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STRUCTURAL AND INFRARED SPECTROSCOPIC CHARACTERIZATION OF $Co_6C(CO)_{12}S_2$: A HIGH-NUCLEARITY CARBIDO CARBONYL CLUSTER SPONTANEOUSLY FORMED FROM DICOBALT OCTACARBONYL AND CARBON DISULPHIDE *

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Summary

$Co_6C(CO)_{12}S_2$ (I) has been isolated in crystalline form from the mixture of more than a dozen of carbonyl products formed when $Co_2(CO)_8$ reacts at room temperature with CS_2. Crystals of I are monoclinic with space group *Cc*, and lattice constants $a = 16.250(5)$, $b = 9.413(4)$, $c = 16.036(5)$ Å, $\beta = 116.77(4)°$. Structure refinement gave $R = 0.034$ for 1974 reflections. The CCo_6S_2 core of the molecule possesses idealized D_{3h} geometry. It is composed of a Co_6 trigonal prism, enclosing a C atom in the centre, and the triangular faces are capped symmetrically by the two S atoms. The core contains two sorts of Co—Co distances: short ones (2.432 Å) along the triangular edges, and long ones (2.669 Å) along the lateral edges. The average Co—C distance is 1.94 Å, and the average Co—S distance 2.192 Å.

^{13}CO-enriched samples were prepared photochemically and their IR spectra used in the assignment of the C—O stretching frequencies. The C—O stretching force constant was calculated to be 1670(2) Nm^{-1}.

By the use of $^{13}CS_2$, I has also been obtained in a selectively carbido-^{13}C-labelled form. The vibrational frequencies of the carbide atom were observed,

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* Dedicated to the memory of Professor Paolo Chini.

and that at 819 cm^{-1} (^{13}C : 790 cm^{-1}) assigned to the species A_2'', and that at 548 cm^{-1} (^{13}C : 535.5 cm^{-1}) to species E'. For the Co-C(carbide) force constant a value of 155 Nm^{-1} was calculated. The cobalt—sulphur stretching frequencies were found at 309 cm^{-1} (A_2'') and 239 cm^{-1} (E'). The Co—S stretching force constant, 78 Nm^{-1}, is considerably lower than that obtained for $SCo_3(CO)_9$, viz. 112 Nm^{-1}.

Introduction

Chini and coworkers were the first to prepare carbido carbonyl transition metal clusters in a directed synthesis, where the carbido atom stems from an external, non-carbonyl source: these were the $[Rh_6C(CO)_{15}]^{2-}$ and $[Co_6C(CO)_{15}]^{2-}$ dianions [1]. If we disregard the conversion of metal carbonyl compounds already containing an interstitial carbon atom by degradation, oxidation or condensation with other carbonyls [2], until recently all other metal carbido carbonyls were made (rather fortuitously, and very often in small yields, along with several other products) by pyrolysis of pure carbonyls or by heating or irradiating their solutions, or more selectively by reduction of a neutral metal carbonyl by a metal carbonyl anion [3]. These methods have in common that the source of the carbide atom is a carbonyl group, although in the case of $[Fe_5C(CO)_{15}]$ (the first metal carbonyl carbide, which was obtained in very small yield when $Fe_3(CO)_{12}$ and 1-pentyne or methylphenylacetylene were heated in petroleum ether [4]), surprisingly enough the origin of the carbidic carbon has not yet been demonstrated.

In this paper we report in detail on the structural and IR-spectroscopic characterization of a carbido carbonyl cluster compound which also contains two sulphur atoms per molecule, viz. $Co_6C(CO)_{12}S_2$. (For preliminary reports on some aspects of this study see refs. 5 and 6.) It is not only one of the still rare examples of non-carbonylic origin, but also the first and up to now the only one in which the interstitial carbidic carbon atom originates from CS_2, as has been proven by the use of $^{13}CS_2$ in the synthesis. But unlike Chini's above-mentioned Rh- and Co-carbido carbonyls, the title compound was not the product of a directed synthesis; it was rather one of at least 14 different products in the reactions of $Co_2(CO)_8$ with CS_2 (as neat liquid or in hydrocarbon solvent) at room temperature [7,8], and therefore represents only one additional item of information in the large and complex puzzle of CS_2 activation by cobalt carbonyls. Among the fully characterized complexes formed in the reaction [8—11], the title compound is unique in several respects: it is among the major products, representing 20 to 35% of the soluble carbonyls regardless of the $Co_2(CO)_8/CS_2$/solvent ratios, and it seems to be the only closed high-nuclearity [2b] cluster and the only interstitial carbide among the products.

The roots of our research activity in this field go back to investigations of the solvent effect on the IR spectra of metal carbonyls [12] and to the attempt to unravel the complex reactions of cobalt carbonyls with sulphur and organic sulphur compounds [13,7]. During the intervening approximately 15 years, CS_2 activation by transition metal complexes in general has received increasing attention [14]. However, only two other cases of $M_X(CO)_YC_VS_W$ clusters formed from pure (unsubstituted) metal carbonyls and CS_2 have been reported: namely the recently prepared $Os_3(CO)_8(CS)S_2$ [15] and $Fe_4(CO)_{12}(CS)S$ [16], which are low-nuclearity, low-symmetry, non-carbido thiocarbonyl complexes.

Experimental

Preparation of $Co_6C(CO)_{12}S_2$ (I)

Compound I was prepared from the reaction of $Co_2(CO)_8$ with CS_2. In a typical preparation *, 5 g of $Co_2(CO)_8$ were dissolved in petroleum ether under a stream of nitrogen at room temperature. 3.5 ml CS_2 (1 : 4 molar ratio) were then added and the mixture was set aside overnight. It was then filtered and the solvent removed in vacuo. The solid was dissolved in a small amount of $CHCl_3$ and the solution subjected to TLC (support: Kieselgel 60 $PF_{254+366}$ Merck; eluent: petroleum ether). The complex appeared as a dark green band near the top of the plates. Extraction with $CHCl_3$ and crystallization from n-heptane at —20° C gave black crystals of pure $Co_6C(CO)_{12}S_2$ (yield: ca. 3% with respect to the starting $Co_2(CO)_8$, ca. 30% of the carbonyl complexes originally dissolved in the reaction mixture). It is stable in air, soluble in CCl_4 and $CHCl_3$, and sparingly soluble in hydrocarbon solvents, and decomposes without melting.

