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The Crystal Structure of a Bridged Chromium(III) Complex: Di-μ-hydroxo-tetrakis-μ-hydroxo Bis(tetrammine Chromium(III)) Bis(diammine Chromium(III))

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The crystal structure of rhodosochloride tetrahydrate $[Cr_4(OH)_6(NH_3)_{12}]Cl_6,4H_2O$ has been determined by means of 3-dimensional X-ray methods. Space group $P2_1/c$. $a=8.26$ Å, $b=17.95$ Å, $c=13.74$ Å, $\beta=130.0°$.

The centrosymmetrical complex has four chromium atoms in a plane. The six hydroxo ligands form bridges between the chromium atoms. Four hydroxo ligands are nearly coplanar with the 4 chromium atoms and form together with these an 8-membered ring with alternating chromium and hydroxo groups. Two hydroxo groups form a double bridge over the 8-ring between the two nearest neighbour chromium atoms. These two chromium have two ammonia molecules in the *cis* position and four hydroxo ligands. The two other chromium have two hydroxo groups in the *cis* position and four ammonia ligands. In the octahedrons surrounding the chromium atoms the measured distances ar.

Cr—O 1.90—2.03 Å
Cr—N 2.05—2.19 Å

The octahedral angles are only slightly distorted. The angles Cr—O—Cr in the 8-ring are 133° and in the double bridge 96°. Cr—Cr distances 2.91, 3.61, and 6.62 Å.

The chlorine and the water molecules form 3-dimensional nets in which the complexes are enmeshed. The shortest distances between chlorine and water molecules and between chlorine and chlorine are:

Cl—H_2O 3.10—3.19 Å
Cl—Cl 4.00—4.26 Å.

As a part of the structural study of the polynuclear Cr(III) and Co(III) hydroxo complexes of the formula $[Me_2(OH)_3(NH_3)_6]X_3$ which is going on in this laboratory,[1] this investigation of $[Cr_4(OH)_6(NH_3)_{12}]Cl_6,4H_2O$ has been taken up.

The compound studied in this work was originally synthesized by S. M. Jørgensen [2] in 1884 and the crystals used were essentially prepared by his method.[3] In this paper Jørgensen's name for the salt, rhodosochloride, will be used.

The rhodoso ion and the ethylenediamine analogue, the latter of which was prepared by Pfeiffer [4] in 1901, show no apparent acid-base properties. Pfeiffer [5] suggested the formula $[Cr\{(OH)_2Cr(NH_3)_4\}_3]^{3+}$ for the rhodoso ion. This formula is analogous to that of the cobalt complex with the same stoichiometric composition, corresponding to Werner's "brown salts" [6] and is normally quoted for the rhodoso ion.

Evidence has, however, been presented suggesting that the chromium and the cobalt series (ammonia and ethylenediamine) probably have different structures. This conclusion of Schäffer [7] was based on a simple comparison of the visible spectra. No resemblance was found, whereas the spectra of the diol tetrammine bis(metal(III)) complexes of Co(III) and Cr(III) are very similar.

It was possible for Jørgensen by treatment of the rhodosochloride with hydrochloric acid to isolate chloroaquatetrammine chromium(III) chloride in an amount corresponding to just half of the total chromium in the complex. Schäffer and Andersen [8] succeeded in identifying both *cis* tetraquadiammine and *cis* diaquatetrammine chromium(III) ions by bridge cleaving experiments. The formation of such products is incompatible with the structure assumed for the Co(III) complex in the brown salts, *i.e.* 4 coplanar cobalt atoms with trigonal symmetry where the central cobalt atom has 6 hydroxo ligands and the central cobalt octahedron forming double hydroxo bridges to the three other cobalt octahedrons by sharing edges.

It is possible to account for the results from the cleavage experiments of the rhodoso complex in terms of structures with four consecutive chromium octahedrons sharing edges.[7,9] However, the results of the X-ray investigation presented here are incompatible with such structures.

EXPERIMENTAL

The crystals of rhodosochloride were selected from preparations of Schäffer. They were prepared essentially by the method of Jørgensen [3] as mentioned above. The difference was that the spontaneous reduction of the ammonium chloride ammonia solvent by the chromium(II) ammine did not take place so rapidly with modern chemicals [10,11] because of the lack of an unknown catalyst. After some months, however, the chromium(II) system did become completely oxidized and large crystals of rhodosochloride had formed.

More recent work by Schäffer and Andersen [8] on the chromium(III) ammonia system, brought to almost equilibrium through the combined action of chromium(II) and charcoal, has led to a fast procedure for preparing the rhodoso complex.

It has been confirmed through X-ray powder diagrams that rhodosochloride tetrahydrate prepared by this method has the same crystal structure as the corresponding compound prepared by Jørgensen's method.

Reprecipitation from an ammonium chloride solution gives a product with the same composition but with a different powder diagram and these crystals were not used. The chemical analysis of the sample,* from which the crystals were taken: Found: Cr 26.02; N 21.08; Cl 26.85. Calc.: Cr 26.02; N 21.03; Cl 26.61.

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

Density measured by flotation is 1.69 g/ml. The monoclinic crystals are crimson and form strongly pleochroitic needles. (The needle axis is chosen as the *a* axis). The crystals were examined in polarized light on a heating table. Diagonal stripes were observed on (010) at 55–56°. The crystals were destructed by further heating.

