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Bis(N^1-isopropyl-2-methyl-1,2-propanediamine)-μ-oxalato-oxalatodicopper(II) Monohydrate

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Abstract. $[Cu_2(C_7H_{18}N_2)_2(C_2O_4)_2].H_2O$, monoclinic, $P2_1/c$, $a = 8·551\ (8)$, $b = 11·876\ (9)$, $c = 26·353\ (9)$ Å, $\beta = 99·37\ (7)°$, $Z = 4$, $D_m = 1·46$, $D_c = 1·463$ Mg m^{-3}. Final $R = 0·063$ ($R_w = 0·044$) for 3318 observed reflections. The dimeric complex contains two independent Cu atoms linked by an oxalate bridge. The coordination of Cu(1) is distorted square pyramidal, the basal plane comprising two N atoms of a diamine molecule and two O atoms of an oxalate ion. Another O atom, from the bridging oxalate ion, is at the apex of the pyramid. The coordination of Cu(2) is square planar, with two N atoms of the other diamine molecule and two O atoms of the bridging oxalate ion forming the base.

Introduction. Blue crystals of the title compound were prepared by adding N^1-isopropyl-2-methyl-1,2-propanediamine to copper(II) oxalate hemihydrate in the molar ratio 1:1 in a methanol–ethanol mixture and evaporating the resulting solution. The space group was determined from systematic absences. Cell parameters and intensities of 6319 unique reflections (including systematic absences) with $3 < 2\theta < 55°$ were measured on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å) and the ω-scan technique. Of these, 3318 reflections with $I > 2\sigma(I)$ were regarded as observed. The structure was solved by *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier methods of XRAY 76 (Stewart, 1976). Isotropic full-matrix least-squares refinement converged to $R = 0·10$ and refinement with anisotropic temperature factors reduced R to 0·075. At this stage H atoms were determined from a difference map. Refinement with fixed isotropic temperature factors for H (U = 0·06 Å^2) moved H′(O9) into a chemically doubtful position, and it was therefore returned and held in the position indicated by the difference map. The final refinement converged to $R = 0·063$ and R_w = 0·044. The weighting scheme was $w = 4F_o^2/\sigma^2(I_o)$. Scattering factors for H were those of Stewart, Davidson & Simpson (1965) and for Cu^{2+}, O, N and C those of Cromer & Mann (1968). Final positional parameters with equivalent values of temperature factors for non-hydrogen atoms are given in Table 1 (Hamilton, 1959). Coordinates for H atoms with their bond lengths are given in Table 2. Bond lengths and angles for non-hydrogen atoms are listed in Table 3. The structure of the molecule with the atom numbering is shown in Fig. 1.*

Table 1. *Fractional coordinates* (×10^5) *for* Cu *and* (×10^4) *for* O, N *and* C *with e.s.d.'s in parentheses, and* B_{eq} *values* (Å^2)

