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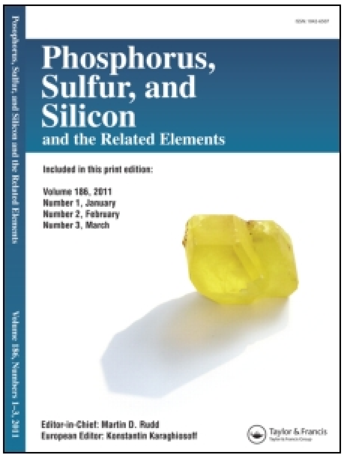

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Synthesis and Structures of New Polynuclear Tin Chalcogen Compounds

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Novel tin chalcogen ring and cage compounds are accessible by the reaction of $[\{Cp^*(CO)_2Fe\}SnCl_3]$ with chalcogen transfer reagents like Ag_2O, Na_2S and $E(SiMe_3)_2$ (E = S, Se).

Keywords: Tin; Chalcogen; Cage compounds; Crystal structure

1. INTRODUCTION

Di- and trifunctional tin halides of the type R_2SnCl_2 and $RSnCl_3$ (R = $\{(CO)_4Co\}$, $\{Cp(CO)_2Fe\}$, $\{Cp(CO)_3Mo\}$, etc.) react with silylated chalcogens $E(SiMe_3)_2$ (E = S, Se, Te) to give organometal substituted tin chalcogen compounds [1, 2]. We now have been interested to use $[\{Cp^*(CO)_2Fe\}SnCl_3]$ (1) ($Cp^* = Me_5C_5$), which contains the sterically demanding Me_5C_5 ligand, as starting compound for the synthesis of new $\{Cp^*(CO)_2Fe\}$ substituted tin chalcogen rings and cages.

2. RESULTS

2.1. Synthesis and structure of $[\{Cp^*(CO)_2Fe\}SnCl_3]$ (1)

The starting compound $[\{Cp^*(CO)_2Fe\}SnCl_3]$ (1) is obtained from the insertion reaction of $SnCl_2$ into the Fe-Cl bond of $[Cp^*(CO)_2FeCl]$. The X-ray crystal structure determination [3] revealed, that 1 contains a tin atom which is coordinated nearly tetrahedrally by three chlorine atoms and the iron atom of the $\{Cp^*(CO)_2Fe\}$ fragment. The molecular geometry of 1 is unexecptional with Sn-Fe (246.0(1) pm) and Sn-Cl distances (235.7(1)-236.2(2) pm) lying in the expected ranges. The steric influence of the bulky $\{Cp^*(CO)_2Fe\}$ group leads to relatively large Fe-Sn-Cl angles (118.3(1)-120.6(1)°) and comparatively small Cl-Sn-Cl angles (98.5(1)-97.0(1)°).

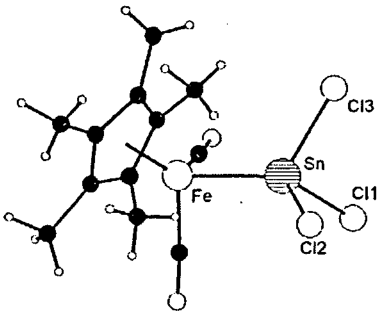
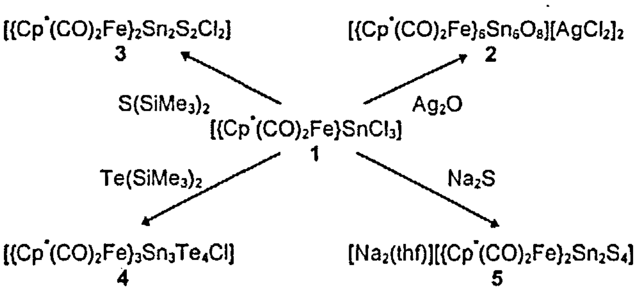


FIGURE 1. The molecular structure of **1**
Selected bond lenghts (pm) and angles (°):
Sn-Fe 246.0(1), Sn-Cl(1) 235.7(1), Sn-Cl(2) 236.2(2), Sn-Cl(3) 236.1(1), Cl(1)-Sn-Cl(2) 99.6(1), Cl(1)-Sn-Cl(3) 97.0(1), Cl(2)-Sn-Cl(3) 98.5(1), Fe-Sn-Cl(1) 118.3(4), Fe-Sn-Cl(2) 118.4(1), Fe-Sn-Cl(3) 120.6(1)

2.2. *The synthesis of {Cp*(CO)$_2$Fe} substituted tin chalcogen compounds*

Scheme 1 summarizes the reactions of **1** with the chalcogen transfer reagents Ag_2O, $S(SiMe_3)_2$, $Te(SiMe_3)_2$ and Na_2S.



