Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE POTASSIUM SALT OF THE HEXANUCLEAR CARBONYL COBALTATE $[Co_6(CO)_{14}]^{4-}$

V. G. ALBANO, P. L. BELLON, P. CHINI AND V. SCATTURIN
Istituto di Chimica Generale ed Inorganica dell' Università, Via G. Venezian, 21, 20133 Milan (Italy)

(Received December 23rd, 1968)

SUMMARY

The crystal and molecular structure of the potassium salt of the tetradecacarbonylhexacobaltate tetraanion $K_4[Co_6(CO)_{14}]\cdot 6\,H_2O$ has been determined by tridimensional X-ray data measured by counter methods. The structure has been refined by least squares on F down to an R factor of 0.06. The salt crystallizes in the monoclinic space group $C^5_{2h}=P^2_{1/n}$ with the following cell constants: $a=12.00(1)$ Å, $b=10.04(1)$ Å, $c=12.00(1)$ Å, $\beta=90.0°$ (1), there are 2 formula units per cell.

The structure is composed of a tetragonal body centered packing of anions with the cavities occupied by potassium ions and water molecules.

The anion $[Co_6(CO)_{14}]^{4-}$ possesses an inversion center and contains an octahedral cluster of metal atoms surrounded by 14 CO groups; 6 of them are linearly bonded one for each cobalt atom and the other 8 CO groups are triply bridged on all the octahedral faces. The metal atoms cluster and its CO's environment deviate from the holosymmetry OO_h. When all the distortions are taken into account the anion can be assigned the symmetry S_6.

The Co–Co mean distance is 2.50 Å; the Co–C and the C–O distances are 1.70 Å and 1.17 Å for linearly bonded groups; for triply bridged groups the Co–C distances are scattered in the range 1.89(1)–2.31(1) Å, the C–O mean distance is 2.21 Å.

INTRODUCTION

The isoelectronic series of octahedral carbonylic clusters $Co_6(CO)_{16}$, $[Co_6(CO)_{15}]^{2-}$, $[Co_6(CO)_{14}]^{4-}$ and $[Ni_2Co_4(CO)_{14}]^{2-}$ has recently been synthesized[1–6]. These species are analogous to other hexanuclear species of the second transition series, such as $Rh_6(CO)_{16}$ (ref. 7), $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{14}$ (arene) (ref. 8, 9). The bonding scheme in all these species is filled by a total of 86 electrons. One major problem is the meaning of this number, in term of an energy spectrum for allocating electrons, although some interpretative approaches have been proposed[4,7,10].

The first member of the present series, $Co_6(CO)_{16}$, is assumed to have the same structure as $Rh_6(CO)_{16}$. This is based upon the observations that the two crystalline species are strictly isomorphous[2] and also that their IR spectra are very similar[1]. Thus in this cluster the 6 cobalt atoms are linearly bonded, each to 2 carbonyl groups, and the remaining 4 CO groups are triply bridged on alternating faces of the octahedron. A rearrangement of this structure takes place when one CO group is replaced by 2 electrons in the anion $[Co_6(CO)_{15}]^{2-}$ (ref. 4). In this cluster 9 CO groups are linearly bonded, 3 are bridging on edges and 3 are bridging on faces, with a decrease in the overall symmetry respect to the neutral species.

This paper deals with the X-ray structure determination of the potassium salt of the tetraanion $[Co_6(CO)_{14}]^{4-}$, as a part of a more general program of structural studies on these clusters. Apart from the obvious interest of such determination from the point of view of stereochemistry and bonding, there are difficulties in the chemical determination of the molecular complexity of these compounds and furthermore the rearrangement of ligands in going from one compound to another is almost impossible to understand on the basis of IR spectra only.

EXPERIMENTAL

Tetrapotassium tetradecacarbonylhexacobaltate crystallizes in beatiful redish-black crystals. The compound was formulated as $K_4[Co_6(CO)_{14}] \cdot 6\ H_2O$, the formula weight being 1010. The compound is unstable upon exposure to the atmosphere and for collection of the diffraction pattern it was necessary to enclose it in a Lindemann-glass capillary.

