

tures of metal-tris complexes involving copper(II) are $[\text{Cu}(\text{trisH}_{-1})_2]\text{NaClO}_4 \cdot \text{H}_2\text{O}$,¹⁰ $[\text{Cu}(\text{trisH}_{-1})\text{Cl}]_4$,¹¹ $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]_2\text{Br}_2$,¹¹ and $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$.¹² Thermoanalytical studies were not considered in any of these articles.

Experimental

Reagents. All the starting materials were Merck analytical grade reagents (unless otherwise indicated) and they were used without further purification.

Preparation of $[\text{Cu}(\text{trisH}_{-1})_2]$. 0.015 mol of tris was dissolved in 50 cm³ of ethanol by refluxing. 0.0075 mol of CuBr_2 (B. D. H. Ltd., minimum 98%) was dissolved in 40 cm³ of ethanol and added to the hot tris solution. The mixture was refluxed for 15 min, allowed to cool down to room temperature, and then an ethanolic solution of KOH (0.015 mol per 40 cm³ EtOH) was added. The color of the solution turned blue, and blue precipitation appeared. The solution was filtered, precipitation discarded and the clear solution was allowed to stand at room temperature overnight. The dark violet crystals were filtered, washed with ethanol and dried in air.

Preparation of $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$. Single crystals of the monohydrate could best be obtained from a water synthesis of tris and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. 0.04 mol of tris and 0.01 mol of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in a minimum amount of water in separate beakers. The solutions were combined, heated for 15–30 min and then filtered. The blue prismatic crystals were formed by slow evaporation at room temperature. The crystallization of the complex may take a few weeks.

Preparation of $[\text{Cu}(\text{trisH}_{-1})_2] \cdot 5\text{H}_2\text{O}$. The best results were obtained when CuSO_4 or $\text{Cu}(\text{CH}_3\text{COOH})_2$ was used as starting materials. 0.04 mol of tris and 0.01 mol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were dissolved in a minimum amount of water in separate beakers. The solutions were combined

and filtered. Crystallization usually takes place within half an hour, but if the solution needs a longer period of time to crystallize, it is preferable to store it at the temperature of 15–20°C. The pentahydrate crystals are plate-shaped and their violet color is anisotropic; the crystal looks blue-violet from two directions and from the third direction the color is more reddish.

Thermal analysis. The thermal behavior of the complexes was determined with a Perkin-Elmer TGA7 thermobalance in air and nitrogen atmospheres. Sample size varied between 7.0 ± 0.5 mg, heating rate was 2°C min⁻¹ and gas flow was 50 cm³ min⁻¹. The temperature range in air was from 25 to 500°C, and in a nitrogen atmosphere the samples were heated up to 900°C. When analyzing the samples in a nitrogen atmosphere, the oven was flushed with nitrogen for 30–45 min before the run was started to remove oxygen from the equipment. The observed weight losses were calculated for each compound in both atmospheres. The results are reported in Table 1.

X-Ray structure measurements. The single-crystal X-ray measurements were done with an Enraf-Nonius CAD-4 diffractometer using Mo K_α radiation. A summary of X-ray data collection parameters and structural refinement is given in Table 2. For all three cases the unit-cell dimensions and the orientation matrix were obtained from a least-squares fitting of 25 centered reflections. During data collection, an intensity check was made every 60 min with two reflections; the orientation matrix was also controlled after every 400–500 reflections. No significant decay in intensity was observed during data collection. The intensities were corrected for Lorentz and polarization effects.

The diffraction data of the pentahydrate were collected using a unit cell with the space group $P2/n$ [$a = 10.087(2)$, $b = 6.340(3)$, $c = 12.907(2)$ Å, $\beta = 95.80(1)^\circ$] but, since the standard choice of the glide direction is c , the unit cell was changed before refinement.

