High Nuclearity Carbonyl Clusters of Rhodium. Part 3.[1,2] Crystal and Molecular Structure of Hexadeca-μ-carbonyl-enneacarbonyl-*polyhedro*-tetradecarhodate(4−) in its Tetraethylammonium Salt

By **Gianfranco Ciani** * and **Angelo Sironi**, Istituto di Chimica Generale ed Inorganica dell'Università e Centro del C.N.R., Via G. Venezian 21, 20133 Milano, Italy
Secondo Martinengo, Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione del C.N.R., Via G. Venezian 21, 20133 Milano, Italy

The title compound, $[NEt_4]_4[Rh_{14}(CO)_{25}]$, crystallises in the tetragonal space group *P4/ncc*, with unit-cell dimensions $a = 17.060(3)$, $c = 27.220(6)$ Å, and $Z = 4$. The structure has been solved by Patterson and Fourier methods from *X*-ray single-crystal counter data and refined by least-squares methods to $R = 0.046$ for 1 224 significant reflections. The $[Rh_{14}(CO)_{25}]^{4-}$ anion contains a metal-atom cluster which can be described as a distorted fragment of a body-centred cubic lattice, of C_{4v} idealized symmetry, with one interstitial metal atom which exhibits eight short metal–metal bonds (mean 2.638 Å), four longer contacts (3.076 Å), and one very long interaction [3.372(4) Å] with the capping atom on the four-fold axis. The Rh–Rh surface interactions are very scattered, ranging from 2.724(2) to 3.325(2) Å. There are nine terminally bound carbonyls (mean Rh–C and C–O, 1.80 and 1.17 Å respectively) and 16 edge-bridging groups. Of these, 12 are symmetric (mean Rh–C and C–O, 1.99 and 1.19 Å) and four, on the Rh(3)–Rh(5) edges, are markedly asymmetric [Rh(3)–C(6) 1.91(2) and Rh(5)–C(6) 2.33(2) Å].

LARGE carbonyl cluster compounds usually contain metal arrangements which are fragments of metallic lattices, with the exception of many species with interstitial main-group elements which show less compact metal arrays. Examples of nearly undistorted closest-packed clusters have been characterized, for instance, in the anions $[Os_{10}C(CO)_{24}]^{2-}$,[3] $[Fe_6Pd_6H(CO)_{24}]^{3-}$,[4] $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ ($n = 2$,[5] 3,[1] or 4 [2]), and $[Rh_{22}(CO)_{37}]^{4-}$.[6]

A metallic lattice of slightly lower compactness than the closest packing (c.c.p., h.c.p., or mixed) is the body-centred cubic (b.c.c.) packing, which can also be derived by distortion of the cubic close packing (c.c.p.). A cluster which resembles a fragment of b.c.c. packing is present in the anion $[Rh_{14}(CO)_{25}]^{4-}$. We reported a brief account of the synthesis and structure of the tetraethylammonium salt in 1978.[7] Subsequently we have performed, on a different sample, another *X*-ray data collection of the NEt_4^+ salt in order to obtain more accurate structural parameters. In a recent note Vidal and Schoening,[8] together with a synthesis of $[Rh_{14}(CO)_{25}]^{4-}$ under high pressure, reported some structural data for the salt previously investigated by us.

In this paper we report the complete results of our more recent structural analysis of $[NEt_4]_4[Rh_{14}(CO)_{25}]$, which are discussed in comparison with those of the other known high-nuclearity rhodium cluster species.

EXPERIMENTAL

Crystal Data.—$C_{57}H_{80}N_4O_{25}Rh_{14}$, $M = 2\,662.0$, Tetragonal, $a = 17.060(3)$, $c = 27.220(6)$ Å, $U = 7\,922.2$ Å^3, $D_m = 2.22(3)$, $Z = 4$, $D_c = 2.24$ g cm^{-3}, $F(000) = 5\,120$, space group *P4/ncc* (no. 130) from systematic absences, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ (Mo-K_α) = 28.2 cm^{-1}.