	x	y	z	B_{eq}
Cu(1)	7447 (9)	23013 (6)	62040 (3)	2·95
Cu(2)	−23679 (9)	−7211 (7)	70809 (3)	3·23
O(1)	1115 (5)	842 (4)	5876 (2)	4·19
O(2)	3070 (6)	−411 (4)	5881 (2)	5·38
O(3)	3046 (5)	2280 (3)	6436 (2)	3·65
O(4)	5061 (5)	1053 (4)	6496 (2)	5·64
O(5)	555 (5)	1803 (4)	7025 (2)	4·29
O(6)	−1331 (5)	507 (4)	6797 (2)	3·94
O(7)	704 (6)	1074 (4)	8027 (2)	5·12
O(8)	−1188 (5)	−199 (4)	7734 (2)	4·08
O(9)	−1268 (8)	1502 (6)	4961 (2)	7·37
N(1)	565 (5)	4011 (4)	6165 (2)	2·73
N(2)	−1595 (6)	2301 (4)	5967 (2)	3·06
N(3)	−3574 (5)	−1238 (4)	6402 (2)	3·02
N(4)	−3250 (6)	−2063 (4)	7374 (2)	3·71
C(1)	2553 (8)	507 (5)	6006 (2)	3·62
C(2)	3667 (7)	1338 (6)	6345 (2)	3·59
C(3)	−1064 (7)	4293 (5)	5900 (2)	3·25
C(4)	−2278 (7)	3434 (5)	6032 (2)	3·19
C(5)	−3847 (8)	3584 (6)	5657 (3)	5·41
C(6)	−2530 (8)	3556 (6)	6592 (3)	4·83
C(7)	1853 (7)	4552 (5)	5927 (2)	3·32
C(8)	1698 (8)	5826 (6)	5900 (3)	4·88
C(9)	1982 (8)	4016 (6)	5417 (2)	4·25
C(10)	−315 (7)	1029 (5)	7121 (2)	3·30
C(11)	−241 (7)	619 (5)	7680 (2)	3·36
C(12)	−4262 (7)	−2376 (5)	6482 (2)	3·54
C(13)	−4688 (7)	−2453 (5)	7023 (2)	3·21
C(14)	−5059 (9)	−3671 (6)	7144 (3)	5·07
C(15)	−6066 (9)	−1694 (7)	7086 (3)	5·43
C(16)	−2674 (9)	−1179 (6)	5955 (3)	4·24
C(17)	−3670 (11)	−1548 (8)	5453 (3)	6·93
C(18)	−1108 (9)	−1798 (7)	6079 (3)	6·10

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35314 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Fractional coordinates* (×10³) *for* H *atoms and their bond lengths* (Å) *with e.s.d.'s in parentheses*

	x	*y*	*z*	*d*
H(N1)	61 (6)	416 (5)	648 (2)	0·85 (5)
H(N2)	−196 (6)	178 (5)	615 (2)	0·87 (6)
H'(N2)	−175 (6)	207 (5)	567 (2)	0·83 (6)
H(N3)	−433 (6)	−75 (5)	632 (2)	0·87 (5)
H(N4)	−338 (7)	−202 (5)	763 (2)	0·71 (6)
H'(N4)	−231 (6)	−261 (5)	741 (2)	1·03 (6)
H(C3)	−99 (6)	423 (5)	553 (2)	1·00 (6)
H'(C3)	−135 (6)	508 (5)	596 (2)	0·98 (6)
H(C5)	−436 (6)	427 (5)	569 (2)	0·94 (6)
H'(C5)	−354 (7)	350 (5)	533 (2)	0·94 (6)
H''(C5)	−455 (6)	305 (5)	576 (2)	0·94 (6)
H(C6)	−307 (6)	423 (5)	662 (2)	0·93 (6)
H'(C6)	−138 (6)	349 (5)	685 (2)	1·10 (5)
H''(C6)	−321 (6)	292 (5)	666 (2)	0·98 (6)
H(C7)	276 (6)	438 (5)	613 (2)	0·89 (5)
H(C8)	89 (7)	610 (5)	568 (2)	0·89 (5)
H'(C8)	165 (6)	622 (5)	627 (2)	1·10 (6)
H''(C8)	260 (7)	618 (5)	584 (2)	0·92 (6)
H(C9)	107 (7)	407 (5)	516 (2)	0·95 (5)
H'(C9)	273 (7)	428 (5)	526 (2)	0·87 (6)
H''(C9)	218 (6)	314 (5)	542 (2)	1·05 (6)
H(C12)	−345 (6)	−290 (5)	644 (2)	0·95 (6)
H'(C12)	−511 (7)	−253 (5)	623 (2)	0·92 (5)
H(C14)	−599 (6)	−404 (5)	690 (2)	1·04 (5)
H'(C14)	−406 (6)	−417 (5)	715 (2)	1·04 (6)
H''(C14)	−526 (7)	−388 (5)	747 (2)	0·95 (6)
H(C15)	−592 (6)	−90 (5)	702 (2)	0·97 (6)
H'(C15)	−685 (6)	−190 (5)	684 (2)	0·90 (5)
H''(C15)	−626 (6)	−165 (5)	744 (2)	0·98 (6)
H(C16)	−253 (6)	−33 (5)	591 (2)	1·02 (6)
H(C17)	−449 (6)	−92 (5)	537 (2)	1·02 (5)
H'(C17)	−378 (6)	−221 (5)	543 (2)	0·79 (6)
H''(C17)	−296 (6)	−142 (5)	518 (2)	1·02 (6)
H(C18)	−28 (6)	−144 (5)	644 (2)	1·18 (5)
H'(C18)	−56 (7)	−162 (5)	585 (2)	0·85 (6)
H''(C18)	−137 (6)	−255 (5)	604 (2)	0·92 (6)
H(O9)	−171 (8)	112 (6)	475 (3)	0·77 (7)
H'(O9)	−57 (–)	80 (–)	514 (–)	1·09 (–)

