X-Ray Diffraction Analysis of the Disordered Crystal and Molecular Structure of $[\{Co_3(CO)_9C\}_2SCO]$: * its Identity with the Previously Reported '$[\{Co_3(CO)_9(CS)\}_2]$'

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The title compound, obtained from the reaction of $[Co_2(CO)_8]$ with CS_2, has been fully characterized by *X*-ray diffraction analysis. The incorrectness of the previously reported formulation, $[\{Co_3(CO)_9(CS)\}_2]$, is ascribed to the disordered $-S-C(O)-$ chain joining the two $CCo_3(CO)_9$ entities. The compound is triclinic, space group $P\bar{1}$, with $a = 8.794(4)$, $b = 12.576(4)$, $c = 8.113(4)$ Å, $\alpha = 105.14(3)$, $\beta = 113.32(4)$, $\gamma = 95.61(1)°$, and $Z = 1$. The cobalt atoms were located by the conventional Patterson method and the C, O, and S atoms by subsequent Fourier-difference maps. The final *R* value was 0.046 for 2 021 reflections with $I > 3\sigma(I)$. The central part of the molecule, $\rangle C-S-C(O)-C\langle$, is planar, with large π-electron delocalization and with different orientations with respect to the two Co_3 triangles. Its vibrational modes correspond to the i.r. bands at 1 642 [ν(C–O)], 1 137 [ν(C–C)], and 924 and 768 cm^{-1} [ν(S–C)].

Among the numerous products of the reaction between $[Co_2(CO)_8]$ and CS_2, a complex, previously designated as ' Complex IV ',[1] was obtained and on the basis of only a preliminary *X*-ray analysis it was assigned the formula $[\{Co_3(CO)_9(CS)\}_2]$.[2] However, at the time of the structural analysis only a very small quantity of the compound was available and its identity with ' Complex IV ' was established only on the basis of the ν(CO) region of the solution i.r. spectrum.

Subsequent repeated preparations enabled additional spectral studies and analyses during which an i.r. absorption band at 1 642 cm^{-1}, characteristic of an ' organic ' carbonyl group, was noticed. This band was not reported in the early study [1] and then in the subsequent investigations it was at first attributed to an impurity. At that time the results of the *X*-ray studies which showed the relative centrosymmetric positions of two $CCo_3(CO)_9$ units seemed to substantiate the composition of the molecule.

However, the band at 1 642 cm^{-1} proved to be genuine since it was exhibited by all the subsequent preparations and retained the same relative intensity, even after a series of attempted purifications and recrystallizations. Hence it was necessary to assume the presence of a $\rangle C=O$ group in the bridging unit connecting the two $CCo_3(CO)_9$ entities. At this point, a precise elemental analysis was carried out which yielded the atomic ratio Co : S = 6 : 1, rather than 3 : 1 as required by the formula given in the preliminary study.[2]

In the light of these supplementary findings it became obvious that the correct molecular formula is $(OC)_9Co_3C-S-C(O)-CCo_3(CO)_9$. We have repeated the analysis of the *X*-ray diffraction data in order to find the source of the first erroneous structural assignment for the bridging group, and to reconcile the structure with the i.r. spectral and analytical data. It was found that the two heavy-atom $CCo_3(CO)_9$ entities were related to each other by a non-crystallographic centre of symmetry and the $-S-C(O)-$ chain was disordered over two inversion-related locations. This unprecedented type of disorder had led us to the previous incorrect formulation.

Experimental

Preparation.—The complex $[\{Co_3(CO)_9C\}_2SCO]$ was prepared from $[Co_2(CO)_8]$ and CS_2 (molar ratio 1 : 4) in light petroleum (b.p. 40–70 °C) at room temperature under a slow stream of nitrogen. After *ca.* 8 h the reaction mixture was filtered, the solvent removed *in vacuo*, and the residue subjected to thin-layer chromatography (t.l.c.) (adsorbent, Kieselgel 60 $PF_{254-366}$; eluant, light petroleum). The compound appeared as a dark brown band, close to the baseline, together with another still unidentified compound (' Complex VII ') whose characterization is in progress.† The two complexes were separated by further t.l.c. Black crystals of pure $[\{Co_3(CO)_9C\}_2SCO]$ were obtained by crystallization from n-heptane {yield less than 1%, with respect to the starting $[Co_2(CO)_8]$}.

