Oxidative Stannylation with $K_6Sn_2Se_6/SnCl_2$: Synthesis and Crystal Structures of $SnCl_3$-Substituted *pseudo*-Tetrahedral Cobalt(III) Complexes

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The ternary Zintl phase $K_6Sn_2Se_6$ was recently shown to mildly oxidize Cp*-ligated Co^{II} complexes, although Sn in the formal +III oxidation state usually tends to be a reducing species. Depending on the reaction conditions, different ratios of Co^{II} and Co^{III} were observed within the product molecules. Cyclovoltammetric investigations indicated that reversible electron transfer occurred between some of the isolated molecules synthesized that way. In order to study the redox behavior of the oxidizing Sn^{III} species in the reaction system, large excesses of Sn^{II} were added to the solvent THF. A suppression of the $Co^{II} \rightarrow Co^{III}$ transition was expected if the oxidation was reversible. Herein we report the synthesis and crystal structures of $[Co_2(\mu\text{-}Cl)_3(thf)_6][CoClCp^*(SnCl_3)_2]$ (**1**) and $[Li(thf)_4][CoCp^*(SnCl_3)_3]$ (**2**) formed from reactions of $[CoClCp^*]_2$ with $K_6Sn_2Se_6$ in the presence of $SnCl_2$ in THF. The results show that oxidation could not be inhibited, indicative of irreversible redox mechanisms. Additionally, one observes the formal insertion of $SnCl_2$ units in Co–Cl bonds. For completion of the 18-electron configuration, the Cp^*Co^{III} 14-electron fragment forms sterically strained anionic structures that may in the future be relevanct as precursors for the formation of Cp*Co-coated heteroatomic aggregates. Furthermore, the cation in **1** is one of the few examples of threefold μ_2-bridged binuclear Co^{II} complexes.

Introduction

In the course of our current studies on the chemical reactivity of binary Zintl anions, we recently synthesized and structurally characterized compounds $[Co_3Cp^*_3(\mu_3\text{-}Se)_2]$, $[Co_3Cp^*_3(\mu_3\text{-}Se)_2][CoCl_2(\mu\text{-}Cl)_2Li(thf)_2]$, and $[Co_4Cp^*_4(\mu_3\text{-}Se)_4]$ which were obtained from reactions of ternary Zintl salt $K_6Sn_2Se_6$[1] with $[CoClCp^*]_2$ under different reaction conditions.[2] Due to unusual oxidation by Sn in the formal +III oxidation state, both Co^{II} and Co^{III} were observed in the mixed valence products as well as Se^{2-} ligands from $K_6Sn_2Se_6$. In order to explore whether the occurring redox processes (which have been shown to be reversible for the isolated products) − can be suppressed by addition of Sn^{II}, we treated $K_6Sn_2Se_6$ with $[CoClCp^*]_2$ in the presence of large excesses of $SnCl_2$ (see Experimental Section). The use of different ratios of Co^{II}/Sn^{II} and slightly varied reaction conditions yielded compounds $[Co_2(\mu\text{-}Cl)_3(thf)_6][CoClCp^*(SnCl_3)_2]$ (**1**) or $[Li(thf)_4][CoCp^*(SnCl_3)_3]$ (**2**) in good yields [Equation (1) or Equation (2)]. Compounds **1** and **2** were structurally characterized by single-crystal X-ray analysis.[3]

$$\begin{array}{c} K_6Sn_2Se_6 + 4\,SnCl_2 + 6\,CoCl_2 + 2\,LiCp^* \\ \Big\downarrow \text{THF} \\ 2\,[Co_2(\mu\text{-}Cl)_3(THF)_6][CoClCp^*(SnCl_3)_2] + 3\,K_2Se + 2\,SnSe + Li_2Se \\ (\mathbf{1}) \end{array} \qquad (1)$$

$$\begin{array}{c} K_6Sn_2Se_6 + 7\,SnCl_2 + 2\,CoCl_2 + 2\,LiCp^* \\ \Big\downarrow \text{THF} \\ 2\,[Li(THF)_4][CoCp^*(SnCl_3)_3] + 3\,K_2Se + 3\,SnSe \\ (\mathbf{2}) \end{array} \qquad (2)$$