Table 1. Thermal decomposition of tris, $[\text{Cu}(\text{trisH}_{-1})_2]$ (1), $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$ (2) and $[\text{Cu}(\text{trisH}_{-1})_2] \cdot 5\text{H}_2\text{O}$ (3).

Compound	Lost in reaction	Air atmosphere			Nitrogen atmosphere		
		$T/^\circ\text{C}$	Weight loss/%		$T/^\circ\text{C}$	Weight loss/%	
			Δ Obs.	Δ Theor.		Δ Obs.	Δ Theor.
tris	tris	25–450	99.7	100.0	25–900	100.0	100.0
1	2 trisH ₋₁	168–450	73.5	73.8	178–450	69.8	79.1
	Total reaction	25–450	73.7	73.8	25–900	73.2	79.1
2	H ₂ O	120–165	6.4	5.6	123–163	5.9	5.6
	2 trisH ₋₁	165–430	69.3	69.7	168–450	66.2	74.7
	Total reaction	25–430	75.6	75.3	25–900	75.1	80.3
3	5 H ₂ O	63–99	21.3	22.9	37–110	21.8	22.9
	2 trisH ₋₁	117–450	58.2	56.9	162–450	55.1	61.0
	Total reaction	25–450	79.7	79.8	25–900	79.8	83.9

Table 2. Crystallographic experimental data for [Cu(trisH₋₁)₂] (1), [Cu(trisH₋₁)₂(H₂O)] (2) and [Cu(trisH₋₁)₂]·5H₂O (3).

Compound	1	2	3
Unit cell determination:			
Formula	CuO ₆ N ₂ C ₈ H ₂₀	CuO ₇ N ₂ C ₈ H ₂₂	CuO ₁₁ N ₂ C ₈ H ₃₀
Formula weight/g mol ⁻¹	303.80	321.81	393.88
Color	Violet	Blue	Violet
Crystal size/mm	0.40 × 0.20 × 0.20	0.20 × 0.20 × 0.15	0.15 × 0.15 × 0.15
T/°C	21 ± 1	21 ± 1	21 ± 1
Reflections for lattice measurement	25	25	25
θ-Range for lattice measurement/°	6–13	7–14	7–14
a/Å	6.261(1)	12.928(3)	10.087(2)
b/Å	10.109(1)	10.783(1)	6.340(3)
c/Å	10.028(1)	10.066(5)	15.557(1)
β/°	116.86(1)	116.59(2)	124.36(1)
V/Å ³	566.3(1)	1254.8(7)	821.2(5)
Z	2	4	2
d _{calc} /g cm ⁻³	1.78	1.70	1.59
λ(Mo K _α)/Å	0.710 73	0.710 73	0.710 73
μ(Mo K _α)/cm ⁻¹	19.51	17.71	13.84
F(000)	318	676	418
Space group	P2 ₁ /c	C2/c	P2/c
Data collection and refinement:			
θ range for data collection/°	2–35	2–35	2–30
Scan method	ω/2θ	ω/2θ	ω/2θ
Scan speed in ω/° min ⁻¹	0.87–5.50	0.79–16.50	0.79–16.50
Scan width in ω/°	0.80 + 0.34 tan θ	0.50 + 0.34 tan θ	0.50 + 0.34 tan θ
No. of measured refls.	2601	2880	2588
Reflections used in refinement, I > 3σ(I)	2029	1841	1759
Absorption correction (min./max.)	0.85/1.09	0.90/1.07	0.92/1.12
Max. shift/error	0.00	0.00	0.00
Max. in final Δρ/e Å ⁻³	0.39	0.43	0.28
No. of parameters refined	79	83	102
R	0.023	0.026	0.026
R _w ^a	0.027	0.029	0.032
S = [Σw(F _o - F _c) ² /(n - m)] ^{1/2}	0.502	1.156	0.713

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

The initial position of the copper atom was solved by direct methods (SHELXS-86),¹³ and the remaining non-hydrogen atoms were found by alternating the least-squares full-matrix cycles of refinement and difference syntheses. The model was first refined with isotropic temperature factors to convergence, then the calculated

hydrogens were placed in the model and refined as riding atoms with fixed isotropic parameters ($B = 5.00 \text{ \AA}^2$). After the absorption correction with the DIFABS program¹⁴ the model was refined again with isotropic thermal parameters. Finally, after the anisotropic refinement, the missing hydrogens were located from a difference

Table 3. Atomic positional parameters and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for [Cu(trisH₋₁)₂] (1).

