Crystal and Molecular Structure of Bis(tetraethylammonium) 1,2;2,3;3,1-Tri-μ-hydrido-μ_3-oxo-1,1,1,2,2,2,3,3,3-enneacarbonyl-*triangulo*-trirhenate(2—)

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The title compound, $[NEt_4]_2[Re_3H_3O(CO)_9]$, crystallizes in the orthorhombic space group *Pnma* with cell constants a = 15.05(2), b = 12.32(1), c = 18.35(2) Å, Z = 4. The structure has been determined by vector methods from single-crystal *X*-ray counter data and refined by block-diagonal least squares to a conventional R value of 0.032 for 1 147 independent reflections. The anion contains an equilateral triangle of metal atoms (mean Re–Re 2.968 Å) capped by a symmetric triply bridging oxo-ligand (mean Re–O 2.12 Å). The carbonyl groups are all terminally bonded, three for each rhenium atom (mean Re–C and C–O 1.88 and 1.18 Å). The overall idealized anion symmetry is C_{3v}. The carbonyl disposition implies that the three hydrido-ligands lie in bridging positions on the Re_3 triangular edges.

UNTIL 1975 the known polynuclear carbonylhydridorhenium compounds with direct metal–metal bonds and more than two rhenium atoms were $[Re_3H_{3-x}(CO)_{12}]^{x-}$ (x = 0,[1] 1,[2] or 2 [3]), $[Re_4H_6(CO)_{12}]^{2-}$,[4] $[Re_3H(CO)_{14}]$,[5] and $[Re_4H_4(CO)_{12}]$.[6] In that year we began, in collaboration with Freni and her co-workers, to study the products of the reaction of $[Re_2(CO)_{10}]$ with alcoholic K[OH] solutions. New polynuclear carbonylhydrido-species, besides the already known $[Re_4H_6(CO)_{12}]^{2-}$, are obtainable in this way. The first to be fully characterized was $[Re_4H_4(CO)_{15}]^{2-}$, containing an unusual tetrametal array.[7,8] It reacts in boiling ethanol to give species such as $[Re_3H_3(CO)_{10}]^{2-}$ (an unsaturated anion),[9] $[Re_3H_3O(CO)_9]^{2-}$,[9] $[Re_4H_4(CO)_{13}]^{2-}$,[10] and other unidentified derivatives.

In this paper we report the complete results of the *X*-ray analysis on $[NEt_4][Re_3H_3O(CO)_9]$. A preliminary account has already appeared.[9] The structure determination shows the presence and bonding of the oxo-ligand and allows an indirect location of the hydrido-ligands in bridging positions. The nature of the hydrido-ligands was, in fact, uncertain since they give an n.m.r. signal (τ 22.8) which is intermediate between the values usually found for terminal and for bridging hydrides.

EXPERIMENTAL

Crystal Data.—$C_{25}H_{43}N_2O_{10}Re_3$, M = 1 090, Orthorhombic, a = 15.05(2), b = 12.32(1), c = 18.35(2) Å, U = 3 402.4 Å^3, D_m = 2.16(2), Z = 4, D_c = 2.13 g cm^{-3}, $F(000)$ = 2 048. From systematic absences, two space groups were possible, $Pn2_1a$ [non-standard setting for $Pna2_1$ (no. 33)] or *Pnma* (no. 62). Mo-K_α radiation (λ 0.710 7 Å), μ(Mo-K_α) = 113.3 cm^{-1}.

Intensity Measurements.—The crystal sample was an elongated prism of dimensions 0.25 × 0.31 × 0.86 mm. The intensity data were measured on a PAILRED diffractometer with Mo-K_α graphite-monochromatized radiation, by the ω-scan method for $2\theta \leqslant 42°$. The total number of reflections collected was 3 999. Three reflections were remeasured at regular intervals showing a total decay of *ca.* 15% at the end of the data collection. The integrated intensities were corrected for Lorentz, polarization, and decay effects. The absorption correction was computed using the method of refs. 11 and 12, the transmission factors being very small and ranging from 0.08 to 0.14. After removing all data having $\sigma(I)/I > 0.25$, a set of 2 199 reflections was obtained, the number of independent reflections being 1 147.

