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Copper(II) Complexes of 2-Amino-2-hydroxymethyl-1,3-propanediol. Part 5. Synthesis, Structure and Thermal Behavior of *cis*-[2-Amino-2-hydroxymethyl-1,3-propanediol-*O,O',N*][2-amino-2-hydroxymethyl-1,3-propanediolato-*O,N*]aquacopper(II) Halide Monohydrate, $[Cu(C_4H_{10}NO_3)(C_4H_{11}NO_3)(H_2O)]X \cdot H_2O$, where $X = F^-$, Cl^-, Br^-, I^-

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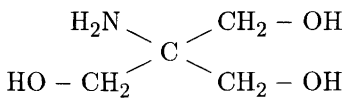
The structures of the chloride, bromide and iodide compounds with 2-amino-2-hydroxymethyl-1,3-propanediol (= tris) as a ligand have been determined by single-crystal X-ray analysis. The chloride and bromide compounds are isomorphic, with the following crystal data: (Cl^-) triclinic space group $P\bar{1}$ with four complexes in a cell of dimensions $a = 6.482(2)$, $b = 11.805(1)$, $c = 19.767(3)$ Å, $\alpha = 88.22(1)$, $\beta = 83.67(2)$, $\gamma = 90.30(2)°$, $V = 1502.6(6)$ Å^3, $R = 0.035$ (6084 reflections); (Br^-) $a = 6\,574(1)$, $b = 11.929(2)$, $c = 19.792(2)$ Å, $\alpha = 88.09(1)$, $\beta = 83.43(1)$, $\gamma = 89.72(1)°$, $V = 1541.1(4)$ Å^3, $R = 0.039$ (5519 reflections). With the iodide compound, the unit-cell volume is only half of what is observed with the chloride and bromide analogs, and the crystal data are as follows: space group $P\bar{1}$ with two complexes in a cell of dimensions $a = 6.677(1)$, $b = 11.582(1)$, $c = 11.838(3)$ Å, $\alpha = 63.02(2)$, $\beta = 100.09(2)$, $\gamma = 100.92(1)°$, $V = 796.9(3)$ Å^3, $R = 0.030$ (3735 reflections). The unit cell of the fluoride compound is determined by X-ray powder diffraction, and the results suggest that it is isomorphous with the chloride and bromide compounds [$a = 6.498(9)$, $b = 11.857(13)$, $c = 19.50(3)$ Å, $\alpha = 88.6(2)$, $\beta = 83.3(2)$, $\gamma = 90.7(1)°$, $V = 1491.7$ Å^3].

The complexes are mononuclear with two tris ligands and one water coordinated to the copper ion in a distorted octahedral arrangement (4 + 2); two amino and two hydroxymethyl groups are in the basal plane, and a water molecule and one terminal hydroxymethyl oxygen are forming the longer apical bonds. The dimeric structure of the complexes, the hydrogen-bonding network, and the non-isomorphic behavior as well as the disorder of the iodide compound are also discussed. Thermal behavior is characterized by TG in air and nitrogen atmospheres.

The ligand 2-amino-2-hydroxymethyl-1,3-propanediol (= tris) is primarily used as a buffering medium in many biochemical applications, because its buffering region is in the physiological pH range. The inhibitory effect of tris relative to other buffers is also known, and the inhibitory mechanism often involves the metal binding capacity of tris. As a weak base, tris is also used as a primary standard for HCl, even though it has a fairly low molecular weight, 121.1. Various other names, such as tris(hydroxymethyl)aminomethane, THAM or Trizma Base, are also used for the ligand.[1,2]



The tris-ligand, like amino alcohols, forms two distinctly different bond types with metal cations. One type of bonding involves a normal coordination bond between the metal and a lone-pair of oxygen or nitrogen atoms. The other type involves a classical coordinate–covalent bond with an alkoxy oxygen[3] (these deprotonated forms are abbreviated trisH$_{-1}$). Both coordination types are observed in the structures of the title compounds.

This article continues our previous study of the solid copper–tris compounds. The structures published earlier are the three basic *trans* complexes, [Cu(trisH$_{-1}$)$_2$], [Cu(trisH$_{-1}$)$_2$(H$_2$O)] and [Cu(trisH$_{-1}$)$_2$]·5H$_2$O,[4] four *cis* complexes, [Cu(trisH$_{-1}$)(tris)(NO$_3$)] and [Cu(trisH$_{-1}$)(tris)]Na(ClO$_4$)$_2$,[5] [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$SO$_4$ and [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$CrO$_4$,[6] as well as two *trans* compounds with potassium halide, [Cu(trisH$_{-1}$)$_2$]-KF·3H$_2$O and [Cu(trisH$_{-1}$)$_2$]KBr·2H$_2$O.[7] None of these compounds is related by isomorphism.

Experimental

Reagents. The reagents used were tris (Sigma, 99–99.5%), CuF$_2$·2H$_2$O (Fluka, purum, ~97%), CuCl$_2$·2H$_2$O (Merck, p.a.), CuBr$_2$ (B. D. H., >98%), CuI (Fluka, >98%) and NaI (J. T. Baker, 'Baker Analyzed'). CuCl (Merck, p.a.) and CuBr (Fluka, purum) were also used as reference materials in the TG analysis. All the reagents were used without further purification.

Preparation of [Cu(trisH$_{-1}$)(tris)(H$_2$O)]X·H$_2$O, where X = F, Cl, Br, I. General procedure. The following reagents, 0.04 mol of tris and 0.01 mol of copper halide, were dissolved in a minimum amount of distilled water in separate beakers, combined and heated for 15–30 min. The blue complex solution was filtered and concentrated with a rotavapor into a syrupy solution with a volume of 5–10 cm^3.

In the case of the fluoride compound (**1**), the synthesis needed an ethanol addition to crystallize the product (40 cm^3 of EtOH per concentrated reaction solution). The light-blue, needle-shaped crystals produced lost their clarity and started to crack when they were removed from the mother liquor. The crystal quality was also poor, and in spite of numerous attempts, it was not possible to prepare crystals suitable for single-crystal X-ray measurements. The existence of the fluoride compound is based on TG, IR and X-ray powder diffraction measurements.

The chloride (**2**) and bromide (**3**) compounds crystallized directly from the concentrated water solution overnight (if not, then the solution was concentrated more). Medium-blue, rod-shaped crystals were produced in both cases.

Since no copper(II) iodide was available, because of the reductive properties of iodide, problems arose with the iodide compound (**4**). When CuI was used as a starting material, copper was in the wrong oxidizing state, and the stoichiometric ratio of copper and iodide differed from the other reactions above. The best yield of the iodide compound was obtained according to the following procedure: 0.02 mol of tris was dissolved in 45 cm^3 of ethanol, 0.005 mol of CuI was wetted with 25 cm^3 of EtOH and this slurry was added to the tris solution. CuI was sparingly soluble in ethanol, but in the presence of tris, it was slowly oxidized to copper(II) by oxygen in the air. This was observed as a color change from colorless to blue and the disappearance of solid CuI, when the solution was kept in an open beaker. This oxidation step took a few days, but the reaction speed could be increased by stirring the mixture occasionally. When most of the copper iodide was dissolved and the blue color had become intense, the solution on top was separated from the unreacted CuI by decantation, then 0.005 mol of NaI was added in a small amount of ethanol, and the mixture was allowed to crystallize at room temperature. Similar ethanol reactions with a higher CuI content (0.01 mol), and without NaI addition also yielded compound **4** as a product.

