# Tin(IV) Complexes with 2-Hydroxybenz(2-Hydroxynaphth)aldehyde Nicotinoylhydrazones (H<sub>2</sub>Ns, H<sub>2</sub>Nnf). Molecular and Crystal Structures of [SnCl<sub>3</sub>(HNnf)] · 2DMF

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**Abstract**—The reaction of  $SnCl_4$  with 2-hydroxybenz(2-hydroxynaphth)aldehyde nicotinoylhydrazones (H<sub>2</sub>Ns, H<sub>2</sub>Nnf) in CH<sub>3</sub>OH gave non-electrolyte complexes [SnCl<sub>3</sub>(HNs)] (I) and [SnCl<sub>3</sub>(HNnf)] (II), which were recrystallized to give the solvates [SnCl<sub>3</sub>(HNs)]  $\cdot$  DMF (III) and [SnCl<sub>3</sub>(HNnf)]  $\cdot$  2DMF (IV). It was found by IR spectroscopy that the ligands in I–IV are protonated at the N(Py) and coordinated in the tridentate chelating mode through the azomethine nitrogen atom and oxy and oxyazine oxygen atoms. The thermolysis of I–IV and electron impact-induced fragmentation of I and II are accompanied by the formation of the complexes [SnCl<sub>2</sub>(Ns)] and [SnCl<sub>2</sub>(Nnf)]. The molecular and crystal structures of IV were determined by X-ray diffraction (CIF file CCDC no. 816105).

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### INTRODUCTION

Previously, in a study of complexation of GeCl<sub>4</sub> with nicotinoylhydrazones of 2-hydroxybenz-  $(H_2N_s)$ and 2-hydroxy-1-naphthaldehydes (H<sub>2</sub>Nnf) in methanol, we found that the composition and structure of the complexes vary depending on the aldehyde moiety:  $[GeCl_2(Ns + HCl)CH_3OH (Ge : H_2Ns molar)]$ ratio of 1 : 1) and  $[Ge(Ns \cdot HCl)_2]$  (1 : 2),  $[Ge(Nnf \cdot$  $HCl_{2}$  (Ge :  $H_{2}Nnf = 1 : 2$ ) [1, 2]. In all complexes, the ligand occurs in the same form protonated at the pyridine nitrogen and connected to germanium(IV) via the azomethine nitrogen atom and oxyazine and oxy oxygen atoms. It was expedient to elucidate how the composition and structure of the complexes being formed are affected by the replacement of the central atoms using the same hydrazones as ligands. This information is also of interest for elucidating the regularities in the variation of complexing ability in the series of Lewis acids, tetrachlorides of the electronic analogues of Ge(IV) and Sn(IV).

The present study is devoted to the products formed in the reaction of  $SnCl_4$  with 2-hydroxybenzand 2-hydroxynaphthaldehyde nicotinoylhydrazones in methanol. The results of this study can be used to estimate the complexing properties of  $SnCl_4$  with respect to the considered ligands in comparison with these properties of  $GeCl_4$  and to obtain new data about the structure of new Sn(IV) coordination compounds with hydrazones.

#### EXPERIMENTAL

Commercial special-purity grade  $SnCl_4$ ,  $\rho = 4.02 \text{ g/cm}^3$ ; reagent grade nicotinic acid hydrazide, high-purity grade 2-hydroxybenz- and 2-hydroxy-1-naphthaldehydes, and analytical grade organic solvents (methanol, acetonitrile, DMF, and diethyl ether) were used.

Nicotinoylhydrazones were synthesized by condensation of nicotinic acid hydrazide with equimolar amounts of aldehydes in methanol according to the general procedure of hydrazone synthesis [3] and recrystallized from acetonitrile. The product purity was verified by TLC on Silufol UV-254 plates in chloroform : acetone = 1 : 10 (H<sub>2</sub>Ns) and chloroform : methanol = 20 : 1 (H<sub>2</sub>Nnf) eluent systems. Yield, % (mp, °C): H<sub>2</sub>Ns, 78 (190); H<sub>2</sub>Nnf, 87 (240).