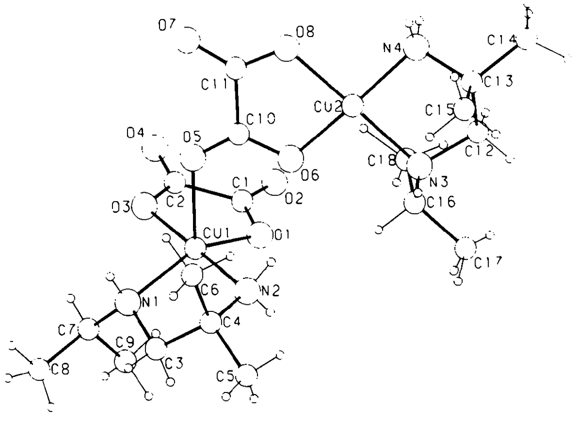

Fig. 1. View of the complex with the atom numbering.

Table 3. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu(1)–O(1)	1·984 (5)	Cu(2)–O(6)	1·921 (5)
Cu(1)–O(3)	1·963 (4)	Cu(2)–O(8)	1·950 (4)
Cu(1)–N(1)	2·038 (5)	Cu(2)–N(3)	2·010 (5)
Cu(1)–N(2)	1·997 (5)	Cu(2)–N(4)	1·974 (6)
Cu(1)–O(5)	2·273 (4)		
C(1)–C(2)	1·551 (9)	C(10)–C(11)	1·542 (8)
C(1)–O(1)	1·285 (8)	C(10)–O(5)	1·235 (8)
C(1)–O(2)	1·241 (8)	C(10)–O(6)	1·275 (7)
C(2)–O(3)	1·278 (8)	C(11)–O(7)	1·243 (7)
C(2)–O(4)	1·240 (8)	C(11)–O(8)	1·288 (8)
N(1)–C(3)	1·491 (7)	N(3)–C(12)	1·502 (8)
N(1)–C(7)	1·496 (8)	N(3)–C(16)	1·511 (9)
N(2)–C(4)	1·488 (8)	N(4)–C(13)	1·488 (7)
C(3)–C(4)	1·535 (9)	C(12)–C(13)	1·531 (9)
C(7)–C(8)	1·520 (10)	C(16)–C(17)	1·516 (10)
C(7)–C(9)	1·507 (9)	C(16)–C(18)	1·517 (11)
C(4)–C(5)	1·542 (9)	C(13)–C(14)	1·525 (10)
C(4)–C(6)	1·531 (10)	C(13)–C(15)	1·514 (10)
N(1)–Cu(1)–N(2)	85·5 (2)	N(3)–Cu(2)–N(4)	85·9 (2)
N(1)–Cu(1)–O(3)	95·3 (2)	N(3)–Cu(2)–O(6)	95·1 (2)
N(2)–Cu(1)–O(1)	95·0 (2)	N(4)–Cu(2)–O(8)	95·0 (2)
O(1)–Cu(1)–O(3)	84·4 (2)	O(6)–Cu(2)–O(8)	84·1 (2)
N(1)–Cu(1)–O(1)	149·8 (2)	N(3)–Cu(2)–O(8)	179·2 (2)
N(2)–Cu(1)–O(3)	179·2 (2)	N(4)–Cu(2)–O(6)	174·7 (2)
O(5)–Cu(1)–N(1)	106·9 (2)		
O(5)–Cu(1)–N(2)	94·3 (2)		
O(5)–Cu(1)–O(1)	103·2 (2)		
O(5)–Cu(1)–O(3)	85·6 (2)		
Cu(1)–O(1)–C(1)	111·6 (4)	Cu(2)–O(6)–C(10)	114·6 (4)
Cu(1)–O(3)–C(2)	112·3 (4)	Cu(2)–O(8)–C(11)	112·7 (4)
O(1)–C(1)–O(2)	124·7 (6)	O(5)–C(10)–O(6)	126·2 (6)
O(1)–C(1)–C(2)	115·3 (5)	O(5)–C(10)–C(11)	120·0 (5)
O(2)–C(1)–C(2)	120·0 (6)	O(6)–C(10)–C(11)	113·8 (5)
O(3)–C(2)–O(4)	125·9 (6)	O(7)–C(11)–O(8)	126·3 (5)
O(3)–C(2)–C(1)	115·4 (5)	O(7)–C(11)–C(10)	119·2 (6)
