New Carbide Clusters in the Cobalt Sub-group. Part 6.[1-5] Crystallographic Characterization of the Tetramethylammonium Salt of the Paramagnetic Anion Carbidohexa-μ-carbonyl-octacarbonyl-*polyhedro*-hexacobaltate(1−)

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The title complex crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions a = 12.17(1), b = 13.28(1), c = 8.67(1) Å, α = 97.78(8)°, β = 89.93(8)°, γ = 98.93(8)°, and Z = 2. The structure has been solved from X-ray single-crystal counter data and refined by least-squares calculations to R = 0.07 for 1 689 significant diffraction intensities. The $[Co_6C(CO)_{14}]^-$ paramagnetic anion contains 87 valence electrons and the metal atom cluster is a distorted octahedron of C_{2v} idealized symmetry. The Co–Co distances are in the range 2.53—2.92 Å, indicating the antibonding character of the extra electron. The carbide atom is located in the cluster cavity with average Co–C distance 1.90 Å. The carbonyl ligands are bonded edge-bridging (six) and terminally (eight), and conform to the cluster symmetry. The uneven lengthenings of the Co–Co interactions and the ligand stereochemistry give evidence that the unpaired electron is essentially located outside the cluster in front of the longest Co–Co edge.

THE anion $[Co_6C(CO)_{14}]^-$ is the first example of a paramagnetic octahedral cluster[6] and contains 87 valence electrons, one more than expected. Its structure is of great interest because it shows the striking stereochemical effects of the one electron exceeding the ' magic ' number.

This complex is best prepared by simple stoicheiometric oxidation of the prismatic dianion $[Co_6C(CO)_{15}]^{2-}$ [reaction (1), thf = tetrahydrofuran]. This new reaction shows a difference between cobalt and rhodium, because the anion $[Rh_6C(CO)_{15}]^{2-}$, under similar conditions, is oxidized to rhodium(I) derivatives which, in certain solvents such as water, give addition products on the fraction still unreacted.[2-4]

$$[Co_6C(CO)_{15}]^{2-} + FeCl_3 \xrightarrow[25\,^{\circ}C,\ N_2]{thf} [Co_6C(CO)_{14}]^- + FeCl_2 + CO + Cl^- \quad (1)$$

We report here a detailed structural analysis of the anion. A preliminary communication on the structure and on other syntheses has already been reported;[6] more detailed accounts on the synthesis and chemical behaviour will be published elsewhere.[7]

EXPERIMENTAL

Crystal Data.—$C_{19}H_{12}Co_6NO_{14}$, M = 831.7, Triclinic, a = 12.17(1), b = 13.28(1), c = 8.67(1) Å, α = 97.78(8), β = 89.93(8), γ = 98.23(8)°, U = 1 373.8 Å^3, D_m = 1.98 g cm^{-3}, Z = 2, D_c = 2.01 g cm^{-3}, $F(000)$ = 814, space group $P\bar{1}$ (no. 2), Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 37.4 cm^{-1}.

Intensity Measurements.—A crystal with dimensions 0.03 × 0.17 × 0.42 mm was mounted on a Philips PAILRED diffractometer. Nine levels of the reciprocal lattice, hk0—8, were explored within the sphere $3 < \theta < 23°$. 4 230 Reflection intensities were collected with the ω-scan method at a scan rate of 1° min^{-1}. The backgrounds were counted for 1 min at both extremes of the scan range. During the data collection a 7% decrease of some standard reflections was observed. The integrated intensities were reduced to F_o values by correction for Lorentz, polarization, decay, and absorption effects. The transmission factors were found in the range 0.57—0.89. A final set of 1 689 reflections was obtained after removing all those with $I < 4\sigma(I)$.

Determination of the Structure.—The structure was solved by conventional Fourier methods and refined by least-squares to R 0.071 and R' 0.085. The block-diagonal approximation was used with 9 × 9 blocks for the cobalt atoms, for which the thermal motion was treated anisotropically, and 4 × 4 blocks for the light atoms. The hydrogen atoms of the tetramethylammonium cation were placed in their expected positions but not refined. The observations were weighted according to the formula $w = 1/(28 - 0.4F_o + 0.004F_o^2)$ where the coefficients of the polynomial were chosen on the basis of an analysis of $\Sigma w\Delta^2$. The atomic scattering factors were taken from ref. 8 for cobalt, oxygen, nitrogen, and carbon, and from ref. 9 for hydrogen. All the computations were carried out on a UNIVAC 1108 computer at the computing centre of Milan University, using local programs.

