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The Crystal Structure of Potassium Perchromate

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The crystal structure of potassium perchromate has been determined by two- and three-dimensional X-ray methods. The perchromate crystallizes in the space group $I\,\bar{4}2m$, with $a = 6.703 \pm 0.003$ Å and $c = 7.632 \pm 0.003$ Å The length of the bond between the two oxygen atoms in a peroxide group is 1.489 ± 0.022 Å. The oxidation number of +5 for the chromium has been confirmed.

The crystal structure of potassium perchromate, K_3CrO_8, has previously been determined by Wilson [1], who, by means of powder diffraction data, found the oxygen-oxygen single bond in the peroxide group to be 1.34 ± 0.06 Å, a rather uncertain and somewhat low value in comparison with those obtained by other authors [6,7]. This would justify a refinement of the structure. It would also be of interest to establish definitely if chromium is surrounded by four equidistant O_2^{2-}-ions and consequently has the oxidation number +5, or if it might be enclosed both by O_2^{2-} and O_2^{-}-ions.

EXPERIMENTAL

Preparation and analysis. K_3CrO_8 was prepared according to Riesenfeld [2] by adding hydrogen peroxide to a cooled, alkaline solution of potassium chromate. The temperature did not exceed −5°C. The crystals were filtered, and dried with alcohol and ether. The chromium content was determined by converting the sample into chromate, adding KI and titrating the liberated iodine with a thiosulfate solution. The potassium content was determined as potassium perchlorate. (Found: K 39.6; Cr 17.5. Calc. for K_3CrO_8: K 39.5; Cr 17.5.)

Magnetometric measurement. K_3CrO_8 has been found to be paramagnetic and the moment was determined by the Gouy method which gave the approximate value $\chi_M = 1\,240 \pm 30$ units, clearly indicating the existence of a single unpaired electron found also by Tjabbes [4] and Klemm and Werth [5].

X-Ray methods. In order to determine the cell dimensions accurately powder photographs of Guinier type were taken using Cu $K\alpha$ radiation and with NaCl as reference substance. Due regard was taken to film shrinkage according to Hägg by copying a scale on the films before development.

The structural investigation was based on single crystal methods. Multiple-film equi-inclination Weissenberg photographs were taken with rotation about $[1\bar{1}0]$ (layer lines 0, 1, 2 and 4), [100] (layer lines 0, 1, 2, and 3) and [001] (layer lines 0, 1, 2, 4 and 6) using molybdenum radiation. Thin tinfoils were placed between the films in order to increase the absorption. The reflexion intensities were estimated by visual comparison with standard scales. A subjective correction was made for variation in spot shape. As molybdenum radiation was used and the crystals were only 0.1 mm thick no correction was made for absorption. The reflexion intensities were corrected using Lorentz and polarization factors.

As the perchromate was decomposed in a few days under the influence of the X-rays it was necessary to use new crystals after about 20 h exposure.

DETERMINATION OF THE STRUCTURE

The cell dimensions were obtained from powder diffraction data by the method of least squares. K_3CrO_8 is tetragonal with

$$a = 6.703 \pm 0.003 \text{ Å}.$$
$$c = 7.632 \pm 0.003 \text{ Å}.$$

Calculated and observed $\sin^2\Theta$-values are given in Table 1.

Table 1. X-ray powder diffraction data for K_3CrO_8.

$h\,k\,l$	$10^4 \cdot \sin^2\Theta_{obs}$	$10^4 \cdot \sin^2\Theta_{calc}$
1 0 1	233	234
1 1 0	265	265
0 0 2	408	408
2 0 0	530	529
1 1 2	672	673
2 1 1	763	763
2 0 2	936	937
2 2 0	1 058	1 058
3 0 1	1 290	1 292
3 1 0	1 324	1 323
2 2 2	1 465	1 466
0 0 4	1 631	1 632
3 1 2	1 730	1 731
3 2 1	1 821	1 821
4 0 0	2 118	2 116
2 0 4	2 166	2 162
3 3 0	2 381	2 382
4 0 2	2 526	2 524
4 2 0	2 645	2 645
2 2 4	2 691	2 691
3 3 2	2 789	2 789
4 1 3	3 170	3 167
4 0 4	3 750	3 749
5 1 2	3 847	3 847
5 2 1	3 940	3 938
4 2 4	4 272	4 278
6 0 0	4 762	4 761
5 3 2	4 901	4 905

