Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

{μ-*N*,*N*′-Bis[2-(dimethylamino)ethyl]oxamidato(2−)-κ^6*N*,*N*′,*O*′:*N*″,*N*‴,*O*}bis[(2,2′-bipyridine-κ^2*N*,*N*′)copper(II)] bis(perchlorate)

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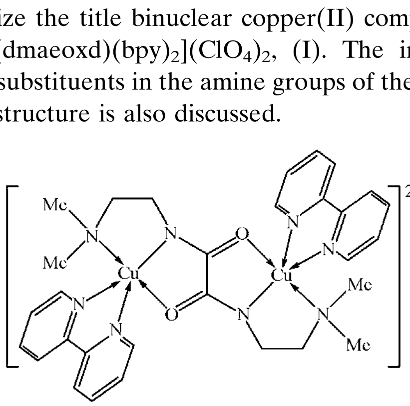
Received 19 November 2007
Accepted 18 December 2007
Online 9 February 2008

In the crystal structure of the title complex, [Cu$_2$(C$_{10}$H$_{20}$N$_4$O$_2$)(C$_{10}$H$_8$N$_2$)$_2$](ClO$_4$)$_2$, the deprotonated dmaeoxd^{2-} ligand {H$_2$dmaeoxd is *N*,*N*′-bis[2-(dimethylamino)ethyl]oxamide} occupies an inversion centre at the mid-point of the central C—C bond and is thus in a *trans* conformation. The two Cu^{II} atoms are located in slightly distorted square-based pyramidal environments. The binuclear units interact with each other *via* π–π interactions to form a one-dimensional chain extending in the *c* direction.

Comment

There has been great interest in the crystal engineering of self-assembled supramolecular architectures formed through relatively weak interactions such as hydrogen bonds and π–π stacking interactions (Blake *et al.*, 1999; Lin *et al.*, 2003). It is well known that *N*,*N*′-disubstituted oxamides could be good candidates for the formation of polynuclear complexes, because their coordinating ability towards transition metal ions can be modified and tuned by changing the nature of the amide substituents (Ojima & Nonoyama, 1988). A typical feature of these ligands is an easy transformation of *cis*–trans conformations, which makes it practical to design tunable molecular materials with desired properties (Chen *et al.*, 1998). To date, many polynuclear complexes containing oxamide bridges have been synthesized and their properties studied extensively (Messori *et al.*, 2003; Wang *et al.*, 2004). However, as far as we are aware, there are few studies of the influence of substituents in the amine groups of the bridging ligand on their coordination environments and supramolecular structures. Taking into account the above facts and in continuation of our work on polynuclear complexes with bridging oxamide groups (Li *et al.*, 2003, 2004), we chose *N*,*N*′-bis[2-(dimethylamino)ethyl]oxamide (H$_2$dmaeoxd) as the bridging ligand and 2,2′-bipyridine as the terminal ligand to synthesize the title binuclear copper(II) complex formulated as [Cu(dmaeoxd)(bpy)$_2$](ClO$_4$)$_2$, (I). The influence of the methyl substituents in the amine groups of the bridging ligand on the structure is also discussed.



(I)

The molecular structure of (I) (Fig. 1) consists of a centrosymmetric dinuclear copper(II) cation and two uncoordinated perchlorate anions. The [Cu$_2$(dmaeoxd)(bpy)$_2$]$^{2+}$ cation lies on an inversion centre at the middle of the C15—C15^i bond [symmetry code: (i) $-x$, $-y$, $2 - z$] and thus has a *trans* conformation, which is similar to another complex, [Cu(apox)(bpy)$_2$](NO$_3$)$_2$, (II) [H$_2$(apox) is *N*,*N*′-bis(3-aminopropyl)oxamide; Boyd & Rickard, 2006]. The N4/O1/C15/C15^i/N4^i/O1^i bridging group is planar, and atom Cu1 is displaced by 0.069 (4) Å from this plane. The Cu⋯Cu separation through the bridge is 5.249 (2) Å. Within the oxamide fragment, the C—O and C—N bonds have partial double-bond character [N4—C15 = 1.292 (4) Å and C15—O1 = 1.263 (3) Å; Table 1], while the length of the C15—C15^i single bond [1.533 (5) Å] is between the value of 1.541 (3) Å

