leren Bindungslängen) erscheint aufgrund der Fehlordnung nicht sinnvoll.

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Potassium μ-Oxo-decachloroditungstate(IV)

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Abstract. $K_4W_2OCl_{10}$, M.W. 894·6, tetragonal, $I4/mmm$, $a=7{\cdot}132$ (2), $c=17{\cdot}648$ (5) Å, $V=897{\cdot}7$ Å^3, $d_x=3{\cdot}31$ g cm^{-3}, $Z=2$, $F(000)=804$. Full-matrix least-squares refinement yielded a final $R=0{\cdot}038$. The W–O–W bridge is linear with W–O = 1·871 (1) Å.

Introduction. The compound was prepared by reduction of potassium tungstate in hydrochloric acid with tin (Olsson, 1913). It crystallizes as square plates, red-violet in transmitted and dark green in reflected light. Weissenberg photographs showed that the crystals are tetragonal. The systematic absences $h+k+l=2n+1$ indicated five possible space groups, $I4/mmm$, $I\bar{4}2m$, $I4mm$, $I\bar{4}m2$ and $I422$. The centrosymmetric space group $I4/mmm$ (No. 139) was assumed. The subsequent refinement confirmed this choice. All measurements for a crystal of approximate dimensions 0·02 × 0·02 × 0·04 mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with scintillation counter and graphite monochromator. The cell parameters were determined from a least-squares refinement of the setting angles of 15 reflexions given by the automatic centring program [λ(Mo $K\alpha$) = 0·71069 Å].

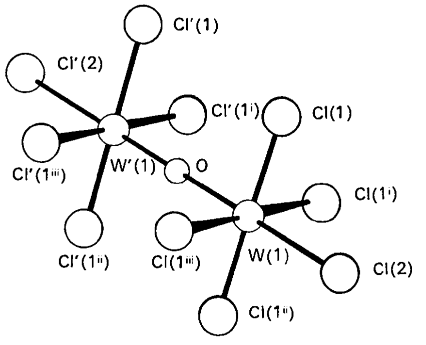

Fig. 1. Perspective view of the $W_2OCl_{10}^{4-}$ ion.

Intensities of 720 independent reflexions were measured up to $2\theta=70°$ with the variable θ–2θ scan technique. The scan rate varied from 2·0 to 20·0° min^{-1} depending on the intensity of reflexion. After each group of 15 reflexions the intensity of a standard reflexion was measured and no significant change in intensity was observed. The intensities were corrected for Lorentz and polarization factors, but not for absorption ($\mu R=0{\cdot}16$).

The crystallographic system and cell parameters suggested isomorphism of $K_4W_2OCl_{10}$ and its Re analogue $K_4Re_2OCl_{10}.H_2O$ (Morrow, 1961). This assumption was confirmed by a Patterson synthesis, which indicated that the W atoms occupy twofold special positions with site symmetry $4mm$ ($00z$; $00\bar{z}$). Because the Patterson synthesis showed no significant differences in location of atoms belonging to both analogues, the parameters of Re, K, Cl and O (except the O atom of the water molecule) were applied in refinement. For the assumed model

$$R_1=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}113 \quad \text{and}$$
$$R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0{\cdot}121\ .$$

Full-matrix least-squares refinement with isotropic thermal parameters for 505 reflexions with $I>3\sigma(I)$ reduced R_1 to 0·055 and R_2 to 0·060. Several cycles of full-matrix refinement with anisotropic thermal parameters yielded the final values $R_1=0{\cdot}038$ and $R_2=0{\cdot}043$.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30884 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates and thermal parameters* ($\times 10^2$) *with e.s.d.'s*

Anisotropic thermal parameters are in the form:

$$\exp\,[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0	0	0·10602 (4)	131 (2)	131 (2)	121 (2)	0	0	0
K(1)	0	0·5	0	350 (21)	189 (16)	249 (15)	0	0	0
K(2)	0	0·5	0·25	486 (19)	486 (19)	319 (20)	0	0	0
Cl(1)	0·2387 (2)	0·2387 (2)	0·1115 (1)	197 (5)	197 (5)	301 (8)	−58 (6)	−28 (5)	−28 (5)
Cl(2)	0	0	0·2424 (3)	401 (16)	401 (16)	131 (14)	0	0	0
O	0	0	0	153 (38)	153 (38)	141 (54)	0	0	0

