The Structure of Organothio-metal Tricarbonyl Tetramers: *X*-Ray Analysis of $[Re(CO)_3SMe]_4$

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Summary The structure of the tetrameric $[Re(CO)_3SMe]_4$ has been established by *X*-ray crystallographic analysis.

ORGANOTHIO-TRICARBONYLS of manganese and rhenium, $[M(CO)_3SR]_4$, have resulted[1-6] from several reactions involving the metal pentacarbonyl halide and the organothio-derivatives RSH,[2,6] $RSSnMe_3$,[1] $RSSiMe_3$,[3] RSCN,[4] and $RSCH_2SnMe_3$.[5] The last two routes are somewhat surprising and indicate that there is a considerable driving force to form these very stable compounds.

The compounds, which at first were considered[1,2] to be trimers, $[M(CO)_3SR]_3$, with D_{3h} symmetry, have now been shown to be tetrameric.[4,6] However there has been some controversy regarding the nature of this tetrameric structure (*cf.* ref. 7 Figures I—III). Although mass spectroscopic evidence seemed to favour a distorted tetrahedral structure with metal–metal bonds and the thio-groups bridging the edges of the tetrahedron,[6] the full-range i.r. and Raman spectra[7,8] indicated a T_d structure which requires no metal–metal bonds and the sulphur atoms lying off the centres of the four triangular faces. It has also been shown[7] that the structures in the solid state and in solution are the same. Furthermore, the electronic spectra of the $[M(CO)_3SR]_4$ complexes do not reveal the outstandingly intense bands at low energy present in the spectra of metal carbonyl clusters with metal–metal bonds. In the latter types the transitions producing these bands are assigned as $\sigma \rightarrow \sigma^*$, involving electrons in the metal–metal bonds.[9] In fact, the tetramers have very similar electronic spectra to the corresponding dimers, $[M(CO)_4SR]_2$, which have no metal–metal bonds.

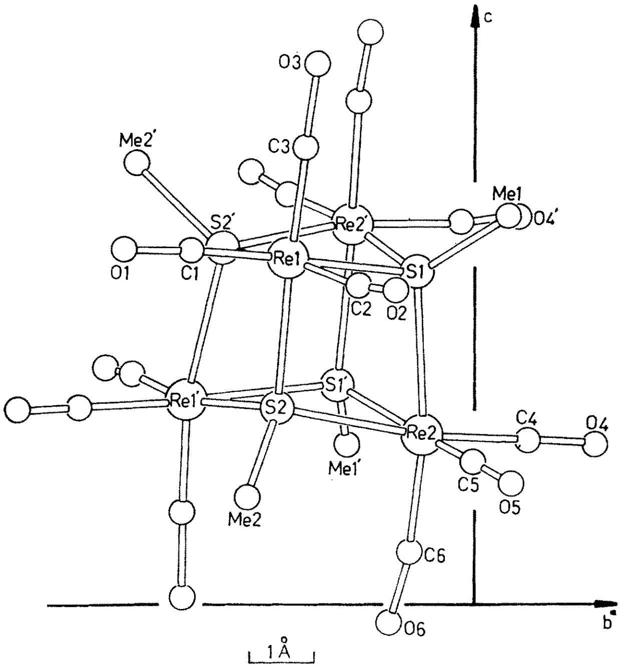

FIGURE. *View of the* $[Re(CO)_3SMe]_4$ *molecule down the* a-*axis*

We have now carried out a determination of the solid-state molecular structure of one of these species by *X*-ray diffraction techniques to provide definitive information on the structure.

Crystals of $[Re(CO)_3SCH_3]_4$ are trigonal, $a = 10·07(1)$, $c = 25·92(2)$ Å, $Z = 3$, space group $P3_121(D_3^4)$. The structure was determined with Mo-K_α diffractometer data from Patterson and Fourier syntheses; full-matrix least-squares refinement reduced R to 0·046 for 817 observed reflexions. The rhenium and sulphur atoms were given anisotropic thermal parameters, and the carbon and oxygen atoms isotropic thermal parameters. Interatomic distances and angles are summarized in the Table, and a view of the molecule is shown in the Figure.

