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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE NEW CLUSTER DIANION μ-IODOTETRA-μ_3-CARBONYLDI-μ-CARBONYLDECACARBONYL-*polyhedro*-HEPTARHODATE(2—) IN ITS TETRAETHYLAMMONIUM SALT

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Summary

The tetraethylammonium salt of the cluster anion $[Rh_7(CO)_{16}I]^{2-}$ crystallizes in the $P\bar{1}$ space group with cell constants a = 20.06(2), b = 11.08(1), c = 10.42(1) Å, α = 83.14(8)°, β = 96.46(8)°, γ = 102.06(8)°, Z = 2. A set of 2532 diffraction intensities, collected by counter methods, was used for resolution and refinement of the structure. The metal atom cluster consists of a monocapped octahedron similar to that found in $[Rh_7(CO)_{16}]^{3-}$. Ten of the CO ligands are coordinated terminally, two edge-bridging and four face-bridging; the iodine atom is in an edge-bridging position. Stereochemistry and bond parameters of this dianion are discussed in connection with the structure of the trianion $[Rh_7(CO)_{16}]^{3-}$ and the presence of an electron pair in a cluster antibonding orbital is demonstrated.

Introduction

Studies of rhodium carbonyl clusters are increasing the knowledge of species containing new metal atom polyhedra or new stereochemistries about clusters of known geometry. The new cluster anion $[Rh_7(CO)_{16}I]^{2-}$ can be prepared by several different routes [1], one of which is as follows:

$$[NMe_4]_3[Rh_7(CO)_{16}] + I_2 \rightarrow [NMe_4]_2[Rh_7(CO)_{16}I] + [NMe_4]I$$

This reaction implied that: (i) the metal atom cluster is very probably a monocapped octahedron similar to that found in $[Rh_7(CO)_{16}]^{3-}$ [2], (ii) the ligand insertion can be described as an electrophilic attack of the I^+ species on the cluster, and (iii) if the iodine ligand is terminally bound as in $[Rh_6(CO)_{15}I]^-$

[3], the new complex is isoelectronic with $[Rh_7(CO)_{16}]^{3-}$, fulfilling the rule that equal cluster geometries require the same number of valency electrons. Decisions on other molecular features, such as the ligand stereochemistry and the actual location of the iodine atom required a detailed structural study.

In this paper the single crystal X-ray structure determination of the new anion in the salt $[NEt_4]_2[Rh_7(CO)_{16}I]$ is described, and the structure compared with those of the anions $[Rh_6(CO)_{15}I]^-$ and $[Rh_7(CO)_{16}]^{3-}$.

Experimental

Crystal data

$C_{32}H_{40}IN_2O_{16}Rh_7$, $M = 1555.2$, triclinic, $a = 20.06(2)$, $b = 11.08(1)$, $c = 10.42(1)$ Å, $\alpha = 83.14(8)°$, $\beta = 96.46(8)°$, $\gamma = 102.06(8)°$, $U = 2237.6$ Å^3, $D_m = 2.29$ (by flotation), $Z = 2$, $D_c = 2.31$ g cm^{-3}, $F(000) = 1484$. Space group $P\bar{1}$ (C_i, No. 2). Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) 32.09 cm^{-1}.

Intensity measurements

For the collection of the diffraction data a multifaced crystal (0.12 × 0.12 × 0.22 mm) was mounted on a Pailred linear equi-inclination diffractometer and graphite monochromatized Mo-K_α radiation was used. A hemisphere was explored within the following limiting angles, $3° \leqslant \theta \leqslant 23°$ and $0° \leqslant \mu \leqslant 17.9°$, in 10 levels ($hk$0-9) of the reciprocal lattice. Reflections were monitored by the ω-scan technique within an angular interval ($\Delta\omega$) increasing, as a function of Y and μ, from 2.6° to 6.0°, at a rate of 1°/min. Background counts for 60 sec were made at both the extreme points of the scan. Some standard reflections, sampled after completion of each layer, revealed no crystal decay.

The integrated intensities were corrected for Lorentz and polarization factors (the latter including the effect of the monochromator [4]). The transmission coefficients, calculated for a large set of well-spaced reflections using the method of refs. 5 and 6, were found in the range 0.72-0.75 so that no absorption correction was applied. All intensities having $\sigma(I)/I > 0.25$ were discarded and a set of 2532 reflections was used for the structure resolution and refinement.

