

Fig. 1. Structure of $\text{TlBr}_3 \cdot 2(\text{pyridine})$ showing intermolecular distances and angles (e.s.d.'s $\sim 0.01 \text{ \AA}$, 0.4°).

1979) which are trigonal bipyramidal. The $\text{Tl}-\text{N}$ distances [av. $2.44(2) \text{ \AA}$] compare with average values $2.364(8) \text{ \AA}$ in $\text{TlCl}_3 \cdot (1,10\text{-phenanthroline})$ (Baxter & Gafner, 1972) and $2.43(2) \text{ \AA}$ in $\text{TlCl}_3 \cdot 3(\text{pyridine})$ (Jeffs, Small & Worrall, 1984c). The large distortions in the equatorial $\text{Br}-\text{Tl}-\text{Br}$ angles ($112.9-131.1^\circ$) and the planarity of all eight heavy atoms indicate a weak but significant interaction between Br and Tl atoms on pairs of adjacent molecules (Fig. 1).

It should be noted that the separation of the bridging Br atoms, 3.97 \AA , is the van der Waals value; closer approach of the bridged Tl and Br in adjacent molecules would either shorten this distance or increase the distortion of the $\text{Br}-\text{Tl}-\text{Br}$ angle. The compound may be regarded as being intermediate between

five-coordinate monomers, e.g. $\text{TlBr}_3\text{-dioxane}$, and six-coordinate halogen-bridged dimers, e.g. $\text{TlCl}_3 \cdot (1,10\text{-phenanthroline})$. Stronger bridging bonds would be expected in $\text{TlCl}_3 \cdot 2(\text{pyridine})$ since the more electronegative Cl will enhance the Lewis acid strength of thallium and favour dimer formation. Thallium compounds involving strongly electron-withdrawing groups, but with shorter halogen-bridging distances have already been reported, e.g. in five-coordinate $[(p\text{-HC}_6\text{F}_4)_2\text{TLX}(\text{OPPh}_3)]_2$ (Henrik, McPartlin, Matthews, Deacon & Phillips, 1980) and in the four-coordinate halides $(p\text{-HC}_6\text{F}_4)_2\text{TLX}$ (Deacon, Phillips, Henrik & McPartlin, 1979) ($X=\text{Cl}, \text{Br}$).

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The Structure of Bis[2-amino-2-hydroxymethyl-1,3-propanediolato(1-)-O,N]copper(II)-Sodium Perchlorate Monohydrate, $[\text{Cu}(\text{C}_4\text{H}_{10}\text{NO}_3)_2] \cdot \text{NaClO}_4 \cdot \text{H}_2\text{O}^*$

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Abstract. $M_r = 444.27$, monoclinic, $C2/c$, $a = 14.2872(6)$, $b = 10.9454(4)$, $c = 11.1921(5) \text{ \AA}$, $\beta = 96.290(3)^\circ$, $Z = 4$, $V = 1739.6(6) \text{ \AA}^3$, $D_x =$

$1.697(1)$, $D_m = 1.70(1) \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu(\text{Mo } K\alpha) = 1.54 \text{ mm}^{-1}$, $F(000) = 916$, $T = 293 \text{ K}$, $R = 0.044$ for 2826 reflections. The structure consists of uncharged $\text{Cu}[\text{NH}_2\text{C}(\text{CH}_2\text{O})\text{(CH}_2\text{OH})_2]_2$ complexes, Na^+ , ClO_4^- and water. The Cu

* Metal Complexes with Mixed Ligands. 24.

coordination is a square-planar CuN₂O₂ chromophore, with the distances Cu—N = 1.999 (2) and Cu—O (deprotonated) = 1.908 (2) Å. The Na atom is situated at a centre of symmetry and is octahedrally surrounded by oxygens from the Cu-bonded ligand, the perchlorate group and the water molecule; distances Na—O = 2.334 (2), 2.516 (3) and 2.305 (3) Å respectively. The Cu complexes are thus connected *via* electrostatic O—Na—O bridges in addition to hydrogen bonds.

Introduction. The buffer region of 2-amino-2-hydroxymethyl-1,3-propanediol (H₃tham) covers the physiological pH range and H₃tham is therefore a favoured buffer in biochemical studies. As all pH buffers contain a basic site they are potential ligands for metal ions. Statements have been made that chelates with H₃tham are formed in aqueous solutions with the basic amino group forming a binding site (Kemula, Bracha-czek & Hulanicki, 1962; Bai & Martell, 1969; Brignac & Mo, 1975; Fischer, Haring, Tribolet & Sigel, 1979). It is also predicted that a proton is lost from the metal-bonded hydroxyl oxygen of H₃tham at least when copper is involved, *i.e.* Cu(H₂tham)₂ is formed (Hall, Swisher, Brannon & Lidén, 1962; Bai & Martell, 1969). Non-aqueous solution data, collected by Dotson (1972), indicated that a proton was removed from the hydroxyl O atom of the ligand when coordinated to certain metallic ions. As no complete crystal structure determination of *M*(H₃tham) compounds (mere structural suggestions are available) could be found in the literature an X-ray crystal structure investigation was undertaken. So far the Ni(H₃tham)₂ [or Ni(tris)₂] structure has been published (Ivarsson, 1982) and in this paper the molecular and crystal structure of Cu(H₂tham)₂ is presented.

