CRYSTAL STRUCTURE OF SODIUM DICHROMATE

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CRYSTAL STRUCTURE OF SODIUM DICHROMATE

$Na_2Cr_2O_7 \cdot 2H_2O$

In the first X-ray diffraction study of sodium dichromate, for monoclinic crystals of $Na_2Cr_2O_7 \cdot 2H_2O$ the following were established: $a = 6.05$, $b = 10.5$, $c = 12.6$ Å; $\beta = 94.9°$; $Z = 4$; $a : b : c = 0.576 : 1 : 1.200$; space group $P2_1/m$. From analysis of the Patterson projection function it followed that the Cr atoms are located in mirror planes. The existence of $[HCrO_4]^-$ anions was also rejected (^{1}).

For the present investigation, crystals of $Na_2Cr_2O_7 \cdot 2H_2O$ were grown from aqueous solution. Two specimens ($0.15 \times 0.2 \times 0.8$ mm^3 and $0.15 \times 0.2 \times 0.2$ mm^3) gave good X-ray photographs. Unit-cell parameters were obtained from rotation photographs and zero-layer reciprocal-lattice photographs: $a = 6.21$, $b = 10.90$, $c = 12.94$ Å; $\beta = 95°$; $a : b : c = 0.569 : 1 : 1.186$. These data, better than (^{1}), agree with the results of careful goniometric measurements (^{2}): $a : b : c = 0.5698 : 1 : 1.1824$; $\beta = 94°55'$.

The three-dimensional experimental material for the X-ray structure analysis consisted of 900 nonzero reflections $0kl$—$4kl$ and $h0l$—$h2l$ (MoK_α radiation, $\max \sin\vartheta/\lambda = 0.55$ Å^{-1}).

From the three-dimensional Patterson function constructed from this hkl set, the hemimorphic space group was determined fairly unambiguously as $P2_1$ (absence of maxima on the v axis). Most of the strong Patterson peaks are concentrated in the planes ($u0w$) and ($u\,^1/_2w$), and this justifies the assumption that all the heavier Cr atoms are located in two sections ($y = 0$ and $y = {}^1/_2$). This, however, does not facilitate analysis of the Patterson function, but rather complicates it, since peaks of bonds and interactions from crystallographically different chromium atoms, without leaving the two sections, overlap. Nevertheless, from the complex network of these peaks it proved possible to isolate the "principal system" —four tetrads of atoms

Table 1

$Na_2Cr_2O_7 \cdot 2H_2O$. Coordinates of the basis atoms

Fig. 1 and Fig. 2: crystal-structure projections

Figure 1: Fig. 1 and Fig. 2: crystal-structure projections

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Cr_1	0.146	0	0.952	O_6	0.330	0.439	0.182
Cr_2	0.052	0.458	0.834	O_7	0.282	0.591	0.333
Cr_3	0.343	0.948	0.487	O_8	0.059	0.447	0.971
Cr_4	0.346	0.450	0.306	O_9	0.190	0.346	0.349
Na_1	0.183	0.771	0.728	O_{10}	0.400	0.917	0.626
Na_2	0.384	0.298	0.029	O_{11}	0.084	0.913	0.456
Na_3	0.149	0.254	0.513	O_{12}	0.492	0.366	0.570
Na_4	0.466	0.769	0.254	O_{13}	0.392	0.092	0.468
O_1	0.385	0.974	0.012	O_{14}	0.121	0.859	0.220
O_2	0.131	0.932	0.840	$(H_2O)_1$	0.355	0.690	0.073
O_3	0.114	0.152	0.939	$(H_2O)_2$	0.194	0.478	0.698
O_4	0.011	0.094	0.200	$(H_2O)_3$	0.155	0.643	0.568
O_5	0.305	0.432	0.806	$(H_2O)_4$	0.475	0.176	0.184

Cr. The lighter Na, O, and H_2O were fixed in a cycle of three-dimensional syntheses of the electron density $\rho(xyz)$. The value of the R-factor thus achieved (for all atoms) was 23%. Refinement by the least-squares method reduced R_{hkl} to 8.3%. The coordinates of the basis atoms are given in Table 1. The structure is characterized by 77 independent positional parameters. The temperature correction common to all atoms is $B \approx 2.2$ Å^2.

Each of the 4 crystallographically independent Cr atoms is surrounded tetrahedrally by 4 oxygen atoms. The $[HCrO_4]^-$ groups mentioned above are absent, but, as expected, the Cr tetrahedra are joined pairwise into $[Cr_2O_7]^{2-}$ diorthogroups. Among the Cr–O distances (as also in (^{3})) the distances to the bridging O atoms stand out as lengthened: Cr_1—O_8 1.78 Å

Fig. 1. Structure of sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$. Projection yz, with alternating layers of cation polyhedra and anionic Cr_2O_7 diorthogroups. The cation layers break up into corrugated chains with a link consisting of three Na octahedra (connected through common edges) and one Na trigonal prism (connected with a trio of octahedra by common vertices). The H_2O molecules are marked by circles.

