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Cyclopentadienylcobalt complexes containing sulfosalt units: synthesis and structure of $[(C_5Me_4Et)_3Co_3AsS_5]I$ and $[(C_5Me_4Et)_3Co_3AsSe_5][Cr(CO)_5I]$

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Abstract

The reaction of K_3AsS_3 with $[Cp^{\#}Co(CO)I_2]$ ($Cp^{\#} = Cp^*$ (C_5Me_5) or Cp^x (C_5Me_4Et)) in DMF at 120°C gave violet $[Cp_2^{\#}Co_2As_2S_3]$ **1**$^{\#}$, dark brown $[Cp_3^{\#}Co_3AsS_6]I$ **2**$^{\#}$, and dark brown $[Cp_3^{\#}Co_3AsS_5]I$ **3**$^{\#}$. Whereas compounds **1**$^{\#}$ are already known, **2**$^{\#}$ and **3**$^{\#}$ were characterized by IR, ^{1}H-NMR and mass spectra. A crystal structure determination of **3**(Cp)^x reveals a salt-like character with $[Cp_3^xCo_3AsS_5]^+$ cations and iodide in a 1:1 ratio. In the cation the three Co atoms are connected by a μ_3-S and a μ_3-AsS_4 ligand, thus forming a distorted Co_3AsS_4-cube. An additional sulfur atom is inserted into one of the As–S edges. The reaction of $[Cp_2^{\#}Co_2I_4]$ with $K_2As_4Se_6$ in DMF at 120°C gave the brown salts $[Cp_3^{\#}Co_3AsSe_5]I$ **5**$^{\#}$. For characterization, compound **5**(Cp^x) was reacted with $[Cr(CO)_5THF]$. An X-ray diffraction analysis of the resulting $[Cp_3^xCo_3AsSe_5][Cr(CO)_5I]$ **8**(Cp^x) reveals a molecular structure similar to that of **3**(Cp)^x, but with a $[Cr(CO)_5I]^-$ anion. In the cation all sulfur atoms are replaced by Se atoms. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Arsenic; Sulfur; Selenium; Mixed ligands

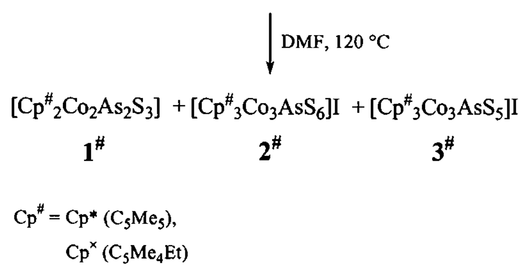
1. Introduction

The structure determining features of sulfosalt compounds are ψ-EX_3 pyramids (E = As, Sb, Bi; X = S, Se, Te) having a lone pair at E [1]. The ability of simple sulfosalt anions like $[AsS_3]^{3-}$ to undergo condensation reactions in the presence of suitable metal cations leads to the formation of an impressive number of extended solid state structures [2]. However, little is known on the stabilization of small ψ-EX_3 units by organometallic complex fragments [3]. Examples include the introduction of $[AsS_3]^{3-}$ as the bridging ligand in a dinuclear Ti complex [4] or the oxidative decarbonylation of binary transition metal carbonyls by mixed E/X cage anions [5]. In this paper we report on the metathesis reactions of K_3AsS_3 with $[Cp^{\#}Co(CO)I_2]$ ($Cp^{\#} = Cp^*$ (C_5Me_5) or Cp^x (C_5Me_4Et)) and of $K_2As_4Se_6$ with $[Cp_2^{\#}Co_2I_4]$.

2. Results

2.1. The system $K_3AsS_3/[Cp^{\#}Co(CO)I_2]$

Reaction of K_3AsS_3 with $[Cp^{\#}Co(CO)I_2]$ (molar ratio 2:3) in DMF at 120°C gave the already known [6] violet complexes $[Cp_2^{\#}Co_2As_2S_3]$ **1**$^{\#}$, the dark brown compounds $[Cp_3^{\#}Co_3AsS_6]I$ **2**$^{\#}$ in 18 (Cp*) and 16% yield (Cp^x), and $[Cp_3^{\#}Co_3AsS_5]I$ **3**$^{\#}$ (62 (Cp*) and 63% yield (Cp^x)) (Eq. (1)). At lower temperatures a decrease of the yields was observed.



$$3\,[Cp^{\#}Co(CO)I_2] + 2\,K_3AsS_3 \xrightarrow{DMF,\ 120\ °C} \underset{\mathbf{1}^{\#}}{[Cp^{\#}{}_2Co_2As_2S_3]} + \underset{\mathbf{2}^{\#}}{[Cp^{\#}{}_3Co_3AsS_6]I} + \underset{\mathbf{3}^{\#}}{[Cp^{\#}{}_3Co_3AsS_5]I} \quad (1)$$

$Cp^{\#} = Cp^*$ (C_5Me_5),
Cp^x (C_5Me_4Et)

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Complexes **1**$^{\#}$ were identified by comparison of their color and ^{1}H-NMR spectra with samples prepared from [$Cp_2^{\#}Co_2(CO)_2$] and As_4S_4 [6]. Complexes **2**$^{\#}$ and **3**$^{\#}$ were characterized by means of IR, positive FDMS, and ^{1}H-NMR spectroscopy. Correct elemental analyses are available only for **3**(Cp^x), for it was very difficult to crystallize the compounds. Fortunately, in the case of **3**(Cp^x) single crystals suitable for X-ray determination were obtained. An unexpected result of the crystallographic study (see below) is the ionic nature of this compound.

