Se—Ag—Se bond, whereas it is very large along the other direction, resulting in a very oblate ellipsoid.

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Hexaamminechromium(III) Aquapentachloromanganate(II)

BY WILLIAM CLEGG*

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

Abstract. $[Cr(NH_3)_6][MnCl_5(H_2O)]$, monoclinic, $P2_1/c$, $a = 17.203$ (3), $b = 11.417$ (2), $c = 14.912$ (3) Å, $\beta = 92.64$ (2)°, $Z = 8$, $D_o = 1.82$, $D_c = 1.836$ g cm^{-3}. The compound was prepared in an attempt to produce the $[MnCl_5]^{3-}$ anion. The structure consists of $[Cr(NH_3)_6]^{3+}$ and $[MnCl_5(H_2O)]^{3-}$ ions.

Introduction. Initial cell parameters were obtained from precession photographs (Mo $K\alpha$ radiation), which also indicated the space group $P2_1/c$ ($h0l$ reflexions absent for odd l, $0k0$ absent for odd k). The asymmetric unit contains two cations and two anions.

A yellow crystal with faces parallel to the unit-cell faces was mounted, in a Lindemann-glass tube, on a Hilger & Watts Y290 four-circle diffractometer, with c slightly misaligned from the φ axis. Unit-cell parameters and the orientation matrix were refined by least squares from 12 reflexions ($2\theta > 40°$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, Zr filter). Intensities were collected for all unique reflexions with $2\theta \leq 55°$ (θ–2θ scan, 2 s count at each of 50 steps of 0.02° in θ, background counts of 25 s at each end of the scan range; calibrated attenuators were inserted into the beam for intense reflexions). Three standard reflexions monitored periodically showed no significant intensity variation. The crystal was measured with a travelling microscope for absorption corrections (Gaussian integration method;

$\mu = 25.65$ cm^{-1}; transmission factors range from 0.293 to 0.454). Of 6722 measured reflexions, 608 with $I < 0$

Table 1. *Atomic coordinates* $(\times 10^5)$ *of the non-hydrogen atoms*

	x	y	z
Cr(1)	12700 (2)	68670 (3)	13256 (3)
N(11)	10809 (18)	80124 (23)	23729 (17)
N(12)	15138 (15)	54983 (21)	22141 (17)
N(13)	1153 (14)	63542 (22)	12808 (18)
N(14)	10042 (14)	82141 (19)	4310 (16)
N(15)	24379 (14)	73134 (22)	13646 (18)
N(16)	14469 (15)	58151 (20)	2261 (16)
Cr(2)	38352 (2)	19151 (3)	36501 (3)
N(21)	46507 (14)	32359 (20)	37638 (16)
N(22)	30036 (14)	31031 (19)	40356 (17)
N(23)	35792 (15)	23811 (22)	23274 (16)
N(24)	47113 (14)	7995 (21)	32747 (17)
N(25)	40535 (14)	14181 (21)	49765 (16)
N(26)	30010 (15)	5854 (20)	35440 (18)
Mn(1)	12140 (2)	18679 (4)	11650 (3)
Cl(11)	14430 (5)	24101 (7)	28065 (5)
Cl(12)	968 (4)	4505 (6)	14489 (5)
Cl(13)	2005 (4)	35136 (6)	9702 (5)
Cl(14)	22344 (4)	33060 (6)	6735 (5)
Cl(15)	22453 (4)	2767 (6)	13101 (6)
O(1)	9720 (14)	14166 (20)	−3028 (15)
Mn(2)	37461 (2)	68568 (4)	38622 (3)
Cl(21)	39722 (5)	82823 (6)	26500 (5)
Cl(22)	51698 (4)	61712 (6)	40280 (5)
Cl(23)	39804 (5)	85037 (6)	50301 (5)
Cl(24)	23151 (4)	72119 (8)	39545 (5)
Cl(25)	34801 (4)	52709 (6)	26679 (5)
O(2)	35913 (13)	55244 (19)	49594 (15)

* Present address: Anorganisch-Chemisches Institut der Universität, Tammannstrasse 4, 3400 Göttingen, Federal Republic of Germany.

