

New Carbide Clusters in the Cobalt Sub-group. Part 5.¹⁻⁴ Crystallographic Characterization of Deca- μ -carbonyl-carbido-octacarbonyl-*polyhedro*-octacobaltate(2-) in its Bis(benzyltrimethylammonium) Salt

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The title complex crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions $a = 19.02(2)$, $b = 10.37(1)$, $c = 12.81(1)$ Å, $\alpha = 116.43(8)$, $\beta = 88.90(8)$, $\gamma = 95.53(8)^\circ$, and $Z = 2$. The structure has been determined by conventional methods from X-ray single-crystal counter data and refined by least-squares calculations to R 0.064 for 3 539 significant diffraction intensities. The $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$ anion contains a deformed tetragonal antiprism of metal atoms (D_2 idealized symmetry) with an average Co-Co distance of 2.52 Å. The carbide atom occupies the centre of the cluster; two kinds of Co-C(carbide) distances are present (means 1.99 and 2.15 Å). There are eight terminal carbonyl ligands, one per metal atom, and the other ten carbonyls range from partially bent to symmetrically edge-bridging.

THE chemistry of the carbide clusters of cobalt parallels that of rhodium as far as the anions $[\text{M}_6\text{C}(\text{CO})_{15}]^{2-}$ are concerned,⁵ but the products obtained from the hexa-

nuclear dianions are different for the two metals. Rhodium gives species such as $[\text{Rh}_8\text{C}(\text{CO})_{19}]$,² $[\text{Rh}_{15}\text{C}_2(\text{CO})_{28}]^-$,³ and $[\text{Rh}_{12}\text{C}_2(\text{CO})_{25}]$,⁴ while only two cobalt species have been ascertained so far, $[\text{Co}_6\text{C}(\text{CO})_{14}]^-$ and $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$. The last anion has been obtained by

¹ V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J.C.S. Dalton*, 1973, 651.

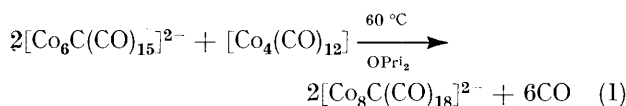
² V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J.C.S. Dalton*, 1975, 305.

³ V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J.C.S. Dalton*, 1976, 970.

⁴ V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J.C.S. Dalton*, preceding paper.

⁵ V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J.C.S. Chem. Comm.*, 1974, 300.

the condensation reaction (1). Its structure may be similar to that of the isoelectronic $[\text{Rh}_8\text{C}(\text{CO})_{19}]^{2-}$ but the



replacement of one carbonyl group by an electron pair and the non-compact structure of the Rh_8 cluster make possible not only ligand rearrangements on the cluster surface but also structural changes in the metal-atom framework. In fact the Co_8 cluster has been found to be different from, but rationally related to, the Rh_8 cluster. We describe here a detailed structural analysis of $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$ based on a crystallographic study. Preliminary data on the synthesis and structure of this anion have already been reported;⁶ a more detailed account of the synthesis will be published elsewhere.

EXPERIMENTAL

Crystal Data.— $\text{C}_{39}\text{H}_{32}\text{Co}_8\text{N}_2\text{O}_{18}$, $M = 1\,287.46$, Triclinic, $a = 19.02(2)$, $b = 10.37(1)$, $c = 12.81(1)$ Å, $\alpha = 116.43(8)$,