The Laue symmetry $2/m$ was determined from precession photographs. Systematic absences indicate a space group $C_{2h}^5 = P2_{1/n}$. This space group refers to the reduced cell, whereas the standard setting, having space group $P2_{1/c}$ is related to the present one in the following way: $a_1 = -a$, $b_1 = b$ and $c_1 = a + c$. The unit cell parameters, determined from film data were refined on the Pailred diffractometer using an ω-lag procedure outlined by Hornstra[11]. The refined cell parameters at 25° are $a = 12.00(1)$ Å, $b = 10.04(1)$ Å, $c = 12.00(1)$ Å, $\beta = 90.0°(1)$, $V = 1446$ Å^3. Agreement between observed and computed specific gravities was obtained for $Z = 2$ ($\rho_{calc} = 2.32$ g/cm^3, $\rho_{obs} = 2.3(1)$ g/cm^3: the latter value was determined by picnometric measurements). The Z value shows that the independent part of the structure is one half of the unit formula reported above and also that the metal atom cluster possesses a center of symmetry.

The diffraction intensities have been measured with a Pailred linear equi-inclination diffractometer, the incident beam being Mo-$K\alpha$ radiation monochromatized by a Si[111] single crystal slice. In order to avoid systematic double reflection effects as much as possible (the cell is a pseudo-tetragonal one) the direction $a + c$ was oriented along the ω-axis; the integrated intensities up to the 15th level (maximum equi-inclination angle 17°) were collected in the range $3° < \Upsilon < 50°$. The ω-scan method, a reliable procedure with monochromatic radiation, was used in the measurement of the diffraction profiles. Few standard reflections of the zero level were checked periodically to see whether any crystal decay was taking place. No significant variation of the intensities of these standards was noticed.

From the entire set of measurements (about 2500 reflections) all the data having a relative counting statistical error $\sigma(I)/I > 0.25$ were suppressed. The final set (2007 reflections) were corrected for systematic effects. The absorption corrections were computed by the method of Busing and Levy[12]. Because of the low linear absorption factor ($\mu = 43.1$ cm^{-1}), a 216 points (6^3) sampling was adopted. Twelve crystal faces were measured on a Stoe optical goniometer equipped with a Leitz screw-micrometer. The crystal dimensions were (in cm) 0.039 along the ω-axis and 0.039×0.027 normally to it, the volume being 2.11×10^{-5} cm^3. Due to the fact that the crystal section normal to the rotation axis is almost hexagonal the transmission factors vary only from 0.377 to 0.399.

STRUCTURE SOLUTION AND REFINEMENT

The structure has been solved by direct methods. The structure factors brought on absolute scale by the Wilson statistical extrapolation[13], were transformed into E values.

A set of 170 E's, greater the 1.8, were applied to Σ_2 relationship of Karle and Hauptmann[14]. The signs of 3 origin determining reflections were kept constant and 4 other reflections were given all the possible sign combinations. The 16 starting sets were used to attribute the signs to the remaining normalized F_o's. The correct sign set was the one obtained with the minimum number of iterations.

A Fourier synthesis based upon the contribution of the 170 E disclosed the position of cobalt and potassium atoms. The reliability index based on their contribution only and computed for all the F_o's was $R=0.35$. A difference Fourier map has shown the positions of all the light atoms of the structure. The R value computed with the contribution of all the atoms was 0.26.

The structure was refined by least squares in the block diagonal approximation because of the limited computing facilities. The blocks were 9×9 for atoms treated anisotropically (see below) and 4×4 for the atoms treated isotropically. The scale factor was correlated with the mean overall temperature factor of the structure in a 2×2 block[15]. The minimized function was $\Sigma w(F_o - K \cdot |F_c|)^2$. The atomic scattering factors, used in the least squares as well as in structure factors computations, were chosen as follows: for Co the T.F.D. statistical model curves[16] corrected for the real part of the anomalous dispersion[17], for K^+ (also corrected for anomalous dispersion), O and C the curves from self-consistent variational field method[18].

