

## The Crystal Structure of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

With a Discussion of the Relation between Bond Number  
and Interatomic Distances

ANDERS BYSTRÖM and KARL-AXEL WILHELMI

*Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden*

Very little is known on the crystal chemistry of the dichromates and the polychromates. The symmetry and the cell dimensions have been determined for  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  by Gossner and Mussngug<sup>1</sup>.  $\text{K}_2\text{Cr}_2\text{O}_7$  is triclinic with  $a = 7.50$  kX,  $b = 7.38$  kX,  $c = 13.40$  kX,  $\alpha = 82.0^\circ$ ,  $\beta = 96.26^\circ$ ,  $\gamma = 90.85^\circ$ , and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is monoclinic with  $a = 7.78$  kX,  $b = 7.54$  kX,  $c = 13.27$  kX, and  $\beta = 93.7^\circ$ . The space group for  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is  $C_{2h}^3$  or  $C_{2h}^6$  according to Gossner and Mussngug. There are four formula units in the unit cell.

It is our intention to study the crystal chemistry of the dichromates and polychromates as part of an investigation of the chromium oxides. The present paper reports a determination of the structure of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .

### UNIT CELL AND SPACE GROUP

A determination of the unit cell from powder photographs (CrK radiation,  $\lambda_\alpha = 2.2909$  Å) gave the following cell dimensions, agreeing well with Gossner's and Mussngug's values:

$$a = 13.26 \pm 0.01 \text{ \AA}, \quad b = 7.54 \pm 0.02 \text{ \AA}, \quad c = 7.74 \pm 0.02 \text{ \AA}, \quad \beta = 93.2^\circ$$

Weissenberg photographs (Cu-K radiation) of the reflexions  $hk0$ ,  $h0l$ ,  $h1l$ ,  $h2l$ ,  $0kl$ ,  $1kl$ , and  $2kl$  showed that the space group is  $C_{2h}^6-C2/c$ .

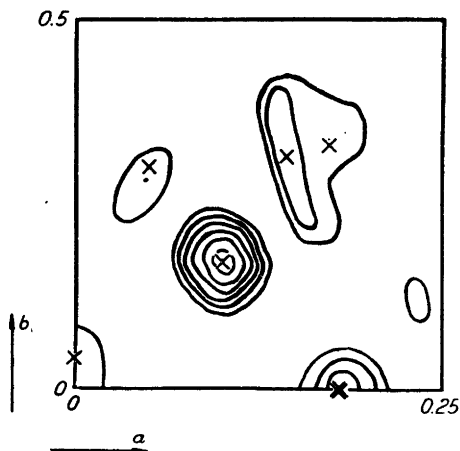


Fig. 1.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . Projection of the electron density on (001).

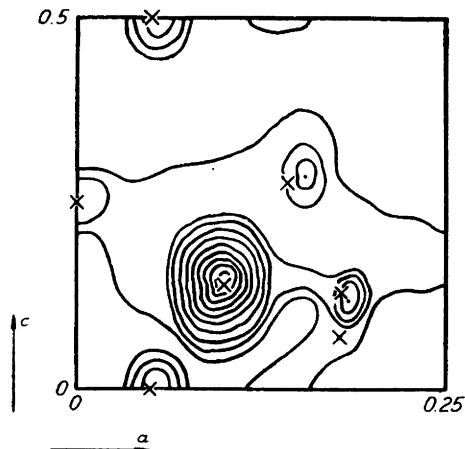


Fig. 2.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . Projection of the electron density on (010). The positions of the atoms from the trial and error process are marked with asterisks, the maxima in the Fourier projections are marked with points.

#### DETERMINATION OF THE STRUCTURE

Approximate values of the  $x$  and  $y$  parameters of the Cr atoms were derived from a Patterson projection in (001). These parameter values rendered it possible to guess the signs of most of the reflexions  $hk0$ . A two dimensional Fourier synthesis of these reflexions showed maxima belonging to the oxygen atoms also. A trial and error process, followed by a new Fourier synthesis, gave the final values of the  $x$  and  $y$  parameters. A similar procedure for the  $h0l$  reflexions gave the  $z$  parameters for the atoms. The final Fourier projections in (001) and (010) are shown in Figs. 1 and 2. Table 1 gives a comparison between observed and calculated  $F$  values.

