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Synthesis and X-ray structure of cobalt–sulfur clusters containing iodides as bridging and terminal ligands

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Abstract

By reacting anhydrous CoI_2 with PEt_3 in a 1:2 ratio in the presence of $S[Si(CH_3)_3]_2$, a mixture of $[Co_6(\mu_3\text{-}S)_6(\mu_3\text{-}I)_2(PEt_3)_6][Co(PEt_3)I_3]_2$ (**1**) and $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3I_3(PEt_3)_4]$ (**2**) is obtained. When the reaction is carried out with the halide and phosphine in a 1:1 ratio, only **1** is formed. The molecular structures of **1** and **2** were established by single-crystal X-ray diffraction study. Crystal data for **1**: monoclinic, space group $P2_1/a$, $Z=2$, $a=31.965(12)$, $b=11.902(5)$, $c=11.805(5)$ Å, $\beta=98.77(8)°$. Crystal data for **2**: cubic, space group $Pa\bar{3}$, $a=21.280(8)$ Å, $Z=8$. **1** contains a novel octahedral species in which two iodide ligands replace two triply bridging sulfides. **2** displays a monocapped prismane geometry, with three cobalt atoms coordinated to a terminal iodine ligand.

Introduction

Transition metal–sulfur clusters have been investigated basically with the aim both to simulate analogous complexes involved in important biological processes and to design new materials of magnetic and conductimetric interest [1]. The most characteristic property of these compounds, i.e. the ability to act as electron reservoir, is found in clusters containing the M_3S unit, a triangle of metal atoms capped by a triply bridging sulfur.

In recent years we have described iron [2], cobalt [3], nickel [4] and rhodium [5] sulfur clusters with triangular, octahedral and cofacial bioctahedral metal frameworks. Common to all these species is the presence, as a building block, of the M_3S fragment, the monotertiary phosphine ligands always occupying terminal positions [2–5].

Here we report the syntheses and structures of two cobalt clusters of formulae $[Co_6(\mu_3\text{-}S)_6(\mu_3\text{-}I)_2(PEt_3)_6][Co(PEt_3)I_3]_2$ (**1**) and $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3I_3(PEt_3)_4]$ (**2**) containing iodide as bridging or terminal ligand. The compound **1** contains a novel octahedral species in which two iodide ligands replace two triply bridging sulfides. As far as we know, among octahedral clusters, species containing triply bridging both halides and chalcogenides have been previously reported only for molybdenum [6]. Additionally the title compounds may be of interest as potential starting material to obtain other highly condensed species by metathetical reactions.

Experimental

All operations were performed under nitrogen. All reagents were reagent grade and were degassed prior to use.

Synthesis of $[Co_6(\mu_3\text{-}S)_6(\mu_3\text{-}I)_2(PEt_3)_6][Co(PEt_3)I_3]_2$ *(1) and* $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3I_3(PEt_3)_4]$ *(2)*

3.13 g (0.01 mol) of anhydrous CoI_2 were added to a solution of 2.36 g (0.02 mol) of PEt_3 in 30 cm^3 of THF. The resulting mixture was stirred for 5 h, then 1.78 g (0.01 mol) of $S[Si(CH_3)_3]_2$ was added and the solution was stirred for a further 4 days. The resulting mixture was filtered and n-butanol (20 cm^3) was added to the solution. After evaporation of the solvent in a current of nitrogen a black solid precipitated. This was filtered, washed with n-butanol and n-hexane and dried in a current of nitrogen. The crude solid was treated with benzene (30 cm^3) and acetone (2 cm^3); the resulting mixture was filtered to yield a black solid and a black solution. The solid, essentially **1**, was recrystallized from dichloromethane/n-butanol. n-butanol (20 cm^3) was added to the solution and by evaporation of the solvent black crystals of **2** were obtained.

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Anal. Calc. for $C_{48}H_{120}Co_8I_8P_8S_6$ (**1**): C, 21.97; H, 4.61; Co, 17.96. Found: C, 21.85; H, 4.60; Co, 16.27%. Yield: 20%. Calc. for $C_{24}H_{60}Co_7I_3P_4S_6$ (**2**): C, 19.76; H, 4.15; S, 13.19; Co, 28.29. Found: C, 19.83; H, 4.09; S, 13.49; Co, 30.45%. Yield: 15%.