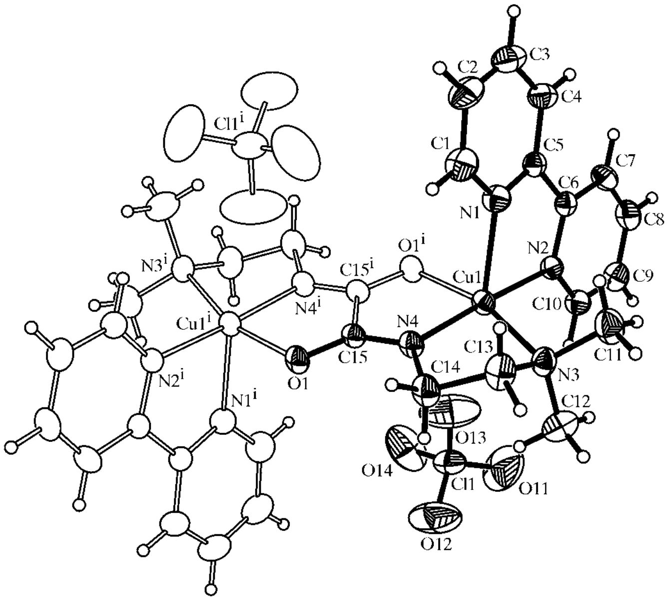


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x$, $-y$, $2 - z$.]

DOI: 10.1107/S0108270107067558

in [H_4dmaeoxd]$(NO_3)_2$ (Sun *et al.*, 2006) and that of 1.520 Å in compound (II).

Due to the rigidity of the ligands, the pentacoordinated Cu^{II} atom has a distorted square-pyramidal geometry. Atom N1 of the bpy ligand occupies the apical position, while the other N atom, N2, together with two N atoms (N3 and N4) and one O atom ($O1^i$) from the dmaeoxd ligand, form the basal coordination plane, with a maximum deviation of 0.0238 (13) Å for atom N4. Atom Cu1 is displaced out of the basal plane towards the apex by 0.0751 (17) Å. The axial Cu1—N1 distance of 2.218 (3) Å is significantly longer than those in the basal plane. The bis-tridentate dmaeoxd ligand produces two five-membered chelate rings with each Cu^{II} atom. The ring formed by the ethylenediamine fragment adopts a twist form, with puckering parameters (Cremer & Pople, 1975) of φ = 56.7 (4)° and Q = 0.448 (3) Å. In the ring, the Cu1—N3(amine) distance [2.092 (3) Å] is longer than the Cu1—N4(amidic) distance [1.903 (2) Å] by 0.189 (4) Å. This difference is larger than that of 0.0698 (18) Å in compound (II), in which the corresponding Cu—N bonds are in a six-membered ring. The dihedral angle between the oxamide bridge and the coordination basal plane is 8.07 (15)°, which is much smaller than the angle of 19.7° in compound (II).

The terminal bpy ligand is present in the usual chelating bidentate mode, with a bite angle of 78.36 (10)°. The C5—N1, C6—N2 and C5—C6 distances of 1.332 (4), 1.351 (4) and 1.494 (4) Å, respectively, are typical C═N and Csp^2—Csp^2 values. The 12-atom plane of the bpy ligand (r.m.s. deviation 0.0238 Å) is nearly perpendicular to the oxamide bridge, with a dihedral angle of 84.03 (7)°, which is larger than the angle of 72.5° in compound (II).

Compared with compound (II), the bpy ligands of the title compound do not contribute to C—H···O hydrogen bonds. In addition, due to the substitution of the H atoms of the primary amine by a methyl group, the dmaeoxd ligand does not participate in any hydrogen bonds, which is different from eight other reported binuclear complexes bridged by oxen [H_2oxen is *N*,*N*′-bis(2-aminoethyl)oxamide] (Cambridge Structural Database, Version 5.28; Allen, 2002). The pyridine rings of the bpy ligand are involved in offset π–π stacking interactions, by means of which, as shown in Fig. 2, the $[Cu_2(dmaeoxd)(bpy)_2]^{2+}$ cations assemble into a one-dimensional chain extending in the *c* direction. There is a 3.793 (2) Å separation between the centroids of the N2/C6–C10 rings at (x, y, z) and ($-x$, $-y$, $-z + 1$), with a plane-to-plane separation of 3.404 Å, which is the only significant π–π interaction. Further investigation concerning the influence of substituents on supramolecular structure is in progress in our laboratory.

