Crystal and Molecular Structure of Tetrakis(tricarbonyl-μ_3-methanethiolato-rhenium)

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Crystals of the title compound are trigonal, a = 10·07(1), c = 25·92(2) Å, Z = 3, space-group $P3_121$. The structure was determined by Patterson and Fourier syntheses and refined by full-matrix least squares calculations to R 0·054 for 812 observed reflexions. The molecule lies on a crystallographic two-fold axis. The structure is an almost regular tetrahedron of rhenium atoms, with each sulphur atom equidistant from the three nearest rhenium atoms and the C–S bonds normal to the triangular planes of the tetrahedron. The Re–S distances are all equivalent [2·48—2·52(1) Å]. The very long Re · · · Re distances [3·853—3·957(3) Å] confirm the absence of any formal direct metal–metal bonds and any interaction between the rhenium atoms must be through the triply bridging sulphur atoms. Each sulphur atom is symmetrically bound to three rhenium atoms, the Re–S–Re angles being almost equal and just less than the tetrahedral angle.

THE very stable organothiolato-tricarbonyls of manganese and rhenium, $[M(CO)_3(SR)]_4$, have been prepared [1-6] from several reactions involving the halogeno(pentacarbonyl)metal compound and various organothiolato-derivatives.

These compounds have been shown to be tetrameric,[4,6] although there has been some controversy regarding the nature of this tetrameric structure (*cf.* ref. 7, Figures I—III). Mass spectroscopic data [6] indicated a distorted tetrahedral structure with metal–metal bonds and the thio-groups bridging the edges of the tetrahedron, but the full-range i.r. and Raman spectra [7,8] favoured a T_d structure with no metal–metal bonds and the sulphur atoms lying off the centres of the four triangular faces. Further support for the latter structure has been found in the electronic spectra of the $[M(CO)_3(SR)]_4$ complexes, since they do not show the very intense bands at low energy which are present in the spectra of metal carbonyl clusters with metal–metal bonds. The tetramers have very similar electronic spectra to the corresponding dimers, $[M(CO)_4(SR)]_2$, which have no metal–metal bonds. Furthermore, it has been shown [7] that the structures in the solid state and in solution are the same. The structure of one of these species, $[Re(CO)_3(SMe)]_4$ was discussed briefly,[9] and a detailed description of the structure analysis is now given.

EXPERIMENTAL

Crystals of $[Re(CO)_3(SMe)]_4$ from chloroform–hexane are pale yellow, with no well developed, simple faces. The space-group and initial unit-cell parameters were determined from Weissenberg and precession photographs, accurate unit-cell parameters being obtained later by a least-squares treatment of 20 $\sin^2\theta$ (hkl) values measured on a General Electric XRD 6 diffractometer.

Crystal Data.—$C_{16}H_{12}O_{12}Re_4S_4$, M = 1269·4, Trigonal, a = 10·07(1), c = 25·92(2) Å, U = 2276·21 Å^3, D_m = 2·80 (by flotation), Z = 3, D_c = 2·78. For Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 172 cm^{-1}. Space-group $P3_121$ (D_3^4) from absent spectra: $00l$, $l \neq 3n$.

Intensity data were collected on a Datex-automated General Electric XRD 6 diffractometer using a θ—2θ scan at 2° min^{-1} in 2θ. All reflexions with 2θ(Mo-K_α) $\leqslant$ 45° were measured. Of the 1188 independent reflexions, 371 had intensities $<3\sigma(I)$ above background, where $\sigma(I)$ is defined by: $\sigma^2(I) = S + B + (0{\cdot}05\ S)^2$, and S = scan count, B = background. These reflexions were classified as unobserved. A check scaling reflexion was monitored every 30 reflexions; its intensity had fallen off by 10% of its starting value at the end of the data collection. Lorentz and polarization corrections were applied and the structure amplitudes were derived; no corrections were made for absorption (crystal dimensions: 0·20 × 0·20 × 0·25 mm).