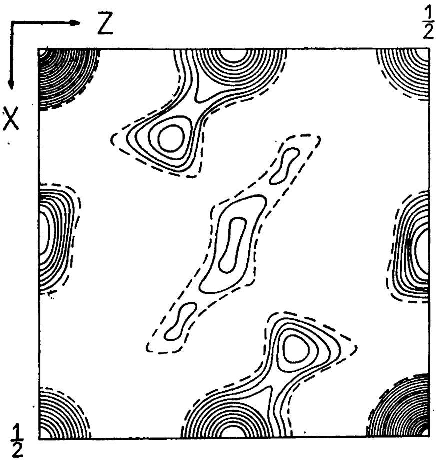


Fig. 1. Patterson projection on (010).

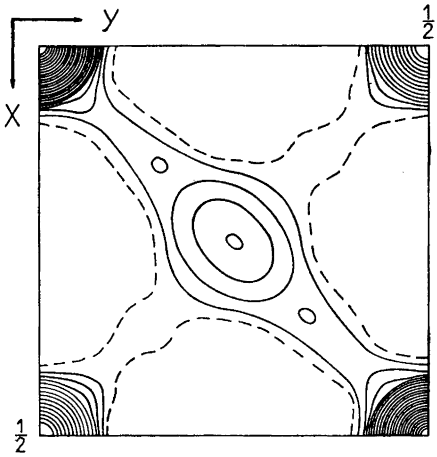


Fig. 2. Patterson projection on (001).

In all photographs only reflexions from planes of the following types were observed:

hkl with $h + k + l = 2n$
$hk0$ with $h + k = 2n$
hhl with $l = 2n$
$0kl$ with $k + l = 2n$
$00l$ with $l = 2n$

The following space groups are thus possible:
$I4/mmm$ (No. 139), $I4mm$ (No. 107), $I\bar{4}m2$ (No. 119), $I\bar{4}2m$ (No. 121) and $I422$ (No. 97).

The experimentally determined density [1] is 2.79, from which the number of molecules per unit cell appears to be 2 (1.94).

From a Patterson projection on (010) (Fig. 1) it was concluded that the heavy atoms (Cr and K) are situated at (0;0), (0;$\frac{1}{4}$), (0;$\frac{1}{2}$), (0;$\frac{3}{4}$), ($\frac{1}{2}$;0), ($\frac{1}{2}$;$\frac{1}{4}$), ($\frac{1}{2}$;$\frac{1}{2}$) and ($\frac{1}{2}$;$\frac{3}{4}$), whereas the oxygen co-ordinates are of the general type.

Further information could be obtained from a Patterson projection on (001) (Fig. 2), which shows that the Cr and K atoms occupy the positions (0;0), (0;$\frac{1}{2}$), ($\frac{1}{2}$;0) and ($\frac{1}{2}$;$\frac{1}{2}$) and that the oxygen parameters seem to be of the type (x;x).

Of the possible space groups only $I\bar{4}2m$ is consistent with all these observations. According to this space group the positions of the heavy atoms will be the following

2 *a* 000
2 *b* 00 1/2
4 *d* 0 1/2 1/4, 1/2 0 1/4

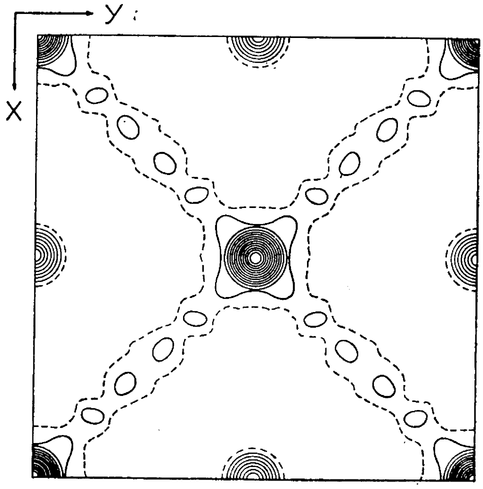


Fig. 3. Projection of the electron density in K_3CrO_8 on (001) (arbitrary units).

