

## Structure of Sodium Perchlorate–Tris(1,4-dioxane) at 293 K. A More Ordered Form of the Silver Perchlorate–Tris(1,4-dioxane) Structure

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**Abstract.**  $C_{12}H_{24}ClNaO_{10}$ , rhombohedral,  $R\bar{3}$ ,  $a = 7.62$  (1) Å,  $\alpha = 91.2$  (2)°,  $D_x = 1.45$  g cm<sup>-3</sup>,  $Z = 1$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 25$  cm<sup>-1</sup>. The Na<sup>+</sup> ion is coordinated by six dioxane molecules. The ClO<sub>4</sub><sup>-</sup> ion lies along the threefold axis, occupying two centrosymmetrically-related sites with equal probability.

**Introduction.** The structure of the 1,4-dioxane (dx) complex AgClO<sub>4</sub>·3dx at room temperature was reported by Prosen & Trueblood (1956). They found a cubic cell ( $a = 7.66$  Å) with Ag at (0,0,0), Cl at ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ), and dioxane O atoms on the cell edges. Because of extensive disorder, the dioxane C and the perchlorate O atoms could not be located. Barnes & Duncan (1972) reported that powder photographs of NaCl·3dx, NaClO<sub>4</sub>·3dx, and NaBF<sub>4</sub>·3dx were very similar to that of AgClO<sub>4</sub>·3dx, but whereas AgClO<sub>4</sub>·3dx showed no phase changes between room temperature and the onset of thermal decomposition at 358 K, NaClO<sub>4</sub>·3dx underwent two reversible phase changes at 317.6 and 369.2 K. To clarify the behaviour of these compounds the structure of NaClO<sub>4</sub>·3dx has now been determined at 293 K.

Colourless, cube-like crystals of NaClO<sub>4</sub>·3dx were grown from aqueous solution. Weissenberg photographs indicated a rhombohedral lattice (confirmed by cell measurements with a Wooster four-circle diffractometer), with Laue symmetry  $\bar{3}$  and space group  $R\bar{3}$  or  $R\bar{3}$ . Equi-inclination Weissenberg photographs of levels

0–7kl were scanned by the SRC Microdensitometer Service; 410 unique reflections were above background. The cell parameters are very similar to those of cubic AgClO<sub>4</sub>·3dx, and a Patterson synthesis agreed with the location of Na and Cl at (0,0,0) and ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) respectively. The structure was expanded by Fourier syntheses in  $R\bar{3}$ . Several models were considered for

Table 2. *Interatomic distances (Å) and bond angles (°)*

Na–O(1)	2.432 (3)	O(2)–Cl–O(2) <sup>ii</sup>	103.5 (5)
Cl–O(2)	1.482 (10)	O(2)–Cl–O(3)	114.9 (6)
Cl–O(3)	1.219 (22)	C(1) <sup>i</sup> –O(1)–C(2)	109.4 (2)
C(1)–O(1) <sup>i</sup>	1.430 (5)	O(1) <sup>i</sup> –C(1)–C(2)	110.5 (2)
C(2)–O(1)	1.452 (5)	C(2)–O(1)–Na	129.1 (2)
C(1)–C(2)	1.506 (6)	O(1)–Na–O(1) <sup>ii</sup>	88.0 (4)
C(1)–H(1)	0.96		
C(1)–H(2)	1.07		
C(2)–H(3)	0.97		
C(2)–H(4)	1.00		

Symmetry code: (i)  $-x, 1-y, -z$ ; (ii)  $z, x, y$ .

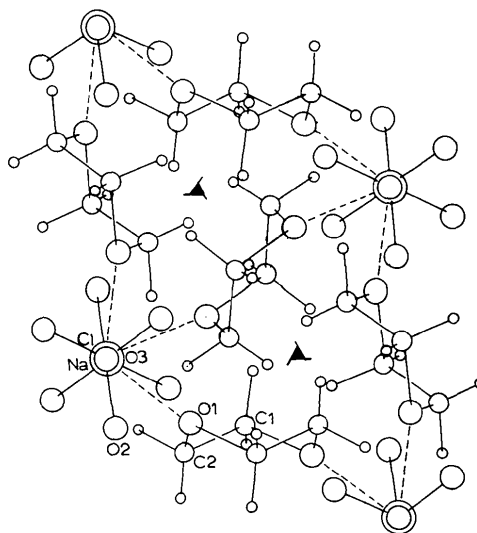


Fig. 1. The structure of NaClO<sub>4</sub>·3C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> projected down [111]. O(3) eclipses the Cl and Na atoms on the triad axis.