Structure Solution and Refinement.—The structure solution was based on a three-dimensional Patterson map which revealed the metal-atom positions. Assuming the centrosymmetric *Pnma* space group, the Re_3 triangle was found in a special position on the symmetry plane at $y = \frac{1}{4}$, with Re(1) lying on the plane and the other two rhenium atoms being on opposite sides of the plane. After a preliminary refinement of the metal atoms, a successive difference-Fourier synthesis revealed the remaining non-hydrogen-atom positions. Since all the carbonyl groups conformed to the C_s symmetry required by the space group *Pnma* we continued the refinement in this group. The two $[NEt_4]^+$ cations were also found in special positions on mirror planes, resulting in disorder; in both cases the nitrogen atom and one external carbon atom lie on the plane and in the cation containing N(1) two external carbon atoms are correlated by the mirror plane.

The refinement was carried out by the least-squares method in the block-diagonal approximation. The central NC_4 moieties of the cations were treated as rigid groups (tetrahedral geometry, N–C 1.52 Å). Anisotropic thermal factors were assigned to the rhenium atoms only. The

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resulting reliability indices were R 0.038 and R' 0.053, where $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$.

The disorder of the cations gave rather scattered C–C bond distances. At this stage we tried to remove this disorder by assuming the non-centrosymmetric space group $Pn2_1a$. All the possible cases were attempted, taking into account also the effects of the anomalous dispersion (for Re). The best results gave reliability indices R 0.036 and R' 0.050. The decrease is significant at a >0.005 confidence level.[13] However, the parameters of the anionic atoms widely oscillated in the non-centrosymmetric refinements because of correlation, so that, as previously suggested in similar cases (see ref. 14 and refs. therein), it was decided to accept the centrosymmetric *Pnma* space group, considering that the reported errors may be optimistic.[14]

In the final refinement all the anionic atoms were treated anisotropically. The observations were weighted according to the formula $w = 1/(A + BF_o + CF_o^2)$ where, in the final cycles, A, B, and C had values 48.5, −0.52, and 0.0023 respectively and were chosen on the basis of an analysis of $\Sigma w(F_o - k|F_c|)^2$. Atomic scattering factors were taken from ref. 15 for all the atoms, those for rhenium being corrected for the effects of anomalous dispersion.[16] The final values of the reliability indices were R 0.032 and R' 0.039. The final difference-Fourier synthesis was flat except for some residual peaks not exceeding 0.9 eÅ^{-3} near to the metal atoms. No direct evidence of the presence of the hydrogen atoms was found.

TABLE 1

Final positional parameters (× 10^4, Re × 10^5)

Atom	*x*	*y*	*z*
Re(1)	17 302(7)	25 000	−8 694(6)
Re(2)	25 899(4)	12 936(6)	3 363(4)
O	3 020(10)	2 500	−401(7)
C(1)	1 877(12)	1 395(17)	−1 574(10)
O(1)	1 948(10)	697(13)	−2 008(6)
C(2)	514(20)	2 500	−1 087(12)
O(2)	−278(15)	2 500	−1 146(11)
C(3)	2 840(11)	73(17)	−220(11)
O(3)	3 028(11)	−690(13)	−579(8)
C(4)	3 619(13)	1 084(16)	909(10)
O(4)	4 251(9)	949(14)	1 273(7)
C(5)	1 988(13)	405(17)	1 002(9)
O(5)	1 592(11)	−106(13)	1 423(7)
N(1)	4 726(9)	−2 500	1 332(7)
C(6)	3 809(13)	−2 004(22)	1 439(10)
C(7)	4 770(19)	−3 043(15)	589(9)
C(8)	5 427(17)	−1 613(17)	1 376(15)
C(9)	4 895(16)	−3 338(14)	1 923(10)
C(10)	3 012(21)	−2 767(31)	1 365(16)
C(11)	4 521(24)	−2 500	−59(19)
C(12)	5 639(19)	−1 079(28)	1 969(15)
N(2)	4 325(11)	2 500	3 494(9)
C(13)	3 702(19)	1 779(24)	3 057(15)
C(14)	4 804(23)	3 274(16)	2 982(14)
C(15)	5 002(20)	1 799(24)	3 889(17)
C(16)	3 789(19)	3 146(17)	4 046(15)
C(17)	2 974(28)	2 500	2 663(21)
C(18)	5 511(23)	2 845(31)	2 493(18)
C(19)	4 623(29)	648(43)	4 171(25)
C(20)	4 436(25)	3 871(37)	4 532(19)

The results of the refinement are reported in Table 1. The final list of observed and calculated structure factor moduli is given in Supplementary Publication No. SUP 22056 (7 pp.).* All the computations were carried out on a UNIVAC 1106 computer at the computing centre of Milan University, with local programs.

