The five-membered rings in each molecule are slightly different in conformation. In cation 1 the thiazolidine ring adopts a flattened envelope conformation with C(12) 0·054 (8) Å out of the four-atom plane while the dihydrothiazolyl ring has a twist conformation with C(15) and C(16) deviating by −0·157 (9) and 0·054 (8) Å from the S(13)C(14)-N(12) plane. In cation 2 both five-membered rings have flattened pseudo half-chair conformations (Table 3). The torsion angles, −1·0 (6)° for C(13)—N(11)—C(14)—N(12), −2·6 (5)° for C(11)—N(11)—C(14)—S(13) and 0·8 (7)° for C(23)—N(21)—C(24)—N(22), 1·5 (6)° for C(21)—N(21)—C(24)—S(23), indicate that these fragments are essentially coplanar.

The orientations of the heterocyclic rings around the inter-ring C—N bonds are such that the exocyclic S atom of the thiazolidinethione moiety and the endocyclic S atom of the dihydrothiazolyl ring are *cis* with intramolecular S···S distances 2·972 (3) and 2·971 (3) Å, respectively, in the two independent cations.

There are six hydrogen bonds, each having a Cl atom as acceptor (Table 4, deposited). All H atoms bonded to N and O participate in the hydrogen-bonding network.

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Table 3. *Least-squares planes*

Values are given in the following order: atoms defining the plane, equation of plane, deviations of atoms from the plane (Å) with e.s.d.'s in parentheses.

Plane 1:	S(12), N(11), C(11), C(13) $-0{\cdot}8682X - 0{\cdot}2533Y - 0{\cdot}42672Z + 0{\cdot}40657 = 0$ S(12) −0·000 (2), N(11) −0·002 (5), C(11) 0·003 (6), C(13) 0·003 (7), S(11) 0·019 (2), C(12) 0·054 (8), C(14) −0·006 (6), N(12) 0·014 (5)
Plane 2:	S(13), C(14), N(12) $-0{\cdot}8567X - 0{\cdot}2386Y - 0{\cdot}4572Z + 3{\cdot}9853 = 0$ C(15) −0·157 (9), C(16) 0·054 (8), N(11) −0·023 (5)
Plane 3:	C(22), C(23), N(21) $-0{\cdot}7857X - 0{\cdot}1026Y - 0{\cdot}6101Z + 2{\cdot}8675 = 0$ S(22) −0·024 (2), C(21) 0·015 (6), S(21) 0·055 (2), C(24) −0·019 (6)
Plane 4:	N(22), C(24), S(23) $-0{\cdot}7696X - 0{\cdot}1152Y - 0{\cdot}6280Z + 2{\cdot}7610 = 0$ C(25) 0·104 (7), C(26) −0·028 (8), N(21) 0·007 (5)

Interplanar angles (°):

1–2	2·0 (5)
3–4	1·6 (6)

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Structure of Copper Zinc Cyclohexylenediaminetetraacetate Hexahydrate

BY A. FUERTES, C. MIRAVITLLES AND E. MOLINS

Instituto 'Jaime Almera', CSIC, c/ Martí i Franqués, s/n. Apartado 30102, 08028 *Barcelona, Spain*

AND E. ESCRIVÁ AND D. BELTRÁN

Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Valencia,
c/ Dr Moliner, 50, *Burjasot, Valencia, Spain*

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Abstract. Pentaaquazinc(II) [*N,N,N',N'*-tetrakis(carboxymethyl)-1,2-cyclohexanediaminato]cuprate(II) monohydrate, $[Zn(H_2O)_5][Cu(C_{14}H_{18}N_2O_8)].H_2O$, $M_r = 579{\cdot}3$, orthorhombic, $Pbc2_1$, $a = 10{\cdot}868$ (3), $b = 11{\cdot}139$ (8), $c = 17{\cdot}432$ (5) Å, $V = 2110$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}823$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}248$ mm^{-1}, $F(000) = 1196$, room temperature, $R = 0{\cdot}030$, $wR = 0{\cdot}034$ for 1780 observed reflections $[I > 2\sigma(I)]$. The structure is characterized by dinuclear entities in which the two metal atoms are linked through a $\mu(O,O')$-type carboxylate bridge. The Cu atom is bound to two N atoms and to four O atoms from the cdta ligand in a tetragonally elongated octahedral environment. The Zn atom displays nearly regular octahedral coordination being bound to five water molecules and to an O atom from the bridging

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carboxylate group. The different molecules interact through hydrogen bonds between the water molecules and the O atoms from the carboxylate groups.

