

## OXIDATIVE ADDITION REACTIONS OF Sn(II) AND Pb(II) WITH SOME HYDRAZIDE AND HYDRAZONE

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### تفاعلات الاضافة المصحوبة بالأكسدة للقصدير الثنائي والرصاص الثنائي مع بعض مشتقات الهيدرازيد والهيدرازون

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ص . ب ٢٧١٣ - الدوحة - قطر

تتحول مركبات القصدير من التكافؤ الثنائي إلى التكافؤ الرباعي بيسر وذلك باستخدام كواشف أكسدة. وقد تم استخدام مشتقات الأرتوكينون لأكسدة كثير من الفلزات الانتقالية وقليل من فلزات المجموعة الرئيسية، كما تم تحضير المتراكبات قيد الدراسة بتفاعل مشتقات كل من بنزويل الهيدرازيد وبنزويل بنزويل الهيدرازون مع كلوريد القصدير الثنائي ونواتر الرصاص، تم تحضير متراكبات بالإضافة بتفاعل مرتبطات معطاء متعادلة مثل ١، ١٠ - فينانثرولين و٢، ٢ - ثنائي البيريدين مع المتراكبات المحضرة، بينما تفاعل اليود بالأكسدة مع متراكبات القصدير مكوناً متراكب رباعي التكافؤ سداسي الارتباط ولم يتأكسد متراكب الرصاص، كذلك تفاعل كل من رباعي كلورو ورباعي برومو بنزوكينون ليعطي نواتج أكسدة مصحوبة بالإضافة وتفاعلت أيضاً مشتقات النافثوكينون مكونة متراكبات القصدير الرباعي والرصاص الرباعي عند درجة الحرارة العادية.

**Key Words:** Oxidative, addition reactions, tin(II), lead(II) metal complexes, hydrazide, hydrazone.

**Running Title:** Oxidative addition reactions of Sn(II) and Pb(II) ... ..

#### ABSTRACT

Bivalent tin compounds can be easily transformed to tetravalent compounds by oxidizing agents. The use of ortho-quinones for oxidation of transition metals has been the subject of many publications, but few analogous studies for main group metals have been reported. In continuation of earlier work on ligands containing hydrazide, we now report that the reaction of  $\text{SnCl}_2$  with both benzhydrazide (BH) benzyl benzhydrazone (BBH) in alcohol gives  $\text{Sn}(\text{BH})\text{Cl}_2$  and  $\text{Sn}(\text{BBH})\text{Cl}_2$ . A series of adducts involving neutral donors such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) are also formed. Upon oxidation of  $\text{Sn}(\text{BH})\text{Cl}_2$  with  $\text{I}_2$ , the product may be six coordinate tin (IV) complex  $\text{Sn}(\text{BH})\text{I}_2\text{Cl}_2$ . The reaction with tetrachloro-(TCQ) and tetrabromo-(TBQ) benzoquinone ( $\text{o-O}_2\text{C}_6\text{X}_4$ ,  $\text{X}=\text{Cl}$  or  $\text{Br}$ ) gives the oxidative addition products  $\text{Sn}(\text{BH})\text{C}_6\text{X}_4\text{O}_2\text{Cl}_2$ . Finally Sn(II) and Pb(II) complexes react smoothly at room temperature with naphthoquinone to form Sn(IV) and Pb(IV) complexes.

## INTRODUCTION

Tin (II) compounds are easily transformed to tin (IV) compounds by oxidizing agents.<sup>(1)</sup> The reaction of organotin(II) compounds were studied.<sup>(2-4)</sup> Some oxidative addition reactions of dicyclopentdienyl tin, tin dimethoxide, and tin bis(acetylacetonate) were investigated.<sup>(3,4)</sup> The reaction of organotin(II) compounds bearing SnOC bonds with carbonyl compounds and p-benzoquinone have been studied.<sup>(5)</sup> There are a number of reactions involving tin(II) halides which result in the formation of materials containing tin-metal bonds in the (IV) oxidation state.<sup>(6)</sup> The use of organotins in industry has increased over the last three decades as a result of their application in fungicides, antifouling paints, insecticides, agricultural pesticide purposes and as stabilizers for polyvinyl chloride and related plastics.<sup>(7)</sup> Tin (IV) antimonate was of particular interest due to its high cation-exchange capacity and selectivity for some elements.<sup>(8)</sup> The reaction mechanisms for some organotin compounds were mentioned.<sup>(9)</sup> Oxidative addition of tin(II) derivatives with some thiosemicarbazide were done.<sup>(10)</sup> In our present work we are concerned with the preparation, characterization and oxidative addition reactions of Sn(II) and Pb(II) complexes of some hydrazide and hydrazone derivatives.

