New Carbide Clusters in the Cobalt Subgroup. Part 16.[1] Preparation and Structural Characterization of μ_6-Carbido-penta-μ-carbonyl-octacarbonyl-*octahedro*-hexacobaltate(2−) as its Tetraethylammonium Salt ‡

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The new anion $[Co_6C(CO)_{13}]^{2-}$ has been prepared by refluxing a solution of $[Co_6C(CO)_{15}]^{2-}$ in tetrahydrofuran under nitrogen; the loss of CO causes rearrangement of the metal cluster from trigonal prismatic to octahedral; the reaction is reversible, and on simple exposure to CO the starting anion is regenerated. The new anion has been characterized by single-crystal *X*-ray diffraction on the salt $[NEt_4]_2[Co_6C(CO)_{13}]$ which crystallizes in the monoclinic space group C_2, with cell constants a = 20.750(2), b = 11.470(2), c = 16.097(2) Å, β = 91.968(3)°, and Z = 4. The structure has been solved from 6 066 reflections, collected by counter methods and refined by least-squares calculations to R = 0.0295. The dianion possesses idealized C_2 symmetry and contains a distorted octahedron of cobalt atoms, whose cavity is occupied by the carbide atom. Five carbonyl ligands are bridging on opposite edges of the three octahedron equators, and eight are terminal. The dianion is not isostructural with the isoelectronic congener $[Rh_6C(CO)_{13}]^{2-}$, thus showing a new way of arranging 13 CO ligands on an octahedral core of metal atoms.

We have already reported that on pyrolysis of the $[Co_6C(CO)_{15}]^{2-}$ anion[2] in bis(2-methoxyethyl) ether at 140 °C or at reflux a mixture of high-nuclearity species is formed, among which the anions $[Co_{11}C_2(CO)_{22}]^{3-}$ and $[Co_{13}C_2(CO)_{24}]^{4-}$ were isolated.[3,4] However, under these drastic conditions, all the intermediate steps of the pyrolysis were lost. Since we are interested in these intermediate species to clarify the mechanism of cluster growth, and we had previously found that on pyrolysis of the trigonal-prismatic anion $[Rh_6C(CO)_{15}]^{2-}$ (ref. 5) the first product formed was the octahedral anion $[Rh_6C(CO)_{13}]^{2-}$,[6] we reinvestigated the behaviour of $[Co_6C(CO)_{15}]^{2-}$ under milder conditions to search for a similar species. We have now isolated, and we report here, the new octahedral anion $[Co_6C(CO)_{13}]^{2-}$, which is isoelectronic, but not isostructural, with the rhodium analogue.

Results and Discussion

Synthesis and Chemical Characterization of the Anion $[Co_6C(CO)_{13}]^{2-}$.—The anion $[Co_6C(CO)_{13}]^{2-}$ is prepared by heating $[Co_6C(CO)_{15}]^{2-}$ at reflux under nitrogen in tetrahydrofuran (thf) solution according to reaction (1). The

$$[Co_6C(CO)_{15}]^{2-} \longrightarrow [Co_6C(CO)_{13}]^{2-} + 2\,CO \quad (1)$$

decarbonylation is complete in 1—2 h, and the product is isolated by precipitation with propan-2-ol. Crystals of the $[NEt_4]^+$ salt suitable for *X*-ray analysis can be obtained from thf–propan-2-ol by the slow diffusion technique. Solutions of the brown $[Co_6C(CO)_{13}]^{2-}$ anion are immediately oxidized in air, while crystals are stable for a few hours. The i.r. spectrum of the $[NEt_4]^+$ salt in thf solution shows bands at 2 020vw, 1 963vs, 1 938m (sh), and 1 804m cm^{-1} (Figure 1).

