

# Copper(II) Complexes of 2-Amino-2-hydroxymethyl-1,3-propanediol. Part 2. Synthesis, Structure and Thermal Behavior of *cis*-[2-Amino-2-hydroxymethyl-1,3-propanediol(1,3-)-*O,O',N*][2-amino-2-hydroxymethyl-1,3-propanediolato(1-)-*O,N*]nitratocopper(II), $[\text{Cu}(\text{C}_4\text{H}_{10}\text{NO}_3)(\text{C}_4\text{H}_{11}\text{NO}_3)(\text{NO}_3)]$ , and *cis*-[2-Amino-2-hydroxymethyl-1,3-propanediol(1,3-)-*O,O',N*][2-amino-2-hydroxymethyl-1,3-propanediolato(1,3-)-*O,O',N*]copper(II) Sodium Bis(perchlorate), $[\text{Cu}(\text{C}_4\text{H}_{10}\text{NO}_3)(\text{C}_4\text{H}_{11}\text{NO}_3)]\text{Na}(\text{ClO}_4)_2$

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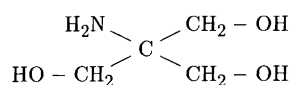
Kotila, S. and Valkonen, J., 1993. Copper(II) Complexes of 2-Amino-2-hydroxymethyl-1,3-propanediol. Part 2. Synthesis, Structure and Thermal Behavior of *cis*-[2-Amino-2-hydroxymethyl-1,3-propanediol(1,3-)-*O,O',N*][2-amino-2-hydroxymethyl-1,3-propanediolato(1-)-*O,N*]nitratocopper(II),  $[\text{Cu}(\text{C}_4\text{H}_{10}\text{NO}_3)(\text{C}_4\text{H}_{11}\text{NO}_3)(\text{NO}_3)]$ , and *cis*-[2-Amino-2-hydroxymethyl-1,3-propanediol(1,3-)-*O,O',N*][2-amino-2-hydroxymethyl-1,3-propanediolato(1,3-)-*O,O',N*]copper(II) Sodium Bis(perchlorate),  $[\text{Cu}(\text{C}_4\text{H}_{10}\text{NO}_3)(\text{C}_4\text{H}_{11}\text{NO}_3)]\text{Na}(\text{ClO}_4)_2$ . – Acta Chem. Scand. 47: 957–964.

The crystal structures of two copper(II) complexes with 2-amino-2-hydroxymethyl-1,3-propanediol (= tris, deprotonated form abbreviated  $\text{trisH}_{-1}$ ) as ligand were determined by the conventional single-crystal X-ray diffraction technique. The blue crystals of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  were refined to the final *R*-value of 0.032 for 3418 reflections. The compound crystallizes in monoclinic space group  $P2_1/c$  with four molecules in a cell of dimensions  $a = 10.246(2)$ ,  $b = 6.950(1)$ ,  $c = 21.313(3)$  Å,  $\beta = 110.54(1)^\circ$ ,  $V = 1421.2(4)$  Å<sup>3</sup>. The crystal structure of the blue perchlorate complex,  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$ , is triclinic with the following crystal data: space group  $P\bar{1}$ ,  $a = 9.946(1)$ ,  $b = 11.793(2)$ ,  $c = 8.853(2)$  Å,  $\alpha = 109.39(1)^\circ$ ,  $\beta = 112.72(1)^\circ$ ,  $\gamma = 82.02(1)^\circ$ ,  $V = 903.4(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.043$  for 4646 reflections.

Both complexes are mononuclear with two tris ligands coordinated to the metal ion via amino and hydroxymethyl groups in a *cis* arrangement. In the nitrate compound, the copper atom has an octahedral sphere of coordination with two pairs of oxygen and nitrogen atoms in the square plane and two weaker apical interactions with nitrate oxygen and a terminal hydroxymethyl oxygen (4 + 2). The perchlorate molecule has a similar, tetragonally distorted octahedral structure (4 + 2), but this time the apical bonds are formed with two terminal hydroxymethyl groups. The molecules form hydrogen-bonded dimers in both structures.

The thermal behavior of the complexes was studied by TG in air and nitrogen atmospheres.

The complex formation of tris (deprotonated form abbreviated  $\text{trisH}_{-1}$ ) with various transition metals in aqueous and non-aqueous solutions has been widely studied.<sup>1–6</sup>



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The early studies in solution already predicted the displacement of an alcoholic proton, as well as formation of different types of bridges involving deprotonated hydroxy groups.<sup>1–4</sup> The solid-state chemistry of tris is less well known. So far, the following crystal structures of tris–metal complexes have been published:  $[\text{Ni}(\text{tris})_2](\text{ClO}_4)_2$ ,<sup>7</sup>  $[\text{Cu}(\text{trisH}_{-1})_2]\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ,<sup>8</sup>  $[\text{Cu}(\text{trisH}_{-1})\text{Cl}]_4$ ,<sup>9</sup>  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]_2\text{Br}_2$ <sup>9</sup> and  $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$ .<sup>10</sup>

The aim of the present study was to obtain information about copper(II)-tris complexes containing different types of anions. Our previous article discussed the structures and thermal behavior of the basic *trans* complexes with three stages of crystalline water,  $[\text{Cu}(\text{trisH}_{-1})_2]$ ,  $[\text{Cu}(\text{trisH}_{-1})_2(\text{H}_2\text{O})]$  and  $[\text{Cu}(\text{trisH}_{-1})_2] \cdot 5\text{H}_2\text{O}$ .<sup>11</sup> In this article we report molecular and crystal structures and the thermal behavior of two new copper(II)-tris complexes,  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  and  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$ .

