (14)°, which is very similar to the value of 78.6° in **B** with the same [4+2] quasi-octahedral coordination geometry, whereas with a much elongated [4+1] square-pyramidal geometry, approximately parallel angles of 15.30 and 27° are found in **A** and **C**, respectively.

The bis-tridentate dmoxp ligand produces five- and six-membered chelate rings; the bite angles are 82.95 (11) and 97.01 (12)°, respectively. The five-membered ring has an envelope conformation, while the six-membered ring is intermediate between half-boat and twist-boat conformations; the corresponding puckering parameters (Cremer & Pople, 1975) are $\varphi = 180$ (2)°, $Q = 0.096$ (3) Å and $\theta = 121.5$ (4)°, and $\varphi = 341.4$ (5)° and $Q = 0.550$ (5) Å, respectively. The oxamide bridge is planar within experimental uncertainties. The dihedral angle between the oxamide bridge and the coordination plane is 10.48 (6)°. The C6=N2 and C6—C6ⁱ distances of 1.299 (5) and 1.492 (7) Å are typical C=N and Csp²—Csp² values, respectively. Given that the C6—O1 distance of 1.282 (4) Å is in accordance with those of (O=C)—O[−] fragments in many examples (Delgado *et al.*, 2006; Berg *et al.*, 2002; Nash & Schaefer, 1969), the oxamide is best described as N=C—O[−] rather than as delocalized.

The perchlorate anions stabilize the crystal structure *via* hydrogen bonds with methanol and HIm ligands (Table 2). As illustrated in Fig. 2, the perchlorate anions bridge the dinuclear copper(II) cationic complexes to form a two-dimensional hydrogen-bonding network parallel to the (101) plane. Owing to the substitution of the H atoms of the primary amine of oxpn by methyl groups, the dmoxp ligand does not participate in any hydrogen bonding, which is different from the situation for the oxpn or oxen ligands in compounds **A–C**. By contrast, the HIm ligand contributes to not only the hydrogen bonds but also the π – π stacking interactions. Along the *a* axial direction, the complexes are assembled by N4—H4⋯O1ⁱⁱ hydrogen bonds [symmetry code: (ii) $x + 1, y, z$] and the stacking between the aromatic rings of HIm and HIm^{vi} [symmetry code: (vi) $-x + 1, -y, -z$] (Fig. 3); the nearest separation is 3.092 (6) Å (C8⋯C8^{vi}). This parallel edge–edge π – π stacking is also found in compounds **A** (3.282 Å) and **B** (3.097 Å). The separations of **A** and **B** were calculated according to the data in the Cambridge Structural Database (Allen, 2002).

Experimental

The H₂dmoxp ligand was prepared according to a reported method (Ojima & Yamada, 1970). An ethanol solution (5 ml) of copper(II) perchlorate hexahydrate (0.2 mmol, 0.0741 g) was added slowly to an ethanol solution (5 ml) containing H₂dmoxp (0.1 mmol, 0.0258 g) and piperidine (0.2 mmol, 0.017 g). The mixture was stirred quickly for 30 min, then a methanol solution (5 ml) of imidazole (0.2 mmol, 0.0136 g) was added dropwise to the mixture. The reaction solution was heated at 333 K with stirring for 6 h. The resulting solution was filtered and concentrated by slow evaporation at room temperature for several days, whereupon dark-blue crystals (yield 0.0477 g, 61%) of the compound suitable for X-ray analysis were obtained from the solution.

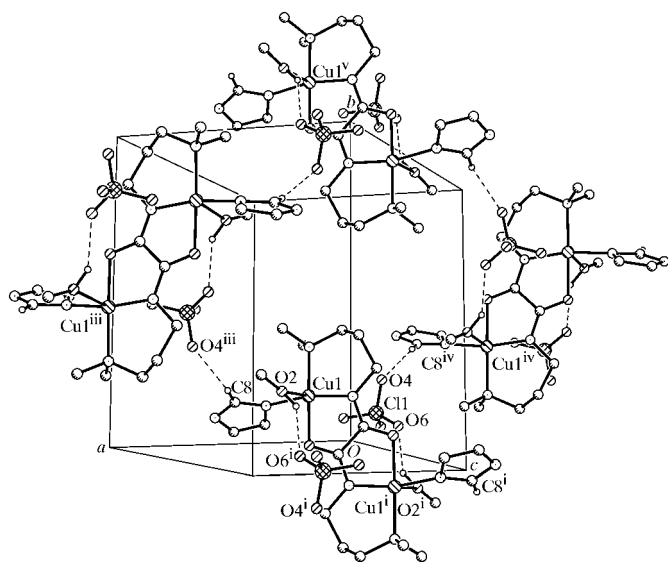


Figure 2

The two-dimensional hydrogen-bonded structure parallel to the (101) plane. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, -y, -z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $x, y + 1, z$.]

