

Synthesis and Tin(IV) Coordination Chemistry of the Novel Tripod $N(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_3$

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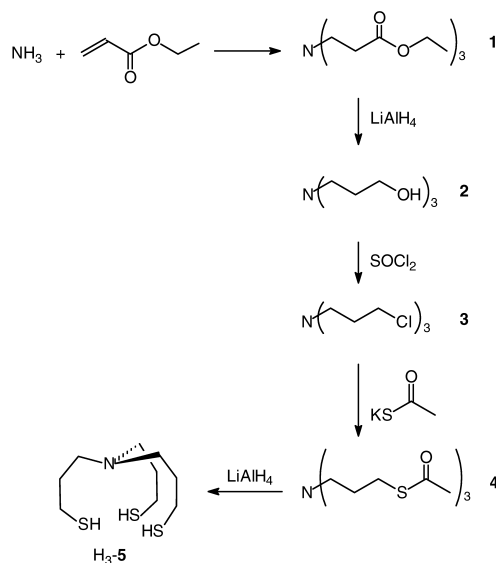
The novel tetradentate ligand $N(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_3$, **H₃-5** was synthesized from tripropanolamine via the trichloride, subsequent reaction with potassium thioacetate and reduction with LiAlH_4 . Ligand **H₃-5** reacts with MeSnCl_3 under formation of the centrosymmetric dinuclear complex $[\text{MeSn}(\mathbf{5})_2]_2$, **6**, which was shown by X-ray structure analysis to contain two tetrahedrally coordinated tin atoms and two bridging thiolato functions.

Key words: Tin, Tripodal Ligand, Trithiol

Introduction

Only few aliphatic, symmetrically substituted tripodal ligands are described in the literature. The NN_3 ligands tren ($N(\text{CH}_2\text{CH}_2\text{NH}_2)_3$) [1] and trpn ($N(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$) [2] have been known for some time and more recently topological unsymmetrical ligands of this type containing C_2 and C_3 bridges between the central nitrogen atom the primary amine donors have been reported [3]. Ligands providing an NO_3 donor set like triethanolamine [4] have also been studied. Some years ago we reported on the aliphatic NS_3 ligand $N(\text{CH}_2\text{CH}_2\text{SH})_3$ and its coordination chemistry with Tc^{III} and Re^{III} [5].

The difference in the ligand arm lengths (C_2 in tren vs. C_3 in trpn) causes significant differences in the properties of the NN_3 ligands and the metal complexes they form. For example, ligand trpn is significantly more basic compared to tren, owing to the larger separation and consequently reduced electrostatic interaction of the ammonium groups after protonation [3b–3c]. On the other hand, trpn forms



Scheme 1. Synthesis of the **H₃-5**.

six-membered chelate rings with metal ions while tren yields exclusively five-membered chelate rings. Molecular mechanics calculations have shown that such five-membered chelate rings are particularly suitable for the stabilization of the late transition metals of the first row [6]. It has been shown that the complex formation constants for the tren complexes are 4–6 orders of magnitude larger than those of the corresponding trpn complexes [7]. To study the effects caused by a variation of the ligand arm lengths with NS_3 ligands, we synthesized the previously unknown ligand $N(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_3$, **H₃-5** (Scheme 1) and studied its coordination chemistry with Sn^{IV} .

Experimental Section

Manipulations concerning the synthesis of the ligand and the complex were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. Compounds **1**, **2** and **3** were prepared according to published procedures [8].

Tris(3-acetylthiopropyl)amine, $N(\text{CH}_2\text{CH}_2\text{CH}_2\text{SC(O)CH}_3)_3$ **4**: To a solution of 25 g (0.221 mol) of potassium thioacetate in 200 ml of ethanol at 50 °C was added 16.5 g (0.067 mol) of tris(3-chloropropyl)amine **3** dissolved in 50 ml of ethanol. The reaction mixture was heated under reflux for 6 h. The resulting suspension was filtered while still hot to separate KCl. The solvent was removed and the oily residue was ex-

tracted several times with diethyl ether. The orange diethyl ether extract was diluted with an equal volume of pentane and this solution was worked up chromatographically (SiO₂). Removal of the solvents yielded a yellow oil. – Yield: 15.1 g (61.7%). – ¹H NMR (250 MHz, CDCl₃): δ = 2.86 (t, 6 H, CH₂S), 2.50 (t, 6 H, NCH₂), 2.32 (s, 9 H, CH₃CO), 1.76 (quin, 6 H, CH₂CH₂CH₂). – ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ = 52.56 (NCH₂), 30.55 (CH₃), 26.94 (CH₂S), 22.37 (CH₂CH₂CH₂).