IR (v, cm<sup>-1</sup>): 3380–3370 v(OH), 3220–3200, 3190 v(NH), 3050, 2930 v(CH)<sub>ring</sub>, 1680–1670 v(C=O), 1625–1623 v(C=N), 1600, 1580, 1490 v(C=C)<sub>ring</sub>, 1560–1540  $\delta$ (NH), 1290–1286 v(Ph–O).

The complexes  $[SnCl_3(HNs)]$  (I) and  $[SnCl_3(HNnf)]$  (II) were prepared by adding  $SnCl_4$  (0.002 mole, 0.23 mL) to hot (50°C) solutions of  $H_2Ns$  and  $H_2Nnf$  (0.002 moles in 25 mL and in 40 mL of methanol, respectively) with continuous stirring. The stirring was continued for additional 10 min at 50°C. The precipitates thus formed were immediately

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separated on a glass filter, washed with hot methanol  $(2 \times 10 \text{ mL})$ , and dried at 80°C to a constant weight. The yields were 85% (I) and 77% (II).

For  $C_{13}H_{10}N_3O_2Cl_3Sn$  (I) anal. C, 33.54; H, 2.15; N, 9.03; Cl, 22.87; Sn, 25.53. calcd., %:

Found, %: C, 33.58; H, 2.18; N, 9.10; Cl, 22.91; Sn, 25.44.

For  $C_{17}H_{12}N_3O_2Cl_3Sn$  (II)

anal. C, 39.61; H, 2.33; N, 8.15; Cl, 20.65; Sn, 23.05. calcd., %:

Found, %: C, 39.68; H, 2.35; N, 8.21; Cl, 20.69; Sn, 22.89.

The solvates  $[SnCl_3(HNs)] \cdot DMF$  (III) and  $[SnCl_3(HNnf)] \cdot 2DMF$  (IV) were isolated from saturated (40°C) solutions of I and II in a mixed solvent (CH<sub>3</sub>OH : DMF = 1 : 3) as a result of isothermal evaporation for 24–32 h at 20°C. After preliminary isolation of crystals of IV suitable for X-ray diffraction, the precipitates were separated, washed with cold methanol (2 × 5 mL), and dried at 80°C to a constant weight. The yields were 60% (III) and 52% (IV).

For C<sub>16</sub>H<sub>17</sub>N<sub>4</sub>O<sub>3</sub>Cl<sub>3</sub>Sn (III)

anal. C, 35.68; H, 3.16; N, 10.41; Cl, 19.77; Sn, 22.06. calcd., %:

Found, %: C, 35.74; H, 3.13; N, 10.50; Cl, 19.81; Sn, 21.83.

For  $C_{23}H_{26}N_5O_4Cl_3Sn$  (IV)

anal. C, 41.72; H, 3.93; N, 10.58; Cl, 16.08; Sn, 17.94. calcd., %:

Found, %: C, 41.78; H, 3.90; N, 10.65; Cl, 15.94; Sn, 17.86.

Analysis of the complexes for C, H, N was performed on a semiautomatic CHN analyzer; chlorine was quantified by mercurometry [4], and tin was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES) on an Optima-2100 DV Perkin Elmer instrument. The molar electrical conductivity  $\lambda$  of  $10^{-3}$  M solutions of **I–IV** in DMF was measured using an Economics Expert digital instrument and the electrolyte type was determined according to the tables [5].

Thermogravimetric measurements were carried out on a Paulik–Paulik–Erdey Q-derivatograph. The samples were heated in air from 20 to 1000°C at a rate of 10°C/min. The sample weight was 100 mg, a platinum crucible without a lid served as the sample holder, and calcined alumina was used as the reference.

The IR absorption spectra  $(400-4000 \text{ cm}^{-1})$  of samples of **I–IV** as KBr pellets were recorded on a Specord 75 IR spectrophotometer and mass spectra were run on an MX-1321 instrument with direct sample injection into the ion source at an ionizing voltage of 70 eV and a source temperature of 220°C.

