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CRYSTAL AND MOLECULAR STRUCTURE OF THE ANION PHOSPHIDO-DI-μ-CARBONYLTETRADECACARBONYL HEXACOBALTATE(1 –) IN ITS TETRAPHENYLPHOSPHONIUM SALT

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Summary

The tetraphenylphosphonium salt of the anion $[Co_6P(CO)_{16}]^-$ crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions a = 10.115(4), b = 21.233(9), c = 20.585(8) Å, β = 91.76(6)°, and Z = 4. The structure has been determined by direct methods from X-ray single-crystal counter data and refined by least-squares calculations to R = 0.059 for 4698 significant diffraction intensities. The anion contains an open array of metal atoms consisting of four triangles linked in a chain sorrounding a semi-interstitial phosphide atom. The nine Co–Co bond distances fall into three classes: four have mean values of 2.574 Å, an other four have mean values of 2.656 Å, and one, very long, has a value of 2.934(2) Å. The phosphorus atom lies in an exposed position so that it is coordinated to all six metals, with Co–P bonds in the range 2.165–2.268(2) Å. Of the 16 carbonyl groups 14 are terminally bound (mean Co–C and C–O distances 1.78 and 1.14 Å) and two are symmetrically bridging (mean Co–C and C–O distances 1.90 and 1.17 Å, respectively).

Introduction

A number of carbonyl cluster compounds containing interstitial main group elements are known. In addition to a wide variety of carbide species [1], interstitial nitrides, such as $[M_6N(CO)_{15}]^-$ (M = Co, Rh) [2] and $[PtRh_{10}N(CO)_{21}]^{3-}$ [3], phosphides, such as $[Rh_9P(CO)_{21}]^{2-}$ [4] and $[Rh_{10}P(CO)_{22}]^{3-}$ [5], arsenides, such as $[Rh_{10}As(CO)_{22}]^{3-}$ [6], and sulphides, such as $[Rh_{10}S(CO)_{22}]^{2-}$ [7] and $[Rh_{17}S_2(CO)_{32}]^{3-}$ [8], have been characterized. Less common are species containing atomic ligands in semi-interstitial or exposed positions, an example being the carbide $Fe_5C(CO)_{15}$ [9].

In this paper we report the complete results of a single crystal X-ray investigation of the PPh_4^+ salt of the anion $[Co_6P(CO)_{16}]^-$; a brief account of the synthesis and

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TABLE 1 [a,b]. FINAL POSITIONAL AND THERMAL PARAMETERS WITHIN $[Co_6P(CO)_{16}][PPh_4]$

