

Synthesis and structure of a dinuclear cobalt carbonyl derivative containing methylthioformate as a five-electron donor ligand

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Received 16 September 1996

Abstract

Dicobalt octacarbonyl reacts with an excess of $(\text{MeSCS}_2)_2$ to form several sulfur-containing cobalt carbonyl derivatives; on addition of PPh_3 , the complex $\text{Co}_2(\text{CO})_2(\text{PPh}_3)_2(1,3\text{-}\eta\text{-S}_2\text{CSMe})(\mu\text{-}1,2\text{-}\eta\text{-SCSMe})$ (**1**) could be isolated from the reaction mixture. The structure of complex **1** was determined by X-ray crystallography; it contains a methyl dithioformate ligand in which the ligand donates five electrons to the cluster and the CS group is bound perpendicular to the Co_2 core.

Keywords: Cobalt carbonyl; Dithioformate; Thioxanthate

1. Introduction

Several metal carbonyl complexes containing dithioesters as ligands have been described already. In these complexes the dithioester may be bonded either to one [1–14], two [12,15–21], or five [22] metal atoms. The number of electrons donated by the ligand to the metal(s) in order to achieve the 18-electron configuration in these complexes is one [2,3,5,12,14], three [1,4–11,13,14,16,19], four [20], or six [12,15,17,18,21,22]. We report now the synthesis and structure of an alkyl dithioformate-substituted dinuclear cobalt carbonyl derivative in which the dithioester ligand is a five-electron donor.

2. Results and discussion

Dicobalt octacarbonyl reacts at room temperature in dichloromethane solution with bis(methylthio(thiocarbonyl))disulfide, $(\text{MeSCS}_2)_2$, to give a complex mixture of different cobalt carbonyl derivatives. Evaporat-

ing the reaction mixtures to dryness and dissolving the residues in hexane, the solutions showed IR spectra which suggested that the main products may belong to the well-known class of $\text{Co}_2(\text{CO})_7(\mu\text{-}3\text{-S})(\mu\text{-L})$ complexes [23,24]. This result would not be surprising, since almost all complexes of this type described till now were formed by reacting $\text{Co}_2(\text{CO})_8$ and different organic sulfur compounds. In order to characterize these complexes by transforming them into well-crystallizing products, efforts were undertaken to prepare PPh_3 -substituted derivatives.

However, when product mixtures obtained by using an excess of the organic sulfur compound $[(\text{MeSCS}_2)_2:\text{Co}_2(\text{CO})_8]$ 0.56–1.25:1; equal to S:Co 3.75–1.67:1] were treated with excess PPh_3 , a complex with an unusually high S:Co ratio (5:2) and a very simple IR spectrum in the ν_{CO} region (1973vs, 1932m cm^{-1} in Nujol) was obtained. The structure of this unexpected complex was determined by X-ray crystallography, and found to be that shown in Fig. 1. Table 1 lists some relevant bond lengths and angles.

As can be seen from Fig. 1, $\text{Co}_2(\text{CO})_2(\text{PPh}_3)_2(1,3\text{-}\eta\text{-S}_2\text{CSMe})(\mu\text{-}1,2\text{-}\eta\text{-SCSMe})$ (**1**) is a dinuclear complex in which the $\text{Co}_2\text{P}_2\text{C}_2\text{S}_2$ core has essentially C_2 symmetry and contains two different sulfur-containing organic ligands. One of these is methyl trithiocarbonate

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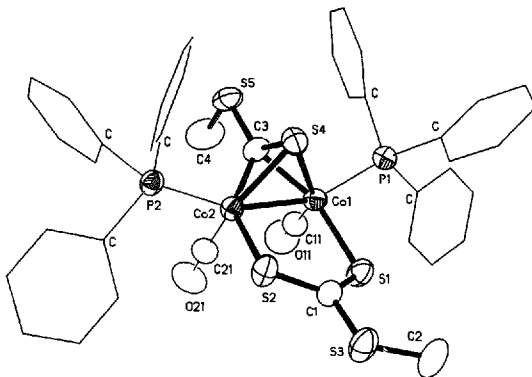


Fig. 1. ORTEP plot (50% probability) of complex **1**, $\text{Co}_2(\text{CO})_2(\text{PPh}_3)_2(1,3\text{-}\eta\text{-S}_2\text{CSMe}(\mu\text{-}1,2\text{-}\eta\text{-SCSMe}))$.