**X-ray diffraction.** The experimental set of reflections for the monoclinic polymorph crystal of **IV** was collected on a Bruker SMART CCD diffractometer ( $\lambda$ Mo $K_{\alpha}$  radiation). The absorption corrections were applied by the SADABS program [6]. The structure was solved by the direct method. All non-hydrogen atoms were located from the difference Fourier maps and refined on  $F_{hkl}^2$  in the anisotropic approximation. All hydrogen atoms (except for H(N) found in the difference map) were placed into the geometrically calculated positions and included in the refinement in the riding model with U(H) = 1.2 U(C), where U(C) is the equivalent thermal factor of the carbon atom bearing this H atom.

Experimental data collection and structure refinement details are summarized in the table. The calculations were carried out by SHELXTL software [7]. The atom coordinates, bond lengths. bond angles, and thermal parameters are deposited with the Cambridge Crystalloraphic Data Centre (CCDC no. 816105; www.ccdc.cam.uk/conts/retrieving.html or deposit@ ccdc.cam.ac.uk).

# **RESULTS AND DISCUSSION**

The study of the reaction of SnCl<sub>4</sub> with nicotinovlhydrazones in methanol showed that, irrespective of the aldehyde moiety (2-hydroxybenz- or 2-hydroxy-1-naphth-), complexes with the same Sn : ligand : Cl molar ratio of 1 : 1 : 3 are formed. They are yellow (I) and orange (II) compounds readily soluble in DMF and DMSO and moderately soluble in acetonitrile. According to electrical conductivity measurements, the compounds were non-electrolytic in DMF ( $\lambda =$ 37.6 (I), 401.3 (II)  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>). Hence, all chlorine atoms of I and II are in the inner sphere and are covalently bonded to tin atoms. Since the complexes are not charged, they can be described as [SnCl<sub>3</sub>(HNs) (I) and [SnCl<sub>3</sub>(HNnf)] (II). They do not undergo solvolysis in a DMF solution, as indicated by invariability of the  $\lambda$  values with time.

The crystal solvates formed by complexes I and II, namely,  $[SnCl_3(HNs)] \cdot DMF$  (III) and  $[SnCl_3(HNnf)] \cdot 2DMF$  (IV), were isolated from a  $CH_3OH-DMF$  solvent mixture. The thermolysis of III and IV, unlike the thermolysis of I and II, starts with the endotherm corresponding to desolvation in the 160–190°C temperature range with the TG-mass loss of 14% (for III, 1 mole of DMF) or 22% (for IV, 2 moles of DMF) and then continues similarly to I and II.

More precisely, one mole of HCl is eliminated at 290–360°C, which gives rise to an endotherm ( $T_{\text{max}} = 350^{\circ}$ C), the TG mass loss being 8.0 (I) and 7.5% (II) ( $\Delta m_{\text{theor}}$ , %: I, 7.8; II, 7.1). The contents of tin and chlorine in the products formed upon maintenance of

Crystal data and refinement d	letails for [SnCla	(HNnf)] · 2DMF ( <b>IV</b> )

Parameter	Value	
Formula	$C_{17}H_{12}N_{3}O_{2}Cl_{3}Sn \cdot 2(C_{3}H_{7}NO)$	
M	661.53	
Temperature, K	120	
System	Monoclinic	
Space group	$P2_1/c$	
a, Å	12.3115(8)	
b, Å	17.431(1)	
<i>c</i> , Å	13.6124(9)	
β, deg	114.843(1)	
$V, Å^3$	2650.9(3)	
Ζ	4	
$\rho$ (calcd.), g cm <sup>-3</sup>	1.658	
Crystal color; habit	Yellow prism	
Crystal size, mm	$0.50\times0.30\times0.20$	
μ, cm <sup>-1</sup>	1.306	
T <sub>min</sub> /T <sub>max</sub>	0.434/0.655	
$2\theta_{\text{max}}$ , deg	58.0	
Total number of reflections	28822	
Number of independent reflections $(R_{int})$	6964 (0.0615)	
$R_1$ (on F for reflections with $I > 2\sigma(I)$ )	0.0398 (4485)	
$wR_2$ (on $F^2$ for all reflections)	0.0700	
Number of refined parameters	325	
GOOF	0.993	
$\Delta \rho_{\text{max}} / \rho_{\text{min}}, e / \text{Å}^3$	0.265/-0.187	

the complexes at 290°C confirm this conclusion. The subsequent destruction of complexes and high-temperature burning out of the organic part of the molecules is accompanied by several exotherms at  $T_{\rm max} = 420$  ( $\uparrow$ ) (I, II), 550 ( $\uparrow$ ) (II), and 610°C ( $\uparrow$ ) (I, II). The thermolysis ends at 700 (I) and 640°C (II) with the formation of a solid residue identified as SnO<sub>2</sub> according to chemical analysis data and TG calculations.