TABLE I

Final positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Co(1)	3 189(0)	60(2)	-278(1)
Co(2)	3 396(0)	2 529(2)	1 354(1)
Co(3)	2 968(1)	481(1)	1 851(1)
Co(4)	2 033(0)	831(1)	-575(1)
Co(5)	2 240(1)	3 354(1)	1 132(1)
Co(6)	1 461(0)	1 418(1)	1 399(1)
Co(7)	2 051(1)	-919(1)	255(1)
Co(8)	2 428(1)	2 779(1)	2 841(1)
C(0)	2 481(5)	1 293(10)	991(8)
C(1)	3 875(7)	-978(14)	-866(11)
O(1)	4 319(6)	-1 722(12)	-1 322(10)
C(2)	3 977(7)	1 817(13)	125(11)
O(2)	4 462(6)	2 041(11)	-354(10)
C(3)	3 988(8)	3 371(15)	2 521(13)
O(3)	4 393(6)	3 923(12)	3 319(10)
C(4)	2 648(8)	-1 222(16)	1 709(13)
O(4)	2 563(6)	-2 267(11)	1 873(9)
C(5)	1 509(8)	-953(14)	-1 030(12)
O(5)	1 101(6)	-1 767(11)	-1 758(9)
C(6)	2 830(7)	133(14)	-1 592(11)
O(6)	2 965(5)	-134(10)	-2 568(9)
C(7)	1 597(7)	1 246(14)	-1 515(11)
O(7)	1 296(7)	1 520(12)	-2 179(10)
C(8)	3 310(8)	4 158(14)	1 179(11)
O(8)	3 576(6)	5 128(10)	1 045(9)
C(9)	2 076(7)	4 009(14)	141(11)
O(9)	1 970(6)	4 532(12)	-491(10)
C(10)	2 071(8)	4 912(15)	2 448(12)
O(10)	1 881(6)	5 959(12)	3 115(10)
C(11)	1 065(8)	2 604(15)	944(12)
O(11)	602(6)	3 055(11)	699(9)
C(12)	689(8)	417(15)	1 413(12)
O(12)	147(7)	-214(13)	1 395(11)
C(13)	1 455(7)	2 582(13)	3 035(10)
O(13)	1 024(6)	3 034(10)	3 771(9)
C(14)	2 843(7)	1 583(12)	3 435(10)
O(14)	2 953(5)	1 607(9)	4 350(8)
C(15)	2 606(9)	4 249(16)	4 160(13)
O(15)	2 694(7)	5 185(14)	5 115(12)
C(16)	2 621(8)	-2 144(15)	-739(12)
O(16)	2 759(6)	-3 281(11)	-1 370(9)
C(17)	1 413(7)	-2 123(13)	407(10)
O(17)	999(6)	-2 940(11)	516(10)
C(18)	3 858(8)	239(15)	1 930(12)
O(18)	4 427(6)	16(12)	2 019(10)

TABLE I (Continued)

Atom	x/a	y/b	z/c
N(1)	497(6)	3 958(11)	-3 111(9)
C(19)	147(9)	4 938(16)	-3 477(13)
C(20)	1 281(9)	4 383(17)	-2 968(14)
C(21)	219(8)	4 088(15)	-1 966(12)
C(22)	394(7)	2 392(13)	-4 069(10)
N(2)	4 013(6)	3 581(12)	-2 668(9)
C(29)	3 298(11)	3 376(20)	-2 183(17)
C(30)	4 510(10)	4 490(19)	-1 646(16)
C(31)	3 950(9)	4 356(16)	-3 398(13)
C(32)	4 268(9)	2 093(17)	-3 376(14)
C(23)	-361(4)	1 783(12)	-4 364(7)
C(24)	-700(4)	1 080(12)	-3 761(7)
C(25)	-1 400(4)	494(11)	-4 042(8)
C(26)	-1 760(4)	611(12)	-4 927(7)
C(27)	-1 420(4)	1 314(12)	-5 530(7)
C(28)	-721(4)	1 900(11)	-5 249(8)
C(33)	4 953(4)	2 074(15)	-3 947(8)
C(34)	5 579(5)	2 181(10)	-3 357(6)
C(35)	6 223(4)	2 156(13)	-3 896(9)
C(36)	6 242(4)	2 023(15)	-5 026(8)
C(37)	5 616(5)	1 915(10)	-5 616(6)
C(38)	4 971(4)	1 941(13)	-5 077(9)
H(24)	-419	989	-3 071
H(25)	-1 664	-51	-3 572
H(26)	-2 304	156	-5 145
H(27)	-1 700	1 406	-6 218
H(28)	-456	2 447	-5 718
H(34)	5 566	2 285	-2 476
H(35)	6 711	2 240	-3 436
H(36)	6 744	2 004	-5 445
H(37)	5 630	1 812	-6 496
H(38)	4 484	1 857	-5 537
H(221)	631	2 336	-4 867
H(222)	648	1 695	-3 789
H(191)	225	6 045	-2 788
H(192)	381	4 886	-4 276
H(193)	-415	4 589	-3 628
H(201)	1 383	5 494	-2 294
H(202)	1 534	3 660	-2 717
H(203)	1 490	4 301	-3 791
H(211)	302	5 213	-1 313
H(212)	-343	3 729	-2 069
H(213)	498	3 414	-1 694
H(321)	4 331	1 581	-2 806
H(322)	3 882	1 430	-4 069
H(291)	3 105	4 429	-1 672
H(292)	2 927	2 712	-2 902
H(293)	3 354	2 840	-1 629
H(301)	4 317	5 547	-1 154
H(302)	4 535	3 952	-1 087
H(303)	5 034	4 621	-1 964
H(311)	3 766	5 413	-2 864
H(312)	4 465	4 493	-3 744
H(313)	3 573	3 723	-4 115