Another proof for the ionic character of **3**(Cp^x) is its transformation into [$Cp_3^xCo_3AsS_5$]PF_6 by an anion exchange with NH_4PF_6 in aqueous EtOH (Eq. (2)). Analytically pure **4**(Cp^x) was isolated in 90% yield.

$$\underset{\mathbf{3}(Cp^x)}{[Cp^x{}_3Co_3AsS_5]I} \xrightarrow[EtOH/H_2O]{NH_4PF_6} \underset{\mathbf{4}(Cp^x)}{[Cp^x{}_3Co_3AsS_5]PF_6} \qquad (2)$$

The IR spectra of **1**$^{\#}$–**3**$^{\#}$ exhibit the characteristic absorptions of the organic ligands, whereas that of **4**(Cp^x) shows an additional ν_{P-F} absorption at 845 cm^{-1}. The ^{1}H-NMR spectra of **2**(Cp*) and **3**(Cp*) exhibit two resonances in a 2:1 ratio originating from the Cp* ligands. The NMR spectra of **2**(Cp^x) and **4**(Cp^x) show four singlets in the ratio 2:2:4:4 for the diasterotopic ring CH_3 resonances, whereas the spectrum of **3**(Cp^x) contains a 2:2:2:2:2:2 pattern. Two quartets in the ratio 2:1 are observed for the CH_2 signals of the ethyl groups of both compounds, but only one triplet for the methyl groups. The interpretation of these data is supported by the crystallographic result obtained for **3**(Cp^x), which show two Co atoms (Co(1) and Co(3) in Fig. 1) to be equivalent.

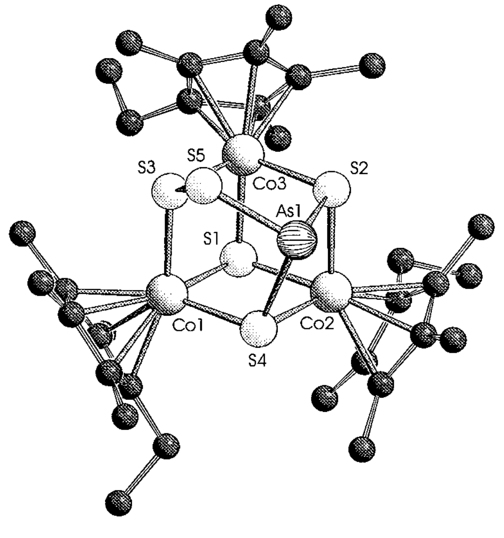
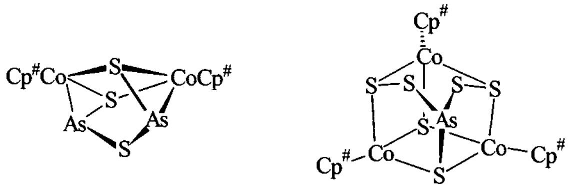


Fig. 1. Structure of the cation [$Cp_3^xCo_3AsS_5$]$^+$ of **3**(Cp^x). Only one of the three possible positions of the S(5)–As(1) unit is shown.



1$^{\#}$ **[2**$^{\#}$**]**$^+$

Scheme 1.

The structure of [$Cp_2^*Co_2As_2S_3$] **1**(Cp*) has already been determined previously [6a]. In this complex (and consequently in **1**(Cp^x)) a S–As–S–As–S chain bridges both Cp*Co moieties, thus forming a basket (Scheme 1).

From mass spectra it is evident that complexes [$Cp_3^{\#}Co_3AsS_6$]I **2**$^{\#}$ contain one additional sulfur compared to complexes **3**$^{\#}$. Therefore, the structure of **2**(Cp^x) may be derived from the structure of **3**(Cp^x) (see below) by insertion of the additional S atom into another As–S–Co bond of the cation of **3**(Cp^x), thus forming a second As–S–S arm (Scheme 1). This view is supported by the ^{1}H-NMR data which suggest the presence of two equivalent Co centers. Whereas the $As(S)(S_2)_2$ ligand is still unknown, complexes containing the analogous $As(Se)(Se_2)_2$ ligand have been synthesized from [$M(CO)_6$] (M = Mo, W) and [As_2Se_6]$^{2-}$ [7] or [WSe_4]$^{2-}$ and As_4Se_4 [8].

The crystal structure of **3**(Cp^x) consists of [$Cp_3^xCo_3AsS_5$]$^+$ cations (Fig. 1) and iodide in a 1:1 ratio. The core of the cation contains a distorted Co_3AsS_4-cube with an additional sulfur atom S(5) being inserted into an As–S edge of this cube. This insertion may take place between each of the three As–S edges, connecting S(5) to S(3), S(2) or S(4), respectively, and thus moving As(1) in three different directions away from the ideal cube corner. Unfortunately, all three orientations are found in the examined crystal. A refinement of this threefold orientation disorder leads to a ratio of 47.5:42.5:10 in the above given sequence for the position of the S(5)–As(1) unit.

The inorganic cores of all three structural arrangements possess a symmetry plane passing through the atoms As(1), S(5), S(3), S(1), and Co(2) in Fig. 1. The equivalency of the Co(1) and Co(3) centers is in agreement with the observed ^{1}H-NMR spectra. The overall geometry of the cation is related to that of [$Cp_3^xCo_3As_2S_4$]: formally, the replacement of S(3) in **3** by an As atom leads to the μ_3-As_2S_3 ligand [9], which provides one electron less than μ_3-AsS_4. The distances between S(1) and each of the three Co atoms in both clusters are comparable (Table 1). The relatively short bond lengths S(3)–S(5) and As(1)–S(5) in **3**(Cp^x) will not be discussed because of the triple disorder of S(5).

