C(12)	−0.6595 (4)	0.2406 (4)	1.0057 (2)	0.0183 (6)
C(13)	−0.4779 (4)	0.3091 (4)	0.8965 (2)	0.0161 (6)
C(14)	−0.8363 (4)	0.2231 (5)	1.0367 (3)	0.0252 (7)
S(2)	−0.23738 (10)	−0.10552 (9)	0.41566 (6)	0.0196 (2)
N(21)	−0.2679 (3)	0.1000 (3)	0.5770 (2)	0.0179 (5)
N(22)	−0.2005 (4)	0.2287 (4)	0.4495 (2)	0.0246 (6)
C(23)	−0.2328 (4)	0.0969 (4)	0.4842 (2)	0.0181 (6)
C(22)	−0.2976 (4)	−0.0548 (4)	0.5983 (2)	0.0176 (6)
C(21)	−0.2867 (4)	−0.1787 (4)	0.5187 (2)	0.0201 (6)
C(24)	−0.3348 (5)	−0.0652 (4)	0.7011 (2)	0.0240 (7)

Table 4. *Bond lengths (Å) and angles (°) for the $[CuCl_4]^{2-}$ anion in (1) and (2)*

	(1)		(2)	
	100 K	200 K	100 K	295 K*
Cu—Cl(1)	2.258 (1)	2.2552 (9)	2.256 (1)	2.257 (1)
Cu—Cl(2)	2.254 (1)	2.2513 (8)	2.272 (1)	2.235 (1)
Cu—Cl(3)	2.235 (2)	2.234 (2)	2.239 (1)	2.264 (1)
Cu—Cl(4)	2.242 (2)	2.239 (1)	2.243 (1)	2.234 (1)
Cl(2)—Cu—Cl(1)	143.09 (4)	142.24 (4)	95.31 (4)	95.6 (1)
Cl(3)—Cu—Cl(1)	94.70 (6)	94.99 (4)	132.15 (4)	130.6 (1)
Cl(3)—Cu—Cl(2)	96.88 (6)	97.04 (4)	98.66 (4)	98.8 (1)
Cl(4)—Cu—Cl(1)	97.12 (5)	97.61 (4)	101.28 (5)	101.7 (1)
Cl(4)—Cu—Cl(2)	96.02 (5)	95.99 (3)	137.64 (4)	137.1 (1)
Cl(3)—Cu—Cl(4)	140.23 (5)	139.66 (4)	98.40 (4)	99.0 (1)

* Data from Fernández *et al.* (1987) (modified atom-labelling scheme).

The diffractometer was equipped with a low-temperature device (Cosier & Glazer, 1986). Data were collected (*CAD*-4 *Software*; Enraf–Nonius, 1989) with profile analysis over all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Cell refinement was performed using *CRYSDA* (Beurskens *et al.*, 1992) and data reduction was achieved using *DATAR* (local program). The structure was solved by Patterson methods using the *DIRDIF* (Beurskens *et al.*, 1992) phase-expansion procedure (*SHELXS*86; Sheldrick, 1990). Isotropic least-squares refinement was performed using a local version of *SHELX*76 (Sheldrick, 1976; Van der Maelen Uría, 1991). Refinement was completed using *SHELXL*93 (Sheldrick, 1993). For compound (1), the apparently anomalous difference between the transmission factors of the absorption corrections of the 100 and 200 K data sets is thought to arise from the nature of the refined absorption correction method. For compound (1) at 100 and 200 K, C—H and NH_2 (planar) H atoms were included using a riding model; the coordinates of N—H11/21 were refined freely. A common isotropic *U* was included for all H atoms. For compound (2), C—H H atoms were riding, while all N—H H atoms were refined freely; all H-atom displacement parameters were refined freely. Further geometrical calculations were made with *PARST* (Nardelli, 1983). Molecular graphics were produced using *EUCLID* (Spek, 1982) and *SHELXL*93 was used to to prepare the material for publication. All calculations were made at the University of Oviedo on VAX computers of the Scientific Computer Center and the X-ray group.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Disodium [*N*,*N*′-(1,3-Propanediyl)bis(oxamato-*N*,*O*)]cuprate(II) Hexahydrate

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Abstract

In order to obtain structural parameters for a comparison with polynuclear metal complexes derived from the $[Cu(C_7H_6N_2O_6)]^{2-}$ complex anion, the X-ray study of the title compound, $Na_2[Cu(C_7H_6N_2O_6)].6H_2O$, has been carried out. The molecular structure parameters are in agreement with the geometrical parameters of derived polynuclear complexes, in particular, with respect to the loss of planarity of the CuN_2O_2 moiety.