A typical side product in the reactions was the *trans* monohydrate, [Cu(trisH$_{-1}$)$_2$(H$_2$O)],[4] especially if the concentrations were too dilute.

Thermal analysis. Thermal behavior of the complexes in air and nitrogen atmospheres was determined with a Perkin-Elmer thermogravimetric analyzer TGA7. The sample size was 7.00 ± 0.50 mg, and the crystalline samples were analyzed with a heating rate of 2°C min^{-1} and a gas flow of 50 cm^3 min^{-1}. Temperature ranges were 25–800 and 25–950°C in air and nitrogen, respectively. To obtain an oxygen-free nitrogen atmosphere, the equipment was flushed for 30 min with nitrogen before the temperature program was initiated. Thermogravimetric results are reported in Table 1.

X-Ray measurements

Powder diffraction. The X-ray powder diffraction pattern of **1** was recorded on a Philips PW 1840 powder diffractometer with β-filtered CuK_α radiation (λ = 1.54060 Å). The diffraction pattern was scanned from 5 to 80° (in 2θ) with a receiving slit of 0.1° and a step width of 0.002° per 1 s. The data were analyzed with Philips APD[8] software using K_{α_2} stripping, and the peak positions were calibrated with an internal silicon powder standard (20% of Standard Reference Material 640b).[9] ITO[10] and TREOR90[11] programs failed to find a unit cell with a comparable geometry, probably because the crystal quality (and therefore the data set) was not very good. However, when the unit-cell parameters of the chloride compound were used as initial values in the PIRUM[12] program, 68 out of 69 strongest lines (in the 2θ range 5–50) could be indexed, and the number of single indexed lines was 10. On the other hand, the calculated powder pattern of the chloride compound (produced by the CERIUS[13] program) showed that reflections (004), (200) and (040) have a moderate intensity, and they can be used to estimate the unit-cell edges *a*, *b* and *c*. When

Table 1. Thermal decomposition of [Cu(trisH$_{-1}$)(tris)(H_2O)]F · H_2O (**1**), [Cu(trisH$_{-1}$)(tris)(H_2O)]Cl · H_2O (**2**), [Cu(trisH$_{-1}$)(tris)(H_2O)]Br · H_2O (**3**) and [Cu(trisH$_{-1}$)(tris)(H_2O)]I · H_2O (**4**).

Compound	Lost in reaction	T/°C	Weight loss (%) Δ Obs.	Δ Theor.
Air atmosphere				
1	2 H_2O	25–85	9.5	10.0
	Org.	122–382	48.4	62.6 (Org.)
	Org.+F+58.4% Cu (as CuF↑)	382–570	32.9	5.3 (F)
	Total reaction → CuO (41.6% of theor.)	25–570	90.8	77.9
2	2 H_2O	25–92	9.3	9.6
	Org.	122–388	48.8	59.9 (Org.)
	Org.+Cl+57.7% Cu (as CuCl↑)	388–570	32.9	9.4 (Cl)
	Total reaction → CuO (42.3% of theor.)	25–570	91.0	78.9
3	2 H_2O	25–98	8.2	8.6
	Org.	123–398	45.3	53.5 (Org.)
	Org.+Br	398–560	28.5	19.0 (Br)
	Total reaction → CuO	25–560	82.0	81.1
4	2 H_2O	25–130	6.8	7.7
	Org.	130–364	43.5	48.2 (Org.)
	Org.+I	364–455	32.3	27.1 (I)
	Total reaction → CuO	25–455	82.5	83.0
Nitrogen atmosphere				
1	2 H_2O	25–58	9.2	10.0
	Org.	128–478	61.5	67.0
	Org. (incomplete)	478–950	4.0	
	Total reaction → CuF	25–950	74.7	77.0
2	2 H_2O	25–90	9.7	9.6
	Org.	151–474	61.8	64.1
	Org.	474–950	4.3	
	Total reaction → CuCl	25–950	75.8	73.7
3	2 H_2O	25–125	8.4	8.6
	Org.	135–420	57.5	57.3
	Br (incomplete)	420–950	12.9	19.0
	Total reaction → Cu	25–950	78.8	84.9
4	2 H_2O	25–139	7.5	7.7
	Org.	139–420	49.0	51.6
	I	420–700	28.4	27.1
	Total reaction → Cu	25–840	86.5	86.4

corresponding peaks in the fluoride pattern were assigned as above, better values were obtained for the unit-cell edges. After introducing these new values for the edges, along with the angles from the chloride structure, the PIRUM refinement was completed with all 69 peaks indexed, and 25 of them were single indexed lines. The possibility that the unit cell would be the small one (similar to the unit cell of **4**), was checked by PIRUM analysis using the small unit-cell parameters of the chloride compound; the results showed that four significant lines were unindexed, so the compatibility was better with the large unit cell. The final indexing pattern and the observed and calculated reflections are listed in Table 2.

Single-crystal measurements All of the data were collected on a computer-controlled Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator and molybdenum X-ray tube. Crystals were mounted on a glass fiber and measured in an air atmosphere. Lattice parameters were determined by a least-squares fit of 25 centered reflections. Two standard reflections were monitored after every 60 min as an intensity check, and they showed that no decomposition occurred with compound **2** (0.2% gain in intensity in 152.1 h), but with compounds **3** and **4** the total loss in intensity was 8.5% in 149.4 h and 3.2% in 85.7 h, respectively. Crystal orientation was checked at an interval of 500 reflections with three standard reflections. Lorentz and polarization effects were taken into account, and the absorption correction was done by the DIFABS[14] program for compounds **2** and **3**; an empiric absorption correction (Ψ-scan) was done for compound **4**. A summary of the crystallographic parameters is presented in Table 3.

The structure solution and refinement procedure was identical to our previous studies on copper–tris complexes.[4–7] The programs used were SHELXS-86[15] (structure solution by direct methods), MolEN[16] (refinement) and SCHAKAL[17] (illustrations). Anisotropic thermal parameters were used for the non-hydrogen atoms, and hydrogens were refined as riding atoms with fixed isotropic thermal parameters, $B = 5.00$ Å^2. The largest peaks in the final difference Fourier maps were in the vicinity of copper or halide atoms (or disordered water in **4**).

