Crystal and Molecular Structure of $[Co_8(CO)_{21}(\mu_5\text{-}CS_2)(\mu_5\text{-}C_2S)]$:† a Thiocarbonyl Group as a Six-electron Donor

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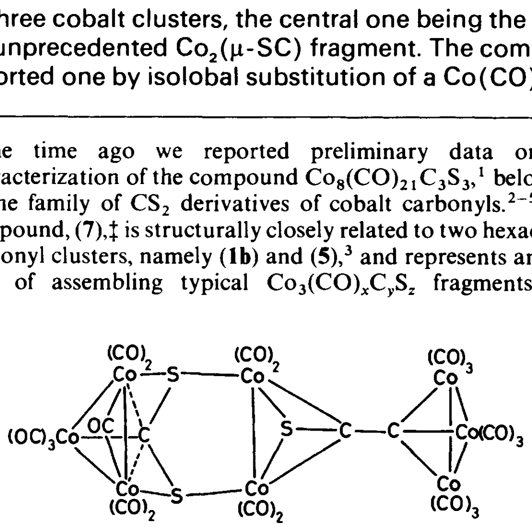
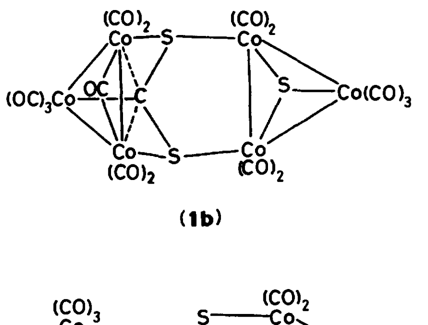
The compound $[Co_8(CO)_{21}(\mu_5\text{-}CS_2)(\mu_5\text{-}C_2S)]$, a minor product of the reaction between $[Co_2(CO)_8]$ and CS_2, has been characterized by *X*-ray diffraction analysis. The crystals are monoclinic, space group *Cc*, with a = 9.208(4), b = 15.864(6), c = 25.36(1), β = 96.39(3)°, and Z = 4. The Co atoms were located by the Patterson method, the S, C, and O atoms by Fourier difference maps. The final R was 0.0899 for 3 206 reflections with $F > 6\sigma(F)$. The structure consists of an assembly of three cobalt clusters, the central one being the most interesting part of the complex, as it shows an unprecedented $Co_2(\mu\text{-}SC)$ fragment. The compound is formally derived from a previously reported one by isolobal substitution of a $Co(CO)_3$ group by a C–R group [R = $CCo_3(CO)_9$].

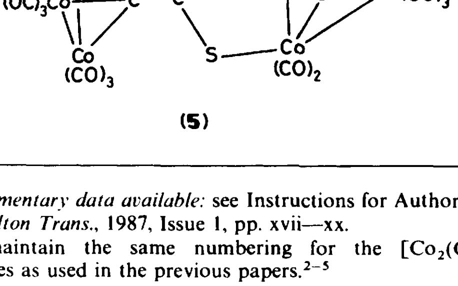
Some time ago we reported preliminary data on the characterization of the compound $Co_8(CO)_{21}C_3S_3$,[1] belonging to the family of CS_2 derivatives of cobalt carbonyls.[2–5] This compound, (**7**),‡ is structurally closely related to two hexacobalt carbonyl clusters, namely (**1b**) and (**5**),[3] and represents another way of assembling typical $Co_3(CO)_xC_yS_z$ fragments, like $[Co_3(CO)_7(CS_2)]$, $[Co_3(CO)_9S]$, and $[Co_3(CO)_9C]$, which are presumably the 'building blocks' formed in the reaction between $[Co_2(CO)_8]$ and CS_2.



(**7**)



(**1b**)



(**5**)

The structural similarity between the complexes (**1b**) and (**7**) is evidenced when the latter is ideally derived from the former by isolobal substitution[6] of the $Co(CO)_3$ fragment by the C–R fragment [R = $CCo_3(CO)_9$], so giving an unprecedented type of co-ordination of the SCR group to a binuclear Co_2 unit. An analogous framework has been found in the iron compounds $[Fe_5(CO)_{13}(\mu_4\text{-}CS)(\mu_3\text{-}S)_2]$[7] and $[Fe_2(CO)_6\{\mu\text{-}SC(C_{10}H_{18})\}]$.[8] A detailed structural analysis of compound (**7**) and its comparison with similar complexes is the subject of the present paper.

Experimental

Preparation of the Complex.—The reaction between $[Co_2(CO)_8]$ and CS_2 gives rise to a great variety of different cobalt carbonyl clusters, as previously described.[2–5] The following procedure is the best way to obtain complex (**7**), the yield of which is very poor (less than 1% with respect to all carbonyl products).

