New Carbide Clusters in the Cobalt Sub-group. Part 9.[1-8] Preparation and Crystallographic Characterization of Dicarbidododeca-μ-carbonyl-dodecacarbonyl-*polyhedro*-tridecacobaltate(4−) as its Tetrakis(benzyltrimethylammonium) Salt $[N(CH_2Ph)Me_3]_4[Co_{13}C_2(CO)_{24}]\cdot Me_2CO$

By **Vincenzo G. Albano** * and **Dario Braga**, Istituto Chimico ' G. Ciamician ' della Università, via F. Selmi 2, 40126 Bologna, Italy
(the late) **Paolo Chini** and **Gianfranco Ciani**, Istituto di Chimica Generale e Inorganica della Università, 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, via G. Venezian 21, 20133 Milano, Italy

The title complex has been prepared by refluxing the dianion $[Co_6C(CO)_{15}]^{2-}$ in diglyme under nitrogen for 8 h. The crystal structure of this new species has been determined in the salt $[N(CH_2Ph)Me_3]_4[Co_{13}C_2(CO)_{24}]\cdot Me_2CO$. It crystallizes in the monoclinic space group $P2_1/c$ with cell constants a = 14.057(7), b = 20.24(1), c = 30.66(1) Å, β = 113.06(5)°, and Z = 4. The structure has been solved from 4 234 X-ray single-crystal diffraction intensities, collected by counter methods, and refined by least-squares calculations down to R = 0.082. The tetra-anion is paramagnetic and contains a $Co_{13}C_2$ cluster in which the metal atoms are arranged in such a way as to form two prismatic cavities in which two isolated carbon atoms are encapsulated. Average bond distances are Co–Co 2.57, Co–C(carbide) 1.98 Å. The CO ligands are terminal (12) and edge-bridging (12) and conform to the idealized cluster symmetry C_2. The unusual cluster geometry found in this species is a compromise between contrasting tendencies of the metal atoms towards close-packed polyhedra and the carbon atoms towards prismatic interstices.

WHEN located in the interstices of metal-atom polyhedra, carbon and other main-group atoms not only act as inner ligands contributing their valence electrons to the cluster orbitals, but are also able to stabilize high nuclearity polyhedra which are quite different from those found in homonuclear clusters. This happens since, although carbon has been found in trigonal-prismatic, octahedral, and tetragonal-antiprismatic cavities, it exhibits a strong preference for the prismatic cavity. As a consequence, polyhedra which reach a compromise between the tendency to close packing, to maximize the metal–metal interactions, and the steric requirements of the interstitial atoms are favoured.

The crystal structures of the carbido-carbonyl clusters of cobalt illustrate well the factors governing the cluster geometry. The two known hexanuclear species $[Co_6C(CO)_{15}]^{2-}$ (ref. 9) and $[Co_6C(CO)_{14}]^{-}$ (ref. 6) contain prismatic and octahedral clusters respectively, but, while the prismatic cavity is regular, the octahedral one is swollen by the presence of an extra electron occupying an antibonding cluster orbital in order to make the cavity big enough for the interstitial carbon. This fact is confirmed by the somewhat opposite situation found in the dianion $[Co_8C(CO)_{18}]^{2-}$ in which a tetragonal-antiprismatic cavity is present.[5] This cavity is wider than necessary and a deformation takes place in order to reduce it to the ideal size.

More recently the pyrolysis of the prismatic dianion $[Co_6C(CO)_{15}]^{2-}$ has afforded two new species, $[Co_{11}C_2(CO)_{22}]^{3-}$ (ref. 8) and $[Co_{13}C_2(CO)_{24}]^{4-}$, which are further examples of the peculiar steric effects of the interstitial carbon atoms. In these anions, two new metal-atom polyhedra have been discovered. The $Co_{11}C_2$ unit contains two bonded carbon atoms [C–C 1.62(5) Å] and a composite cavity consisting of a tetragonal antiprism and a trigonal prism sharing a face, similar to that found in $[Rh_{12}C_2(CO)_{25}]$.[4]

