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Formation of a Bridging Sulfide in $[Co_4(\mu_3\text{-}S)(SCH_2CH_2S)_3(PPh_3)_3Cl]$ via Disruption of the C–S Bond from Dithiolate

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Introduction

A few transition metal complexes with mixed phosphine and thiolate ligands are known,[1-3] but none contains bridging sulfide formed through the capture of the sulfur atom from the starting thiolates. Recently we have shown that the reaction of $CoX(PPh_3)_3$ (X = Cl, Br) with thiolate or dithiolate is a route to cobalt–sulfur cluster compounds, such as $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6Br]$, $[Co_6(\mu_3\text{-}S)_8(PPh_3)_6]\cdot L$ (L = solvents), and $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_4X_3]$ (X = Cl, Br).[4-6] The substitution of SEt^- for S^{2-} as the source of sulfur in the last complex also led to the same product. In the present reaction system the sulfur atoms dissociated completely from the thiolate or dithiolate reactants and were incorporated into the cluster building process without any original thiolate ligands coordinated. Holm and Henkel et al.[7,8] reported the trinuclear complexes $[M_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ (M = Fe, Co) (**2**) formed in the reaction of MCl_2–$Na_2(S_2\text{-}o\text{-}xyl)$–$Li_2S$, in which the bridged sulfur atom was directly provided by S^{2-}. By varying the reaction conditions in the $CoX(PR_3)_3$–dithiolate system, we have now obtained a tetranuclear compound with simultaneous ligations of phosphine, dithiolate, and sulfide, in which the dithiolate functions not only as a ligand but also as a donor of S^{2-} ion through the cleavage of a C–S bond. In this note we describe the synthesis and structural characterization of $[Co_4(\mu_3\text{-}S)(SCH_2CH_2S)_3(PPh_3)_3Cl]$ (**1**).

Experimental Section

All operations were carried out under an atmosphere of pure dinitrogen using conventional Schlenk techniques. Acetonitrile was dried and degassed before use. Cobalt chloride, triphenylphosphine, and 1,2-ethanedithiol were purchased from the Aldrich Chemical Co. $CoCl(PPh_3)_3$ and Na_2edt (H_2edt = 1,2-ethanedithiol) were prepared according to literature methods.[9,10]

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, and proton NMR spectra were measured on a Varian FT-80A spectrometer with CD_2Cl_2 as solvent and $SiMe_4$ as internal standard, downfield shifts being regarded as positive. Magnetic susceptibility was measured for the crystalline sample at room temperature on a homemade Gouy–Faraday magnetic balance using the Faraday method. Elemental analyses were carried out by the Analytical Chemistry Group of this Institute.

Preparation of $[Co_4(\mu_3\text{-}S)(SCH_2CH_2S)_3(PPh_3)_3Cl]$. To a stirred suspension of $CoCl(PPh_3)_3$ (2.64 g, 3 mmol) in acetonitrile (50 mL) was added the white powder of Na_2edt (0.41 g, 3 mmol), resulting in a brown solution. After the reaction mixture was stirred for 3 h at room temperature, it was filtered, and the filtrate was reduced in volume by half. The deep brown crystalline product of the title compound was obtained from the filtrate kept at 4 °C for several days. This material was collected, washed with ether, and dried in vacuo, affording 0.43 g (42%) of the title compound. IR (KBr) (cm^{-1}): PPh_3, 3053 (m), 745 (s), 694 (s), 522 (s), 507 (s); edt, 2910 (m), 465 (m), 303 (s). ^1H NMR (CD_2Cl_2): δ 7.34, 6.54 (m, 45, PPh_3), –9.0 ppm (br, 12, edt). Anal. Calcd for $C_{60}H_{57}ClCo_4P_3S_7$: C, 52.73; H, 4.20; P, 6.80; S, 16.42. Found: C, 52.53; H, 4.38; P, 6.78; S, 16.02.

Crystal Data. A single crystal of **1** was obtained by recrystallization from acetonitrile/ether. Determination of cell constants and data collection were carried out at room temperature with Mo Kα radiation on a Rigaku AFC5R four-circle diffractometer in the range of $2° < 2\theta < 50.2°$. A total of 3743 reflections were measured, and 2636 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. Intensity data used in the structure determination and refinement were corrected for Lorentz–polarization factors, linear decay, and empirical absorption (DIFABS correction). The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final conventional factors are $R = 0.046$ and $R_w = 0.064$. All calculations were carried out on a VAX 11/785 computer with the TEXSAN program package. Crystallographic data appear in Table I, and the atomic coordinates and thermal parameters are listed in Table II. The selected interatomic distances and angles are in Table III.