Dicobalt octacarbonyl and carbon disulphide (molar ratio 1:2.5) were allowed to react in light petroleum (b.p. 40—70 °C) at room temperature under a slow stream of nitrogen. The reaction mixture was filtered and subjected to dry column chromatography (nylon-foil tubing filled with Woelm DCC Silica). Repeated washings with light petroleum removed all other products, leaving complex (**7**) at the top of the column. This zone was cut off and the complex extracted by a small quantity of chloroform. The solution was diluted by an equal volume of light petroleum and allowed to crystallize at −20 °C. I.r. spectrum: (n-heptane solution) 2 107w, 2 092m, *ca.* 2 067m, (sh), 2 065s, 2 060s, 2 050s, br, 2 041s, 2 029m, 2 021m, 2 008w, 2 002w, 1 996m, 1 816m; (KBr disc) 1 385w, 870m, 760m, 730m, 567m, 552m, 535m, 510s, 497s, *ca.* 480m (sh), *ca.* 435m (sh), 425m, 385w, and 365w cm^{-1}.

Collection and Reduction of X*-Ray Data.*—Owing to the very poor quality of the crystals, the intensity measurements were performed using two individual crystals (approximate dimensions 0.20 × 0.20 × 0.02 and 0.20 × 0.25 × 0.02 mm respectively). The crystal data and the main experimental

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ We maintain the same numbering for the $[Co_2(CO)_8]$–CS_2 complexes as used in the previous papers.[2–5]

Table 1. Experimental and crystal data for $[Co_8(CO)_{21}(\mu_5\text{-}CS_2)(\mu_5\text{-}C_2S)]$

Space group	Cc (C_s^4, no. 9)
a/Å	9.208(4)
b/Å	15.864(6)
c/Å	25.36(1)
β/°	96.39(3)
U/Å^3	3 681.5
M	1 191.8
Z	4
D_c/g cm^{-3}	2.15
μ(Mo-K_α)/cm^{-1}	36.2
F(000)	2 304
Diffractometer	Nicolet $R3$ (crystal sealed in Lindemann glass capillary)
Radiation	Mo-K_α (graphite monochromated, λ = 0.7107 Å)
Scan technique	ω
Scan width/°	1.0
Scan speed/° min^{-1}	2—12
Scan range (2θ)/°	2—50
Ratio of total background time to scan time	0.5
Check reflections	1 every 50
Collected reflections	4 861
Reflections with $F > 6\sigma(F)$	3 206
R	0.0899
R'	0.0926

Table 2. Fractional atomic co-ordinates

Atom	X/a	Y/b	Z/c
Co(1)	0.000 00	0.056 1(2)	1.000 00
Co(2)	0.046 9(5)	0.208 6(2)	0.987 5(2)
Co(3)	0.187 4(5)	0.101 3(2)	0.943 7(2)
Co(4)	0.442 2(5)	0.188 0(2)	1.094 2(2)
Co(5)	0.397 0(5)	0.037 3(2)	1.105 4(2)
Co(6)	0.600 6(5)	0.205 8(2)	1.249 2(2)
Co(7)	0.552 8(5)	0.056 5(2)	1.261 0(2)
Co(8)	0.809 6(5)	0.104 7(2)	1.253 6(2)
S(1)	0.257 9(8)	0.136 9(4)	1.131 5(3)
S(2)	0.634 1(8)	0.200 8(4)	1.158 7(3)
S(3)	0.576 9(8)	0.011 1(4)	1.174 6(3)
C(1)	0.181 2(24)	0.121 8(13)	1.019 6(10)
C(2)	0.274 7(28)	0.119 1(15)	1.064 6(11)
C(3)	0.653 5(23)	0.109 0(13)	1.196 9(9)
C(11)	−0.070 1(34)	0.063 1(20)	1.066 3(14)
O(11)	−0.118 9(28)	0.068 6(15)	1.102 4(11)
C(12)	0.065 1(34)	−0.050 4(20)	1.005 2(13)
O(12)	0.093 0(28)	−0.119 9(17)	1.005 3(11)
C(13)	−0.162 8(36)	0.044 8(19)	0.952 5(14)
O(13)	−0.270 7(28)	0.038 0(16)	0.929 1(11)
C(21)	−0.016 8(35)	0.248 8(21)	1.045 8(14)
O(21)	−0.053 9(36)	0.276 8(20)	1.085 4(15)
C(22)	0.174 5(32)	0.293 3(19)	0.978 0(13)
O(22)	0.247 0(23)	0.342 9(14)	0.971 1(9)
C(23)	−0.104 7(33)	0.233 3(19)	0.937 3(14)
O(23)	−0.200 0(26)	0.244 9(15)	0.905 2(10)
C(31)	0.329 7(35)	0.163 8(20)	0.926 9(14)
O(31)	0.423 8(29)	0.211 1(16)	0.912 7(11)
C(32)	0.280 3(44)	0.000 1(27)	0.937 9(17)
O(32)	0.348 7(33)	−0.057 7(19)	0.934 2(13)
C(33)	0.068 5(30)	0.104 6(17)	0.882 9(12)
O(33)	−0.010 2(32)	0.100 0(17)	0.844 1(12)
C(41)	0.395 1(29)	0.296 2(17)	1.092 9(11)
O(41)	0.357 5(26)	0.364 6(14)	1.091 2(10)
C(42)	0.561 0(32)	0.187 0(18)	1.046 5(13)
O(42)	0.626 5(30)	0.185 3(17)	1.010 7(11)
C(51)	0.290 6(26)	−0.054 5(15)	1.116 9(10)
O(51)	0.216 1(28)	−0.105 3(16)	1.130 8(11)
C(52)	0.510 6(38)	0.000 6(22)	1.060 9(15)
O(52)	0.581 7(28)	−0.027 3(16)	1.025 3(12)
C(61)	0.414 8(36)	0.252 2(21)	1.243 1(14)
O(61)	0.309 3(29)	0.280 9(16)	1.244 7(11)
C(62)	0.710 1(33)	0.292 3(20)	1.272 7(14)
O(62)	0.784 5(26)	0.347 9(17)	1.289 5(11)
C(63)	0.570 9(30)	0.140 7(17)	1.314 0(13)
O(63)	0.575 0(28)	0.152 4(17)	1.358 9(12)
C(71)	0.361 8(32)	0.049 9(18)	1.261 1(12)
O(71)	0.237 3(36)	0.057 6(20)	1.269 0(15)
C(72)	0.600 6(38)	−0.038 7(23)	1.298 7(16)
O(72)	0.641 8(31)	−0.096 2(18)	1.320 5(13)
C(81)	0.886 2(27)	0.006 2(16)	1.233 4(11)
O(81)	0.951 0(26)	−0.050 6(16)	1.219 6(11)
C(82)	0.925 3(40)	0.179 3(22)	1.226 5(16)
O(82)	0.002 9(28)	0.230 9(16)	1.211 8(11)
C(83)	0.888 1(38)	0.106 6(21)	1.323 8(16)
O(83)	0.938 6(29)	0.104 2(17)	1.365 6(12)