The preparation and structure of the tetra-anion $[Co_{13}C_2(CO)_{24}]^{4-}$ are described in this paper. This compound had been previously tentatively formulated as a monohydride since its e.s.r. spectrum at room temperature had not revealed unpaired electrons. The actual stereogeometry did not rule out this possibility and showed a possible hydrogen location. However, in spite of many attempts, it has not been possible to substantiate experimentally the presence of such a hydrogen atom. This induced us to reinvestigate the magnetic behaviour and it has now been found that at low temperature (123 K) an intense symmetric signal appears in the e.s.r. spectrum of the powdered sample at g = 2.13 (peak-to-peak linewidth 300 G).† No hyperfine structure has been observed either at this temperature or in liquid helium. The signal disappears at room temperature.[10] This result indicates the presence of one unpaired electron which has been confirmed by measurement of the magnetic moment, *ca.* 1.45 B.M.

EXPERIMENTAL

All operations were performed in the absence of oxygen. The solvents were distilled and stored under nitrogen. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. The magnetic moment was measured by the Evans' method [11] on a 15% solution in MeCN, with $SiMe_4$ as reference, on a Bruker 80 spectrometer. It was computed without taking into account the density-dependent term but introducing standard diamagnetic corrections.

Preparation of $[N(CH_2Ph)Me_3]_4[Co_{13}C_2(CO)_{24}]\cdot Me_2CO$.—The starting material, $Na_2[Co_6C(CO)_{15}]\cdot n(Me_2CH)_2O$, was prepared by a modification of the original synthesis.[12] A

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† Throughout this paper: 1 G = 10^{-4} T; 1 B.M. = 9.274 × 10^{-24} A m².

mixture of $[Co_3(CO)_9CCl]$ *(1.52 g, 3.2 mmol) and finely* powdered $Na[Co(CO)_4]$ (9.6 mmol) in di-isopropyl ether (40 cm^3) was stirred under nitrogen at 60 °C for 70—90 min and the resulting reddish brown crystalline powder filtered off (yield 80—90%). A solution of $Na_2[Co_6C(CO)_{15}]\cdot n(Me_2CH)_2O$ (0.9 g) in diglyme, $(MeOCH_2CH_2)_2O$ (15 cm^3), was refluxed, with stirring under nitrogen, for 8 h on an oil-bath at 175 °C. The reddish brown solution turned black and a black oil separated out. At the end of the reaction the mixture was evaporated to dryness *in vacuo* on an oil-bath at 80 °C. The tarry residue was dissolved in methanol (20 cm^3) and the solution was filtered. The compound was obtained as its benzyltrimethylammonium salt by slow dropwise addition of a solution of $[N(CH_2Ph)Me_3]Cl$ (1 g) in methanol (5 cm^3), with stirring. The product separated out as a crystalline powder. Occasionally, a tar was formed initially, but this crystallized on subsequent stirring (2—3 h). The product was filtered off from the brown mother-liquor,* washed with methanol (6 × 5 cm^3), and vacuum dried. It was further purified by dissolution in the minimum amount of acetone, addition of propan-2-ol, and evaporation of the acetone *in vacuo*, yield *ca.* 50%. Crystals suitable for *X*-ray analysis were obtained from an acetone solution by slow diffusion of propan-2-ol {Found: Co, 35.1; $[N(CH_2Ph)Me_3]^+$, 27.65. Calc. for $C_{69}H_{70}Co_{13}N_4O_{25}$: Co, 36.1; $[N(CH_2Ph)Me_3]^+$, 28.3%}.

The i.r. spectrum in MeCN solution showed bands at 1 960vs and 1 945 (sh) cm^{-1} in the terminal carbonyl-stretching region, and at 1 785ms and 1 758mw cm^{-1} in the bridging carbonyl region.

The $[N(CH_2Ph)Me_3]^+$ salt is very soluble in acetonitrile, soluble in acetone, sparingly soluble in ethyl methyl ketone (emk), and insoluble in tetrahydrofuran, methanol, and propan-2-ol. It can be obtained as crystals containing emk by addition of emk to a highly concentrated solution in MeCN (0.5 g in 2—3 cm^3) and subsequent concentration *in vacuo*.

