X-Ray Crystal Structures of Two Products Formed in the Reaction of Dicobalt Octacarbonyl with Carbon Disulphide: Dodecacarbonylcarbidohexacobalt Disulphide, $Co_6C(CO)_{12}S_2$, and Bis-(enneacarbonyltricobaltcarbon) Disulphide, $(CO)_9Co_3CSSCCo_3(CO)_9$

By GYÖRGY BOR*
(*Department of Industrial and Engineering Chemistry, Swiss Federal Institute of Technology (ETH),* CH-8092 *Zurich, Switzerland*)

and GIULIANA GERVASIO,* ROSANNA ROSSETTI, and PIER LUIGI STANGHELLINI
(*Institute of Chemistry, University of Turin,* I-10125 *Turin, Italy*)

Summary Two complexes formed in the reaction of dicobalt octacarbonyl with carbon disulphide were identified through *X*-ray crystallography as $Co_6C(CO)_{12}S_2$ (**1**) and $[(CO)_9Co_3CS]_2$ (**2**); the cluster core of (**1**) is composed of a trigonal prism of six cobalt atoms capped symmetrically by two sulphur atoms, and containing a carbide atom in the centre, whereas (**2**) is a *trans*-disulphide of the enneacarbonyltricobaltcarbon cluster, showing distortion of the idealized threefold local symmetry of the Co_3CS entities presumably owing to repulsive interactions between the sulphur and (equatorial) carbonyl-C atoms.

DICOBALT OCTACARBONYL reacts at room temperature with carbon disulphide either neat[1] or in the presence of hydrocarbon solvents.[2,3] Among the complex cobalt carbonyl derivatives formed, sulphur-containing ones like $SCo_3(CO)_9$[4,5] and sulphur-free carbon derivatives like $[(CO)_9Co_3C]_2$[6,7] have been identified.[2] In addition, five different C_xS_y-containing derivatives have been separated by column chromatography.[1,2] The composition of two of these has been established by *X*-ray analysis: $(CO)_9Co_3CSCS(CO)_7Co_3S$[8] and $(CO)_8Co_3(CS_2)(CO)_7Co_3S$.[9]

We now report that for this reaction, performed in hexane solvent under nitrogen at room temperature, with $CS_2:Co_2(CO)_8$ ratios between 0·5:1 and 100:1, two novel products, characterized previously[2] only by their i.r. spectra, were separated by t.l.c., and characterized by *X*-ray analysis.

Among the products stable on t.l.c. a green compound, designated previously[2] as 'Complex III,' is always present in considerable quantities (20—35% from t.l.c. analysis, based upon the soluble products). Deep-green crystals (obtained by cooling an n-heptane solution of the complex to -20 °C) of $Co_6(CO)_{12}CS_2$ (**1**) are monoclinic, space group *Cc*, with $a = 16{\cdot}250(5)$, $b = 9{\cdot}413(4)$, $c = 16{\cdot}036(5)$ Å, $\beta = 116{\cdot}77(4)°$, $U = 2189{\cdot}41$ Å^3, $Z = 4$.† The cobalt and sulphur atoms were located with the aid of direct methods and an initial Patterson synthesis. Subsequent Fourier-difference maps revealed the carbon and oxygen atom positions. The present *R* value is 0·066 after isotropic refinement of 1975 observed reflections with $I > \sigma(I)$.

---

† The intensity measurements were made on a Philips PW 110 four-circle automatic diffractometer (Mo-K_α graphite-monochromatized radiation, $\lambda = 0{\cdot}7107$ Å, θ–2θ scanning).

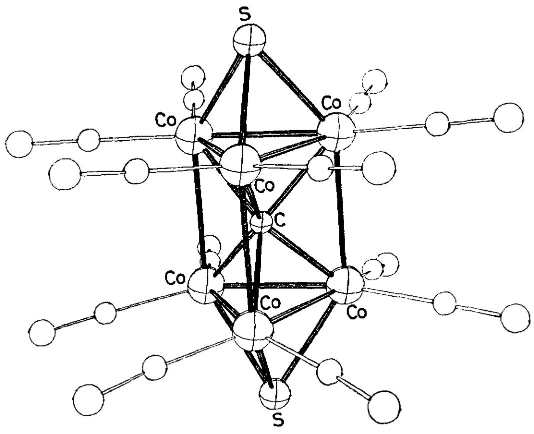

FIGURE 1. Molecular structure of $Co_6C(CO)_{12}S_2$. Significant averaged bond lengths and angles with the estimated standard deviations in parentheses are: Co–Co(triangular faces) 2·437(4); Co–Co(rectangular faces) 2·669(5); Co–S 2·194(6); Co–C(carbide) 1·94(2) Å; Co–S–Co 67·4(2)°.