Table 2. X-Ray powder diffraction data for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]F · H$_2$O (**1**) [a=6.498(9), b=11.857(13), c=19.50(3) Å, α=88.6(2), β=83.3(2), γ=90.7(1)°, V=1491.7 Å^3].[a]

h	k	l	$2\theta_{obs}$/°	$2\theta_{calc}$/°	d_{obs}/Å	I/I_{max}
0	1	1	8.627	8.636	10.2415	100
0	−1	1	8.847	8.844	9.9873	24
1	0	−1	14.938	14.938	5.9282	5
1	1	2	17.202	17.279	5.1507	14
1	0	3	18.107	18.259	4.8925	19
0	0	4	18.192	18.312	4.8726	18
−1	1	2	18.672	18.735	4.7484	6
−1	−1	2	18.977	19.104	4.6727	6
0	1	4	19.512	19.608	4.5458	3
1	2	1	20.557	20.558	4.3170	3
−1	2	1	20.972	20.954	4.2325	4
−1	−2	1	21.397	21.441	4.1494	6
−1	−1	3	22.102	22.086	4.0186	2
−1	2	2	22.607	22.674	3.9300	8
0	0	5	22.912	22.945	3.8784	5
1	2	3	23.607	23.578	3.7657	9
1	−2	3	23.742	23.768	3.7446	9
0	3	2	24.062	24.084	3.6955	11
−1	2	3	25.047	25.146	3.5524	8
1	0	5	25.397	25.387	3.5042	8
−1	−2	3	25.852	25.848	3.4436	5
0	3	3	26.042	26.110	3.4189	8
1	1	5	26.387	26.380	3.3750	6
0	−3	3	26.752	26.748	3.3297	6
0	2	5	27.207	27.148	3.2751	10
−1	−3	1	27.412	27.404	3.2510	8
2	0	0	27.672	27.624	3.2211	9
2	1	2	29.137	29.155	3.0624	4
−2	−1	1	29.653	29.691	3.0102	7
1	−2	5	29.778	29.788	2.9979	7
0	4	0	30.248	30.248	2.9524	9
−2	1	2	30.984	30.953	2.8839	11
2	0	4	31.429	31.455	2.8441	13
−1	2	5	31.664	31.650	2.8235	9
2	−2	2	31.855	31.868	2.8070	12
0	0	7	32.335	32.337	2.7664	6
−2	−2	1	32.630	32.637	2.7421	8
0	1	7	33.011	33.029	2.7113	5
1	4	0	33.461	33.452	2.6759	5
1	0	7	33.656	33.706	2.6608	6
−2	−2	2	34.167	34.143	2.6222	6
1	−1	7	34.692	34.713	2.5837	10
2	2	4	34.952	34.967	2.5650	19
−2	2	3	35.503	35.503	2.5265	7
0	−4	4	35.953	35.926	2.4959	8
2	3	2	36.408	36.405	2.4657	12
1	3	6	37.073	37.036	2.4230	8
2	2	5	37.224	37.253	2.4135	8
2	3	3	37.429	37.414	2.4008	6
−2	1	5	38.909	38.859	2.3128	6
−1	2	7	39.444	39.467	2.2827	5
−1	−4	4	39.625	39.605	2.2727	5
0	5	3	40.150	40.145	2.2441	7
0	4	6	40.795	40.757	2.2101	9
−2	0	6	41.795	41.794	2.1595	10
−1	−4	5	42.401	42.382	2.1301	7
−2	−1	6	42.736	42.739	2.1141	9
2	4	4	44.106	44.084	2.0516	17
−3	−1	2	44.981	44.999	2.0137	17
1	−3	8	45.131	45.133	2.0074	16
0	−5	5	45.362	45.350	1.9977	14
−3	−2	1	45.872	45.860	1.9766	11
−1	−5	4	46.102	46.146	1.9673	13
−2	4	4	46.312	46.303	1.9589	11
3	2	4	46.773	46.776	1.9406	10
2	5	0	47.945	47.944	1.8959	9
3	−1	6	48.650	48.643	1.8701	9
1	−3	9	49.225	49.229	1.8496	8
2	−3	8	50.255	50.273	1.8140	8

[a] Input values for the least-squares program: a=6.442, b=11.809, c=19.490 Å, α=88.22, β=83.67, γ=90.30°.

The main problem in solving these structures was deciding which unit cell and space group were the correct ones. Both chloride and bromide compounds could also be solved in a unit cell with half of the volume (similar cell as with the iodide compound) with $P1$ as a space group, but the convergence of the refinement and the e.s.d.s of the results were much poorer than in the large unit cell. The unit cell of the iodide compound had been consistently the small one, but originally the structure could be solved only in $P1$ (R = 0.040). To confirm the unit cell, the iodide compound was also forced to the large unit cell ($a' = -a$, $b' = -b+c$, $c' = b+c$), but the structure was not refineable in the large unit cell. Furthermore, the total number of reflections fulfilling the $3\sigma(I)$ criterion did not increase when the large unit cell was introduced. The centrosymmetric choice of the space group was also supported by the fact that the compounds are racemic mixtures of optical enantiomers. Because of the larger crystal dimensions of the iodide compound, the data set is more biased by absorption. When the empirical absorption correction was introduced to the iodide compound, the structure was also solved in the centrosymmetric space group $P\bar{1}$. The rotation photographs of aligned crystals support the chosen unit-cell edges. A similar structural case, in which the iodide compound possesses higher symmetry than other halide analogs, is observed with tris–hydrogen-halide salts, trisH$^+ \cdot X^-$ (X = F, Cl, Br, I).[18]

The final atomic positional parameters and equivalent isotropic temperature factors are given in Tables 4–6. Tables of bond angles, anisotropic thermal parameters, least-squares planes, coordinates of hydrogen atoms, as well as listings of observed and calculated structure factors, are available from the author on request.

Results and discussion

Thermal analysis. The thermal behavior of the title compounds is summarized in Table 1. The thermal decomposition process of all complexes is quite similar. The fluoride and chloride compounds show identical behavior, and correspondingly, the heavier bromide and iodide analogs have similar decomposition patterns in both atmospheres.

Table 3. Crystallographic experimental data for $[Cu(trisH_{-1})(tris)(H_2O)]Cl \cdot H_2O$ (**2**), $[Cu(trisH_{-1})(tris)(H_2O)]Br \cdot H_2O$ (**3**) and $[Cu(trisH_{-1})(tris)(H_2O)]I \cdot H_2O$ (**4**).

Compound	**2**	**3**	**4**
Unit-cell determination			
Formula	$CuClO_8N_2C_8H_{25}$	$CuBrO_8N_2C_8H_{25}$	$CuIO_8N_2C_8H_{25}$
Formula weight	376.29	420.74	467.74
Color	Blue	Blue	Blue
Crystal size/mm	0.20×0.20×0.13	0.18×0.14×0.10	0.25×0.20×0.15
T/°C	21±1	21±1	21±1
Reflections for lattice measurements	25	25	25
θ-Range for lattice measurement/°	9–12	5–13	9–13
a/Å	6.482 (2)	6.574 (1)	6.677 (1)
b/Å	11.805 (1)	11.929 (2)	11.582 (1)
c/Å	19.767 (3)	19.792 (2)	11.838 (3)
α/°	88.22 (1)	88.09 (1)	63.02 (2)
β/°	83.67 (2)	83.43 (1)	100.09 (2)
γ/°	90.30 (2)	89.72 (1)	100.92 (1)
V/Å^3	1502.6 (6)	1541.1 (4)	796.9 (3)
Z	4	4	2
d_{calc}/g cm^{-3}	1.66	1.81	1.95
λ(MoK_α)/Å	0.71073	0.71073	0.71073
μ(MoK_α)/cm^{-1}	16.70	40.23	33.23
F(000)	788	860	466
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Data collection and refinement			
θ-Range for data collection/°	2–30	2–30	2–30
Scan method	ω/2θ	ω/2θ	ω/2θ
Scan speed in ω/° min^{-1}	0.87–5.50	1.03–5.50	0.92–5.50
Scan width in ω/°	0.80+0.34 tan θ	0.90+0.34 tan θ	0.80+0.34 tan θ
No. of measured reflections	8718	8962	4635
Reflections used in refinement, $I > 3\sigma(I)$	6084	5519	3735
Absorption correction (min./max.)	0.85/1.17	0.84/1.11	0.88/1.00
Max. shift/error	0.00	0.00	0.00
Max. in final Δρ/e Å^{-3}	0.63	1.08	1.41
No. of parameters refined	361	361	197
R	0.035	0.039	0.030
R_w[a]	0.043	0.039	0.032
$S=[\Sigma w(F_o-F_c)^2/(n-m)]^{1/2}$	1.469	1.638	1.019

[a] $w = 1/\sigma^2(F_o)$.

