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Preliminary communication

A NEW COBALT CARBONYL—CARBON DISULPHIDE CLUSTER CONTAINING A Co_3C AND A Co_3S PYRAMID SYMMETRICALLY LINKED BY A CS_2-BRIDGE: *sym*-$SCo_6(CO)_{16}C(CS_2)$

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Summary

sym-$(CO)_9Co_3C(CS_2)Co_3(CO)_7S$ has been isolated from the mixture formed in the reaction of $Co_2(CO)_8$ with CS_2. This is the fifth member of the $C_mS_nCo_p(CO)_q$ family identified by X-ray diffraction studies. The molecular structure of the title compound is discussed and briefly compared with that of the asymmetric isomer and related compounds.

Dicobalt octacarbonyl reacts with carbon disulphide at room temperature [1—3]. Besides sulphur derivatives, e.g. $SCo_3(CO)_9$, and sulphur-free carbon derivatives, as $[(CO)_9Co_3C]_2$, compounds belonging to the family of $C_mS_nCo_p(CO)_q$ clusters are among the CO-containing products of this complex reaction. The following members of this family have been characterized so far by X-ray diffraction: $SCo_6(CO)_{16}C(CS_2)$ ("Ia") [4], $SCo_6(CO)_{15}(CS_2)$ ("Ib") [5,6], $S_2Co_6(CO)_{12}C$ ("III") [3] and $Co_6(CO)_{18}C_2S_2$ ("IV")* [3].

We now report the preparation and structural characterization of a new compound "V" not observed previously among the products. Compound V was isolated by TLC from the reaction mixture obtained from $Co_2(CO)_8/CS_2$ in molar ratios between 1/2 and 1/50 in n-hexane at room temperature under nitrogen for 10—72 hours by TLC. It was eluted after $[Co_3(CO)_7S_2]_2S_2$ (III) and $Co_4(CO)_{12}$, but before Ib, and often overlapped with $\{(CO)_9Co_3C\}_2CO$. It was obtained in ca. 15% yield (based on the soluble carbonyl complexes), as dark brown crystals, stable in air, only slightly soluble in hydrocarbons but soluble in CCl_4 and

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*The labellings Ia, Ib, III, and IV correspond to those used in our previous papers [2,3]. Compounds Ia and Ib were initially formulated as two isomers of the composition $Co_4(CO)_{12}CS_2$ [1,2]. These formulae proved to be in error and should be replaced by those given above.

chloroform. The IR spectrum in the C—O stretching region shows the following absorptions (in hexane): 2107m, 2078s, 2065.5s, 2055.5m, 2050w, 2046.5m, 2034m, and 2015vw cm^{-1}. In the medium-IR region (KBr pellet) three bands are found, at 1166.5, 991, and 742 cm^{-1}, whereas between 700 and 200 cm^{-1} bands were observed (in KBr pellets) at 631, 613, 524, 512, 495, 479, 467, 456, 440, 429, 408, 390, 379, 357, 347, 313, and 210 cm^{-1}.

Crystals suitable for X-ray analysis were obtained by slow cooling of a dilute n-heptane solution at −20°C. They belong to the triclinic $P\bar{1}$ space group, with a 12.822(4), b 13.399(4), c 8.851(4) Å, α 100.07(4), β 85.72(3). and γ 106.20(4)°; $Z = 2$. The cobalt atoms were located on a Patterson tridimensional map, and the carbon, oxygen and sulphur atoms by subsequent Fourier-difference syntheses. The atoms were satisfactorily refined by least-squares method in the $P\bar{1}$ space group to the final value of $R = 0.090$ for 2839 reflections.

The structure of compound V can be regarded as formed by the two distorted tetrahedral cluster units Co_3C and Co_3S, linked by a symmetric CS_2 bridge which is C-bonded to the apical carbon atom of the first cluster and S-bonded to two cobalt atoms of the second (Fig. 1). It is the isomer of complex Ia [4], the main structural difference being the mode of bondong of the CS_2-bridge: in complex Ia this is S-bonded to the apical C-atom of the Co_3C unit, and is bonded to two cobalt atoms of the Co_3S cluster by the C and the second S atom of the S—C—S bridge. We refer to Ia as the asymmetric isomer of $Co_6(CO)_{16}C_2S_3$.

