

[μ_3 -*cis*-*N*-(2-Aminoethyl)-*N'*-(2-carboxylatophenyl)oxamidato(3-)]bis-(2,2'-diamino-4,4'-bi-1,3-thiazole)-tetracopper(II) bis(2,4,6-trinitrophenolate)

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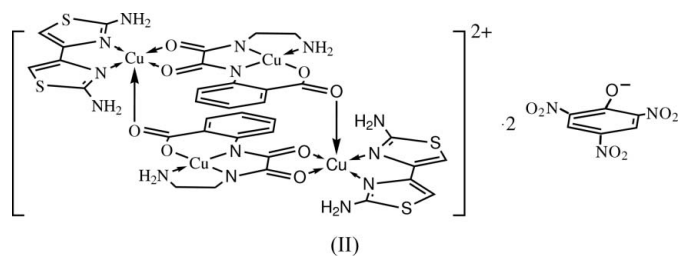
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The title complex, $[\text{Cu}_4(\text{C}_{11}\text{H}_{10}\text{N}_3\text{O}_4)_2(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)_2](\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2$, consists of a circular tetracopper(II) cation with an embedded inversion centre and two uncoordinated picrate (2,4,6-trinitrophenolate) anions. The Cu^{II} cations at the inner sites of *N*-(2-aminoethyl)-*N'*-(2-carboxylatophenyl)oxamidate(3-) (oxbe) have square-planar environments and those at the outer sites are in square-pyramidal geometries. The separations of pairs of Cu^{II} cations bridged by *cis*-oxamide and carboxylate groups are 5.2217 (5) and 5.2871 (5) Å, respectively. The tetracopper(II) cations and picrate anions are connected by N—H...O hydrogen bonds into a two-dimensional network parallel to the (010) plane, and these two-dimensional networks are assembled by two types of π - π stacking interactions into a three-dimensional supramolecular structure.

Comment

Many studies have been devoted to the crystal engineering of metal coordination complexes with supramolecular architectures formed through relatively weak interactions such as hydrogen bonds and π - π stacking interactions (Blake *et al.*, 1999; Lin *et al.*, 2003). *N,N'*-Disubstituted oxamides, which can afford symmetric and asymmetric oxamidate bridges by switching conformation between *cis* and *trans* (Ojima & Nonoyama, 1988; Ruiz *et al.*, 1999), have a typical ability to form three-dimensional supramolecular architectures (Zhang *et al.*, 2001; Delgado *et al.*, 2006; Sun *et al.*, 2007, 2008). Compared with studies dealing with symmetric *N,N'*-disubstituted oxamide polynuclear systems (Nakatani *et al.*, 1991; Lloret *et al.*, 1992; Santana *et al.*, 2004; Tang *et al.*, 2005), relatively few studies of asymmetric *N,N'*-disubstituted

oxamide polynuclear complexes have been reported to date, owing to difficulties in their synthesis (Matović *et al.*, 2005; Zang *et al.*, 2003). However, polynuclear complexes bridged by asymmetric *N,N'*-disubstituted oxamide ligands containing aromatic groups are characterized by connecting into a three-dimensional supramolecular structure *via* hydrogen bonds and π - π stacking, while they have shown outstanding magnetic properties (Yu *et al.*, 1989, 1991; Larionova *et al.*, 1997; Zang *et al.*, 2003; Tao, Zang, Cheng *et al.*, 2003; Tao, Zang, Hu *et al.*, 2003; Tao, Zang, Mei *et al.*, 2003; Tao *et al.*, 2004; Matović *et al.*, 2005; Zhu *et al.*, 2007), which prompted us to design and synthesize this type of polynuclear complex to explore their particular structures and functionalities.