Thermal decomposition starts with the dehydration of water (normally in one step, but sometimes two steps are observed with compounds **3** and **4**). The dehydration temperatures show that water in the fluoride compound is most easily dehydrated, and the dehydration temperature rises, when the weight of the halide increases. In an air atmosphere, the organic ligand decomposes in two successive phases, and the latter is accompanied by the simultaneous degradation of halide. With the bromide and iodide compounds the last degradation step is clear, and the final product is CuO, but with the fluoride and chloride compounds, the final weight is much less than what is expected for CuO (see the theoretical values in Table 1). The most likely explanation is that covalent copper halides are formed during the decomposition process of the fluoride and chloride compounds,[19] and as a consequence, 58% of copper is sublimated as CuF or CuCl, and 42% of copper remains as CuO. Similar behavior was also observed with copper fluorides and chlorides, when samples of $CuF_2 \cdot 2H_2O$, CuCl, $CuCl_2 \cdot 2H_2O$, CuBr, $CuBr_2$ and CuI were each analyzed as a reference material in the same conditions.

In nitrogen atmosphere, most of the organic part is decomposed by 500°C, but the process produces some carbon, which may interfere with the interpretation above 500°C.[4,5] With the fluoride and chloride compounds the TG curve is quite featureless above 500°C, and the final product is copper(I) halide. The bromide and iodide compounds decompose further giving elemental copper as the final residue (with the bromide compound the last step is still incomplete at 950°C).

Molecular structures. The molecular structures of the complexes are shown in Figs. 1 and 2, and the bond lengths describing these molecules are listed in Table 7. The angles characterizing the distortion of the coordination sphere of copper are shown in Table 8.

The complex molecules in all structures are mononuclear cation complexes with two tris ligands (one of them is deprotonated) and one water molecule coordi-

Table 4. Atomic positional parameters and equivalent isotropic temperature factors[a] with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]Cl · H$_2$O (**2**).

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Molecule 1				
Cu100	−0.48621(6)	0.23944(3)	0.64546(2)	1.087(6)
OW100	−0.8181(4)	0.2284(2)	0.6081(2)	2.50(5)
O111	−0.5694(4)	0.3621(2)	0.7100(1)	1.51(4)
O112	−0.1316(4)	0.3498(2)	0.6732(1)	1.94(4)
O113	−0.2557(4)	0.5757(2)	0.5124(1)	2.19(5)
O121	−0.5383(3)	0.1243(2)	0.7173(1)	1.33(4)
O122	−0.0022(4)	0.0165(2)	0.5982(2)	2.66(5)
O123	−0.3179(4)	−0.1024(3)	0.5216(1)	2.65(5)
N111	−0.4164(4)	0.3675(2)	0.5785(1)	1.29(4)
N121	−0.3932(4)	0.1132(2)	0.5845(1)	1.36(4)
C111	−0.5451(5)	0.4709(3)	0.6772(2)	1.61(5)
C112	−0.3741(5)	0.4687(3)	0.6176(2)	1.17(5)
C113	−0.1580(5)	0.4575(3)	0.6406(2)	1.72(6)
C114	−0.3854(6)	0.5787(3)	0.5759(2)	1.85(6)
C121	−0.5445(5)	0.0154(3)	0.6883(2)	1.47(5)
C122	−0.3809(5)	0.0075(3)	0.6263(2)	1.24(5)
C123	−0.1681(5)	0.0021(3)	0.6511(2)	1.85(6)
C124	−0.4343(6)	−0.0963(3)	0.5869(2)	2.09(6)
Molecule 2				
Cu200	−0.01073(6)	0.73989(3)	0.15009(2)	1.168(6)
OW200	−0.3576(4)	0.7166(3)	0.1095(2)	3.07(6)
O211	−0.1072(4)	0.8641(2)	0.2121(1)	1.68(4)
O212	0.3303(4)	0.8426(2)	0.1784(1)	2.01(4)
O213	0.2369(4)	1.0680(2)	0.0164(1)	2.21(5)
O221	−0.0813(3)	0.6244(2)	0.2196(1)	1.32(4)
O222	0.2525(5)	0.3853(3)	0.2066(2)	2.91(6)
O223	0.1651(5)	0.3961(3)	0.0278(1)	2.90(6)
N211	0.0586(4)	0.8667(2)	0.0825(1)	1.24(4)
N221	0.0917(4)	0.6123(2)	0.0909(1)	1.58(5)
C211	−0.0751(5)	0.9734(3)	0.1795(2)	1.67(6)
C212	0.1017(5)	0.9673(3)	0.1219(2)	1.18(5)
C213	0.3139(5)	0.9524(3)	0.1472(2)	1.87(6)
C214	0.1019(6)	1.0772(3)	0.0785(2)	1.85(6)
C221	−0.1043(5)	0.5197(3)	0.1874(2)	1.51(5)
C222	0.0749(5)	0.5034(3)	0.1314(2)	1.28(5)
C223	0.2755(5)	0.4823(3)	0.1623(2)	1.92(6)
C224	0.0209(6)	0.4059(3)	0.0872(2)	1.98(6)
Cl1	0.0767(1)	0.75424(9)	0.55432(5)	2.61(2)
Cl2	−0.5736(1)	0.75191(9)	−0.03443(5)	2.71(2)
OW1	0.5737(6)	0.2397(3)	0.1973(2)	4.29(8)
OW2	−0.0824(6)	0.2462(3)	0.2762(2)	4.97(9)

[a] $B_{eq}=\frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

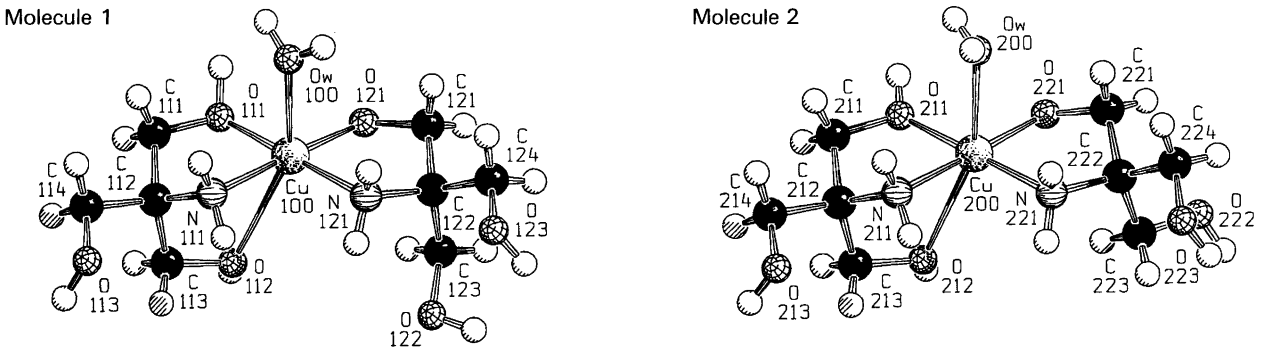


Fig. 1. SCHAKAL projections of cation complexes 1 and 2 in the chloride (**2**) and bromide (**3**) compounds (coordinates taken from **2**).