Anisotropic atoms

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Co(1)	−165(1)	2571(1)	−361(1)	103(1)	−4(1)	12(1)	19(1)	0(1)	19(1)
Co(2)	913(1)	3136(1)	842(1)	74(1)	−12(1)	−9(1)	23(1)	−4(1)	27(1)
Co(3)	−593(1)	3716(1)	8(1)	97(1)	−16(1)	−9(1)	17(1)	0(1)	28(1)
Co(4)	149(1)	1990(1)	729(1)	95(1)	4(1)	−4(1)	20(1)	0(1)	20(1)
Co(5)	−2637(1)	2965(1)	−221(1)	84(1)	−12(1)	−17(1)	20(1)	5(1)	25(1)
Co(6)	−978(1)	2711(1)	1604(1)	100(1)	10(1)	6(1)	30(1)	−2(1)	19(1)
P(1)	−1175(2)	2840(1)	558(1)	72(1)	−7(1)	−2(1)	19(1)	0(1)	18(1)
O(1)	1899(7)	3199(4)	−1050(3)	216(9)	−67(8)	87(7)	45(2)	−4(4)	42(2)
O(2)	−1376(8)	1858(4)	−1425(3)	218(11)	−18(8)	−25(8)	44(2)	−31(3)	36(2)
O(3)	3550(6)	2660(4)	605(4)	100(7)	11(8)	22(8)	53(2)	−14(5)	64(3)
O(4)	1450(8)	3798(4)	2031(4)	164(9)	−59(9)	−14(8)	80(3)	−57(4)	45(2)
O(5)	−458(10)	4429(4)	−1199(3)	315(14)	−100(10)	−40(9)	53(2)	41(3)	37(2)
O(6)	−1873(8)	4645(4)	815(4)	217(11)	27(8)	54(10)	34(2)	−29(4)	68(3)
O(7)	2280(7)	1460(4)	1557(3)	144(8)	40(7)	−42(7)	46(2)	7(4)	42(2)
O(8)	−1642(8)	917(3)	595(4)	224(10)	−71(7)	−55(8)	31(1)	9(3)	48(2)
O(9)	−2807(8)	3407(3)	−1576(3)	218(10)	−24(8)	−33(7)	39(2)	17(3)	29(1)
O(10)	−3999(8)	1763(3)	−213(4)	210(10)	−77(7)	−28(9)	33(2)	3(4)	57(2)
O(11)	−4465(7)	3765(4)	460(4)	142(8)	14(7)	32(8)	40(2)	−10(4)	61(3)
O(12)	758(9)	2216(5)	2655(4)	259(12)	99(11)	−62(8)	88(4)	10(5)	32(2)
O(13)	−2132(8)	3849(4)	2177(4)	190(9)	33(8)	45(8)	43(2)	−26(4)	48(2)
O(14)	−3131(8)	1815(4)	1674(4)	180(9)	−6(8)	80(8)	35(2)	−3(4)	68(3)
O(15)	1684(7)	1550(3)	−329(3)	228(9)	89(7)	30(7)	38(2)	−1(3)	30(1)
O(16)	1938(6)	4288(3)	321(4)	140(7)	−69(6)	−35(7)	34(1)	10(4)	61(2)
C(1)	1037(10)	2988(4)	−777(4)	159(11)	−32(9)	28(8)	29(2)	−7(4)	28(2)
C(2)	−950(9)	2147(4)	−1006(4)	147(11)	3(8)	−5(8)	25(2)	1(3)	25(2)
C(3)	2511(9)	2835(5)	704(5)	106(9)	1(9)	−4(9)	34(2)	−15(4)	38(2)
C(4)	1160(9)	3512(5)	1582(5)	107(10)	−29(10)	0(9)	49(3)	−18(5)	34(2)
C(5)	−509(10)	4147(4)	−746(4)	161(11)	−49(8)	−25(9)	27(2)	10(4)	32(2)
C(6)	−1367(9)	4288(4)	504(5)	118(9)	−13(8)	8(9)	20(2)	−7(4)	44(3)
C(7)	1463(8)	1680(4)	1224(4)	108(9)	−2(7)	−7(7)	26(2)	5(3)	27(2)
C(8)	−946(9)	1338(4)	654(4)	164(11)	−10(8)	−21(8)	21(2)	9(3)	26(2)
C(9)	−2727(9)	3245(4)	−1049(4)	124(9)	−16(8)	−18(7)	27(2)	5(3)	25(2)
C(10)	−3462(8)	2225(4)	−222(4)	123(9)	−37(7)	−31(8)	22(2)	9(3)	32(2)

[illegible]	−3762(8)	3453(4)	184(5)	95(8)	5(7)	1(9)	25(2)	3(4)	43(3)
C(12)	128(10)	2417(6)	2237(4)	148(12)	40(12)	−1(9)	57(4)	−9(5)	25(2)
C(13)	−1675(9)	3410(5)	1941(4)	118(10)	−9(9)	13(8)	42(3)	−12(4)	28(2)
C(14)	−2286(9)	2161(4)	1650(4)	113(9)	4(8)	16(8)	29(2)	−1(4)	35(2)
C(15)	920(8)	1884(4)	−94(4)	122(9)	30(7)	7(7)	24(2)	−7(3)	27(2)
C(16)	1109(9)	3908(4)	368(4)	113(9)	−18(7)	−14(8)	19(2)	−7(4)	37(2)
P(2)	4207(2)	4623(1)	2907(1)	67(1)	0(1)	2(1)	19(1)	3(1)	24(1)