Intensity Measurements.—A crystal of dimensions 0.14 × 0.26 × 0.30 mm was mounted on an automatic BASIC diffractometer.[9] Intensity data, corresponding to $\frac{1}{16}$ of the reciprocal lattice, were collected with the ω scan method, using graphite monochromatized Mo-K_α radiation, within the range $3.5 < \theta < 25°$. A total of 4 022 diffraction intensities was measured, with a scan width of 1.0° and a scan speed of 0.033° s^{-1}; the background was measured at each side of the scan range for half of the peak-scanning time. One standard reflection, repeated at regular intervals, showed no crystal decay. The integrated intensities were reduced to F_o values by correction for Lorentz, polarization, and absorption effects. The transmission factors were calculated following the method of Busing and Levy,[10] and were found in the range 0.51—0.67. After removing all the reflections having $\sigma(I)/I > 0.30$ a final set of 1 224 independent reflections was used in the structure solution and refinements.

Structure Solution and Refinement.—The structure solution was based on Patterson and Fourier methods. The anion was found to lie in a special position about a four-fold crystallographic symmetry axis (*c* in Wyckoff notation) while the NEt_4^+ cations are in general positions.

The structure was refined by block-matrix least squares, with the metal atoms treated anisotropically and the others isotropically. The hydrogen atoms of the cations were not considered. The final values of the conventional agreement indices *R* and *R'* were both equal to 0.046.

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 128.3, −0.68, and 0.0016, chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors for all atoms were taken from ref. 11. Corrections for both the real and imaginary parts of the anomalous dispersion were taken from ref. 12.

The final difference-Fourier map was flat except for some residual peaks not exceeding 1.0 e Å^{-3}, near to the metal atoms.

The results of the refinements are reported in Table 1. The final list of observed and calculated factors and thermal parameters are given in Supplementary Publication No. SUP 23265 (8 pp.).†

All the computations were performed on a UNIVAC 1100/

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1

Final positional parameters ($\times 10^4$) within the salt $[NEt_4]_4[Rh_{14}(CO)_{25}]$ with estimated standard deviations in parentheses

Atom	x	y	z
Rh(1)	2 500	2 500	1 294(1)
Rh(2)	1 949(1)	1 481(1)	1 944(1)
Rh(3)	1 910(1)	1 409(1)	724(1)
Rh(4)	772(1)	1 987(1)	1 328(1)
Rh(5)	2 500	2 500	55(1)
C(1)	−123(17)	1 784(17)	1 623(11)
C(2)	560(14)	3 551(14)	2 078(9)
C(3)	338(11)	2 695(11)	795(6)
C(4)	824(10)	1 068(10)	872(6)
C(5)	1 331(12)	2 148(12)	2 400(7)
C(6)	1 312(13)	3 169(13)	25(8)
C(7)	2 500	2 500	−605(15)
O(1)	−699(14)	1 640(15)	1 840(8)
O(2)	−24(11)	3 885(11)	2 143(6)
O(3)	−286(8)	2 759(8)	615(4)
O(4)	372(8)	578(8)	742(4)
O(5)	1 052(10)	2 078(9)	2 806(5)
O(6)	963(9)	3 373(9)	−314(5)
O(7)	2 500	2 500	−1 040(13)
N	550(9)	−1 983(10)	1 149(5)
C(8)	841(15)	−1 358(15)	794(9)
C(9)	596(16)	−2 863(16)	953(10)
C(10)	−303(16)	−1 909(15)	1 289(10)
C(11)	1 096(17)	−1 852(17)	1 609(11)
C(12)	382(18)	−1 353(18)	291(11)
C(13)	1 466(21)	−3 037(20)	778(12)
C(14)	−484(18)	−1 039(19)	1 491(11)
C(15)	938(20)	−2 452(25)	2 012(12)

80 computer at the Computing Centre of Milan University, using local programs.

DISCUSSION

The crystal structure consists of the packing of discrete $[Rh_{14}(CO)_{25}]^{4-}$ anions and NEt_4^+ cations in the ratio 1 : 4, as illustrated in Figure 1.