The weights w were the reciprocal of the F_o's variance. This variance was computed from the variance of the corresponding F_o^2 assumed to be[19]: $V(F_o^2) = V_{cs}(F_o^2) + (A \cdot F_o^2)^2$, where $V_{cs}(F_o^2)$ is the counting statistical variance and A a parameter which in the present case was chosen in such a way as to make $\Sigma(w \cdot \Delta^2)/n$, the weighted mean quadratic error, approximately constant over the entire range of F_o's[15]. In the first cycles $A=0.03$ was used; for final ones a more suitable model with $A=0.07$ was chosen.

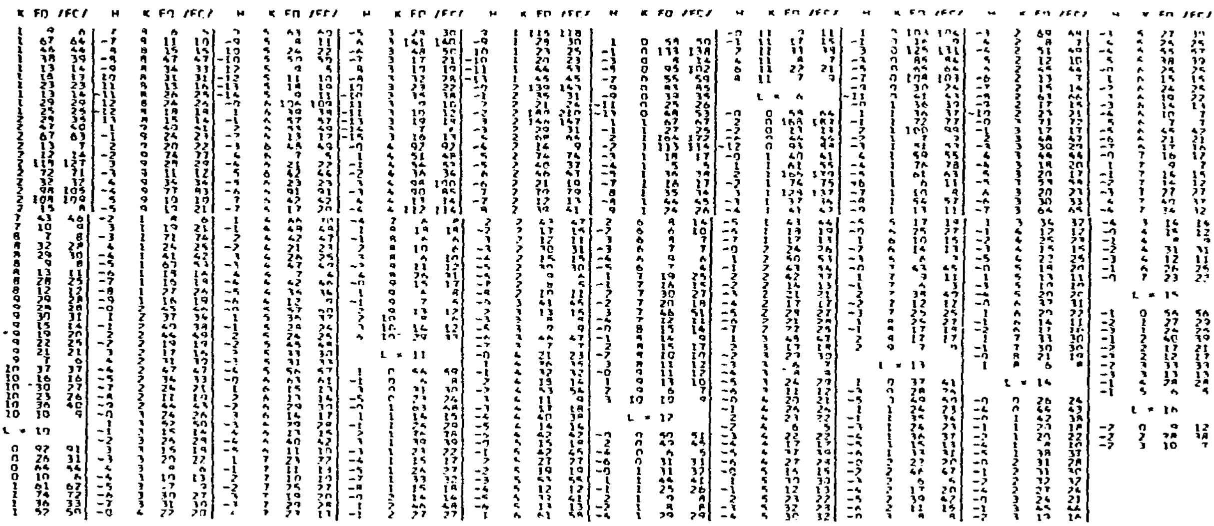
A preliminary refinement was done on the positions and thermal isotropic factors of the metal atoms only ($R=0.15$). After that the general isotropic refinement on all the atoms was undertaken; this refinement led to the reliability indices $R = \Sigma(|F_o - K \cdot |F_c||)/\Sigma F_o = 0.08$ and $R_w = [\Sigma w(F_o - K \cdot |F_c|)^2/\Sigma w \cdot F_o^2]^{\frac{1}{2}} = 0.10$. Further least squares cycles were finally computed with anisotropic thermal parameters for the metal atoms. The final reliability indices were: $R' = 0.060$ and $R'_w = 0.070$. The value of the error fit function was 1.57. A final electron density map has shown residual peak heights of $0.5 e^-/\text{Å}^3$ or less.

All the computations referred upon in this paper were done on an IBM 7040 computer. The program used were local versions of the following entries of the "1966 International World List of Crystallographic Programs": 7528, 7531, 7532, 7535 for

TABLE 1

OBSERVED AND CALCULATED STRUCTURE FACTORS MODULI IN ELECTRON UNITS FOR $K_4[Co_6(CO)_{14}]\cdot 6\ H_2O$

H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/	H	K	FO	/FC/
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]



Fourier analysis and S.F.L.S. computation. Counter data reduction and absorption corrections were based upon Fortran IV programs prepared in the authors' Laboratory.

