N,N′-Bis(2-ammonioethyl)oxamide diaquabis-(oxalato-$\kappa^2 O,O′$)cuprate(II) dihydrate

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Key indicators

The title compound, $(C_6H_{16}N_4O_2)[Cu(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$, consists of a $[Cu(ox)_2(H_2O)_2]^{2-}$ dianion (ox is oxalate), a doubly protonated N,N′-bis(2-ammonioethyl)oxamide dication (H_4aeoxd^{2+}) and two uncoordinated water molecules. Both the cation and the anion are centrosymmetric. The structural components are linked into a three-dimensional supramolecular structure by a combination of strong N—H···O and O—H···O, and weak C—H···O hydrogen bonds.

Comment

Both diaquabis(oxalato-$\kappa^2 O,O′$)cuprate(II) group, $[Cu(ox)_2(H_2O)_2]^{2-}$, and N,N′-bis(2-ammonioethyl)oxamide, H_2aeoxd, have played a key role as bridging ligands in the synthesis of polynuclear complexes (Andruh *et al.*, 1996; Novosad *et al.*, 2000; Chen *et al.*, 1998; Yan *et al.*, 1998). The crystal structures of other salts of $[Cu(ox)_2(H_2O)_2]^{2-}$ (Andruh *et al.*, 1996; Novosad *et al.*, 2000) and H_4aeoxd^{2+} (Su *et al.*, 1999) have already been determined.

(I)
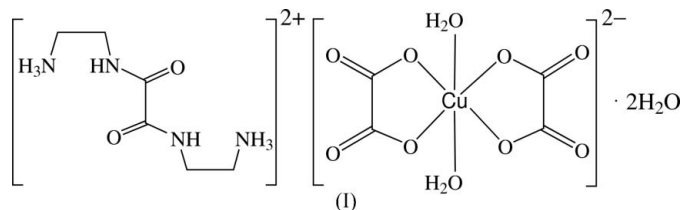
Here we report the self-assembling title compound, (I), which contains these two components together. The molecular structure is illustrated in Fig. 1 and selected geometric para-
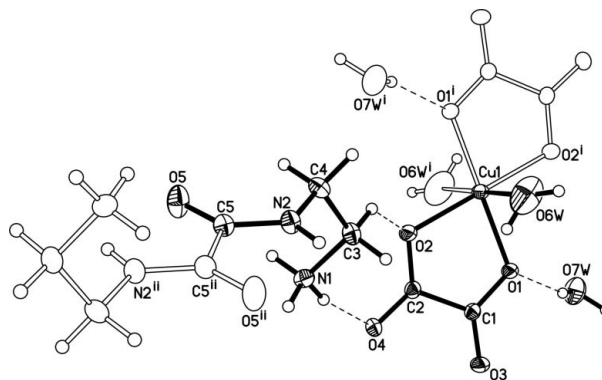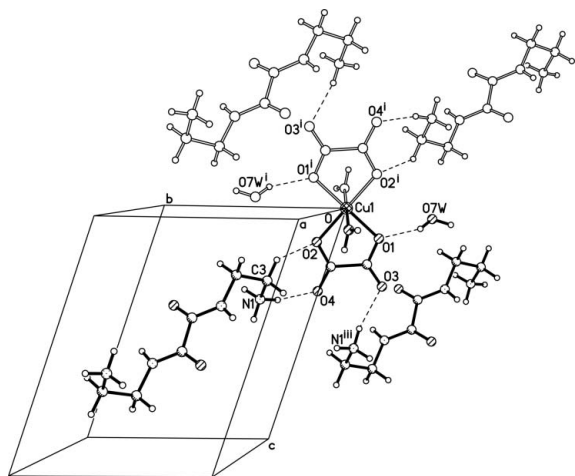

Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Full displacement ellipsoids (for the asymmetric unit) and open ellipsoids (for the symmetry-related parts) are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $-x + 1$, $-y + 1$, $-z + 1$.]
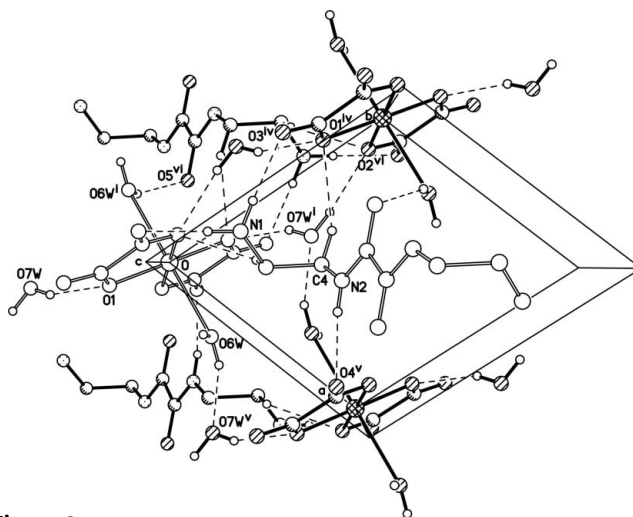
Figure 2
The two-dimensional hydrogen-bonded (dashed lines) network parallel to the ($\bar{1}$10) plane. The symmetry-related part of the [Cu(ox)$_2$(2H$_2$O)]$^{2-}$ ion and the two hydrogen-bonded H$_4$aeoxd^{2+} ions are shown as open circles and hollow bonds. [Symmetry codes: (i) $-x$, $-y$, $-z$; (iii) $-x$, $-y$, $1 - z$.]

Figure 3
A view of the three-dimensional supramolecular structure. The central layer is shown in open circle and hollow bonds. H atoms not involved in hydrogen bonds (dashed lines) have been omitted for clarity. [Symmetry codes: (i) $-x$, $-y$, $-z$; (iv) x, $1 + y$, z; (v) $1 + x$, y, z; (vi) $-x$, $-y + 1$, $-z$.]

meters are presented in Table 1. The cation and anion each lie on a symmetry centre. The interatomic bond distances and angles are comparable to those reported in the literature (Su *et al.*, 1999; Novosad *et al.*, 2000).

Non-bonding interactions consist of two types of classical (N—H···O and O—H···O) and one type of non-classical (C—H···O) hydrogen bonds (Table 2), leading to an extensive three-dimensional supramolecular structure. Parallel to the ($\bar{1}$10) plane, one [Cu(ox)$_2$(2H$_2$O)]$^{2-}$ dianion is connected to two uncoordinated water molecules through O7W—H7B···O1 hydrogen bonds; it is simultaneously connected with four neighbouring H$_4$aeoxd^{2+} dications *via* N1—H1B···O4, C3—H3A···O2 and N1—H1A···O3^{ii} [symmetry code: (ii) $-x$, $-y$, $1 - z$] hydrogen bonds. Each H$_4$aeoxd^{2+} ion is also linked to four adjacent [Cu(ox)$_2$(2H$_2$O)]$^{2-}$ ions, forming a two-dimensional hydrogen-bonding network (Fig. 2). Each layer is further connected through other hydrogen bonds, resulting in a three-dimensional hydrogen-bonding network.

Experimental

All reagents were of AR grade. The ligand H$_2$aeoxd, its mononuclear compound Cu(aeoxd), and oxovanadium(IV) oxalate dihydrate, were prepared according to literature methods (Ojima & Nonoyama, 1988; Sathyanarayana & Patel, 1965). The original scope of this work was to prepare a heterodinuclear oxamide-bridged copper(II)–oxovanadium(IV) complex, but during the synthetic process the title compound and an orange compound were obtained. To an aqueous solution (10 ml) of Cu(aeoxd) (20.4 mg, 0.1 mmol) was added drop-wise an aqueous solution (5 ml) of oxovanadium(IV) oxalate dihydrate (19.1 mg, 0.1 mmol). The mixture was stirred continuously at 333 K for 5 h and a small amount of a green precipitate formed. The solution was then filtered and the filtrate allowed to stand at room temperature for several days, giving blue and orange crystals. The orange crystals were too small to be suitable for X-ray diffraction so we only determined the structure of the blue crystals. Analysis

calculated: C 24.62, H 4.96, N 11.48%; found: C 24.55, H 4.92, N 11.56%.