Complexes comprising a tetrachalcogenoarsenate(III) ligand are still very rare. The only sulfur-derived example is described in the anion [$Pt_3(AsS_4)_3$]$^{3-}$ in which

Table 1
Selected distances (Å) and angles (°) of $[Cp^x_3Co_3AsS_5]I$ **3**(Cp^x)

Co(1)–S(1)	2.266(2)	Co(3)–S(2)	2.246(2)
Co(1)–S(3)	2.220(2)	Co(3)–S(3)	2.230(2)
Co(1)–S(4)	2.225(2)	As(1)–S(2)	2.326(2)
Co(2)–S(1)	2.267(2)	As(1)–S(4)	2.356(2)
Co(2)–S(2)	2.249(2)	As(1)–S(5)	2.208(5)
Co(2)–S(4)	2.229(2)	S(3)–S(5)	2.049(4)
Co(3)–S(1)	2.262(2)		
S(3)–Co(1)–S(1)	84.5(1)	Co(3)–S(2)–Co(2)	95.2(1)
S(4)–Co(1)–S(1)	84.2(1)	Co(1)–S(3)–Co(3)	96.6(1)
S(3)–Co(1)–S(4)	96.9(1)	Co(1)–S(4)–Co(2)	96.9(1)
S(2)–Co(2)–S(1)	85.1(1)	As(1)–S(2)–Co(2)	84.9(1)
S(4)–Co(2)–S(1)	84.1(1)	As(1)–S(4)–Co(2)	84.6(1)
S(4)–Co(2)–S(2)	93.2(1)	As(1)–S(4)–Co(1)	107.0(1)
S(2)–Co(3)–S(1)	85.3(1)	As(1)–S(2)–Co(3)	110.1(1)
S(3)–Co(3)–S(1)	84.4(1)	S(5)–As(1)–S(2)	98.7(1)
S(3)–Co(3)–S(2)	93.5(1)	S(5)–As(1)–S(4)	100.4(1)
S(5)–S(3)–Co(1)	111.7(1)	S(2)–As(1)–S(4)	88.1(1)
S(5)–S(3)–Co(3)	114.2(1)	S(3)–S(5)–As(1)	96.7(2)

$$\begin{tikzcd}
{[Cp^{\#}_2Co_2I_4] + 1.4\ K_2As_4Se_6} \arrow[r, "DMF", "120\ ^\circ C"'] & {\begin{array}{c}[Cp^{\#}_3Co_3AsSe_5]I \\ \mathbf{5}^{\#}\end{array}} \arrow[d, "NH_4PF_6"] \\
 & {\begin{array}{c}[Cp^{\#}_3Co_3AsSe_5]PF_6 \\ \mathbf{6}^{\#}\end{array}}
\end{tikzcd}$$

Scheme 2.

three Pt(II) centers are bridged by three $[AsS_2(S_2)]^{3-}$ ligands [10].

2.2. Reaction of $K_2As_4Se_6$ with $[Cp^{\#}_2Co_2I_4]$

Reaction of $[Cp^{\#}_2Co_2I_4]$ with $K_2As_4Se_6$ in DMF at 120°C gave after 16 h the brown salts $[Cp^{\#}_3Co_3AsSe_5]I$ **5**$^{\#}$ in 95 (**5**(Cp^*)) and 91% (**5**(Cp^x)) yield (Scheme 2). The best yields were obtained in the molar ratio 1:1.4. At 20°C the reaction rate was much lower. Additionally, other compounds were observed, identification of which was impossible. Positive and negative LSI mass spectrometry of **5**$^{\#}$ provided a first hint for the salt-like character of these compounds, for the cations $[\mathbf{5}^{\#}]^+$ as well as iodide were found.

Recrystallization experiments gave a microcrystalline material only for **5**(Cp^x), but C, H elemental analyses agreed only roughly with the composition $[Cp^x_3Co_3AsSe_5]I$. The final proof was possible by the reaction of **5**(Cp^x) with $[Cr(CO)_5THF]$ and a crystal structure determination of one of the products (see below).

The ionic character of compounds **5**$^{\#}$ is also supported by their transformation into the PF_6 salts **6**$^{\#}$ by metathesis with NH_4PF_6 in aqueous EtOH (Scheme 2). For $[Cp^x_3Co_3AsSe_5]PF_6$ **6**(Cp^x) a satisfying elemental analysis was obtained. The IR spectra of **6**$^{\#}$ exhibit ν_{P-F} absorptions at 825 cm^{-1} as the only significant bands. The ^{1}H-NMR spectra of **5**$^{\#}$ and **6**$^{\#}$ show patterns closely related to those of compounds **3**$^{\#}$ containing the tetrathioarsenate(III) ligand. Although the resolution is not as good the observed similarities may indicate similar solid state structures. This has been confirmed by an X-ray diffraction analysis of **8**(Cp^x) (see below).