A sample labelled selectively by ^{13}C in the central carbido position was prepared similarly by the use of $^{13}CS_2$ (90% ^{13}C, furnished by Stohler Isotope Chemicals).

The ^{13}CO ligand-enrichment was performed photochemically. A hexane solution of I, under ca. 1 bar of a ^{13}CO-enriched (approximately 13% ^{13}C) gas, was stirred at 0° C in sunlight for ca. 12 h. Chromatography showed that no by-products were formed, whereas an attempted thermal exchange reaction at 85° C resulted in extensive decomposition and formation of at least one unidentified carbonylic by-product.

Crystal data

$a = 16.250(5)$, $b = 9.413(4)$, $c = 16.036(5)$ Å, $\beta = 116.77(4)°$, monoclinic system, $V = 2189.41$ Å^3, $M = 765.85$, $Z = 4$, space group Cc or $C2/c$ from extinctions, $D_c = 2.32$ g cm^{-3}, $D_m = 2.33$, Mo-K_α radiation, graphite monochromatized, $\lambda = 0.7107$ Å. μ(Mo-K_α) is 45.2 cm^{-1}.

Crystal structure determination

A crystal sealed under nitrogen in a glass capillary was mounted on a Philips PW 1100 diffractometer and a range $2° < \theta < 25°$ was explored. 2300 reflection intensities were collected with the θ—2θ scan method at a scan rate of 0.05° sec^{-1}; the scan width was 2.00° and the background was measured for 10 sec before and after the scanning range.

Three standard reflections (006, 040, 600) were checked after every ~240 measures, but no radiation damage was discovered. With the aid of an initial

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* Additional details will be given elsewhere in a comprehensive account of our studies of this reaction.

TABLE 1

ATOMIC FRACTIONAL COORDINATES WITH THE ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x/a	*y/b*	*z/c*
Co(1)	0.2084	0.6232(1)	0.9675
Co(2)	0.3383(1)	0.6794(1)	0.9368(1)
Co(3)	0.2382(1)	0.8681(1)	0.9408(1)
Co(4)	0.3162(1)	0.6554(1)	1.1503(1)
Co(5)	0.4461(1)	0.7116(2)	1.1193(1)
Co(6)	0.3461(1)	0.9004(1)	1.1237(1)
S(1)	0.1947(2)	0.7019(3)	0.8331(2)
S(2)	0.4381(2)	0.7768(3)	1.2462(2)
C(1)	0.2069(8)	0.4341(12)	0.9609(9)
C(2)	0.1058(7)	0.6477(11)	0.9777(7)
C(3)	0.4117(7)	0.7765(13)	0.8965(8)
C(4)	0.3759(8)	0.4996(13)	0.9333(8)
C(5)	0.2873(8)	1.0128(12)	0.9022(9)
C(6)	0.1406(9)	0.9564(13)	0.9364(10)
C(7)	0.2296(7)	0.6774(12)	1.1902(8)
C(8)	0.3344(8)	0.4707(14)	1.1726(8)
C(9)	0.5040(7)	0.5414(13)	1.1462(9)
C(10)	0.5353(7)	0.8107(11)	1.1039(7)
C(11)	0.2635(9)	0.9952(14)	1.1463(9)
C(12)	0.4102(8)	1.0521(13)	1.1169(9)
C(13)	0.3160(6)	0.7404(9)	1.0394(7)
O(1)	0.2039(9)	0.3121(9)	0.9587(10)
O(2)	0.0394(6)	0.6633(12)	0.9858(7)
O(3)	0.4566(7)	0.8328(12)	0.8703(7)
O(4)	0.3980(7)	0.3884(10)	0.9289(9)
O(5)	0.3164(8)	1.1015(10)	0.8767(8)
O(6)	0.0765(7)	1.0174(11)	0.9292(10)
O(7)	0.1780(7)	0.6899(11)	1.2191(7)
O(8)	0.3434(9)	0.3497(10)	1.1863(9)
O(9)	0.5419(7)	0.4371(11)	1.1686(11)
O(10)	0.5904(5)	0.8685(10)	1.0939(6)
O(11)	0.2130(8)	1.0581(11)	1.1621(9)
O(12)	0.4532(9)	1.1481(11)	1.1168(10)

Patterson three-dimensional map and using direct methods the cobalt and sulphur atoms were located. The structure was solved by assuming a *Cc* space group, and the subsequent satisfactory refinement confirmed the choice. Fourier-difference maps allowed location of the other atoms. The carbonyl groups were located with some difficulty owing to the dominating effects of the cobalt and sulphur atoms on the diffractions. The refinement with the SHELX 76 [17] program, initially isotropic, then anisotropic for all the atoms, led to $R = 0.034$ for 1974 reflections with $I > 3\sigma(I)$. Owing to the satisfactory behaviour of $\Sigma w \Delta^2$, the weights were kept at a unitary value. No absorption correction was applied. The atomic fractional coordinates are listed in Table 1 and the thermal parameters in Table 2. A list of observed and calculated structure factors is available on request (from G.G.)