## EXPERIMENTAL

All the chemicals used were of from BDH. Stannous Chloride was dehydrated by dissolving it in acetic anhydride.<sup>(10)</sup> Benzhydrazide (BH) and benzyl benzhydrazone (BBH) were prepared according to the literature method.<sup>(11)</sup> Tin and lead analyses were estimated by the standard methods.<sup>(12)</sup> Carbon and hydrogen microanalysis were carried out on Cairo University Microanalyses Unit. Inorganic halogen analysis by the Volhard method.<sup>(13)</sup> <sup>1</sup>Hnmr spectra were recorded with a Jeol JNM Fourier Transform nmr spectrophotometer using d<sub>6</sub>-DMSO as a solvent at Tanta University, Egypt. The equipment and the methods employed for recording the molar conductance and Infrared spectra were the same as reported earlier.<sup>(14)</sup>

### Synthesis of Sn(II) complexes:

In a typical experiment, to a weighted amount of stannous chloride (2.2g, 0.01 mol.) was added the calculated amount of benzhydrazide (1.4g, 0.01mol), using absolute ethanol (50ml) as the reaction medium. A white precipitate after reflux for one hour was formed. The solid compound was collected, washed with diethyl ether and dried *in vacuo*.

The separated complex (2.8g, 90%) was identified as (BH)SnCl<sub>2</sub>.2H<sub>2</sub>O.C<sub>2</sub>H<sub>5</sub>OH. By the same way with the molar ratio 1:1, [(BBH)(Sn).2H<sub>2</sub>O]Cl<sub>2</sub>.C<sub>2</sub>H<sub>5</sub>OH complex was prepared by the reaction of benz benzyl hydrazone with SnCl<sub>2</sub>.

### Synthesis of Pb(II) complex:

As reported above, to a weighted amount of lead nitrate (1.65g, 5mmol), dissolved in the least amount of water, was added to the calculated amount of benzhydrazide (0.7g, 5mmol) using absolute ethanol as the reaction medium. The solid precipitate that formed was collected, washed with diethyl ether and dried *in vacuo*. The solid compound was identified as (BH)Pb(NO<sub>3</sub>)<sub>2</sub>.C<sub>2</sub>H<sub>5</sub>OH.

### Formation of adduct

#### Synthesis [(BH)SnCl<sub>2</sub>.phen.]5H<sub>2</sub>O.C<sub>2</sub>H<sub>5</sub>OH:

In a typical experiment, 1,10-phenanthroline (0.19g, 1.05 mmol) was added to a solution of (BH)SnCl<sub>2</sub> (0.04g, 1.01mmol.) in ethanolic solution (30ml). A yellow product, was obtained after one hour of stirring at room temperature, the solid was collected, washed with ether, and dried *in vacuo*; yield of (BH)SnCl<sub>2</sub>.phen.5H<sub>2</sub>O.C<sub>2</sub>H<sub>5</sub>OH (0.5g, 91%). Adduct with Pb(II) complex was not formed.

### Oxidation of Sn(II) complexes

#### Reaction with I<sub>2</sub>

#### Synthesis of [Sn(BH)Cl<sub>2</sub>]<sub>2</sub>.2H<sub>2</sub>O.C<sub>2</sub>H<sub>5</sub>OH

(BH)SnCl<sub>2</sub> (0.41 g, 1 mmol) was suspended in diethyl ether (20 ml), and iodine (0.25 g, 1 mmol) in the same solvent (20 ml) was added. The orange solid immediately turned brown; stirring was continued over night, and the resulting solid in collected, washed and dried as in other experiment, yield of (BH)SnCl<sub>2</sub> (0.65 g, 98%).

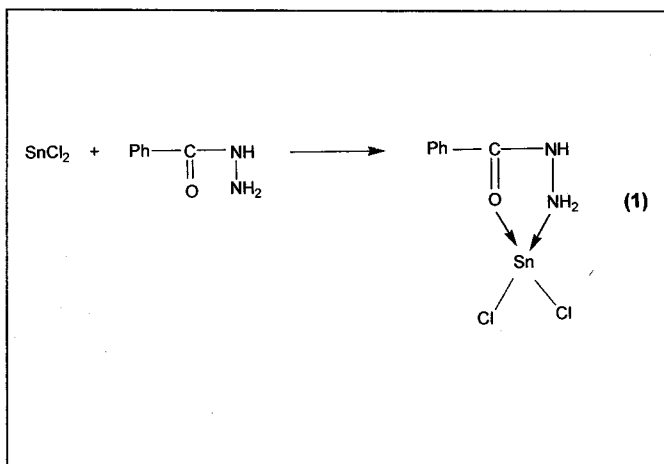
#### Reactions with tetrahalogeno-ortho-quinones (o-O<sub>2</sub>C<sub>6</sub>X<sub>4</sub>; X=Cl, Br)