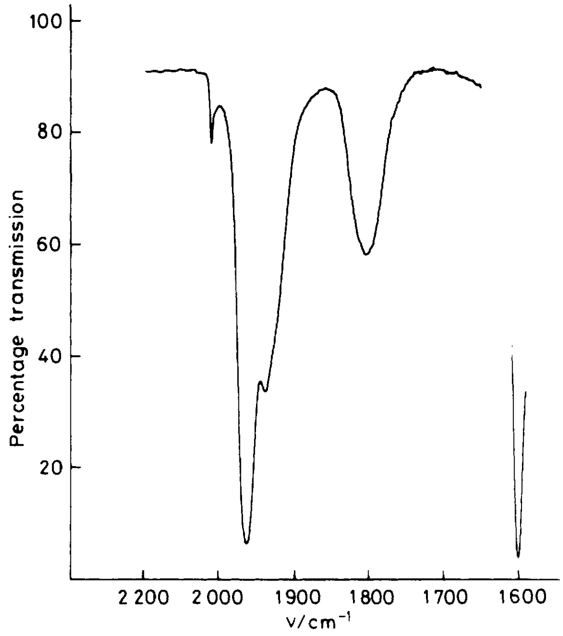

Figure 1. The i.r. spectrum of $[NEt_4]_2[Co_6C(CO)_{13}]$ in thf solution

Similarly to the rhodium analogue, the $[Co_6C(CO)_{13}]^{2-}$ anion takes up immediately carbon monoxide according to the reverse of reaction (1), thus regenerating the starting trigonal-prismatic anion; this reaction is best performed using CO diluted with nitrogen, in order to slow down the subsequent decomposition of $[Co_6C(CO)_{15}]^{2-}$.[2]

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* For correspondence on structural characterization.

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‡ *Supplementary data available* (No. SUP 56458, 12 pp.): H-atom co-ordinates, thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Co(1)–Co(3)	2.884(1)	Co(6)–C(01)	1.859(4)	Co(6)–C(8)	1.758(5)	N(1)–C(16)	1.508(5)
Co(1)–Co(4)	2.481(1)	Co(1)–C(1)	1.757(4)	Co(6)–C(11)	1.985(4)	N(1)–C(18)	1.534(6)
Co(1)–Co(5)	2.505(1)	Co(1)–C(9)	1.884(4)	C(1)–O(1)	1.136(5)	N(1)–C(20)	1.498(6)
Co(1)–Co(6)	2.648(1)	Co(1)–C(10)	1.908(4)	C(2)–O(2)	1.121(6)	C(14)–C(15)	1.509(6)
Co(2)–Co(3)	2.466(1)	Co(2)–C(2)	1.756(4)	C(3)–O(3)	1.142(5)	C(16)–C(17)	1.520(7)
Co(2)–Co(4)	2.926(1)	Co(2)–C(11)	1.877(4)	C(4)–O(4)	1.156(5)	C(18)–C(19)	1.481(7)
Co(2)–Co(5)	2.714(1)	Co(2)–C(12)	1.886(4)	C(5)–O(5)	1.159(5)	C(20)–C(21)	1.529(7)
Co(2)–Co(6)	2.498(1)	Co(3)–C(3)	1.748(3)	C(6)–O(6)	1.156(5)	N(2)–C(22)	1.484(7)
Co(3)–Co(4)	2.465(1)	Co(3)–C(12)	1.970(4)	C(7)–O(7)	1.108(6)	N(2)–C(24)	1.536(8)
Co(3)–Co(6)	2.746(1)	Co(3)–C(13)	1.879(4)	C(8)–O(8)	1.125(7)	C(22)–C(23)	1.508(9)
Co(4)–Co(5)	2.671(1)	Co(4)–C(4)	1.739(4)	C(9)–O(9)	1.151(5)	C(24)–C(25)	1.470(1)
Co(5)–Co(6)	2.659(1)	Co(4)–C(9)	1.987(4)	C(10)–O(10)	1.165(5)	N(3)–C(26)	1.500(5)
Co(1)–C(01)	1.878(4)	Co(4)–C(13)	1.909(4)	C(11)–O(11)	1.173(5)	N(3)–C(28)	1.510(5)
Co(2)–C(01)	1.876(4)	Co(5)–C(5)	1.757(4)	C(12)–O(12)	1.161(5)	C(26)–C(27)	1.499(8)
Co(3)–C(01)	1.869(3)	Co(5)–C(7)	1.791(4)	C(13)–O(13)	1.188(5)	C(28)–C(29)	1.530(7)
Co(4)–C(01)	1.865(4)	Co(5)–C(10)	1.992(4)	N(1)–C(14)	1.496(5)	Co(4) · · · C(5)	2.764(4)
Co(5)–C(01)	1.855(3)	Co(6)–C(6)	1.757(4)				