$\beta = 88.90(8)$, $\gamma = 95.53(8)^\circ$, $U = 2\,252.33$ Å³, $D_m = 1.86$, $Z = 2$, $D_c = 1.90$ g cm⁻³, $F(000) = 1\,280$, space group $P\bar{1}$ (no. 2), Mo- K_α radiation, $\lambda = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 30.59$ cm⁻¹.

Intensity Measurements.—A thick tabular crystal, dimensions $0.13 \times 0.28 \times 0.36$ mm, was mounted on a PALLERD linear equi-inclination diffractometer. The reciprocal lattice layers $hk0$ —13 were explored within the limiting angles $3 < \theta < 25^\circ$ and $0 \leq \mu \leq 21.13^\circ$ by use of graphite-monochromatized Mo- K_α radiation. Integrated diffraction intensities for 7 686 reflections were measured with the ω -scan method at a scan rate of 1° min⁻¹ and within an angular interval ($\Delta\omega$) varying, as a function of μ , between 1.6 and 3.0° . Background was counted for 24 s at the extreme points of the scan range. The crystal stability was periodically tested during data collection; no significant

⁶ V. G. Albano, P. Chini, G. Ciani, M. Sansoni, D. Strumolo, B. T. Heaton, and S. Martinengo, *J. Amer. Chem. Soc.*, 1976, **98**, 5027.

decay was detected. Integrated intensities were reduced to F_o values by correction for Lorentz and polarization factors. The absorption correction was computed by the methods of refs. 7 and 8, and the transmission factors found were in the range 0.44–0.70. A final set of 3 539 independent reflections was obtained after removing all those having $\sigma(I)/I > 0.25$.

block-diagonal least squares to R 0.064 and R' 0.076. The final difference-Fourier map was rather flat except for some residual peaks, not exceeding $1.2 \text{ e } \text{Å}^{-3}$, near to the cobalt atoms. In the refinement, weights were applied to the observations according to $w = 1/(A + BF_o + CF_o^2)$; in the final cycles A , B , and C had values of 17.2, -0.36 , and 6.6×10^{-3} , and were chosen on the basis of an

TABLE 2
Bond distances (Å) and relevant angles (°)