Isotropic atoms

Phenyl carbon atoms

Atom	x	y	z	$B(\mathring{A}^2)$
Cp(11)	4357(9)	3785(2)	2840(2)	4.0(1)
Cp(12)	4199(7)	3410(2)	3387(2)	5.8(2)
Cp(13)	4258(7)	2758(2)	3335(2)	6.6(2)
Cp(14)	4477(9)	2479(2)	2735(2)	7.5(2)
Cp(15)	4635(7)	2854(2)	2188(2)	6.9(2)
Cp(16)	4576(7)	3506(2)	2240(2)	5.3(2)
Cp(21)	4772(6)	5006(3)	2194(2)	3.9(1)
Cp(22)	5929(5)	5361(2)	2228(2)	5.0(1)
Cp(23)	6392(5)	5650(3)	1672(2)	6.4(2)
Cp(24)	5698(6)	5583(3)	1082(2)	5.8(2)
Cp(25)	4541(5)	5228(2)	1048(2)	5.2(2)
Cp(26)	4078(5)	4940(3)	1604(2)	4.6(1)
Cp(31)	2526(4)	4844(3)	3019(2)	3.6(1)
Cp(32)	2015(4)	5384(2)	2722(2)	4.5(1)
Cp(33)	691(5)	5542(2)	2791(3)	5.5(2)
Cp(34)	−120(4)	5160(3)	3157(2)	6.1(2)
Cp(35)	390(4)	4620(2)	3454(2)	6.5(2)
Cp(36)	1713(5)	4462(2)	3385(3)	5.4(2)
Cp(41)	5212(5)	4867(2)	3590(2)	3.6(1)
Cp(42)	4886(4)	5402(2)	3941(2)	5.0(1)
Cp(43)	5709(5)	5603(2)	4455(2)	6.1(2)
Cp(44)	6856(5)	5269(2)	4617(2)	5.9(2)
Cp(45)	7181(4)	4734(2)	4265(2)	5.2(2)
Cp(46)	6359(5)	4533(2)	3751(2)	4.7(1)

Phenyl hydrogen atoms

Atom	x	y	z	$B(\mathring{A}^2)$
H(12)	4042	3611	3818	5.8
H(13)	4145	2489	3728	6.6
H(14)	4520	2010	2698	7.5
H(15)	4793	2654	1758	6.9
H(16)	4690	3776	1848	5.3
H(22)	6428	5410	2653	5.0
H(23)	7224	5905	1697	6.4
H(24)	6031	5791	683	5.8
H(25)	4042	5181	624	5.2
H(26)	3247	4685	1580	4.6
H(32)	2599	5659	2460	4.5
H(33)	324	5931	2578	5.5
H(34)	−1071	5275	3206	6.1
H(35)	−192	4346	3717	6.5
H(36)	2081	4074	3599	5.4
H(42)	4063	5643	3826	5.0
H(43)	5476	5988	4709	6.1
H(44)	7447	5414	4986	5.9
H(45)	8006	4495	4382	5.2
H(46)	6593	4150	3499	4.7

[a] All parameters $\times 10^4$ except for the isotropic B factors. [b] The b_{ij} are the coefficients of $\exp-(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})$.

structure appeared previously [10]. The anion contains a phosphide ligand, bound to an open hexametal array, in a semi-interstitial position, intermediate between the situation for an external bridging phosphide ligand, as for instance in $[Co(\eta^5\text{-}C_5H_5)(\mu_3\text{-}P)]_4$ [11], and that for a completely encapsulated phosphorus atom.

Experimental

Crystal data. $C_{40}H_{20}Co_6O_{16}P_2$, $M = 1172.1$, Monoclinic, $a = 10.115(4)$, $b = 21.233(9)$, $c = 20.585(8)$ Å, $\beta = 91.76(6)°$, $U = 4420.2$ Å^3, $D_m = 1.73(2)$ (by flotation), $D_c = 1.76$ g cm^{-3}, $Z = 4$, $F(000) = 2320$, Space Group $P2_1/c$ (No. 14), Mo-K_α radiation (λ 0.7107 Å), μ(Mo-K_α) = 23.4 cm^{-1}.

Intensity measurements. A crystal of dimensions $0.17 \times 0.18 \times 0.34$ mm was mounted on the BASIC automatic diffractometer [12]. Diffraction intensities were collected in the range $3° < \theta < 25°$ by the ω-scan method, using graphite monochromatized Mo-K_α radiation. A total of 8570 reflections was measured and no decay of the sample was observed during the collection. The intensities were corrected for Lorentz and polarization effects but not for absorption. After rejection of all data having $\sigma(I)/I > 0.40$, a set of 4698 significant data was used in the structure solution and refinement.