Co(1)–C(1)–O(1)	176.4(5)	Co(5)–C(7)–O(7)	176.5(4)	Co(6)–C(11)–O(11)	138.3(4)
Co(2)–C(2)–O(2)	176.9(3)	Co(6)–C(8)–O(8)	176.1(3)	Co(2)–C(11)–O(11)	141.2(4)
Co(3)–C(3)–O(3)	179.2(4)	Co(4)–C(9)–O(9)	136.1(4)	Co(3)–C(12)–O(12)	136.6(3)
Co(4)–C(4)–O(4)	175.0(4)	Co(1)–C(9)–O(9)	144.2(4)	Co(2)–C(12)–O(12)	143.9(4)
Co(5)–C(5)–O(5)	172.7(4)	Co(5)–C(10)–O(10)	136.2(4)	Co(4)–C(13)–O(13)	138.1(4)
Co(6)–C(6)–O(6)	173.7(5)	Co(1)–C(10)–O(10)	143.8(4)	Co(3)–C(13)–O(13)	140.8(4)

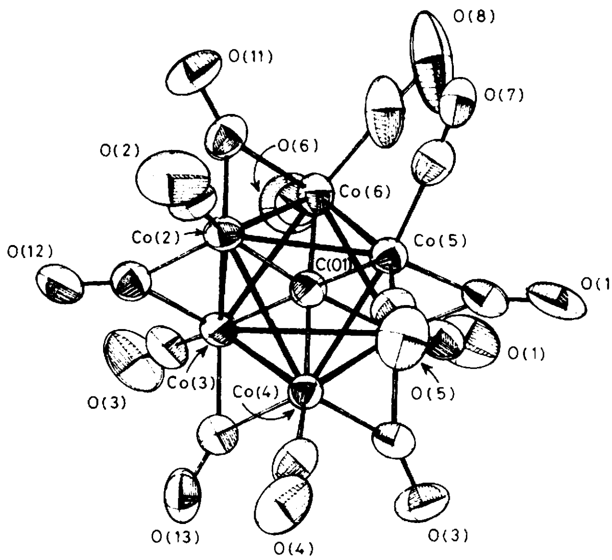

Figure 2. The structure of the dianion $[Co_6C(CO)_{13}]^{2-}$ showing 50% probability thermal ellipsoids. Carbon atoms of the CO groups bear the same numbering as the O atoms. The idealised two-fold axis passes through C(13)–O(13) and the mid-point of the Co(5)–Co(6) bond

Structural Characterization of the Anion $[Co_6C(CO)_{13}]^{2-}$.—The crystal consists of $[Co_6C(CO)_{13}]^{2-}$ anions and $[NEt_4]^+$ cations; the independent part of the unit cell contains one anion and two cations. One cation is in general position [N(1)] and adopts a conformation of S_4 idealized symmetry. Two further cations, of half occupancy located around two-fold symmetry axes at 0,*y*,0 [N(2)] and 0,*y*,0.5 [N(3)] form the remaining independent $[NEt_4]^+$ cation. The latter cations show D_{2d} idealized symmetry and their S_4 axes are coincident with the C_2 space group operations.