## Experimental

**Reagents.** All the reagents were Merck 'pro analyse' grade (unless otherwise indicated) and were used as obtained without further purification.

**Preparation of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$ .** The blue crystals of the nitrate complex were crystallized from water solution with a metal-ligand-anion stoichiometric ratio of 1 : 4 : 8. 0.01 mol of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 0.04 mol of tris and 0.06 mol of  $\text{NaNO}_3$  were dissolved in a minimum amount of distilled water in separate beakers with moderate heating. The complex was formed by adding copper solution to the tris solution and finally pouring the  $\text{NaNO}_3$  solution into the blue complex mixture. The solution was warmed for 15 min to promote the coordination

of nitrate oxygen to the complex, and then the solution was concentrated with a rotavapor to a volume of 10–15 cm<sup>3</sup>. Blue, rod-shaped crystals were formed within a few days at room temperature. Crystals were filtered, washed with a small amount of cold water, and dried in air.

**Preparation of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$ .** The light blue crystals of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$  were crystallized from solution with a metal-ligand-anion stoichiometric ratio 1 : 4 : 8. 0.01 mol of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Frederic Smith Chemical Co.) 0.04 mol of tris, and 0.06 mol of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (B.D.H. Ltd., laboratory reagent, 'low in chloride' grade) were dissolved in a minimum amount of distilled water in separate beakers. First, Cu(II) perchlorate solution was added to the tris solution, and then the sodium perchlorate solution was added to the complex solution. Excessive water was removed with a rotavapor until the final volume was ~10 cm<sup>3</sup>. The complex was crystallized by adding 40 cm<sup>3</sup> of methanol that had been saturated with anhydrous  $\text{NaClO}_4$ . Crystallization time may vary from a few days to weeks (at room temperature), but the process can be speeded up by a further addition of saturated  $\text{NaClO}_4$ -MeOH solution after a few days. Clear blue prismatic crystals were filtered, washed with water-methanol solution, and dried in air.

**Table 1.** Thermal decomposition of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  (1) and  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$  (2).

Compound	Lost in reaction	T/°C	Weight loss/%	
			Δ Obs.	Δ Theor.
Air atmosphere:				
1	Org.	150–292	53.1	—
	Org.	292–345	4.2	—
	Org. + NO <sub>3</sub>	345–420	21.2	—
	Total reaction → CuO	25–420	78.6	78.3
2	Org. + ClO <sub>4</sub>	157–289	42.6	—
	Org.	289–408	18.2	—
	O <sub>2</sub> (NaClO <sub>4</sub> )	408–440	6.5	6.1
	O <sub>2</sub> (NaClO <sub>4</sub> )	440–474	7.6	6.1
	Total reaction → CuO + NaCl	157–474	74.9	73.8
	NaCl	720–820	11.6	11.2
Total reaction → CuO	25–900	84.9	84.9	
Nitrogen atmosphere				
1	Org.	164–290	63.9	—
	Org.	290–390	4.5	—
	Org. total	164–390	68.4	65.8
	NO <sub>3</sub>	390–970	14.5	16.9
	Total reaction → Cu	25–970	83.1	82.7
2	Org. + ClO <sub>4</sub>	185–290	43.4	—
	Org.	290–333	4.8	—
	O <sub>2</sub> (NaClO <sub>4</sub> ) (+ org.)	333–384	7.4	6.1
	O <sub>2</sub> (NaClO <sub>4</sub> )	384–446	5.6	6.1
	Org.	446–720	10.7	—
	NaCl	720–840	11.9	11.2
	Total reaction → Cu	25–950	86.4	87.9

**Thermal analysis.** Thermal behavior of the complexes in air and nitrogen atmospheres was determined with a Perkin-Elmer thermogravimetric analyzer TGA7. The sample size of the nitrate compound was  $7.00 \pm 0.50$  mg; the amount of the perchlorate compound was smaller (3.20–3.30 mg) because of the risk of explosion. The crystalline samples were analyzed with heating rate  $2^\circ\text{C min}^{-1}$  and gas flow  $50 \text{ cm}^3 \text{ min}^{-1}$ . The temperature range with the nitrate complex was 25–500°C in air and 25–970°C in a nitrogen atmosphere. Both perchlorate curves were run from 25 to 950°C. When a nitrogen atmosphere was used, the equipment was flushed for 30–45 min with nitrogen before the start of the temperature program to remove oxygen from the oven. Observed and theoretical weight losses are reported in Table 1.