Atom	x	y	z	B _{eq} /Å ²
Cu100	0.000	0.000	0.000	1.192(3)
O111	-0.0047(2)	-0.0376(1)	0.1885(1)	1.44(2)
O112	0.2967(2)	-0.3555(1)	0.3106(1)	1.62(2)
O113	0.7657(2)	-0.2241(1)	0.2843(1)	2.55(2)
N111	0.3350(2)	-0.0673(1)	0.0988(1)	1.21(2)
C111	0.2318(2)	-0.0616(1)	0.3009(1)	1.35(2)
C112	0.3694(2)	-0.1412(1)	0.2352(1)	1.03(2)
C113	0.2585(2)	-0.2777(1)	0.1841(1)	1.31(2)
C114	0.6351(2)	-0.1537(2)	0.3460(2)	1.53(2)

$$^a B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

Table 4. Atomic positional parameters and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for [Cu(trisH₋₁)₂(H₂O)] (2).

Atom	x	y	z	B _{eq} /Å ²
Cu100	0.000	0.26885(3)	0.250	1.211(4)
OW100	0.000	0.0649(2)	0.250	3.27(4)
O111	0.00643(9)	0.2822(1)	0.4468(1)	1.50(2)
O112	-0.1696(1)	0.5617(1)	0.4090(1)	2.24(2)
O113	-0.3919(1)	0.4054(1)	0.1391(1)	2.14(3)
N111	-0.1724(1)	0.2974(1)	0.1760(1)	1.37(2)
C111	-0.1051(1)	0.2923(2)	0.4398(2)	1.58(3)
C112	-0.1880(1)	0.3589(2)	0.2976(2)	1.26(2)
C113	-0.1545(1)	0.4947(2)	0.2976(2)	1.69(3)
C114	-0.3128(1)	0.3487(2)	0.2743(2)	1.67(3)

^a See Table 3.

Table 5. Atomic positional parameters and equivalent isotropic temperature factors^a with e.s.d.s in parentheses for [Cu(trisH₋₁)₂] · 5H₂O (3).

Atom	x	y	z	B _{eq} /Å ²
Cu100	0.000	0.000	0.000	1.651(6)
OW1	0.000	-0.8208(4)	-0.250	2.56(5)
OW2	-0.2862(2)	-0.6467(3)	-0.3073(1)	3.72(5)
OW3	-0.3052(2)	-0.2437(3)	-0.2490(1)	2.90(4)
O111	0.0119(1)	0.0935(3)	0.12221(9)	1.83(3)
O112	-0.4792(2)	0.0778(3)	-0.1265(1)	3.23(4)
O113	-0.2035(2)	0.6389(3)	-0.0480(1)	2.86(4)
N111	-0.1781(2)	0.2063(3)	-0.0764(1)	2.10(4)
C111	-0.0827(2)	0.2746(4)	0.1023(1)	1.93(4)
C112	-0.2323(2)	0.2760(3)	-0.0102(1)	1.55(4)
C113	-0.3533(2)	0.1168(4)	-0.0207(2)	2.35(5)
C114	-0.3067(2)	0.4958(4)	-0.0417(1)	2.18(4)

^aSee Table 3.

Table 6. Bond distances (Å) with e.s.d.s in parentheses for [Cu(trisH₋₁)₂] (1), [Cu(trisH₋₁)₂(H₂O)] (2) and [Cu(trisH₋₁)₂] · 5H₂O (3).