Recently, we reported the crystal structure of a cyclic tetracopper(II) complex bridged by the *N*-(2-aminoethyl)-*N'*-(2-carboxylatophenyl)oxamidate (oxbm) ligand and end-capped with 2,2'-bipyridine (bpy), namely, $[\text{Cu}_4(\text{oxbm})_2(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$, (I) (Gu *et al.*, 2009). That study revealed that the terminal ligands (bpy) and counter-ions (Cl^-) played a dominant role in the construction of the three-dimensional supramolecular structure. In order to understand better the influence of terminal ligands and counter-ions on the crystal structure of these compounds, it was found necessary to

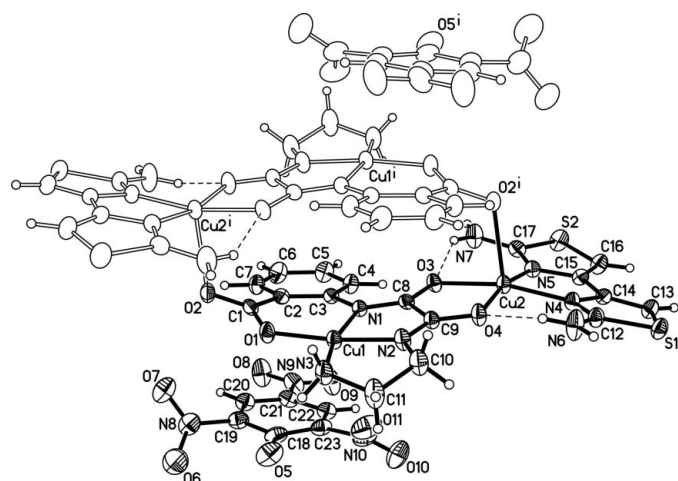


Figure 1

The molecular structure of (II), showing the atom-numbering scheme. The reference asymmetric unit is shown as shaded ellipsoids and filled bonds, while boundary ellipsoids and open bonds represent the symmetry-related half of the tetracopper(II) complex cation. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dotted lines indicate hydrogen bonds. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

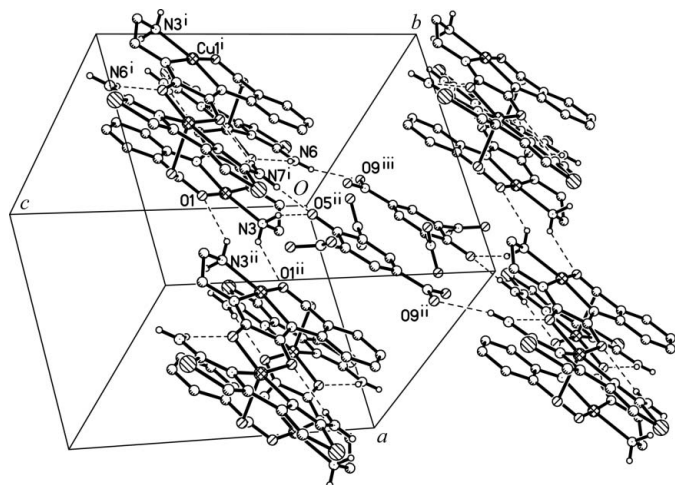


Figure 2

A view of a two-dimensional hydrogen-bonded structure of (II), parallel to the *ac* plane. Hydrogen bonds are shown as dotted lines and H atoms not involved in hydrogen bonds have been omitted for clarity. [Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y, z - 1$.]

synthesize a series of tetranuclear complexes of essentially analogous skeletal structure except for the terminal ligands and counter-ions. As an extension of our work, in this paper, the novel tetranuclear copper(II) complex, $[\text{Cu}_4(\text{oxbe})_2(\text{dabt})_2](\text{pic})_2$ (dabt is 2,2'-diamino-4,4'-bi-1,3-thiazole and pic is picrate), (II), has been synthesized using $\text{Na}[\text{Cu}(\text{oxbe})]$, with oxbe as the bridging ligand, and dabt and picrate anions as terminal ligand and counter-ion, respectively, and its crystal structure is reported here.

