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Crystal and Molecular Structure of Copper Iminodiacetate Dihydrate

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Abstract

Copper iminodiacetate dihydrate, $[\mathrm{Cu(CH_2COO)_2NH}].2\mathrm{H_2O}$ crystallizes in the orthorhombic space group *Pbca* with unit-cell dimensions a = 10·228 (2), b = 10·419 (2) and c = 13·688 (3) Å. The structure was solved by direct methods using diffractometric X-ray data and refined by a full-matrix least-squares method to a final R value of 0·062. The Cu ion is coordinated in the form of a distorted octahedron, the distances around the Cu atom being Cu—O*W*(1) = 1·991 (3), Cu—O*W*(2) = 2·410 (3), Cu—O(1) = 1·945 (3), Cu—N = 2·014 (3), Cu—O(4) = 2·494 (3), Cu—O(3′) of the neighbouring molecule = 1·961 (3) Å.

Introduction

Iminodiacetic acid constitutes the functional group of an important and useful resin, commercially known as Chelex 100, where iminodiacetic acid is introduced into a matrix of a styrene divinyl benzene polymer. This resin shows unusually high preference for Cu and other heavy metals and thus makes this resin uniquely suitable for detection, estimation and removal of trace metals from biological fluids and enzyme systems (Siegel & Degens, 1960). Moreover ligand-exchange chromatography on Cu-loaded Chelex 100 (Goldstein, 1967) has been found to be an extremely useful technique for the rapid separation of nucleic acid compounds.

Experimental

The compound was prepared by Dr Sunil Kr. Datta of our Institute by neutralizing iminodiacetic acid with the requisite amount of basic copper carbonate. The excess copper carbonate was filtered off and the filtrate adjusted to pH 4. Slow evaporation yielded blue prismatic crystals of copper iminodiacetate. Preliminary unit-cell parameters were determined from rotation, oscillation and Weissenberg photographs while accurate cell parameters were obtained from the diffractometer measurements. Systematic absences of the types $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$ and $hk0$ for $h = 2n + 1$ indicate that the space group is *Pbca*. The crystal data are summarized in Table 1.

Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs using Ni-filtered Cu $K\alpha$ radiation. 838 independent reflections were estimated visually and necessary correction terms were applied. The coordinates of the Cu atom were determined from a three-dimensional Patterson synthesis and the Cu atom was found to be situated on the glide plane perpendicular to the a axis. As a result of this a spurious mirror appeared on the Cu-phased Fourier map which made the faithful identification of peaks difficult. So attempts were made to solve the structure by direct methods. At this stage intensity data were collected on an automatic Stoe

Table 1. *Crystal data*

Copper iminodiacetate dihydrate, $[\mathrm{Cu(CH_2COO)_2NH}].2\mathrm{H_2O}$,
M_r = 230·64, space group *Pbca*,
a = 10·228 (2), b = 10·419 (2), c = 13·688 (3) Å, Z = 8,
D_m = 2·303, D_c = 2·305 Mg m^{-3}.

Table 2. *Positional parameters* (×10^4) *of non-hydrogen atoms with their e.s.d.'s in parentheses*

	x	y	z
Cu	2434 (1)	2023 (1)	4281 (0)
N	3640 (3)	1527 (3)	3181 (2)
O(1)	1908 (3)	3442 (3)	3446 (2)
O(2)	2278 (4)	4362 (3)	2011 (2)
O(3)	6547 (3)	2106 (3)	4636 (2)
O(4)	4587 (3)	3050 (3)	4626 (2)
O*W*(1)	3013 (4)	618 (3)	5167 (2)
O*W*(2)	631 (4)	681 (3)	3790 (2)
C(1)	3573 (4)	2536 (4)	2417 (3)
C(2)	2520 (4)	3508 (4)	2633 (3)
C(3)	4985 (4)	1300 (4)	3540 (3)
C(4)	5391 (4)	2240 (4)	4328 (3)