Table 2. *Bond lengths* (Å) *and angles* (°)

Cr(1)-N(11)	2·074 (3)	Cr(2)-N(21)	2·061 (3)	Mn(1)-Cl(11)	2·538 (2)	Mn(2)-Cl(21)	2·476 (2)
Cr(1)-N(12)	2·079 (3)	Cr(2)-N(22)	2·072 (3)	Mn(1)-Cl(12)	2·562 (2)	Mn(2)-Cl(22)	2·572 (2)
Cr(1)-N(13)	2·069 (3)	Cr(2)-N(23)	2·071 (3)	Mn(1)-Cl(13)	2·571 (2)	Mn(2)-Cl(23)	2·582 (2)
Cr(1)-N(14)	2·073 (3)	Cr(2)-N(24)	2·070 (3)	Mn(1)-Cl(14)	2·536 (2)	Mn(2)-Cl(24)	2·505 (2)
Cr(1)-N(15)	2·071 (3)	Cr(2)-N(25)	2·075 (3)	Mn(1)-Cl(15)	2·542 (2)	Mn(2)-Cl(25)	2·566 (2)
Cr(1)-N(16)	2·066 (3)	Cr(2)-N(26)	2·090 (3)	Mn(1)-O(1)	2·268 (3)	Mn(2)-O(2)	2·259 (3)
N(11)-Cr(1)-N(12)	91·6 (2)	N(21)-Cr(2)-N(22)	88·5 (2)	Cl(11)-Mn(1)-Cl(12)	94·5 (1)	Cl(21)-Mn(2)-Cl(22)	95·1 (1)
N(11)-Cr(1)-N(13)	91·1 (2)	N(21)-Cr(2)-N(23)	90·3 (2)	Cl(11)-Mn(1)-Cl(13)	90·3 (1)	Cl(21)-Mn(2)-Cl(23)	89·4 (1)
N(11)-Cr(1)-N(14)	88·2 (2)	N(21)-Cr(2)-N(24)	88·3 (2)	Cl(11)-Mn(1)-Cl(14)	92·4 (1)	Cl(21)-Mn(2)-Cl(24)	97·0 (1)
N(11)-Cr(1)-N(15)	90·5 (2)	N(21)-Cr(2)-N(25)	91·1 (2)	Cl(11)-Mn(1)-Cl(15)	90·9 (1)	Cl(21)-Mn(2)-Cl(25)	89·2 (1)
N(12)-Cr(1)-N(13)	88·5 (2)	N(22)-Cr(2)-N(23)	88·7 (2)	O(1)-Mn(1)-Cl(12)	84·9 (2)	O(2)-Mn(2)-Cl(22)	82·5 (2)
N(12)-Cr(1)-N(15)	90·0 (2)	N(22)-Cr(2)-N(25)	90·7 (2)	O(1)-Mn(1)-Cl(13)	87·9 (2)	O(2)-Mn(2)-Cl(23)	91·2 (2)
N(12)-Cr(1)-N(16)	92·1 (2)	N(22)-Cr(2)-N(26)	90·9 (2)	O(1)-Mn(1)-Cl(14)	88·1 (2)	O(2)-Mn(2)-Cl(24)	85·4 (2)
N(13)-Cr(1)-N(14)	90·4 (2)	N(23)-Cr(2)-N(24)	91·5 (2)	O(1)-Mn(1)-Cl(15)	90·9 (2)	O(2)-Mn(2)-Cl(25)	90·2 (2)
N(13)-Cr(1)-N(16)	89·2 (2)	N(23)-Cr(2)-N(26)	90·0 (2)	Cl(12)-Mn(1)-Cl(13)	88·3 (1)	Cl(22)-Mn(2)-Cl(23)	92·2 (1)
N(14)-Cr(1)-N(16)	91·2 (2)	N(24)-Cr(2)-N(25)	89·3 (2)	Cl(12)-Mn(1)-Cl(15)	93·5 (1)	Cl(22)-Mn(2)-Cl(25)	89·5 (1)
N(15)-Cr(1)-N(16)	89·3 (2)	N(25)-Cr(2)-N(26)	88·1 (2)	Cl(13)-Mn(1)-Cl(14)	88·2 (1)	Cl(23)-Mn(2)-Cl(24)	88·2 (1)
N(11)-Cr(1)-N(16)	176·3 (2)	N(21)-Cr(2)-N(26)	179·4 (2)	Cl(14)-Mn(1)-Cl(15)	89·9 (1)	Cl(24)-Mn(2)-Cl(25)	90·5 (1)
N(12)-Cr(1)-N(14)	178·7 (2)	N(22)-Cr(2)-N(24)	176·9 (2)	Cl(12)-Mn(1)-Cl(14)	172·3 (1)	Cl(22)-Mn(2)-Cl(24)	167·9 (1)
N(13)-Cr(1)-N(15)	177·8 (2)	N(23)-Cr(2)-N(25)	178·0 (2)	Cl(13)-Mn(1)-Cl(15)	177·8 (1)	Cl(23)-Mn(2)-Cl(25)	177·9 (1)
				Cl(11)-Mn(1)-O(1)	178·1 (2)	Cl(21)-Mn(2)-O(2)	177·5 (2)

