A New Type of Oxide Structure: the Crystal Structure of Rhenium(VII) Oxide

By B. KREBS,* A. MÜLLER, and H. BEYER
(*Anorganisch-Chemisches Institut der Universität, Göttingen, Germany*)

DIRHENIUM HEPTOXIDE Re_2O_7 is one of the few important binary transition metal oxides, the structures of which were previously unknown.[1]

Attempts to predict the structure by methods other than X-ray diffraction have lead to ambiguous or wrong results.

We examined the structure by X-ray methods. Yellow, hygroscopic crystals of Re_2O_7 were obtained by treating Re powder with excess oxygen in a flow system at 500°, followed by slow sublimation. The compound crystallizes in the space group $P2_12_12_1$ (D_2^4, No. 19) [2] with $a = 12{\cdot}508$, $b = 15{\cdot}196$, $c = 5{\cdot}448$ Å, $U = 1035{\cdot}5$ Å^3, $D_m = 6{\cdot}14$, $D_c = 6{\cdot}21$ g./cm.^{3}, $Z = 8$. A total of 1102 unique nonzero intensities were recorded on Weissenberg (Cu-K_α) and precession (Mo-K_α) photographs (all integrated). The data were measured photometrically. Special care was taken of the absorption effects. The structure was solved from Patterson and Fourier syntheses. The least-squares refinement converged to an R factor of 5·3%, with anisotropic temperature factors for Re. Anomalous dispersion corrections were applied to Re, from which the absolute configuration could be determined

The structure is based on an unusual combination of different structural features: mainly covalently bonded ReO_6 octahedra and ReO_4 tetrahedra are connected through sharing corners to form polymeric double layers along the (010) face.[3] A double layer of this kind is shown in Figure 1. It has only van der Waals contacts to neighbouring layers and consists of chains c along the axes of ReO_6 octahedra sharing corners, every other chain being part of the upper or lower half of the double layer, respectively. These chains are connected by the ReO_4 tetrahedra to form the layers, every tetrahedron sharing one corner with each of two octahedra. The resulting double layers can be described as a system of "rings" of 4 polyhedra (t.-o.-t.-o.), which are themselves connected

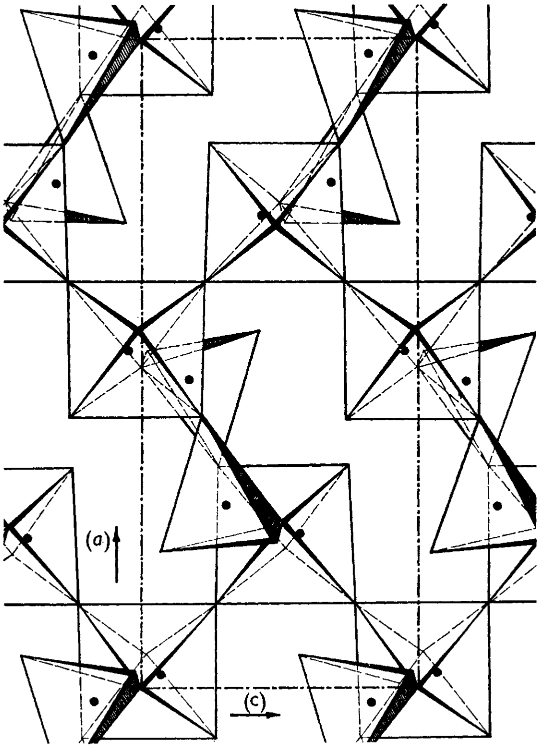

FIGURE 1. *Crystal structure of* Re_2O_7: *one of the two double layers perpendicular to* b, *related to each other by a twofold screw axis*: ●, Re; corners of the polyhedra, O.

through corners of the octahedra resulting in a polymeric arrangement. In Figure 1 these "rings" are perpendicular to the plane of the paper. Figure 2 shows this structure element with the bond distances determined (σ = 0·02—0·03 Å). Re–Re distances bonded through O range from 3·678 to 3·774 Å (σ = 0·002 Å). Between the layers the shortest (nonbonded) Re–Re distances are >4·66 Å. Every octahedron is linked to two octahedra and to two tetrahedra. The octahedral environment is strongly distorted: the central Re atom is displaced from the centre parallel to one of the threefold axes of the octahedron, resulting in the fact that there is a "long" and a "short" Re–O bond distance in every Re(o.)–O–Re(o.) bridge. All terminal Re–O bonds are shorter than corresponding bridging bonds, according to their higher bond orders.[4] Observed O–Re–O bond angles are 76—104° in the distorted octahedra, 104—113° in the tetrahedra. Re–O–Re bond angles were found at values from 147·0 to 152·9°.

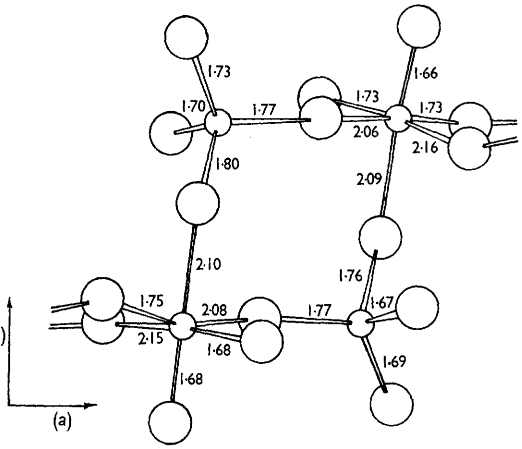

FIGURE 2. *Asymmetrical unit of the* Re_2O_7 *structure with bond distances in* Å. *Direction of view approximately along the* c *axis.*

If the partly heteropolar character of the Re–O bonds >2·0 Å is stressed, the lattice can, in an idealized form, be regarded as an arrangement of ReO_4^- (the tetrahedra) and ReO_3^+ ions.

From this crystal structure the mechanism of evaporation can be explained: thermal cleavage of two of the long Re–O bonds per octahedron, together with a slight change in hybridisation at the Re atom is sufficient to give the Re_2O_7 molecule with tetrahedral co-ordination as it is observed in the gas phase.[1] An analogous mechanism is to be assumed for the hydrolysis to solid "perrhenic acid" which has, according to our crystal structure determination,[5] to be formulated as dirhenium-dihydrato-heptoxide $Re_2O_7(OH_2)_2$. The complicated i.r. spectrum[1,6] and the unusual physical properties of Re_2O_7 can be interpreted on the basis of its crystal structure.

We thank Prof. Dr. O. Glemser for generous support of our work, and G. Wagner for preparing the oxide.

(*Received, January* 15*th*, 1968; *Com.* 049.)

---

[1] B. Krebs and A. Müller, *Z. Naturforsch.*, 1968, in the press.

[2] A. Müller and B. Krebs, *Naturwiss.*, 1965, **52**, 55; see also K. A. Wilhelmi, *Acta Chem. Scand.*, 1954, **8**, 693.

[3] A different structural principle which links MeO_4 and MeO_6 polyhedra is realized in $Na_2Mo_2O_7$, I. Lindquist, *Acta Chem. Scand.*, 1950, **4**, 1066; 1960, **14**, 960; M. Seleborg, *ibid.*, 1967, **21**, 499.

[4] In the ReO_4^- ion (formal bond order 7/4) bond distances of about 1·77 Å were found (J. C. Morrow, *Acta Cryst.*, 1960, **13**, 443).

[5] H. Beyer, O. Glemser, and B. Krebs, *Angew. Chem.*, in the press.

[6] K. Ulbricht and H. Kriegsmann, *Z. Chem.*, 1967, **7**, 224.