Synthesis of [$Co_7(\mu_4$-$S)_3(\mu_3$-$S)_3I_3(PEt_3)_4$] (2)

3.13 g (0.01 mol) of anhydrous CoI_2 were added to a solution of 1.18 g (0.01 mol) of PEt_3 in 30 cm^3 of THF. The resulting mixture was stirred for 5 h, then 1.78 g (0.01 mol) of $S[Si(CH_3)_3]_2$ was added and the solution was further stirred for 4 days. After filtration n-butanol (20 cm^3) was added to the solution and black crystals of **2** precipitated. The crystals were recrystallized from a mixture of benzene/acetone (in small percentage)/n-butanol. Yield: 35%.

Crystallography

Crystal data

Details are given in Table 1. Unit cell parameters for both the compounds were determined from 20 and 25 randomly selected reflections for **1** and **2**, respectively. The intensities after correction for background were corrected for Lorentz-polarization effects. The intensities were assigned a standard deviation $\sigma(I)$, calculated as previously described with instability factor k of 0.03 for both **1** and **2** [7]. An X-ray absorption correction was applied to **1** [8] and **2** [9].

TABLE 1. Details of crystal data[a]

	1	**2**
Formula	$C_{48}H_{120}Co_8I_8P_8S_6$	$C_{24}H_{60}Co_7I_3P_4S_6$
M	2624.37	1458.27
a (Å)	31.965(12)	21.280(8)
b (Å)	11.902(5)	
c (Å)	11.805(5)	
β (°)	98.77(8)	
Space group	$P2_1/a$	$Pa\bar{3}$
U (Å^3)	4438.7	9636.4
Z	2	8
D_{calc} (g cm^{-3})	1.96	2.01
μ (cm^{-1})	370.4 (Cu Kα)	46.5 (Mo Kα)
$F(000)$	2528	5664
Crystal habit	parallelepiped	cube
Dimensions (mm)	0.025×0.30×0.375	0.18×0.18×0.18
Diffractometer	Philips PW 1100	Enraf Nonius CAD4
Radiation (Å)	1.5418	0.7107
Scan speed (° s^{-1})	0.08	0.09
Scan width ($A+B$ tan θ)	$A=0.8$, $B=0.15$	$A=0.8$, $B=0.35$
Max. deviation of standard intensities (%)	2	10
2θ Limits (°)	5–120	5–50
Total data	7321	3300
Data used	2889 ($I>3\sigma(I)$)	760 ($I>2\sigma(I)$)
Final variables	262	93

[a] Details common to both compounds: color, black; monochromator, graphite crystal; scan method, ω–2θ; background time, half scan time; standards, 3 every 120 s; temperature, 22 °C.

Solution and refinements of the structures

All calculations were performed by using the SHELX 76 [8] and ORTEP [10] programs on a SEL 32/77 computer. Atomic scattering factors for the appropriate neutral atoms were taken from ref. 11 for non-hydrogen atoms and from ref. 12 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms [13]. During the refinement the function $\Sigma w(|F_o|-|F_c|)^2$ was minimized, the weights w being defined as $w=1/\sigma^2(F_o)$. Patterson and Fourier maps enabled the locations of all the non-hydrogen atoms for both the structures. Full-matrix least-squares refinements were carried out with anisotropic thermal parameters assigned to cobalt, sulfur, iodine and phosphorus atoms. Hydrogen atoms in calculated positions were introduced in **1**, but were not refined. Refinements converged to R_w and R factors of 0.096, 0.095 and 0.058 and 0.085 for **1** and **2**, respectively. Difference Fourier maps calculated at the end of the refinement showed residual electron density in the proximity of the ethylenic chains and of the $[CoI_3(PEt_3)]^-$ anion, which are affected by high thermal motion. This fact can partially account for the rather poor R factor values. Final positional parameters of **1** are given in Table 2. Owing to the isostructurality of **2** with already reported clusters [14, 15], refinement of the structure is not reported here (see 'Supplementary material').

