Copper(II) Complexes of 2-Amino-2-hydroxymethyl-1,3-propanediol. Part 3. Synthesis, Structure and Thermal Behavior of Bis-*cis*[2-amino-2-hydroxymethyl-1,3-propanediol-*O,N*][2-amino-2-hydroxymethyl-1,3-propanediolato-*O,N*]aquacopper(II) Sulfate and Chromate, [Cu(C$_4$H$_{10}$NO$_3$)(C$_4$H$_{11}$NO$_3$)(H$_2$O)]$_2$X, where X=SO$_4^{2-}$, CrO$_4^{2-}$

Sirpa Kotila* and Jussi Valkonen

Department of Chemistry, University of Jyväskylä, FIN-40500 Jyväskylä, Finland

Kotila, S. and Valkonen, J., 1994. Copper(II) Complexes of 2-Amino-2-hydroxymethyl-1,3-propanediol. Part 3. Synthesis, Structure and Thermal Behavior of Bis-*cis*[2-amino-2-hydroxymethyl-1,3-propanediol-*O,N*][2-amino-2-hydroxymethyl-1,3-propanediolato-*O,N*]aquacopper(II) Sulfate and Chromate, [Cu(C$_4$H$_{10}$NO$_3$)(C$_4$H$_{11}$NO$_3$)(H$_2$O)]$_2$X, where X = SO$_4^{2-}$, CrO$_4^{2-}$. – Acta Chem. Scand. 48: 200–208 © Acta Chemica Scandinavica 1994.

Crystal structures of the title compounds with 2-amino-2-hydroxymethyl-1,3-propanediol (= tris, deprotonated form abbreviated trisH$_{-1}$) as ligand have been determined from single-crystal X-ray data. The blue [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$SO$_4$ compound crystallizes in the triclinic space group P$\bar{1}$ with two complexes in a cell of dimensions $a = 6.213(2)$, $b = 11.009(4)$, $c = 11.248(1)$ Å, $\alpha = 70.88(1)$, $\beta = 72.87(2)$, $\gamma = 79.67(2)°$, $V = 691.76(3)$ Å^3, $R = 0.032$ (2169 reflections). The space group of the green [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$CrO$_4$ compound is also P$\bar{1}$, but the unit cell is twice as large, containing four complexes, and the dimensions are $a = 6.424(1)$, $b = 10.735(1)$, $c = 21.578(2)$ Å, $\alpha = 98.60(1)$, $\beta = 89.97(1)$, $\gamma = 72.63(1)°$, $V = 1402.5(3)$ Å^3, $R = 0.033$ (4698 reflections).
  Both complexes are mononuclear and have a square-pyramidal coordination sphere with two amino and two hydroxymethyl groups in the basal plane and a water molecule as the apical ligand. The complexes form dimers with their optical enantiomorphs via strong hydrogen bonds, which involve the deprotonated hydroxymethyl groups [O···O distances 2.509(3)–2.525(4) Å]. The disorder of the terminal hydroxymethyl groups and the anions has been determined, and the three-dimensional network of hydrogen bonding is discussed. Thermal behavior was characterized by TG in air and nitrogen atmospheres.

2-Amino-2-hydroxymethyl-1,3-propanediol (tris) is a common buffering agent in biochemical and sea-water[1] studies, because its buffering range lies in the physiological pH area 7–9. The ligand also has various other names, such as tris(hydroxymethyl)aminomethane (tham), Trizma Base or less often used Tromethamine and Trometamol.[2]

H$_2$N—C—CH$_2$-OH
OH-CH$_2$ ... CH$_2$-OH
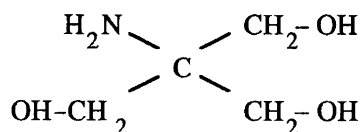
* To whom correspondence should be addressed.

Tris forms chelates with metallic cations mainly via the amino group and one or two of the hydroxymethyl groups. Alcoholic ligands also have two distinctly different bond types with metal cations. One type involves a normal metal–oxygen coordination bond, whereas the second type includes a covalent coordination bond with the alkoxy oxygen.[3] These deprotonated species are abbreviated trisH$_{-1}$.

Our special interest is the solid-state chemistry of tris compounds and the aim of this study is to reveal the variety of copper(II)–tris compounds containing different anions. In our earlier articles we reported the structures and thermal behavior of three *trans* complexes, [Cu(trisH$_{-1}$)$_2$], [Cu(trisH$_{-1}$)$_2$(H$_2$O)] and [Cu(trisH$_{-1}$)$_2$]·5H$_2$O[4] as well as two *cis*-complexes, [Cu(trisH$_{-1}$)(tris)-

$(NO_3)]$ and $[Cu(trisH_{-1})(tris)]Na(ClO_4)_2$.[5] In this paper we concentrate on two new copper(II)–tris complexes, $[Cu(trisH_{-1})(tris)(H_2O)]_2SO_4$ and $[Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4$.

Experimental

Reagents. All the reagents were used without further purification.

