Refinements of the Crystal Structures of KTcO₄, KReO₄ and OsO₄. The Bond Lengths in Tetrahedral Oxo-Anions and Oxides of d^0 Transition Metals

By Bernt Krebs and Klaus-Dieter Hasse

Fakultät für Chemie, Universität Bielefeld, Bielefeld, Germany (BRD)

From single-crystal structure redeterminations of KTcO₄ (scheelite type, $a = 5·630$, $c = 12·867$ Å), of KReO₄ (scheelite type, $a = 5·674$, $c = 12·668$ Å) and of OsO₄ (monoclinic, $C2/c$, $a = 9·379$, $b = 4·515$, $c = 8·630$ Å, $\beta = 116·58°$), precise metal–oxygen bond lengths were obtained: Tc–O 1·711 (3), Re–O 1·719 (5), Os–O 1·684 (7) and 1·710 (7) Å (uncorrected). The Re–O and Os–O values are much more in line with the trend to be expected within the complete series of the isoelectronic MO_4^{n-} species (M: d^0 transition metal) than those previously determined. 'Effective ionic radii' are derived for Tc^{VII}, Re^{VII}, Ru^{VIII} and Os^{VIII}.

Introduction

The simple tetrahedral oxo-anions and oxides of the transition metals with d^0 configuration (VO_4^{3-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, MnO_4^-, TcO_4^-, ReO_4^-, RuO_4, OsO_4) are of considerable interest for the understanding of the nature of transition metal–oxygen bonds. In going from the V to the VIII transition metal groups of the periodic table, a continuous decrease of metal–oxygen bond lengths within the isoelectronic series of this class of compounds is to be expected as a result of the contraction of the metal electron shells, together with an increase in bond strength (increasing π bond contributions). The bond-strength increase can be demonstrated most clearly, besides the results of other methods, from the stretching force constants (*e.g.* Krebs & Müller, 1967; Müller & Krebs, 1967; Krebs, Müller & Fadini, 1967).

Structural and bond-length data which are available for all the species cited above except for TcO_4^-, show in general the predicted trends. Clarification is, however, needed in the cases of ReO_4^- and OsO_4. For ReO_4^- the only known structure analysis (of $KReO_4$) reports a Re–O bond length of 1·77 (3) Å (Morrow, 1960) which seems rather long; the Os–O value in solid OsO₄ [average 1·74 (2) Å; Ueki, Zalkin & Templeton, 1965] is at variance with the gas phase electron diffraction result [$r_g = 1·712$ (3) Å; Seip & Stølevik, 1966], the significance of this difference being doubtful due to the large error of the X-ray value. Gilli & Cruickshank (1973) showed that this discrepancy is not caused by neglect of anomalous dispersion in the case of the X-ray data.

To obtain a more reliable base for the discussion of the Me–O bonding in this series of compounds, the crystal structures of KTcO₄, KReO₄ and OsO₄ were refined on the basis of counter data.

Experimental

In order to avoid impurities, KTcO₄ and KReO₄ were prepared *via* the volatile oxides. ⁹⁹Tc (Oak Ridge) and

Re (Degussa) were reacted with O₂ in a closed system to give Tc₂O₇ and Re₂O₇. The oxides were sublimed and dissolved in equivalent amounts of aqueous KOH, the salts being crystallized from the solution by slow evaporation. OsO₄ single crystals were prepared by reaction of Os(Degussa) with O₂ and subsequent slow sublimation in a closed system which had a provision for cooling during the mounting of the crystals in a sealed capillary. For the X-ray intensity measurements ground spheres of KTcO₄ (radius 0·048 mm; $\mu = 42·9$ cm⁻¹) and of KReO₄ (radius 0·022 mm; $\mu = 323·2$ cm⁻¹) were used; in the case of OsO₄ the data were collected on a prismatic crystal with dimensions $0·086 \times 0·066 \times 0·028$ mm ($\mu = 411·4$ cm⁻¹). In all three cases absorption corrections were applied and secondary extinction was corrected for. For KTcO₄ (KReO₄) a full non-equivalent set of 390 (487) reflexions with $\sin \theta / \lambda < 0·77$ (0·82) Å⁻¹ was collected on a Hilger–Watts four-circle diffractometer at 20°C (Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, scintillation counter ω–2θ scan), 349 (404) of which were considered to be significant with $I > 2\sigma(I)$. For OsO₄ data collection was done at 17°C on a Philips four-circle diffractometer (graphite monochromator, Mo $K\alpha$ radiation, $\lambda = 0·7107$ Å, scintillation counter, ω–2θ mode), a full set of 488 [444 above $2\sigma(I)$] reflexions with $\sin \theta / \lambda < 0·71$ Å⁻¹ being measured.

