

The Crystal Structure of Di- μ -hydroxotetrakis- μ -hydroxobis-(tetraminechromium(III)) bis(diamminechromium(III)) Bromide Dihydrate

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The crystal structure of rhodoso bromide dihydrate $[\text{Cr}_4(\text{OH})_6(\text{NH}_3)_{12}]\text{Br}_6 \cdot 2\text{H}_2\text{O}$ has been determined by means of 3-dimensional X-ray methods. Space group *Pbca*. $a=22.58 \text{ \AA}$, $b=13.93 \text{ \AA}$, $c=10.00 \text{ \AA}$.

The centrosymmetrical complex found is analogous to that of rhodoso chloride tetrahydrate, an eight-membered ring of alternating chromium and hydroxo groups.

In the octahedrons surrounding the chromium atoms the measured distances are

Cr—O	1.95—2.00 \AA
Cr—N	2.07—2.13 \AA

The octahedral angles are only slightly distorted. The angles Cr—O—Cr in the 8-ring are 134° and 135° and in the double bridge 96° . Cr—Cr distances 2.91 \AA , 3.61 \AA , 3.63 \AA , and 6.62 \AA .

The bromine-water net surrounding the complex differs from the chloride tetrahydrate. The hydroxo groups have no water contact, a single bromine bridges two complexes, and there are halogen ammonia contacts. The shortest distances between bromine and water molecules and between bromine and bromine are:

Br—H ₂ O	3.34 \AA	Br—Br	4.23 \AA
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As a part of the structural study of the polynuclear Cr(III) and Co(III) complexes of the formula $[\text{Me}_2(\text{OH})_3(\text{NH}_3)_2]\text{X}_3$ the halogenides of the ion $[\text{Cr}_4(\text{OH})_6(\text{NH}_3)_{12}]^{6+}$ have been taken up.

The tetrahydrates of chloride, bromide, and iodide were originally synthesized by Jørgensen,¹ and in this paper Jørgensen's name for the complex ion, rhodoso, will be used.

From the description in Jørgensen's paper the hydrates mentioned above could be expected to be isomorphous. It has been possible to isolate 2 tetra-

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hydrates of the chloride, 1 dihydrate and 1 tetrahydrate of the bromide, and 1 tetrahydrate of the iodide. However, powder diagrams show that only the tetrahydrates of the bromide and iodide are isomorphous.

The recent structural investigation² of one of the chloride tetrahydrates showed that the rhodoso ion is centrosymmetrical and has 4 chromium atoms in a plane forming a rhomboid. The 6 hydroxo ligands form bridges between the octahedrally surrounded chromium atoms. 4 hydroxo groups are nearly coplanar with the chromium atoms and form together with these an eight-membered ring with alternating chromium and hydroxo groups. Two hydroxo groups form a double bridge over the eight-ring forming a planar four-ring together with the 2 chromium atoms in the shortest distance. These two chromium atoms have 2 NH_3 in the *cis* position. The two other chromium atoms have 2 hydroxo groups in the *cis* position. This structure was shown to be in excellent agreement with the bridge cleaving experiments of Andersen and Schäffer.³

The structure investigation on the bromide dihydrate was taken up simultaneously with that of the chloride. The results given below reproduce the structure of the rhodoso ion in detail, whereas the characteristics of the two halogenide-water nets are different.

EXPERIMENTAL

The crystals of rhodoso bromide used in the single crystal analyses were selected from preparations of Schäffer.³ They were prepared from a solution of rhodoso chloride by precipitation with ammonium bromide and reprecipitated. The chemical analyses of the sample from which the crystals were taken: * Found: Cr 20.97; N 16.47; Br 46.63. Calc.: Cr 20.20; N 16.32; Br 46.53. The sample contains a small amount of chloride (0.5 %), which explains that the analytical figures are a little high. Preparations from a later synthesis excluding chloride have now appeared³ showing the same powder diagram. The dihydrate is prepared from a saturated solution at 30° by reprecipitation with ammonium bromide. The tetrahydrate is precipitated from a dilute solution after standing at 0° over NaBr in a desiccator. The isomorphous iodide was prepared after Jørgensen¹ from a solution of the chloride by precipitation with NH_4I . The 2 tetrahydrates of the chloride² are not isomorphous as mentioned above.