Introduction. *N,N'*-1,2-Cyclohexanediylbis[(*N*-carboxymethyl)glycine] (cdta) can form solid bimetallic carboxylate-bridged coordination compounds of stoichiometry $[M(OH_2)_x][M'(\text{cdta})(OH_2)_y].zH_2O$. Recently we have proved (Fuertes, Miravitlles, Escrivá & Beltrán, 1984; Fuertes, Miravitlles, Escrivá, Martínez-Tamayo & Beltrán, 1985) the existence of four structural families for this system, namely: (I) $[Cu(OH_2)_4][Cu(\text{cdta})]$; (II) $[M(OH_2)_5][M'(\text{cdta})].H_2O$ [(M,M') = (Mn,Cu), (Co,Cu), (Ni,Cu), (Zn,Cu), (Ni,Ni), (Mn,Ni) and (Mn,Zn)]; (III) $[Cu(OH_2)_4][Ni(\text{cdta})].3H_2O$; and (IV) $[M(OH_2)_4][M'(\text{cdta})(OH_2)].4H_2O$ [(M,M') = (Zn,Zn), (Co,Co), (Mn,Co), (Zn,Co)]. The bridging through COO groups provides magnetic exchange pathways between the paramagnetic centers; therefore the correlated study of crystal structure and magnetic properties in these compounds is of great interest. Previously the crystal structure of $[Cu(OH_2)_4][Cu(\text{cdta})]$ [family (I)] has been solved and reported together with a magnetic-property study (Fuertes, Miravitlles, Escrivá, Coronado & Beltrán, 1986). In the present work we report the crystal structure of the title compound, as representative of the structural type (II).

Experimental. Suitable blue crystals were prepared by slow cooling of a water–propanone solution of $Zn(NO_3)_2.6H_2O$, $Cu(NO_3)_2.4H_2O$ and the tetrasodium salt of cdta in equimolar ratio. D_m not determined. Crystals 0·2 × 0·2 × 0·5 mm. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell constants refined from 25 reflections ($5° < \theta < 18°$). 2180 reflections ($1° < \theta < 25°$) ($h = 0$ to 12; $k = 0$ to 13; $l = 0$ to 20) measured with the variable-speed ω–2θ technique, of which there are 50 standard reflections, 112 equivalent reflections through $-x, \frac{1}{2}+y, z$, and 109 equivalent reflections through $x, \frac{1}{2}-y, \frac{1}{2}+z$; $2\theta_{\max} = 50°$. 1929 unique reflections but only 1780 with $I > 2\sigma(I)$ (from counting statistics) were used in the refinement. Variation of standard reflections 211, $5\bar{2}\bar{7}$, 222 and 114, ±0·91%. Data corrected for Lorentz–polarization but not absorption. Structure solved by multisolution direct methods (*MULTAN*11/84; Main, Germain & Woolfson, 1984), using the 230 highest E values; 12 non-H atoms found in first E map; remaining non-H atoms were located by subsequent Fourier syntheses. Full-matrix least-squares refinement with anisotropic temperature factors (*SHELX*76, Sheldrick, 1976). Six H atoms were located in a difference Fourier map and 12 H atoms of the ligand were placed in calculated positions. The H atoms of the six water molecules were omitted from the model. Additional refinement with all non-H atoms treated anisotropically and fixed thermal parameters for H atoms ($U = 0·0668$ Å^2) converged at $R = 0·030$, $wR = 0·034$, $S = 1·54$ for the 1780 observed reflections and 289 variables. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/[\sigma^2(F_o) + 0·0099F_o^2]$ with $\sigma^2(F_o)$ from counting statistics. $(\Delta/\sigma)_{\max}$ in last least-squares cycle <0·5. Max. value in final difference density map was 0·65 e Å^{-3} located near the Zn atom. Atomic form factors from *SHELX*76 (Sheldrick, 1976) and atomic scattering factors and corrections for anomalous dispersion for Zn and Cu atoms were taken from *International Tables for X-ray Crystallography* (1974). The geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975) and *DISTAN* (Burzlaff, Böhme & Gomm, 1977) and molecular illustrations were drawn with *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The atomic parameters are given in Table 1.* A perspective view of the molecule with the atomic numbering scheme is shown in Fig. 1. Table 2 gives bond distances and angles for the complex.

