Crystal Structure of Tri-μ-carbonyl-octacarbonyl-iodo-*tetrahedro*-tetracobaltate(1−) as Its Tetraethylammonium Salt

By **Vincenzo G. Albano** * and **Dario Braga**, Istituto Chimico ' G. Ciamician ' dell'Università, via F. Selmi 2, 40126 Bologna, Italy
Giuliano Longoni, Stefano Campanella, Alessandro Ceriotti, and **Paolo Chini**, Istituto di Chimica Generale dell'Università e Centro del CNR, via G. Venezian 21, 20133 Milano, Italy

The complex $[NEt_4][Co_4(CO)_{11}I]$ crystallizes in the orthorhombic space group *Cmca* with unit-cell dimensions a = 16.97(1), b = 26.72(1), c = 12.10(1) Å, and Z = 8. The structure has been solved from *X*-ray single-crystal counter data and refined by least-squares calculations to R = 0.063 for 1 874 significant diffraction intensities. The structure of the anion is derived from that of the parent $[Co_4(CO)_{12}]$. Three of the carbonyl groups are edge-bridging, defining a basal triangle, and eight are terminal, two per metal atom. The iodine atom, contrary to expectation, is terminally bonded to the apical cobalt atom. The molecular symmetry is C_s-*m*. The Co–I distance is 2.642(2) Å, and the Co–Co interactions have mean values 2.47 and 2.52 Å for the bridged and unbridged edges, respectively. A slight disorder, caused by the presence of 2% of an isomer with the iodine in a basal position, is present.

ALTHOUGH dodecacarbonyltetracobalt has been known for a long time [1] and its structure reported three times,[2] the first anionic derivatives, $[Co_4(CO)_{11}X]^-$ (X = Br, I, NCS, COOR, or CONHR), have been prepared only now.[3] It seemed that the structure of these new species could be inferred from the known stereochemistries of substituted derivatives of $[Ir_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$, namely $[Ir_4(CO)_{11}Br]^-$,[4] $[Ir_4(CO)_{10}H_2]^{2-}$,[5] $[Ir_4(CO)_{10}(PPh_3)_2]$,[6] $[Ir_4(CO)_9(PPh_3)_3]$,[6] $[Rh_4(CO)_8\{P(OPh)_3\}_4]$,[7] and $[Rh_4(CO)_8(Ph_2PCH_2PPh_2)_2]$.[2c] All these species contain three bridging ligands on the edges of a basal triangle, as in the C_{3v} structure of $[Co_4(CO)_{12}]$ and $[Rh_4(CO)_{12}]$,[2b] and the substituents are terminally bonded in the basal triangle. Apical substitution takes place only when there are four substituents. A striking feature is that the T_d unbridged structure of $[Ir_4(CO)_{12}]$ [8] turns into the bridged C_{3v} one upon ligand substitution. This structural evidence suggests that the presence of bridging carbonyl ligands and the consequent four-co-ordination of the basal metal atoms are particularly effective in improving the mechanism of charge equalization. In fact, when the entering ligands are better donors, charge accumulation on the metal atoms is prevented *via* π back bonding, and with electronegative species *via* improved σ donation. The latter effect is well documented in the structures of $[Ir_4(CO)_{11}Br]^-$ (ref. 4) and $[Rh_6(CO)_{15}I]^-$ (ref. 9) in which the bridging ligands (double bridging in the former and triple bridging in the latter) exhibit shorter distances from the metal atom bearing the halogen.

We decided to determine the crystal structure of $[Co_4(CO)_{11}I]^-$ more for the sake of completeness than in the hope of finding a new type of stereochemistry. The new anion was strongly expected to be isostructural with $[Ir_4(CO)_{11}Br]^-$. The outcome, on the contrary, has shown that, in this case, iodine prefers the apical location and that extrapolations can be misleading in this kind of structure.

EXPERIMENTAL

Crystal Data.—$C_{19}H_{20}Co_4NO_{11}$, M = 800.5, Orthorhombic, a = 16.97(1), b = 26.72(1), c = 12.10(1) Å, U = 5 486.6 Å^3, D_m = 1.90, Z = 8, D_c = 1.94 g cm^{-3}, $F(000)$ = 3 199.7, space group *C2cb* (no. 41) or *Cmca* (no. 64), the latter being used in the refinement, Mo-K_α radiation (λ = 0.710 7 Å), μ(Mo-K_α) = 33.8 cm^{-1}.

Intensity Measurements.—A crystal fragment with average thickness 0.2 mm was mounted on a Philips PW 1010 diffractometer. Diffraction intensities in one octant of the reciprocal lattice were measured in the range $3 < \theta < 26°$ by the ω-scan method, with scan width 1.2° and speed 1.8° min^{-1}. The background was measured at both sides of the reflections for a total time equal to the peak scanning time. Weak reflections were measured up to five times. 2 509 Diffraction intensities were collected, 1 874 of which $[F_o > 3\sigma(F_o)]$ were used for the computations. The integrated intensities were reduced to F_o values by correction for Lorentz and polarization effects, and a correction for absorption was applied.

