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CRYSTAL AND MOLECULAR STRUCTURE OF THE CESIUM SALT OF THE HEXANUCLEAR CARBONYL COBALTATE $[Co_6(CO)_{15}]^{2-}$

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SUMMARY

The salt $Cs_2[Co_6(CO)_{15}]\cdot 3H_2O$ crystallizes in the space group $P2_{1/c}$ with the following cell constants: $a = 9.26$ Å, $b = 23.97$ Å, $c = 14.31$ Å, $\beta = 122° 54'$, $z = 4$. 1300 independent non-zero reflections were measured on precession photographs. The anion $[Co_6(CO)_{15}]^{2-}$ is built up of an octahedral cluster of cobalt atoms surrounded by 15 carbonylic groups. Three of these are triply bonded on faces, three doubly bonded on edges and nine are terminal. The idealized symmetry of the anion is C_{3v}. Layers of these anions are parallel to (1,0,0) plane and present channels, along [1,0,0] direction, in which cesium ions and water molecules are located.

INTRODUCTION

The synthesis of some compounds containing a cluster of six cobalt atom derivatives, which has been performed recently[1-3] has proved that $[Rh_6(CO)_{16}]$ is not exceptional[4] and also that the presence of an excess of two electrons is a general characteristic of this class of compounds. This is confirmed also by the compounds containing a cluster of six ruthenium atoms[5]. This electron excess appears to be related to the stability and chemical behaviour of these octahedral clusters, as there is no tendency to lose or gain electrons.

Therefore it is of considerable interest to obtain structural information on these cluster compounds in order to correlate the structures within a common electronic scheme of bonding. The present analysis is part of this program, and it is primarily concerned with the elucidation of the geometry of these complexes.

EXPERIMENTAL

The pentadecacarbonylhexacobaltate dianion can be obtained in association with several cations. The cesium salt was chosen for the present investigation because it crystallizes in a suitable form and it is stable enough upon exposure to the atmosphere, at least for the time needed to be sealed in a capillary tube.

The unit formula, as determined in the present analysis is $Cs_2[Co_6(CO)_{15}]\cdot 3H_2O$. The chemical analysis suggests a largely variable composition with respect to the water, from 4 to 0 molecules per cation[6]. These numbers depend upon the drying conditions but correspond to different individuals: one is described in the present

TABLE 1. ATOMIC POSITIONAL AND THERMAL PARAMETERS WITH THEIR e.s.d.

Atoms with anisotropic temperature factors[a]

Atom	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Cs1	0.9504(2)	0.1622(1)	0.1891(1)	0.01013(20)	−0.00025(27)	0.00691(17)	0.00203(3)	0.00045(11)	0.00488(7)
Cs2	0.4452(2)	0.1214(1)	0.1423(1)	0.01078(21)	−0.00047(27)	0.01031(21)	0.00127(2)	−0.00030(11)	0.00871(10)
Co1	0.6920(4)	0.3465(1)	0.1625(2)	0.00672(34)	−0.00049(45)	0.00575(32)	0.00091(5)	−0.00005(14)	0.00325(13)
Co2	0.4257(4)	0.3174(1)	0.1574(2)	0.00539(35)	−0.00008(45)	0.00368(33)	0.00074(5)	0.00015(15)	0.00294(14)
Co3	0.4607(4)	0.4175(1)	0.1178(2)	0.00661(37)	0.00062(46)	0.00317(32)	0.00075(5)	0.00028(14)	0.00260(14)
Co4	0.7435(4)	0.4217(1)	0.3016(2)	0.00628(34)	−0.00196(46)	0.00532(31)	0.00072(5)	−0.00027(15)	0.00317(13)
Co5	0.7125(4)	0.3243(1)	0.3408(2)	0.00593(36)	0.00042(45)	0.00380(30)	0.00067(5)	−0.00004(16)	0.00277(13)
Co6	0.4825(4)	0.3924(1)	0.2957(2)	0.00673(34)	0.00076(48)	0.00487(32)	0.00086(5)	−0.00030(17)	0.00270(14)