Determination and refinement of the structure

A three-dimensional Patterson function showed peaks compatible with the presence of a monocapped octahedron of metal atoms, and indicated a centrosymmetric arrangement of the two anions in the cell. The $P\bar{1}$ space group was therefore assumed and confirmed by successful refinement of the structure. After preliminary refinement of the metal atom parameters by least-squares, a difference map showed most of the CO ligands and two very dominant peaks in the vicinity of the metal atom cluster. These peaks were attributed to a disordered location of the iodine ligand and of a carbonyl group on two tetrahedral edges of the cluster. A refinement of the iodine parameters with fixed occupancy factor 0.5 gave significantly different thermal factors (3.7 and 6.9 Å^2), and suggested that the two locations were unevenly occupied by the I/CO couple. The disorder was therefore treated by a variable occupancy factor and the

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TABLE 1

POSITIONAL AND THERMAL PARAMETERS FOR THE ANISOTROPIC ATOMS[a,b]

Atom	x	y	z	b_{11}[c]	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Rh(1)	2918 (1)	1701 (1)	1556 (2)	21 (1)	−1 (1)	18 (1)	61 (1)	9 (3)	88 (2)
Rh(2)	2896 (1)	−9 (1)	−154 (2)	24 (1)	−1 (1)	12 (1)	48 (1)	6 (3)	105 (2)
Rh(3)	3911 (1)	2074 (1)	−136 (2)	14 (1)	0 (1)	12 (1)	74 (1)	20 (3)	102 (2)
Rh(4)	2989 (1)	3578 (1)	−478 (2)	22 (1)	7 (1)	24 (1)	55 (1)	9 (3)	92 (2)
Rh(5)	1914 (1)	1486 (1)	−528 (2)	13 (1)	−3 (1)	13 (1)	75 (1)	16 (3)	107 (2)
Rh(6)	2916 (1)	1840 (1)	−2224 (2)	22 (1)	1 (1)	15 (1)	60 (1)	2 (3)	87 (2)
Rh(7)	1869 (1)	3459 (1)	−2595 (2)	22 (1)	24 (1)	8 (1)	91 (1)	12 (3)	106 (2)
I	2420 (1)	2702 (2)	−4579 (3)	37 (1)	31 (2)	15 (3)	128 (3)	−5 (5)	117 (3)
I′	2481 (2)	5634 (4)	−1409 (5)	36 (1)	26 (4)	23 (5)	80 (4)	3 (9)	149 (6)

[a] All values X 10^4. [b] The numbers in parentheses here and in the successive tables are the estimated standard deviations on the last significant digits. [c] 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 2

POSITIONAL AND THERMAL PARAMETERS OF THE ISOTROPIC ATOMS[a]

