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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE TETRAETHYLAMMONIUM SALT OF TETRAHYDRIDOPENTADECACARBONYLTETRARHENATE(2—) IN TWO CRYSTALLOGRAPHIC FORMS

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Summary

The structure of the title compound, $(NEt_4)_2[H_4Re_4(CO)_{15}]$, is reported in two crystallographic modifications, I and II. Both forms are monoclinic and the cell constants are as follows: I, *a* 11.355(2), *b* 21.204(4), *c* 17.416(3) Å, β 94.15(2)°, space group $P2_1/c$; II, *a* 21.831(4), *b* 17.584(3), *c* 11.446(2) Å, β 96.02(2)°, space group $P2_1/n$. Two sets of 3042 (I) and 2870 (II) independent diffraction intensities, collected by counter methods, were used for the solution and refinement of the two structures. The final conventional *R* factors have values 5.5% (I) and 6.3% (II), respectively. The crystal packings are compared, showing different conformations of the $(NEt_4)^+$ cations. The anions contain a tetrametal cluster formed by an isosceles triangle plus an apically bound metal atom; the carbonyl groups are all terminally bonded to the rhenium atoms. Some differences, present both in the metal atom clusters and in the carbonyl dispositions, are discussed and compared with a third, previously reported, crystallographic modification of the same compound.

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Introduction

The synthesis and brief description of the X-ray structure of the salt $(NEt_4)_2$-$[H_4Re_4(CO)_{15}]$, containing an unusual tetrametal cluster have been recently reported [1]. The anion exhibits in solution interesting fluxional behavior involving two of the hydridic hydrogens, which has been studied by analysis of the PMR spectra at different temperatures [2]. It possesses a high reactivity in boiling ethanol, giving rise to various hydridocarbonyl cluster anions such as $[H_3Re_3(CO)_{10}]^{2-}$, $[H_3Re_3(\mu_3\text{-}O)(CO)_9]^{2-}$ [3] and $[H_4Re_4(CO)_{13}]^{2-}$ [4].

Very recently, two new crystallographic modifications of the same substance have been obtained by recrystallization, both monoclinic (forms I and II). This gave the opportunity of studying the molecular structure of the cluster anion in different crystal environments. Furthermore, the structural data of the previously reported modification (form III) were of poor quality because of decomposition of the crystals upon X-ray irradiation [1]. For these reasons, and also in order to ascertain whether some chemical transformation occurred, we have carried out a complete structure analysis on the two new forms. In this paper the resulting structures, together with the previous one, are compared and discussed.

Experimental

The compound, $C_{31}H_{44}N_2O_{15}Re_4$, mol. wt. 1429.6, gives yellow monoclinic crystals; the crystal data of the three forms are reported in Table 1.

Intensity measurements

Intensity data of forms I and II were collected on a Philips PW1100 four-circle automatic diffractometer, using graphite monochromatized Mo-K_α radiation (λ 0.7107 Å), by the ω-scan method, within the limits $3° < \theta < 22°$. The crystal sample of form I was a multifaced polyhedron of dimensions 0.26 × 0.31 × 0.34 mm, while that of II was an elongated prism measuring 0.08 × 0.13 × 0.53 mm. Since the compound showed a marked decay upon X-ray irradiation [1] fast measurements were performed, with scan speeds of 0.1°/sec (I) and 0.15°/sec (II). The scan widths were 1° and 1.4°, respectively, and the total background

TABLE 1

CRYSTAL DATA FOR THE THREE FORMS OF $(NEt_4)_2[H_4Re_4(CO)_{15}]$

	I	II	III
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a	11.355(2)	21.831(4)	11.60(1)
b	21.204(4)	17.584(3)	20.68(2)
c	17.416(3)	11.446(2)	17.97(2)
β	94.15(2)	96.02(2)	95.90(10)
U	4182.3	4369.6	4287.9
D_m	2.23(2)	2.20(2)	2.20(2)
D_c	2.27	2.17	2.21
Z	4	4	4

counting times were equal to the peak scanning times. The total numbers of the collected reflections were 5161(I) and 5338(II). At the end of the data measurements the amounts of decay resulted to be 10% for I and 21% for II. The intensities were corrected for Lorentz, polarization, decay and absorption effects (μ(Mo-K_α) equal to 122.7 and 117.3 cm^{-1} for I and II, respectively). After rejection of all data having $\sigma(I)/I > 0.25$ two sets of 3042 (I) and 2870 (II) independent non-zero reflections were used in the solution and refinement of the structures.

Solution and refinement of the structures

The metal atom positions were obtained through Patterson function analysis. After preliminary refinements of the rhenium parameters successive difference-Fourier syntheses revealed all the non-hydrogen atom positions. The structures were refined by the least-squares method in the block-diagonal approximation. Anisotropic temperature factors were assigned to the rhenium atoms only. The contribution of the cationic hydrogen atoms was taken into account in the structure factors calculations (ideal tetrahedral geometry, C—H 1.08 Å, B equal to 8 Å^2).