The crystal is dissymmetric (space group C_2) because the anion $[Co_6C(CO)_{13}]^{2-}$ adopts a chiral geometry of C_2 idealized symmetry and molecules of the same chirality have preferred to pack together in the same crystal. This is not the first case in which chiral cluster compounds have been characterized but they had always been found to give racemic crystals; as in the case of $[Rh_8C(CO)_{19}]$ with C_1 point symmetry,[7] $[Co_8C(CO)_{18}]^{2-}$ (D_2),[8] and $[Co_{13}C_2(CO)_{24}]^{4-}$ (C_2).[4] The anion consists of a Co_6C core arranged in a distorted octahedron of metal atoms with the carbide atom in the cavity. Of the 13 carbonyl ligands five are bonded in edge-bridging position and eight linearly. The bridged edges are on opposite sides of the octahedron equators and the edges of two opposite triangular faces are free of ligands. Therefore if these faces are taken as basal (see Figure 2), the bridging ligands are found on five out of the six inter-basal edges. The cobalt atoms connected by the unbridged inter-basal edge [Co(5) and Co(6)] bear two terminal ligands and the idealized two-fold axis bisects this edge.

The Co–Co interactions are distinctly different for bridged and unbridged edges (see Table 1). The bridged edges are shorter and in the range 2.465(1)—2.505(1), average 2.483(1) Å. The unbridged edges show longer and more scattered values in the range 2.648(1)—2.926(1), average 2.750(1) Å. While the former set of values are within the expected range for cobalt clusters, the latter are significantly longer than normal. The longest edge is comparable only to the value found in the paramagnetic species $[Co_6C(CO)_{14}]^-$, 2.916(4) Å.[9] The same effect has been detected not only in the congener anion $[Rh_6C(CO)_{13}]^{2-}$, but also in other isoelectronic hexanuclear species with a low ligand-to-metal ratio such as $[Ni_6(CO)_{12}]^{2-}$ (ref. 10) and $[Pt_6(CO)_{12}]^{2-}$,[11] confirming that the bonding mechanism of the bridging CO groups strengthens the spanned metal–metal interactions.

The Co–C(carbide) distances are found to be in the range 1.86(1)—1.88(1), average 1.87(1) Å. The apparent radius of carbon turns out to be 0.55 Å, almost equal to the value of 0.56 Å found in $[Co_6C(CO)_{14}]^-$ (ref. 9) and shorter than that in $[Rh_6C(CO)_{13}]^{2-}$, 0.60 Å.[6] These values cannot be considered true bond radii because they depend on the value chosen for the metal radius, *i.e.* one half of the average metal–metal bond in the compound under consideration. The cobalt–carbonyl interactions Co–C and C–O average 1.76, 1.14, and 1.93, 1.17 Å, for terminal and bridging ligands, respectively. A feature of interest