The idealized molecular structure of (**1**) belongs to point group D_{3h}. It is composed of a trigonal prism of six cobalt atoms, and each triangular face of this prism is symmetrically capped by a sulphur atom. A carbide atom in the centre of the prism completes the carbonyl-bearing core of the molecule. The carbonyl ligands are all terminally bonded and are in equivalent positions. The two carbonyl layers are inclined away from each other (Figure 1).

The two S atoms and the carbide atom lie on the molecular axis; however, they are at a non-bonding distance [3·02(2) Å]. There are two sets of Co–Co distances: the lateral ones are long [2·669(5) Å], whereas the triangular ones are short [2·437(4) Å]. The latter type of Co–Co bond is the shortest reported so far for structures containing the Co_3S entity: *cf.* 2·637(3) Å in $SCo_3(CO)_9$,[5] 2·460(5) Å in $SCo_6(CO)_{11}(SEt)_4$,[10] or 2·474(7) and 2·531(5) Å in $[SCo_3(CO)_7]_2S_2$.[11] Consequently the Co–S distances [av. 2·194(6) Å] are longer, and the Co–S–Co angles more acute [67·4(2)°] than the corresponding values reported so far. The cluster (**1**) has 90 valence electrons, equal to $[Co_6C(CO)_{15}]^{2-}$, which is the only example reported to have a trigonal prismatic structure of the Co_6C unit.[12] Structural details have been determined only for the analogous rhodium cluster dianion,[13] hence no direct comparison of the Co–Co distances can be made. It seems relevant that the difference between the short and long metal–metal bond lengths is significantly greater in the case of (**1**) (23·2 pm) than that found in the Rh_6C cluster (av. 3 pm).

'Complex IV' of ref. 2 was found to have the composition $[Co_3(CO)_9CS]_2$ (**2**). In our recent experiments this product represented *ca.* 10% of the t.l.c. resistant part if the CS_2: $Co_2(CO)_8$ ratio was high (50—100: 1). With lower ratios its relative yield was lower.

Brown crystals of (**2**) (obtained by cooling an n-heptane solution of the complex to -20 °C) are triclinic, space group $P\bar{1}$, with $a = 8{\cdot}794(4)$, $b = 12{\cdot}576(4)$, $c = 8{\cdot}113(4)$ Å, $\alpha = 105{\cdot}14(3)$, $\beta = 113{\cdot}32(4)$, $\gamma = 95.61(1)°$, $U = 774{\cdot}60$ Å^3 $Z = 2$.† The initial Patterson map was interpreted in terms of cobalt positions. Subsequent Fourier-difference maps then showed positions of the S, C, and O atoms. Isotropic refinement based on 2258 observed reflections with $I > \sigma(I)$ led to $R = 0{\cdot}095$. Complex (**2**) contains two enneacarbonyltricobaltcarbon pyramids[14] connected by a *trans*-disulphide bridge (Figure 2). The molecule has a centre of symmetry and the atoms C(10), S,S', and C(10') are coplanar.