SCHEME 1. Reactions of **1** with chalcogen transfer reagents

2.2.1 *The synthesis of [{Cp*(CO)$_2$Fe}$_6$Sn$_6$O$_8$][AgCl$_2$]$_2$ (2)*

On treatment with Ag_2O, **1** reacts in aqueous acetone to give a yellow solution and a white precipitate of AgCl. After filtration, removal of the solvent and recrystallisation from thf/n-heptane, yellow orange crystals of $[\{Cp^*(CO)_2Fe\}_6Sn_6O_8][AgCl_2]_2$ (**2**) can be obtained. **2** is ionic in character and contains $[\{Cp^*(CO)_2Fe\}_6Sn_6O_8]^{2+}$ cations and $[AgCl_2]^-$ anions. The cluster cation (Fig. 2) consists of an octahedral arrangement of six $\{Cp^*(CO)_2Fe\}Sn$ groups. Each of the 8 triangular faces of the Sn_6-octahedron is capped by a μ_3-oxygen atom. The resulting Sn_6O_8 cage can be described as a distorted rhombic dodecahedron, which consists of 12 Sn_2O_2 four-membered rings. In the cluster cation, the tin atoms exhibit a square-pyramidal coordination geometry with four oxygen atoms in the basal sites of the square pyramid and the iron atom of the {$Cp^*(CO)_2Fe$} group in the apex. The Sn-O distances vary from 209.2(3) to 212.5(3) pm. This is in accordance with the Sn-O bond lengths observed in other tin oxygen clusters, e. g. $[\{BuSn)_{12}O_{14}(OH)_6]^{2+}$, [4, 5], $[(^iPrSn)_{12}O_{14}(OH)_6]^{2+}$ [6]. The $[AgCl_2]^-$ anion (Fig. 4) is almost linear with Ag-Cl distances of 230.5(3) pm and a Cl-Ag-Cl angle of 178.0(1)°. Similiar values have been observed in $[K(2,2,2\text{-crypt})][AgCl_2]$ [7].

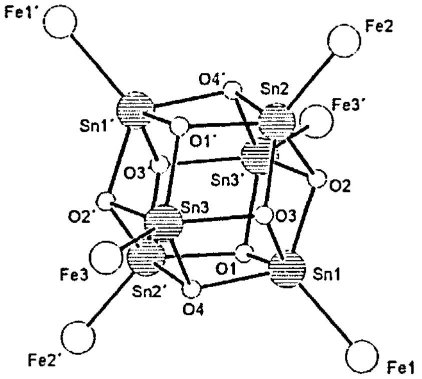


FIGURE 2.
The molecular structure of the cluster cation $[\{Cp^*(CO)_2Fe\}_6O_8]^{2+}$ (the CO and Cp^* groups are omitted for clarity)

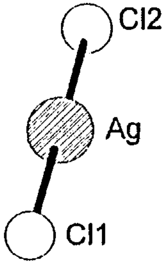


FIGURE 3.
The molecular structure of the $[AgCl_2]^-$ anion

2.2.2 The synthesis of Sn-S and Sn-Te derivatives

For the synthesis of Sn-S and Sn-Te derivatives, $S(SiMe_3)_2$, $Te(SiMe_3)_2$ and Na_2S were used as chalcogen sources.

