Hexacobalt Hexadecacarbonyl and its Derivatives

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FOLLOWING the recent Communication[1] on some derivatives of the pentadecacarbonylhexacobaltate(—II) anion, $Co_6(CO)_{15}^{2-}$, the isolation of a derivative of the tetradecacarbonylhexacobaltate(—IV), $Co_6(CO)_{14}^{4-}$, and of the hexacobalt hexadecacarbonyl, $Co_6(CO)_{16}$, is now reported.

The $Co_6(CO)_{14}^{4-}$ anion can be prepared by reduction of $K_2Co_6(CO)_{15}$ with lithium metal in tetrahydrofuran. The same anion is more easily obtained from $Co_4(CO)_{12}$ with sodium or lithium metal in tetrahydrofuran at room temperature: the rapidly-formed green-yellow $Co_6(CO)_{15}^{2-}$ is slowly transformed into the red-brown $Co_6(CO)_{14}^{4-}$. In all cases alkali tetracarbonylcobaltate(—I) is also present.

The salt, $K_4Co_6(CO)_{14}$, was isolated as dark red crystals, which are soluble in water, but insoluble in tetrahydrofuran. The corresponding sodium and lithium salts are soluble in tetrahydrofuran: these solutions absorb carbon monoxide giving tetracarbonylcobaltate(—I) derivatives. The solutions containing the $Co_6(CO)_{14}^{4-}$ anion show two main infrared absorptions at about 1890 and 1660 cm.$^{-1}$ and these low wave-numbers are explained by the high ratio between negative charges and the number of CO ligands.

The formation of the Co_6-carbonyl cluster, either from $[Co(C_2H_5OH)_x][Co(CO)_4]_2$ derivatives[1] or by reaction of $Co_4(CO)_{12}$ with alkali metals, suggests that this Co_6-cluster is derived by dimerization of the intermediate species $Co_3(CO)_8$. This species can be formed in the first case by loss of ethanol or in the second case according to the equation:

$$Na + Co_4(CO)_{12} \longrightarrow NaCo(CO)_4 + Co_3(CO)_8$$

Mild oxidising agents, such as $FeCl_3$, react with aqueous solutions of $Co_6(CO)_{15}^{2-}$ or $Co_6(CO)_{14}^{4-}$ derivatives giving mixtures of carbonyl compounds. Extraction of these mixtures with n-pentane gives at first a fraction consisting mainly of $Co_4(CO)_{12}$, followed by slow extraction of $Co_6(CO)_{16}$. The hexacobalt hexadecacarbonyl, obtained as black, air-sensitive crystals, begins to decompose at 100—110° and is sparingly soluble in toluene and n-pentane. With basic solvents (such as acetone, methanol, diethyl ether, and pyridine) there is a rapid reaction yielding tetracarbonylcobaltate(−I) derivatives. The infrared spectrum is similar to that of $Rh_6(CO)_{16}$, as can be seen from the following data (Nujol mull):

$Co_6(CO)_{16}$: 2103w, 2061s, 2057sh, 2026w, 2020w, 2018w, 1806w, 1772s,

$Rh_6(CO)_{16}$: 2105w, 2070s, 2047w, 2040w, 2022mw, 2020mw, 1833w, 1793s,

and probably the two compounds have the same structure.[2]

The series $Co_6(CO)_{16}$, $Co_6(CO)_{15}^{2-}$, and $Co_6(CO)_{14}^{4-}$ provide the first example of the possibility of substituting more than one mole of carbon monoxide with doublets of electrons in cluster-carbonyl compounds. The two anions parallel the recent report on the two hydridocarbonyls, $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$.[3]

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[1] P. Chini, *Chem. Comm.*, 1967, 29.

[2] E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

[3] B. F. Johnson, R. D. Johnston, J. Lewis, and N. Robinson, *Chem. Comm.*, 1966, 851.