Infrared Spectra.—Spectra of CCl_4 solutions (CO stretching region) and of CsI pellets (1 800—300 cm^{-1}) of the complex were recorded on a Perkin-Elmer 325 grating spectrometer (slit width *ca.* 1 cm^{-1}). Bands were observed at 2 112w, 2 101m, 2 092w, 2 070s, 2 060m, *ca.* 2 057w (sh), 2 050m, 2 040s, 2 016w, 1 642m, 1 137m, 924m, *ca.* 818w, 768s, 689m, 656m, 593s, *ca.* 546w (sh), 527s, 506s, 495s, 470m, 450w,br, 438w, 430w, *ca.* 394w (sh), 387m, and 321w cm^{-1}.

Crystallography.—*Crystal data.* $C_{21}Co_6O_{19}S$, $M = 941.88$, Triclinic, space group $P\bar{1}$ (no. 2), $a = 8.794(4)$, $b = 12.576(4)$, $c = 8.113(4)$ Å, $\alpha = 105.14(3)$, $\beta = 113.32(4)$, $\gamma = 95.61(1)°$, $U = 774.60$ Å^3, $Z = 1$, $D_c = 2.02$ g cm^{-3}, $F(000) = 456$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 31.6 cm^{-1}.

Intensity measurements. 2 724 Intensities were collected on a Philips PW1100 automatic diffractometer, in the range

* μ-(2-Oxo-3-thiabutanediylidyne-μ_3-C^1:μ_3-C^4)-bis(nonacarbonyl-*triangulo*-tricobalt).

Supplementary data available (No. SUP 23586, 14 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

† *Note added in proof:* the formula and structure of ' Complex VII ' have since been established as $C_8(CO)_{21}C_3S_3$ (G. Gervasio, R. Rossetti, P. L. Stanghellini, and G. Bor, XXII Int. Conf. Coordination Chem., Budapest, 23rd–27th August, 1982, Abstracts, p. 762.

$2 < \theta < 25°$ using the θ—2θ scan method at a scan rate of 0.067° s^{-1}, with a scan width of 2.0°. The backgrounds were counted for 10 s at both extremes of the scan range. During the data collection three standard reflections were measured every 240 intensities, but no radiation damage was observed.

Solution and refinement of the structure. The structure was solved [3] by the initial location of the Co in a three-dimensional Patterson map and subsequent determination of C, O, and S atoms from a sequence of Fourier-difference maps. The formulation of the complex as $\{Co_3(CO)_9C\}_2S_2$ with the inversion centre on the S–S bond yielded an R value of 0.0567 for 2 021 reflections with $I > 3\sigma(I)$, with anisotropic refinement of all the atoms. The distances and angles, as well as the thermal parameters of all the atoms, were in agreement with the structure proposed in ref. 2. The final Fourier-difference map showed no abnormal peaks, only some positive and negative peaks at 0.7—0.8 e $Å^{-3}$ and a positive one at 1.5 e $Å^{-3}$.

However, the i.r. spectrum (solid state or n-hexane solution) did not agree in any way with the proposed structure, indicating unequivocally the presence of a ketonic CO group (see later). This non-congruence can tentatively be explained by the presence of a C_{ap}–C(O)–S–C'_{ap} chain joining the two $Co_3(CO)_9$ groups; if the chain were 50% oriented in the alternative position C_{ap}–S–C(O)–C'_{ap}, and $C_{ap}Co_3(OC)_9$ and $C'_{ap}Co_3(CO)_9$ were related by a pseudo-inversion centre, superimposition of the S atom on the CO group would result, simulating a crystallographic inversion centre over the whole structure. This new structure is strongly supported by the elemental analysis, which gives unequivocally a Co : S ratio of 6 : 1. Hence a re-examination of the structure was necessary at this point.