Treatment of **1** with $S(SiMe_3)_2$ affords $[\{Cp^*(CO)_2Fe\}_2Sn_2S_2Cl_2]$ (**3**), which contains a four-membered Sn_2S_2 ring with an alternating arrangement of Sn and S atoms (Fig. 4). **3** is situated about a crystallographic center of inversion, and therefore the Sn_2S_2 ring is exactly planar. The tin atoms are coordinated almost tetrahedrally by two bridging S atoms, a terminal {$Cp^*(CO)_2Fe$} group and a chlorine atom. The terminal substituents are *trans* with respect to the ring plane. Although **3** contains two Sn-Cl bonds, no further reaction with $S(SiMe_3)_2$ occurs, even if an excess of $S(SiMe_3)_2$ is added and elevated temperatures are applied. This means that the reactive Sn-Cl bonds are protected effectively by the sterically demanding {$Cp^*(CO)_2Fe$} groups.

$[\{Cp(Ph_3P)Ni\}_2Sn_2S_2Cl_2]$, which is an analogue of **3** shows a similar low reactivity towards $S(SiMe_3)_2$ [8].
The Te derivative $[\{Cp^*(CO)_2Fe\}_3Sn_3Te_4Cl]$ (**4**) is obtained from the reaction of **1** with $Te(SiMe_3)_2$. Unlike **3**, **4** contains a bicyclic Sn_3Te_4-core, which consists of a Sn_3Te_3 ring (with chair conformation) and an additional μ_2-bridging Te atom (Fig. 5). The tin atoms exhibit two coordination modes: Sn1 and Sn2 are coordinated roughly tetrahedrally by three bridging Te atoms and a terminal $\{Cp^*(CO)_2Fe\}$ group, whereas Sn3 is bound to two tellurium atoms, a terminal Cl atom and a $\{Cp^*(CO)_2Fe\}$ group. In contrast to **3**, the four-membered ring Sn1-Te1-Sn2-Te2 is puckered with a folding angle of 26° (with respect to the line Te1-Te2). The Sn_3Te_4 framework of **4** is closely related to the structure of $[\{Cp(CO)_2Fe\}_3Sn_3Se_4Cl]$ [9].

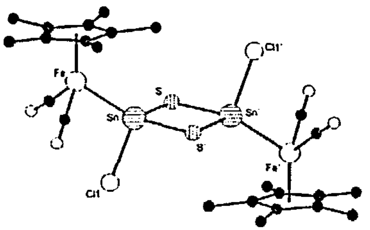


FIGURE 4.
The molecular structure of **3** (H atoms omitted for clarity)
Selected bond lenghts (pm) and angles (°): Fe-Sn 247.6(1), Sn-S 243.9(1), Sn-S' 243.8(1), Sn-Cl(1) 241.6(2), Sn-S-Sn' 86.2(1), Cl(1)-Sn-S' 101.6(1), Cl(1)-Sn-S 102.7(1), S-Sn-S' 93.8(1), Cl(1)-Sn-Fe 105.8(1), S'-Sn-Fe 126.2(1), S-Sn-Fe 123.2(1)

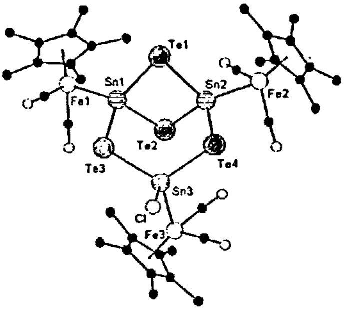


FIGURE 5.
The molecular structure of **4** (H atoms omitted for clarity)
Selected bond lengths (pm) and angles (°): Sn-Fe 252.4(1)-253.7(2), Sn-Te 276.3(1)-280.5(1), Sn(3)-Cl 247.1(3), Te(1)-Sn(1)-Te(2) 96.2(1), Te(2)-Sn(1)-Te(3) 101.9(1), Te(1)-Sn(1)-Te(3) 106.6(1), Te(2)-Sn(2)-Te(4) 105.8(1), Te(1)-Sn(2)-Te(2) 95.7(1), Te(1)-Sn(2)-Te(4) 104.8(1), Cl-Sn(3)-Te(3) 93.1(1), Cl-Sn(3)-Te(4) 96.8(1)