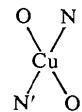
Experimental. NaOH solution was added to a blue solution with the composition [Cu²⁺] = 0.25 M, [H₃tham] = 0.50 M and [ClO₄⁻] = 3.0 M. At pH ~ 9.5 the solution turned violet and crystals were formed, one such, *ca* 0.24 × 0.28 × 0.30 mm, used for structure analysis; *D*_m by flotation in CCl₄—CHBr₃, Syntex *R3* four-circle diffractometer, graphite-monochromatized Mo *K*_α, 3749 reflections \pm *hkl* with $2\theta < 65^\circ$, 2826 with $I \geq 2\sigma(I)$, Lp correction, empirical absorption correction (transmission factors 0.785–1.000), standard reflections: 226, 333, 311; Patterson synthesis and standard Fourier methods, anisotropic full-matrix refinement minimizing $\sum(\Delta F)^2$, H (from ΔF synthesis) isotropic ($B = 4$ Å²), final $R = 0.044$, $wR = 0.051$, $w = 1/\{[1.5\sigma(F_0)]^2 + (0.035F_0)^2\}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), $(\Delta/\sigma)_{\text{max}} < 10\%$. Computer programs supplied with the Syntex *R3* crystallographic system, final calculations with programs described by Antti (1976). DG Nova 3, CD Cyber 1972, computers of the

Department of Inorganic Chemistry, Umeå, and the University of Umeå respectively.

Discussion. Final atomic positional parameters are given in Table 1.*

The structure is built up from uncharged Cu[NH₂C(CH₂O)(CH₂OH)₂]₂ complexes, Na⁺ and ClO₄⁻ ions and water molecules. The Cu complexes are connected in a three-dimensional framework by electrostatic O—Na—O bridges and hydrogen bonds (Fig. 1).

In the Cu[NH₂C(CH₂O)(CH₂OH)₂]₂ complex, the metal ion lies at a centre of symmetry, surrounded by two bidentate H₃tham ligands in a square-planar arrangement. Each ligand is attached to the Cu atom by an amino group, Cu—N = 1.999 (2) Å, and a deprotonated hydroxymethyl oxygen, Cu—O = 1.908 (2) Å. For symmetry reasons the atoms



are coplanar, with the angle N—Cu—O' = 94.1 (3)°. The Cu—N distance is of the same order as found in other Cu—amino bonds (Ivarsson, Lundberg & Ingri, 1972). According to Hathaway & Hodgson (1973) a normal short Cu—O distance is *ca* 2.00 Å but Cu—O distances of 1.90 Å are frequent in square-coplanar Cu complexes. An effect of the metal interaction on bonding distances within the ligand is only noticed in the N—C(4) bond, which is significantly longer than the corresponding bond in the 'non-metal-bonding' H₃tham, 1.490 (3) and 1.472 (2) Å respectively. The same situation occurs in the Ni—H₃tham interaction (Ivarsson, 1982). Distances and angles are given in Table 2.

The sodium–oxygen arrangement: The Na⁺ ion coordinates in an octahedral arrangement of six O atoms, two each from water molecules,† perchlorate groups† and OH groups† from H₃tham. The Na⁺ in this structure is a central ion in the bridging framework since it bridges the Cu complexes in addition to forming —Na—ClO₄—Na—ClO₄— connection chains.

The perchlorate group: Owing to the symmetry there are only two different oxygens in the perchlorate group. O(4) is connected to the Na⁺ ion and O(5) is connected to the amino group of the Cu complex *via* a hydrogen bond [O(5)—N = 3.184 (3) Å]. The O(4) atoms are

* Lists of structure factors and anisotropic thermal parameters, fractional atomic coordinates for H atoms and hydrogen-bond distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38899 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Symmetry operation $\frac{1}{2} - x, \frac{1}{2} - y, z$ applied.

situated in the axial position of an octahedral Cu coordination, but the distance 3.414 (2) Å indicates a very weak interaction.

The Cl—O distances are approximately equal and in good agreement with values found in earlier investigations.

