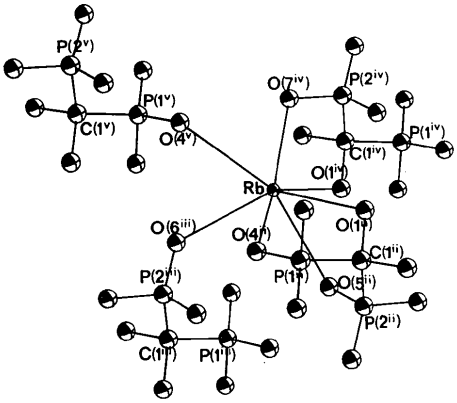

Fig. 1. *ORTEP* (Johnson, 1976). Environnement de l'atome de rubidium.

L'étude de la conformation des molécules HEDP montre que les groupes PO_3 sont en position éclipsée avec un écart maximal de 14°. La longueur des liaisons P—O est influencée par la nature des interactions entre l'atome d'oxygène et l'atome d'hydrogène voisin: deux liaisons longues (1,571 et 1,554 Å) aboutissent à un groupement hydroxyle; deux liaisons de longueur moyenne (1,530 et 1,528 Å) sont impliquées dans une liaison symétrique par pont hydrogène; deux liaisons courtes (1,487 et 1,492 Å) où l'atome d'oxygène est accepteur de liaisons hydrogène. D'aprés les longueurs des liaisons P—O et les positions déterminées pour les atomes d'hydrogène, chaque groupe phosphonate conserve un proton et partage le deuxième proton H(45) avec un groupe phosphonate d'un coordinat HEDP voisin, conférant ainsi à l'acide hydroxyéthyldiphosphonique la possibilité de se comporter comme un monoacide.

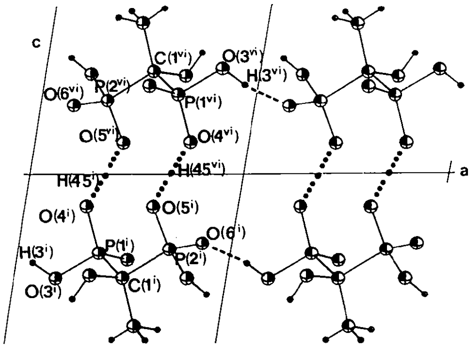

Fig. 2. *ORTEP* (Johnson, 1976). Liaisons hydrogène entre molécules HEDP. Projection partielle selon l'axe *y*. Code de symétrie: (i) x, y, z; (vi) $1-x, 1-y, -z$.

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catena-Triaqua-μ-[1,3,5-benzenetricarboxylato(2—)]-copper(II)

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Abstract. $[Cu(C_9H_4O_6)(H_2O)_3]_n$, $M_r = 325{\cdot}73$, monoclinic, $P2_1/n$, $a = 8{\cdot}570\,(1)$, $b = 18{\cdot}855\,(1)$, $c = 6{\cdot}845\,(3)$ Å, $\beta = 92{\cdot}87\,(2)°$, $V = 1104{\cdot}7$ Å^3, $Z = 4$, $D_m = 2{\cdot}0$, $D_x = 1{\cdot}96$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 21{\cdot}00$ cm^{-1}, $F(000) = 660$, $T = 293$ K, $R = 0{\cdot}030$, $wR = 0{\cdot}027$ $[w = 1/\sigma^2(F_o)]$ for 1625 reflexions with $|F_o| > 2\sigma(|F_o|)$. Only two of the three carboxylic groups of the acid act as ligands to Cu atoms, bridging them to give polymeric chains. The Cu atoms show a distorted pyramidal coordination geometry involving the two carboxylic O atoms and three water molecules.

Introduction. The present work is part of structural studies on copper complexes with polybasic benzenecarboxylic acids containing three or more carboxyl groups. Up to now only the structure of a complex of 1,2,4,5-benzenetetracarboxylic acid has been reported (Usubaliev, Shnulin & Mamedov, 1982). On the other hand a number of structures of copper complexes with *o*-phthalic acid have been published. Here a variety of

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters in catena-triaqua-μ-[1,3,5-benzenetricarboxylato(2−)]-copper*(II)

$B_{eq} = \frac{1}{3}(\sum B_{ii} + 2B_{13}\cos\beta)$.