Table 1. *Atomic parameters* ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Na	0	0	0
Cl	5000	5000	5000
O(1)	241 (4)	3170 (4)	-268 (4)
O(2)	5124 (21)	5329 (20)	3097 (14)
O(3)	4057 (17)	4057 (17)	4057 (17)
C(1)	1007 (7)	5901 (6)	1299 (6)
C(2)	1680 (6)	4355 (6)	270 (7)
H(1)	1930	6710	1680
H(2)	350	5430	2430
H(3)	2540	3650	880
H(4)	2440	4800	-680

the  $\text{ClO}_4^-$  ion. The most satisfactory involved an averaged centrosymmetric structure (see below). Full-matrix least-squares refinement was continued in  $R\bar{3}$  with anisotropic thermal parameters for all non-hydrogen atoms, and converged at  $R = 0.065$  after all H atoms had been located. The positions and thermal parameters ( $U = 0.05 \text{ \AA}^2$ ) of the H atoms were not refined. Scattering factors were from *International Tables for X-ray Crystallography* (1974). G. M. Sheldrick's *SHELX 76* program system was used in all calculations. The final atomic positions are given in Table 1, bond lengths and angles in Table 2.\*

**Discussion.** In the low-temperature form of the  $\text{MX}_3\text{dX}$  structure (Fig. 1) the chair-conformation dioxane molecule occupies a fixed position with quite small thermal motion. Its O atoms, O(1), lie  $0.27 \text{ \AA}$  from a cell edge, and the molecule has no crystallographically-imposed symmetry other than an inversion

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33406 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

centre. The  $\text{NaO}_6$  octahedron is slightly elongated along the crystal threefold axis; the Na—O(1) distance (Table 2) is within the normal range. One O atom, O(3), of the  $\text{ClO}_4^-$  ion is present as two half-atoms on the threefold axis, but the Cl—O(3) distance is very short and both Cl and O(3) refine with large anisotropic thermal parameters. The remaining O atom, O(2), is on a general sixfold position at a reasonable distance from Cl, but its thermal parameters are also large and the O(2)—Cl—O(2)<sup>ii</sup> angle is only  $103.5^\circ$ . These observations, and the positions of the stronger peaks ( $ca 0.5 \text{ e \AA}^{-3}$ ) in the final difference map, suggest that the above model is too simple. However, attempts to refine the structure with half Cl atoms at  $\pm(x, x, x)$  ( $x \simeq 0.49$ ) were unsatisfactory, and other models required an excessive number of parameters.

#### References

- BARNES, J. C. & DUNCAN, C. S. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1732–1734.  
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press.  
 PROSEN, R. J. & TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9**, 741–746.

*Acta Cryst.* (1978). **B34**, 1985–1988

## Bis(*p*-tolyl isocyanide)octadecacarbonylhexaosmium

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**Abstract.**  $\text{Os}_6(\text{CO})_{18}(\text{CNC}_6\text{H}_4\text{CH}_3)_2$ , monoclinic,  $P2_1/c$ ,  $a = 10.570$  (3),  $b = 16.768$  (5),  $c = 23.752$  (3)  $\text{\AA}$ ,  $\beta = 101.71$  (7) $^\circ$ ,  $U = 4122 \text{ \AA}^3$ ,  $D_m = 2.96$  (2),  $Z = 4$  for  $D_x = 2.983 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo } K\alpha) = 178.2 \text{ cm}^{-1}$ . The structure was refined to an  $R$  of 0.064 for 3400 unique diffractometer data. An unusual cluster geometry is found, in which one isocyanide bridges three Os atoms whereas the other acts as a terminal ligand. All carbonyls are terminal, but the pattern of short C...Os interactions and Os—Os lengths can be correlated with the formal oxidation states of the Os atoms.

**Introduction.** The title compound was isolated as red prismatic crystals (Eady & Malatesta, 1976) from the reaction between  $\text{Os}_6(\text{CO})_{18}$  and *p*-tolyl isocyanide. Spectroscopic evidence indicated that the two isocyanides were differently coordinated, but full structural elucidation required a crystal structure determination.

7182 reflexions were measured on a Nonius CAD-4 four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and a crystal  $0.10 \times 0.20 \times 0.13 \text{ mm}$ .  $L_p$  and numerical absorption corrections