Final atom positions are reported in Table 1 and bond distances and angles in Table 2. Observed and computed structure factors and thermal parameters are given in Supplementary Publication No. SUP 22601 (9 pp.).†

DISCUSSION

The crystal contains discrete anions $[Co_6C(CO)_{14}]^-$ whose stereochemistry is illustrated in Figure 1. The metal-atom cluster is a distorted octahedron with the carbide atom allocated in the cavity. The carbonyl ligands are co-ordinated linearly (eight) and edge-bridging (six). Atoms Co(1) and Co(3) bear two terminal ligands and the others only one. The bridging ligands span all the edges having either Co(2) or Co(4) at one

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

corner. The molecule conforms, with slight deviations due to packing effects, to C_{2v} symmetry and the two-fold axis bisects the edges Co(2)–Co(4) and Co(1)–Co(3).

According to idealized C_{2v} symmetry the cluster edges fall into the following non-equivalent sets of increasing length: (*i*) six bridged edges with mean value 2.533(3) Å; (*ii*) edge Co(1)–Co(3) 2.663(4) Å; (*iii*) four unbridged edges with mean length 2.770(3) Å; and (*iv*) Co(2)–Co(4) 2.916(4) Å. All these edges and their average, 2.66 Å, are longer than the values found in other cobalt clusters: 2.51 Å in $[Co_6(CO)_{15}]^{2-}$ (ref. 10), 2.50 Å in $[Co_6(CO)_{14}]^{4-}$ (ref. 11), and 2.52 Å in $[Co_8C(CO)_{18}]^{2-}$ (ref. 5).

The Co–C(carbide) distances are of two types with mean values 1.85 and 1.93 Å, the longer values being the distances from Co(2) and Co(4). The calculated radius of carbon in this species is 0.56 Å. This value, in spite of the cluster deformation, is only slightly smaller than the values found in other octahedral cavities: 0.57 Å in $[Fe_5C(CO)_{15}]$ (ref. 12) and $[Fe_6C(CO)_{16}]^{2-}$ (ref. 13), 0.60 Å in $[Ru_6C(CO)_{17}]$ (ref. 14), $[Ru_6C(CO)_{14}(C_9H_{12})]$ (ref. 15), and $[Rh_{15}(C)_2(CO)_{28}]^-$ (ref. 3).