Determination of the Structure.—The structure was solved and refined using the SHELX package of crystallographic programs.[10] At first the space group *Aba*2 was used but, when the C_s-*m* and C_2-2 symmetries of the anion and cation, respectively, became apparent the refinement was completed in the space group *Cmca* down to R 0.066. A difference-Fourier map, computed after refinement, revealed numerous residual peaks in the range 1.1—0.7 e Å^{-3}. Five were located in the vicinity of the tetrahedron edges at *ca.* 1.4 Å from the cobalt atoms, one on the mirror plane and two symmetry-related pairs in general positions. The other peaks were satellites of the oxygen atoms, with average distances of 0.6 and 1.3 Å from the oxygens and carbons, respectively. As we were confident of the quality of our data, we considered that the spurious peaks were physically significant and tried to explain them in terms of partial disorder in the crystal. The peaks in the region of the metal-atom tetrahedron were ' bridging ' all the edges except Co(3)–Co(3'), the one orthogonal to the mirror plane. The peaks could be related to each other and to either Co(3) or Co(3') on the basis of reasonable bond lengths, giving the images of two symmetry-equivalent cobalt tetrahedra, as shown in Figure 1. The most convincing model for disorder generation appeared to be a 180° rotation around the direction of the three-fold axis of the tetrahedron passing through Co(3′) [accompanied by the crystallographically equivalent operation about the axis containing Co(3)]. This arises because the directions in question are the sites of two-fold symmetry axes of the idealized icosahedron whose vertices are defined by the ligands. The mechanism of disorder seemed to be the same as in the crystals of [$Co_4(CO)_{12}$] in which, however, the occupancy factor of the two molecular orientations was 0.5.[2b] In the present case the refined occupancy factor of the cobalt atoms indicated that 98 out of 100 molecules had the main orientation, and two were statistically distributed in the two equivalent faint images. Such partial disorder was explained by the fact that the iodine atom was not affected by this effect, and as a consequence two kinds of molecules were present in the crystal. The real crystal was therefore a solid solution of two structural isomers, packed in such a way as to maintain the Co–I vectors iso-oriented, in order not to perturb the interion interactions.

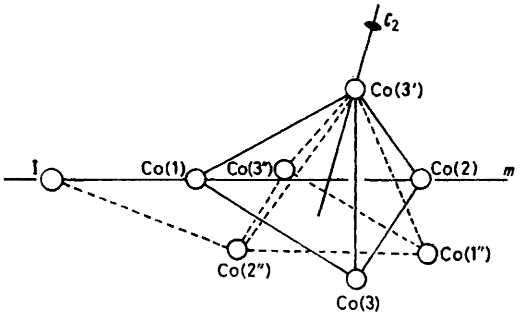

FIGURE 1 Sketch showing the model of disorder in terms of rotation about a C_2 axis of the idealized icosahedron defined by the ligands (coincident with a three-fold axis of the cobalt tetrahedron). Solid lines define the main image, dashed lines one of the faint images. The image produced by the crystallographic mirror plane has been omitted for sake of clarity. The different role of the iodine ligand in the two molecular images is clearly shown if one bears in mind that the edge-bridged triangles are Co(2), Co(3), Co(3′) and Co(2″), Co(3′), Co(3″), respectively

TABLE 1

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

Atom	*x*	*y*	*z*
I	0	3 749(1)	5 635(1)
Co(1)	0	4 016(1)	3 532(1)
Co(2)	0	3 985(1)	1 457(1)
Co(3)	729(1)	3 340(1)	2 484(1)
Co(1″)	553(32)	3 583(21)	1 578(45)
Co(2″)	446(32)	3 563(21)	3 551(45)
Co(3″)	0	4 227(30)	2 642(67)
C(1)	816(7)	4 434(4)	3 773(11)
O(1)	1 315(6)	4 702(4)	3 913(9)
C(2)	0	3 819(6)	66(14)
O(2)	0	3 720(5)	−868(12)
C(3)	0	4 644(6)	1 383(13)
O(3)	0	5 072(5)	1 340(11)
C(4)	1 080(6)	2 869(4)	1 577(8)
O(4)	1 307(5)	2 571(3)	983(8)
C(5)	1 465(6)	3 324(4)	3 500(8)
O(5)	1 958(5)	3 295(3)	4 144(8)
C(6)	1 129(5)	3 901(3)	1 676(8)
O(6)	1 715(5)	4 101(3)	1 429(7)
C(7)	0	2 905(5)	3 297(11)
O(7)	0	2 576(4)	3 875(9)
N	2 500	1 168(4)	2 500
C(8)	1 773(6)	1 483(4)	2 610(8)
C(9)	1 765(8)	1 844(5)	3 569(10)
C(10)	2 603(6)	839(4)	3 523(9)
C(11)	1 978(8)	483(5)	3 730(12)
H(1)	1 708(6)	1 697(4)	1 859(8)
H(2)	1 276(6)	1 234(4)	2 703(8)
H(3)	1 218(8)	2 050(5)	3 569(10)
H(4)	2 252(8)	2 102(5)	3 491(10)
H(5)	1 820(8)	1 639(5)	4 335(10)
H(6)	2 646(6)	1 082(4)	4 233(9)
H(7)	3 146(6)	632(4)	3 430(9)
H(8)	2 110(8)	272(5)	4 469(12)
H(9)	1 928(8)	231(5)	3 037(12)
H(10)	1 428(8)	681(5)	3 840(12)