parameters are listed in Table 1. The cell parameters were obtained from the refinement of the θ angles of 24 accurately centred reflections. A reference reflection showed no significant decrease during the measurements on both crystals.

An absorption correction was applied according to the method of ref. 9 (relative transmission-factor ranges: 1.0—0.7 and 1.0—0.6 respectively); a secondary extinction correction was not made.

Resolution of the Structure.—Heavy atoms were located using the Patterson method and the S, C, and O atoms were subsequently found using Fourier difference maps. In the last cycles of refinement, the data corresponding to the two crystals were merged and the two scale factors were refined. The weighting scheme was $w = 1/[\sigma(F)^2 + aF^2]$ where the coefficient $a = 0.002$ corresponds to a satisfactory constancy of $\Sigma w\Delta^2$ over various ranges of $|F_o|$. Owing to the poor quality of the crystals and consequently to the low quality of the measurements, only the Co and S atoms were anisotropically refined. For the refinement the programs of SHELX 76[10] were used and the best planes were calculated by the method of ref. 11.

Tables 2—5 list the final fractional co-ordinates, the mean thermal displacements for Co and S, and the bond distances and angles respectively.

Results

The structure of the molecule (Figure 1) is formed by three fragments: a distorted square pyramid, $Co_3(C)S_2$, and two 'tetrahedral' clusters, Co_2SC and Co_3C respectively. The inner Co_2SC fragment is linked to the $Co_3(C)S_2$ cluster along one edge and to the Co_3C unit *via* one vertex, in a staggered arrangement, as shown in Figure 2(*a*) and (*b*). All the carbonyl groups are terminal, except one which bridges the Co–Co edge of the square face of the pyramid. The whole structure has an idealized non-crystallographic mirror plane passing through the atoms marked with an asterisk [Figure 2(*a*)]: the equation of the plane is: $1.70X + 15.47Y - 3.58Z + 1.49 = 0$ for fractional co-ordinates with $\chi^2 = 0.97$.*

There is a striking similarity between complexes (7) and (**1b**). The $(CO)_8Co_3CS_2$ fragment, characterized by the presence of a μ_5-CS_2 ligand, does not show significant differences, which are present mainly in the central Co_2SC fragment and are

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* The distances (Å) of atoms from the mean plane are: Co(3) 0.003(7), Co(8) 0.000(7), S(1) −0.004(12), C(1) 0.032(39), C(2) −0.011(45), and C(3) 0.004(37); X, Y, and Z correspond to the fractional co-ordinates X/a, Y/b, and Z/c respectively.