Table 2. Fractional atomic co-ordinates

Atom	x	y	z	Atom	x	y	z
Co(1)	0.309 76(2)	0.620 56	0.824 97(3)	O(10)	0.348 5(2)	0.691 2(4)	0.994 1(2)
Co(2)	0.409 49(2)	0.369 96(6)	0.752 47(3)	C(11)	0.355 9(2)	0.251 5(4)	0.791 7(3)
Co(3)	0.328 74(2)	0.488 48(6)	0.675 18(3)	O(11)	0.351 8(2)	0.149 6(3)	0.794 6(2)
Co(4)	0.407 44(2)	0.624 43(6)	0.739 76(3)	C(12)	0.386 5(2)	0.363 7(4)	0.638 3(2)
Co(5)	0.405 49(2)	0.514 30(6)	0.885 84(3)	O(12)	0.396 7(2)	0.316 3(3)	0.576 3(2)
Co(6)	0.306 16(3)	0.389 78(6)	0.827 00(3)	C(13)	0.371 2(2)	0.617 1(4)	0.629 5(3)
C(01)	0.361 6(1)	0.500 5(4)	0.784 2(2)	O(13)	0.374 7(2)	0.669 4(3)	0.566 1(2)
C(1)	0.229 7(2)	0.664 2(4)	0.839 8(3)	N(1)	0.326 1(1)	0.493 0(3)	0.331 6(2)
O(1)	0.177 0(2)	0.687 4(4)	0.847 2(3)	C(14)	0.372 7(2)	0.509 8(5)	0.403 2(3)
C(2)	0.485 1(2)	0.301 4(4)	0.760 9(3)	C(15)	0.437 8(2)	0.452 4(5)	0.397 6(3)
O(2)	0.533 2(2)	0.257 7(4)	0.768 8(3)	C(16)	0.261 2(2)	0.542 0(4)	0.353 0(3)
C(3)	0.265 4(2)	0.478 0(4)	0.601 5(2)	C(17)	0.262 4(3)	0.668 9(5)	0.380 1(4)
O(3)	0.223 5(2)	0.471 4(4)	0.554 2(2)	C(18)	0.315 9(2)	0.362 8(4)	0.313 9(3)
C(4)	0.476 1(2)	0.700 7(4)	0.712 7(3)	C(19)	0.296 1(3)	0.290 0(4)	0.384 7(4)
O(4)	0.522 6(2)	0.744 9(3)	0.690 6(3)	C(20)	0.354 0(3)	0.548 2(5)	0.256 3(3)
C(5)	0.481 6(2)	0.580 7(4)	0.881 7(3)	C(21)	0.310 2(3)	0.546 5(7)	0.173 2(3)
O(5)	0.532 7(2)	0.621 2(4)	0.887 9(3)	N(2)	0.0	−0.013 5(4)	0.0
C(6)	0.227 2(2)	0.392 3(4)	0.784 5(3)	C(22)	0.000 2(4)	−0.087 6(6)	−0.075 6(4)
O(6)	0.173 5(2)	0.389 8(4)	0.763 4(3)	C(23)	0.009 1(4)	−0.024 4(8)	−0.156 6(4)
C(7)	0.417 2(2)	0.427 9(4)	0.977 7(3)	C(24)	−0.059 4(4)	0.066 4(6)	−0.006 2(4)
O(7)	0.425 1(2)	0.369 9(4)	1.032 1(2)	C(25)	−0.121 0(4)	0.003 3(10)	−0.013 2(5)
C(8)	0.288 6(2)	0.337 1(6)	0.926 4(3)	N(3)	0.0	1.016 91(41)	0.5
O(8)	0.276 2(2)	0.308 6(7)	0.990 8(3)	C(26)	0.045 9(2)	0.940 1(5)	0.454 9(3)
C(9)	0.349 2(2)	0.750 7(4)	0.776 3(2)	C(27)	0.094 8(2)	1.000 2(7)	0.403 3(4)
O(9)	0.345 5(2)	0.850 0(3)	0.766 9(2)	C(28)	−0.036 0(2)	1.097 5(4)	0.440 7(3)
C(10)	0.349 7(2)	0.637 9(4)	0.932 6(3)	C(29)	−0.074 2(3)	1.036 9(6)	0.370 3(4)

in this molecule is that it is not isostructural with the isoelectronic anion $[Rh_6C(CO)_{13}]^{2-}$ in which the ligands adopt an achiral arrangement with C_s idealized symmetry. The ligand geometry in $[Co_6C(CO)_{13}]^{2-}$ can be more usefully compared to that in the dianions $[M_6(CO)_{12}]^{2-}$ (M = Ni or Pt) in order to demonstrate that the bridging ligands are located on the interbasal edges in the former and on the basal ones in latter pair.

The ligand arrangement adopted in $[Co_6C(CO)_{13}]^{2-}$ is characterized by three-co-ordination of each of the cobalt atoms. In $[Rh_6C(CO)_{13}]^{2-}$, in contrast, the number of rhodium–carbonyl interactions was unevenly distributed and a uniform distribution of electrons was achieved through asymmetric interactions of the bridging ligands and incipient bending of some terminal groups. In the cobalt species the ligand distribution can be considered more regular but the ligand-to-metal electron donation is surely unbalanced because Co(5) and Co(6), which bear two terminal ligands, are richer in electrons than the other metal atoms. In fact a compensation mechanism is set up through a system of asymmetric bridging ligands which conveys charge on atoms Co(1) and Co(2). Atoms Co(3) and Co(4) seem to remain deficient of electrons but some localization of anionic charge could help in equalizing the number of electrons around each cobalt atom. The present work confirms our previous considerations[6] that the ligand stereogeometry is mainly controlled by the need for an even distribution of the electrons provided to the metal core when repulsive inter-ligand interactions are not at work.

