Acta Chemica Scandinavica A 28 (1974) 541—545

The Crystal Structure of Ammonium Dichromate, $(NH_4)_2Cr_2O_7$

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The crystal structure of the room temperature form of ammonium dichromate has been redetermined by X-ray diffraction. Least squares refinement with 950 reflections gave a final R-value of 0.039 for 52 parameters. The intensity data were collected on a semi-automatic diffractometer using monochromatized Mo$K\alpha$-radiation.

The dichromate ions are in the eclipsed form with terminal oxygen atoms *trans* to the bridging oxygen atom. The symmetry is approximately C_{2v}. The Cr – O (bridge) distance is 1.781 Å, e.s.d. 0.002 Å and the mean Cr – O (terminal) is 1.634 Å, e.s.d. 0.002 Å. The Cr – O – Cr angle is 121.0°, e.s.d. 0.19°. There is no evidence for an abnormally long Cr – O (bridge) distance.

The crystal structure of the room temperature form of ammonium dichromate has been redetermined to obtain more precise values of the bond lengths and angles. The structure was first solved by Byström and Wilhelmi,[1] henceforth referred to as B and W, who obtained an exceptionally large value, 1.91 Å, for the Cr – O (bridge) distance. Although B and W attributed the apparent lengthening of the bond to errors in the atomic coordinates, Luu and Hillaire [2] claimed from their interpretation of the solid-state Raman-spectrum that the lengthening was real and could be explained by invoking hydrogen bonding.

We now find no evidence for an abnormally long Cr – O bond.

EXPERIMENTAL

Intensity data were collected using a linear diffractometer of the Arndt-Phillips [3] design. Mo$K\alpha$-radiation monochromatized [4] by means of a graphite crystal was employed in conjunction with a scintillation counter and a pulse height analyser. The background – peak – background technique was used. The crystal was mounted with its [010] axis, the needle axis, as rotation axis.

Reflections hkl with $0 \leq k \leq 9$ and for which $\sin\theta/\lambda < 0.7$ were measured giving 1040 independent reflections of which 957 had $I > 2\sigma_c(I)$ where $\sigma_c(I)$ is the square root of the total number of counts for the reflection.

The crystal used was 0.7 mm in length and 0.20 by 0.25 mm in cross section. No correction was made for absorption.

CRYSTAL DATA

$(NH_4)_2Cr_2O_7$, M = 252.1. Monoclinic, $a = 13.26 \pm 0.01$ Å, $b = 7.54 \pm 0.02$ Å, $c = 7.74 \pm 0.02$ Å, $\beta = 93.2°$, $U = 772.6$ Å^3, $Z = 4$, $D_c = 2.17$, $F(0,0,0) = 504$. The cell dimensions are those given by B and W. The possible space groups are $C2/c$ (C_{2h}^6, No. 15) and Cc (C_s^4, No. 9); the morphology shows the space group to be $C2/c$.

The orange crystals are tabular on (100) and bounded by {101} and {111}, the largest dimension is in the [010] direction.

Observed and calculated structure factors, atomic coordinates and thermal vibration parameters are listed in Tables 1 – 3. Bond distances, angles, and torsion angles are given in Tables 4 – 6. The estimated standard deviations do not include the errors in the cell dimensions.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by the heavy atom method. Least-squares refinement of atomic coordinates, thermal parameters, scale factor, and an isotropic extinction parameters gave a final R-value of 0.039 for 950 reflections and 52 parameters, the weighted R-value was $r = 0.062$. Only those reflections for which $\sin\theta/\lambda < 0.7$

Table 1. Observed and calculated structure factors: h, k, l, $10|F_{obs}|$, $10|F_{calc}|$.

