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Tin Tetrachloride Chelates with 4-Dimethylaminobenzaldehyde Pyridinoylhydrazones. Molecular and Crystal Structures of [$SnCl_4$(γ-Idb · H)] · CH_3CN and [$SnCl_4$(γ-Idb · H)] · DMF

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Abstract—The reactions of $SnCl_4$ with 4-dimethylaminobenzaldehyde pyridinoylhydrazones (α-HPdb, β-HNdb, and γ-HIdb) afford complexes [$SnCl_4$(Pdb · H)] (**I**); [$SnCl_4$(Ndb · H)] · *n*Solv, Solv = 0 (**II**), CH_3OH (**IIa**); and [$SnCl_4$(Idb · H)] · *n*Solv, Solv = 0 (**III**), CH_3OH (**IIIa**), CH_3CN (**IIIb**), DMF (**IIIc**). The complexes are thermally stable to 310–340°C, and desolvation occurs in ranges of 145–190°C (CH_3OH), 160–230°C (CH_3CN), and 160–190°C (DMF). It is found by IR spectroscopy that the complexes include the form of ligands protonated at N(Py), where the ligands are bonded to tin according to the bidentate-cyclic mode through the azomethine nitrogen atom and the oxygen atom of the oxyazine group. The molecular and crystal structures of complexes **IIIb** and **IIIc** are determined by X-ray diffraction analyses (CIF files CCDC nos. 1055248 and 1055249, respectively).

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INTRODUCTION

Investigations aimed at synthesizing complexes of organotin compounds with various chelating ligands became active in recent years, and the synthesis conditions, properties and crystal structures for these complexes were determined [1–3]. An information about their biological activity was of special interest [4–6]. The coordination compounds based on tin tetrachloride, in particular, with various aroyl- and pyridinoylhydrazones known due to their biological activity, are poorly studied in this respect [7–9]. Therefore, we started to study the complex formation of tin tetrachloride with benzaldehyde 2-R-benzoylhydrazones (R = H, OH). Methanol was used as a solvent. However, this attempt was unsuccessful because of the competitive interaction of the latter with $SnCl_4$, which was not suppressed even by the introduction of the donor substituent $–N(CH_3)_2$ into the aldehyde fragment of hydrazones. The complexes with the same coordination mode {$SnCl_4ON$} but different O,N-coordinated forms of hydrazone, namely, amide (O(C–O)–N(CH=N)) and imide (O(C–O)–N(CH=N), in the presence of the vacant nitrogen atom of the $–N(CH_3)_2$ group were obtained due to the replacement of methanol by aprotic but also polar acetonitrile [10].

The purpose of this work is to extend a series of the studied ligands, to develop procedures of syntheses of the tin tetrachloride complexes with dimethylaminobenzaldehyde pyridinoylhydrazones (α-HPdb, β-HNdb, and γ-HIdb) using different solvents (methanol, acetonitrile, dimethylformamide (DMF)), and to reveal the influence of the solvent nature, the presence of two donor atoms in the ligand molecules (NPy and $–N(CH_3)_2$), and the position of the nitrogen atom in the heterocycle on their formation, compositions, and structures.

EXPERIMENTAL

Tin tetrachloride $SnCl_4$ (special purity grade, ρ = 2.03 g/mL); hydrazides of picolinic, nicotinic, and isonicotinic acids (special purity grade); and 4-dimethylaminobenzaldehyde (reagent grade) were used. All organic solvents used were of special purity grade.

Synthesis of pyridinoylhydrazones was carried out by the condensation of 4-dimethylaminobenzaldehyde with an equimolar amount of hydrazide of the corresponding acid in methanol using the general procedure used for the synthesis of hydrazones [11], and then the product was recrystallized from acetonitrile. The purity was monitored by TLC on Silufol UV-254 plates in a chloroform–acetone (1 : 10) mixture used as an eluent. The yields were as follows: (melting points are given in parentheses): HPdb, 83% (190°C); HNdb, 77% (148°C); and HIdb, 88% (202°C).