diffractometer using Zr-filtered Mo $K\alpha$ radiation and altogether 2131 reflections were measured in the $\theta/2\theta$ scanning mode. The background was measured by a stationary-crystal and stationary-counter technique on each side of the peak. Three standard reflections were monitored after each group of 100 measurements. They did not show any noticeable change in intensity. Initial attempts to solve the structure by direct methods using the program *MULTAN* (Main, Germain & Woolfson, 1970) failed, probably due to the special position of the Cu ion. Moreover, the fact that Cu is a dominant scatterer makes the successful application of direct methods, which requires all the atoms to be of nearly equal scattering power, rather difficult. So, the contribution of the Cu atom to the observed structure amplitudes was calculated on the basis of the Cu position known from the Patterson synthesis and $|F_{\mathrm{Cu}}|$, thus obtained, subtracted from the $|F_{\mathrm{obs}}|$, a procedure allowed in centric structures at least for the large amplitudes, *i.e.* the large E's used for direct methods. The 150 largest E's were phased by *MULTAN* and an E map calculated with the most consistent phase set revealed all the non-hydrogen atoms. The coordinates of these atoms were refined isotropically using the full-matrix least-squares refinement program *ORFLS* (Busing, Martin & Levy, 1962). After three cycles of refinement, the R value was reduced to 0·11. Two more cycles of refinement using anisotropic temperature factors resulted in an R value of 0·084. At this stage 17 reflections were excluded from the intensity data because of inaccuracy in their intensity estimation. A three-dimensional difference Fourier was then calculated which revealed H atoms attached to two water molecules OW(1) and OW(2). The positions of the remaining H atoms were located stereochemically. Two more cycles of refinement were carried out by taking into account the contribution of H atoms in structure factor calculations. The final R value was 0·062. Positional parameters of the non-hydrogen atoms together with their standard deviations obtained from the correlation matrix are given in Table 2.* The atomic parameters of the H atoms are given in Table 3.

Table 3. *Positional parameters* ($\times 10^4$) *of hydrogen atoms*

	x	y	z
H(C1)	4438	2977	2374
H'(C1)	3382	2118	1769
H(C3)	5037	404	3806
H'(C3)	5604	1370	2976
H(N)	3295	700	2901
H(W1)	2839	4951	611
H'(W1)	3978	544	5018
H(W2)	1608	579	3987
H'(W2)	4613	4985	3493

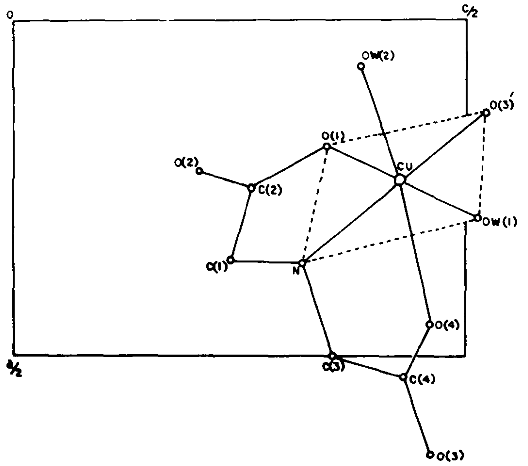

Fig. 1. Atomic numbering of copper iminodiacetate dihydrate.

Discussion

The atomic numbering scheme of the molecule is shown in Fig. 1. The Cu ion is coordinated in a distorted octahedron and the approximate square plane around Cu is formed by the imino N atom, the O atom of the water molecule OW(1), the carboxyl O atom O(1) and another carboxyl O atom O(3) of the neighbouring molecule, *i.e.* O(3') (Fig. 2). The O(3') atom acts as a bridging ligand between two adjacent molecules. The octahedral coordination is completed by the remaining

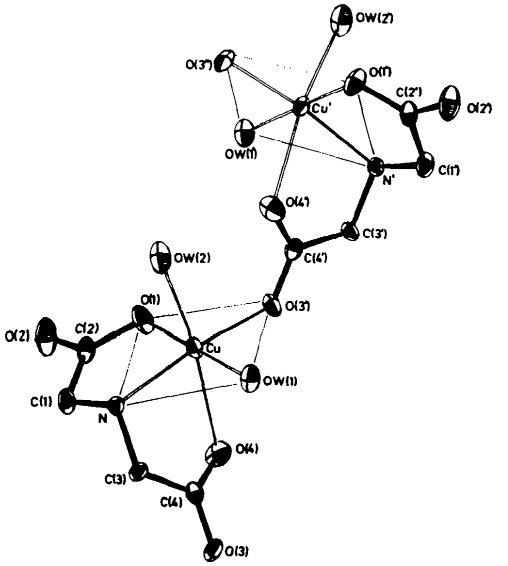

Fig. 2. Arrangement of adjacent molecules of copper iminodiacetate dihydrate. *ORTEP* plot (Johnson, 1965) of thermal ellipsoids of the atoms scaled to 50% probability.