**X-Ray structure measurements.** Single-crystal X-ray measurements were carried out with an Enraf-Nonius CAD-4 diffractometer using  $\text{Mo } K_\alpha$  radiation. Crystals

were mounted on a glass fiber and measured in an air atmosphere. All relevant crystallographic information is given in Table 2. Accurate unit-cell parameters were obtained by a least-squares analysis of 25 centered reflections. The calculations were done on a MicroVAX 3100 computer using the MolEN<sup>12</sup> program supplied by Enraf-Nonius. Intensity data on each compound were collected by a  $\omega/2\theta$  scanning method, with two ( $\text{NO}_3^-$ ) or three ( $\text{ClO}_4^-$ ) standard reflections recorded for an intensity check every 60 min. Similarly, the orientation matrix was confirmed at an interval of 500 reflections. The data were corrected for linear decay, since a decay of 2.3% (72.8 h) was observed for the nitrate compound, and there was a total gain in intensity of 10.0% (91.3 h) during data collection for the perchlorate complex. In addition, Lorentz and polarization effects were taken into account, and absorption correction was done by the DIFABS<sup>13</sup> program.

The positions of the heavy atoms (Cu, Na, Cl) were solved by direct methods with the SHELXS-86<sup>14</sup>

Table 2. Crystallographic experimental data for  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  (1) and  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})\text{Na}(\text{ClO}_4)_2]$  (2).

Compound	1	2
Unit cell determination:		
Formula	$\text{CuO}_9\text{N}_3\text{C}_8\text{H}_{21}$	$\text{CuCl}_2\text{NaO}_{14}\text{N}_2\text{C}_8\text{H}_{21}$
Formula weight/g mol <sup>-1</sup>	366.81	526.70
Color	Blue	Blue
Crystal size/mm	$0.18 \times 0.15 \times 0.08$	$0.30 \times 0.18 \times 0.13$
<i>T</i> /°C	$21 \pm 1$	$21 \pm 1$
Reflections for lattice measurement	25	25
$\theta$ -Range for lattice measurement/°	8–13	9–13
<i>a</i> /Å	10.246(2)	9.946(1)
<i>b</i> /Å	6.950(1)	11.793(2)
<i>c</i> /Å	21.313(3)	8.853(2)
$\alpha$ /°	90.00	109.39(1)
$\beta$ /°	110.54(1)	112.72(1)
$\gamma$ /°	90.00	82.02(1)
<i>V</i> /Å <sup>3</sup>	1421.2(4)	903.4(2)
<i>Z</i>	4	2
<i>d</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.71	1.94
$\lambda(\text{Mo } K_\alpha)$ /Å	0.71073	0.71073
$\mu(\text{Mo } K_\alpha)$ /cm <sup>-1</sup>	15.86	16.05
<i>F</i> (000)	764	538
Space group	$P2_1/c$	$P\bar{1}$
Data collection and refinement:		
$\theta$ -Range for data collection/°	2–32.5	2–30
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan speed in $\omega$ /° min <sup>-1</sup>	0.92–5.50	0.59–5.50
Scan width in $\omega$ /°	$0.60 + 0.34 \tan \theta$	$0.50 + 0.34 \tan \theta$
No. of measured refls.	5502	5254
Reflections used in refinement $I > 3\sigma(I)$	3418	4646
Absorption correction (min./max.)	0.77/1.18	0.85/1.26
Max. shift/error	0.00	0.00
Max. in final $\Delta\rho/e \text{ \AA}^{-3}$	0.39	0.97
No. of parameters refined	190	253
<i>R</i>	0.032	0.043
<i>R</i> <sub>w</sub> <sup>a</sup>	0.035	0.055
$S = [\sum w(F_o - F_c)^2 / (n - m)]^{1/2}$	1.103	1.326

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

Table 3. Atomic positional parameters and equivalent isotropic temperature factors<sup>a</sup> with e.s.d.s in parentheses for [Cu(trisH<sub>-1</sub>)(tris)(NO<sub>3</sub>)] (1).

Atom	x	y	z	B <sub>eq</sub> /Å <sup>2</sup>
Cu100	0.31081(3)	0.72289(4)	0.49991(1)	1.389(4)
O111	0.4874(2)	0.6421(3)	0.57072(8)	1.77(3)
O112	0.4171(2)	1.0431(3)	0.55832(9)	2.37(4)
O113	0.3046(2)	0.6283(3)	0.71379(9)	3.13(4)
O121	0.3852(2)	0.6746(2)	0.43011(7)	1.48(3)
O122	0.1324(2)	1.1818(3)	0.36446(9)	2.35(4)
O123	0.0672(2)	0.8215(3)	0.24460(8)	2.66(4)
N111	0.2467(2)	0.7720(3)	0.57679(8)	1.52(3)
N121	0.1371(2)	0.8118(3)	0.42740(9)	1.55(3)
C111	0.4808(2)	0.6652(4)	0.6364(1)	1.81(4)
C112	0.3726(2)	0.8195(3)	0.6347(1)	1.48(4)
C113	0.4163(2)	1.0231(4)	0.6245(1)	2.02(4)
C114	0.3467(3)	0.8145(4)	0.7012(1)	2.41(5)
C121	0.2760(2)	0.6790(3)	0.3666(1)	1.55(4)
C122	0.1676(2)	0.8345(3)	0.3647(1)	1.33(3)
C123	0.2292(2)	1.0342(3)	0.3648(1)	1.63(4)
C124	0.0348(2)	0.8061(4)	0.3040(1)	1.81(4)