In complex V the CS_2-bridge and the Co(4) and Co(5) atoms form a five-membered ring (Fig. 2) which is strictly planar. This plane is inclined with respect to the Co_3 planes of Co_3S and Co_3C by 161 and 82°, respectively, and thus

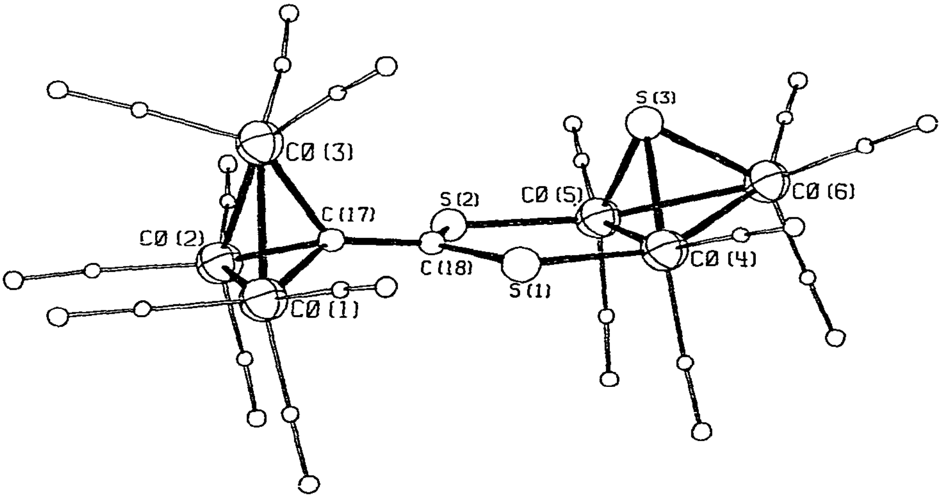

Fig. 1. Perspective view of the molecular structure of *sym*-$(CO)_9Co_3C(CS_2)Co_3(CO)_7S$. The more relevant bond lengths and angles with the estimated standard deviations in parentheses are:

Co(1)—Co(2)	2.471(3) Å
Co(1)—Co(3)	2.464(3)
Co(2)—Co(3)	2.478(3)
Co—C(17) (av.)	1.89(2)
Co—S(3) (av.)	2.154(5)
Co(4)—S(1)	2.233(5)
Co(5)—S(2)	2.242(5)
C(17)—C(18)	1.49(2)

Co(4)—Co(5)	2.479(3) Å
Co(4)—Co(6)	2.524(3)
Co(5)—Co(6)	2.532(4)
C(18)—S(1)	1.71(2)
C(18)—S(2)	1.67(2)

C(17)—C(18)—S(1)	116(1)°
C(17)—C(18)—S(2)	118(1)°
S(1)—C(18)—S(2)	126(1)°

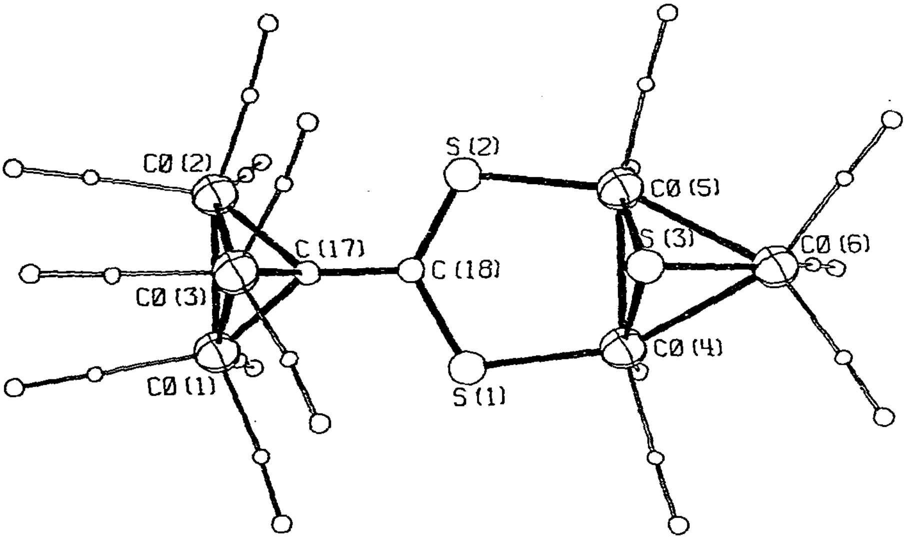

Fig. 2. Top-view of the structure.

