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Preliminary communication

A binuclear disulfide-bridged derivative of cobalt carbonyl $Co_2(CO)_6(C_6F_5SSC_6F_5)$

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More than 30 years ago Hieber and Spacu[1] described the preparation of a dinuclear cobalt carbonyl derivative of the type $[(RS)Co(CO)_3]_2$ ($R = C_2H_5$), to which they assigned a structure analogous to that of the corresponding $[(RS)Fe(CO)_3]_2$ compounds[1–4]. Applying the inert gas rule, and regarding the two RS-bridges as three-electron donors, these authors suggested, however, that there was no metal–metal bond in the cobalt compound, in contrast to the iron analogue. For the compound with $R = C_6H_5$ they proposed the monomeric structure $C_6H_5SCo(CO)_3$.

Subsequently there have been several unsuccessful attempts to reproduce the above results, but instead of the mono- and bi-nuclear compounds, trimeric, tetrameric, pentameric, and hexameric cluster compounds have been obtained containing metal–metal bonds and also doubly- and triply-bridging RS-groups[5,6]. Since the high electronegativity of the perhalo-organic groups decreases the basicity of the lone pairs on the S atom and hence the tendency of sulfur to form multiple bridges[7], the reactions of perfluoro- and perchlorophenylthio compounds with dicobalt octacarbonyl have now been studied.

Equimolar amounts of $Co_2(CO)_8$ and $C_6F_5SSC_6F_5$ [8] react in hexane under N_2 at room temperature. The reaction (which can be monitored by the IR spectrum) is complete in 0.5 h, and $Co_2(CO)_6(C_6F_5SSC_6F_5)$, (I), crystallizes on cooling; it forms black crystals (m.p. 100°) which dissolve readily in organic solvents to give greenish-brown solutions. It is very air-stable even in solution.

Elementary analysis is consistent with the formula assigned, and the dimeric formulation is in accord with the observed molecular weight. The mass spectrum shows, in addition to peaks from the fragmentation of the fluoroaromatic groups, only the lower members of the fragmentation series $(C_6F_5S)_2Co_2(CO)^+_{6-n}$ with $n = 4$–6, the complete series $C_6F_5S_2Co_2(CO)^+_{6-n}$ (arising from splitting off of a C_6F_5 group), and a very intense peak due to the $Co_2S_2^+$ cluster.

The IR spectrum shows five C–O stretching bands at 2111m, 2081 vs, 2066s, 2059m-s, 2049w (and 2033vw: ^{13}CO) cm^{-1} (hexane solution, ± 1 cm^{-1}), with a general pattern and intensity distribution identical with that reported[9] for the acetylene-bridged derivatives $Co_2(CO)_6(RC{\equiv}CR')$. Thus the structure of (I) must be analogous with the known[10] structures of the acetylene complexes. Since no binuclear metal carbonyl derivatives containing non-planar bridging ligands are known without metal—metal bonds, the Co—Co bond must be present in (I). The diamagnetism (indicated by NMR) excludes the usual formulation having separated three-electron donor RS-bridges, and we suggest the structure shown in Fig.1, in which the S—S bond is retained, and the sulfur atoms act as two-electron donors. This assumption is confirmed by the high C—O stretching frequencies, which are 20–40 cm^{-1} higher than those of $Fe_2(CO)_6(SC_6F_5)_2$ [11] in which the sulfur atoms are three-electron donors and give some partial negative charge to the Fe atoms and so cause a low-energy shift of the C—O frequencies. The frequencies of (I), however, fall into the region reported[12] for $Co_2(CO)_6(CF_3C{\equiv}CH)$, in which the carbon atoms are also formally two-electron donors.

In this formulation the sulfur atoms have 10 electrons on their valence shells (sp^3d hybridization) and, because of the presence of the lone pairs, the fluoroaromatic rings are probably in a twisted configuration, as indicated in Fig.1. An X-ray study is in progress.

The reaction of $Co_2(CO)_8$ with C_6F_6SH was also investigated. (I) is formed also in this reaction, but is not the only product. During the chromatography of the reaction products the first compound eluted (in small quantity) has (apart from a general shift towards higher frequencies due to the electronegative character of the C_6F_5 group: 2096m, 2057vs, and 2038.5s cm^{-1}) exactly the same IR spectrum in the C—O stretching region as compounds obtained with alkyl and aryl thiols or disulfides[5], which were formulated as $Co_3(CO)_6(S)(SR)$. Thus we tentatively ascribe such a formula to the compound found in the first fraction ($R = C_6F_5$). The second fraction eluted with hexane contains an unknown product with C—O stretching frequencies at 2074s, 2064m-s, 2058 vs, 2049m-s, 2038 , and 2028w cm^{-1}. Compound (I) is eluted as the third fraction. The difference between the results for this reaction and those for the reaction involving bis(pentafluorophenyl) disulfide, which gives (I) as the sole product, represents additional chemical evidence for the presence of the S—S bond in compound (I).

Formation of the same type of compound was observed in the reaction of $Co_2(CO)_8$ with $C_6Cl_5SSC_6Cl_5$, as shown by the analogous IR spectrum in the C—O stretching region: 2107m, 2079vs, 2062.5s, 2056.5m-s, and 2046w cm^{-1} (hexane solution, ± 1 cm^{-1}); we formulate this product as $Co_2(CO)_6(C_6Cl_5SSC_6Cl_5)$. It has a similar greenish-brown colour to (I), but is much less stable.

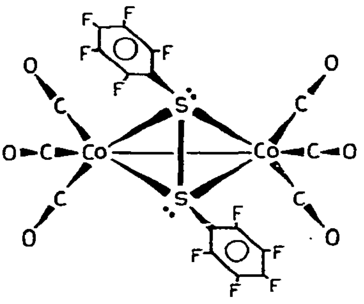

Fig.1. Suggested structure of the compound $Co_2(CO)_6(C_6F_5SSC_6F_5)$.

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