Table 1 is the list of observed and computed structure factors moduli in electron units. In Tables 2 and 3 the positional and the thermal parameters of cobalt and

TABLE 2

FINAL ATOMIC COORDINATES[a] FOR ANISOTROPICALLY REFINED ATOMS OF $K_4[Co_6(CO)_{14}]\cdot 6\,H_2O$

Atoms	x/a	y/b	z/c	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Co1	−1362(1)	34(1)	565(1)	22(0)	−0(1)	5(1)	69(1)	−14(1)	35(0)
Co2	535(1)	−364(1)	1336(1)	36(0)	−3(1)	−12(1)	57(0)	7(1)	23(0)
Co3	108(1)	1726(1)	245(1)	39(0)	−4(1)	−11(1)	36(0)	−1(1)	40(0)
K1	−3004(2)	−3359(2)	566(2)	55(1)	−21(2)	2(2)	89(2)	0(2)	37(1)
K2	628(2)	−3878(2)	2735(2)	41(1)	−5(2)	−12(2)	77(1)	−0(2)	57(1)

[a] All values $\times 10^{-4}$; anisotropic temperature factors are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

TABLE 3

FINAL ATOMIC COORDINATES[a] FOR ISOTROPICALLY REFINED ATOMS OF $K_4[Co_6(CO)_{14}]\cdot 6\,H_2O$

Atoms	x/a	y/b	z/c	B (Å^2)	Atoms	x/a	y/b	z/c	B (Å^2)
C1	−2728(7)	80(8)	999(7)	2.4(1)	O3	719(7)	4401(8)	810(7)	5.0(1)
C2	1011(7)	−387(8)	2661(7)	2.4(1)	OF135	−1952(5)	2644(5)	−863(5)	2.7(1)
C3	425(7)	3334(8)	544(7)	2.3(1)	OF123	−943(5)	1864(6)	2451(5)	3.3(1)
CF135	−1265(7)	1808(8)	−655(7)	2.5(1)	OF126	−1238(5)	−2335(5)	1997(5)	2.6(1)
CF123	−704(7)	1309(8)	1595(7)	2.6(1)	OF234	2400(5)	1577(6)	1244(5)	2.8(1)
CF126	−860(7)	−1478(8)	1381(7)	2.5(1)	OA1	999(6)	3486(7)	3316(6)	4.3(1)
CF234	1607(7)	998(8)	845(7)	2.3(1)	OA2	−2954(7)	3998(8)	976(7)	5.2(1)
O1	−3627(7)	13(8)	1345(7)	5.1(1)	OA3	5007(6)	2501(7)	306(6)	4.4(1)
O2	1424(7)	−351(8)	3546(7)	5.4(1)					

[a] All values $\times 10^4$.

potassium and, respectively, of carbon and oxygen atoms are reported together with their e.s.d.'s.

DESCRIPTION OF THE CRYSTAL STRUCTURE

As pointed out in the experimental part of this paper the unit cell contains 2 units $K_4[Co_6(CO)_{14}]\cdot 6\ H_2O$ and the fourfold space group multiplicity requires the crystallographically independent part to be one half of the unit formula. This means that only 2 potassium atoms and 3 water molecules are independent, and also that the anion $[Co_6(CO)_{14}]^{4-}$ must possess a twofold symmetry operator that in this case has to be one of the inversion centers of the space group.

The unit cell is pseudo-tetragonal and can be regarded as the result of the packing of the large spherical anions (see next section) in a body centered tetragonal lattice; in fact in the space group $P2_{1/n}$ the inversion center at 0,0,0 is equivalent to the inversion center at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

The cavities in the anion packing are occupied by potassium ions and water molecules. All the oxygen atoms of the carbonyl groups are involved in the coordination around the cations. Each CO group displays one or two $O{-}K^+$ contacts. The water molecules are involved in single or double contacts with potassium ions and in loose hydrogen bonds with oxygen atoms. All the $O{-}K^+$ contacts and the O–H ... O interactions are reported in Table 4.