Two refinements were tried: (*i*) in the $P1$ space group; (*ii*) in the $P\bar{1}$ space group with an occupancy factor of 0.5 for the C, O, and S atoms of the disordered chain. Refinement (*i*) did not give satisfactory results since there are high correlation factors arising from the inversion centre that operate over the greatest part of the molecule, causing the R factor to oscillate during the refinement. In (*ii*) an examination of the final Fourier-difference map suggested that the residual peak of 1.5 e $Å^{-3}$ was due to the O atom of the ketonic group. The S and O atoms were then provided with an occupancy factor of 0.5 and refined in order to locate the C atom. The latter was assigned to one of the several small peaks which resulted and was subsequently introduced in the refinement with an occupancy factor of 0.5. The first cycles of refinement gave poor values for the distances and angles, but subsequently the atoms settled in satisfactory positions, significantly lowering the R value to 0.0456 for 2 021 reflections (anisotropic cycle). Even though the thermal parameter of the O atom is slightly high, we adopt the formulation $[\{Co_3(CO)_9C\}_2SCO]$ for the compound based on the lowered R, the reasonable final distances and angles, and, in particular, the i.r. and elemental analysis data.

The weighting scheme was $w = 1/[\sigma(F)^2 + aF^2]$, where a was varied in order to maintain $\Sigma w\Delta^2$ satisfactorily constant for the amplitude in various ranges of $|F_o|$. Fractional atomic co-ordinates are reported in Table 1, bond distances and angles in Table 2.

Discussion

Description of the Structure.—The molecular structure is formed by two $CCo_3(CO)_9$ units, centrosymmetrically related, joined by a –C(O)–S– chain (Figure 1). The complex belongs to the series of compounds with two trigonal pyramidal CCo_3 clusters bonded directly *via* the two C_{ap} atoms,[4] or by means of a CO ketonic group [5] or of a linear C_2 chain.[6] The Co_3 triangles are nearly equilateral and the Co–Co distances lie in the usual range.[7] The average Co–C_{ap} bond length (1.892 Å) and the dihedral angle between the Co_3 and the CoC_{eq} planes (28—30°) are close to corresponding reported values.[8]

