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A re-investigation of the crystal structure of $(NH_4)_2CrO_4$.

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The crystal structure of ammonium chromate, $(NH_4)_2CrO_4$, has been redetermined with three-dimensional X-ray data from a linear diffractometer. The space group is $C2/m$ with unit-cell parameters $a=12{\cdot}21$, $b=6{\cdot}258$, $c=7{\cdot}630$ Å, $\beta=115°10'$. The CrO_4^{2-} ion, with Cr–O$=1{\cdot}658\pm0{\cdot}004$ Å, does not depart significantly from regular tetrahedral geometry. The hydrogen atoms have been located, although there is nuclear magnetic resonance evidence that the NH_4^+ ions are undergoing continous thermal re-orientation in the crystal.

Introduction

The crystal structure of ammonium chromate, $(NH_4)_2CrO_4$, was first investigated by Bujor (1931, 1944) who reported the unlikely Cr–O bond distances of 1·60 and 1·98 Å. A complete redetermination of the crystal structure was therefore undertaken as part of a general study of the structures of tetrahedral oxyanions. A summary of our results has already been published (Stephens & Cruickshank, 1969).

Unknown to us, a similar investigation was simultaneously undertaken by Gatehouse & Leverett (1969), referred to hereafter as GL, who have reported the correct space group and anion geometry, although they were unable to locate the hydrogen atoms. GL used Cu $K\alpha$ radiation and photographic methods to record 465 intensities, whereas in our investigation Mo $K\alpha$ radiation was used in conjunction with a linear diffractometer to obtain the integrated intensities of 966 reflexions. The greater resolution and accuracy of the Mo data have enabled us to locate the hydrogen atoms and to determine the geometry of the chromate ion with significantly greater precision.

In the interests of brevity, this report is confined to those aspects of the structure not already discussed by GL.

Experimental

A small single crystal (approx. 0·2 × 0·3 × 0·8 mm) was used for the collection of intensity data on a Hilger–Watts linear diffractometer with Mo $K\alpha$ radiation and balanced Zr/Sr filters. The integrated intensities of 966 independent reflexions (all above background) were measured. Lorentz and polarization corrections were applied but absorption corrections ($\mu R\simeq0{\cdot}8$) were not. The unit-cell parameters were refined on the diffractometer and are listed in Table 1 with those of GL.

Table 1. *Unit-cell parameters for* $(NH_4)_2CrO_4$

	This work	GL
a	12·21 (1) Å	12·300 (2) Å
b	6·258 (3)	6·294 (5)
c	7·630 (4)	7·664 (2)
β	115·2 (2)°	115·6 (1)°
Space group	$C2/m$	$C2/m$

A polycrystalline sample of $(NH_4)_2CrO_4$ was also investigated at room temperature by nuclear magnetic resonance (n.m.r.) techniques, and the proton line-width was measured. The radio frequency (r.f.) excitation was held at 16MHz and the magnetic field swept linearly through the resonance condition. The first derivative of the absorption was plotted directly by a chart recorder, and the r.f. power and modulation were kept low enough to ensure that the line-width was not artificially increased.

Structure solution and refinement

The structure was solved directly from the three-dimensional Patterson function, which clearly showed the positions of all (non-hydrogen) atoms. These positions were used as the starting point for full-matrix least-squares (l.s.) refinement. The structure was refined to an R index of 5·5% with anisotropic vibration parameters on all atoms except Cr,* and with weights calculated to make $\langle w\Delta^2\rangle$ essentially independent of $|F_o|$. A correction for secondary extinction (Zachariasen, 1963) was also included in the l.s. refinement following Larson's (1967) procedure. Scattering curves for Cr^{3+} and O^- were taken from *International Tables for X-ray Crystallography* (1962). The scattering curve for a spherical NH_4^+ ion (Davis & Whitaker, 1966) was used instead of the usual curve for nitrogen.

A three-dimensional difference synthesis revealed small, tetrahedrally arranged, peaks about 1 Å from each nitrogen atom. Hydrogen atoms were placed at these positions and the scattering curves (*International Tables*, 1962) for neutral nitrogen and hydrogen were then used. L.s. refinement was continued for three cycles in which the parameters of all atoms were varied, with the exception of the hydrogen atom vibration parameters which were fixed at 0·038 Å^2. Weights were calculated from $w=1/(0{\cdot}4-0{\cdot}06|F_o|+0{\cdot}003|F_o|^2)$ and in the final cycle the average shift/error was 0·06. The final R index was 3·14% and the l.s. residual ($[\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$) was 3·73%.