X-Ray technique. The cell dimensions were determined from Guinier powder diagrams using Cu-radiation and Si as internal standard. Weissenberg and oscillation diagrams were taken using Cu and Cr radiation and multiple film technique. The dimensions of the crystals were by rotation around the *a* axis $0.21 \times 0.01 \times 0.04$ mm and by rotation around the *b* axis $0.04 \times 0.03 \times 0.04$ mm. The data from the crystal rotated around the *a* axis were mainly used in projections (155 reflections) and scaling. The crystal rotated around the *b* axis was a fragment cut perpendicular to the *a* axis. The quality of the two data sets differed so much that only the data from the crystal rotated around the *b* axis were used in the 3-dimensional refining of the structures (10 layer lines and 1012 reflections registered).

Computing methods. The least squares refinement [12] was carried out on I.B.M. 7090. All other programs were carried out on Gier. Apart from the Fourier program [13] the programs used were in Algol 3 and Algol 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 were refined by a random search method [10] applied on the $\sin^2\theta$-values from the powder diagram. The mean deviation between calculated and observed $\sin^2\theta$-values was 6×10^{-5} (32 observed reflections).

The resulting lattice constants are

$$a = 8.26_0 \text{ Å}, \quad b = 17.95_3 \text{ Å}, \quad c = 13.73_5 \text{ Å}, \quad \beta = 129.0_9°.$$

The observed density is 1.69 g/ml. The calculated density with 2 formula units in the unit cell is 1.70 g/ml.

The diffraction symmetry shown by the data was $2/m$. The systematic absence of the reflections $h0l$ for $l \neq 2n$, $0k0$ for $k \neq 2n$ indicated that the space group was $P2_1/c$ assuming that the absence was not accidental.

The general position in this group is

$$x,y,z; \quad -x,-y,-z; \quad -x,y+1/2,1/2-z; \quad x,1/2-y,1/2+z.$$

(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 a fourfold position and as there are 8 chromium atoms in the unit cell, 2 of the chromium atoms have to be connected to each other in a relatively short distance by a symmetry element, if the complex is tetranuclear. The shape of the unit cell indicated that this had to be a symmetry center, and according to this the complex itself had to be centrosymmetrical.

Two-dimensional Buerger methods were used after centrosymmetrical structures composed of four consecutive chromium octahedral complexes

sharing edges mentioned above were considered as most unlikely on the basis of the 2-dimensional Fourier-projections along the a and b axes.

The applied minimum function was

$$\underset{j}{\text{Min}}\ P((u,v,w)+(u_j,v_j,w_j))$$

where $P(u,v,w)$ is the Patterson function and j the index of the seeking vector.

The intensities were connected to the absolute scale by means of Wilson's method. One, two, or three seeking vectors were used simultaneously. A characteristic minimum function along the a axis is given in Fig. 2 together with the Patterson function, Fig. 1. The marked figure in Fig. 2 occurred in many of the Buerger maps along this axis. Assuming that this had to be connected to the complex, it confirmed the exclusion of the centrosymmetrical structure of 4 chromium octahedron sharing edges as considered above. It also indicated the possibility that one pair of the centrosymmetrical chromium atoms should be nearly at the same distances from atoms in the other pair.

After assuming this position for the two chromium atoms, two chlorine and two of the lighter atoms were detected in Fourier-projections along the

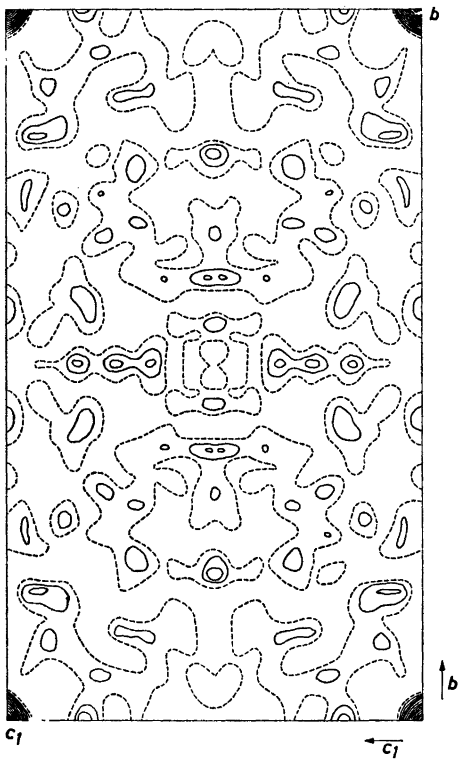

Fig. 1. Patterson projection along [100] on the bc_1 plane. $\bar{c}_1=\bar{a}+\bar{c}$ (arbitrary scale).

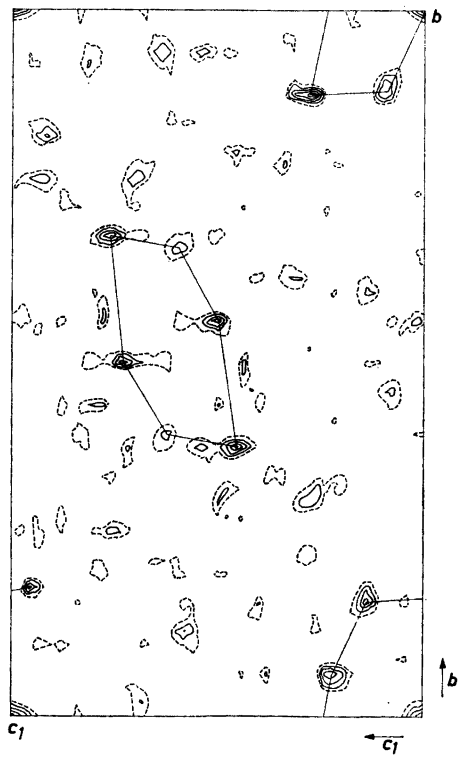

Fig. 2. 2-dimensional Buerger-Min. function on the bc_1 plane. $\bar{c}_1=\bar{a}+\bar{c}$ (arbitrary scale).

a axis. Difficulties arose about the placing of the third chlorine and the two water molecules even though three more atoms (N,O) would be reasonably placed from 3-dimensional Fourier and difference syntheses.