Synthesis of [$SnCl_4$(Pdb · H)] (I), [$SnCl_4$(Ndb · H)] (II), and [$SnCl_4$(Idb · H)] (III). Tin tetrachloride (0.001 mol) was added with continuous stirring to acetonitrile solutions (15–20 mL) of the corresponding hydrazone (0.001 mol) saturated at the boiling temperatures. In the case of compound **III**, a precipitate was formed almost immediately. For the isolation of compounds **I** and **II**, the corresponding solutions were kept at 50–55°C to the onset of crystallization (5–10 min) and left to stay at 20°C for complete precipitation. Precipitates of complexes **I–III** were separated on the Schott filter, washed with acetonitrile, and dried at 80°C to a constant weight. The yields were the following (color is indicated in parentheses): 84.3% (orange), 67.6% (orange), and 86.6% (vinous) for compounds **I**, **II**, and **III**, respectively. For $C_{15}H_{16}N_4OSnCl_4$ anal. calcd. (%): C, 34.97; H, 3.11; N, 8.16; Cl, 27.59; Sn, 23.06. Found (%) for **I**: C, 34.87; H, 3.10; N, 8.18; Cl, 27.61; Sn, 22.96. Found for **II** (%): C, 34.94; H, 3.06; N, 8.21; Cl, 27.56; Sn, 23.10. Found for **III** (%): C, 34.95; H, 3.08; N, 8.11; Cl, 27.51; Sn, 22.98.

Synthesis of solvates $[SnCl_4(Ndb \cdot H)] \cdot CH_3OH$ (IIa) and $[SnCl_4(Idb \cdot H)] \cdot CH_3OH$ (IIIa). Tin tetrachloride (0.001 mol) was added to suspensions containing hydrazones (0.001 mol) in methanol (20 mL). This resulted in the formation of colored solutions, and precipitates crystallized almost immediately. Then all reaction mixtures were left to stay for evaporation at 30–35°C for complete precipitation, separated while they remained warm, and treated similarly to compounds **I–III**. The yields were the following (color is indicated in parentheses): for **IIa**, 85.4% (yellow-orange); for **IIIa**, 89.2 (red-vinous). For $C_{16}H_{20}N_4O_2SnCl_4$ anal. calcd. (%): C, 35.12; H, 3.66; N, 7.68; Cl, 25.97; Sn, 21.71. Found for **IIa** (%): C, 35.10; H, 3.56; N, 7.73; Cl, 25.87; Sn, 21.68. Found for **IIIa**, C, 35.16; H, 3.59; N, 7.73; Cl, 25.91; Sn, 21.65.

The crystals of solvate **$[SnCl_4(Idb \cdot H)] \cdot CH_3CN$ (IIIb)** suitable for X-ray diffraction analysis were isolated by crystallization at 20°C from a solution obtained by the addition of an equimolar amount of $SnCl_4$ to a solution of Hidb (0.0005 mol) in CH_3CN (25 mL) at 40°C. The crystals of solvate **$[SnCl_4(Idb \cdot H)] \cdot DMF$ (IIIc)** were isolated from a solution of compound **III** in a CH_3OH–DMF (1 : 3) mixture saturated at 40°C due to isothermal evaporation for 24–32 h at 20°C.

Elemental analyses of the complexes were carried out on a semiautomated CHN analyzer. The chlorine content was determined mercurometrically [12]. The content of tin was determined by atomic emission spectroscopy with inductively-coupled plasma on an Optima–2100 DV instrument (PerkinElmer). The molar electric conductivity (λ) of DMF solutions of the complexes (10^{-3} mol/L) was measured on an Ekspert-002 conductometer at 25°C. The type of electrolyte was determined according to the tabulated data [13].

The thermal stability of the compounds was studied in platinum crucibles on a Q-1500 D Paulik– Paulik–Erdey derivatograph in air in a range of 20–1000°C (the heating rate was 10°C/min, the DTA and DTG sensitivity was 1/5 of the maximum value, Al_2O_3 served as a reference, and the weighed sample was 100 mg). The IR absorption spectra (4000–400 cm^{-1}) of the ligands and complexes in KBr pellets were recorded on a Shimadzu FTIR-8400S spectrophotometer.

The X-ray diffraction analyses of compounds **IIIb** and **IIIc** were carried out on a Bruker APEX-II CCD diffractometer at 100 K (λMoK_α radiation). The calculations were performed using the SHELXTL (version 5.1) program package [14]. The unit cell parameters and conditions for recording and refinement of structures **IIIb** and **IIIc** are given in Table 1. The bond lengths and bond angles are given in Table 2.