As no heavy peaks have appeared in the Patterson projection, except the one at origo it seemed very probable that the Cr atoms occupy the position 2 *a* and the K atoms 2 *b* and 4 *d*.

That this assumption is correct is indicated by the close agreement between observed and calculated structure factors arrived at in the final stage of the investigation.

The signs of the structure factors were calculated on the assumption that the chromium and potassium positions alone determined these. Two Fourier projections were synthesised, one (see Table 2, column 1) on (001) (Fig. 3) and one (Table 2, column 2) on (010) (Fig. 4).

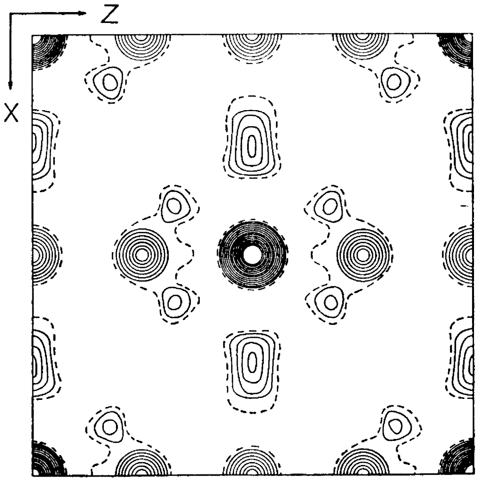


Fig. 4. Projection of the electron density in K_3CrO_8 on (010) (arbitrary units).

Table 2. Atomic parameters obtained from the various Fourier syntheses.

Atom		1	2	3	4	5	6
O_1	x	0.138	0.117	0.134	0.125	0.132	0.1355
	y	0.138	—	0.135	—	0.132	0.1355
	z	—	0.175	—	0.183	0.183	0.1825
O_2	x	0.207	0.200	0.203	0.208	0.206	0.2050
	y	0.207	—	0.204	—	0.206	0.2050
	z	—	0.000	—	0.011	0.011	0.0075

The heavy peaks all occurred at the above-mentioned positions for potassium and chromium. The oxygen parameters thus obtained are subject to great errors, however, because of the considerable differences in the electron densities between the chromium and potassium atoms on the one hand and the oxygen atoms on the other hand.

In order to attain greater accuracy two difference syntheses were produced (Table 2, columns 3 and 4) by subtracting the contributions of the chromium and potassium atoms from the structure factors with due regard to the temperature factor. The parameters obtained from these two projections were in better agreement with each other, but there was still great uncertainty in the $O_{(2)}$-position because of the overlapping. A (F_o-F_c)-synthesis was tried but with the aid of this it was not possible to get sufficiently exact parameter displacements. It was therefore necessary to make a three-dimensional Fourier analysis in order to resolve the peaks.

Three-dimensional refinement

The final atomic co-ordinates from the (010)- and (001)-projections, which are shown in column 5 of Table 2, were used to calculate $\sum_r f_r A_r$ and $\sum_r f_r B_r$ in the expression

$$|F(hkl)| = \{[\sum_r f_r A_r]^2 + [\sum_r f_r B_r]^2\}^{\frac{1}{2}} \quad ,$$

where the notation is that adopted in the International Tables for X-ray Crystallography [10]. The phase angle $\alpha(hkl)$ could thereafter be deduced by means of the equation

$$\alpha(hkl) = \tan^{-1}\left\{\frac{[\sum_r f_r B_r]}{[\sum_r f_r A_r]}\right\}$$