Experimental

General.—The experimental conditions were as reported in a previous paper.[2] The starting anion $[Co_6C(CO)_{15}]^{2-}$ was prepared as already described.[2]

Synthesis of $[NEt_4]_2[Co_6C(CO)_{13}]$.—$[NEt_4]_2[Co_6C(CO)_{15}]$ (0.18 g) in thf (6 cm^3) under nitrogen was refluxed while stirring in an oil-bath at 80 °C until the i.r. bands of the starting dianion were replaced by those of Figure 1 (1.5—2 h was required). During the reaction the colour changed from reddish to brown. The resulting solution was concentrated in vacuum to *ca.* 4 cm^3, filtered, and carefully layered with propan-2-ol (25 cm^3) to give, after some days, when the diffusion of the solvents was complete, the product as well formed crystals which were filtered off, washed with propan-2-ol and vacuum dried. Yields were 70—80% (Found: C, 35.95; H, 3.90; N, 2.80. Calc. for $C_{30}H_{40}Co_6N_2O_{13}$: C, 36.4; H, 4.05; N, 2.85%). The bis(triphenylphosphine)iminium salt was prepared in a similar way.

Crystallography.—Crystal data. $C_{30}H_{40}Co_6N_2O_{13}$, M = 990.3, monoclinic, a = 20.750(2), b = 11.470(2), c = 16.097(2) Å, β = 91.968(3)°, U = 3 829.4 Å^3, Z = 4, D_c = 1.72 g cm^{-3}, $F(000)$ = 2 000, possible space groups C_2 (no. 5), C_m (no. 8), or $C2/m$ (no. 12), Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 86.3 cm^{-1}.

A suitable crystal of dimensions 0.5 × 0.2 × 0.03 mm was mounted on an Enraf-Nonius CAD4 diffractometer. The crystal was sealed in a Lindeman glass capillary to prevent decomposition. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 well centred high-angle (θ) reflections. Diffraction intensities were measured, at room temperature, in the range $2 < \theta < 27°$ by the ω–2θ scan method, with scan interval $(0.7 + 0.35 \tan\theta)°$, a pre-scan speed of 10° min^{-1} and pre-scan acceptance $\sigma(I)/I < 0.3$. Reflections that did not match the acceptance condition were considered weak; the others were measured to a desired $\sigma(I)/I = 0.02$ for a maximum time of 100 s. 6 472 Intensities were collected in the octants $\pm h$, $\pm k$, $+l$, 6 066 of which $[I_o > 2.5\sigma(I_o)]$ were used in the structure solution.

Structure solution and refinement. The integrated intensities were reduced to F_o values, an empirical absorption correction was applied by azimuthal scanning of 12 reflections $[\chi > 80°]$, with relative transmission factors in the range 0.69—1.0. For all computations the SHELX package of crystallographic programs was used.[12] The structure was solved by combined use of Patterson and direct methods. The Patterson map revealed that the most probable space group was C_2 and its choice was confirmed by successful refinement of the structure. After locating the six cobalt atoms all the light-atom positions were determined by difference-Fourier syntheses. All atoms were allowed to vibrate anisotropically. Hydrogen atoms were added in calculated positions and not refined. In the least-squares calculations the observations were weighted according to the formula $w = K/[\sigma^2(F) + |g|*F^2]$, where both K and g were refined (1.0 and 0.0016, respectively). As a full set of intensity data had been collected the determination of the absolute configuration was attempted. The final agreement indices for the correct enantiomer were $R = 0.0295$ and $R' = 0.0326$, those for the inverted structure model were $R = 0.032$ and $R' = 0.036$. A final difference-Fourier map showed residual peaks of less than 1 e Å^{-3} in proximity to the metal atoms. The final atom co-ordinates of all refined atoms are reported in Table 2.

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