Atom	x	y	z	B (Å^2)	Atom	x	y	z	B (Å^2)
C(1)	3676 (10)	507 (10)	1387 (22)	3.5 (4)	O(15′)	2168 (16)	2173 (29)	−4660 (29)	1.0 (4)
O(1)	4012 (7)	80 (14)	2143 (16)	4.7 (3)	C(16)	1320 (15)	4311 (28)	−3639 (34)	7.2 (7)
C(2)	2412 (11)	605 (21)	2724 (25)	4.4 (5)	O(16)	910 (12)	4626 (23)	−4295 (27)	10.0 (6)
O(2)	2084 (11)	−123 (10)	3429 (23)	8.3 (5)	N(1)	3692 (9)	−2948 (16)	−5238 (19)	4.1 (4)
C(3)	3435 (13)	2083 (24)	2714 (28)	5.7 (6)	C(17)	3246 (23)	−1897 (36)	−5447 (33)	5.5 (6)
O(3)	3818 (12)	3214 (21)	3515 (26)	9.2 (6)	C(18)	3162 (21)	−4180 (30)	−5172 (40)	5.5 (6)
C(4)	2334 (12)	−1340 (22)	687 (26)	4.6 (5)	C(19)	4091 (19)	−2823 (39)	−3927 (32)	5.5 (6)
O(4)	1907 (10)	−2161 (19)	1232 (22)	7.5 (5)	C(20)	4111 (19)	−2820 (33)	−6306 (34)	5.5 (6)
C(5)	3336 (14)	−990 (26)	−905 (30)	6.3 (6)	C(17′)	4153 (17)	−3947 (29)	−5190 (33)	3.5 (4)
O(5)	3686 (11)	−1569 (21)	−1226 (25)	9.0 (6)	C(18′)	4140 (17)	−1713 (23)	−5169 (27)	3.5 (4)
C(6)	4547 (15)	1527 (28)	−809 (33)	7.3 (7)	C(19′)	3290 (15)	−2088 (30)	−6651 (24)	3.5 (4)
O(6)	4979 (15)	1184 (27)	−1324 (33)	12.5 (9)	C(20′)	3202 (14)	−3315 (26)	−4276 (28)	3.5 (4)
C(7)	4557 (14)	3206 (25)	710 (30)	6.1 (6)	C(21)	4622 (14)	−1590 (26)	−3894 (31)	6.2 (6)
O(7)	4964 (14)	3892 (25)	1295 (31)	11.5 (8)	C(22)	4669 (15)	−3651 (28)	−6184 (33)	7.0 (7)
C(8)	2147 (9)	2904 (17)	800 (20)	2.8 (4)	C(23)	2706 (18)	−2266 (33)	−4315 (39)	9.0 (9)
O(8)	1810 (7)	3359 (14)	1395 (16)	4.9 (3)	C(24)	2729 (18)	−4256 (32)	−6659 (39)	8.9 (9)
C(9)	2119 (12)	307 (22)	−1908 (25)	4.5 (5)	N(2)	0	0	5000	5.5 (7)
O(9)	1750 (8)	−434 (15)	−2526 (18)	5.7 (4)	C(25)	647 (15)	994 (38)	4951 (45)	6.1 (6)
C(10)	3588 (10)	3639 (18)	−1928 (22)	3.2 (4)	C(26)	12 (21)	−309 (41)	6703 (30)	6.1 (6)
O(10)	3965 (7)	4265 (13)	−2518 (15)	4.2 (3)	C(27)	−103 (25)	−1023 (33)	4504 (42)	6.1 (6)
C(11)	3410 (17)	1250 (31)	−3165 (37)	8.2 (8)	C(28)	−615 (17)	750 (30)	4867 (45)	6.1 (6)
O(11)	3742 (13)	861 (24)	−3869 (20)	10.9 (7)	C(29)	−533 (19)	−1818 (35)	5448 (42)	9.9 (10)
C(12)	3453 (16)	4904 (29)	301 (35)	7.6 (8)	C(30)	638 (20)	1471 (37)	3299 (44)	10.4 (11)
O(12)	3789 (15)	5711 (28)	787 (34)	12.5 (8)	N(3)	0	5000	0	6.4 (7)
C(13)	1233 (13)	389 (25)	212 (29)	5.9 (6)	C(31)	598 (20)	5310 (56)	−845 (47)	8.1 (8)
O(13)	798 (13)	−412 (24)	576 (29)	10.9 (7)	C(32)	−83 (32)	3495 (31)	308 (54)	8.1 (8)
C(14)	1193 (11)	2351 (21)	−1561 (25)	4.6 (5)	C(33)	−660 (21)	5095 (54)	−903 (44)	8.1 (8)
O(14)	614 (9)	2161 (17)	−1560 (21)	6.9 (4)	C(34)	74 (22)	5591 (47)	1119 (43)	8.1 (8)
C(15)	2226 (15)	4634 (25)	−1335 (31)	5.1 (4)	C(35)	−679 (22)	4579 (41)	−2266 (50)	11.9 (12)
O(15)	2101 (15)	5552 (25)	−1118 (31)	5.1 (4)	C(36)	−738 (14)	3180 (26)	1324 (31)	6.6 (7)
C(15′)	2147 (16)	2404 (29)	−3619 (29)	1.0 (4)					

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[a] $x, y, z \times 10^4$.

implied carbonyl group was constrained to a fixed C—O distance, 1.15 Å. The final value of the occupancy factor was 0.637(5) for the unprimed I, C(15) and O(15) atoms (see Tables 1 and 2).