it occupies two equatorial positions of the Co_3S cluster. The (non-bonded) S···S distance of 2.69 Å is very favourable in substituting two vicinal equatorial CO groups of $SCo_3(CO)_9$: the resulting Co(4)—Co(5)—S angles (95°, av.) are very similar to those found for the Co—Co—C angles in $SCo_3(CO)_9$, viz. 96.5° (av.) [7]. It should be emphasized that the removal of the "excess" electron from the paramagnetic $SCo_3(CO)_9$ by the remainder of the molecule results in shortening

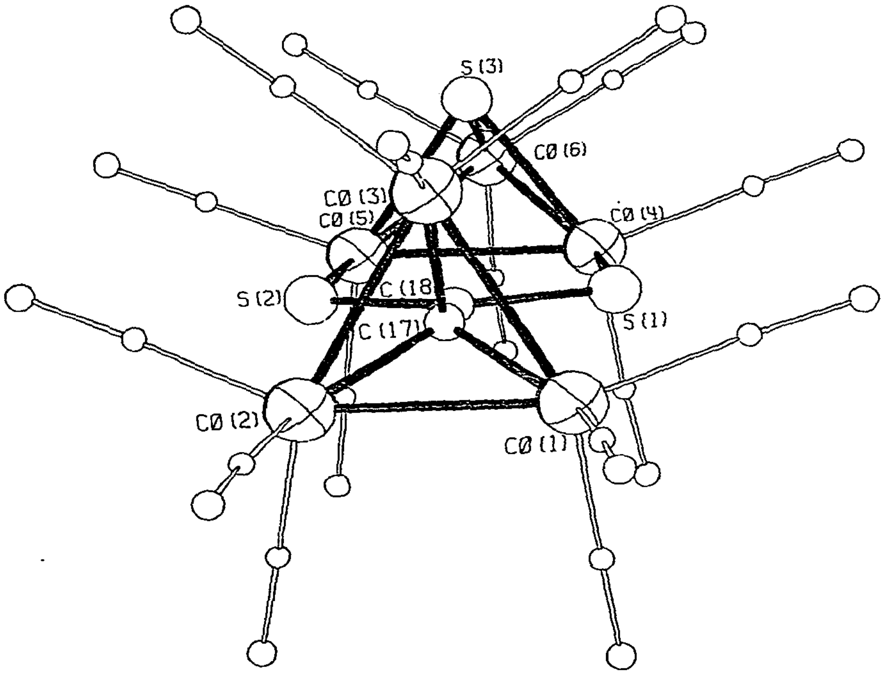

Fig. 3. Oblique view from the Co(1)—Co(2)—Co(3) face.

of the Co—Co distances of the Co_3S unit, as found in $SCo_2Fe(CO)_9$ [8] and in clusters containing the $SCo_3(CO)_x$ ($x = 6$ or 7) fragment [4,9,10].

Moreover, the Co_3S cluster does not possess a threefold symmetry, as the bridged Co—Co bond is significantly shorter (2.479(3) Å) than the other metal—metal distances (2.524(3) and 2.532(4) Å). A similar shortening of the bridged Co—Co edge was previously found in Ia [4] and $\{Co_3(CO)_7S_6\}_2S_2$ [9]. The similarity between the Co_3S clusters in these three complexes is not confined only to the Co—Co distances but also includes the other distances and angles.

The apical C(17) atom lies roughly on the plane defined by the five-membered ring, so that the planarity of the C(17)—CS_2 bridge suggests an sp^2 hybridisation of C(18). This is supported by the values of the C—C—S and S—C—S angles, which are not far from 120°. The length of the C—S bonds indicate a partial double bond character [11], and the value of the C(17)—C(18) bond (1.49(2) Å) agrees with the values reported by Brice and Penfold [12] for σ C_{ap}—$C(sp^2)$ bond in the Co_3C—C systems. The CS_2 group bonded to the former unit can be considered as a dithiocarboxylato substituent, and its bonding characteristics are similar to those of an allylic group.

Within the $(CO)_9Co_3C$ fragment all bonds are consistent with the values previously reported [13], and at this stage of refinement, there is no evidence of significant distortion of the Co_3C—C framework from the local C_{3v} symmetry. The Co(1)—Co(2) edge is parallel to the plane of the five-membered ring, as better shown in Fig. 3, and so the molecule possesses an idealised C_s symmetry.

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