Rhodoso bromide dihydrate shows no loss in weight when dried over P_2O_5 . The orthorhombic diamond-shaped crystals are crimson and show extinction along the diagonals. The diagonal through the acute angle is taken as *b* and that through the obtuse angle as *c*. The crystals are plates perpendicular to the long *a* axis. The density as measured by flotation is 2.17 g/ml.

X-Ray technique. The cell dimensions were determined from Guinier powder diagrams using Cu-radiation and Si as internal standard. The lattice constants were refined by a random search method⁴ applied on the $\sin^2\theta$ -values from the powder diagram. The mean deviation between calculated and observed $\sin^2\theta$ -values was 0.5×10^{-5} . Weissenberg, oscillation and precession diagrams were taken using Cu-radiation and the multiple film technique. The data from the crystal rotated around the *c* axis were mainly used in projections and for scaling. Only the data from the crystal rotated around the *b* axis were used in the 3-dimensional refining of the structure (8 layerlines and 1300 of 1710 possible reflections registered). The dimensions of the crystal were $0.12 \times 0.24 \times 0.19$ mm. Absorption corrections were omitted.

Computing methods. The least squares refinement⁵ was carried out on I.B.M. 7090. All other programs were carried out on Gier. Apart from the Fourier program⁶ the

* I am much indebted to H. Buchwald for carrying out the analysis.

programs used were in Algol 3 and 4. The perspective drawing program was written by J. Steensgaard Madsen, the program of 3-dimensional Buerger Min. function, plotting programs, and refinement of cell dimensions by B. Svejgaard, Department of Numerical Analysis.

UNIT CELL AND SPACE GROUP

The lattice constants are

$$a = 22.58_1 \text{ \AA} \quad b = 13.93_1 \text{ \AA} \quad c = 10.00_1 \text{ \AA}$$

The observed density is 2.17 g/ml, the calculated density 2.17 g/ml. $Z=4$.

The diffraction symmetry is mmm . The systematic absence of the reflections $0kl$ for $k=2n$, $hk0$ for $h \neq 2n$ indicated that the space group was $Pbca$ assuming that this absence was not accidental.

The general position is

$$x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, z;$$

$$x, \frac{1}{2}-y, \frac{1}{2}+z; \bar{x}, \frac{1}{2}+y, \frac{1}{2}+z; \frac{1}{2}+x, y, \frac{1}{2}-z; \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z.$$

(The atoms in the following are marked: atoms having the same first indices belong to the same set of equivalent positions. The second indices follow the sequence of the positions given above).

STRUCTURE DETERMINATION

As the space group has an 8 fold position and as there are 4 formula units with 4 Cr atoms each in the unit cell, 2 of the Cr atoms have to be connected in a relatively short distance by a symmetry element. As the complex found in the chloride has a symmetry center, the complex was assumed to be placed centrosymmetrically. The long axis (8 Å) of the assumed complex had to be placed rather close to the $a-b$ plane on account of the dimensions of the unit cell.

Table 1. Atomic co-ordinates and standard deviations, expressed as fractions of the cell edges, and the isotropic thermal parameters in Å².