The product is highly sensitive to air in solution; oxidation in the solid state is slower. It reacts slowly with carbon monoxide resulting in complete destruction of the cluster and formation of Co^{2+} and $[Co(CO)_4]^-$.

Crystal Data.—$C_{69}H_{70}Co_{13}N_4O_{25}$, $M = 2\,121.3$, Monoclinic, $a = 14.057(7)$, $b = 20.24(1)$, $c = 30.66(1)$ Å, $\beta = 113.06(5)°$, $U = 8\,026.16$ Å^3, $D_m = 1.77$, $Z = 4$, $D_c = 1.75$ g cm^{-3}, space group $P2_1/c$ (no. 14), $F(000) = 4\,252$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 25.76 cm^{-1}.

Intensity Measurements.—A thick tabular crystal with dimensions 0.10 × 0.15 × 0.25 mm was mounted on a Siemens diffractometer. Diffraction intensities were measured in two octants of the reciprocal lattice in the range $3.5 < \theta < 23°$ by the ω scan method, with scan interval 1.3°, and speed 3° min^{-1}. The background was measured at both sides of the reflections for a total time equal to the peak scanning time. 10 987 Diffraction intensities were collected, 4 234 of which $[F_o > 5\sigma(F_o)]$ were used for the structure solution and refinement. The integrated intensities were reduced to F_o values, and an experimental correction for absorption was applied.

For all the computations, the SHELX package of crystallographic programs was used.[13] The cobalt atoms were located by a straightforward application of direct methods and, after a preliminary refinement of their parameters, a difference-Fourier synthesis showed the light atoms. The structure was refined by least-squares calculations and, due to the high number of atoms, the normal matrix was divided in blocks of ten atoms each. Only the cobalt atoms were treated anisotropically. The phenyl rings were treated as rigid groups (C–C 1.395 Å, C–C–C angle 120°) whilst the hydrogen atoms were omitted due to the vast number of atoms in the structure model. The final agreement indices were $R = 0.082$ and $R' = 0.086$. A final Fourier map showed residual peaks lower than 0.9 e Å^{-3} in the vicinity of the oxygen atoms and the phenyl rings. The co-ordinates of all the refined atoms are reported in Table 1.