This quantity was used in the expression for the electron density

$$\varrho_{xyz} = \frac{8}{V_c} \sum_h \sum_k \sum_l |F(hkl)| \{\cos 2\pi hx \; \cos 2\pi ky \; \cos 2\pi lz \; \cos\alpha(hkl) - \sin 2\pi hx \; \sin 2\pi ky \; \sin 2\pi lz \sin\alpha(hkl)\}.$$

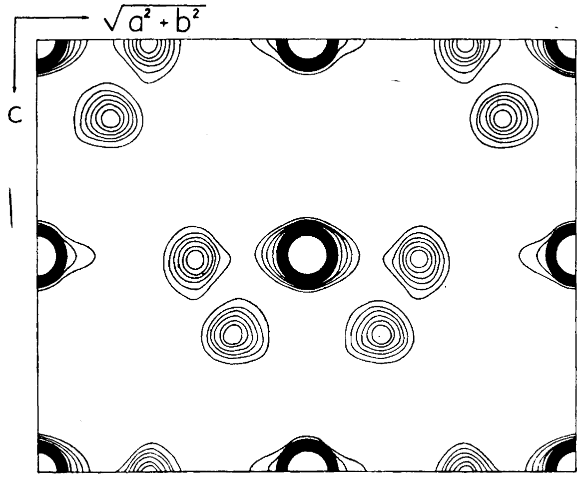


Fig. 5. The electron density of K_3CrO_8 in the plane $(1\bar{1}0)$. Contours at 2 e/Å^3. The curves are not drawn in the centers of the heavy atoms.

In the first stage of the calculation the quantities $\underset{h\ k}{\Sigma\Sigma}|F(hkl)|\cos 2\pi hx \cos 2\pi ky \cos\alpha(hkl)$ and $\underset{h\ k}{\Sigma\Sigma}|F(hkl)| \sin 2\pi hx \sin 2\pi ky \sin\alpha(hkl)$ were determined with $h = 0-8$, 10 and $k = 0-8$, 10, and with x taken at intervals of 1/200 of the cell side, and with y at intervals of 1/60 of the cell side. With the aid of these two-dimensional data one-dimensional Fourier syntheses were computed in the z-direction, with z taken at intervals of 1/200 of the cell side. Because $x_1 = y_1$ and $x_2 = y_2$ it was sufficient to calculate the electron density in the plane $(1\bar{1}0)$ (Fig. 5).

Final parameter values of the oxygen atoms are given in column 6 of Table 2. The arrangement of the atoms is given in Table 3. In Table 4 are

Table 3. Arrangement of the atoms in K_3CrO_8.

Atom	x	y	z	Atom	x	y	z
Cr_1	0	0	0	O_5	0.6355	0.6355	0.6825
Cr_2	1/2	1/2	1/2	O_6	0.7050	0.7050	0.5075
K_1	0	0	1/2	O_7	0.8645	0.8645	0.1825
K_2	1/2	1/2	0	O_8	0.7950	0.7950	0.0075
K_3	0	1/2	1/4	O_9	0.1355	0.8645	0.8175
K_4	1/2	0	3/4	O_{10}	0.6355	0.3645	0.3175
K_5	1/2	0	1/4	O_{11}	0.2050	0.7950	0.9925
K_6	0	1/2	3/4	O_{12}	0.7050	0.2950	0.4925
O_1	0.1355	0.1355	0.1825	O_{13}	0.8645	0.1355	0.8175
O_2	0.2050	0.2050	0.0075	O_{14}	0.7950	0.2050	0.9925
O_7	0.3645	0.3645	0.6825	O_{15}	0.3645	0.6355	0.3175
O_4	0.2950	0.2950	0.5075	O_{16}	0.2950	0.7050	0.4925

Table 4. Values of observed and calculated structure factors for K_3CrO_8 including the phase angle α(hkl).

