SHORT-FORMAT PAPERS

The Structure of $(ND_4)_2Cr(SO_4)_2.6D_2O$ at 4·3 K by Neutron Diffraction

By Brian N. Figgis and Edward S. Kucharski

School of Chemistry, University of Western Australia, Nedlands, WA 6009, Australia

and J. Bruce Forsyth

Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England

Abstract. Di($^2H_4$)ammonium hexa[($^2H_2$)aqua]chromium(II) disulfate, $[ND_4]_2[Cr(D_2O)_6](SO_4)_2$, $M_r = 407\cdot1$, monoclinic, $P2_1/a$, $a = 9\cdot488\,(2)$, $b = 12\cdot816\,(4)$, $c = 6\cdot097\,(2)$ Å, $\beta = 107\cdot11\,(1)°$, $V = 708\cdot6\,(7)$ Å^3, $Z = 2$, $D_m = 1\cdot90\,(1)$, $D_x = 1\cdot91$ g cm^{-3}, neutron, $\lambda = 1\cdot176$ Å, $\mu = 0\cdot255$ cm^{-1}, $F(000) = 463$ fm, $T = 4\cdot3$ K, $R(F) = 0\cdot018$ for 1018 unique reflections, deuteration 95·1 (3)% for ammonium, 94·2 (2)% for water. The structure is very similar to the hydrogen-bonded network in the other isomorphous ammonium Tutton salts studied at 4 K. The CrO_6 octahedron has a large Jahn–Teller distortion with a tetragonal elongation of Cr···O(8) = $2\cdot389\,(1)$, Cr···O(7) = $2\cdot080\,(1)$, Cr···O(9) = $2\cdot054\,(1)$ Å. The cell parameters and CrO_6-octahedron geometry are virtually the same as those found in the previous 84 K X-ray charge-density study on the hydrogenous salt.

Experimental. The following operations were carried out in an argon atmosphere with the rigorous exclusion of air. Chromous Tutton salt (Figgis, Kucharski & Reynolds, 1990) was twice recrystallized from warm D_2O and a large pale blue plate-like crystal with major face (20$\bar{1}$) was grown by slow cooling of a saturated D_2O solution. Such crystals are stable in dry air for some hours.

Two crystals were cut from the large single crystal (No. 1 $5\cdot4 \times 3\cdot2 \times 0\cdot8$ mm, No. 2 $6\cdot0 \times 3\cdot0 \times 0\cdot8$ mm). Crystal No. 1 was mounted with **b** as the rotation axis and No. 2 was mounted with the rotation axis perpendicular to both (20$\bar{1}$) and **b**, in a helium gas flow cryostat on the D15 lifting arm normal-beam diffractometer at the Institut Laue–Langevin. Cell parameters were obtained from 18 reflections from each crystal, in the range $19 < 2\theta <$ 117°, well separated in angle, refining both sets to mutually consistent values. 956 reflections were measured in the first crystal orientation and 1372 in the second. $2\theta/\omega$ scans were used, $(\sin\theta)/\lambda < 0\cdot76$ Å^{-1}, $|h| < 14$, $|k| < 18$, $|l| < 9$, some reflections being omitted due to lifting-arm angle restriction and limitations of normal-beam geometry. One standard measured after every 40 reflections showed no systematic variation with time. Scaled squares of structure-factor moduli were obtained using the profile analysis program *COLL5N* (Lehmann & Larsen, 1974). These intensity data were merged to $R_{int} = 0\cdot017$ and $0\cdot019$ for the unique sets of 487 reflections [$462 > 3\sigma(I)$] for crystal No. 1 and 594 [$556 > 3\sigma(I)$] for crystal No. 2. Both data sets were corrected for absorption, the maximum and minimum transmission factors being 0·970 and 0·936. The structure was refined using *ASRED* (Figgis, Reynolds & Williams, 1980), starting at the 84 K X-ray structure. Both data sets were refined together on $|F^2|$, weights $w = (\sigma|F^2|)^{-2}$, with separate scale, isotropic type II extinction (Becker & Coppens, 1974, 1975), and multiple scattering corrections, but common anisotropic thermal and positional parameters. There were 180 parameters in all. The largest correction factor for extinction was 1·37 (No. 1) and 1·33 (No. 2). Deuterium site populations were refined to estimate the degree of deuteration. Initially all the deuterium site populations were refined separately, but in final refinement water and ammonium-ion deuterium populations were constrained separately to be equal. Deuteration values of 94·2 (2)% for H_2O and 95·1 (3)% for $(NH_4)^+$ were obtained. Scattering lengths were taken from Koester & Steyerl (1980). Refinement converged [$(\Delta/\sigma)_{max} < 0\cdot06$] to $R(F^2) = 0\cdot023$, $wR(F^2) = 0\cdot029$, $S = 1\cdot83$ and $R(F) = 0\cdot018$