A perspective view of (II) is depicted in Fig. 1, and selected bond distances and angles are listed in Table 1. The molecular structure of (II) consists of a circular tetranuclear copper(II) cation, $[\text{Cu}_4(\text{oxbe})_2(\text{dabt})_2]^{2+}$, located on an inversion centre, and two uncoordinated symmetrically related pic anions. The tetracopper(II) cation can be considered as a pair of *cis*-oxamidate-bridged dinuclear copper(II) complexes assembled through carboxylate bridges to form a cyclic tetranuclear system. The separations of the Cu^{II} cations through the oxamide and carboxylate bridges are 5.2217 (5) and 5.2871 (5) Å, respectively. The oxamide group chelates to atoms Cu1 and Cu2 with typical bite angles of 84.42 (10) and 83.44 (8)°, respectively. The carboxylate group bridges the Cu^{II} cations in a skew-skew fashion, with torsion angles of $\text{Cu1}-\text{O1}-\text{C1}-\text{O2} = -157.0$ (2)° and $\text{Cu2}^i-\text{O2}-\text{C1}-\text{O1} = 104.8$ (3)° [symmetry code: (i) $-x, 1 - y, 1 - z$], which are similar to those found in other related complexes (Duan *et al.*, 2006; Tong *et al.*, 1997; Gu *et al.*, 2009).

In complex (II), the two Cu^{II} cations are in different coordination environments, which are distinct from those in complex (I). Atom Cu1, at the inner site of oxbe trianionic ligand, has a distorted square-planar geometry formed by N1, N2, N3 and O1, of which the maximum displacement from the coordination plane is 0.0401 (15) Å for atom N2. Atom Cu1 is displaced only 0.0770 (14) Å from the plane towards O11 from a nitro group, with a $\text{Cu1}\cdots\text{O11}$ distance of 2.770 (3) Å. Such

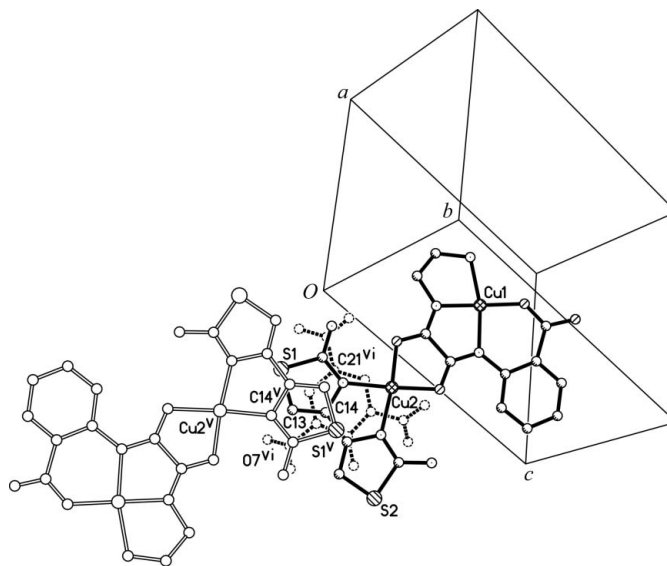


Figure 3

A perspective view of the π - π stacking interactions in (II), viewed perpendicular to the thiazole ring containing atom S1. H atoms have been omitted for clarity. [Symmetry codes: (v) $-x - 1, -y, -z$; (vi) $-x, -y, -z + 1$.]

a distance is too long to be considered a normal coordination bond. Furthermore, the bond valences (Shields *et al.*, 2000) around Cu1 are 0.550, 0.468, 0.598 and 0.467 units for O1, N1, N2 and N3, respectively, with a sum of 2.083. In comparison, O11 only contributes 0.049 to the bond valence, less than 3% of the total Cu1 valence, and can thus be reasonably ignored. In complex (I), atom Cu1 has a square-pyramidal geometry and the corresponding displacement from the basal plane is 0.2403 (13) Å, with an axial Cu—Cl bond length of 2.6832 (16) Å. The bond valence of the apical Cl atom is 0.158. In complex (II), the environment around atom Cu2 can be best described as a distorted square-pyramidal geometry, similar to that in complex (I), with τ values of 0.12 (Addison *et al.*, 1984). Atom Cu2 is coordinated by the outer O atoms (O3 and O4) of the oxamide group and atoms N4 and N5 of the dabt molecule, which define the basal plane with deviations in the range 0.0037 (11)–0.0041 (12) Å. Atom Cu2 is displaced 0.2004 (12) Å out of the basal plane towards apical carboxylate atom O2^i , with a $\text{Cu2}-\text{O2}^i$ bond length of 2.341 (2) Å.

