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Synthesis, Structure and Electrochemical Properties of a Ferrocene-Bridged Bis[tris(arylselenolato)stannyl] Compound

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Two ferrocene-bridged bis[tris(arylselenolate)stannyl] compounds with the general formula $(RSe)_3Sn–Fc–Sn(SeR)_3$ [Fc = ferrocene; R = Ph (**1**), 1-Np (**2**)] were synthesized and characterized by means of NMR spectroscopy (**1**, **2**) as well as X-ray diffraction (**1**). It was shown by DFT calculations that the observed mixed *cis*/*trans* conformation of the SePh groups in **1** represents the global minimum on the energy hyperface in the presence of an Fc bridge between the two tin atoms. Investigation of the electrochemical behavior of **1** indicated the electrochemically driven conversion under cleavage of the tin–selenium bond.

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Introduction

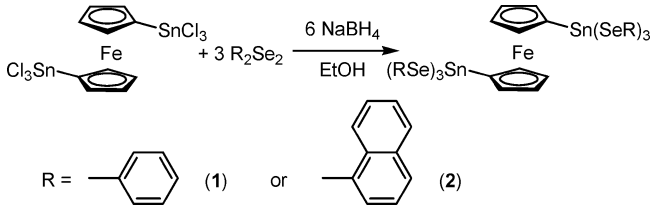
During the last decades, organotin and (organochalcogenolato)tin compounds have been extensively developed due to their interesting catalytic or biological activities, as well as their precursor function for the generation of tin chalcogenide films for opto-electronic applications.[1–11] Stannoxanes, for example, catalyze the formation of acetals or esters from alcohols and ketones[12] or acids and alcohols,[13] respectively. $[Ph_3Sn(SR)]$ (HSR = 2-mercaptobenzoxazole or 5-chloro-2-mercaptobenzothiazole) exhibits lipoxygenase inhibitory activities.[14] Tetrakis(thiophenolato)tin was used for the syntheses of thin films of SnS and SnS_2.[15] Additionally, organotin chlorides were used as starting materials for the synthesis of a number of cyclic compounds $R_6Sn_3S_3$ or adamantine-type structures $(RSn)_4S_6$ (e.g. R = C_6F_5, C_6H_4F, Ph, C_6H_4Me, Me, CMe_2CH_2COMe, C_2H_4COOH) by reactions with $S(SiMe_3)_2$ or $Na_2S·9H_2O$.[16] The employment of tin thiolates recently resulted in the formation of ternary clusters like $[Cu_4Sn_3(edt)_6(\mu_3\text{-}O)(PPh_3)_4](ClO_4)_2·3CH_2Cl_2$, $[(Ph_3P)_2Cu]_2SnS(edt)_2·2CH_2Cl_2·H_2O$, $[(Ph_3P)_2Cu]_2SnS(edt)_2·2DMF·H_2O$ and $[(Ph_3P)Cu]_2Sn(SPh)_6·3H_2O$, synthesized by reactions of $[Cu(PPh_3)_2(MeCN)_2]ClO_4$ with $Sn(edt)_2$ (edt = ethane-1,2-dithiolate),[17] by reaction of $[(PPh_3)_3CuBr]$ with $(Bu_4N)_2[Sn_3S_4(edt)_3]$, or by reaction of $Sn(SPh)_4$ with CuCN and PPh_3.[18] Bis(trichlorostannyl)organyl compounds were used to synthesize a series of bis[tris(arylchalcogenolato)stannyl] derivatives, and their reactivity was studied by our group.[19] We have also reported a heterometallic, heterovalent $Cu^I/Sn^{II/IV}/S$ cluster, $[(Ph_3PCu^I)_6\{(CH_2)_4Sn^{IV}S_2\}_6Cu^I_4Sn^{II}]$, synthesized by treating bis(trichlorostannyl)butane with $Na_2S·9H_2O$ and $[CuCl(Ph_3P)_3]$ under solvothermal condition.[20] The Corrigan group used ferrocene-bridged chalcogenido ligands to synthesize several nanoclusters.[21] However, the reactivity of ferrocene-bridged ditin compounds towards arylchalcogenolate or chalcogenide was not investigated so far.

In this paper, we report the syntheses, characterization, optical and electrochemical properties of two novel arylselenolato-substituted tinorganyl compounds according to the general formula $(RSe)_3Sn–Fc–Sn(SeR)_3$, (Fc = ferrocene; **1**: R = Ph; **2**: R = 1-Np). The title compounds are currently being explored with respect to their applicability as synthons in the preparation of heterometallic, mixed coordination/organometallic polymers.

