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NOTE

Sulphur-containing metal carbonyls
IX.* New carbon disulphide complexes of cobalt

Previously we have reported the preparation of $Co_4(CO)_{10}CS_2$ (I, A isomer)** as the first transition metal–carbon disulphide complex[2]. As mentioned in that paper, in the reaction between cobalt carbonyl and carbon disulphide some additional hexane-soluble, carbonyl derivatives are also formed[3]. The appearance of recent publications on transition metal–thiocarbonyl complexes[4-7] prompts us to give some details on the above mentioned complexes, since we believe that one (or two) of them represents the first example of a cobalt carbonyl thiocarbonyl complex.

If $Co_2(CO)_8$ is treated in hexane solution (25 g/l) with a threefold excess of CS_2 (at room temperature, under N_2 for 24 h) and the reaction product is worked up after filtration [solid residue, 15.5% of $Co_2(CO)_8$ introduced] by chromatography (silica gel column, low activity grade, freshly activated at 180°, 3 h; length 5 m, diameter 5 cm for 2 l solution) the following complexes are eluted by hexane in the given sequence (identified by their IR spectra): $[Co_2(CO)_5S]_2$[8,9], $Co_3(CO)_9S$[10,9], $[Co_3(CO)_9C]_2$[11], "Complex III", $Co_3(CO)_6CS_2$ (II), and (IA)[2]. With 20% benzene in hexane "Complex IV" is eluted. The fractions containing (II) are collected, evaporated to dryness *in vacuo* and crystallized from hexane yielding 1.48% of a black crystal powder, $Co_3(CO)_6CS_2$. (Found: C, 19.66; Co, 40.2; S, 15.35. $C_7Co_3O_6S_2$ calcd.: C, 19.96; Co, 42.01; S, 15.23%.)

If the reaction is carried out with a $Co_2(CO)_8/CS_2$ ratio of 2 and in higher dilution (12.5 g $Co_2(CO)_8$/l), after working up as given previously the elution sequence is the following: with hexane, $[Co_2(CO)_5S]_2$, $Co_3(CO)_9S$, $[Co_3(CO)_9C]_2$, "Complex III"; with 20% benzene in hexane, $Co_4(CO)_{10}CS_2$ (I, B isomer). The fractions containing (IB) are collected, evaporated and the black powder obtained is crystallized from 40–50° warm toluene, cooled successively to −15°. Shiny black crystals of $Co_4(CO)_{10}CS_2$ are obtained. (Yield: 8.1%.) (Found: C, 22.28, 22.13; Co, 40.80, 39.10; S, 10.75, 10.80. $C_{11}Co_4O_{10}S_2$ calcd.: C, 22.30; Co, 39.83; S, 10.83%.)

The C–O and C–S stretching frequencies of all complexes prepared or detected in these reactions are given in Table 1.

The two isomers of (I) differ not only in the presence of a bridging CO ligand (or ligands) in (IB), but also in the number and position of the bands assigned tentatively to C–S stretching vibrations. Consequently the bonding of the "CS_2" entity must considerably differ in the two isomers, but X-ray investigations are needed for the clarification of these structures probably representing hitherto unknown types.

The spectrum of (II) has only one band in the middle region suggesting that the carbon disulphide is split in this molecule into a sulphur atom and a thiocarbonyl group. Its formula is hence better represented as $Co_3(CO)_6(S)(CS)$. We suggest a

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* For Part VIII see ref. 1.

** *Note added in proof.* According to recent X-ray diffraction results of Wei and Dahl the actual composition of (IA) is more likely $Co(CO)_{16}C_2S_3$. (Private communication by Professor L. F. Dahl, July 1967).

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TABLE I

C–O[a] AND C–S[b] STRETCHING FREQUENCIES OF THE COBALT CARBONYL–CARBON DISULPHIDE COMPLEXES
In cm^{-1}; relative intensities in parentheses.

Band type	*(IA)*[2]	*(IB)*	*(II)*	*"Complex III"*	*"Complex IV"*
Terminal C–O	2107.0 (0.5)	2106 (0.1)	2100 (2.1)		2112 (0.2)
	2083.3 (4.2)	2085 (7.5)	2077 (9.3)	2058.8 (10)	2101 (1.3)
	2063.8 (10)	2059 (10)	2060 (10)	2031.0 (1.6)	2070.5 (10)
	2048.0 (5.6)	2052 (3.2)	2053 (5.0)		2059 (1.7)
	2042.0 (3.2)	2033 (0.9)	2047 (2.9)		2050 (2.2)
	2029.2 (1.7)	2018.5 (1)	2035 (2.5)		2041 (3.8)
	~2022 (sh)	2015 (sh)			
Bridging C–O		1838 (1.1)			
C–S	1021	873	1011	821	1134
	900	732			926
	754				770

[a] In n-hexane solution. [b] In KBr pellet.

structure being constructed of a triangle of three $Co(CO)_2$ entities bonded to an apical trivalent sulphur atom like in $Co_3(CO)_9S$[9,10,12], the CS group bridging on the other side of the Co_3 cluster.

"Complexes III and IV" are formed in very small yields and up till now we were not able to obtain reasonable analytical compositions for them. The presence of only one band in the middle infrared region and of only two C–O stretching bands for "Complex III" suggestst a thiocarbonyl complex of high molecular symmetry.

The formation of the sulphur-free compound $[Co_3(CO)_9C]_2$[11] is noteworthy, since it indicates an interesting desulphurization reaction in which the sulphur-containing complexes $Co_3(CO)_9S$ and $[Co_2(CO)_5S]_2$ are also formed. The mechanism of the formation of $[Co_3(CO)_9C]_2$, which undoubtedly contains a C–C bond is, however, unclear.

Hungarian Oil and Gas Research,
Institute "MÁFKI",
Veszprém (Hungary)

E. KLUMPP
G. BOR
L. MARKÓ

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