Results and discussion

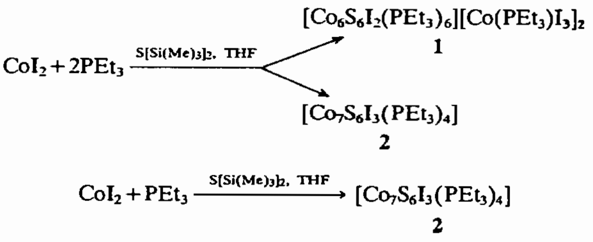
The sulfur clusters so far reported generally contain thiolato, tertiary phosphines or halide groups as ancillary ligands [16]. Fenske *et al.* [14] have reported that the reactions of $CoCl_2$ with monotertiary phosphines and $E[Si(CH_3)_3]_2$ (E = S, Se, Te) allow the formation of Co6 and Co7 clusters of formulae $[Co_6E_8(PR_3)_6]^{0,1+}$ and $[Co_7E_6(PR_3)_4Cl_3]$ or $[Co_7E_6(PR_3)_5Cl_2]$, respectively. The composition of the cluster mixtures depends on the ratio M:E:PR_3, the solvent, the R substituents of the PR_3 ligands.

Recently during the preparation of the complexes $[Ni_3S_2(PEt_3)_5X]^+$ (X = Cl, Br, I) we have found that the metathesis of halogen with sulfur in the reaction of $NiX_2(PR_3)_2$ with $S[Si(CH_3)_3]_2$ is favoured in the order Cl > Br > I [17]. Moreover the 'soft' iodide

TABLE 2. Positional parameters ($\times 10^4$) for **1**

Atom	*x*	*y*	*z*
I1	632(1)	3569(2)	3749(2)
I2	1102(1)	1332(4)	2034(5)
I3	2164(2)	−1009(5)	3209(6)
I4	1670(1)	−367(4)	−243(4)
Co1	−177(1)	4027(4)	3633(4)
Co2	475(1)	5639(4)	4285(4)
Co3	379(1)	3789(4)	5750(4)
Co4	1803(2)	436(6)	1819(6)
S1	−204(2)	2832(6)	5058(6)
S2	785(2)	5276(6)	6055(6)
S3	−53(2)	5656(6)	2831(6)
P1	−417(3)	2944(7)	2188(6)
P2	972(3)	6451(8)	3489(7)
P3	791(3)	2507(7)	6668(7)
P4	2305(3)	1873(9)	1925(10)
C1	−340(9)	3457(29)	771(25)
C2	102(11)	3542(36)	542(32)
C3	−166(9)	1561(25)	2221(24)
C4	−334(11)	784(29)	1206(27)
C5	−969(9)	2712(28)	1996(26)
C6	−1128(11)	2022(31)	2972(30)
C7	1010(10)	5912(28)	2070(26)
C8	1337(15)	6396(44)	1455(40)
C9	919(10)	7964(27)	3271(27)
C10	535(11)	8310(34)	2451(31)
C11	1521(10)	6414(29)	4286(27)
C12	1733(15)	5194(38)	4333(40)
C13	616(11)	1097(27)	6366(27)
C14	616(13)	672(36)	5177(32)
C15	1333(9)	2579(28)	6352(27)
C16	1591(17)	1629(44)	6893(45)
C17	857(12)	2562(32)	8259(29)
C18	1049(12)	3647(32)	8818(32)
C19	2739(28)	1758(79)	1017(76)
C20	2947(31)	582(90)	1606(84)
C21	2601(28)	2221(77)	3275(77)
C22	2282(39)	2424(107)	4234(105)
C23	2015(36)	3287(103)	1324(95)
C24	2358(44)	4213(127)	1927(117)

seems rather suitable to bind metal centers in such compounds. Bearing in mind the above considerations we have investigated the reaction of CoI_2 with PEt_3 and $S[Si(CH_3)_3]_2$ in different molar ratios, in order to try to synthesize iodine containing cobalt sulfur clusters. The results are summarize in the following scheme:



Both clusters, which contain the same valence electron number, 98, are diamagnetic, the paramagnetism of **1**, μ_{eff}(r.t.) = 6.35 BM, being due to the presence of the tetrahedral high spin $[CoI_3(PEt_3)]^-$ anion. **1** behaves as a 1:2 electrolyte in nitroethane solution.