#### Synthesis of (Br<sub>4</sub>C<sub>6</sub>O<sub>2</sub>) SnCl<sub>2</sub>(BH)

A solution of o-O<sub>2</sub>C<sub>6</sub>Br<sub>4</sub> (0.43g, 1 mmol.) in diethyl ether (20 ml) was added to (BH)SnCl<sub>2</sub> (0.41g, 1mmol) in the same solvent. The red solution of o-O<sub>2</sub>C<sub>6</sub>Br<sub>4</sub> change to brown. The mixture was stirred for 4h, by which time a brown solid had formed washed with ether and dried *in vacuo*. The product is (o-Br<sub>4</sub>C<sub>6</sub>O<sub>2</sub>)Sn(BH)Cl<sub>2</sub> yield (0.73 g, 95%). Analogous oxidative addition process was also identified with o-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub> to yields, Sn(BH)Cl<sub>2</sub>-o-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub> (0.61 g, 96%).

## RESULTS AND DISCUSSION

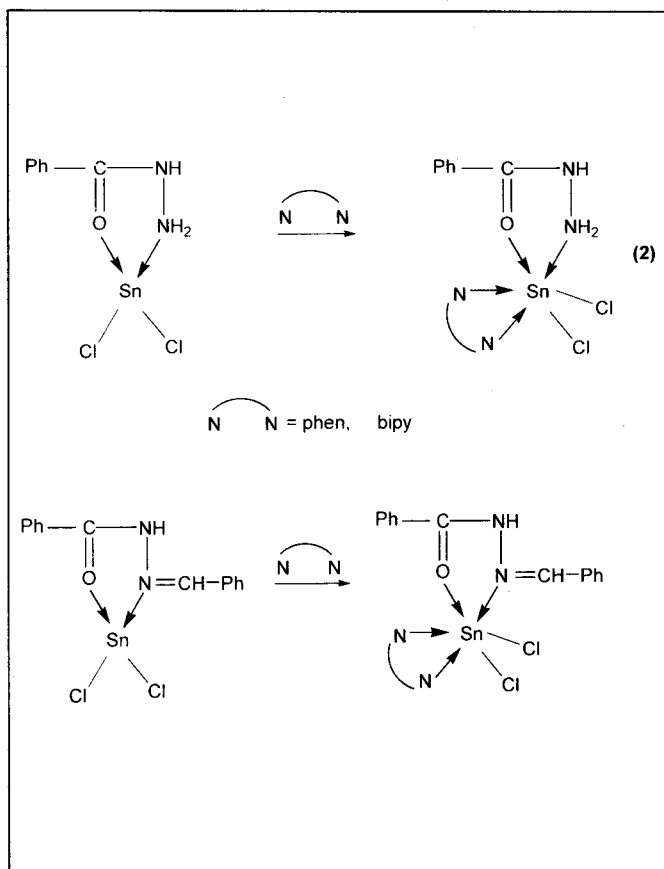
The reaction of tin(II) derivatives of Benzhydrazide and hydrazone in the presence of 1,10-phenanthroline, *n*-Bu<sub>4</sub>NI, I<sub>2</sub> and ortho quinones are a simple and efficient route to a series of novel Sn(II) and Sn(IV) compounds which have not have been previously reported.



The resulting complexes (table I) are solid, stable to atmospheric exposure and are soluble in common organic solvents such as acetone, DMF and DMSO.

Adducts (BH)SnCl<sub>2</sub> and (BBH)SnCl<sub>2</sub> and (BH)Pb(NO<sub>3</sub>)<sub>2</sub>