TABLE 1

Final positional parameters (× 10^4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co(1)	2 693(2)	1 279(2)	−1 849(3)
Co(2)	2 676(2)	1 093(2)	1 031(3)
Co(3)	3 038(2)	3 323(2)	−1 309(3)
Co(4)	3 070(2)	3 366(2)	1 624(3)
Co(5)	1 378(2)	2 289(2)	285(3)
Co(6)	4 366(2)	2 233(2)	219(3)
C(0)	2 856(15)	2 260(14)	−108(22)
C(1)	1 518(18)	1 062(16)	−3 121(25)
O(1)	824(16)	995(15)	−4 056(24)
C(2)	3 770(20)	1 053(18)	−3 170(29)
O(2)	4 438(16)	933(15)	−4 094(24)
C(3)	2 530(21)	262(19)	2 365(31)
O(3)	2 421(15)	−270(14)	3 340(22)
C(4)	1 971(18)	3 645(17)	−2 409(27)
O(4)	1 274(17)	3 849(15)	−3 203(25)
C(5)	4 231(18)	3 596(16)	−2 477(26)
O(5)	4 983(15)	3 709(13)	−3 287(21)
C(6)	3 246(21)	4 054(19)	3 441(31)
O(6)	3 353(15)	4 572(14)	4 651(22)
C(7)	118(20)	2 336(18)	−571(29)
O(7)	−756(17)	2 340(16)	−1 145(25)
C(8)	5 660(18)	2 196(16)	−684(26)
O(8)	6 470(15)	2 130(13)	−1 305(21)
C(9)	2 503(20)	79(18)	−895(28)
O(9)	2 365(14)	−824(13)	−1 101(21)
C(10)	3 172(19)	4 517(17)	267(28)
O(10)	3 335(16)	5 415(14)	544(23)
C(11)	970(17)	1 178(15)	1 311(25)
O(11)	282(14)	680(13)	1 868(21)
C(12)	4 362(17)	1 130(15)	1 268(25)
O(12)	4 915(14)	631(13)	1 885(20)
C(13)	1 414(20)	3 341(18)	1 880(28)
O(13)	887(15)	3 830(14)	2 732(22)
C(14)	4 770(18)	3 279(16)	1 804(26)
O(14)	5 484(14)	3 765(13)	2 575(21)
N	−1 974(14)	2 823(12)	4 546(20)
C(15)	−3 097(24)	2 183(22)	4 614(35)
C(16)	−1 094(22)	2 131(19)	4 496(31)
C(17)	−1 925(23)	3 297(21)	3 076(34)
C(18)	−1 810(31)	3 551(28)	6 068(46)
H(151)	−3 735	2 673	4 650
H(152)	−3 223	1 612	3 595
H(153)	−3 133	1 808	5 647
H(161)	−286	2 583	4 447
H(162)	−1 138	1 756	5 529
H(163)	−1 227	1 560	3 477
H(171)	−1 125	3 759	3 008
H(172)	−2 043	2 699	2 090
H(173)	−2 571	3 776	3 070
H(181)	−1 012	4 027	6 073
H(182)	−2 460	4 030	6 178
H(183)	−1 841	3 110	7 031

TABLE 2

Bond distances and carbon–carbon contacts (Å), and relevant angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Co(1)–Co(2)	2.543(4)	C(6)–O(6)	1.17(3)
Co(1)–Co(3)	2.663(4)	C(7)–O(7)	1.18(3)
Co(1)–Co(5)	2.779(4)	C(8)–O(8)	1.13(3)
Co(1)–Co(6)	2.760(4)	C(9)–O(9)	1.18(3)
Co(2)–Co(4)	2.916(4)	C(10)–O(10)	1.17(3)
Co(2)–Co(5)	2.537(4)	C(11)–O(11)	1.14(3)
Co(2)–Co(6)	2.532(4)	C(12)–O(12)	1.18(3)
Co(3)–Co(4)	2.537(4)	C(13)–O(13)	1.17(3)
Co(3)–Co(5)	2.755(4)	C(14)–O(14)	1.16(3)
Co(3)–Co(6)	2.767(4)	N–C(15)	1.51(3)
Co(4)–Co(5)	2.519(4)	N–C(16)	1.51(3)
Co(4)–Co(6)	2.533(4)	N–C(17)	1.49(4)
Co(1)–C(0)	1.85(2)	N–C(18)	1.52(4)
Co(2)–C(0)	1.93(2)	C(1) ··· C(2)	2.74(3)
Co(3)–C(0)	1.85(2)	C(1) ··· C(4)	3.37(3)
Co(4)–C(0)	1.94(2)	C(1) ··· C(7)	3.23(3)
Co(5)–C(0)	1.84(2)	C(1) ··· C(9)	2.83(3)
Co(6)–C(0)	1.87(2)	C(2) ··· C(5)	3.32(3)
Co(1)–C(1)	1.77(2)	C(2) ··· C(8)	3.22(3)
Co(1)–C(2)	1.77(2)	C(2) ··· C(9)	2.84(4)
Co(1)–C(9)	1.88(3)	C(3) ··· C(6)	4.95(4)
Co(2)–C(9)	1.99(2)	C(3) ··· C(9)	2.80(3)
Co(2)–C(3)	1.70(3)	C(3) ··· C(11)	2.62(4)
Co(2)–C(11)	2.11(2)	C(3) ··· C(12)	2.60(3)
Co(2)–C(12)	2.05(2)	C(4) ··· C(5)	2.76(3)
Co(3)–C(4)	1.75(2)	C(4) ··· C(7)	3.20(3)
Co(3)–C(5)	1.79(2)	C(4) ··· C(10)	2.77(3)
Co(3)–C(10)	1.94(2)	C(5) ··· C(8)	3.25(4)
Co(4)–C(6)	1.71(2)	C(5) ··· C(10)	2.91(3)
Co(4)–C(10)	2.04(2)	C(6) ··· C(10)	2.90(4)
Co(4)–C(13)	2.02(2)	C(6) ··· C(13)	2.60(3)
Co(4)–C(14)	2.10(2)	C(6) ··· C(14)	2.58(4)
Co(5)–C(7)	1.72(3)	C(7) ··· C(11)	2.69(4)
Co(5)–C(11)	1.83(2)	C(7) ··· C(13)	2.72(3)
Co(5)–C(13)	1.82(2)	C(8) ··· C(12)	2.71(3)
Co(6)–C(8)	1.76(2)	C(8) ··· C(14)	2.74(3)
Co(6)–C(12)	1.83(2)	C(9) ··· C(11)	3.05(3)
Co(6)–C(14)	1.83(2)	C(9) ··· C(12)	3.00(3)
C(1)–O(1)	1.16(3)	C(10) ··· C(13)	2.93(3)
C(2)–O(2)	1.15(3)	C(10) ··· C(14)	3.13(4)
C(3)–O(3)	1.17(3)	C(11) ··· C(12)	4.14(3)
C(4)–O(4)	1.18(3)	C(13) ··· C(14)	4.06(4)
C(5)–O(5)	1.16(3)		