The anion lies on a four-fold crystallographic axis, passing through the metal atoms Rh(1) and Rh(5). The entire anion, of idealized C_{4v} symmetry, is illustrated in Figure 2. Bond distances and angles are reported in Table 2. The metallic polyhedron, shown in Figure 3, can be described as a centred incomplete rhombic dodecahedron (somewhat elongated in the direction of the four-fold axis), *i.e.* essentially a fragment of a body-centred cubic lattice.

In more detail, we can compare this cluster with a monocapped centred cuboctahedron (cubic close packing) [Figure 4(A)] and with a regular incomplete centred rhombic dodecahedron (body-centred cubic packing) [Figure 4(B)], two polyhedra which can be interconverted by distortions. As is well known, in polyhedron (A) the metal–metal bond lengths are all equal and the next-nearest neighbours are at a markedly longer distance (41%), which is decisively non-bonding; the central atom exhibits 12 equal metal–metal bonds. In polyhedron (B) there are two types of metal–metal bonds: a short one and a second [dotted lines in Figure 4(B)] which is 15% longer than the former; the central metal exhibits eight short and five longer bonds. The anion $[Rh_{14}(CO)_{25}]^{4-}$ shows metal–metal interactions which can be approximately divided into three classes: a first set ranging from 2.624(2) to 2.793(2) Å (mean 2.727 Å), a second in the range 2.992(2)—3.076(1) Å (mean 3.034 Å), and a third in the range 3.325(2)—3.372(4) Å (mean 3.334 Å). Assuming that the mean Rh–Rh bond length of the first set is taken as unity, the

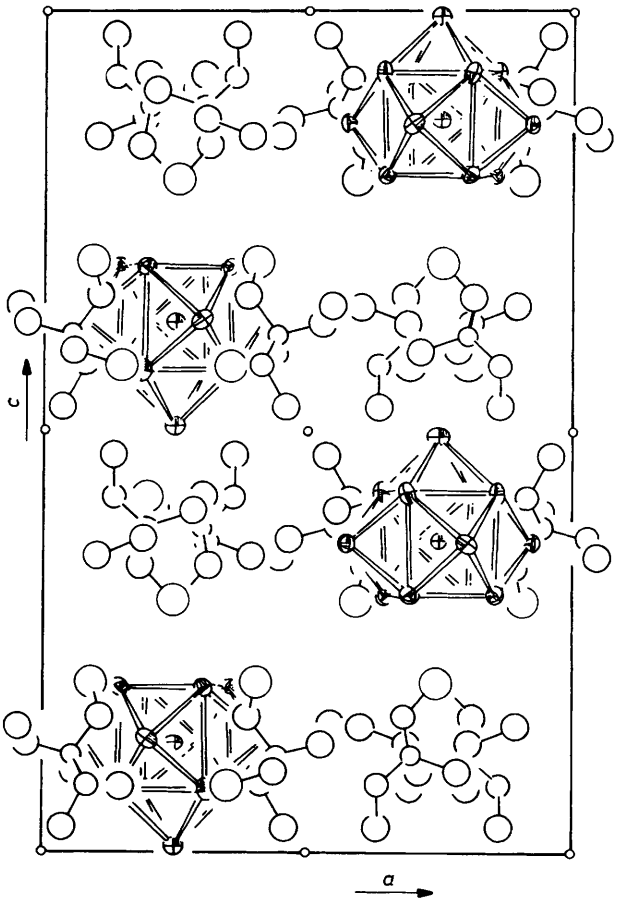


FIGURE 1 A view of the packing in the salt $[NEt_4]_4[Rh_{14}(CO)_{25}]$ (down the *b* axis). The carbonyl ligands have been omitted for clarity

mean Rh–Rh interactions for the other sets are 11 and 22% longer, respectively. We observe therefore that this cluster, although intermediate between polyhedra (A) and (B), is much more similar to (B), the main differences being: (*i*) an elongation of *ca.* 6% (with respect to the ideal value of 3.136 = 1.15 × 2.727 Å) in the direction of the four-fold axis, reflected in the Rh(2)–Rh(3) and Rh(1)–Rh(5) distances, and (*ii*) a contraction of the basal square face, containing Rh(2) and its symmetry-related atoms, which resembles the corresponding basal square face of polyhedron (A), probably due to the lack of a metal capping atom opposite to Rh(5).