Table 2. Atomic coordinates in fractions of cell edges. The estimated standard deviations $\times 10^5$ are given in brackets.

	x	y	z
Cr	0.10148(4)	0.17124(7)	−0.14046(6)
O1	0.05730(21)	0.30327(40)	0.00172(34)
O2	0.17849(19)	0.02802(41)	−0.05279(16)
O3	0.15877(20)	0.28968(38)	−0.28058(34)
O4	0	0.05488(45)	−0.25
NH_4^+	0.35655(23)	0.15412(42)	−0.34526(39)

were used, 7 reflections very close to the rotation axis ($h^2+l^2\leq 2$) were omitted from the refinement.

It was not possible to determine the positions of the hydrogen atoms. Since proton magnetic resonance [5] and inelastic neutron scattering [6,7] both indicate that the ammonium ion is reorienting about random axes the scattering factor for a freely rotating ammonium ion was used. This did not give an appreciably lower R-value than that obtained by refining with a neutral nitrogen atom and no hydrogen atoms ($R=0.040$). Refinement in the lower symmetry space group, Cc, did not give a lower R-value.

COMPUTATIONAL DETAILS

Least squares refinement was carried out using the fullmatrix program LINUS,[8] the quantity minimized was

$$r=\frac{\sum w||F_o|-|F_c||^2}{\sum w|F_o|^2}$$

where $w=1/\sigma^2$, where

$$\sigma=\sqrt{\sigma_c(F_o^2)+(1+K)F_o^2}-|F_o|$$

The parameter K was varied so that $\langle w||F_o|-|F_c||\rangle$ varied as little as possible with the magnitude of F_o.

The atomic scattering factors used were those of Cromer and Waber [9] for chromium and of Cromer and Mann [10] for oxygen and for nitrogen. The scattering factor for the ammonium ion was calculated [11] as

$$f_{NH_4^+}=f_N+3f_H \sin(4\pi rs)/4\pi rs$$

where $r=1.0$ Å, $s=\sin\theta/\lambda$, and f_H is the scattering factor for hydrogen as calculated for a spherically symmetric atom by Stewart, Davidson, and Simpson.[12]

No correction was made for anomalous dispersion or for absorption.

Bond lengths and angles and their standard deviations were calculated using ORFFE,[13] drawings were made using ORTEP.[14]

DISCUSSION

The structure is shown in Fig. 1. The two tetrahedra of the $Cr_2O_7^{2-}$ ion are related by a 2-fold axis through the centre oxygen atom. The compound is isostructural with one of the forms [15] of $Rb_2Cr_2O_7$.

The dimensions of the dichromate ion are very similar to those found for other dichromates. Panagiotopoulos and Brown [16] quote structural data for 12 dichromates for which Cr−O terminal) range from 1.60 Å to 1.62 Å, Cr−O (bridge) from 1.76 Å to 1.80 Å, and the angle Cr−O−Cr from 121° to 141°. We find Cr−O (terminal) = 1.634(2) Å, Cr−O (bridge) = 1.781(3) Å, and Cr−O−Cr = 121.0(2)°. From the torsion angles the mean value of the twist of the CrO_3 groups out of the plane defined by the two chromium

Table 3. Thermal parameters ($\times 10^4$) with their estimated standard deviations. The u_{ij} are defined by: $\exp[-2\pi^2(u_{11}a^{*2}h^2+\cdots 2u_{12}a^*b^*hk+\cdots)]$.

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cr	237(4)	295(3)	204(3)	41(2)	40(2)	19(2)
O1	409(15)	557(16)	253(13)	59(12)	92(11)	−77(12)
O2	406(14)	477(16)	571(18)	136(12)	−82(13)	92(14)
O3	376(14)	476(14)	278(13)	−96(11)	96(11)	23(11)
O4	277(16)	295(15)	279(19)	0	18(14)	0
NH_4^+	317(15)	446(17)	262(14)	45(12)	33(11)	59(12)