Results and Discussion

The structure of **1** in the solid state was determined by a single-crystal X-ray diffraction study with the results shown from different viewpoints in Figure 1. The cluster contains four cobalt atoms in the form of a trigonal pyramid. The three Co(1) atoms form an equilateral triangular basal plane, which is capped by one triply-bridging sulfur atom S(3) below, and are doubly-bridged by one sulfur atom S(2) of the edt^{2-} ligand in each edge of the triangle. Each of the Co(1) atoms in the Co_3 triangle is again bridged to the apical Co(2) atom by another sulfur atom S(1) of the dithiolate ligand along the edges of the Co_4 trigonal pyramid to provide additional stability to the molecule in the sense of locking the apical cobalt atom and the basal tricobalt atoms together. The apical Co(2) atom is terminally coordinated by one chloride atom, while each of the Co(1) atoms is coordinated by one triphenylphosphine ligand. The molecular structure possesses a crystallographic C_3 symmetry with the rotation axis passing through the atoms Cl, Co(2), and S(3) and the center of the basal planes. The two planes of Co_3 and $S(2)_3$ are very close to one another with a distance of 0.04 Å so that Co_3S_3 can be regarded as an irregular hexagon with S(2)–Co(1)–S(2) being 163.50(6)° and Co(1)–S(2)–Co(1) being 76.34(6)° as shown in Figure 1. Unlike $[Co_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ (**2**),[7,8] in which the dithiolate acts as both terminal and bridging ligands, both sulfurs of the edt^{2-} ligand in complex **1** act as doubly-bridged atoms. The Co–Co bond distances of 2.741(2) Å (Table III) within the triangle $Co_3(1)$ are slightly shorter than the corresponding ones of 2.806 Å in compound **2**,[8] shorter than that in $[Co_6(\mu_3\text{-}S)_8(PPh_3)_6]$ (2.870 Å)[5] and much shorter than the nonbonding Co(1)···Co(2) distances (3.3 Å) in **1**. The Co(1)–S(2) bond lengths (2.202(2) and 2.232(2) Å) and Co(1)–S(3) (2.209(8) Å) are slightly shorter than the corresponding ones in compound **2**[7,8] (2.307 and 2.275 Å, respectively). The Co(1)–S(1) and Co(2)–S(1) distances being different from those in general metal–ethanedithiolate complexes[10] are of different lengths 2.249(2) and 2.328(8) Å, respectively.

The molecular of **1** is tetranuclear with one four-coordinate and three five-coordinate cobalt atoms. The coordination sphere of Co(2) is nearly tetrahedral with average bond angles of 109.47°

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Table I. Crystallographic Data for 1

formula: $C_{60}H_{57}ClCo_4P_3S_7$	$T = 296$ K
fw = 1366.64	$\lambda = 0.710\,69$ Å
cryst syst: trigonal	$D_{calcd} = 1.43$ g cm^{-3}
space group: $P\bar{3}$ (No. 147)	μ(Mo Kα) = 14.05 cm^{-1}
$a = 16.505(8)$ Å	obsd data: 2636 ($I > 3.0\sigma(I)$)
$c = 13.401(6)$ Å	$R^a = 0.046$
$V = 3162(3)$ Å^3	$R_w{}^b = 0.064$
$Z = 2$	

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Atomic Coordinates and Thermal Parameters for 1

