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An Exceptionally Electron-Rich Carbonyl Cluster Consisting of a Hexacobalt Octahedron Encompassed by an Octa(μ_3-sulphido) Cube: X-Ray Diffraction Analysis of the Structure of $Co_6(\mu_3\text{-}S_8)(CO)_6 \cdot 3S_8$

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Dicobalt octacarbonyl is known [1] to react with cyclo-octasulphur, in alkane solvents at room temperature. Four sulphur-containing cobalt carbonyl complexes were isolated from the alkane-soluble fraction [1d]. The structures of two of them, *viz.* $Co_3(CO)_9(\mu_3\text{-}S)$ and $Co_4(CO)_{10}(\mu_4\text{-}S)_2$, were correctly predicted from elemental analysis and IR spectral considerations [1d] as shown by subsequent X-ray structure determinations [2, 3]. For $((\mu_3\text{-}S)Co_3(CO)_7)_2(\mu_4\text{-}S_2)$ [4], the X-ray study revealed a structure which was a dimer of that suggested in the first preparative study based upon IR arguments [1d].

However, the fourth compound formed in this reaction (1) labelled 'S-4' in early papers, defied until now attempts at characterization. Unreported elemental analysis gave an extremely high sulphur content (around 65 percent), which did not suggest a reasonable structure. Another curious finding was a single, sharp C–O stretching band in the solution IR spectrum [1b, d], hinting at a structure of very high symmetry.

To identify unequivocally complex *1* we have repeated the preparation with an improved purification method, obtaining the complex *1* in a reasonable yield which allowed us to have suitable crystals for an X-ray diffraction study. In a typical preparation, $Co_2(CO)_8$ and elementary sulphur (molar ratio *ca.* 1:1) were reacted in petroleum ether solution at 40 °C under CO atmosphere, until the starting carbonyl disappeared (*ca.* 7 hrs). The filtered solution was worked up under nitrogen by means of dry-column chromatography (support: Silica Woelm DCC; eluent: petroleum ether). Three bands were developed: a dark-green band (complex *1*), a pink band ($Co_4(CO)_{10}S_2$), and a violet band ($(Co_3(CO)_7\text{-}S)_2S_2$). The green zone was cut-off and the compound was extracted by petroleum ether and crystallized at –20 °C. The yield was *ca.* 10% rel. to the sum of the soluble carbonyl products.

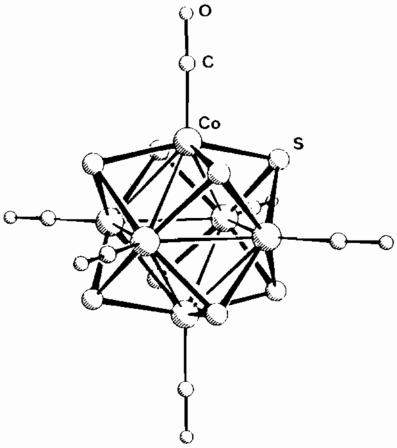

Fig. 1. Structure of $Co_6(\mu_3\text{-}S)_8(CO)_6$. Main bond distances (Å): Co–Co: 2.799(1)–2.818(1), 2.811(1) av.; Co–S: 2.224(2)–2.235(2), 2.228(1) av.; Co–C: 1.739(6)–1.750(6), 1.744(4) av.

The structure indicated the formula $Co_6S_8(CO)_6 \cdot 3S_8$ and consists of discrete octa(μ_3-sulphido) hexacobalt hexacarbonyl clusters, which lie on a crystallographic inversion centre and are surrounded in the lattice by S_8 rings, with a cluster/ring ratio of 1:3. The complex crystallizes in the monoclinic *C2/c* space group, with cell dimensions: $a = 20.456(4)$, $b = 12.385(4)$, $c = 17.600(5)$ Å, $\beta = 90.94(2)°$. An inversion centre on the cluster and a two-fold axis on one S_8 molecule reduce the multiplicity to 4; $Z = 8$ for the other S_8 molecule in a general position.

The structure was solved using 3395 reflections with $Fo > 6\sigma(Fo)$. Data were collected up to $2\theta = 50°$ with monochromatized MoKα radiation. The anisotropic least-squares cycles led to the conventional $R = 0.048$ [5].

The cluster component of *1* consists of a Co_6 octahedron encapsulated in an S_8 cube: the sulphur atoms cap symmetrically all Co_3 faces of the octahedron, and correspondingly the cobalt atoms cap all S_4 faces of the cube, generating a tetrahexahedron with an idealised O_h symmetry. The relative positions of the cobalt and sulphur atoms are inverted with respect to the recently reported $[Co_8S_6(SC_6H_5)_8]^{4-}$, in which a Co_8 cube is circumscribed by an S_6 octahedron [6]. Each cobalt atom bears a terminal carbonyl group (Fig. 1).

Previous examples of octahedral cobalt clusters with the same ligand coordination are the $[Co_6(\mu_3\text{-}CO)_8(CO)_6]^{4-}$ tetraanion (*2*) [7] and the $[Co_6(\mu_3\text{-}$

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$S)_8(PEt_3)_6]^+$ cation (*3*) [8]. The most important feature of the new structure is the large Co–Co separation (2.881 Å av.). This value should be compared with those reported for *2* (2.50 Å) and for *3* (2.79 Å). On the other hand the Co–S distances are similar to those found in other Co–S clusters (2.16 Å, av.) [9].

An electron count shows that cluster *1* is a 98-electron complex, in contrast to 2 (86 electrons) and *3* (97 electrons). Hence it appears that the great excess of electrons in the cluster weakens substantially the Co–Co bonds and that the normal length Co–S bonds are responsible for holding together the 'blown-up' Co_6 framework.

The compound is quite stable on air. Even if no special cluster – S_8 interactions seem to be present in the lattice, attempts to eliminate the S_8 molecules by vacuum sublimation resulted in decomposition of the complex.

The observation of only one ν(C–O) band in solution (at 2058.0 cm^{-1} in n-heptane; $^{13}C–O$ satellite at 2013 cm^{-1}) is in agreement with the selection rules of point group O_h. In a CsI pellet this band is broadened and has three components (at 2050, 2046 and 2035 cm^{-1}) as a consequence of lower site symmetry (C_2). Resolution of these components occurs upon cooling to *ca.* 80 K.

In the frequency region between 700 and 200 cm^{-1} absorptions appear at 516(s), 472(m), 374(m), 310(w) and 241(w) cm^{-1} (CsI), which belong to the known types of carbonyl deformation and Co–CO stretching modes and to the Co–S stretching modes.

Comparison with the IR spectrum on CsI pellets, of elementary sulfur shows that the absorptions of the S_8 rings are apparently of much lower intensity.

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