and 946 with $0 < I < 3\sigma(I)$ (based on counting statistics) were rejected.

The structure was solved from the 5168 unique reflexions by Patterson and Fourier methods, with the help of constrained refinement to overcome the problem of pseudosymmetry in the positions of the metal atoms alone. The quantity minimized by full-matrix least squares was $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w = 1/\sigma^2(F_o)$]. Complex scattering factors for uncharged atoms were those of Cromer & Waber (1974) and Cromer & Ibers (1974).

With Cr, Mn and Cl atoms anisotropic and N isotropic, a difference synthesis revealed two major peaks assigned to O atoms of H_2O ligands attached to Mn. Inclusion of these atoms with isotropic thermal parameters reduced R (= $\sum |\Delta|/\sum |F_o|$) from 11·47 to 7·15% and R_w [= $(\sum w\Delta^2/\sum wF_o^2)^{1/2}$] from 17·43 to

8·9%. Further refinement with all atoms anisotropic (R = 3·75%, R_w = 6·02%) followed by a difference map revealed the positions of 17 of the 20 H atoms. These positions, together with calculated positions for the other three, were refined to idealized positions by applying geometrical constraints (N—H=O—H = 0·87 Å, H—N—H = 107°, H—O—H = 104°; threefold symmetry for Cr—NH_3 groups, twofold for Mn—OH_2) (Churchill, 1973; Clegg, Greenhalgh & Straughan, 1975), and these constraints were maintained during the remaining refinement. An overall isotropic thermal parameter was refined for the H atoms of each ion. The final values of R and R_w were 2·91 and 4·36% [3·69 and 4·60% including the reflexions with $0 < I < 3\sigma(I)$]. All shift/e.s.d. ratios in the last cycle were <0·02. An analysis of variance showed no systematic trends with indices, sin θ or $|F_o|$; 258 parameters were refined. A final difference synthesis showed no significant features. Atomic coordinates are given in Table 1,* and bond lengths and angles in Table 2.

Discussion. Complexes of empirical formula $Cr(NH_3)_6MCl_5$ can be prepared from [$Cr(NH_3)_6$]Cl_3, MCl_2 and HCl in solution in water or water/methanol for M = Co, Zn, Pd, Hg (Greenhalgh, 1977). Of these, the Hg complex contains trigonal-bipyramidal [$HgCl_5$]$^{3-}$ anions (Clegg, Greenhalgh & Straughan, 1975) and is isostructural with the corresponding Cu (Raymond, Meek & Ibers, 1968) and Cd complexes (Epstein & Bernal, 1971), which can be prepared in the same way. The Zn and Co complexes contain distorted tetrahedral [MCl_4]$^{2-}$ anions, which show a significant
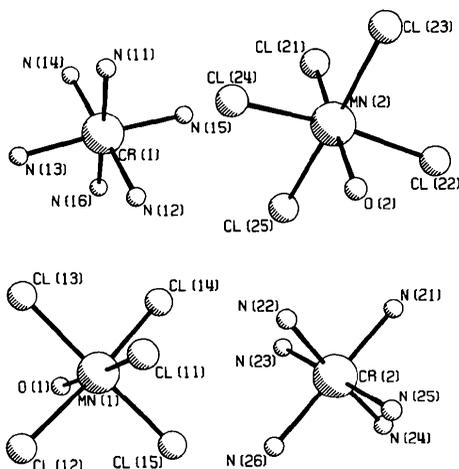
Fig. 1. Perspective view of the four crystallographically independent ions, showing the numbering scheme adopted. H atoms are omitted for clarity.