## Nitrate:

N1	0.1362(2)	0.3119(3)	0.5177(1)	2.12(4)
O1	0.1942(2)	0.3927(3)	0.48183(9)	2.85(4)
O2	0.1372(3)	0.3885(3)	0.5707(1)	4.33(5)
O3	0.0771(2)	0.1547(3)	0.5007(1)	3.00(4)

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

Table 4. Atomic positional parameters and equivalent isotropic temperature factors<sup>a</sup> with e.s.d.s in parentheses for [Cu(trisH<sub>-1</sub>)(tris)]Na(ClO<sub>4</sub>)<sub>2</sub> (2).

Atom	x	y	z	B <sub>eq</sub> /Å <sup>2</sup>
Cu100	0.02923(4)	0.28996(3)	0.38352(4)	1.097(7)
O111	0.1647(2)	0.4168(2)	0.5588(3)	1.33(4)
O112	0.1438(3)	0.2059(2)	0.6207(3)	2.22(5)
O113	0.4811(3)	0.0849(3)	0.4105(4)	2.84(6)
O121	-0.1241(2)	0.3787(2)	0.4664(3)	1.10(4)
O122	-0.1192(3)	0.3732(2)	0.1398(3)	2.05(5)
O123	-0.4040(4)	0.0782(3)	0.1545(4)	4.04(8)
N111	0.2074(3)	0.2091(2)	0.3417(3)	1.34(5)
N121	-0.1239(3)	0.1693(2)	0.2160(3)	1.48(5)
C111	0.3142(3)	0.3785(3)	0.5921(4)	1.39(6)
C112	0.3220(3)	0.2413(3)	0.5173(4)	1.21(5)
C113	0.2887(4)	0.1758(3)	0.6210(4)	1.96(6)
C114	0.4749(3)	0.2061(3)	0.5128(4)	1.78(6)
C121	-0.2562(3)	0.3116(3)	0.3716(4)	1.37(6)
C122	-0.2610(3)	0.2420(3)	0.1891(4)	1.41(6)
C123	-0.2608(4)	0.3267(3)	0.0891(4)	2.03(7)
C124	-0.3965(4)	0.1658(4)	0.0831(5)	2.58(8)
Na1	0.0416(2)	0.4078(1)	0.7628(2)	2.27(3)

<sup>a</sup> See Table 3.

program, and the remaining non-hydrogen atoms were located by a difference Fourier method. The refinement was done using full-matrix least-squares techniques with anisotropic temperature factors for all non-hydrogen atoms and isotropic thermal parameters with fixed  $B = 5.00 \text{ \AA}^2$  for all hydrogen atoms. The final  $R$ -values were  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.032$  for the nitrate complex and  $R = 0.043$  for the perchlorate complex. The corresponding weighted  $R_w$ -values (with unit weighting) were 0.035 for the nitrate and 0.055 for the perchlorate compound, respectively. All shift/error values were  $< 0.01$  in the last refinement cycle.

Scattering factors and real and imaginary dispersion corrections for atomic scattering factors were taken from Ref. 15. The figures were drawn with the SCHAKAL<sup>16</sup> program. The final atomic positional parameters and equivalent isotropic temperature factors are given in Tables 3 and 4. The relevant molecular bond distances and angles for the complexes and anions are reported in Tables 5 and 6. Tables of anisotropic thermal parameters,

Table 5. Bond distances (Å) with e.s.d.s in parentheses for [Cu(trisH<sub>-1</sub>)(tris)(NO<sub>3</sub>)] (1) and [Cu(trisH<sub>-1</sub>)(tris)]-Na(ClO<sub>4</sub>)<sub>2</sub> (2).

Bond distance/Å	1	2
Cu100-O111	1.987(1)	1.966(2)
Cu100-O112	2.596(2)	2.431(3)
Cu100-O121	1.925(2)	1.968(2)
Cu100-O122	—	2.518(3)
Cu100-O1(NO <sub>3</sub> )	2.553(2)	—
Cu100-N111	1.997(2)	1.997(3)
Cu100-N121	2.002(2)	2.000(2)
O111-C111	1.433(3)	1.437(4)
O112-C113	1.419(3)	1.434(5)
O113-C114	1.419(4)	1.423(4)
O121-C121	1.422(2)	1.433(4)
O122-C123	1.425(3)	1.431(5)
O123-C124	1.422(3)	1.402(7)
N111-C112	1.476(2)	1.490(3)
N121-C122	1.484(3)	1.487(4)
C111-C112	1.534(3)	1.535(4)
C112-C113	1.523(3)	1.525(6)
C112-C114	1.532(4)	1.532(5)
C121-C122	1.540(3)	1.536(4)
C122-C123	1.525(3)	1.539(6)
C122-C124	1.526(3)	1.518(5)