	x	y	z	B_{eq}(Å^2)
Cu	0·82085 (5)	0·27359 (2)	0·20996 (7)	1·46
O(1)	0·9462 (3)	0·1889 (1)	0·2339 (4)	1·84
O(2)	0·7331 (3)	0·1263 (1)	0·2784 (5)	2·78
O(3)	0·7109 (3)	0·3622 (1)	0·2036 (4)	1·95
O(4)	0·4802 (3)	0·3110 (1)	0·2391 (4)	2·12
O(5)	0·0484 (3)	0·5845 (1)	0·2968 (4)	2·49
O(6)	0·0050 (3)	0·4706 (1)	0·2338 (5)	3·73
O(7)	0·7487 (3)	0·2475 (2)	−0·0601 (4)	3·05
O(8)	0·8590 (4)	0·2890 (2)	0·4956 (4)	3·17
O(9)	1·0399 (3)	0·3293 (1)	0·1229 (5)	2·72
C(1)	0·4965 (4)	0·4372 (2)	0·2423 (5)	1·23
C(2)	0·3358 (4)	0·4446 (2)	0·2519 (5)	1·42
C(3)	0·2694 (4)	0·5120 (2)	0·2588 (6)	1·52
C(4)	0·3646 (4)	0·5722 (2)	0·2571 (5)	1·38
C(5)	0·5261 (4)	0·5645 (2)	0·2489 (5)	1·26
C(6)	0·5921 (4)	0·4973 (2)	0·2407 (5)	1·26
C(7)	0·5665 (4)	0·3647 (2)	0·2278 (5)	1·43
C(8)	0·0955 (4)	0·5186 (2)	0·2611 (6)	1·95
C(9)	0·8754 (4)	0·1298 (2)	0·2537 (5)	1·55

Table 2. *Bond lengths* (Å) *and angles* (°) *in catena-triaqua-μ-[1,3,5-benzenetricarboxylato(2−)]-copper*(II)

Cu—O(1)	1·927 (2)	O(6)—C(8)	1·200 (4)
Cu—O(3)	1·917 (2)	C(1)—C(2)	1·389 (5)
Cu—O(7)	1·982 (3)	C(1)—C(6)	1·398 (5)
Cu—O(8)	1·987 (3)	C(1)—C(7)	1·498 (5)
Cu—O(9)	2·257 (3)	C(2)—C(3)	1·394 (5)
O(1)—C(9)	1·278 (4)	C(3)—C(4)	1·398 (5)
O(2)—C(9)	1·241 (4)	C(3)—C(8)	1·497 (5)
O(3)—C(7)	1·258 (4)	C(4)—C(5)	1·395 (5)
O(4)—C(7)	1·259 (4)	C(5)—C(6)	1·391 (5)
O(5)—C(8)	1·332 (4)	C(5)—C(9)	1·494 (5)
O(3)—Cu—O(1)	174·4 (1)	C(4)—C(3)—C(2)	120·0 (3)
O(7)—Cu—O(1)	91·1 (1)	C(4)—C(3)—C(8)	121·0 (3)
O(7)—Cu—O(3)	93·7 (1)	C(3)—C(4)—C(5)	119·8 (3)
O(8)—Cu—O(1)	88·5 (1)	C(4)—C(5)—C(6)	120·1 (3)
O(8)—Cu—O(3)	87·2 (1)	C(4)—C(5)—C(9)	118·6 (3)
O(8)—Cu—O(7)	169·2 (1)	C(6)—C(5)—C(9)	121·4 (3)
O(8)—Cu—O(9)	95·4 (1)	C(1)—C(6)—C(5)	119·9 (3)
O(9)—Cu—O(1)	86·6 (1)	O(4)—C(7)—O(3)	124·2 (3)
O(9)—Cu—O(3)	90·2 (1)	C(1)—C(7)—O(3)	116·3 (3)
O(9)—Cu—O(7)	95·4 (1)	C(1)—C(7)—O(4)	119·4 (3)
C(9)—O(1)—Cu	117·7 (2)	O(6)—C(8)—O(5)	122·1 (3)
C(7)—O(3)—Cu	121·1 (2)	C(3)—C(8)—O(5)	113·0 (3)
C(2)—C(1)—C(6)	120·1 (3)	C(3)—C(8)—O(6)	124·9 (3)
C(2)—C(1)—C(7)	119·7 (3)	O(2)—C(9)—O(1)	122·4 (3)
C(6)—C(1)—C(7)	120·1 (3)	C(5)—C(9)—O(1)	116·4 (3)
C(3)—C(2)—C(1)	120·0 (3)	C(5)—C(9)—O(2)	121·1 (3)
C(2)—C(3)—C(8)	119·0 (3)		

coordination modes are found, *e.g.* bidentate chelating and monodentate carboxylic groups (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1981) and bidentate bridging carboxylate groups (Prout, Carruthers & Rossotti, 1971).

Experimental. Blue acicular crystals by diffusion of an aqueous solution of $Cu(ClO_4)_2$ into 1,3,5-benzenetricarboxylic acid in ethanol. D_m by flotation in an aqueous solution of thallium(I) formate/malonate. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$, graphite monochromator. Crystal of about 0·30 × 0·10 × 0·08 mm. Lattice parameters from 25 reflexions, $9·3 < \theta < 15·6°$; intensity measurement $2 \leq \theta \leq 25°$ ($-10 \leq h \leq 10$; $0 \leq k \leq 22$; $0 \leq l \leq 8$), three intensity-control reflexions every hour of data collection, two reflexions for orientation every 200 reflexions, no significant decay. 2012 reflexions measured, Lp correction, no correction for absorption. 1625 reflexions with $|F_o| > 2\sigma(|F_o|)$ were used for structure refinement. The position of the Cu atom was obtained from a Patterson synthesis, O- and C-atom positions from subsequent Fourier syntheses. After refining all non-H atoms with anisotropic thermal parameters, H-atom positions were taken from a difference Fourier map and were added to the model for final calculation with fixed isotropic thermal parameters of 0·08 Å^2, benzene H atoms riding on the C atoms with C—H bond lengths fixed at 1·08 Å and constraints of O—H bond lengths being not shorter than 0·85 Å and angles H—O—H in the water molecules not smaller than 104°. Full-matrix least-squares refinement on F converged at $R = 0·030$, $wR = 0·027$ [$w = 1/\sigma^2(F_o)$]. Max. Δ/σ on final cycle = 0·144 (H-atom coordinate), $\Delta\rho$ fluctuations within +0·39, −0·40 e Å^{-3}. All calculations were performed with