Structure solution and refinement. The structure was solved by direct methods, which gave the metal atoms positions. After a preliminary refinement a successive difference-Fourier map showed the positions of all the non-hydrogen atoms.

The refinements were carried out by block-matrix least-squares. All the anionic atoms and the P atom of the cation were treated anisotropically. The phenyl groups of the cation were treated as rigid groups (D_{6h} symmetry, C–C 1.392 Å). The phenyl hydrogen atoms were located in their ideal positions (C–H 1.08 Å) with an isotropic thermal factor equal to that of the corresponding carbon atom. The final values of the conventional R and R_w factors are 0.059 and 0.065, respectively.

During the refinements weights were applied according to the formula $w = 1/(A + BF_0 + CF_0^2)$; in the final cycles A, B and C had values 19.5, -0.43 and 0.0072, respectively, chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 13 for Co, P, O and C and from ref. 14 for hydrogen. For Co and P both the real and imaginary part of the anomalous scattering were taken into account [15]. The final difference-Fourier map was flat, showing residual peaks not exceeding 0.6 e/Å^3.

The results of the refinements are reported in Table 1. A final list of observed and calculated structure factors moduli can be obtained on application to the authors. All the computations were performed on a UNIVAC 1100/80 computer using local programs.

Results and discussion

The crystal structure consists of discrete $[Co_6P(CO)_{16}]^-$ anions and PPh_4^+ cations in the ratio 1/1, separated by normal Van der Waals' contact distances.

The anion is illustrated in Fig. 1. It exhibits an overall idealized C_2 symmetry, with the two-fold axis passing through the P atom and the middle of the Co(1)–Co(2) edge. It contains a six-metal array consisting of a chain of four edge-sharing triangles surrounding a "semi-interstitial" phosphorus atom. The Co_6P moiety is

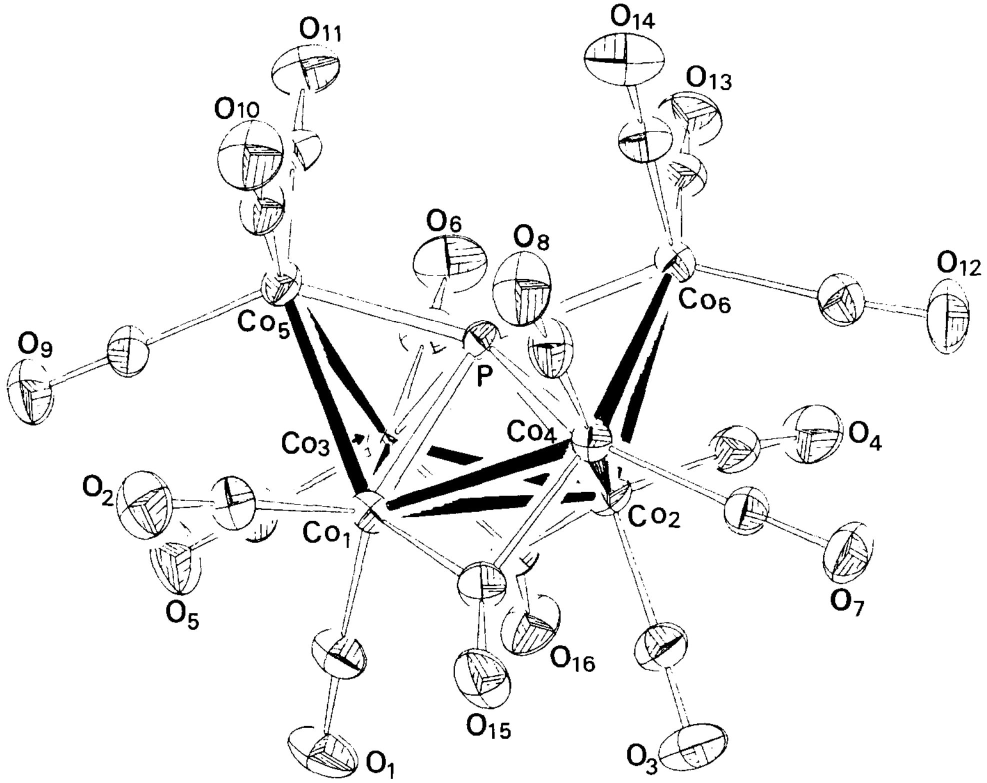


Fig. 1. A view of the anion $[Co_6P(CO)_{16}]^-$. The carbonyl groups are indicated by the labels of their oxygen atoms.

shown in Fig. 2. The four cobalt triangles are folded with the following dihedral angles: 143.3° between planes Co(1,2,3) and Co(1,2,4), 122.9° between planes Co(1,2,3) and Co(1,3,5), and 122.0° between planes Co(1,2,4) and Co(2,4,6).