Considering only the co-ordination about the central metal atom Rh(1), it shows eight short contacts (mean 2.638 Å) and four contacts *ca.* 17% longer [with the capping atoms Rh(4) and its symmetry-related atoms] of 3.076(1) Å, a situation very close to that of a b.c.c.

lattice atom. The fifth contact, Rh(1)–Rh(5), is markedly longer, 3.372(4) Å.

The 25 carbonyl ligands are disposed nine terminally and 16 edge-bridging (four asymmetric), as illustrated in Figure 2. Four surface metal atoms, Rh(3) and its equivalent atoms, are not co-ordinated to the terminal

TABLE 2

Interatomic distances (Å) and selected angles (°) within the salt $[NEt_4]_4[Rh_{14}(CO)_{25}]$ *

(*a*) Distances

Rh(1)–Rh(2)	2.652(3)	Rh(4)–C(3)	2.03(2)
Rh(1)–Rh(3)	2.624(2)	Rh(4)–C(4)	2.00(2)
Rh(1)–Rh(4)	3.076(1)	Rh(5)–C(6)	2.33(2)
Rh(1)–Rh(5)	3.372(4)	Rh(5)–C(7)	1.80(4)
Rh(2)–Rh(2^{iii})	2.793(2)	C(1)–O(1)	1.17(4)
Rh(2)–Rh(3)	3.325(2)	C(2)–O(2)	1.16(3)
Rh(2)–Rh(4)	2.755(2)	C(3)–O(3)	1.18(2)
Rh(2)–Rh(4^{iii})	2.752(2)	C(4)–O(4)	1.19(2)
Rh(3)–Rh(3^{iii})	2.992(2)	C(5)–O(5)	1.21(3)
Rh(3)–Rh(4)	2.729(2)	C(6)–O(6)	1.15(3)
Rh(3)–Rh(4^{iii})	2.724(2)	C(7)–O(7)	1.18(6)
Rh(3)–Rh(5)	2.791(3)	N–C(8)	1.52(3)
Rh(2)–C(2^{iii})	1.83(2)	N–C(9)	1.59(3)
Rh(2)–C(5)	1.99(2)	N–C(10)	1.51(3)
Rh(2)–C(5^{iii})	1.99(2)	N–C(11)	1.58(3)
Rh(3)–C(3^{iii})	1.96(2)	C(8)–C(12)	1.58(4)
Rh(3)–C(4)	1.98(2)	C(9)–C(13)	1.59(5)
Rh(3)–C(6^{iii})	1.91(2)	C(10)–C(14)	1.61(4)
Rh(4)–C(1)	1.76(3)	C(11)–C(15)	1.53(5)

(*b*) Angles

Rh(2)–Rh(1)–Rh(2^{ii})	96.3(1)	Rh(4)–C(4)–O(4)	135(1)
Rh(2)–Rh(1)–Rh(2^{iii})	63.5(1)	Rh(3)–C(4)–Rh(4)	86.5(7)
Rh(2)–Rh(1)–Rh(3)	78.1(1)	Rh(2)–C(5)–O(5)	136(2)
Rh(2)–Rh(1)–Rh(3^{ii})	174.4(1)	Rh(2^{iv})–C(5)–O(5)	134(2)
Rh(3)–Rh(1)–Rh(3^{ii})	107.5(1)	Rh(2)–C(5)–Rh(2^{iv})	89.2(9)
Rh(3)–Rh(1)–Rh(3^{iii})	69.5(1)	Rh(3^{iv})–C(6)–O(6)	150(2)
Rh(4)–Rh(1)–Rh(4^{ii})	176.6(1)	Rh(5)–C(6)–O(6)	129(2)
Rh(4)–Rh(1)–Rh(4^{iii})	89.9(1)	Rh(3^{iv})–C(6)–Rh(5)	81.7(8)
Rh(4)–Rh(1)–Rh(5)	91.7(1)	Rh(3)–Rh(2)–C(2^{iii})	99.1(8)
Rh(4)–C(1)–O(1)	177(3)	Rh(2)–Rh(3)–C(6^{iii})	175.9(7)
Rh(2^{iv})–C(2)–O(2)	177(2)	Rh(3)–Rh(4)–C(1)	145(1)
Rh(5)–C(7)–O(7)	180	Rh(3^{iv})–Rh(4)–C(1)	139(1)
Rh(3^{iv})–C(3)–O(3)	140(2)	Rh(3)–Rh(5)–C(3)	130.7(1)
Rh(4)–C(3)–O(3)	133(2)		
Rh(4)–C(3)–Rh(3^{iv})	86.3(7)	C–N–C	102(2)—116(2)
Rh(3)–C(4)–O(4)	139(2)	N–C–C	109(2)—113(2)