MeSCS_2 , which is coordinated through two sulfur atoms parallel to the two cobalt atoms in a way similar to the arrangement adopted by the closely related MeOCS_2 ligand in $\text{Co}_3(\text{CO})_7(\mu\text{-}3\text{-S})(\mu\text{-}1,3\text{-}\eta\text{-S}_2\text{C}(\text{OMe}))$ [24]. The pentaatomic $\text{Co}_2\text{S}_2\text{C}$ ring is puckered, while the S(1), S(2), C(1) and S(3) atoms lie on a plane, thus suggesting a π delocalization on these four atoms, with a

greater double bond character on the shorter C(1)–S(1) and C(1)–S(2) bonds (1.687(6) Å av.) compared with the C(1)–S(3) bond (1.742(6) Å). The extension of the π delocalization to the C(1)–S(3) bond is also confirmed by the small deviation of C(2) from the mean plane (0.15 Å), as already found in $\text{Co}_3(\text{CO})_7(\mu\text{-}3\text{-S})(\mu\text{-}1,3\text{-}\eta\text{-S}_2\text{C}(\text{OMe}))$ [24] and in $\text{Co}_3(\text{CO})_5(\text{PPh}_3)_2(\mu\text{-}3\text{-}\eta\text{-S}_2\text{CSBu}^t)$ [25]. The asymmetry of the angles around C(1) is a consequence of this rough coplanarity, which gives rise to a C(2) ... S(1) contact (3.113 Å), significantly shorter than the sum of the van der Waals radii.

The other ligand is methyl dithioformate MeSCS , which through its CS group is also coordinated to both cobalt atoms but occupies a position perpendicular to the two metals. The C(3), C(4), S(4) and S(5) atoms lie on a plane with a mean deviation from it of 0.032 Å; this planarity and the values of the C(3)–S(4) and C(3)–S(5) bond lengths (1.724(6) Å av.) suggest a π delocalization along the SCS chain. The C(3)–S bond lengths are in the range of those observed in other compounds (1.720–1.737 Å), having a similar arrangement of the M_2CS 'tetrahedron' (M = Mo, W, Fe, or Co) [20,21,26–32].

Two features of the structure of complex **1** deserve a mention. One of these is that the CS group uses five electrons in bonding to the two metals to satisfy the 18-electron rule. This is a bonding mode which has been observed in metal carbonyl chemistry only in a few cases up to now [20,27–32], and none of these is a dithioester complex. The other is the symmetry of the M_2CS 'tetrahedron', in the sense that the two metal atoms are identical and have the same arrangement of ligands in their coordination sphere, which is also rather rare [20,21,27,28,33,34]. Owing to the odd number of

Table 1
Selected bond lengths (Å) and bond angles (°) for complex **1**

Co(1)–Co(2)	2.435(1)	S(3)–C(1)	1.742(6)
Co(1)–S(1)	2.301(2)	S(3)–C(2)	1.782(8)
Co(1)–S(4)	2.230(2)	S(4)–C(3)	1.722(6)
Co(1)–P(1)	2.232(2)	S(5)–C(3)	1.727(5)
Co(1)–C(11)	1.747(6)	S(5)–C(4)	1.779(8)
Co(1)–C(3)	1.938(5)	P(1)–C	1.834(6)
Co(2)–S(2)	2.287(2)	P(1)–C	1.835(6)
Co(2)–S(4)	2.226(2)	P(1)–C	1.827(6)
Co(2)–P(2)	2.232(2)	P(2)–C	1.809(6)
Co(2)–C(21)	1.745(6)	P(2)–C	1.827(6)
Co(2)–C(3)	1.936(6)	P(2)–C	1.835(6)
S(1)–C(1)	1.689(6)	C(11)–O(11)	1.141(8)
S(2)–C(1)	1.685(6)	C(21)–O(21)	1.145(8)
Co(2)–Co(1)–S(1)	94.7(1)	Co(1)–S(4)–C(3)	57.0(2)
Co(2)–Co(1)–S(4)	56.8(1)	Co(2)–S(4)–C(3)	57.0(2)
S(1)–Co(1)–S(4)	106.3(1)	C(3)–S(5)–C(4)	102.2(3)
Co(2)–Co(1)–P(1)	154.3(1)	Co(1)–C(11)–O(11)	176.7(6)
Co(2)–Co(1)–C(11)	102.9(2)	Co(2)–C(21)–O(21)	177.9(6)
S(1)–Co(1)–C(11)	102.3(2)	S(1)–C(1)–S(2)	127.1(3)
Co(2)–Co(1)–C(3)	51.0(2)	S(1)–C(1)–S(3)	121.0(3)
Co(1)–Co(2)–S(2)	98.7(1)	S(2)–C(1)–S(3)	111.8(3)
Co(1)–Co(2)–S(4)	57.0(1)	Co(1)–C(3)–Co(2)	77.9(2)
Co(1)–Co(2)–P(2)	158.6(1)	Co(1)–C(3)–S(4)	74.8(2)
Co(1)–Co(2)–C(21)	91.5(2)	Co(2)–C(3)–S(4)	74.7(2)
Co(1)–S(1)–C(1)	109.3(2)	Co(1)–C(3)–S(5)	139.0(3)
Co(2)–S(2)–C(1)	107.3(2)	Co(2)–C(3)–S(5)	137.4(3)
C(1)–S(3)–C(2)	105.8(3)	S(4)–C(3)–S(5)	126.3(3)
Co(1)–S(4)–Co(2)	66.2(1)		