Table 1. *Atomic fractional positional coordinates* ($\times 10^5$, *except* z, $\times 10^4$) *and equivalent isotropic thermal parameters* ($\mathring{A}^2 \times 10^4$)

$$U_{eq} = (1/3)[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)].$$

	x	y	z	U_{eq}
Cr	0	0	0	32 (5)
S	38855 (14)	14300 (12)	7482 (2)	29 (2)
O(3)	37822 (8)	23627 (6)	6030 (1)	58 (2)
O(4)	52915 (7)	8856 (6)	7718 (1)	55 (2)
O(5)	26507 (7)	7162 (6)	6341 (1)	47 (2)
O(6)	37695 (7)	17254 (6)	9775 (1)	54 (2)
O(7)	16228 (7)	10507 (8)	1711 (1)	61 (3)
O(8)	−18365 (11)	11761 (7)	494 (2)	68 (3)
O(9)	713 (10)	−7189 (6)	3042 (2)	50 (3)
N	12703 (6)	36448 (6)	3777 (1)	57 (2)
D(11)	4395 (9)	34568 (11)	2313 (2)	175 (5)
D(12)	20473 (11)	30652 (7)	4209 (2)	181 (4)
D(13)	8386 (9)	37642 (7)	5116 (2)	171 (3)
D(14)	17676 (11)	43270 (7)	3504 (2)	180 (4)
D(15)	20672 (9)	9363 (10)	3358 (1)	147 (4)
D(16)	23965 (8)	12512 (7)	1038 (1)	154 (3)
D(17)	−28440 (8)	10696 (9)	−452 (2)	156 (3)
D(18)	−16093 (15)	18980 (7)	271 (3)	168 (4)
D(19)	−8557 (8)	−6872 (7)	3421 (2)	154 (3)
D(20)	4213 (11)	−14421 (7)	3283 (2)	135 (4)

Table 2. *Bond lengths* ($\mathring{A}$) *and angles* ($°$)

Directly bonded atoms

Cr—O(7)	2·0802 (9)	S—O(3)	1·473 (2)
Cr—O(8)	2·389 (1)	S—O(4)	1·474 (2)
Cr—O(9)	2·054 (1)	S—O(5)	1·488 (2)
O(7)—D(15)	0·979 (1)	S—O(6)	1·483 (2)
O(7)—D(16)	0·975 (1)	N—D(11)	1·030 (1)
O(8)—D(17)	0·970 (1)	N—D(12)	1·025 (1)
O(8)—D(18)	0·969 (1)	N—D(13)	1·027 (1)
O(9)—D(19)	0·974 (1)	N—D(14)	1·030 (1)
O(9)—D(20)	0·981 (1)		

O(7)—Cr—O(8)	89·32 (4)	O(3)—S—O(4)	109·9 (1)
O(7)—Cr—O(9)	90·84 (4)	O(3)—S—O(5)	108·29 (9)
O(8)—Cr—O(9)	90·04 (4)	O(3)—S—O(6)	110·4 (1)
Cr—O(7)—D(15)	116·7 (1)	O(4)—S—O(5)	108·7 (1)
Cr—O(7)—D(16)	119·82 (8)	O(4)—S—O(6)	110·16 (8)
Cr—O(8)—D(17)	117·7 (1)	O(6)—S—O(5)	109·3 (1)
Cr—O(8)—D(18)	112·6 (1)	D(12)—N—D(13)	109·2 (1)
Cr—O(9)—D(19)	113·79 (8)	D(12)—N—D(14)	109·1 (1)
Cr—O(9)—D(20)	118·6 (1)	D(12)—N—D(11)	111·3 (1)
D(16)—O(7)—D(15)	108·71 (9)	D(13)—N—D(14)	108·1 (1)
D(18)—O(8)—D(17)	105·8 (1)	D(13)—N—D(11)	109·94 (9)
D(19)—O(9)—D(20)	107·1 (1)	D(14)—N—D(11)	109·2 (1)