The reaction of **1** with Na_2S in thf leads to a complete substitution of the Cl atoms and the ionic compound $[Na_2(thf)][\{Cp^*(CO)_2Fe\}_2Sn_2S_4]$ (**5**) (Fig. 6) is obtained. The $[\{Cp^*(CO)_2Fe\}_2Sn_2S_4]^{2-}$ anion contains a four-membered Sn_2S_2 ring. Additionally, the tin atoms are bound to a terminal S atom and a $\{Cp^*(CO)_2Fe\}$ group. In contrast to **2**, the $\{Cp^*(CO)_2Fe\}$ are in a *cis* arrangement and the Sn_2S_2 ring is slightly folded. In **5**, the Sn-S distances can be divided into two groups. As expected, the endocyclic Sn-S bond lengths (246.8(1)-248.7(1) pm) are comparable with the corresponding values in **3**, whereas the exocyclic Sn-S bonds are much shorter (234.6(1) and 237.9(1) pm). Similar terminal Sn-S distances have been observed in thiostannates like $[SnS_4]^{4-}$ [10] or $[PhSnS_3]^{3-}$ [11].

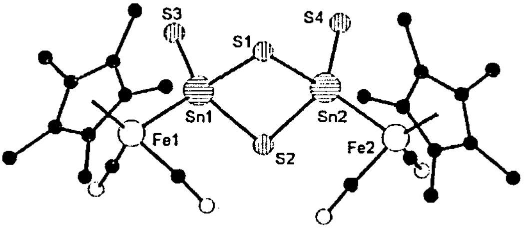


FIGURE 6. The molecular structure of the $[\{Cp^*(CO)_2Fe\}_2Sn_2S_4]^{2-}$anion

2.3 *Synthesis of a mixed tin-sulfur-nickel cluster*

Thiostannates like **5** could be considered as potential ligands for the synthesis of polynuclear transition metal complexes. Currently we are investigating the reactivity of **5** and some related thiostannates, e. g. $[RSnS_3]^{3-}$ (R = Me, Ph, $\{Cp(CO)_2Fe\}$), towards transition metal halides [12]. Recently we found that $[MeSnS_3]^{3-}$, which is accessible by the cleavage of the adamantane like $Me_4Sn_4S_6$ by sulfide ions, reacts with $[Cl_2Ni(PEt_3)_2]$ in aqueous thf to give $[(Me_2Sn_2S_4)S_2Ni_3(PEt_3)_4]$ (**6**).

6 (Fig. 7) contains a $Sn_2S_6Ni_3$ cluster framework which can be divided formally into two parts consisting of a $Me_2Sn_2S_4$ fragment and a Ni_3S_2 unit. The $Me_2Sn_2S_4$ part is related very closely to the structure of the $[\{Cp^*(CO)_2Fe\}_2Sn_2S_4]^{2-}$ anion observed in **5**. The "terminal" sulfur atoms of the $Me_2Sn_2S_4$ unit (S3 and S4) are bound to two Ni atoms of the Ni_3S_2 cluster unit. The Ni_3S_3 cluster fragment consists of three Ni atoms in a triangular arrangement and two μ_3-S atoms. The coordination of the Ni atoms is almost square planar. Ni1 and Ni3 have similar coordination spheres consisting of the μ_3-bridging sulfur atoms S5 and S6, a terminal sulfur atom of the $Me_2Sn_2S_4$ fragment (S3 or S4, respectively) and a PEt_3 ligand. Ni2, which is not bound to the $Me_2Sn_2S_4$ part, is coordinated by two phosphine ligands and the sulfur atoms S5 and S6. Like in the isolectronic Ni_3 cluster $[Cl_2Ni_3(Ph_3P)_4]$ [13], the Ni-Ni distances are rather long (290.0(1)-297.5(1) pm) without any significant Ni-Ni interactions.