Additional data on the crystal structures of compounds **IIIb** and **IIIc** were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1055248 and 1055249, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

It is established from the data of elemental analysis and thermogravimetry and the electroconductivity measurements that the tin tetrachloride complexes (**I–III**) are formed regardless of the position of the nitrogen atom in the heterocycle and solvent nature: nonelectrolytes (λ of their DMF solutions ranges from 52 to 57 Ohm^{-1} cm^2 mol^{-1} [13]) or their solvates with the molar ratio Sn : HL : Cl = 1 : 1 : 4. The complexes are well soluble in DMF and dimethyl sulfoxide and are almost insoluble in acetonitrile, methanol, and nitrobenzene.

The thermogravimetric (TG) curves of the solvated complexes exhibit endotherms of desolvation in ranges of 155–190 (175↓) for **IIa** and 160–200 (180↓)°C for **IIIa**. This was proved by the calculations for thermogravimetry (mass loss, $\Delta m = 5.8$ and 6.0% nearly coincides with Δm_{theor} ($-CH_3OH$) = 5.6%) and elemental analyses of the products obtained by the storage of the complexes at 180°C to a constant weight. Complexes **IIIb** and **IIIc** were desolvated at higher temperatures (160–235 (230↓) and 180–220 (215↓)°C). This was confirmed by the experimental results for compounds **IIa** and **IIIa**: Δm (TG) ≈ Δm of storage (8.0 ≈ 7.6 for **IIIb** and 12.5 ≈ 12.4% for **IIIc** and Δm_{theor} ($-CH_3CN = 7.19$; $-DMF = 12.11\%$) (for CH_3CN, 7.19%; for DMF, 12.11%). It can be concluded that the in the studied solvents the obtained complexes do not decompose, the more so the high-temperature thermolysis stages of desolvated complexes **II** and **III** are completely identical. Complexes **I–III** are thermally stable up to 310–340°C (Table 3), and their thermolysis proceeds in two stages.

The transition to the second stage for complexes **II** and **III** was accompanied by the formation of a stable

Table 1. Experimental and crystallographic data for structures **IIIb** and **IIIc**

Parameter	Value	
	IIIb	**IIIc**
Empirical formula	$C_{17}H_{19}Cl_4N_5OSn$	$C_{18}H_{23}Cl_4N_5O_2Sn$
FW	569.86	601.90
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	*Pbca*
Z	4	8
a, Å	7.8682(3)	15.8723(15)
b, Å	14.8453(6)	10.9218(9)
c, Å	18.9392(7)	27.800(2)
β, deg	96.2200(10)	90
V, Å^3	2199.19(15)	4819.2(7)
ρ_{calcd}, g/cm^3	1.721	1.659
μ_{Mo}, cm^{-1}	16.66	15.28
F(000)	1128	2400
$2\theta_{max}$, deg	61	60
Number of measured reflections	28768	30002
Number of independent reflections	6718	7144
Number of reflections with $I > 2\sigma(I)$	5505	3923
Number of refined parameters	256	275
R_1 ($I > 2\sigma(I)$)	0.0337	0.0483
wR_2 (for all reflections)	0.0790	0.0959
GOOF	1.019	1.002
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.835/–1.081	0.940/–1.087

phase in a narrow temperature range of 42–440°C. The results of analysis of the products of the isothermal storage at 410°C showed that the products contained almost no chlorine (3.0–4.2%) and the tin content for **II** decreased by 9%. This indicates that chloride ions are removed at this thermolysis stage and for **II** this is accompanied by the elimination to the gas phase and removal of tin-containing particles. The oxidation and destruction of the organic moiety of all complexes occur in a range of 440–680°C and are accompanied by the intense exothermal effect with a mass loss. According to the elemental analysis data, the final thermolysis product is SnO_2, which is characteristic of the tin chloride complexes [15]. The weight of SnO_2 is lower than the theoretical value (28.5%) only in the case of complex **II** (Table 3).