The two metal atoms lie on two different octahedral coordination sites. The Cu atom, occupying the 'chelated' position, is bound to two N atoms and to four O atoms from the cdta ligand. The Zn atom, which occupies the 'hydrated' position, is bound to five O atoms from water molecules and to an O atom belonging to a bridging carboxylate group. In this way, the structure is characterized by dinuclear entities in which the two metal atoms are linked through a $\mu(O,O')$-type carboxylate bridge.

The cdta ligand is hexadentate in the complex $[Cu(\text{cdta})]^{2-}$ forming five-membered chelate rings. For these we use here the classification, established by Weakliem & Hoard (1959), into the three types E, G and R. The E ring is the ethylenediamine ring M—N—C—C′—N'—M, the G rings are the glycine rings whose mean planes are more nearly parallel to the N—M—N′ plane [in this case these are Cu—N(10)—C(11)—C(12)—O(11)—Cu and Cu—N(20)—C(21)—C(22)—O(21)—Cu], and the R rings are the glycine rings whose mean planes are more nearly perpendicular to the N—M—N' plane [in the title compound these are Cu—N(10)—C(31)—C(32)—O(31)—Cu and Cu—N(20)—C(41)—C(42)—O(41)—Cu].

The six ligand atoms around the Cu^{2+} ion define a tetragonally elongated (along the Cu—O_R bonds) octahedron, the basal plane being formed by the two N atoms and two O atoms [O(11), O(21)] from type-G

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* Lists of H-atom coordinates, anisotropic thermal parameters, the equations of the least-squares planes, and structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42682 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

carboxylates. So, the Cu—N and Cu—O_G bond distances [$\bar{d}_{\text{Cu—N}} = 2{\cdot}037\ (22)$; $\bar{d}_{\text{Cu—O}_G} = 1{\cdot}991\ (17)$ Å] are considered as normal when these ligands coordinate in the equatorial plane (Tomlinson, Hathaway, Billing & Nichols, 1969; Fuertes, Miravitlles, Escrivá, Coronado & Beltrán, 1986), while the axial Cu—O_R bonds are longer and these apical ligands should be considered as weakly bonded or semi-coordinated to the Cu atom.

Table 1. *Fractional coordinates* (×10⁴, Zn *and* Cu ×10⁵) *and equivalent isotropic temperature factors* (Å²) *for non-hydrogen atoms, with e.s.d.'s in parentheses*