However, instead of suppressing the oxidative effect of $K_6Sn_2Se_6$ by excess Sn^{II}, Co^{II} was again partly oxidized to Co^{III}, while $SnCl_2$ was formally inserted in Co−Cl bonds in both cases. However, the formation of the counterion $[Co_2(\mu\text{-}Cl)_3(thf)_6]^+$ is evidence of a stepwise mechanism, rather than of a direct insertion. This was possibly initialized by the partial ionization of $CoCl_2$ in THF giving $CoCl^+$ and Cl^-, followed by the aggregation of THF-solvated $CoCl^+$ with $CoCl_2$ to yield $[Co_2(\mu\text{-}Cl)_3(thf)_6]^+$, while Cl^- reacted with $SnCl_2$ to form the $SnCl_3{}^-$ anion. The latter finally coordinated to the Cp*-ligated Co^{III} center resulting from the oxidation reaction. Although we were not yet in the position to identify all reaction by-products with certainty, one further hint existed for the reduction of the Sn centers to Sn^{II} rather than for an oxidation to Sn^{IV}: Small $SnSe^+$ peaks were always found in the mass spectra of the primary reaction precipitates, whereas no further Sn products − such as $SnCl_4$, $SnSe_2$ or $SnCl_2$ − were observed either in the mass spectrum or in the NMR measurement of the reaction solution. Moreover, unwanted oxidation of Co^{II} by traces of oxygen in the reaction mixture can be excluded as the products are not formed by means of pure selenide donors such as K_2Se or $Se(SiMe_3)_2$ instead of $K_6Sn_2Se_6$. The observations ultimately suggest the irreversibility of the oxidation by Sn^{III} in the investigated system which correlates with the precipitation of insoluble SnSe during the reaction.

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A $[Co_2(\mu\text{-}Cl)_3(thf)_6]^+$ complex similar to the cation in **1** was already reported by Sobola and co-workers[4] but has, in contrast to the analog iron and nickel species,[4,5] not yet been structurally determined. The molecular structure of the complex cation in **1** is shown in Figure 1.

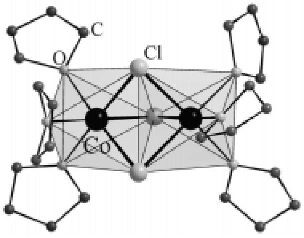

Figure 1. Molecular structure of the cation in **1** in the crystal; the drawn polyhedra illustrate the octahedral environment around the Co centers; H atoms are omitted for clarity; selected distances [pm] and angles [°]: Co−Cl 242.6(6)−248.0(6), Co−O 207.6(2)−216.0(2), Co···Co 302.4(4); Cl−Co−Cl 85.4(2)−86.8(2), O−Co−O 87.2(6)−91.4(5), O−Co−Cl(*cis*) 90.1(4)−95.5(4), O−Co−Cl(*trans*) 175.7(4)−179.2(4)

Three oxygen atoms and three μ_2-Cl ligands surround the two Co atoms to form two face-sharing octahedra. Featuring nearly perfect octahedral angles, a slight trigonal compression results from the Co−O distances being naturally shorter than the Co−Cl bonds. The cation in **1** represents one of the few examples of octahedrally coordinated Co^{II} ions and also of threefold μ_2-bridged binuclear Co^{II} complexes. Another example is a cation coordinated terminally by 1,4,7-trimethyl-1,4,7-triazacyclononan.[6] More frequently, either the terminal ligands are negatively charged as in $[Co_2(\mu\text{-}Cl)_3(C_5Me_4R)_2]^+$ (R = Me, Et)[7,8] and thus give reason for a Co^{III} compound, or the Co^{II} complex is only doubly μ_2-Cl bridged, leading to the preferred tetrahedral coordination pattern. For instance, the latter is found in $[Co_2Cl_4(\mu\text{-}Cl)_2]^{2-}$,[9,10] in the trinuclear dianion $[\{CoCl_2\}_2\{Co(thf)_2\}(\mu_2\text{-}Cl)_4]^{2-}$ [11] or in the tetranuclear complex $[\{CoCl(thf)\}_2\{Co(thf)_2\}_2(\mu\text{-}Cl)_6]$.[12]

The anions in **1** (Figure 2) or **2** (Figure 3) are strongly related and only differ in one ligand at the Co center. Formal substitution of one $SnCl_3$ group in **2** for a Cl ligand in **1** correlates with the larger excess of $SnCl_2$ in the reaction mixture yielding **2** relative to that in the reaction leading to **1**. Both structures exhibit 18 electrons at the Co atom.