Bond distance/Å	1	2	3
Cu100–O111	1.941(1)	1.950(1)	1.929(2)
Cu100–OW100	—	2.200(2)	—
Cu100–N111	1.991(1)	2.032(1)	1.985(2)
O111–C111	1.419(1)	1.416(2)	1.411(3)
O112–C113	1.417(2)	1.419(2)	1.423(2)
O113–C114	1.420(2)	1.423(2)	1.425(3)
N111–C112	1.486(2)	1.483(2)	1.480(3)
C111–C112	1.529(2)	1.530(2)	1.536(2)
C112–C113	1.526(2)	1.527(2)	1.520(3)
C112–C114	1.532(1)	1.527(2)	1.527(3)

Table 7. Bond angles (°) with e.s.d.s in parentheses for [Cu(trisH₋₁)₂] (1), [Cu(trisH₋₁)₂(H₂O)] (2) and [Cu(trisH₋₁)₂] · 5H₂O (3).

Angle/°	1	2	3
O111–Cu100–O111 ^a	180.0(0)	171.54(6)	180.0(0)
O111–Cu100–OW100	—	94.23(4)	—
O111–Cu100–N111	85.67(4)	84.40(5)	85.39(7)
O111–Cu100–N111 ^a	94.33(4)	94.32(5)	94.61(7)
N111–Cu100–OW100	—	98.70(4)	—
N111–Cu100–N111 ^a	180.0(0)	162.60(6)	180.0(0)
Cu100–O111–C111	109.73(9)	112.09(8)	112.1(1)
Cu100–N111–C112	108.17(9)	107.30(8)	110.2(1)
O111–C111–C112	109.7(1)	110.7(1)	111.3(2)
O112–C113–C112	109.51(9)	110.4(2)	112.2(2)
O113–C114–C112	112.1(1)	111.9(2)	110.9(2)
N111–C112–C111	104.9(1)	105.4(1)	106.3(2)
N111–C112–C113	106.90(9)	106.6(1)	108.4(2)
N111–C112–C114	111.6(1)	111.5(1)	110.9(2)
C111–C112–C113	111.2(1)	111.7(1)	109.4(2)
C111–C112–C114	111.7(1)	111.1(1)	111.1(2)
C113–C112–C114	110.4(1)	110.4(1)	110.6(2)

^aSymmetry operation applied is $-x, -y, -z$ for 1 and 3, and $-x, y, \frac{1}{2} - z$ for 2.

Fourier map and refined isotropically with fixed thermal parameters. The final R (R_w) values for the non-hydrate, monohydrate and pentahydrate were 0.023 (0.027), 0.026 (0.029) and 0.026 (0.032), respectively.

The calculations were all performed on a MicroVAX 3100 computer using the MolEN¹⁵ structure determination program. The scattering factors and real and imaginary dispersion corrections for atomic scattering factors were taken from Ref. 16. The figures were drawn using the SCHAKAL¹⁷ program. The final positional parameters for the structures are given in Tables 3–5, and the selected bond distances and angles are listed in Tables 6 and 7. Tables of anisotropic thermal parameters, coordinates of hydrogen atoms and listings of observed and calculated structure factors are available from the authors on request.

Results and discussion

Syntheses. The syntheses given in the Experimental section are only examples of possible reactions, because the title compound crystallizes with varying amount of crystalline water from a number of synthesis having different copper(II) or copper(I) salts and tris as starting materials. In an ethanolic solution, tris was observed to react even with metallic copper powder, giving the non-hydrous [Cu(trisH₋₁)₂] as the product.

The degree of crystalline water depends mainly on the solvent, the reaction temperature and the crystallization temperature. The non-hydrous complex crystallizes from various methanolic or ethanolic syntheses containing different Cu(II) salts and tris as starting materials. The product is very often a mixture of non-hydrate and monohydrate compounds, especially when the reaction mixture is refluxed for a long period of time.