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

W—O	1·871 (1)	K(2)–Cl(1)	3·513 (2)	O—W–Cl(1)	92·31 (5)
W—Cl(1)	2·410 (2)	Cl(1)–O	3·110 (2)	Cl(1)–W–Cl(1^{ii})	175·37 (7)
W—Cl(2)	2·406 (5)	Cl(1)–Cl(2)	3·336 (4)	Cl(1)–W–Cl(2)	87·69 (8)
K(1)–Cl(1)	3·201 (2)				

A subsequent difference map showed no significant peaks. Attempted refinement in non-centrosymmetric space groups was unsuccessful. A linear W–O–W system in which the W–O distances are not equal was also considered but without success. The function minimized was $\sum w(|F_o|-|F_c|)^2$ with $w=[\sigma^2(F)+0{\cdot}0001F_o^2]^{-1}$. Scattering factors for neutral atoms corrected for anomalous dispersion (Templeton, 1962) were taken from Cromer & Waber (1974). All calculations were performed with the Syntex XTL Structure Determination System (NOVA 1200 computer and additional external disk memory). The final parameters are listed in Table 1. In Table 2 the interatomic distances and valence angles are given.

Discussion. The structure consists of discrete binuclear $Cl_5W\text{–}O\text{–}WCl_5^{4-}$ anions and K^+ cations. The anion is isostructural with that in the above-mentioned Re compound and also with $Ru_2OCl_{10}^{4-}$ (Mathieson, Mellor & Stephenson, 1952) and $Os_2OCl_{10}^{4-}$ (Tebbe & Schnering, 1973). Two W atoms of distorted octahedral geometry are linked by the O atom with site symmetry $4/mmm$, forming the linear W–O–W group. The W–O distance, 1·871 (1) Å, is longer than the 1·819 Å in Na_2WO_4 (Okada, Morikawa, Marumo & Iwai, 1974) but shorter than the W–O(bridging) distance (1·93 Å) in $[W_2O_{11}(H_2O)_2]^{2-}$ (Einstein & Penfold, 1964). A similar lengthening of the metal–oxygen bond going from tetrahedral MO_4^{n-} to octahedral oxygen-bridged compounds was found for Re complexes, *viz.* 1·77 Å in $KReO_4$ (Morrow, 1960), 1·86 Å in $Re_2OCl_{10}^{4-}$ and 1·912 Å in $Re_2O_3en_2Cl_4$ (Glowiak, Lis & Jeżowska-Trzebiatowska, 1972). Practically no differences in W–Cl bond lengths *cis* and *trans* to the bridging O atom are observed [2·410 (2) and 2·406 (5) Å, respectively]. Thus the geometry of the Cl atoms is very close to that in $Ru_2OCl_{10}^{4-}$ and $Re_2OCl_{10}^{4-}$. On the other hand, some deviation from this equivalency of M–Cl bonds occurs in $Os_2OCl_{10}^{4-}$, which exhibits Os–Cl(*trans*) = 2·433 (7) Å, slightly but appreciably greater than Os–Cl(*cis*) = 2·371 (6) Å. Each W atom is displaced towards the O bridge by 0·097 Å from the plane of the *cis* Cl atoms. This displacement is rather small in comparison with that in the Os compound (0·152 Å). The Cl–O and Cl–Cl non-bonding distances (Table 2) are of the same order as those in $Ru_2OCl_{10}^{4-}$ and $Re_2OCl_{10}^{4-}$. Unlike the Ru and Re analogues, $K_4W_2OCl_{10}$ was found to be anhydrous. The results are in good agreement with infrared studies (Colton & Rose, 1968). The structure of $K_4W_2OCl_{10}$ has confirmed earlier suggestions of the presence of two equivalent W^{IV} d^2 central atoms leading to a linear W–O–W bridge. In the case of d^2 central atoms the formation of bent M–O–M bridges must be ruled out (Jeżowska-Trzebiatowska, 1971).

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