(*b*) Angles

Co(1)–C(0)–Co(3)	92.1(9)	Co(3)–C(10)–O(10)	147(2)
Co(2)–C(0)–Co(4)	99.6(9)	Co(4)–C(10)–O(10)	133(2)
Co(1)–C(0)–Co(2)	84.5(8)	Co(2)–C(11)–O(11)	132(2)
Co(3)–C(0)–Co(4)	83.8(8)	Co(5)–C(11)–O(11)	148(2)
Co(5)–C(0)–Co(6)	160.5(12)	Co(2)–C(12)–O(12)	133(2)
Co(1)–C(1)–O(1)	172(2)	Co(6)–C(12)–O(12)	145(2)
Co(1)–C(2)–O(2)	176(2)	Co(4)–C(13)–O(13)	133(2)
Co(2)–C(3)–O(3)	177(2)	Co(5)–C(13)–O(13)	146(2)
Co(3)–C(4)–O(4)	177(2)	Co(4)–C(14)–O(14)	133(2)
Co(3)–C(5)–O(5)	176(2)	Co(6)–C(14)–O(14)	147(2)
Co(4)–C(6)–O(6)	176(2)	Co(1)–C(9)–O(9)	141(2)
Co(5)–C(7)–O(7)	178(2)	Co(2)–C(9)–O(9)	135(2)
Co(6)–C(8)–O(8)	177(2)	Co(3)–C(10)–O(10)	145(2)
Co(1)–C(9)–O(9)	145(2)	Co(4)–C(10)–O(10)	133(2)
Co(2)–C(9)–O(9)	132(2)		

The non-equivalence of the terminal CO groups is evident only for the Co–C distances. These have a mean value of 1.70 Å for the groups bonded to Co(2) and Co(4) and 1.76 Å for the others. The bridging groups are all asymmetric with Co–C distances of 1.85 and 2.05 Å. The C–O values are not significantly different for terminal and bridging groups, their mean value being 1.16 Å.

The particular features of this anion, *i.e.* the lengthening of the Co–Co interactions and the low molecular symmetry, give evidence of the antibonding character of the 87th valence electron. The bond lengthening is detectable in all the octahedron edges and is a maximum for Co(2)–Co(4), which is some 0.4 Å longer than the normal value. Such a distortion has never been observed in octahedral clusters with 86 valence electrons, including the carbido-derivatives $[Ru_6C(CO)_{17}]$ (ref. 14), $[Ru_6C(CO)_{14}(C_9H_{12})]$ (ref. 15), and $[Fe_6C(CO)_{16}]^{2-}$ (ref. 13). In particular the clusters with fourteen ligands, $[Co_6(CO)_{14}]^{4-}$ (ref. 11) and $[Co_4Ni_2(CO)_{14}]^{2-}$ (ref. 16) have idealized O_h symmetry. One could imagine that in the hypothetical $[Co_6C(CO)_{14}]$ the first unoccupied orbitals are degenerate. As a consequence the insertion of the one electron in this energy level would produce a Jahn–Teller deformation of the cluster in order to remove the orbital degeneracy. A recent study by Lauher [17] on the bonding in the rhodium clusters confirms this view showing that, in the octahedral Rh_6C cluster, the first unoccupied level has t_{1u} symmetry. The new ligand arrangement conforms to the lower cluster symmetry.