Atoms with isotropic temperature factors

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
CF125	0.6376(34)	0.2740(11)	0.2075(18)	2.77(52)	OB46	0.6430(20)	0.4931(7)	0.4189(11)	2.66(33)
OF125	0.6646(21)	0.2282(7)	0.1983(11)	2.75(33)	C41	0.8781(29)	0.4781(10)	0.3391(16)	2.34(44)
CF134	0.6978(31)	0.4273(11)	0.1461(17)	2.61(48)	O41	0.9670(29)	0.5162(11)	0.3676(17)	5.58(53)
OF134	0.7494(22)	0.4571(8)	0.1020(12)	3.08(36)	C51	0.8315(30)	0.2697(10)	0.4297(16)	2.24(45)
C21	0.3402(29)	0.2700(10)	0.2083(16)	2.00(42)	O51	0.9210(26)	0.2369(8)	0.4921(14)	3.93(41)
O21	0.2856(24)	0.2373(8)	0.2365(13)	3.94(40)	CB45	0.9058(31)	0.3754(11)	0.4210(18)	2.73(48)
C22	0.3022(30)	0.2944(11)	0.0167(16)	2.48(47)	OB45	1.0383(22)	0.3743(8)	0.5024(13)	3.90(40)
O22	0.2182(24)	0.2805(8)	−0.0722(13)	3.99(41)	C61	0.3489(38)	0.4089(14)	0.3392(22)	4.17(68)
C31	0.4507(34)	0.4888(12)	0.1410(20)	3.50(58)	O61	0.2634(25)	0.4245(9)	0.3709(14)	4.61(46)
O31	0.4226(21)	0.5347(8)	0.1539(12)	3.18(35)	CB56	0.5882(29)	0.3373(10)	0.4063(16)	2.06(41)
C32	0.3444(25)	0.4151(9)	−0.0279(14)	1.57(37)	OB56	0.5746(23)	0.3195(8)	0.4807(13)	3.60(39)
O32	0.2685(23)	0.4134(9)	−0.1240(13)	4.04(41)	CF236	0.2841(31)	0.3860(11)	0.1383(17)	2.64(46)
C11	0.9069(41)	0.3332(15)	0.2253(23)	4.58(72)	OF236	0.1297(22)	0.3915(8)	0.0918(12)	3.32(36)
O11	1.0524(28)	0.3191(10)	0.2626(16)	5.39(53)	O1	0.8554(26)	0.1222(10)	0.3534(14)	4.71(46)
C12	0.6259(35)	0.3341(12)	0.0236(20)	3.43(54)	O2	0.7238(25)	0.0552(9)	0.1376(14)	4.56(43)
O12	0.5883(25)	0.3257(9)	−0.0654(14)	4.16(42)	O3	0.9478(27)	0.0068(9)	0.3602(15)	4.54(45)
CB46	0.6335(27)	0.4552(9)	0.3679(15)	1.65(38)					

[a] The temperature factors are in form: $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$

paper, another is obtained as a crystalline powder when the compound is drastically dehydrated.

The salt $Cs_2[Co_6(CO)_{15}]\cdot 3H_2O$ crystallizes monoclinic in the space group $P2_{1/c}$, with the following cell constants[3]: $a = 9.26(2)$ Å; $b = 23.97(3)$ Å; $c = 14.31(2)$ Å; $\beta = 122° 54'(10')$; $V = 2668$ Å^3. The density measured with the picnometric method is 3.0 g/cm^3 and compares with a density of 2.93 g/cm^3 which can be computed if one assumes 4 formula units per cell. The unit cell dimensions and the intensities were measured from precession photographs taken with Mo-$K\alpha$ radiation, using samples of nearly regular mean radius of 0.12 mm.

The measurement of the intensities was made photometrically on the following levels of the reciprocal lattice: h0l, h1l, h2l, h3l, h4l, 0kl, 1kl, 2kl, and hhl. A total of 1300 non-zero reflections have been measured. The intensities were corrected for Lorentz and polarization factors and the data taken on the different levels were scaled using the procedure described by Hamilton, Rollet and Sparks[7]. No absorption corrections were applied ($\mu = 66$ cm^{-1}).