Infrared spectra

Spectra were recorded with a Perkin Elmer Model 325 grating spectrometer. The spectral slit width was 0.9 to 1.0 cm^{-1} in the 2000 cm^{-1} and 800 cm^{-1}

TABLE 2

ATOMIC THERMAL PARAMETERS ($\times 10^4$ FOR Co AND $\times 10^3$ FOR S, C AND O ATOMS) [a]

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(1)	276(6)	355(7)	356(7)	—19(6)	145(6)	—37(6)
Co(2)	314(7)	397(7)	322(7)	—31(6)	182(6)	—6(6)
Co(3)	316(7)	341(7)	392(7)	82(6)	160(6)	49(6)
Co(4)	331(7)	391(7)	309(7)	38(6)	165(6)	—3(6)
Co(5)	246(6)	436(8)	328(7)	15(6)	117(5)	16(6)
Co(6)	385(7)	346(7)	395(8)	—74(6)	221(6)	—49(6)
S(1)	37(1)	61(2)	29(1)	0(1)	10(1)	—6(1)
S(2)	39(1)	70(2)	27(1)	—6(1)	11(1)	—7(1)
C(1)	48(4)	48(4)	69(5)	2(4)	41(4)	1(4)
C(2)	36(4)	47(4)	35(4)	11(4)	17(3)	3(4)
C(3)	39(4)	56(5)	49(4)	4(4)	20(4)	1(4)
C(4)	49(4)	53(5)	56(4)	—13(4)	33(4)	—11(4)
C(5)	56(4)	42(4)	60(5)	—2(4)	24(4)	4(4)
C(6)	60(5)	44(4)	86(5)	6(4)	42(4)	7(4)
C(7)	38(4)	52(4)	38(4)	4(4)	9(3)	0(4)
C(8)	53(4)	8(5)	52(4)	6(4)	38(4)	10(4)
C(9)	36(4)	47(4)	81(5)	—4(4)	28(4)	—4(4)
C(10)	39(4)	35(4)	41(4)	9(4)	8(4)	0(4)
C(11)	55(4)	59(5)	66(5)	—2(4)	38(4)	—3(4)
C(12)	53(4)	45(4)	71(5)	—22(4)	30(4)	—9(4)
C(13)	37(4)	22(3)	30(3)	—1(3)	19(3)	6(3)
O(1)	124(5)	38(4)	153(5)	—13(4)	90(4)	—15(4)
O(2)	44(4)	120(5)	76(4)	22(4)	39(3)	19(4)
O(3)	86(4)	92(5)	89(4)	—3(4)	66(4)	—25(4)
O(4)	96(4)	50(4)	136(5)	—35(4)	72(4)	3(4)
O(5)	118(5)	54(4)	111(5)	21(4)	73(4)	—16(4)
O(6)	60(4)	72(5)	186(6)	29(5)	69(4)	29(4)
O(7)	76(4)	96(5)	81(4)	—5(4)	62(4)	—3(4)
O(8)	134(5)	51(4)	131(5)	42(4)	87(4)	29(4)
O(9)	67(4)	57(4)	204(6)	35(5)	59(4)	26(4)
O(10)	41(3)	87(4)	66(4)	10(4)	25(3)	—21(4)
O(11)	112(5)	68(5)	153(5)	—26(4)	100(4)	8(4)
O(12)	125(5)	74(4)	171(5)	—52(4)	114(4)	—53(4)

[a] Expression of the form $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^{\star}b^{\star} + 2U_{13}hla^{\star}c^{\star} + 2U_{23}klb^{\star}c^{\star})]$ with the units of U_{ij} being Å^2.

region (slit program 4.5). In the C—O stretching region spectra were recorded on saturated hexane solutions, with an 0.5 mm pathlength (needed because of the very poor solubility), and with solvent compensation. C—O spectra were scanned with 5- or 10-fold wavenumber scale expansion (1 cm on the chart = 5 or 2.5 cm^{-1}); ordinate expansion (5×) was used for the weak satellites. The 1000—220 cm^{-1} region was scanned on CsI or KBr pellets (0.4 to 1.2 mg sample in 300 mg CsI or KBr); the KBr absorption was compensated by placing a pellet of KBr in the reference beam.

Results and discussion

Description of the structure

The basic framework of the molecule (Fig. 1) is a regular trigonal prism of six cobalt atoms encapsulating a carbidic C. Its two triangular faces are capped

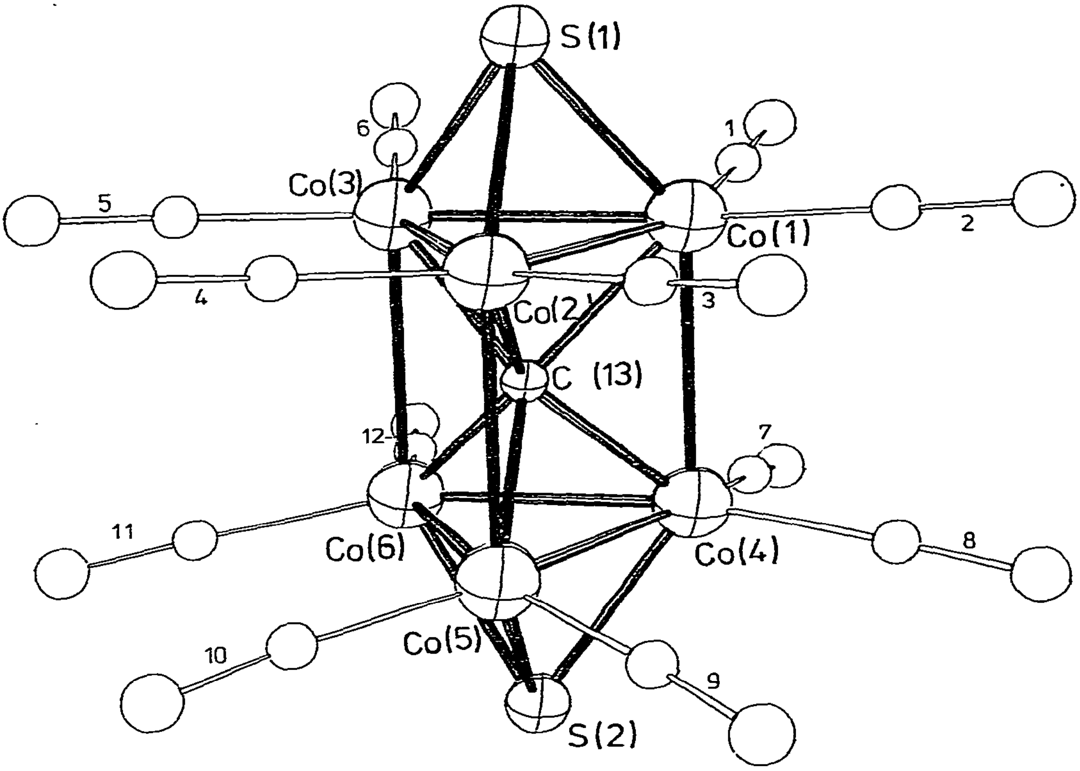

Fig. 1. The molecular structure of $Co_6C(CO)_{12}S_2$ (I) in the crystalline state; isolated numbers refer to the carbonyl groups rather than to individual atoms.

by S atoms, and two CO groups are terminally bound to each metal atom. The idealized symmetry is D_{3h}, with the threefold axis passing through the carbidic C and the S atoms. The present compound is the only example of a prismatic cluster of cobalt atoms *; other similar frameworks have been found only as part of more complex structures [3b].