Table 3. Root-mean-square displacements (Å) of atoms along the principal axis of their vibration ellipsoids

Atom	$(\bar{U}^2)_{\mathrm{min.}}^{\frac{1}{2}}$	$(\bar{U}^2)_{\mathrm{mid.}}^{\frac{1}{2}}$	$(\bar{U}^2)_{\mathrm{max.}}^{\frac{1}{2}}$
Co(1)	0.140	0.185	0.190
Co(2)	0.147	0.175	0.211
Co(3)	0.160	0.171	0.204
Co(4)	0.131	0.170	0.189
Co(5)	0.141	0.156	0.203
Co(6)	0.166	0.190	0.218
Co(7)	0.189	0.198	0.217
Co(8)	0.152	0.187	0.204
S(1)	0.124	0.179	0.205
S(2)	0.137	0.183	0.232
S(3)	0.145	0.202	0.226

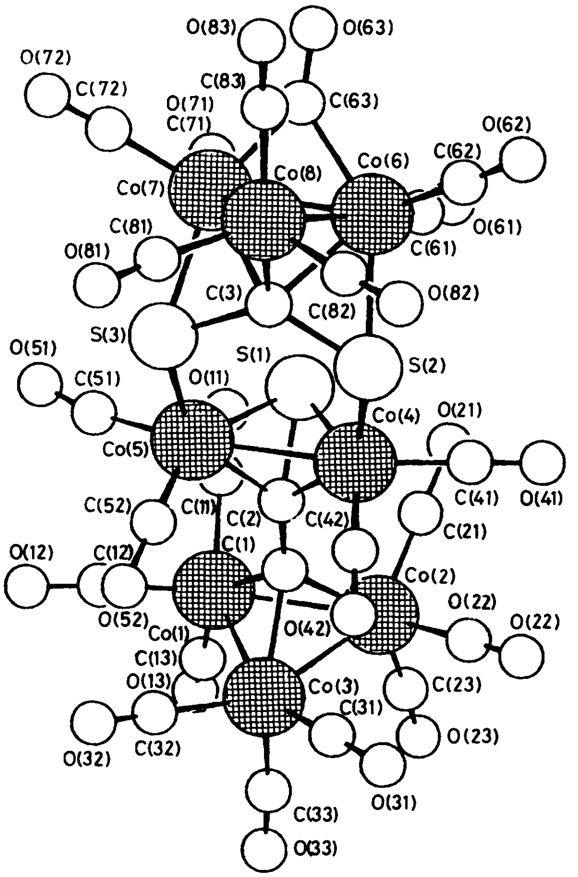

Figure 1. View of one molecule of $[Co_8(CO)_{21}(\mu_5\text{-}CS_2)(\mu_5\text{-}C_2S)]$ with the atom labelling scheme

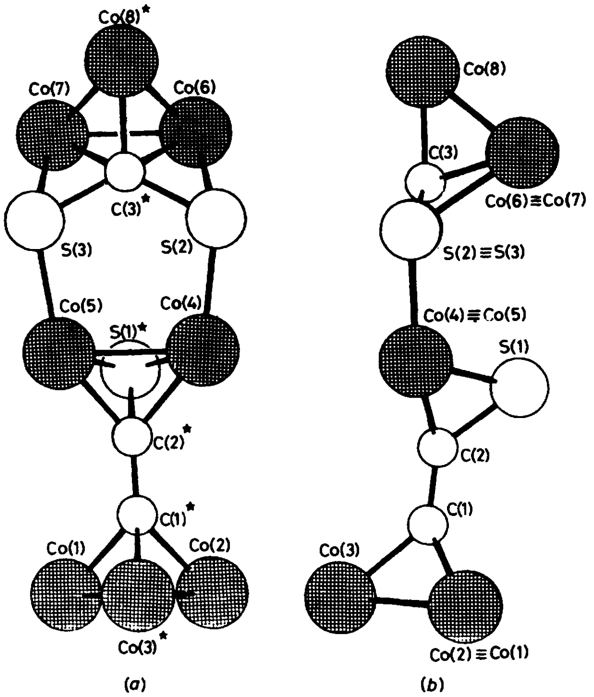

Figure 2. (*a*) View of the skeleton of the molecule showing the mirror plane. (*b*) Projection of the skeleton perpendicular to the mirror plane

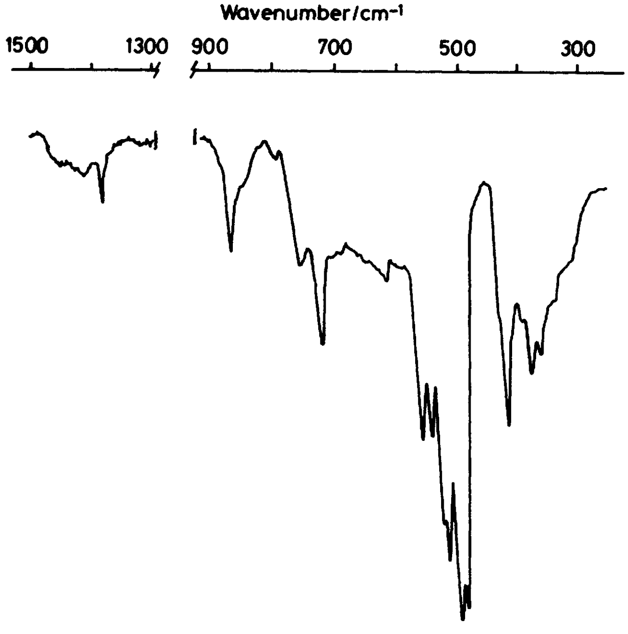

Figure 3. I.r. spectrum of complex (7) in the mid-frequency region (KBr disc)