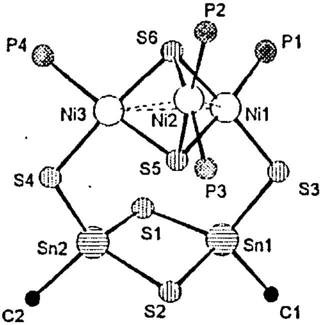


FIGURE 7. The molecular structure of 6 (H atoms and ethyl groups omittet for clarity)
Selected bond lengths (pm) and angles (°): Sn(1)-S(1) 243.7(1), Sn(1)-S(2) 244.1(1), Sn(1)-S(3) 235.0(1), Sn(2)-S(1) 243.3(1), Sn(2)-S(2) 244.3(1), Sn(2)-S(4) 235.7(1), Ni(1)-S(3) 224.4(1), Ni(1)-S(5) 217.1(1), Ni(1)-S(6) 219.2(1), Ni(1)-Ni(2) 290.6(1), Ni(1)-Ni(3) 297.5(1), Ni(2)-S(5) 218.8(1), Ni(2)-S(6) 220.4(1), Ni(2)-Ni(3) 290.0(1), Ni(3)-S(4) 224.1(1), Ni(3)-S(5) 217.8(1), Ni(3)-S(6) 219.0(1), S(1)-Sn(1)-S(2) 93.5(1), S(1)-Sn(1)-S(3) 113.3(1), S(2)-Sn(1)-S(3) 121.0(1), S(1)-Sn(2)-S(2) 93.5(1), S(1)-Sn(2)-S(4) 114.4(1), S(2)-Sn(2)-S(4) 120.2(1), Sn(1)-S(1)-Sn(2) 85.2(1), Sn(1)-S(2)-Sn(2) 84.9(1), Ni(1)-S(3)-Sn(1) 106.5(1), Ni(3)-S(4)-Sn(2) 106.2(1)

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[3] Crystal structure determinations: The data collection was performed on a Stoe IPDS imaging plate diffraction system at 220 K with MoK$_\alpha$-radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97 [14]. The molecular drawings were generated with DIAMOND [15]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). a) 1, $C_{12}H_{15}Cl_3FeO_2Sn$, monoclinic, $P2_1/c$, $Z = 4$, $a = 1184.4(3)$ pm, $b = 996.2(2)$ pm, $c = 1418.3(4)$ pm, $\beta = 91.57(3)°$, $V = 1672.8(7)\times10^6$ pm^3. 12578 reflections collected in the 2Θ range 5.8–56°, 3045

unique reflections, 233 parameters, $R_1(I>2\sigma(I)) = 0.031$, wR_2(all data) = 0.102. CCDC: 147192. b) $3\times 2CH_2Cl_2$, $C_{26}H_{34}Cl_6Fe_2O_4S_2Sn_2$, orthorhombic, Pbca, Z = 4, a = 1204.0(4) pm, b = 1287.5(8) pm, c = 2429.2(8) pm, V = 3766(3)$\times 10^6$pm^3. 16053 reflections in the 2Θ range 4.8–50°, 3055 unique reflections, 250 parameters, $R_1(I>2\sigma(I)) = 0.031$, wR_2(all data) = 0.087. CCDC: 147193. c) 4×2 thf, $C_{44}H_{45}ClFe_3O_8Sn_3Te_4$, triclinic, $P\bar{1}$, Z = 2, a = 1400.3(2) pm, b = 1418.4(3) pm, c = 1506.6(4) pm, $\alpha = 95.44(3)°$, $\beta = 100.04(3)°$, $\gamma = 98.03(2)°$, V = 2895.6(11)$\times 10^6$ pm^3. 25880 reflections in the 2Θ range 3.6–50°, 9584 unique reflections, 589 parameters, $R_1(I>2\sigma(I)) = 0.047$, wR_2(all data) = 0.113. CCDC: 147194. d) 6×2 thf, $C_{34}H_{82}Ni_3O_2P_4S_6Sn_2$, triclinic, $P\bar{1}$, Z = 2, a = 1129.4 (2) pm, b = 1329.1(3) pm, c = 1890.3(3) pm, $\alpha = 87.81(2)°$,. $\beta = 81.86(2)°$, $\gamma = 71.11(2)°$, V = 2896(1) $\times 10^6$ pm^3. 22761 reflections in the 2Θ range 4.2–52°, 9548 unique reflections, 410 parameters, $R_1(I>2\sigma(I)) = 0.035$, wR_2(all data) = 0.101. CCDC: 147195.

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