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Structure of K_4OBr_2

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Abstract. Tetrapotassium dibromide oxide, K_4OBr_2, $M_r = 332{\cdot}2$, tetragonal, $I4/mmm$, $a = 5{\cdot}145\,(2)$, $c = 16{\cdot}527\,(4)$ Å, $V = 437{\cdot}49$ Å^3, $Z = 2$, $D_x = 2{\cdot}522$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 109{\cdot}11$ cm^{-1}, $F(000) = 308$, $T = 294$ K, $R = 0{\cdot}0428$ for 197 unique reflections with $F_o > 2\sigma(F_o)$. The yellow compound crystallizes in the *anti*-K_2NiF_4 structure type and is isotypic with the colourless Na_4OI_2.

Introduction. Recently we described the preparation of Na_3OCl and of Na_3OBr (Sabrowsky, Paszkowski, Reddig & Vogt, 1988) and the crystal structure of Na_4OI_2 (Sabrowsky, Hippler, Sitta, Vogt & Walz, 1990) as part of our investigations into the existence of ternary alkali-metal chalcogenide halides. Na_3OCl and Na_3OBr crystallize in the *anti*-perovskite structure type whereas Na_4OI_2 forms crystals with the *anti*-K_2NiF_4 structure. We have now succeeded in preparing single crystals of K_4OBr_2 and determining their structure. The results are presented here.

Experimental. Polycrystalline samples of K_4OBr_2 can be obtained by sintering a corresponding stoichiometric mixture of K_2O and KBr in closed silver or corundum crucibles between 573 and 623 K in vacuum. Well shaped yellow single crystals of K_4OBr_2 were grown from these mixtures at 623 K in silver crucibles. The crystals are very sensitive to air and moisture. D_m was not measured. A crystal with the approximate dimensions $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}05$ mm was used for the data collection. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 25 diffraction maxima in the θ range 13·5–18°. The intensity measurements were carried out on a Philips PW 1100/15 four-circle diffractometer at 294 K with graphite-monochromated Mo $K\alpha$ radiation applying the ω–2θ scan technique. A total of 683 reflections were collected in the range $3 \le 2\theta \le 60°$ (h: $-7 \rightarrow 7$, k: $0 \rightarrow 7$, l: $0 \rightarrow 19$). Three strong reflections monitored periodically exhibited no significant intensity variation. The data were corrected for Lorentz and polarization effects, leading to 197 unique reflections (nine unobserved unique reflections) with $F_o > 2\sigma(F_o)$ ($R_{\text{int}} = 0{\cdot}0291$). Absorption was corrected empirically by final $F_o - F_c$ comparison using *DIFABS* (Walker & Stuart, 1983) (min. correction: 0·758; max. correction: 1·560). The structural model was verified by Patterson and Fourier methods using *SHELX76* (Sheldrick, 1976). Least-squares refinement on F with anisotropic thermal parameters led to the atomic parameters given in Table 1.* Final $R = 0{\cdot}0428$, $wR = 0{\cdot}0339$, $\{w = k/[\sigma^2(F) + gF^2];\ k = 1{\cdot}3973,\ g = 0{\cdot}0\}$, $(\Delta/\sigma)_{\max} = 0{\cdot}03$, $(\Delta\rho)_{\max} = 1{\cdot}33$, $(\Delta\rho)_{\min} = -1{\cdot}62$ e Å^{-3}. Atomic scattering factors and f', f'' values were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. K_4OBr_2 crystallizes in the *anti*-K_2NiF_4 structure type (Fig. 1) and is isotypic with Na_4OI_2. The structure can be derived from the *anti*-perovskite structure as we have shown earlier (Sabrowsky, Hippler, Sitta, Vogt & Walz, 1990). The oxygen anion is coordinated octahedrally by six potassium ions. The structure involves two crystallographically different potassium ions, both octahedrally coordinated. K(1) is surrounded by two oxygen and four bromide ions, K(2) has one oxygen and five bromide neighbours. The coordination of the bromide anions is ninefold. A Br^- anion is surrounded by a square plane of four K^+ ions approximately in the plane $z = 0{\cdot}15$. Above this plane a fifth K^+ ion completes a square pyramid about the Br^- anion and below it a further square plane of four K^+ ions, twisted about z by 45° relative to the first, also participates in the

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52764 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and thermal parameters* (Å^2) *for* K_4OBr_2