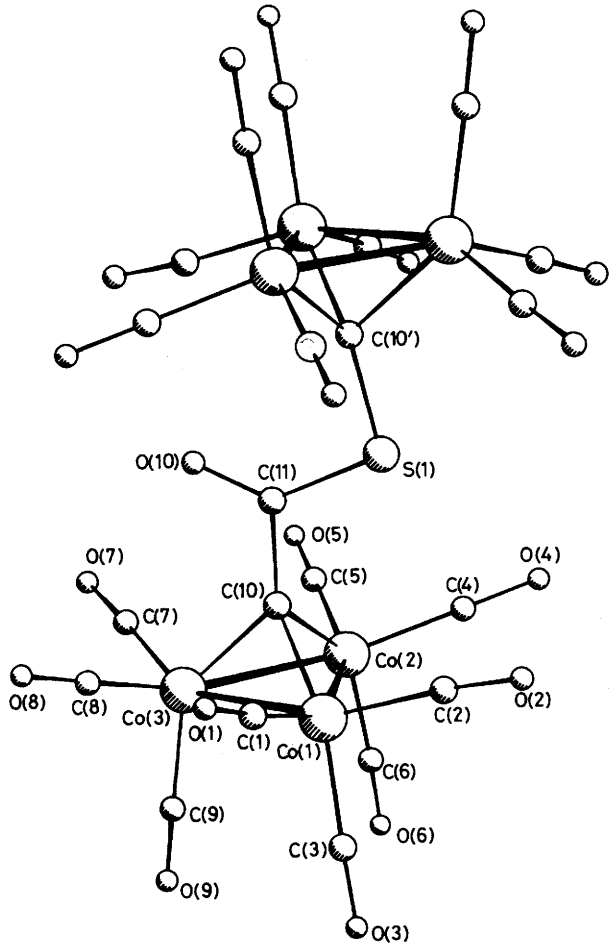

Figure 1. Molecular structure of $[\{Co_3(CO)_9C\}_2SCO]$

The most interesting part of the molecule is the –C(O)–S– chain, but the disorder of the structure gives rise to high estimated standard deviations (e.s.d.s) of the positional parameters of the CO group, preventing an accurate analysis of the bonds. Nevertheless, the C(11) atom is clearly coplanar with S(1), O(10), C(10), and C(10'),* showing a formal sp^2 hybridization. The angles around C(11) are not equal (115, 115, and 130°), probably owing either to the asymmetry of the atoms bonded to it or to crystal-packing effects. Other compounds with a ketonic CO group show the same behaviour, $[Co_3(CO)_9\{COC(O)Me\}]$,[9] or have nearly equal angles, $[Co_3(CO)_9\{CC(O)Ph\}]$ [10] and $[\{Co_3(CO)_9C\}_2CO]$.[5] The CO bond length has a plausible value [1.206(17) Å], *cf.* $[Co_3(CO)_9\{CC(O)Ph\}]$ [1.235(9) Å],[10] $[\{Co_3(CO)_9C\}_2CO]$ (1.24 Å),[5] and $[Co_3(CO)_9\{COC(O)Me\}]$ (1.20 Å).[9] In spite of the high σ value, the C(10)–C(11) bond [1.554(22) Å] is longer than the C–C bond in some Co_3C–C– frameworks probably because in these cases a partial π-electron density is delocalized on the C–C unit, *cf.* 1.46 Å in $[(OC)_9Co_3(CC_2H)Co_2(CO)_6]$,[11] 1.473(8) Å in $[Co_3(CO)_9\{CC(O)Ph\}]$,[10] and 1.478(16) Å in

* The equation of the plane is $7.29X - 5.48Y + 1.24Z = 0.00$ for fractional atomic co-ordinates and the distances (Å) from it are: −0.002(10) for C(10), 0.001(10) for C(10'), 0.000(7) for S(1), −0.003(31) for O(10), and 0.016(34) for C(11); $\chi^2 = \Sigma(d/\sigma)^2 = 0.30$.

Table 1. Fractional atomic co-ordinates with the e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Co(1)	0.040 56(10)	0.256 57(6)	−0.062 42(10)	C(11)	0.026 6(22)	0.050 9(19)	0.082 3(18)
Co(2)	0.324 40(10)	0.225 16(6)	0.116 97(11)	O(1)	−0.313 0(7)	0.2361(8)	−0.117 7(10)
Co(3)	0.167 43(10)	0.316 26(6)	0.288 45(10)	O(2)	−0.036 6(10)	0.112 7(5)	−0.445 0(8)
C(1)	−0.175 8(9)	0.246 9(8)	−0.097 6(10)	O(3)	0.133 4(8)	0.472 8(5)	−0.116 4(9)
C(2)	−0.005 0(10)	0.163 7(6)	−0.295 1(9)	O(4)	0.351 7(9)	0.056 1(6)	−0.191 0(10)
C(3)	0.097 6(9)	0.390 0(6)	−0.094 2(9)	O(5)	0.559 0(9)	0.154 8(7)	0.422 3(9)
C(4)	0.340 1(9)	0.122 1(6)	−0.071 8(10)	O(6)	0.539 6(7)	0.434 3(5)	0.152 3(10)
C(5)	0.467 0(10)	0.181 1(7)	0.304 9(11)	O(7)	0.3526(8)	0.279 4(6)	0.649 9(8)
C(6)	0.459 1(8)	0.352 9(6)	0.135 6(10)	O(8)	−0.141 9(8)	0.321 1(7)	0.342 5(10)
C(7)	0.285 7(9)	0.293 2(6)	0.510 4(9)	O(9)	0.310 3(8)	0.556 6(4)	0.368 1(8)
C(8)	−0.021 2(9)	0.320 6(6)	0.321 0(9)	O(10)	−0.003 2(25)	0.044 2(11)	0.212 5(20)
C(9)	0.256 5(9)	0.465 4(5)	0.340 8(9)	S(1)	−0.016 4(5)	−0.051 0(3)	−0.126 9(5)
C(10)	0.111 0(7)	0.171 5(4)	0.104 3(7)				

Table 2. Interatomic distances (Å) and angles (°) (primes indicate atoms related by the centre of symmetry)

Co(1)–Co(2)	2.474(1)	Co(2)–C(4)	1.792(7)	Co(3)–C(10)	1.899(5)	C(7)–O(7)	1.119(9)
Co(1)–Co(3)	2.473(1)	Co(2)–C(5)	1.808(8)	C(1)–O(1)	1.140(9)	C(8)–O(8)	1.143(8)
Co(1)–C(1)	1.795(8)	Co(2)–C(6)	1.835(7)	C(2)–O(2)	1.121(8)	C(9)–O(9)	1.127(8)
Co(1)–C(2)	1.802(7)	Co(2)–C(10)	1.885(5)	C(3)–O(3)	1.138(8)	C(10)–C(11)	1.554(22)
Co(1)–C(3)	1.815(7)	Co(3)–C(7)	1.805(7)	C(4)–O(4)	1.145(9)	C(10′)–S(1)	1.745(7)
Co(1)–C(10)	1.892(5)	Co(3)–C(8)	1.783(7)	C(5)–O(5)	1.130(9)	C(11)–O(10)	1.206(17)
Co(2)–Co(3)	2.480(1)	Co(3)–C(9)	1.828(6)	C(6)–O(6)	1.131(8)	C(11)–S(1)	1.711(14)