Preparation of [Cu(trisH_{-1})(tris)(H_2O)]_2SO_4. 0.03 mol of $CuSO_4·5H_2O$ (J.T. Baker, minimum 99.0%) was placed into a 250 cm^3 round-bottomed flask with a reflux condenser and was dissolved in 15 cm^3 of distilled water. Then 0.09 mol of tris (Sigma, 99–99.5%) was added and the mixture was gently refluxed for 5 h. The complex solution was cooled to room temperature, poured into a beaker, and three 15 cm^3 portions of methanol added, whereupon a thick syrupy solution formed on the bottom of the beaker. After the cloudy methanol solution on the top had been discarded, the syrupy complex solution was dissolved in a minimum volume of water–methanol (1:1 v/v) solution by heating. The solution was filtered, and the compound crystallized within a few days. The bright blue rod-shaped crystals were filtered, washed with a cold water–methanol (1:1) solution and dried in air.

Preparation of [Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4. The chromate compound was crystallized from a water solution with a metal–ligand–anion stoichiometric ratio of 1:4:2.

The following compounds, 0.04 mol of tris (Sigma, 99–99.5%), 0.01 mol of $CuCl_2·2H_2O$ (Merck, p.a.), and 0.02 mol of Na_2CrO_4 (Merck, puriss.), were dissolved in a minimum amount of distilled water in separate beakers by moderate heating. The solutions were cooled to room temperature, and the complex was formed by adding the copper solution to the tris solution and finally pouring the sodium chromate solution into the blue complex mixture. The green solution was filtered and concentrated with a rotavapor to a volume of ~ 10 cm^3. The dark green needle-shaped crystals, formed within a week at room temperature, were separated with vacuum filtration (with no washing, because the compound is very soluble in water) and dried in air. If the complex solution is too dilute or has been heated during the procedure, some monohydrate, $[Cu(trisH_{-1})_2(H_2O)]$,[4] might result as a side-product.

Thermal analysis. The thermal behavior of the complexes in air and nitrogen atmospheres was determined with a Perkin-Elmer thermogravimetric analyzer TGA7. The sample size of the sulfate compound was 7.00 ± 0.50 mg; the amount of the chromate compound was smaller (4.00–4.30 mg), because the needle-shaped crystals took more space. 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 with the sulfate and chromate compounds were 25–900 and 25–950°C, respectively, in both atmospheres. To remove oxygen from the oven when a nitrogen atmosphere was used, the equipment was flushed for 30–45 min with nitrogen before the

Table 1. Thermal decomposition of $[Cu(trisH_{-1})(tris)(H_2O)]_2SO_4$ (**1**) and $[Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4$ (**2**).

Compound	Lost in reaction	$T/°C$	Weight loss (%)	
			Δ Obs.	Δ Theor.
Air atmosphere				
1	2 H_2O	52–128	4.9	4.9
	Org.	148–468	66.4	65.1
	$1\frac{1}{2}$ O_2 (SO_4)	575–715	4.6	6.5
	Total reaction			
	→CuS+CuO	25–800	75.4	76.4
2	2 H_2O	38–87	4.9	4.7
	Org.	109–323	64.0	64.4
	Total reaction			
	→2 CuO+$\frac{1}{2}$ Cr_2O_3	25–323	68.9	69.1
Nitrogen atmosphere				
1	2 H_2O	25–123	4.9	4.9
	Org.	170–900	60.3	65.0
	Total reaction			
	→Cu_2SO_4 (+C)	25–900	65.2	69.9
2	2 H_2O	25–95	4.8	4.7
	Org.	95–780	61.3	63.4
	2 O_2 (CrO_4)	780–950	8.1	8.4
	Total reaction			
	→2 Cu+Cr (+C)	25–950	74.2	76.5

temperature program was initiated. Observed and theoretical weight losses are reported in Table 1.

X-Ray structure measurements. Diffracted intensities were measured with an Enraf-Nonius CAD-4 diffractometer and with monochromatized MoKα radiation. Crystals were mounted on a glass fiber and measured in air. The lattice parameters were calculated by least-squares fitting of 25 centered reflections. Crystal data and experimental details are presented in Table 2.

During the data collection the decay of crystals was monitored with three reflections every 60 min, and the orientation of the crystal was checked every 500 reflections. The total gain in intensity was 10.5% in 27.7 h for the sulfate compound, and for the chromate compound the total loss in intensity was 12.5% in 136.4 h. In addition to the correction for the decay, Lorentz and polarization effects were also taken into account and the absorption correction was done by the DIFABS[6] program.

Positions of the heavy atoms (Cu, Cr) were determined

by direct methods with the SHELXS-86 program;[7] the remaining non-hydrogen atoms were located from difference Fourier maps, and their coordinates were refined to convergence by the full-matrix least-squares method. Hydrogen atoms were placed in their calculated positions $(CH_2, NH_2, d = 0.95 \text{ Å})$ after the isotropic refinement of the displacement parameters, and most of the OH and H_2O hydrogens were found from the residual electron density map after the anisotropic refinement of the displacement parameters. All hydrogens were refined as riding atoms with fixed isotropic displacement parameters $B = 5.00 \text{ Å}^2$. After all atoms in the complex molecules had been determined, the R-values were still 0.054 (SO_4) and 0.037 (CrO_4), and the maxima in residual electron density maps were $2.89\ e\ \text{Å}^{-3}\ (SO_4)$ and $1.42\ e\ \text{Å}^{-3}$ (CrO_4). A closer analysis of the difference Fourier map showed that the terminal hydroxymethyl groups in both compounds were disordered, having two possible orientations. The multiplicities were found by presuming that the isotropic displacement parameters of both orientations would be equal in magnitude. In the sulfate com-

Table 2. Crystallographic experimental data for $[Cu(trisH_{-1})(tris)(H_2O)]_2SO_4$ (1) and $[Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4$ (2).