$$B_{\text{eq}} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)
Cu	−16775 (6)	5852 (6)	2040	1·9 (1)
Zn	−22459 (7)	−18673 (6)	−28260 (7)	2·2 (1)
N(10)	−1093 (5)	1251 (4)	−806 (3)	1·8 (2)
N(20)	−3103 (5)	1803 (4)	183 (4)	2·2 (2)
O(1)	−3214 (4)	−249 (5)	−2909 (4)	3·0 (2)
O(2)	−694 (4)	−927 (4)	−3141 (3)	2·7 (2)
O(3)	−1094 (5)	−3443 (4)	−2864 (4)	3·2 (2)
O(4)	−3717 (5)	−2950 (4)	−2556 (3)	3·1 (2)
O(5)	−2770 (5)	−2211 (5)	−4023 (4)	3·4 (2)
O(6)	3629 (5)	1634 (5)	−984 (4)	3·6 (2)
O(11)	−1 (5)	−170 (4)	224 (3)	2·7 (2)
O(12)	1901 (5)	464 (6)	−36 (4)	3·5 (2)
O(21)	−2602 (4)	−107 (4)	1073 (3)	2·5 (2)
O(22)	−4544 (5)	−277 (5)	1469 (3)	3·5 (2)
O(31)	−2477 (6)	−864 (5)	−536 (4)	3·8 (2)
O(32)	−2029 (6)	−1623 (5)	−1669 (3)	3·3 (2)
O(41)	−839 (5)	2051 (5)	937 (3)	3·2 (2)
O(42)	−1481 (5)	3586 (4)	1645 (3)	2·7 (2)
C(10)	−1808 (6)	2409 (6)	−916 (4)	2·1 (3)
C(11)	239 (6)	1468 (6)	−668 (4)	2·4 (3)
C(12)	761 (6)	507 (6)	−125 (4)	2·3 (3)
C(20)	−3141 (6)	2212 (6)	−649 (4)	2·5 (3)
C(21)	−4151 (6)	1053 (6)	420 (4)	2·6 (3)
C(22)	−3752 (6)	163 (6)	1043 (4)	2·6 (3)
C(30)	−3939 (7)	3331 (6)	−788 (5)	3·0 (3)
C(31)	−1266 (8)	327 (6)	−1418 (4)	3·1 (3)
C(32)	−1985 (7)	−791 (6)	−1180 (4)	2·5 (3)
C(40)	−3870 (8)	3701 (7)	−1642 (5)	4·1 (3)
C(41)	−2884 (7)	2772 (7)	751 (5)	3·1 (3)
C(42)	−1629 (6)	2801 (6)	1137 (4)	2·2 (3)
C(50)	−2559 (8)	3988 (7)	−1853 (5)	3·6 (3)
C(60)	−1701 (8)	2890 (8)	−1735 (5)	3·4 (3)

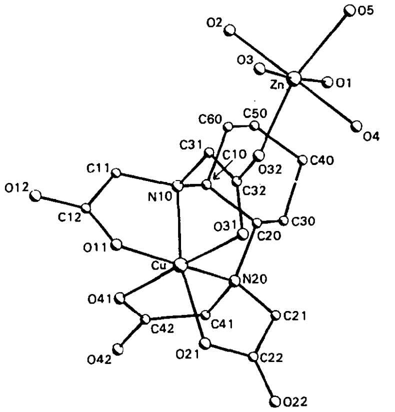

Fig. 1. Perspective view and atomic numbering of the title compound.

This kind of distortion is a result of the Jahn–Teller effect and its extent has been parametrized by Hathaway & Billing (1970) through the tetragonality, T (defined as the mean in-plane Cu—L bond length divided by the mean out-of-plane bond length, R_S/R_L), which in this case is 0·89. This value is greater than that found in the analogous complex $Cu_2(cdta).4H_2O$ ($T = 0{\cdot}82$) (Fuertes, Miravitlles, Escrivá, Coronado & Beltrán, 1986), indicating a lower distortion of the $[Cu(cdta)]^{2-}$ octahedron in the title compound.

The cdta conformation is *E,G/R*, according to the notation suggested by Porai-Koshits, Pozhidaev & Polynova (1974). In this conformation, within the three types established for edta complexes, the methylene groups of the *E* and *G* rings in the $N(CH_2)_3$ cluster lie on one side of the *N—M—N′* plane and the methylene