Tris(3-mercaptopropyl)amine, N(CH₂CH₂CH₂SH)₃, H₃-5: A sample of 5 g of **4** dissolved in 20 ml of THF was added dropwise to a suspension of 2 g of LiAlH₄ in 50 ml of THF. During the addition the temperature was kept at 0 °C with an ice-bath. The reaction mixture was stirred at r.t. for 6 h. It was then hydrolyzed with 4.5 ml of degassed water. To this was added 30 ml of diethyl ether and the suspension was saturated with CO₂ by addition of dry ice. Solids were removed by filtration and the solvent was removed to leave a yellow oil. – Yield: 2.3 g (71.0%). – ¹H NMR (250 MHz, CDCl₃): δ = 2.59 (t, 6 H, CH₂S), 2.52 (t, 6 H, NCH₂), 1.76 (quin, 6 H, CH₂CH₂CH₂) 1.4 (s, 3 H, SH). – ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ = 52.64 (NCH₂), 31.2 (CH₂CH₂CH₂), 22.64 (CH₂S). – C₉H₂₁NS₃ (236.43): calcd. C 45.14, H 8.84, N 5.85; found C 44.89, H 8.69, N 6.15.

Di[tris(3-thiolatopropyl)amine]methylstannane, [MeSn(5)]₂, **6**: Under argon 180 mg (0.75 mmol) of H₃-5 and 230 mg (2.2 mmol) of triethylamine in 5 ml of THF were added to 180 mg (0.75 mmol) of methyltin trichloride in 40 ml of THF. The solution was heated to reflux for 2 h. The solvent was decanted from the yellow solid, and the solid was washed with methanol. The residue was extracted with 30 ml of hot pyridine. Upon cooling to –30 °C colorless needles of **6** precipitated from the pyridine solution over 2 weeks. The needles are only sparingly soluble in pyridine. Owing to the poor solubility in all common organic solvents no NMR spectra could be recorded. – Yield: 270 mg (73%). – C₂₀H₄₂N₂S₆Sn₂ (740.30): calcd. C 32.45, H 5.72, N 3.78; found C 32.99, H 5.87, N 3.73.

X-ray structure determination: Formula C₂₀H₄₂N₂S₆Sn₂, M = 740.30, colorless crystal, 0.41 × 0.38 × 0.38 mm, *a* = 10.969(2), *b* = 12.834(2), *c* = 11.744(2) Å, β = 117.96(2)°, *V* = 1460.3(4) Å³, ρ_{calcd} = 1.684 g cm^{–3}, μ = 21.51 cm^{–1}, empirical multi-scan absorption correction (0.7319 ≤ *T* ≤ 0.9977), *Z* = 2, monoclinic, space group *P*2₁/*a*, λ = 0.71073 Å, *T* = 293(2) K, ω-2θ scans, 2507 reflections collected (*h*, *k*, ±*l*), [(sin θ)/λ]_{max} = 0.595 Å^{–1}, 2385 independent and 2196 observed reflections [*I* ≤ 2σ(*I*)], 138 refined parameters, *R* = 0.0302, w*R*₂ = 0.0744 (refinement on |*F*²|), max. residual electron density 0.497 (–0.689) e Å^{–3}, hydrogen atom positions calculated and refined as riding atoms. Diffraction data were collected on an Enraf Nonius CAD-4 diffractometer. Programs used: structure solution SHELXS-97 [9], structure refinement SHELXL-97 [10],

graphics ORTEP3 [11]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-217322. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

Tin(IV) complexes with tripodal NO₃ ligands, the alkylstannatranes [RSn(OCH₂CH₂)₃N], have been known for some time. Normally they exhibit a trigonal-bipyramidal coordination geometry [12,13]. However, trinuclear species with two hexacoordinated (octahedral) and one heptacoordinated (pentagonal-bipyramidal) tin(IV) centers are also known [14]. The formation of such polynuclear aggregates is inhibited by the presence of sterically demanding alkyl groups R at the tin atom [15].

Alkyltin thiolates are normally obtained by the reaction of alkyltin(IV) halogenides with thiols in the presence of a base. They are moderately stable towards hydrolysis and show a lesser tendency to associate to polynuclear complexes than the comparable alkoxides [16]. For example, the S₂-ligand 1,2-bis(mercaptopropan-2-yl)ethane reacts with RSnCl₃ to give the mononuclear, square-pyramidal, anionic complexes [RSn(SCH₂CH₂S)₂][–] [17]. Even monomeric, tetrahedral tin tetrathiolates [Sn(SCH₂CH₂S)₄] are known, which react with Lewis bases under formation of octahedral complexes *trans*-[Sn(SCH₂CH₂S)₂(base)₂] (base = pyridine, alkyl amine) [18]. The NS₂ ligands RN(CH₂CH₂SH)₂ react with tin(II) to give a dinuclear tetrahedrally coordinated tin(II) complex which reacts with disulfides or thiols under formation of trigonal-bipyramidal tin(IV) complexes with an NS₄ coordination environment [19].