	1	2
Unit cell determination:		
Formula	$Cu_2SO_{18}N_4C_{16}H_{46}$	$Cu_2CrO_{18}N_4C_{16}H_{46}$
Formula weight	741.71	761.64
Color	Blue	Green
Crystal size/mm	0.18×0.15×0.13	0.23×0.15×0.05
$T/°C$	21±1	21±1
Reflections for lattice measurement	25	25
θ-Range for lattice measurement/°	5–12	8–13
$a/\text{Å}$	6.213(2)	6.424(1)
$b/\text{Å}$	11.009(4)	10.735(1)
$c/\text{Å}$	11.248(1)	21.578(2)
$\alpha/°$	70.88(1)	98.60(1)
$\beta/°$	72.87(2)	89.97(1)
$\gamma/°$	79.67(2)	72.63(1)
$V/\text{Å}^3$	691.76(3)	1402.5(3)
Z	1	2
$d_{calc}/\text{g cm}^{-3}$	1.78	1.80
$\lambda(MoK\alpha)/\text{Å}$	0.71073	0.71073
$\mu(MoK\alpha)/\text{cm}^{-1}$	16.98	19.62
$F(000)$	388	792
Space group	$P\bar{1}$	$P\bar{1}$
Data collection and refinement:		
θ-Range for data collection/°	2–25	2–30
Scan method	$\omega/2\theta$	ω/θ
Scan speed in $\omega/°$ min^{-1}	1.03–16.50	0.79–5.50
Scan width in $\omega/°$	0.50+0.34 tan θ	0.70+0.34 tan θ
No. of measured reflections	2438	8131
Reflections used in refinement, $I > 3\sigma(I)$	2169	4698
Absorption correction (min./max.)	0.98/1.02	0.84/1.27
Max. shift/error	0.00	0.00
Max. in final $\Delta\rho/e\ \text{Å}^{-3}$	0.68	0.45
No. of parameters refined	223	424
R	0.032	0.033
$R_w{}^a$	0.040	0.035
$S = [\Sigma w(F_o - F_c)^2/(n-m)]^{1/2}$	1.018	1.332

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

Table 3. Atomic positional parameters and equivalent isotropic displacement parameters[a] with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$SO$_4$ (1).

Atom	x	y	z	$B_{eq}/\text{Å}^2$
Molecule				
Cu100	0.14192(7)	0.51101(4)	0.18142(4)	1.202(8)
OW100	0.5269(4)	0.5125(3)	0.1513(3)	2.77(7)
O111	0.0574(4)	0.6557(2)	0.0379(2)	1.61(5)
O112[b]	0.3640(8)	0.8352(5)	0.2093(5)	5.2(1)
O112B[c]	0.283(2)	0.9464(9)	0.049(1)	3.2(3)
O113[b]	−0.1993(8)	0.9808(4)	0.1866(4)	3.4(1)
O113B[c]	−0.288(2)	0.811(1)	0.351(1)	5.0(3)
O121	0.1839(4)	0.3879(2)	0.0866(2)	1.41(5)
O122	−0.2076(5)	0.1936(3)	0.4560(3)	3.03(7)
O123	0.3203(7)	0.0178(3)	0.3386(3)	4.37(9)
N111	0.0598(6)	0.6439(3)	0.2758(3)	1.85(7)
N121	0.1514(5)	0.3577(3)	0.3382(3)	1.48(6)
C111	−0.0690(6)	0.7618(3)	0.0836(3)	1.84(8)
C112	0.0310(6)	0.7751(3)	0.1872(3)	1.57(7)
C113	0.2615(7)	0.8278(4)	0.1240(4)	2.91(9)
C114	−0.1317(7)	0.8610(4)	0.2646(4)	2.53(9)
C121	0.279(6)	0.2692(3)	0.1567(3)	1.63(7)
C122	0.1572(6)	0.2384(3)	0.3026(3)	1.32(7)
C123	−0.0834(6)	0.2108(4)	0.3241(4)	2.14(8)
C124	0.2881(7)	0.1267(4)	0.3818(4)	2.29(9)
Sulfate				
S1	0.500	0.500	0.500	1.95(3)
O1[d]	0.487(1)	0.4062(7)	0.6332(6)	4.1(2)
O2[d]	0.2496(9)	0.5189(7)	0.4972(5)	3.3(1)
O3[d]	0.554(1)	0.6221(6)	0.5039(7)	4.3(2)
O4[d]	0.623(1)	0.4515(7)	0.3991(6)	5.2(2)

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$. [b] pp = 0.72. [c] pp = 0.28. [d] pp = 0.50.

pound the molecule has two disordered hydroxymethyl groups, and the multiplicities of these orientations are 72 and 28% for molecules A and B, respectively. In the chromate compound there is one disordered hydroxymethyl group in each molecule; in this case multiplicities of 84% (molecules 1A and 2A) and 16% (molecules 1B and 2B) were found. The hydrogens of these disordered hydroxy groups were not found from the difference Fourier map. When the disorder was included in the model, the major peaks in the final difference Fourier map were located close to the copper atoms and sulfate or chromate ions. The sulfate structure was also solved in the non-centrosymmetric space group *P*1 to confirm the disorder.