$h\,k\,l$	F_{obs}	F_{calc}	$\alpha°(hkl)$
2 0 0	85	77	0
4 0 0	73	74	0
6 0 0	76	83	0
8 0 0	66	66	0
1 0 0 0	62	60	0
1 1 0	43	42	0
3 1 0	20	21	180
2 2 0	132	146	0
4 2 0	75	79	0
6 2 0	61	66	0
8 2 0	58	68	0
1 0 2 0	47	47	0
3 3 0	47	46	0
4 4 0	101	99	0
6 4 0	61	60	0
8 4 0	41	45	0
1 0 4 0	56	66	0
5 5 0	26	22	0
6 6 0	60	64	0
8 6 0	71	59	0
1 0 6 0	60	48	0
7 7 0	36	23	0
8 8 0	69	65	0
1 0 1	36	45	0
3 0 1	30	35	180
5 0 1	27	27	0
2 1 1	30	35	265
4 1 1	10	8	62
6 1 1	20	14	61
3 2 1	35	37	333
5 2 1	28	24	127
7 2 1	20	15	17
5 4 1	17	15	344
0 0 2	34	29	0
2 0 2	24	24	180
4 0 2	37	39	0
1 1 2	128	117	347
3 1 2	118	105	355
5 1 2	91	87	8
7 1 2	48	54	2
9 1 2	57	60	354
2 2 2	41	47	321
3 3 2	93	87	355
5 3 2	55	51	9
7 3 2	84	82	2
5 5 2	83	80	353
7 5 2	57	52	357
9 5 2	64	62	8
7 7 2	66	59	359
9 7 2	59	43	4
9 9 2	72	46	349
3 0 3	17	10	0

Table 4, continued.

h k l	F_{obs}	F_{calc}	$\alpha^\circ(hkl)$
5 0 3	36	36	0
4 1 3	30	26	4
3 2 3	24	23	16
4 3 3	17	20	189
0 0 4	110	133	0
2 0 4	60	65	0
4 0 4	86	89	0
6 0 4	57	67	0
1 1 4	15	16	53
3 1 4	18	15	80
5 1 4	19	18	304
2 2 4	102	109	14
4 2 4	63	65	357
6 2 4	71	66	345
8 2 4	52	67	7
4 4 4	70	68	359
6 4 4	61	65	5
8 4 4	57	56	356
5 5 4	29	19	38
6 6 4	57	60	8
8 6 4	55	53	356
8 8 4	52	53	2
1 0 5	33	31	0
3 0 5	29	30	180
3 2 5	24	22	22
5 4 5	19	13	11
0 0 6	49	49	0
1 1 6	81	86	350
3 1 6	50	57	359
5 1 6	63	66	5
7 1 6	85	64	0
2 2 6	30	24	323
3 3 6	83	87	356
5 3 6	59	57	5
7 3 6	53	59	2
5 5 6	62	75	355
7 5 6	38	41	357
7 7 6	67	69	359
2 1 7	17	17	267
3 2 7	18	14	330
0 0 8	43	65	0
2 0 8	43	54	0
4 0 8	61	82	0
1 1 8	12	9	246
2 2 8	48	75	356
4 2 8	39	56	4
4 4 8	39	50	355
6 4 8	42	61	3
6 6 8	36	51	352
0 0 10	26	20	0
1 1 10	35	64	1
2 2 10	23	13	45
3 3 10	39	66	1
5 5 10	44	63	7

given observed structure factors and those calculated using the values of the atomic parameters given in Table 3. In Table 4 are also included the phase angles $\alpha(hkl)$ used in computing the electron density in the plane $(1\bar{1}0)$.

The structure factor disagreements,

$$R = \frac{\Sigma(|F_{\text{calc}}|-|F_{\text{obs}}|)}{\Sigma|F_{\text{obs}}|}$$

of the final coordinates are $R_{hkl} = 13.2$ %, $R_{hk0} = 8.4$ % and $R_{h0l} = R_{0kl} = 17.4$ %, excluding those terms too weak to be observed.

