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Synthesis and molecular structure of $[(C_5Me_5)_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}SbS_4I)]$, a tricobalt complex with the tripodal ψ-SbS_4-ligand

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Abstract

The reaction of K_3SbS_3 with $[Cp^*_2Co_2I_4]$ ($Cp^* = C_5Me_5$) gave dark brown $[Cp^*_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}SbS_4I)]$ (**1**) in 22% yield. Complex **1** was characterized by ^1H-NMR and mass spectra. The crystal structure determination reveals as the central feature a distorted Co_3SbS_4 cube with the fifth sulfur atom being inserted into one of the three Sb–S edges. The coordination sphere around the Sb atom in the unprecedented tripodal ψ-$Sb(S_2)S_2$-ligand is extended by a weakly coordinated iodine atom [$d(Sb\text{–}I) = 3.215(1)$ Å].

Keywords: Cobalt; Antimony; Sulfur; Mixed ligands

1. Introduction

Mixed ligands from Group 15 and 16 elements are useful reagents for the coordination of metal ions [1]. Several strategies have been developed to introduce such species in soluble transition metal complexes [1,2]. Recently, the metathesis reaction [3] of thio- or selenoarsenates(III) with cyclopentadienylmetal halide derivatives was shown to be an alternative synthetic method for the formation of hybrid clusters from transition metal and main group elements. Usually, the mixed ligands in these compounds are unstable in the free state, e.g. the $\mu,\eta^{1:3}$-AsS_2-ligand [4], which is a higher homologue of NO_2^-, and μ_3-$As(X_2)X_2$-ligands (X = S, Se) [5], which are members of the vast family of simple sulfosalts. It is striking that analogous Sb–S ligands do not exist although $[\psi\text{-}SbS_3]^{3-}$ and $[SbS_4]^{3-}$ ions are well known building blocks in networks of various dimensionality [6]. Recently, transition metal cations have been incorporated into thioantimonate(III) networks, and soluble complex anions like $[Sb_4S_6]^{2-}$ or $[Sb_{12}Se_{20}]^{4-}$ are also known [7]. In this study we report on the reaction of K_3SbS_3 with $[Cp^*_2Co_2I_4]$, which gives a trinuclear cobalt complex containing a tripodal ψ-SbS_4-ligand.

2. Results

The reaction of $[Cp^*_2Co_2I_4]$ with excess K_3SbS_3 in boiling THF gave the dark brown compound $[Cp^*_3Co_3SbS_5I]$ in 22% yield (Eq. (1)). The relatively low yield may be explained by the formation of at least another, presumably structurally related compound, which is difficult to separate. As a possible formula for this by-product one may consider $[Cp^*_3Co_3SbS_6I]$. This assumption is based on the product distribution in the related reaction of $[Cp^*Co(CO)I_2]$ with K_3AsS_3, which gives $[Cp^*_3Co_3AsS_5I]$ and $[Cp^*_3Co_3AsS_6I]$ [5]. Attempts to carry out the reaction described in Eq. (1) in boiling acetone or DMF did not increase the yield of **1**.

$$[(C_5Me_5)_2Co_2I_4] \xrightarrow[\text{THF, 65 °C}]{K_3SbS_3} \underset{\mathbf{1}}{[(C_5Me_5)_3Co_3SbS_5I]} + \ldots \quad (1)$$

Correct elemental analysis was obtained for **1**. The complex was further characterized by means of positive ESI mass spectrometric analysis. The parent ion is assigned to the $[Cp^*_3Co_3SbS_5]^+$ cation as the dominat-

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ing ion, indicating a facile loss of the weakly coordinated iodine. The ^{1}H-NMR spectrum of **1** contains two resonances in a 2:1 ratio originating from the Cp* ligands. This suggests the presence of two equivalent Co centers, what is in agreement with the crystallographic result.

The crystal structure of **1** is shown in Fig. 1. The core of the molecule contains a distorted Co_3SbS_4 cube with the fifth sulfur atom [S(5)] being inserted into the Sb(1)–S(4) edge of this cube. Alternatively, one may describe the structure as composed of a Co_3-triangle bridged by a μ_3-S- and a μ_3-$Sb(S_2)S_2$-ligand. As in other tricobalt compounds belonging to this structural type [4,5] a disorder is observed for the edge Sb(1)–S(5). Insertion of S(5) may also take place between the edge Sb(1)–S(2) and two different Sb-positions were found as well. The ratio for both orientations is 92:8. A disorder is also found for one of the Cp* ligands [(C(21)–C(30)] giving rise to two orientations in a 59:41 ratio.