In the water syntheses, the formation of monohydrate versus pentahydrate depends again on the temperature and the choice of the anion. Heating up the reaction mixture promotes the coordination of water to the copper ion, leading to the monohydrate structure. On the other hand, one can affect the final product with the choice of the anion. Anions which do not participate in protolytic reactions (Cl⁻, Br⁻) lead more often to the monohydrate structure, while anions which affect the pH of the solution by making it more alkaline (SO₄²⁻, Ac⁻) usually give the pentahydrate form. The crystallization of the complex below room temperature (15–20°C) also promotes the formation of the pentahydrate structure.

Thermal analysis. The thermal decomposition of the Cu(trisH₋₁)₂ · n H₂O complexes took place in two basic stages; the dehydration of crystalline water was followed by the degradation of the organic part in two or three overlapping reactions leading to CuO in an air atmosphere and metallic copper in a nitrogen atmosphere.

The temperature of dehydration depends clearly on the coordination of water; in the pentahydrate structure, where the water molecules are not coordinated to copper

but are bonded to the structure by hydrogen bonding, the cleavage of water happens in one step between 63–99°C, whereas the coordinated water in the monohydrate structure lasts until 120–165°C. The thermal behavior of the ligand and the complexes is summarized in Table 1.

Molecular structures. The basic structure in all three cases is a mononuclear neutral complex with two deprotonated tris molecules covalently bonded to the copper atom in a *trans* configuration (Fig. 1).

The non-hydrate and pentahydrate complexes are almost identical, with square-planar structures, differing

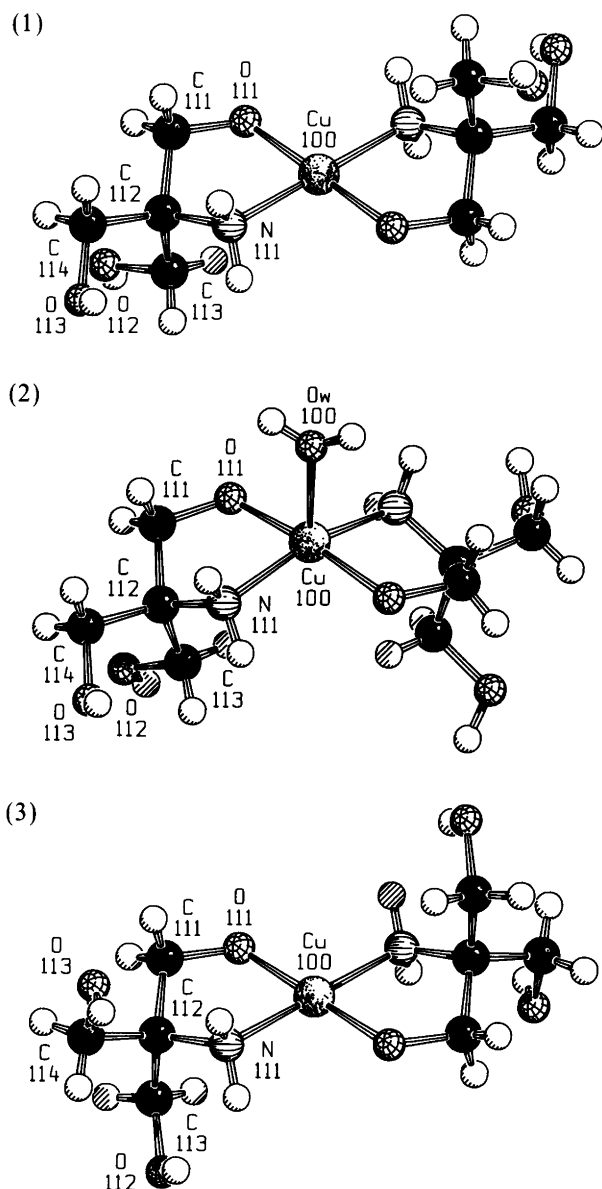


Fig. 1. SCHAKAL projections of the molecules $[\text{Cu}(\text{trisH}_{-1})_2]$ (1), $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$ (2) and $[\text{Cu}(\text{trisH}_{-1})_2] \cdot 5\text{H}_2\text{O}$ (3). The other half of the molecule is generated by inversion with respect to the copper atom in the case of 1 and 3, and by two-fold rotation around the Cu100–Ow100 bond (two-fold axis) in the case of 2.