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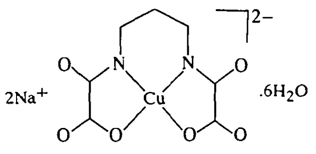
Comment

Magnetostructural correlations in binuclear or trinuclear copper(II) complexes have been investigated exhaustively during the last two decades. It is now well established that $C_2X_2Y_2$ (X, Y = O, N, S) ligands are efficient in the propagation of the magnetic interaction when they bridge two copper(II) centres, resulting in antiferromagnetic coupling. It has been shown in binuclear and trinuclear systems that it is possible to tune the magnitude of this interaction by retaining the same bridging ligand and changing the terminal ligands. In order to determine the influence of different ligands on the copper(II) coordination polyhedron, it is interesting to compare the geometry of the mononuclear complex with those of the binuclear or trinuclear systems. The structure and magnetic properties of a trinuclear complex with the [N,N'-(1,3-propanediyl)bis(oxamato)]cuprate(II) moiety as central group have been reported previously (Costa *et al.*, 1993). In the present paper, we report the crystal structure of the mononuclear compound, disodium [N,N'-(1,3-propanediyl)bis(oxamato-N,O)]cuprate(II) hexahydrate, (I).



(I)

The structure of (I) consists of mononuclear [N,N'-(1,3-propanediyl)bis(oxamato)]cuprate(II) anions (Fig. 1), sodium cations and water molecules coordinated to sodium cations. The Cu atom displays near square-planar coordination with a slight tetrahedral distortion (D = 6%; Gali, Bonnet & Anderson, 1979), with two O atoms and the two deprotonated amide N atoms of the oxamate group forming the coordination plane; this distortion was 3% in $[Cu(H_2O)(Me_2tn)_2][Cu(pba)].3H_2O$, where Me_2tn is N,N'-dimethylpropanediamine and pba is N,N'-(1,3-propanediyl)bis(oxamate) (Ribas *et al.*, 1991). The Cu—O distances of 1.961 (4) and 1.967 (5) Å and Cu—N distances of 1.922 (5) and 1.924 (5) Å are in good agreement with the distances observed in the previously mentioned trinuclear complex (Costa *et al.*, 1993). The Cu atom is displaced by 0.016 (4) Å from the least-squares plane defined by the four coordinated atoms. These lengths are 0.125 (4) and 0.057 (4) Å in molecules A and B, respectively, of the trinuclear complex, where a perchlorate ion is coordinated in the fifth position. The dihedral angles between the coordination plane and the two planes defined by the oxamate groups [4.2 (2) and 3.2 (1)°] reveal a planar conformation of the complex unit. These angles are 4.8 (6) and 6.9 (7)° for molecule A and 7.3 (6) and 7.1 (6)° for molecule B in the trinuclear complex.

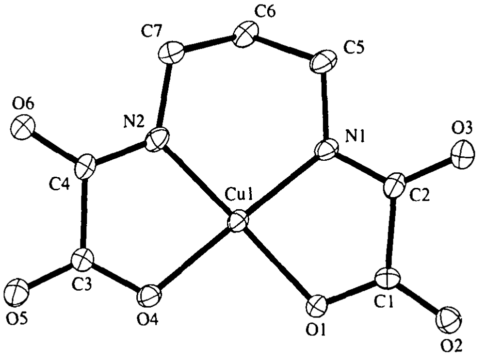


Fig. 1. An *ORTEP*II view (Johnson, 1976) of the 1,3-propanediylbis(oxamato)cuprate(II) anion showing the numbering scheme and 50% probability displacement ellipsoids.

Each NaO_6 polyhedron has a different environment. Thus, the Na1 atom is coordinated by four O atoms of four oxamate groups and two water O atoms, while the Na2 polyhedron is formed by five water O atoms and one O atom of an oxamate ligand. The octahedra are slightly distorted; the distortion parameter is 0.055 for Na1 and 0.028 for Na2 (Urtiaga, Pizarro, Cortes, Goñi & Larramendi, 1994). The Na1···Na2 distance is 4.046 (4) Å.

