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Crystallographic and Magnetic Study of Catena-μ-iodo-bis-{μ-{[2-(3-aminopropyl)amino]ethanolato-*N*,*N*′,μ-O}copper(II)} Iodide Dihydrate

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with two independent dimeric units in a cell of dimensions $a=8.105(7)$, $b=11.294(10)$, $c=11.931(12)$ Å, $\alpha=83.34(8)$, $\beta=74.36(7)$, $\gamma=78.83(7)°$. The crystal structure has been determined by the heavy atom method from 3987 independent reflections collected with an automatic four-circle diffractometer and refined by block-diagonal least-squares method to an R value of 0.043.

The structure consists of $[Cu_2(C_5H_{13}N_2O)_2]^{2+}$ dimers, where Cu···Cu distances are 2.976 and 2.969 Å. Each copper(II) ion has square-pyramidal (4+1)-coordination with the two oxygen atoms and two nitrogen atoms in the basal plane and an iodide ion in the apical position. The coordinated iodide ion (Cu–I; 2.996 and 3.026 Å) lies between two dimers, giving rise to a polymeric structure.

The temperature dependence of the magnetic susceptibility, studied in the range 93.2–303.2 K, shows an intramolecular antiferromagnetic coupling with a singlet-triplet separation of 65 cm^{-1}.

Earlier crystallographical investigations performed at this Department have shown the 1:1-complexes formed by copper(II) salts and 2-[(3-aminopropyl)-amino]ethanol (H*L*) to have tetranuclear structures with a cubane-type Cu_4O_4 core.[1–5] In the core eight Cu–O distances were found to be short and four long. The effect of the anion on the geometry of the Cu_4O_4 core was apparent in the lengths of the stretched Cu–O distances. Magnetically all copper(II) complexes of the amine studied thus far have proved to be identical.[6–7] They have normal magnetic moments (μ_{eff} about 1.9 B.M.) at room temperature.

It might be expected from the ionic radii of halogenides X^- that the Cu–X distances would increase in the anion order $F^- < Cl^- < Br^- < I^-$. However X-ray structural analyses have shown that the bromide ion is located nearer the copper(II) ion in $(CuLBr)_4.3H_2O$[3] than the chloride ion is in $(CuLCl)_4.4H_2O$.[1] Correspondingly, the stretched Cu–O distances are longer in the former compound than in the latter. The present structure was solved in order to study further the effect of halogenides on the configuration of {2-[(3-aminopropyl)amino]ethanolato}copper(II) complexes.

EXPERIMENTAL

Preparation and analyses of the compound. The complex was prepared by adding 5 cm^3 of 67 % hydroiodic acid and 0.045 mol of amine to a solution containing 0.020 mol $CuCO_3$ in 250 cm^3 water. The white CuI precipitate formed was filtered off and the dark blue solution was left to evaporate at room temperature. After a few days dark blue crystalline prisms and needles were formed.

Copper, diamine and iodide was analyzed by conventional methods. Calc: Cu 19.51; *L* 35.98; I 38.97; H_2O 5.53 %. Found: Cu 19.56; *L* 36.4; I 38.8; H_2O 5.5 %.

Physical measurements. The crystal used for data collection was a brick-like prism having approximate dimensions 0.2 × 0.3 × 0.9 mm. Both the crystal and intensity data were measured on an automatic Syntex $P2_1$ four-circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda=0.7107$ Å). The cell dimensions were obtained by least-squares refinement of setting angles for 14 well-centered reflections.

The intensity data were collected by the ω-scan technique at room temperature, using a scan range

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of 1.0°, scan speed 2.0–20.0° min^{-1} depending upon the peak intensity, and 2θ values between 5.0 and 55.0°. Of the 5063 reflections recorded, 3987 independent reflections had $I > 3\sigma(I)$ and were regarded as observed. The intensity of a standard reflection recorded after every hundredth measurement varied about ±1 % during the data collection. Data were corrected for Lorentz and polarization effects and for absorption from ϕ-scan data.