mainly in orientation of the terminal hydroxy groups. The four-coordination around copper is planar owing to symmetry reasons and the metal–ligand distances range from 1.929(2) Å (Cu–O) to 1.991(1) Å (Cu–N). The five-membered chelate rings are also nearly planar; the ring is in an *envelope* conformation with Cu100, O111, N111 and C111 defining the plane, and C112 is the atom which is bent out of the plane. The deviations of C112 from this least-squares plane are $-0.582(1)$ Å for the non-hydrate and $-0.491(2)$ Å for the pentahydrate molecule. Furthermore, the terminal hydroxymethyl groups can take an axial or an equatorial position in relation to this chelate plane. The corresponding C113 and C114 distances from the plane are $-2.094(1)$ and $-0.255(2)$ Å for the non-hydrate and $-2.010(3)$ and $0.022(2)$ Å for the pentahydrate.

In the monohydrate complex the copper atom has a square-pyramidal five-coordination with tris molecules in the basal plane and the oxygen atom of the water molecule occupies the apical position. The deviations of O111, N111, O111' and N111' atoms from the least-squares plane range from 0.074(1) to 0.089(1) Å, and the copper atom is displaced 0.226(1) Å from this plane toward the apex of the pyramid. The metal–ligand distances in the equatorial plane of the coordination sphere range from 1.950(1) Å (Cu–O) to 2.032(1) Å (Cu–N), while the apical bond length is a little longer, Cu–Ow = 2.200(2) Å. The chelate rings in the monohydrate molecule are nearly planar, with C112 deviating $-0.602(2)$ Å from the Cu100–O111–N111–C111 least-squares plane. The corresponding axial and equatorial C113 and C114 distances are $-2.109(2)$ Å and $-0.296(2)$ Å. The dihedral angle between the two-fold symmetry related Cu100–O111–N111–C111 planes is $161.30(3)^\circ$. The monohydrate molecule is an optically active complex with two possible enantiomers, which are mirror images of each other, but because the synthesis is not stereoselective and the product is a racemic mixture, the compound crystallizes in a centrosymmetric space group where both enantiomers are present.

All the bond lengths and angles summarized in Tables 6 and 7 are consistent with the previously reported structures of tris-containing copper complexes.^{10–12}

Crystal structures. The projections of the crystal structures and hydrogen bonding of $\text{Cu}(\text{trisH}_{-1})_2$ complexes are presented in Fig. 2.

In the $[\text{Cu}(\text{trisH}_{-1})_2]$ structure the copper atom is located at the inversion center and surrounded by two symmetry-related tris ligands. The molecule forms 14 hydrogen bonds with six surrounding complex units via all OH and NH_2 hydrogens. Two short hydrogen bond distances ($\text{O} \cdots \text{O} = 2.60\text{--}2.79$ Å) are found from the deprotonated metal-bonded hydroxy group (O111) to the adjacent terminal hydroxymethyl groups. The amino-hydrogen contacts ($\text{N} \cdots \text{O} = 2.90\text{--}2.97$ Å) to the neighboring hydroxymethyl are also shorter than in the monohydrate structure (in the pentahydrate structure,

