

trans*-Bis(2-aminoanilinium- κN^2)bis(oxalato- $\kappa^2 O, O')$ copper(II)*Tony D. Keene, Michael B. Hursthouse and Daniel J. Price***

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Key indicators

Single-crystal X-ray study

 $T = 120\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$ R factor = 0.035 wR factor = 0.091

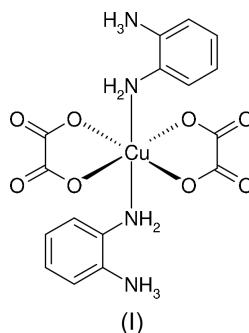
Data-to-parameter ratio = 14.2

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

The title compound, $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_9\text{N}_2)_2]$, crystallizes in the space group $P2_1/c$, with the Cu atom located at a centre of symmetry. It is a neutral coordination complex in which the metal exhibits a tetragonally elongated octahedral *trans*- CuO_4N_2 coordination environment. Extensive intermolecular hydrogen bonding between the oxalate anions and the ammonium cations determines the molecular packing in the crystal.

Comment

The title complex, (I), was grown from aqueous solution by a gel crystallization technique. It crystallizes in the monoclinic space group $P2_1/c$, with the Cu atom located at a centre of symmetry. The structure comprises planar $[\text{Cu}(\text{ox})_2]^{2-}$ units (ox is oxalate), which have long axial contacts to the amino groups of monoprotonated 1,2-phenylenediamine cations (Fig. 1). All bond lengths and angles are in accordance with standard values (Orpen *et al.*, 1992). All amine H atoms are involved in linear hydrogen bonds. In each complex, two H atoms form intramolecular bonds, while the remaining eight H atoms link to six neighbouring molecules, forming a three-dimensional network (Fig. 2).



While the majority of metal–oxalate compounds form low-solubility polymeric structures, discrete mononuclear complexes can be formed when the oxalate bridging potential is reduced. One way to achieve this is to saturate the metal coordination sphere, either by using high oxalate/metal ratios, or by some inert capping ligand. This has been demonstrated with chelating amines and kinetically inert ions such as Cr^{III} (Lethbridge *et al.*, 1970; Rochon & Massarweh, 1999; Russell *et al.*, 2001) and Co^{III} (Yasui *et al.*, 1987; Lappin *et al.*, 1993), resulting in a *cis*- $[\text{M}(\text{ox})_2\text{X}_2]$ species. For Cu^{II} , the favoured square-planar coordination geometry with weak axial interactions means that, although it is seldom seen in structural studies (Insausti *et al.*, 1994), *trans*- $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})_2]^{2-}$ is the dominant solution species under high oxalate concentration. A consequence of the facile displacement of water is that, in

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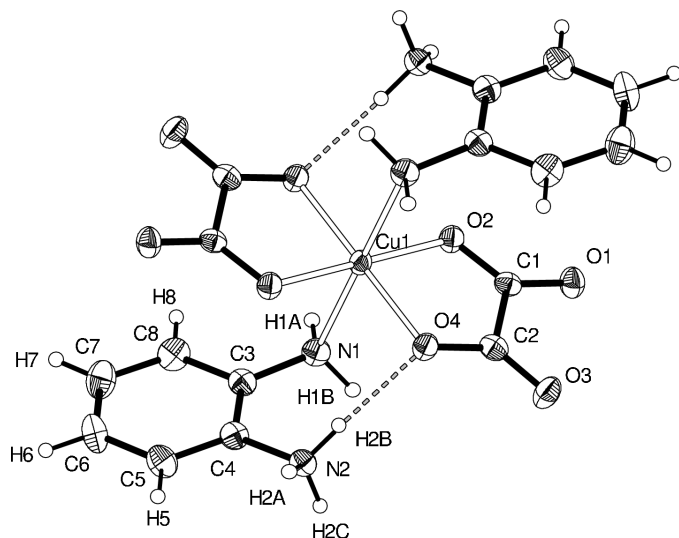


Figure 1
The molecular structure of (I), showing the numbering scheme in the asymmetric unit. Dashed lines depict intramolecular hydrogen bonding. Displacement ellipsoids are shown at the 70% probability level.