Crystal data

(C$_6$H$_{16}$N$_4$O$_2$)[Cu(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·2H$_2$O	γ = 70.51 (3)°
	V = 474.4 (2) Å^3
M_r = 487.88	Z = 1
Triclinic, $P\bar{1}$	D_x = 1.708 Mg m^{-3}
a = 6.7889 (14) Å	Mo $K\alpha$ radiation
b = 7.5799 (15) Å	μ = 1.23 mm^{-1}
c = 10.255 (2) Å	T = 298 (2) K
α = 72.49 (3)°	Block, blue
β = 83.48 (3)°	0.45 × 0.38 × 0.29 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2535 measured reflections
	1703 independent reflections
φ and ω scans	1518 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	R_{int} = 0.019
	θ_{max} = 25.2°
T_{min} = 0.595, T_{max} = 0.702	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.037	$+ 0.3253P]$
$wR(F^2)$ = 0.101	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
1703 reflections	$\Delta\rho_{max}$ = 0.63 e Å^{-3}
134 parameters	$\Delta\rho_{min}$ = −0.53 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9464 (19)	Cu1—O6W	2.550 (3)
Cu1—O2	1.9471 (19)		
O1—Cu1—O2	84.76 (8)	O1^i—Cu1—O6W	88.98 (10)
O1—Cu1—O6W	91.02 (10)	O2—Cu1—O6W	89.54 (12)
O1^i—Cu1—O2	95.24 (8)	O2^i—Cu1—O6W	90.46 (12)

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

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···O3[ii]	0.89	2.05	2.912 (3)	164
N1—H1B···O4	0.89	2.05	2.926 (3)	167
N1—H1C···O3[iii]	0.89	2.01	2.858 (3)	159
N2—H2···O4[iv]	0.86	2.18	2.903 (3)	141
O6W—H6A···O5[v]	0.85	2.53	3.307 (5)	153
O6W—H6B···O7W[iv]	0.85	2.05	2.860 (4)	159
O7W—H7B···O1	0.85	2.03	2.828 (3)	156
O7W—H7A···O2[v]	0.85	2.13	2.972 (3)	171
C3—H3A···O2	0.97	2.58	3.329 (4)	135
C4—H4B···O1[iii]	0.97	2.59	3.502 (4)	158

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

H atoms of water molecules were located in a difference Fourier map and were refined in riding mode (Nardelli, 1999), with $U_{iso}(H) = 0.08$ Å^2 and O—H = 0.85 Å; all other H atoms were placed in calculated positions, with C—H = 0.97 Å and N—H = 0.89 (protonated primary amine) or 0.86 Å (secondary amine), and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(protonated primary amine).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Andruh, M., Melanson, R., Stager, C. V. & Rochon, F. D. (1996). *Inorg. Chim. Acta*, **251**, 309–317.
Bruker (2002). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, Z.-N., Zhang, H.-X., Su, C.-Y., Zhou, Z.-Y., Zheng, K.-C. & Kang, B.-S. (1998). *Inorg. Chem.* **37**, 3877–3880.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.
Novosad, J., Messimeri, A. C., Papadimitriou, C. D., Veltsistas, P. G. & Woollins, J. D. (2000). *Transition Met. Chem.* **25**, 664–669.
Ojima, H. & Nonoyama, K. (1988). *Coord. Chem. Rev.* **92**, 85–111.
Sathyanarayana, D. N. & Patel, C. C. (1965). *J. Inorg. Nucl. Chem.* **27**, 297–302.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Su, C.-Y., Zhang, W.-J. & Kang, B.-S. (1999). *Acta Cryst.* C**55**, 636–637.
Yan, C.-W., Li, Y.-T., Su, Y.-Z. & Liao, D.-Z. (1998). *Polyhedron*, **17**, 1311–1316.