Nearly the same changes are observed in the IR spectra of compounds **I–III** (Table 4) in the range of vibrations of the main functional groups: the ν(NH) and ν(C=O) stretching vibrations are absent, the σ(NCO) and σ(NCH) vibrations undergo changes, and new frequencies ν(Sn–N) and ν(Sn–O) appear [1, 15]. This indicates that the bidentate-cyclic coordination through the azomethine nitrogen atom and the oxygen atom of the oxyazine group of the enol form of the ligand occurs in complexes **I–III**. The negative charge appeared on the coordination mode of tin in complexes **I–III** should be compensated. This is possible only due to the protonation of the vacant nitrogen atoms, but it is unclear which of them is protonated. This question was answered by the results of X-ray diffraction analyses of crystalline solvates **IIIb** and **IIIc**. The structures of molecules $\{SnCl_4(Idb \cdot H)\}$ are nearly identical. The highest differences that do not exceed 0.015 Å are observed for the Sn(1)–N(3) and Sn(1)–Cl(4) bonds. Taking into account that the molecular structures of $SnCl_4(Idb \cdot H)$ in compounds **IIIb** and **IIIc** are similar, we considered spe-

Table 2. Selected bond lengths, bond angles, and hydrogen bond parameters in structures **IIIb** and **IIIc**

Bond	*d*, Å	
	IIIb	**IIIc**
Sn(1)–O(1)	2.1010(17)	2.095(3)
Sn(1)–N(3)	2.175(2)	2.189(3)
Sn(1)–Cl(4)	2.3823(6)	2.3666(11)
Sn(1)–Cl(1)	2.3965(7)	2.3821(12)
Sn(1)–Cl(3)	2.4013(6)	2.4070(11)
Sn(1)–Cl(2)	2.4312(7)	2.4380(10)
O(1)–C(1)	1.304(3)	1.297(5)
N(2)–C(1)	1.309(3)	1.303(5)
N(2)–N(3)	1.386(3)	1.385(4)
N(3)–C(7)	1.310(3)	1.311(5)
C(1)–C(2)	1.485(3)	1.486(6)
Angle	ω, deg	
N(3)Sn(1)Cl(4)	168.51(6)	166.78(10)
O(1)Sn(1)Cl(3)	169.53(5)	169.16(8)
Cl(1)Sn(1)Cl(2)	175.43(2)	173.87(4)
C(1)N(2)N(3)	111.25(19)	111.6(3)
C(7)N(3)N(2)	119.3(2)	118.3(3)
H···N(O)	2.02	1.74
N···N	2.857(4)	2.628(5)
N–H···O	153	170

cific features of the structure using compound **IIIb** as an example, since structure **III** is characterized by lower *R* factors and standard deviations of the atomic coordinates.

The coordination polyhedron of the tin atom $\{SnCl_4ON\}$ in structure **IIIb** is a distorted octahedron (Fig. 1). The axial positions are occupied by the azomethine nitrogen atom N(1) and chlorine atom Cl(4), whereas the oxazine oxygen atom O(1) of the HIdb ligand and three chlorine atoms Cl(1), Cl(2), and Cl(3) lie in the equatorial plane (Fig. 1). The hydrazone molecules in the complex exist in the zwitterionic form with the protonated nitrogen atom N(1) of the pyridine rings of the hydrazide fragment and the negatively charged coordination mode of tin. The structure of the HIdb ligand corresponds to the enol form with some contribution of the ketone form: in the oxyazine fragment N(3)–C(1)–O(1), the N(3)–C(1) bond length (1.309 Å) is closer to the standard length of the ordinary bond (C(sp^3)–N 1.33 Å [16]) than to that of the double bond (C(sp^2)=N 1.279 Å [16] (Table 2). At the same time, the C(1)–O(1) distance (1.305 Å) is intermediate between the length of the standard C=O double bond (in urea, 1.265 Å) [16] and bond lengths in enols C=C–OH (1.333 Å) and enol esters (alcohols) C=C–O–Alk (1.354 Å).

The electron density delocalization is observed in the five-membered metallocycle: the N(2)–N(3) (1.386 Å) and N(3)–C(7) (1.310 Å) bond lengths are close to the average values for the N(sp^2)–N(sp^3) (1.401 Å) and C(sp^2)–(C=N) 1.279 Å bonds [16]. In crystals of compounds **IIIb** and **IIIc**, molecules $\{SnCl_4(Idb \cdot H)\}$ form hydrogen bonds N–H···N and N–H···O with solvate molecules of acetonitrile and DMF. The hydrogen bonds of the pyridinium fragment with DMF are stronger than those with acetonitrile (Table 2). In structure **IIIb** (Fig. 2), a weak π–π stacking interaction is observed between the phenyl substituents. In structure **IIIc** (Fig. 3), a weak π–π stacking interaction is observed between the phenyl substituents and pyridine fragment.