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

N(10)—Cu	2·014 (5)	C(12)—O(11)	1·275 (8)
N(20)—Cu	2·059 (5)	C(12)—O(12)	1·249 (8)
O(11)—Cu	2·008 (5)	C(22)—O(21)	1·286 (8)
O(21)—Cu	1·974 (5)	C(22)—O(22)	1·239 (8)
O(31)—Cu	2·242 (6)	C(32)—O(31)	1·246 (9)
O(41)—Cu	2·265 (5)	C(32)—O(32)	1·261 (9)
O(1)—Zn	2·092 (5)	C(42)—O(41)	1·248 (8)
O(2)—Zn	2·060 (4)	C(42)—O(42)	1·254 (8)
O(3)—Zn	2·157 (4)	C(20)—C(10)	1·537 (8)
O(4)—Zn	2·057 (5)	C(60)—C(10)	1·529 (10)
O(5)—Zn	2·197 (5)	C(12)—C(11)	1·537 (9)
O(32)—Zn	2·048 (5)	C(30)—C(20)	1·537 (9)
C(10)—N(10)	1·518 (8)	C(22)—C(21)	1·533 (9)
C(11)—N(10)	1·487 (8)	C(40)—C(30)	1·546 (11)
C(31)—N(10)	1·494 (8)	C(32)—C(31)	1·528 (9)
C(20)—N(20)	1·520 (9)	C(50)—C(40)	1·506 (12)
C(21)—N(20)	1·472 (8)	C(42)—C(41)	1·521 (8)
C(41)—N(20)	1·485 (9)	C(60)—C(50)	1·551 (11)

N(20)—Cu—N(10)	88·8 (2)	C(21)—N(20)—Cu	101·8 (3)
O(11)—Cu—N(10)	83·3 (2)	C(21)—N(20)—C(20)	114·7 (5)
O(11)—Cu—N(20)	163·6 (2)	C(41)—N(20)—Cu	110·2 (4)
O(21)—Cu—N(10)	167·2 (2)	C(41)—N(20)—C(20)	115·0 (5)
O(21)—Cu—N(20)	83·6 (2)	C(41)—N(20)—C(21)	110·4 (6)
O(21)—Cu—O(11)	106·6 (2)	C(12)—O(11)—Cu	109·5 (4)
O(31)—Cu—N(10)	83·4 (2)	C(22)—O(21)—Cu	111·8 (4)
O(31)—Cu—N(20)	99·9 (2)	C(32)—O(31)—Cu	107·8 (5)
O(31)—Cu—O(11)	93·4 (2)	C(32)—O(32)—Zn	140·2 (5)
O(31)—Cu—O(21)	87·9 (2)	C(42)—O(41)—Cu	111·3 (4)
O(41)—Cu—N(10)	95·8 (2)	C(20)—C(10)—N(10)	108·8 (5)
O(41)—Cu—N(20)	80·7 (2)	C(60)—C(10)—N(10)	112·1 (6)
O(41)—Cu—O(11)	85·8 (2)	C(60)—C(10)—C(20)	113·9 (6)
O(41)—Cu—O(21)	93·1 (2)	C(12)—C(11)—N(10)	110·2 (5)
O(41)—Cu—O(31)	178·9 (2)	O(12)—C(12)—O(11)	124·1 (6)
O(2)—Zn—O(1)	87·4 (2)	C(11)—C(12)—O(11)	117·8 (5)
O(3)—Zn—O(1)	172·2 (2)	C(11)—C(12)—O(12)	118·0 (6)
O(3)—Zn—O(2)	86·0 (2)	C(10)—C(20)—N(20)	107·8 (5)
O(4)—Zn—O(1)	97·5 (2)	C(30)—C(20)—N(20)	114·2 (6)
O(4)—Zn—O(2)	174·5 (2)	C(30)—C(20)—C(10)	111·6 (5)
O(4)—Zn—O(3)	88·9 (2)	C(22)—C(21)—N(20)	110·3 (5)
O(5)—Zn—O(1)	87·4 (2)	O(22)—C(22)—O(21)	123·9 (6)
O(5)—Zn—O(2)	92·7 (2)	C(21)—C(22)—O(21)	117·1 (5)
O(5)—Zn—O(3)	88·8 (2)	C(21)—C(22)—O(22)	119·0 (6)
O(5)—Zn—O(4)	85·1 (2)	C(40)—C(30)—C(20)	109·9 (6)
O(32)—Zn—O(1)	90·7 (2)	C(32)—C(31)—N(10)	115·6 (6)
O(32)—Zn—O(2)	95·8 (2)	O(32)—C(32)—O(31)	123·1 (7)
O(32)—Zn—O(3)	94·1 (2)	C(31)—C(32)—O(31)	121·2 (6)
O(32)—Zn—O(4)	86·7 (2)	C(31)—C(32)—O(32)	115·8 (6)
O(32)—Zn—O(5)	171·2 (2)	C(50)—C(40)—C(30)	109·7 (6)
C(10)—N(10)—Cu	105·2 (4)	C(42)—C(41)—N(20)	117·1 (6)
C(11)—N(10)—Cu	103·0 (4)	O(42)—C(42)—O(41)	125·2 (6)
C(11)—N(10)—C(10)	112·4 (5)	C(41)—C(42)—O(41)	118·6 (6)
C(31)—N(10)—Cu	109·3 (4)	C(41)—C(42)—O(42)	116·2 (6)
C(31)—N(10)—C(10)	115·5 (5)	C(60)—C(50)—C(40)	111·7 (6)
C(31)—N(10)—C(11)	110·5 (5)	C(50)—C(60)—C(10)	110·7 (7)
C(20)—N(20)—Cu	103·6 (4)		