Structure Determination and Refinement.—The positions of the two rhenium atoms in the asymmetric unit were determined from a three-dimensional, unsharpened Patterson synthesis. Two cycles of full-matrix least-squares refinement of these positions and a scale-factor (with constant isotropic B of 3·0 Å^2), gave R 0·22. A subsequent three-dimensional Fourier summation based on these positions revealed all remaining atoms, excluding the methyl hydrogens. Refinement proceeded with full-matrix least-squares calculations, finally with the rhenium and sulphur atoms having anisotropic temperature factors, the parameters refined being β_{ij} in the equation: $f = f^\circ \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{33}kl)$ where f° is the tabulated [10] scattering factor and f is the value corrected for thermal motion. Five reflexions, thought to be suffering from extinction errors (011, 013, 104, 025, and 106) were given zero weight in the final cycles of refinement. A weighting scheme of the form: $w = 1/\sigma^2(F_o)$ was used throughout, and its usefulness confirmed from an analysis of $w(|F_o| - |F_c|)^2$, average values of which over ranges of $|F_o|$ were approximately constant. The unobserved reflexions were given zero weight. Convergence was reached at R 0·054 for the 812 reflexions included in the refinement, the maximum parameter shift in the final cycle being 0·5σ. The final positional and thermal parameters

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are given in Table 1. Measured and calculated structure-factors are listed in Supplementary Publication No. SUP 20333 (4 pp., 1 microfiche).*

TABLE 1

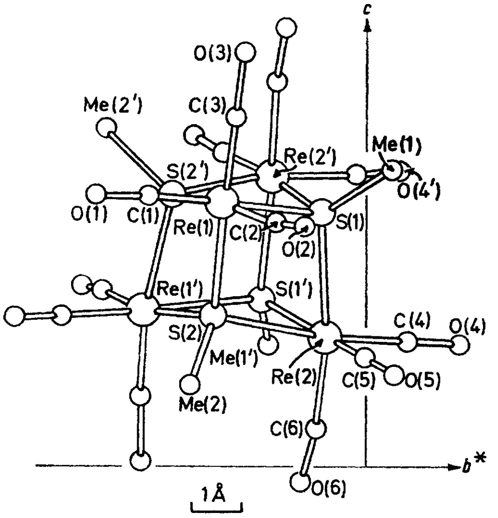
Final positional parameters (fractional) and thermal parameters (B and $10^4\beta_{ij}$), with standard deviations in parentheses

Atom	x	y	z	B/Å^2
Re(1)	0·1858(2)	−0·3256(2)	0·2088(1)	
Re(2)	0·1251(2)	−0·0898(2)	0·1031(1)	
S(1)	0·1452(9)	−0·1007(9)	0·1997(4)	
S(2)	0·0996(11)	−0·3492(10)	0·1181(5)	
O(1)	0·1947(39)	−0·6209(42)	0·2138(16)	6·13(92)
O(2)	0·5246(45)	−0·1378(43)	0·1879(17)	6·87(92)
O(3)	0·2430(38)	−0·2798(39)	0·3287(16)	6·20(83)
O(4)	0·1266(37)	0·2126(40)	0·1008(14)	5·27(77)
O(5)	0·4655(44)	0·0719(47)	0·0721(17)	7·27(92)
O(6)	0·0497(35)	−0·1389(37)	−0·0123(15)	5·58(76)
C(1)	0·2033(51)	−0·5015(57)	0·2140(21)	4·30(103)
C(2)	0·4021(55)	−0·2067(55)	0·1951(20)	4·64(99)
C(3)	0·2183(56)	−0·3055(57)	0·2792(22)	5·72(113)
C(4)	0·1318(45)	0·0993(42)	0·1044(17)	2·91(81)
C(5)	0·3287(55)	0·0041(58)	0·0869(21)	5·45(103)
C(6)	0·0900(42)	−0·1168(44)	0·0318(17)	2·93(74)
C(Me1)	0·2853(45)	0·0598(44)	0·2350(16)	3·18(81)
C(Me2)	0·1883(48)	−0·4066(52)	0·0666(19)	4·31(99)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	69(2)	86(2)	12(0)	50(2)	−1(1)	4(1)
Re(2)	64(2)	57(2)	10(0)	23(2)	0(1)	2(1)
S(1)	59(11)	41(11)	11(2)	25(9)	3(4)	−4(4)
S(2)	99(14)	59(12)	16(2)	29(11)	8(5)	−3(4)

DISCUSSION

The Figure shows the molecule of [Re(CO)$_3$(SMe)]$_4$ viewed down a. Bond lengths and angles with their standard deviations are listed in Table 2.