The oxbe ligand coordinates Cu1 with a six-membered and two five-membered chelate rings. The five-membered Cu1/N2/C10/C11/N3 ring has a twist conformation, with puckering parameters (Cremer & Pople, 1975) $Q = 0.302$ (4) Å and $\varphi = 122.0$ (6)°, and the remaining five-membered Cu1/N1/C8/C9/N2 ring is almost planar, as expected. The puckering parameters of the Cu1/O1/C1–C3/N1 six-membered ring are $Q = 0.205$ (3) Å, $\theta = 78.1$ (8)° and $\varphi = 112.4$ (7)°. The Cu1–N3 bond is longer than the Cu1–N1 and Cu1–N2 bonds (Table 1), which is consistent with the stronger donor abilities of the deprotonated amide N atoms compared with the primary amine N atoms (Jubert *et al.*, 2002).

Comparison of complexes (I) and (II) shows that they share the same metal ion and an analogous oxamidate-bridged

skeletal structure. The main differences between them are the terminal ligands and the counter-ions [dabt and pic in (II) and bpy and Cl⁻ in (I)]. The substitution of Cl⁻ by pic contributes not only to changing the coordination geometries of the Cu^{II} cations (due to the larger space occupied by pic) but also affects the intermolecular interactions. The pic anions and dabt terminal ligands are better hydrogen-bond acceptors and donors than chloride anions and bpy ligands, which results in a stronger two-dimensional network formed by N—H...O hydrogen bonds, parallel to the (010) plane (Fig. 2 and Table 2). Furthermore, there are two types of offset π - π stacking interactions in complex (II) (Table 3 and Fig. 3). One is observed between the two thiazole rings containing atoms S1 and S1^v [symmetry code: (v) $-1 - x, -y, -z$], with a closest separation of 3.375 (4) Å (C13^v). The other is between the S1 thiazole ring and the picrate benzene ring at $(-x, -y, 1 - z)$ [symmetry code (vi)]; the closest distance between atom C20^{vi} and the thiazole plane is 3.436 (4) Å. These stackings form stronger interlayer interactions than those in complex (I), where only one type of π - π stacking occurs with a nearest separation of 3.421 (4) Å. These stacking interactions assemble the hydrogen-bonded layers into a three-dimensional supramolecular structure.

It is clear from the above discussion that terminal ligands and counter-ions play an important role in the construction of the three-dimensional supramolecular structures of these compounds, and further investigations involving different sets are in progress in our laboratory.

Experimental

All reagents were of analytical reagent grade. Na[Cu(oxbe)] was prepared according to the method of Tao, Zang, Mei *et al.* (2003). For the preparation of the title complex, [Cu₄(oxbe)₂(dabt)₂](pic)₂, (II), a methanolic solution (5 ml) of Cu(pic)₂·6H₂O (0.0628 g, 0.1 mmol) was added dropwise to an aqueous solution (5 ml) of Na[Cu(oxbe)] (0.0335 g, 0.1 mmol) with continuous stirring. The mixture was stirred quickly for 1 h and then dabt (0.0199 g, 0.1 mmol) in methanol (5 ml) was added dropwise. The solution obtained was stirred at 333 K for 6 h. The resulting solution was then filtered and the filtrate allowed to stand at room temperature for two weeks to give well shaped green crystals of (II) suitable for X-ray analysis (yield 69%). Analysis calculated for C₄₆H₃₆Cu₄N₂₀O₂₂S₄: C 34.46, H 2.26, N 17.47%; found: C 34.61, H 2.18, N 17.71%.