The final values of the reliability indices R and R', $\{R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}\}$, were 0.055 and 0.078 (I) and 0.063 and 0.075 (II), respectively. The observations were weighted according to the formula $w = 1/(A + BF_o + CF_o^2)$; in the final cycles A, B and C had values 226.5, —2.4, 1.1×10^{-2} (I) and 70.0, 1.0, 3×10^{-3} (II), chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 5 for Re, O, N and C, and from ref. 6 for hydrogen. The rhenium factor was corrected both for the real and imaginary part of the anomalous dispersion [7]. The final difference-Fourier maps were rather flat except for some peaks up to ca. 2 e/Å^3 in the vicinity of the rhenium atoms.

The results of the refinements are reported in Table 2 for I and in Table 3 for II. Lists of observed and computed structure factors moduli and tables of coordinates for the cationic hydrogens can be obtained on application to the authors. All computations were performed on a UNIVAC 1106 computer.

Description of the structures and discussion

The crystal structures consist of discrete $[H_4Re_4(CO)_{15}]^{2-}$ anions and $(NEt_4)^+$ cations in the ratio 1 : 2. The best way to compare the packings is to show the projections of the cell contents down the shortest axis. i.e. down a in form I (Fig. 1) and down c in form II (Fig. 2). In these two views, although of different symmetry, the disposition of the centroids of anions and cations is similar, but their relative orientations are unlike. At the molecular level differences are present both in the anion geometries and, especially, in the conformations of the cations. In form II the two crystallographically independent $(NEt_4)^+$ have essentially the same *transoid* conformation with approximate D_{2d} symmetry. In form I one cation, 2 (see Fig. 1), maintains this conformation while the second, 1, assumes a less usual 'nordic-cross' arrangement of S_4 symmetry. These two kinds of conformation, characterized by N—C torsion angles close to 180° or ±60°, are the only stable ones predictable for $(NEt_4)^+$ in the free state and should be comparable in energy. The packing of the previous form III resembles that of

(continued on p. 242)

TABLE 2

POSITIONAL AND THERMAL PARAMETERS IN FORM I [a, b]

Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re(1)	34976(11)	12199(6)	26038(7)	680(9)	−33(10)	17(10)	212(3)	−5(6)	241(4)
Re(2)	26159(12)	2941(6)	12416(7)	957(11)	−17(11)	0(11)	199(3)	−26(6)	283(4)
Re(3)	18591(11)	16623(6)	11443(7)	706(10)	0(10)	27(10)	218(3)	46(6)	263(4)
Re(4)	15884(12)	9634(6)	39009(7)	858(11)	9(10)	141(11)	204(3)	28(6)	265(4)

Isotropic atoms

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
C(11)	4435(26)	631(14)	3221(17)	3,9(6)	C(42)	621(27)	786(15)	4691(18)	4,5(6)
O(11)	4958(22)	270(12)	3581(14)	6,3(8)	O(42)	63(21)	713(11)	5222(13)	5.8(5)
C(12)	4802(33)	1430(18)	2107(22)	5,9(3)	C(43)	1746(28)	94(16)	3625(19)	4.7(6)
O(12)	5652(27)	1574(15)	1818(18)	8,4(7)	O(43)	1671(27)	−433(14)	3393(18)	8.4(7)
C(13)	3916(26)	1865(14)	3297(16)	3,9(6)	C(44)	1243(41)	1852(22)	3922(27)	8.0(11)
O(13)	4164(22)	2280(12)	3710(15)	6,6(6)	O(44)	1104(27)	2402(14)	3889(17)	8.2(7)
C(21)	4240(30)	468(17)	856(20)	5,2(7)	N(1)	2573(24)	−2175(13)	4970(15)	5.0(6)
O(21)	5101(21)	565(12)	661(14)	6,0(5)	CT(11)	3174(34)	−2784(18)	4925(22)	6.1(8)
C(22)	2030(32)	62(18)	220(21)	5,9(8)	CT(12)	1797(31)	−2064(16)	4232(20)	5.3(7)
O(22)	1756(26)	−87(15)	−405(17)	8,3(7)	CT(13)	1702(41)	−2134(22)	5544(26)	7.9(11)
C(23)	1029(36)	192(19)	1571(23)	6,8(9)	CT(14)	3594(38)	−1664(21)	5016(25)	7.4(10)
O(23)	22(34)	184(13)	1795(16)	7,3(6)	CT(15)	2474(35)	−3386(20)	4791(24)	6.7(9)
C(24)	2982(36)	−533(20)	1535(23)	6,8(9)	CT(16)	2354(41)	−2062(23)	3475(27)	8.2(11)
O(24)	3092(29)	−1060(15)	1717(19)	9,0(8)	CT(17)	2215(56)	−2252(32)	6308(38)	12.2(18)
C(31)	934(27)	1384(15)	242(17)	4,3(5)	CT(18)	3075(51)	−1025(27)	5092(34)	10.3(15)
O(31)	505(20)	1247(11)	−336(13)	5,7(5)	N(2)	2761(20)	4024(11)	2579(13)	3.7(4)
C(32)	3223(28)	1809(15)	626(18)	4,6(6)	CT(21)	3203(29)	3374(15)	2416(19)	4.8(7)
O(32)	4165(21)	1896(11)	329(13)	5,9(5)	CT(22)	3603(35)	4376(20)	3074(23)	6.6(9)
C(33)	404(29)	1567(16)	1714(19)	4,9(7)	CT(23)	2566(40)	4411(23)	1848(27)	8.2(11)
O(33)	−417(23)	1592(13)	2024(15)	6,8(6)	CT(24)	1636(38)	3940(20)	2976(25)	7.0(10)
C(34)	1442(28)	2495(15)	945(18)	4,6(5)	CT(25)	4299(45)	3320(25)	1991(30)	9.1(12)
O(34)	1187(21)	3036(11)	793(14)	6,0(5)	CT(26)	4089(39)	4010(21)	3822(26)	7.6(10)
C(41)	3019(28)	1026(15)	4591(18)	4,5(6)	CT(27)	2067(48)	5061(27)	1990(31)	10.0(14)
O(41)	3747(25)	1006(13)	5059(16)	7,6(6)	CT(28)	625(50)	3661(28)	2570(33)	10.3(15)