View of molecule down a

The molecules lie on crystallographic two-fold axes at positions (x, 0, 5/6), (0, x, 1/6), ($\bar{x}$, $\bar{x}$, 1/2). The structure is an almost regular tetrahedron of rhenium atoms with each sulphur atom equidistant from the three nearest rhenium atoms and the C(Me)–S bonds normal to the triangular planes of the tetrahedron, within experimental error. This structural arrangement is very similar to that found for [Et$_3$AsCuI]$_4$,[11] Os$_4$O$_4$(CO)$_{12}$,[12] [Mo(OH)(CO)$_2$NO]$_4$,4[OPPh$_3$],[13] [ZnO(OMe)]$_4$,[14] and related compounds.[15] In all these structures the metal atoms are at the corners of a fairly regular tetrahedron with metal–metal separations being long enough to rule out the possibility of any formal direct metal–metal bonding. In this study, the Re · · · Re separations are very long, 3·853—3·957(3) Å, compared to the Re–Re distances

TABLE 2

Interatomic distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

Re(1)–S(1)	2·51(1)	Re(2)–C(5)	1·83(5)
Re(1)–S(2)	2·48(1)	Re(2)–C(6)	1·88(4)
Re(1)–S(2′)	2·50(1)	S(1)–C(Me1)	1·78(4)
Re(2)–S(1)	2·52(1)	S(2)–C(Me2)	1·85(5)
Re(2)–S(2)	2·52(1)	C(1)–O(1)	1·16(5)
Re(2)–S(1′)	2·50(1)	C(2)–O(2)	1·09(5)
Re(1)–C(1)	1·87(5)	C(3)–O(3)	1·31(6)
Re(1)–C(2)	1·92(5)	C(4)–O(4)	1·17(4)
Re(1)–C(3)	1·85(6)	C(5)–O(5)	1·25(5)
Re(2)–C(4)	1·87(5)	C(6)–O(6)	1·20(5)

(*b*) Non-bonded distances

Re(1) · · · Re(1′)	3·909(3)	Re(1) · · · Re(2′)	3·853(2)
Re(1) · · · Re(2)	3·872(2)	Re(2) · · · Re(2′)	3·957(3)

(*c*) Angles

S(1)–Re(1)–S(2)	77·9(3)	S(2)–Re(2)–C(5)	94·5(1·6)
S(1)–Re(1)–S(2′)	77·8(3)	S(1′)–Re(2)–C(6)	98·9(1·1)
S(2)–Re(1)–S(2′)	75·8(4)	S(2)–Re(2)–C(6)	95·1(1·2)
S(1)–Re(1)–C(1)	176·3(1·4)	C(4)–Re(2)–C(5)	91·0(2·0)
S(2′)–Re(1)–C(2)	169·7(1·5)	C(4)–Re(2)–C(6)	94·2(1·8)
S(2)–Re(1)–C(3)	169·4(1·6)	C(5)–Re(2)–C(6)	86·0(2·0)
S(2)–Re(1)–C(1)	100·0(1·6)	Re(1)–S(1)–Re(2)	100·7(3)
S(2′)–Re(1)–C(1)	98·9(1·4)	Re(1)–S(1)–Re(2′)	100·8(3)
S(1)–Re(1)–C(2)	93·8(1·5)	Re(2)–S(1)–Re(2′)	104·1(3)
S(2)–Re(1)–C(2)	96·8(1·6)	Re(1)–S(1)–C(Me1)	111·1(1·2)
S(1)–Re(1)–C(3)	95·4(1·6)	Re(2)–S(1)–C(Me1)	121·1(1·4)
S(2′)–Re(1)–C(3)	94·9(1·5)	Re(2′)–S(1)–C(Me1)	116·2(1·3)
C(1)–Re(1)–C(2)	89·4(2·0)	Re(1)–S(2)–Re(1′)	103·4(4)
C(1)–Re(1)–C(3)	86·4(2·4)	Re(1)–S(2)–Re(2)	101·4(4)
C(2)–Re(1)–C(3)	91·8(2·2)	Re(1′)–S(2)–Re(2)	100·1(3)
S(1)–Re(2)–S(2)	76·7(3)	Re(1)–S(2)–C(Me2)	120·9(1·5)
S(1)–Re(2)–S(1′)	75·1(3)	Re(1′)–S(2)–C(Me2)	114·8(1·4)
S(2)–Re(2)–S(1′)	77·6(3)	Re(2)–S(2)–C(Me2)	113·3(1·5)
S(1)–Re(2)–C(6)	170·6(1·2)	Re(1)–C(1)–O(1)	171(4)
S(1′)–Re(2)–C(5)	170·9(1·6)	Re(1)–C(2)–O(2)	179(5)
S(2)–Re(2)–C(4)	169·5(1·3)	Re(1)–C(3)–O(3)	175(4)
S(1)–Re(2)–C(4)	93·6(1·3)	Re(2)–C(4)–O(4)	173(4)
S(1′)–Re(2)–C(4)	96·2(1·2)	Re(2)–C(5)–O(5)	175(5)
S(1)–Re(2)–C(5)	99·0(1·7)	Re(2)–C(6)–O(6)	172(3)