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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 33878 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

carboxyl O(4) atom and the O atom of the remaining water molecule, O*W*(2). The Cu—O*W*(2) bond is almost perpendicular to the approximate square plane. The distances from Cu of atoms forming the square plane, *i.e.* Cu—O(1), Cu—O(3′), Cu—N, and Cu—O*W*(1), are 1·945 (3), 1·961 (3), 2·014 (3) and 1·991 (3) Å respectively. The Cu—N distance is in close agreement with 1·98–2·04 Å reported for rectangular coordination complexes by Freeman, Robinson & Schoone (1964). The two apical bond distances Cu—O*W*(2) and Cu—O(4) are 2·410 (3) and 2·494 (3) Å respectively, which are typical of those found in tetragonally elongated octahedral Cu^{II} complexes (Hathaway & Billig, 1970; Hathaway & Hodgson, 1973). Bond distances and angles are summarized in Tables 4 and 5.

The square plane around the Cu ion is almost 'ideal' and the Cu ion is shifted towards the apical O*W*(2) atom by 0·133 Å (Table 6). The acetate groups together with the Cu ion form two five-membered rings having a Cu—N bond common to both rings. The dihedral angle between these two planes is 107°. It is to be noted that C—O bonds of both the carboxyl groups are of unequal lengths: C(2)—O(1) > C(2)—O(2) and C(4)—O(3) > C(4)—O(4), although the carboxyl groups are ionized. This is as expected because O(1)$^-$ and O(3)$^-$ are coordinated equatorially to the positively charged metal atom Cu^{2+}. The equations of least-squares planes and the deviations of individual atoms from these planes are given in Table 6. The N—H bond distance is 1·01 Å and the average C—H and O—H bond distances in the molecule are 1·00 and 0·92 Å respectively. The angles in the water molecules, *i.e.* H(*W*1)—O*W*(1)—H′(*W*1) and H(*W*2)—O*W*(2)—H′(*W*2), are 106·9 and 108·3° respectively. The O*W*(1) atom acts as an acceptor forming a hydrogen bond with O*W*(2) of the same complex molecule, the distance O*W*(1)—O*W*(2) being 3·08 Å and the angle O*W*(2)—H(*W*2)···O*W*(1) 146·2°. The imino N atom also forms a hydrogen bond with O(2) of the neighbouring molecule; the corresponding distance N—O(2) is 2·92 Å and the angle N—H···O(2) is 163·5°. Adjacent molecules are linked in endless chains parallel to the *a* axis. A stereoview of the three-dimensional packing of the molecules is shown in Fig. 3.

Table 4. *Bond distances* (Å) *with their standard deviations in parentheses*

Cu—N	2·014 (3)	N—C(1)	1·484 (5)
Cu—O(1)	1·945 (3)	C(1)—C(2)	1·507 (6)
Cu—O(4)	2·494 (3)	C(2)—O(1)	1·278 (5)
Cu—O*W*(1)	1·991 (3)	C(2)—O(2)	1·257 (5)
Cu—O*W*(2)	2·410 (3)	C(3)—C(4)	1·516 (5)
Cu—O(3′)	1·961 (3)	C(4)—O(3)	1·262 (5)
N—C(3)	1·480 (5)	C(4)—O(4)	1·247 (5)

Table 5. *Bond angles* (°) *with their standard deviations in parentheses*

O(1)—Cu—N	85·7 (1)	N—Cu—O*W*(1)	94·8 (1)
O(1)—Cu—O*W*(2)	93·8 (1)	O*W*(2)—Cu—O(3′)	97·2 (1)
O(1)—Cu—O(3′)	88·0 (1)	N—C(1)—C(2)	111·8 (3)
O(1)—C(2)—O(2)	122·1 (4)	N—C(3)—C(4)	112·9 (3)
O(1)—C(2)—C(1)	118·9 (4)	C(1)—N—Cu	108·4 (2)
O(3)—C(4)—C(3)	115·0 (3)	C(1)—N—C(3)	113·0 (3)
O(3)—C(4)—O(4)	125·8 (4)	C(1)—C(2)—O(2)	119·0 (4)
O(4)—Cu—N	73·2 (1)	C(2)—O(1)—Cu	114·7 (3)
O(4)—Cu—O*W*(1)	86·4 (1)	C(3)—N—Cu	111·2 (2)
O*W*(1)—Cu—O*W*(2)	88·4 (1)	C(3)—C(4)—O(4)	119·3 (3)
O*W*(1)—Cu—O(3′)	91·0 (1)	C(4)—O(4)—Cu	103·3 (3)

Table 6. *Least-squares planes*

Equations of the planes

Plane 1: $-0·7839X - 0·5409Y - 0·3048Z = -5·0107$
Plane 2: $0·0836X + 0·7816Y - 0·6180Z = -1·4118$
Plane 3: $-0·7018X - 0·5713Y - 0·4253Z = 5·4265$

Deviations (Å) of atoms from the planes

Plane 1		Plane 2		Plane 3	
N	−0·095*	Cu	−0·017*	Cu	−0·354*
O(1)	0·103*	N	0·052*	N	0·275*
O(3′)	−0·098*	O(1)	0·001*	O(3)	−0·234*
O*W*(1)	0·091*	O(2)	0·024*	O(4)	0·374*
Cu	0·133	C(1)	−0·055*	C(3)	−0·098*
O*W*(2)	2·540	C(2)	−0·004*	C(4)	0·035*
O(4)	−2·316				

* Atoms included in calculating the particular plane.