The IR spectra of complexes exhibit no v(OH), v(NH), or v(C=O) bands present in the spectra of hydrazones and, instead, new bands appear at 560– 550 cm<sup>-1</sup> v(Sn–O) and 445 -432 cm<sup>-1</sup> v(SnN) [8]. The v(C=N) band shifts to lower frequency by 10– 12 cm<sup>-1</sup> and the bending modes of the pyridine ring shift to higher frequency (~1010, 635, and 415 cm<sup>-1</sup> in the spectra of **I**–**IV** and ~996, 620, and 400 cm<sup>-1</sup> in the

spectra of the ligands). The results indicate that in I-IV, the ligand is bonded to tin via the azomethine nitrogen atom and the oxygen atoms of the oxyazine and hydroxy groups. Since the changes in the  $\delta(Py)$  region could be caused by both the hydrazone coordination involving the N(Py) atom and protonation [1, 2], the final conclusion about the structure of the tin polyhedron in these complexes was based on X-ray diffraction study of **IV**.

The structure of **IV** contains two DMF solvent molecules. The complex molecule is shown in Fig. 1. The molecule has a zwitter-ion structure, the pyridine nitrogen atom being protonated and the negative charge being delocalized on the O(2)C(11)N(2)hydrazine moiety. The coordination polyhedron of tin,  $\{SnCl_3O_2N\}$ , is a somewhat extended octahedron; the axial Sn-Cl(2) and Sn-Cl(3) bonds are longer than the equatorial Sn-Cl(1) bond (Sn-Cl(1)), Sn-Cl(2), 2.4089(8); Sn-Cl(3), 2.3574(8);2.4260(8); Sn-O(1), 2.024(2); Sn-O(2), 2.092(2); Sn-N(1), 2.152(2) Å). The axial Cl(2) atom is involved in the  $Cl(2)\cdots H(1A)-C(1)$  hydrogen bond, which results in shortening of the Sn-Cl(2) bond compared to the other axial bond (Sn-Cl(3)). The substantial decrease in the Sn–Cl(1) distance is typical of equatorial bonds and apparently reflects the *trans*-effect of nitrogen.

In the central moiety of the HNnf<sup>-</sup> ligand, the bond lengths (N(1)–N(2), 1.409(3); C(1)–N(1), 1.291(4); C(12)–N(2), 1.305(4); C(11)–O(1), 1.335(4); C(12)–O(2), 1.305(3) Å) are typical of coordinated nicotinoylhydrazones. The negative charge is likely to be concentrated on the oxygen atom of the nicotinoyl residue, because the C(12)=O(2) bond is substantially longer than the C=O  $\rightarrow$  Sn coordination bonds [9]. The C(11)–O(1) distances are equal to typical  $C(sp^2)$ –O  $\rightarrow$  metal bond lengths with deprotonated hydroxy group [1, 2, 10].

The strong hydrogen bonds, C(1)– H(1*A*)…Cl(2*A*) and N(3)–H(3N)…O(2S) (H…Cl 2.82, H…O 1.81 Å), combine the molecules into dimeric associates {Sn<sub>2</sub>Cl<sub>6</sub>(Me<sub>2</sub>NCHO)<sub>2</sub>} (Fig. 2). Furthermore, weak  $\pi$ – $\pi$  stacking interaction occurs between the parallel aromatic systems, the distance between the planes of the pyridine and naphthalene rings being 3.44 Å and the dihedral angle being 7.4° (Fig. 3).

The packing of the dimeric associates in the crystal (Fig. 4) is determined by hydrogen bonding between the methyl hydrogens of the solvent molecules and the chlorine atoms; the Cl…H distances (2.8-2.9 Å) are shorter than the sum of the van der Waals radii of Cl and H (2.97 Å) [11].

