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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 = 0.031

wR factor = 0.079

Data-to-parameter ratio = 13.2

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

N,N'-(2-Ammonioethyl)ethane-1,2-diaminium di- μ -oxalato-bis[aquaoxalatocuprate(II)]

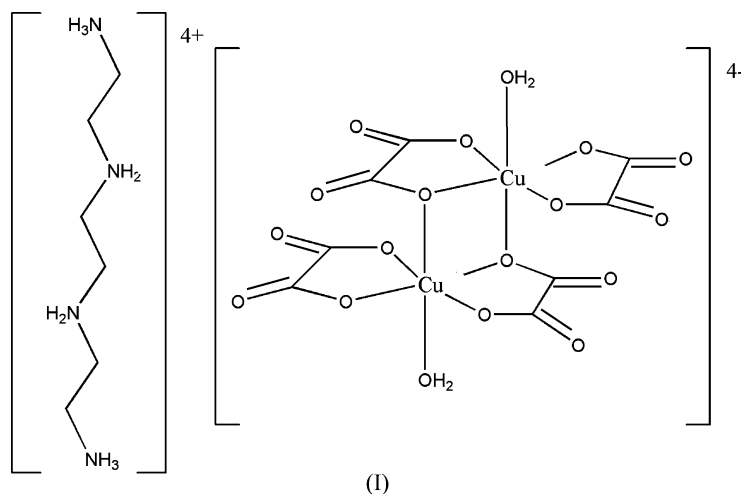
The asymmetric unit of the title compound, $(\text{C}_6\text{H}_{22}\text{N}_4)[\text{Cu}_2(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]$, contains one-half of a $\text{C}_6\text{H}_{22}\text{N}_4^{4+}$ cation and one-half of a $[\text{Cu}_2(\text{ox})_4(\text{H}_2\text{O})_2]^{4-}$ anion (ox is oxalate). The $[\text{Cu}(\text{ox})_2(\text{H}_2\text{O})]^{2-}$ units dimerize around an inversion center, giving an octahedrally distorted CuO_6 coordination. The cation is also centrosymmetric. Extensive hydrogen bonding between the oxalate, the coordinated water molecules and the cations determines the crystal packing and may explain the strong interactions observed between the chelate $\text{Cu}(\text{ox})_2$ planes of the $[\text{Cu}_2(\text{ox})_4(\text{H}_2\text{O})_2]^{4-}$ anion.

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Comment

The title complex, (I), obtained as a by-product in our experiment, consists of $[\text{C}_6\text{H}_{22}\text{N}_4]^{4+}$ cations and the rare $[\text{Cu}_2(\text{ox})_4(\text{H}_2\text{O})_2]^{4-}$ dimeric anions (ox is oxalate), which have only been observed in $(\text{C}_6\text{H}_{14}\text{N}_2)[\text{Cu}_2(\text{ox})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$, (II) (Keene *et al.*, 2004). Cations and anions are both centrosymmetric. In the anion, two oxalates and one water molecule are coordinated to one Cu^{2+} , forming half of the dimer (Fig. 1).



The two parts of the dimer are connected through the bridging atom O7 and its symmetry-related counterpart. The structure of the $[\text{Cu}_2(\text{ox})_4(\text{H}_2\text{O})_2]^{4-}$ dimer reveals a very similar arrangement to that of the same anion in (II). However, the interaction between the chelate $\text{Cu}(\text{ox})_2$ planes is much stronger in the title compound. Indeed, the $\text{Cu}-\text{O}$ distance between the two chelate planes is 2.669 (2) Å, compared with 2.906 (1) Å in (II). Similarly, the $\text{Cu}\cdots\text{Cu}$ distance is 3.405 (1) Å, whereas it is 3.818 (8) Å in (II). Moreover, the $\text{O}7-\text{Cu}1-\text{O}7$ angle is 85.90 (9)°, larger than the value of 78.04° in (II). This stronger interaction may result

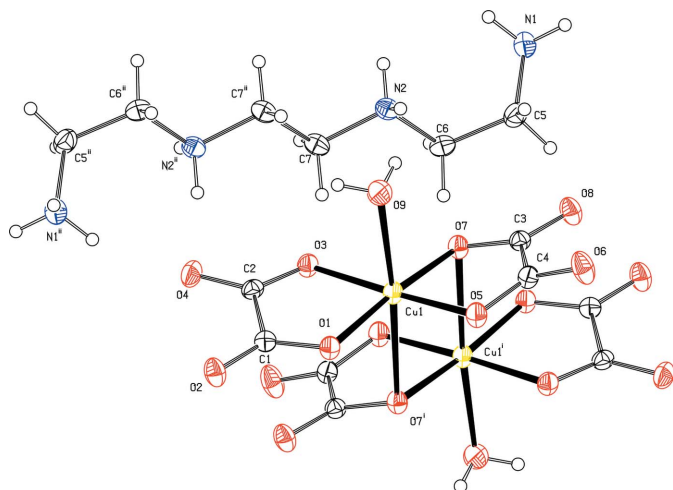


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, 2 - z$.]