O(4)–C(2)–C(1)	118·7 (6)	O(8)–C(11)–C(10)	114·6 (5)
Cu(1)–O(5)–C(10)	121·9 (4)		
Cu(1)–N(1)–C(3)	107·7 (3)	Cu(2)–N(3)–C(12)	107·9 (3)
Cu(1)–N(1)–C(7)	113·2 (4)	Cu(2)–N(3)–C(16)	115·3 (4)
Cu(1)–N(2)–C(4)	110·8 (3)	Cu(2)–N(4)–C(13)	109·7 (4)
N(1)–C(3)–C(4)	111·1 (5)	N(3)–C(12)–C(13)	110·0 (5)
N(1)–C(7)–C(8)	112·5 (5)	N(3)–C(16)–C(17)	112·5 (6)
N(1)–C(7)–C(9)	110·9 (5)	N(3)–C(16)–C(18)	110·6 (5)
C(8)–C(7)–C(9)	113·4 (6)	C(17)–C(16)–C(18)	113·6 (7)
N(2)–C(4)–C(3)	106·5 (5)	N(4)–C(13)–C(12)	105·2 (5)
N(2)–C(4)–C(5)	110·4 (5)	N(4)–C(13)–C(14)	110·2 (5)
N(2)–C(4)–C(6)	108·4 (5)	N(4)–C(13)–C(15)	109·0 (5)
C(3)–N(1)–C(7)	113·8 (4)	C(12)–N(3)–C(16)	114·3 (5)
C(3)–C(4)–C(5)	109·2 (5)	C(12)–C(13)–C(14)	109·9 (5)
C(3)–C(4)–C(6)	111·2 (5)	C(12)–C(13)–C(15)	111·9 (5)
C(5)–C(4)–C(6)	111·2 (6)	C(14)–C(13)–C(15)	110·5 (6)

Discussion. The structure consists of dimeric complexes and water molecules. The neutral complex contains two independent Cu atoms with different coordination linked by an oxalate bridge. The coordination of Cu(1) is distorted square pyramidal. The two N atoms of one diamine molecule and two O atoms from an oxalate ion forming the base of the pyramid show a large tetrahedral distortion, as can be seen from their displacements from the mean plane through them (Table 4). Cu(1) is displaced 0·261 (1) Å towards the apex of the pyramid which is occupied by an O atom of the bridging oxalate ion. The distortion from regular square-pyramidal stereochemistry follows from the values of the angles N(1)–Cu(1)–O(1) and N(2)–

Table 4. *Least-squares planes and deviations* (Å) *of individual atoms*

The equations of the planes are in the form $Ax + By + Cz = D$, where x,y,z are fractional coordinates.