The hydrogen-bond system (Fig. 2): Two short hydrogen-bond distances are found from the deprotonated metal-bonded hydroxymethyl group, one to the water molecule, Aq—O(1) = 2.678 (4) Å, and one to the non-metal-bonded hydroxymethyl group from an adjacent Cu complex, O(1)—O(2) = 2.603 (2) Å. Besides the above-mentioned hydrogen bond the water molecule is also linked with an adjacent water molecule

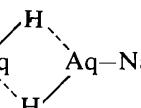
forming a $-\text{Na}-\text{Aq}$  arrangement.

Table 2. Distances (Å) and angles (°) with e.s.d.'s in parentheses

Cu—O(1)	1.908 (2)	O(1)—Cu—N	94.1 (1)
Cu—N	1.999 (2)	O(1)*—Cu—N	85.9 (1)
		Cu—O(1)—C(1)	112.1 (1)
		Cu—N—C(4)	107.3
O(1)—C(1)	1.419 (3)	C(1)—C(4)—C(2)	110.7 (2)
O(2)—C(2)	1.417 (3)	C(1)—C(4)—C(3)	109.7 (2)
O(3)—C(3)	1.423 (3)	C(1)—C(4)—N	105.8 (2)
N—C(4)	1.490 (3)	C(2)—C(4)—C(3)	110.5 (2)
C(1)—C(4)	1.525 (3)	C(2)—C(4)—N	111.9 (2)
C(2)—C(4)	1.527 (3)	C(3)—C(4)—N	108.0 (2)
C(3)—C(4)	1.538 (3)	C(4)—C(1)—O(1)	110.6 (2)
		C(4)—C(2)—O(2)	110.4 (2)
		C(4)—C(3)—O(3)	112.8 (2)
Na—O(3)	2.334 (2)	O(3)—Na—O(4)	90.0 (2)
Na—O(4)	2.516 (3)	O(3)—Na—Aq	92.2 (1)
Na—Aq	2.305 (3)	O(4)—Na—Aq	93.6 (2)
Cl—O(4)	1.425 (3)	O(4)—Cl—O*(4)	112.1 (2)
Cl—O(5)	1.418 (3)	O(4)—Cl—O(5)	108.1 (2)
		O(4)—Cl—O*(5)	109.2 (2)
		O(5)—Cl—O*(5)	110.2 (2)

* Symmetry operation $\frac{1}{2} - x, \frac{1}{2} - y, z$ applied.

Table 1. Fractional atomic coordinates ($\times 10^4$) and the equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ac\beta_{13}\cos\beta).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Cu	2500	2500	5000	1.89 (1)
N	2331 (1)	3953 (2)	3916 (2)	2.16 (4)
C(1)	1210 (1)	4332 (2)	5326 (2)	2.36 (5)
C(2)	1442 (2)	5924 (2)	3771 (2)	2.93 (5)
C(3)	2719 (2)	5515 (2)	5460 (2)	2.61 (5)
C(4)	1921 (1)	4949 (2)	4602 (2)	2.01 (4)
O(1)	1603 (1)	3264 (2)	5901 (2)	2.25 (4)
O(2)	2121 (1)	6585 (2)	3199 (2)	3.72 (5)
O(3)	3503 (1)	5879 (2)	4863 (2)	3.35 (5)
O(4)	0465 (2)	1470 (3)	3441 (2)	4.71 (9)
O(5)	0686 (2)	2939 (3)	2028 (2)	6.77 (9)
Cl	0	2197 (2)	2500 (2)	2.82 (2)
Aq	4557 (3)	3531 (3)	3572 (3)	6.16 (15)
Na	5000	5000	5000	2.38 (4)

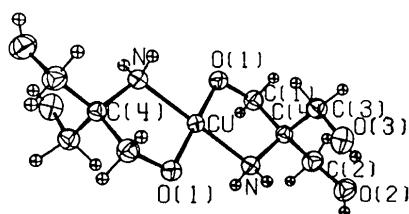


Fig. 1. Perspective view of the Cu complex unit (ORTEP; Johnson, 1976).

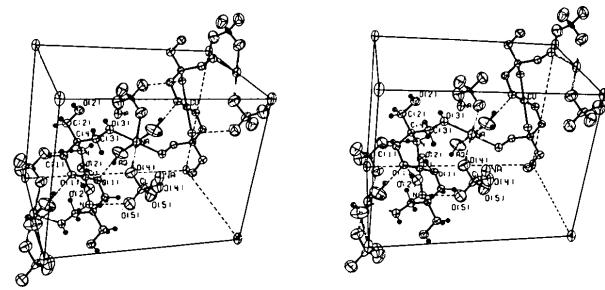


Fig. 2. A stereoscopic representation of the structure. Hydrogen bonds are indicated by dashed lines. Thermal ellipsoids enclose 50% probability.

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