In the calculations of the  $F$  values, scattering factors for  $\text{O}^{2-}$  and  $\text{Cr}^{6+}$  have been used. The values for  $\text{Cr}^{6+}$  were calculated from the expression  $f_{\text{Cr}^{6+}} = f_{\text{Cr}} - \frac{6}{4} (f_{\text{Ti}} - f_{\text{Ti}^{4+}}) \cdot f_{\text{NH}_4^+}$  was assumed to be equal to  $f_{\text{O}^{2-}}$ .

The following parameter values were obtained:

	$x$	$y$	$z$
8 Cr in 8( $f$ ):	$0.100 \pm 0.002$	$0.175 \pm 0.003$	$0.139 \pm 0.003$
8 $\text{O}_1$ in 8( $f$ ):	$0.050 \pm 0.005$	$0.300 \pm 0.010$	$0.000 \pm 0.010$
8 $\text{O}_2$ in 8( $f$ ):	$0.144 \pm 0.005$	$0.311 \pm 0.010$	$0.278 \pm 0.010$
8 $\text{O}_3$ in 8( $f$ ):	$0.178 \pm 0.005$	$0.000 \pm 0.010$	$0.070 \pm 0.010$
4 $\text{O}_4$ in 4( $e$ ):	0	$0.042 \pm 0.010$	$0.250 \pm 0.010$
8 $\text{NH}_4$ in 8( $f$ ):	$0.172 \pm 0.005$	$0.333 \pm 0.010$	$0.667 \pm 0.010$

The errors are derived from the trial and error calculations.

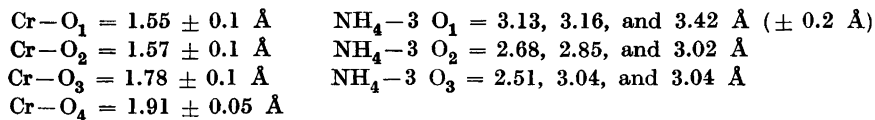
Table 1. Weissenberg Photographs of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . Comparison between  $F_{\text{obs}}$  and  $F_{\text{calc}}$ -  
Cu-K Radiation.

$hkl$	$F_{\text{obs}}$	$F_{\text{calc}}$	$hkl$	$F_{\text{obs}}$	$F_{\text{calc}}$
200	30	37	150	30	22
400	140	- 140	350	30	- 23
600	25	12	550	50	- 45
800	30	- 10	750	-	- 22
1000	80	54	950	55	61
1200	55	47	1150	50	79
1400	65	- 69	1350	30	- 21
1600	30	- 40			
			060	120	147
110	50	68	260	-	2
310	-	- 11	460	110	- 86
510	-	- 12	660	55	- 16
710	-	- 9	860	-	- 3
910	60	53	1060	50	53
1110	90	65	1260	-	39
1310	-	- 11			
1510	30	- 26	170	20	31
			370	-	- 13
020	100	- 117	570	20	- 6
220	30	- 45	770	-	0
420	75	91	970	-	- 11
620	45	72	1170	-	- 1
820	-	- 14			
1020	-	- 2	080	80	- 82
1220	-	11	280	20	- 34
1420	25	25	480	30	50
1620	35	46	680	30	42
			880	-	- 27
130	-	13			
330	20	- 40	190	65	- 41
530	90	158	390	-	- 21
730	35	62	590	60	72
930	105	- 127			
1130	70	- 55	1602	70	80
1330	45	25	1402	40	- 69
1530	85	57	1202	105	- 123
			1002	30	15
040	-	2	802	30	3
240	20	0	602	50	6
440	30	33	402	-	42
640	50	39	202	130	- 163
840	30	- 19	002	35	- 41
1040	30	- 20	202	130	199
1240	-	- 3	402	55	56
1440	-	12	602	80	- 68