STRUCTURE RESOLUTION AND REFINEMENT

The structure has been resolved using the Sayre method applied to the 200 strongest normalized structure factors. A Fourier map obtained with these coefficients showed the heavy atom positions. After a preliminary refinement of positional and thermal parameters of these atoms, a difference Fourier computed with all the observed structure factors showed 30 peaks interpreted as 15 CO groups. No clear indications were obtained regarding the water molecules. The model was refined by block-diagonal least squares[8] using the following procedure: first the heavy atoms were refined isotropically with constant contributions of the light atoms, then the refinement was extended to all the atoms, the heavy ones being refined anisotropically. After the convergence of this refinement, a difference map showed the presence of 3 residual peaks, which could be recognized as the oxygen atoms of the water molecules. A final refinement was then performed by least squares. The reliability index was at end $R = 0.058$ and the minimized function $(\Sigma w\cdot\Delta^2/\Sigma w\cdot F_0^2)^{\frac{1}{2}} = 0.08$.

The atomic scattering factors, from self-consistent wave functions for carbon and oxygen and from a Thomas–Fermi–Dirac statistical model for cobalt and cesium atoms, were used[9]. The weights were assigned according the Cruikshank criterion assuming $w = 1/(a + F_0 + c\cdot F_0^2)$ with $a = 5.0$ and $c = 0.02$.

The results of the refinement are reported in the tables: Table 1 gives atomic positional and thermal parameters, Table 2 is a list of the observed and calculated structure factors.

