Short communication

The Crystal Structure of Tris{di-μ-hydroxo-tetraamminechromium(III)} chromium(III) Dithionate Tetrahydrate

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In a recent work,[1] it was shown that it was possible to isolate salts of the chromium analogue of "Werner's optically active inorganic ion",[2] $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, from NH_4^+/NH_3 buffer solutions of chromium(II) after charcoal-catalyzed spontaneous oxidation to chromium(III). The identification of the complex was based on cleavage experiments in solution and evaluation of the powder diagrams of the dithionate salts of the chromium and the cobalt complexes. These two complexes are the ammonia analogues of "Werner's brown salts" of cobalt(III) and ethylenediamine.[3] Werner suggested on the basis of experimental results that the complex had a central cobalt atom surrounded by three other cobalt atoms in a trigonal array with the central cobalt atom octahedrally coordinated to six bridging hydroxide groups. This was later confirmed through X-ray structure investigations of some of the Δ/Λ isomers.[4]

Our earlier attempts to solve the structure of the cobalt ammonia complex encountered difficulties due to disorder in the available crystals.[5] However, the dithionate of the chromium complex gave crystals more suitable for investigating this type of structure. These dithionate crystals were grown from dilute solutions of the bromide[1] through reprecipitation with lithium or sodium dithionate followed by washing with water and air drying.

The monoclinic crystals of the compound $[Cr\{(OH)_2Cr(NH_3)_4\}_3](S_2O_6)_3 \cdot 4\ H_2O$ form pleochroitic red-orange/violet plates with parallel extinction and the [10$\bar{1}$] axis along the length of the plates. The 2-fold axis is perpendicular to the longest edge of the plate. The large face is (101). The space group was determined through Weissenberg and precession photographs to be $P2_1/n$. The analogous cobalt salt shows the same mor-

Table 1. Crystal data for $[Cr_4(NH_3)_{12}(OH)_6](S_2O_6)_3 \cdot 4\ H_2O$.

Space group: Monoclinic $P2_1/n$	Crystal size: $0.2 \times 0.4 \times 0.1$ mm^3
a = 18.533(5) Å	Independent reflections used in calculations:
b = 9.736(1) Å	3447 including 644 LT ($F^2 < 2\sigma(F^2)$)
c = 20.067(7) Å	No. of parameters: 452
β = 98.69(2)°	R = 0.05, R_w = 0.08
Z = 4	$1/w = \sigma^2(F) + 0.03\ F + 0.002\ F^2$
V = 3579 Å^3	
μ(Mo$K\alpha$) = 4.7 cm^{-1}	

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Table 2. Fractional coordinates.

Atom	x	y	z
Cr1	.52978 (6)	.25695 (12)	.23341 (6)
Cr2	.58768 (7)	.23101 (13)	.38074 (6)
Cr3	.62199 (7)	.22983 (13)	.12315 (6)
Cr4	.36897 (6)	.29328 (13)	.19422 (6)
O12	.5126 (3)	.1493 (5)	.3130 (3)
O22	.6065 (3)	.3381 (6)	.3016 (3)
O13	.6033 (3)	.1305 (5)	.2053 (3)
O23	.5525 (3)	.3600 (5)	.1537 (3)
O14	.4461 (3)	.1692 (5)	.1752 (2)
O24	.4518 (3)	.3834 (5)	.2524 (3)
N12	.6633 (4)	.0844 (7)	.3580 (4)
N22	.5575 (4)	.1033 (7)	.4553 (4)
N32	.6709 (4)	.3218 (8)	.4475 (4)
N42	.5139 (4)	.3753 (7)	.4048 (4)
N13	.5380 (4)	.1213 (7)	.0653 (3)
N23	.6978 (4)	.0889 (7)	.0974 (4)
N33	.6317 (4)	.3450 (8)	.0368 (4)
N43	.7083 (4)	.3349 (7)	.1811 (4)
N14	.3514 (4)	.1735 (7)	.2759 (3)
N24	.2916 (3)	.1809 (7)	.1298 (4)
N34	.2911 (3)	.4314 (7)	.2195 (4)
N44	.3870 (4)	.4263 (7)	.1153 (3)
S1	.26627 (12)	.30217 (25)	.41929 (10)
S2	.34791 (11)	.25636 (22)	.50294 (11)
S3	.10469 (11)	.27039 (22)	.25190 (11)
S4	.02320 (14)	.29825 (26)	.16684 (14)
S5	.87138 (12)	.21505 (24)	.45630 (11)
S6	.86005 (12)	.25036 (22)	.35040 (11)
O11S	.2127 (3)	.3803 (8)	.4476 (3)
O21S	.2420 (4)	.1685 (8)	.3935 (4)
O31S	.3030 (4)	.3811 (8)	.3750 (3)
O12S	.4035 (3)	.1854 (7)	.4735 (4)
O22S	.3689 (4)	.3854 (7)	.5329 (4)
O32S	.3115 (4)	.1715 (9)	.5466 (4)
O13S	.1673 (3)	.2230 (7)	.2249 (3)
O23S	.0741 (4)	.1699 (6)	.2928 (3)
O33S	.1146 (4)	.4029 (6)	.2835 (3)
O14S	.9641 (4)	.3663 (7)	.1915 (4)
O24S	.0571 (4)	.3865 (9)	.1228 (3)
O34S	.0054 (5)	.1593 (8)	.1449 (6)
O15S	.9400 (3)	.1447 (7)	.4737 (3)
O25S	.8092 (3)	.1316 (7)	.4633 (4)
O35S	.8680 (4)	.3495 (7)	.4860 (3)
O16S	.7861 (3)	.3014 (7)	.3332 (3)
O26S	.9154 (3)	.3484 (6)	.3411 (3)
O36S	.8720 (4)	.1163 (6)	.3220 (3)
O1W	.1911 (4)	.3990 (7)	.0724 (4)
O2W	.8515 (4)	.1166 (7)	.1810 (3)
O3W	.0610 (4)	.3545 (10)	.4217 (4)
O4W	.0995 (9)	.1053 (17)	.0573 (8)

phology, has the same space group and a similar powder diagram.[1]

