ACTA CHEMICA SCANDINAVICA 17 (1963) 1563–1566

Least-Squares Refinement of the Crystal Structure of Potassium Peroxochromate

ROLF STOMBERG

Department of Inorganic Chemistry, Chalmers University of Technology, Göteborg, Sweden

In the peroxochromate ion, CrO_8^{3-}, which consists of a central Cr(V) ion surrounded by four peroxo groups, the oxygen-oxygen bond distance in the peroxo groups is 1.47 ± 0.03 Å, and the chromium ion is nearer to one oxygen of each peroxo group than it is to the other, according to a least squares refinement of a previous structure determination by Fourier methods.

The structure of the peroxochromate ion has been investigated by Wilson [1] and later by Stomberg and Brosset [2]. They have determined the crystal structure of K_3CrO_8 by three-dimensional Fourier methods, showing that, in the peroxochromate ion, the chromium atom is dodecahedrally surrounded by the eight oxygen atoms and has the unusual oxidation state of +5. They have found the O-O distance in the peroxo groups to be 1.49 ± 0.02 Å, the Cr-O_I distance 1.90 ± 0.02 Å and the Cr-O_{II} distance 1.94 ± 0.02 Å.

CRYSTAL STRUCTURE AND ITS REFINEMENT

K_3CrO_8 crystallizes in the space group $I\,\bar{4}2\,m$, with $a = 6.703 \pm 0.003$ Å and $c = 7.632 \pm 0.003$ Å. There are two molecules in the unit cell, in which Cr occupies the position 2a, K_I 2b, K_{II} 4d, and O_I and O_{II} 8i, with $x_I = 0.1355$, $z_I = 0.1825$, $x_{II} = 0.2050$, and $z_{II} = 0.0075$. These parameters gave a value for the R factor of 0.13.

The chemical bonding in the peroxochromate ion has been the subject of a ligand field calculation by Swalen and Ibers [3], who have carried out a least-squares refinement of the structure with the aid of the observed $F(hkl)$-values reported by Stomberg and Brosset. Their refinement led to the appreciably lower value of 1.405 ± 0.039 for the O_I-O_{II} distance. This value is, however, not unreasonable, for Stomberg [4] has recently shown that in the adduct molecule $CrO_5 \cdot C_5H_5N$ the O-O distances in the peroxo groups are 1.41 ± 0.03 Å. Swalen and Ibers, however, gave equal weight to all observed reflexions in their least-squares refinement.

Table 1. Weighting analysis.

sin Θ	Number of reflexions	$\overline{w(\|F\|_o - \|F_c\|)^2}$ normalized
0.00 – 0.32	36	0.8
0.32 – 0.47	30	1.1
0.47 – 0.65	23	1.2

Table 2. Parameters for K_3CrO_8 obtained by the present least-squares refinement. The standard deviations have been determined both by the least-squares programme and by Cruickshank's method [12]. Both methods showed good agreement with each other in this case.

Atom	Position	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B Å^2	$\sigma(B)$ Å^2
Cr	2a	0		0		0		1.7	0.1
K_I	2b	0		0		½		2.3	0.1
K_{II}	4d	0		½		¼		2.4	0.1
O_I	8i	0.1355	0.0023	0.1355	0.0023	0.1788	0.0021	1.6	0.2
O_{II}	8i	0.2079	0.0020	0.2079	0.0020	0.0082	0.0022	2.5	0.2

In the present investigation, Cruickshank's weighting scheme,

$$w(hkl) = \frac{1}{a + |F_o| + c|F_o|^2},$$

was used with $a = 16$ and $c = 0.0160$. For a weighting scheme to be satisfactory, the normalized average value of $w(hkl)\ [|F_o| - |F_c|]^2$ should be approximately unity, irrespective of the reflexions entering into the calculation of the average value (see Table 1).

The following parameters were determined from the 109 observed structure factors: a scale factor for each zone, the five isotropic parameters and the four oxygen positional parameters. The atomic scattering factors of Freeman and Watson [5] for Cr, Freeman [6] for K, and Hoerni and Ibers [7] for O, and the Ås-