It had been expected that it should have been possible to determine some of the phases from information lying in the differences between the two data sets where Cu and Cr radiation were used, respectively. The Wilson plot for the Cr-radiation was, however, so poor for the small sin θ values that the uncertainty in the correlation of the sets of data was too large. Isomorphous substitution failed on the rhodosobromide where only the dihydrate was isolated (*Pbca*). But three dimensional Buerger minimum functions, where the vectors between a chromium atom and the inverse atom were used as seeking vectors, gave together with several successive Fourier and difference syntheses the remaining atoms.

The atom positions were refined by minimizing the expression $\sum(|F_o|-k|F_c|)^2/\sum(F_o)^2$ until the R residue $\sum||F_o|-k|F_c||/\sum|F_o|$ was 0.18 by approximation with a quadratic. The minimalisation was then carried on by isotropic least squares refinement [12] until the R residue was 0.112.

The resulting atomic coordinates are given in Table 1, the observed and calculated F values in Table 2. The atoms are numbered as given on p. 2673. The Buerger Map, Fig. 2, shows a good agreement with the resulting Fourier projection along the *a* axis given in Fig. 3.

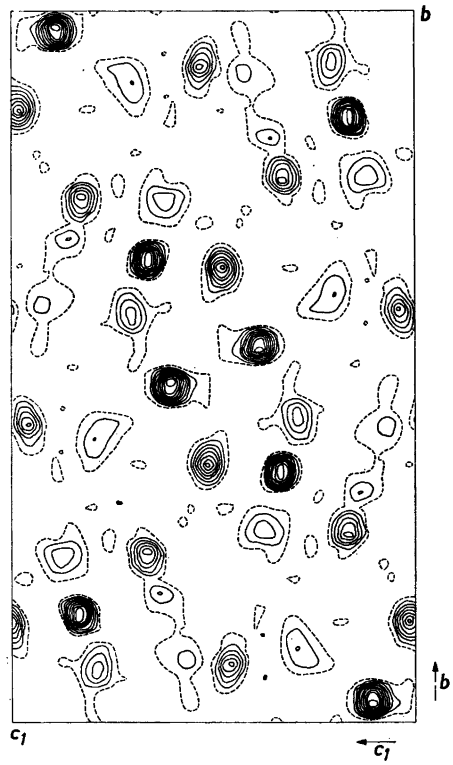

Fig. 3. Electron density projection along [100] on the bc_1 plane. $\bar{c}_1=\bar{a}+\bar{c}$ (arbitrary scale).

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}	0.0262	0.0286	0.1087	0.0007	0.0004	0.0004	1.16	0.10
Cr_{21}	0.7277	0.1506	0.8356	0.0008	0.0004	0.0005	1.49	0.10
O_{11}	0.1868	0.0273	0.0488	0.0027	0.0014	0.0016	1.17	0.37
O_{21}	0.8386	0.0705	0.8034	0.0028	0.0014	0.0017	1.14	0.30
O_{31}	0.8899	0.1214	0.0160	0.0030	0.0015	0.0018	1.50	0.41
N_{11}	0.8373	0.0217	0.1601	0.0039	0.0019	0.0023	3.58	0.57
N_{21}	0.2570	0.0887	0.2747	0.0038	0.0018	0.0022	3.54	0.57
N_{31}	0.5595	0.1825	0.6497	0.0045	0.0020	0.0027	4.81	0.71
N_{41}	0.6096	0.2378	0.8715	0.0042	0.0020	0.0024	4.20	0.63
N_{51}	0.9670	0.2315	0.8810	0.0038	0.0018	0.0022	3.20	0.54
N_{61}	0.4794	0.0831	0.7908	0.0043	0.0020	0.0025	4.54	0.67
Cl_{11}	0.4396	0.1431	0.0198	0.0012	0.0007	0.0008	2.29	0.17
Cl_{21}	0.0686	0.2335	0.6724	0.0015	0.0008	0.0009	3.71	0.23
Cl_{31}	0.1337	0.0770	0.4659	0.0014	0.0008	0.0008	3.01	0.20
O_{11}^{w}	0.8034	0.0889	0.5888	0.0040	0.0019	0.0023	4.52	0.66
O_{21}^{w}	0.6458	0.1060	0.3007	0.0043	0.0020	0.0026	3.84	0.60

DESCRIPTION OF THE STRUCTURE

The complex found in the structure is centrosymmetric and contains four octahedral chromium(III) subunits. The chromium(III) is *cis* coordinated to diamino tetrahydroxo groups and tetramino dihydroxo groups. This explains the results found by cleavage experiments mentioned above.

Distances and angles within the complex are given in Tables 3 and 4. The distances found seem to be in agreement with the results from the relatively few crystallographic investigations [1,15,16] of polynuclear hydroxo ammine Cr(III) and Co(III) complexes.