interaction with the remaining Cl^- ion to give incipient formation of a fifth M–Cl bond (Clegg, 1976). Spectroscopic and X-ray photographic data indicate that the Pd complex contains square-planar $[PdCl_4]^{2-}$ and Cl^- anions with no significant bonding interaction (Greenhalgh, 1977; Clegg, 1977). With $MnCl_2$, the same method gives a complex initially formulated as $[Cr(NH_3)_6][MnCl_5]$, but the IR spectrum is inconsistent with this and suggests the possibility of bridged species $[Mn_2Cl_x]^{(x-4)-}$ (Greenhalgh, 1977). The crystal structure was determined in order to resolve this difficulty.

The complex actually contains $[MnCl_5(H_2O)]^{3-}$ anions. These and the $[Cr(NH_3)_6]^{3+}$ cations have an essentially octahedral coordination geometry, cis angles
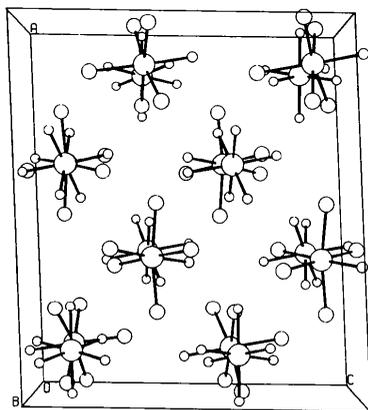
Fig. 2. The contents of one unit cell.

in the anions differing from 90° by rather more than is observed in the cations. The ions are held together by Coulombic forces and by a network of weak N—H···Cl hydrogen bonds.

The geometries of the two independent cations and two independent anions are shown in Fig. 1, and the contents of one unit cell in Fig. 2.

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An X-ray Diffraction Study of Nickel Thiosulphate Hexahydrate

By Y. ELERMAN, A. AYDIN URAZ AND N. ARMAĞAN

University of Ankara Faculty of Science, Department of Physics, Beşevler, Ankara, Turkey

Abstract. $NiS_2O_3.6H_2O$, $M_r = 463.02$, orthorhombic, *Pnma*, $a = 9.282$ (5), $b = 14.444$ (9), $c = 6.803$ (3) Å, $Z = 4$, $V = 912.1$ Å^3, $D_x = 2.03$, $D_m = 1.92$ g cm^{-3} (flotation), μ(Cu $K\alpha$) $= 73.27$ cm^{-1}. The title compound is isostructural with $MgS_2O_3.6H_2O$. The structure was refined by a full-matrix least-squares method to an R (excluding zero-weight data) of 0.056 for 248 reflexions and an R (including zero-weight data) of 0.072 for 266 reflexions. The S—S and S—O bond distances in the $S_2O_3^{2-}$ anion are 2.015 (7) and 1.465 (10) Å respectively. The bond angle O—S—O is 110.2 (6)°. The H atom positions were found from a difference Fourier synthesis.

Introduction. The first structural investigation of $NiS_2O_3.6H_2O$ was made by Brunt (1946) who proposed that it was isomorphous with $MgS_2O_3.6H_2O$. In this study, which is based on the data collected at room temperature, Brunt's proposition is justified and the results are compared with those of the other ionic thiosulphates.

The diffraction data were collected employing a