For the following discussion it is, however, more useful to regard I as constructed formally of two trigonal pyramids of $Co_3(CO)_9S$ (II) fused base to base by replacing the three axial CO groups on both units by direct (lateral) Co—Co linkages. The structural data for the pyramidal Co_3S entities (Table 3) reveal that the Co—S bonds are slightly longer in I (2.191 Å av. vs 2.139 Å av.) whereas the Co—Co bonds are much shorter than in II [18].

Dahl et al. [19] pointed out that the geometry of a triangular metal cluster system is very sensitive to the antibonding electrons, by showing that the Co—Co distance values in Co_3 frameworks correlate well with the number of electrons in the MO's with mainly antibonding Co—Co character. The average bond length (Co_3 triangle only) of I (2.432 Å) is close to that in $Co_3(C_5H_5)_3(CO)(S)$ (2.452 Å; no antibonding electrons), shorter than that in $[Co_5(C_5H_5)_3S_2]^+$

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* Chini and coworkers have suggested a prismatic shape for the $[Co_6C(CO)_{15}]^{2-}$ ion, but no structural data have been reported. cf. ref. 1b.

TABLE 3

SELECTED VALUES OF INTERATOMIC DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Co(1)—Co(2)	2.433(2)	
Co(1)—Co(3)	2.433(2)	
Co(1)—Co(4)	2.669(2)	
Co(2)—Co(3)	2.428(2)	
Co(2)—Co(5)	2.667(2)	
Co(3)—Co(6)	2.672(2)	
Co(4)—Co(5)	2.435(2)	
Co(4)—Co(6)	2.433(2)	
Co(5)—Co(6)	2.431(2)	
Co(1)—S(1)	2.195(3)	
Co(2)—S(1)	2.181(3)	
Co(3)—S(1)	2.197(3)	
Co(4)—S(2)	2.203(3)	
Co(5)—S(2)	2.184(3)	
Co(6)—S(2)	2.191(3)	
Co(1)—C(13)	1.946(9)	
Co(2)—C(13)	1.925(9)	
Co(3)—C(13)	1.934(9)	
Co(4)—C(13)	1.949(10)	
Co(5)—C(13)	1.936(9)	
Co(6)—C(13)	1.934(9)	
Co—C_{CO}	av. 1.78	range 1.76(1)—1.84(1)
C—O	av. 1.13	range 1.12(1)—1.16(1)

(2.591 Å; one antibonding electron) and in $Co_3(CO)_9S$ (2.637 Å; one antibonding electron), and shorter again than that in $Co_3(C_5H_5)_3S_2$ (2.687; two antibonding electrons) [19b]. This suggests that the linkage of two Co_3S units through the assistance of the central C atom effectively removes the electron density from the antibonding MO of the Co_3S unit thereby shortening the Co—Co bond and increasing its strength.

The average lateral (inter-triangle) distance between the cobalt atoms on the other hand is much longer (2.669 Å), and permits the interstitial C atom to be accommodated. An apparent covalent radius of 0.72 Å can be calculated on the basis of the average Co—C and the (shorter) Co—Co distances (along the edges of the triangle), in agreement with analogous radii in the trigonal prismatic cavity of Rh (0.74 Å) [3b], in the square antiprismatic cavity of Co (0.74 Å) [3b], and in the trigonal prismatic cavity of Co (0.69 Å) [20].

The comparison between II and I further reveals that the Co—S—Co angle has drastically decreased (from 76.1° av. to 67.4° av.) (Table 4). On one hand this is connected with the contraction of the Co_3 triangle. On the other hand the angle CO_{ax}—Co—Co in II (97° av) is obviously reduced to 90°, as it corresponds to the one formed by two adjacent edges of the rectangular faces in the prismatic structure of I, while all the angles not comprising the Co_3 ring do not change appreciably (viz. CO_{eq}—Co—CO_{eq}: 101° vs. 98°; S—Co—CO_{ax} resp. S—Co(*i*)—Co(*i* + 3): 142.6° vs. 140.1°; CO_{eq}—Co—CO_{ax} resp. CO_{eq}—CO(*i*)—Co(*i* + 3): 100.8° vs. 96.7° av.). Therefore, in I the equatorial CO groups are forced down towards the Co_3 plane (from 25° in II to between 3 and 10°) while the Co—S bonds straighten up and their length increases by approxi-

TABLE 4

SELECTED VALUES OF BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	Average	Range
Co—Co—Co (triangular face)	60.0	59.9(1)— 60.1(1)
Co—Co—Co (rectangular face)	90.0	89.8(1)— 90.3(1)
Co—S—Co	67.4	67.2(1)— 67.5(1)
C_{CO}—Co—C_{CO}	98.2	97.1(6)—100.0(5)
Co—Co(lateral)—S	140.1	139.3(1)—140.7(1)
Co—Co(lateral)—C_{CO}	96.7	93.7(3)—100.1(4)
Co—C(carbidic)—Co [a]	77.8	77.6(4)— 78.0(4)
Co—C(carbidic)—Co [b]	87.1	86.5(4)— 87.4(4)

[a] Both Co atoms belong to the same triangle. [b] The two Co atoms are on the same lateral edge of the prism.

mately 0.05 Å. This must be accompanied by a weakening of the bond (see paragraph on the vibrational frequencies of the sulphur atoms).