Fig. 2. $Na_2Cr_2O_7 \cdot 2H_2O$. Projection xz, with discretely protruding polar Cr_2O_7 groups, trios of Na octahedra, and Na prisms connecting them into a single chain.

(the other Cr_1—O distances are 1.62, 1.64, and 1.68), Cr_2—O_8 1.78 (as against 1.59, 1.65, and 1.66 Å), Cr_3—O_{10} 1.84 Å (the others are 1.59, 1.63, and 1.67),

Fig. 3. $Na_2Cr_2O_7 \cdot 2H_2O$. Projection xz. Superposition of two layers with nonuniform arrangement of large particles: 10 O (per cell) in the lower layer and 8 $(4+4)$ $O + H_2O$ in the upper layer.

Figure 2: Fig. 3. $Na_2Cr_2O_7 \cdot 2H_2O$. Projection xz. Superposition of two layers with nonuniform arrangement of large particles: 10 O (per cell) in the lower layer and 8 $(4+4)$ $O + H_2O$ in the upper layer.

Cr_4—O_{10} 1.78 (the remaining ones are 1.62, 1.63, and 1.64 Å); the lengthened Cr—O bonds, together with the distances in the diorthogroups Cr_1—Cr_2 3.17 Å and Cr_3—Cr_4 3.16 Å, determine the angles: Cr_1—O_8—Cr_2 125° and Cr_3—O_{10}—Cr_4 122°. In the tetrahedra the O–O edges range from 2.63 to 2.81 Å.

The Na cations occupy 4 independent crystallographic positions, with Na–O distances within the range 2.31-2.64 Å. For each Na a coordination number of 6 is characteristic; the seventh Na–O distance = 3.2 Å (the smallest) clearly does not enter into the coordination sphere. Three Na polyhedra are fairly regular octahedra; the fourth Na polyhedron is close to a trigonal prism, inclined because of the displacement of the bases relative to one another.

In the yz projection (Fig. 1), layers of Na octahedra perpendicular to the b axis are clearly seen, alternating with layers of Cr_2O_7 groups. In the cationic layers, trios of mutually edge-sharing Na octahedra of three types (Fig. 2) and, through NaO_6 prisms (which have only common vertices with the octahedral Na), are linked into an infinite corrugated

chain, with a link of $3+1$ Na polyhedra, which extends in the diagonal direction $\mathbf{a}+\mathbf{c}$. The dichromate groups Cr_2O_7 fasten the Na chains into a layer through O atoms at the bases of their tetrahedra and, at the same time, through the apices of the tetrahedra bind the layers to one another. These single O apices in their (anion) layer alternate with an equal number of H_2O molecules, each of which is shared by two Na octahedra.

The crystal structure of $Na_2Cr_2O_7 \cdot 2H_2O$ may be regarded as metastable. The bridging O, which connects Cr tetrahedra into a dichromate group, is strongly strained (more than +3 charges converge on it), despite the "compensating" elongation of the bridging Cr–O bonds. The remaining O atoms bear an uncompensated negative charge (the inverse effect), sufficient for the rigid attachment of sodium atoms. Hydrated sodium dichromate nevertheless absorbs additional moisture from the air and is partially destroyed, and therefore in chemical technology the more expensive but stable K bichromate is used as the dichromate. The cause of the instability of $Na_2Cr_2O_7 \cdot 2H_2O$ may be sought in the features of the packing of oxygen atoms in the ac planes (Fig. 3).

Fig. 3. $Na_2Cr_2O_7 \cdot 2H_2O$. Projection xz. Superposition of two layers with nonuniform arrangement of large particles: 10 O (per cell) in the lower layer and 8 $(4+4)$ $O + H_2O$ in the upper layer.

In Na dichromate, one O atom accounts for $V_O \approx 24\ \text{Å}^3$, i.e., a value not much exceeding V_O in ordinary oxygen compounds (according to Shibald[4]), provided that 36 O atoms (together with H_2O) are distributed uniformly over their four levels. But in $Na_2Cr_2O_7 \cdot 2H_2O$ the 36 O atoms (more precisely, 28 O and 8 H_2O) are distributed nonuniformly: in two layers there are 4 O and 4 H_2O each (i.e., 8 atoms), while in the other two there are 10 O atoms (without H_2O) (Fig. 3).

Thus, already within a single (polyhedral) layer there is a mismatch between two (upper and lower) planar nets. Their dimensions a and c are determined by the layer with 10 O atoms. The number 10 in the polar structure of Na dichromate corresponds to the concentration in one (anion) layer of the bases of two dichromate groups with 5 O atoms from each. The water-oxygen layer with the apices of the same groups proves to be unfilled; it coincides in the direction a with a purely oxygen layer, but is sparse in the direction c. The apparent natural tendency of this layer to become denser in order to agree with the purely oxygen layer entails absorption of H_2O from the air, with the consequence—the destruction of the rigidity of the structure, i.e., of the principal criterion of the stability of $Na_2Cr_2O_7 \cdot 2H_2O$.

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Note: Figure translations are in progress. See original paper for figures.