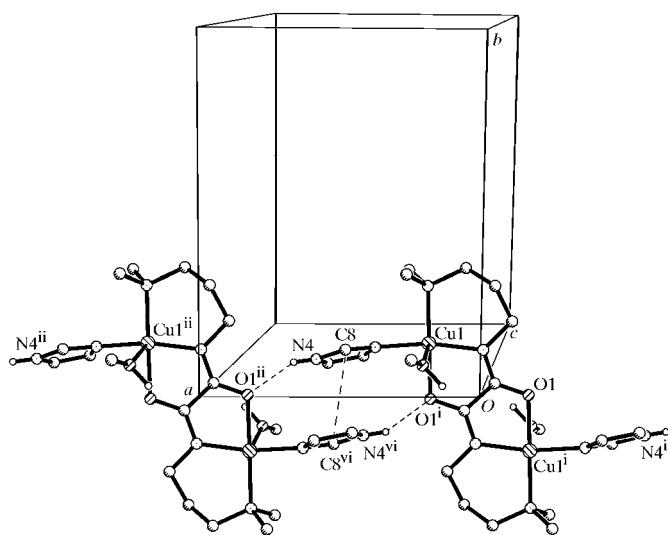


Figure 3

The packing of (**I**), showing π – π stacking interactions between imidazole groups and a one-dimensional hydrogen-bonded structure along the *a* axis. Dashed lines indicate hydrogen bonds and the π – π interaction. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x + 1, y, z$; (vi) $-x + 1, -y, -z$.]

Crystal data

$[\text{Cu}_2(\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_2)(\text{C}_3\text{H}_4\text{N}_2)_2(\text{CH}_4\text{O})_2](\text{ClO}_4)_2$	$V = 1578.0 (7) \text{ \AA}^3$
$M_r = 782.60$	$Z = 2$
Monoclinic, $P2_1/n$	$D_x = 1.647 \text{ Mg m}^{-3}$
$a = 10.023 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.084 (3) \text{ \AA}$	$\mu = 1.59 \text{ mm}^{-1}$
$c = 12.317 (3) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 102.328 (4)^\circ$	Block, dark blue
	$0.50 \times 0.14 \times 0.09 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer	8761 measured reflections
φ and ω scans	3121 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2201 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.504$, $T_{\max} = 0.870$	$R_{\text{int}} = 0.042$
	$\theta_{\max} = 26.1^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 1.6075P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.117$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.03$	$\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$
3121 reflections	$\Delta\rho_{\min} = -0.33 \text{ e \AA}^{-3}$
203 parameters	
H-atoms parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	2.064 (3)	C5—N2	1.463 (5)
Cu1—N2	1.955 (3)	C6—N2	1.299 (5)
Cu1—N3	1.982 (3)	C6—O1	1.282 (4)
Cu1—O1 ⁱ	2.022 (3)	C6—C6 ⁱ	1.492 (7)
N1—Cu1—N2	97.01 (12)	N3—Cu1—O1 ⁱ	85.68 (11)
N1—Cu1—N3	94.04 (13)	C5—N2—C6	117.6 (3)
N1—Cu1—O1 ⁱ	176.09 (13)	C5—N2—Cu1	128.9 (2)
N2—Cu1—N3	167.84 (13)	C6—N2—Cu1	113.2 (2)
N2—Cu1—O1 ⁱ	82.95 (11)	C6—O1—Cu1 ⁱ	110.6 (2)

Symmetry code: (i) $-x, -y, -z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O6 ⁱ	0.98	2.06	2.907 (6)	144
N4—H4 \cdots O1 ⁱⁱ	0.86	2.06	2.855 (4)	153
C8—H8 \cdots O4 ⁱⁱⁱ	0.93	2.47	3.317 (6)	152

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

The hydroxy H atoms of the methanol molecules were located in a difference Fourier map and refined using a riding model (O—H = 0.98 \AA) and the $U_{\text{iso}}(\text{H})$ value was refined. The other H atoms were

positioned geometrically, with an N—H distance of 0.86 \AA and C—H distances of 0.93 (Csp²—H), 0.97 (CH₂) and 0.96 \AA (CH₃), and were then treated as riding, with $U_{\text{iso}}(\text{H})$ values of 1.2 $U_{\text{eq}}(\text{C}, \text{N})$ and 1.5 $U_{\text{eq}}(\text{methyl C})$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3043). Services for accessing these data are described at the back of the journal.

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