We became interested in the coordination chemistry of the novel ligand H₃-5 with the RSn^{IV} complex fragment. Previous studies with the ligand N(CH₂CH₂SH)₃, possessing ethanediyl bridges between the central nitrogen atom and the S donors indicated, that this ligand forms mononuclear trigonal-bipyramidal tin(IV) complexes [15], isostructural with the mononuclear alkylstannatranes [14] having N and R in the axial positions. Trigonal-bipyramidal complexes were also obtained from N(CH₂CH₂SH)₃, a monodentate co-ligand and Re^{III} and Tc^{III} [5]. Reaction of H₃-5 with MeSnCl₃ in THF in the presence of

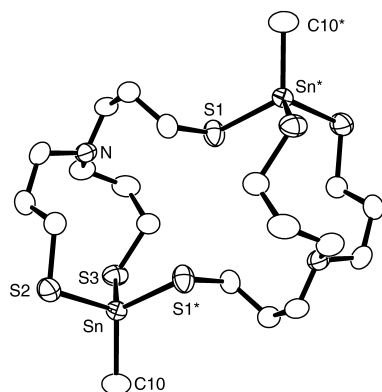


Fig. 1. Molecular structure of $[\text{MeSn}(\mathbf{5})]_2$, **6**. Hydrogen atoms have been omitted. Starred atoms represent transformed coordinates of the type 1- x , - y , - z . Selected bond lengths [\AA] and angles [$^\circ$]: Sn-S2 2.3940(9), Sn-S3 2.3970(9), Sn-S1* 2.3881(11), Sn-C10 2.119(3), range S-C 1.836(3)-1.840(3), range N-C 1.464(4)-1.469(4); S2-Sn-S3 113.90(3), S2-Sn-S1* 102.40(3), S2-Sn-C10 108.27(12), S3-Sn-S1* 108.28(3), S3-Sn-C10 108.49(13), S1*-Sn-C10 115.59(12), range Sn-S-C 99.45(10)-105.33(11), range C-N-C 110.3(3)-112.0(2).

triethylamine yields a white powder **6**, which is insoluble in most organic solvents. The characterization of **6** was complicated by this poor solubility. The CHN analysis revealed a composition consistent with the formulation $[\text{MeSn}(\mathbf{5})]$. Compound **6** was sparingly soluble in hot pyridine. From such a solution colorless crystals of **6** were obtained.

The X-ray structure analysis of **6** revealed a new coordination mode of an NS_3 ligand at the MeSn^{IV} complex fragment. Instead of the expected trigonal-bipyramidal complex, the dinuclear complex $[\text{MeSn}(\mathbf{5})]_2$, **6** (Fig. 1) was obtained. In **6** two of the ligand arms coordinate to one tin atom, while the third ligand arm is coordinated in a bridging fashion to a

second tin atom. Neither the central nitrogen atom nor pyridine solvent molecules are coordinated. Thus an almost perfect SnCS_3 tetrahedron is formed. This is surprising, since most tetrahedral Sn^{IV} thiolato complexes, when dissolved in nitrogen bases, form octahedral complexes with a *trans*-configuration of the nitrogen donors [18]. The absence of pyridine coordination is surprising, and it is unique in Sn^{IV} coordination chemistry that an N-centered tripod of type NX_3 ($\text{X} = \text{S}, \text{O}, \text{N}$) is not N-coordinated. The absence of pyridine coordination might be explained with the reduced Lewis acidity of the tin center in an SnCS_3 environment. The lack of intramolecular nitrogen coordination is based on the geometric situation found with ligand **5**³⁻. The coordination of the central nitrogen atom in a chelating fashion would lead to six-membered chelate rings which have been shown to be much less stable than five-membered rings [6]. All reported alkylstannatranes with intramolecular N-coordination exhibit five-membered chelate rings.

The coordination environment around tin is best described as tetrahedral with S-Sn-S and S-Sn-C angles in the range from 102.40(3) $^\circ$ to 115.59(12) $^\circ$. The deviation from tetrahedral coordination in **6** is much less than observed for the tetrathiolate $[\text{Sn}(\text{SCH}_2\text{CH}_2\text{S})_2]^-$ [18a]. In the absence of a strong chelate effect for six-membered rings the formation of an unstrained coordination polyhedron can be taken as another driving force for the formation of the dinuclear complex **6**. A similar observation was made for cyclotristannathianes and -adamantanes, where an increase of the coordination number at tin would induce strain. Consequently, no reaction with Lewis bases was observed [20].

Acknowledgements

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