The final agreement indices were *R* 0.063 and *R*′ 0.076.

TABLE 2

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

Co(1)–I	2.642(2)	C(2) · · · C(6)	2.7(1)
Co(2″)–I	2.68(5)	C(3) · · · C(6)	2.8(1)
Co(1)–Co(2)	2.512(3)	C(4) · · · C(4′)	3.7(1)
Co(1)–Co(3)	2.529(2)	C(4) · · · C(5)	2.7(1)
Co(2)–Co(3)	2.458(2)	C(4) · · · C(6)	2.7(1)
Co(3)–Co(3′)	2.475(2)	C(4) · · · C(7)	2.8(7)
Co(2″)–Co(3″)	2.2(1)	C(5) · · · C(6)	2.8(1)
Co(2″)–Co(1″)	2.4(1)	C(5) · · · C(7)	2.7(1)
Co(3″)–Co(1″)	2.4(1)		
Co(3′)–Co(2″)	2.45(7)	Co(1)–C(1)–O(1)	179(1)
Co(3′)–Co(3″)	2.68(8)	Co(2)–C(2)–O(2)	178(1)
Co(3′)–Co(1″)	2.52(7)	Co(2)–C(3)–O(3)	180(1)
Co(1)–C(1)	1.80(1)	Co(3)–C(4)–O(4)	179(1)
Co(2)–C(2)	1.74(2)	Co(3)–C(5)–O(5)	177(1)
Co(3)–C(3)	1.76(2)	Co(2)–C(6)–O(6)	139(1)
Co(3)–C(4)	1.77(1)	Co(3)–C(6)–O(6)	142(1)
Co(3)–C(5)	1.75(1)	Co(3)–C(7)–O(7)	140(1)
Co(2)–C(6)	1.95(1)	I–Co(1)–C(1)	90.7(4)
Co(3)–C(6)	1.91(1)	C(1)–Co(1)–C(1′)	101(1)
Co(3)–C(7)	1.96(1)	I–Co(1)–Co(2)	162.4(2)
C(1)–O(1)	1.12(1)	C(1)–Co(1)–Co(3′)	153.8(4)
C(2)–O(2)	1.16(2)	I–Co(1)–Co(3)	106.9(2)
C(3)–O(3)	1.15(2)	C(1)–Co(1)–Co(3)	98.5(4)
C(4)–O(4)	1.14(1)	C(1)–Co(1)–Co(2)	100.5(4)
C(5)–O(5)	1.15(2)	Co(1)–Co(2)–C(2)	167.1(5)
C(6)–O(6)	1.17(1)	Co(1)–Co(3)–C(4)	168.9(3)
C(7)–O(7)	1.12(1)	Co(1)–Co(2)–C(3)	91.0(5)
I · · · C(1)	3.2(1)	Co(1)–Co(3)–C(5)	90.8(3)
I · · · C(5)	3.8(1)	Co(1)–Co(2)–C(6)	82.4(3)
I · · · C(7)	3.6(1)	Co(1)–Co(3)–C(6)	82.6(3)
C(1) · · · C(1′)	2.8(1)	Co(1)–Co(3)–C(7)	88.1(3)
C(1) · · · C(3)	3.3(1)	C(2)–Co(2)–C(3)	102(1)
C(1) · · · C(5)	3.2(1)	C(2)–Co(2)–C(6)	95.9(3)
C(1) · · · C(6)	3.0(1)	C(4)–Co(3)–C(5)	100(1)
C(2) · · · C(3)	2.7(1)	C(4)–Co(3)–C(6)	97.0(4)
C(2) · · · C(4)	3.6(1)	C(4)–Co(3)–C(7)	95.8(5)