All calculations were done on a MicroVAX 3100 computer with the MolEN[8] structure-determination package. The atomic scattering factors and real and imaginary dispersion corrections for scattering factors were taken from Ref. 9. The figures were drawn with the SCHAKAL program.[10] The final atomic positional parameters and equivalent isotropic displacement parameters are given in Tables 3 and 4. The relevant molecular bond distances and angles for the complexes and anions are listed in Tables 5 and 6. Tables of anisotropic displacement parameters, coordinates of hydrogen atoms and listings of observed and calculated structure factors are available from the authors upon request.

Results and discussion

Thermal analysis. The thermal behavior of the compounds, determined in air and nitrogen atmospheres, is summarized in Table 1.

Molecular structures. The molecular structures of the complexes are presented in Figs. 1 and 2, and the bond lengths and angles characterizing the molecules are listed in Tables 5 and 6.

The complex molecules in both structures are mononuclear cation complexes with two tris ligands (one of them deprotonated) and one water molecule coordinated to the copper atom. The coordination sphere around copper is square-pyramidal five-coordination with tris molecules in the basal plane (*cis* configuration) and a water molecule occupying the apical position.

In the sulfate compound the metal–ligand distances in the equatorial plane range from 1.924(3) (Cu–O) to 2.009(2) Å (Cu–N), and the apical bond with water is a little longer 2.317(3) Å (Cu–OW). In the square pyramid the deviations of O111, N111, O121 and N121 from the least-squares plane differ by from 0.059(3) to 0.064(3) Å and the copper atom is displaced 0.1694(5) Å from this plane towards the apex of the pyramid. The five-membered chelate rings have an *envelope* conformation, where C112 and C122 are the atoms bent out of the planes.

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Table 4. Atomic positional parameters and equivalent isotropic displacement parameters [a] with e.s.d.s in parentheses for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$CrO$_4$ (**2**).

Atom	x	y	z	$B_{eq}/Å^2$
Molecule 1				
Cu100	0.23135(6)	0.99737(4)	0.90917(2)	1.328(7)
OW100	0.5878(4)	0.9934(3)	0.9241(1)	2.75(6)
O111	0.2050(4)	0.8435(2)	0.9449(1)	1.72(4)
O112	0.7450(4)	0.6711(3)	0.8096(2)	3.15(6)
O113	0.3717(5)	0.5093(3)	0.7952(1)	3.13(6)
O121	0.1334(4)	1.1153(2)	0.9873(1)	1.50(4)
O122[b]	−0.3005(6)	1.4023(4)	0.9601(2)	3.37(8)
O122B[c]	−0.241(3)	1.322(2)	0.8557(9)	3.3(4)
O123	0.3264(5)	1.3817(3)	0.8929(2)	3.08(6)
N111	0.2988(5)	0.8685(3)	0.8295(1)	1.86(6)
N121	0.1716(5)	1.1610(3)	0.8685(1)	1.75(5)
C111	0.2066(6)	0.7338(3)	0.8981(2)	1.91(6)
C112	0.3556(5)	0.7303(3)	0.8421(1)	1.29(5)
C113	0.5929(6)	0.6837(4)	0.8598(2)	2.16(7)
C114	0.3156(6)	0.6415(3)	0.7841(2)	1.92(6)
C121	0.1512(5)	1.2421(3)	0.9791(2)	1.65(6)
C122	0.0597(5)	1.2769(3)	0.9164(2)	1.53(6)
C123	−0.1836(6)	1.2942(4)	0.9152(2)	2.46(8)
C124	0.1017(6)	1.4030(4)	0.9024(2)	2.16(7)
Molecule 2				
Cu200	0.22865(6)	1.00264(4)	0.59082(2)	1.334(7)
OW200	0.5803(4)	1.0069(3)	0.5760(1)	2.82(6)
O211	0.0482(4)	1.1571(2)	0.5549(1)	1.67(4)
O212	0.4153(4)	1.3287(3)	0.6904(2)	3.16(6)
O213	−0.1193(5)	1.4904(3)	0.7048(1)	3.19(7)
O221	0.2489(4)	0.8848(2)	0.5128(1)	1.50(4)
O222[b]	0.1022(6)	0.5981(4)	0.5399(2)	3.35(8)
O222B[c]	0.079(3)	0.681(2)	0.6431(9)	3.1(4)
O223	0.7085(5)	0.6184(3)	0.6073(2)	3.18(6)
N211	0.1680(5)	1.1316(3)	0.6704(1)	1.79(5)
N221	0.3327(5)	0.8387(3)	0.6314(1)	1.72(5)
C211	−0.0589(6)	1.2660(4)	0.6021(2)	1.91(7)
C212	0.0850(5)	1.2697(3)	0.6579(1)	1.35(5)
C213	0.2763(6)	1.3169(4)	0.6405(2)	2.20(7)
C214	−0.0426(6)	1.3584(4)	0.7158(2)	1.91(7)
C221	0.3927(6)	0.7585(3)	0.5209(2)	1.69(6)
C222	0.3369(5)	0.7225(3)	0.5836(2)	1.54(6)
C223	0.1095(6)	0.7063(4)	0.5849(2)	2.32(7)
C224	0.5043(6)	0.5967(4)	0.5972(2)	2.18(7)
Chromate				
Cr1	0.74858(9)	1.00001(7)	0.74999(3)	1.708(9)
O1[d]	0.684(1)	1.1016(6)	0.6945(3)	3.0(1)
O2[d]	1.006(1)	0.9217(9)	0.7370(3)	5.2(2)
O3[d]	0.710(1)	1.0815(8)	0.8190(3)	5.9(2)
O4[d]	0.603(1)	0.8984(6)	0.7404(3)	4.2(1)
O5[d]	0.785(1)	0.8988(6)	0.8050(3)	3.1(1)
O6[d]	0.500(1)	1.1019(8)	0.7592(3)	4.1(2)
O7[d]	0.790(2)	0.918(1)	0.6815(4)	6.3(2)
O8[d]	0.927(1)	1.0790(7)	0.7628(3)	5.3(1)