Table 5. Atomic positional parameters and equivalent isotropic temperature factors[a] with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H_2O)]Br · H_2O (**3**).

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Molecule 1				
Cu100	−0.49163(7)	0.24051(4)	0.64586(2)	1.485(8)
OW100	−0.8201(5)	0.2315(3)	0.6081(2)	3.01(7)
O111	−0.5761(5)	0.3616(2)	0.7102(1)	1.97(5)
O112	−0.1408(5)	0.3485(3)	0.6741(2)	2.40(6)
O113	−0.2649(5)	0.5722(3)	0.5137(2)	2.58(6)
O121	−0.5413(4)	0.1254(2)	0.7171(1)	1.64(5)
O122	−0.0087(5)	0.0242(3)	0.5982(2)	3.02(7)
O123	−0.3145(5)	−0.0951(3)	0.5214(2)	2.88(6)
N111	−0.4220(5)	0.3680(3)	0.5798(2)	1.64(6)
N121	−0.3991(5)	0.1163(3)	0.5848(2)	1.68(6)
C111	−0.5504(7)	0.4706(3)	0.6778(2)	1.98(7)
C112	−0.3813(6)	0.4679(3)	0.6192(2)	1.48(6)
C113	−0.1682(6)	0.4556(4)	0.6422(2)	2.07(7)
C114	−0.3925(7)	0.5768(4)	0.5764(2)	2.13(8)
C121	−0.5443(6)	0.0182(3)	0.6874(2)	1.78(7)
C122	−0.3822(6)	0.0111(3)	0.6257(2)	1.45(6)
C123	−0.1703(7)	0.0078(4)	0.6505(2)	2.26(8)
C124	−0.4281(7)	−0.0914(4)	0.5864(2)	2.38(8)
Molecule 2				
Cu200	−0.01217(8)	0.74097(4)	0.15116(2)	1.593(8)
OW200	−0.3534(6)	0.7220(4)	0.1110(2)	3.78(8)
O211	−0.1065(5)	0.8637(2)	0.2136(1)	2.10(5)
O212	0.3267(5)	0.8433(3)	0.1800(2)	2.42(6)
O213	0.2243(5)	1.0664(3)	0.0182(2)	2.71(6)
O221	−0.0764(5)	0.6260(2)	0.2205(1)	1.80(5)
O222	0.2563(7)	0.3896(3)	0.2059(2)	4.03(8)
O223	0.1628(6)	0.4026(3)	0.0279(2)	3.47(7)
N211	0.0568(5)	0.8670(3)	0.0847(2)	1.57(6)
N221	0.0884(6)	0.6151(3)	0.0915(2)	2.03(6)
C211	−0.0769(7)	0.9724(4)	0.1810(2)	1.98(7)
C212	0.0966(6)	0.9669(3)	0.1238(2)	1.52(6)
C213	0.3059(7)	0.9518(4)	0.1488(2)	2.29(8)
C214	0.0944(7)	1.0750(4)	0.0800(2)	2.31(8)
C221	−0.0957(7)	0.5225(4)	0.1884(2)	2.21(8)
C222	0.0773(7)	0.5072(3)	0.1319(2)	1.83(7)
C223	0.2801(7)	0.4872(4)	0.1609(2)	2.63(9)
C224	0.0262(8)	0.4108(4)	0.0878(2)	2.65(9)
Br1	0.08263(7)	0.74961(4)	0.55804(3)	2.660(8)
Br2	−0.57674(8)	0.75367(5)	−0.03887(3)	3.11(1)
OW1	0.5762(8)	0.2466(4)	0.2062(2)	5.8(1)
OW2	−0.0582(8)	0.2417(4)	0.2690(2)	5.8(1)

[a] See Table 4.

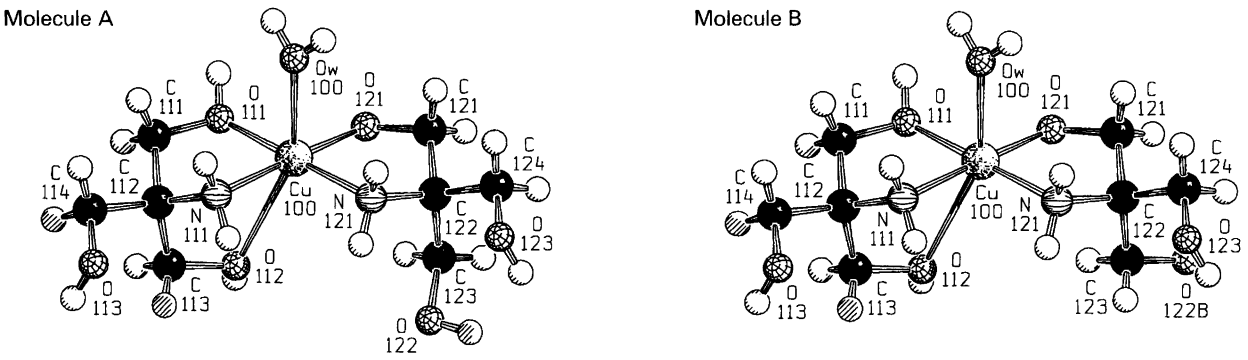


Fig. 2. SCHAKAL projection of the disordered cation complex in the iodide compound (**4**) (molecule A 87% and B 13%).

Table 6. Atomic positional parameters and equivalent isotropic temperature factors[a] with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H_2O)]I · H_2O (**4**).