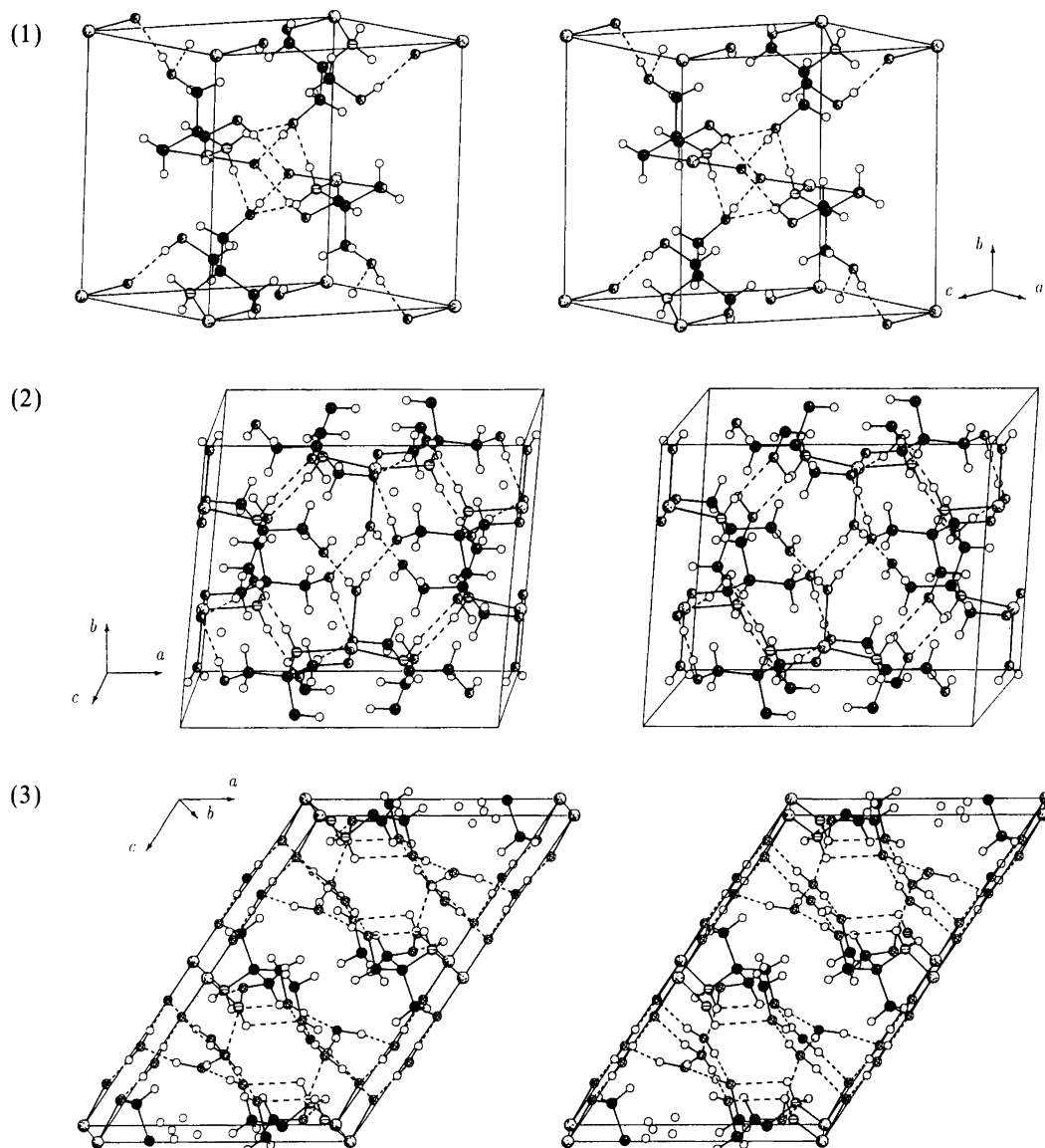


Fig. 2. Stereoscopic representations of hydrogen bonding for $[\text{Cu}(\text{trisH}_{-1})_2]$ (1), $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$ (2) and $[\text{Cu}(\text{trisH}_{-1})_2] \cdot 5\text{H}_2\text{O}$ (3). Hydrogen bonds are indicated by dashed lines.

the NH_2 hydrogen bonds are even shorter, but they are intramolecular bonds).