atom	x	y	z	B(eq)[a]
Co(1)	0.74343(5)	0.44078(5)	0.77466(5)	2.67(3)
Co(2)	0.6667	0.3333	0.9917(1)	3.10(5)
Cl	0.6667	0.3333	1.1605(2)	4.2(1)
S(1)	0.779991)	0.4806(1)	0.9357(1)	3.24(5)
S(2)	0.8391(1)	0.3841(1)	0.7715(1)	3.00(5)
S(3)	0.6667	0.3333	0.6596(2)	2.84(8)
P	0.8415(1)	0.5746(1)	0.6985(1)	3.11(6)
C(1)	0.8903(4)	0.4832(4)	0.9532(4)	3.5(2)
C(2)	0.8978(4)	0.4094(4)	0.8948(5)	3.6(2)
C(11)	0.9592(4)	0.6340(4)	0.7529(4)	3.6(2)
C(12)	1.0196(4)	0.5990(5)	0.7374(5)	4.3(3)
C(13)	1.1051(5)	0.6393(6)	0.7863(6)	5.3(3)
C(14)	1.1304(5)	0.7117(6)	0.8510(6)	6.0(3)
C(15)	1.0723(6)	0.7455(5)	0.8678(6)	5.6(3)
C(16)	0.9864(5)	0.7077(5)	0.8184(5)	4.7(3)
C(21)	0.8566(5)	0.5622(4)	0.5653(4)	3.9(2)
C(22)	0.7761(5)	0.5159(5)	0.5085(5)	5.2(3)
C(23)	0.7825(8)	0.5042(6)	0.4049(6)	6.8(4)
C(24)	0.866(1)	0.5390(8)	0.3610(6)	7.8(5)
C(25)	0.9434(8)	0.5831(7)	0.4148(7)	7.3(5)
C(26)	0.9420(5)	0.5963(5)	0.5168(5)	5.2(3)
C(31)	0.8150(5)	0.6702(4)	0.7002(5)	4.2(3)
C(32)	0.7750(5)	0.6850(5)	0.7841(6)	5.1(3)
C(33)	0.7590(7)	0.7582(6)	0.7886(8)	7.1(5)
C(34)	0.7816(8)	0.8182(7)	0.708(1)	8.4(6)
C(35)	0.8237(8)	0.8064(7)	0.6282(8)	8.2(5)
C(36)	0.8400(6)	0.7323(5)	0.6209(6)	6.1(4)
H(1)	1.0008	0.5461	0.6928	3.9
H(2)	1.1488	0.6154	0.7725	3.9
H(3)	1.1905	0.7376	0.8816	3.9
H(4)	1.0944	0.7972	0.9131	3.9
H(5)	0.9467	0.7333	0.8306	3.9
H(6)	0.7156	0.4914	0.5386	4.2
H(7)	0.7232	0.4679	0.3625	4.2
H(8)	0.8561	0.5292	0.2893	4.2
H(9)	1.0008	0.6061	0.3766	4.2
H(10)	1.0010	0.6284	0.5542	4.2
H(11)	0.7582	0.6438	0.8406	4.8
H(12)	0.7266	0.7662	0.8495	4.8
H(13)	0.7675	0.8686	0.7197	4.8
H(14)	0.8355	0.8511	0.5758	4.8
(H15)	0.8667	0.7210	0.5602	4.8
H(16)	0.9406	0.5437	0.9335	4.2
H(17)	0.8983	0.4758	1.0232	4.2
H(18)	0.8696	0.3524	0.9333	4.3
H(19)	0.9622	0.4282	0.8850	4.3

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

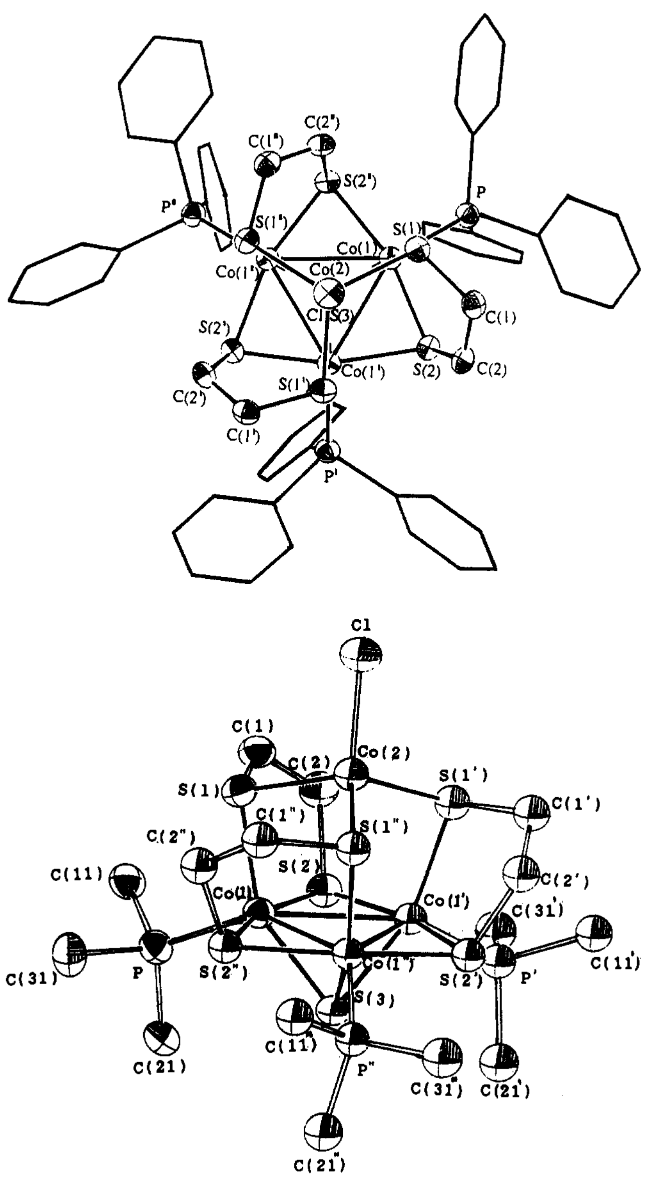

Figure 1. Top (top) and side (bottom) views of $[Co_4(\mu_3\text{-}S)(SCH_2CH_2S)_3(PPh_3)_3Cl]$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for 1