Crystal data

[Cu ₄ (C ₁₁ H ₁₀ N ₃ O ₄) ₂ (C ₆ H ₆ N ₄ S ₂) ₂ · (C ₆ H ₂ N ₃ O ₇) ₂]	$\beta = 98.134 (1)^\circ$
$M_r = 1603.34$	$\gamma = 105.059 (1)^\circ$
Triclinic, $P\bar{1}$	$V = 1404.91 (4) \text{ \AA}^3$
$a = 10.5528 (2) \text{ \AA}$	$Z = 1$
$b = 10.9391 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 13.1938 (2) \text{ \AA}$	$\mu = 1.74 \text{ mm}^{-1}$
$\alpha = 102.367 (1)^\circ$	$T = 296 \text{ K}$
	$0.15 \times 0.13 \times 0.11 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer	13345 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	6527 independent reflections
$T_{\min} = 0.780, T_{\max} = 0.831$	4897 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.876 (2)	Cu2—O3	2.0145 (19)
Cu1—N1	1.985 (2)	Cu2—O4	1.919 (2)
Cu1—N2	1.894 (2)	Cu2—N4	1.982 (2)
Cu1—N3	2.045 (2)	Cu2—N5	1.964 (2)
Cu2—O2 ⁱ	2.341 (2)		
O1—Cu1—N1	95.46 (9)	O2 ⁱ —Cu2—O3	85.08 (8)
N1—Cu1—N2	84.42 (10)	O1—Cu1—N2	173.15 (11)
N2—Cu1—N3	81.51 (10)	O1—Cu1—N3	98.33 (9)
O3—Cu2—O4	83.44 (8)	N1—Cu1—N3	165.85 (10)
N4—Cu2—N5	82.54 (9)	O4—Cu2—N5	167.33 (10)
O2 ⁱ —Cu2—O4	102.56 (9)	O4—Cu2—N4	91.25 (9)
O2 ⁱ —Cu2—N5	89.85 (9)	N5—Cu2—O3	100.37 (9)
O2 ⁱ —Cu2—N4	107.11 (9)	N4—Cu2—O3	167.55 (9)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3B...O1 ⁱⁱ	0.85	2.31	3.025 (3)	141
N3—H3A...O5 ⁱⁱ	0.94	2.28	3.161 (4)	157
N6—H6A...O4	0.86	2.07	2.772 (3)	138
N6—H6B...O9 ⁱⁱⁱ	0.86	2.25	3.043 (4)	152
N7—H7A...O3	0.86	2.31	3.050 (3)	145
N7—H7B...O5 ^{iv}	0.86	2.14	2.932 (3)	153

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y, z - 1$; (iv) $x - 1, y, z$.

Table 3

Geometric parameters of π - π stacking interactions (Å, °).

R1 denotes the thiazole ring consisting of atoms N4/C12/S1/C13/C14 and R2 is the C18—C23 benzene ring. $Cg\cdots Cg$, α and β denote the centroid-centroid separation, the dihedral angle between the ring planes and the offset angle, respectively. The separation is the perpendicular distance of the specified atom of the second ring from the plane of the first ring.

First ring	Second ring	$Cg\cdots Cg$	α	β	Separation
R1	R1 ^v	3.4785 (17)	0	13.78	C13 ^v 3.375 (4), C14 ^v 3.378 (3)
R1	R2 ^{vi}	3.7852 (18)	5.70 (16)	21.55	C20 ^{vi} 3.436 (4), C21 ^{vi} 3.529 (4)

Symmetry codes: (v) $-x - 1, -y, -z$; (vi) $-x, -y, 1 - z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	433 parameters
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.69 \text{ e \AA}^{-3}$
6527 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$

The primary amine H atoms were found in a difference Fourier map and all other H atoms were placed in calculated positions. All H atoms were refined using a riding model, with N—H = 0.86 Å, C—H = 0.93 (aromatic) or 0.97 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP (Siemens, 1994) and CAMERON (Watkin *et al.*, 1993); 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: BG3125). Services for accessing these data are described at the back of the journal.

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