2.3. Reaction of $[Cp^x_3Co_3AsSe_5]I$ 5(Cp^x) with $[Cr(CO)_5THF]$

Reaction of $[Cp^x_3Co_3AsSe_5]I$ **5**(Cp^x) with excess $[Cr(CO)_5THF]$ (THF, 20°C, 16 h) gave **7**(Cp^x) in 75% and **8**(Cp^x) in 8% yield (Eq. (3)). From positive LSI mass spectroscopy there is evidence for the presence of the same cation as in **5**(Cp^x). However, negative LSIMS shows significant differences in the anionic part. Thus, in the mass spectrum of **7**(Cp^x) a fragment of composition $[\{Cr(CO)_5\}_2I]^-$ is dominating, whereas in the spectrum of **8**(Cp^x) the main peak corresponds to $[Cr(CO)_5I]^-$. This finding is also supported by the IR spectra, which exhibit significant differences in the region of terminal CO absorptions. A full characterization by means of elemental analyses and X-ray crystallography confirms **8**(Cp^x) to be a salt of composition $[Cp^x_3Co_3AsSe_5][Cr(CO)_5I]$. On this basis, for **7**(Cp^x) a formulation as $[Cp^x_3Co_3AsSe_5][\{Cr(CO)_5\}_2I]$ is very likely.

$$\begin{array}{c}[Cp^x_3Co_3AsSe_5]I \\ \mathbf{5}(Cp^x)\end{array} \xrightarrow{[Cr(CO)_5THF]} \begin{array}{c}[Cp^x_3Co_3AsSe_5][\{Cr(CO)_5\}_2I] \\ \mathbf{7}(Cp^x) \\ + \\ [Cp^x_3Co_3AsSe_5][Cr(CO)_5I] \\ \mathbf{8}(Cp^x)\end{array} \qquad (3)$$

The IR spectra show strong absorptions at 2065, 2045, 1940, and 1880 for **7**(Cp^x) and 1920 and 1860 cm^{-1} for **8**(Cp^x). The more complex pattern in the case of **7**(Cp^x) may be explained by the $[\{Cr(CO)_5\}\mu\text{-}I\{Cr(CO)_5\}]^-$ anion. The ^{1}H-NMR spectra of **7**(Cp^x) and **8**(Cp^x) are practically identical with that of **5**(Cp^x), thus excluding coordination of the $Cr(CO)_5$ fragments at one of the lone pairs of the inorganic core of the molecule. The spectroscopic findings have been confirmed by the solid state structure of **8**(Cp^x).

Single crystals of **8**(Cp^x) were obtained from toluene. The crystal structure consists of four molecular units in the cell and each molecular unit contains a $[Cp^x_3Co_3AsSe_5]^+$ cation and a $[Cr(CO)_5I]^-$ anion. The geometry of the cation (Fig. 2) is analogous to that of **3**(Cp^x), but with Se atoms instead of sulfur. As in **3**(Cp^x) the core may be derived from a distorted cubane-like structure, the additional Se atom (Se(5)) being inserted in one of the three As–Se edges. The

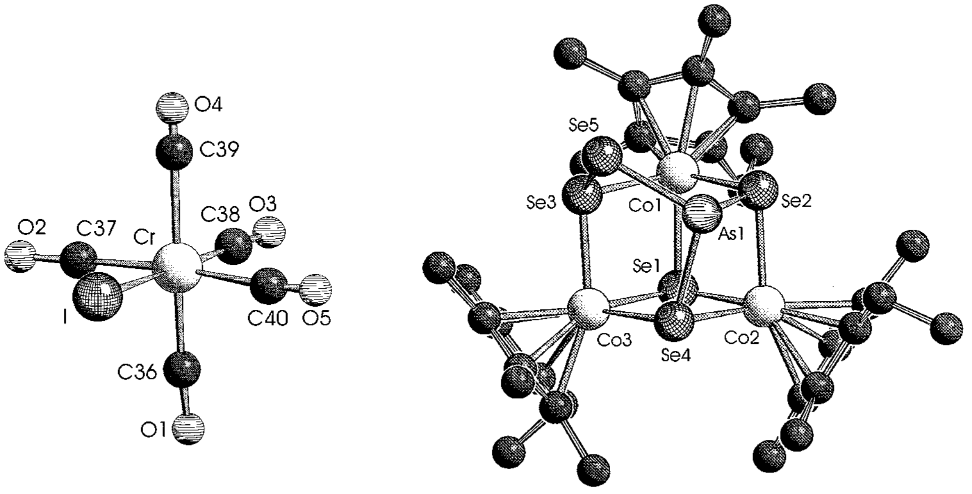


Fig. 2. Structure of **8**(Cp^x) showing the cation $[Cp^x_3Co_3AsSe_5]^+$ (right) and the anion $[Cr(CO)_5I]^-$ (left). Only one of the two positions of the As(1)–Se(5) unit is shown.

atoms As(1) and Se(5) exist in this crystal in only two different orientations, the degree of disorder being 91:9. In Fig. 2 a symmetry plane goes through As(1), Se(1), Se(3), Se(5), and Co(2). Consequently, two of the Co centers are chemically equivalent, which is in accord with the ^{1}H-NMR spectra.

Due to the larger covalent radius of Se the Co–Se, As–Se, and Se–Se bonds are by ca. 0.1 Å longer than in the related sulfur cation [**3**(Cp^x)]$^+$ (Table 2). To our knowledge **8**(Cp^x) contains the first example of a tetraselenoarsenate(III) ligand. Sulfur derived examples have been described aside from **3**(Cp^x) in the anion $[Pt_3(AsS_4)_3]^{3-}$ [10]. Very recently the new mixed Zintl ion $[M_7As_3Q_{13}]^{4-}$ has been described containing bridging $[AsQ_4]^{3-}$ units (M = Cu, Ag; Q = Se, Te) [11]. Two $[AsTe_4]^{3-}$ ligands are part of $[Fe_2(CO)_4As_2Te_8]^{2-}$ [12].

The structure of the $[Cr(CO)_5I]^-$ anion is presented in Fig. 2. It is similar to that already described in the literature [13] with the exception of the CO groups 'C(39)' and 'C(40)'. The corresponding Cr–C bonds are too long, being compensated by too short C–O bonds (Table 2). As a possible explanation we suggest a slight disorder of iodine, which may occupy to some degree the positions of the CO groups 'C(39)' and 'C(40)'. This would result in a shift of electron density towards the middle of the CO dumb-bells.