TABLE 1

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

Atom	*X*	*Y*	*Z*
Co(1)	758(2)	7 998(2)	4 030(1)
Co(2)	2 564(2)	8 015(2)	4 024(1)
Co(3)	996(2)	8 189(2)	3 246(1)
Co(4)	936(2)	6 987(2)	3 067(1)
Co(5)	662(2)	6 674(2)	3 839(1)
Co(6)	2 487(2)	6 807(2)	3 823(1)
Co(7)	2 207(2)	7 083(2)	4 588(1)
Co(8)	1 531(2)	7 370(2)	5 248(1)
Co(9)	638(2)	6 475(2)	4 659(1)
Co(10)	−659(2)	7 293(2)	4 141(1)
Co(11)	249(2)	8 179(2)	4 747(1)
Co(12)	2 126(2)	8 241(2)	4 779(1)
Co(13)	−470(2)	7 505(2)	3 326(1)
C(0)	866(14)	7 413(10)	4 559(6)
C(1)	1 310(15)	7 410(11)	3 683(7)
C(2)	3 430(17)	8 594(12)	4 369(8)
O(2)	4 070(12)	8 969(8)	4 602(5)
C(3)	466(19)	8 867(13)	2 958(9)
O(3)	98(14)	9 371(10)	2 740(7)
C(4)	249(17)	6 512(12)	2 581(8)
O(4)	−226(14)	6 204(10)	2 256(7)
C(5)	1 037(18)	5 853(13)	3 896(8)
O(5)	1 198(12)	5 282(9)	3 885(5)
C(6)	3 174(19)	6 111(13)	3 965(9)
O(6)	3 632(13)	5 583(9)	4 079(6)
C(7)	2 839(17)	6 338(12)	4 823(8)
O(7)	3 274(12)	5 869(9)	5 000(6)
C(8)	2 506(18)	7 361(12)	5 797(9)
O(8)	3 206(14)	7 379(9)	6 180(6)
C(9)	765(21)	5 656(15)	4 751(9)
O(9)	812(16)	5 068(12)	4 820(7)
C(10)	−1 879(17)	7 301(11)	3 709(7)
O(10)	−2 749(13)	7 258(8)	3 446(6)
C(11)	−199(19)	8 924(14)	4 792(9)
O(11)	−609(13)	9 434(9)	4 807(6)
C(12)	2 655(18)	8 763(12)	5 233(8)
O(12)	3 040(13)	9 118(8)	5 556(6)
C(13)	−1 457(19)	7 664(12)	2 803(9)
O(13)	−2 165(14)	7 768(9)	2 467(7)
C(14)	−435(16)	8 364(11)	3 566(7)
O(14)	−918(11)	8 852(8)	3 486(5)
C(15)	1 228(16)	8 827(12)	4 318(7)
O(15)	1 118(11)	9 403(8)	4 222(5)
C(16)	2 333(19)	8 523(13)	3 495(9)
O(16)	2 783(14)	8 927(10)	3 350(6)
C(17)	3 569(17)	7 424(11)	3 987(7)
O(17)	4 485(13)	7 442(9)	4 079(6)
C(18)	1 070(20)	7 746(14)	2 729(10)
O(18)	1 104(13)	7 846(9)	2 354(7)
C(19)	2 227(19)	6 623(13)	3 185(9)
O(19)	2 623(12)	6 323(8)	2 952(6)
C(20)	−599(16)	6 552(11)	3 332(7)
O(20)	−1 219(11)	6 145(7)	3 133(5)
C(21)	3 242(17)	7 569(11)	4 994(8)
O(21)	4 132(11)	7 594(7)	5 267(5)
C(22)	867(18)	6 584(12)	5 300(8)
O(22)	681(13)	6 330(9)	5 608(6)
C(23)	640(15)	7 949(11)	5 399(8)
O(23)	472(12)	8 110(8)	5 721(6)

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* The brown mother-liquor contained other anions, among which it has been possible to isolate and characterize the anion $[Co_{11}C_2(CO)_{22}]^{3-}$.[8]

TABLE 1 (*continued*)

Atom	*X*	*Y*	*Z*
C(24)	−817(18)	6 464(12)	4 368(8)
O(24)	−1 497(12)	6 069(8)	4 331(5)
C(25)	−1 070(17)	7 797(11)	4 551(8)
O(25)	−1 825(12)	7 869(7)	4 633(5)
N(1)	3 453(17)	3 864(12)	5 086(8)
C(26)	4 358(28)	3 910(18)	4 934(12)
C(27)	3 232(24)	3 132(17)	5 157(11)
C(28)	3 830(25)	4 197(17)	5 555(12)
C(29)	2 489(24)	4 212(16)	4 740(11)
C(30)	2 216(24)	3 586(14)	4 276(10)
C(31)	1 413(24)	3 141(14)	4 211(10)
C(32)	988(24)	2 780(14)	3 791(10)
C(33)	1 366(24)	2 864(14)	3 436(10)
C(34)	2 169(24)	3 308(14)	3 501(10)
C(35)	2 594(24)	3 669(14)	3 922(10)
N(2)	2 802(16)	913(11)	4 603(7)
C(36)	1 689(19)	1 055(12)	4 271(9)
C(37)	2 796(21)	484(14)	5 012(10)
C(38)	3 387(23)	1 527(16)	4 797(10)
C(39)	3 333(19)	485(13)	4 332(9)
C(40)	3 439(14)	836(8)	3 918(5)
C(41)	2 652(14)	788(8)	3 467(5)
C(42)	2 759(14)	1 098(8)	3 083(5)
C(43)	3 654(14)	1 455(8)	3 149(5)
C(44)	4 441(14)	1 503(8)	3 600(5)
C(45)	4 333(14)	1 193(8)	3 984(5)
N(3)	1 925(15)	9 367(10)	1 801(7)
C(46)	2 500(20)	9 621(14)	2 296(9)
C(47)	2 275(17)	8 685(12)	1 763(8)
C(48)	761(19)	9 369(13)	1 662(9)
C(49)	2 095(15)	9 839(10)	1 428(7)
C(50)	3 203(11)	9 896(11)	1 503(7)
C(51)	3 693(11)	9 435(11)	1 323(7)
C(52)	4 740(11)	9 505(11)	1 413(7)
C(53)	5 298(11)	10 036(11)	1 682(7)
C(54)	4 809(11)	10 497(11)	1 862(7)
C(55)	3 761(11)	10 427(11)	1 773(7)
N(4)	2 015(15)	5 543(10)	1 612(7)
C(56)	1 435(19)	5 313(12)	1 112(9)
C(57)	2 657(21)	6 172(14)	1 607(9)
C(58)	1 272(22)	5 698(14)	1 837(10)
C(59)	2 744(18)	5 006(12)	1 927(8)
C(60)	3 461(13)	4 697(9)	1 693(6)
C(61)	4 416(13)	4 984(9)	1 770(6)
C(62)	5 073(13)	4 690(9)	1 584(6)
C(63)	4 776(13)	4 109(9)	1 321(6)
C(64)	3 822(13)	3 822(9)	1 244(6)
C(65)	3 164(13)	4 116(9)	1 430(6)
O(1)	4 668(23)	6 950(17)	2 381(10)
C(66)	4 749(33)	7 565(25)	2 553(16)
C(67)	5 278(28)	8 068(20)	2 406(13)
C(68)	4 364(35)	7 518(23)	2 944(18)