<i>hkl</i>	$F_{\text{obs}}$	$F_{\text{calc}}$	<i>hkl</i>	$F_{\text{obs}}$	$F_{\text{calc}}$
80 $\bar{2}$	130	- 134	008	75	59
100 $\bar{2}$	30	- 63	20 $\bar{8}$	100	114
120 $\bar{2}$	80	70	40 $\bar{8}$	-	- 34
140 $\bar{2}$	-	27	60 $\bar{8}$	70	- 94
160 $\bar{2}$	-	- 48			
1404	70	83	021	70	- 101
1204	30	- 11	022	30	27
1004	75	- 98	023	60	- 60
804	85	- 51	024	35	32
604	40	54	025	90	96
404	120	123	026	45	- 73
204	30	32	027	-	26
004	60	- 51	028	35	- 51
20 $\bar{4}$	30	3	029	50	- 59
40 $\bar{4}$	50	54			
60 $\bar{4}$	110	83	041	35	58
80 $\bar{4}$	-	26	042	20	33
100 $\bar{4}$	110	- 92	043	65	82
120 $\bar{4}$	40	- 66	044	70	43
140 $\bar{4}$	40	56	045	110	- 112
			046	30	- 41
1206	30	39	047	-	- 12
1006	-	26	048	-	- 18
806	30	- 70	049	30	56
606	80	- 101			
406	-	2	061	-	- 15
206	85	103	062	-	- 18
006	85	48	063	20	- 14
20 $\bar{6}$	75	- 57	064	70	- 65
40 $\bar{6}$	100	- 75	065	-	- 1
60 $\bar{6}$	-	- 4	066	40	36
80 $\bar{6}$	60	37	067	-	7
100 $\bar{6}$	-	1			
120 $\bar{6}$	50	- 40	081	50	- 52
			082	-	- 34
608	-	- 22	083	-	- 12
408	25	- 40	084	-	- 27
208	25	- 12	085	30	41

## DESCRIPTION OF THE STRUCTURE

The following interatomic distances are obtained:



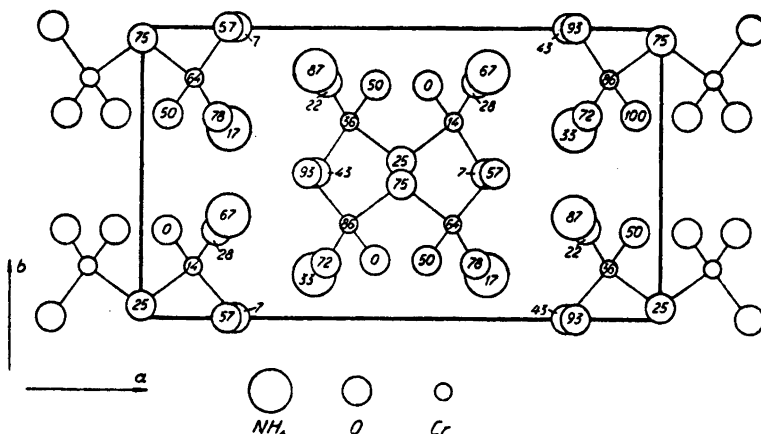


Fig. 3.  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ . Projection of the structure on (001). The figures denote the heights of the atoms in fractions of  $c$ . Superimposed oxygen atoms are symmetrically displaced.

The shortest O—O distances are:

$$\begin{array}{lll} \text{O}_1-\text{O}_2 = 2.43 \text{ \AA}, & \text{O}_1-\text{O}_3 = 2.86 \text{ \AA}, & \text{O}_2-\text{O}_3 = 2.89 \text{ \AA}, \\ \text{O}_1-\text{O}_4 = 2.85 \text{ \AA}, & \text{O}_3-\text{O}_4 = 2.82 \text{ \AA}, & \text{O}_2-\text{O}_4 = 2.79 \text{ \AA} \end{array}$$

The structure is shown in Fig. 3. The chromium atoms are surrounded by four oxygen atoms, situated in the corners of a distorted tetrahedron. Two tetrahedra share one corner so that a  $\text{Cr}_2\text{O}_7^{2-}$  group is formed. The  $\text{Cr}-\text{O}_4-\text{Cr}$  angle is  $115^\circ$  and the  $\text{Cr}-\text{Cr}$  distance in the bridge 3.2  $\text{\AA}$ . The  $\text{Cr}-\text{Cr}$  distances between different  $\text{Cr}_2\text{O}_7^{2-}$  groups are much longer, being 4.8  $\text{\AA}$ . In  $\text{CrO}_3$ , the distance  $\text{Cr}-\text{Cr}$  between adjacent atoms in the same chain is 3.3  $\text{\AA}$  and the angle  $\text{Cr}-\text{O}-\text{Cr} = 136^\circ$ .