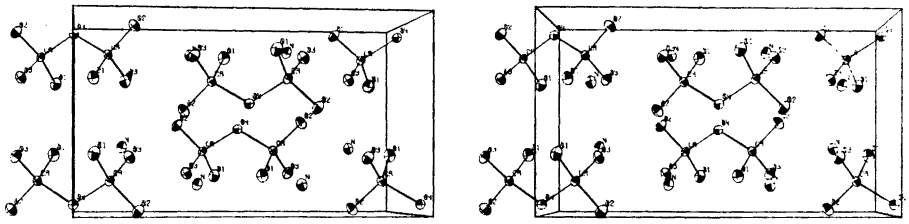

Fig. 1. Stereoscopic view of the unit cell contents as seen down the *c*-axis. The *a*-axis is horizontal.

Table 4. Bond lengths l, and bond lengths corrected for riding motion, l_{corr}, and their estimated standard deviations.

	l	l_{corr}
Cr – O1	1.618(3)	1.632(3)
Cr – O2	1.610(3)	1.632(3)
Cr – O3	1.626(3)	1.637(3)
Cr – O4	1.781(2)	

Table 5. Angles and their estimated standard deviations.

	θ	$\sigma(\theta)$
O1 – Cr – O2	111.8	0.15
O1 – Cr – O3	108.4	0.17
O1 – Cr – O4	109.5	0.12
O2 – Cr – O3	109.9	0.15
O2 – Cr – O4	108.3	0.16
O3 – Cr – O4	108.8	0.11
Cr – O4 – Cr	121.0	0.19

Table 6. Torsion angles (°) and their standard deviations. The torsion angle is defined as 0° when the 4 atoms are coplanar and the two oxygen atoms are *cis* to each other, and as 180° when the two oxygen atoms are in the *trans* position.

	θ	$\sigma(\theta)$
Cr′ – O4 – Cr – O1	56.67	0.12
Cr′ – O4 – Cr – O2	178.86	0.12
Cr′ – O4 – Cr – O3	−61.68	0.11

atoms and the bridging oxygen atoms are $\alpha_1 = 2.05°$ and α_2, the twist of the CrO_3 group related by the 2-fold axis is $-\alpha_1$. Panagiotopoulos and Brown [16] found a correlation between the Cr – O – Cr angle, the antisymmetric twist $(\alpha_1 - \alpha_2)$, and the amplitude of the antisymmetric torsion mode, each of these tending to increase together. For ammonium dichromate $\alpha_1 - \alpha_2$ is very small, 4.1°, the Cr – O – Cr is one of the smallest observed and unlike most of the dichromates studied the thermal vibration of the central oxygen atom is not larger than that of the terminal atoms.

There is no evidence for an abnormally long Cr – O (bridge) bond, the extreme value found by B and W is partly explained by the fact that the reflections were indexed according to a cell with $\beta = 86.8°$ whereas they used $\beta = 93.2°$ in their calculations. The confirmation of the long bond by Raman spectroscopy would seem to call for a reinterpretation of the Raman data.

The nearest neighbour distances to the nitrogen atom are given in Table 7, showing that there are many ways in which the ammonium

Table 7. Nitrogen-oxygen distances less than 3.5 Å. The nitrogen atom has the coordinates as in Table 2, the symmetry operations show how the oxygen positions are related to those in Table 2. The standard deviations are ~0.004 Å.

N – O1	2.853	$\frac{1}{2}-x, \frac{1}{2}-y, -z$
N – O1	2.991	$\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$
N – O1	3.150	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$
N – O2	2.957	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$
N – O2	3.101	$x, -y, -\frac{1}{2}+z$
N – O2	3.493	x, y, z
N – O3	2.885	x, y, z
N – O3	2.923	$\frac{1}{2}-x, \frac{1}{2}-y, z-1$
N – O3	2.926	$\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$

ion could be hydrogen-bonded to the oxygen atoms so that there is the possibility of either static or dynamic disorder.

Acknowledgement. The linear diffractometer was provided by Carlsbergfondet.

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Received February 20, 1974.