group of the *R* ring lies on the other. The other two types are called *E,R/G* (with the CH_2 groups of the *E* and *R* rings separated through the *N—M—N′* plane from that of the *G* ring) and *trans-E* (or centrosymmetric *trans* structure for edta). The *E,G/R* conformation is characteristic of the octahedral complexes containing the hexadentate cdta ligand, and it is also present in $Cu_2(cdta).4H_2O$ and $CuNi(cdta).7H_2O$ (Fuertes, Miravitlles, Escrivá, Martínez-Tamayo & Beltrán, 1985). The cyclohexane ring is in the chair form, and its conformation is defined by the planes *A*[C(20),C(30),C(50),C(60)], *B*[C(30),C(40),C(50)] and *C*[C(10),C(20),C(60)]. The angles between the *A–B* and *A–C* planes are, respectively, 54·3 (7) and 45·7 (7)°.

The carboxylate groups are, in general, asymmetric. The interplay between the bond lengths and angles in them does not obey the first relationship described by Borthwick (1980), probably due to the perturbations produced by the metal—O bonds and hydrogen bonds. However, it follows fairly well the remaining *R*2, *R*3 and *R*4 relationships. The formulae of the four relations are: *R*1, $\varphi_1-\varphi_2=-100\ (r_1-r_2)$; *R*2, $1/r_i=0{\cdot}65\times\sin\varphi_j+0{\cdot}22$ ($i\neq j$; $i,j\in\{1,2\}$); *R*3, $\varphi_i=243-100r_i$ ($i\in\{1,2\}$) and *R*4, $r_1r_2\cos(\alpha/2)\simeq0{\cdot}73$, where φ_i and α are the C—C—O and O—C—O angles (°), respectively, and r_i is the C—O distance (Å).

The COO_G groups show the greatest differences between the two C—O bond distances, having $d_{C-Oj1} > d_{C-Oj2}$. The COO_R groups are more symmetrical and show the inverse relation $d_{C-Oj1} < d_{C-Oj2}$ owing to the weaker interaction of O*j*1 with the Cu^{2+} ion. This result has also been found in the $Cu_2(cdta).4H_2O$ and $MnCu(edta).6H_2O$ complexes (Solans, Font-Altaba, Oliva & Herrera, 1983).

The structural function of the bridging carboxylate is, after the terminology established by Porai-Koshits (1980), intermediate between *a*-2-*s* and *a*-2-*a* (nearer to *a*-2-*a*), as can be seen from the torsion angles Cu—O(31)—C(32)—O(32) = 164·0 (6)° and O(31)—C(32)—O(32)—Zn = 139·8 (7)°.