The Co–Co interactions can be divided into three classes. There is a very long and weakly-bonding interaction, the Co(1)–Co(2) edge of 2.934(2) Å, and the other eight bonds belong to two sets of four, a longer set, involving the external Co(5) and Co(6) atoms, with a mean value of 2.656 Å, and a shorter set, involving the other Co atoms, of mean value 2.574 Å. A long Co–Co interaction comparable to the Co(1)–Co(2) one was previously found in the paramagnetic species $[Co_6C(CO)_{14}]^-$, 2.916(4) Å, the lengthening being ascribed in that case to the presence of one extra electron (exceeding the usual number of 86) in an antibonding cluster orbital [16]. The other Co–Co bond lengths are, on the other hand, comparable with the corresponding values found in many cobalt carbonyl clusters.

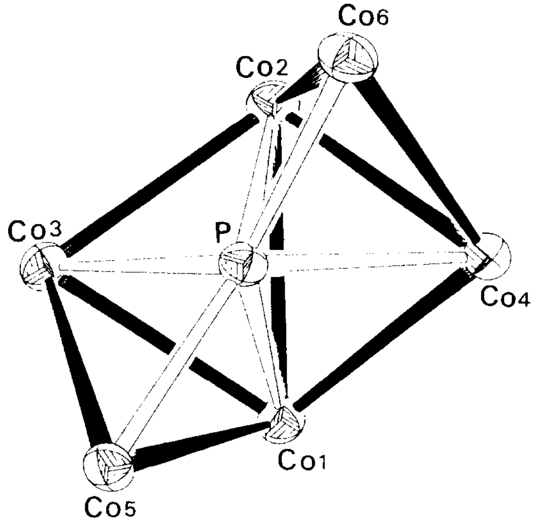
Of the sixteen CO groups fourteen are terminal and two symmetric edge-bridging. The cobalt atoms Co(5) and Co(6) bear three terminal carbonyl groups whereas each of the other metal atoms is connected to one edge-bridging and to two terminal CO groups. The mean values of the Co–C and C–O interactions are 1.78 and 1.14 Å, respectively, for the terminal and 1.90 and 1.17 Å, respectively, for the bridging groups.

The phosphide ligand is bound to all the six cobalt atoms, in such a way that it can be considered a "semi-interstitial" ligand, as indicated also by the Co(5)–P–Co(6) angle of 142.2(1)°. The Co–P bonds belong to two classes: two bonds, with the Co(5) and Co(6) atoms, are significantly shorter (mean 2.170 Å) than the other four (mean 2.263 Å). These bond lengths are comparable with the corresponding Co–P interactions in $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ (mean 2.244 Å) [17] and in $[Co(\eta^5\text{-}C_5H_5)(\mu_3\text{-}P)]_4$ (two sets of mean values 2.216 and 2.256 Å) [11].

The situation of the exposed phosphorus atom in $[Co_6P(CO)_{16}]^-$ is intermediate between that of an external bridging P atom, as in $[Co(\eta^5\text{-}C_5H_5)(\mu_3\text{-}P)]_4$, and that of an interstitial atom, as in $[Rh_9P(CO)_{21}]^{2-}$ [4] and in $[Rh_{10}P(CO)_{22}]^{3-}$ [5]. This is the only known example of a semi-interstitial location for an element of the third period, but analogous exposed positions are known for C and N atoms; for example, in the square pyramidal species $Fe_5C(CO)_{15}$ [9] and $HFe_5N(CO)_{14}$ [18] and in the butterfly species $Fe_4C(CO)_{13}$ [19] and $[Fe_4N(CO)_{12}]^-$ [20]. These exposed atoms are also of interest in respect of their unusual reactivities [21,22].

The present hexametal array is uncommon and a rather similar cluster has been found only in the recently characterized species $Co_6(\mu_4\text{-}S)(C_2)(CO)_{14}$ [23], containing a Co_4 square with two opposite edges bridged by two cobalt atoms; the metal arrangement surrounds an exposed dicarbide group.