Bond distances and relevant angles are listed in Table 2. Thermal parameters and structure factors are reported in Supplementary Publication No. SUP 23206 (28 pp.).*

TABLE 2

Distances (Å) and relevant angles (°) with estimated standard deviations in parentheses

Co(1)–Co(2)	2.546(5)	Co(8)–C(8)	1.70(2)
Co(1)–Co(3)	2.581(5)	Co(9)–C(9)	1.68(3)
Co(1)–Co(5)	2.735(4)	Co(10)–C(10)	1.71(2)
Co(1)–Co(7)	2.789(4)	Co(11)–C(11)	1.66(3)
Co(1)–Co(10)	2.579(5)	Co(12)–C(12)	1.67(2)
Co(1)–Co(11)	2.591(5)	Co(13)–C(13)	1.69(2)
Co(1)–Co(12)	2.400(3)	Co(1)–C(14)	1.87(2)
Co(1)–Co(13)	2.390(4)	Co(1)–C(15)	1.89(2)
Co(2)–Co(3)	2.560(4)	Co(2)–C(16)	1.84(3)
Co(2)–Co(6)	2.513(5)	Co(2)–C(17)	1.89(2)
Co(2)–Co(7)	2.735(5)	Co(3)–C(16)	1.86(2)
Co(2)–Co(12)	2.659(5)	Co(3)–C(18)	1.86(3)
Co(3)–Co(4)	2.489(5)	Co(4)–C(18)	1.90(3)
Co(3)–Co(13)	2.572(5)	Co(4)–C(19)	1.86(3)
Co(4)–Co(5)	2.620(5)	Co(5)–C(20)	1.86(2)
Co(4)–Co(6)	2.510(4)	Co(6)–C(17)	1.88(2)
Co(4)–Co(13)	2.620(5)	Co(6)–C(19)	1.88(2)
Co(5)–Co(6)	2.598(5)	Co(7)–C(21)	1.79(2)
Co(5)–Co(7)	2.602(4)	Co(8)–C(22)	1.88(3)
Co(5)–Co(9)	2.560(5)	Co(8)–C(23)	1.90(2)
Co(5)–Co(10)	2.688(5)	Co(9)–C(22)	1.87(3)
Co(5)–Co(13)	2.423(4)	Co(9)–C(24)	1.88(2)
Co(6)–Co(7)	2.586(5)	Co(10)–C(24)	1.86(2)
Co(7)–Co(8)	2.614(5)	Co(10)–C(25)	1.88(3)
Co(7)–Co(9)	2.608(5)	Co(11)–C(23)	1.91(2)
Co(7)–Co(12)	2.430(4)	Co(11)–C(25)	1.88(2)
Co(8)–Co(9)	2.517(4)	Co(12)–C(15)	1.90(2)
Co(8)–Co(11)	2.474(4)	Co(12)–C(21)	1.98(2)
Co(9)–Co(10)	2.513(4)	Co(13)–C(14)	1.88(2)
Co(10)–Co(11)	2.538(4)	Co(13)–C(20)	1.94(2)
Co(10)–Co(13)	2.649(5)	C(2)–O(2)	1.18(3)
Co(11)–Co(12)	2.604(5)	C(3)–O(3)	1.22(3)
C(0)–Co(1)	1.96(2)	C(4)–O(4)	1.14(3)
C(0)–Co(5)	2.59(2)	C(5)–O(5)	1.18(3)
C(0)–Co(7)	1.97(2)	C(6)–O(6)	1.23(3)
C(0)–Co(8)	1.95(2)	C(7)–O(7)	1.14(3)
C(0)–Co(9)	1.97(2)	C(8)–O(8)	1.20(3)
C(0)–Co(10)	2.04(2)	C(9)–O(9)	1.21(4)
C(0)–Co(11)	1.97(2)	C(10)–O(10)	1.17(2)