2.4. Conclusions

K_3AsS_3 and $K_2As_4Se_6$ are convenient sources for sulfosalt ligands as has been demonstrated in their reactions with $[Cp^{\#}Co(CO)I_2]$ and $[Cp^{\#}_2Co_2I_4]$. Although the mixed main group element sources are structurally very different, the products exhibit close structural similarities. In all cases the ψ-AsX_3 (X = S, Se) pyramid has formed having one (**3**($Cp^{\#}$), **5**($Cp^{\#}$)) or two (**2**($Cp^{\#}$)) dichalcogeno side arms. This means that the As/X ratio in the products is lower as in the inorganic precursors. This may indicate the participation of fragmentation/insertion pathways, as far as the AsS_3 ligand is concerned. The original idea to coordinate the As_4Se_6 cage as a whole could not be realized. Thus far, the $[As_4Se_6]^{2-}$ ligand has been stabilized by means of large cations, e.g. $[PPh_4]^+$ [14] or [K(2.2.2-crypt)]$^+$ [15], but no example is known for a transition metal cluster containing the intact ligand [7,11].

Table 2
Selected distances (Å) and angles (°) of $[Cp^x_3Co_3AsSe_5][Cr(CO)_5I]$ **8**(Cp^x)

Co(1)–Se(1)	2.389(1)	As(1)–Se(2)	2.429(1)
Co(1)–Se(2)	2.337(1)	As(1)–Se(4)	2.416(1)
Co(1)–Se(3)	2.313(1)	As(1)–Se(5)	2.334(1)
Co(2)–Se(1)	2.378(1)	Cr–C(36)	1.86(1)
Co(2)–Se(2)	2.365(1)	Cr–C(37)	1.89(1)
Co(2)–Se(4)	2.369(1)	Cr–C(38)	1.85(1)
Co(3)–Se(1)	2.391(1)	Cr–C(39)	2.05(1)
Co(3)–Se(3)	2.310(1)	Cr–C(40)	2.01(1)
Co(3)–Se(4)	2.339(1)	I–Cr	2.792(2)
Se(3)–Se(5)	2.387(1)		
Se(1)–Co(1)–Se(3)	82.9(1)	Co(1)–Se(3)–Co(3)	98.7(1)
Se(1)–Co(1)–Se(2)	85.8(1)	Co(2)–Se(4)–Co(3)	95.9(1)
Se(2)–Co(1)–Se(3)	99.0(1)	Se(5)–Se(3)–Co(1)	107.6(1)
Se(1)–Co(2)–Se(2)	85.5(1)	Se(5)–Se(3)–Co(3)	108.1(1)
Se(1)–Co(2)–Se(4)	84.7(1)	As(1)–Se(2)–Co(1)	108.9(1)
Se(2)–Co(2)–Se(4)	90.1(1)	As(1)–Se(2)–Co(2)	87.1(1)
Se(1)–Co(3)–Se(3)	82.9(1)	As(1)–Se(4)–Co(2)	87.3(1)
Se(1)–Co(3)–Se(4)	85.1(1)	As(1)–Se(4)–Co(3)	109.1(1)
Se(3)–Co(3)–Se(4)	98.8(1)	Se(2)–As(1)–Se(5)	100.9(1)
Co(1)–Se(1)–Co(2)	93.4(1)	Se(4)–As(1)–Se(5)	101.9(1)
Co(1)–Se(1)–Co(3)	94.5(1)	Se(2)–As(1)–Se(4)	87.4(1)
Co(2)–Se(1)–Co(3)	94.3(1)	Se(3)–Se(5)–As(1)	95.3(1)
Co(1)–Se(2)–Co(2)	95.1(1)		

3. Experimental

All manipulations were carried out under nitrogen by Schlenk techniques. ^{1}H-NMR spectra were recorded at 250 MHz. K_3AsS_3 was prepared from K, S_8 and As_2S_3 in liquid NH_3 [16]. $K_2As_4Se_6$ was obtained as a red-brown powder from K and As_4Se_4 in liquid NH_3 [14,15] and was employed without further purification. $[Cp^{\#}Co(CO)I_2]$ and $[Cp_2^{\#}Co_2I_4]$ were prepared following the literature [17].

3.1. Reaction of K_3AsS_3 with $[Cp^{\#}Co(CO)I_2]$

A suspension of 0.19 g (0.67 mmol) of K_3AsS_3 and 1 mmol of $[Cp^{\#}Co(CO)I_2]$ in 50 ml of DMF was stirred for 16 h at 120°C. After vacuum distillation of the solvent the brown residue was suspended in toluene, filtered and washed with 3 × 10 ml of toluene to give a solid (named A). The filtrates were concentrated to 15 ml and then chromatographed on SiO_2 (column 5 cm, Ø 3 cm). Elution with toluene gave a violet band containing $[Cp_2^{\#}Co_2As_2S_3]$ **1**$^{\#}$ in 16 (Cp*) and 12% (Cp^x) yield. The products are spectroscopically identical with independently prepared samples [6]. Elution with acetone gave a brown band which was combined with solid A. This solid was dissolved in CH_2Cl_2–toluene (1:1) and chromatographed on silanized SiO_2 (column 15 cm, Ø 3 cm). Elution with CH_2Cl_2–toluene (1:1) gave a brown band, the first 50 ml of which were discarded. The following 100 ml contained brown $[Cp_3^{\#}Co_3AsS_6]I$ **2**$^{\#}$ (Cp*, 18; Cp^x, 16% yield). Elution with CH_2Cl_2 gave brown $[Cp_3^{\#}Co_3AsS_5]I$ **3**$^{\#}$ (Cp*, 62; Cp^x, 63%). Crystallization succeeded only in the case of **3**(Cp*) (from CH_2Cl_2 by stepwise layering with toluene and pentane) and **3**(Cp^x) (from acetone and stepwise addition of toluene and pentane).

