Crystal and Molecular Structures of New Cobalt Carbonyl Clusters

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THE preparation of three different hexanuclear cluster carbonyl compounds of cobalt has been recently reported.[1,2] These clusters were formulated as follows:

hexadecacarbonylhexacobalt $Co_6(CO)_{16}$,
pentadecacarbonylhexacobaltate(−II) $[Co_6(CO)_{15}]^{2-}$,
tetradecacarbonylhexacobaltate(−IV) $[Co_6(CO)_{14}]^{4-}$.

Each of the metal atoms in these clusters as well as those in the compounds $Rh_6(CO)_{16}$, $Ru_6C(CO)_{17}$, and $Ru_6C(CO)_{14}$(arene) which have been described recently,[3,4] contains a third of an electron in excess of that of the noble gas configuration. The total of two extra electrons seems related to the stability of this kind of cluster as there is no tendency to lose[3] or gain electrons,[5] as previously speculated.

This behaviour is exemplified by the following redox reactions of $[Co_6(CO)_{15}]^{2-}$ cluster:

$$\begin{tikzcd}
Co_6(CO)_{16} & {[Co_6(CO)_{15}]^{2-}} \arrow[l, "\mathrm{Fe}^{3+}"', "+\mathrm{CO}"] \arrow[d, "-\mathrm{CO}"', "\mathrm{Na}"] \\
 & {[Co_6(CO)_{14}]^{4-}}
\end{tikzcd}$$

Here are some preliminary results of a crystallographic study undertaken to elucidate the stereochemical and electronic structure of these clusters in the compounds,

$Co_6(CO)_{16}$ (I), $Cs_2[Co_6(CO)_{15}],3H_2O$ (II), and
$K_4[Co_6(CO)_{14}],8H_2O$ (III)

which are crystalline solids, rather unstable in air and deeply coloured [black (I), green-black (II), red-black (III)].

The crystal data are given in Table 1. As a comparison, in the first column are the cell constants of the $Rh_6(CO)_{16}$ as reported by Dahl.[3] The first two compounds are obviously isomorphous, so that the structure already reported for the neutral rhodium cluster can also be assigned to the corresponding cobalt compound.

The structure of $Cs_2[Co_6(CO)_{15}],3H_2O$ is fully resolved. Three-dimensional data were collected from precession photographs (Mo-K_α radiation) and 1300 observed reflections were used for solving the structure. A Fourier synthesis of the strongest reflections was computed with phases obtained with the Sayre method and showed the metal cluster and the cations. All of the CO and H_2O groups were subsequently found in a difference Fourier. A least-square isotropic refinement using a block diagonal program written for the IBM 7040 computer, brought the reliability index to 0·085.

The crystal structure can be described in terms of anionic layers packed in such a way as to form, along the *a* direction, channels in which the caesium cations and the water molecules are located.

The metal cluster (Figure) is a distorted octahedron of C_{3v} symmetry, with an average distance Co–Co of 2·49 Å. However, nine out of the twelve edges have a mean length of 2·52(1) Å and the remaining three (namely, those defining the octahedral face 4–5–6) give a value of 2·46(1) Å. This difference is significant at this stage of refinement and relates to the special type of bonding on this face.

Three kinds of metal–carbon bonds appear in the structure. Nine carbonyls are terminally-bonded, three are bridged to edges, and three are bridged on faces. The mean values of cobalt–carbon and carbon–oxygen distances are given in Table 2, together with the angles Co–C–O.

