Redetermination of the Crystal Structure of the Tetrameric Chromium(III) Ammine Complex $[Cr_4(NH_3)_{12}(OH)_6]Cl_6 \cdot 4H_2O$ at 110 K

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Recent correlations between structural properties and magnetic interactions in oligomeric hydroxo-bridged chromium(III) complexes have called upon more accurate knowledge of the position of the hydrogen atoms in the hydroxo bridges[1,2] than normally available from room temperature data. The title tetrameric chromium(III) ammine complex, the so-called "rhodoso" chloride, was among the first of this class of compounds to be characterized structurally.[3] This work was done using film data with Cu-radiation (1012 refl.) and with crystalline material which was not of the best quality. Since this publication the methods of data collection have been greatly improved as has the method of synthesis for the compound,[2] so it seemed reasonable to us to redetermine the structure and in particular to obtain accurate information about the hydrogen atoms.

Intensity data were collected on Enraf-Nonius Cad 4 diffractometer at 110(1) K and the XRAY 76[4] system of programs was used in the calculations. Table 1 gives the crystal data, information on data collection and refinement, and Table 2 gives the resulting parameters.

The morphology and all major features of the earlier determined structure were found to be correct. However, significantly more accurate values for bond lengths and angles have been obtained (Table 3). The Cr–N and Cr–O are "normal",[5,7] and the distances involving hydrogen are also as would be expected. The rhodoso ion is placed to have a symmetry center and shown in Figs. 1 and 2. The differences for the hydrogen bonds in the three groups NH_3, H_2O and OH may not be significant.

The 8-membered ring Cr_4O_4 in the rhodoso ion has alternating Cr and O atoms (Figs. 1 and 2) and for the best plane through the 4 oxygen and the Cr1 and the Cr1′ the maximum deviation is 0.003 Å. The Cr2 lies a distance of 0.35 Å out of this plane and is probably stabilized in this position by hydrogen bonding between a hydrogen of a NH_3 group in the Cr2 octahedron and O1 in the double bridge. The H···O distance is 1.930 Å and the N–O distance is 2.885 Å. In

Table 1. Crystal data, data collection and reduction characteristics.[a]

$[Cr_4(NH_3)_{12}(OH)_6]Cl_6.4H_2O$	Space group $P\,2_1/c$ (No.14)
110(1) K (CAD 4)	room temp. (Guinier)
a=8.243(2) Å	a=8.260(2) Å
b=17.916(2) Å	b=17.953(2) Å
c=13.650(3) Å	c=13.735(2) Å
β=129.84(2)°	β=129.99(4)°
V=1547.7 Å^3	
F(000) 824	
Z=2	
D_m=1.69 D_x=1.763 g cm^{-3}	
Crystal dimensions 0.09×0.09×0.29 mm^3	
μ(Mo$K\alpha$)=19.1 cm^{-1}	
$0.05<\sin\theta/\lambda<0.79$	
Total measured refl. 7663	
Indep. refl. 5839 including 1701 LT ($F^2<2\sigma(F^2)$) in calculations	
Number of variables 245	
R= 0.028 R_w= 0.038	
1/weight $\sigma^2(F)-0.025\|F\|+0.0013\,F^2$	

[a] No correction for absorption was applied. Corrections for anomalous dispersion and scattering factors for Cr(0) were taken from (Ref. 5), scattering factors for the other atoms from XRAY 76.[4]

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Table 2. Fractional coordinates for the complex. Tables of anisotropic temperature factors and observed and calculated structure factors are available upon request.

Atom	X	Y	Z
Cr1	.02337(04)	.02912(01)	.10830(02)
Cr2	.72274(04)	.14932(01)	.82997(02)
Cl1	.43385(06)	.14352(02)	.01373(04)
Cl2	.05706(07)	.23252(02)	.66482(04)
Cl3	.12066(07)	.07812(03)	.46314(04)
N1	.83140(23)	.02199(09)	.15643(14)
N2	.24970(24)	.09025(09)	.27285(14)
N3	.55017(25)	.18090(09)	.63898(14)
N4	.58438(25)	.23560(09)	.85615(16)
N5	.96403(24)	.22183(09)	.87880(16)
N6	.47779(24)	.08201(09)	.78429(14)
O1	.19073(18)	.02515(07)	.05182(11)
O2	.84141(19)	.06571(06)	.80119(12)
O3	.88535(19)	.12147(07)	.00970(12)
O1W	.79638(26)	.08618(09)	.58401(15)
O2W	.63594(23)	.11015(08)	.29941(14)
H1N1	.8948(42)	.0269(14)	.2333(28)
H2N1	.7460(38)	.0589(13)	.1201(23)
H3N1	.7726(40)	.0184(14)	.1350(25)
H1N2	.2603(44)	.0759(16)	.3323(27)
H2N2	.3759(52)	.0864(17)	.2965(29)
H3N2	.2246(45)	.1385(17)	.2662(27)
H1N3	.6045(53)	.3369(19)	.1076(32)
H2N3	.4229(47)	.3378(17)	.0847(28)
H3N3	.5371(32)	.2688(13)	.1258(20)
H1N4	.6125(46)	.2232(19)	.3481(28)
H2N4	.4490(41)	.2672(14)	.3057(24)
H3N4	.6104(42)	.2698(17)	.4243(28)
H1N5	.9413(51)	.2621(20)	.3145(33)
H2N5	.9740(47)	.2433(20)	.4274(31)
H3N5	.0751(46)	.3063(18)	.4095(27)
H1N6	.5409(38)	.4574(14)	.3158(23)
H2N6	.3697(43)	.4265(15)	.2039(26)
H3N6	.4335(36)	.4032(13)	.3236(22)
H10	.2245(47)	.0609(17)	.0455(28)
H20	.8420(43)	.4305(15)	.2532(27)
H30	.9283(42)	.1526(14)	.0524(26)
H1W1	.8794(49)	.3800(20)	.0934(28)
H2W1	.8010(52)	.4436(19)	.0447(32)
H1W2	.7654(44)	.0999(14)	.3445(25)
H2W2	.6034(48)	.1147(18)	.2325(31)