A comparison of the results of studying the complex formation of $SnCl_4$ with 4-dimethylaminobenzaldehyde benzoyl-(2-hydroxybenzoyl)hydrazones [10] and those obtained in this work suggests that the

Table 3. Thermal stability of the complexes studied

Compound	Temperature range ΔT (T_{max}, °C)↑↓	Δm (TG), %	$SnO_{2\,pract}$, %
$[SnCl_4(Pdb \cdot H)]$ (**I**)	310–455 (330↓↑)	30.0	
	455–680 (480↑, 600↑)	42.0	28.0
$[SnCl_4(Ndb \cdot H)]$ (**II**)	340–425 (350↓↑, 410↑)	40.0	
	440–670 (610↓)	42.0	18.0
$[SnCl_4(Idb \cdot H)]$ (**III**)	320–420 (350↓↑, 410↑)	29.5	
	440–680 (640↑)	41.0	29.5

Table 4. IR spectral data for the hydrazones and tin(IV) complexes

Compound	ν(NH)	ν(CH)	ν(C=O)	ν(C=N)	δ(CH)	σ(NCH) (δ(NCO))	ν(Sn–N)	ν(Sn–O)
HPdb	3220	3020 2980	1669	1620	1598 1480	1545		
$[SnCl_4(Pdb \cdot H)]$ (**I**)		3067 2900		1610	1600 1473	1518	446	552
HNdb	3210	3097 3034	1670	1625	1598 1480	1560 1520		
$[SnCl_4(Ndb \cdot H)]$ (**II**)		3081 2918		1615	1580 1490	1525	448	568
HIdb	3204	2980	1660	1630	1588 1480	1565		
$[SnCl_4(Idb \cdot H)]$ (**III**)		2923		1612	1600 1497	1520	450	553

complexes with pyridinoylhydrazones are characterized by a higher stability, since they are formed not only in acetonitrile but also in methanol, and they do not undergo exchange interaction with solvent molecules and are isolated as solvates **IIa** and **IIIa**. Aprotic highly polar acetonitrile and DMF favor the crystallization of solvates $[SnCl_4(Idb \cdot H)] \cdot Solv$ (Solv = CH_3CN (**IIIb**), DMF (**IIIc**)). Of two donor nitrogen

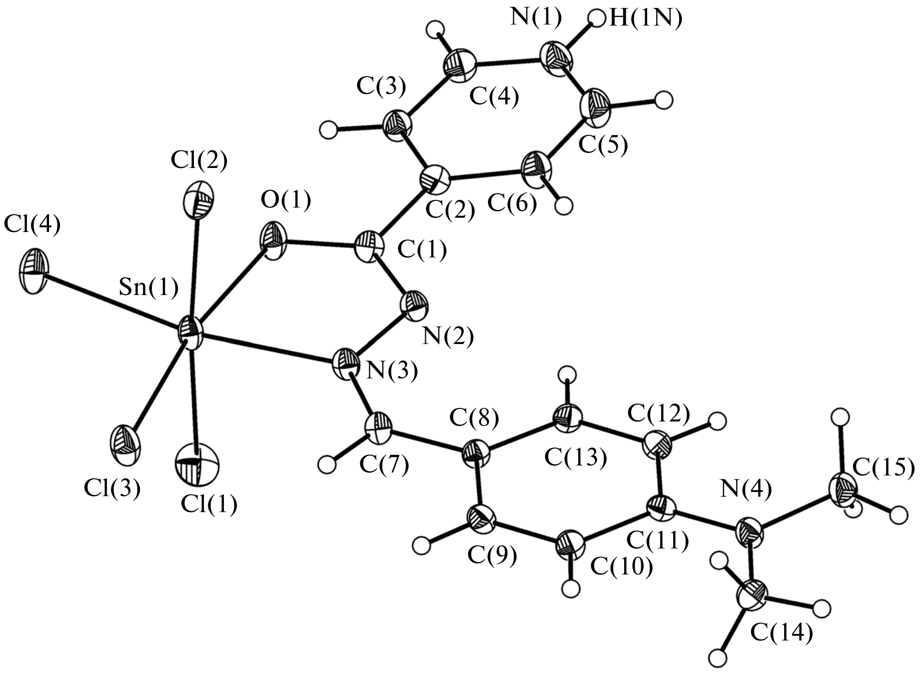

Fig. 1. Molecular structure of compound **III**.