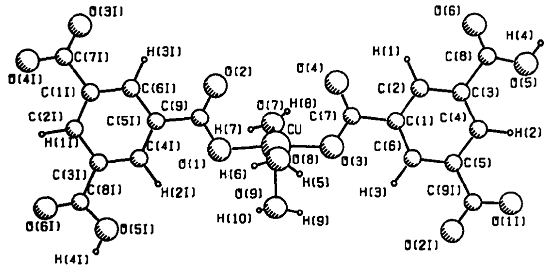

Fig. 1. Surroundings of the Cu atom and numbering scheme [symmetry code: (I) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$].

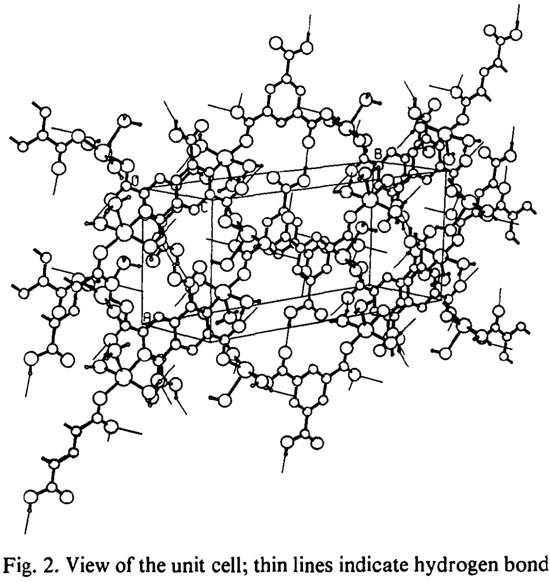

Fig. 2. View of the unit cell; thin lines indicate hydrogen bonds.

*SHELX*76 (Sheldrick, 1976) using scattering factors of Cromer & Mann (1968).

Discussion. Atomic positions and equivalent isotropic thermal parameters are given in Table 1,* bond lengths and angles in Table 2. Fig. 1 shows the environment of the Cu atom; Fig. 2 is a perspective view of the unit cell. The coordination polyhedron is a square pyramid formed by two monodentate carboxylic groups of different acid molecules and three water molecules, the base of the pyramid being slightly distorted towards a tetrahedron. An analogous coordination sphere was observed in copper(II) 1,2,4,5-benzenetetracarboxylate decahydrate (Usubaliev, Shnulin & Mamedov, 1982). As two of the carboxyl groups act as ligands, polymeric zigzag chains are formed, which run along **b**. These are connected into sheets *via* hydrogen bonding: O(5)—H(4)···O(2^{i}) [O(5)···O(2^{i}) = 2·566 Å]. Intermolecular distances O(7)···O(4^{ii}) = 2·705 Å and O(8)···O(4^{ii}) = 2·690 Å indicate hydrogen bonding between neighbouring sheets. [Symmetry code: (i) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$.]

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44844 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Tetrachlorotris(triphenylphosphine oxide)thorium(IV)

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Abstract. $[ThCl_4\{OP(C_6H_5)_3\}_3]$, $M_r = 1208·73$, triclinic, $P\bar{1}$, $a = 10·668\,(7)$, $b = 13·857\,(7)$, $c = 20·141\,(6)$ Å, $\alpha = 98·23\,(4)$, $\beta = 77·98\,(4)$, $\gamma = 100·67\,(8)$°, $V = 2845\,(5)$ Å^3, $Z = 2$, $D_x = 1·411$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 30·212$ cm^{-1}, $F(000) = 1192$, $T = 295\,(1)$ K, $R = 0·052$ for 4671 observed reflections with $I > 3\sigma(I)$. The Th atom is seven-coordinate in an approximate capped-octahedral environment with an O in the capping position and three Cl atoms in the capped face. The packing in the crystal is dictated by van der Waals interactions.

Introduction. Numerous substituted tertiary phosphine oxide complexes of thorium and uranium tetrahalides are now known but very few structural data are available for complexes of the type ThX_4L_3 (X = Cl or Br; L = oxygen-donor ligand). The structure analysis of the title compound has been undertaken with the aim of clarifying the stoichiometric and conformational changes induced by relatively bulky oxygen-donor ligands.

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