Table 2 gives the final atomic parameters with their e.s.d.'s as derived from the inverse l.s. matrix. The fractional coordinates obtained by GL are also listed in this table. Their coordinates agree with ours within the e.s.d.'s, but are of lower precision.

Discussion

Fig. 1 shows the structure projected on to the ac plane. The tetrahedral groups which lie on the mirror plane at $y=\frac{1}{4}$

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* The Cr atom, with its regular, isolated tetrahedral environment, may not be markedly anisotropic in its thermal motion. With this assumption, the redundancy between the interlayer scale factors and the U_{22} parameters can be avoided.

are shown in heavy outline while those lying at $y=0$ are shown in lighter outline. The broken lines indicate N···O distances (Table 4). This figure is essentially the same as that of GL except for the inclusion of the hydrogen atoms.

All interatomic distances within the chromate tetrahedron were corrected for librational thermal motion (Cruickshank, 1961). Both the uncorrected and corrected distances, and the angles subtended at the Cr atom are listed in Table 3 together with the GL values for comparison.

The chromate group is regular with a mean (corrected) Cr-O bond distance* of 1·658 Å. We estimate the standard deviation of this mean as 0·004 Å. The root-mean-square

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* The GL cell dimensions are systematically about 0·6% larger than ours. If their values are used, the corrected mean Cr–O distance increases by 0·010 Å to 1·668 Å. However we have no evidence to suggest how either determination can be in error, and we prefer to use our own values.

Table 2. *Final parameters*

(*a*) Final atomic positions

	x/a		*y/b*		*z/c*	
	This work	GL	This work	GL	This work	GL
Cr	0·17184 (3)	0·17184 (14)	0	0	0·21239 (5)	0·21223 (24)
O(1)	0·3181 (2)	0·3182 (9)	0	0	0·3579 (3)	0·3549 (13)
O(2)	0·0905 (2)	0·0903 (7)	0	0	0·3374 (3)	0·3382 (12)
O(3)	0·1407 (1)	0·1405 (5)	0·2152 (2)	0·2174 (11)	0·0767 (2)	0·0754 (8)
N(1)	0·5171 (2)	0·5160 (9)	0	0	0·2516 (4)	0·2512 (14)
H(1)	0·4492 (56)		0		0·2637 (79)	
H(3)	0·5822 (51)		0		0·3860 (82)	
H(5)	0·5233 (34)		0·1203 (60)		0·1841 (50)	
N(2)	0·8405 (2)	0·8409 (9)	0	0	0·2650 (3)	0·2660 (14)
H(2)	0·9064 (51)		0		0·2496 (79)	
H(4)	0·8564 (49)		0		0·3897 (84)	
H(6)	0·7954 (34)		0·1160 (62)		0·2039 (49)	

(*b*) Final vibration parameters (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr		0·0167 (2) (isotropic)				
O(1)	0·0193 (8)	0·0472 (12)	0·0302 (10)	0	0·0037 (7)	0
O(2)	0·0306 (10)	0·0491 (12)	0·0279 (15)	0	0·0176 (8)	0
O(3)	0·0353 (7)	0·0201 (7)	0·0290 (6)	0·0010 (4)	0·0114 (5)	0·0041 (4)
N(1)	0·0381 (12)	0·0207 (10)	0·0270 (11)	0	0·0145 (9)	0
N(2)	0·0299 (10)	0·0204 (9)	0·0250 (11)	0	0·0121 (8)	0
H(all)		0·038 (isotropic)				

Table 3. *Bond distances* (Å) *and angles* (°) *in the chromate tetrahedron*

	This work		
	uncorrected	corrected	GL
Cr–O(1)	1·654 (4)	1·669	1·654 (6)
Cr–O(2)	1·644 (3)	1·659	1·665 (6)
Cr–O(3) (2)	1·641 (2)	1·652	1·665 (6)
Mean (r.m.s. deviation)	1·645 (6)	1·658 (7)	1·662 (5)
O(1)···O(2)	2·716	2·741	2·749
O(1)···O(3) (2)	2·676	2·695	2·681
O(2)···O(3) (2)	2·679	2·701	2·718
O(3)···O(3′)	2·693	2·710	2·736
Mean (r.m.s. deviation)	2·687 (15)	2·707 (17)	2·714 (25)