The monohydrate, $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$, has a doubly primitive C-centered lattice with four molecules in a unit cell. The asymmetric unit is half of the molecule and the other half is generated by two-fold rotation along the $\text{Cu100}-\text{OW100}$ bond (the copper atom and the coordinated water are located at the two-fold rotation axis). There is, again, an extensive framework of hydrogen bonds; one molecule forms 14 hydrogen bonds with seven adjacent complexes, utilizing all OH, NH_2 and H_2O hydrogens in bonding. The most distinctive bonding modes are the $\text{Cu100}-\text{O111} \cdots \text{O113} \cdots \text{OW100} \cdots \text{O113} \cdots \text{O111}'-\text{Cu100}-\text{O111} \cdots$ chains which lie in the direction of the c -axis.

In the crystal structure of the pentahydrate, the copper atom is positioned in the center of symmetry which also lies in the c -glide plane. In addition, the two-fold axis passes through the OW1 atom (crystalline water) in the b -direction. The general structure of the pentahydrate consists of layers of molecules divided by layers of crystalline water parallel to the ab -plane. Because of this layer-like structure, direct intermolecular hydrogen bonding between molecules is hindered and all the hydrogen bonds formed are between molecules and crystalline water. In addition, in this structure, the NH_2 hydrogen bonds have only an intramolecular effect on the orientation of the terminal hydroxymethyl groups. In the framework, the most characteristic hydrogen bond chain is $\text{Cu100}-\text{O111} \cdots \text{OW1} \cdots \text{O111}'-\text{Cu100}-\text{O111} \cdots$,

which also includes the strongly bonding O111 hydroxy group. The other interactions within the molecule layers are weak van der Waals type $\text{CH}_2 \cdots \text{CH}_2$ contacts. The layer structure of the pentahydrate explains the anisotropy observed in the crystal color (see Experimental).

References

1. Ramette, R. W., Culberson, C. H. and Bates, R. G. *Anal. Chem.* **49** (1977) 867.
2. Dotson, R. L. *J. Inorg. Nucl. Chem.* **34** (1972) 3131.
3. Dotson, R. L. *J. Inorg. Nucl. Chem. Lett.* **9** (1973) 215.
4. Hall, J. L., Simmons, R. B., Morita, E., Joseph, E. and Gavlas, J. F. *Anal. Chem.* **43** (1971) 634.
5. Bai, K. S. and Martell, A. E. *J. Inorg. Nucl. Chem.* **31** (1969) 1697.
6. Boyd, P. D., Pilbrow, J. R. and Smith, T. D. *Aust. J. Chem.* **24** (1971) 59.
7. Brignac, P. J. and Mo, C. *Anal. Chem.* **47** (1975) 1465.
8. Bologni, L., Sabatini, A. and Vacca, A. *Inorg. Chim. Acta* **69** (1983) 71.
9. Eilerman, D. and Rudman, R. *J. Chem. Phys.* **72** (1980) 5656.
10. Ivarsson, G. J. M. *Acta Crystallogr., Sect. C* **40** (1984) 67.
11. Masi, D., Mealli, C., Sabat, M., Sabatini, A., Vacca, A. and Zanobini, F. *Helv. Chim. Acta* **67** (1984) 1818.
12. Colombo, M. F., Austrilino, L., Nascimento, O. R., Castellano, E. E. and Tabak, M. *Can. J. Chem.* **65** (1987) 821.
13. Sheldrick, G. M. In: Sheldrick, G. M., Krüger, C. and Goddard, R., Eds., *Crystallographic Computing 3*, Oxford University Press, Oxford 1985, pp. 175–189.
14. Walker, N. and Stuart, D. *Acta Crystallogr., Sect. A* **39** (1983) 158.
15. *MolEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands 1990.
16. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
17. Keller, E., *SCHAKAL, a FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models*, University of Freiburg, Freiburg 1987.

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