essentially ascribed to the isolobal substitution of $Co(CO)_3$ by $C\text{–}CCo_3(CO)_9$ and to the steric hindrance of the long chain. The significant differences between the cluster geometries of (7) and (**1b**) are: (*i*) longer Co(4,5)–S distances in (7) (within 4σ); (*ii*) shorter Co(4)–Co(5) distances (within 10σ); (*iii*) an opening of the nest formed by the Co(6)Co(7)S(2)S(3)Co(4)Co(5)S(1) atoms [S(2,3)Co(4,5)S(1) 107.2° in (7) *vs.* 102.3° in (**1b**), and Co(4,5) ⋯ Co(6,7) 4.051 *vs.* 3.965 Å].

A decrease in the Co–Co distance as a consequence of the $Co(CO)_3$ *vs.* $CCCo_3(CO)_9$ isolobal substitution is also evidenced, *e.g.*, in the pair of complexes, $[Co_3(CO)_9(\mu_3\text{-}CH)]$[12] and $[Co_5(CO)_{15}(\mu_5\text{-}C_3H)]$[13] which are structurally related to the compounds (**1b**) and (7), the difference being an apical μ_3-CH group instead of μ_3-S. Sulphur Co_3S clusters show a sensitivity to substitution greater than Co_3C clusters: the Co–Co distances involved in substitution are 2.499(1) and 2.448(5) Å respectively for (**1b**) and (7) S clusters *vs.* 2.479(7) and 2.447(4) Å for $[Co_3(CO)_9(\mu_3\text{-}CH)]$[12] and $[Co_5(CO)_{15}(\mu_5\text{-}C_3H)]$[13] CH clusters.

Other complexes where a quite similar arrangement takes place are $[Co_8(CO)_{24}C_6]\cdot 0.5C_6H_6$[14] and $[Co_8(CO)_{24}C_6]$,[15] in which the acetylene is substituted by $CCo_3(CO)_9$; also in this

Table 4. Interatomic distances (Å)

Co(1)–Co(2)	2.483(5)	Co(4)–S(2)	2.279(7)	Co(7)–S(3)	2.340(9)	C(22)–O(22)	1.058(33)
Co(1)–Co(3)	2.466(5)	Co(4)–C(2)	1.969(25)	Co(7)–C(3)	2.129(23)	C(23)–O(23)	1.143(36)
Co(1)–C(1)	1.983(22)	Co(4)–C(41)	1.770(27)	Co(7)–C(63)	1.891(31)	C(31)–O(31)	1.229(39)
Co(1)–C(11)	1.871(35)	Co(4)–C(42)	1.720(31)	Co(7)–C(71)	1.762(29)	C(32)–O(32)	1.123(44)
Co(1)–C(12)	1.792(32)	Co(5) · · · Co(7)	4.076(6)	Co(7)–C(72)	1.816(38)	C(33)–O(33)	1.158(37)
Co(1)–C(13)	1.824(34)	Co(5)–S(1)	2.184(7)	Co(8)–C(3)	1.918(22)	C(41)–O(41)	1.138(31)
Co(2)–Co(3)	2.475(5)	Co(5)–S(3)	2.314(8)	Co(8)–C(81)	1.811(26)	C(42)–O(42)	1.145(38)
Co(2)–C(1)	1.965(22)	Co(5)–C(2)	1.938(26)	Co(8)–C(82)	1.781(37)	C(51)–O(51)	1.251(42)
Co(2)–C(21)	1.770(36)	Co(5)–C(51)	1.797(24)	Co(8)–C(83)	1.846(40)	C(52)–O(52)	1.140(32)
Co(2)–C(22)	1.819(31)	Co(5)–C(52)	1.724(37)	S(1)–C(2)	1.743(29)	C(61)–O(61)	1.078(36)
Co(2)–C(23)	1.823(32)	Co(6)–Co(7)	2.434(5)	S(2)–C(3)	1.745(23)	C(62)–O(62)	1.168(36)
Co(3)–C(1)	1.960(24)	Co(6)–Co(8)	2.498(5)	S(3)–C(3)	1.773(22)	C(63)–O(63)	1.150(36)
Co(3)–C(31)	1.735(32)	Co(6)–S(2)	2.348(9)	C(1)–C(2)	1.352(32)	C(71)–O(71)	1.192(39)
Co(3)–C(32)	1.831(44)	Co(6)–C(3)	2.119(22)	C(11)–O(11)	1.068(38)	C(72)–O(72)	1.110(40)
Co(3)–C(33)	1.789(29)	Co(6)–C(61)	1.853(34)	C(12)–O(12)	1.133(36)	C(81)–O(81)	1.156(32)
Co(4)–Co(5)	2.448(5)	Co(6)–C(62)	1.767(31)	C(13)–O(13)	1.105(36)	C(82)–O(82)	1.174(40)
Co(4) · · · Co(6)	4.063(6)	Co(6)–C(63)	1.986(31)	C(21)–O(21)	1.182(44)	C(83)–O(83)	1.108(42)
Co(4)–S(1)	2.188(7)	Co(7)–Co(8)	2.511(5)				

