(*sh*) cm⁻¹. Previously reported IR ($\tilde{\nu}_{CO}$) frequencies for this compound: 2073 (*vs*), 2031 (*m*), 2016 (*vs*), 1994 (*w*) cm⁻¹ [in hexane; Schmid & Etzrodt (1977)].

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Structure of Na₃OCl

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Abstract. $M_r = 120\cdot422$, cubic, *Pm3m*, $a = 4\cdot496$ (2) Å, $V = 90\cdot88$ Å³, $Z = 1$, $D_x = 2\cdot200$ g cm⁻³, λ(Mo *K*α) = 0·71069 Å, $\mu = 11\cdot58$ cm⁻¹, $F(000) = 58$, $T = 293$ K, $R = 0\cdot0269$ for 74 unique observed reflections. The compound crystallizes in the perovskite structure type. The Na atom is coordinated by two O atoms (axial) and four Cl atoms (equatorial) in a distorted octahedral environment. Oxygen is surrounded octahedrally by six Na atoms and chlorine is coordinated by 12 Na atoms.

Introduction. Recently we described the preparation of Na₃OCl and Na₃OBr (Sabrowsky, Paszkowski, Reddig & Vogt, 1988) as part of our investigations on the existence of ternary alkali metal chalcogenide halides. In agreement with the rule of Goldschmidt (1926) the compounds should crystallize in the anti-perovskite structure type. Meanwhile we succeeded in preparing single crystals of Na₃OCl. We present here the results of the single-crystal structure determination.

Experimental. Polycrystalline samples of Na₃OCl can be obtained by sintering a stoichiometric mixture of Na₂O and NaCl in closed silver crucibles between 573 and 873 K in an argon atmosphere (3 bar). Well shaped colourless single crystals of Na₃OCl were grown from equimolar mixtures of Na₂O and NaCl at 873 K. The crystals are sensitive to air and moisture. D_m was not measured. A crystal with the dimensions 0·1 × 0·1 × 0·1 mm was used for the data collection. The unit-cell parameters were determined by least-squares treatment of the adjusted angular settings of 25 reflections ($2\theta = 14 - 26°$) measured on

a Syntex *R*3 diffractometer. The intensity measurements were carried out at 293 K with graphite-monochromatized Mo $K\alpha$ radiation and the ω–2θ scan technique. A total of 579 reflections were collected from $2\theta = 3$–$58°$ (h $0\rightarrow7$, k $0\rightarrow7$, l $-7\rightarrow7$) and 74 of these were unique ($R_{int} = 0.0225$). 74 reflections with $F_o > 2\sigma(F_o)$ were considered as observed and used in the refinement. Three strong reflections ($20\bar{2}$, 202, 022) monitored periodically during data collection exhibited no significant intensity variation. The data were corrected for Lorentz and polarization effects. A correction for absorption was not made. The structure was solved by Patterson and Fourier methods using *SHELX*76 (Sheldrick, 1976). Least-squares refinement (on *F*) with anisotropic parameters led to the atomic parameters given in Table 1.* Final $R = 0.0269$, $wR = 0.0269$ (unit weights), $(\Delta/\sigma)_{max} = 0.7$, $\Delta\rho_{max} = 0.53$, $\Delta\rho_{min} = -0.7$ e Å^{-3}. Atomic scattering factors and f', f'' values were from *International Tables for X-ray Crystallography* (1974). Fig. 1 shows a schematic representation of the structure with selected interatomic distances; e.s.d.'s are 0.002 Å.

Discussion. The single-crystal investigation confirms the perovskite-type structure of Na$_3$OCl according to our earlier powder work (Sabrowsky *et al.*, 1988). Oxygen is surrounded octahedrally by six Na atoms ($d_{Na-O} = 2.248$ Å). Chlorine is coordinated by 12 Na atoms ($d_{Na-Cl} = 3.179$ Å). The geometry about the six-coordinate Na atom involves a distorted octahedron. The axial positions are occupied by two O atoms ($d_{Na-O} = 2.248$ Å). In the equatorial plane the Na atom is coordinated by four Cl atoms ($d_{Na-Cl} = 3.179$ Å). In comparison to the sum of the molecular volumes of Na$_2$O and NaCl (52.92 cm^3 mol^{-1}) a volume dilatation of 3.42% is observed for the formation of Na$_3$OCl ($V_M = 54.73$ cm^3 mol^{-1}). Relative to sodium oxide the Na—O distance in the present structure is shorter whereas the Na—Cl distance in Na$_3$OCl is much longer than in NaCl. In spite of the volume dilatation we attribute the stability of Na$_3$OCl in the first approximation to the favourable Madelung energy for this compound in contrast to the Madelung energies of the starting materials. The Madelung constant for Na$_3$OCl is given by $M(CaTiO_3)/4 = M(Na_3OCl) = 6.18872$ (Hoppe, 1956; Ladd & Lee, 1965). Using the equation $U_M = -(Me^2/4\pi\varepsilon_0 R)N_L(1 - 1/n)$ with $R = R(O—Na) = 2.25$ Å and $n = 7.4$ the energy is calculated to be $U_M(Na_3OCl) = -3306$ kJ mol^{-1} whereas $U_M(NaCl) = -778$ kJ mol^{-1} and $U_M(Na_2O) = -2481$ kJ mol^{-1}

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52550 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and anisotropic thermal parameters* (Å^2) *for* Na$_3$OCl