## Nitrate:

N1-O1	1.254(3)	—
N1-O2	1.246(3)	—
N1-O3	1.240(3)	—

## Perchlorates:

C11-O1	—	1.427(4)
C11-O2	—	1.421(5)
C11-O3	—	1.413(4)
C11-O4	—	1.402(5)
C12-O5	—	1.428(3)
C12-O6	—	1.409(4)
C12-O7	—	1.422(5)
C12-O8	—	1.444(5)

**Table 6.** Bond angles (in °) with e.s.d.s in parentheses for [Cu(trisH<sub>-1</sub>)(tris)(NO<sub>3</sub>)] (1) and [Cu(trisH<sub>-1</sub>)(tris)]-Na(ClO<sub>4</sub>)<sub>2</sub> (2).

Angle/°	1	2
O111–Cu100–O112	76.19(6)	77.23(9)
O111–Cu100–O121	92.04(7)	87.67(9)
O111–Cu100–O1(NO <sub>3</sub> )	96.52(6)	—
O111–Cu100–O122	—	106.67(9)
O111–Cu100–N111	84.22(7)	84.43(9)
O111–Cu100–N121	177.81(8)	174.1(1)
O112–Cu100–O1(NO <sub>3</sub> )	159.79(7)	—
O112–Cu100–O122	—	172.9(1)
N111–Cu100–N121	96.96(8)	101.4(1)
Cu100–O111–C111	111.6(1)	111.9(2)
Cu100–O121–C121	109.8(1)	108.6(2)
Cu100–O1–N1(NO <sub>3</sub> )	127.4(2)	—
Cu100–N111–C112	106.3(1)	102.9(2)
Cu100–N121–C122	108.5(1)	103.4(2)
O111–C111–C112	109.7(2)	109.7(2)
O112–C113–C112	109.8(2)	109.8(3)
O113–C114–C112	111.0(2)	111.7(3)
O121–C121–C122	111.1(2)	109.5(3)
O122–C123–C122	111.6(2)	112.5(3)
O123–C124–C122	109.1(2)	112.3(3)
N111–C112–C111	106.0(2)	106.4(2)
N111–C112–C113	107.6(2)	107.8(3)
N111–C112–C114	112.6(2)	111.9(3)
N121–C122–C121	106.2(2)	104.3(2)
N121–C122–C123	108.2(2)	108.9(3)
N121–C122–C124	110.0(2)	112.9(3)
C111–C112–C113	114.0(2)	112.4(3)
C111–C112–C114	108.7(2)	108.6(3)
C113–C112–C114	108.0(2)	109.8(3)
C121–C122–C123	110.2(2)	111.9(3)
C121–C122–C124	110.6(2)	112.2(3)
C123–C122–C124	111.4(2)	106.7(3)
Nitrate:		
O1–N1–O2	120.5(2)	—
O1–N1–O3	120.3(2)	—
Perchlorates:		
O1–Cl1–O2	—	108.1(3)
O1–Cl1–O3	—	111.0(3)
O1–Cl1–O4	—	107.8(3)
O5–Cl2–O6	—	112.9(2)
O5–Cl2–O7	—	111.2(2)
O5–Cl2–O8	—	107.8(3)

coordinates of hydrogen atoms, and listings of observed and calculated structure factors are available from the authors on request.

## Results and discussion

**Thermal analysis.** The thermal behavior of the complexes under study is summarized in Table 1. The thermal decomposition of [Cu(trisH<sub>-1</sub>)(tris)(NO<sub>3</sub>)] in an air atmosphere begins at 150°C with the decomposition of the organic part. The major degradation reaction occurring between 150 and 292°C consists of two unresolved processes with peaks in the DTG curve at 204 and 230°C.

The small intermediate step (292–345°C) is due to the organic ligand, and the final step (345–420°C) involves the simultaneous decomposition of the remaining organic residue and nitrate group. The final product in an air atmosphere is CuO.

In a nitrogen atmosphere the overall decomposition processes of the nitrate compound takes place at elevated temperature. The major degradation reactions of the organic part are poorly resolved, and the following step (290–390°C) is very broad and flat. The decomposition of the nitrate group is a slow and broad process which starts around 400°C and has a maximum in the DTG curve at ~800°C. The final residue in a nitrogen atmosphere is metallic copper.

The perchlorate compound contains two types of perchlorate groups after the organic part begins to decompose: those attracted to the copper cation, which decompose in a similar manner as in copper(II) perchlorate, with the production of CuO in air and metallic copper in nitrogen atmosphere, respectively, and those that behave like NaClO<sub>4</sub>, giving NaCl as a stable intermediate product in both atmospheres. The formula [Cu(trisH<sub>-1</sub>)(tris)]ClO<sub>4</sub>·NaClO<sub>4</sub> would better describe the thermal behavior of the perchlorate compound.