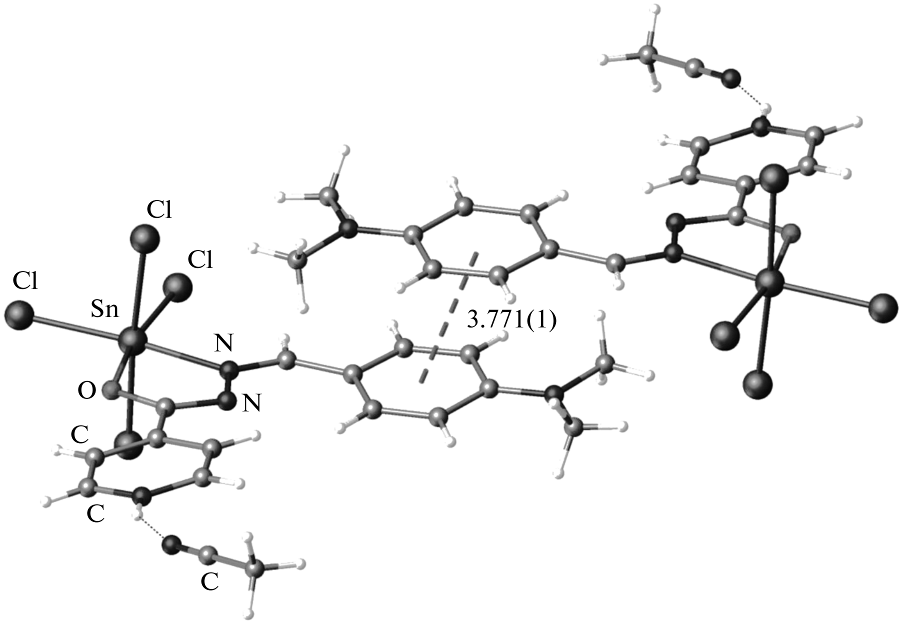

Fig. 2. Stacking interaction in structure **IIIb**. The distance between the centers of the phenyl substituents is indicated.

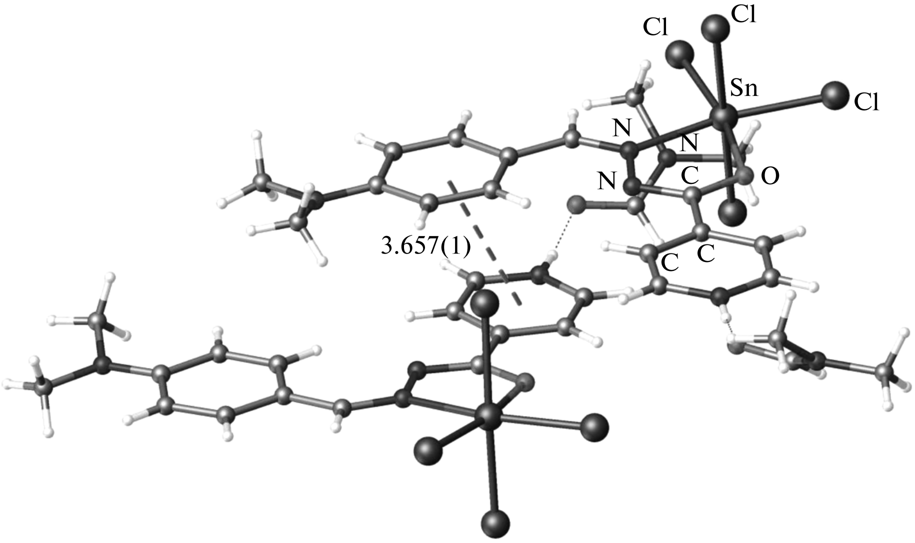

Fig. 3. Stacking interaction in structure **IIIc**. The distance between the centers of the phenyl substituents is indicated.

atoms (of the N(Py) and 4-$N(CH_3)_2$ groups) in the molecules of the complexes, the former is protonated being more basic, regardless of its position in the heterocycle. This is contrary to the fact that the α-pyridine atom (potential coordination site) could be bound to tin.

Thus, all coordination compounds synthesized earlier [10] and in this work are unusual chelates of tin tetrachloride with the zwitterionic form of hydrazone coordinated through the bidentate mode (N,O).

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