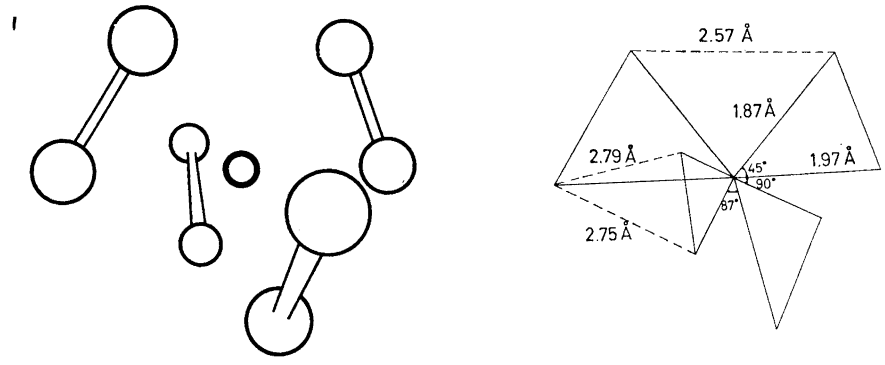

Fig. 1. Bond lengths and angles in the peroxochromate ion.

Table 3. Observed and calculated structure factors for K_3CrO_8.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\alpha°$ (hkl)	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\alpha°(hkl)$
2	0	0	87.7	77.2	0	3	2	3	20.6	18.8	13
4	0	0	66.1	64.7	0	2	2	4	88.8	88.4	15
6	0	0	54.9	53.5	0	4	2	4	43.3	45.2	356
8	0	0	34.9	32.4	0	6	2	4	39.5	36.0	343
10	0	0	21.7	15.5	0	8	2	4	23.4	24.0	9
1	0	1	38.4	41.5	0	3	2	5	18.4	17.2	24
3	0	1	28.7	29.6	180	2	2	6	22.1	17.2	334
5	0	1	22.0	20.0	0	3	2	7	11.2	10.4	331
0	0	2	35.6	28.9	0	2	2	8	27.1	36.6	352
2	0	2	24.1	22.0	180	4	2	8	19.6	22.7	5
4	0	2	32.3	34.6	0	6	2	8	18.9	19.0	5
3	0	3	15.5	12.6	0	2	2	10	9.7	8.3	42
5	0	3	26.8	26.8	0	3	3	0	39.0	38.8	0
0	0	4	103.0	113.0	0	3	3	2	66.0	69.0	354
2	0	4	52.7	57.5	0	5	3	2	33.8	35.1	8
4	0	4	67.5	68.2	0	7	3	2	42.9	38.7	2
6	0	4	35.5	36.2	0	4	3	3	12.2	12.5	189
1	0	5	27.8	25.5	0	3	3	6	49.7	51.3	357
3	0	5	23.1	17.3	180	5	3	6	29.8	27.9	5
0	0	6	40.5	39.9	0	7	3	6	20.3	18.0	2
0	0	8	26.6	34.1	0	3	3	10	13.4	19.6	2
2	0	8	25.6	28.6	0	4	4	0	70.9	71.1	0
4	0	8	31.5	37.7	0	6	4	0	33.8	30.7	0
0	0	10	11.7	9.6	0	8	4	0	16.7	14.8	0
1	1	0	41.2	38.7	0	10	4	0	15.2	16.2	0
3	1	0	17.8	17.4	180	5	4	1	10.5	12.6	348
2	1	1	27.3	31.7	266	4	4	4	42.4	39.8	359
4	1	1	8.2	6.7	58	6	4	4	29.6	28.9	6
6	1	1	12.8	10.9	51	8	4	4	20.0	18.1	356
1	1	2	119.4	113.0	347	5	4	5	9.6	10.0	10
3	1	2	98.0	93.3	355	4	4	8	15.6	16.6	355
5	1	2	64.5	63.5	8	6	4	8	13.4	17.4	2
7	1	2	29.0	27.8	4	5	5	0	13.6	15.4	0
9	1	2	21.8	20.6	350	5	5	2	42.4	40.8	350
4	1	3	22.2	22.6	4	7	5	2	22.1	20.1	355
1	1	4	12.0	13.8	56	9	5	2	17.4	16.4	12
3	1	4	13.5	13.8	61	5	5	4	13.1	12.1	35
5	1	4	12.1	13.9	314	5	5	6	23.9	28.1	355
1	1	6	57.5	63.2	352	7	5	6	11.1	10.8	356
3	1	6	33.2	36.4	0	9	5	6	11.9	10.7	8
5	1	6	34.0	32.8	4	5	5	10	9.6	12.9	13
7	1	6	34.7	25.3	1	6	6	0	23.3	25.8	0
2	1	7	10.3	11.8	282	8	6	0	20.0	17.7	0
1	1	8	6.7	5.9	281	10	6	0	11.2	8.6	0
3	1	8	10.5	7.9	2	6	6	4	19.2	20.6	13
1	1	10	14.2	23.0	4	8	6	4	13.3	13.0	353
2	2	0	131.8	135.4	0	6	6	8	7.9	11.3	348
4	2	0	65.5	64.0	0	7	7	0	9.5	11.1	0
6	2	0	42.6	42.8	0	7	7	2	17.1	15.6	358
8	2	0	29.3	28.0	0	9	7	2	10.2	8.2	6
10	2	0	15.7	13.2	0	7	7	6	13.2	15.9	359
3	2	1	28.7	31.4	332	8	8	0	13.8	14.0	0
5	2	1	21.8	15.7	114	8	8	4	9.0	8.7	4
7	2	1	11.8	10.4	16	9	9	2	7.0	7.0	344
2	2	2	39.5	43.3	320						