Hydrogen bonds

O(3)—D(20)	1·705 (1)	O(5)—D(15)	1·761 (1)
O(3)—D(12)	1·918 (1)	O(5)—D(14)	1·858 (1)
O(4)—D(17)	1·808 (1)	O(6)—D(16)	1·803 (1)
O(4)—D(13)	1·864 (1)	O(6)—D(18)	1·843 (1)
O(5)—D(19)	1·752 (1)	O(6)—D(11)	1·875 (1)

N—D(11)—O(6)	171·5 (1)	O(7)—D(16)—O(6)	175·5 (1)
N—D(12)—O(3)	156·81 (9)	O(8)—D(17)—O(4)	178·4 (1)
N—D(13)—O(4)	171·47 (8)	O(8)—D(18)—O(6)	178·2 (1)
N—D(14)—O(5)	161·5 (1)	O(9)—D(19)—O(5)	170·7 (1)
O(7)—D(15)—O(5)	173·18 (9)	O(9)—D(20)—O(3)	172·7 (1)

$[3\sigma(I)$ cut]. Maximum and minimum peak heights in the final difference Fourier map were 300 and -300 μm^{-2}. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. The principal interatomic distances and angles

obtained using the *XTAL* system (Hall & Stewart, 1989) are given in Table 2.* *ORTEP* diagrams of the unit-cell contents projected down the b axis, and of the $Cr(OD_2)_6^{2+}$ cation are given in Figs. 1 and 2, respectively.

Related literature. The structure is consistent with that of the V^{II} (Deeth, Figgis, Forsyth, Kucharski & Reynolds, 1988), Ni^{II} (Fender, Figgis & Forsyth, 1986*b*), Mn^{II} (Fender, Figgis, Forsyth, Reynolds &
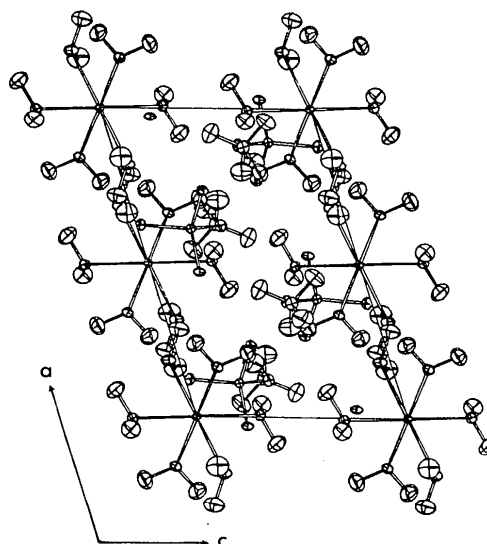
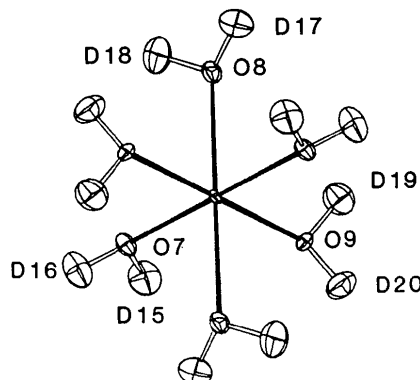Fig. 1. View of the unit cell projected down the b axis. The thermal ellipsoids are drawn at the 80% probability level.

Fig. 2. View of the $[Cr(D_2O)_6]^{2+}$ cation projected onto the plane defined by the O(7), O(8) and O(9) atoms. The thermal ellipsoids are drawn at the 80% probability level.

Stevens, 1986) and Fe^{II} (Figgis, Kucharski, Reynolds & Tasset, 1989) ammonium Tutton salts measured at helium temperatures by neutron diffraction. Those were precursors, as in this case, to the spin-density measurements by the polarized neutron-diffraction experiment (Deeth, Figgis, Forsyth, Kucharski & Reynolds, 1989; Figgis, Forsyth, Kucharski, Reynolds & Tasset, 1990; Fender *et al.*, 1986; Fender, Figgis & Forsyth, 1986*a*). The chromous Tutton salt structure has been determined at 295 and 84 K by X-ray diffraction (Figgis, Kucharski & Reynolds, 1990). The unit-cell dimensions and CrO_6 octahedron of this structure determination are virtually the same as those found in the 84 K X-ray structure. In the present structure, of course, the hydrogen positions are much better defined. There are sulfate and ammonium ions present, each close to a regular tetrahedron in shape [av. S—O = 1·480 (8) Å, av. O—S—O = 109·5 (12)°, av. N—D = 1·028 (3) Å, av. H—N—H 109·4 (17)°]. There are also $Cr(OD_2)_6^{2+}$ ions, but these show the expected Jahn–Teller distortion from regular octahedral geometry: Cr—O(8), 2·389 Å, is much longer than the other two Cr—O bonds, which average 2·068 (14) Å. There is a complex hydrogen-bonding network which differs only in detail from that seen in the other members of the series. The observation from the 84 K X-ray structure that D(13) is hydrogen bonded only to O(4), and not also to O(3) as it is in the other members in the series is confirmed.