Re(1′) · · · Re(1) · · · Re(2)	59·36(4)
Re(1′) · · · Re(1) · · · Re(2′)	59·84(4)
Re(2) · · · Re(1) · · · Re(2′)	61·62(5)
Re(1) · · · Re(2) · · · Re(1′)	60·80(5)
Re(1) · · · Re(2) · · · Re(2′)	58·95(4)
Re(1′) · · · Re(2) · · · Re(2′)	59·42(4)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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of 3·02 Å in $Re_2(CO)_{10}$ [16] and of 2·956—3·024 Å in the $Re_4(CO)_{16}^{2-}$ ion,[17] and even long compared to the distance of 3·392 Å in $HRe_2Mn(CO)_{14}$,[18] which is believed to have a hydrogen atom between the two Re atoms. This confirms the absence of any formal direct metal–metal bond of the type found in $Re_2(CO)_{10}$ or $Re_4(CO)_{16}^{2-}$ and thus any interaction between the Re atoms must be through the triply bridging sulphur atoms. The four Re · · · Re distances are highly significantly different (30σ in the extremities of the range), but there seems to be no chemical reason for this. It might arise if the three Re–S bonds were not equivalent, but there is no suggestion from the values obtained [2·48—2·52(1) Å] that this is so. The difference may be a result of omission of corrections for absorption and anomalous dispersion, or due to crystal packing effects, although there does not seem to be any unusually short intermolecular contact. A similar situation is found in $Os_4O_4(CO)_{12}$ in which the Os · · · Os distances of 3·253(4) and 3·190(4) are significantly different (15σ). Again the Os–O distances are equivalent and the difference has been attributed to crystal packing. This anomaly had also been previously observed in the $Re_4(CO)_{16}^{2-}$ ion.

This seems to be the first structure in which the sulphur atom of an organothiolato-group is symmetrically bound to three like metal atoms and has no non-bonding electrons. The Re–S distances [2·48—2·52(1) Å] agree fairly well with the value predicted (2·55 Å) from the sum of the covalent radii of 1·51 [19] for rhenium and 1·04 [20] for sulphur. The only other report of a Re–S bond distance appears to be the mean value of 2·325(1) Å found in $Re(S_2C_2Ph_2)_3$.[21] The use of all possible valence electrons of the sulphur atom for bonding has previously been observed,[22-25] and in two compounds, $Co_5(CO)_{10}(SEt)_5$ [22] and $SCo_6(CO)_{11}(SEt)_4$,[23] the organothiolatosulphur atoms are equidistant from three metal atoms. However in these complexes two of the Co–S(μ_3)–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(Me)–S–Re angles are conversely slightly greater than tetrahedral. The sulphur atom is therefore slightly further from the triangular face of rhenium atoms than the ideal tetrahedral co-ordination position. Nevertheless, these sulphur atoms are probably nearer to being tetrahedrally bonded and sp^3 hybridized than any others which have been observed. The much more acute metal–sulphur–metal angle found in doubly bridged species, and in the other triply bridged species discussed, is almost certainly caused by the metal–metal bond shortening the distance between the metal atoms, compared to the situation in the present triply bridged species. The rhenium atoms are octahedrally co-ordinated 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. The Re–C distances [1·83—1·92(5), mean 1·87(5) Å] agree well with the values found in $HRe_2Mn(CO)_{11}$ [18] [1·82—2·05, mean 1·95(3) Å] and $[Bu^n_4N]_2[Re_4(CO)_{16}]$ [17] [1·86—1·96, mean 1·91(4) Å]. The Re–C–O angles range from 171—179(4)° indicating no significant deviation from linearity, although significant deviations have often been found in such complexes and can be rationalized in terms of simple MO considerations.[26,27]

The C–O distances [1·09—1·31(5) Å] and C(Me)–S distances [1·78 and 1·85(4) Å] are in good agreement with the generally accepted values.

The closest intermolecular approaches are 3·13 for C · · · O contacts, 3·14 for O · · · O contacts, and 3·71 Å for C · · · C contacts, which indicate that the intermolecular forces are of the van der Waals type.

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