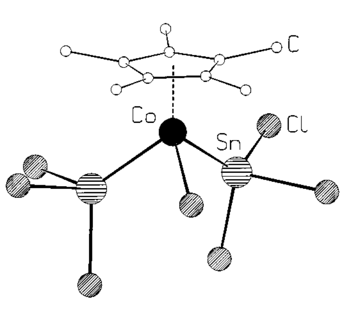

Figure 2. Molecular structure of the anion in **1** in the crystal; H atoms are omitted for clarity; selected distances [pm] and angles [°]: Co−Sn 247.4(3)−247.5(3), Sn−Cl 235.0(7)−240.3(7), Co−Cl 224.1(7), Co−C 207.1(2)−209.3(3); Sn−Co−Sn 96.2(1), Sn−Co−Cl 83.4(2)−87.2(2), Sn−Co−Cp*(*centroid*) 124.8(3)−127.1(2), Cl−Co−Cp*(*centroid*) 125.5(2), Cl−Sn−Cl 94.8(3)−97.6(3), Co−Sn−Cl 112.4(2)−125.9(2)

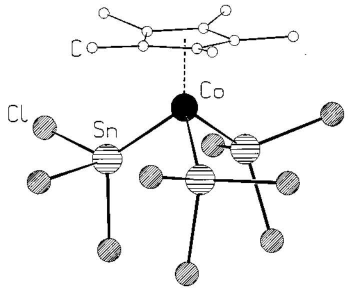

Figure 3. Molecular structure of the anion in **2** in the crystal; H atoms are omitted for clarity; selected distances [pm] and angles [°]:Co−Sn 247.1(1)−248.1(1), Sn−Cl 234.2(7)−241.1(5), Co−C 209.1(8)−215.1(7); Sn−Co−Sn 90.8(4)−93.6(4), Sn−Co−Cp*(*centroid*) 122.6(3)−125.8(3), Cl−Sn−Cl 91.3(1)−100.4(1), Co−Sn−Cl 114.1(1)−126.3(2)

In the complex anions, one Cp* ring and three further ligands *pseudo*-tetrahedrally coordinate the Co atom. Due to the steric demand of the Cp* groups, the angles around the Co center enclosed by the other ligands decrease by more than 13° with regard to the ideal tetrahedral angle of 109.47°. Steric problems that occur in the structures become clear when considering the Sn−Co−Cl angles in **1** which are narrowed even beyond orthogonal angles. In **2**, three bulky $SnCl_3$ groups inhibit this relaxation. The Sn atoms, two in **1** or three in **2**, are also placed in the center of distorted rather than ideal tetrahedra. Cl−Sn−Cl angles that are at least 9° smaller than 109.47° correspond to Cl−Sn−Co angles somewhat more obtuse than perfect tetrahedral angles. Showing similar Co−Sn bond lengths, the steric influence of the different substituents in the anions of **1** or **2** can mainly be seen from slightly elongated Co−C distances in **2** with regard to the corresponding distances in **1**.

Besides the fact that the syntheses of partly oxidized **1** and **2** suggest that the mild oxidant $K_6Sn_2Se_6$ acts irreversibly, the anions in the described products could also be relevant for another reason. Similar to other organometal-substituted tin halides, both complexes could serve to synthesize heteroatomic aggregates ligated by organometallic fragments. For example, compounds of the type $[ML_n(SnCl_3)]$ (L = Cp, CO, PR_3; R = organic group; M = Fe, Ni)[13,14] or $[(ML_n)_2(SnCl_3)_2]$ (L = Cp, CO; M = Fe, Co)[15,16] that are obtained in analogous insertion reactions (without redox processes) of either $[Cp(CO)_2Fe]Cl$, $[Co(CO)_4]Cl$ or $[NiCp(PPh_3)]Cl$ with $SnCl_2$, form organometallic saturated binary rings or cages when reacted with silylated chalcogens $E(SiMe_3)_2$ (E = S, Se, Te) or Na_2Se.[17] However, whereas the L_nM fragments of the quoted compounds contain 17 valence electrons and therefore provide only one metal−chlorine bond each for insertion of $SnCl_2$, the Cp^*Co^{III} fragments in **1** and **2** formally exhibit 14 valence electrons at the Co center. Thus, owing to the larger electronic requirements, one observes the coordination to three $SnCl_3$ units or to two $SnCl_3$ units and one Cl ligand. Whether these molecules can aggregate with silylated main-group elements, or whether the *ipso* position of two or even three $SnCl_3$ ligands at the metal center would result in a sterically overloaded product shall be further investigated.