TABLE 4

O–H····O AND $O{-}K^+$ CONTACTS IN $K_4[Co_6(CO)_{14}]\cdot 6\ H_2O$

Atoms[a]	Distance (Å)	Atoms[a]	Distance (Å)
O–H ... O contacts		*K2–O contacts*	
OA1–O123	2.87(2)	K2–O1	2.87(1)
OA2–O135	2.87(2)	K2–O3	2.89(1)
OA3–OA1	2.86(2)	K2–O135	3.02(1)
		K2–O345	2.87(1)
K1–O contacts			
K1–O2	2.84(1)	K2–O234	2.70(1)
K1–O123	2.70(1)	K2–OA1	2.70(1)
K1–O234	2.91(1)	K2–OA1	2.72(1)
K1–O345	2.92(1)	K2–OA3	2.84(1)
K1–OA2	2.70(1)		
K1–OA3	2.76(1)		

[a] The atoms are labelled according to Fig. 2 and Tables 2 and 3; the oxygen atoms listed may come from different molecules.

In this way the anions are connected together through $O{-}K^+{-}O$ bridges, the connections being extended throughout the crystal structure. It is apparent that a number of contacts $K^+{-}O$ supported by carbonyl groups are in the same range of length at the $K^+{-}OH_2$ contacts. The low values of the frequences of the CO stretching modes in this compound [ν(CO) at about 1918, 1895, 1885 and 1635 cm^{-1}][24] indicate that extensive π bonding is present. The π component of the Me–CO bond increases the permanent dipole moment of the ligand itself with the result that the negative charge on the oxygen atom is augmented (see, for instance ref. 20). The comparison between the water–cation and the carbonyl–cation contacts might give an idea of what the negative charge on the oxygen atom of the CO group is, although caution must be exercized in such a kind of approach.

THE ANION $[Co_6(CO)_{14}]^{4-}$

A perspective view of the centrosymmetric tetraanion tetradecacarbonylhexacobaltate is shown in Fig. 1. In Fig. 2 bond lengths and angles together with their e.s.d.'s are reported.