Co(1)–Co(1)	2.741(2)	Co(2)–Cl	2.261(3)
Co(1)–S(2)	2.202(2)	S(1)–C(1)	1.815(6)
Co(1)–S(2)	2.232(2)	S(2)–C(2)	1.853(6)
Co(1)–S(3)	2.210(2)	P–C(11)	1.835(6)
Co(1)–S(1)	2.249(2)	P–C(21)	1.828(6)
Co(2)–S(1)	2.329(2)	P–C(31)	1.835(7)
Co(1)–P	2.228(2)	C(1)–C(2)	1.504(8)
S(2)–Co(1)–S(3)	83.74(4)	Co(1)–S(3)–Co(1′)	76.66(8)
S(2)–Co(1)–P	95.33(6)	C(21)–P–C(11)	106.3(3)
S(2)–CO(1)–S(2″)	163.50(6)	C(21)–P–C(31)	102.3(3)
S(2)–Co(1)–S(1)	89.90(6)	C(21)–P–Co(1)	114.1(2)
S(2)–Co(1)–Co(1′)	52.32(5)	C(2)–C(1)–S(1)	113.6(4)
S(2)–Co(1)–Co(1″)	112.31(5)	C(1)–C(2)–S(2)	113.7(4)
S(3)–Co(1)–P	108.44(7)	P–Co(1)–S(2)	98.18(6)
S(3)–Co(1)–S(1)	150.10(7)	P–Co(1)–S(1)	101.21(7)
S(3)–Co(1)–Co(1′)	51.68(4)	P–Co(1)–Co(1′)	141.11(5)
C(1)–S(1)–Co(1)	104.5(2)	P–Co(1)–Co(1″)	139.55(5)
C(1)–S(1)–Co(2)	104.8(2)	S(1)–Co(1)–Co(1′)	105.47(4)
Co(1)–S(1)–Co(2)	92.67(7)	S(1)–Co(1)–Co(1″)	102.08(4)
C(2)–S(2)–Co(1)	106.9(2)	Cl–Co(2)–S(1)	108.81(5)
C(2)–S(2)–Co(1′)	112.3(2)	S(1)–Co(2)–S(1)	110.13(5)
Co(1)–S(2)–Co(1′)	76.34(6)		

for the CoS_3Cl unit. The Co(1) atoms are each coordinated in a distorted square-pyramidal geometry of the CoS_4P unit with three bridging sulfur atoms from edt^{2-} ligands and one sulfide forming the basal plane and one phosphorus atom in the apical position.

In the ^{1}H NMR spectrum a broad peak at high field (δ −9.0 ppm) for symmetry-related $SCH_2CH_2S^-$ as compared to the narrow peaks near 3.0–1.0 ppm for diamagnetic complexes with coordinated edt^{2-} [11] may arise from compound **1** paramagnetism. The solid magnetic susceptibility has been determined, and the magnetic moment of 6.4 μ_B (298 K) is consistent with the above

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^{1}H NMR resonances. According to the crystal data and geometry of the cluster framework, compound **1** can be considered as two magnetic centers, Co(2)$^{3+}$ and 3 Co(1)$^{2+}$, with high-spin $S = 2$ and $S = {}^3/_2$, respectively. From the equation $\mu_{eff} = (\mu_1{}^2 + \mu_2{}^2)$, a total of magnetic moment (6.24 μ_B) can be calculated, which is comparable to the experimental value (6.4 μ_B).

Beside its interesting stereochemistry, compound **1** is significant in its synthetic process. The reactions of low-valent cobalt with thiolate in the presence of PPh_3 for rather long reaction times are shown to lead to a series of polynuclear cobalt–sulfide clusters,[4–6] in which the bridged sulfur atoms were completely originated from the thiolate reactants. With simply variation of the conditions in the reaction system, for example, by shortening of the reaction time, the sulfur-containing ligands can be captured in the formation of cobalt complexes. In this reaction, the dithiolate plays a dual role both producing the bridging chelate fragments and providing the sulfur atom capping the metal triangles. Beside the demonstration of the synthetic potential for the formation of transition metal sulfides, the disruption of the C–S bond found in this system may be related to the mechanism of industrially important hydrodesulfurization catalytic processes.[12,13] Although the cleavage of the C–S bond is documented in $[ReS(edt)_2]^-$ [14] and $[NbS(edt)(SC_2H_4SC_2H_4S)]^-$ [15] complexes, which are mononuclear with terminal sulfur atoms, this is the first example of polynuclear cluster formation with bridging sulfur atoms both directly from a dithiolate and captured from the cleavage of the C–S bond of a dithiolate. Further research on the formation mechanism of this type of reaction is under way.

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Supplementary Material Available: Tables listing crystal data and experimental parameters, anisotropic thermal parameters, bond distances, and bond angles (4 pages). Ordering information is given on any current masthead page.

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