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Sodium Chromate Tetrahydrate[*]

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Abstract. $Na_2CrO_4.4H_2O$: monoclinic, $P2_1/c$, a = 6·186 (4), b = 11·165 (4), c = 12·20 (1) Å, β = 104·95 (10)°, Z = 4, d_x = 1·91 g cm^{-3} at 23 °C. The crystals were grown from aqueous solution at 25–29 °C. The structure was determined from X-ray diffraction data for 1844 independent reflections (R = 0·11). The average Cr–O bond distance is 1·64 (4) Å. Each sodium ion has either five or six oxygen atoms (from water and chromate) as neighbors. All of the hydrogen atoms are involved in hydrogen bonds with O–O distances ranging from 2·76 to 2·86 Å. $Na_2SeO_4.4H_2O$ is isomorphous, with a = 6·22 (2), b = 11·18 (4), c = 12·18 (4) Å, and β = 105 (1)°.

Introduction. Sodium chromate crystallizes as the decahydrate (below 19·5°), the hexahydrate (19·5–25·9°) and the tetrahydrate (25·9–63°) (*Gmelins Handbuch*, 1962), and a sesquihydrate is reported to be stable in the neighborhood of 70° (Borchardt, 1958). We determined the structure of the tetrahydrate as a by-product of a study of several decahydrates (Ruben, Templeton, Rosenstein & Olovsson, 1961).

A yellow crystal of dimensions 0·19 × 0·08 × 0·05 mm was enclosed in a thin-walled quartz capillary to prevent gain or loss of water. Intensities of 1844 independent reflections, all of those within a quadrant of the sphere of reflection out to $2\theta = 55°$ were measured using Zr-filtered Mo $K\alpha$ radiation (λ = 0·70926 Å for $K\alpha_1$) with the stationary-crystal stationary-counter technique. Systematic absences corresponded to $P2_1/c$. No correction was made for absorption, μ = 15·7 cm^{-1}, nor extinction. For the full-matrix least-squares refinements, the data were weighted as described elsewhere (Sime, Dodge, Zalkin & Templeton, 1971) with p = 0·05. Zero weight was assigned to 537 reflections with $I < \sigma(I)$. We used atomic form factors for spherical hydrogen from Stewart, Davidson & Simpson (1965) and for other atoms those of Cromer & Waber (1965) with dispersion corrections for Na and Cr according to Cromer (1965).

The sodium and chromium positions were deduced from a three-dimensional Patterson function, and oxygen atoms were found with a subsequent difference map. Hydrogen positions were derived from an analysis of the hydrogen bonding; only three of the eight hydrogen peaks were observable in the difference maps. The positional and anisotropic thermal parameters of all of the atoms with the exception of hydrogen were refined by least squares. A common isotropic thermal parameter for all hydrogen atoms refined to B_H = 7·8 Å^2 (σ = 1·2 Å^2). The other parameters are listed in Tables 1 and 2. The R_1 index ($R_1 = \sum|\Delta F|/\sum|F_o|$) was 0·11 for all 1844 data, and 0·068 for the 1307 non-zero weighted data; the weighted index, $R_2 = (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}$, was 0·061. The goodness of fit was 1·02. In the final cycle no parameter shifted more than 0·02σ.[*]

Table 1. *Atomic coordinates*

In this and the following tables, estimated standard deviations of the last digits are indicated in parentheses. Hydrogen positions are estimates derived from the hydrogen bonding and were not refined. Coordinates for the hydrogen atoms are × 10^3, for other atoms × 10^4.

	x	y	z
Cr	2644 (2)	4003·2 (9)	2400·3 (9)
Na(1)	2482 (4)	5720 (2)	4971 (2)
Na(2)	4776 (4)	6791 (2)	1124 (2)
O(1)	3750 (8)	4286 (5)	3734 (4)
O(2)	3392 (8)	2641 (4)	2122 (4)
O(3)	3473 (8)	4939 (5)	1596 (4)
O(4)	− 146 (7)	4086 (5)	2137 (4)
O(5)	2069 (8)	4063 (4)	9337 (4)
O(6)	3486 (8)	7431 (5)	9203 (4)
O(7)	1325 (8)	7275 (5)	6121 (5)
O(8)	1183 (8)	4425 (4)	6214 (4)
H(1)	142	468	885
H(2)	253	435	1009
H(3)	236	692	876
H(4)	452	740	876
H(5)	19	789	597
H(6)	92	681	670
H(7)	192	373	651
H(8)	84	492	676

Cell dimensions of the isomorphous $Na_2SeO_4.4H_2O$ were derived from precession and Weissenberg photographs.