The molecular structure of **1** consists of discrete $[Co_6S_6I_2(PEt_3)_6]^{2+}$ cluster cations and $[CoI_3(PEt_3)]^-$ anions. The perspective view of the cluster cation is given in Fig. 1 and selected bond distances and angles in Table 3.

The cation **1** is isostructural with the series $[M_6(\mu_3\text{-}S)_8(PEt_3)_6]^{n+}$ (M = Fe, Co; *n* = 2, 1, 0) [2, 3], where two iodine atoms substitute two sulfur ligands, and therefore is built up of an octahedral cobalt framework, whose triangular faces are triply bridged by six sulfur and two iodine atoms. Since the cation lies on a centre of inversion, the two iodine ligands bridge two centrosymmetrically related faces. Moreover the metal framework may be considered to possess idealized O_h symmetry, the values of the Co–Co–Co bond angles being very close to 60 and 90°. Each metal atom is additionally coordinated to a triethylphosphine group. Therefore each cobalt atom is linked to three sulfur, one iodine and one phosphorus in a distorted square pyramidal environment. The metal–metal separation averaging 2.82(1) Å is fully comparable with that of 2.817(3) Å reported for the parent compound $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]$, which contains the same number of valence electrons [3]. It is interesting to note that the edges of the two faces capped by the iodine ligand are significantly longer (2.851(6), 2.850(6),

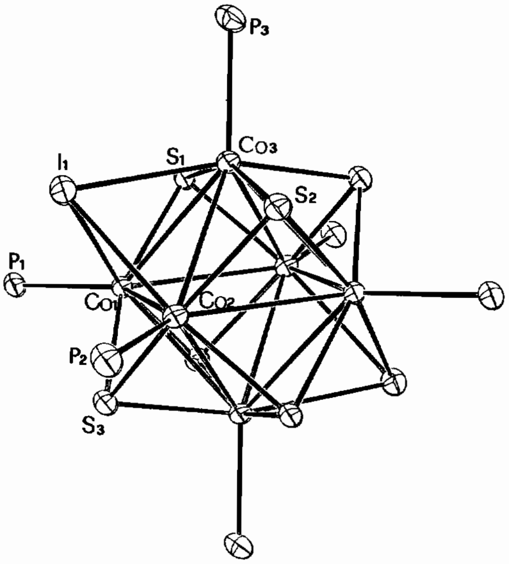


Fig. 1. Perspective view of the cluster cation $[Co_6(\mu_3\text{-}S)_6(\mu_3\text{-}I)_2(PEt_3)_6]^{+2}$. ORTEP drawing with 30% probability ellipsoids.