In the decomposition of the perchlorate compound in an air atmosphere, the main decomposition process (157–289°C) appears as two distinctive peaks in the DTG curve at 216 and 271°C. The first peak is due to the organic ligand and the second to the perchlorate groups associated with the copper ion. The following slow process (289–408°C) is due to the decomposition of the organic part; the subsequent sharp peaks indicate the decomposition of NaClO<sub>4</sub>, which leads to a mixture of CuO and NaCl as a stable intermediate product. The last phase in the TG curve at 720–820°C is the sublimation of NaCl leading to CuO as the final product at 900°C.

The decomposition reactions of the perchlorate compound in a nitrogen atmosphere are basically the same as in air. The major differences are that the organic part decomposes at a higher temperature, and the degradation of perchlorate groups is less fierce and occurs at a lower temperature than in an air atmosphere. As a result the TG curve is less resolved, and the NaClO<sub>4</sub> peaks and the broad organic peak have changed position. The intermediate phase is not so clear this time because copper(II) is reduced to metallic copper in several successive reactions (CuO → Cu<sub>2</sub>O → Cu), which are still occurring when NaCl begins to decompose. The end product in a nitrogen atmosphere is metallic copper.

The interpretation above is based on our earlier study of thermal behavior of three copper(II)–tris complexes<sup>11</sup> and on the TG runs of various alkali metal and copper(II) perchlorates in air and nitrogen atmospheres.

A comparison of the present thermogravimetric results with those published earlier<sup>11</sup> reveals certain differences. All the compounds discussed previously, [Cu(trisH<sub>-1</sub>)<sub>2</sub>], [Cu(trisH<sub>-1</sub>)<sub>2</sub>(H<sub>2</sub>O)], and [Cu(trisH<sub>-1</sub>)<sub>2</sub>]·5H<sub>2</sub>O, are mononuclear *trans* isomers with two deprotonated

ligands in square-planar or square-pyramidal coordination. In the TG curves of these *trans* complexes the main derivative peak (due to the decomposition of the organic part) is more symmetric, with the peak at 194–198°C in air and 209–217°C in a nitrogen atmosphere. With the present *cis* complexes,  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  and  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$ , the degradation of the organic part is more complex, resulting in a derivative peak with at least two observable maxima. The reason for this behavior may be the unequal coordination of deprotonated and nonprotonated ligands. Moreover, the coordination number is higher in the nitrate and perchlorate complexes, since the terminal hydroxymethyl groups participate in coordination (and are more strongly bonded to the structure). The existence of a hydrogen in the metal-coordinated hydroxy group also allows dimeric structure (see section on Crystal Structure), which may affect the thermal behavior of the nitrate and perchlorate compounds.

**Molecular structures.** The molecular structures of the nitrate and perchlorate complexes are presented in Fig. 1, and the representative bond lengths and angles are listed in Tables 5 and 6.

The  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  molecule is a mononuclear uncharged complex with two tris ligands (of which one is deprotonated) and one coordinated nitrate

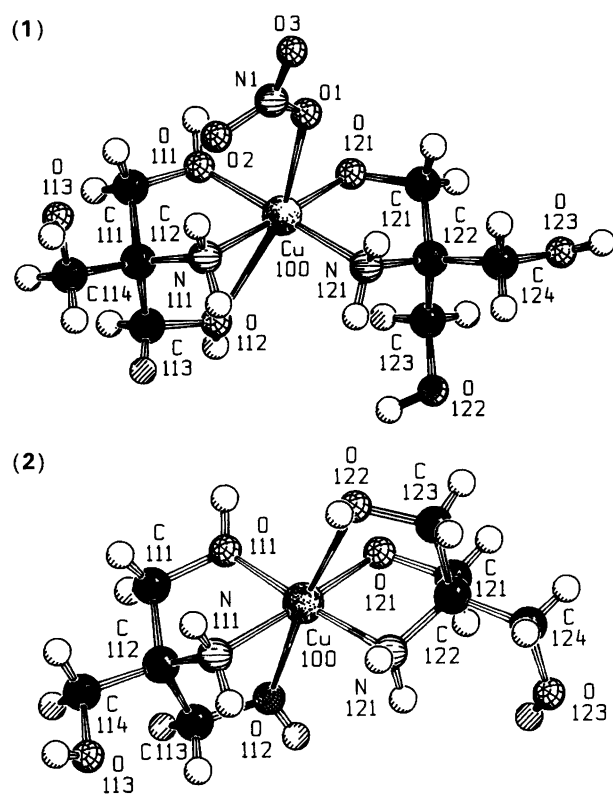


Fig. 1. SCHAKAL projections of the  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  molecule (1) and the cation complex of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]\text{Na}(\text{ClO}_4)_2$  (2).

group. The nonprotonated tris unit is coordinated to the copper ion via one amino and two hydroxymethyl groups, whereas the negatively charged  $\text{trisH}_{-1}$  ligand has coordination bonds to copper only by amino nitrogen and deprotonated hydroxy oxygen. The coordination sphere is a tetragonally distorted octahedron with four shorter bonds in a square plane and two longer bonds perpendicular to this plane. In the basal plane there are two pairs of Cu–O and Cu–N bonds (in a *cis* arrangement), all of which lie in the range 1.92–2.01 Å. The two apical bonds involve coordinated nitrate oxygen and one terminal hydroxymethyl group from the nonprotonated side of the molecule. These apical bond lengths are 2.553(2) and 2.596(2) Å.