Another interesting stereochemical feature shows that the preferred location of the antibonding electron is just outside the metal-atom cluster, in front of the Co(2)–Co(4) edge. The experimental position of the terminal CO ligands bonded to Co(2) and Co(4) should be in the equatorial symmetry plane with the carbon atoms about 3.3 Å apart (dotted lines in Figure 2), the normal van der Waals contact between carbon atoms linked to different metal atoms. In fact this is the value observed for the terminal ligands bound to Co(1) and Co(3). The actual C(3) · · · C(6) contact is 4.9 Å, while the contacts of these atoms with the neighbouring bridging ligands are in the range 2.6—2.9 Å. It is evident that the electron present in front of the Co(2)–Co(4) edge repels C(3) and C(6) and these atoms, in their turn, push away the bridging ligands so that they are all asymmetric in the same direction, the longer distances being those from Co(2) and Co(4). Another way of looking at the ligand asymmetry is that these bridging carbonyls are strongly associated with the metal–metal bonds,[18] and thus they are affected by the antibonding orbital localized around Co(2) and Co(4).

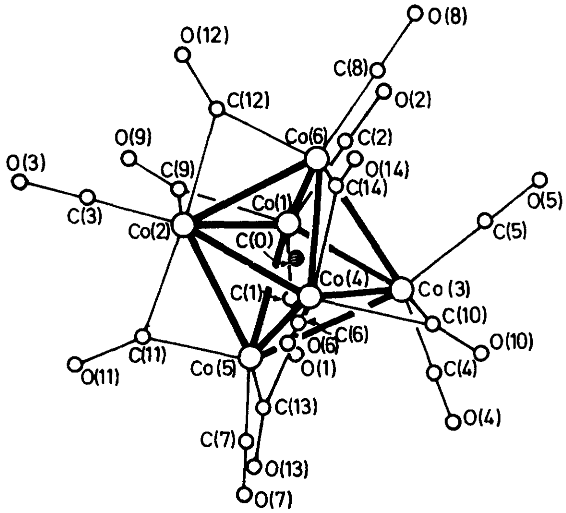

FIGURE 1 View of the anion $[Co_6C(CO)_{14}]^-$

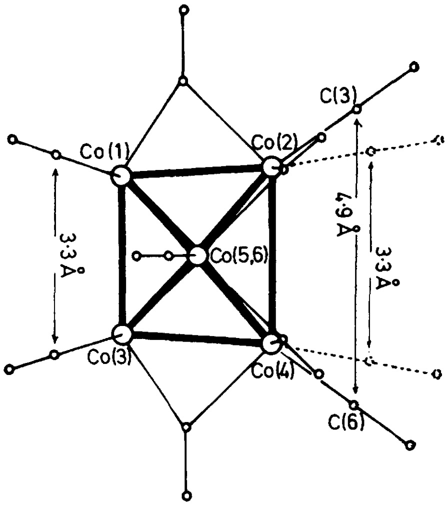

FIGURE 2 Schematic projection of the anion in the idealized symmetry plane containing the elongated edge. The expected positions of the terminal ligands bonded to Co(2) and Co(4) are represented by dotted lines

The charge localization in the vicinity of the Co(2)–Co(4) edge is also in agreement with the already cited shorter values of the Co(2)–C(3) and Co(4)–C(6) interactions, explicable in terms of stronger π back-bonding that helps in dispersing the charge, and thus increases the repulsion between these terminal ligands.

In carbonyl chemistry this cluster represents the first example of a paramagnetic species. Undoubtedly the additional bonds from the central carbide play a crucial role in stabilizing this particular electronic configuration. Therefore this species provides further evidence for the belief that interstitial carbides can stabilize unusual structures.[19]

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