DISCUSSION

The structure consists of discrete $[Re_3H_3O(CO)_9]^{2-}$ anions and $[NEt_4]^+$ cations in the ratio 1 : 2. The packing down the *a* axis is shown in Figure 1. Both the disordered cations (see the Experimental section) have a ' nordic-cross ' conformation of approximate S_4 symmetry.

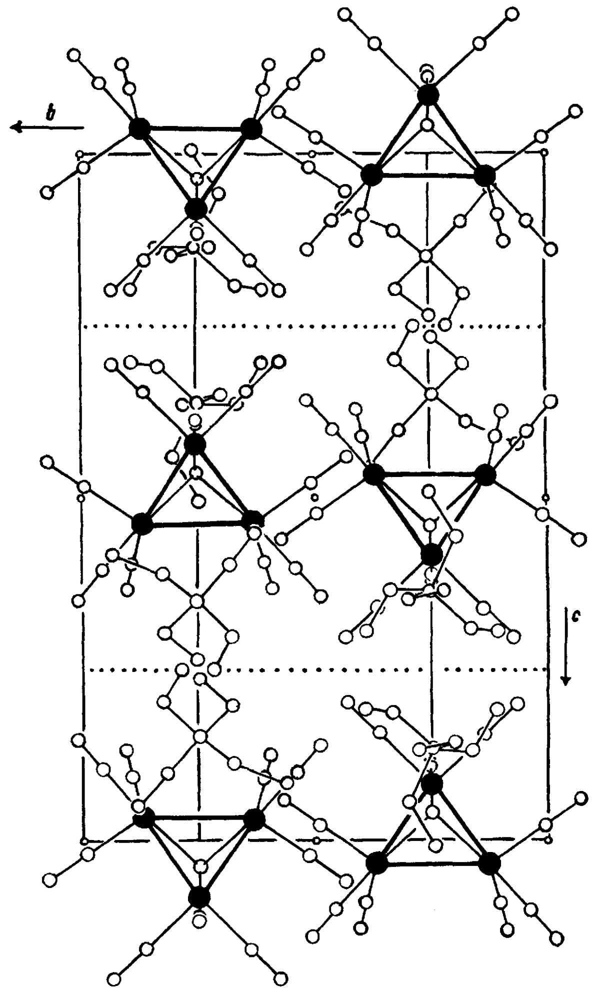

FIGURE 1 Projection of the structure of $[NEt_4]_2[Re_3H_3O(CO)_9]$ down the *a* axis. For clarity the images of the disordered cations are not shown

The structure of the anion is depicted in Figure 2. It lies on a crystallographic mirror plane passing through Re(1), O, and the middle of the Re(2)–Re(2') edge and contains a nearly equilateral metal-atom triangle capped by a triple bridging oxo-ligand. The nine CO groups are terminally bonded, each rhenium atom bearing one ' axial ' and two ' equatorial ' such ligands. The three

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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hydridic hydrogen atoms (not directly located) can be placed (see below) in bridging positions on the Re_3 triangular edges, by the side opposite from the μ_3-oxo-ligand, with Re–H bonds nearly *trans* to the equatorial CO groups, as shown in Figure 2. Ignoring the Re–Re bonds, the co-ordination around the metal atoms is approximately octahedral. The overall anion symmetry is C_s, but it can be well idealized as C_{3v}. The more interesting bond parameters are reported in Table 2. The anion, according to the effective atomic number rule, is a saturated triangular cluster possessing 48 valency electrons.