[a] The Re parameters × 10^5; the other ones × 10^4, except for the isotropic B factors. [b] The b_{ij} values are the coefficients of exp $-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS IN FORM II [a]

Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re(1)	36489(6)	24382(7)	65420(10)	169(3)	35(6)	−107(8)	256(4)	−15(11)	506(9)
Re(2)	46385(6)	11212(7)	71398(11)	177(3)	85(6)	−120(9)	280(4)	−105(12)	695(10)
Re(3)	34272(6)	10144(7)	82011(11)	180(3)	−50(6)	−138(9)	275(4)	51(12)	637(10)
Re(4)	40284(7)	37408(7)	85477(12)	230(3)	0(7)	−81(10)	264(4)	−165(13)	761(11)

Isotropic atoms

Atom	x	y	z	$B(Å^2)$	Atom	x	y	z	$B(Å^2)$
C(11)	4010(13)	3155(17)	5613(26)	3.5(6)	C(42)	4174(16)	4535(21)	9603(32)	5.1(8)
O(11)	4233(12)	3600(16)	4969(24)	6.6(6)	O(42)	4226(14)	5038(18)	10286(28)	8.4(8)
C(12)	3337(14)	1887(18)	5236(28)	4.0(6)	C(43)	4841(19)	3759(24)	8194(37)	6.3(9)
O(12)	3080(11)	1578(15)	4354(23)	6.0(6)	O(43)	5330(15)	3754(19)	7813(29)	9.0(8)
C(13)	2911(17)	2971(21)	6488(32)	5.3(8)	C(44)	3249(17)	3453(21)	9051(32)	5.0(7)
O(13)	2460(12)	3353(15)	6359(22)	6.1(6)	O(44)	2799(13)	3257(16)	9347(25)	6.9(6)
C(21)	4238(17)	595(22)	5839(32)	5.3(8)	N(1)	716(11)	2237(14)	7616(22)	4.0(5)
O(21)	4007(16)	253(20)	4950(30)	9.3(9)	CT(11)	1162(16)	2678(20)	8567(32)	5.0(8)
C(22)	4890(17)	194(21)	7781(33)	5.4(8)	CT(12)	133(16)	2757(20)	7291(30)	4.7(7)
O(22)	5091(14)	−384(18)	8215(27)	8.1(7)	CT(13)	562(15)	1510(19)	8199(29)	4.2(6)
C(23)	4989(13)	1626(17)	8509(26)	3.5(6)	CT(14)	1001(17)	2161(21)	6447(32)	5.3(8)
O(23)	5248(12)	1936(16)	9376(23)	6.5(5)	CT(15)	1301(17)	3466(22)	8224(33)	5.3(8)
C(24)	5361(20)	1294(25)	6403(39)	7.0(10)	CT(16)	−212(19)	2949(25)	8369(37)	6.4(9)
O(24)	5791(13)	1418(16)	5935(25)	7.0(6)	CT(17)	138(24)	956(30)	7376(46)	8.8(13)
C(31)	3651(16)	63(20)	8850(30)	4.8(7)	CT(18)	1571(19)	1618(25)	6518(37)	6.6(10)
O(31)	3782(11)	−537(14)	9346(22)	5.8(5)	N(2)	2528(13)	4420(17)	2760(25)	4.9(6)
C(32)	3036(16)	526(20)	6849(31)	4.8(7)	CT(21)	2341(22)	3949(28)	3797(43)	7.9(11)
O(32)	2785(14)	203(17)	6000(26)	7.6(7)	CT(22)	2757(26)	3971(33)	1822(50)	9.8(14)
C(33)	3844(14)	1510(18)	9538(28)	3.9(6)	CT(23)	3025(25)	4941(32)	3405(48)	9.4(14)
O(33)	4055(12)	1763(16)	10459(24)	6.8(6)	CT(24)	1969(19)	4896(25)	2110(27)	6.5(9)
C(34)	2676(15)	1099(19)	8879(30)	4.6(7)	CT(25)	1854(31)	3250(39)	3347(58)	11.8(18)
O(34)	2248(11)	1187(13)	9405(21)	5.4(5)	CT(26)	3301(25)	3361(33)	2285(48)	9.4(14)
C(41)	3705(17)	4394(22)	7258(32)	5.3(8)	CT(27)	3193(37)	5545(47)	2364(70)	15.9(23)
O(41)	3504(14)	4815(19)	6482(27)	8.2(8)	CT(28)	1671(21)	5413(27)	3013(41)	7.6(11)

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[a] See footnotes on Table 2.