Extensive disorder was present in the two tetraethylammonium cations. One of these cations was in general positions and showed double images of the methylene groups, arranged at the vertices of a cube centered at the central nitrogen atom. Nitrogen and methyl groups were substantially ordered. The other cation had the same kind of disorder but was distributed about two crystallographic inversion centres, assuming, on average, precise C_i symmetry. As the half-weighted methylene groups oscillated during the refinement they were constrained to a rigid-body geometry and arranged at the vertices of a regular tetrahedron with a centre-to-vertex distance 1.52 Å, while the central nitrogen atoms and the methyl groups were refined individually. One average thermal factor was used for each rigid group.

The whole structure was refined by the least-squares method in the block-diagonal approximation. The function $\Sigma w(F_o - k|F_c|)^2$ was minimized until all parameter shifts became $<(1/3)\sigma$. The final values of the reliability indices were $R = 0.056$ and $R' = 0.076$, $\{R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}\}$. The thermal factor was treated anisotropically for the heavy atoms only. 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 40.0, 1.15 and 0.0003, and were chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 7; the rhodium factor was corrected for the real part of the anomalous dispersion [8].

A final difference-Fourier synthesis revealed background fluctuations in the interval ±0.9 e/Å^3. The results of the refinement are reported in Tables 1 and 2. The final list of observed and computed structure factor moduli can be obtained on application to the authors.

All calculations were performed on a UNIVAC 1106 computer.

Description of the structure and discussion

The crystal structure consists of discrete anions and cations affected by partial disorder; the crystal packing and the average structure is drawn in Fig. 1. In Fig. 2 the stronger of the two molecular images of the $[Rh_7(CO)_{16}I]^{2-}$ anion is depicted. Selected interatomic distances and angles for the compound are reported in Table 3. The metal atom polyhedron is a monocapped octahedron with idealized C_{3v} symmetry about which ten CO ligands are arranged terminally, two edge-bridging and four face-bridging. The iodine atom is bridging one of the tetrahedral edges.

Some comments are necessary for clarifying the iodine—carbonyl disorder in the anion. The halogen atom is distributed on two tetrahedral edges and the dihedral angle defined by the planes containing the iodine images is lower than that containing the carbonyl group images. These images are related by a mirror plane of the idealized C_{3v} point group of the metal atom cluster. The main cause of disorder in the anion can be found in the comparable hindrance of iodine and carbonyl group, as confirmed by other experimental findings of I/CO disorder (see, for instance, refs. 9 and 10). However, the different shapes of the two ligands and the low symmetry of the environment determine, through