[a]See Table 3. [b]pp=0.84. [c]pp=0.16. [d]pp=0.50.

These carbons are located at the opposite sides of the coordination plane, leading to an *anti* conformer. Furthermore, the terminal hydroxymethyl groups can take an axial or an equatorial position in relation to this chelate plane. On the non-deprotonated side of the complex both terminal hydroxy groups are disordered, having two possible orientations with multiplicities of 0.72 and 0.28. The orientations refer to two different ways of forming hydrogen bonds with the neighboring groups. The angles between these different orientations are 96.8(8)° (O112–C113–O112B) and 112.7(7)° (O113–C114–O113B). The dihedral angle between the chelate planes is 13.5(3)°.

The asymmetric unit of the chromate compound contains two almost identical complex molecules (Fig. 2),

Table 5. Bond distances (in Å) with e.s.d.s in parentheses for $[Cu(trisH_{-1})(tris)(H_2O)]_2SO_4$ (**1**) and $[Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4$ (**2**).

Bond distance	1	2	Bond distance	2
Cu100–OW100	2.317(3)	2.301(3)	Cu200–OW200	2.297(3)
Cu100–O111	1.983(2)	1.975(3)	Cu200–O211	1.983(2)
Cu100–O121	1.924(3)	1.930(2)	Cu200–O221	1.928(2)
Cu100–N111	1.990(3)	1.997(3)	Cu200–N211	1.997(3)
Cu100–N121	2.009(2)	2.016(3)	Cu200–N221	2.017(3)
O111–C111	1.439(4)	1.429(4)	O211–C211	1.428(4)
O112–C113	1.328(8)	1.421(5)	O212–C213	1.414(5)
O112B–C113	1.31(1)	–	–	–
O113–C114	1.394(5)	1.414(5)	O213–C214	1.412(5)
O113B–C114	1.22(1)	–	–	–
O121–C121	1.412(4)	1.435(4)	O221–C221	1.430(4)
O122–C123	1.423(5)	1.411(5)	O222–C223	1.411(5)
O122B–C123	–	1.39(2)	O222B–C223	1.35(2)
O123–C124	1.397(6)	1.402(5)	O223–C224	1.411(5)
N111–C112	1.477(4)	1.486(4)	N211–C212	1.485(4)
N121–C122	1.485(5)	1.488(4)	N221–C222	1.489(4)
C111–C112	1.529(6)	1.531(5)	C211–C212	1.522(5)
C112–C113	1.523(6)	1.523(5)	C212–C213	1.528(5)
C112–C114	1.533(5)	1.527(5)	C212–C214	1.523(4)
C121–C122	1.540(4)	1.529(5)	C221–C222	1.531(5)
C122–C123	1.512(6)	1.519(5)	C222–C223	1.522(5)
C122–C124	1.523(5)	1.528(6)	C222–C224	1.523(5)

Sulfate or chromate (X = S, Cr)

	1	2
X–O1	1.505(6)	1.707(6)
X–O2	1.541(6)	1.621(6)
X–O3	1.461(8)	1.589(7)
X–O4	1.376(8)	1.626(8)
X–O5	–	1.696(7)
X–O6	–	1.635(6)
X–O7	–	1.580(7)
X–O8	–	1.620(8)