Table 4. Interatomic distances and angles in K_3CrO_8. The superscripts refer to the several equivalent positions as they appear in *International Tables*, Vol. I.

$Cr^1 - O_I^1$	1.874 ± 0.019 Å
$Cr^1 - O_{II}^1$	1.972 ± 0.018
$K_I^1 - O_I^1$	2.769 ± 0.017
$K_I^1 - O_{II}^6$	2.771 ± 0.018
$K_{II}^1 - O_I^1$	2.664 ± 0.016
$O_I^1 - O_{II}^1$	1.472 ± 0.025
$O_I^1 - O_{II}^6$	2.920 ± 0.025
$O_I^5 - O_I^6$	2.568 ± 0.042
$O_I^7 - O_{II}^6$	2.751 ± 0.027
$O_{II}^6 - O_{II}^7$	2.790 ± 0.037
$O_I^1 - Cr^1 - O_{II}^1$	45.9 ± 0.6°
$Cr^1 - O_I^1 - O_{II}^1$	71.1 ± 1.4
$Cr^1 - O_{II}^1 - O_I^1$	64.0 ± 1.4
$O_{II}^6 - Cr^2 - O_{II}^7$	90.1 ± 1.3
$O_I^6 - Cr^2 - O_I^5$	86.5 ± 1.2

brink-Brändén [8] least-squares programme for the FACIT electronic computer were used. After six cycles, the refinement converged to the parameters listed in Table 2, the maximum shift after the final cycle being 0.00011 in the z-coordinates and 0.00005 in the x-coordinates and the mean values of these shifts being 0.00009 and 0.00005, respectively. From these parameters, the $|F_c|$'s shown in Table 3 were calculated. The reliability index $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for all observed reflexions was found to be 0.085.

In Table 4 some bond distances and angles and some interatomic distances are listed. The errors listed in Table 4 include the effects of correlation between parameters. Fig. 1 shows the refined structure of the CrO_8^{3-} ion.

DISCUSSION

The present least-squares refinement of the crystal structure of K_3CrO_8 shows that the Cr-O_I distance, 1.87 ± 0.02 Å, is significantly shorter than the Cr-O_{II} distance, 1.97 ± 0.02 Å. (Swalen and Ibers report the values 1.846 ± 0.022 Å and 1.944 ± 0.024 Å, respectively.) That this should be the case was first pointed out by Hoard [9], and the ligand field calculation by Swalen and Ibers is in agreement with this observation. The $O_I - O_{II}$ distance, 1.47 ± 0.03 Å, is, however, not significantly smaller than the value, 1.49 Å, usually found in peroxo groups [10,11].

REFERENCES

1. Wilson, I. A. *Arkiv Kemi, Mineral. Geol.* **15 B** (1942) No. 5.
2. Stomberg, R. and Brosset, C. *Acta Chem. Scand.* **14** (1960) 441.
3. Swalen, J. D. and Ibers, J. A. *J. Chem. Phys.* **37** (1962) 17.
4. Stomberg, R. *Nature* **196** (1962) 570.
5. Freeman, A. J. and Watson, R. E. *Acta Cryst.* **14** (1961) 231.
6. Freeman, A. J. *Acta Cryst.* **12** (1959) 261.
7. Hoerni, J. A. and Ibers, J. A. *Acta Cryst.* **7** (1954) 744.
8. Åsbrink, S. and Brändén, C. I. *Private communication.*
9. Hoard, J. L., Silverton, J. V., Glen, G. L. and Willstadter, E. *Proc. 7th Intern. Conf. Coordination Chemistry* (1962) 73.
10. Abrahams, S. C., Collin, R. L. and Lipscomb, W. N. *Acta Cryst.* **4** (1951) 15.
11. Vannerberg, N. G. *Arkiv Kemi* **14** (1959) 17.
12. Cruickshank, D. W. J. *Acta Cryst.* **2** (1949) 65.

Received March 5, 1963.