The five-membered chelate rings are almost planar, with C112 deviating from the Cu100–O111–N111–C111 plane by  $-0.649(2)$  Å and C122 from the Cu100–O121–N121–C121 plane by  $-0.511(2)$  Å. The corresponding distances between the equatorial and axial hydroxymethyl carbons and these planes are  $-2.146(3)$  Å (C113) and  $-0.424(3)$  Å (C114) from the Cu100–O111–N111–C111 plane and  $-2.034(2)$  Å (C123) and  $-0.008(3)$  Å (C124) from the Cu100–O121–N121–C121 plane. The dihedral angle between the two planes is  $175.9(5)^\circ$ . The N–O bond lengths of the nitrate ion [N1–O1 1.254(3) Å, N1–O2 1.246(3) Å and N1–O3 1.240(3) Å] are very similar, indicating that the nitrate ion is only weakly bonded to the copper(II) ion.<sup>17</sup> The observed bond lengths and angles are consistent with the copper-tris structures<sup>7–11</sup> published earlier, as well as with the nitrate complexes of the same type of amino alcohols.<sup>17,18</sup>

The perchlorate molecule is the same type of complex as the nitrate molecule described above, except that it has a unit charge +1 and the deprotonated tris ligand, like the nonprotonated ligand, forms three coordination bonds with copper. In the  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]^+$  molecule the coordination sphere is a tetragonally distorted octahedron with Cu–O and Cu–N bonds in the plane ranging from 1.96 to 2.00 Å. The apical interactions are caused by two axial hydroxymethyl groups which are bent toward the copper(II) ion from the opposite sides of the plane. The bond distances in apical direction are 2.431(3) Å (Cu100–O112) and 2.518(3) Å (Cu100–O122). The five-membered chelate rings are *envelope* conformers with C112 deviating from the Cu100–O111–N111–C111 plane by  $-0.690(3)$  Å. The corresponding deviation of C122 on the other side is 0.712(3) Å. The distances of equatorial and axial hydroxymethyl carbons from the chelate planes are  $-2.164(4)$  Å (C113),  $-0.529(4)$  Å (C114), 2.193(4) Å (C123) and 0.686(4) Å (C124). All the bond lengths and angles summarized in Tables 5 and 6 are in good agreement with the previously reported structures of perchlorate-containing metal-tris complexes.<sup>7,8</sup>

Both complex molecules have two optical isomers that are mirror images of each other. Since the syntheses are not stereoselective, both isomers are found in equal proportions in the crystal structures, and the compounds are not optically active.