both having one disordered hydroxy group (O122 and O222) on the deprotonated side of the complex, and the multiplicities of these two possible orientations are 0.84 (molecules 1A and 2A) and 0.16 (molecules 1B and 2B). In the five-coordination spheres of copper atoms the metal–ligand distances are in the range 1.93–2.02 Å, where the shortest bond length refers to the covalent coordination bond of the alkoxy group. The apical coordination bonds with water are 2.301(3) and 2.297(3) Å in molecules 1 (Cu100–OW100) and 2 (Cu200–OW200), respectively. In the square-pyramidal structure the deviations of the oxygen and nitrogen atoms from the least-
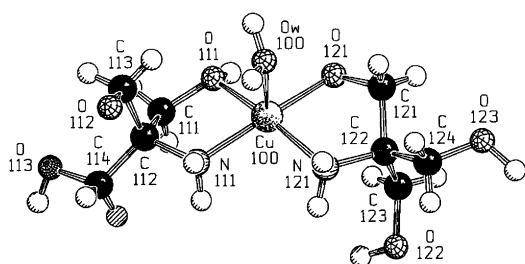
squares plane range from 0.079(3) to 0.087(3) Å, and the corresponding distances of the copper atoms from that plane towards the apex of the pyramid are 0.1898(4) and 0.1873(4) Å for molecules 1 and 2, respectively. The conformation of the five-membered chelate rings is also *anti* as in the sulfate compound. The dihedral angle between the chelate planes is 13.7(2)° in both complex molecules, and the angles between the two orientations of the disordered hydroxy groups are 109.1(8)° (O122–C123–O122B) and 109.7(10)° (O222–C223–O222B).

The complex molecules in the sulfate and chromate compounds are optically active with two possible enantiomers. Because the syntheses are not stereoselective, the product is a racemic mixture, and the compounds crystallize in centrosymmetric space groups where both enantiomers are present in equal amounts. The bond lengths and angles obtained for the molecules are consistent with the previously reported structures of copper–tris complexes.[4,5]

Crystal structures. Stereoscopic projections of the crystal structures and the hydrogen bonding framework for both compounds are presented in Figs. 3 and 4.

Very often sulfate and chromate compounds have isomorphic structures, because the anions share the same

Fig. 1. SCHAKAL drawing of the cation complex A (72%) in $[Cu(trisH_{-1})(tris)(H_2O)]_2SO_4$ (**1**).

Table 6. Bond angles (in °) with e.s.d.s in parentheses for $[Cu(trisH_{-1})(tris)(H_2O)]_2SO_4$ (**1**) and $[Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4$ (**2**).

Angle	1	2	Angle	2
O111–Cu100–O121	92.6(1)	92.6(1)	O211–Cu200–O221	92.56(9)
O111–Cu100–OW100	106.0(1)	104.1(1)	O211–Cu200–OW200	104.1(1)
O111–Cu100–N111	83.3(1)	83.1(1)	O211–Cu200–N211	83.1(1)
O111–Cu100–N121	166.7(1)	164.3(1)	O211–Cu200–N221	164.4(1)
O121–Cu100–N111	172.8(1)	172.8(1)	O221–Cu200–N211	172.9(1)
O121–Cu100–N121	86.3(1)	86.5(1)	O221–Cu200–N221	86.4(1)
N111–Cu100–N121	96.4(1)	96.1(1)	N211–Cu200–N221	96.3(1)
Cu100–O111–C111	111.7(2)	113.1(2)	Cu200–O211–C211	112.6(2)
Cu100–O121–C121	108.5(2)	107.5(2)	Cu200–O221–C221	107.5(2)
Cu100–N111–C112	111.7(2)	111.2(2)	Cu200–N211–C212	111.3(2)
Cu100–N121–C122	108.8(2)	108.0(2)	Cu200–N221–C222	108.2(2)
O111–C111–C112	108.2(3)	109.2(3)	O211–C211–C212	109.7(2)
O112–C113–C112	113.3(4)	113.5(3)	O212–C213–C212	113.6(3)
O112B–C113–C112	121.8(6)	–	–	–
O113–C114–C112	113.6(3)	109.9(3)	O213–C214–C212	110.1(3)
O113B–C114–C112	117.0(7)	–	–	–
O121–C121–C122	110.4(3)	109.7(3)	O221–C221–C222	110.2(2)
O122–C123–C122	111.6(4)	110.7(3)	O222–C223–C222	109.9(3)
O122B–C123–C122	–	104.9(8)	O222B–C223–C222	105.0(8)
O123–C124–C122	111.1(4)	110.1(3)	O223–C224–C222	110.1(3)
N111–C112–C111	106.6(3)	105.8(2)	N211–C212–C211	106.0(3)
N111–C112–C113	109.0(3)	110.1(3)	N211–C212–C213	109.7(2)
N111–C112–C114	109.1(3)	109.3(3)	N211–C212–C214	109.5(3)
N121–C122–C121	105.7(3)	105.7(2)	N221–C222–C221	105.2(3)
N121–C122–C123	108.5(3)	107.6(3)	N221–C222–C223	107.1(3)
N121–C122–C124	110.1(3)	111.6(3)	N221–C222–C224	111.9(3)
C111–C112–C113	110.0(3)	109.2(3)	C211–C212–C213	109.4(3)
C111–C112–C114	110.4(3)	111.4(3)	C211–C212–C214	111.8(2)
C113–C112–C114	111.5(4)	110.9(2)	C213–C212–C214	110.4(3)
C121–C122–C123	109.8(3)	111.6(3)	C221–C222–C223	111.5(3)
C121–C122–C124	110.5(3)	111.0(3)	C221–C222–C224	111.3(3)
C123–C122–C124	112.0(3)	109.3(3)	C223–C222–C224	109.7(3)

Sulfate or chromate (X=S, Cr)

Angle	1	2
O1–X–O2	100.7(3)	105.3(4)
O1–X–O3	106.9(4)	111.6(3)
O1–X–O4	114.5(4)	108.7(3)
O5–X–O6	–	108.9(3)
O5–X–O7	–	111.2(4)
O5–X–O8	–	105.6(4)

charge and tetrahedral geometry. In this case the sulfate and chromate compounds proved to be non-isomorphic, even though they possess many similarities in structure.