Crystal data and refinement

Unit-cell constants were obtained by least-squares refinement of the four-circle coordinates of 14 reflexions.

Crystal data

KTcO₄: tetragonal, $I4_1/a$, scheelite structure as predicted by Boyd (1959) and McDonald & Tyson (1962), $a = 5·630$ (2), $c = 12·867$ (4) Å, $V = 407·8$ Å³, $Z = 4$, $D_c = 3·27$, $D_o = 3·24$ (3) g cm⁻³, all at 20°C. Previous powder data [$a = 5·654$, $c = 13·030$ Å, McDonald & Tyson (1962)] are significantly different from these new values.

KReO₄: isomorphous with KTcO₄, $I4_1/a$, $a = $

5·674 (2), $c = 12·688$ (4) Å, $V = 408·5$ Å³, $Z = 4$, $D_c = 4·70$, $D_o = 4·68$ (2) g cm⁻³, all at 20°C. The cell constants correspond quite well to previous data [5·680 and 12·703 Å, Morrow (1960); 5·660 and 12·667 Å, Lock & Turner (1975)].

OsO₄: monoclinic, $C2/c$, $a = 9·379$ (4), $b = 4·515$ (2), $c = 8·630$ (3) Å, $\beta = 116·58$ (4)°, $V = 326·8$ Å³, $Z = 4$, $D_c = 5·17$, $D_o = 5·11$ (5) g cm⁻³, all at 17°C. The cell constants are in excellent agreement with those given by Ueki et al. (1965).

The refinement by full-matrix least squares was started for KTcO₄ and KReO₄ with the metal atom coordinates taken from the KReO₄ structure determination by Morrow (1960), for OsO₄ with the Os coordinates given by Ueki et al. (1965). All oxygen coordinates were taken from subsequent difference Fourier syntheses; the least-squares refinement was then completed with anisotropic temperature factors for all atoms. Scattering curves for Os, Re, Tc, K and O were taken from International Tables for X-ray Crystallography (1968). Anomalous scattering corrections were applied to Os, Re, Tc and K (Cromer & Liberman, 1970.. Introduction of anisotropic temperature factors for the O atoms, which improved the R values about 1%, was shown to be highly justified by Hamilton's (1965) statistical test.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/[\sigma(F_o^2)]^2$; $\sigma(F_o^2) = \{[\sigma(I)]^2 + (0·03I)^2\}^{1/2}/Lp$; I: net intensity. Reflexions with $\sigma(I) > 2I$ were excluded from the refinement ($w = 0$). The final R values after convergence were

	KTcO₄	KReO₄	OsO₄
R_1	0·029	0·042	0·051
R_2	0·034	0·041	0·046

where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}$ for all measured reflexions, including weak ones. Shifts in the last cycle were below $0·04\sigma$; the highest maxima in the difference syntheses (in the vicinity of the heavy metals) were below 1·2 e Å⁻³.*

The final atomic coordinates and thermal parameters are given in Table 1. Table 2 lists the interatomic distances and bond angles within the TcO₄⁻, ReO₄⁻ and OsO₄ tetrahedra.† The transition metal–oxygen bond distances were corrected for librational oscillations of the tetrahedra (Cruickshank, 1956; Schomaker & Trueblood, 1968); the corrected distances are given in Table 2.

---

* The programs used for the calculations on a PDP10 included local versions of the DATAP (M. Dobler), ORFLS (W. R. Busing, K. O. Martin, H. A. Levy) and FORDAP (A. Zalkin) programs.

† Lists of the observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31445 (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 anisotropic temperature factor coefficients (U values multiplied by 10^4)

The temperature factors are expressed in the form

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

E.s.d.'s are given in parentheses in units of the last decimal. Origins at Ī.

(a) KTcO₄

		x	y	z
Tc	4(a)	0	0·25	0·125
K	4(b)	0	0·25	0·625
O	16(f)	0·1089 (4)	0·0254 (4)	0·2008 (2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tc	207 (2)	207 (2)	226 (2)	0	0	0
K	290 (4)	290 (4)	249 (5)	0	0	0
O	295 (10)	304 (10)	317 (10)	54 (9)	2 (8)	69 (8)

(b) KReO₄

		x	y	z
Re	4(a)	0	0·25	0·125
K	4(b)	0	0·25	0·625
O	16(f)	0·1166 (10)	0·0310 (9)	0·2027 (5)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	138 (1)	138 (1)	164 (1)	0	0	0
K	313 (8)	313 (8)	281 (11)	0	0	0
O	300 (26)	206 (22)	252 (20)	−7 (18)	−14 (19)	75 (17)