Discussion. Each of the eight hydrogen atoms can be assigned unambiguously to a hydrogen bond (Table 3). Only one of these bonds is from one water molecule to another; all of the others are between water and chromate oxygen atoms.

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[*] A table of observed structure factors, their estimated standard deviations, and their discrepancies has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30192 (8 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Thermal parameters* (Å^2)

Anisotropic temperature factors have the form exp $[-\frac{1}{4}(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	1·37 (4)	1·41 (4)	1·69 (4)	−0·03 (4)	0·53 (3)	−0·05 (4)
Na(1)	2·0 (1)	2·1 (1)	2·2 (1)	−0·04 (9)	0·47 (9)	−0·16 (9)
Na(2)	1·9 (1)	2·1 (1)	2·6 (1)	0·2 (1)	0·7 (1)	0·2 (1)
O(1)	2·1 (2)	3·7 (3)	2·3 (2)	0·5 (2)	0·5 (2)	−0·3 (2)
O(2)	2·1 (2)	2·0 (2)	2·4 (2)	−0·2 (2)	0·9 (2)	−0·3 (2)
O(3)	2·9 (2)	2·2 (2)	3·0 (2)	−0·6 (2)	1·2 (2)	0·2 (2)
O(4)	1·9 (2)	2·8 (2)	2·4 (2)	0·2 (2)	0·4 (2)	0·0 (2)
O(5)	2·8 (2)	2·3 (2)	2·5 (2)	0·4 (2)	0·6 (2)	0·4 (2)
O(6)	2·3 (2)	3·0 (2)	2·6 (2)	−0·6 (2)	1·3 (2)	−0·8 (2)
O(7)	2·3 (2)	3·0 (2)	3·4 (3)	−0·2 (2)	1·3 (2)	0·2 (2)
O(8)	3·2 (2)	1·8 (2)	2·4 (2)	0·6 (2)	0·7 (2)	0·3 (2)

Table 3. *Hydrogen-bond distances and angles*

Arrows point away from the hydrogen donors. The two distances refer to the first and second atoms and the second and third atoms respectively.

	Distances (Å)		Angle (°)
O(3) ← O(5) → O(4)	2·84 (1)	2·80 (1)	110·0 (2)
O(2) ← O(6) → O(4)	2·82 (1)	2·84 (1)	99·0 (2)
O(5) ← O(7) → O(4)	2·85 (1)	2·86 (1)	101·7 (2)
O(2) ← O(8) → O(4)	2·76 (1)	2·81 (1)	112·8 (3)
O(7) → O(5) → O(3)	2·85 (1)	2·84 (1)	117·2 (2)
O(7) → O(5) → O(4)	2·85 (1)	2·80 (1)	102·9 (2)

The two sodium ions are each coordinated to oxygen atoms from both water and chromate ions. Na(1) is at the center of a distorted octahedron of six oxygen atoms with Na–O distances ranging from 2·36 to 2·46 Å (Tables 4 and 5). Na(2) is coordinated to five oxygen atoms at distances from 2·35 to 2·38 Å.

Table 4. *Other interatomic distances* (Å)

Distances in parentheses have been corrected for thermal motion assuming a 'riding' model.

Cr——O(1)	1·625 (5) (1·637)
Cr——O(2)	1·650 (5) (1·655)
Cr——O(3)	1·605 (5) (1·618)
Cr——O(4)	1·675 (5) (1·684)
Na(1)–O(8)	2·359 (6)
Na(1)–O(8)	2·381 (5)
Na(1)–O(6)	2·414 (6)
Na(1)–O(7)	2·453 (6)
Na(1)–O(1)	2·456 (6)
Na(1)–O(1)	2·463 (5)
Na(2)–O(3)	2·345 (6)
Na(2)–O(2)	2·348 (6)
Na(2)–O(5)	2·367 (5)
Na(2)–O(7)	2·375 (5)
Na(2)–O(6)	2·382 (6)
Na(2)–O(1)	2·922 (6)
O(5)—O(4)	2·80 (1)
O(5)—O(3)	2·84 (1)
O(6)—O(2)	2·82 (1)
O(6)—O(4)	2·84 (1)
O(6)—O(7)	3·00 (1)
O(7)—O(5)	2·85 (1)
O(7)—O(4)	2·86 (1)
O(8)—O(2)	2·76 (1)
O(8)—O(4)	2·81 (1)