	This work	GL
O(1)–Cr–O(2)	110·9 (1)	111·9 (5)
O(1)–Cr–O(3)	108·5 (1)	107·8 (5)
O(2)–Cr–O(3)	109·3 (1)	109·4 (5)
O(3)–Cr–O(3′)	110·2 (1)	110·5 (6)

Table 4. *Bond distances and angles in the ammonia tetrahedra*

N(1)–H(1)	0·87 (8) Å	H(1)–N(1)–H(3)	106 (5)°
N(1)–H(3)	0·99 (5)	H(1)–N(1)–H(5) (2)	111 (3)
N(1)–H(5) (2)	0·93 (4)	H(3)–N(1)–H(5) (2)	111 (3)
		H(5)–N(1)–H(5′)	107 (5)
N(2)–H(2)	0·86 (7)	H(2)–N(2)–H(4)	111 (5)
N(2)–H(4)	0·89 (6)	H(2)–N(2)–H(6) (2)	109 (3)
N(2)–H(6) (2)	0·91 (4)	H(4)–N(2)–H(6) (2)	111 (3)
		H(6)–N(2)–H(6′)	106 (4)
Mean (r.m.s. deviation)	0·91 (4)	Mean (r.m.s. deviation)	110 (2)

(r.m.s.) deviation of the individual distances from the mean is 0·007 Å. The r.m.s. deviation of the O-Cr-O angles from 109·5° is 0·9°. The corrected O···O distances have a r.m.s. deviation of 0·016 Å from their mean of 2·707 Å.

Both ammonium tetrahedra are regular within the e.s.d.'s. The average N–H distance is 0·91 Å with an 0·04 Å r.m.s. deviation. These ions are oriented as shown in Fig. 1 to form the maximum number of nearly-equal hydrogen bonds with the surrounding oxygen atoms. The 8 oxygen atoms surrounding N(1) belong to 6 different chromate tetrahedra, while the 8 oxygen atoms about N(2) belong to 5 different tetrahedra. Each chromate group makes 16 O···N contacts with 11 adjacent NH_4^+ ions and there are 22 O···O contacts between 3·12 and 3·98 Å in length to other chromate groups. The uncorrected N-H distances and H-N-H angles are given in Table 4.

The n.m.r. results indicate that both ammonium ions are undergoing some rotational motion, as the proton resonance line-width is only 4·8 gauss, as compared with 12–15 gauss for a stationary NH_4^+ ion (Gutowsky & Pake, 1948). The type of rotational motion is evidently one of rapid re-orientation with the ions spending only a small portion of time in transitions, since otherwise the hydrogen atoms would not have shown up in the difference electron density synthesis, nor could their positions have been refined by the l.s. program.

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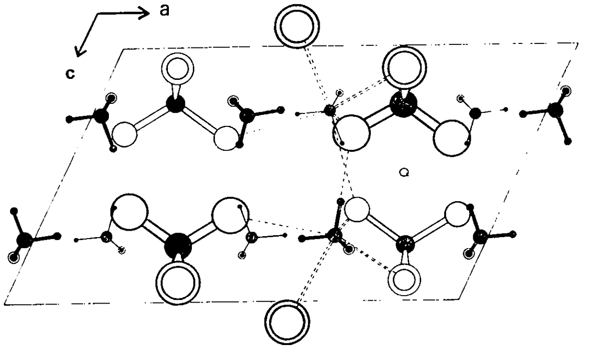

Fig. 1. Projection of the structure down the **b** axis. The open circles represent oxygen atoms. The broken lines indicate the 8 N···O distances for each nitrogen atom.

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Erratum: The structure of bis-π-cyclopentadienyl(toluene-3,4-dithiolato)molybdenum.

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A correction to *Acta Cryst.* (1969), B25, 2013.

In Table 1 of the title paper (Knox & Prout, 1969) the fifth line from the bottom should read:

C(13)	4509(19)	2189(14)	8518(24)	871(69)

Reference

Knox, J. R. & Prout, C. K. (1969). *Acta Cryst.* B**25**, 2013.