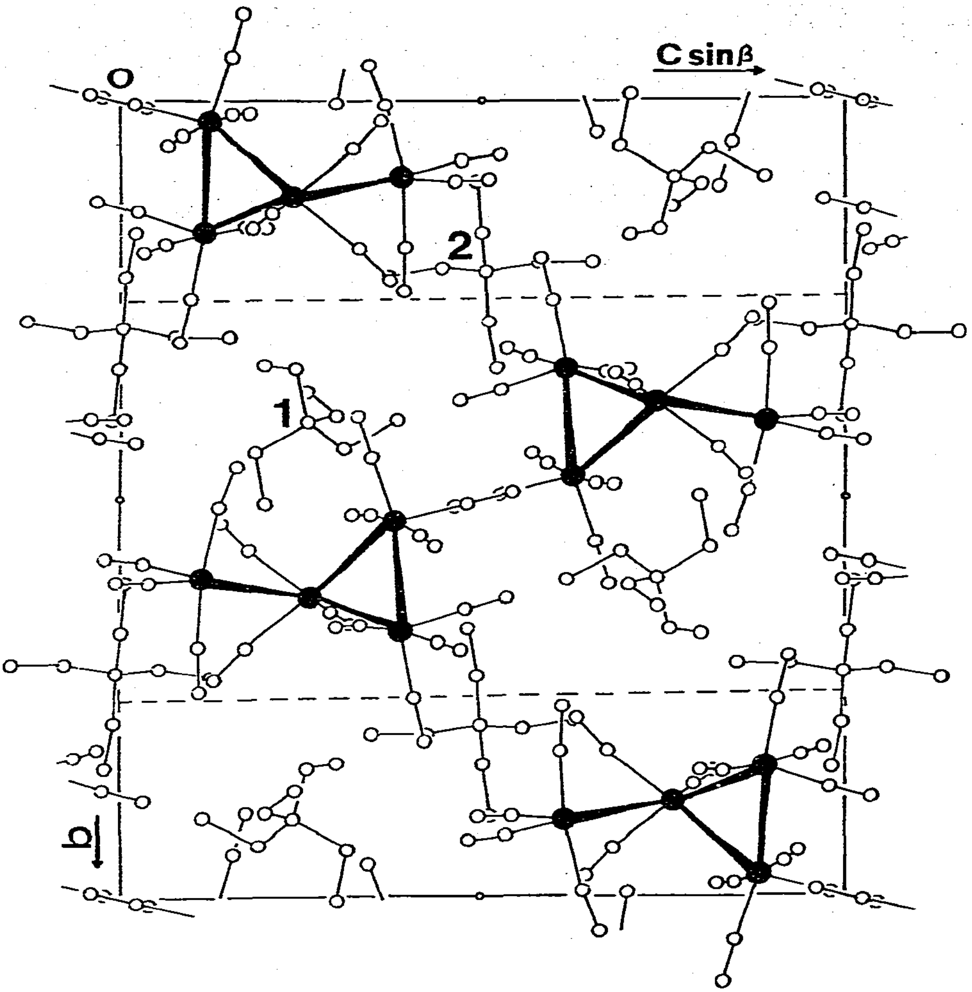

Fig. 1. Projection of form I down the *a* axis.

I; one cation is very similar to 2 while the other, lying at the position of 1, is disordered.

The surprising ability of this salt to give various crystallographic modifications can probably be ascribed, not only to the different cationic conformations, but also to the flexibility of the open-cluster anion (see below). The packing efficiency, on the basis of the computed density, is I > III > II. A view of the anion $[H_4Re_4(CO)_{15}]^{2-}$, with the atomic numbering, is depicted in Fig. 3. It contains a tetrametal array, consisting of an isosceles triangle [Re(1)Re(2)Re(3)] plus an apical metal atom, Re(4), bound to Re(1). All the fifteen carbonyl groups are terminally bonded to the rhenium atoms, occupying octahedral coordination sites. Tables 4 and 5 give a comparison of the bond lengths and bond angles in the different forms.