Observed structure factors have been corrected for thermal vibrations by the factor exp $[B(\sin \Theta/\lambda)^2]$ with $B = 2.0 \times 10^{-16}$ cm^2, determined by the method of least squares from the final structure factors. An isotropic temperature factor has been applied in spite of the fact that the (F_o-F_c)-synthesis showed the existence of somewhat different magnitudes in the thermal vibrations in the x- and z-directions.

Accuracy of the determination

The standard deviations $\sigma(x)$ and $\sigma(z)$ of atomic coordinates were estimated from the differences ΔF between the magnitudes of observed and calculated values of the structure factors according to Cruickshank's method[3], where

$$\sigma(x) = \frac{2\pi[\Sigma h^2(F_o-F_c)^2]^{\frac{1}{2}}}{a \cdot V \cdot \dfrac{\partial^2\varrho}{\partial x^2}}$$

and

$$\sigma(z) = \frac{2\pi[\Sigma l^2(F_o-F_c)^2]^{\frac{1}{2}}}{c \cdot V \cdot \dfrac{\partial^2\varrho}{\partial z^2}};$$

here a and c are the cell edges and V the cell volume.

As proposed by Shoemaker, Donohue, Schomaker and Corey[8] these values have been increased by the factor of 1.3 as the structure has no centre of symmetry but the projections are centro-symmetric.

The values of $\frac{\partial^2\varrho}{\partial x^2}$ and $\frac{\partial^2\varrho}{\partial z^2}$ were obtained from the values of the electron density in the neighbourhood of the final Fourier peaks. Mean values for the oxygen atoms are

$$\frac{\partial^2\varrho}{\partial x^2} = 610 \text{ and } \frac{\partial^2\varrho}{\partial z^2} = 625 \text{ e/Å}^5$$

The standard deviations of the oxygen atomic positions are thus $\sigma(x) = 0.0084$ and $\sigma(z) = 0.0096$ Å. The standard deviations in the bond lengths are 0.022 Å for O_1-O_2 and 0.015 Å for K—O and Cr—O. The probable error in the bond angles is 1°.

Table 5. Interatomic distances.

Cr_1-O_1	1.895 Å
Cr_1-O_2	1.944
K_1-O_1	2.743
K_1-O_4	2.797
K_3-O_1	2.661
O_1-O_2	1.489
O_1-O_4	2.905
O_3-O_5	2.569
O_4-O_{10}	2.744
O_4-O_{12}	2.751

Description of the structure

Bond lengths and other interatomic distances are given in Table 5 and bond angles in Table 6. Fig. 6 shows the arrangement of the oxygen atoms about the chromium atom. From this figure, and from the data obtained, it follows that the chromium atom in K_3CrO_8 is surrounded by eight oxygen atoms, four being at a distance of 1.895 Å and four at 1.944 Å. The discrepancy between these two values is not significant. Thus the close agreement between the bond lengths indicates that the chromium atom is bonded to eight oxygen atoms. This 8-coordination with the symmetry $\bar{4}\ 2\ m$ has a dodecahedral configuration.

The length of the bond between the two oxygen atoms, as a peroxide ion is 1.489 Å, close to values found in other peroxy compounds [6,7]. The shortest distances between oxygen atoms not belonging to the same peroxide ion are 2.91 Å, 2.57 Å, 2.75 Å, and 2.74 Å.

The potassium atoms are also 8-coordinate, the shortest potassium-oxygen distances being 2.74 Å, 2.80 Å, and 2.66 Å.

DISCUSSION

The likely configurations for a complex ion or a molecule of formula AB_8 are four in number, [9,11] namely the cube, the Archimedean antiprism with symmetry $\bar{8}2m$, the dodecahedron with symmetry $\bar{4}2m$ and the face-centered trigonal prism. The need to use *f*-orbitals of the central atom in forming cubic bonds has been quoted as unfavourable [11], although it is believed that diketone complexes of Ce(IV), Th(IV) *etc.* have cubic arrangements [15].