Complex **2**(Cp*): $C_{30}H_{45}AsCo_3IS_6$ (976.7) — PI-FDMS (CH_2Cl_2): 848.9 ($[C_{30}H_{45}AsCo_3S_6]^+$) — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.44$ (s, 15), 1.46 (s, 30). Complex **2**(Cp^x): $C_{33}H_{51}AsCo_3IS_6$ (1018.8) — PI-FDMS (CH_2Cl_2): 891.0 ($[C_{33}H_{51}AsCo_3S_6]^+$) — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.01$ (t, 9; $^3J_{H-H} = 7.5$ Hz), 1.43 (s, 6), 1.46 (s, 6), 1.47 (s, 12), 1.49 (s, 12), 2.08 (q, 4; $^3J_{H-H} = 7.5$ Hz), 2.10 (q, 2; $^3J_{H-H} = 7.5$ Hz).

Complex **3**(Cp*): Anal. Found: C, 36.98; H, 4.72. Calc. for $C_{30}H_{45}AsCo_3IS_5$ (944.6): C, 38.14; H, 4.80% — PI-FDMS (CH_2Cl_2): 816.6 ($[C_{30}H_{45}AsCo_3S_5]^+$) — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.49$ (s, 15), 1.51 (s, 30). Complex **3**(Cp^x): Anal. Found: C, 40.18; H, 5.21. Calc. for $C_{33}H_{51}AsCo_3IS_5$ (986.7): C, 40.17; H, 5.21% — PI-FDMS (CH_2Cl_2): 859.1 ($[C_{33}H_{51}AsCo_3S_5]^+$) — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.03$ (t, 9; $^3J_{H-H} = 7.5$ Hz), 1.482 (s, 6), 1.505 (s, 6), 1.511 (s, 6), 1.512 (s, 6), 1.527 (s, 6), 1.532 (s, 6), 2.12 (q, 4; $^3J_{H-H} = 7.5$ Hz), 2.13 (q, 2; $^3J_{H-H} = 7.5$ Hz).

*3.2. Synthesis of $[Cp_3^xCo_3AsS_5]PF_6$ **4**(Cp^x)*

The solutions of 50 mg (0.3 mmol) of NH_4PF_6 in 7 ml of H_2O and 148 mg (0.15 mmol) of $[Cp_3^xCo_3AsS_5]I$ **3**(Cp^x) in 7 ml of EtOH were combined to give a brown precipitate, which was filtered and washed with 3 × 5 ml of H_2O and then 3 × 3 ml of Et_2O. The dried residue was dissolved in CH_2Cl_2 and filtered. After evaporation of the solvent $[Cp_3^xCo_3AsS_5]PF_6$ **4**(Cp^x) was obtained in 90% yield. Recrystallization occurred from CH_2Cl_2 which was layered with ether.

Complex **4**(Cp^x): Anal. Found: C, 39.43; H, 5.25. Calc. for: $C_{33}H_{51}AsCo_3F_6PS_5$ (1004.8): C, 39.45; H, 5.12% — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.02$ (t, 9; $^3J_{H-H} = 7.5$ Hz), 1.47 (s, 6), 1.49 (s, 6), 1.50 (s, 12), 1.52 (s, 12H), 2.11 (q, 4; $^3J_{H-H} = 7.5$ Hz), 2.12 (q, 2; $^3J_{H-H} = 7.5$ Hz) — IR (KBr, cm^{-1}): 845 (vs; ν_{P-F}).

3.3. Reaction of $K_2As_4Se_6$ with $[Cp_2^{\#}Co_2I_4]$

The mixture of 0.45 g (0.53 mmol) of $K_2As_4Se_6$, 0.37 mmol of $[Cp_2^{\#}Co_2I_4]$ and 50 ml of DMF was stirred for 16 h at 120°C. After removal of the solvent in vacuo the brown residue was dissolved in CH_2Cl_2, filtered and washed with CH_2Cl_2 until the washings were colorless. The filtrate was concentrated to 20 ml and then transferred to the top of a column containing SiO_2 (8 cm, Ø 3 cm). Impurities were eluted with 50 ml of CH_2Cl_2 and 50 ml of toluene–acetone (1:1). The brown compounds $[Cp_3^{\#}Co_3AsSe_5]I$ **5**$^{\#}$ were eluted with acetone in yields of 95 (**5**(Cp*)) and 91% (**5**(Cp^x)). Crystals suitable for elemental analysis were only obtained for **5**(Cp^x) by dissolving it in warm toluene followed by slow cooling to −20°C.

Complex **5**(Cp*): $C_{30}H_{45}AsCo_3ISe_5$ (1179.1): PI-LSIMS(NBA–CH_2Cl_2): 1052.7($[C_{30}H_{45}AsCo_3Se_5]^+$) — NI-LSIMS (NBA–$CH_2Cl_2$): 126.8 ($I^-$) — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.57$ (s, 15), 1.59 (s, 30). Complex **5**(Cp^x): Anal. Found: C, 33.78; H, 4.21. Calc. for $C_{33}H_{51}AsCo_3ISe_5$ (1221.2): C, 32.46; H, 4.21% — PI-FDMS (CH_2Cl_2): 1094.7 ($[C_{33}H_{51}AsCo_3Se_5]^+$) — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.028$ (t, 3; $^3J_{H-H} = 7.5$ Hz), 1.033 (t, 6; $^3J_{H-H} = 7.5$ Hz), 1.569 (s, 6), 1.573 (s, 6), 1.592 (s, 6), 1.594 (s, 6), 1.596 (s, 6), 1.599 (s, 6), 2.16 (q (br), 6).