The strain in the individual chelate rings has been analyzed in terms of the deviation (*t*) of the sum of the angles on each ring from the idealized values proposed by Weakliem & Hoard (1959) for an *E* ring (527·9°) and a glycinate ring (538·9°).

The *t* values for the title compound have been compared with those for related complexes in a previous work (Fuertes, Miravitlles, Escrivá, Coronado & Beltrán, 1986). The strains of the *E* and *G* rings are similar [$t_E=-13{\cdot}7\ (9)°$, $\bar{t}_G=-14{\cdot}7\ (9)°$]. However, the *G* rings are more strained than the *R* ones [$\bar{t}_R=-1{\cdot}3\ (10)°$]. This result is general in edta and edta-like complexes and arises from the cumulative bond-angle strains in forming a *G* ring.

The coordination polyhedron of the Zn atom is a slightly distorted octahedron, with normal Zn—O distances for this type of environment (Constable, 1984). The six water molecules are involved in hydrogen bonds with the O atoms from carboxylate groups and with symmetry-related water molecules (Table 3), assuring the intermolecular packing (Fig. 2).

The strongest hydrogen bonds are formed by the uncoordinated and weakly Cu-bonded O atoms from carboxylate groups [O(22), O(41), O(42)]. This result is normal and also explains the similar bond distances C(42)—O(41) and C(42)—O(42).

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

A—B		*B—A—C*	
$O(1)-O(22^{i})$	2·730 (5)	$Zn-O(1)-O(22^{i})$	131·4 (3)
$O(1)-O(42^{ii})$	2·754 (6)	$Zn-O(1)-O(42^{ii})$	104·8 (3)
		$O(22^{i})-O(1)-O(42^{ii})$	110·8 (4)
$O(2)-O(41^{iii})$	2·632 (5)	$Zn-O(2)-O(41^{iii})$	116·1 (3)
$O(2)-O(42^{ii})$	2·770 (5)	$Zn-O(2)-O(42^{ii})$	105·2 (3)
		$O(41^{iii})-O(2)-O(42^{ii})$	124·1 (4)
$O(3)-O(21^{iv})$	2·955 (5)	$Zn-O(3)-O(21^{iv})$	98·2 (3)
$O(3)-O(42^{iii})$	2·930 (5)	$Zn-O(3)-O(42^{iii})$	127·4 (3)
		$O(21^{iv})-O(3)-O(42^{iii})$	108·5 (4)
$O(4)-O(6^{v})$	2·780 (5)	$Zn-O(4)-O(6^{v})$	107·3 (3)
$O(4)-O(22^{iv})$	2·756 (5)	$Zn-O(4)-O(22^{iv})$	122·2 (3)
		$O(6^{v})-O(4)-O(22^{iv})$	120·0 (4)
$O(5)-O(12^{iii})$	2·792 (5)	$Zn-O(5)-O(12^{iii})$	113·0 (3)
$O(5)-O(21^{iv})$	2·998 (5)	$Zn-O(5)-O(21^{iv})$	96·0 (3)
		$O(12^{iii})-O(5)-O(21^{iv})$	135·2 (4)
$O(6)-O(12)$	2·822 (5)	$O(12)-O(6)-O(4^{vi})$	132·6 (4)
$O(6)-O(4^{vi})$	2·780 (5)	$O(12)-O(6)-O(32^{vi})$	98·8 (4)
$O(6)-O(32^{vi})$	2·867 (5)		

Symmetry code: (i) $-1-x, -y, -\frac{1}{2}+z$; (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $-x, -y, -\frac{1}{2}+z$; (iv) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$; (v) $-x, -\frac{1}{2}+y, z$; (vi) $-x, \frac{1}{2}+y, z$.