The cobalt atoms are formally 8-co-ordinated

TABLE 1

Crystallographic data

	$Rh_6(CO)_{16}$	$Co_6(CO)_{16}$	$Cs_2[Co_6(CO)_{15}],3H_2O$	$K_4[Co_6(CO)_{14}],8H_2O$
a (Å)	17·00	16·38 (2)	9·26 (1)	11·97 (1)
b (Å)	9·78	9·47 (1)	23·97 (3)	10·04 (1)
c (Å)	17·53	16·89 (2)	14·31 (2)	12·00 (1)
β	121°45′	121°40′ (20′)	122°54′ (20′)	90°00′ (20′)
Space group	*I*2/*a*	*I*2/*a*	*P*2$_1$/*c*	*P*2$_1$/*n*
Z	4	4	4	2
D_m (g. cm.^{3})	2·87	2·3	3·0	2·3
D_c (g. cm.^{3})	2·86	2·36	2·93	2·37

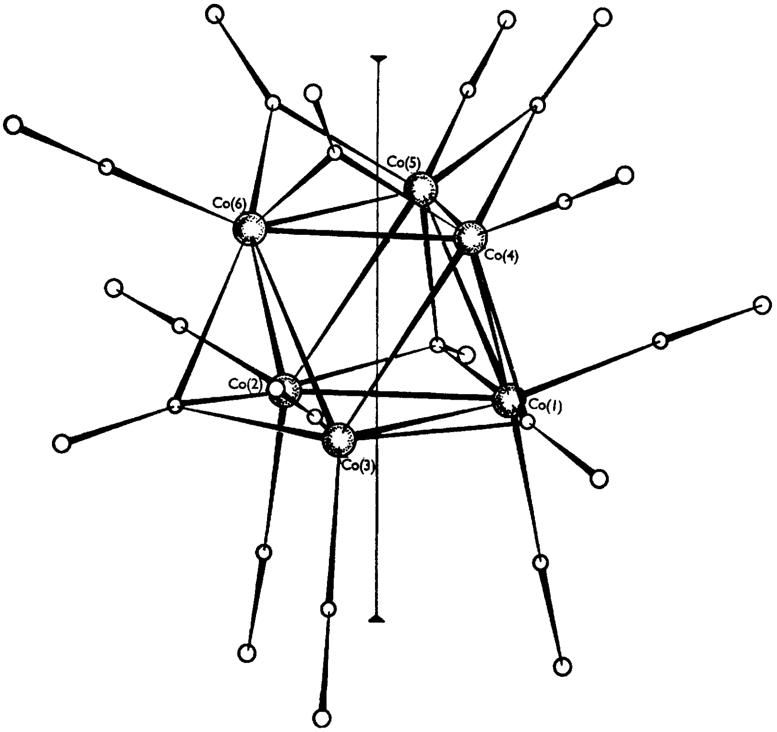

FIGURE. *Projection of the anion pentadecacarbonylhexacobaltate*(-II) $[Co_6(CO)_{15}]^{2-}$.

TABLE 2

Average values of interatomic distances and angles of the CO *groups in the anion* $[Co_6(CO)_{15}]^{2-}$.

	Co–C (Å)	C–O(Å)	Co–C–O
Terminal	1·74	1·15	175°
Bridged on edges ..	1·90	1·17	139°
Bridges on fences ..	2·00	1·19	133°

The atoms **1**, **2**, and **3** (see Figure) have the same co-ordination as the corresponding rhodium atoms in $Rh_6(CO)_{16}$ whereas the remaining cobalt atoms are co-ordinated through a different scheme. The ligand environment of this cluster can be derived from the neutral molecule $Rh_6(CO)_{16}$ by the subtraction of a face-bonded CO and a subsequent rearrangement of three linearly bonded groups into edge-bridging positions.

This rearrangement may be explained by assuming that in $[Co_6(CO)_{16}]$ the metal atoms on a face are bonded to a carbon monoxide using three molecular orbitals of the same type as that found in a cyclopropenyl methyl group.[6] The substitution of a CO molecule with a pair of electrons should formally charge the octahedral face with three pairs of electrons in the appropriate molecular orbitals. The pairs may now give nucleophilic attraction to three linear carbonyls, pushing the CO groups into edge-bridging positions.

(*Received, December* 19*th*, 1967; *Com.* 1359.)

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