The refinement comprised anisotropic treatment of the heavy atoms, occupancy factors for all the cobalt peaks, one thermal factor for all the faint cobalt images, constrained geometry, and two thermal factors for the methylene and methyl groups, respectively. In Table 1 the coordinates of the structure model are reported, double-primed atoms being related to the unprimed ones by the pseudo-rotation-generating disorder. Table 2 lists bond distances, relevant intramolecular non-bonded contacts, and angles. Thermal parameters and structure factors are available as Supplementary Publication No. SUP 22791 (13 pp.).*

DISCUSSION

The crystal contains discrete cations [NEt_4]$^+$, placed about two-fold axes (special position *e*) and two isomers

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

of the anion [$Co_4(CO)_{11}I$]$^-$ in the mol ratio 98 : 2. The main isomer has crystallographic symmetry C_s-m (special position *f*). Its structure, depicted in Figure 2, is derived from the C_{3v} structure of [$Co_4(CO)_{12}$].[2] Three of the CO ligands are edge-bridging, defining a basal triangle, and eight are terminal, two per cobalt atom. The iodine is terminally bonded to the apical cobalt. The second isomer contains the iodine atom in an axial position of the basal triangle and is isostructural with [$Ir_4(CO)_{11}Br$]$^-$.[4] This isomer, although occupying the same site as the main isomer, does not match the symmetry plane (see Experimental section) and is statistically distributed on either side of it. Its bond parameters will not be discussed because of their high standard deviations.

The Co–Co distances form two sets with mean lengths 2.47(1) and 2.52(1) Å for bridged and unbridged edges, respectively. The shortening effect of the bridging ligands (0.05 Å) is significant and smaller differences in either set do not cause overlap of the two sets of values. These minor differences show the perturbing effect of the iodine on the cluster orbitals. The overall mean value [2.493(16) Å] is not affected and is equal to that found in [$Co_4(CO)_{12}$], 2.49 [2b] and 2.492 Å.[2c]

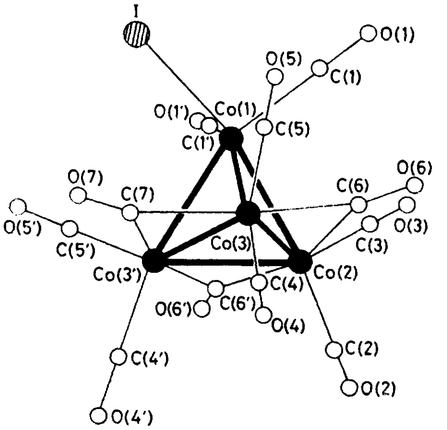

FIGURE 2 Structure of the apical isomer. Atoms I, Co(1), Co(2), and three CO groups lie in the crystallographic mirror plane

The cobalt–carbonyl interactions in the basal triangle are normal; the mean Co–C and C–O distances are 1.755(7) and 1.150(4) Å for the terminal ligands and 1.940(15), and 1.145(25) Å for the bridging groups. The bond distances of the apical carbonyl groups [1.80(1) and 1.12(1)Å] indicate a lower degree of π back bonding, as a consequence of the polar character of the Co(1)–I interaction. The same effect was noticed in [$Rh_6(CO)_{15}I$]$^-$.[9]

The Co–I distance [2.642(2) Å] is longer than the sum of the covalent radii. In fact the apparent radius of iodine in this complex is 1.39 Å, *cf.* 1.34 Å found[9] in [$Rh_6(CO)_{15}I$]$^-$ and 1.33 Å in the element itself. The augmented atomic dimension indicates that iodine is more negatively charged in this complex than in [$Rh_6(CO)_{15}I$]$^-$, as a consequence of the lower electronegativity of cobalt.

In order to explain the unexpected apical co-ordination of the halogen in this complex one should take into account both electronic and steric factors. As already illustrated, the basal location of the substituents in Rh_4 and Ir_4 tetrahedra can be justified assuming that the disturbance introduced in the molecules can be better minimized when a greater number of CO groups are co-ordinated to the site undergoing substitution. It is possible that, due to the lower electronegativity of cobalt, two terminal ligands in the apical site can manage as well as one terminal and two bridging in the basal positions, in other words the energy gain in basal substitution is not so high as in rhodium and iridium derivatives. Consequently the contribution of steric effects becomes determining in this rather extreme case. Although an analysis of the non-bonded contacts (see Table 2) does not give evidence of a much higher hindrance of iodine, one should keep in mind that the contacts among ligands bonded to the same metal atom, being substantially shorter than the sum of the van der Waals radii, are surely repulsive. In the present case the local alleviation of one contact on the apical cobalt should give a greater contribution to the energetic balance in favour of the apical isomer because the Co_4 cluster is the smallest in its subgroup and iodine is apparently the most cumbersome among the substituents encountered so far. The energy difference between the apical and basal isomer is surely a small one, as demonstrated by the presence of both species in the crystal. The mol ratio 49 : 1 is not an indication of equilibrium between the two isomers; it probably reflects just the solubility of the latter in the crystal lattice of the former.

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