The magnetic data of the compound were measured over the temperature range 93.2–303.2 K by the Gouy method, using a Newport Instruments variable temperature Guoy balance. Copper(II) sulfate pentahydrate was used for calibration.[8] Diamagnetic corrections were applied with Pascal's constants for the atoms of the amine and the calculated correction values for iodide ion and the water molecule.[9]

CRYSTAL DATA

$[Cu_2(C_5H_{13}N_2O)_2I]I.2H_2O$, $FW = 651.26$
Crystal system: Triclinic
Space group: $P\bar{1}$ (No. 2)
$a = 8.105(7)$, $b = 11.294(10)$, $c = 11.931(12)$ Å
$\alpha = 83.34(8)$, $\beta = 74.36(7)$, $\gamma = 78.83(7)°$
$V = 1029.3(16)$ Å^3, $Z = 2$, $F(000) = 628$,
$\mu(MoK\alpha) = 52.0$ cm^{-1}
$D_m = 2.10(1)$ g cm^{-3} (flotation technique),
$D_x = 2.10$ g cm^{-3}

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by the heavy atom method. The positions of two independent iodine atoms were located from a three-dimensional Patterson function in the non-centrosymmetric space group $P1$. The other non-hydrogen atoms were located from successive Fourier syntheses.

In the calculation of F_c, atomic scattering factors computed from numerical Hartree-Fock wave functions were used for all non-hydrogen atoms and scattering factors reported by Stewart *et al.* for hydrogen atoms.[10,11] The anomalous dispersion coefficients for copper and iodine atoms were included in the calculations.[12]

After refinement by block-diagonal least-squares techniques the R value was 0.090 for the non-hydrogen atoms with isotropic thermal parameters in the space group $P1$ ($R = \sum \| F_o| - |F_c \| / \sum |F_o|$). Because a centre of symmetry was found in the array of atoms, the space group was changed to the centrosymmetric $P\bar{1}$. The R value then dropped to 0.097 with isotropic thermal parameters and 0.047 with anisotropic thermal parameters. In minimizing the function $w(|F_o| - |F_c|)^2$ the weighting scheme $w = 1/(30.0 + |F_o| + 0.01|F_o|^2)$ was used.

The positions of the hydrogen atoms of the water molecules were located from a difference Fourier map. The hydrogen atoms of the amine were placed in calculated positions. A fixed isotropic thermal parameter value ($U = 0.05$ Å^2) was used for all hydrogen atoms. After the location of the hydrogen atoms and two subsequent cycles of refinement the R-value converged to the value 0.043. The computations were performed on a UNIVAC 1108 computer with the X-Ray 76 program system.[13] The figures were drawn by the ORTEP program.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The atomic coordinates and thermal parameters with their standard deviations for non-hydrogen atoms are given in Table 1 and the coordinates of hydrogen atoms in Table 2. A list of observed and calculated structure factors can be obtained from the authors.

The structure contains two crystallographically independent $Cu(C_5H_{13}N_2O)^+$ units, which comprise two separate dimers each having a centre of symmetry. The labeling of the atoms in the dimers with bond lengths and angles is shown in Fig. 1. The Cu···Cu distances in the dimers are 2.969(1) Å (Cu1) and 2.976(1) Å (Cu2). The values are shorter than those of tetranuclear cations of this amine but are in agreement with those of other dimeric alkoxy-bridged Cu(II) complexes.[8]

The coordination around each copper(II) ion is distorted square-pyramidal (4+1) with two nitrogen atoms and two oxygen atoms in the basal plane and an iodide ion in the apical position. The interatomic distances between the copper(II) ion and the basal atoms (1.961–2.026 Å) are typical for coordination bonds. The Cu–I1 distances, 2.996(1) Å for Cu1 and 3.026(1) Å for Cu2($1-x$, $1-y$, $\bar{z}$), are somewhat longer than the coordination bond distance 2.70 Å found in trigonal bipyramidal (3+2) copper(II) coordination.[14-15] However, the apical bond distance involving oxygen and nitrogen atoms is found to be elongated by about 20 % in the square-pyramidal (4+1)-coordination.[16] Because