The three metal atom clusters are very similar; however, minor but significant differences are present. The most symmetric one is that of form I, in which

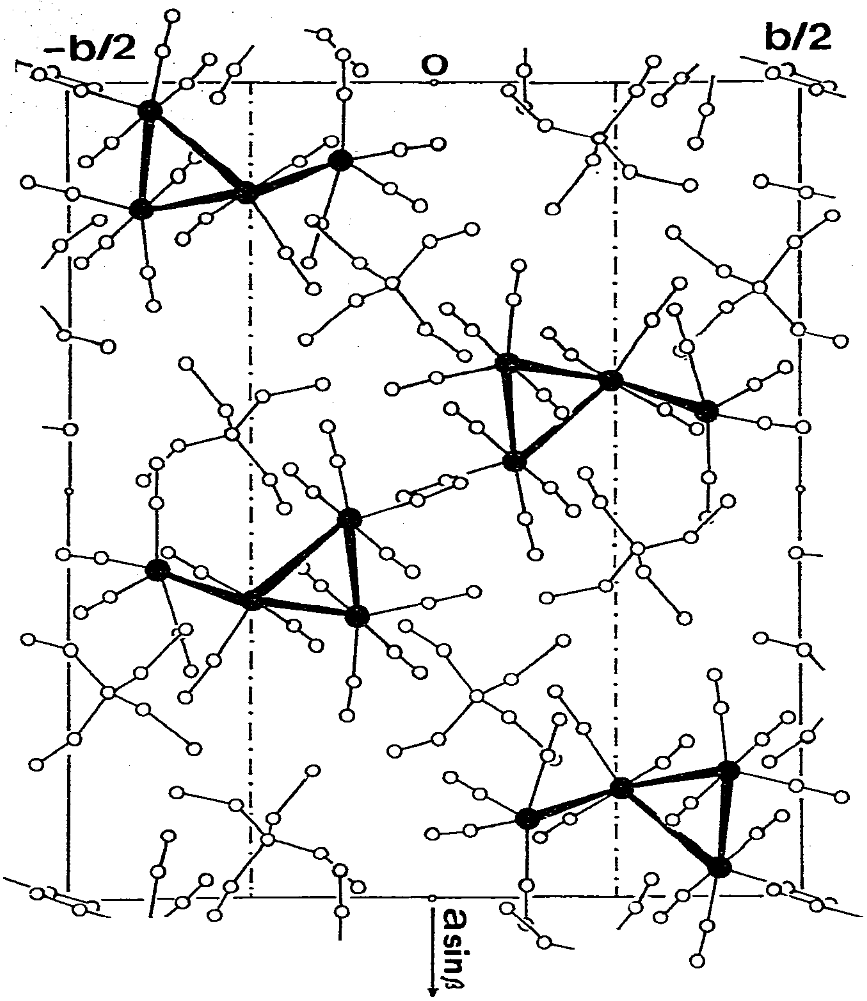

Fig. 2. Projection of form II down the c axis.

the two long trianglular edges, Re(1)—Re(2) and Re(1)—Re(3), and the angles Re(4)—Re(1)—Re(2) and Re(4)—Re(1)—Re(3) are nearly equal, thus almost exactly conforming to ideal C_s symmetry. In form III the two long triangular edges become somewhat different (ca. 0.02 Å) and in form II also the two above angles show a certain difference (ca. 4°). It is noteworthy that packing factors may have some influence not only on the bond angles but even on the metal—metal distances.

The Re—Re bond lengths and the positions of the hydridic atoms (not directly located) have already been discussed [1]. The short Re(2)—Re(3) edge, 3.03 Å, has a typical value for a normal single bond. The other three Re—Re bonds are lengthened by the presence of edge-bridging hydrido ligands, as found in many similar situations [8]. The fourth hydrido ligand must, on the basis of steric considerations, be terminally bound to Re(4), *trans* to CO(41) (see Fig. 3). These hydrides

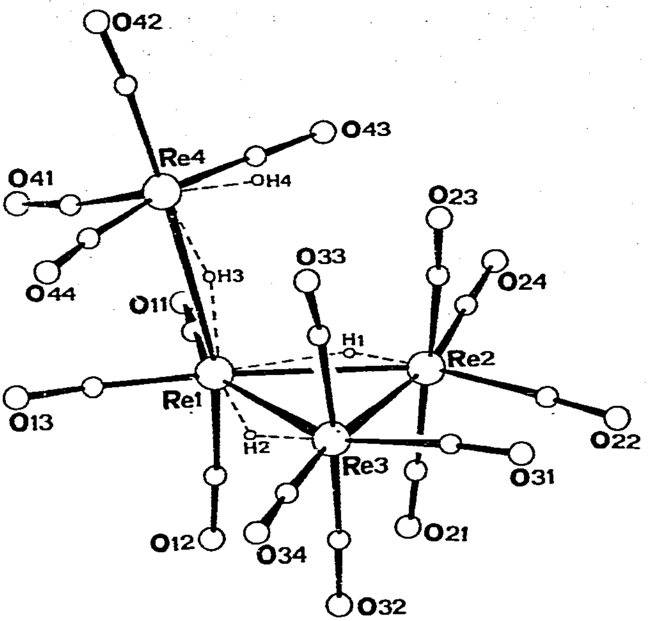

Fig. 3. View of the anion $[H_4Re_4(CO)_{15}]^{2-}$ (in form I) with the postulated hydridic atoms positions.

belong, therefore, to three classes, as shown by PMR spectra at temperatures lower than 0°C, i.e. H(1) and H(2) (τ 26.93), which are equivalent, H(3) (τ 25.95) and H(4) (τ 15.04); at higher temperatures the latter two are fluxional, giving only one signal (τ 20.57 ppm) [2]. In order to attain the EAN for the metals the two net negative charges of the anion must be equally shared by the four rhenium atoms.