The crystal packing is determined by the sodium ions and hydrogen bonds. The anions are stacked in a columnar fashion along the c axis. The distances between the copper ions are 3.583 (2) [Cu···Cu(1 − x, 1 − y, −z)] and 3.662 (2) Å [Cu···Cu(1 − x, 1 − y, 1 − z)]. The sodium octahedra form a zigzag chain along the the b axis, with the junctions between octahedra beimg alternately vertices and edges.

Experimental

The title compound was prepared as described by Nonoyama, Ojima & Nonoyama (1976).

Crystal data

$Na_2[Cu(C_7H_6N_2O_6)].6H_2O$
M_r = 431.75
Triclinic
$P\bar{1}$
a = 11.194 (2) Å
b = 10.492 (2) Å
c = 6.976 (2) Å
α = 94.62 (2)°
β = 97.78 (2)°
γ = 102.54 (2)°
V = 787.3 (3) Å^3
Z = 2
D_x = 1.821 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 12–25°
μ = 1.506 mm^{-1}
T = 293 (2) K
Prism
0.5 × 0.3 × 0.3 mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans

2667 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 29.99°

Absorption correction:
ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.475$, $T_{\max} = 0.894$
2692 measured reflections
2692 independent reflections

$h = -15 \rightarrow 15$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: 4%

Refinement

Refinement on F^2
$R(F) = 0.0719$
$wR(F^2) = 0.1872$
$S = 1.076$
2569 reflections
218 parameters
Only H-atom U's refined
$w = 1.4202/[\sigma^2(F) + 0.002960F^2]$