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

		x	y	z	U_{11}	U_{22}	U_{33}	U_{eq}
K(1)	4(*c*)	0	0·5	0	0·0395 (21)	0·0105 (16)	0·0584 (22)	0·0361 (20)
K(2)	4(*e*)	0	0	0·1553 (2)	0·0512 (13)	0·0512 (13)	0·0236 (18)	0·0420 (15)
O	2(*a*)	0	0	0	0·0092 (34)	0·0092 (34)	0·0142 (61)	0·0108 (43)
Br	4(*e*)	0	0	0·3539 (1)	0·0322 (6)	0·0322 (6)	0·0272 (8)	0·0304 (7)

$U_{23} = U_{13} = U_{12} = 0$. $T = \exp[-2\pi^2U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

Table 2. *Interatomic distances* (Å) *for* K_4OBr_2

K(1)—O	2·573	2*
K(1)—Br	3·528 (1)	4
K(1)—K(1)	3·638	4
K(1)—K(2)	3·634 (2)	4
K(2)—O	2·567 (3)	1
K(2)—Br	3·282 (3)	1
K(2)—Br	3·641 (3)	4

* Number of equivalent bonds involving the first atom of the pair.

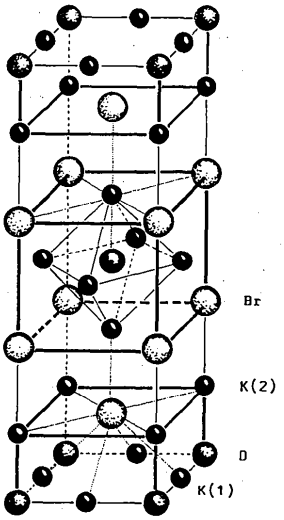

Fig. 1. A perspective drawing of the unit cell of K_4OBr_2.

coordination polyhedron of the Br^- anion (for atomic coordinates and interatomic distances see Tables 1 and 2).

Related to the sum of the molar volumes of K_2O (40·4 cm^3) and KBr (43·3 cm^3), a volume dilation of +3·8% is observed for the formation of K_4OBr_2 (V_m = 131·8 cm^3 mol^{-1}).

Besides K_4OBr_2 the perovskite-phase K_3OBr [a = 5·22 (4) Å] (Hippler, Sitta, Vogt & Sabrowsky, 1989) also exists, as expected by the rules given by Goldschmidt (1926). The coexistence of K_4OBr_2 and K_3OBr can be explained by an estimation of the lattice energies (U_L) for these compounds. Using the Madelung constant [$M(K_2NiF_4) = 7{\cdot}47461$ (Hoppe & Wald, 1989)] and the Born–Landé equation $U_L = -(Me^2/4\pi\varepsilon_oR)N_L(1-1/n)$ with $R = R(\mathrm{O—K}) =$ 2·57 Å and the Born exponent $n = 9$, the lattice energy value for K_4OBr_2 is $U_L(K_4OBr_2) = -3591{\cdot}8$ kJ mol^{-1} whereas $U_L(\mathrm{KBr}) = -658{\cdot}3$ kJ mol^{-1} [$R(\mathrm{KBr}) = 3{\cdot}30$ Å, $n = 9{\cdot}5$] and $U_L(K_2O) = -2206{\cdot}9$ kJ mol^{-1} [$R(\mathrm{O—K}) = 2{\cdot}79$ Å, $n = 8{\cdot}3$]. This leads to a difference of $-68{\cdot}3$ kJ mol^{-1} for the formation of K_4OBr_2 in comparison with $K_2O + 2\,\mathrm{KBr}$.

For K_3OBr the lattice energy is calculated to be $U_L = -2920{\cdot}0$ kJ mol^{-1} using the Madelung constant $M(K_3OBr) = 6{\cdot}18872$ (Hoppe, 1956; Ladd & Lee, 1965), $R(\mathrm{O—K}) = 2{\cdot}61$ Å, $n = 8{\cdot}8$. Taking the above values for K_2O and KBr, the difference relative to K_3OBr is $-54{\cdot}8$ kJ mol^{-1}.

These calculations show that both compounds are stable against decomposition to KBr and K_2O. It is mainly a question of the K_2O/KBr ratio and the reaction temperature which determines whether K_3OBr or K_4OBr_2 is formed.

An interesting difference between the sodium and the potassium compounds involves the colours. All sodium compounds are colourless whereas the potassium compounds show colours ranging from yellow to orange. To discover the reason for this difference in colour, physical measurements and further preparation of comparable compounds with rubidium and caesium are already in progress.

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