Both structures consist of anions and hydrogen-bonded cationic dimers, which contain the optically active complex and its enantiomer. The dimer has a step-like structure (in which there is an inversion center in the middle of the eight-membered ring) and the apical water ligands are pointing outwards. The hydrogen bonds in the dimer include the deprotonated hydroxy groups, so the donor–acceptor distances are short [O···O distances 2.525(4) Å (SO₄) and 2.509(3)–2.510(3) Å (CrO₄)]. The corresponding Cu···Cu distances in the dimers are 4.9866(7) Å (SO₄) as well as 4.9012(6) and 4.9031(6) Å (CrO₄).

In both structures the anions (SO_4^{2-} and CrO_4^{2-}) are disordered, having two centrosymmetrically related orientations, where the multiplicities for oxygen atoms are 0.50. The sulfate anion is in a special position, and the other
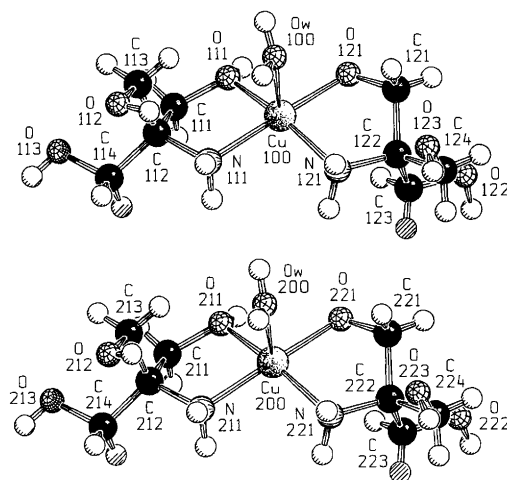

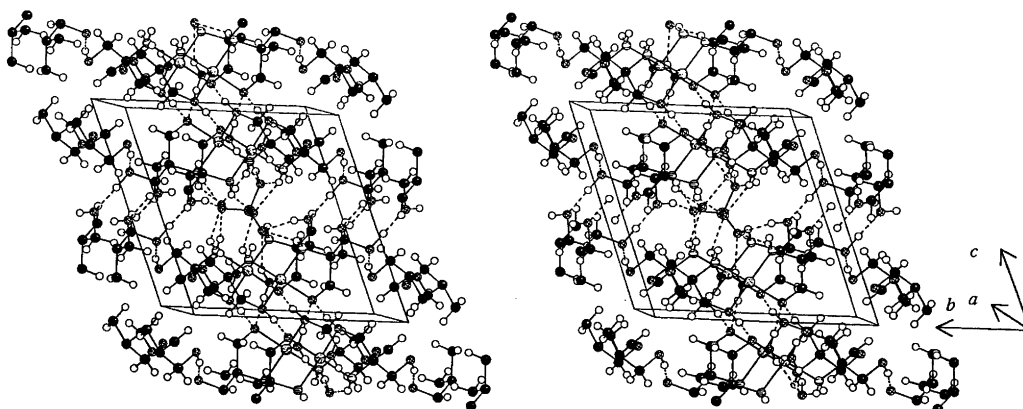*Fig. 2.* SCHAKAL drawings of the cation complexes 1A and 2A (84%) in $[Cu(trisH_{-1})(tris)(H_2O)]_2CrO_4$ (**2**).

Fig. 3. Stereoscopic representation of hydrogen bonding for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$SO$_4$ (**1**) (molecule A, 72%). Hydrogen bonds are indicated by dashed lines, and sulfate is shown in one of the two centrosymmetric orientations.

set of oxygens is generated by symmetry, whereas the chromate anion is in a general position and has two sets of oxygens (O1–O4 and O5–O8). The geometry of both anion types is not regular, indicating that the hydrogen-bonding surroundings are different for each oxygen.[11,12] Nevertheless, the average bond lengths and angles (SO$_4$, 1.47 Å and 107°; CrO$_4$, 1.63 Å and 109°) are normal for these anions.[11–14]

The differences in the structures arise from the fact that the unit cell of the sulfate compound contains only one dimer, whereas the unit cell of the chromate compound contains two dimers,of which one is tilted around to form almost a mirror image of the other (see packing diagrams

in Figs. 5 and 6). The reason for this non-isomorphic packing lies in the difference of the anion size and therefore changes in the hydrogen-bonding network.