Results and Discussion

Syntheses

1,1′-Bis[tris(arylselenolato)stannyl]ferrocene compounds were prepared by treating 1,1′-bis(trichlorostannyl)ferrocene with NaSeR, generated in situ by sodium borohydride reduction of diphenyl diselenide (**1**) or dinaphthyl diselenide (**2**) in ethanol (Scheme 1). Compounds **1** and **2** were charac-



Scheme 1. Syntheses of compounds **1** and **2**.

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terized by means of NMR spectroscopy. Details of the experimental procedures are given in the Experimental Section.

Crystal Structures

Compound **1** was structurally characterized by means of single-crystal X-ray diffraction,[22,23] whereas for **2**, no crystals were obtained. However, the congruence of all analytical data served to identify the composition. Figure 1 shows the molecular structure and provides selected interatomic distances and angles of compound **1**. A fragment of the packing of the molecules within the crystal lattice is shown in Figure 2.

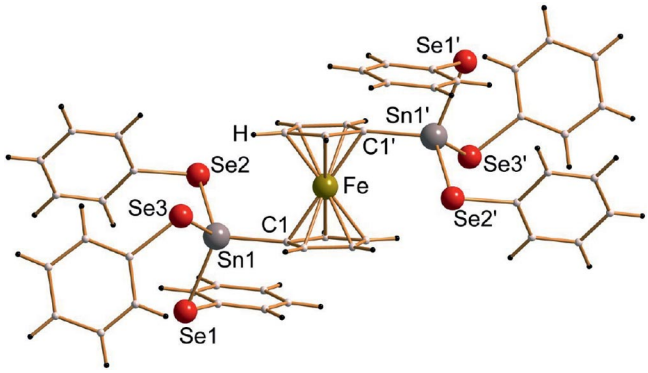

Figure 1. (a) Molecular structure of **1**, selected distances [pm] and angles [°] in **1**: Sn–C 210.40(7), Sn–Se 250.58(11)–254.13(11), C–Se 191.5(8)–194.2(7); C–Sn–Se 104.85(19)–113.20(2), Se–Sn–Se 106.47(3)–111.83(4), C–Se–Sn 92.00(2)–96.00(2).

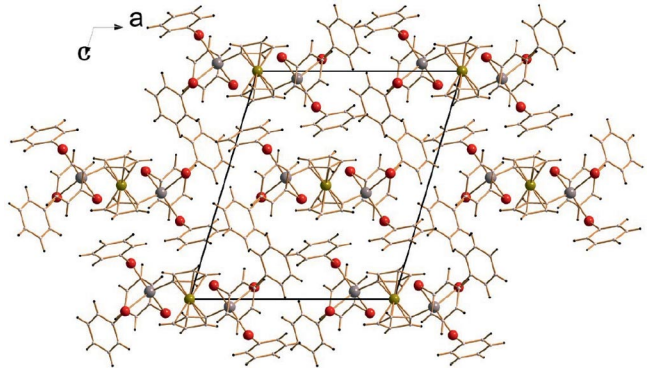

Figure 2. Fragment of the packing of the molecules of **1** within the crystal, viewed along crystallographic *b* axis.

Compound **1** crystallizes as orange needles in the monoclinic space group $P2_1/n$ (No. 14) with two formula units in the unit cell. The two [Sn(SePh)$_3$] units bind to different cyclopentadienyl rings of the bridging ferrocene entity. According to the inversion symmetry of the molecule, both the Cp rings and the [Sn(SePh)$_3$] groups adopt a staggered conformation. This way, the steric hindrance of the bulky substituents is minimized. The coordination geometry around the tin atoms is distorted tetrahedral with distances Sn–C 210.40(7) and Sn–Se 250.58(11)–254.13(11) pm. Although all six connections C1–Sn–Se–C_{Ph} are in accord with a *gauche*-type conformation, a more *trans*-like arrangement of four selenophenolato ligands is observed: those containing Se2, Se3, Se2′, Se3′ are oriented away from the bridging ferrocene residue with dihedral angles C1–Sn–Se–C_{Ph} of 137.20 or 162.30°. The remaining two selenophenolato groups at Se1 and Se1′ atoms are oriented rather *cis*-like toward the bridging ferrocene residue with a dihedral angle of 72.48°. This *cis*/*trans* mixed conformation of the C1–Sn–Se–C_{Ph} connections in **1** does not only seem to be favorable for a dense packing of the rod-like molecules within the crystal; according to density functional theory (DFT)[24] calculations of the isolated molecules, using the program system Turbomole,[25] the all-*trans*-type conformer is by 340 kJ mol^{-1} higher in energy for the most stable arrangement of the three Ph rings upon rotation about the Se–C_{Ph} bonds. This significant energetic disadvantage is the result of a systematically observed distortion of the geometry at the Sn atoms away from a trigonal pyramid toward a less favorable see-saw geometry, which is driven by the incongruent tendency to form intramolecular Cp–H···Se interactions and to minimize the steric interaction between the three SePh groups at the same time. Conformers with more than one *cis*-type SePh ligand per Sn atom evolved not to be a local minimum on the energy hypersurface owing to unacceptable steric repulsions between the Cp rings and the backward orientated Ph substituents.