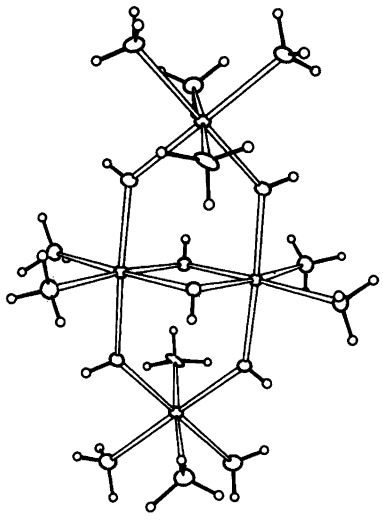

Fig. 1. The rhodoso ion. Ellipsoids include 50 % probability.

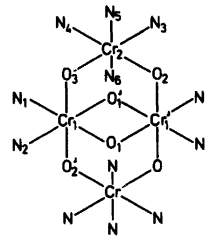

Fig. 2. Numbering scheme for the rhodoso ion.

rhodoso bromide dihydrate[8] this N–O distance was 2.83 Å. A similar feature was found in the trinuclear Cr-complex ion referred to above.[2] The difference between this latter ion, $Cr_3(NH_3)_{10}(OH)_4^{5+}$, and the rhodoso ion is that one of the $-(OH)Cr(NH_3)_4(OH)-$ fragments of the rhodoso ion has been replaced by 2 NH_3. An O–H–O of analogous character to the NH–O is found in the other trinuclear complex ion, $Cr_3(C_6H_{15}N_5)_3(OH)_5^{4+}$ (Ref. 9).

In the present structure the hydrogen bond H1–O1 in the double bridge forms an angle of 49.3° with the plane Cr1–O1–Cr1′ whereas the other corresponding angles for the H–O bonds are small.

The chloride-water net surrounding the cations shows only small changes in contact distances (0.05 Å) from the earlier investigation. The hydrogen bond distances in this net and from the rhodoso ion are included in Table 4. As in the earlier investigations O1 and O3 have hydrogen bonds to Cl1 and Cl2 and O2 to Ow2. Each water molecule forms 2 hydrogen bonds to chlorine and has 2 contacts with the complex ion through a hydrogen of OH or NH_3. Each chlorine atom has contacts through 2 hydrogen bonds.

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Table 3. Bond lengths and selected contact distances in Å and angles in degrees for the complex ion and for the water molecules.

Cr1–O1	1.966(2)	Cr2–O2	1.962(2)	
Cr1–O1	1.973(1)	Cr2–O3	1.962(2)	
Cr1–O2	1.972(1)	Cr2–N3	2.095(2)	
Cr1–O3	1.970(1)	Cr2–N4	2.083(2)	
Cr1–N1	2.070(2)	Cr2–N5	2.095(2)	
Cr1–N2	2.087(1)	Cr2–N6	2.075(2)	
O–H	0.66–0.73			
Ow–H	0.77–0.88			
N–H	0.80–0.91			
O1–H16N	2.12(2)	O1–N6	2.885(2)	
$O_1Cr_1O_1'$	84.38(7)	other Cr1 octahedron angles		86.67–94.19
$O_2Cr_2O_3$	91.57(6)	other Cr2 octahedron angles		87.05–92.50
Cr1O2Cr1'	95.61(6)	O–H angle with this plane		49.3
Cr1'O2Cr2	133.36(9)	O–H angle with this plane		2.7
Cr1O3Cr2	134.47(8)	O–H angle with this plane		17.7

Table 4. Selected intermolecular hydrogen bonds in Å with d(A···B) less than 3.3 Å.

A–H···B	d(H···B)	d(A···B)
O1–H1O···Cl1	2.51(4)	3.181(2)
O2–H2O···O1w	2.11(4)	2.765(3)
O3–H3O···Cl2	2.37(2)	3.080(1)
N2–H22N···O2w	2.16(5)	2.986(3)
N3–H13N···O1w	2.27(5)	3.084(3)
N4–H14N···O2w	2.18(4)	2.972(2)
O1w–H11w···Cl2	2.31(3)	3.110(2)
O1w–H21w···Cl3	2.52(3)	3.179(2)
O2w–H22w···Cl1	2.40(4)	3.164(2)
O2w–H12w···Cl3	2.52(3)	3.179(2)

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