Table 6. Bond angles.

$O_1-Cr_1-O_2$	45.6°
$Cr_1-O_1-O_2$	68.9
$Cr_1-O_2-O_1$	65.5
$O_4-Cr_2-O_{16}$	89.8
$O_4-Cr_2-O_{10}$	91.2
$O_3-Cr_2-O_5$	95.4
$O_3-O_{12}-O_5$	55.8
$O_1-K_1-O_4$	63.9

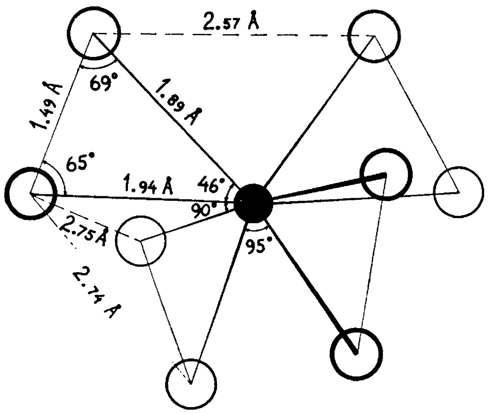
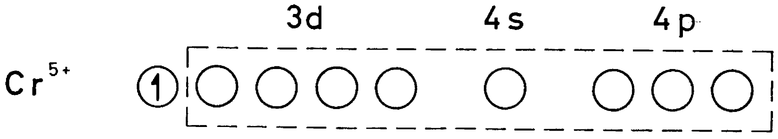


Fig. 6. Bond lengths and bond angles in K_3CrO_8.

According to the literature [14] other molecules and ions with co-ordination number 8 are 8-quinolinol chelates of tetrapositive metals; cyano- and fluorocomplexes such as $Mo(CN)_8^{4-}$, $W(CN)_8^{4-}$, and TaF_8^{3-}; and oxalato complexes such as $U(C_2O_4)_4^{4-}$. So far only the antiprismatic and the dodecahedral arrangements have been established for a discrete group AB_8.

Hoard and Nordsieck [9] have found that $Mo(CN)_8^{4-}$ has the dodecahedral arrangement with the carbon atoms at the vertices, and that the symmetry of the complex ion can be approximated to $\bar{4}2m$. The present investigation has shown that CrO_8^{3-} has the symmetry $\bar{4}2m$ and that the geometrical arrangement of the oxygen atoms surrounding the central chromium atom is dodecahedral. One would have expected the same configuration for $Mo(CN)_8^{4-}$, CrO_8^{3-} and TaF_8^{3-}, but Hoard *et al.* [12] have shown by X-ray analysis that TaF_8^{3-} has the arrangement of an Archimedean antiprism.

According to Kimball [11] the dodecahedral, antiprismatic and face-centered trigonal prismatic configurations are given by appropriate linear combinations of *spd*-orbitals, but Higman [13] has concluded that one *f*-orbital is required for the $Mo(CN)_8^{4-}$-arrangement. This conclusion does not seem adequate as there are no available *f*-orbitals in CrO_8^{3-}. It is highly probable that the bonds are d^4sp^3-hybrids because the paramagnetism of the substance is in accordance with the orbital configuration



The stability of this arrangement has also been found to occur with Mo^{5+} in $Mo(CN)_8^{3-}$ which is not oxidized to $Mo(CN)_8^{2-}$. This is in contrast to other Mo(V) compounds which are readily oxidized to Mo(VI).

It is rather remarkable that the two non-isoelectronic ions $Mo(CN)_8^{4-}$ and CrO_8^{3-} have the same configuration. It should also be pointed out that the structure of the $Mo(CN)_8^{3-}$-ion, which is isoelectronic with CrO_8^{3-}, has not yet been determined.

Finally it should be mentioned that $Cr(O_2)_4^{4-}$ does not seem to exist. This may be explained by assuming that the configuration with a single electron in the 3*d* orbital has a stabilizing effect.

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