Table 5. *Additional angles* (°)

O(1)–Cr——O(2)	108·5 (4)
O(1)–Cr——O(3)	111·5 (4)
O(1)–Cr——O(4)	109·1 (3)
O(2)–Cr——O(3)	108·9 (4)
O(2)–Cr——O(4)	110·0 (4)
O(3)–Cr——O(4)	108·8 (4)
O(1)–Na(1)–O(1)	89·6 (3)
O(1)–Na(1)–O(6)	99·4 (3)
O(1)–Na(1)–O(7)	175·5 (3)
O(1)–Na(1)–O(8)	102·1 (3)
O(1)–Na(1)–O(8)	89·3 (3)
O(1)–Na(1)–O(6)	87·5 (3)
O(1)–Na(1)–O(7)	90·1 (3)
O(1)–Na(1)–O(8)	90·5 (3)
O(1)–Na(1)–O(8)	175·4 (3)
O(6)–Na(1)–O(7)	76·1 (2)
O(6)–Na(1)–O(8)	158·4 (3)
O(6)–Na(1)–O(8)	97·1 (3)
O(7)–Na(1)–O(8)	82·5 (3)
O(7)–Na(1)–O(8)	91·3 (3)
O(8)–Na(1)–O(8)	85·4 (3)
O(1)–Na(2)–O(2)	59·4 (2)
O(1)–Na(2)–O(3)	161·4 (3)
O(1)–Na(2)–O(5)	97·7 (3)
O(1)–Na(2)–O(6)	78·1 (2)
O(1)–Na(2)–O(7)	81·3 (2)
O(2)–Na(2)–O(3)	104·4 (3)
O(2)–Na(2)–O(5)	98·4 (3)
O(2)–Na(2)–O(6)	137·4 (3)
O(2)–Na(2)–O(7)	92·7 (3)
O(3)–Na(2)–O(5)	93·4 (3)
O(3)–Na(2)–O(6)	117·2 (3)
O(3)–Na(2)–O(7)	91·2 (3)
O(5)–Na(2)–O(6)	88·6 (3)
O(5)–Na(2)–O(7)	166·6 (3)
O(6)–Na(2)–O(7)	78·1 (3)
O(2)–O(1)—O(3)	59·6 (2)
O(2)–O(1)—O(4)	61·2 (2)
O(3)–O(1)—O(4)	59·7 (2)
O(1)–O(2)—O(3)	60·4 (2)
O(1)–O(2)—O(4)	60·0 (2)
O(3)–O(2)—O(4)	59·6 (2)
O(1)–O(3)—O(2)	60·0 (2)
O(1)–O(3)—O(4)	60·5 (2)
O(2)–O(3)—O(4)	61·6 (2)
O(1)–O(4)—O(2)	58·8 (2)
O(1)–O(4)—O(3)	59·8 (2)
O(2)–O(4)—O(3)	58·8 (2)

The chromate ion is moderately distorted from regular tetrahedral shape. The O–Cr–O bond angles range from 108·5 to 111·5°. The average Cr–O bond length is 1·639 Å when uncorrected for thermal motion, and is 1·649 Å after correction for thermal motion assuming the 'riding' model. The individual bond lengths vary from 1·605 to 1·675 Å (uncorrected) and this variation appears to be statistically significant. We attribute it to hydrogen bonding and other crystal packing effects because the Cr–O distance is longer when oxygen has a larger number of sodium and hydrogen neighbors. McGinnety (1972) has discussed similar effects in potassium chromate.

References

BORCHARDT, H. J. (1958). *J. Phys. Chem.* **62**, 166–169.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Gmelins Handbuch der anorganischen Chemie (1962). Vol. 52B, pp. 468–472. Weinheim: Verlag Chemie.

MCGINNETY, J. A. (1972). *Acta Cryst.* B**28**, 2845–2852.

RUBEN, H. W., TEMPLETON, D. H., ROSENSTEIN, R. D. & OLOVSSON, I. (1961). *J. Amer. Chem. Soc.* **83**, 820–824.

SIME, R. J., DODGE, R. P., ZALKIN, A. & TEMPLETON, D. H. (1971). *Inorg. Chem.* **10**, 537–541.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.