Co(1)–Co(2)	2.482(4)	Co(8)–C(0)	2.18(1)	Co(3)–C(18)	1.75(2)
Co(1)–Co(3)	2.598(4)	Co(1)–C(1)	1.71(2)	C(1)–O(1)	1.17(2)
Co(1)–Co(4)	2.503(4)	Co(1)–C(2)	2.12(2)	C(2)–O(2)	1.16(2)
Co(1) ··· Co(5)	3.711(4)	Co(2)–C(2)	1.82(2)	C(3)–O(3)	1.18(2)
Co(1)–Co(7)	2.515(4)	Co(2)–C(3)	1.73(2)	C(4)–O(4)	1.19(2)
Co(2)–Co(3)	2.536(4)	Co(3)–C(4)	1.74(2)	C(5)–O(5)	1.18(2)
Co(2)–Co(5)	2.501(4)	Co(7)–C(4)	2.35(2)	C(6)–O(6)	1.18(2)
Co(2)–Co(8)	2.571(4)	Co(4)–C(5)	1.86(2)	C(7)–O(7)	1.18(2)
Co(2) ··· Co(4)	3.381(4)	Co(7)–C(5)	1.95(2)	C(8)–O(8)	1.16(2)
Co(3)–Co(7)	2.517(4)	Co(1)–C(6)	1.86(2)	C(9)–O(9)	1.19(2)
Co(3)–Co(8)	2.464(4)	Co(4)–C(6)	1.95(2)	C(10)–O(10)	1.13(2)
Co(3) ··· Co(6)	3.255(5)	Co(4)–C(7)	1.70(2)	C(11)–O(11)	1.15(2)
Co(4)–Co(5)	2.555(4)	Co(2)–C(8)	1.82(2)	C(12)–O(12)	1.16(2)
Co(4)–Co(6)	2.571(4)	Co(5)–C(8)	2.12(2)	C(13)–O(13)	1.20(2)
Co(4)–Co(7)	2.484(4)	Co(5)–C(9)	1.73(2)	C(14)–O(14)	1.18(2)
Co(5)–Co(6)	2.522(4)	Co(5)–C(10)	1.79(2)	C(15)–O(15)	1.18(2)
Co(5)–Co(8)	2.553(4)	Co(8) ··· C(10)	2.63(2)	C(16)–O(16)	1.15(2)
Co(6)–C(7)	2.566(4)	Co(6)–C(11)	1.80(2)	C(17)–O(17)	1.15(2)
Co(6)–Co(8)	2.449(4)	Co(5)–C(11)	2.27(2)	C(18)–O(18)	1.15(2)
Co(7) ··· Co(8)	3.802(5)	Co(6)–C(12)	1.72(2)	N(1)–C(20)	1.50(2)
Co(1)–C(0)	2.12(1)	Co(6)–C(13)	1.90(2)	N(1)–C(21)	1.50(2)
Co(2)–C(0)	1.99(1)	Co(8)–C(13)	1.87(1)	N(1)–C(22)	1.54(2)
Co(3)–C(0)	1.95(1)	Co(3)–C(14)	1.86(1)	C(22)–C(23)	1.50(2)
Co(4)–C(0)	2.03(1)	Co(8)–C(14)	1.95(2)	N(2)–C(29)	1.52(2)
Co(5)–C(0)	2.16(1)	Co(8)–C(15)	1.71(2)	N(2)–C(30)	1.51(2)
Co(6)–C(0)	2.00(1)	Co(1)–C(16)	2.26(2)	N(2)–C(31)	1.49(2)
Co(7)–C(0)	2.14(1)	Co(7)–C(16)	1.79(2)	N(2)–C(32)	1.52(2)
		Co(7)–C(17)	1.73(1)	C(32)–C(33)	1.48(2)
Co(2)–C(0)–Co(3)	80.2(4)	Co(8)–C(10)–O(10)	126(2)		
Co(2)–C(0)–Co(4)	114.6(6)	Co(6)–C(11)–O(11)	155(2)		
Co(2)–C(0)–Co(6)	140.5(5)	Co(5)–C(11)–O(11)	130(2)		
Co(3)–C(0)–Co(4)	144.5(5)	Co(6)–C(12)–O(12)	176(2)		
Co(3)–C(0)–Co(6)	111.0(6)	Co(6)–C(13)–O(13)	137(1)		
Co(4)–C(0)–Co(6)	79.2(5)	Co(8)–C(13)–O(13)	140(1)		
Co(1)–C(0)–Co(5)	120.4(6)	Co(3)–C(14)–O(14)	141(1)		
Co(1)–C(0)–Co(7)	72.4(3)	Co(8)–C(14)–O(14)	138(1)		
Co(1)–C(0)–Co(8)	142.0(6)	Co(8)–C(15)–O(15)	174(2)		
Co(5)–C(0)–Co(7)	140.3(6)	Co(1)–C(16)–O(16)	131(1)		
Co(5)–C(0)–Co(8)	72.0(3)	Co(7)–C(16)–O(16)	153(1)		
Co(7)–C(0)–Co(8)	123.2(6)	Co(7)–C(17)–O(17)	178(2)		
Co(1)–C(1)–O(1)	176(3)	Co(3)–C(18)–O(18)	175(2)		
Co(1)–C(2)–O(2)	135(1)	C(22)–N(1)–C(19)	110(1)		
Co(2)–C(2)–O(2)	147(1)	C(22)–N(1)–C(20)	107(1)		
Co(2)–C(3)–O(3)	179(2)	C(22)–N(1)–C(21)	112(1)		
Co(3)–C(4)–O(4)	161(1)	C(19)–N(1)–C(20)	110(1)		
Co(7)–C(4)–O(4)	125(1)	C(19)–N(1)–C(21)	110(1)		
Co(4)–C(5)–O(5)	141(2)	C(20)–N(1)–C(21)	109(1)		
Co(7)–C(5)–O(5)	138(1)	N(1)–C(22)–C(23)	115(1)		
Co(1)–C(6)–O(6)	142(2)	C(32)–N(2)–C(29)	108(1)		
Co(4)–C(6)–O(6)	136(1)	C(32)–N(2)–C(30)	111(1)		
Co(4)–C(7)–O(7)	179(1)	C(32)–N(2)–C(31)	111(1)		
Co(2)–C(8)–O(8)	149(1)	C(29)–N(2)–C(30)	108(1)		
Co(5)–C(8)–O(8)	132(1)	C(29)–N(2)–C(31)	110(1)		
Co(5)–C(9)–O(9)	177(1)	N(2)–C(32)–C(33)	116(1)		
Co(5)–C(10)–O(10)	165(2)				

