

Fig. 1. Two different views of the unit cell of RbGa₇, with thermal ellipsoids shown at the 50% probability level.

direct Ga–Ga bonds occurring between Ga(1) and Ga(2); the linkage between adjacent sheets is ensured, along the *z* axis, by double bifurcated bonds involving Ga(4) as centers and occurring between Ga(3) and Ga(5). Ga(1) and Ga(2) have seven, Ga(3) and Ga(5) have six and Ga(4) has four coordinating Ga atoms at less than 3.5 Å. Ga(4) is coordinated to its four neighboring Ga atoms (3, 4 and 5) nearly tetrahedrally (120.1, 96.7, 120.5 and 96.7°).

Rb atoms occupy vacant channels parallel to the *y* axis and bordered by Ga atoms (3, 4 and 5). These alkaline atoms form zig-zag chains parallel to the *y* axis with mean Rb–Rb distance and angle of 4.135 Å and 106°; their contact distances with Ga atoms range from 3.713 (3) to 3.842 (3) Å.

In conclusion, this structure presents some analogies with that of K₃Ga₁₃ (Belin, 1980). Although in the latter, both the concentration of the alkaline-metal

atoms and the symmetry of the crystal are higher, Ga atoms have the ability to coordinate to each other within icosahedra arranged around inversion centers. However, in K₃Ga₁₃ the structure is more complex since Ga atoms are also coordinated within 11 vertex polyhedra. In both structures, connections between such polyhedra are ensured through direct and bifurcated Ga–Ga bonds; the stacking of Ga atoms is not compact, leaving holes where the alkaline-metal atoms can reside.

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Acta Cryst. (1981). B37, 2062–2064

The Structure of Tetrakis(tricarbonyl- μ_3 -hydroxo-rhenium)–Benzene (1 : 2)

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(Received 16 March 1981; accepted 7 May 1981)

Abstract. [Re(CO)₃OH]₄·2C₆H₆, *M_r* = 1305.18, cubic, *Pn*3*m*, *a* = 11.343 (2) Å, *V* = 1454.42 Å³,

Z = 2, *d_c* = 2.96, *d_o* = 3.0 Mg m⁻³, $\mu(\text{Mo } K\alpha) = 16.9 \text{ mm}^{-1}$. Final weighted *R* = 0.029 for 225 observed independent reflections. The structure consists of discrete tetramers, four Re and four O atoms occupy-

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ing the corners of a distorted cube. There are two benzene rings per formula unit in the lattice. The compound is most probably the first characterized example of a benzene ring using both faces as acceptors for $\text{OH}\cdots\pi$ hydrogen bonding.

Introduction. Except for the X-ray structure analysis, the chemical and physical properties of the title compound, $[\text{Re}(\text{CO})_3\text{OH}]_4 \cdot 2\text{C}_6\text{H}_6$ (I), have been reported (Herberhold, Süss, Ellermann & Gäbelein, 1978). Based on IR and NMR data, a cubane-like structure with four Re and four O atoms at the edges of a distorted cube was proposed but no solvent molecules in the crystals analogous to the two benzene rings in (I) had been reported (Herberhold *et al.*, 1978). We now report the molecular structure of (I).

The crystal and molecular structure of tetrakis(tricarbonyl- μ_3 -methanethiolato-rhenium) (II) and of tetrakis(tricarbonyl- μ_3 -methoxo-rhenium) (III) have been described earlier (Harrison, Marsh & Trotter, 1972; Atwood, 1977, unpublished, quoted in Herberhold *et al.*, 1978) allowing a comparison with (I). The latter was prepared by a procedure similar to those reported in the literature (Herberhold *et al.*, 1978).

Single crystals were obtained by recrystallizing (I) from benzene solutions which were heated to 323–333 K and very slowly cooled down to room temperature. A yellow, sparkling, strongly refracting crystal ($0.4 \times 0.4 \times 0.3$ mm) mounted on top of a glass capillary was used for the investigation. Lattice parameters were derived from the setting angles of 25 machine-centred reflections (Syntex R3, monochromatic Mo $K\alpha$ radiation). Data collection (θ - 2θ scans, $2\theta < 70^\circ$) yielded 225 observed independent reflections with $I > 3.0\sigma(I)$. Lorentz and polarization corrections as well as an empirical (ψ scans) absorption correction were applied.

The crystal system is cubic with space group $Pn3m$ (O_h^2), origin at centre ($3m$). The positions of the atoms were taken from Patterson and Fourier maps, all atoms occupying special positions [Re $8(e)$, μ_3 -oxygen O(2) $8(e)$, carbonyl carbon and oxygen C(1), O(1) $24(k)$ and benzene carbon C(6) $24(i)$; *International Tables for X-ray Crystallography*, 1969]. Final refinement by a cascade-matrix procedure with anisotropic temperature factors converged with a weighted $R = 0.029$ (unweighted $R = 0.040$).^{*} The weighting scheme was $W = 1/\sigma^2(F)$. Calculations were carried out on a Nova 3 computer; the plot was drawn on a Tektronix plotter. The program package was *SHELXTL* (Sheldrick, 1979).

Discussion. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2; Fig. 1 shows a

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36168 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$, $\times 10^5$ for Re) and equivalent isotropic temperature factors ($\times 10^3$, $\times 10^4$ for Re)

| | x | y | z | $U_{\text{eq}} (\text{Å}^2)^*$ |
|-------------------|-----------|-----------|------------|--------------------------------|
| Re | 14141 (7) | 14141 (7) | 14141 (7) | 247 (2) |
| O(μ_3) | 3328 (10) | 3328 (10) | 3328 (10) | 17 (4) |
| C(1) | 1405 (16) | 1405 (16) | -243 (17) | 35 (5) |
| O(1) | 1402 (11) | 1402 (11) | -1290 (13) | 61 (4) |
| C _{ring} | 5000 | 4146 (19) | 5854 (19) | 108 (16) |

* $U_{\text{eq}} = \frac{1}{3} \text{trace } \bar{U}$, \bar{U} signifying the diagonalized U matrix.