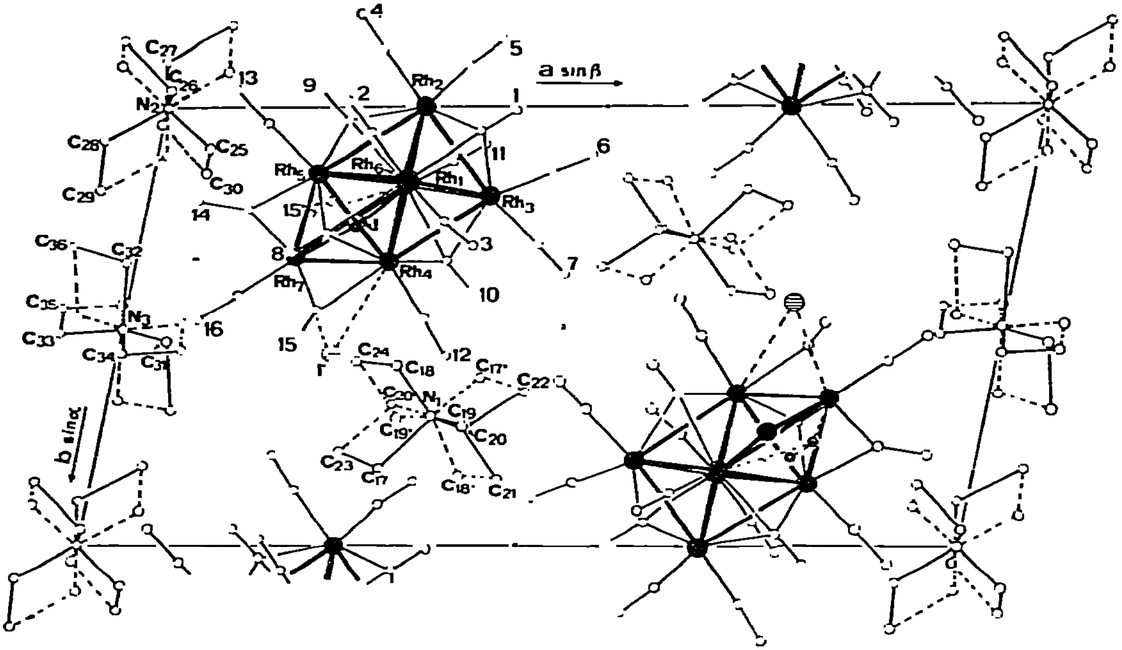

Fig. 1. Projection of the structure down the *c* axis. For clarity only the oxygen atoms of the CO groups are labelled.

small differences in Van der Waal's contacts, the uneven population of the two molecular images. On the other hand, an inspection of the inter-ionic contacts does not reveal unusually short values. The disorder in the $[NEt_4]^+$ cations is therefore essentially independent of the packing and, in fact, it has often been found in salts of this cation.

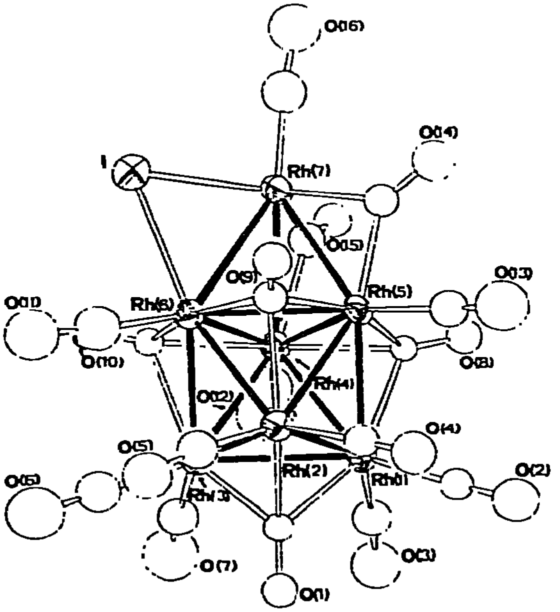

Fig. 2. Perspective ORTEP drawing of the anion.

TABLE 3

SELECTED BOND DISTANCES AND ANGLES IN $[N(C_2H_5)_4]_2[Rh_7(CO)_{16}I]$

Distances (Å)

