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[(Triphos)Co(CS$_2$)Cr(CO)$_5$]. A Dinuclear Heterometal Complex Containing a CS$_2$ Bridging Group

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Few dinuclear metal complexes containing a CS$_2$ molecule as a bridging group are known [1–7] and only two structures of such complexes have been determined by direct X-ray analysis. The [Cl(PPh$_3$)$_2$-Pt(CS$_2$)Pt(PPh$_3$)$_2$]BF$_4$ complex has been found to contain the Pt–dithioformato fragment linked to the second metal through two sulfur atoms [6]. Another dinuclear CS$_2$ derivative, of formula [(triphos)Co-(CS$_2$)Co(triphos)](BPh$_4$)$_2$, recently prepared in this laboratory, has been found to contain a bridging CS$_2$ molecule, π-bonded to one cobalt through a C=S linkage and σ-bonded to the other metal through the two terminal sulfur atoms [7].

A novel dinuclear metal complex of formula [(triphos)Co(CS$_2$)Cr(CO)$_5$], triphos = 1,1,1-tris-(diphenylphosphinomethyl)ethane, has been prepared in this laboratory and has been completely investigated by X-ray analysis.

The crystal structure consists of a dinuclear complex molecule [(triphos)Co(CS$_2$)Cr(CO)$_5$] which has methylene chloride molecules interspersed in the lattice. In Fig. 1 a perspective view of the skeleton of the molecule is shown. The CS$_2$ group has been found to hold together the (triphos)Co and the Cr(CO)$_5$ fragments. The cobalt atom is coordinated both by the three phosphorus atoms of the triphos ligand and by the C=S linkage, through π-bonding. The other sulfur atom of the CS$_2$ group is σ-bonded to the chromium atom, which is thus hexacoordinated in a distorted octahedral geometry. The two independent complex molecules of the asymmetric unit are chemically equivalent, differing only in some conformational distortions that probably result from packing forces. As the differences in bond distances are not significant, they are discussed in terms of averaged values from the two independent molecules.

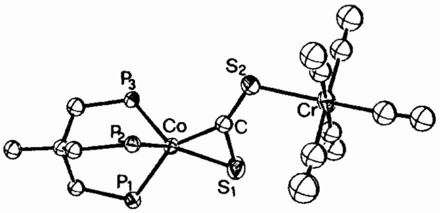

Fig. 1. Skeleton of the complex molecule [(triphos)Co-(CS$_2$)Cr(CO)$_5$]. Important distances (Å) and angles (deg) are: Co–P(av) = 2.218(7), Co–S(1) = 2.200(8), Co–C = 1.86(2), Cr–S(2) = 2.444(7), C–S(1) = 1.66(3), C–S(2) = 1.63(3), C–Co–S(1) = 47.4(8), S(2)–C–S(1) = 136.2(1.3), C–S(2)–Cr = 113.4(9).

Bond lengths and bond angles within the Co–CS$_2$ linkage compare well with those reported for monomeric transition metal complexes containing a terminal π-bonded CS$_2$ group. Indeed the values of the C–S(1) and C–S(2) bonds (1.66(3) and 1.63(3) Å), although somewhat longer than the C–S distance in the free CS$_2$ molecule (1.55 Å) [8], resemble the values of 1.68(1) and 1.62(1) Å found for [(triphos)-Co(CS$_2$)] [9] and 1.676(7) and 1.615(8) found for [Fe(η^2-CS$_2$)(CO)$_2$(PMe$_3$)(PPh$_3$)] [10]. The increase in both C–S(1) and C–S(2) distances with respect to the free ligand suggests that the π-coordination of the CS$_2$ reduces the bond order of both C–S linkages.

The I.R. spectrum, nujol mulls, shows four bands in the ν(CO) stretching region at 2055, 1982, 1930 and 1887 cm^{-1}, as expected for a LCr(CO)$_5$ complex [11] and a band at 1110 cm^{-1} attributable to the C=S stretch which agrees well with those found in other complexes containing a bridging CS$_2$ group [3–5].

The magnetic moment of 1.95 μ_B, indicative of one unpaired electron, is in agreement with 17 valency electrons, supplied by the d^9 cobalt atom, the three phosphorus atoms of the triphos ligand and by the double bond of the CS$_2$ molecule.

Experimental

A solution of Cr(CO)$_5$(THF) formed *in situ* by UV irradiation of the corresponding hexacarbonyl complex [12] (175 mg, 0.875 mmol in 60 ml of THF) was added under nitrogen to a solution of [(triphos)-Co(CS$_2$)] [9] (500 mg, 0.658 mmol in 250 ml of THF) kept at –10 °C. The reaction mixture was kept for 6 h at room temperature. The solvent was removed under vacuum and the resulting residue extracted with methylene chloride (40 ml). Black crystals were obtained on addition of ethanol (30 ml) and slow evaporation of the solvent. They were recrystallized from the same solvents and dried under

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a nitrogen stream. *Anal.* Calcd. for $C_{47.25}H_{39.5}Cl_{0.5}$-$CoCrO_5P_3S_2$: C, 58.32; H, 4.09; Co, 6.05; Cr, 5.34, S, 6.59. Found: C, 58.20; H, 4.12; Co, 5.95; Cr, 5.10; S, 6.48.

The crystals are monoclinic, space group $P2_1/n$, with a = 25.23(2), b = 18.43(1), c = 22.19(2) Å, β = 114.8(1)°, D_c = 1.38 g cm^{-3} for Z = 8, λ(MoKα) = 0.7107 Å, μ(MoKα) = 8.37 cm^{-1}.

Integrated reflection intensities were measured on a Philips PW 1100 automatic computer controlled diffractometer. From a total of 9274 independent reflections 3618 were considered observed with $I \geqslant 3\,\sigma(I)$ and were rescaled to account for decomposition of the crystals. The structure analysis, requiring determination of the parameters for two independent unit formulae of the complex, was solved by the heavy atom method. Owing to the large number of variables (121 non-hydrogen atoms) the structure refinement was carried out by blocking the least-squares matrix and by constraining the phenyl groups as rigid bodies. Anisotropic thermal vibration was assumed for Co, Cr, S and P atoms. Hydrogen atoms were introduced in their calculated positions but not refined. Convergence was reached with R = 0.079 and R_w = 0.088, respectively.

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