Co(2)–Co(1)–Co(3)	60.2(0)	C(7)–Co(3)–C(10)	103.4(3)	C(6)–Co(2)–C(10)	141.9(3)
Co(2)–Co(1)–C(1)	147.9(2)	C(8)–Co(3)–C(9)	102.8(3)	Co(1)–Co(3)–Co(2)	59.9(0)
Co(2)–Co(1)–C(2)	98.7(2)	C(8)–Co(3)–C(10)	102.7(3)	Co(1)–Co(3)–C(7)	151.4(2)
Co(2)–Co(1)–C(3)	101.2(2)	C(9)–Co(3)–C(10)	141.7(2)	Co(1)–Co(3)–C(8)	99.4(2)
Co(2)–Co(1)–C(10)	48.9(2)	Co(1)–C(1)–O(1)	176.8(8)	Co(1)–Co(3)–C(9)	98.7(2)
Co(3)–Co(1)–C(1)	95.9(2)	Co(1)–C(2)–O(2)	174.6(7)	Co(1)–Co(3)–C(10)	49.1(2)
Co(3)–Co(1)–C(2)	154.3(2)	Co(1)–C(3)–O(3)	179.1(6)	Co(2)–Co(3)–C(7)	97.2(2)
Co(3)–Co(1)–C(3)	100.0(2)	Co(2)–C(4)–O(4)	179.2(8)	Co(3)–C(8)–O(8)	178.5(7)
Co(3)–Co(1)–C(10)	49.4(2)	Co(2)–C(5)–O(5)	178.5(8)	Co(3)–C(9)–O(9)	178.2(6)
C(1)–Co(1)–C(2)	97.0(3)	Co(2)–C(6)–O(6)	177.0(6)	Co(1)–C(10)–Co(2)	81.9(2)
C(1)–Co(1)–C(3)	104.0(4)	Co(3)–C(7)–O(7)	176.7(7)	Co(1)–C(10)–Co(3)	81.4(2)
C(1)–Co(1)–C(10)	99.7(3)	Co(1)–Co(2)–C(6)	99.8(2)	Co(1)–C(10)–C(11)	129.3(7)
C(2)–Co(1)–C(3)	98.2(3)	Co(1)–Co(2)–C(10)	49.2(2)	Co(2)–C(10)–Co(3)	81.9(2)
C(2)–Co(1)–C(10)	106.4(3)	Co(3)–Co(2)–C(4)	153.6(2)	Co(2)–C(10)–C(11)	129.7(8)
C(3)–Co(1)–C(10)	143.2(3)	Co(3)–Co(2)–C(5)	97.3(2)	Co(3)–C(10)–C(11)	133.7(5)
Co(1)–Co(2)–Co(3)	59.9(0)	Co(3)–Co(2)–C(6)	98.8(2)	Co(1′)–C(10′)–S(1)	135.6(4)
Co(1)–Co(2)–C(4)	99.3(2)	Co(3)–Co(2)–C(10)	49.3(2)	Co(2′)–C(10′)–S(1)	134.7(4)
Co(1)–Co(2)–C(5)	150.4(2)	C(4)–Co(2)–C(5)	95.4(3)	Co(3′)–C(10′)–S(1)	121.3(3)
Co(2)–Co(3)–C(8)	151.1(2)	C(4)–Co(2)–C(6)	100.8(3)	C(10)–C(11)–O(10)	115.1(1.5)
Co(2)–Co(3)–C(9)	100.4(2)	C(4)–Co(2)–C(10)	105.3(3)	C(10)–C(11)–S(1)	114.9(9)
Co(2)–Co(3)–C(10)	48.8(2)	C(5)–Co(2)–C(6)	102.5(3)	O(10)–C(11)–S(1)	129.9(1.9)
C(7)–Co(3)–C(8)	94.4(3)	C(5)–Co(2)–C(10)	102.1(3)	C(10′)–S(1)–C(11)	102.3(8)
C(7)–Co(3)–C(9)	102.5(3)				