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters[a] ($\times 10^3$). Estimated standard deviations are given in parentheses.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I1	4216(1)	4414(1)	−1928(1)	28(1)	51(1)	25(1)	−10(1)	−2(1)	−6(1)
I2	−2016(1)	772(1)	2581(1)	40(1)	37(1)	39(1)	−6(1)	−10(1)	−3(1)
Cu1	1358(1)	3961(1)	182(1)	24(1)	22(1)	28(1)	−2(1)	−11(1)	−2(1)
Cu2	4144(1)	6118(1)	4454(1)	24(1)	22(1)	28(1)	−5(1)	−9(1)	−0(1)
O1	−446(5)	4375(4)	−689(4)	23(2)	21(2)	31(2)	−2(1)	−9(2)	−7(2)
O2	6322(5)	5518(4)	4911(4)	29(2)	22(2)	31(2)	−10(2)	−12(2)	1(2)
N1	3016(8)	3523(5)	1191(6)	35(3)	37(3)	44(3)	−6(2)	−20(3)	4(3)
N2	991(7)	2241(5)	210(5)	29(3)	28(3)	38(3)	−6(2)	−9(2)	−4(2)
N3	1836(7)	6750(5)	4117(5)	29(3)	32(3)	37(3)	−4(2)	−14(2)	−5(2)
N4	4534(7)	7768(5)	4726(5)	34(3)	23(2)	31(3)	−8(2)	−5(2)	−4(2)
C1	4325(10)	2405(7)	954(8)	33(4)	43(4)	65(5)	−4(3)	−25(4)	14(4)
C2	3472(10)	1300(7)	1018(7)	43(4)	33(3)	50(4)	7(3)	−15(3)	4(3)
C3	2557(11)	1282(7)	50(7)	48(4)	28(3)	52(4)	7(3)	−10(3)	−4(3)
C4	−10(10)	2237(6)	−668(6)	44(4)	27(3)	44(4)	−6(3)	−12(3)	−12(3)
C5	−1353(8)	3367(6)	−551(6)	30(3)	28(3)	44(4)	−2(2)	−14(3)	−7(3)
C6	1708(10)	7894(7)	3354(7)	47(4)	38(4)	42(4)	4(3)	−23(3)	−6(3)
C7	2154(10)	8944(6)	3888(7)	51(4)	21(3)	46(4)	6(3)	−15(3)	4(3)
C8	4069(11)	8782(6)	3875(8)	52(4)	24(3)	59(5)	−9(3)	−16(4)	13(3)
C9	6363(9)	7628(6)	4803(7)	39(3)	31(3)	52(4)	−16(3)	−19(3)	5(3)
C10	6745(9)	6435(7)	5467(6)	38(4)	42(4)	31(3)	−15(3)	−10(3)	−12(3)
O(W1)[b]	416(7)	4723(6)	−3134(5)	37(3)	69(4)	39(3)	−10(3)	−13(2)	−1(3)
O(W2)[b]	233(10)	2775(7)	3409(6)	82(5)	77(5)	49(4)	−36(4)	10(3)	−22(3)

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\cdots+2hka^*b^*U_{12}+\cdots)]$. [b] The oxygen atom of a water molecule.

Table 2. Fractional atomic coordinates ($\times 10^3$) for hydrogen atoms.[a]

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
H1(O_w1)	50(12)	460(8)	−234(8)	H1(C5)	−211(12)	337(8)	14(8)
H2(O_w1)	131(11)	442(8)	−374(8)	H2(C5)	−208(12)	360(8)	−106(8)
H1(O_w2)	59(11)	341(8)	310(8)	H1(N3)	141(11)	628(8)	389(8)
H2(O_w2)	−73(12)	251(8)	435(8)	H2(N3)	115(11)	682(8)	471(8)
H1(N1)	355(11)	403(8)	103(8)	H1(C6)	252(12)	778(8)	260(8)
H2(N1)	246(12)	341(8)	181(8)	H2(C6)	50(12)	799(8)	323(8)
H1(C1)	505(11)	218(8)	146(8)	H1(C7)	129(11)	905(8)	466(8)
H2(C1)	511(12)	254(8)	17(8)	H2(C7)	184(11)	963(8)	335(8)
H1(C2)	439(11)	63(8)	97(8)	H1(C8)	427(11)	958(8)	407(8)
H2(C2)	258(12)	133(8)	182(8)	H2(C8)	480(11)	861(8)	310(8)
H1(C3)	230(11)	45(8)	2(8)	H1(N4)	381(11)	791(8)	549(8)
H2(C3)	339(12)	138(8)	−70(8)	H1(C9)	713(12)	759(8)	407(8)
H1(N2)	32(12)	210(8)	92(8)	H2(C9)	653(11)	823(8)	513(8)
H1(C4)	74(12)	214(8)	−140(8)	H1(C10)	796(11)	629(8)	556(8)
H2(C4)	−60(12)	149(8)	−63(8)	H2(C10)	608(12)	643(8)	636(8)

[a] Fixed $U_{iso}=0.05$ Å^2 for all atoms.