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
Cr ₁₁	0.0302	0.0368	0.8808	0.0001	0.0003	0.0003	1.51	0.06
Cr ₃₁	0.1304	0.9674	0.1437	0.0001	0.0004	0.0003	1.71	0.07
O ₁₁	0.0063	0.0853	0.0605	0.0006	0.0014	0.0014	1.66	0.28
O ₂₁	0.0483	0.9328	0.1943	0.0006	0.0015	0.0015	1.93	0.29
O ₃₁	0.1059	0.0036	0.9639	0.0006	0.0013	0.0013	1.37	0.27
N ₁₁	0.0590	0.9860	0.6932	0.0009	0.0020	0.0022	2.90	0.45
N ₂₁	0.0622	0.1733	0.8278	0.0008	0.0019	0.0019	2.14	0.37
N ₃₁	0.1592	0.9358	0.3415	0.0010	0.0022	0.0023	3.43	0.49
N ₄₁	0.2175	0.9994	0.0858	0.0009	0.0020	0.0023	3.08	0.47
N ₅₁	0.1164	0.1099	0.1930	0.0009	0.0021	0.0020	2.76	0.42
N ₆₁	0.3530	0.1754	0.5917	0.0010	0.0021	0.0023	3.28	0.49
Br ₁₁	0.1593	0.1601	0.5400	0.0001	0.0003	0.0003	3.39	0.07
Br ₂₁	0.4700	0.1890	0.9647	0.0001	0.0003	0.0002	3.05	0.06
Br ₃₁	0.3048	0.1342	0.2754	0.0001	0.0003	0.0003	3.47	0.07
O ₁₁ ^w	0.2196	0.1554	0.8452	0.0010	0.0020	0.0024	5.31	0.56

RHODOSO BROMIDE DIHYDRATE

Table 2. Continued.

Table with multiple columns (h, k, l, Fo, Fo) and rows of numerical data, appearing as a grid of values.

coordinated to diamino tetrahydroxo groups and to tetradiamino dihydroxo groups. The same feature is found in the analogous ethylene derivative $[\text{Cr}_4(\text{OH})_6(\text{en})_6]^{6+}$.⁷ This explains the results of chemical cleavage experiments on both complexes.³

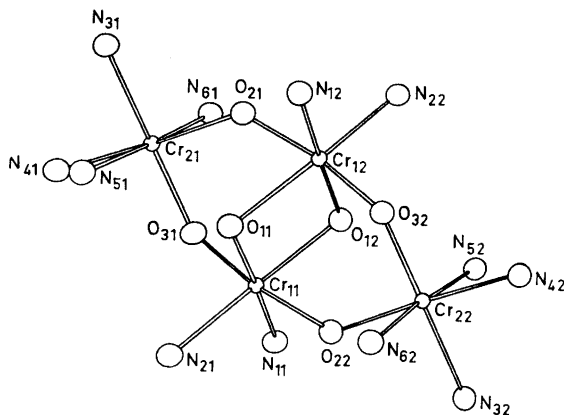


Fig. 1. The complex ion $[\text{Cr}_4(\text{OH})_6(\text{NH}_3)_{12}]^{6+}$. Indices p. 277.

Table 3. Calculated distances in Å within the complex. Chromium distances greater than 3.5 Å are included, other distances of this order are not given. (Standard deviations in brackets).