(c) OsO₄

		x	y	z
Os	4(e)	0	0·25940 (8)	0·25
O(1)	8(f)	0·1125 (8)	0·0366 (17)	0·1927 (12)
O(2)	8(f)	0·1177 (8)	0·4832 (21)	0·4190 (9)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os	263 (2)	221 (2)	210 (2)	0	128 (2)	0
O(1)	427 (32)	533 (38)	542 (44)	−73 (33)	269 (35)	−11 (44)
O(2)	425 (32)	664 (43)	188 (25)	−40 (38)	−30 (23)	−110 (29)

Table 2. *Interatomic distances and bond angles with standard deviations*

KTcO₄

		Corrected	Multiplicity
Tc—O	1·711 (3) Å	1·724 Å	4
O——Tc–O^I	110·5 (2)°		2
O——Tc–O^{II}	109·0 (2)		4
O$\cdots$O^I	2·811 (4) Å		1
O$\cdots$O^{II}	2·785 (4)		2
K——O^{III}	2·794 (3)		4
K——O^{IV}	2·864 (3)		4

KReO₄

Re—O	1·719 (5) Å	1·733 Å	4
O——Re–O^I	110·0 (3)°		2
O——Re–O^{II}	109·2 (3)		4
O$\cdots$O^I	2·816 (10) Å		1
O$\cdots$O^{II}	2·802 (10)		2
K——O^{III}	2·785 (6)		4
K——O^{IV}	2·872 (6)		4

OsO₄

Os$\cdots$O(1)	1·684 (7) Å	1·698 Å	2
Os$\cdots$O(2)	1·710 (7)	1·727	2
O(1)——Os–O(1)^V	106·7 (4)°		1
O(1)——Os–O(2)	110·7 (3)		2
O(1)——Os–O(2)^V	110·6 (3)		2
O(2)——Os–O(2)^V	107·6 (4)		1
O(1)$\cdots$O(1)^V	2·702 (14) Å		1
O(1)$\cdots$O(2)	2·793 (11)		2
O(1)$\cdots$O(2)^V	2·791 (11)		2
O(2)$\cdots$O(2)^V	2·760 (14)		1

The indices refer to the following transformations of the parameters in Table 1: (I) $\bar{x},\frac{1}{2}-y,z$; (II) $-\frac{1}{4}+y,\frac{1}{4}-x,\frac{1}{4}-z$; (III) $\frac{1}{4}+y,\frac{1}{4}-x,\frac{1}{4}+z$; (IV) $\frac{1}{2}-x,\bar{y},\frac{1}{2}+z$; (V) $\bar{x},y,\frac{1}{2}-z$.

Discussion

The Tc–O and Re–O bond lengths in the slightly but significantly distorted TcO₄⁻ and ReO₄⁻ tetrahedra in KTcO₄ and KReO₄ are equal within the limits of error. This effect of the 'lanthanide contraction' is similarly observed in bonds of the homologous pairs Hf–Zr, Nb–Ta and Mo–W to other elements.

The Tc–O bond length of 1·711 (3) Å* is comparable to the mean value [1·714 Å; single values 1·649 (6)$\cdots$ 1·840 (1) Å] within the distorted TcO₄ tetrahedra of the dimeric Tc₂O₇ molecules in the solid (Krebs, 1971).

The present result for the Re–O bond [1·719 (5) Å] shows the previously reported value [1·77 (3) Å; Mor-

---

* For the purpose of comparison with other (mostly uncorrected) bond distances the uncorrected values are used.
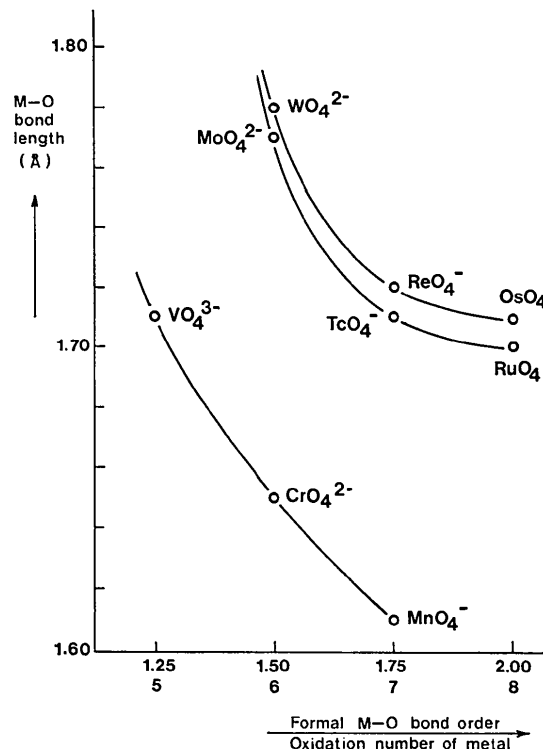

Fig. 1. Metal–oxygen bond lengths in tetrahedral d^0 transition metal oxo-anions and oxides in relation to the group numbers of the metals.