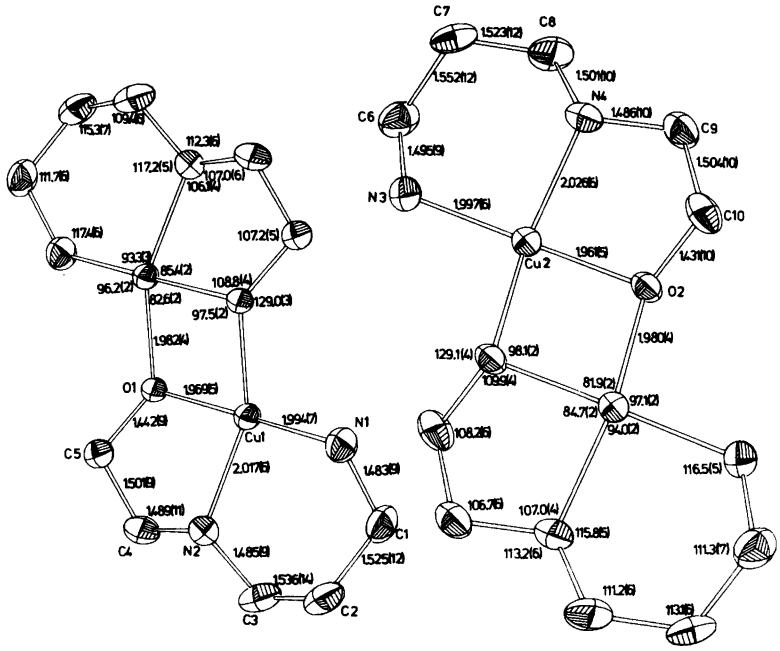

Fig. 1. View of the dimeric cations with bond lengths and angles. Estimated standard deviations are in parentheses.

the Cu−I distances in the present compound display the same elongation, it can be assumed that I1 is attached to two Cu(II) ions by coordination bonds, producing a polymeric structure (Fig. 2). The Cu···I distance that indicates weak interaction is found to be much longer, 3.42−3.87 Å.[17]

The deviation of the Cu(II) ions (0.28 and 0.29 Å, Table 3) from the basal least-squares planes towards the iodide ions is also in agreement with the assumption of a strong interaction between the ions. There is, however, a tetrahedral distortion in the coordination sphere; for the deviations of the basal atoms from the least-squares planes are 0.18−0.23 Å and the dihedral angles between the planes CuN_2 and CuO_2 are 29.4° for Cu1 and 28.7° for Cu2. The respective values are less

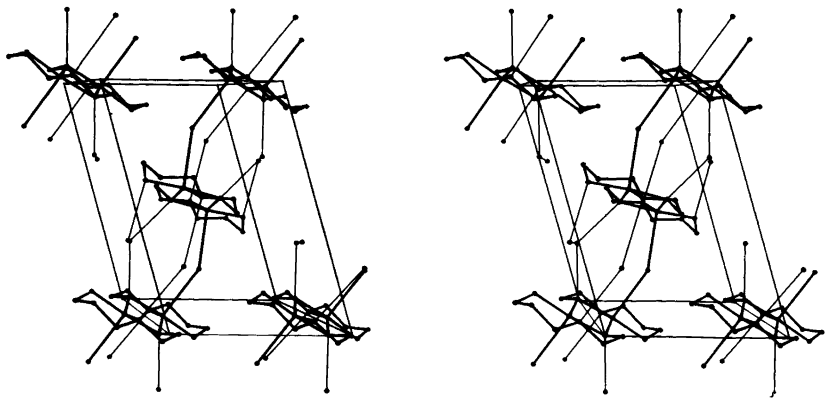

Fig. 2. Stereo view of the packing. Possible hydrogen bonds are shown in fine lines.

Table 3. Least-squares planes through the four basal atoms in the copper(II) coordination sphere and the distances (Å) of some atoms from these planes.

Plane 1:	N1	N2	O1	$O1^{I}$	Cu1	I1
	−0.18	0.20	−0.23	0.21	−0.29	−3.28
Plane 2:	N3	N4	O2	$O2^{II}$	Cu2	$I1^{III}$
	−0.18	0.20	−0.23	0.21	−0.28	−3.29

Equivalent positions: I $\bar{x},1-y,\bar{z}$ II $1-x,1-y,1-z$ III $1-x,1-y,\bar{z}$

(0.12−0.18 Å and 10.6−14.6°) in the tetranuclear complexes of this amine having octahedral (4+2)-coordination.

The configuration of the tridentately coordinated amine is similar to that of the amine in the tetranuclear Cu(II) complexes. It has chair conformation and both the bond lengths and the angles are normal for the amine. The amine hydrogen atoms lie within 0.76−1.06 Å of the parent atoms. The bonded atoms around each amine atom are tetrahedrally oriented indicating sp^3-hybridization.