Atom	*x*	*y*	*z*	B_{eq}/Å^2	
Molecule					
Cu100	0.85487(5)	0.59438(3)	0.60926(3)	1.434(6)	
OW100	1.2195(4)	0.6251(3)	0.6569(2)	3.21(6)	
O111	0.8807(3)	0.6474(2)	0.4252(2)	1.79(4)	
O112	0.4869(4)	0.6671(2)	0.4801(2)	2.25(5)	
O113	0.7565(4)	1.0486(2)	0.4180(2)	2.62(5)	
O121	0.8321(3)	0.4107(2)	0.6507(2)	1.55(4)	
O122	0.4215(4)	0.4373(3)	0.8674(3)	2.95(6)	pp=0.87
O122B	0.459(3)	0.233(2)	0.886(2)	3.0(4)	pp=0.13
O123	0.7884(4)	0.3947(2)	1.0638(2)	3.08(6)	
N111	0.8534(4)	0.7851(2)	0.5511(2)	1.58(4)	
N121	0.8225(4)	0.5365(2)	0.7932(2)	1.71(5)	
C111	0.8853(5)	0.7855(3)	0.3513(3)	2.01(6)	
C112	0.7743(4)	0.8408(2)	0.4144(2)	1.46(5)	
C113	0.5431(5)	0.8036(3)	0.4045(3)	2.16(6)	
C114	0.8246(5)	0.9902(3)	0.3508(3)	2.15(6)	
C121	0.8616(5)	0.3368(3)	0.7854(3)	1.79(5)	
C122	0.7619(4)	0.3928(3)	0.8537(2)	1.51(5)	
C123	0.5294(5)	0.3662(3)	0.8312(3)	2.21(6)	
C124	0.8420(5)	0.3327(3)	0.9947(3)	2.29(6)	
I1	0.65016(4)	0.82268(3)	0.81298(2)	3.233(5)	
OW1A	0.764(2)	0.942(1)	0.939(1)	6.8(3)[b]	pp=0.34
OW1B	0.888(4)	0.995(2)	1.012(2)	8.6(6)[b]	pp=0.22
OW1C	0.426(3)	1.001(3)	0.996(3)	9.1(7)[b]	pp=0.22
OW1D	0.732(5)	0.995(3)	1.014(3)	10.7(8)[b]	pp=0.22

[a] See Table 4.
[b] Refined isotropically.

nated to the copper atom. The coordination sphere around copper is a distorted octahedron with tris molecules coordinated via amino and hydroxymethyl groups in the basal plane (*cis* configuration), and the apical positions are occupied by water and one terminal hydroxymethyl oxygen from the non-protonated ligand. The basal plane of the O111, N111, O121 and N121 (or O211, N211, O221 and N221) atoms is almost planar, and the copper atom is displaced 0.019–0.060 Å towards the apical water molecule. Furthermore, the five-membered chelate rings are in an *envelope* conformation, where Cu100, O111, N111, C111 (or corresponding set) are the atoms

Table 7. Bond distances (in Å) with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H_2O)]Cl · H_2O (**2**), [Cu(trisH$_{-1}$)(tris)(H_2O)]Br · H_2O (**3**) and [Cu(trisH$_{-1}$)(tris)(H_2O)]I · H_2O (**4**).

Bond	**2**	**3**	**4**	Bond	**2**	**3**
Cu100–OW100	2.355(3)	2.366(3)	2.397(2)	Cu200–OW200	2.486(3)	2.482(4)
Cu100–O111	1.997(2)	1.993(3)	2.008(2)	Cu200–O211	1.999(2)	1.997(3)
Cu100–O112	2.752(3)	2.768(2)	2.717(2)	Cu200–O212	2.638(3)	2.674(3)
Cu100–O121	1.936(2)	1.935(3)	1.936(2)	Cu200–O221	1.922(2)	1.921(3)
Cu100–N111	1.994(3)	1.992(3)	1.995(2)	Cu200–N211	1.991(3)	1.984(3)
Cu100–N121	1.999(3)	1.991(3)	2.006(2)	Cu200–N221	2.006(3)	2.006(3)
O111–C111	1.422(4)	1.434(5)	1.431(3)	O211–C211	1.428(4)	1.433(5)
O112–C113	1.427(4)	1.427(5)	1.432(3)	O212–C213	1.428(4)	1.427(6)
O113–C114	1.432(4)	1.417(5)	1.424(5)	O213–C214	1.433(4)	1.416(5)
O121–C121	1.426(4)	1.426(5)	1.424(3)	O221–C221	1.422(4)	1.420(5)
O122–C123	1.420(4)	1.408(5)	1.426(6)	O222–C223	1.417(5)	1.440(6)
O122B–C123	–	–	1.40(2)	–	–	–
O123–C124	1.426(4)	1.413(5)	1.430(5)	O223–C224	1.426(4)	1.406(6)
N111–C112	1.482(4)	1.487(5)	1.483(3)	N211–C212	1.481(4)	1.483(5)
N121–C122	1.483(4)	1.484(5)	1.487(5)	N221–C222	1.490(4)	1.489(5)
C111–C112	1.527(4)	1.513(5)	1.525(5)	C211–C212	1.529(4)	1.515(5)
C112–C113	1.525(4)	1.526(6)	1.521(4)	C212–C213	1.524(5)	1.523(6)
C112–C114	1.524(5)	1.533(6)	1.536(4)	C212–C214	1.533(5)	1.530(6)
C121–C122	1.535(4)	1.530(5)	1.531(5)	C221–C222	1.530(4)	1.517(6)
C122–C123	1.514(5)	1.529(6)	1.525(4)	C222–C223	1.515(5)	1.525(7)
C122–C124	1.530(5)	1.518(6)	1.527(4)	C222–C224	1.528(5)	1.529(6)

Table 8. Bond angles (in °) of the coordination sphere of copper with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]Cl · H$_2$O (**2**), [Cu(trisH$_{-1}$)(tris)(H$_2$O)]Br · H$_2$O (**3**) and [Cu(trisH$_{-1}$)(tris)(H$_2$O)]I · H$_2$O (**4**).[a]

Angle	2	3	4	Angle	2	3
OW100–Cu100–O111	93.1(1)	92.8(1)	92.01(9)	OW200–Cu200–O211	93.0(1)	92.9(1)
OW100–Cu100–O112	154.61(9)	154.6(1)	155.03(7)	OW200–Cu200–O212	158.6(1)	158.0(1)
OW100–Cu100–O121	95.6(1)	95.9(1)	96.43(9)	OW200–Cu200–O221	89.9(1)	91.0(1)
OW100–Cu100–N111	89.1(1)	89.3(1)	88.7(1)	OW200–Cu200–N211	90.8(1)	91.0(1)
OW100–Cu100–N121	89.4(1)	89.4(1)	89.3(1)	OW200–Cu200–N221	88.6(1)	88.7(1)
O111–Cu100–O112	71.96(8)	72.2(1)	73.70(8)	O211–Cu200–O212	74.58(9)	74.0(1)
O111–Cu100–O121	91.44(9)	92.0(1)	92.16(9)	O211–Cu200–O221	92.64(9)	92.9(1)
O111–Cu100–N111	84.2(1)	83.8(1)	83.9(1)	O211–Cu200–N211	83.8(1)	83.5(1)
O121–Cu100–N121	86.5(1)	86.2(1)	86.4(1)	O221–Cu200–N221	85.7(1)	85.5(1)
N111–Cu100–O112	69.44(9)	69.2(1)	69.79(8)	N211–Cu200–O212	70.9(1)	70.3(1)
N111–Cu100–N121	97.7(1)	97.9(1)	97.5(1)	N211–Cu200–N221	97.8(1)	98.0(1)

[a] Other angles in the structures are normal to these copper–tris complexes.[4–7]

defining the plane, and C112 (or C122, C212, C222) are the atoms bent out of the plane. In each molecule, these five-membered rings are bent in the same direction, meaning that the complex is a *syn* conformer. Terminal hydroxymethyl groups can take an axial or an equatorial position in relation to these planes. The complex molecules are also optically active, with two possible enantiomers. The product contains both enantiomers in equal amounts.