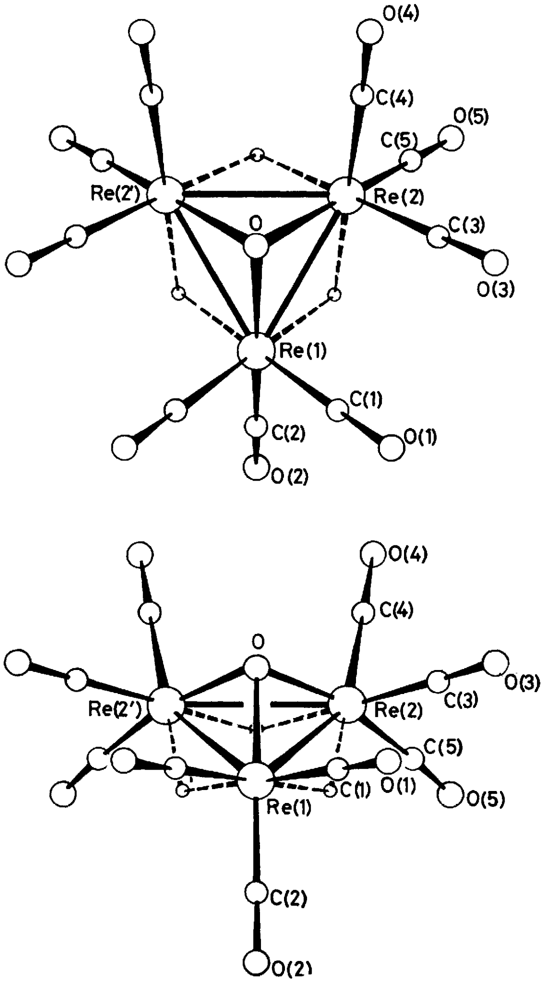

FIGURE 2 Two views of the anion $[Re_3H_3O(CO)_9]^{2-}$ with the postulated hydride atom positions

The Re–Re distances (mean 2.97 Å) have values typical for normal single bonds, similar to the values found for the unbridged metal–metal distances in $[Re_2(CO)_{10}]$ (3.02 Å),[17] $[Re_4(CO)_{16}]^{2-}$ (2.96—3.02 Å),[18] $[Re_3H_2(CO)_{12}]^-$ (3.03 Å),[2] and $[Re_3H(CO)_{12}]^{2-}$ (3.00 Å) The Re–C and C–O bond lengths (means 1.88 and 1.18 Å)[3] are comparable with the corresponding interactions in many rhenium compounds, in particular with the mean values in $[Re_4H_4(CO)_{15}]^{2-}$ [form (I), 1.91 and 1.16 Å; form (II), 1.88 and 1.20 Å] [8] and in $[Re_4(CO)_{16}]^{2-}$ (1.91 and 1.19 Å).[18] There is no significant difference between the axial and equatorial carbonyls.

TABLE 2

Bond distances and angles within the anion $[ReH_3O(CO)_9]^{2-}$

Distances (Å)			
Re(1)–Re(2)	2.963 (1)	Re(2)–C(4)	1.89(2)
Re(2)–Re(2′)	2.973 (1)	Re(2)–C(5)	1.87(2)
Re(1)–O	2.123 (15)	C(1)–O(1)	1.18(2)
Re(2)–O	2.112 (10)	C(2)–O(2)	1.20(4)
Re(1)–C(1)	1.89(2)	C(3)–O(3)	1.18(3)
Re(1)–C(2)	1.87(3)	C(4)–O(4)	1.17(2)
Re(2)–C(3)	1.86(2)	C(5)–O(5)	1.16(2)
Angles (°)			
Re(1)–Re(2)–Re(2′)	59.9(1)	O–Re(1)–C(1)	99.8(6)
Re(2)–Re(1)–Re(2′)	60.2(1)	O–Re(1)–C(2)	168.5(8)
Re(1)–Re(2)–O	45.8(4)	O–Re(2)–C(3)	98.9(7)
Re(2)–Re(1)–O	45.5(3)	O–Re(2)–C(4)	101.6(7)
Re(2′)–Re(2)–O	45.3(3)	O–Re(2)–C(5)	167.7(7)
Re(1)–O–Re(2)	88.8(5)	C(1)–Re(1)–C(1′)	92.1(8)
Re(2)–O–Re(2′)	89.4(5)	C(1)–Re(1)–C(2)	88.2(7)
Re(2)–Re(1)–C(1)	95.7(6)	C(3)–Re(2)–C(4)	91.7(8)
Re(2)–Re(1)–C(1′)	145.2(6)	C(3)–Re(2)–C(5)	89.1(9)
Re(2)–Re(1)–C(2)	125.9(5)	C(4)–Re(2)–C(5)	87.3(8)
Re(1)–Re(2)–C(3)	94.8(6)	Re(1)–C(1)–O(1)	178(2)
Re(1)–Re(2)–C(4)	147.3(6)	Re(1)–C(2)–O(2)	173(2)
Re(1)–Re(2)–C(5)	124.7(6)	Re(2)–C(3)–O(3)	178(2)
Re(2′)–Re(2)–C(4)	97.9(6)	Re(2)–C(4)–O(4)	179(2)
Re(2′)–Re(2)–C(3)	144.1(6)	Re(2)–C(5)–O(5)	177(2)
Re(2′)–Re(2)–C(5)	125.7(6)		