Table 3. *Structural and bonding data for tetrahedral d^0 transition-metal oxo-anions and oxides*

	Experimental M–O bond lengths(Å)	Method	Mean value (Å)	'Effective ionic radius'^{a} of M (Å)	M–O stretching^b force constant (mdyn Å^{-1})
VO₄³⁻	c	X	1·71	0·355	4·80
CrO₄²⁻	c	X	1·65	0·30	5·65
MoO₄²⁻	c	X	1·77	0·42	5·93
WO₄²⁻	c	X	1·78^d	0·42	6·48
MnO₄⁻	1·607 (5)^e	X	1·61	0·26	5·93
	1·610 (4)^f	X			
TcO₄⁻	1·711 (3)^g	X	1·71	0·35^g	6·78
ReO₄⁻	1·719 (5)^g	X	1·72	0·36^g	7·56
	1·723 (4)^h	X			
RuO₄	1·706 (3)^i	e.d.	1·70	0·35^g	6·96
OsO₄	1·712 (3)^j	e.d.	1·71	0·36^g	8·29
	1·675 (5)^g	X			

Notes: (a) According to Shannon & Prewitt (1969); for CN 4, d^0 configuration, based on $r(^{IV}O^{2-}) = 1·40$ Å. (b) Müller & Diemann (1974). (c) Several X-ray structure determinations exist for these ions. A list of references is given, *e.g.* by Shannon & Prewitt (1969, 1970). Compilations of VO₄³⁻ data: Brown & Shannon (1973), of MoO₄²⁻ data: Schröder (1975). TiO₄⁴⁻, NbO₄³⁻ and TaO₄³⁻ (Barker & Wood, 1972) may be added to this group of compounds, if more reliable structural data are available. (d) Contrary to Shannon & Prewitt (1970) who assign equal radii to Mo^{VI} and W^{VI}, the difference of about 0·01 Å seems significant from the large number of literature data. (e) Palenik (1967): KMnO₄. (f) Boonstra (1968): AgMnO₄. (g) This paper. (h) Lock & Turner (1975): KReO₄. (i) Schäfer & Seip (1967). (j) Seip & Stølevik (1966).

row (1960)], which was accepted as the normal Re^{VII}–O bond length, to be considerably too high. This is in good agreement with a recent independent refinement of the $KReO_4$ structure [Re–O 1·723 (4) Å; Lock & Turner (1975)] and confirms the X-ray results for the ReO_4 tetrahedra in the polymeric Re_2O_7 structure [average Re–O 1·74 Å; single values 1·68 (3)···1·80 (2) Å; Krebs, Müller & Beyer (1969)], for the tetrahedral ReO_3S^- ions in $RbReO_3S$ [av. Re–O 1·730 Å, single values 1·717 (15)···1·745 (13) Å; Krebs & Kindler (1969)], and is close to the values for ReO_3Cl [Re–O 1·702 (3) Å] and for ReO_3F [Re–O 1·692 (3) Å] from microwave spectra (Amble, Miller, Schawlow & Townes, 1952; Lotspeich, Javan & Engelbrecht, 1959).

The details of the remaining structural features are very similar in $KTcO_4$ and $KReO_4$. Besides the almost identical K–O distances (Table 2), nonbonded O···O contact distances in the tristetrahedral KO_8 polyhedra of $KTcO_4$ ($KReO_4$) are: 3·087 (3·080), 3·413 (3·357), 3·335 (3·452), 3·707 (3·728) Å, with additional interionic contacts at 3·244 (3·148) Å. Every O has one Tc(Re)+two K as neighbours.

The mean Os–O bond length of 1·697 Å found in the present study agrees better with the gas phase electron diffraction results [$r_g = 1·712$ (3) Å; Seip & Stølevik (1966)] than the less precise previous X-ray value of 1·74 Å [single values 1·76 (3) and 1·71 (3) Å; Zalkin & Templeton (1965)] and fits better into the isoelectronic series of analogous tetrahedra. The OsO_4 tetrahedra show significant angular distortion, apparently caused by intermolecular packing forces.