The four chromium atoms lie in a plane forming an eight-membered ring with alternating hydroxo groups (Fig. 4). The hydroxo groups are only slightly out of the plane (O_{21}, 0.22 Å, O_{31} 0.18 Å). The two remaining hydroxo groups form a double bridge over the ring between the two chromium atoms (Cr_{11}

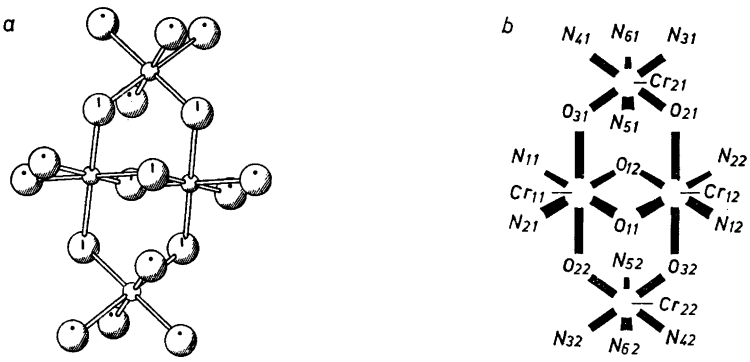

Fig. 4. The complex ion $[Cr_4(OH)_6(NH_3)_{12}]^{6+}$ *a* and a schematical model *b*. Indices p. 2673.

Table 2. Observed and calculated structure factors.