TABLE 3. Selected bond distances (Å) and angles (°) for **1**

Cation			
Co(1)–Co(2)	2.851(6)	Co(2)–I(1)	2.612(5)
Co(1)–Co(3)	2.850(6)	Co(2)–S(1′)	2.205(8)
Co(1)–Co(2′)	2.796(6)	Co(2)–S(2)	2.214(8)
Co(1)–Co(3′)	2.802(6)	Co(2)–S(3)	2.215(8)
Co(2)–Co(3)	2.846(6)	Co(2)–P(2)	2.191(10)
Co(2)–Co(3′)	2.806(6)	Co(3)–I(1)	2.624(5)
Co(1)–I(1)	2.625(5)	Co(3)–S(1)	2.229(8)
Co(1)–S(1)	2.213(8)	Co(3)–S(2)	2.192(9)
Co(1)–S(2′)	2.194(9)	Co(3)–S(3′)	2.205(9)
Co(1)–S(3)	2.221(9)	Co(3)–P(3)	2.191(9)
Co(1)–P(1)	2.183(8)		
I(1)–Co(1)–S(1)	88.8(3)	S(1′)–Co(2)–S(3)	88.4(3)
I(1)–Co(1)–S(2′)	163.7(3)	S(1′)–Co(2)–P(2)	97.8(4)
I(1)–Co(1)–S(3)	87.9(3)	S(2)–Co(2)–S(3)	155.7(4)
I(1)–Co(1)–P(1)	98.3(3)	S(2)–Co(2)–P(2)	104.0(3)
S(1)–Co(1)–S(2′)	88.7(3)	S(3)–Co(2)–P(2)	100.4(3)
S(1)–Co(1)–S(3)	156.2(3)	I(1)–Co(3)–S(1)	88.5(2)
S(1)–Co(1)–P(1)	99.5(3)	I(1)–Co(3)–S(2)	88.4(3)
S(2′)–Co(1)–S(3)	87.8(3)	I(1)–Co(3)–S(3′)	163.8(3)
S(2′)–Co(1)–P(1)	98.0(3)	I(1)–Co(3)–P(3)	97.5(3)
S(3)–Co(1)–P(1)	104.3(3)	S(1)–Co(3)–S(2)	156.0(4)
I(1)–Co(2)–S(1′)	164.5(3)	S(1)–Co(3)–S(3′)	88.0(3)
I(1)–Co(2)–S(2)	88.3(2)	S(1)–Co(3)–P(3)	103.4(4)
I(1)–Co(2)–S(3)	88.4(2)	S(2)–Co(3)–S(3′)	88.3(3)
I(1)–Co(2)–P(2)	97.7(3)	S(2)–Co(3)–P(3)	100.7(3)
S(1′)–Co(2)–S(2)	88.4(3)	S(3′)–Co(3)–P(3)	98.7(3)
Anion			
Co(4)–I(2)	2.531(8)	Co(4)–I(4)	2.589(8)
Co(4)–I(3)	2.531(9)	Co(4)–P(4)	2.336(12)
I(2)–Co(4)–I(3)	123.0(3)	I(3)–Co(4)–I(4)	110.6(3)
I(2)–Co(4)–I(4)	103.2(3)	I(3)–Co(4)–P(4)	102.8(4)
I(2)–Co(4)–P(4)	107.3(4)	I(4)–Co(4)–P(4)	109.5(4)

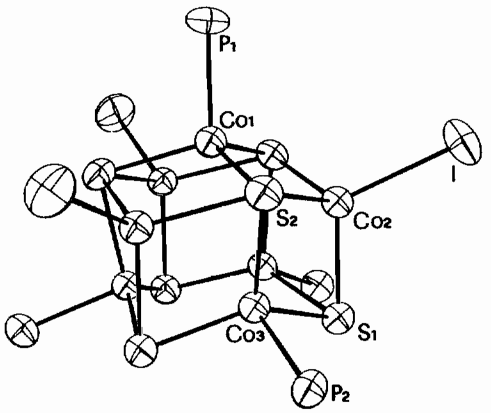


Fig. 2. Perspective view of the cluster unit $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3I_3(PEt_3)_4]$. ORTEP drawing with 30% probability ellipsoids.

2.846(6) Å) than those relative to the faces capped by the sulfur ligands (2.796(6), 2.802(6), 2.806(6) Å). The values of μ_3-S–Co of 2.210(4) (av.) Å as well as μ_3-I–Co of 2.620(4) (av.) Å and Co–P of 2.188(3) (av.) Å are well within the normal range.

In the anion the cobalt displays a tetrahedral geometry being coordinated by three iodine and a triethylphosphine group.

The crystal structure of **2** consists of cluster molecular unit of $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3I_3(PEt_3)_4]$, whose perspective view is given in Fig. 2. The cluster molecule is isostructural with the iron cluster $[Fe_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PEt_3)_4Cl_3]$ [15] and with the cobalt cluster $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh)_5Cl_2]$ [14], which possesses one electron more than **2**. It displays a monocapped prismane moiety, with crystallographically imposed C_{3v} symmetry, the three-fold axis passing through the Co1–P1 bond. Due to the isostructurality of the above clusters we compare only the Co–Co distances of **2** with those reported for the 99 electrons species $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_5Cl_2]$ [14]. The observed difference (2.555(7)–2.581(7) versus 2.574(2)–2.652(2) Å) is of the same order as that found at the variance of one electron in the couples $[Fe_6S_8(PEt_3)_6]^{n+}$, $n=2$, 1 (90/91 electrons) and $[Co_6S_8(PEt_3)_6]^{n+}$, $n=1$, 0 (97/98 electrons) [2, 3].

Supplementary material

Final parameters and bond distances and angles of compound **2**, as well as thermal parameters and lists of structure factors of both compounds, are available from the authors on request.

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