$\text{Cr}_{11}-\text{O}_{11}$	1.97(1)	$\text{Cr}_{21}-\text{N}_{11}$	4.53(2)
$\text{Cr}_{11}-\text{O}_{12}$	1.99(1)	$\text{Cr}_{21}-\text{N}_{12}$	4.77(2)
$\text{Cr}_{11}-\text{O}_{22}$	1.97(1)	$\text{Cr}_{21}-\text{N}_{21}$	4.79(2)
$\text{Cr}_{11}-\text{O}_{31}$	1.95(1)	$\text{Cr}_{21}-\text{N}_{22}$	4.62(2)
$\text{Cr}_{11}-\text{N}_{11}$	2.11(2)	$\text{O}_{11}-\text{O}_{12}$	2.68(2)
$\text{Cr}_{11}-\text{N}_{21}$	2.10(2)	$\text{O}_{11}-\text{O}_{21}$	2.84(2)
$\text{Cr}_{21}-\text{O}_{21}$	1.98(1)	$\text{O}_{11}-\text{O}_{22}$	2.68(2)
$\text{Cr}_{21}-\text{O}_{31}$	1.94(1)	$\text{O}_{11}-\text{O}_{31}$	2.83(2)
$\text{Cr}_{21}-\text{N}_{31}$	2.12(2)	$\text{O}_{11}-\text{O}_{32}$	2.69(2)
$\text{Cr}_{21}-\text{N}_{41}$	2.09(2)	$\text{O}_{11}-\text{N}_{12}$	2.91(2)
$\text{Cr}_{21}-\text{N}_{51}$	2.09(3)	$\text{O}_{11}-\text{N}_{21}$	3.03(2)
$\text{Cr}_{21}-\text{N}_{61}$	2.06(2)	$\text{O}_{11}-\text{N}_{62}$	2.83(2)
$\text{Cr}_{11}-\text{Cr}_{12}$	2.93(0)	$\text{O}_{21}-\text{O}_{31}$	2.82(2)
$\text{Cr}_{11}-\text{Cr}_{21}$	3.60(0)	$\text{O}_{21}-\text{N}_{12}$	2.90(2)
$\text{Cr}_{11}-\text{Cr}_{22}$	3.63(0)	$\text{O}_{21}-\text{N}_{22}$	2.89(2)
$\text{Cr}_{11}-\text{O}_{31}$	3.47(1)	$\text{O}_{21}-\text{N}_{31}$	2.90(2)
$\text{Cr}_{11}-\text{O}_{32}$	3.48(1)	$\text{O}_{21}-\text{N}_{51}$	2.87(3)
$\text{Cr}_{11}-\text{N}_{31}$	5.62(2)	$\text{O}_{21}-\text{N}_{61}$	2.90(3)
$\text{Cr}_{11}-\text{N}_{32}$	4.83(2)	$\text{O}_{31}-\text{N}_{11}$	2.90(2)
$\text{Cr}_{11}-\text{N}_{41}$	4.72(2)	$\text{O}_{31}-\text{N}_{21}$	2.91(2)
$\text{Cr}_{11}-\text{N}_{42}$	5.62(2)	$\text{O}_{31}-\text{N}_{41}$	2.79(2)
$\text{Cr}_{11}-\text{N}_{51}$	4.48(2)	$\text{O}_{31}-\text{N}_{51}$	2.95(3)
$\text{Cr}_{11}-\text{N}_{62}$	4.44(2)	$\text{O}_{31}-\text{N}_{61}$	2.73(2)
$\text{Cr}_{11}-\text{N}_{61}$	3.81(2)	$\text{N}_{31}-\text{N}_{41}$	3.00(3)
$\text{Cr}_{11}-\text{N}_{62}$	3.96(2)	$\text{N}_{31}-\text{N}_{61}$	2.95(3)
$\text{Cr}_{21}-\text{Cr}_{22}$	6.61(0)	$\text{N}_{31}-\text{N}_{51}$	3.00(3)
$\text{Cr}_{21}-\text{O}_{11}$	3.77(1)	$\text{N}_{41}-\text{N}_{51}$	2.91(3)
$\text{Cr}_{21}-\text{O}_{12}$	3.35(1)	$\text{N}_{41}-\text{N}_{61}$	2.95(3)

Distances and angles within the complex are given in Tables 3 and 4.

The four chromium atoms lie in a plane forming an eight-membered ring with alternating hydroxo groups (Fig. 1). The hydroxo groups are slightly out of the plane (0.18 Å).

Table 4. Angles in degrees within the complex.