Rh(1)—Rh(2)	2.742(5)	Rh(5)—C(8)	2.16(2)	N(1)—C(19)	1.51(4)
Rh(1)—Rh(3)	2.741(5)	Rh(2)—C(9)	2.31(3)	N(1)—C(20)	1.45(4)
Rh(2)—Rh(3)	2.740(5)	Rh(5)—C(9)	2.18(3)	N(1)—C(17′)	1.58(4)
Rh(1)—Rh(4)	2.780(5)	Rh(6)—C(9)	2.10(2)	N(1)—C(18′)	1.48(3)
Rh(1)—Rh(5)	2.788(5)	Rh(3)—C(10)	2.45(2)	N(1)—C(19′)	1.59(3)
Rh(2)—Rh(5)	2.796(5)	Rh(4)—C(10)	2.11(2)	N(1)—C(20′)	1.45(4)
Rh(2)—Rh(6)	2.789(5)	Rh(6)—C(10)	2.11(2)	C(17)—C(23)	1.65(6)
Rh(3)—Rh(4)	2.782(5)	Rh(4)—C(15)	2.09(3)	C(18)—C(24)	1.69(6)
Rh(3)—Rh(6)	2.779(5)	Rh(7)—C(15)	1.93(3)	C(19)—C(21)	1.55(4)
Rh(4)—Rh(5)	2.755(4)	Rh(6)—C(15′)	2.14(3)	C(20)—C(22)	1.58(5)
Rh(4)—Rh(6)	2.788(5)	Rh(7)—C(15′)	1.88(4)	C(17′)—C(22)	1.51(5)
Rh(5)—Rh(6)	2.760(5)	Rh(5)—C(14)	2.04(3)	C(18′)—C(21)	1.56(4)
Rh(4)—Rh(7)	2.893(5)	Rh(7)—C(14)	1.96(2)	C(19′)—C(24)	1.61(4)
Rh(5)—Rh(7)	2.886(5)	Rh(7)—C(16)	1.79(3)	C(20′)—C(23)	1.67(5)
Rh(6)—Rh(7)	3.000(5)	C(1)—O(1)	1.16(3)	N(2)—C(25)	1.52(3)
Rh(6)—I	2.684(6)	C(2)—O(2)	1.17(3)	N(2)—C(26)	1.77(3)
Rh(7)—I	2.740(6)	C(3)—O(3)	1.19(4)	N(2)—C(27)	1.27(4)
Rh(4)—I′	2.672(7)	C(4)—O(4)	1.15(3)	N(2)—C(28)	1.61(4)
Rh(7)—I′	2.823(7)	C(5)—O(5)	1.14(4)	C(25)—C(30)	1.74(6)
Rh(1)—C(1)	2.17(2)	C(6)—O(6)	1.18(5)	C(28)—C(29)	1.36(6)
Rh(2)—C(1)	2.18(2)	C(7)—O(7)	1.16(4)	N(3)—C(31)	1.53(5)
Rh(3)—C(1)	2.16(2)	C(8)—O(8)	1.19(3)	N(3)—C(32)	1.64(4)
Rh(1)—C(2)	1.84(2)	C(9)—O(9)	1.18(3)	N(3)—C(33)	1.55(4)
Rh(1)—C(3)	1.81(3)	C(10)—O(10)	1.15(2)	N(3)—C(34)	1.38(5)
Rh(2)—C(4)	1.85(2)	C(11)—O(11)	1.21(5)	C(32)—C(36)	1.68(7)
Rh(2)—C(5)	1.83(2)	C(12)—O(12)	1.14(4)	C(33)—C(35)	1.59(7)
Rh(3)—C(6)	1.80(4)	C(13)—O(13)	1.17(4)		
Rh(3)—C(7)	1.83(3)	C(14)—O(14)	1.14(3)		
Rh(4)—C(12)	1.83(3)	C(15)—O(15)	1.15		
Rh(5)—C(13)	1.80(3)	C(15′)—O(15′)	1.15		
Rh(6)—C(11)	1.73(4)	C(16)—O(16)	1.20(4)		
Rh(1)—C(8)	2.26(2)	N(1)—C(17)	1.59(5)		
Rh(4)—C(8)	2.14(2)	N(1)—C(18)	1.54(4)		

Angles (°)

Rh(1)—C(1)—O(1)	133(2)	Rh(5)—C(8)—O(8)	134(2)
Rh(2)—C(2)—O(2)	133(2)	Rh(2)—C(9)—O(9)	129(2)
Rh(3)—C(3)—O(3)	133(2)	Rh(5)—C(9)—O(9)	132(2)
Rh(1)—C(2)—O(2)	177(2)	Rh(6)—C(9)—O(9)	138(2)
Rh(1)—C(3)—O(3)	172(3)	Rh(3)—C(10)—O(10)	125(2)
Rh(2)—C(4)—O(4)	179(2)	Rh(4)—C(10)—O(10)	136(2)
Rh(2)—C(5)—O(5)	170(3)	Rh(6)—C(10)—O(10)	137(2)
Rh(3)—C(6)—O(6)	178(3)	Rh(5)—C(14)—O(14)	131(2)
Rh(3)—C(7)—O(7)	177(3)	Rh(7)—C(14)—O(14)	136(2)
Rh(4)—C(12)—O(12)	178(3)	Rh(4)—C(15)—O(15)	133(3)
Rh(5)—C(13)—O(13)	172(3)	Rh(7)—C(15)—O(15)	135(3)
Rh(6)—C(11)—O(11)	177(3)	Rh(6)—C(15′)—O(15′)	115(3)
Rh(7)—C(16)—O(16)	175(3)	Rh(7)—C(15′)—O(15′)	145(3)
Rh(1)—C(8)—O(8)	129(2)	Rh(6)—I—Rh(7)	67.1(3)
Rh(4)—C(8)—O(8)	136(2)	Rh(4)—I′—Rh(7)	63.5(3)