$[C(OC)_9Co_3(CS_2)Co_3(CO)_7S]$.[12] The C(10)–C(11) bond length is close to the $C–C_{ap}$ distance in $[Co_3(CO)_9(CMe)]$ [1.53(3) Å] [13] and to the aliphatic C–C single bond (1.54 Å), but the unreliability of the values does not allow one to draw a definite conclusion about the C–C bond order. Both S–C bond lengths [C(10′)–S(1) 1.745(7), C(11)–S(1) 1.711(14) Å] correspond to a bond order greater than one,[14] indicating a considerable π-electron delocalization over the whole planar C–C(O)–S–C chain, as in an allylic group. The chain is folded more than expected, as the CSC angle is much more acute (102°) than the CSCr angle in $[\{(C_5H_5)Co\}_3(S)CSCr(CO)_5]$ (121°) [15] or the COC angle in $[Co_3(CO)_9\{COC(O)Me\}]$ (122.9°),[9] probably because of crystal-packing effects, on the more flexible part of the chain.

The orientation of the chain with respect to the two Co_3 clusters differs in that the C_{ap}–C bond is nearly perpendicular to the Co_3 triangle, whereas the C_{ap}–S bond is inclined towards Co(3). The complex shows both structural situations typical of Co_3C–R clusters, *i.e.* the C–R bond can be (*i*) perpendicular to the Co_3 plane or (*ii*) folded towards a Co atom or a Co–Co bond. Case (*i*) is, as expected, typical for small R groups (R = H,[7] Cl,[16] or CH_3 [13]), but it also occurs when R is a long or bulky chain [R = $O–Zr(\eta\text{-}C_5H_5)_2OCCo_3(CO)_9$,[17] $O–ZrCl(\eta\text{-}C_5H_5)_2$,[17] $CCo_3(CO)_9$,[4] or $C_2CCo_3(CO)_9$ [6]], indicating that the steric hindrance of R is not the driving force for the deformation. On the other hand, all the compounds showing deformation (*ii*) have bulky R groups especially when they possess symmetry lower than C_{3v}. In some cases, the folding of the C–R bond could be due to an interaction between R and the Co atoms and/or the carbonyl groups and is accompanied by an asymmetric tilting of the equatorial CO groups towards the Co_3 plane (*e.g.* $[\{Co_3(CO)_9C\}_2CO]$ [5] and $[(OC)_9Co_3(CC_2H)Co_2(CO)_6]$ [11]). In other examples, as in our case, the CO tilting is absent and the deformation can presumably be attributed to crystal-packing effects, *cf.* $[(OC)_9Co_3C(CS_2)Co_3(CO)_7S]$,[12] $[\{Co_3(CO)_9C\}_2$-

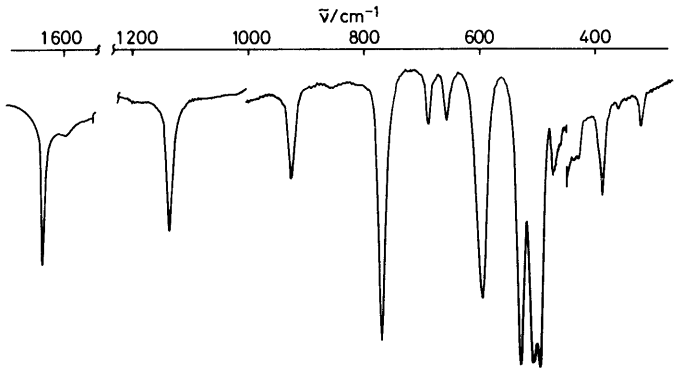

Figure 2. I.r. spectrum of $[\{Co_3(CO)_9C\}_2SCO]$ in the 1 650—300 cm^{-1} region (CsI pellet)

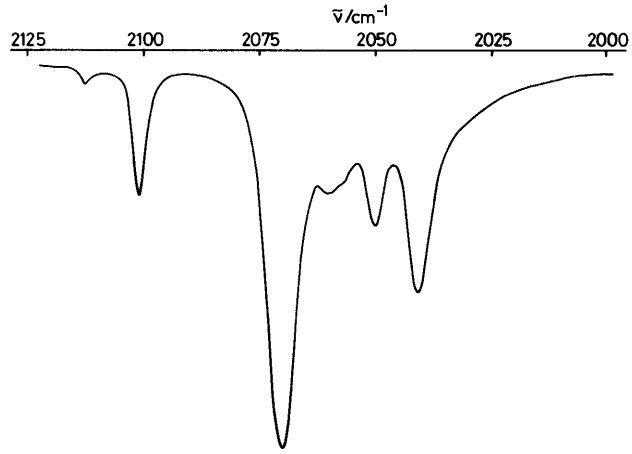

Figure 3. I.r. spectrum of $[\{Co_3(CO)_9C\}_2SCO]$ in the CO stretching region (solvent CCl_4)