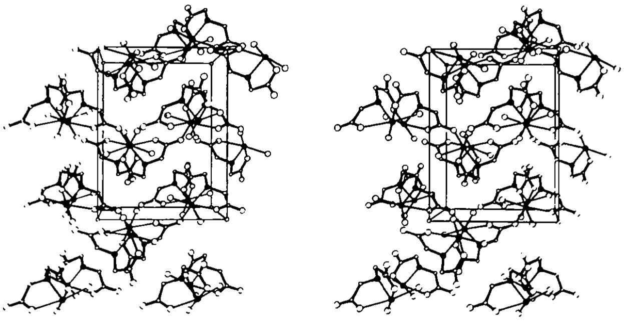

Fig. 3. Stereoview of the three-dimensional packing of copper iminodiacetate dihydrate.

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Structures of Polyether Complexes. V.* Molecular Structure of Bis(8-quinolyloxyethyl) Ether–Rubidium Iodide, a Linear Polyether Circularly Embracing a Metal Ion

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Abstract

The title compound (DGOE.RbI) crystallizes in space group *Pnma* with $a = 9{\cdot}955$ (2), $b = 18{\cdot}163$ (3), $c = 12{\cdot}242$ (3) Å. The structure was solved from 1821 X-ray diffractometer data and refined by least squares to $R = 6{\cdot}4\%$. The linear ligand wraps around the cation in a circular manner, with the quinoline planes tilted like the wings of a butterfly and forming a dihedral angle of 66·8°. Rb^+ is coordinated to two symmetry-related I^- ions at distances of 3·691 and 3·903 Å and to all heteroatoms of DGOE as follows: $Rb^+\cdots N$ 2·97, $Rb^+\cdots$O(quinoline) 3·067, $Rb^+\cdots$O(aliphatic) 3·174 Å. The latter distance is 0·3 Å longer than expected and might not represent true coordination.

Introduction

Relatively long, linear polyether ligands wrap around metal ions in more than one turn to form complexes displaying a helical or S-shaped configuration (Saenger, Brand, Vögtle & Weber, 1977; Saenger, Brand, Reddy, Suh & Weber, 1978; Suh & Saenger, 1978). In this connection it was of interest to study the structure of a complex formed by a short linear ligand, DGOE.RbI (Fig. 1) (Vögtle & Sieger, 1977).

Experimental

When a hot, saturated methanol/ethyl acetate solution of DGOE.RbI was allowed to cool, yellowish, tabular crystals were obtained; crystal data are given in Table 1. The space-group ambiguity, *Pnma* or a reindexed $Pna2_1$, was resolved in favour of the former (with the *m* plane passing through the molecule) after the structure was solved with *MULTAN* (Main, Germain & Woolfson, 1970) and refined by full-matrix least squares in both space groups. The final *R* is 6·4% for all the measured 1821 data.

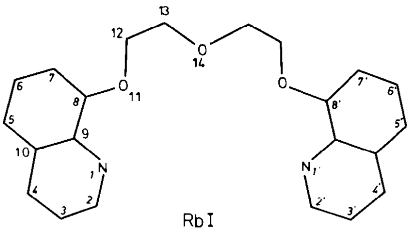

Fig. 1. Chemical structure of the DGOE.RbI complex.

Results and discussion

Geometric data and the numbering scheme are displayed in Fig. 2, a diagram of the structure is in Fig. 3,

Table 1. *Crystallographic data*

Chemical formula: $C_{22}H_{20}N_2O_3.RbI$, $M_r = 572{\cdot}8$
Space group: *Pnma*
$a = 9{\cdot}955$ (2), $b = 18{\cdot}163$ (3), $c = 12{\cdot}242$ (3) Å
$V = 2213{\cdot}5$ Å^3, $Z = 4$, $D_c = 1{\cdot}719$ Mg m^{-3}, m.p. 498 K
1821 X-ray intensities were collected in the $2\theta/\omega$ scan mode; stationary background on both sides of scan.
Data were corrected for Lorentz-polarization, but not for absorption; size of crystal: 0·1 × 0·3 × 0·2 mm.
$R = \sum||F_o| - |F_c||/\sum|F_o| = 6{\cdot}4\%$ for all data.

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* Part IV: Suh & Saenger (1978).

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