Electrochemical Behavior

Cyclovoltammetric measurements were performed in order to investigate both the influence of the substitution of ferrocene by two Sn(SR)$_3$ groups and to explore the electrochemical stability of **1**. The cyclic voltammogram is given in Figure 3.

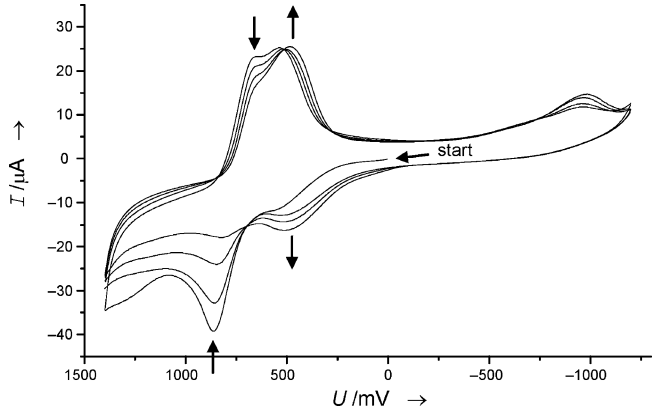

Figure 3. Multiple cyclic voltammogram of compound **1** at a scan rate of 200 mV s^{-1} in dichloromethane.

The figure shows the electrochemical behavior of compound **1** in dichloromethane. The strong oxidation peak of the first scan at +860 mV seems to have its quasi-reversible counter peak at a reduction potential of +660 mV. A second reduction peak at +485 mV overlaps with the first peak. In the second cycle, we observed that the previous shoulder at +510 mV increases, while a strong decrease of the firstly

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observed oxidative peak at +860 mV occurs. On the reverse scan the first reduction peak at +660 mV decreases, while the peak at +485 mV increases. In the third cycle isosbestic points are clearly recognizable indicating that compound **1** is electrochemically transformed into a new product. In control experiments we were able to show that PhSn(SePh)$_3$ did not produce any eletroanalytically relevant peaks in the region in question. The electroanalytical investigation of $FcSnCl_3$ showed an almost reversible redox couple at +705 mV for the oxidation peak and +475 mV for the corresponding reduction peak vs. Ag/AgCl. Therefore, we propose that the carbon–tin bond is not cleaved during the cyclic voltammograms of **1**. The cleavage of a tin–selenium bond seems most likely. Another weak reduction peak is observed at ca. –950 mV. It may arise from the decomposition process of **1** or be due to further impurities. The nature of the electrochemically generated product could not be elucidated so far.

UV/Vis Spectroscopy

The solid-state optical properties of compounds **1** and **2** were investigated by recording UV/Vis spectra (Figure 4). One observes a smooth onset of absorption at 2.23 eV (556 nm; **1**) and 2.29 eV (541 nm; **2**), respectively, which reflect Se(p)→Sn(p)-based LMCT transitions within the crystals. No bands are observed that can be assigned to d→d transitions, which indicates that even the modification of the Cp rings by two bulky Sn(SePh)$_3$ groups does not provoke a high-spin situation at the transition-metal center.

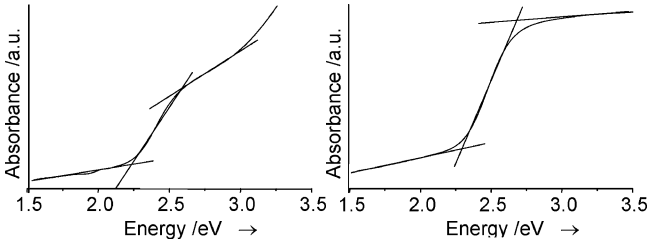

Figure 4. UV/Vis spectra of compounds **1** and **2**, recorded as suspension of single crystals in nujol oil.

Conclusions

Two ferrocene-bridged bis[tris(arylselenolato)stannyl] compounds were prepared and characterized. The molecular structure of compound **1** was additionally optimized by DFT calculations. In accordance with these investigations, a *cis*/*trans* mixed orientation of the selenophenolate groups is favored. We were able to show by cyclic voltammery that the compound is electrochemically converted into another species, probably under Sn–Se bond cleavage. We are about to study the reactivity of such compounds containing Lewis-basic chalcogenolato groups towards transition-metal complexes in order to produce novel ternary metal-organic frameworks.