Determination of the Structure.—The structure was solved by interpretation of the Patterson function. The trial co-ordinates of the eight cobalt atoms were first refined and then used for phasing the reflections. A subsequent difference-Fourier map showed the peaks of all the remaining non-hydrogen atoms. The structure was refined by

⁷ W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

⁸ G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

analysis of $\Sigma w\Delta^2$. Atomic scattering factors were taken from ref. 9 for non-hydrogen atoms; the contribution of the anomalous dispersion for cobalt was taken into account.¹⁰ The hydrogen atoms of the cations were placed, after each cycle of refinement, in their expected positions with a C–H distance of 1.08 Å and their contributions to the

⁹ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

¹⁰ 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

structure factors were computed (scattering factor from ref. 11).

Final atomic positions are in Table 1, and bond distances and angles in Table 2. Structure factors and thermal parameters are given in Supplementary Publication No. SUP 22202 (16 pp.).* The calculations were carried out on a UNIVAC 1106 computer at the computing centre of Milan University, using local programs.

DISCUSSION

The crystal structure consists of discrete ions, all the interionic contacts being normal. The structure of the anion is illustrated in Figure 1 and a view of the metal-atom cluster is shown in Figure 2. The cobalt atoms are disposed in two parallel layers (interplanar distance 2.12 Å), each containing a rhomb of metal atoms. The mutual orientation of the rhombic moieties is staggered, so that the polyhedron can be defined as a tetragonal antiprism. The carbide atom occupies the centre of the cluster. The idealized symmetry of the metal-atom cluster is only D_2 (D_{4h} in the regular antiprism) because the antiprism is significantly elongated