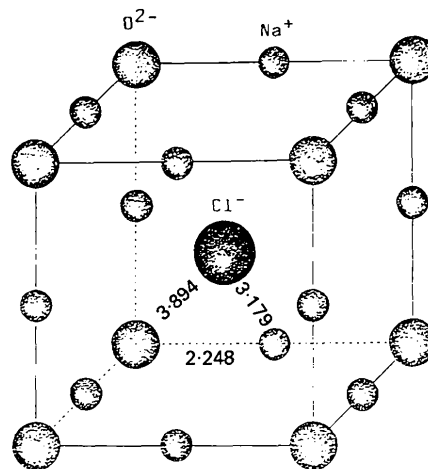|		x	y	z	$U_{11} = U_{22} = U_{33}$	
O	1(a)	0.0	0.0	0.0	0.0133 (8)	
Cl	1(b)	0.5	0.5	0.5	0.0281 (4)	
					U_{11}	$U_{22} = U_{33}$
Na	3(d)	0.5	0.0	0.0	0.0125 (8)	0.0543 (9)

$U_{12} = U_{13} = U_{23} = 0$

Fig. 1. Structure of Na$_3$OCl and selected interatomic distances (Å).

(Ladd & Lee, 1964). This shows a difference of -47 kJ mol^{-1}. Furthermore the existence of Na$_4$OBr$_2$ and Na$_4$OI$_2$ (Sabrowsky, Hippler, Sitta, Vogt & Walz, 1990) can be explained by the Madelung energies whereas Na$_4$OCl$_2$ [calculated Madelung energy for formation $+30$ kJ mol^{-1} using $M(K_2NiF_4) = 7.47461$ (Hoppe & Wald, 1989), $R = R(O—Na) = 2.25$ Å and $n = 7.47$] was not found.

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Structure of Dipotassium Aquadioxotetraperoxodivanadate(V) Trihydrate

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Abstract. $K_2[V_2O_2(O_2)_4(H_2O)].3H_2O$, $M_r = 412\cdot4$, triclinic, $P1$, $a = 6\cdot501$ (3), $b = 7\cdot882$ (3), $c = 7\cdot501$ (3) Å, $\alpha = 107\cdot18$ (5), $\beta = 95\cdot50$ (5), $\gamma = 116\cdot20$ (5)°, $V = 317\cdot8$ Å^3, $Z = 1$, $D_x = 2\cdot15$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 22\cdot59$ cm^{-1}, $F(000) = 204$, $T = 153$ K, $R = 0\cdot026$ for 1966 unique reflections. The core of the structure is a dimeric diperoxo complex of V^V atoms with purely inorganic ligands, $[V_2O_2(O_2)_4(H_2O)]^{2-}$. The coordination polyhedron of each V atom can be described as a pentagonal pyramid. Within the dimeric peroxo complex the coordination polyhedra are chemically non-equivalent and are connected to each other by sharing one O atom of the peroxo group. In the structure there is a hydrogen-bond network including O atoms of complexes and water molecules.

Introduction. Up to now, the structures of only four dimeric peroxovanadates have been determined by the single-crystal X-ray method: $(NH_4)_4[O\{VO(O_2)_2\}_2]$ (Stomberg, Olson & Svensson, 1984), $(Hbpy)[H\{VO(O_2)_2bpy\}_2].xH_2O_2.(6-x)H_2O$, $x \approx 0\cdot5$ (Szentivanyi & Stomberg, 1984), $(NH_4)_3[HO\{VO(O_2)_2\}_2].H_2O$ (Campbell, Flanagan, Griffith & Skapski, 1985) and $[N(CH_3)_4]_2[V_2O_2(O_2)_4(H_2O)].2H_2O$ (Lapshin, Smolin, Shepelev, Gyepesova & Schwendt, 1989). It may be noted here that the anion composition of the latter peroxovanadate represents an analogue of that in the title compound. As part of our study of peroxovanadates, we have carried out the structural study of the present compound which provides information on the influence of the cation on the configuration of the complex anion.

Experimental. A crystal suitable for X-ray crystallography was selected from a sample prepared by dissolving 1·38 g (10 mmol) KVO_3 in 15 cm^3 of 15% H_2O_2 at 273 K. Then 8 cm^3 ethanol and several drops of H_2SO_4 solution (1 mol dm^{-3}) were added to the solution. After three months at 245 K, yellow crystals could be isolated; they were washed with ethanol and stored at 245 K in a desiccator. To prevent decomposition of the crystal investigated, dimensions $0\cdot35 \times 0\cdot30 \times 0\cdot45$ mm, the data were collected at $T = 153$ K by using a nitrogen gas stream cooling device. Reflection data were recorded using an automatic three-circle normal-beam single-crystal X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters from 14 reflections ($14 < \theta < 33°$). Intensity data were collected with the ω–2θ scan method; integrated intensity values were obtained with the modified Oatley & French (1982) profile analysis procedure. Data were collected for $2\theta < 81°$. One control reflection, monitored every 30 reflections, showed no significant variation in intensity. 2408 reflections measured, 1966 unique reflections having $I > 4\sigma(I)$ were used in the analysis; index range: $-11 \leq h \leq 11$, $-14 \leq k \leq 13$, $0 \leq l \leq 6$. Values of I were corrected for Lorentz and polarization effects, no absorption corrections were applied. V atoms were located by Patterson methods and all non-H atoms and H atoms were located in successive difference Fourier syntheses. Calculations were carried out on a BESM-6 computer using the locally modified crystallographic program system *RENTGEN*-75 (Andrianov, Safina & Tarnopolsky, 1974). Seven