electrons furnished by the CS group, this is only possible because the methyl trithiocarbonate ligand also donates an odd number of electrons (three) to the two cobalt atoms.

The CO and $\text{P}(\text{C}_6\text{H}_5)_3$ ligands on the two Co atoms are nearly eclipsed. The crystal packing shows a short contact (2.91 Å) between S(5) and a H phenylic atom of a molecule at $x, -0.5 - y, -0.5 + z$; this contact is in the plane of the C(3), C(4), S(4) and S(5) atoms, with angles of 123° (C(3)–S(5)–H) and 134° (C(4)–S(5)–H).

In agreement with its structure, complex **1** shows only one signal in its ^{31}P NMR spectrum at 38.4 ppm. The ^{13}C spectrum exhibits a triplet at 242.6 ppm (C1, $^3\text{J}(\text{PCoSC})$ 16.5 Hz), a broadened singlet at 210.1 ppm ($(\text{CO})_2$), a further, slighter broadened singlet at 138 ppm (assigned to C(3)) and, apart from the aromatic carbons of the phenyl rings, two sharp singlets of the S-methyl groups (24.3 and 21.9 ppm). The value of the chemical shift of C3 falls within the range observed for μ -methylene complexes (100–200 ppm) [35].

Experiments to characterize further complexes formed in the same reaction and to get some information about the mechanism of formation of **1** are in progress.

3. Experimental section

3.1. General methods

All manipulations were carried out under Ar by standard Schlenk techniques using deoxygenated, dry solvents. Infrared spectra were recorded on a Specord IR 75 (Carl Zeiss, Germany) spectrometer and were calibrated with benzene (1959.6 cm^{-1}). ^{31}P and ^{13}C NMR spectra were obtained at 293 K on a Varian Unity 300 spectrometer. $\text{Co}_2(\text{CO})_8$ was prepared according to the literature method [36].

3.2. Synthesis

3.2.1. Preparation of $(\text{MeSCS}_2)_2$

The method of Knoth and Gattow [37] was somewhat modified in the sense that NaNO_2/HCl was used as an oxidant [38] instead of I_2 . 8.0 g (0.143 mol) KOH was dissolved in 40 ml water, and after cooling 7.6 ml (approx. 6.2 g, 0.13 mol) MeSH and 8.6 ml (10.9 g, 0.143 mol) CS_2 added. The reaction mixture was stirred at 0°C until it became homogeneous. Following this, 8.0 g (0.116 mol) NaNO_2 , 8 ml MeOH and finally 10 ml conc. HCl were added under stirring at 0°C . The product slowly crystallized from the solution. Filtration and washing with cold water yielded 15.0 g $(\text{MeSCS}_2)_2$ (0.122 mol, 94% calculated on MeSH). M.p. 89°C (lit. $89\text{--}90^\circ\text{C}$) [37].

