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Key indicators

Single-crystal X-ray study

$T = 298$ K

Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å

R factor = 0.033

wR factor = 0.088

Data-to-parameter ratio = 12.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

$[\mu\text{-trans-}N,N'\text{-Bis(3-aminopropyl)oxamidato(2-)}]\text{-bis}[(\text{methanol})\text{picratocopper(II)}]$

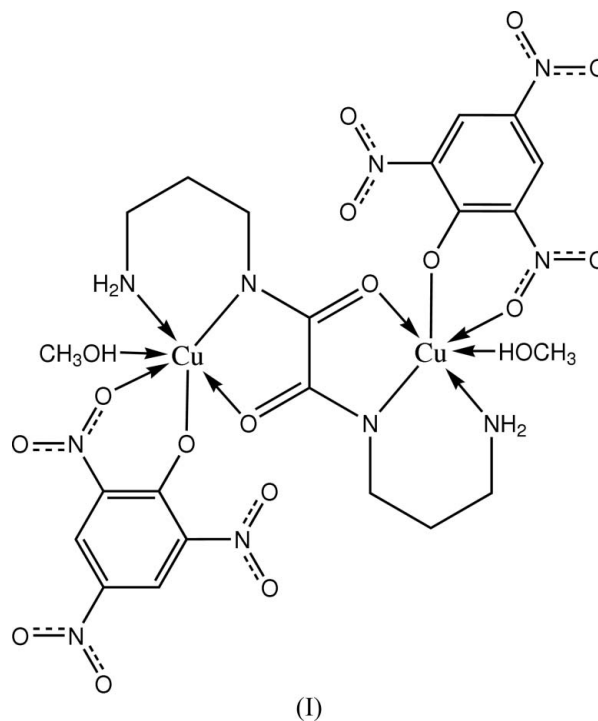
The title complex, $[\text{Cu}_2(\text{C}_6\text{H}_2\text{N}_3\text{O}_7)_2(\text{C}_8\text{H}_{16}\text{N}_4\text{O}_2)(\text{CH}_3\text{OH})_2]$, contains a centrosymmetric binuclear unit in which the oxamide ligand (at a centre of symmetry) acts in a bis-tridentate fashion and the picrate anion binds to copper(II) in a bidentate mode. The Cu^{II} atom displays a distorted octahedral coordination with axial elongation. The binuclear molecules are linked by hydrogen bonds, forming a three-dimensional supramolecular architecture.

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Comment

Oxamido compounds and their complexes have been investigated extensively (Ruiz *et al.*, 1999) by virtue of their bioactivities (Barta-Szalai *et al.*, 2004) and the versatile bridging function (Ojima & Nonoyama, 1988). We selected N,N' -bis(3-aminopropyl)oxamide (oxpn) as a bridging ligand and picrate as a terminal group to synthesize a new binuclear copper(II) complex, (I), with a three-dimensional supramolecular structure *via* hydrogen bonds. As far as we know, it is the first crystal structure of an oxamide complex using picrate as a terminal group.



The title complex (Fig. 1) forms a centrosymmetric binuclear molecule with an inversion centre at the mid-point of the $\text{C4}-\text{C4}^i$ bond [symmetry code: (i) $2 - x, -y, -z$]. The Cu

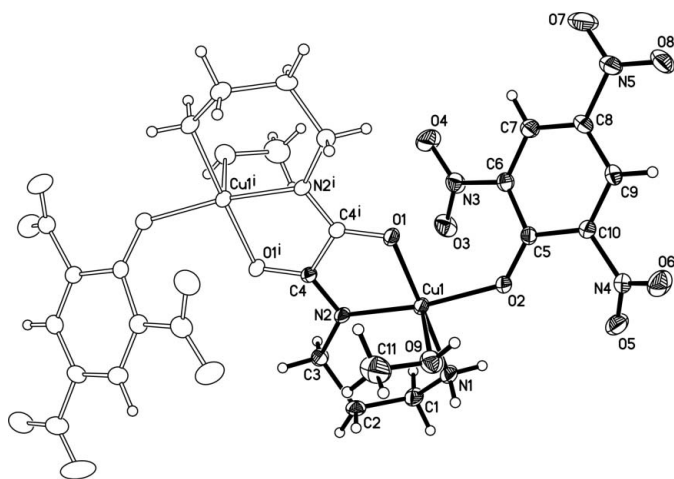


Figure 1
The molecular structure of (I), with 30% probability displacement ellipsoids. [Symmetry code: (i) $2 - x, -y, -z$.]