C(0)–Co(12)	2.34(2)	C(11)–O(11)	1.19(3)
C(1)–Co(1)	1.95(2)	C(12)–O(12)	1.17(3)
C(1)–Co(2)	2.06(2)	C(13)–O(13)	1.14(3)
C(1)–Co(3)	2.00(2)	C(14)–O(14)	1.17(3)
C(1)–Co(4)	1.95(2)	C(15)–O(15)	1.20(3)
C(1)–Co(5)	1.90(2)	C(16)–O(16)	1.22(4)
C(1)–Co(6)	1.96(2)	C(17)–O(17)	1.21(3)
C(1)–Co(7)	2.64(2)	C(18)–O(18)	1.19(4)
C(1)–Co(13)	2.31(2)	C(19)–O(19)	1.22(4)
Co(2)–C(2)	1.72(2)	C(20)–O(20)	1.18(2)
Co(3)–C(3)	1.64(2)	C(21)–O(21)	1.20(2)
Co(4)–C(4)	1.72(2)	C(22)–O(22)	1.19(3)
Co(5)–C(5)	1.73(3)	C(23)–O(23)	1.15(3)
Co(6)–C(6)	1.67(3)	C(24)–O(24)	1.21(3)
Co(7)–C(7)	1.76(2)	C(25)–O(25)	1.19(3)
Co(2)–C(2)–O(2)	176(2)	Co(8)–C(22)–O(22)	135(2)
Co(3)–C(3)–O(3)	178(3)	Co(9)–C(22)–O(22)	141(2)
Co(4)–C(4)–O(4)	179(3)	Co(8)–C(23)–O(23)	140(2)
Co(5)–C(5)–O(5)	172(2)	Co(11)–C(23)–O(23)	139(2)
Co(6)–C(6)–O(6)	176(3)	Co(9)–C(24)–O(24)	136(2)
Co(7)–C(7)–O(7)	176(2)	Co(10)–C(24)–O(24)	139(2)
Co(8)–C(8)–O(8)	177(2)	Co(10)–C(25)–O(25)	138(2)
Co(9)–C(9)–O(9)	177(3)	Co(11)–C(25)–O(25)	137(2)
Co(10)–C(10)–O(10)	172(2)	N(1)–C(26)	1.52(5)
Co(11)–C(11)–O(11)	174(2)	N(1)–C(27)	1.55(4)
Co(12)–C(12)–O(12)	179(2)	N(1)–C(28)	1.48(4)
Co(13)–C(13)–O(13)	175(3)	N(1)–C(29)	1.53(3)
Co(1)–C(14)–O(14)	140(2)	N(2)–C(36)	1.52(3)
Co(13)–C(14)–O(14)	141(1)	N(2)–C(37)	1.53(4)
Co(1)–C(15)–O(15)	140(1)	N(2)–C(38)	1.48(4)
Co(12)–C(15)–O(15)	141(1)	N(2)–C(39)	1.58(4)
Co(2)–C(16)–O(16)	139(2)	N(3)–C(46)	1.50(3)
Co(3)–C(16)–O(16)	133(2)	N(3)–C(47)	1.48(3)
Co(2)–C(17)–O(17)	136(2)	N(3)–C(48)	1.52(3)
Co(6)–C(17)–O(17)	140(2)	N(3)–C(49)	1.58(3)
Co(3)–C(18)–O(18)	141(2)	N(4)–C(56)	1.50(3)
Co(4)–C(18)–O(18)	136(2)	N(4)–C(57)	1.56(4)
Co(4)–C(19)–O(19)	136(2)	N(4)–C(58)	1.49(4)
Co(6)–C(19)–O(19)	139(2)	N(4)–C(59)	1.55(3)
Co(5)–C(20)–O(20)	142(2)	O(1)–C(66)	1.34(6)
Co(13)–C(20)–O(20)	138(1)	C(67)–C(66)	1.43(7)
Co(7)–C(21)–O(21)	148(2)	C(68)–C(66)	1.50(8)
Co(12)–C(21)–O(21)	132(2)		