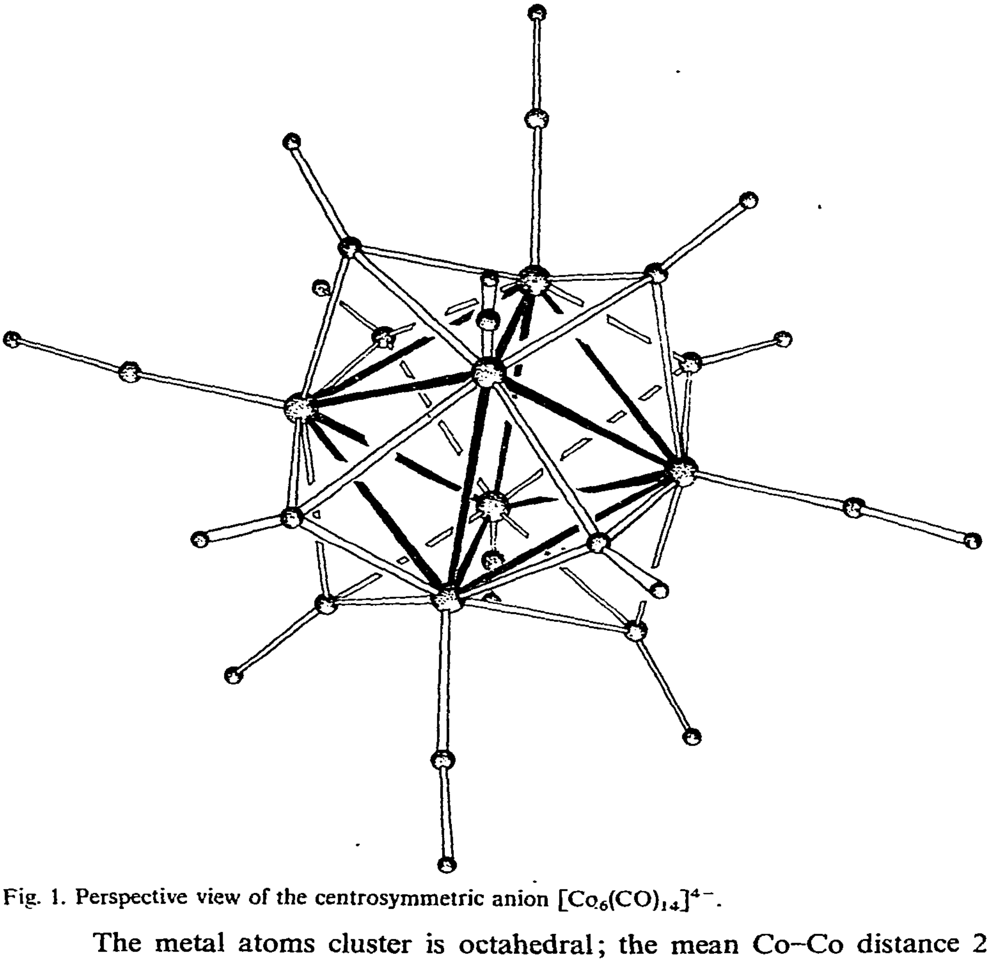


Fig. 1. Perspective view of the centrosymmetric anion $[Co_6(CO)_{14}]^{4-}$.

The metal atoms cluster is octahedral; the mean Co–Co distance 2.50 Å compares well with the corresponding mean of 2.51 Å found in the dianion[4] $[Co_6(CO)_{15}]^{2-}$. In the present cluster the Co–Co distances fall into the range 2.466(2)–2.534(2) Å; the distortion can be rationalized by dividing the intermetallic bonds into two classes: 6 edges of the octahedron in the range 2.510(2)–2.534(2) Å contour two faces related by the inversion center; the other 6 edges are in the range 2.466(2)–2.491(2) Å. In this way the symmetry of the metal cluster can be idealized as D_{3d} with the faces bordered by the longer metal–metal distances normal to the $\bar{3}$ operator.