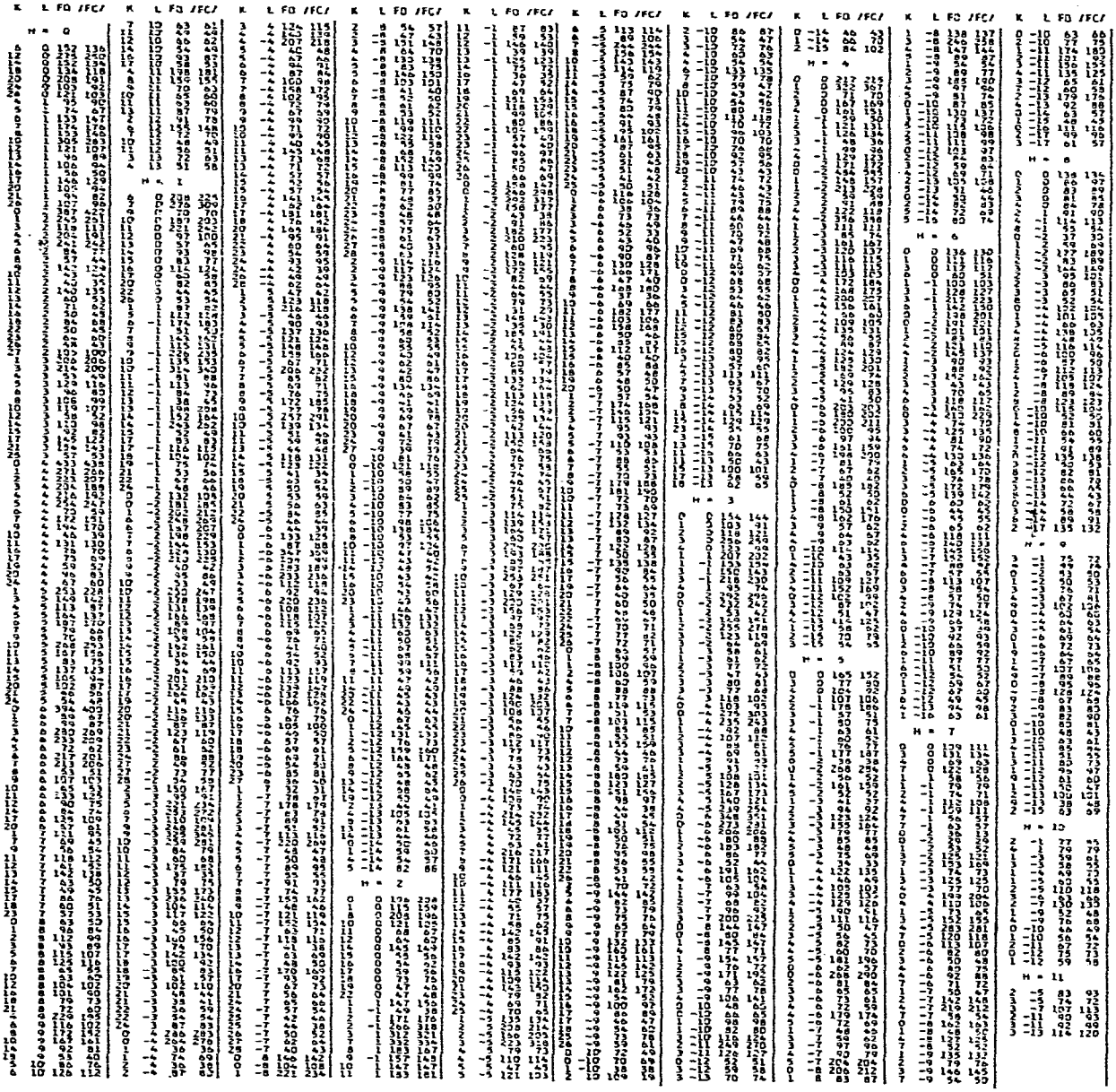
PACKING AND COORDINATION AROUND THE CATIONS

Fig. 1 shows the projection of the structure along the [1,0,0] axis. The crystal consists of anionic layers parallel to the (1,0,0) plane. Along the axis there are channels which are occupied by the cesium ions and the water molecules.

The two non equivalent cesium ions define a direction nearly parallel to the a axis, as it can be seen from Table 1, and their separation is exactly $a/2$. Each cation exhibits eight contacts with oxygen atoms of water and of carbonyl groups, ranging

TABLE 2

OBSERVED AND CALCULATED STRUCTURE FACTORS MODULI IN ELECTRONS



from 3.0 Å to 3.5 Å. No regular coordination polihedra can be assigned to these cations, but there exists a limited regularity consisting of a distorted square of oxygen atoms perpendicular to the vector Cs1–Cs2 and shared by the two cations. It is noteworthy that this square is formed from two water molecules (O1 and O2 in Fig. 1) and two carbonyl oxygen atoms. The third water molecule (O3 in Fig. 1) is not coordinated to the cesium ions and displays contacts with the neighboring oxygens in the order of