The oxo-ligand forms a symmetric triple bridge. μ_3-Oxo-groups are not unusual, *e.g.* in $[\{OsO(CO)_3\}_4]$ [19] and in $[Mo_4Cl_6O_6(OPr)_6]$,[20] but this seems to be only the second example of such a ligand in a triangular cluster, the first being $[Co_3O(\eta\text{-}C_5H_5)_3(CO)]$.[21] The mean Re–O distance (2.12 Å) compares well with other Re–O single bonds: Re–O(EtOH) (2.16 Å) in $[ReBr_4(NO)(HOEt)]^-$,[22] Re–O(carboxyl) (mean 2.09 Å) in $[Re_2Cl_5O(O_2CEt)(PPh_3)_2]$,[23] and Re–O(carboxyl) (mean 2.11 Å) in $[Re_2Cl_3O(O_2CEt)_2(PPh_3)_2]$.[24] It is longer, as expected, than the mean Re–O(double bridge) distances found in the above two Re_2 species (1.89 and 1.92 Å, respectively).

The anion geometry resembles that of the isoelectronic species $[Ru_3H_3(CMe)(CO)_9]$,[25] containing a μ_3-ethylidyne ligand. In that structure the hydrido-ligands were directly located in bridging positions analogous to those postulated here (Ru–H 1.812 Å, Ru–H–Ru 103°). The carbonyl disposition in these two hydridic species is very similar, but quite different from that found in the related non-hydridic compounds of formula $[M_3(CO)_9X]$ (X =

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triple-bridging ligand) (see Table 3). In particular the X–M–C_{ax} and M–M–C_{ax} angles are markedly larger in the former species, due to the steric repulsions of the hydridic atoms. Assuming average C_{3v} parameters for $[Re_3H_3O(CO)_9]^{2-}$ and locating the hydrido-ligands exactly *trans* to the equatorial carbonyl groups, the Re–H bond and the Re–H–Re angle may be estimated as *ca.* 1.80 Å and 111°. These values are reasonable and are comparable with similar parameters listed in ref. 25.

TABLE 3

Mean bond angles (°) in some $[M_3(CO)_9H_3(\mu_3\text{-}X)]$ and $[M_3(CO)_9(\mu_3\text{-}X)]$ cluster species

				M–M–C_{eq}			
Compound	X–M–C_{ax}	X–M–C_{eq}	M–M–C_{ax}	*cis*	*trans*	C_{eq}–M–C_{eq}	C_{ax}–M–C_{eq}
$[Re_3H_3O(CO)_9]^{2-}$ [a]	168	100	125	96	145	92	88
$[Ru_3H_3(CMe)(CO)_9]$ [b]	162	96	120	95	142	90	97
$[Co_3S(CO)_9]$ [c]	143	103	97	96	152	101	101
$[Co_2FeS(CO)_9]$ [d]	145	103	97	98	154	98	100
$[Co_3Se(CO)_9]$ [e]	146	102	96	97	153	100	100
$[Co_2FeSe(CO)_9]$ [e]	147	102	97	98	154	99	100
$[Co_2FeTe(CO)_9]$ [e]	149	100	96	97	154	99	99
$[Co_3(CMe)(CO)_9]$ [f]	142	103	99	97	151	97	102

[a] This work. [b] Ref. 25. [c] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229. [d] D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6027. [e] C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93** 6032. [f] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 261.

As noted above, the Re–Re bonds are normal and are not lengthened by the presence of the bridging hydrido-ligands. Lengthening is usually found in the presence of such ligands, the Re–Re bond lengths ranging from 3.14 Å in $[Re_3H(CO)_{12}]^{2-}$ (ref. 3) to 3.39 Å in $[MnRe_2H(CO)_{14}]$.[26] A different situation arises when another bridging ligand X is present for the same M–M bond. Normal metal–metal distances are also found in $[Ru_3H_3(CMe)(CO)_9]$ and in $[Os_3H(OMe)(CO)_{10}]$ (a species with an Os–Os bond doubly bridged by a hydrido- and a methoxo-ligand).[27] Thus the presence of X prevents the M–M bond lengthening, probably because this would imply too weak M–X bonds.*

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* *Note added in proof:* This effect, observed in other hydridic cluster compounds, has been recently discussed (M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843) in *reporting the structure of* $[Ru_3H(CNMe_2)(CO)_{10}]$.

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