Experimental Section

All reactions were carried out with exclusion of air and moisture, either under dry nitrogen or under argon (glove box). All solvents were dried and freshly distilled prior to use.

$[Co_2(\mu\text{-}Cl)_3(thf)_6][CoClCp^*(SnCl_3)_2]$ (1): $CoCl_2$ (26 mg, 0.20 mmol) and LiCp* (28 mg, 0.20 mmol) were stirred at room temperature for 20 min in THF (2 mL), resulting in a brown−black solution of $[CoClCp^*]_2$. After cooling down to −40 °C, $SnCl_2$ (133 mg, 0.70 mmol) in THF (1.5 mL) was added. During warming up to room temperature, the color changed to dark brown. Addition of $K_6Sn_2Se_6$ (28 mg, 0.03 mmol) at −78 °C terminated the synthesis. After 10 weeks at −40 °C, bundles of fine blue−black needle-like crystals of **1** appeared; yield: 0.071 g (0.053 mmol; 80%). − $C_{34}H_{63}Cl_{10}Co_3O_6Sn_2$ (1336.621): calcd. C 30.55, H 4.75; found C 30.52, H 4.68.

$[Li(thf)_4][CoCp^*(SnCl_3)_3]$ (2): $CoCl_2$ (78 mg, 0.60 mmol) and LiCp* (85 mg, 0.60 mmol) were stirred at room temperature for 20 min in THF (2 mL), resulting in a brown−black solution of $[CoClCp^*]_2$. A saturated solution (6 mL) of $SnCl_2$ (1.950 g, 10.28 mmol) in THF was added, causing a color change to dark blue. $K_6Sn_2Se_6$ (95 mg, 0.10 mmol) was introduced into the reaction mixture at −78 °C. After addition of 10 mL of toluene, the sample was stored at −40 °C. Within one week, large red−black cube-like crystals of **2** were found; yield: 454 mg (0.39 mmol; 65%). − $C_{26}H_{47}Cl_9CoLiO_4Sn_3$ (1164.739): calcd. C 26.81, H 4.07; found C 26.97, H 4.02.

Acknowledgments

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[3] Data of the X-ray structure analyses. Mo-K_α radiation, graphite monochromator, imaging plate diffractometer STOE IPDS with rotating anode (Schneider); structure solution by direct methods and full-matrix least-squares refinement on F^2; used programs: SHELXS-86,[18] SHELXL-97.[19] − **2**: monoclinic, space group $P2_1$ (No. 4), $Z = 2$, $a = 1164.7(2)$, $b = 1408.8(3)$, $c = 1480.8(3)$ pm, $\beta = 97.40(3)°$, $V = 2572.2(9) \cdot 10^6$ pm^3, $\rho_{calcd.} = 1.726$ g·cm^{-3}, $2\theta = 4-46°$, 6341 reflections measured, 4830 independent reflections [$R_{int} = 0.084$], 3772 with $I > 2\sigma(I)$, μ(Mo-K_α) = 2.641 mm^{-1}; 351 parameters (positions of nonhydrogen atoms except the partly twofold disordered atoms of the THF ligands were refined employing anisotropic displacement parameters; C and O atoms of the THF molecules were refined isotropically assuming split positions wherever necessary; H atoms were calculated for ideal positions and were not refined). Maximum peak on the final difference Fourier map: 1.129 e$^-$·Å^{-3}. $R_1 = 0.072$, $wR_2 = 0.177$. − **3**: orthorhombic, space group $Pca2_1$ (No. 29), $Z = 4$, $a = 2150.1(4)$, $b = 990.5(2)$, $c = 2006.8(4)$ pm, $V = 4273.7(15) \cdot 10^6$ pm^3, $\rho_{calcd.} = 1.810$ g·cm^{-3}, $2\theta = 4-48°$, 17785 reflections measured, 6660 independent reflections [$R_{int} = 0.052$], 6238 with $I > 2\sigma(I)$, μ(Mo-K_α) = 2.705 mm^{-1}; 372 parameters (positions of nonhydrogen atoms except the partly twofold disordered atoms of the THF ligands were refined employing anisotropic displacement parameters; Cl8 and Cl9 show twofold disorder; therefore, adequate split positions were assigned; C and O atoms of the THF molecules were refined isotropically assuming split positions wherever necessary; H atoms were calculated for idealized positions and were not refined). Maximum peak on the final difference Fourier map: 1.849 e$^-$·Å^{-3}. $R_1 = 0.048$, $wR_2 = 0.133$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137021 and CCDC-137022. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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