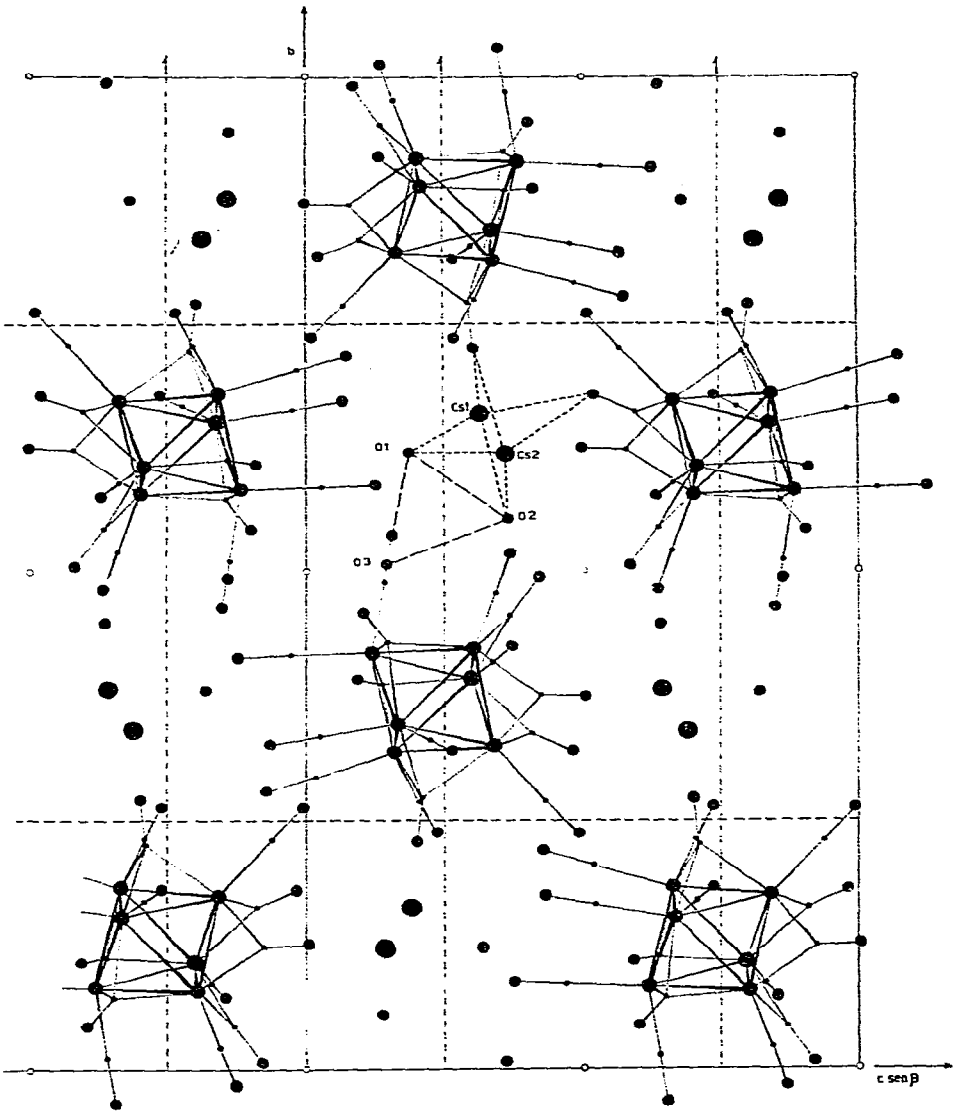


Fig. 1. Projection of the structure along the [1,0,0] axis.

2.8–2.9 Å. This seems to exclude the presence of a definite hydrogen bond in favor of a clathrating situation.

STRUCTURE OF THE ANION $[Co_6(CO)_{15}]^{2-}$

The anion is built upon an octahedral cluster of cobalt atoms surrounded by 15 carbonylic groups. Three of these are triply bonded on faces, three are doubly bonded on edges, and nine are terminal.

The overall symmetry is C_{3v}. Fig. 2 shows a projection along the threefold symmetry axis of the anion. Figs. 3 and 4 record distances, with e.s.d., and some of the

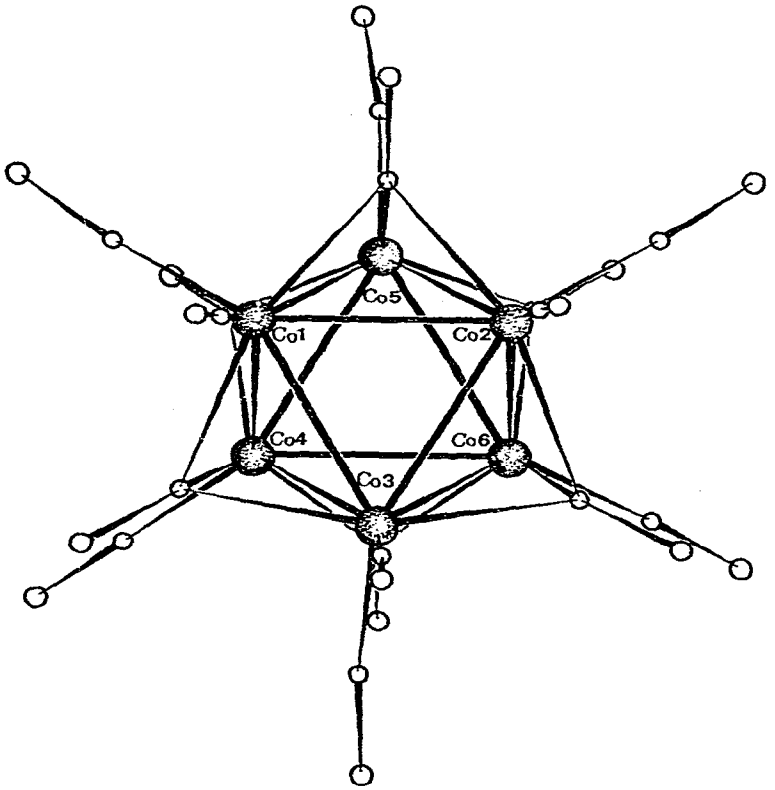


Fig. 2. Projection of the anion $[Co_6(CO)_{15}]^{2-}$ along the threefold symmetry axis.

bond angles. The distances involving the metal atoms bridged by edge carbon monoxide groups, labelled Co4, Co5, and Co6, have a mean value of 2.47 Å whereas the other nine metal–metal distances have a mean value of 2.52 Å. The difference of 0.05 Å although small is significant in relation to the e.s.d. The overall mean of 2.51 Å is in agreement with a number of Co–Co distances which have been reported[10].

