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A Reinvestigation of the Crystal Structure of Potassium Perrhenate

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Abstract. $KReO_4$ was prepared by the conventional method [Peacock, R. D. (1966). *The Chemistry of Technetium and Rhenium*, p. 32. Amsterdam: Elsevier] and recrystallized from a 0·01*M* aqueous solution at 5°C, tetragonal $I4_1/a$, $Z=4$, $a=5{\cdot}660$ (2), $c=12{\cdot}667$ (4) Å, $V=405{\cdot}8$ Å^3, $D_{\text{calc}}=4{\cdot}73$, $D_{\text{obs}}=4{\cdot}68$ (2) g cm^{-3}. The ReO_4^- ion is essentially tetrahedral [Re–O = 1·723 (4) Å] and two types of oxygen atom form a rough tristetrahedron about the potassium ion [K–O = 2·779 (4), 2·851 (4) Å].

Introduction. 1025 reflexions were collected in all four quadrants for $0<\theta<27{\cdot}5°$ on a Syntex $P\bar{1}$ diffractometer using graphite monochromatized Mo $K\alpha$ ($\lambda=0{\cdot}7107$ Å) radiation at 23°C. Of these reflexions, 719 were greater than 3σ and 214 were between 3σ and 1σ. The remaining 92 ($\leq 1\sigma$) were rejected. On averaging equivalent reflexions, a set containing 195 reflexions greater than 3σ and 41 between 3σ and 1σ was obtained and was used in subsequent calculations. A standard reflexion was counted every 50 reflexions, and an analysis of the data showed only random fluctuations in the intensity of the standard reflexion; the maximum deviation was ± 3 %. The crystal used had been ground to a sphere of radius 0·025 mm (maximum deviation 5 %) and absorption corrections were applied because $\mu=325{\cdot}0$ cm^{-1}. Secondary extinction corrections were made with the method of Larsen (1967). Unit-cell parameters were obtained by least-squares refinement of 15 accurately centred reflexions in the range $20°<2\theta<30°$. The space group was $I4_1/a$, as discovered by Morrow (1960), and a trial structure was found by using the positional parameters of Morrow for K and Re, and determining the oxygen-atom positions from electron difference maps.* Subsequent refinement using a full-matrix least-squares method applied to those reflexions with $F_o>3\sigma$,* with all atoms having anisotropic thermal parameters, minimized $\sum\omega(F_o-F_c)^2$ and was terminated when $R_1=(\sum||F_o|-|F_c||/\sum|F_o|)=0{\cdot}0197$ and $R_2=(\sum\omega(|F_o|-|F_c|)^2/\sum\omega F_o^2)^{1/2}=0{\cdot}0163$. A weighting function, ω, was chosen so that $\omega|F_o-F_c|^2$ would be locally independent of F_o. The final function used was $\omega=[42{\cdot}0\text{–}0{\cdot}672|F_o|+0{\cdot}00276|F_o|^2]$.†

Inclusion of anisotropic thermal parameters for oxygen made a significant difference to the refinement. With unit weights, and isotropic thermal parameters for oxygen, $R_2=0{\cdot}0317$. When anisotropic thermal parameters were used, $R_2=0{\cdot}0262$; application of the significance test (Hamilton, 1965) shows that this is significant at better than the 99·9 % confidence level.

A number of different combinations of scattering curves were tried to see whether they had any effect on the structure solution. K^+, K^0, O^- and O^0 were taken from *International Tables for X-ray Crystallography* (1962), Re^{3+} from Thomas & Umeda (1957) and Re from Cromer & Waber (1965). Anomalous dispersion corrections were applied to potassium (*International Tables for X-ray Crystallography* 1962) and rhenium (Cromer, 1965). No preferred set was obtained and final refinement was made with K^0, O^0 and Re. In the last cycle of refinement no parameter shifted by more than 1/100th of its error and an electron density difference map had no valleys or peaks outside the limits $-0{\cdot}54$ e Å^{-3} to $+0{\cdot}43$ e Å^{-3}. The final parameters are given in Table 1.‡