Data were collected on an Enraf-Nonius Cad 4 diffractometer at room temperature. The crystal data are given in Table 1. The X-ray system of programs[6] and DIRDIF[7] were used in the calculations. From the Patterson function together with MULTAN,[8] the chromium atoms should lie in a plane almost perpendicular to the 2-fold axis. DIRDIF gave the positions of the rest of the atoms except those of hydrogen which could not be located. Anisotropic refinement gave reasonable temperature factors. One water molecule, O4W, had a population of ½. The coordinates of the atoms are given in Table 2.

Fig. 1 shows the complex ion. Distances and angles are given in Table 3. The complex has the expected D_3 symmetry. The chromium nitrogen distances are in agreement with results from other chromium ammine complexes. The chromium-chromium distances, 2.986(2)–3.005(2) Å, and the chromium-oxygen distances, 1.952(6)–1.987(6) Å, agree with those found, for example in Ref. 9, for the group of dimeric chromium complexes with double hydroxo bridges. The three independent dithionate ions has the expected D_{3d} symmetry within small deviations. Distances and angles are given in Table 4.

A hydrogen bond net is formed throughout the structure connecting all oxygen and nitrogen atoms in the complex to water or oxygen in dithionate, and from oxygen in dithionate to water (2.82–2.94 Å). Only one oxygen, O15S, has no contact. The hydrogen bond lengths from oxygen in the complex are 2.783(8)–2.998(8) Å and from nitrogen 2.85(1)–3.15(1) Å.

Tables of anisotropic temperature factors and F_{obs} are available from the authors upon request.

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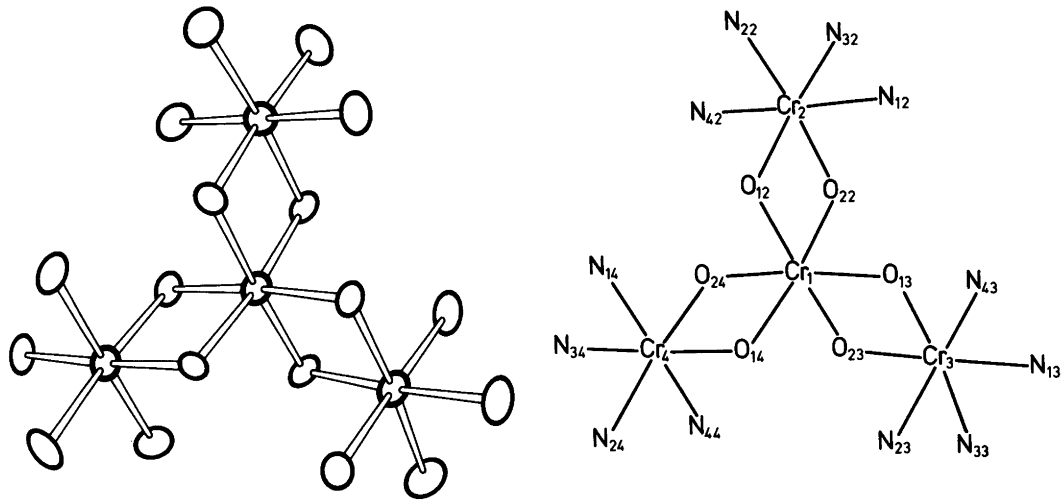

Fig. 1. Perspective drawing of the $[Cr\{(OH)_2Cr(NH_3)_4\}_3]^{6+}$ ion and sketch of the ion to show the numbering of the atoms. The thermal ellipsoids enclose 50% probability.

Table 3. Bond lengths in Å and angles in degrees in the complex ion.

Cr1–O12	1.976(5)	Cr2–N12	2.099(7)
Cr1–O22	1.982(5)	Cr2–N22	2.086(8)
Cr1–O13	1.981(5)	Cr2–N32	2.082(7)
Cr1–O23	1.987(5)	Cr2–N42	2.068(8)
Cr1–O14	1.989(5)	Cr3–N13	2.083(6)
Cr1–O24	1.980(5)	Cr3–N23	2.084(7)
Cr2–O12	1.960(5)	Cr3–N33	2.094(8)
Cr2–O22	1.974(5)	Cr3–N43	2.097(7)
Cr3–O13	1.987(5)	Cr4–N14	2.077(7)
Cr3–O23	1.969(5)	Cr4–N24	2.089(7)
Cr4–O14	1.953(5)	Cr4–N34	2.090(7)
Cr4–O24	1.986(5)	Cr4–N44	2.111(7)

Octahedral angles in the bridges		Octahedral angles outside the bridges	
O12Cr1O22	80.8(2)	O–Cr–O	87.9(2)–97.9(2)
O13Cr1O23	81.1(2)	O–Cr–N	88.5(3)–95.4(3)
O14Cr1O24	81.5(2)	N–Cr–N	87.7(3)–93.0(3)
O12Cr2O22	81.3(2)		
O13Cr3O23	81.4(2)		
O14Cr4O24	82.3(2)		

Table 4. Bond lengths in Å and angles in degrees for the 3 dithionate ions. Number of determinations [ ].

S–S	[3]	2.119(3)–2.131(3)
S–O	[18]	1.421(7)–1.455(7)
O–S–O	[18]	111.3(5)–118.1(6)
S–S–O	[18]	103.2(4)–105.8(3)

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