Bond shortening between metal atoms supporting multiple bridges of carbonyl groups has been often reported, *e.g.* in $[Fe_3(CO)_{12}]$ (ref. 11), $[HFe_3(CO)_{11}]^-$ (ref. 12), $[Fe_4(CO)_{13}]^{2-}$ (ref. 13), and in $[Rh_3(\pi\text{-}Cp)_3(CO)_3]$ (ref. 14). This effect is not present in compounds *e.g.* $[Co_4(CO)_{12}]$ (ref. 11), $[Rh_4(CO)_{12}]$ (ref. 15), $[Ir_4(CO)_{10}(PPh_3)_2]$ (ref. 16) and $[Ir_4(CO)_9(PPh_3)_3]$ (ref. 16), having single bridges between metal atoms.

The various kinds of carbonyl groups display a variety of Co–C and C–O bond lengths. For terminal groups the mean Co–C and C–O distances are 1.74 Å and 1.15 Å, respectively. These groups are essentially linear, the angle Co–Ĉ–O varying between 171° and 180°, as it is generally found. Double bridging CO groups have the following Co–C, C–O and Co–Ĉ–O mean values: 1.90 Å, 1.17 Å, and 140°. These bridges are symmetric within the standard deviations. We can compare the above distances and angles with those found in $[Co_2(CO)_8]$ (1.19 Å, 1.21 Å, 137°)[17], in $[Co_2(CO)_9HCCH]$ (1.98 Å, 1.19 Å)[18], in $[Co_4(CO)_{10}(Et_2C_2)]$ (1.84–1.97 Å, 1.17 Å)[19] and in several carbonylic compounds of other transition elements[20]. The

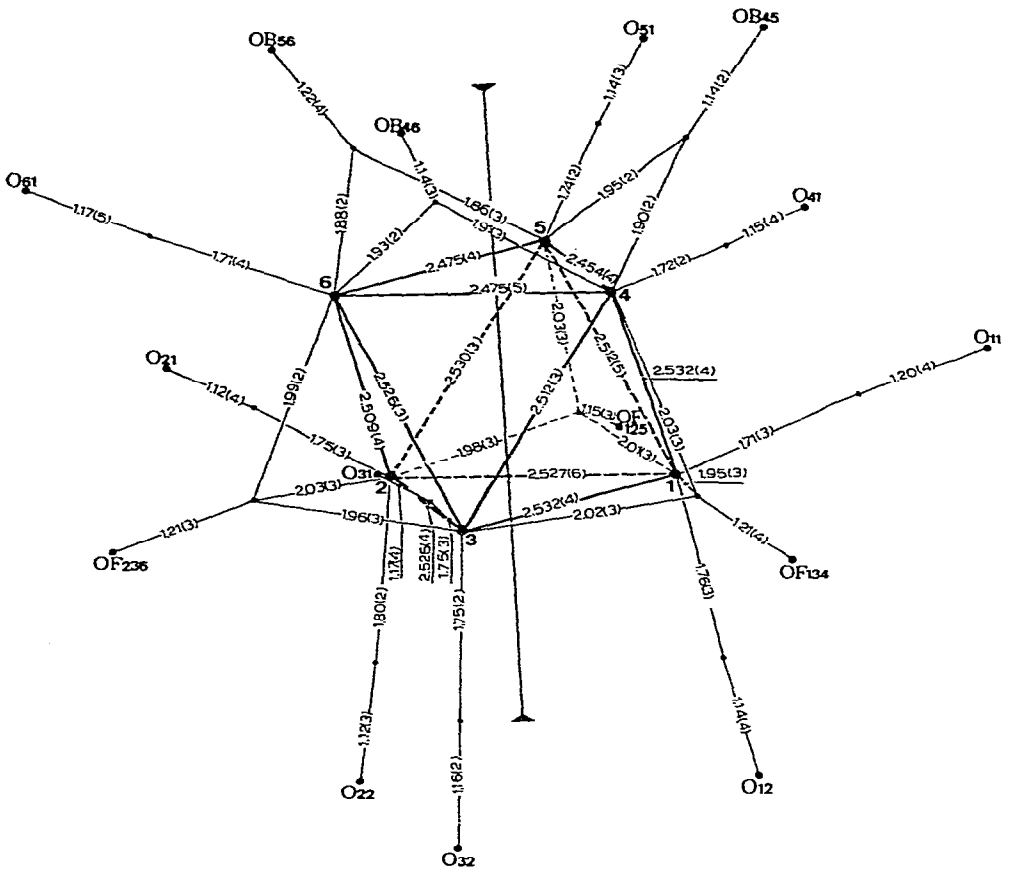


Fig. 3. Bond distances in the anion $[Co_6(CO)_{15}]^{2-}$ with their e.s.d.