The cluster geometry of $[Co_6P(CO)_{16}]^-$ can be rationalized considering the dimensions of the cobalt and phosphorus atoms. Using a covalent radius of 1.10 Å for P and assuming a reasonable radius of 1.28 Å for Co, the radius ratio r_P/r_{Co} results equal to 0.860, which, in the light of the theoretical values reported in Table 3, shows that a phosphide atom cannot occupy the cavity of an octahedron or of a regular trigonal prism of cobalt atoms. The known compounds with these types of clusters show that the cluster cages possess a certain elasticity which enables them



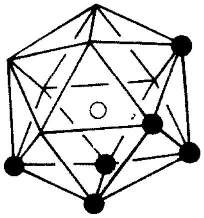


Fig. 2. A view of the Co_6P moiety approximately down the idealized two-fold axis.

Fig. 3. The relationship between the Co_6 array and the icosahedron.

TABLE 2

BOND DISTANCES AND ANGLES WITHIN THE SALT $[Co_6P(CO)_{16}][PPh_4]$

Distances (Å)

Co(1)–Co(2)	2.934(2)	Co(5)–C(9)	1.806(9)
Co(1)–Co(3)	2.587(2)	Co(5)–C(10)	1.779(9)
Co(1)–Co(4)	2.573(1)	Co(5)–C(11)	1.768(10)
Co(1)–Co(5)	2.661(2)	Co(6)–C(12)	1.803(11)
Co(2)–Co(3)	2.574(2)	Co(6)–C(13)	1.793(11)
Co(2)–Co(4)	2.562(1)	Co(6)–C(14)	1.769(10)
Co(2)–Co(6)	2.670(2)	C(1)–O(1)	1.143(13)
Co(3)–Co(5)	2.642(2)	C(2)–O(2)	1.132(12)
Co(4)–Co(6)	2.650(2)	C(3)–O(3)	1.139(12)
Co(1)–P(1)	2.253(2)	C(4)–O(4)	1.136(14)
Co(2)–P(1)	2.265(2)	C(5)–O(5)	1.110(13)
Co(3)–P(1)	2.265(2)	C(6)–O(6)	1.124(13)
Co(4)–P(1)	2.268(2)	C(7)–O(7)	1.154(11)
Co(5)–P(1)	2.165(2)	C(8)–O(8)	1.142(12)
Co(6)–P(1)	2.175(2)	C(9)–O(9)	1.139(11)
Co(1)–C(1)	1.749(10)	C(10)–O(10)	1.122(12)
Co(1)–C(2)	1.772(9)	C(11)–O(11)	1.137(13)
Co(1)–C(15)	1.898(9)	C(12)–O(12)	1.137(14)
Co(2)–C(3)	1.770(10)	C(13)–O(13)	1.153(14)
Co(2)–C(4)	1.731(11)	C(14)–O(14)	1.130(13)
Co(2)–C(16)	1.920(9)	C(15)–O(15)	1.164(12)
Co(3)–C(5)	1.807(10)	C(16)–O(16)	1.170(11)
Co(3)–C(6)	1.785(10)	P(2)–Cp(11)	1.791(5)
Co(3)–C(16)	1.899(9)	P(2)–Cp(21)	1.786(6)
Co(4)–C(7)	1.778(9)	P(2)–Cp(31)	1.786(5)
Co(4)–C(8)	1.777(10)	P(2)–Cp(41)	1.786(6)
Co(4)–C(15)	1.902(9)		

Angles (deg.)