h	k	l	Fo	Fc
−10	0	8	32	−42
−10	0	10	31	30
−10	0	12	19	22
−9	0	4	23	23
−9	0	6	56	−58
−9	0	8	–	−5
−9	0	10	<	20
−9	0	12	–	1
−8	0	2	31	37
−8	0	4	20	−18
−8	0	6	50	−41
−8	0	8	–	−4
−8	0	10	–	3
−8	0	12	16	15
−8	0	14	–	0
−8	0	16	34	−36
−7	0	2	41	42
−7	0	4	41	40
−7	0	6	52	43
−7	0	8	–	−3
−7	0	10	44	47
−7	0	12	64	55
−7	0	14	46	−38
−7	0	16	48	−38
−6	0	2	47	46
−6	0	4	22	18
−6	0	6	83	−77
−6	0	8	41	−33
−6	0	10	92	94
−6	0	12	23	−26
−6	0	14	38	45
−6	0	16	<	−11
−5	0	2	120	111
−5	0	4	19	−23
−5	0	6	101	−110
−5	0	8	131	130
−5	0	10	45	46
−5	0	12	23	19
−5	0	14	39	41
−5	0	16	26	−18
−4	0	2	60	56
−4	0	4	174	−167
−4	0	6	132	−121
−4	0	8	20	17
−4	0	10	41	−35
−4	0	12	46	32
−4	0	16	35	−47
−3	0	2	39	−33
−3	0	4	117	−124
−3	0	6	67	−65
−3	0	8	36	−30
−3	0	10	62	72
−3	0	12	47	49
−3	0	14	45	−32
−2	0	2	52	44
−2	0	4	111	−114
−2	0	6	84	−76
−2	0	8	13	17
−2	0	10	38	31
−2	0	12	39	−41
−2	0	14	49	−47
−1	0	2	128	121
−1	0	4	163	−142
−1	0	6	80	−92
−1	0	8	37	42
−1	0	10	23	−13
−1	0	12	–	−5
−1	0	14	44	−29
0	0	4	61	63
0	0	6	87	102
0	0	8	–	5
0	0	10	–	12
0	0	12	–	3
1	0	0	134	117
1	0	2	48	−43
1	0	4	11	3
1	0	6	14	−20
1	0	8	<	−18
1	0	10	46	41
2	0	0	57	46
2	0	2	58	60
2	0	4	14	5
2	0	6	–	−11
2	0	8	67	79
2	0	10	46	53
3	0	0	16	−15
3	0	2	60	−57
3	0	4	89	−91
3	0	6	–	−4
3	0	8	40	48
4	0	0	27	38
4	0	2	95	−100
4	0	4	<	−18
4	0	6	<	26
5	0	0	–	8
5	0	2	40	−40
5	0	4	–	−25
5	0	6	17	−17
6	0	0	–	−6
6	0	2	20	−17
6	0	4	26	−28
7	0	0	49	46
−10	1	11	25	25
−9	1	9	33	32
−9	1	10	–	6
−9	1	11	31	29
−8	1	5	28	−32
−8	1	8	36	44
−8	1	9	–	0
−8	1	10	–	14
−8	1	11	63	55
−8	1	13	24	34
−8	1	14	18	25
−7	1	2	25	27
−7	1	4	30	−31
−7	1	5	–	10
−7	1	6	21	26
−7	1	8	26	29
−7	1	9	–	1
−7	1	10	42	−45
−7	1	11	76	82
−7	1	12	–	9
−7	1	13	<	17
−7	1	14	–	6
−7	1	15	–	−29
−6	1	2	33	−29
−6	1	4	25	−26
−6	1	5	31	−28
−6	1	6	53	60
−6	1	7	110	−103
−6	1	8	–	−15
−6	1	9	–	−2
−6	1	10	–	−7
−6	1	11	–	19
−6	1	12	58	65
−6	1	13	<	−27
−6	1	14	–	−9
−5	1	1	61	69
−5	1	2	–	−11
−5	1	3	36	36
−5	1	4	43	37
−5	1	5	87	−82
−5	1	6	12	−14
−5	1	7	32	−38
−5	1	8	<	−12
−5	1	9	32	34
−5	1	10	48	52
−5	1	11	–	−9
−5	1	12	–	−1
−5	1	13	–	−6
−5	1	14	<	−17
−4	1	1	77	74
−4	1	2	22	−22
−4	1	3	33	−32
−4	1	4	100	−97
−4	1	5	105	−95
−4	1	6	26	−11
−4	1	7	49	−50
−4	1	8	–	4
−4	1	9	–	−6
−4	1	10	30	−27
−4	1	11	–	−6
−4	1	12	–	−7
−4	1	13	26	−21
−4	1	14	25	21
−3	1	1	–	0
−3	1	2	44	44
−3	1	3	65	70
−3	1	4	–	4
−3	1	5	113	−103
−3	1	6	59	53
−3	1	7	–	0
−3	1	8	28	−26
−3	1	9	53	51
−3	1	10	–	−13
−3	1	11	52	57
−3	1	12	33	33
−3	1	13	–	−12
−3	1	14	–	−11
−2	1	1	116	109
−2	1	2	112	−117
−2	1	3	63	61
−2	1	4	<	12
−2	1	5	19	13
−2	1	6	–	5
−2	1	7	26	−36
−2	1	8	58	−61
−2	1	9	69	61
−2	1	10	–	−5
−2	1	11	39	35
−2	1	12	37	−40
−2	1	14	42	−40
−1	1	1	127	119
−1	1	2	–	7
−1	1	3	29	−32
−1	1	4	134	155
−1	1	5	31	−30
−1	1	6	24	−25
−1	1	7	30	33
−1	1	8	18	23
−1	1	9	44	49
−1	1	10	36	37
−1	1	11	–	−15
−1	1	12	14	−17
0	1	1	127	121
0	1	2	27	35
0	1	3	66	−69
0	1	4	53	−54
0	1	5	–	−7
0	1	6	–	−6
0	1	7	28	36
1	1	0	69	75
1	1	1	82	−88
1	1	2	86	−71
1	1	3	119	−115
1	1	4	–	−7
1	1	5	68	−81
1	1	6	32	34
1	1	7	20	−28
2	1	0	58	−57
2	1	1	20	20
2	1	2	26	−23
2	1	3	–	4
2	1	4	72	84
2	1	5	72	−68
2	1	6	–	−25
2	1	7	–	−5
2	1	8	–	−19
2	1	9	53	61
3	1	0	86	−66
3	1	1	56	57
3	1	2	9	25
3	1	3	32	−30
3	1	4	–	−1
3	1	5	47	−66
3	1	6	36	−43
4	1	1	33	34
4	1	2	32	41
6	1	3	27	−29
6	1	4	16	18
−10	2	11	28	28
−9	2	6	17	−19
−9	2	7	38	−40
−9	2	11	–	3
−9	2	12	33	37
−8	2	13	41	−39
−8	2	5	26	−36
−8	2	6	–	−4
−8	2	7	–	9
−8	2	8	28	−30
−8	2	9	45	41
−8	2	10	16	20
−8	2	11	–	−11
−8	2	12	27	33
−8	2	13	–	−1
−8	2	14	25	−25
−7	2	1	48	47
−7	2	2	35	31
−7	2	4	–	3
−7	2	5	23	−33
−7	2	6	–	−10
−7	2	7	16	21
−7	2	8	–	−11
−7	2	9	<	−22
−7	2	10	28	20
−7	2	11	40	−41
−7	2	12	–	13
−7	2	13	–	−6
−7	2	14	37	−32
−7	2	15	35	−31
−7	2	16	25	−21
−6	2	3	42	−38
−6	2	4	–	−3
−6	2	5	48	45
−6	2	6	42	37
−6	2	7	<	−13
−6	2	8	<	−13
−6	2	9	15	−22
−6	2	10	31	27
−6	2	11	58	56
−6	2	12	<	10
−6	2	13	<	−13
−6	2	14	<	−22
−6	2	15	<	−13
−6	2	16	18	−27
−6	2	17	31	31
−5	2	1	–	8
−5	2	3	71	71
−5	2	4	<	14
−5	2	5	45	41
−5	2	6	42	−43
−5	2	7	–	−2
−5	2	8	34	−34
−5	2	9	47	43
−5	2	10	42	43
−5	2	11	–	11
−5	2	12	28	27
−5	2	13	36	−45
−5	2	14	22	−29
−5	2	15	–	11
−4	2	1	–	−16
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0	2	8	–	10
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2	2	0	54	−38
2	2	1	56	54
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2	2	6	–	−12
2	2	7	<	−12
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3	2	5	–	−11
3	2	6	–	−6
3	2	7	–	14
3	2	8	31	38
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4	2	1	69	69
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4	2	6	–	−5
4	2	7	38	46
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5	2	5	–	14
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−6	3	12	–	12
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Table 2. Continued.

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-7	6	2	-	-5
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-7	6	6	31	-31
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0	6	2	39	40
0	6	3	52	-61
0	6	4	55	-52
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0	6	7	29	37
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0	6	12	25	23
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1	6	4	53	-50
1	6	5	-	-12
1	6	6	60	-65
1	6	7	13	-13
1	6	11	23	-26
2	6	1	9	-11
2	6	2	51	38
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3	6	5	33	44
3	6	7	24	27
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4	6	5	<	18
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0	9	4	49	-50
0	9	5	31	-39
0	9	6	41	-51
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0	9	8	14	10
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0	9	10	46	-50
1	9	0	23	34
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1	9	6	53	63
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Table 2. Continued.