Table 5. Bond angles (°)

Co(2)–Co(1)–Co(3)	60.0(1)	Co(5)–Co(4)–C(2)	50.6(7)	C(61)–Co(6)–C(63)	93.7(1.4)	Co(1)–C(1)–Co(2)	77.9(8)
Co(2)–Co(1)–C(1)	50.7(6)	Co(5)–Co(4)–C(41)	154.8(9)	C(62)–Co(6)–C(63)	104.5(1.4)	Co(1)–C(1)–Co(3)	77.4(8)
Co(2)–Co(1)–C(11)	98.0(1.0)	Co(5)–Co(4)–C(42)	101.7(1.0)	Co(6)–Co(7)–Co(8)	60.7(1)	Co(1)–C(1)–C(2)	129.4(1.7)
Co(2)–Co(1)–C(12)	149.9(1.0)	S(1)–Co(4)–S(2)	107.4(3)	Co(6)–Co(7)–S(3)	98.5(2)	Co(2)–C(1)–Co(3)	78.1(9)
Co(2)–Co(1)–C(13)	98.8(1.0)	S(1)–Co(4)–C(2)	49.2(8)	Co(6)–Co(7)–C(3)	54.9(6)	Co(2)–C(1)–C(2)	133.2(1.6)
Co(3)–Co(1)–C(1)	50.9(7)	S(1)–Co(4)–C(41)	99.6(9)	Co(6)–Co(7)–C(63)	52.9(9)	Co(3)–C(1)–C(2)	137.6(1.7)
Co(3)–Co(1)–C(11)	146.8(1.0)	S(1)–Co(4)–C(42)	152.3(1.0)	Co(6)–Co(7)–C(71)	104.6(1.0)	Co(4)–C(2)–Co(5)	77.6(1.0)
Co(3)–Co(1)–C(12)	93.8(1.0)	S(2)–Co(4)–C(2)	146.6(8)	Co(6)–Co(7)–C(72)	146.9(1.2)	Co(4)–C(2)–S(1)	71.9(1.0)
Co(3)–Co(1)–C(13)	102.9(1.1)	S(2)–Co(4)–C(41)	95.6(9)	Co(8)–Co(7)–S(3)	80.6(2)	Co(4)–C(2)–C(1)	134.6(1.8)
C(1)–Co(1)–C(11)	96.2(1.2)	S(2)–Co(4)–C(42)	90.2(1.0)	Co(8)–Co(7)–C(3)	48.0(6)	Co(5)–C(2)–S(1)	72.5(1.1)
C(1)–Co(1)–C(12)	102.3(1.2)	C(2)–Co(4)–C(41)	110.5(1.1)	Co(8)–Co(7)–C(63)	80.1(8)	Co(5)–C(2)–C(1)	138.5(1.8)
C(1)–Co(1)–C(13)	145.5(1.2)	C(2)–Co(4)–C(42)	105.0(1.3)	Co(8)–Co(7)–C(71)	165.0(1.0)	S(1)–C(2)–C(1)	134.3(1.9)
C(11)–Co(1)–C(12)	97.8(1.4)	C(41)–Co(4)–C(42)	99.7(1.3)	Co(8)–Co(7)–C(72)	96.8(1.1)	Co(6)–C(3)–Co(7)	69.9(7)
C(11)–Co(1)–C(13)	105.0(1.5)	Co(4)–Co(5)–S(1)	56.0(2)	S(3)–Co(7)–C(3)	46.5(6)	Co(6)–C(3)–Co(8)	76.3(8)
C(12)–Co(1)–C(13)	101.6(1.4)	Co(4)–Co(5)–S(3)	98.4(2)	S(3)–Co(7)–C(63)	150.9(9)	Co(6)–C(3)–S(2)	74.1(8)
Co(1)–Co(2)–Co(3)	59.6(1)	Co(4)–Co(5)–C(2)	51.8(7)	S(3)–Co(7)–C(71)	100.5(1.0)	Co(6)–C(3)–S(3)	136.3(1.2)
Co(1)–Co(2)–C(1)	51.4(6)	Co(4)–Co(5)–C(51)	155.9(8)	S(3)–Co(7)–C(72)	101.3(1.2)	Co(7)–C(3)–Co(8)	76.5(8)
Co(1)–Co(2)–C(21)	99.5(1.1)	Co(4)–Co(5)–C(52)	97.5(1.2)	C(3)–Co(7)–C(63)	104.7(1.0)	Co(7)–C(3)–S(2)	136.3(1.2)
Co(1)–Co(2)–C(22)	149.3(9)	S(1)–Co(5)–S(3)	107.1(3)	C(3)–Co(7)–C(71)	123.0(1.2)	Co(7)–C(3)–S(3)	73.0(8)
Co(1)–Co(2)–C(23)	99.7(9)	S(1)–Co(5)–C(2)	49.6(8)	C(3)–Co(7)–C(72)	128.9(1.3)	Co(8)–C(3)–S(2)	117.9(1.2)
Co(3)–Co(2)–C(1)	50.8(7)	S(1)–Co(5)–C(51)	100.8(8)	C(63)–Co(7)–C(71)	92.8(1.3)	Co(8)–C(3)–S(3)	116.5(1.2)
Co(3)–Co(2)–C(21)	149.5(1.1)	S(1)–Co(5)–C(52)	149.6(1.2)	C(63)–Co(7)–C(72)	102.5(1.5)	S(2)–C(3)–S(3)	122.8(1.3)
Co(3)–Co(2)–C(22)	94.1(1.0)	S(3)–Co(5)–C(2)	148.1(8)	C(71)–Co(7)–C(72)	97.6(1.5)	Co(1)–C(11)–O(11)	175(3)