The most stable arrangement of a  $\text{Cr}_2\text{O}_7^{2-}$  group, consisting of two joined tetrahedra, would seem to imply equilinear bonds from the two Cr atoms to the shared oxygen atom. Actually these two bonds form an angle of  $115^\circ$ . A satisfactory explanation of this strong distortion of the dichromate group has not been found. It may be due to the formation of strong  $\text{N}-\text{H}-\text{O}$  bonds, but the accuracy of the  $\text{NH}_4-\text{O}$  (or rather  $\text{N}-\text{O}$ ) distances is so low that it is not possible to decide whether this explanation is likely to be the real one. If this is the case, these bent  $\text{Cr}_2\text{O}_7^{2-}$  groups ought not to exist in dichromates of the alkali metals. An attempt to solve the structure of another dichromate will be made.

Previous investigations on chromates and  $\text{CrO}_2\text{Cl}_2$  have shown, that for an oxygen atom bonded to only one Cr atom the distance  $\text{Cr}-\text{O}$  is close to

1.60 Å (see table in ref. 2 p. 1140). As will be seen the distances Cr—O<sub>1</sub> and Cr—O<sub>2</sub> found agree with this figure. However, the distance Cr—O<sub>3</sub> is considerably longer. No reasonable explanation for this effect has been found, but a considerable part of the difference may be due to errors in the parameters.

For oxygen atoms bonded to two Cr atoms, Cr—O distances of  $1.79 \pm 0.05$  Å were found in CrO<sub>3</sub><sup>2</sup>. Again in (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, the corresponding distances are considerably longer (Cr—O<sub>4</sub>), being  $1.91 \pm 0.10$  Å. However, this difference in distances may also be due to errors in parameters.

#### ESTIMATION OF THE EFFECT OF BOND NUMBER ON INTERATOMIC DISTANCES

In a recent paper, Pauling<sup>3</sup> suggested a formula relating interatomic distances and coordination number in metals and alloys:

$$\begin{aligned} r(1) - r(n) &= 0.300 \log n \\ n &= \text{bond number} \\ r(1) &= \text{radius for bond number 1.} \\ r(n) &= \text{radius for bond number } n. \end{aligned}$$

A similar logarithmic relation may also hold for the bonds (dominatingly) covalent in character in other compounds. In V<sub>2</sub>O<sub>5</sub> there are oxygen atoms bonded to one, two, and three V atoms with the following distances<sup>4</sup>:

$$d_1 = \text{O—V} = 1.54 \pm 0.06; \quad d_2 = \text{O—2 V} = 1.77 \pm 0.03; \quad d_3 = \text{O—3 V} = 1.93 \pm 0.05$$

$d_3$  is a mean value of three distances 1.88, 1.88 and 2.02 Å (see below). The errors denote maximal errors derived from a trial and error process and from two dimensional Fourier projections, so that the distances are probably rather more accurate than the errors would indicate.

Assuming a similar equation to Pauling's to be valid, we can calculate one of these distances, knowing two of them.

$$\begin{aligned} \Delta_{1,2} &= -d_1 + d_2 = 2 K \log 2 & \frac{\Delta_{1,2}}{\Delta_{1,3}} &= \frac{\log 2}{\log 3} \\ \Delta_{1,3} &= -d_1 + d_3 = 2 K \log 3 \end{aligned}$$

From  $\Delta_{1,2} = -1.54 + 1.77 = 0.23$ , we calculate  $\Delta_{1,3} = 0.36$  Å, which is close to the observed value 0.39 Å. The value of the constant  $K$  in the equation used:

$$r_{\text{V}}(n_1) + r_{\text{O}}(n_1) - r_{\text{V}}(n_2) + r_{\text{O}}(n_2) = 2 K \log \frac{n_2}{n_1}$$

is calculated from the observed values of  $\Delta_{1,2}$  and  $\Delta_{1,3}$  and found to be 0.38 and 0.41 respectively, with a mean value of 0.39. As was seen, the corresponding value of the constant in Pauling's equation was 0.300.