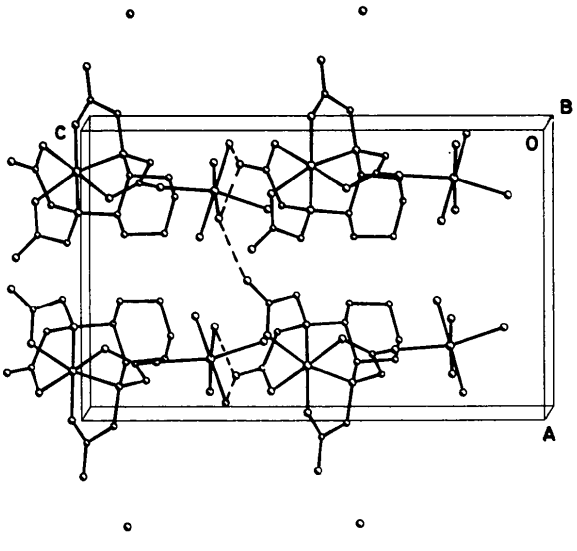

Fig. 2. A view of the unit-cell contents, viewed approximately along the [010] direction. Hydrogen bonds are indicated by dashed lines.

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Structure of an Orthorhombic Form of 2,2′-Biphenylenemercury

By N. A. A. Al-Jabar, J. Bowen Jones, D. S. Brown and A. G. Massey

*Department of Chemistry, Loughborough University of Technology, Loughborough LE*11 3*TU, England*

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Abstract. 1,2;1,3;2,3-Tris(μ-2,2′-biphenylene)-trimercury, $[Hg_3(C_{12}H_8)_3]$, $M_r = 1058·3$, orthorhombic, $Pbca$, $a = 26·857$ (16), $b = 11·458$ (6), $c = 19·110$ (44) Å, $U = 5880$ Å^3, $Z = 8$, $D_m = 2·398$, $D_x = 2·391$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 153·44$ cm^{-1}, $F(000) = 3840$, $T = 293$ K, $R = 0·053$ for 1898 reflexions with $I > 3\sigma(I)$. The biphenylenemercury molecule is trimeric, $(C_6H_4C_6H_4Hg)_3$, and chiral. The Hg atoms form a triangle with Hg···Hg contacts in the range 3·461 (1) to 3·637 (2) Å, slightly greater than accepted van der Waals distances. The C—Hg—C angles are 176·3 (9)–178·9 (8)°.

Introduction. When Wittig first prepared 2,2′-biphenylenemercury he assumed it was a simple monomer (Wittig & Herwig, 1954) but later quoted ebullioscopic evidence to prove its tetrameric nature (Wittig & Lehmann, 1957). However, mass spectral analysis (Awad, Brown, Cohen, Humphries & Massey, 1977; Al-Jabar & Massey, 1984) and an X-ray study of triclinic crystals (Stender, Hinrichs, Kopf & Klar, 1981) showed some samples of the molecule to be trimeric. As both the trimeric and tetrameric species appear equally feasible we have searched for evidence of a tetramer. We found that the bulk of our biphenylenemercury samples separates from a variety of solvents as orthorhombic crystals which take on a surprising array of physical shapes from apparent cubes and truncated rods to perfectly formed hexagons. Again, even in this new crystal form biphenylenemercury is trimeric; so far we have been unable to obtain any evidence for a tetrameric species although the perfluorinated analogue has been detected mass spectroscopically (Al-Jabar & Massey, 1984).

Experimental. Preparation by the method of Neugebauer, Kos & Schleyer (1982); colourless crystals grown from toluene; D_m by flotation in hexane–dibromomethane; crystal (0·38 × 0·13 × 0·08 mm) mounted about **c**; Stoe Weissenberg diffractometer, $\sin\theta/\lambda < 0·6$ Å^{-1}; lattice parameters from maximizing fit of axial row reflexions; 5123 reflexions measured, 1898 with $I > 3\sigma(I)$; h 0–34, k 0–14, l 0–15; standard check reflexions on each layer, no significant changes; absorption corrections applied, $t_{\min}$ 0·25, $t_{\max}$ 0·33; Hg positions found by direct methods and C