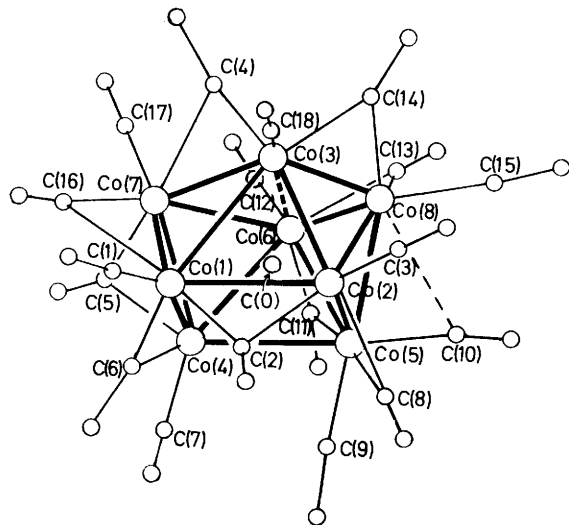


FIGURE 1 Structure of the anion $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$. The cobalt atoms are labelled in such a way as to show the simple derivation of the tetragonal antiprism from the bicapped trigonal prism (see text). The atoms Co(1)—Co(6) define the prismatic unit, and Co(7) and Co(8) are the capping atoms. It should be noted that the choice of the capping atoms is not unique in the antiprism, the present choice being the one most evident in the projection of the anion down the a axis

along one of the two-fold symmetry axes (C_2' in Figure 2). The Co—Co distances [2.464—2.598(4) Å, mean 2.52 Å] are in good agreement with those found in other polyhedra of cobalt atoms, e.g. 2.49 in $[\text{Co}_4(\text{CO})_{12}]^{12}$, 2.51 in $[\text{Co}_6(\text{CO})_{15}]^{2-}$,¹³ and 2.50 Å in $[\text{Co}_6(\text{CO})_{14}]^{4-}$.¹⁴ The

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

¹¹ J. B. Forsyth and M. Wells, *Acta Cryst.*, 1959, **12**, 412.

¹² C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 4792.

¹³ V. G. Albano, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1968, **15**, 423.

¹⁴ V. G. Albano, P. L. Bellon, P. Chini, and V. Scatturin, *J. Organometallic Chem.*, 1969, **16**, 461.

spread of the distances can be attributed to the presence of a variety of bridging carbonyl ligands. The mean lengths for symmetrically bridged (six), asymmetrically bridged (four), and unbridged edges (six) are 2.484, 2.527, and 2.556(2) Å respectively. The well

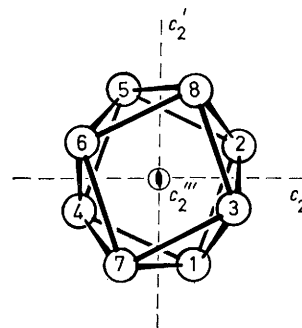


FIGURE 2 The metal-atom cluster and the idealized symmetry operations

known shortening effect¹⁵ of bridging carbonyl groups is clearly demonstrated in the present anion because other sources of deformation of the Co—Co interactions seem to be absent.

Although the cluster geometry is a new one, it is derived from the prismatic cluster of the parent anion $[\text{Co}_6\text{C}(\text{CO})_{15}]^{2-}$ by insertion of two extra cobalt atoms on the rectangular faces of the prism. The bicapped prism so obtained is turned into a tetragonal antiprism [planes Co(1,2,4,5) and Co(3,6,7,8)] by stretching the interbasal edge [Co(3)—Co(6)] lying between the capped faces (broken line in Figure 1). The structure of the Co_8 cluster indicates that the non-compact configuration adopted by the metal-atom polyhedron in $[\text{Rh}_8\text{C}(\text{CO})_{19}]$ may be a consequence of the steric hindrance caused by the extra CO ligand. It is not clear why cobalt and rhodium do not give the same isoelectronic species, but the fact is not unique. It may be worth mentioning that, while most carbonylic clusters having 86 valence electrons are octahedral, $[\text{Pt}_6(\text{CO})_{12}]^{2-}$ (ref. 16) is prismatic and, even more exceptionally, $[\text{Os}_6\text{H}_2(\text{CO})_{18}]^{17}$ contains a monocapped pyramid of metal atoms.