Co(3)–Co(2)–C(23)	103.5(1.0)	S(3)–Co(5)–C(51)	95.0(8)	Co(6)–Co(8)–Co(7)	58.1(1)	Co(1)–C(12)–O(12)	173(3)
C(1)–Co(2)–C(21)	99.1(1.3)	S(3)–Co(5)–C(52)	90.0(1.2)	Co(6)–Co(8)–C(3)	55.5(7)	Co(1)–C(13)–O(13)	171(3)
C(1)–Co(2)–C(22)	100.7(1.1)	C(2)–Co(5)–C(51)	109.6(1.1)	Co(6)–Co(8)–C(81)	149.7(8)	Co(2)–C(21)–O(21)	177(3)
C(1)–Co(2)–C(23)	146.9(1.2)	C(2)–Co(5)–C(52)	103.7(1.4)	Co(6)–Co(8)–C(82)	92.7(1.1)	Co(2)–C(22)–O(22)	178(3)
C(21)–Co(2)–C(22)	97.1(1.4)	C(51)–Co(5)–C(52)	102.4(1.4)	Co(6)–Co(8)–C(83)	104.5(1.1)	Co(2)–C(23)–O(23)	177(3)
C(21)–Co(2)–C(23)	101.9(1.4)	Co(7)–Co(6)–Co(8)	61.2(1)	Co(7)–Co(8)–C(3)	55.5(7)	Co(3)–C(31)–O(31)	176(3)
C(22)–Co(2)–C(23)	101.8(1.4)	Co(7)–Co(6)–S(2)	97.6(2)	Co(7)–Co(8)–C(81)	99.1(8)	Co(3)–C(32)–O(32)	174(4)
Co(1)–Co(3)–Co(2)	60.4(1)	Co(7)–Co(6)–C(3)	55.2(6)	Co(7)–Co(8)–C(82)	147.1(1.2)	Co(3)–C(33)–O(33)	175(3)
Co(1)–Co(3)–C(1)	51.7(6)	Co(7)–Co(6)–C(61)	102.6(1.1)	Co(7)–Co(8)–C(83)	101.8(1.1)	Co(4)–C(41)–O(41)	176(3)
Co(1)–Co(3)–C(31)	154.8(1.1)	Co(7)–Co(6)–C(62)	144.9(1.1)	C(3)–Co(8)–C(81)	95.9(1.1)	Co(4)–C(42)–O(42)	172(3)
Co(1)–Co(3)–C(32)	98.9(1.3)	Co(7)–Co(6)–C(63)	49.4(9)	C(3)–Co(8)–C(82)	96.7(1.4)	Co(5)–C(51)–O(51)	169(3)
Co(1)–Co(3)–C(33)	96.2(9)	Co(8)–Co(6)–S(2)	80.7(2)	C(3)–Co(8)–C(83)	154.6(1.2)	Co(5)–C(52)–O(52)	174(3)
Co(2)–Co(3)–C(1)	51.0(6)	Co(8)–Co(6)–C(3)	48.2(6)	C(81)–Co(8)–C(82)	101.3(1.4)	Co(6)–C(61)–O(61)	173(4)
Co(2)–Co(3)–C(31)	99.4(1.1)	Co(8)–Co(6)–C(61)	163.4(1.0)	C(81)–Co(8)–C(83)	99.4(1.4)	Co(6)–C(62)–O(62)	178(3)
Co(2)–Co(3)–C(32)	155.6(1.4)	Co(8)–Co(6)–C(62)	94.3(1.0)	C(82)–Co(8)–C(83)	100.0(1.6)	Co(6)–C(63)–Co(7)	78(1)
Co(2)–Co(3)–C(33)	93.8(9)	Co(8)–Co(6)–C(63)	78.8(8)	Co(4)–S(1)–Co(5)	68.1(2)	Co(6)–C(63)–O(63)	138(3)
C(1)–Co(3)–C(31)	104.5(1.3)	S(2)–Co(6)–C(3)	45.6(6)	Co(4)–S(1)–C(2)	58.8(9)	Co(7)–C(63)–O(63)	144(2)
C(1)–Co(3)–C(32)	106.8(1.5)	S(2)–Co(6)–C(61)	98.8(1.1)	Co(5)–S(1)–C(2)	57.9(8)	Co(7)–C(71)–O(71)	167(3)
C(1)–Co(3)–C(33)	139.5(1.1)	S(2)–Co(6)–C(62)	102.9(1.1)	Co(4)–S(2)–Co(6)	121.9(3)	Co(7)–C(72)–O(72)	174(3)
C(31)–Co(3)–C(32)	96.2(1.6)	S(2)–Co(6)–C(63)	146.7(9)	Co(4)–S(2)–C(3)	110.3(8)	Co(8)–C(81)–O(81)	171(2)
C(31)–Co(3)–C(33)	100.4(1.4)	C(3)–Co(6)–C(61)	120.7(1.2)	Co(6)–S(2)–C(3)	60.2(8)	Co(8)–C(82)–O(82)	176(4)
C(32)–Co(3)–C(33)	101.7(1.6)	C(3)–Co(6)–C(62)	127.7(1.2)	Co(5)–S(3)–Co(7)	121.4(3)	Co(8)–C(83)–O(83)	177(3)
Co(5)–Co(4)–S(1)	55.9(2)	C(3)–Co(6)–C(63)	101.8(1.0)	Co(5)–S(3)–C(3)	108.0(8)		
Co(5)–Co(4)–S(2)	97.6(2)	C(61)–Co(6)–C(62)	101.9(1.4)	Co(7)–S(3)–C(3)	60.5(8)		