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.70$ e Å^{-3}
$\Delta\rho_{\min} = -0.60$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	0.47111 (7)	0.45692 (7)	0.23553 (12)	0.0235 (2)
Na1	0.0207 (2)	0.3968 (3)	−0.1873 (4)	0.0338 (6)
Na2	0.1306 (3)	−0.0115 (3)	0.1723 (4)	0.0365 (6)
O1	0.3474 (4)	0.2913 (4)	0.2248 (7)	0.0283 (9)
O2	0.1446 (4)	0.2227 (4)	0.2326 (8)	0.0334 (10)
O3	0.1196 (5)	0.4775 (5)	0.2108 (10)	0.0448 (13)
O4	0.6081 (4)	0.3684 (4)	0.2204 (7)	0.0286 (9)
O5	0.8129 (4)	0.4211 (5)	0.2126 (7)	0.0332 (10)
O6	0.8012 (4)	0.6806 (4)	0.2047 (7)	0.0330 (10)
N1	0.3343 (5)	0.5384 (5)	0.2527 (8)	0.0267 (10)
N2	0.5959 (5)	0.6152 (5)	0.2354 (8)	0.0287 (11)
C1	0.2384 (6)	0.3109 (5)	0.2305 (9)	0.0245 (11)
C2	0.2266 (6)	0.4552 (6)	0.2299 (10)	0.0276 (12)
C3	0.7104 (5)	0.4497 (5)	0.2155 (9)	0.0238 (11)
C4	0.7066 (5)	0.5965 (5)	0.2198 (8)	0.0230 (11)
C5	0.3403 (6)	0.6798 (6)	0.2645 (11)	0.0330 (14)
C6	0.4700 (6)	0.7589 (6)	0.3614 (10)	0.0290 (12)
C7	0.5741 (7)	0.7485 (6)	0.2467 (11)	0.0331 (14)
O11	0.0799 (5)	−0.2317 (5)	0.0050 (8)	0.0359 (11)
O12	−0.0312 (5)	0.3164 (6)	−0.5205 (8)	0.0425 (12)
O13	−0.0919 (5)	−0.0572 (5)	0.1701 (8)	0.0397 (12)
O14	0.3540 (5)	0.0291 (5)	0.1473 (9)	0.0455 (13)
O15	0.6219 (6)	0.0963 (5)	0.2261 (9)	0.0472 (14)
O16	0.1718 (6)	−0.0678 (6)	0.5000 (9)	0.0498 (14)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—N1	1.922 (5)	C6—C7	1.519 (10)
Cu1—N2	1.924 (5)	Na1—O3^{i}	2.258 (6)
Cu1—O1	1.961 (4)	Na1—O6^{ii}	2.325 (5)
Cu1—O4	1.967 (5)	Na1—O12	2.358 (6)
O1—C1	1.287 (8)	Na1—O5^{ii}	2.397 (6)
O2—C1	1.242 (7)	Na1—O11^{iii}	2.405 (6)
O3—C2	1.261 (8)	Na1—O3	2.835 (7)
O4—C3	1.278 (7)	Na1—Na1^{i}	3.403 (6)
O5—C3	1.249 (7)	Na1—Na2^{iii}	4.046 (4)
O6—C4	1.244 (7)	Na2—O11	2.416 (5)
N1—C2	1.307 (8)	Na2—O16	2.416 (7)
N1—C5	1.466 (7)	Na2—O2	2.426 (5)
N2—C4	1.313 (8)	Na2—O13	2.430 (6)
N2—C7	1.469 (8)	Na2—O14	2.476 (7)
C1—C2	1.549 (8)	Na2—O13^{iii}	2.559 (6)
C3—C4	1.548 (8)	Na2···Na2^{iii}	3.589 (6)
C5—C6	1.541 (9)		
N1—Cu1—N2	97.3 (2)	O3^{i}—Na1—O6^{ii}	162.7 (2)
N1—Cu1—O1	84.9 (2)	O3^{i}—Na1—O12	92.3 (2)
N2—Cu1—O1	177.0 (2)	O6^{ii}—Na1—O12	84.5 (2)
N1—Cu1—O4	178.2 (2)	O3^{i}—Na1—O5^{ii}	92.2 (2)
N2—Cu1—O4	84.5 (2)	O6^{ii}—Na1—O5^{ii}	71.5 (2)
O1—Cu1—O4	93.4 (2)	O12—Na1—O5^{ii}	98.0 (2)
C1—O1—Cu1	111.7 (3)	O3^{i}—Na1—O11^{iii}	99.6 (2)
C3—O4—Cu1	112.0 (4)	O6^{ii}—Na1—O11^{iii}	97.6 (2)
C2—N1—C5	119.6 (5)	O12—Na1—O11^{iii}	108.0 (2)
C2—N1—Cu1	114.0 (4)	O5^{ii}—Na1—O11^{iii}	150.8 (2)
C5—N1—Cu1	125.9 (4)	O3^{i}—Na1—O3	97.0 (2)
C4—N2—C7	120.4 (5)	O6^{ii}—Na1—O3	85.9 (2)
C4—N2—Cu1	114.7 (4)	O12—Na1—O3	170.4 (2)
C7—N2—Cu1	125.0 (4)	O5^{ii}—Na1—O3	79.0 (2)
O2—C1—O1	124.4 (5)	O11^{iii}—Na1—O3	73.2 (2)
O2—C1—C2	119.5 (6)	O11—Na2—O16	97.8 (2)
O1—C1—C2	116.0 (5)	O11—Na2—O2	160.0 (2)
O3—C2—N1	129.2 (6)	O16—Na2—O2	101.3 (2)
O3—C2—C1	118.3 (5)	O11—Na2—O13	82.3 (2)
N1—C2—C1	112.5 (5)	O16—Na2—O13	93.0 (2)
O5—C3—O4	125.6 (5)	O2—Na2—O13	90.7 (2)
O5—C3—C4	117.7 (5)	O11—Na2—O14	94.8 (2)
O4—C3—C4	116.6 (5)	O16—Na2—O14	90.7 (2)
O6—C4—N2	127.6 (6)	O2—Na2—O14	90.9 (2)
O6—C4—C3	120.3 (5)	O13—Na2—O14	175.6 (2)
N2—C4—C3	112.1 (5)	O11—Na2—O13^{iii}	84.3 (2)
N1—C5—C6	110.7 (5)	O16—Na2—O13^{iii}	177.8 (2)
C7—C6—C5	115.2 (6)	O2—Na2—O13^{iii}	76.7 (2)
N2—C7—C6	111.3 (5)	O13—Na2—O13^{iii}	88.0 (2)
Na1^{iii}—O11—Na2	114.1 (2)	O14—Na2—O13^{iii}	88.4 (2)
Na2—O13—Na2^{iii}	92.0 (2)		

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CFEO* (Solans, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a diagram of the crystal packing, have been deposited with the IUCr (Reference: KA1157). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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