Infrared spectroscopic studies

1. The C—O stretching region

Only two strong bands, at 2059 and 2031 cm^{-1}, are observed in the stretching region IR spectrum of I in hexane solution (Fig. 2), apart from two

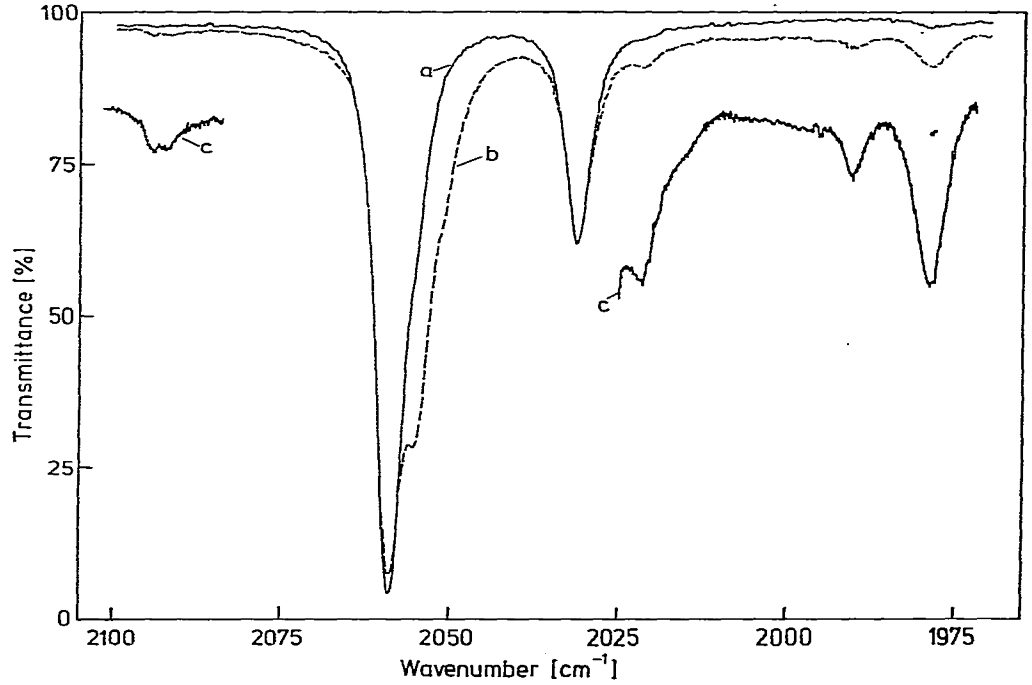

Fig. 2. IR spectrum of $Co_6C(CO)_{12}S_2$ in the C—O stretching region (saturated n-hexane solution, path-length 0.5 mm): (a) natural $^{12}CO/^{13}CO$ abundance; (b) ^{13}CO enriched sample (approximately 10% ^{13}CO corresponding to ca. 37.5% $(^{12}CO)_{11}(^{13}CO)$ and ca. 22% $(^{12}CO)_{10}(^{13}CO)_2$ species; (c) same as (b), but with 5-fold ordinate expansion.

weak absorptions due to ^{13}CO substituted species (as confirmed by isotope enrichment studies). One of those is a weak band at 1979 cm^{-1} readily visible under routine conditions, the other is a weak shoulder at 2055 cm^{-1} (merged in the low-energy wing of the strong band) barely discernible even in an expanded wavenumber scale spectrum.

Even in the early studies the simplicity of the spectrum was taken to indicate a high molecular symmetry [7b]. The interpretation of the spectra became feasible, however, only when X-ray analysis showed that the molecule of I belongs to point group D_{3h}.

The C—O stretching modes of I give rise to normal vibrations of A_1' (R), A_1'' (—), A_2' (—), A_2'' (IR), $2E'$ (IR, R) and $2E''$ (R) symmetries (characters in parenthesis indicate spectral activities). The problem of frequency assignment proved to be highly complex, and we cannot offer such a complete and unambiguous solution as in earlier cases [21].

First of all we did not succeed in recording the Raman spectrum, because the crystals of I have a very dark colour and are only slightly soluble. Then there is the striking fact that out of the three IR-active modes predicted by selection rules, only two can be observed directly in the all-^{12}CO spectrum and assigned (unequivocally, by systematic exclusion of all other possible combinations through C—O factored force field calculations): E', ν_5 to 2059 and A_2'', ν_4 to 2031 cm^{-1}. The lower E' mode (ν_6), although IR-allowed, simply does not show a detectable intensity. A similar case of an unexpected extremely low intensity of one of the IR-active E' modes in the spectrum of $Ru_3(CO)_{12}$ was recently subjected to a quantitative analysis [22]. It can be explained by a cancellation of the sum of the local oscillating C—O dipole moment by an induced dipole moment between the metal centers. With μ'_{xy} assumed to be ca. 1.4 and $\mu'_z \simeq 1.2$ * the intensity ratios calculated were the same as those observed in the spectrum: $I_5(2059) : I_4(2031) : I_6(\sim 2022) \cong 1.0 : 0.21 : 0.00$.

The position of ν_6 at ~2022 cm^{-1} can be derived with reasonable accuracy (±1 cm^{-1}) from a mono ^{13}CO band in the spectrum of an enriched sample at 2021.5 cm^{-1}. A satellite at 2094 cm^{-1} permits the frequency of the IR-inactive, totally symmetric in-phase A_1' mode (ν_1) to be estimated straightforwardly as 2096.5 ± 0.5 cm^{-1}. This is confirmed by another small band at 2092 cm^{-1} (observed at 10% ^{13}CO-enrichment) assigned to the $\{CCo_6S_2\}(^{12}CO)_{10}(^{13}CO)_2$ species (calculated frequency values for its 9 isotopomers are between 2091.4 and 2092.1 cm^{-1}), The shoulder at 2055 cm^{-1} is obviously a mono-^{13}CO satellite of the E' fundamental at 2059 cm^{-1}. The other IR-inactive modes (2) E'', A_1'', and A_2' must occupy (in decreasing order) the low-energy end of the terminal C—O stretching region according to the relative phase rules of Orgel [23] and Kaesz et al. [24] **.

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* μ'_{xy} and μ'_z are the changes of the induced metal—metal dipole moment in the xy plane or along the z axis, respectively. Values are given relative to the unit local C—O dipole moment derivative, i.e. $(\partial\mu_{CO}/\partial R) = 1$. For details see ref. 22.