case the Co–Co distances are quite close [2.461(8) and 2.469(6) Å] to those found in the above complexes.

The μ-SC group may be related to a μ-C_2 acetylenic group, in that the C(2)–S(1) distance [1.74(3) Å] lies between a single and a double bond* and correspondingly the S(1)–C(2)–C(1) angle [134.3(2)°] largely diverges from linearity. This group formally donates five electrons to the Co_2 unit. The additional electron, compared to bridging acetylenic ligands which are four-electron donors, is needed to balance the fact that the 'chelating' $(CO)_8Co_3(C)S_2$ unit, which takes the place of two CO ligands, is a three-electron donor.

The C(1)–C(2) bond links two tetrahedral clusters and its value [1.35(3) Å] indicates a considerable partial double-bond character through delocalization, in accord with the analogous complexes $[\{Co_3(CO)_9C\}_2]$[16] [1.37(1) Å], $[Co_3(CO)_{24}C_6]\cdot 0.5C_6H_6$[14] [1.37(4) Å], and $[Co_5(CO)_{15}(\mu_5\text{-}C_3H)]$[13] [1.46(2) Å].

The molecules of complex (7) are elongated in a direction prevalently parallel to the longest *c* axis of the cell. The contacts among the molecules are essentially realized through the oxygen atoms.

I.r. Spectra.—The spectrum of the CO stretching region is not meaningful as it consists of a complex envelope of bands, corresponding to the 21 expected active modes. Any attempt at assignment appears valueless, except for the band at 1 816 cm^{-1} due the bridging CO.

The region 1 400—700 cm^{-1} contains absorptions corresponding to the vibration modes of the non-CO ligands (Figure 3), which may be assigned by comparison with the spectra of compounds (**1b**) and (**5**).[3] The two bands at 870 and 730 cm^{-1} are probably the in-plane and out-of-plane vibrations of the carbon atom of the cluster-bonded CS_2 unit; complex (**1b**), with an identical fragment, shows the same absorptions at 830 and 729 cm^{-1}. We assign the band at 1 385 cm^{-1} to the C_{ap}–C stretching vibration. The same mode was found at 1 167 cm^{-1} for (**5**), but the different values of the C–C distance [1.35 Å for (**7**), 1.478 Å for (**5**)] could account for the difference in the frequencies {*cf.* also $[Co_6(CO)_{14}(C_2)S]$:[5] 1 444 cm^{-1}, C–C 1.37 Å}. The absorption at 760 cm^{-1} has no counterpart in the spectra of (**1b**) and (**5**) and could be tentatively assigned mainly to ν(C–S) of the $Co_2(SC)$ fragment.

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* The C–S bond distances of the related complexes in refs. 7 and 8 are 1.71(2) and 1.73(1) Å respectively.