O ₁₁ -Cr ₁₁ -O ₁₂	84	O ₂₁ -Cr ₂₁ -O ₃₁	92
O ₁₁ -Cr ₁₁ -O ₂₂	85	O ₂₁ -Cr ₂₁ -N ₂₁	89
O ₁₁ -Cr ₁₁ -O ₃₁	92	O ₂₁ -Cr ₂₁ -N ₅₁	89
O ₁₁ -Cr ₁₁ -N ₂₁	96	O ₂₁ -Cr ₂₁ -N ₄₁	92
O ₁₂ -Cr ₁₁ -O ₂₂	92	O ₃₁ -Cr ₂₁ -N ₄₁	87
O ₁₂ -Cr ₁₁ -O ₃₁	86	O ₃₁ -Cr ₂₁ -N ₅₁	94
O ₁₂ -Cr ₁₁ -N ₁₁	91	O ₃₁ -Cr ₂₁ -N ₆₁	85
O ₂₂ -Cr ₁₁ -N ₁₁	92	N ₂₁ -Cr ₂₁ -N ₄₁	91
O ₂₂ -Cr ₁₁ -N ₂₁	91	N ₂₁ -Cr ₂₁ -N ₅₁	88
O ₃₁ -Cr ₁₁ -N ₁₁	92	N ₂₁ -Cr ₂₁ -N ₆₁	92
O ₃₁ -Cr ₁₁ -N ₂₁	92	N ₄₁ -Cr ₂₁ -N ₅₁	88
N ₁₁ -Cr ₁₁ -N ₂₁	88	N ₄₁ -Cr ₂₁ -N ₆₁	91
		Cr ₁₁ -O ₁₁ -Cr ₁₂	96
		Cr ₁₁ -O ₂₂ -Cr ₂₂	134
		Cr ₁₁ -O ₃₁ -Cr ₂₁	135

The two hydroxogroups forming double bridge have a distance 2.68 Å. The distance of the chromium atoms in the shortest distance is 2.93 Å. The distances from one of these through the single hydroxo-bridges to the two other chromium atoms are 3.60 Å and 3.62 Å. The distance between the chromium atoms defining the length of the complex is 6.62 Å. In the chloride these distances are 3.61 Å and 6.62 Å. In the ethylene derivative these 3 distances are given as 2.929 Å, 3.606 Å, and 6.554 Å.

The Cr-N distance is in the Cr₁₁ octahedron 2.10 Å and in the Cr₂₁ 2.06-2.13 Å. Apart from these Cr₂₁-N distances, which in the chloride were 2.05-2.19 Å, the analogous distances could be taken as equal within the experimental error.

A short distance of contact, 2.83 Å, is found between one of the hydroxo groups in the double bridge and one of the nitrogens belonging to Cr₂. An analogous result, 2.93 Å, is found for the chloride.

The Cr-O-Cr angles in the single hydroxo bridges are 134° and 135°. For the chloride, both angles were 133° and for the ethylene derivative 131°.

Table 5. Calculated distances outside the complex smaller than 4.5 Å for Br-Br distances, smaller than 3.5 Å for other distances.

Br ₁₁ -Br ₂₇	4.295(4)	N ₄₁ -Br ₃₁	3.32(2)
Br ₁₁ -Br ₃₁	4.231(4)	N ₄₁ -O ₁₁ ^w	3.24(3)
O ₁₁ -Br ₂₃	3.26(1)	N ₅₁ -Br ₂₄	3.48(2)
O ₂₁ -Br ₂₈	3.22(1)	N ₅₁ -Br ₃₄	3.40(2)
O ₃₁ -Br ₂₈	3.36(1)	N ₅₁ -Br ₃₈	3.39(2)
N ₁₁ -Br ₂₈	3.40(2)	Br ₁₁ -O ₁₁ ^w	3.34(2)
N ₃₁ -O ₁₈ ^w	3.01(3)	Br ₁₁ -O ₁₅ ^w	3.50(2)

The Cr—O—Cr angle both for the chloride and the bromide is 96° (in the double bridge) while in the ethylene derivative it is 95° .

Just as for the chloride, the octahedral angles deviate from 90° , but this cannot be interpreted as indicating an appreciable distortion from a regular octahedron.