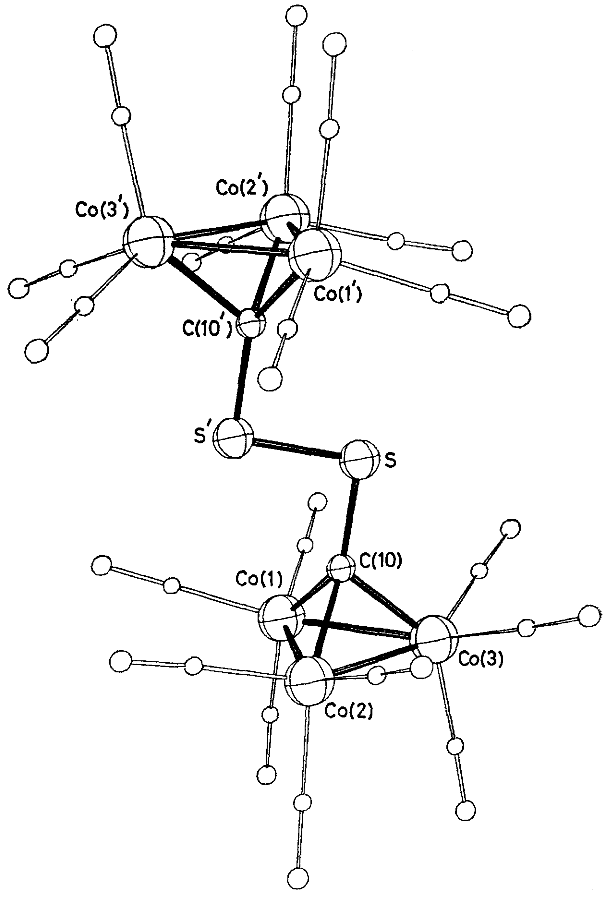

FIGURE 2. Molecular structure of $[(CO)_9Co_3CS]_2$. Significant bond lengths and angles with the estimated standard deviations in parentheses are: Co(1)–Co(2) 2·475(3); Co(1)–Co(3) 2·474(3); Co(2)–Co(3) 2·481(3); Co–C(10) (av.) 1·89(1); C(10)–S 1·73(2); S–S' 1·95(1) Å; Co(1)–C(10)–S 135(1); Co(2)–C(10)–S 134(1); Co(3)–C(10)–S 122(1); C(10)–S–S' 96(1)°.

The idealized geometry of the $(CO)_9Co_3C$ units is similar to that found for other $RCCo_3(CO)_9$ complexes.[14] One unusual feature of the structure of (**2**) is that the directions of the C–S bonds do not point along the local threefold axes of the Co_3C pyramids [*cf.* the angles Co(*i*)–C(10)–S]. This kind of distortion was first reported for $(CO)_9Co_3C(CO)CCo_3(CO)_9$[15] and has now also been found for the $AcOCCo_3(CO)_9$[16] and $R_2NBX_2OCCo_3(CO)_9$[17] derivatives. In the former case the repulsion between the equatorial CO sets of the two $Co_3(CO)_9$ units must be the driving force for such a distortion, whereas for the latter two complexes the distortion can be attributed to repulsive interaction between the orbitals of a heteroatom in the AcO or R_2NBX_2O group and of two vicinal Co–(CO) entities. In the case of (**2**) both effects act in the same direction.

It is interesting that the relatively acute C–S–S bond angles of 96° (the usual valency angles in organic disulphides are between 103 and 107° [18]) 'resist' more strongly the repulsive forces than the orientation of the apical C–S bonds does. Instead, the dihedral angle (between the two C–S–S planes) alters, reaching 180° to minimize the equatorial nonbonded CO interactions; (usual sulphur dihedral angles lie in the range 74—110° [19]). A considerable double bond character of the S–S bond (*ca.* 70% double bond by using Abrahams' approach[19]) is suggested by the shortness of this bond.

(*Received*, 21*st June* 1978; *Com.* 664.)

---

[1] L. Markó, G. Bor, and E. Klumpp, *Angew. Chem.*, 1963, **75**, 248.

[2] E. Klumpp, G. Bor, and L. Markó, *J. Organometallic Chem.*, 1968, **11**, 207.

[3] For reviews on the chemistry of transition-metal CS_2-complexes see: I. S. Butler and A. E. Fenster, *J. Organometallic Chem.*, 1974, **66**, 161; P. V. Yaneff, *Co-ordination Chem. Rev.*, 1977, **23**, 183.

[4] L. Markó, G. Bor, and E. Klumpp, *Chem. and Ind.*, 1961, 1491.

[5] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1229.

[6] G. Bor, L. Markó, and B. Markó, *Chem. Ber.*, 1962, **95**, 333.

[7] M. D. Brice and B. R. Penfold, *Inorg. Chem.*, 1972, **11**, 1381.

[8] C. H. Wei, personal communication; *cf.* C. H. Wei, Oak Ridge Natl. Lab., Biology Div., Annual Progress Report, 1967, p. 325.

[9] J. Blount and L. F. Dahl, unpublished (1968).

[10] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1968, **90**, 3977.

[11] D. L. Stevenson, V. R. Magnusson, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1967, **89**, 3727.

[12] V. G. Albano, P. Chini, S. Martinengo, M. Sansoni, and D. Strumolo, *J.C.S. Chem. Comm.*, 1974, 299.

[13] V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J.C.S. Dalton*, 1973, 651.

[14] G. Pályi, F. Piacenti, and L. Markó, *Inorg. Chem. Acta Rev.*, 1970, **4**, 109; B. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, 1973, **6**, 73.

[15] G. Allegra, E. Mostardini-Peronaci, and R. Ercoli, *Chem. Comm.*, 1966, 549.

[16] V. Bätzel and G. Schmid, *Chem. Ber.*, 1976, **109**, 3339.

[17] V. Bätzel, U. Müller, and R. Allmann, *J. Organometallic Chem.*, 1975, **102**, 109; V. Bätzel, *Z. Naturforsch.*, 1976, **31b**, 342.

[18] O. Foss, in 'Organic Sulfur Compounds,' ed. N. Kharasch, Pergamon Press, New York, 1961, pp. 76—77.

[19] S. C. Abrahams, *Quart. Rev.*, 1956, **10**, 407.