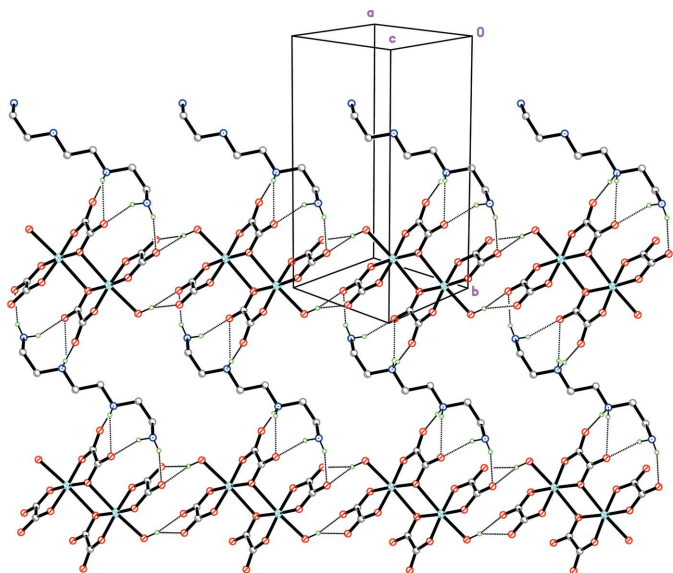


Figure 2
The two-dimensional layer connected by hydrogen bonds (shown as dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity. Colour key: red O, pale blue Cu, grey C, blue N and green H.

from hydrogen-bond interactions between the anions and the $[\text{C}_6\text{H}_{22}\text{N}_4]^{4+}$ cations (Table 1 and Fig. 2).

The occurrence of $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between cations and anions results in the formation of an intricate three-dimensional network (Table 1 and Fig. 2).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China and were used without further purification. 2,2'-(2,5,8,11-Tetraazadodeca-1,11-diene-1,12-diyl)diphenol was synthesized by refluxing N,N' -(ethane-1,2-diyl)diethane-1,2-diamine and salicylaldehyde in a 1:2 molar ratio in 100 ml ethanol overnight at 383 K, followed by rotary evaporation.

The residue was filtered off and washed twice each with ethanol and diethyl ether. 2,2'-(2,5,8,11-Tetraazadodeca-1,11-diene-1,12-diyl)diphenol (3 mmol) was dissolved in 20 ml of ethanol. $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (3 mmol), ZnCl_2 (3 mmol) and oxalic acid (3 mmol) were dissolved in 10 ml water. The two solutions were mixed and stirred for 1 h at room temperature. The solution was filtered and the resulting solid was washed twice each with ethanol and diethyl ether. 0.25 g of the solid was dissolved in 30 ml heated water. 1 M KOH was used to adjust the pH to 6. The solution was filtered, and the filtrate was left to stand at room temperature. Blue crystals of compound (I) were obtained after three months by slow evaporation of the solvent.

Crystal data

$(\text{C}_6\text{H}_{22}\text{N}_4)[\text{Cu}_2(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]$
 $M_r = 665.47$
 Monoclinic, $P2_1/c$
 $a = 9.736(2) \text{ \AA}$
 $b = 14.089(3) \text{ \AA}$
 $c = 9.398(2) \text{ \AA}$
 $\beta = 118.263(2)^\circ$
 $V = 1135.4(4) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.946 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.97 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Pillar, blue
 $0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.589, T_{\max} = 0.694$

6026 measured reflections
 2356 independent reflections
 1971 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 27.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.079$
 $S = 0.98$
 2356 reflections
 179 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e \AA}^{-3}$

Table 1

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2B}\cdots\text{O6}^i$	0.90	1.95	2.840 (3)	172
$\text{N2}-\text{H2A}\cdots\text{O8}^i$	0.90	2.57	3.007 (3)	110
$\text{N2}-\text{H2A}\cdots\text{O4}^{ii}$	0.90	2.05	2.895 (3)	155
$\text{N1}-\text{H1C}\cdots\text{O9}^{iii}$	0.89	2.52	2.979 (3)	113
$\text{N1}-\text{H1C}\cdots\text{O5}^{iii}$	0.89	2.36	3.113 (3)	143
$\text{N1}-\text{H1C}\cdots\text{O1}^{iii}$	0.89	2.30	3.045 (2)	141
$\text{N1}-\text{H1B}\cdots\text{O2}^{iv}$	0.89	2.07	2.917 (3)	160
$\text{N1}-\text{H1A}\cdots\text{O8}^i$	0.89	2.36	2.922 (3)	121
$\text{N1}-\text{H1A}\cdots\text{O4}^{ii}$	0.89	2.05	2.840 (3)	147
$\text{O9}-\text{H92}\cdots\text{O6}^i$	0.82 (3)	1.95 (3)	2.773 (3)	175 (3)
$\text{O9}-\text{H91}\cdots\text{O4}^{iv}$	0.82 (3)	2.46 (2)	3.043 (3)	128 (2)
$\text{O9}-\text{H91}\cdots\text{O2}^v$	0.82 (3)	2.12 (2)	2.905 (3)	158 (3)

Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $x - 1, y, z$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 2, -y + 1, -z + 2$.

H atoms attached to C and N atoms were placed in geometrically idealized positions, with $\text{Csp}^3-\text{H} = 0.97 \text{ \AA}$ and $\text{Nsp}^3-\text{H} = 0.90 \text{ \AA}$ (0.89 \AA terminal), and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ [$1.5U_{\text{eq}}(\text{N})$ for NH_3 groups]. Aqua H atoms were located in difference Fourier maps and refined using a fixed $U_{\text{iso}}(\text{H})$ value (0.066 \AA^2). The O—H distances were restrained to 0.82 (1) \AA .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL/PC*.

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