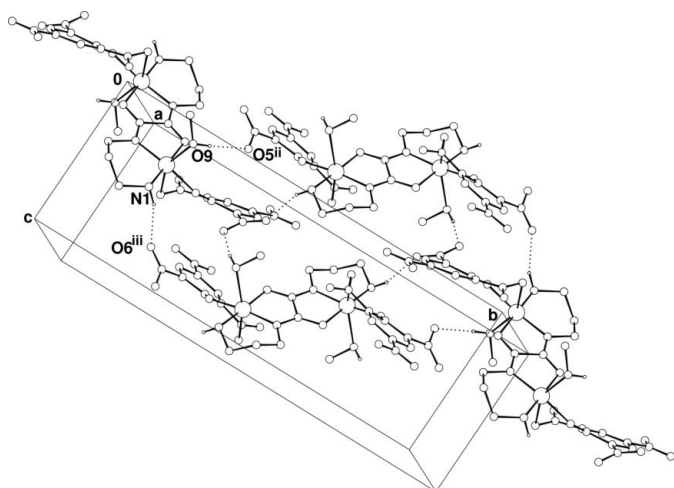


Figure 2
A two-dimensional classical hydrogen-bonding network parallel to the plane (100). Dotted lines indicate hydrogen bonds. [Symmetry codes: (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, z + \frac{1}{2}$.]

atom has a distorted octahedral coordination geometry. The equatorial plane is built up by N1, N2 and O1 of the oxpn^{2-} ligand and the phenolic hydroxyl (O2) from the picrate. The axial coordination sites are occupied by an oxygen (O3) of an *ortho* nitro group of the picrate and the O atom (O9) of a methanol molecule at greater distances (Table 1). Therefore, the coordination polyhedron of each Cu^{II} atom is elongated octahedral (4 + 2) (Tang *et al.*, 2003).

The *N,N'*-bis(3-aminopropyl)oxamidate, oxpn^{2-} , ligand adopts a bis-tridentate *trans* conformation, forming a six-membered chelate ring with each metal ion. This $\text{Cu1-N1-C1-C2-C3-N2}$ ring has a half-chair conformation, the Cremer & Pople (1975) puckering-parameter values being $\varphi = -26.4(4)^\circ$, $\theta = 130.2(2)^\circ$ and $Q = 0.535(3) \text{ \AA}$.

As a terminal group, the picrate anion assumes a bidentate mode, forming a six-membered chelate ring on each metal ion,

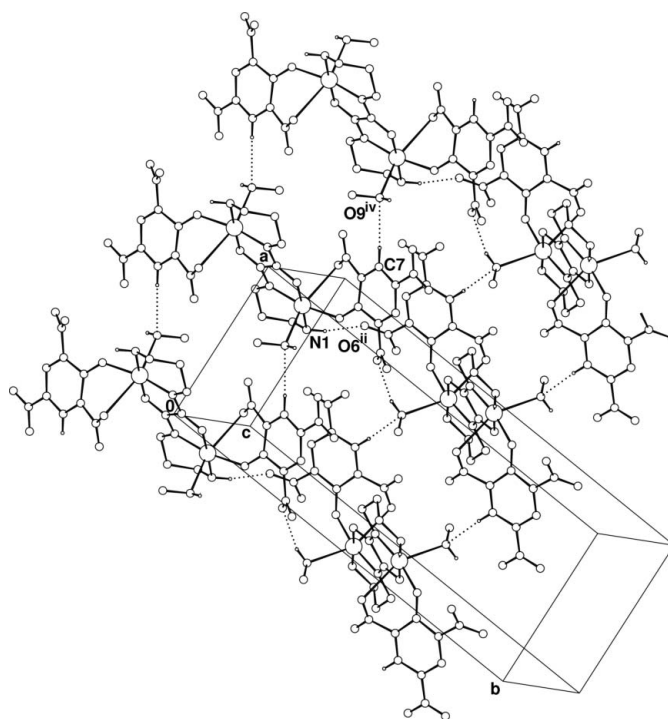


Figure 3
A view of the three-dimensional supramolecular structure with non-classical hydrogen bonding. Dotted lines indicate hydrogen bonds. [Symmetry codes: (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x + 1, y, z$.]