The intermolecular O···O contacts in the OsO_4 structure are at 3·055, 3·073, 3·095, 3·101, 3·157, 3·159, 3·171, 3·223, 3·233, 3·288, 3·346 Å, indicating quite regular packing [σ(O···O): 0·012···0·015 Å].

With the reservations that should be made in directly comparing X-ray diffraction results with gas phase electron diffraction data, Table 3 gives the bond-length data for the complete series of stable tetrahedral d^0 transition metal oxo-anions and oxides. In Fig. 1 the correlation between bond lengths and oxidation numbers (group numbers of the metals) is shown. The continuous decrease of the M–O values within the isoelectronic series from left to right is partly due to the normal increase of nuclear charge–electron shell attraction in the metals and partly to the increase in π bond strength (parallel to a decrease of negative ionic charge) in the strongly covalent bonds. This is shown from the Me–O stretching force constants cited in Table 3. From the Tc–O, Re–O and Os–O bond lengths in $KTcO_4$, $KReO_4$ and OsO_4 the 'effective ionic radii' in the definition of Shannon & Prewitt (1969) can be derived for Tc^{VII}, Re^{VII} and Os^{VIII} with CN 4 (tetrahedral). Subtraction of $r(^{III}O^{2-}) = 1·36$ Å from the Tc–O and Re–O bond lengths observed results in the values 0·35 Å for Tc^{VII} and 0·36 Å for Re^{VII}, as given in Table 3. A value for $r(^IO^{2-})$, which has to be formally used in the calculation of the corresponding effective radius for Os^{VIII}, is not known. From the data derived

by Shannon & Prewitt, it should not be significantly different from the value for CN 2 (1·35 Å). Subtracting this value from the observed bond lengths results in the effective ionic radius of 0·36 Å for Os^{VIII} with CN 4 and (if the gas phase bond length is assumed to be valid also for the solid) of 0·35 Å for Ru^{VIII}; see Table 3.

References

AMBLE, E., MILLER, S. L., SCHAWLOW, A. L. & TOWNES, C. H. (1952). *J. Chem. Phys.* **20**, 192–193.

BARKER, M. G. & WOOD, D. J. (1972). *J. Chem. Soc. Dalton*, pp. 9–13, 2448–2450.

BOONSTRA, E. G. (1968). *Acta Cryst.* **B24**, 1053–1062.

BOYD, G. E. (1959). *J. Chem. Educ.* **36**, 3–14.

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* **A29**, 266–282.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756, 757–758.

GILLI, G. & CRUICKSHANK, D. W. J. (1973). *Acta Cryst.* **B29**, 1983–1985.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.

KREBS, B. (1971). *Z. anorg. allgem. Chem.* **380**, 146–159.

KREBS, B. & KINDLER, E. (1969). *Z. anorg. allgem. Chem.* **368**, 293–307.

KREBS, B. & MÜLLER, A. (1967). *J. Mol. Spectrosc.* **22**, 290–295.

KREBS, B., MÜLLER, A. & BEYER, H. (1969). *Inorg. Chem.* **8**, 436–443.

KREBS, B., MÜLLER, A. & FADINI, A. (1967). *J. Mol. Spectrosc.* **24**, 198–203.

LOCK, C. J. L. & TURNER, G. (1975). *Acta Cryst.* **B31**, 1764–1765.

LOTSPEICH, J. F., JAVAN, A. & ENGELBRECHT, A. (1959). *J. Chem. Phys.* **31**, 633–643.

McDONALD, B. J. & TYSON, G. J. (1962). *Acta Cryst.* **15**, 87.

MORROW, J. C. (1960). *Acta Cryst.* **13**, 443–445.

MÜLLER, A. & DIEMANN, E. (1974). *MTP Int. Rev. Sci.*, *Inorg. Chem. Ser.* II, **5**, 71–110. London: Butterworth.

MÜLLER, A. & KREBS, B. (1967). *J. Mol. Spectrosc.* **24**, 180–197.

PALENIK, G. J. (1967). *Inorg. Chem.* **6**, 503–507.

SCHÄFER, L. & SEIP, H. (1967). *Acta Chem. Scand.* **21**, 737–744.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

SCHRÖDER, F. (1975). *Acta Cryst.* **B31**, 2294–2309.

SEIP, H. M. & STØLEVIK, R. (1966). *Acta Chem. Scand.* **20**, 385–394.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.

SHANNON, R. D. & PREWITT, C. T. (1970). *Acta Cryst.* **B26**, 1046–1048.

UEKI, T., ZALKIN, A. & TEMPLETON, D. H. (1965). *Acta Cryst.* **19**, 157–160.