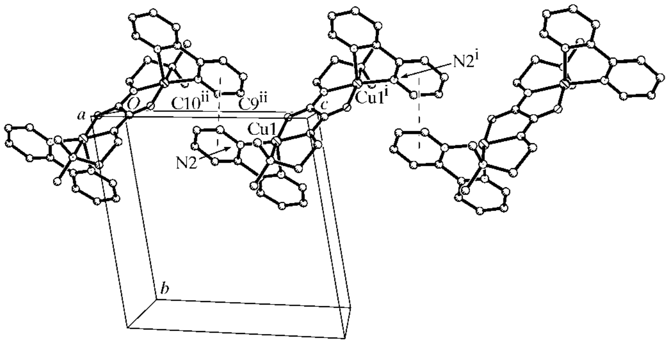


Figure 2
A view showing the π–π stacking interactions, viewed approximately down the *a* axis. H atoms and the ClO_4^- anion have been omitted for clarity. [Symmetry codes: (i) $-x$, $-y$, $2 - z$; (ii) $-x$, $-y$, $1 - z$.]

Experimental

All reagents were of AR grade and were used without further purification. The H_2dmaeoxd ligand was synthesized according to the method of Ojima & Yamada (1970). To a solution of H_2dmaeoxd (0.0230 g, 0.1 mmol) in methanol (10 ml) were added successively piperidine (0.2 mmol) and a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0741 g, 0.2 mmol) in methanol (5 ml). After stirring for 20 min, a solution of bpy (0.0312 g, 0.2 mmol) in methanol (5 ml) was added. The reaction mixture was stirred at 333 K for a further 2 h. The green precipitate which formed was collected by suction filtration, washed several times with methanol and diethyl ether, and dried over P_2O_5 under reduced pressure (yield 0.0637 g, 73%). Green crystals of the title compound suitable for X-ray analysis were obtained from a methanol–acetonitrile (1:1 *v*/*v*) mixture by slow evaporation for one week at room temperature. Analysis calculated for $C_{30}H_{36}Cl_2Cu_2N_8O_{10}$ (%): C 41.58, H 4.19, N 12.93; found (%): C 41.52, H 4.14, N 12.92. IR (KBr pellet, γ, cm^{-1}): 1648 (*vs*), 1474 (*m*), 1442 (*s*), 1090 (*vs*), 770 (*m*), 623 (*s*).

Crystal data

$[Cu_2(C_{10}H_{20}N_4O_2)(C_{10}H_8N_2)_2](ClO_4)_2$
M_r = 866.67
Triclinic, $P\overline{1}$
a = 8.6631 (17) Å
b = 10.144 (2) Å
c = 10.569 (2) Å
α = 79.73 (3)°
β = 78.02 (3)°
γ = 87.08 (3)°
V = 893.9 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.41 mm^{-1}
T = 298 (2) K
0.22 × 0.16 × 0.13 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.747, T_{max} = 0.838
4847 measured reflections
3189 independent reflections
2778 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.110
S = 1.05
3189 reflections
235 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

All H atoms were positioned geometrically, with C—H = 0.93 (Csp^2—H), 0.97 (CH_2) or 0.96 Å (CH_3). They were then treated using a riding model, with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(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).

This project was supported by the National Natural Science Foundation of China (grant No. 30672515) and the Natural Science Foundation of Qingdao City (grant No. 06-2-2-11-jch).

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	1.903 (2)	N1—C5	1.332 (4)
Cu1—N2	1.988 (2)	N2—C6	1.351 (4)
Cu1—O1^{i}	2.045 (2)	N4—C15	1.292 (4)
Cu1—N3	2.092 (3)	C5—C6	1.494 (4)
Cu1—N1	2.218 (3)	C15—C15^{i}	1.533 (5)
O1—C15	1.263 (3)		
N4—Cu1—N2	172.37 (10)	N2—Cu1—N1	78.36 (10)
N4—Cu1—O1^{i}	83.44 (9)	O1^{i}—Cu1—N1	88.81 (10)
N2—Cu1—O1^{i}	92.92 (9)	N3—Cu1—N1	103.12 (11)
N4—Cu1—N3	82.92 (10)	O1—C15—N4	129.1 (2)
N2—Cu1—N3	99.63 (10)	O1—C15—C15^{i}	118.8 (3)
O1^{i}—Cu1—N3	164.14 (10)	N4—C15—C15^{i}	112.2 (3)
N4—Cu1—N1	108.19 (10)		
Cu1—N1—C5—C6	−9.0 (3)	Cu1—N2—C6—C5	6.9 (3)

Symmetry code: (i) $-x, -y, -z+2$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3130). Services for accessing these data are described at the back of the journal.

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