The ψ-$Sb(S_2)S_2$-ligand in **1** is a first example of a tetrathioantimonate(III) ligand with a S_2 side-arm, which may be derived from original $[SbS_3]^{3-}$ by incorporation of an additional sulfur atom. Thus, the series of ψ-tetrachalcogenoarsenate(III) ligands $As(S_2)S_2$ [5,8], $As(Se_2)Se_2$ [5,8,9] and $As(Te_2)Te_2$ [9,10] is extended to the higher homologue Sb. The structural motive of our $Sb(S_2)S_2$-ligand has partially been anticipated in the cyclic dianion $[Sb_2Se_6]^{2-}$ [11]. The Sb–S bond lengths in **1** are in between 2.429(2) and 2.562(2) Å indicating single bonds [6,12]. Due to the larger covalent radius of Sb they are 0.12–0.20 Å (Table 1) longer than the As–S bonds in the related $[(C_5Me_4Et)_3Co_3(\mu_3\text{-}S)(\mu_3\text{-}AsS_4)]I$ [5]. Whereas the latter complex consists of discrete ions, in **1** iodine is weakly coordinated at Sb. This may be concluded from the Sb(1)–I(1) distance of 3.215(1) Å and from a distorted trigonal-bipyramidal configuration of Sb(1) with I(1), S(2) and S(3) in roughly equatorial positions. In this case one may assume the lone pair in the axial position. Although the sum of the covalent radii of Sb and I is 2.73 Å, the range of 3.20 Å has been accepted in the literature for long covalent Sb–I bonds [13].

In conclusion the reaction of K_3SbS_3 with $[Cp^*_2Co_2I_4]$ provides a first example for the introduction of a mixed Sb–S ligand into a soluble transition metal main group hybrid cluster. Work employing other metal halide complexes is in progress showing a strong dependence of the products from the nature of the metal.

Table 1
Selected distances (Å) and angles (°) of $[Cp^*_3Co_3SbS_5I]$ (**1**)

Bond distances	
Co(1)–S(1)	2.264(2)
Co(1)–S(3)	2.237(2)
Co(2)–S(1)	2.269(2)
Co(2)–S(2)	2.241(2)
Co(3)–S(1)	2.253(2)
Co(3)–S(2)	2.255(2)
Co(3)–S(3)	2.260(2)
S(4)–S(5)	2.097(2)
Co(1)–S(4)	2.212(2)
Co(2)–S(4)	2.221(2)
Sb(1)–S(2)	2.454(2)
Sb(1)–S(3)	2.565(2)
Sb(1)–S(5)	2.429(2)
Sb(1)···I(1)	3.215(1)
Bond angles	
S(1)–Co(1)–S(4)	84.2(1)
S(1)–Co(1)–S(3)	84.4(1)
S(3)–Co(1)–S(4)	97.5(1)
S(1)–Co(2)–S(4)	83.9(1)
S(1)–Co(2)–S(2)	84.6(1)
S(2)–Co(2)–S(4)	98.2(1)
S(1)–Co(3)–S(2)	84.6(1)
S(2)–Sb(1)–S(5)	96.2(1)
S(3)–Sb(1)–S(5)	91.8(1)
S(2)–Sb(1)–S(3)	80.3(1)
S(5)–Sb(1)–I(1)	89.4(1)
S(2)–Sb(1)–I(1)	84.8(1)
S(3)–Sb(1)–I(1)	165.1(1)
Co(1)–S(1)–Co(2)	94.4(1)
Co(1)–S(1)–Co(3)	95.4(1)
Co(2)–S(1)–Co(3)	95.0(1)
Co(2)–S(2)–Co(3)	95.7(1)
Co(2)–S(2)–Sb(1)	111.0(1)
Co(3)–S(2)–Sb(1)	90.2(1)
Co(1)–S(3)–Co(3)	96.0(1)
Co(1)–S(3)–Sb(1)	110.9(1)
Co(3)–S(3)–Sb(1)	87.4(1)
Co(1)–S(4)–Co(2)	97.2(1)
Co(1)–S(4)–S(5)	112.2(1)
Co(2)–S(4)–S(5)	112.9(1)
S(4)–S(5)–Sb(1)	99.1(1)

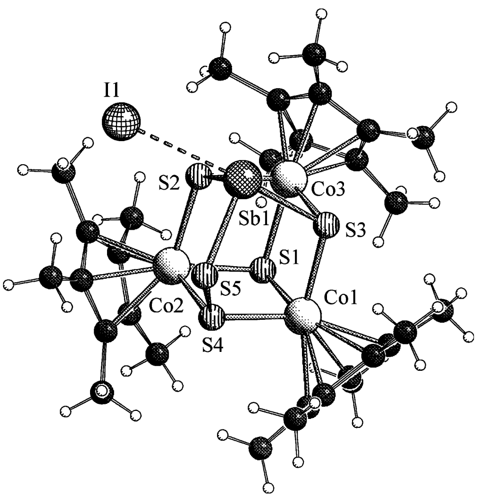

Fig. 1. Structure of $[Cp^*_3Co_3SbS_5I]$ (**1**). Only one of the two positions of the Sb(1)–S(5) unit and one of the disordered Cp* ligands is shown. The solvent (2 THF per molecule) is omitted.