RESULTS AND DISCUSSION

The crystal comprises discrete anions $[Co_{13}C_2(CO)_{24}]^{4-}$ (Figure 1), cations $[N(CH_2Ph)Me_3]^+$, and one acetone molecule per anion. The anion $[Co_{13}C_2(CO)_{24}]^{4-}$ contains a closed polyhedron of metal atoms with no resemblance

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

to any simple geometrical solid, its idealized symmetry being C_2 (Figure 2). It can be described as a three-layer stack containing two squares in the outer layers and three fused triangles (five atoms) in the central one. The layer packing is such that two trigonal-prismatic cavities are formed, each containing a carbon atom. An equivalent description of the cluster is in terms of two prismatic Co_6C units sharing one vertex [Co(1)]. The two prisms are mutually rotated so that the atom in each prism connected to the shared one by the interbase edge [Co(5) and Co(7) respectively] caps a square face of the other prism. The remaining Co atoms [Co(12) and Co(13)] cap a second square face on each prism and are in bridging positions on a basal edge of the other prism. A total of 33 Co–Co interactions is present of which two are within the polyhedron itself. One can assess the degree of compactness of this polyhedron by bearing in mind that in the close-packed M_{13} polyhedra the number of M–M connections is 36. All the outer faces are triangular with the exception of the two uncapped rectangular faces of the prism. Cobalt atoms Co(3), Co(4), Co(6), Co(8), Co(9), and Co(11) have four metal–metal connections; Co(2), Co(10), Co(12), and Co(13) five; Co(5) and Co(7) seven; and Co(1) eight.

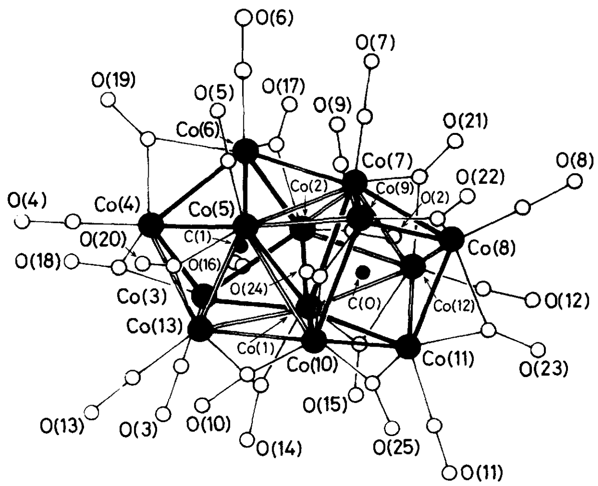

FIGURE 1 The anion $[Co_{13}C_2(CO)_{24}]^{4-}$ showing the atom labelling. The carbon atoms of the CO ligands, not labelled in the figure, are numbered in accordance with the corresponding oxygens