Table 1. *Positional and thermal parameters for* $KReO_4$

Anisotropic temperature factors U_{ij} were obtained from $\beta_{ij}=2\pi^2b_ib_jU_{ij}$ where β_{ij}'s appear as a temperature effect through $\exp[-(\beta_{11}h^2+\ldots2\beta_{12}hk+\ldots)]$ in the structure-factor expression and b_i are the reciprocal-lattice vectors. All parameters have been multiplied by 10^4. E.s.d.'s are given in parentheses. Parameters are given relative to the origin at $\bar{1}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0	2500	1250	137 (4)	137 (4)	168 (3)	–	–	–
K	0	2500	6250	199 (15)	199 (15)	157 (11)	–	–	–
O	1177 (7)	288 (8)	2022 (4)	231 (25)	277 (23)	268 (24)	61 (24)	−46 (18)	93 (19)

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* Programs used were written for a CDC6400 computer and include the X-RAY71 programs *DATCO3* and *DATRDN*. The least-squares program *CUDLS* and Fourier program *SYMFOU* are written locally by J. S. Stephens.

* The selection of $F_o>3\sigma$ is made before absorption corrections are made to F_o.

† An alternative refinement using the weighting scheme $\omega=42{\cdot}0\text{–}0{\cdot}672\ |F_o|+0{\cdot}00276\ |F_o|^2+1250\ (|\sigma/F_o|)^2$ and using all data with $F_o>1\sigma$ was terminated at $R_1=0{\cdot}0248$ and $R_2=0{\cdot}0161$. The parameters and errors were the same as in the above refinement.

‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30940 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. We have been attempting to establish a relationship between Re–O bond distances and the Re–O stretching frequencies and related force constants for a variety of compounds. It has become apparent that most Re–O bond lengths are not known with sufficient accuracy to test any detailed relationship.

The graphical relationships we have developed suggest that accepted Re–O distances for Re(VII) compounds are too long. We would expect the Re–O distances in ReO_3Cl and ReO_4^- to be 1·70 and 1·73 Å respectively. In the most recent edition of Cotton & Wilkinson (1972) the Re–O distance for ReO_3Cl is given as 1·76 Å, and is undoubtedly based on the value of 1·761 (3) Å derived by Amble, Miller, Schawlow & Townes (1952). Other work has shown, however, that the correct value is 1·70 Å (Lotspeich, Javan & Englebrecht, 1959) and the value quoted above is in error, probably because of a printing mistake in the original paper. The published value for the Re–O distance in ReO_4^- is 1·77 (3) Å (Morrow, 1960). The mean value is larger than our expected value, but because of the large error cannot be said to differ significantly. As a result, we have reinvestigated the crystal structure of $KReO_4$ in order to obtain a more reliable value of the Re–O distance.

Our value for the Re–O distance, 1·723 (4) Å, is very close to the expected value and the O–Re–O angles [110·8 (2) and 108·8 (2)] are close to, but significantly different from, the tetrahedral angle. Although the mean distance has changed only 0·05 Å from Morrow's value, there is a marked reduction in the e.s.d.'s and the position of the oxygen atom within the cell has changed by 0·14 Å. A marked decrease has also been made in the temperature factors which are now in the expected order $Re < K < O$ rather than $Re < O < K$ as found by Morrow. In addition, the measured density is much closer to the X-ray density than Smith & Long's (1948) value of 4·38 g cm^{-3}.

Although, as Morrow has noted, $KReO_4$ is structurally like KIO_4 and $KRuO_4$, there appears to be no relationship to the structure of $KMnO_4$ (Palenik, 1967). Apart from the differences in the overall packing, the most noticeable difference is in the packing of the oxygen atoms around the potassium ion. In $KMnO_4$ the packing is based on a distorted Archimedian antiprism. For $KReO_4$ the packing is based on a rough tristetrahedron (or bisbisphenoid) (Buerger, 1971). The two K–O distances [2·779 (4) and 2·851 (4) Å] differ slightly and there is a rotation of 15·8° about the fourfold axis between the two sets of oxygen atoms compared with the ideal structure. The packing about K^+ must be determined by the overall structure, since oxygen–oxygen contacts within this coordination sphere (3·078, 3·347, 3·426, 3·697, 4·263 Å) are considerably longer than the sum of the van der Waals radii and other O–O contacts in the structure (2·801, 2·836, 3·159).

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