Using the value 0.39 for the constant we can calculate the bond numbers of the four longer O—V bonds, with the bond numbers 2 for O—V<sub>1</sub> = 1.54 and 1 for O—2 V = 1.77 Å. For the vanadium atoms we find

	$n$	
V—O = 1.54 Å (one distance)	2.0	(assumed value)
V—O = 1.77 Å ( » » )	1.0	» »
V—O = 1.88 Å (two » )	0.73	(calculated value)
V—O = 2.02 Å (one » )	0.50	» »
V—O = 2.81 Å ( » » )	0.05	» »

Thus for the V atoms  $\sum n = 2.0 + 1.0 + 2 \cdot 0.73 + 0.50 = 4.96$  close to the expected value of 5. It is of interest to note that the sixth bond is much weaker than the other five, and it seems appropriate to call the V atoms five-coordinated, as was done in a previous paper <sup>4</sup>.

The only Cr—O distance in CrO<sub>3</sub> known with reasonable accuracy is that to the shared oxygen atoms in the chain, which is  $1.79 \pm 0.05$  Å<sup>2</sup>. From the distance Cr—O in CrO<sub>2</sub>F<sub>2</sub> with bond number 2, we calculate this distance to be  $1.57 + 0.78 \log 2 = 1.80$  Å, thus almost exactly the same as the observed value. The other Cr—O distances in CrO<sub>3</sub> are almost equally long, being 1.81 Å (expected value 1.57 Å), but their accuracy is very low, as is evident from the structure determination.

The mean Cr—O distance in chromates such as K<sub>2</sub>CrO<sub>4</sub> and CuCrO<sub>4</sub> is calculated to be  $1.57 + 0.78 \log \frac{4}{3} = 1.67$  Å. This is actually the value found by Brandt in CuCrO<sub>4</sub><sup>5</sup> and within the accuracy of the value in CaCrO<sub>4</sub> (1.64 Å)<sup>6</sup>. The distance Cr—O in K<sub>2</sub>CrO<sub>4</sub><sup>7</sup> and Na<sub>2</sub>CrO<sub>4</sub><sup>8</sup> is somewhat lower, 1.60 Å, but the limits of errors may include the calculated value.

The individual bond numbers of the Cr—O<sub>1</sub>, Cr—O<sub>2</sub>, and Cr—O<sub>3</sub> bonds in (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> are difficult to evaluate because of the large errors in the NH<sub>4</sub>—O distances. However an expected mean value for the length of the three bonds is  $1.57 + 0.78 \log \frac{6}{5} = 1.63$  Å. The observed Cr—O distances are rather inaccurate ( $\pm 0.1$  Å) but their mean value, which may be more accurate than the three individual bonds, is actually 1.63 Å, the same as the calculated value. For the fourth Cr—O bond in (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, a value of  $1.57 + 0.78 \log 2 = 1.80$  Å is calculated but the observed value  $1.91 \pm 0.05$  Å indicates that this distance may be somewhat longer. A more accurate determination of the interatomic distances would be of great interest.

## SUMMARY

The crystal structure of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  has been determined. The cell dimensions are:

$$a = 13.26 \pm 0.01 \text{ \AA}, \quad b = 7.54 \pm 0.02 \text{ \AA}, \quad c = 7.74 \pm 0.02 \text{ \AA}, \quad \beta = 93.2^\circ$$

The space group is  $C_{2h}^6 - C2/c$  with the atoms in the positions:

	$x$	$y$	$z$
8 Cr in 8( $f$ ):	0.100 $\pm$ 0.002	0.175 $\pm$ 0.003	0.139 $\pm$ 0.003
8 O <sub>1</sub> in 8( $f$ ):	0.050 $\pm$ 0.005	0.300 $\pm$ 0.010	0.000 $\pm$ 0.010
8 O <sub>2</sub> in 8( $f$ ):	0.144 $\pm$ 0.005	0.311 $\pm$ 0.010	0.278 $\pm$ 0.010
8 O <sub>3</sub> in 8( $f$ ):	0.178 $\pm$ 0.005	0.000 $\pm$ 0.010	0.070 $\pm$ 0.010
4 O <sub>4</sub> in 4( $e$ ):	0	0.042 $\pm$ 0.010	0.250
8 NH <sub>4</sub> in 8( $f$ ):	0.172 $\pm$ 0.005	0.333 $\pm$ 0.010	0.667 $\pm$ 0.010

The  $\text{Cr}_2\text{O}_7^{2-}$  group consists of two tetrahedra sharing one corner. The two bonds in the Cr—O—Cr bridge form an angle of  $115^\circ$ .

The relation between bond numbers and interatomic distances in  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$ , and  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  are discussed.

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