Table 2

Crystal data and parameters of δ -ra collection and refinement for complex **1**

Empirical formula	$\text{C}_{22}\text{H}_{36}\text{Co}_2\text{O}_2\text{P}_2\text{S}_5$
Color; habit	brown; prismatic
Crystal size (mm^3)	$0.20 \times 0.40 \times 0.52$
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 18.039(3)\text{ \AA}$ $b = 10.530(2)\text{ \AA}$ $c = 21.526(4)\text{ \AA}$ $\beta = 92.37(2)^\circ$
Volume	$4085.4(13)\text{ \AA}^3$
Z	4
Formula weight	912.8
Density (calc.)	1.484 g cm^{-3}
Absorption coefficient	1.182 mm^{-1}
2 θ range	$2.0\text{--}55.0^\circ$
Scan type	$\theta\text{--}2\theta$
Scan speed	Variable; $4.00\text{--}20.00^\circ\text{ min}^{-1}$
Scan range	2.00°
Reflections collected	9716
Independent reflections	9289 ($R_{\text{int}} = 2.27\%$)
Observed reflections	5475 ($F > 4.0\sigma(F)$)
Absorption correction	Semi-empirical
Min./max. transmission	0.2104/0.2321
Refinement method	Full-matrix least-squares
Quantity minimized	$\sum w(F_o - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0030F^2$
Number of parameters refined	478
Final R indices (obs. data)	$R = 5.67\%$, $wR = 7.32\%$
R indices (all data)	$R = 10.19\%$, $wR = 12.37\%$
Goodness-of-fit	1.03
Largest and mean Δ/σ	0.111, 0.004
Data-to-parameter ratio	11.5:1
Largest difference peak	1.18 e \AA^{-3}
Largest difference hole	-0.47 e \AA^{-3}
$K = \sum(F_o - F_c)/\sum F_o$; $wR = (\sum(w(F_o - F_c)^2)/\sum(wF_o)^2)^{1/2}$	

3.2.2. Preparation of $\text{Co}_2(\text{CO})_2(\text{PPh}_3)_2(1,3\text{-}\eta\text{-S}_2\text{CSMe})(\mu\text{-}1,2\text{-}\eta\text{-SCSMe})$ (**1**)

513 mg (1.5 mmol) $\text{Co}_2(\text{CO})_8$ and 308 mg (1.25 mmol) $(\text{MeSCS}_2)_2$ (S:Co 5:2) were dissolved under Ar in 20 ml dichloromethane and the solution stirred until the IR spectra of samples taken from the reaction mixture indicated that all $\text{Co}_2(\text{CO})_8$ had been consumed (about 16 h). The dark brown solution was evaporated in vacuo to dryness, the residue dissolved in 20 ml hexane and filtered. To this solution 580 mg (2.21 mmol) PPh_3 was added, and the reaction mixture stored overnight at 0°C . The crystals were filtered and recrystallized from CH_2Cl_2 /hexane by the slow diffusion method. Yield 176 mg (0.193 mmol, 12.9% calculated on cobalt). Anal. Found: Co, 13.3; P, 6.70. Calc.: Co, 12.91; P, 6.78%.

3.3. Crystallography

The crystal data, parameters of data collection and refinement are collected in Table 2. In Table 3 atomic

Table 3

Selected atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for complex I

Atom	x	y	z	U_{eq}
Co(1)	2385(1)	-261(1)	5015(1)	33(1)
Co(2)	2705(1)	1238(1)	4207(1)	33(1)
S(1)	3360(1)	298(2)	5682(1)	45(1)
S(2)	3879(1)	1737(2)	4567(1)	43(1)
S(3)	4873(1)	1429(2)	5613(1)	56(1)
S(4)	2883(1)	-847(1)	4128(1)	40(1)
S(5)	1236(1)	-599(2)	3713(1)	52(1)
F(1)	2168(1)	-2193(1)	5392(1)	34(1)
F(2)	2813(1)	2030(1)	3253(1)	35(1)
C(1)	1632(4)	472(6)	5354(3)	45(2)
O(11)	1119(3)	922(6)	5555(3)	76(2)
C(21)	2165(3)	2423(6)	4531(3)	44(2)
O(21)	1805(3)	3174(5)	4756(3)	66(2)
C(11)	3992(3)	1119(5)	5286(3)	37(2)
C(2)	4923(4)	597(9)	6335(3)	70(3)
C(3)	2016(3)	-171(6)	4157(2)	38(2)
C(4)	536(4)	359(9)	4033(4)	74(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

fractional coordinates of the most relevant atoms are given. The reflections with $-23 \leq h \leq 23$, $0 \leq k \leq 13$, $0 \leq l \leq 28$ were collected on a Siemens P4 automatic diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Two standard reflections were measured every 50 reflections; no decay was detected. For solution (direct methods) and refinement the Siemens SHELXTL, IRIS package was used. Most of the hydrogen atoms coincident with the calculated ones appeared on the last Fourier difference map; therefore they were put in the calculated positions and refined riding on the corresponding carbon atoms with fixed U_{iso} . All other atoms were anisotropically refined.

4. Supplementary material available

Full tables of distances and angles, fractional atomic coordinates and anisotropic thermal parameters. List of observed and calculated structure factors.

Acknowledgements

This work was supported by 40%/60% MURST (Italy) and OTKA grants T-7444 and T-016260 (Hungary).

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