Hydrogen bonding details for the water molecules are shown in Table 4. The water molecule W1 lies between atoms O1 and O2 and the water molecule W2 between atoms O(W1) and N3($\bar{x}$, $1-y$, $1-z$). It is also possible that the iodide ion I2 is hydrogen bonded to the nitrogen atoms N2 and N4($\bar{x}$, $1-y$, $1-z$), but the I···N distances of 3.668(5) and 3.687(5) Å indicate that the possible bonds are very weak. These hydrogen bonds are also indicated in Fig. 2.

The paramagnetic susceptibilities of the complex in the temperature interval 93.2−303.2 K are shown in Fig. 3. In the light of the structural results the susceptibility data were fitted to the Bleaney-Bowers equation

$$\chi'_A = \frac{Ng^2\beta^2}{3kT}\cdot\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + N\alpha \qquad (1)$$

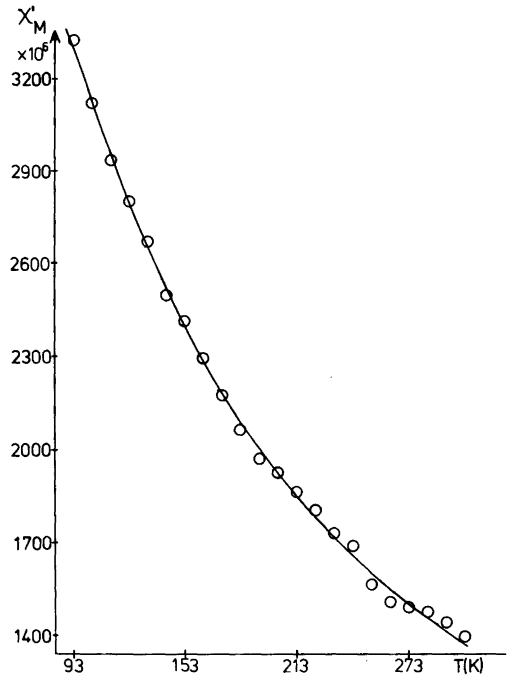

Fig. 3. Experimental temperature dependence of the molar magnetic susceptibility for the complex. The solid curve represents susceptibilities calculated from eqn. (1), with $g=2.15$, $-2J=65$ cm^{-1} and $N\alpha=60\times10^{-6}$ (cgs units).

Table 4. Hydrogen bonding details for water molecules.

X−H···Y	Position of acceptor atom	X···Y (Å)	X−H (Å)	H···Y (Å)	X−H···Y (°)
O(W1)−H1(W1)···O1		2.810(7)	0.96(10)	1.92(9)	154(8)
O(W1)−H2(W1)···O2	$1-x,1-y,\bar{z}$	2.897(6)	0.92(8)	2.06(8)	152(9)
O(W2)−H1(W2)···O(W1)	$\bar{x},1-y,\bar{z}$	2.770(10)	0.84(9)	2.11(9)	136(7)
O(W2)−H2(W2)···N(3)	$x,1-y,1-z$	3.026(8)	1.22(8)	2.01(9)	138(7)

where $-2J$ is equal to the energy separation between the lowest singlet and triplet levels and the other symbols have their usual meanings. The value 60×10^{-6} (cgs units) was used for $N\alpha$ and the values 2.15(6) and 65(1) cm^{-1} were obtained for g and $-2J$, respectively. The magnetic moment, μ_{eff}, of the complex was 1.85 B.M. at room temperature (20 °C; $\mu_{eff} = 2.828(\chi'_M \cdot T)^{\frac{1}{2}}$).

In spite of there being two independent dimeric units in the structure, use of the same coupling constant value for both dimers is justified. The reason is that the structural features, shown to be the dominating ones for magnetic exchange in dioxygen-bridged copper(II) dimers, are almost identical: namely, the Cu–O–Cu angles within the Cu_2O_2 rings and the tetrahedral distortions at the copper(II) coordination (*cf.* above).[18] At the same time, an interdimeric exchange interaction is also possible through an iodo-bridged pathway. This exchange is in all probability very small compared with the intradimer interaction and no attempt was made to include it in calculations.

It is worth mentioning that of the eight 2-[(3-aminopropyl)amino]ethanolato copper(II) complexes (NO_3^-, NO_2^-, ClO_4^-, Cl^-, Br^-, F^-, SO_4^{2-}) studied magnetically in our laboratory, this iodo complex is the first one where the coupling between the neighgbouring copper(II) ions is antiferromagnetic; in all other complexes it is ferromagnetic.[19] Crystallographic investigations have shown that in some of these complexes the four neighbouring copper(II) ions form an almost regular tetrahedron.[1-4]

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