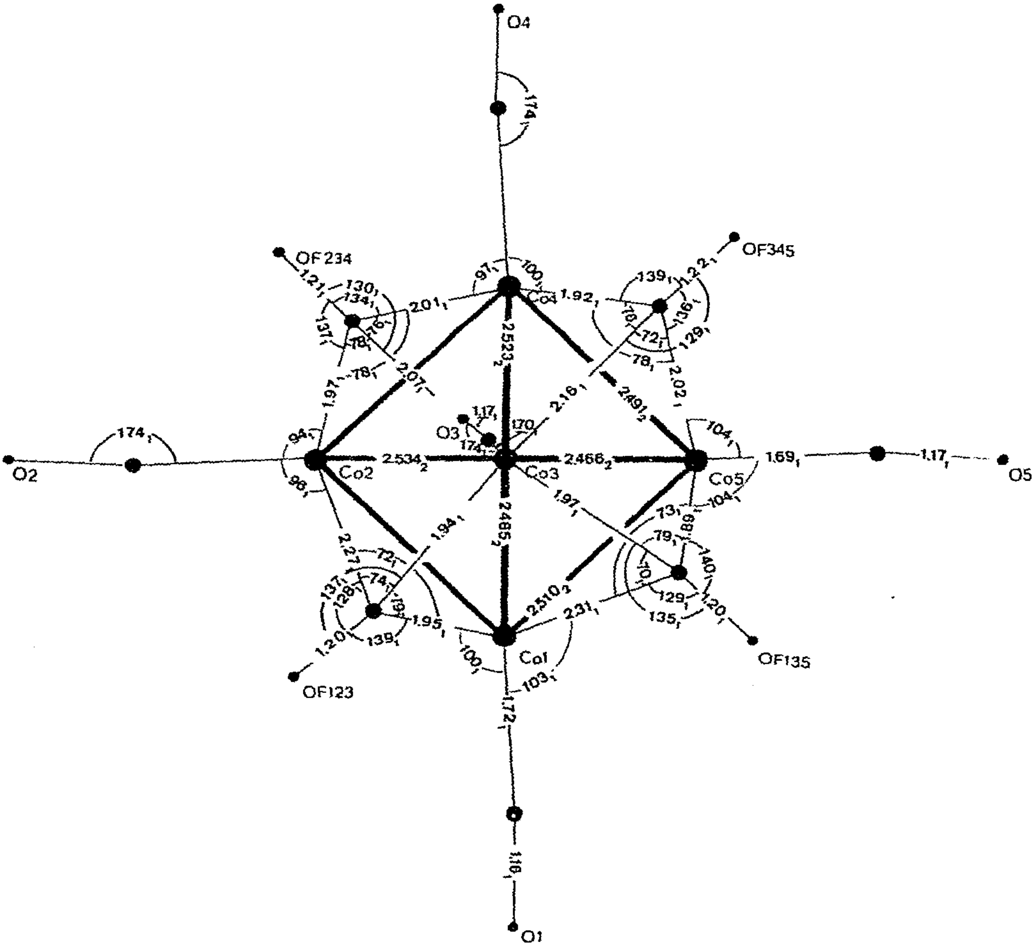


Fig. 2. Distances and angles with their e.s.d. in the anion $[Co_6(CO)_{14}]^{4-}$.

Two kinds of CO groups surround the metal cluster: 6 groups are linearly bonded to the 6 apices of the octahedron and the 8 remaining groups are triply bridged on all the cluster faces. The topological relationship among the 2 kinds of

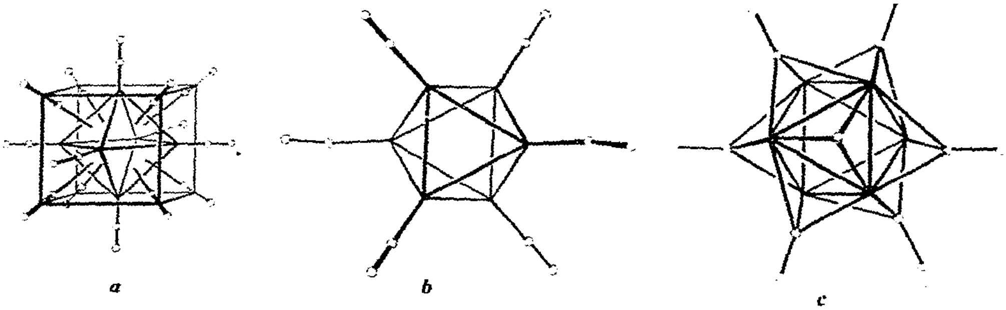


Fig. 3a–c. Topological and symmetry relationships between linear and bridged ligands in the anion $[Co_6(CO)_{14}]^{4-}$.

ligands is clearly understood when the metal atom cluster is inscribed in a cube, as shown in Fig. 3a: the linearly bonded groups point outward from the 6 cube faces and the bridged groups point to the 8 cube apices.

The carbonyl groups will be discussed with reference to Fig. 3b,c. In Figure 3b the linearly bonded carbonyls are represented. These groups are characterized by a narrow distribution of the bond lengths and angles: the three independent Co–C distances are 1.69(1), 1.70(1) and 1.72(1) Å and the corresponding C–O distances are 1.69(1), 1.70(1) and 1.72(1) Å and the corresponding C–O distances are 1.16(1), 1.17(1) and 1.17(1) Å. The mean values for Co–C and C–O 1.70 Å and 1.17 Å can be compared with the corresponding values in $[Co_6(CO)_{15}]^{2-}$ 1.74 Å and 1.15 Å[4]. The shorter metal–carbon and the longer carbon–oxygen distances in the tetraanion, as compared with the dianion, indicate a more efficient d_π–π^* back-donation. All the linearly bonded carbonyls are characterized by a Co–C–O angle of 174°(1). The remarkable constance of this bending is possibly due to an electronic effect which can arise from different interactions of the π^* orbitals of the CO groups with the appropriate metal cluster orbitals[10,21]. The triple bridges formed by 8 CO groups display rather irregular Co–C distances; however these irregularities can be better rationalized by dividing these groups in 2 classes: 2 axial groups, oriented along the $\bar{3}$ axis of the trigonal antiprism and 6 other groups bonded to the remaining faces of the antiprism. The 2 axial CO are almost symmetrically bonded to the basal faces as it can be noticed from the Co–C–Co angles which are in the range 76°(1)–78°(1) and from the Co-C distances in the range 1.97(1)–2.07(1) Å. The 6 other groups display a larger spread of the Co–C–Co angles from 70°(1) to 79°(1). Each bridged group is characterized by 2 shorter Co–C distances [their overall range is 1.89(1)–2.02(1) Å] and a longer one [in the range 2.16(1)–2.31(1) Å]. Distances and angles for these 6 bridged groups follow a pattern (see Fig. 3c) which is no longer in agreement with the D_{3d} point group. The overall symmetry of the anion consistent with these deformations is S_6. Clearly this is the symmetry of the metal cluster orbitals involved in bonding with the CO groups.