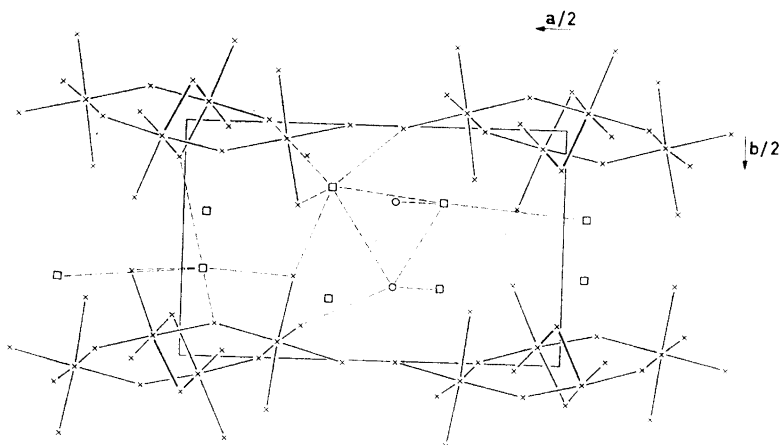


Fig. 2. Projection along [001] showing the shortest distances of contact for bromine and water. \times Atoms belonging to the complex ion. \square Br. \circ H_2O .

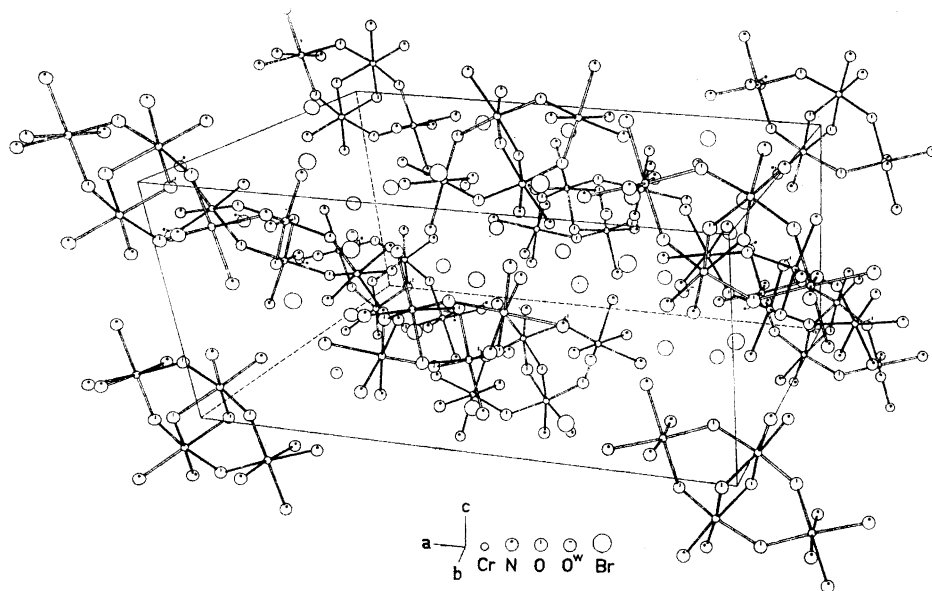


Fig. 3. Perspective drawing of the structure.

The surroundings of the complex differ from those of the chloride (Figs. 2 and 3). Distances are given in Table 5. A single bromine (Br_{21}) bridges the hydroxo group O_{14} in one complex to the hydroxo group O_{27} in another complex in the distances 3.25 and 3.21 Å. Another bromine (Br_{31}) bridges one complex through an NH_3 group (N_{14}) with a distance of 3.31 Å to another complex through a contact to a hydroxo group O_{38} with a distance of 3.36 Å. The third bromine has no contacts to the complex but to the water (3.34 Å) and has short distances to the two other bromines (4.30 and 4.23 Å). There is no bromine layer formed (*cf.* the chloride), and all hydroxo groups have a contact to the surroundings but only through bromine. No bromine lies in the planes formed by $\text{Cr}-\text{O}-\text{Cr}$.

The chromium bromine distances are rather long, the shortest being 4.21 Å. From an electrostatic viewpoint the arrangement of the negative bromide ions seems to be well balanced against the positive complex.

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