Plane through N(1), N(2), O(1) and O(3)

$$-1\cdot557x - 2\cdot715y + 25\cdot370z = 14\cdot663$$

Cu(1)	0·261 (1)	C(3)	−0·587 (10)
N(1)	−0·257 (8)	C(4)	0·298 (11)
N(2)	0·259 (8)	O(1)	−0·269 (6)
C(1)	−0·217 (11)	O(3)	0·266 (8)
C(2)	0·133 (11)		

Plane through N(3), N(4), O(6) and O(8)

$$-6\cdot923x + 6\cdot765y + 7\cdot140z = 6\cdot164$$

Cu(2)	0·044 (1)	C(12)	−0·192 (11)
N(3)	0·044 (8)	C(13)	0·437 (10)
N(4)	−0·044 (9)	O(6)	−0·046 (7)
C(10)	−0·165 (11)	O(8)	0·046 (7)
C(11)	−0·095 (11)		

Cu(1)–O(3), 149·8 (2) and 179·2 (2)° respectively. N(1)–Cu(1)–O(3) is distorted towards the trigonal angle 120°, while N(2)–Cu(1)–O(3) is distorted towards 180° so that the coordination of Cu(1) is nearly trigonal bipyramidal.

The coordination of Cu(2) is square planar. Two N atoms from the other diamine molecule and two O atoms from the bridging oxalate ion are coordinated to Cu(2) in almost regular square-planar arrangement. Cu(2) deviates only 0·044 (1) Å from the N(3), N(4), O(6), O(8) plane.

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···*A*	H···*A*	*D*···*A*	*D*–H···*A*
N(1)–H(N1)···O(8^{i})	2·18 (5)	3·014 (6)	165 (5)
N(2)–H′(N2)···O(9)	2·09 (6)	2·874 (8)	160 (5)
N(3)–H(N3)···O(4^{ii})	2·27 (6)	2·987 (7)	140 (4)
N(4)–H′(N4)···O(5^{iii})	2·05 (5)	2·907 (6)	139 (4)
O(9)–H(O9)···O(2^{iv})	2·04 (7)	2·804 (7)	169 (7)
O(9)–H′(O9)···O(1)	2·22 (6)	3·000 (7)	127 (5)

Symmetry code

(i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$
(ii) $-1 + x, y, z$
(iii) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$
(iv) $-x, -y, 1 - z$

Bond lengths and angles in the diamine molecules and oxalate ions are as expected. The packing is determined by intermolecular hydrogen bonds involving the water molecule, the diamine N atoms, and O atoms from the oxalate ions. The parameters of the hydrogen bonds are listed in Table 5.

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N,N,N′,N′-Tetramethylethylenediammonium Aquabis(malonato)oxovanadate(IV) Dihydrate

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Abstract. $C_6H_{18}N_2^{2+}.C_6H_6O_{10}V^{2-}.2H_2O$, orthorhombic, *Pnma*, $a = 11\cdot185\,(3)$, $b = 18\cdot512\,(3)$, $c = 9\cdot434\,(4)$ Å, $Z = 4$. The structure was refined to $R = 0\cdot038$ for 1409 observed reflections. The crystal structure is formed from $C_6H_{18}N_2^{2+}$ cations, $[VO(H_2O)(C_3H_2O_4)_2]^{2-}$ anions and water molecules. The V atom is coordinated to six O atoms in the form of a distorted octahedron. The malonate ions are chelated in a *trans* arrangement, the lengths of the equatorial bonds being 1·981 (2) and 1·995 (2) Å. The apical sites are taken by the oxo O atom and by a water O atom at 1·589 (4) and 2·281 (4) Å, respectively. The remaining water molecules link the complex anions by hydrogen bonding.

Introduction. The magnetic properties of oxovanadium(IV) complexes with carboxylic acids have been

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