$C_2]$,[6] and $[(OC)_9Co_3COHfCl(\eta\text{-}C_5H_5)_2]$.[17] The best support for this suggestion is given by $[(OC)_9Co_3COBCl_2(NEt_3)]$, in which the two crystallographically independent molecules have different foldings of the C–R chain,[18] or by the two $Co_3(CO)_9CO$ groups in $[\{(OC)_9Co_3CO\}_2(\eta\text{-}C_5H_5)TiCo(CO)_4]$.[19]

I.r. Spectra.—The determination of the correct structure clearly eliminates the ambiguities that were apparent between the i.r. spectra and the ' old ' disulphide structure.

In the medium-frequency region (between 1 200 and 700 cm^{-1}) there are three bands (Figure 2), as reported in the earlier study.[1] The centrosymmetric disulphide,[2] however, could have had only one i.r.-allowed vibration in this region, *viz.* the one belonging to an antisymmetric C–S stretching. Now the observed three bands can directly be assigned to $\nu[C_{ap}\text{–}C(O)]$ at 1 137 cm^{-1}, $\nu[C'_{ap}\text{–}S]$ at 924 cm^{-1}, and $\nu[C(O)\text{–}S]$ at 768 cm^{-1}. The assignment of the last two vibrations involving the sulphur atom is only an approximation in terms of internal co-ordinates and it is based on the observed C–S bond distances. Alternatively, they can be considered as bands belonging to the asymmetrically and symmetrically coupled ($\nu_{asym} > \nu_{sym}$) C–S stretching modes.

Also the pattern of the ν(C–O) region now fits well with the correct structure. The previously suggested disulphide formula, with two $CCo_3(CO)_9$ units that are both chemically and structurally equivalent, did not account for the presence of seven i.r.-active C–O stretching fundamentals (Figure 3). The presence of the inversion centre (point group C_i) would have allowed five bands at most in the i.r. spectrum (one probably with near-zero intensity), all the modes symmetric with respect to the inversion centre being i.r.-inactive; moreover, the in- and out-of-phase coupling of the a_2 modes of the two $Co_3(CO)_9$ units (only ' equatorial ' ligands involved) could not have a non-zero dipole component.

Another approach for predicting the pattern of the C–O stretching region of the spectrum of dimeric $\{(OC)_9Co_3C\}_2S_2$ with a centre of symmetry would have been to invoke the observations of Pályi and Váradi [20] who studied the spectra of several $[Co_3(CO)_9(CR)]$ compounds with highly asymmetric R groups. They found a doubling of the two bands assigned to the *e* modes (with C_{3v} point symmetry), the components of the doublets having about the same intensities. This is not the pattern shown by ' Complex IV '.

The correct structure established in the present study clearly indicates the presence of two chemically non-equivalent $CCo_3(CO)_9$ groups, the electronic effects of the S atom in one case and of the chain-carbonyl group in the other being surely different. The observed i.r. spectrum has features that correspond to the vibrations of two different but coupled $CCo_3(CO)_9$ units. In particular the two bands in the 2 115—2 100 cm^{-1} region clearly show that the in-phase coupling of the two locally totally symmetric vibrations of the $Co_3(CO)_9$ units (belonging to the weaker component at 2 112.5 cm^{-1}) gives rise to an i.r.-active vibration, which could not be the case with a centrosymmetric structure. Consequently, the lower (and stronger) component at 2 101 cm^{-1} must be the out-of-phase coupling of the two locally in-phase motions.

The band with the highest intensity in the spectrum, at 2 070 cm^{-1}, probably arises from that combination of the two local *e* modes in which the dipole vectors add in-phase. At present it seems unsafe to assign the analogous out-of-phase vibration to one of the weak bands around 2 050—2 060 cm^{-1}. A detailed assignment for the lower energy C–O stretching frequencies is also not possible.

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