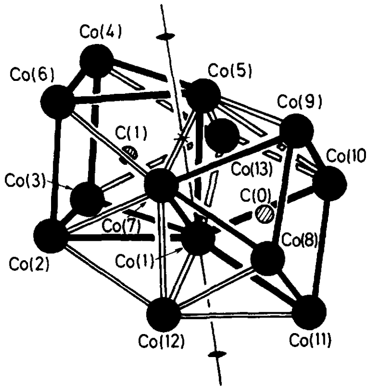

FIGURE 2 The $Co_{13}C_2$ cluster; solid lines define the prismatic moieties

The geometry of the 12 terminal and 12 edge-bridging carbonyl ligands conforms to C_2 cluster symmetry. All the cobalt atoms except Co(1) carry a single terminal ligand, the high connectivity of that atom being the cause of this difference. When this species was suspected to contain a hydrogen ligand it was supposed to be on the idealized two-fold axis terminally bonded to Co(1). The bridging groups span only the in-layer edges, *i.e.* all the square edges of the outer layers and four out of the five edges of the central layer. In this way four- and five-connected metal atoms have three bonding interactions with the outer ligands, seven- and eight-connected atoms only two. It is evident that the ligand geometry is the one which best allows an even electron distribution among the cluster atoms.

The cobalt–cobalt interactions are spread over the range 2.390—2.789(5) Å with overall average 2.57 Å. This value can be compared with that found in $[Co_8C(CO)_{18}]^{2-}$ 2.52,[5] $[Co_6C(CO)_{14}]^-$ 2.66,[6] and $[Co_6CS_2(CO)_{12}]$ 2.51.[14] These distances can be grouped into two main sets, the edges which are bridged by ligands and those which are not. In the first set [range 2.390—2.560(4), average 2.48 Å] there are two subgroups, the edges in the central layer, in which atoms Co(12) and Co(13) are involved, with mean length 2.41 Å and the edges in the outer layers, mean 2.52 Å. In the second set [range 2.546—2.789(5), average 2.62 Å] one should note that the inner distances Co(1)–Co(5) and Co(1)–Co(7) are the longest in the structure with mean value 2.76 Å.

All the cobalt atoms may be considered to be bonded to at least one carbide atom. The distances of the carbide-carbon atoms from their respective prism vertices are in the range 1.90—2.06(2) Å, with average 1.98 Å. The mean distances from the capping atoms are 2.32 and 2.61 Å, the shorter distance being from Co(12) and Co(13) which do not belong to the prismatic moieties. The apparent radius of carbon (taking 1.29 Å for cobalt, the experimental value in this complex) is 0.69 Å, in very good agreement with that (0.68 Å) found [14] in $[Co_6CS_2(CO)_{12}]$. These values are smaller than that (0.73 Å) found [5] in the tetragonal-antiprismatic cavity of $[Co_8C(CO)_{18}]^{2-}$, and indicate that the cavity in a prism of cobalt atoms is rather too small for the carbon atom. The ideal radius of carbon seems to be that in $[Co_8C(CO)_{18}]^{2-}$, in which a cluster deformation takes place in order to reduce the cavity to the optimum size and adjust the four Co–C distances to their best value. This fits very well with the radii found in the prismatic rhodium clusters; 0.74 Å in $[Rh_6C(CO)_{15}]^{2-}$,[1] and 0.72 Å in $[Rh_8C(CO)_{19}]$.[2]

The terminal ligands show normal Co–C and C–O bond lengths with mean distances 1.70 and 1.18 Å respectively. Some deviations from the average values are very probably significant and indicate different degrees of back donation from different metal atoms.

The bridging groups are not significantly distorted with mean bond distances 1.96, 1.19 Å for Co–C and C–O interactions respectively.

Due to the complexity of the cluster, the structural analysis of this anion does not afford a clear rationalization of the role played by the unpaired electron. However, parallelling the explanation put forward for the other paramagnetic anion [7] $[Co_6C(CO)_{14}]^-$, we suggest that an extra electron in an antibonding cluster orbital is needed in order to widen the prismatic cavity which, as discussed above, is not the best size for accommodating an interstitial carbon. This would also provide an explanation for the elongation of the two prism edges Co(1)–Co(5) and Co(1)–Co(7), referred to above.

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