* Asymmetric units: ii $\frac{1}{2} - x, \frac{1}{2} - y, z$; iii $\frac{1}{2} - y, x, z$; iv $y, \frac{1}{2} - x, z$.

CO groups. All the surface metals are connected to three carbonyl ligands, except the capping metal Rh(5), which bears one terminal CO and is bound to four markedly asymmetric CO bridging ligands [Rh(5)–C(6) 2.33(2), Rh(3)–C(6) 1.91(2) Å]. This carbonyl stereochemistry allows a more homogeneous distribution of the anionic charge over the whole cluster surface.

The Rh–C and C–O interactions for the terminal ligands have mean values of 1.80 and 1.17 Å, and for the 12 symmetric edge-bridging ligands, 1.99 and 1.19 Å, respectively.

It is of interest to compare the structure of the anion $[Rh_{14}(CO)_{25}]^{4-}$ with those of the related species $[Rh_{14}H(CO)_{25}]^{3-}$,[13] $[Rh_{14}(CO)_{26}]^{2-}$,[14] and $[Rh_{15}(CO)_{27}]^{3-}$,[7] which have already been briefly described and whose detailed structures will be reported in other papers of this series. The metallic clusters present in these species can be derived from that of $[Rh_{14}(CO)_{25}]^{4-}$ by distortions. In

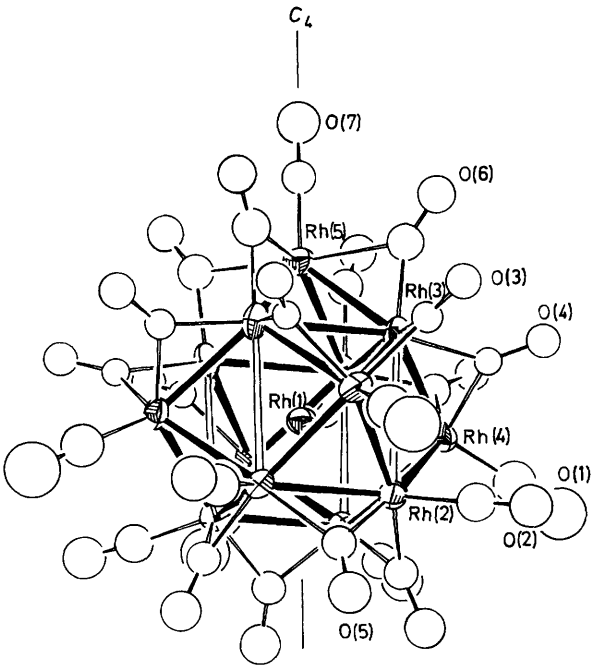


FIGURE 2 A view of the anion $[Rh_{14}(CO)_{25}]^{4-}$. The independent carbonyl ligands are indicated by the labelling of their oxygen atoms