Table 2. Bond distances (Å) and angles ($^\circ$)

| | | | | | |
|--|------------|--------------------------------------|------------|---|------------|
| Re-C(1) | 1.877 (20) | Re-Re | 3.480 (2) | Re-O(μ_3) | 2.207 (8) |
| C(1)-O(1) | 1.187 (25) | C _{ring} -C _{ring} | 1.369 (16) | O(μ_3)-O(μ_3) | 2.156 (10) |
| Re-Re-Re | 60.0 | | | Re-C(1)-O(1) | 179.7 (21) |
| O(μ_3)-O(μ_3)-O(μ_3) | 60.0 | | | C _{ring} -C _{ring} -C _{ring} | 120.0 |
| O(μ_3)-Re-O(μ_3) | 73.9 | | | Re-O(μ_3)-Re | 104.0 (5) |

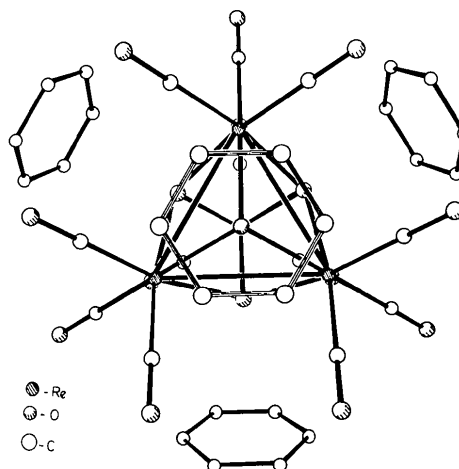


Fig. 1. ORTEP (Johnson, 1965) drawing of (I) viewed along one of the four threefold axes.

view of the cubane-like species together with the benzene rings. Figs. 2 and 3 are schematic drawings of (I) and give the numbering of the atoms and some bond lengths and angles. (I) forms discrete $[\text{Re}(\text{CO})_3\text{OH}]_4$ molecules with T_d symmetry; the benzene rings (two per tetrameric unit) are perpendicular to the four threefold axes of the unit cell with the centres of the rings lying on these axes ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) at a distance of 3.285 Å from the O atoms of the four μ_3 -OH groups. This means that only four benzene rings are needed to match with the eight μ_3 -OH groups of the two molecules ($Z = 2$), or, in other words, that each of the four benzene rings is involved in two $\text{OH}\cdots\pi$ hydrogen bonds. We believe that (I) represents the first characterized example of a benzene ring using both faces as acceptors for such $\text{OH}\cdots\pi$ hydrogen bonding. Only very few

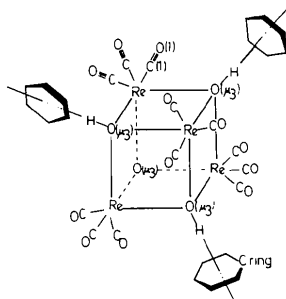


Fig. 2. Schematic drawing of (I) with atom numbering. The fourth benzene ring has been omitted for clarity.

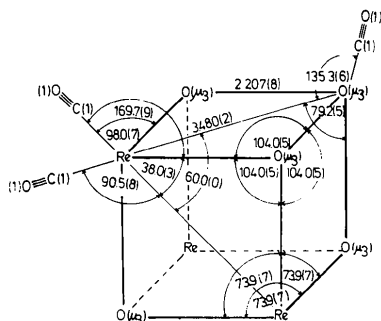


Fig. 3. Schematic drawing of the cube with distances (Å) and angles ($^{\circ}$).

examples of single $\text{OH}\cdots\pi$ hydrogen bonds characterized by X-ray methods are known (McPhail, Sim, Frey & Ott, 1966; Hardy & McNicol, 1976) with hydrogen-benzene distances of about 2.1 Å. Assuming an O-H distance of about 1 Å, the proton-benzene distance in (I) is longer; it should be close to 2.3 Å. This rather longer $\text{OH}\cdots\pi$ hydrogen bond could be due to the fact that the benzene rings in (I) are involved in two such bonds.*

The geometry of (I) can be best described as a distorted cube composed of two tetrahedra having a common centre. In one tetrahedron the corners are occupied by Re, in the other by O atoms (μ_3).

* We thank Professor G. A. Sim for discussion of this feature.

Regarding the μ_3 -OH groups as five-electron donors (Herberhold *et al.*, 1978) no Re-Re bonds need be assumed in order to obey the 18-electron rule for the Re atoms. The Re-Re distances [3.480 (2) Å] are clearly outside the range of Re-Re single bonds.

The Re-C_{carbonyl} distances as well as the C-O distances are within the range of values reported in the literature; the same is valid for the C-C lengths in the benzene rings.

A comparison between (I) and (II) is interesting. In the latter four Re and four S atoms respectively form almost regular tetrahedra (Harrison *et al.*, 1972). In contrast to (I) the Re-Re distances in (II) vary from 3.853–3.957 (3) Å, a phenomenon which has also been reported for the Re-Re distances in $\text{Re}_4(\text{CO})_{16}^{2-}$ (2.956–3.024 Å; Churchill & Bau, 1968) and which has been attributed to crystal packing. Due to the symmetry requirements of the space group, the Re-Re and also the O-O distances are identical in (I); the Re_4 and O_4 tetrahedra are ideal.

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