In the isomorphic chloride and bromide structures, there are two molecules (molecules 1 and 2) in the asymmetric unit, which are structurally quite similar, differing mainly in the orientation of one axial hydroxymethyl group on the deprotonated side and in the positions of the hydrogens in the coordinated water molecule. A closer inspection of the bond lengths shows that there are distinctive differences in the apical bond lengths of the coordination spheres. In molecule 1, the coordination sphere is more distorted with a short Cu100–OW100 bond [2.355 Å (**2**)/2.366 Å (**3**)] and a long Cu100–O112 bond (2.752/2.768 Å), whereas the apical bond lengths in molecule 2 are closer to each other (Cu200–OW200 = 2.486/2.482 Å and Cu200–O212 = 2.638/2.674 Å). In the basal plane, the lengths of the coordination bonds do not vary that much. Furthermore, calculations of the least-squares planes show that the basal plane in molecule 1 is less planar than in molecule 2, and that the dihedral angle between the chelate planes is smaller in molecule 1 (3.7/3.3°) than in molecule 2 (9.0/7.8°).

In the iodide structure (**4**), there is only one molecule in the asymmetric unit, where the axial hydroxymethyl group on the non-protonated side is disordered, having two possible orientations with occupancies 87% (molecule A) and 13% (molecule B). Molecule A is structurally very close to molecule 1 in compounds **2** and **3**; the apical bond lengths, Cu100–OW100 (2.397 Å) and Cu100–O112 (2.717 Å), the planarity of the basal plane and the dihedral angle between the chelate planes (3.3°) are in good agreement with the values mentioned above. On the other hand, molecule B is quite like molecule 2 in compounds **2** and **3** (only the disorder of O122 and two calculated hydrogens riding on carbon C123 are refined, otherwise the structure is the same as in molecule A). It is very likely that the orientation of the O122 group also affects the geometry of the coordination sphere, and that the true structure of the iodide compound consists of two types of molecules, which are closer to molecules 1 and 2 in compounds **2** and **3**, and the statistical structure that is obtained in the refinement is more or less a weighted average of these two molecules, where the weights are given by occupancies.

Similar distorted octahedral coordination spheres have been observed earlier with copper–tris compounds containing nitrate and perchlorate as an anion,[5] [Cu(trisH$_{-1}$)(tris)(NO$_3$)] and [Cu(trisH$_{-1}$)(tris)]Na(ClO$_4$)$_2$.

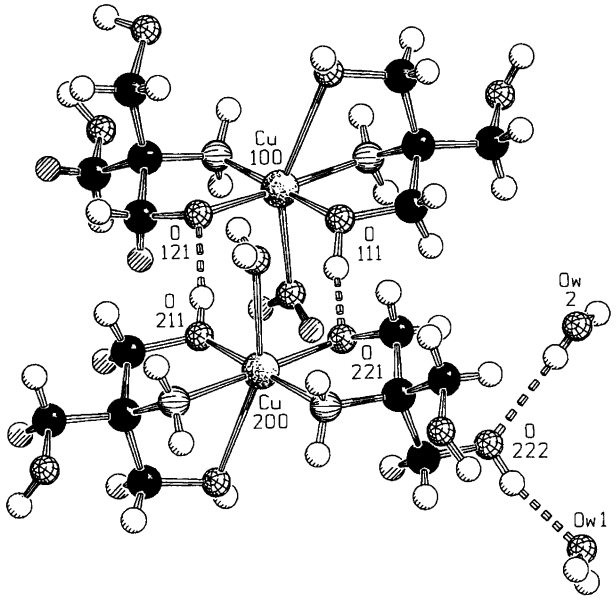


Fig. 3. Example of the dimer structure in the chloride and bromide compounds; cation complex 2 and the optical enantiomer of complex 1 form the hydrogen-bonded associate above, in which crystalline water molecules are attached to the terminal hydroxymethyl group O222 (enantiomer of complex 1 is generated by symmetry operation −1−*x*, 1−*y*, 1−*z*).

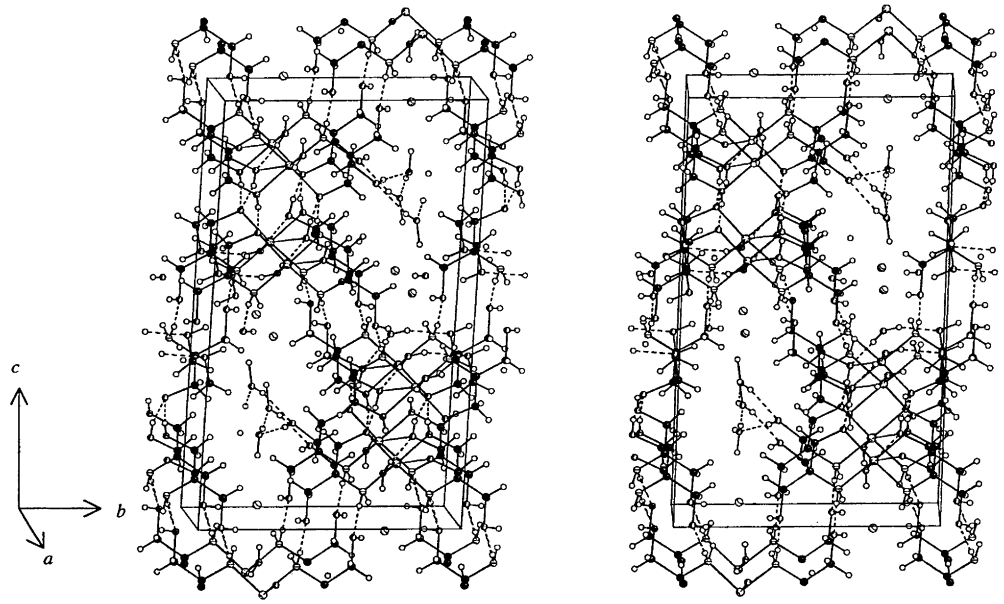


Fig. 4. Stereoscopic representation of hydrogen bonding for the chloride (**2**) and bromide (**3**) compounds (coordinates taken from **2**). Hydrogen bonds are indicated by dashed lines.

Crystal structures. A hydrogen-bonded dimer structure of the complexes is shown in Fig. 3, and stereoscopic projections of the crystal structures and the hydrogen-bonding framework for both compound types are presented in Figs. 4 and 5.