Co(1)–C(1)–O(1)	172.4(9)	Co(1)–Co(2)–C(3)	92.0(3)
Co(1)–C(2)–O(2)	175.7(9)	Co(1)–Co(2)–C(4)	166.4(3)
Co(2)–C(3)–O(3)	177.7(10)	Co(2)–Co(1)–C(1)	87.7(3)
Co(2)–C(4)–O(4)	171.2(10)	Co(2)–Co(1)–C(2)	170.9(3)
Co(3)–C(5)–O(5)	177.8(9)	C(1)–Co(1)–C(2)	101.1(4)
Co(3)–C(6)–O(6)	179.0(9)	C(3)–Co(2)–C(4)	101.5(5)
Co(4)–C(7)–O(7)	177.1(8)	C(5)–Co(3)–C(6)	100.4(5)
Co(4)–C(8)–O(8)	178.7(9)	C(7)–Co(4)–C(8)	102.4(4)
Co(5)–C(9)–O(9)	178.0(9)	C(9)–Co(5)–C(10)	106.2(4)
Co(5)–C(10)–O(10)	178.6(9)	C(9)–Co(5)–C(11)	103.8(4)
Co(5)–C(11)–O(11)	178.1(9)	C(10)–Co(5)–C(11)	102.1(4)
Co(6)–C(12)–O(12)	175.7(10)	C(12)–Co(6)–C(13)	104.5(5)
Co(6)–C(13)–O(13)	177.7(9)	C(12)–Co(6)–C(14)	100.5(5)
Co(6)–C(14)–O(14)	179.1(9)	C(13)–Co(6)–C(14)	102.9(5)
Co(1)–C(15)–O(15)	137.2(7)	Cp(11)–P(2)–Cp(21)	111.1(3)
Co(4)–C(15)–O(15)	137.5(7)	Cp(11)–P(2)–Cp(31)	110.7(4)
Co(2)–C(16)–O(16)	135.7(8)	Cp(11)–P(2)–Cp(41)	107.6(3)
Co(3)–C(16)–O(16)	139.4(8)	Cp(21)–P(2)–Cp(31)	108.5(3)
Co(1)–C(15)–Co(4)	85.3(4)	Cp(21)–P(2)–Cp(41)	109.0(3)
Co(2)–C(16)–Co(3)	84.8(4)	Cp(31)–P(2)–Cp(41)	110.0(3)
Co(5)–P(1)–Co(6)	142.2(1)		

TABLE 3

THE MORE USUAL CAVITIES IN CLUSTER COMPOUNDS SUITABLE TO CONTAIN INTERSTITIAL ATOMS

Type of cavity	Number of metals defining the cavity	r_{int}/r_{met}	Some examples in the cobalt subgroup	
			Co	Rh
Octahedron	6	0.414	$[Co_6C(CO)_{14}]^-$ [a]	$[Rh_6C(CO)_{13}]^{2-}$ [b]
Trigonal prism	6	0.528	$[Co_6N(CO)_{15}]^-$ [c]	$[Rh_6C(CO)_{15}]^{2-}$ [d]
Square antiprism	8	0.646	$[Co_8C(CO)_{18}]^{2-}$ [e]	$[Rh_9P(CO)_{21}]^{2-}$ [f] $[Rh_{10}S(CO)_{22}]^{2-}$ [g]
Cube	8	0.732	–	–
Icosahedron	12	0.902	–	$[Rh_{12}Sb(CO)_{27}]^{3-}$ [h]
Cuboctahedron or Twinned-cuboctahedron	12	1.000	–	$[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ [i]

[a] Ref. 16. [b] V.G. Albano, D. Braga and S. Martinengo, J. Chem. Soc. Dalton, (1981) 717. [c] Ref. 2. [d] V.G. Albano, M. Sansoni, P. Chini and S. Martinengo, J. Chem. Soc. Dalton, (1973) 651. [e] V.G. Albano, P. Chini, G. Ciani, S. Martinengo and M. Sansoni, J. Chem. Soc. Dalton, (1978) 463. [f] Ref. 4. [g] Ref. 7. [h] Ref. 24. [i] G. Ciani, A. Sironi and S. Martinengo, J. Chem. Soc. Dalton, (1981) 519.

to accomodate interstitial atoms, but there are limits which cannot be exceeded. The actual Co_6 open array can be considered part of the surface of a larger polyhedron, namely an icosahedron, as illustrated in Fig. 3, in accord also with the value of the radius ratio r_P/r_{Co}. A comparable radius ratio can be expected for Sb and Rh atoms, and a recently characterized species, the anion $[Rh_{12}Sb(CO)_{27}]^{3-}$, contains an almost icosahedral arrangement of Rh atoms with an encapsulated Sb atom [24].

Finally, the anion possesses 92 valence electrons, corresponding to 46 cluster valence molecular orbitals (CVMOs). This number is higher than in an octahedron (43 CVMOs) or in a trigonal prism (45 CVMOs), in accord with a progressive loss of compactness in these three clusters.

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