** Since different research groups agree in assigning the lowest C—O stretching frequency in the spectrum of $ECo_3(CO)_9$ complexes (E = HC, RC, S, etc.) to the IR-inactive A_2 mode [25], and since the A_1'' and A_2' modes are simply the out-of-phase and in-phase combinations of the A_2 C—O stretches of two coupled $ECo_3(CO)_6$ units, the above-mentioned sequence seems reasonable.

TABLE 5

ASSIGNMENT OF THE C—O STRETCHING MODES OF $Co_6C(CO)_{12}S_2$ (POINT GROUP D_{3h})

ν_i^{CO}	Species	Activity	Frequency (cm^{-1})
ν_1	A_1'	R	2096.5 [b]
ν_2	A_1''	—	2018 [c]
ν_3	A_2'	—	2004 [c]
ν_4	A_2''	IR	2031.0 [a]
ν_5	E'	IR, R	2059.0 [a]
ν_6	E'	IR, R	2022 [c]
ν_7	E''	R	2024 [c]
ν_8	E''	R	2021 [c]

[a] By direct measurement, ±0.5 cm^{-1}. [b] Calculated from isotopic frequencies, ±1 cm^{-1}. [c] Calculated from isotopic frequencies, ±2 ... 4 cm^{-1}.

The assignment of frequency values to these modes on the basis of the remaining two isotopic bands of $\{CCo_6S_2\}(^{12}CO)_{11}(^{13}CO)$ at 2015 and 1979 cm^{-1} proved to be very difficult *. Upon substitution of $\{CCo_6S_2\}(^{12}CO)_{12}$ by one ^{13}CO group, the molecule changes from D_{3h} to C_1. This complete loss of symmetry elements is reflected in the C—O stretching factored force field calculations **, where the variation of the (input) frequency value of any one of the (lower energy) all-^{12}CO modes affects several ^{13}CO bands at the same time. Obviously in this case the concept of isotope satellites (i.e. that every ^{13}CO band derives prevalently from its own parent mode) must be abandoned, at least in the confined region between 1970 and 2025 cm^{-1}. Therefore when several input frequency values are changed in a concerted way, different but equally acceptable solutions can be calculated; thus the lower E' mode may be varied in a range of ±2 cm^{-1} and E'' even within ±4 cm^{-1} without affecting the calculated values unduly. Table 5 lists what we regard as the most probable assignments based on a good agreement between observed and calculated isotopic frequencies (to within ±0.5 cm^{-1}), as well as between the calculated force and interaction contants (given in Table 6) and those found in earlier studies for polynuclear carbonyls [21].

Due to the fact that the frequency values are very closely spaced in the 2025 to 2015 cm^{-1} region, not even the proposed sequence $E'' > E' > E'' > A_1'' > A_2'$ is completely without ambiguity in the sense that at the high-energy end E'' and E' may be changed to $E' > E'' > E'' > A_1'' > A_2'$ without greatly affecting the above mentioned agreement.

It would be very interesting to compare the C—O stretching valence force constant (1670 Nm^{-1}) with the corresponding value for $SCo_3(CO)_9$. One might

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* There was no way of attributing the absorption at 1990 cm^{-1} to monosubstituted species; C—O factored force field calculations show that it is a band of the $\{CCo_6S_2\}(^{12}CO)_{10}(^{13}CO)_2$ species. A favourable resultant at the local oscillating dipoles for several of the nine isotopomers, originating partly in the fact that the ^{13}C—O bonds stretch with a high relative amplitude in this mode, is the main reason why this vibration is relatively intense. In addition also a high induced metal—metal dipole contribution can be calculated for it. In contrast, the lowest C—O stretching mode (calculated to occur in the 1972—1978 cm^{-1} region) was not observed at all, since the above mentioned factors do not reinforce one another.

** Details of the method have been described in ref. 21d.

TABLE 6

C—O STRETCHING FORCE AND INTERACTION CONSTANTS OF $Co_6C(CO)_{12}S_2$

Constant	Type of interaction [a]	Examples [b]	Value [c] (mdyn/Å)
K(C—O)	—	—	16.70
i_c	geminal *cis*	1— 2, 3— 4, ...	0.21
j_1	Δ, vicinal	2— 3, 4— 5, ...	0.19
j_2	Δ, vicinal	1— 4, 2— 5, ...	0.04
j_3	Δ, vicinal	1— 5, 2— 6, ...	0.04
j_4	ΔΔ, vicinal	1— 7, 2— 8, ...	0.18
j_5	ΔΔ, vicinal	1— 8, 2— 7, ...	0.17
j_6	ΔΔ, distal	1—12, 2— 9, ...	0.14
j_7	ΔΔ, distal	1—10, 2—11, ...	0.01
j_8	ΔΔ, distal	1—11, 2—12, ...	0.02

[a] Interaction between CO ligands bound to two cobalt atoms within (Δ) or not within (ΔΔ) the same Co_3 triangle. [b] Ligands are numbered as shown in Fig. 1. [c] Accuracy ±0.02 mdyn/Å; 1 mdyn/Å = 100 Nm^{-1}.

expect a decrease of this value on cluster formation and on decreasing the CO/Co ratio in going from II to I, as in the case of $Co_2(CO)_8 \rightarrow Co_4(CO)_{12}$ (average terminal K_{CO} values of 1705 [26] vs. 1693 Nm^{-1} [21c] and of $Ru(CO)_5 \rightarrow Ru_3(CO)_{12}$ (1675 * [27] vs. 1665.7 Nm^{-1} [21d], if the carbidic C atom does not have a marked influence. Since the spectrum of II [13] has not yet been completely analyzed, we have to postpone such a comparison.

2. *Vibrational frequencies of the interstitial C atom*

No previous report on the assignment of the vibrations of an interstitial carbon atom inside a transition metal cluster, seems to exist. For $Fe_5C(CO)_{15}$, which contains an exposed carbide atom (adapting the nomenclature of Muetterties [3a]), the absorption bands observed at 790 and 770 cm^{-1} by Braye et al. were attributed to the Fe—carbide frequencies [4].

