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MOLECULAR STRUCTURE OF DIRHENIUM DECACARBONYL

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SUMMARY

The molecular structure of $Re_2(CO)_{10}$ has been determined by electron diffraction methods and the following bond lengths found: Re–Re 3.04, Re–C 2.01 and C–O 1.16 Å. Equatorial CO groups of neighbouring rhenium atoms are found to be in an eclipsed conformation.

Only dimanganese decacarbonyl has been studied in detail[1-4] of the series of binuclear carbonyls of the Group VII metals of the type $M_2(CO)_{10}$. A complete X-ray investigation has been undertaken[5] for $Tc_2(CO)_{10}$, but for the $Re_2(CO)_{10}$ molecule only the Re–Re bond length has been established[2]. Because the metal–metal bond energies in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ differ considerably (0.96 and 2.22 eV respectively), it seemed desirable to determine the complete structure of dirhenium decacarbonyl.

Dirhenium decacarbonyl has been prepared by the reaction of $KReO_4$ with carbon monoxide at 270 atm and 270° in an autoclave fitted with a copper piston. The product was purified by repeated crystallization from benzene followed by sublimation *in vacuo*.

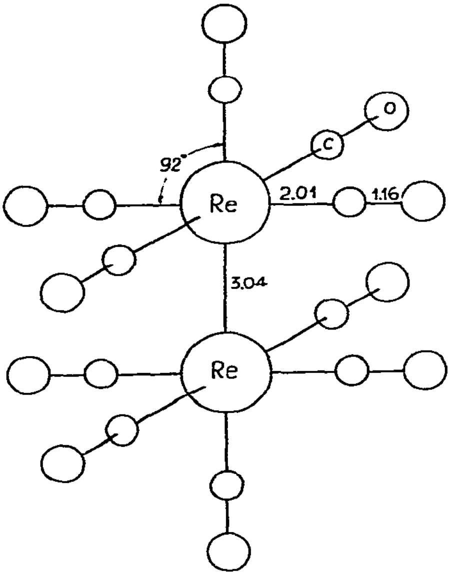
Electron diffraction patterns were recorded using an EG-100M electronograph with an r^3-sector. The nozzle-to-plate distances were ca. 400 and 200 mm, and an accelerating potential of 40 kV was used. The modified molecular intensity function $sM(s)$, calculated in the usual way[7], covers the s range from 1.3 to 27.6 $Å^{-1}$.

A choice of a preliminary model was made on the basis of an analysis of the radial distribution function. It was assumed that the $Re_2(CO)_{10}$ molecule is approximately isostructural with that of $Mn_2(CO)_{10}$, and has D_{4d} symmetry. In addition, the possibility of rotation of the $Re(CO)_5$ groups about the Re–Re bond leading to D_{4h} symmetry was also taken into account. The structure was refined by a least-squares procedure using a version of the stage-by-stage parameter refinement applied to the molecular intensity function[8]. To achieve this refinement, non-nuclear scattering was taken into account in the program for the calculation of the theoretical $sM(s)$ curve[9]. Hartree–Fock potentials[10] for the C and O atoms and Thomas–Fermi–Dirac potentials[11] for the Re atom were used. The final value of discrepancy index is

$$R = \sqrt{\frac{\Sigma\,[sM(s)_{\text{exp}} - k \cdot sM(s)_{\text{theor}}]^2}{\Sigma\,[sM(s)_{\text{exp}}]^2}} = 11.8\%$$

RESULTS AND DISCUSSION

The molecular geometry of $Re_2(CO)_{10}$ is presented in Fig. 1. The data obtained show that the molecule consists of two $Re(CO)_5$ fragments with a Re–Re bond length of 3.04 Å (in crystals 3.02 Å)[2]. In contrast to the analogous manganese and technetium carbonyls the equatorial carbonyl groups in $Re_2(CO)_{10}$ are in an eclipsed configuration (D_{4h} symmetry).



The Re atom exists in a slightly distorted octahedral configuration with the C_{axial}–Re–$C_{equatorial}$ angle equal to 88°. The mean Re–C bond length of 2.01 Å is the same for the axial and equatorial positions. The mean C–O distance is 1.16 Å.

REFERENCES

1 L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, 16 (1963) 419.
2 L. F. Dahl, E. Ishishi and R. E. Rundle, *J. Chem. Phys.*, 26 (1957) 1750.
3 N. I. Gapotchenko, N. V. Alekseev, K. N. Anisimov, N. E. Kolobova and I. A. Ronova, *Zh. Strukt. Khim.*, 9 (1968) 392.
4 A. Almenningen, G. G. Jacobsen and H. M. Seip, *Acta Chem. Scand.*, 23 (1969) 865.
5 M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 4 (1965) 1140.
6 H. J. Svec and G. Junk, *J. Amer. Chem. Soc.*, 89 (1967) 2836.
7 E. N. Vedeneev, *Programme of computing treatment of results of electronographic investigations. Complex EKRAFON.* Computing Centre of Moscow State University, Moscow, 1969.
8 N. I. Gapotchenko and N. V. Alekseev, *Zh. Strukt. Khim.*, 12 (1971) 530.
9 N. I. Gapotchenko, N. V. Alekseev and I. A. Ronova, *Zh. Strukt. Khim.*, 11 (1970) 131.
10 T. G. Strand and R. A. Bonham, *J. Chem. Phys.*, 40 (1964) 1676.
11 R. A. Bonham and T. G. Strand, *J. Chem. Phys.*, 39 (1963) 2200.