The Re—C and C—O distances show more regular values in form II, while in I they are rather scattered. The overall mean values are 1.91 and 1.16 Å (I) and 1.88 and 1.20 Å (II), respectively. However the carbonyl groups are of four kinds: CO *trans* to CO (6), CO *trans* to hydrogen-bridged Re—Re bonds (6), CO *trans* to Re—Re bonds (2) and CO *trans* to a hydrido ligand (1). The Re—C distances corresponding to the first class have, on average, higher values than those belonging to the second (overall mean values on the two structures 1.92 vs. 1.87 Å). A possible explanation is that mutually *trans* carbonyl groups are in competition between themselves for the metal-to-ligand back-donated π electrons.

The corresponding Re—Re—C and C—Re—C angles show large differences in the three forms, up to 13°. The anion possesses a certain flexibility since some torsion of the Re(4)H(CO)$_4$ group is possible about the Re(1)—Re(4) bond. In form II the overall anion geometry conforms well to C_s symmetry since the above torsion angle is very small, ca. 4° (see Fig. 4 above). In form I a deviation of about 15° occurs and owing to the dissymmetric intramolecular non-bonded contacts the disposition of the carbonyl groups becomes highly unsymmetrical. In all cases the basal triangular moiety exhibits large differences between Re—Re—C (equatorial) angles involving hydrogen-bridged and non hydrogen-bridged Re—Re bonds (see Fig. 4 below). The former are enlarged in order to

TABLE 4

BOND DISTANCES (Å) IN $(NEt_4)_2[H_4Re_4(CO)_{15}]$ (in square brackets the metal—metal distances of form III)

Distance	Form I	Form II
Re(1)—Re(2)	3.184(2)	3.192(2) [3.192(8)]
Re(1)—Re(3)	3.181(2)	3.210(2) [3.211(8)]
Re(1)—Re(4)	3.287(2)	3.287(2) [3.288(9)]
Re(2)—Re(3)	3.026(2)	3.029(2) [3.023(8)]
Re(1)—C(11)	1.92(3)	1.88(3)
Re(1)—C(12)	1.82(4)	1.85(3)
Re(1)—C(13)	1.87(3)	1.86(4)
Re(2)—C(21)	2.04(4)	1.89(4)
Re(2)—C(22)	1.92(4)	1.85(4)
Re(2)—C(23)	1.94(4)	1.89(3)
Re(2)—C(24)	1.87(4)	1.89(5)
Re(3)—C(31)	1.92(3)	1.87(4)
Re(3)—C(32)	1.87(3)	1.89(3)
Re(3)—C(33)	2.00(3)	1.91(3)
Re(3)—C(34)	1.86(3)	1.89(4)
Re(4)—C(41)	1.96(3)	1.94(4)
Re(4)—C(42)	1.86(3)	1.85(4)
Re(4)—C(43)	1.93(5)	1.86(4)
Re(4)—C(44)	1.92(3)	1.92(4)
C(11)—O(11)	1.13(4)	1.21(4)
C(12)—O(12)	1.16(5)	1.23(4)
C(13)—O(13)	1.16(4)	1.19(5)
C(21)—O(21)	1.08(4)	1.24(5)
C(22)—O(22)	1.16(5)	1.20(5)
C(23)—O(23)	1.23(5)	1.22(5)
C(24)—O(24)	1.17(5)	1.15(5)
C(31)—O(31)	1.12(4)	1.22(4)
C(32)—O(32)	1.24(4)	1.21(5)
C(33)—O(33)	1.11(4)	1.19(4)
C(34)—O(34)	1.21(4)	1.17(4)
C(41)—O(41)	1.12(4)	1.20(5)
C(42)—O(42)	1.17(4)	1.18(5)
C(43)—O(43)	1.18(6)	1.20(6)
C(44)—O(44)	1.19(5)	1.13(5)
N(1)—CT(11)	1.47(5)	1.58(4)
N(1)—CT(12)	1.52(4)	1.58(4)
N(1)—CT(13)	1.46(6)	1.50(4)
N(1)—CT(14)	1.58(5)	1.54(5)
CT(11)—CT(15)	1.51(6)	1.48(5)
C(12)—CT(16)	1.50(6)	1.55(6)
CT(13)—CT(17)	1.44(8)	1.58(6)
CT(14)—CT(18)	1.49(7)	1.56(6)
N(2)—CT(21)	1.50(4)	1.54(6)
N(2)—CT(22)	1.45(5)	1.46(7)
N(2)—CT(23)	1.52(5)	1.55(6)
N(2)—CT(24)	1.51(5)	1.60(5)
CT(21)—CT(25)	1.50(6)	1.67(8)
CT(22)—CT(26)	1.58(6)	1.64(8)
CT(23)—CT(27)	1.52(8)	1.66(10)
CT(24)—CT(28)	1.43(7)	1.57(7)

lower the H···C non-bonded contacts, with a mean value (on the three forms) of 111° vs. 91° for the others. A similar situation was found in the corresponding moiety of $[H_2Re_3(CO)_{12}]^-$ [9].