Thus, considering the analogy in the composition and IR spectra, it can be concluded that compounds I-IV have the same coordination unit: {SnCl<sub>3</sub>O<sub>2</sub>N}. The arising negative charge is counterbalanced by the hydrazone form protonated at the heterocyclic nitrogen atom.

Attention is drawn by the fact that thermolysis of the complexes is accompanied by dehydrochlorination of their molecules (-1 mole HCl) to give species stable in the temperature range of  $360-420^{\circ}$ C. A study of the mass spectra of I and II demonstrated that the electron impact-induced fragmentation gives rise to species with m/z of 36 [HCl]<sup>+</sup> (I, II), 429 [SnCl<sub>2</sub>(Ns)]<sup>+</sup> (I), and 479 [SnCl<sub>2</sub>(Nnf)]<sup>+</sup> (II). In all probability, these are complexes with five-coordinate Sn(IV) atom, similar to that described in [8]:



The performed study showed that in the case of Sn(IV), unlike Ge(IV), only equimolar complexes are formed regardless of what is the aldehyde moiety in nicotinoylhydrazone.

The Sn(IV) and Ge(IV) complexes contain coordination octahedra of different composition,  $\{SnCl_3O_2N\}$  and  $\{GeCl_2O_2N\}$ , with identical tridentate chelating form of the ligand protonated at N(Py). The positive charge is counterbalanced in different ways: by the total negative charge of the tin coordination unit in I and II and by the chloride ion in  $[GeCl_2(Ns \cdot HCl)CH_3OH]$  and  $[Ge(Ns \cdot HCl)_2]$ .

The initial step of the thermolysis of  $[Ge(Ns \cdot HCl)_2]$ ,  $[Ge(Nnf \cdot HCl)_2]$  and  $[SnCl_3(HNs)]$  (I),  $[SnCl_3(HNnf)]$  (II) is dehydrochlorination; however, in the case of I and II, it occurs at higher temperature, which is attributable to stronger binding of the chloride ion.



Fig. 1. Structure of the complex molecule [SnCl<sub>3</sub>(HNnf)] in IV; the thermal ellipsoids are shown to 50% probability.



Fig. 2. Centrosymmetric dimeric associates  $\{Sn_2Cl_6(Me_2NCHO)_2\}$ .

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Fig. 3.  $\pi$ - $\pi$ -Stacking interactions of the aromatic moieties in IV.



Fig. 4. Packing of molecules in the crystal of IV.

Thus, in relation to the given ligands, it was found that  $GeCl_4$  and  $SnCl_4$  differ considerably in the complexing properties, as indicated by the differences between the compositions and structures of the coordination compounds they form.

## REFERENCES

- 1. Seifullina, I.I., Shmatkova, N.V., and Starikova, Z.A., *Russ. J. Inorg. Chem.*, 2004, vol. 49, no. 3, p. 352.
- Seifullina, I.I., Shmatkova, N.V., Shishkin, O.V., and Zubatyuk, R.I., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 4, p. 486.
- 3. Sharma, C.S., Jadon Gunjan, Singh, H.P., et al., *IJARPB*, 2012, vol. 2, no. 1, p. 28.
- 4. Cheng, F.W., Microchem. J., 1959, vol. 24, no. 6, p. 989.

- 5. Gearly, W.J., Coord. Chem. Rev., 1971, no. 7, p. 81.
- 6. SADABS. Version 2.01. Bruker/Siemens Area Detector Absorption Correction Program, Madison, WI: Bruker AXS, 2001.
- 7. Sheldrick, G.M., Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, vol. 64, p. 112.
- 8. Han Dong Yin, Min Hong, Gang Li, and Da Qi Wang, J. Organomet. Chem., 2005, vol. 690, no. 11, p. 3714.
- 9. Seifullina, I.I., Shmatkova, N.V., and Starikova, Z.A., *Russ. J. Inorg. Chem.*, 2001, vol. 46, no. 8, p. 1150.
- 10. Seifullina, I.I., Shmatkova, N.V., Zubatyuk, R.I., et al., *Russ. J. Inorg. Chem.*, 2013, vol. 58, no. 1, p. 26.
- 11. Zefirov, Yu.V. and Zorkii, P.M., Usp. Khim., 1995, vol. 64, p. 446.

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