3. Experimental

All manipulations were carried out under nitrogen by Schlenk techniques. ^{1}H-NMR spectra were recorded at 400 MHz. K_3SbS_3 was prepared as a bright yellow–brown powder in analogy to K_3AsS_3 [14] from K, S_8, and Sb_2S_3 in stoichiometric amounts in liquid NH_3. $[Cp^*_2Co_2I_4]$ was prepared due to literature methods [15].

3.1. Synthesis of $[Cp^*_3Co_3SbS_5I]$

A mixture of 850 mg (0.95 mmol) of $[Cp^*_2Co_2I_4]$, 560 mg (1.67 mmol) of K_3SbS_3 and 50 ml of THF was stirred for 16 h under reflux. After cooling to room temperature the resulting dark brown solution was filtered over 5 cm of SiO_2. Extraction of the SiO_2 phase with acetone and evaporation of the solvent gave a dark residue which was dissolved in acetone–toluene (5:1). Chromatography on SiO_2 (column 15 cm, ∅ 3 cm) gave upon elution with acetone–toluene (5:1) a light brown band, which was discarded, followed by a broad red–brown band. This band was collected in two equal fractions, the first fraction containing 138 mg (0.14 mmol, 22%) of $[Cp^*_3Co_3SbS_5I]$ (**1**). The second fraction contains **1** along with presumably $[Cp^*_3Co_3SbS_6I]$. The purity was monitored by means of ^{1}H-NMR spectra. Recrystallization of **1** from THF gave black–brown prisms.

Anal. Found: C, 37.00; H, 4.87. Calc. for $C_{30}H_{45}Co_3ISbS_5$ (991.48): C, 36.34; H, 4.47%. PI-ESI-MS: m/z 864.0 ($[Cp^*_3Co_3SbS_5]^+$). ^{1}H-NMR (CD_2Cl_2): δ 1.48 (s, 30H, Me), 1.46 (s, 15H, Me).

3.2. Crystallographic data for *1*·2THF

Dark plates (0.46 × 0.24 × 0.15 mm), triclinic $P\bar{1}$; cell: a, 11.2445(1); b, 13.924(2); c, 15.445(2) Å; α, 87.31(2)°; β, 70.44(2)°; γ, 71.64(1)°; V, 2158.0(5) Å^3, $Z = 2$; absorption correction: numerical. Transmission factor (min/max) 0.7079/0.4582, μ, 2.741 mm^{-1}. F(000) 1140, $D_{calc} = 1.748$ g cm^{-3}; Stoe-IPDS. Mo–K$_\alpha$ radiation, graphite monochromator, 30 004 collected reflections; 7632 unique reflections [$I > 4.0\sigma(I)$]. Structure solution by means of direct methods and Fourier synthesis. $R_1 = 0.0466$, $wR_2 = 0.1290$; residual electron density (max/min) 2.705/−1.119 e Å^{-3}, goodness-of-fit on $F^2 = 1.070$.

During structure refinement the following problems occurred: (a) with the aid of PLATON a further solvent accessible area was found, but it was impossible to refine any reasonable molecule from difference Fourier peaks. Therefore the midpoint, the size and the number of electrons in that void were refined and the contribution to the calculated structure factors of the disordered solvent was taken into account by back-Fourier transformation with the program SQUEEZE [16]. The void was found at (0.5, 0, 0.5) with a size of 290 Å^3. The electron number of 42e$^-$ corresponds exactly to another THF molecule; (b) the Cp* ligand [C(21)–C(30)] showed positional disorder. For the two orientations a ratio of 59:41 was found; (c) the insertion of S(5) between the edges Sb–S(4) and Sb–S(2), respectively, was realized in a 92:8 ratio. Concomitantly, two different Sb-positions Sb(1) and Sb(2) in the same ratio were found. The position of iodine should follow these two different Sb positions, but it was not possible to refine two different iodine positions. The highest residual electron density was found in the vicinity of I(1), indicating that a second position with equal Sb–I distances is plausible.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 190155. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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