The coordination around Re(4) is similar in forms I and II. The C(43)—Re(4)

TABLE 5

BOND ANGLES (DEG.) FOR THE ANION $[H_4Re_4(CO)_{15}]^{2-}$ IN THE THREE FORMS

Angle	Form I	Form II	Form III[a]
Re(2)—Re(1)—Re(3)	56.8(1)	56.5(1)	56.5(2)
Re(1)—Re(2)—Re(3)	61.5(1)	62.0(1)	62.0(2)
Re(1)—Re(3)—Re(2)	61.7(1)	61.5(1)	61.4(2)
Re(2)—Re(1)—Re(4)	102.9(1)	103.9(1)	103.6(2)
Re(3)—Re(1)—Re(4)	102.8(1)	100.0(1)	103.5(3)
Re(2)—Re(1)—C(11)	98(1)	107(1)	103(3)
Re(2)—Re(1)—C(12)	91(1)	89(1)	90(2)
Re(2)—Re(1)—C(13)	171(1)	160(1)	171(2)
Re(3)—Re(1)—C(11)	155(1)	163(1)	159(3)
Re(3)—Re(1)—C(12)	90(1)	90(1)	88(2)
Re(3)—Re(1)—C(13)	114(1)	103(1)	116(2)
Re(4)—Re(1)—C(11)	83(1)	81(1)	80(3)
Re(4)—Re(1)—C(12)	165(1)	167(1)	166(2)
Re(4)—Re(1)—C(13)	80(1)	80(1)	81(2)
C(11)—Re(1)—C(12)	89(1)	92(1)	92(4)
C(11)—Re(1)—C(13)	90(1)	93(1)	86(3)
C(12)—Re(1)—C(13)	87(1)	90(1)	86(3)
Re(1)—Re(2)—C(21)	84(1)	86(1)	89(2)
Re(1)—Re(2)—C(22)	157(1)	153(1)	158(2)
Re(1)—Re(2)—C(23)	95(1)	92(1)	91(2)
Re(1)—Re(2)—C(24)	109(1)	111(1)	111(1)
Re(3)—Re(2)—C(21)	94(1)	86(1)	91(2)
Re(3)—Re(2)—C(22)	97(1)	91(1)	96(2)
Re(3)—Re(2)—C(23)	82(1)	89(1)	86(2)
Re(3)—Re(2)—C(24)	167(1)	173(1)	173(1)
C(21)—Re(2)—C(22)	90(1)	89(2)	87(3)
C(21)—Re(2)—C(23)	175(2)	176(1)	177(3)
C(21)—Re(2)—C(24)	94(2)	94(2)	91(2)
C(22)—Re(2)—C(23)	89(2)	90(1)	92(3)
C(22)—Re(2)—C(24)	94(2)	95(2)	91(3)
C(23)—Re(2)—C(24)	90(2)	91(2)	92(2)
Re(1)—Re(3)—C(31)	145(1)	152(1)	149(2)
Re(1)—Re(3)—C(32)	89(1)	87(1)	88(2)
Re(1)—Re(3)—C(33)	92(1)	92(1)	92(3)
Re(1)—Re(3)—C(34)	124(1)	112(1)	122(2)
Re(2)—Re(3)—C(31)	84(1)	91(1)	87(2)
Re(2)—Re(3)—C(32)	87(1)	92(1)	86(2)
Re(2)—Re(3)—C(33)	97(1)	86(1)	97(2)
Re(2)—Re(3)—C(34)	172(1)	172(1)	174(2)
C(31)—Re(3)—C(32)	95(1)	90(1)	85(3)
C(31)—Re(3)—C(33)	87(1)	90(1)	97(4)
C(31)—Re(3)—C(34)	91(1)	96(1)	89(3)
C(32)—Re(3)—C(33)	176(1)	178(1)	177(3)
C(32)—Re(3)—C(34)	88(1)	92(1)	90(3)
C(33)—Re(3)—C(34)	89(1)	90(1)	88(3)
Re(1)—Re(4)—C(41)	81(1)	81(1)	82(3)
Re(1)—Re(4)—C(42)	175(1)	174(1)	173(2)
Re(1)—Re(4)—C(43)	85(1)	92(1)	87(2)
Re(1)—Re(4)—C(44)	90(1)	82(1)	92(2)
C(41)—Re(4)—C(42)	94(1)	94(2)	91(4)
C(41)—Re(4)—C(43)	97(1)	96(2)	105(3)
C(41)—Re(4)—C(44)	95(2)	97(2)	101(3)
C(42)—Re(4)—C(43)	94(1)	91(2)	95(3)
C(42)—Re(4)—C(44)	93(2)	96(2)	90(3)
C(43)—Re(4)—C(44)	166(2)	165(2)	154(3)