The molecule lies on a crystallographic two-fold axis. Examination of the Figure indicates that the structure is almost a regular tetrahedron with each sulphur atom equidistant from the three nearest rhenium atoms and the C–S bonds normal to the triangular planes of the tetrahedron within experimental error. Probably the most significant features of the structure, which confirm the conclusions of spectroscopic studies, are the Re–S distances, which are all equivalent [2·49—2·53(1) Å], and the Re · · · Re distances. The latter are very long [3·854—3·957(3) Å] compared to the Re–Re distances [3·02 Å] in $Re_2(CO)_{10}$[10] and [2·956—3·024 Å] in the $Re_4(CO)_{16}^{2-}$ ion,[11] and even long compared to the distance [3·392 Å] in $HRe_2Mn(CO)_{14}$,[12] which is believed to have a hydrogen atom between the two Re atoms. This confirms the absence of any formal direct metal–metal bonds of the type found in $Re_2(CO)_{10}$ or $Re_4(CO)_{16}^{2-}$. Any interaction between the rhenium atoms must be through the triply-bridging sulphur atoms. While the four Re · · · Re distances appear to be different, there is no reason to believe that these differences are chemically significant. This anomaly had previously been observed in the $Re_4(CO)_{16}{}^{2-}$ ion.[11]

Interatomic distances (*Å*) *and angles* (*degrees*)

		Mean
Re(1) · · · Re(1')	3·909(3)	
Re(1) · · · Re(2)	3·873(2)	
Re(1) · · · Re(2')	3·854(2)	
Re(2) · · · Re(2')	3·957(3)	
Re–S	2·49—2·53(1)	2·51
$S–CH_3$	1·78, 1·81(5)	1·80
Re–C	1·85—1·93(4)	1·88
C–O	1·10—1·25(5)	1·20
Re · · · Re · · · Re	58·96—61·61(5)	60·0
Re–C–O	172—178(4)	176
C–Re–C	85—93(2)	90
S–Re–S	75·3—77·9(3)	76·9
S–Re–C(*trans*)	169—175(2)	171
S–Re–C(*cis*)	94—100(2)	96
Re–S–Re	100·2—103·9(4)	101·6
$Re–S–CH_3$	111—121(2)	116

This is the first report of the sulphur atom of an organothio-group being symmetrically bound to three like metal atoms and having no non-bonding electrons. The use of all possible valence electrons of the sulphur atom for bonding has previously been observed,[13–16] and in two compounds $Co_5(CO)_{10}(SC_2H_5)_5$[13] and $SCo_6(CO)_{11}(SC_2H_5)_4$,[14] the organothio sulphur atoms are equidistant from three metal atoms. However in these complexes two of the Co–S(triply bridged)–Co angles are *ca.* 120° and the third is only *ca* 60°. In the present case, the Re–S–Re angles are almost equal and just less than the tetrahedral angle. The C(methyl)–S–Re angles are of the same order of magnitude greater than 109°. The sulphur atom is therefore slightly further from the triangular face of rhenium atoms than the ideal tetrahedral co-ordination position. However, these sulphur atoms are probably nearer to being tetrahedrally bonded and sp^3-hybridised than any others which have been observed. The much more acute metal–S–metal angle found in doubly-bridged species, and in the other triply-bridged species discussed above, is almost certainly caused by the metal–metal bond shortening the distance between the metal atoms, compared to the present triply-bridged species. The rhenium atoms are six-co-ordinate and the local symmetry around each of them is C_{3v}. The bonding of each with its nearest neighbours will be similar to that in any mononuclear *cis*-$M(CO)_3L_3$ complex. This conclusion has been tentatively suggested by Braterman,[8] based on the results of an approximate force constant calculation. As a consequence of this comparison, it would be predicted that the CO groups of $[M(CO)_3SR]_4$ would be difficult to substitute with Lewis bases.

Finally it should be noted that the supposedly analogous diphenylphosphino-complexes $[M(CO)_3PPh_2]_n$, M = Mn, Re,[17] cannot now have a similar structure to the $[M(CO)_3SR]_n$ complexes and it seems more likely that these are, as postulated, trimeric. Further structural work is necessary to establish this.

Note added in proof. The crystal structure of $Os_4O_4(CO)_{12}$ has just been reported (*Chem. Comm.*, 1970, 1169). It has the same type of structure with the four metal atoms held together by triply bridging oxygen atoms. Further, the independent, Os–Os distances differ, yet as with the Re—Re distances in the present structure, there is no reason to believe they are chemically different.

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