Experimental Section

General: All manipulations were performed under purified argon by using a double manifold Schlenk line, or under dry N_2 within a glove box. Solvents were dried by standard methods and freshly distilled prior to use. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer. Commercially available reagents were used as received. $Cl_3Sn–Fc–SnCl_3$ was prepared according to the literature.[26]

Synthesis of (R′Se)$_3$Sn–Fc–Sn(SeR′)$_3$: 1,1′-Bis(trichlorostannyl)ferrocene (0.16 mmol) was dissolved in degassed absolute ethanol (5 mL) and added to an ethanolic solution (5 mL) of NaSePh prepared from R_2Se_2 (0.48 mmol) and Na[BH_4] (1.06 mmol) in situ. The mixture was stirred for 24 h. The orange solid was isolated by filtration, washed with ethanol and *n*-hexane, and dried in vacuo. Crystals of **1**, suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a dichloromethane/*n*-hexane (1:1) mixture.

1,1′-Bis[tris(selenophenolato)stannyl]ferrocene (1): Yield: 0.085 g, 0.063 mmol, 40%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 4 H, CpH), 4.28 (s, 4 H, CpH), 7.14–7.50 (m, 30 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.30, 72.47, 74.16 (Cp), 124.23, 129.00, 131.53, 137.08 (Ar) ppm. ^{119}Sn NMR ($CDCl_3$): δ = –49.27 (s) ppm. $C_{46}H_{38}Se_6Sn_2Fe$ (1357.75): C 40.69, H 2.82; found C 40.52, H 2.79.

1,1′-Bis[tris(selenonaphthylato)stannyl]ferrocene (2): Yield: 0.175 g, 0.106 mmol, 32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23 (s, 4 H, CpH), 3.83 (s, 4 H, CpH), 7.1–7.76 (m, 42 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.79, 73.57, 74.32, 124.78, 125.60, 126.19, 126.71, 128.50, 129.02, 129.39, 134.14, 136.15, 136.97 (Ar) ppm. ^{119}Sn ($CDCl_3$): δ = –49.92 (s) ppm. $C_{70}H_{50}Se_6Sn_2Fe$ (1658.17): calcd. C 50.70, H 3.04; found C 50.78, H 3.00.

UV/Vis Spectroscopy: UV/Vis spectra were recorded with a Varian Cary 5000 UV/Vis/NIR spectrometer in the range of 800–200 nm using the double-beam technique. The samples were measured as suspensions in nujol between two quartz plates. The mixture was placed between two quartz plates and rapidly brought into the UV/Vis beam.

Electrochemical Investigations: The voltammetric investigations were carried out with a BAS-100 B/W Electrochemical Analyzer (Bioanalytical Systems, West Lafayette, Indiana, U.S.A.). Potentials were measured against an Ag/AgCl "leek-free" reference electrode (Cypress Systems, Inc., Lawrence, Kansas, U.S.A.); glassy carbon working electrode (3 mm diameter); anhydrous dichloromethane containing tetra-*n*-butylammonium perchlorate as supporting electrolyte (0.1 M) under nitrogen; scan rate: 200 mV s^{-1}; automatic IR compensation.

Methods of the Quantum Chemical Investigations: All calculations were conducted with the Turbomole[25] software package in the version 5.10. The calculations were performed on the DFT level[24] by employing a B88 exchange functional 3-5 and a P86 correlation functional[27] and the Ridft program.[28] Basis sets def2-SV(P)[29] were employed with an effective core potential (ECP-28) at the Sn atoms.[30] All data were taken from optimized local minimum structures, rationalized by analytical calculation of the second derivatives with respect to the vibrational normal modes.[31]

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[22] Details on the measurement and X-ray structural refinement of **1**: Stoe IPDS-II diffractometer (T = 100 K, Mo-K_α radiation, $\lambda_{\text{Mo-}K\alpha}$ = 0.71073 Å, graphite monochromization). Structure solution by direct methods, full-matrix least-squares refinement against F^2 with SHELXS-97 and SHELXL-97 software: Monoclinic, $P2_1/n$, a = 13.978(3) Å, b = 9.971(2) Å, c = 16.213(3) Å, β = 106.59(3)°, V = 2165.5(7) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 2.082 g cm^{-3}, μ(Mo-K_α) = 6.550 mm^{-1}, 2θ = 4.54–51.82°. 12966 reflections measured, 4195 independent reflections [R(int) = 0.0917] of which 3134 with $I > 2\sigma(I)$, 250 parameters, R_1 [$I > 2\sigma(I)$] = 0.0373, wR_2 (all data) = 0.0952, GoF (all data) = 0.900, max. peak/hole 1.995/–1.202 e$^-$ Å^{-3}. CCDC-740251 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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