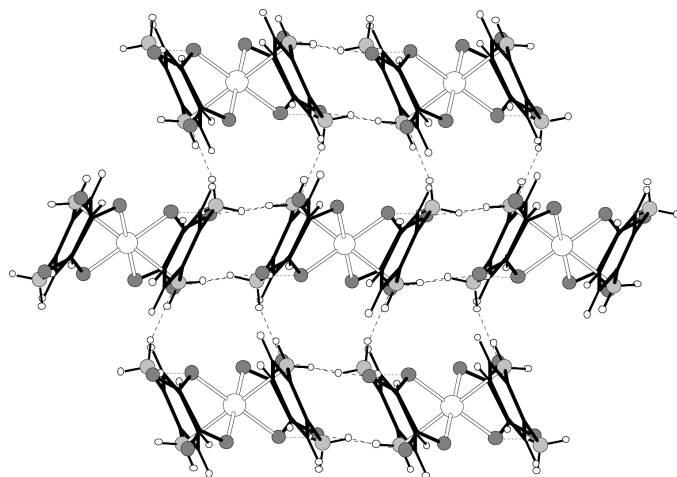


Figure 2
Packing diagram of (I), viewed down the *a* axis.

most $[\text{Cu}(\text{ox})_2]^{2-}$ -containing compounds, Cu exhibits an axial coordination from neighbouring $[\text{Cu}(\text{ox})_2]^{2-}$ units, resulting in polymeric structures (Bloomquist *et al.*, 1981; Gajapathy *et al.*, 1983; Novosad *et al.*, 2000; Lohn, 1969).

The title compound, (I), is one of relatively few examples of mononuclear copper bisoxalate compounds (Savel'eva *et al.*, 1992; Kivekas & Pajunen, 1977; Oshio *et al.*, 2000; Insausti *et al.*, 1994) and the only known example with *trans*-N-donor ligands.

Experimental

Single crystals of (I) were synthesized by a gel-crystallization technique. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (100 mg) was dissolved in distilled water (18 ml). Tetramethoxysilane (2 ml) was added and the mixture stirred until

monophasic, then allowed to set in a test tube. A solution of 1,2-phenylenediammonium oxalate (200 mg) in distilled water (3 ml) was added to the top of the gel. After about 3 weeks, small pale-blue crystals had formed in the gel. IR (KBr, diffuse reflectance, cm^{-1}): 3345 and 3283 ($-\text{NH}_2$ stretch), 3075 (Ar—H stretch), 2900 and 2611 [$\nu(-\text{NH}_3)$], 1674 and 1628 ($-\text{CO}_2$ anti-symmetric stretch), 1504 ($-\text{NH}_3$ bend), 1428 (oxalate $-\text{CO}_2$ symmetric stretch), 1291 (C—O bend), 797 (4 adj. Ar—H bends), 755, 500. UV-vis/NIR (diffuse reflectance on a powdered sample, cm^{-1}): 14500 (*d-d*), 36500 (oxalate absorption). Absorption is consistent with an O_4N_2 coordination sphere.

Crystal data

$[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_9\text{N}_2)_2]$
 $M_r = 457.89$
 Monoclinic, $P2_1/c$
 $a = 11.5768$ (4) Å
 $b = 10.6642$ (3) Å
 $c = 7.5782$ (2) Å
 $\beta = 108.0130$ (10)°
 $V = 889.73$ (5) Å³
 $Z = 2$

$D_x = 1.709$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4249 reflections
 $\theta = 2.9$ – 27.5°
 $\mu = 1.28$ mm⁻¹
 $T = 120$ (2) K
 Block, pale blue
 0.2 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1997)
 $T_{\min} = 0.605$, $T_{\max} = 0.880$
 8409 measured reflections

2023 independent reflections
 1765 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.086$
 $\theta_{\max} = 27.5^\circ$
 $h = -15 \rightarrow 15$
 $k = -13 \rightarrow 13$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.091$
 $S = 1.06$
 2023 reflections
 142 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 0.8605P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.47$ e Å⁻³
 $\Delta\rho_{\min} = -0.56$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O2	1.9579 (14)	O4—C2	1.283 (2)
Cu1—O4	1.9675 (14)	O2—C1	1.264 (3)
Cu1—N1	2.4980 (19)	O3—C2	1.231 (3)
O1—C1	1.248 (2)	C1—C2	1.559 (3)
O2—Cu1—O4 ⁱ	95.24 (6)	O2 ⁱ —Cu1—N1	92.15 (6)
O2—Cu1—O4	84.76 (6)	O4 ⁱ —Cu1—N1	90.60 (6)
O2—Cu1—N1	87.85 (6)	O4—Cu1—N1	89.40 (6)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O3 ⁱⁱ	0.86 (3)	2.33 (3)	3.181 (2)	167 (2)
N2—H2A \cdots O1 ⁱⁱⁱ	0.89	1.93	2.799 (2)	164
N2—H2A \cdots O2 ⁱⁱⁱ	0.89	2.56	3.184 (2)	128
N2—H2B \cdots O4	0.89	2.05	2.925 (2)	166
N2—H2C \cdots O1 ^{iv}	0.89	2.01	2.843 (2)	154
N2—H2C \cdots O3 ^{iv}	0.89	2.49	3.026 (2)	120
N1—H1B \cdots O3 ^{iv}	0.92 (3)	2.05 (3)	2.938 (3)	162 (2)

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

The amino atoms H1A and H1B were located in a difference map and refined freely. All other H atoms were fixed in calculated positions and refined in riding mode.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) in *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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