*3.4. Synthesis of $[Cp_3^{\#}Co_3AsSe_5]PF_6$ (**6**$^{\#}$)*

The compounds $[Cp_3^{\#}Co_3AsSe_5]PF_6$ (**6**$^{\#}$) were prepared from 50 mg (0.3 mmol) of NH_4PF_6 in 7 ml of H_2O and 0.15 mmol of $[Cp_3^{\#}Co_3AsSe_5]I$ (**5**$^{\#}$) in 7 ml of EtOH as described above for $[Cp_3^xCo_3AsS_5]PF_6$ (**4**(Cp^x)). The yields were 92 (**6**(Cp*)) and 89% (**6**(Cp^x)). Crystals were obtained only for **6**(Cp^x) from CH_2Cl_2–ether (1:1).

Table 3
Crystal data for compounds **3**(Cp^x) and **8**(Cp^x)

	3(Cp^x)	**8**(Cp^x)
Empirical formula	$C_{33}H_{51}AsCo_3IS_5$	$C_{38}H_{51}AsCo_3CrIO_5Se_5$
Formula weight	986.65	1412.89
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions		
a, (Å)	11.238(1)	11.131(1)
b, (Å)	11.784(1)	18.608(1)
c, (Å)	14.807(1)	22.616(1)
α, (°)	87.6(1)	
β, (°)	76.0(1)	95.8(1)
γ, (°)	88.9(1)	
V (Å^3)	1900.7(3)	4659.9(6)
Z	2	4
D_{calc} (g cm^{-3})	1.724	2.014
F(000)	992	2719
Crystal size (mm)	$0.26 \times 0.10 \times 0.03$	$0.50 \times 0.08 \times 0.06$
Diffractometer	STOE-IPDS	STOE-IPDS
Temperature (K)	173(1)	173(1)
θ (°)	1.87–25.74	2.12–25.72
No. of reflections collected	15 196	32 746
No. of independent reflections	6766	8828
R_{int}	0.0426	0.0491
No. of observed reflections [$I > 2\sigma$]	4493	6209
μ (mm^{-1})	3.267	6.58
No. of data/restraints/parameters	6766/0/403	8828/0/494
Goodness-of-fit on F^2	0.912	0.954
T_{max}, T_{min}	0.8416, 0.5849	0.7269, 0.2178
Absorption correction	numerical	numerical
R_1, wR_2 [$I > 2\sigma$]	0.0464, 0.1054	0.0485, 0.1315
R_1, wR_2 (all data)	0.0779, 0.1149	0.0723, 0.1413

Complex **6**(Cp*): ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.56$ (s, 15), 1.57 (s, 30). Complex **6**(Cp^x): Anal. Found: C, 31.22; H, 4.15. Calc. for $C_{33}H_{51}AsCo_3F_6PSe_5$ (1239.2): C, 31.98; H, 4.15% — ^{1}H-NMR ($CHCl_3$-*d*): $\delta = 1.02$ (t, 9; $^3J_{H-H} = 7.5$ Hz), 1.554 (s, 12), 1.574 (s, 6), 1.581 (s, 6), 1.585 (s, 12), 2.15 (q (br), 6). IR (KBr, cm^{-1}): 825 (vs) (ν_{P-F}).

3.5. Reaction of [$Cp^x_3Co_3AsSe_5$]I with [$Cr(CO)_5THF$]

195 mg (0.16 mmol) of **5**(Cp^x) was added to a solution of 0.5 mmol of [$Cr(CO)_5THF$] (from 110 mg of [$Cr(CO)_6$]) in 80 ml of THF. The resulting mixture was stirred for 16 h at 20°C. After evaporation of the solvent the brown residue was dissolved in toluene–CH_2Cl_2 (2:1) and chromatographed on SiO_2 (column 15 cm, Ø 3 cm). Elution with toluene–CH_2Cl_2 (2:1) gave a red band of an as yet unidentified product in small quantities. With acetone a broad brown band was eluted containing [$Cp^x_3Co_3AsSe_5$][{$Cr(CO)_5$}$_2$I] **7**(Cp^x) in 75% yield followed by a narrow brown band containing [$Cp^x_3Co_3AsSe_5$][$Cr(CO)_5I$] **8**(Cp^x) in 8% yield. **8**(Cp^x) was recrystallized from toluene, whereas it was impossible to purify **7**(Cp^x) by recrystallization.

Complex **7**(Cp^x): $C_{43}H_{51}AsCo_3Cr_2IO_{10}Se_5$ (1605.3): PI-LSIMS (NBA–acetone): 1095.0 ([$Cp^x_3Co_3AsSe_5$]$^+$) — NI-LSIMS (NBA–acetone): 510.5 ([{$Cr(CO)_5$}$_2$I]$^-$, rel. intensity 100%), 318.7 ([$Cr(CO)_5I$]$^-$, 67%) — IR (KBr, cm^{-1}): 2065 (s), 2045 (m), 1940 (s), 1880 (s) (ν_{C-O}).

Complex **8**(Cp^x): Anal. Found: C, 32.54; H, 3.72. Calc. for $C_{38}H_{51}AsCo_3CrIO_5Se_5$ (1413.2): C, 32.17; H, 3.20% — PI-LSIMS (NBA–acetone): 1095.0 ([$Cp^x_3Co_3AsSe_5$]$^+$) — NI-LSIMS (NBA–acetone): 510.5 ([{$Cr(CO)_5$}$_2$I]$^-$, rel. intensity 65%), 318.7 ([$Cr(CO)_5I$]$^-$, 100%), 126.8 (I$^-$, 8%). — IR (KBr, cm^{-1}): 1920 (s), 1860 (m) (ν_{C-O}).