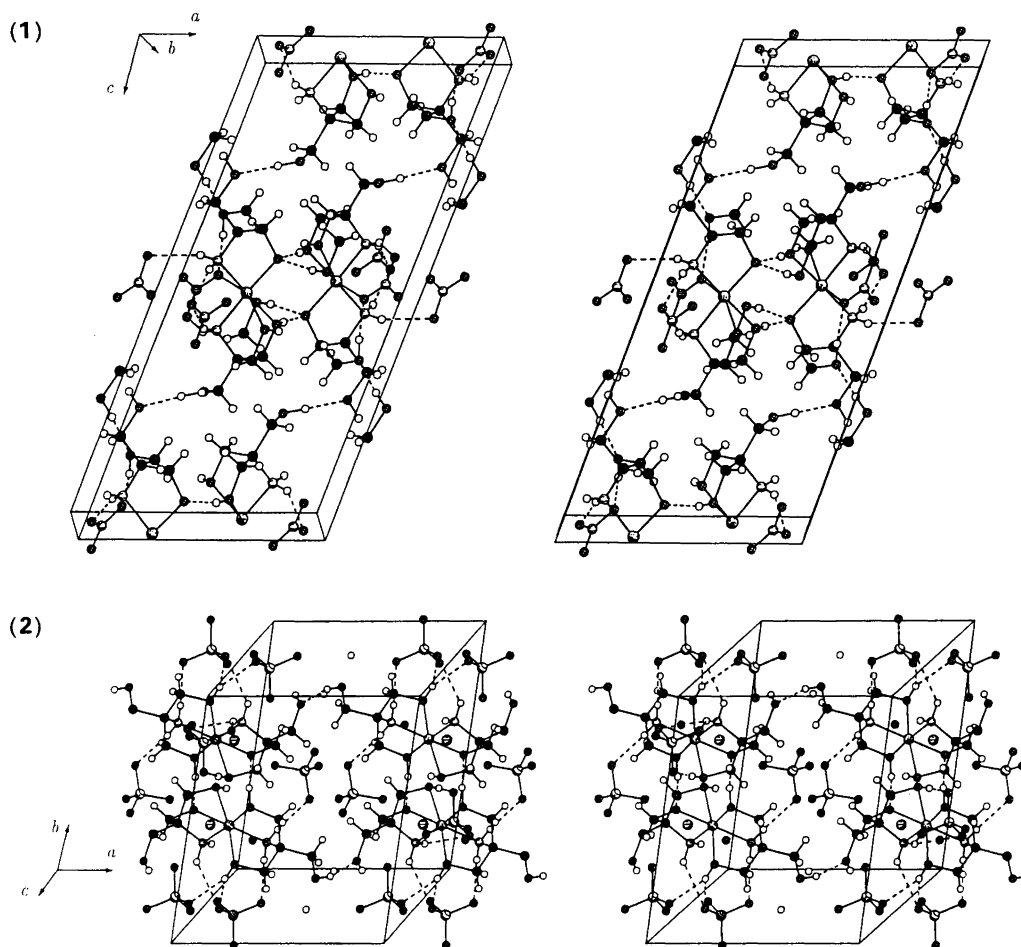


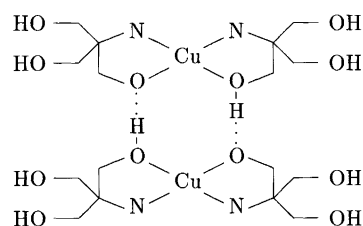
Fig. 2. Stereoscopic representations of hydrogen bonding for  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})(\text{NO}_3)]$  (1) and  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})\text{Na}(\text{ClO}_4)_2]$  (2). Hydrogen bonds are indicated by dashed lines.

**Crystal structures.** Stereoscopic projections of the crystal structures and the hydrogen-bonding framework for both compounds are presented in Fig. 2.

Common to both of these structures is the formation of hydrogen-bonded dimers. Because of the *cis* arrangement and the existence of a hydrogen in every other metal-bonded hydroxymethyl group, the monomer is able to form hydrogen-bonded associates with another mononuclear unit. The dimer is not coplanar; on the contrary, when one looks towards the dimer from one end the monomer units appear to form a step-like structure with an inversion center in the middle of the eight-membered ring. The hydrogen bonds in the dimer structure are strong, with donor-acceptor distances of 2.46–2.56 Å for the  $\text{O}111 \cdots \text{O}121$  contacts.

In the dimer structure of the nitrate compound the nitrate groups are oriented towards one of the monomer units, while the apical bonds with hydroxymethyl groups are directed outwards. The corresponding situation in the perchlorate complex dimer is that the apical bonds of the deprotonated ligands are facing one of the monomers, while the apical bonds of normal tris point outside the

dimer. The simplified scheme of the dimer structure is shown below.



The occurrence of H-bonded polynuclear complexes of this kind has earlier been reported by Masi *et al.*<sup>9</sup>

The crystal structure of the nitrate compound is built up from uncharged molecules which are connected into a three-dimensional framework by extensive hydrogen bonding by OH,  $\text{NH}_2$ , and coordinated nitrate groups. The dimers are polymerized along the *b*-axis by hydrogen bonds between metal-coordinated deprotonated oxygen and apical hydroxymethyl groups of the adjacent

dimer. Coordinated nitrate groups interact mainly with amino hydrogens; first, nitrate forms an intramolecular hydrogen bond with amino hydrogen of the same molecule; then the nitrate groups connect the dimers along the *a*- and *b*-axes by hydrogen bonds with amino hydrogens of the neighboring dimers. The other interactions are hydrogen bonds between noncoordinated terminal hydroxymethyl groups or weak van der Waals forces between  $\text{CH}_2 \cdots \text{CH}_2$  groups.

The crystal structure of the perchlorate compound consists of charged units of  $[\text{Cu}(\text{trisH}_{-1})(\text{tris})]^+$ ,  $\text{Na}^+$  and  $\text{ClO}_4^-$ , so that the interactions are more electrostatic in nature. The hydrogen bonding in this structure occurs primarily between perchlorate oxygens and OH or  $\text{NH}_2$  hydrogens of the molecules, because the interactions between molecules are prevented by perchlorate layers along the crystallographic ( $\bar{1}01$ ) plane. In addition to the hydrogen bond involved in dimerization there is only one other intermolecular hydrogen bond joining the adjacent dimers by noncoordinated terminal hydroxymethyl groups  $\text{O}113 \cdots \text{O}123'$ . Correspondingly, all perchlorate anions are bonded by at least one hydrogen bond to the neighboring dimer. The  $\text{Na}^+$  ions are located in the same *bc*-plane as copper(II) and form a parallelepiped where two copper atoms and two sodium atoms are at the corners. The interatomic distances between these metal ions are 3.138(2) and 4.067(2) Å (Na–Cu), 4.7410(5) Å (Cu–Cu) and 5.505(3) Å (Na–Na), respectively. Otherwise the sodium ions are octahedrally surrounded by three perchlorate oxygens and three oxygens of dimeric hydroxymethyl groups, with distances falling in the range 2.56–2.62 Å.

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