similar to two other copper complexes using bipyridine as ligand (Liang *et al.*, 2001; Simonov *et al.*, 1985). Atom C5 is displaced by $0.126(4) \text{ \AA}$ from the least-squares plane through the other C atoms in the benzene ring; this is due to the steric hindrance arising from the coordination of O3 and has been observed in a few instances (Beer *et al.*, 1995, 1996).

The crystal structure is stabilized by hydrogen bonding. As shown in Fig. 2, a two-dimensional infinite network parallel to the plane (100) is formed *via* two classical hydrogen bonds (entries 1 and 2 in Table 2). The adjacent layers are further connected by non-classical hydrogen bonds between aromatic carbon atom (C7) and methanol (third entry in Table 2) to form a three-dimensional supramolecular architecture (Fig. 3).

Experimental

All reagents were of AR grade and were used without further purification. The H_2oxpn ligand and its mononuclear complex $\text{Cu}(\text{oxpn})$ were prepared according to the literature method (Ojima & Yamada, 1968). The binuclear complex was prepared by the following procedure. A 5 ml methanol solution of 62.7 mg (0.1 mmol) copper(II) picrate hexahydrate was added dropwise to a 15 ml methanol solution of 26.4 mg (0.1 mmol) $\text{Cu}(\text{oxpn})$. The mixture was heated at reflux with stirring for 8 h. The solution was filtered and the filtrate was allowed to stand at room temperature for ten days, giving green crystals (yield 38%). IR (KBr pellet, cm^{-1}): $\nu(\text{N-H})$ 3164 (*s, br*), $\nu(\text{N-C=O})$ 1631 (*vs*), $\nu_{\text{as}}(\text{NO}_2)$ 1557, 1501 (*s*), $\nu_{\text{s}}(\text{NO}_2)$ 1365, 1316 (*s*), $\nu(\text{C-O})$ 1271 (*s*)

Crystal data

[Cu₂(C₆H₂N₃O₇)₂(C₈H₁₆N₄O₂)-
(CH₄O)₂]
M_r = 847.62
 Monoclinic, *P*2₁/*c*
a = 8.7271 (17) Å
b = 22.245 (4) Å
c = 8.2234 (16) Å
 β = 92.739 (3)°
V = 1594.6 (5) Å³
Z = 2
D_x = 1.765 Mg m⁻³
 Mo *K*α radiation
 μ = 1.43 mm⁻¹
T = 298 (2) K
 Block, green
 0.19 × 0.15 × 0.12 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: none
 8436 measured reflections
 2873 independent reflections
 2194 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{max} = 25.2°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.033
wR (*F*²) = 0.088
S = 1.01
 2873 reflections
 237 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.8821P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.36 e Å⁻³
 Δρ_{min} = -0.28 e Å⁻³

Table 1
 Selected bond lengths (Å).

Cu1—N1	1.969 (2)	Cu1—O2	1.9788 (19)
Cu1—N2	1.952 (2)	Cu1—O3	2.624 (3)
Cu1—O1	1.976 (2)	Cu1—O9	2.405 (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>
O9—H9A...O5 ⁱ	0.84	2.23	3.030 (3)	161
N1—H1C...O6 ⁱⁱ	0.90	2.15	3.017 (4)	161
C7—H7...O9 ⁱⁱⁱ	0.93	2.52	3.447 (4)	173

Symmetry codes: (i) *x*, -*y* + ½, *z* - ½; (ii) *x*, -*y* + ½, *z* + ½; (iii) *x* + 1, *y*, *z*.

The O-bound H atom was located in a difference Fourier map, but refined as riding with O—H = 0.84 Å. All other H atoms were placed in calculated positions, with N—H = 0.90 Å and C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl C atoms, respectively. All H atoms were refined in riding mode, with *U*_{iso}(H) = 0.08 Å² (on O), 1.2*U*_{eq}(N, methylene and aromatic C) or 1.5*U*_{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: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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