TABLE 5 (continued)

Angle	Form I	Form II	Form III [a]
Re(1)—C(11)—O(11)	178(3)	177(3)	180
Re(1)—C(12)—O(12)	177(3)	173(3)	
Re(1)—C(13)—O(13)	178(3)	173(3)	
Re(2)—C(21)—O(21)	179(3)	176(3)	
Re(2)—C(22)—O(22)	175(3)	176(3)	
Re(2)—C(23)—O(23)	174(3)	176(3)	
Re(2)—C(24)—O(24)	173(4)	178(4)	
Re(3)—C(31)—O(31)	171(3)	175(3)	
Re(3)—C(32)—O(32)	176(3)	179(3)	
Re(3)—C(33)—O(33)	171(3)	171(3)	
Re(3)—C(34)—O(34)	178(3)	173(3)	
Re(4)—C(41)—O(41)	169(3)	178(3)	
Re(4)—C(42)—O(42)	175(3)	175(3)	
Re(4)—C(43)—O(43)	170(3)	171(4)	
Re(4)—C(44)—O(44)	174(4)	177(3)	

[a] In the refinement of form III the Re—C—O interactions were constrained to linearity with a fixed C—O distance of 1.16 Å.

C(44) angle (166° and 165°, respectively) shows a bending of these CO groups toward the terminal hydrido ligand, H(4), due to its low steric requirement. The amount of bending in form III is larger (154°) but the value is probably unaccu-

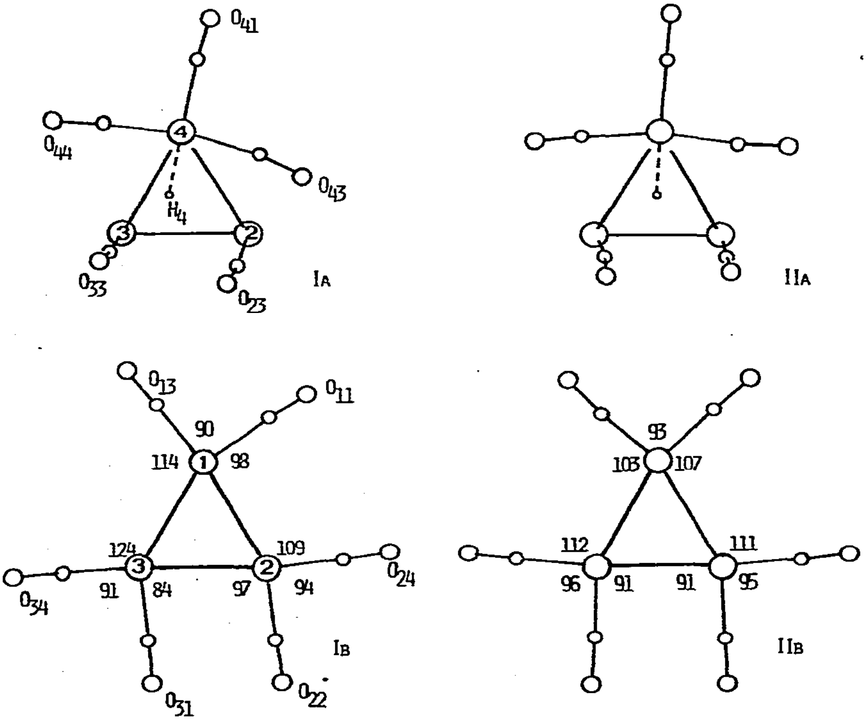

Fig. 4. View of two moieties of the anion in forms I and II; a projection down the Re(4)—Re(1) bond (A) and the basal triangle with the equatorial carbonyl groups (B).

rate because of the linearity imposed on the Re—C—O interactions in that case [1].

It has been pointed out (see, for instance, ref. 8 and refs. therein) that the tendency of metal atoms, at least in three- and tetra-metal clusters, to achieve a complete 18 electron shell enables us to make forecasts of the geometry and bonding in such arrays on the basis of a simple electron count. The EAN rule requires a total number of 60 valency electrons for a tetrahedral cluster. A lower number leads to electron deficient species with metal—metal double bonds (possibly delocalized), while a larger number gives electron rich compounds, with a deficiency of one metal—metal bond for each supplementary electron pair. The present anion possesses 64 valency electrons, thus requiring the breaking of two of the six tetrahedral edges (Re···Re of ca. 5 Å). More electrons imply the absence of surplus metal—metal bonds so that such structures cannot be held together without the presence of bridging ligands, as in the cases of $[\mathrm{Re(SCH_3)(CO)_3}]_4$ [10], $[\mathrm{OsO(CO)_3}]_4$ [11] and $[\mathrm{HW(OH)(CO)_3}]_4$ [12], which are all 72 electrons species with no metal—metal bonds. From this point of view $[\mathrm{H_4Re_4(CO)_{15}}]^{2-}$ is the most electron rich tetrametal cluster ever found.

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