3.6. Crystal structure determinations of 3(Cp^x) and 8(Cp^x)

Data were collected on a STOE-IPDS diffractometer. The structures were solved by direct methods (heavy atom positions) and subsequent difference Fourier syntheses (SHELX-97). Crystal data and refinement details are given in Table 3.

Starting with one orientation of the S(5)–As(1) unit, the difference Fourier syntheses showed reasonable electron density in the vicinity of these two atoms. Geometrically these residues together with the already located atoms seemed to maintain the threefold symmetry along the body diagonal of the cube, formed by sulfur and cobalt atoms. Therefore it became evident, that in the examined crystal the S(5)–As(1) unit exists in three orientations. Refinement of these three orientations with the option PART of the SHELXL-97 program led to a substantial improvement of all structural parameters. The occupation factor for each PART was refined with the restriction that all three values must add to 1.0. The refinement converged and showed, that in the examined crystal the orientation with S(5) connected to S(3), S(2) and S(4), respectively, are present in a ratio of 47.5:42.5:10.

The structure solution of **8**(Cp^x) with direct methods proceeded without problems. The difference Fourier syntheses showed considerable residual electron density in proximity to the uncoordinated As–Se unit. In contrast to **3**(Cp^x) two further electron maxima were found, showing that in this crystal the Se(5)–As(1) unit exists in only two orientations. Again, this disorder was refined with the option PART of the SHELXL-97 program, all parameters improved significantly and the refined occupancy factors of each PART showed, that the two orientations are present in a ratio of 91:9. After refinement there were no residual electron density maxima within the cation.

Difficulties were observed during refinement of the $[Cr(CO)_5I]^-$ anion. A detailed look at the shape of the anisotropic ellipsoids and the interatomic distances revealed anomalies for the CO dumb-bells ‘C(39)’ and ‘C(40)’: the Cr–C distances are too long and the corresponding C–O distances are too short. Consideration of residual electron maxima by difference Fourier syntheses did not result in any disordering of CO groups. Thus, we propose that the iodine atom replaces to a low percentage the position of both dumb-bells in question. Unfortunately, a mathematical treatment of the iodine disorder is not possible, which finally affects the structure solution and the temperature factors.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. CCDC 154643 and 154644 for compounds **8**(Cp^x) and **3**(Cp^x), respectively. 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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References

[1] (a) W. Nowacki, Schweiz. Min. Petr. Mitt. 49 (1969) 109. (b) Y. Takeuchi, R. Sadanaga, Z. Kristallogr. 130 (1969) 346.

[2] For leading reviews see: (a) W.S. Sheldrick, M. Wachhold, Angew. Chem. 109 (1997) 214; Angew. Chem. Int. Ed. Engl. 36 (1997) 206. (b) W.S. Sheldrick, J. Chem. Soc. Dalton Trans. (2000) 3041.

[3] J. Wachter, Angew. Chem. 110 (1998) 782; Angew. Chem. Int. Ed. Engl. 37 (1998) 750.

[4] G.A. Zank, T.B. Rauchfuss, S.R. Wilson, A.L. Rheingold, J. Am. Chem. Soc. 106 (1984) 7621.

[5] (a) G.W. Drake, J.W. Kolis, Coord. Chem. Rev. 137 (1994) 131. (b) J.W. Kolis, D.M. Young, in: S.M. Kauzlarich (Ed.), Chemistry, Structure and Bonding of Zintl Phases and Ions, VCH, Weinheim, 1996, p. 225.

[6] (a) H. Brunner, H. Kauermann, B. Nuber, J. Wachter, M.L. Ziegler, Angew. Chem. 98 (1986) 551; Angew. Chem. Int. Ed. Engl. 25 (1986) 557. (b) H. Brunner, H. Kauermann, L. Poll, B. Nuber, J. Wachter, Chem. Ber. 129 (1996) 657.

[7] S.C. O’Neal, W.T. Pennington, J.W. Kolis, Inorg. Chem. 31 (1992) 888.

[8] S.C. O’Neal, W.T. Pennington, J.W. Kolis, J. Am. Chem. Soc. 113 (1991) 710.

[9] H. Brunner, B. Nuber, L. Poll, J. Wachter, Angew. Chem. 105 (1993) 1699; Angew. Chem. Int. Ed. Engl. 32 (1993) 1628.

[10] J.-H.K. Chou, M.G. Kanatzidis, Inorg. Chem. 33 (1994) 5372.

[11] C. Wang, R.C. Haushalter, Inorg. Chim. Acta 288 (1999) 1.

[12] T.M. Martin, P.T. Wood, G.L. Schimek, W.T. Pennington, J.W. Kolis, Inorg. Chem. 34 (1995) 4385.

[13] P.H. van Rooyen, L. Geer, S. Lotz, Acta Crystallogr. Sect. C 46 (1990) 1432.

[14] M.A. Ansari, J.A. Ibers, J.W. Kolis, S.C. O’Neal, W.T. Pennington, Polyhedron 11 (1992) 1877.

[15] D.M. Smith, C.-W. Park, J.A. Ibers, Inorg. Chem. 35 (1996) 6682.

[16] M.G. Kanatzidis, J.H. Chou, J. Solid State Chem. 127 (1996) 187.

[17] S.A. Frith, J.L. Spencer, W.E. Geiger, J.R. Edwin, J. Edwin, Inorg. Synth. 23 (1985) 15.