Although bond distances and angles are affected by these solid-state effects, the principal structural features of the anion are not obscured and the molecular structure can be discussed in terms of idealized C_s symmetry. The metal atom cluster is very similar to that found in $[Rh_7(CO)_{16}]^{3-}$; the ligand geometry is formally equal to that of the trianion as far as the tetrahedral unit is concerned, but exhibits substantial changes in the basal triangle of the octahedral moiety. The iodine atom has substituted one edge-bridging CO group which, however, remains coordinated and causes a ligand rearrangement in the basal triangle of the octahedral moiety resulting in the formation of a face-bridging group and in the transition of three other carbonyls from edge-bridging to terminal positions. The actual ligand geometry in the octahedral region is very similar to that found in $Rh_6(CO)_{16}$ [11], with four face-bridging ligands on alternating faces of the octahedron.

The Rh—Rh distances range from 2.740(5) to 3.000(5) Å, with mean values 2.77 and 2.93 Å in the octahedral and tetrahedral regions, respectively. These distances can be compared with the average value of 2.76 Å in $[Rh_7(CO)_{16}]^{3-}$ in which there are no significant differences between the two moieties. It should be noted that, while the octahedral values are strictly comparable in the two anions, the tetrahedral edges of the dianion are, on average, 0.16 Å longer than in the trianion. This bond destabilization can be ascribed to the presence of an electron pair in a low-lying antibonding orbital delocalized in the tetrahedral region of the cluster. The source of these electrons can be found in the halogen ligand, which adopts the bridging geometry in order to achieve sufficient interaction between one of its lone pairs and a cluster orbital. This effect shows the topology of the lowest unoccupied cluster orbital and is even more significant if one notes that, although the ligand rearrangement affects the octahedral moiety more than the tetrahedral one, no significant effects on the octahedral rhodium—rhodium distances are observed. The stereochemical consequences of electron pairs in antibonding molecular orbitals have been described recently by Dahl et al. (see ref. 12 and references therein); for instance, $Cp_3Ni_3(\mu_3\text{-}S)_2$ [13] and $Cp_3Ni_3(\mu_3\text{-}CO)_2$ [14] have metal—metal distances of 2.801(5) and 2.39(1) Å, respectively, the sulphide complex having an excess of two electron pairs with respect to the carbonyl complex.

The isolation of only one structural isomer from several different synthetic procedures indicates that the actual location of the halogen is thermodynamically favoured, and that the energy gain deriving from an additional iodine—rhodium bond overcomes the cost of populating an antibonding cluster orbital. The fact that in the $[Rh_6(CO)_{15}I]^-$ anion [3] the iodine atom is in terminal position indicates that the same energetic balance, is unfavourable in this case, and that the separation between the highest occupied and the lowest unoccupied cluster orbitals is very probably larger.

The Rh—I distances are not very reliable because of the iodine—carbonyl disorder; however, the bridge seems slightly but significantly asymmetric and the overall mean value of 2.73 Å is comparable with the distance of 2.71(1) Å found for the terminal iodine in $[Rh_6(CO)_{15}I]^-$. The particularly long rhodium—rhodium distance subtended by this ligand in its preferred location can be described to a size effect of the iodine and to a more pronounced localization of the populated antibonding orbital along this edge. Nevertheless the Rh(6)—Rh(7) interaction remains attractive, as suggested by the very acute value of the Rh(6)—I—Rh(7) angle, 67.1(3)°.

Ten CO ligands are arranged terminally, two edge-bridging and four face-bridging. The linear groups belong to three different classes but their bonding parameters are substantially equivalent except for the group C(11)—O(11) attached to Rh(6), to which a high percentage of iodine is also bound. Excluding this carbonyl group, the Rh—C distances are found in the range 1.79(3)-1.85(2) Å, with mean value 1.82 Å, and the C—O distances in the interval 1.14(4)-1.20(4) Å, with mean value 1.17 Å. Only one of the edge-bridging groups has been well refined and its geometry is regular. Two types of triple-bridging are present in the octahedral moiety. One is symmetrically bound to the triangle opposite to the capped face and has a mean Rh—C value of 2.17 Å; the others occupy alternate side faces and are markedly asymmetric, with Rh—C mean values 2.13 Å (six values) and 2.34 Å (three values); the higher value concerning the interactions with the metal atoms Rh(1), Rh(2) and Rh(3). The C—O mean value for the face-bridging groups is 1.17 Å.

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