A central atom encapsulated into a metal cluster must have three vibrational degrees of freedom, of which, in point group D_{3h}, two should be degenerate. Hence, we can expect one vibration along the z axis (species A_2'') and another in the horizontal xy plane (species E'), both IR active. In order to identify these two vibrational frequencies, we prepared the selectively ^{13}C-labelled carbido cluster by using $^{13}CS_2$ in the synthesis. Two bands, in the middle region (850—500 cm^{-1}) of the spectrum reported in Fig. 3, show considerable frequency shifts upon ^{13}C-substitution: the band at 819 cm^{-1} is shifted to 790 cm^{-1}, and the other at 548 cm^{-1} is shifted to 535.5 cm^{-1}. We assign the first band to A_2'', and the lower one to E'. The extent of coupling of the highest mode with some Co—C—O bending modes is expected to be quite low; in fact, the $\nu(^{13}C)/\nu(^{12}C)$ ratio is 0.965 for the higher band pair, compared with the theoretical value of 0.9606. The second feature in this region lies very near to the Co—C—O bending region, and this vibration must undergo considerable mixing with bending

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* Obtained by the ^{13}CO enrichment method.

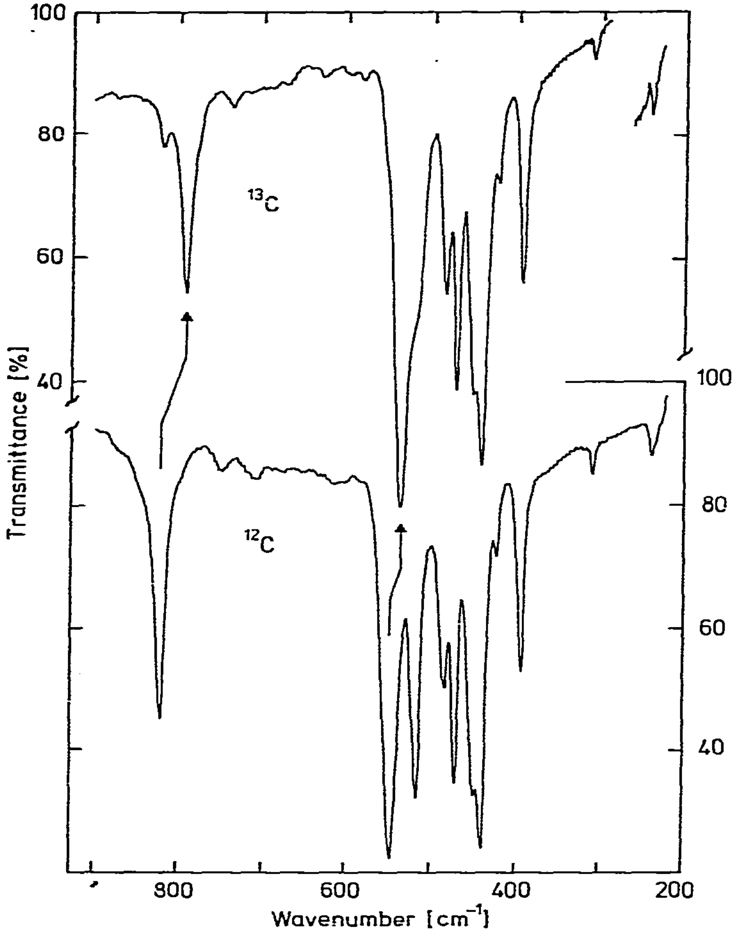

Fig. 3. Low-frequency IR spectrum of selectively carbido ^{13}C-labelled ^{13}CCo$_6$(CO)$_{12}$S$_2$ (90% isotopical purity) and of its natural abundance counterpart (1.2 mg sample in KBr). Filiation lines mark the frequency shifts of the two carbidic vibrations.

modes, as indicated by the fact that the isotopic shift is much smaller and the $\nu(^{13}C)/\nu(^{12}C)$ ratio is 0.977.

That the vibrations in this region are strongly mixed with other vibrational modes is also shown by the considerably reduced relative intensity of the band at 517 cm^{-1}, upon ^{13}C substitution, indicating a change in the P.E.D. (potential energy distribution) of the components of this normal mode, as well as by the small, but real frequency shifts and band shape changes observed in the 500—420 cm^{-1} region, as shown by spectra scanned with wavenumber expansion presented in Fig. 4.

A simple model, shown in Fig. 5, helps to confirm the assignment of the z (A_2'') and xy (E') vibrations. We can obtain expressions for K_z and K_{xy}, the "collective" force constants acting along z axis and in the xy plane, respectively, from the x (or y) and z stretching potential energy components in terms of the individual Co—C force constant k_c and the angle β formed between the

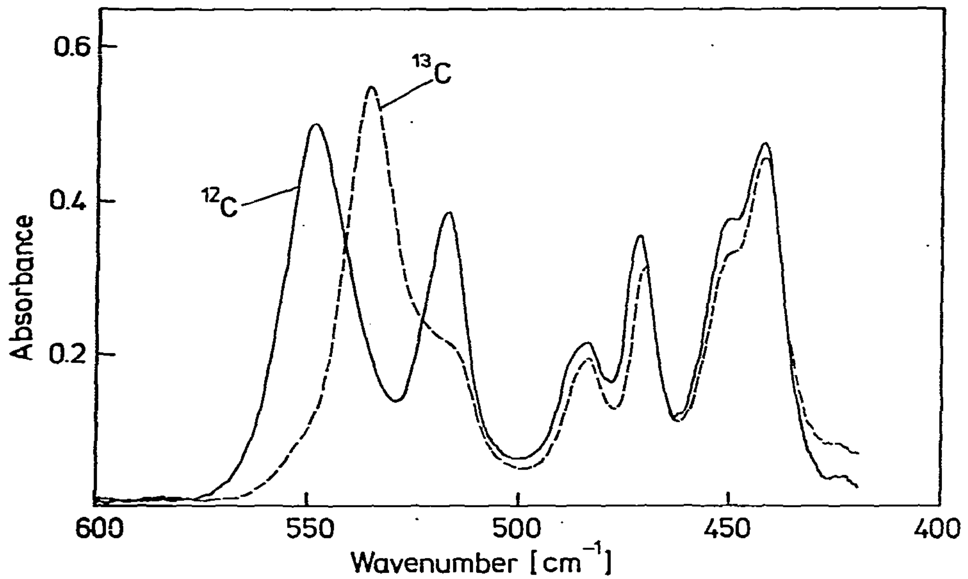

Fig. 4. Spectra of $Co_6C(CO)_{12}S_2$ with natural abundance and carbido ^{13}C-enrichment, recorded with wavenumber scale expansion in the 600—420 cm^{-1} region (same samples as in Fig. 3).