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-4	3	12	50	-49
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-3	3	3	42	41
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-2	3	9	-	14
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-2	3	12	43	-41
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-1	3	1	27	28
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0	3	6	94	100
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0	3	13	24	-28
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3	3	5	<	15
3	3	6	28	39
4	3	0	37	26
4	3	4	-	-2
4	3	5	23	-33
5	3	0	19	-17
5	3	1	42	46
5	3	2	20	-29
5	3	3	27	-30
6	3	3	31	-29
6	3	4	21	21
7	3	0	19	-13
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-8	4	12	-	11
-8	4	13	-	-16
-8	4	14	26	-22
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-7	4	4	<	-13
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-3	4	4	109	-106
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-1	4	3	88	-80
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-1	4	8	<	17
-1	4	9	27	-26
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-1	4	1	47	-45
-1	4	2	13	-15
-1	4	3	-	-8
-1	4	4	95	-107
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-1	4	9	-	4
-1	4	10	-	-3
-1	4	11	34	-32
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-1	4	1	-	13
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-1	4	4	82	-95
-1	4	5	35	41
-1	4	7	30	37
-1	4	0	51	56
-1	4	1	26	-23
-1	4	2	39	-37
-1	4	3	<	10
-1	4	7	28	33
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4	4	1	64	-68
5	4	0	49	51
6	4	0	35	35
6	4	3	28	-27
7	4	0	26	-28
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0	5	2	89	-83
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0	5	5	67	-64
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1	5	2	79	-73
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1	5	7	-	13
1	5	8	17	23
1	5	9	18	19
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2	5	2	49	-49
2	5	3	-	10
2	5	4	40	-48
2	5	5	45	-51
2	5	6	-	17
2	5	7	21	27
2	5	8	22	34
3	5	0	27	30
3	5	1	<	-17
3	5	2	51	-54
3	5	3	27	-36
3	5	4	<	13
3	5	6	13	26
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4	5	2	40	-38
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5	5	1	-	11
5	5	2	43	51
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-5	6	10	-	8
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-4	6	12	<	-9
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-4	6	15	-	7
-4	6	16	11	-21
-3	6	0	49	42
-3	6	1	48	-44
-3	6	2	77	-71
-3	6	3	-	4
-3	6	5	85	102
-3	6	5	43	-41
-3	6	6	-	14
-3	6	7	10	18
-3	6	8	25	-21
-3	6	9	58	47
-3	6	10	72	70
-3	6	11	33	-31
-3	6	12	13	21
-3	6	13	43	-36
-3	6	14	31	-28
-2	6	0	11	-12
-2	6	1	70	64
-2	6	2	59	59
-2	6	3	76	69
-2	6	4	115	120
-2	6	5	18	-20
-2	6	6	72	-72
-2	6	7	81	92

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).

$Cr_{11}-O_{11}$	1.96(3)	$Cr_{21}-N_{11}$	4.57(4)
$Cr_{11}-O_{12}$	1.97(2)	$Cr_{21}-N_{12}$	4.71(4)
$Cr_{11}-O_{22}$	2.03(2)	$Cr_{21}-N_{21}$	4.78(2)
$Cr_{11}-O_{31}$	1.95(2)	$Cr_{21}-N_{22}$	4.58(3)
$Cr_{11}-N_{11}$	2.09(4)	$O_{11}-O_{12}$	2.64(3)
$Cr_{11}-N_{21}$	2.10(2)	$O_{11}-O_{21}$	2.79(2)
$Cr_{21}-O_{21}$	1.90(3)	$O_{11}-O_{22}$	2.79(4)
$Cr_{21}-O_{31}$	1.99(2)	$O_{11}-O_{31}$	2.77(4)
$Cr_{21}-N_{31}$	2.05(3)	$O_{11}-O_{32}$	2.76(4)
$Cr_{21}-N_{41}$	2.06(4)	$O_{11}-N_{12}$	2.88(4)
$Cr_{21}-N_{51}$	2.19(3)	$O_{11}-N_{21}$	2.98(4)
$Cr_{21}-N_{61}$	2.11(4)	$O_{11}-N_{62}$	2.93(4)
$Cr_{11}-Cr_{12}$	2.91(1)	$O_{21}-O_{31}$	2.82(4)
$Cr_{11}-Cr_{21}$	3.61(1)	$O_{21}-N_{12}$	2.90(4)
$Cr_{11}-Cr_{22}$	3.61(1)	$O_{21}-N_{22}$	2.98(4)
$Cr_{11}-O_{21}$	3.49(2)	$O_{21}-N_{31}$	2.75(4)
$Cr_{11}-O_{32}$	3.49(3)	$O_{21}-N_{51}$	3.02(4)
$Cr_{11}-N_{31}$	5.57(3)	$O_{21}-N_{61}$	2.87(4)
$Cr_{11}-N_{32}$	4.74(3)	$O_{31}-N_{11}$	2.90(5)
$Cr_{11}-N_{41}$	4.70(3)	$O_{31}-N_{21}$	2.88(3)
$Cr_{11}-N_{42}$	5.56(4)	$O_{31}-N_{41}$	2.79(4)
$Cr_{11}-N_{51}$	4.61(3)	$O_{31}-M_{51}$	3.04(5)
$Cr_{11}-N_{52}$	4.67(3)	$O_{31}-N_{61}$	2.84(3)
$Cr_{11}-N_{61}$	3.88(2)	$N_{31}-N_{41}$	2.97(5)
$Cr_{11}-N_{62}$	3.92(2)	$N_{31}-N_{51}$	2.91(3)
$Cr_{21}-Cr_{22}$	6.62(1)	$N_{31}-N_{61}$	3.00(5)
$Cr_{21}-O_{11}$	3.69(2)	$N_{41}-N_{51}$	2.87(5)
$Cr_{21}-O_{12}$	3.43(2)	$N_{41}-N_{61}$	2.93(4)

and Cr_{12}). The distance between these two atoms are 2.91 Å. The distance from one of these through the single hydroxo bridge to each of the two other chromium atoms is nearly the same within the experimental error ($Cr_{11}-Cr_{21}$, $Cr_{11}-Cr_{22}$) 3.61 Å. The distance between the chromium atoms defining the length of the complex ($Cr_{21}-Cr_{22}$) is 6.62 Å.