The carbon–oxygen length in all the bridged carbonyls is 1.20(1)–1.22(1) Å; the mean 1.21 Å may be compared with the corresponding mean of 1.19 Å in the dianion[4] $[Co_6(CO)_{15}]^{2-}$. Moreover the CO distance of 1.21 Å compares well with the "ketonic" interactions in metal–acetyl and metal–carboalkoxy compounds in which the CO distances of 1.21(2) Å[22] and respectively, 1.18(2) Å[23] have been found. As far as bond length–bond order relationships are acceptable, this fact suggests that in face-bridged groups the carbon–oxygen bond order is 2 or, in other words, that a total of 2 electrons has been transferred from metal cluster orbitals to the π^* orbitals of the CO groups.

In the present complex all the 8 faces of the octahedron are involved in triple bridges, as compared with 4 faces in the neutral parent species $Co_6(CO)_{16}$ and 3 faces in the dianion $[Co_6(CO)_{15}]^{2-}$ where also 3 double bridges are present. These facts indicate that the formation of triple bridges is very efficient in dissipating the excess of negative charge on the metal atoms. This dissipation of charge through π back-donation mechanism become increasingly important in going from the neutral complex to the tetraanion as it may be seen not only from the already noticed variation of the Co–C and C–O bond lengths, but also from the shifts of the IR CO stretching bands toward lower frequencies[1,3,5].

ACKNOWLEDGEMENTS

The Authors acknowledge the Italian Consiglio Nazionale delle Ricerche for financial support.

REFERENCES

1 P. Chini, *Chem. Commun.*, (1967) 440.
2 V. Albano, P. Chini and V. Scatturin, *Chem. Commun.*, (1968) 163.
3 P. Chini and V. Albano, *J. Organometal. Chem.*, 15 (1968) 433.
4 V. Albano, P. Chini and V. Scatturin, *J. Organometal. Chem.*, 15 (1968) 423.
5 P. Chini, V. Albano and S. Martinengo, *J. Organometal. Chem.*, 16 (1969) 471.
6 P. Chini, S. Martinengo and V. Albano, *Proc. Int. Symp. Metal Carbonyls and Derivatives, Venice 2–4 Sept., 1968*, A-3, *Inorg. Chim. Acta*, (Ed.).
7 E. R. Corey, L. F. Dahl and W. Beck, *J. Amer. Chem. Soc.*, 85 (1963) 1202.
8 B. F. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc., A*, (1968) 2865.
9 R. Mason and W. R. Robinson, *Chem. Commun.*, (1968) 468.
10 S. F. A. Kettle, *J. Chem. Soc., A*, (1967) 314.
11 J. Hornstra, *Report 4021, N.V. Philips Gloeil. Fabr.*, 1965.
12 W. R. Busing and H. A. Levy, *Acta Cryst.*, 10 (1957) 180.
13 A. J. C. Wilson, *Nature*, 150 (1942) 152.
14 H. Hauptmann and J. Karle, *A.C.A. Monograph No. 3*, 1953.
15 D. W. J. Cruickshank and D. E. Pilling, *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, Pergamon Press, London, 1961.
16 L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 26 (1957) 239.
17 *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962.
18 R. Mc. Weeny, *Acta Crystallogr.*, 4 (1951) 513.
19 P. A. Agron, R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, 23 (1967) 1079.
20 T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, 6 (1967) 971.
21 S. F. A. Kettle, *Inorg. Chem.*, 4 (1965) 1661.
22 M. R. Churchil and J. P. Fennessey, *Inorg. Chem.*, 7 (1968) 953.
23 V. Albano, P. L. Bellon and M. Sansoni, *Inorg. Chem.*, in press.
24 Nujol Mull.