three-fold symmetry axis and the single Co—C bonds. Hence:

$K_z = 6\ k_c \cos^2\beta$

$K_{xy} = 3\ k_c \sin^2\beta$

then

$\nu_z/\nu_{xy} = \text{ctg}\,\beta\sqrt{2}$

In complex I, $\beta = 46.5°$ which yields $\nu_z/\nu_{xy} = 1.343$. The observed frequency ratio is 1.495 for the ^{12}C molecule and 1.475 for the ^{13}C-carbidic one. Hence

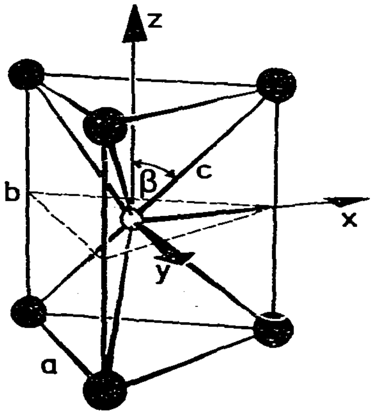

Fig. 5. The geometry of the Co_6C core of I and the notation used in the analysis of the vibration of the interstitial carbon atom.

the higher frequency belongs to the longitudinal vibration, and the lower one to the degenerate vibration in the xy plane. The discrepancy between the observed and calculated frequency ratio must be ascribed to the simplicity of the approach and to the mentioned strong coupling of the lower frequency mode with other vibrations. Without such a coupling the E' mode should occur around 600 cm^{-1}.

An approximate value for the Co—C force constant k_c was calculated from the normal coordinate analysis of the cage, neglecting both Co—C—O and Co—C—Co bending modes. On the basis of symmetry coordinates the F and G matrices are, in this case, both diagonal. Neglecting the interaction constants (whose values are expected not to be too different from zero) the solution of Wilson's equation is thus straightforward.

The secular equation for the A_2'' mode becomes simply:

$$k_c - G_{A_2''}^{-1} \times \lambda_1 = 0$$

where

$$G_{A_2''} = 6\mu_C \times \cos^2\beta + \mu_{Co} \text{ and } \lambda_1 = (4\pi^2c^2/N)\nu_1{}^2$$

The calculated value k_c = 1.55 mdyn/Å seems to be a good approximation *. This compares well with the values ranging from 1.35 to 1.71 mdyn/Å obtained for the Co—C constant of the Co_3CY core of the corresponding enneacarbonyls by a more complete calculation according to Kettle, Oxton et al. [25c,29].

3. *The vibrational frequencies of the sulphur atoms*

Adams [30] has listed the metal—sulphur stretching frequencies, and assigns them to the 210—480 cm^{-1} range. However, no examples of doubly or triply bridging S ligands were available for inclusion in his compilation when his book was written. Iron—sulphur frequencies of the μ_2-S bridges in $S_2Fe_2(CO)_6$ were observed later in the Raman studies by Scovell and Spiro [31a] and by Kettle and Stanghellini [31b] in the region between 332 and 265 cm^{-1}. Recently, Oxton et al. [32] reported frequencies between 238 and 354 cm^{-1} for a number of μ_3-S-bridged cobalt, nickel, and iron cyclopentadienyl and carbonyl complexes.

In the spectrum of I in the region below the lowest Co—(CO) band two weak absorptions are observed at 309 and 239 cm^{-1}, and these are the only likely candidates for the Co—S modes. These frequencies are considerably lower not only than those of the paramagnetic $SCo_3(CO)_9$ (II) [32], but also than those of $SCo_2Fe(CO)_9$ (357, 324 and 319 cm^{-1} [33]) in which the excess electron is not present. In I four vibrations, with dominantly Co—S stretching character can be expected to arise from the in-phase and out-of-phase combinations of the symmetric (a_1) and asymmetric (e) Co—S stretches of two SCo_3 units: A_1' (R), A_2'' (IR), E' (IR, R) and E'' (R). We have no basis for estimating the interaction constants between the two Co_3S entities, but presumably they are quite

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* The same numerical value is obtained if we apply the equation given by Herzberg [28] for the λ_1 vs. k_1 relationship of XY_3 pyramidal molecules, making the substitutions $k_1 = 2\,k_c$ and $m_y = 2\,m_{Co}$; (the influences of λ_2 and of the deformational term are also in this case neglected).

low. This implies small A'_1—A''_2 and E'—E'' frequency separation and it should not influence the assignment of the observed two bands.

Simple force field calculations [28] indicate that the symmetric frequencies (A'_1, A''_2), i.e. in which the displacement of the sulphur atoms occurs along the z-axis, are higher than those belonging to the perpendicular displacements of the S atoms (E, E''). It is interesting to compare the approximate Co—S stretching force constants, calculated from the symmetrical frequency only, for both I and II. The Herzberg equation given for XY_3 pyramidal molecules [28] leads to the same results as calculations with a complete G matrix: for I k (Co—S) = 78 Nm^{-1} can be calculated from the frequency of 309 cm^{-1}, whereas for II the Co—S force constant is 112 Nm^{-1}. Hence the lengthening of the Co—S bonds by 5.2 (av.) pm (from 213.9 to 219.1 pm) is accompanied by a decrease in the value of the force constant by 30%. This considerable weakening of the Co—S bond force constant cannot be attributed entirely to the lengthening of the bond, but can be regarded also as a manifestation of the geometrically less favourable overlap between the Co and S orbitals owing to the more "upright" direction of the Co orbitals, enforced by the longitudinal Co—Co bonds.

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