face bonded carbonyls have the following average distances: Co–C 2.00 Å and C–O 1.19 Å. However the carbon atoms are coordinated to a single face in such a way that only the overall C_{3v} symmetry of the molecule is respected. In fact two of the Co–C distances systematically are longer than the third one with averages 2.02 Å (from six values) and 1.97 Å (from three values).

The bond angle Co–$\hat{C}$–O for these carbonyls has a mean value of 133.3°. If we take into account the above bond asymmetry, the three Co–$\hat{C}$–O angles have averages: 134°, 134° and 131°. The mean angle Co–$\hat{C}$–Co is 78°. These distances and angles are comparable with those found in $[Rh_6(CO)_{16}]$ (2.17 Å, 1.20 Å, 132°, 79.5°)[4], in $[Fe_4(CO)_{13}]^{2-}$, (2.00 Å, 1.20 Å, 134°, 77.9°)[13], in $[Ni_3(\pi\text{-Cp})_3(CO)_2]$, (1.94 Å, 1.19 Å, 134°, 77°)[21] and in $[Fe_4(\pi\text{-Cp})_4(CO)_4]$ (80°)[22].

DISCUSSION

It is interesting to compare the structure of this anion with that of the neutral molecule $[Co_6(CO)_{16}]$. The latter should have the same structure as $[Rh_6(CO)_{16}]$ in view of the strict crystallographic isomorphism[3] and the IR spectral similarity[2].