The chloride and bromide compounds are strictly isomorphic, and they consist of hydrogen-bonded cationic dimers, halides and crystalline water. The dimer structures are formed from complex molecule 1, which is hydrogen-bonded to the optical enantiomer of complex 2, or *vice versa* (Fig. 3). The hydrogen bonds in the dimers include the deprotonated hydroxymethyl groups, so the O···O distances are short [2.532(3)–2.560(3) Å]. The dimer forms a step-like structure, where the apical water ligands are pointing towards the other molecule in the dimer, and the Cu100···Cu200′ distances are 4.9181(5) Å (**2**) and 4.8870(6) Å (**3**). The dimers are stacked along the *a*-axis and polymerized by the hydro-

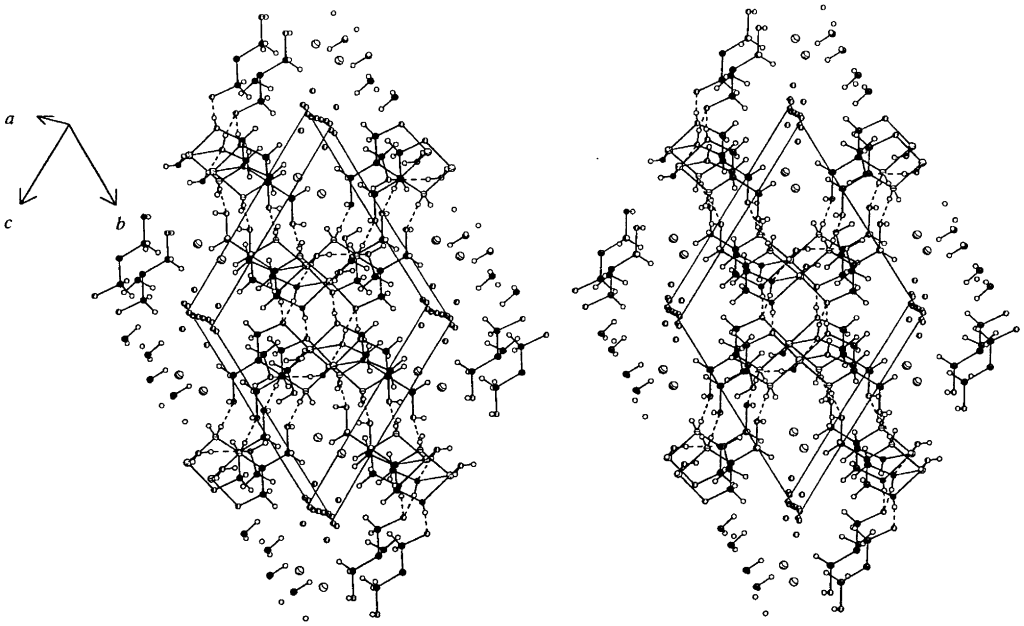


Fig. 5. Stereoscopic representation of hydrogen bonding for the iodide compound (**4**) (molecule A, 87%). Hydrogen bonds are indicated by dashed lines, and all the locations of the disordered water molecule OW1 are approximately along the *a*-axis.

gen bonds between the coordinated water and the coordinated hydroxymethyl groups of the adjacent dimers. The coordinated water OW100 also fixes the position of the free axial hydroxymethyl group O122 in the dimer on the top. In the *bc*-plane the dimers are linked to four neighboring dimers via hydrogen bonds between amino and equatorial hydroxymethyl groups (two N–H···O and N···H–O bonds for each pair). As a result, the compound forms a net-like structure with tunnels along the *a*-direction, and these tunnels are filled with crystalline water (OW1 and OW2) and halides. The halides are located in the hydrophobic cavities, with the hydrogens pointing towards the halide [each halide is surrounded by six hydrogens with Cl–H and Br–H distances in the range 2.22–2.76 Å (**2**) and 2.34–2.84 Å (**3**)]. Similar hydrophobic tunnels have been observed earlier with copper–tris halides containing potassium as a cation.[7] The axial hydroxymethyl group O222 from molecule 2 is turned into the tunnel, and it serves as an arm to which the crystalline water can attach and form a hydrogen-bonded zigzag chain of OW2–H···O222–H···OW1–H···OW2′–H′··· with fixed positions for crystalline water.

Even though the iodide compound is not isomorphic with compounds **2** and **3**, the structures are very similar, and they can be described as isotypic. In the iodide structure, the dimers are formed from the complex molecule and its optical isomer via strong hydrogen bonds [O111···O121′ = 2.565(4) Å]. The eight-membered ring in the dimer contains an inversion center, and the Cu100···Cu100′ separation is 4.8706(6) Å. The stacking of the dimers along the *a*-axis, as well as the net-like structure with tunnels along the *a*-axis and halide occupying the hydrophobic cavities (I–H distances in the range 2.69–3.02 Å) are common features for all these compounds. Nevertheless, since the ionic radius of iodide (2.16 Å) is larger than the radii of chloride (1.81 Å) or bromide (1.95 Å),[20] there is not enough space in the tunnel for the hydroxymethyl arm (O122) in compound **4**. Only 13% of O122 is oriented in a manner suitable for fixing the crystalline water. As a consequence, the crystalline water is disordered along the *a*-axis, having at least four possible locations with occupancies 0.34 or less.

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References

1. Brignac, P. J. Jr. and Mo, C. *Anal. Chem. 47* (1975) 1465.
2. Allen, D. E., Baker, D. J. and Gillard, R. D. *Nature (London) 214* (1967) 906.
3. Dotson, R. L. *Inorg. Nucl. Chem. Lett. 9* (1973) 215.
4. Kotila, S. and Valkonen, J. *Acta Chem. Scand. 47* (1993) 950.
5. Kotila, S. and Valkonen, J. *Acta Chem. Scand. 47* (1993) 957.
6. Kotila, S. and Valkonen, J. *Acta Chem. Scand. 48* (1994) 200.
7. Kotila, S. and Valkonen, J. *Acta Chem. Scand. 48* (1994) 312.
8. *PC-APD Software for Automated Powder Diffraction PW1710*, Version 2.0. N.V. Philips Gloeilampenfabrieken, Eindhoven, The Netherlands 1989.
9. *Standard Reference Material 640b, Silicon Powder 20/d-Spacing Standard for X-Ray Diffraction.* National Bureau of Standards Certificate, Gaithersburg, MD 1987.
10. Visser, J. W. *J. Appl. Crystallogr. 2* (1969) 89.
11. Werner, P.-E., Eriksson, L. and Westdahl, M. *J. Appl. Crystallogr. 18* (1985) 367.
12. Werner, P.-E. *Arkiv Kemi 31* (1969) 513.
13. *CERIUS, a Molecular Modeling Environment for Material Research*, Cambridge Molecular Design, Cambridge, UK 1991.
14. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A 39* (1983) 158.
15. Sheldrick, G. M. In: Sheldrick, G. M., Krüger, C. and Goddard, R., Eds., *Crystallographic Computing 3*, Oxford University Press, Oxford 1985, pp. 175–189.
16. *MolEN, an Interactive Structure Solution Procedure*, Enraf–Nonius, Delft, The Netherlands 1990.
17. Keller, E. *SCHAKAL, a FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models*, University of Freiburg, Freiburg 1987.
18. Rudman, R., Lippman, R., Sake Gowda, D. S. and Eilerman, D. *Acta Crystallogr., Sect. C 39* (1983) 1267.
19. Tummavuori, J. and Suontamo, R. *Finn. Chem. Lett.* (1979) 176.
20. Holtzclaw, H. F. Jr, Robinson, W. R. and Odom, J. D. *General Chemistry*, 9th Edn, D. C. Heath and Co., Lexington, MA 1991.

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