Table 4. Angles in degrees within the complex.

$O_{11}-Cr_{11}-O_{12}$	84	$O_{21}-Cr_{21}-O_{31}$	93
$O_{11}-Cr_{11}-O_{22}$	89	$O_{21}-Cr_{21}-N_{31}$	88
$O_{11}-Cr_{11}-O_{31}$	90	$O_{21}-Cr_{21}-N_{51}$	95
$O_{11}-Cr_{11}-N_{21}$	94	$O_{21}-Cr_{21}-N_{61}$	81
$O_{12}-Cr_{11}-O_{22}$	88	$O_{31}-Cr_{21}-N_{41}$	87
$O_{12}-Cr_{11}-O_{31}$	89	$O_{31}-Cr_{21}-N_{51}$	93
$O_{12}-Cr_{11}-N_{11}$	90	$O_{31}-Cr_{21}-N_{61}$	88
$O_{22}-Cr_{11}-N_{11}$	90	$N_{31}-Cr_{21}-N_{41}$	92
$O_{22}-Cr_{11}-N_{21}$	92	$N_{31}-Cr_{21}-N_{51}$	86
$O_{31}-Cr_{11}-N_{11}$	92	$N_{31}-Cr_{21}-N_{61}$	92
$O_{31}-Cr_{11}-N_{21}$	91	$N_{41}-Cr_{21}-N_{51}$	85
$N_{11}-Cr_{11}-N_{21}$	91	$N_{41}-Cr_{21}-N_{61}$	89
		$Cr_{11}-O_{11}-Cr_{12}$	96
		$Cr_{11}-O_{22}-Cr_{22}$	133
		$Cr_{11}-O_{31}-Cr_{21}$	133

The Cr—O distances in the double bridge are 1.96—1.97 Å. In the single bridges the Cr—O distances are 1.90—1.97 Å. The analogous distances found in $[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+}$ are 1.88—1.99 Å [15,16] and in $[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3+}$ 1.90—2.03 Å.[1]

The Cr—N distances are, in the Cr_{11}-octahedron 2.09—2.10 Å and in the Cr_{21}-octahedron 2.05—2.19 Å. They are in reasonable agreement both with the results mentioned above 1.88—2.02 Å,[15,16] 1.92—2.04 Å [1] and with the results from the investigation of Reinecke salts [17] 2.11—2.15 Å.

Both the Cr—O—Cr angles in the two single hydroxo bridges are 133° and the Cr—O—Cr angle in the double bridge is 96°.

Although the octahedral angles given deviate from 90°, this cannot be interpretated as indicating appreciable distortion from a regular octahedron.

The complexes lie in grooves formed by chlorine-water nets, connected to each other through the complex (Figs. 5 and 6). The centers of the 8-rings are in the *bc* plane. The long axis of the ring is tilted 35° from the *b* axis. The distances outside the complex are given in Tables 5 and 6; the angles connected to the water molecules and the hydroxo groups in Table 7.

Two of the oxygens in the hydroxo groups (O_{31}, O_{11}) have a short distance to chlorine 3.08—3.15 Å. The third (O_{21}) has a water contact (O_{11}^{w}) 2.79 Å. The shortest distances from nitrogen to chlorine and to water, respectively, are 3.30 Å and 3.01 Å. The shortest distance between oxygen atoms, 2.64 Å, is found in the double bridge (O_{11}—O_{12}). The other short distances of this group are 2.76—2.82 Å. The oxygen-nitrogen short distances in the complex are 2.75—3.04 Å and the nitrogen-nitrogen 2.87—3.00 Å. Each oxygen has

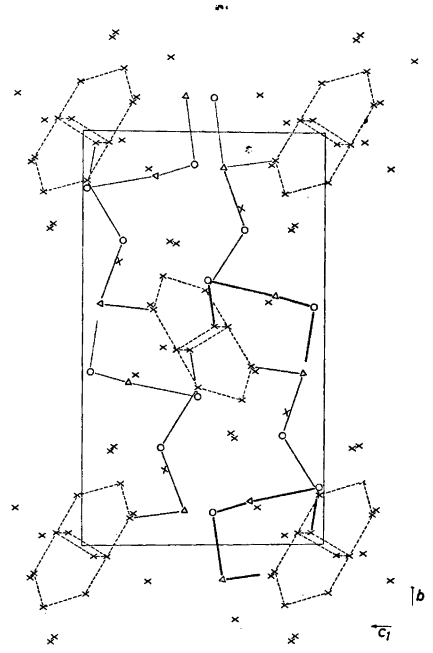

Fig. 5. Chlorine-water nets surrounding the complex ions. Projection along [100] on the bc_1 plane. $c_1 = \bar{a} + \bar{c}$. × Atoms belonging to the complex ion. ○ Cl. △ Water.