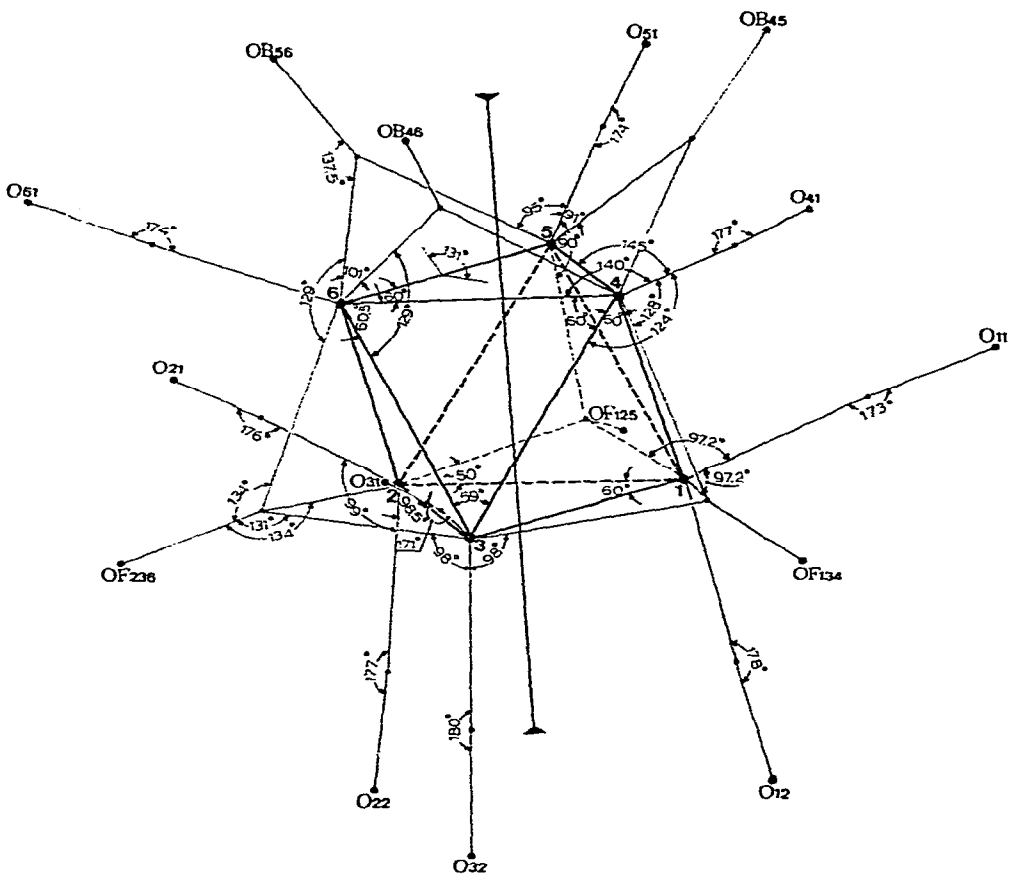


Fig. 4. Some bond angles in the anion $[Co_6(CO)_{15}]^{2-}$.

The present cluster can be derived from a neutral $M_6(CO)_{16}$ molecule by subtraction of one of the four face bridging carbonyl groups. At the same time one terminal carbon monoxide group on each cobalt atom of this face becomes bridged to the edges, so that the entire process results in a change of symmetry from T_d of the neutral molecule to C_{3v} of the present anion.

The geometry of coordination around each metallic atom can be rationalized by keeping the intermetallic bonds separated from the cobalt–carbon bonds. Fixing attention on the latter, we note that the atoms Co1, Co2, Co3, are linked to two linear carbonyls and to two bridged carbonyls on the faces. The planes passing through these groups and the metallic atom are perpendicular to each other: furthermore the angle of the terminal CO's to the cobalt is little different from a tetrahedral angle (C_t–$\hat{C}o$–$C_t = 100°$).

Bearing in mind that the face carbonyl bond may be considered to have four centres, and that therefore the measured angle C_f–$\hat{C}o$–C_f may be greater than that between the atomic orbitals of the metal which contribute to the bond, it may be assumed that the atoms Co1, Co2, Co3 use sp^3 hybrids to link to the two terminal carbonyls and to the two carbonyls bridged on the faces.

The metallic atoms Co4, Co5, Co6 are on the other hand each linked to one terminal, two bridged on edges and one bridged on face CO groups. The carbon atoms of the bridging groups are on a plane roughly perpendicular to the terminal bond Co–C and to the body diagonal of the octahedron. The arrangement of these four carbonyls is that of a triangular pyramid, with the cobalt atom practically on the base plane (0.05 Å outside the triangle of the carbon atoms). Again the bond between the metal and the bridged carbonyls may be considered polycentric, and the geometry suggests that the cobalt uses planar hybrids of sp^2 type for these carbonyls, while the orbital p_z interacts with the terminal carbonyl.

This mode of using the s and p orbitals of the metal leaves all five d orbitals available for the intermetallic bond and for back-donation. Furthermore, with an orientation such as to maintain $d_{x^2-y^2}$ and d_{xy} essentially non-bonding, d_{xz} and d_{yz} directed along the edges and d_{z^2} along the diagonal of the body of the octahedron, the orbitals d_{xz} and d_{yz} can combine with each other in octahedral O_h symmetry to give 12 M.O. of the type t_{1g}, t_{2g}, t_{1u}, t_{2u}, the d_{z^2} to give 6 M.O. of the type a_{1g}, e_g and t_{1u}.

We assume also that the non-bonding orbitals $d_{x^2-y^2}$ and d_{xy} have suitable energy to back-donate on the π^* orbitals of the terminal carbon monoxide groups, and that the polycentric bonds on the faces require 6 electrons for each occupied face $(a_1 + e)$. If this interpretation is correct, the 86 valency electrons (54 of cobalt, 30 of the carbonyls and 2 anionic) are distributed as follows: 48 in molecular orbitals, formed by hybrids of sp type of the metal and σ orbitals of the ligands, 24 in non-bonding d orbitals, 12 in t_{2g} and t_{1u} molecular orbitals formed by overlapping the orbitals d_{xz} and d_{yz} and finally 2 electrons in the bonding orbital a_{1g}. This interpretation is also applicable to the cluster $[Co_6(CO)_{16}]$. In this case the six metallic atoms at the vertices of the octahedron are equivalent and each is linked to two terminal carbonyls and to two carbonyls bridged on the faces. The molecular symmetry T_d involves the use of hybrids sp^3 by the metal, leaving the d orbitals in orientations suitable to form intermetallic molecular orbitals of the type described.

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