Another point of interest in the present anion is the kind of cavity in which the carbide carbon atom is located and the significant deformation of the metal-atom polyhedron. Carbon atoms in transition-metal carbides have been found only exceptionally in tetragonal-antiprismatic cavities, e.g. in Cr_{23}C_6 ,¹⁸ because carbon usually prefers octahedral or trigonal-prismatic cavities. On the other hand the tetragonal-antiprismatic geometry is more common for boron in metal-rich borides.¹⁹ The reluctance of carbon towards eight-coordination is made more evident by the deformation

¹⁵ P. Chini, *Inorg. Chim. Acta Rev.*, 1968, **2**, 31.

¹⁶ J. C. Calabrese, L. F. Dahl, A. Cavalieri, P. Chini, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, 1974, **96**, 2616.

¹⁷ M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Chem. Comm.*, 1976, 883.

¹⁸ A. I. Bowman, P. G. Arnold, E. K. Storms, and N. G. Nereson, *Acta Cryst.*, 1972, **B28**, 3102.

¹⁹ A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1975, p. 840.

of the antiprismatic cavity. This deformation can be easily explained in terms of the relative sizes of the cluster cavity and of the carbide atom. The calculated radius of the cavity (centre-vertex distance) for a regular antiprism of edge 2.52 Å is 2.08 Å, while the expected Co-C distance, on the basis of covalent radii, is *ca.* 2 Å. The effect of the cluster deformation consists in a shortening of four Co-C distances and in a lengthening of the other four, the average distances being 1.99 and 2.15 Å respectively. The shorter value is ideal for a covalent Co-C bond. The deformation seems to imply a limited energy expenditure as only the bond angles in the rhombic faces are affected.

The bonds of the carbide atom can hardly be considered as localized, but the presence of four strong and four weak Co-C interactions has significant effects on the ligand stereochemistry. The carbonyl groups are bound in a variety of geometries. Eight are strictly linear, one per cobalt atom, and the other ten range from partially bent to symmetrically edge-bridging. If all the bent groups are counted as edge-bridging there are 28 cobalt-carbonyl interactions, four cobalt atoms being three-co-ordinate and four being four-co-ordinate. It is significant that the four-co-ordinate atoms are those farthest from the central atom. An inspection of the actual ligand geometry could suggest that this stereochemical rationalization is too idealized and, perhaps, scarcely significant. That is not the case because the asymmetry of some ligands, markedly C(10)-O(10), is

²⁰ E. R. Corey, J. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

justified by the fact that a more symmetric mode of bonding would produce intolerably short non-bonded carbon-carbon contacts. The anion is actually asymmetric but the idealized structure with 10 edge-bridging groups has C_2 symmetry (C_2'' in Figure 2).

The C-O distances are not significantly different in the linear and bridging ligands. An interesting comparison can be made among the bond parameters of the linear groups in $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$, $[\text{Co}_6(\text{CO})_{15}]^{2-}$, and $[\text{Co}_6(\text{CO})_{14}]^{4-}$ (1.72, 1.17; 1.74, 1.15; and 1.70, 1.17 Å for the Co-C and C-O distances respectively). The values for the carbide anion in the present complex lie between those of the other two ions and might indicate an intermediate degree of π back bonding, *i.e.* the effective negative charge per cobalt atom in $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$ is higher than $\frac{1}{4}$ and is intermediate between the value in $[\text{Co}_6(\text{CO})_{15}]^{2-}$ ($\frac{1}{3}$) and that in $[\text{Co}_6(\text{CO})_{14}]^{4-}$ ($\frac{2}{3}$). In other words some electron transfer takes place from the carbide atom to the metal atoms. A charge transfer in the opposite direction seems to be present in all the carbide derivatives of rhodium¹⁻⁴ in which the Rh-C and C-O distances are longer and shorter, respectively, than the values in $[\text{Rh}_6(\text{CO})_{16}]^{20}$ (for a detailed comparison of distances see ref. 21).

The bond parameters in the two benzyltrimethylammonium cations are consistent with each other and with those found in other structures.¹

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²¹ P. Chini, G. Longoni, and V. G. Albano, *Adv. Organometallic Chem.*, 1976, **14**, 285.