In both structures the dimers are stacked along the a-direction and polymerized by OW100–HW$\cdots$O121' (OW200–HW$\cdots$O221') and O122–H$\cdots$O123' (O222–H$\cdots$O223') hydrogen bonds. The dimers have their amino groups oriented towards the sulfate or chromate ions, and the anions connect the dimers with N–H$\cdots$O(SO$_4$ or CrO$_4$) hydrogen bonds in the a- and c-directions. The coordinated water molecule also forms hydrogen-bonded chains with the sulfate or chromate ions in the c-direction, like the OW100–HW$\cdots$O1–S–

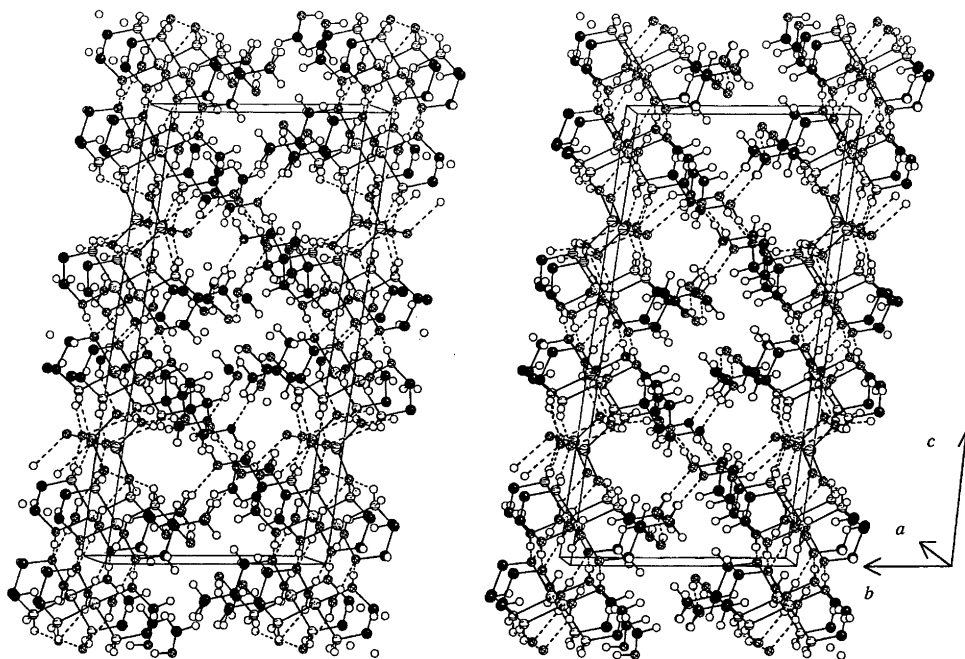*Fig. 4.* Stereoscopic representation of hydrogen bonding for [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$CrO$_4$ (**2**) (molecules 1A and 2A, 84%). Hydrogen bonds are indicated by dashed lines, and chromate is shown in one of the two centrosymmetric orientations.
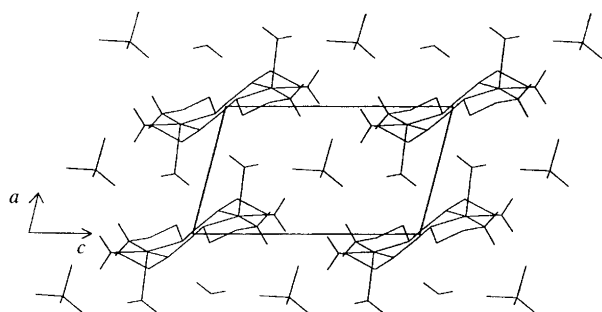
Fig. 5. Packing diagram of the dimers and anions in [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$SO$_4$ (1). Terminal hydroxymethyl groups are omitted for clarity, and anions are shown in one orientation.

O4$\cdots$HW'$-$OW100' chain in the sulfate compound and OW100$-$HW$\cdots$O3$-$Cr$-$O1$\cdots$HW$-$OW200 and OW100$-$HW$\cdots$O5$-$Cr$-$O7$\cdots$HW$-$OW200 chains in the chromate compound. In the bc-plane the interactions are mainly hydrogen bonds between terminal hydroxymethyl

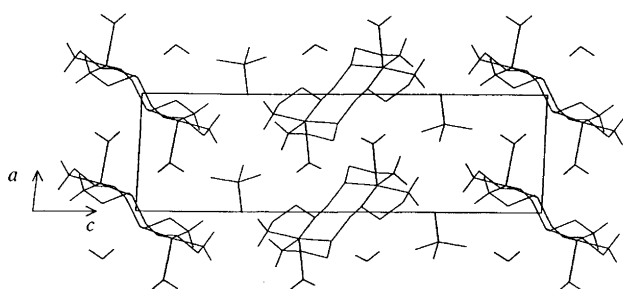Fig. 6. Packing diagram of the dimers and anions in [Cu(trisH$_{-1}$)(tris)(H$_2$O)]$_2$CrO$_4$ (2). Terminal hydroxymethyl groups are omitted for clarity, and anions are shown in one orientation.

groups or weak van der Waals forces between CH$_2\cdots$CH$_2$ groups. The hydrogen bonding of disordered hydroxy groups is not included because these hydrogens could not be located from the difference Fourier map, but otherwise all H$_2$O, OH and NH$_2$ hydrogens are involved in the hydrogen-bonding network.

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