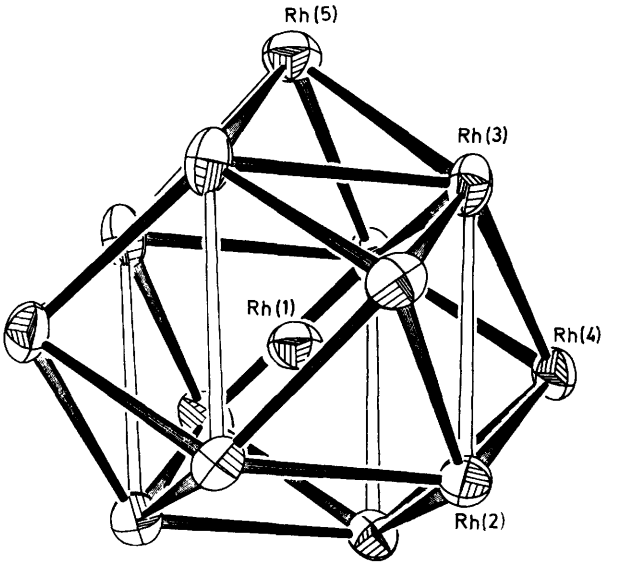
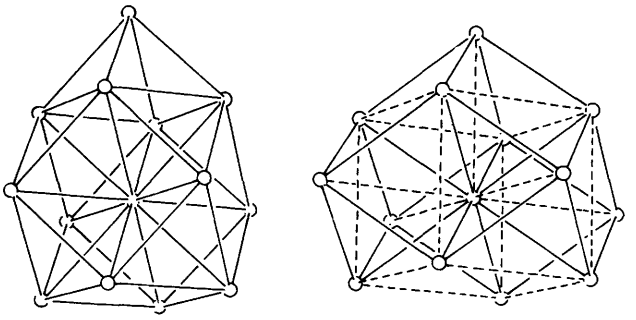


FIGURE 3 The metal-atom cluster of the anion $[Rh_{14}(CO)_{25}]^{4-}$

$[Rh_{14}H(CO)_{25}]^{3-}$ the insertion of a hydride ligand in a semi-interstitial position gives rise to a metallic array intermediate between c.c.p. and b.c.c. packings, with the central metal showing 10 short bonds. In $[Rh_{14}(CO)_{26}]^{2-}$ and in $[Rh_{15}(CO)_{27}]^{3-}$ the presence on the cluster surface of another CO group and of a $Rh(CO)_2$ capping group, respectively, determines metallic arrangements intermediate between closest packing and b.c.c. packing, with the central metal showing nine short bonds.



(A) (B)

FIGURE 4 A monocapped regular cuboctahedron [polyhedron (A)] and an incomplete regular rhombic dodecahedron [polyhedron (B)]

Another interesting feature which can be inferred by comparing these structures concerns the reactivity of $[Rh_{14}(CO)_{25}]^{4-}$ toward electrophiles. The structures of $[Rh_{14}H(CO)_{25}]^{3-}$ and $[Rh_{15}(CO)_{27}]^{3-}$ show that in reactions (1) and (2) the preferred sites of attack are the

$$[Rh_{14}(CO)_{25}]^{4-} + H^+ \longrightarrow [Rh_{14}H(CO)_{25}]^{3-} \quad (1)$$

$$[Rh_{14}(CO)_{25}]^{4-} + [Rh(CO)_2(MeCN)_2]^+ \longrightarrow [Rh_{15}(CO)_{27}]^{3-} + 2MeCN \quad (2)$$

lateral distorted square faces of the cluster (2,3,4,4′ and equivalent faces), which are relatively less crowded with ligands.

The anion $[Rh_{14}(CO)_{25}]^{4-}$ possesses 180 valence electrons, corresponding to 90 cluster valence molecular orbitals (c.v.m.o.s). This is in accord with the result of an extended-Hückel molecular orbital calculation on the bare Rh_{14} cluster,[15] like those performed by Lauher,[16] in order to establish the bonding capabilities of cluster compounds. We note that, on passing from polyhedron (A) to polyhedron (B) of Figure 4 the number of computed c.v.m.o.s decreases from 91 ($6N_{metals} + 7$) to 90 and that this decrease seems to be typically associated with a c.c.p.→b.c.c. conversion, as deduced from a number of computed examples.[17]

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