References

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A30, 129–153.
BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–425.
DEETH, R. J., FIGGIS, B. N., FORSYTH, J. B., KUCHARSKI, E. S. & REYNOLDS, P. A. (1988). *Aust. J. Chem.* 41, 1289–1294.
DEETH, R. J., FIGGIS, B. N., FORSYTH, J. B., KUCHARSKI, E. S. & REYNOLDS, P. A. (1989). *Proc. R. Soc. London Ser. A*, 421, 153–168.
FENDER, B. E. F., FIGGIS, B. N. & FORSYTH J. B. (1986*a*). *Proc. R. Soc. London Ser. A*, 404, 139–145.
FENDER, B. E. F., FIGGIS, B. N. & FORSYTH, J. B. (1986*b*). *Aust. J. Chem.* 39, 1023–1028.
FENDER, B. E. F., FIGGIS, B. N., FORSYTH, J. B., REYNOLDS, P. A. & STEVENS E. (1986). *Proc. R. Soc. London Ser. A*, 404, 127–138.
FIGGIS, B. N., FORSYTH, J. B., KUCHARSKI, E. S., REYNOLDS, P. A. & TASSET, F. (1990). *Proc. R. Soc. London Ser. A*, 428, 113–127.
FIGGIS, B. N., KUCHARSKI, E. S. & REYNOLDS, P. A. (1990). *Acta Cryst.* B46, 577–586.
FIGGIS, B. N., KUCHARSKI, E. S., REYNOLDS, P. A. & TASSET, F. (1989). *Acta Cryst.* C45, 942–944.
FIGGIS, B. N., REYNOLDS, P. A. & WILLIAMS, G. A. (1980). *J. Chem. Soc. Dalton Trans.* pp. 2339–2347.
HALL, S. R. & STEWART, J. M. (1989). Editors. *XTAL2.6 Users Manual.* Univs. of Western Australia, Australia, and Maryland, USA.
KOESTER, L. & STEYERL, A. (1980). *Neutron Physics. Tracts in Modern Physics*, 80, p. 1. Berlin: Springer.
LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A30, 580–584.

Structure of GdMo5O8

BY P. GOUGEON, P. GALL AND M. SERGENT

Laboratoire de Chimie Minérale B, Unité de Recherche Associée au CNRS n° 254, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes CEDEX, France

Abstract. Gadolinium pentamolybdate, $GdMo_5O_8$, $M_r = 764·95$, monoclinic, $P2_1/c$, $a = 7·559$ (3), $b = 8·9926$ (9), $c = 9·923$ (3) Å, $\beta = 109·81$ (2)°, $V = 634·6$ (3) Å^3, $Z = 4$, $D_x = 8·006$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·71073$ Å, $\mu = 197·4$ cm^{-1}, $F(000) = 1352$, $T = 298$ K, $R = 0·028$ for 2098 observed reflections. The title compound is isostructural with $LaMo_5O_8$ and contains bioctahedral $Mo_{10}O_{18}$ cluster units strongly linked by Mo(1)—Mo(1) intercluster bonds [2·674 (1) Å] to form infinite molybdenum oxide chains. These are interconnected through Mo—O—Mo bonds to create channels where the Gd^{3+} ions are located. The Mo—Mo distances in the Mo_{10} cluster lie between 2·598 (1) and 2·832 (1) Å (average 2·746 Å). The Mo—O distances range between 1·994 (5) and 2·142 (5) Å (average 2·074 Å). The Gd^{3+} ions are ten coordinated to O atoms with Gd—O distances ranging from 2·315 (5) to 2·959 (5) Å (average 2·614 Å).

Experimental. Single crystals of $GdMo_5O_8$ were obtained by heating a cold-pressed pellet of a stoichiometric mixture of Gd_2O_3, MoO_3 and Mo in sealed molybdenum crucibles at about 2100 K for 5 min, cooling to 1273 K at a rate of 100 K h^{-1} and finally furnace cooling to room temperature.