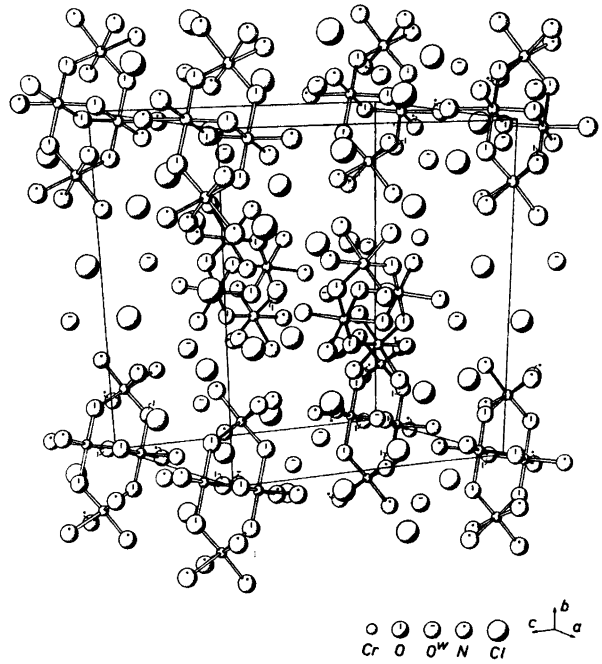

Fig. 6. Perspective drawing of the structure.

Table 5. Distances in Å outside the complex smaller than 3.5 Å. Standard deviations in brackets.

$O_{11}-O_{22}{}^w$	3.39(3)	$N_{41}-O_{24}{}^w$	3.04(5)
$O_{11}-Cl_{11}$	3.15(3)	$N_{41}-Cl_{21}$	3.43(3)
$O_{21}-O_{11}{}^w$	2.79(4)	$N_{41}-Cl_{24}$	3.40(2)
$O_{31}-Cl_{24}$	3.08(3)	$N_{51}-Cl_{11}$	3.44(3)
$N_{11}-O_{12}{}^w$	3.39(4)	$N_{51}-Cl_{21}$	3.46(4)
$N_{11}-Cl_{11}$	3.33(3)	$N_{61}-Cl_{31}$	3.42(3)
$N_{11}-Cl_{31}$	3.38(4)	$O_{11}{}^w-O_{21}{}^w$	3.29(5)
$N_{21}-O_{21}{}^w$	3.01(4)	$O_{11}{}^w-Cl_{21}$	3.10(3)
$N_{21}-Cl_{24}$	3.43(3)	$O_{11}{}^w-Cl_{32}$	3.19(4)
$N_{21}-Cl_{31}$	3.38(4)	$O_{21}{}^w-Cl_{11}$	3.13(3)
$N_{31}-O_{11}{}^w$	3.12(4)	$O_{21}{}^w-Cl_{31}$	3.15(3)
$N_{31}-Cl_{14}$	3.42(4)		
$N_{31}-Cl_{31}$	3.30(3)		

Table 6. Distances between Cl atoms smaller than 4.5 Å. Standard deviations in brackets.

$Cl_{11}-Cl_{21}$	4.00(1)
$Cl_{21}-Cl_{31}$	4.26(2)
$Cl_{31}-Cl_{32}$	4.01(2)

Table 7. Angles in degrees connected to the water molecules and to the hydroxo groups and their nearest neighbours.

$Cl_{21}-O_{11}{}^{w}-Cl_{32}$	133°	$Cr_{11}-O_{22}-H_2O_{12}$	112°
$O_{21}-O_{11}{}^{w}-Cl_{21}$	98°	$Cr_{22}-O_{22}-H_2O_{12}$	114°
$O_{21}-O_{11}{}^{w}-Cl_{32}$	102°	$Cr_{11}-O_{22}-Cr_{22}$	133°
$Cl_{11}-O_{21}{}^{w}-Cl_{31}$	111°	$Cr_{11}-O_{31}-Cl_{24}$	117°
		$Cr_{21}-O_{31}-Cl_{24}$	106°
$Cr_{11}-O_{11}-Cr_{12}$	96°	$Cr_{11}-O_{31}-Cr_{21}$	133°
$Cr_{11}-O_{11}-Cl_{11}$	137°		
$Cr_{12}-O_{11}-Cl_{11}$	117°		

2 chromium, a chlorine or a water-oxygen, and 6—8 nitrogen and oxygen atoms from the hydroxo group in the shortest distance. There is a rather close packing around the atoms in the complex, but the distances seem to be in good agreement with what could be expected from a survey of the literature.

The two oxygens of the water molecules have different surroundings; one ($O_{11}{}^{w}$) has 1 hydroxo group and 2 chlorine (O_{21}, Cl_{11}, Cl_{32}) and lies in the same plane as the hydroxo group and the adjacent chromium atoms, whereas the other ($O_{21}{}^{w}$) has only 2 chlorine (Cl_{11}, Cl_{31}). This is in agreement with what would be expected from the results of the experiments of Jørgensen [3] where a loss in weight corresponding to half the amount of crystal water was observed by desiccation.

The three chlorine atoms differ in surroundings; one (Cl_{11}) has 1 chlorine and 2 oxygen atoms, one from water, the other from a hydroxo group (Cl_{21}, $O_{21}{}^{w}$, O_{11}) in the nearest distance; the second (Cl_{21}) has 2 chlorine and 2 oxygen atoms from a water molecule and a hydroxo group (Cl_{11}, Cl_{21}, $O_{11}{}^{w}$, O_{54}) while the third (Cl_{31}) has 2 chlorine and 2 oxygen from water molecules (Cl_{21}, Cl_{32}, $O_{11}{}^{w}$, $O_{21}{}^{w}$). The Cl—Cl distances mentioned here are 4.00—4.27 Å and the Cl—O distances 3.08—3.19 Å.

The chromium chlorine distances are rather long, the shortest being 4.33 Å. The arrangement of the negative chloride ions seems from an electrostatic viewpoint to be well balanced against the positive complex.

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