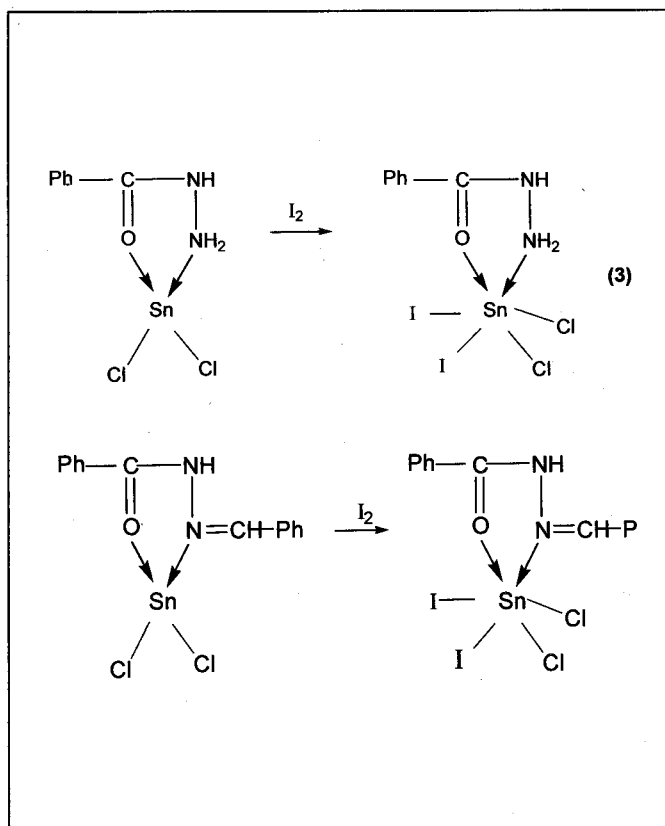
Both bipyridine and 1,10 phenanthroline form 1:1 complexes with (BH)SnCl<sub>2</sub> and (BBH)SnCl<sub>2</sub> (reactions 2). These



salts are 1:2 electrolytes in DMSO (cf conductivities 100-110 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>), established for such salts in this solvent compared with standard range.<sup>(15)</sup> Adducts with (BH)Pb(NO<sub>3</sub>)<sub>2</sub> complex were not formed.

Oxidation of (BH)SnCl<sub>2</sub>

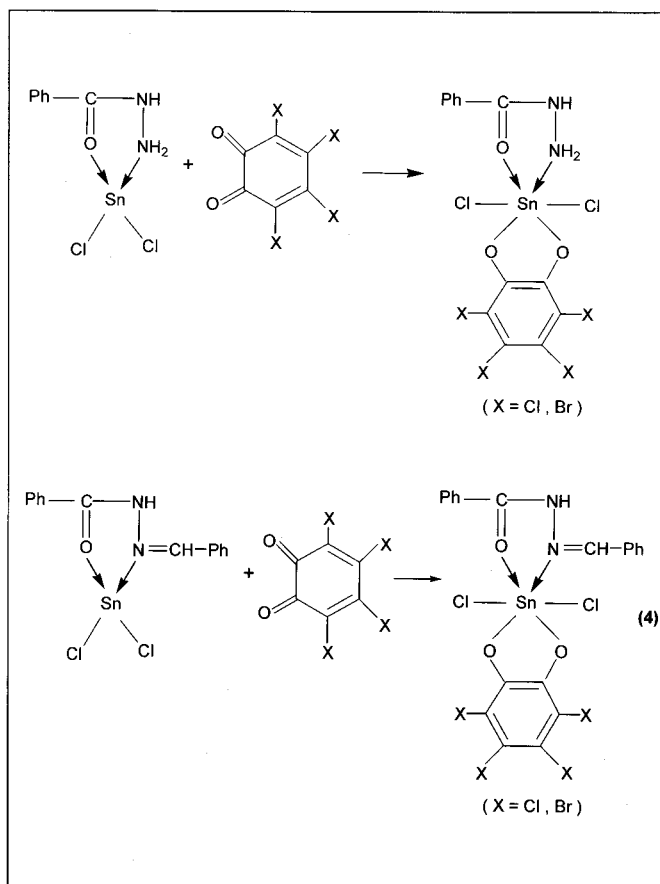
Whatever, the stereochemical influence of the non-bonding pair of electrons in tin, there can be no doubt about their par-



ticipation in the reaction with iodine, where the product is six-co-ordinate tin(IV) complex (BH)SnCl<sub>2</sub>I<sub>2</sub> which result from the oxidative insertion of tin(II) into the I-I bond; analogous reactions are known.<sup>(16,17)</sup> (reactions 3). The reaction of I<sub>2</sub> solution with Pb(BH)(NO<sub>3</sub>)<sub>2</sub> complex was not allowed.

Similarly, when tin(II) derivatives of hydrazide and hydrazone react with the ortho-quinones *o*-O<sub>2</sub>C<sub>6</sub>X<sub>4</sub> (X=Cl, Br), the final product is a six-co-ordinate tin(IV) complexes, the basic process is clearly that of oxidative addition. The reactions 4 are exactly parallel to that of tin(II) catecholates<sup>(18)</sup>, tin(II) halides<sup>(19)</sup> and tin(II) thiosemicarbazides.<sup>(10)</sup>

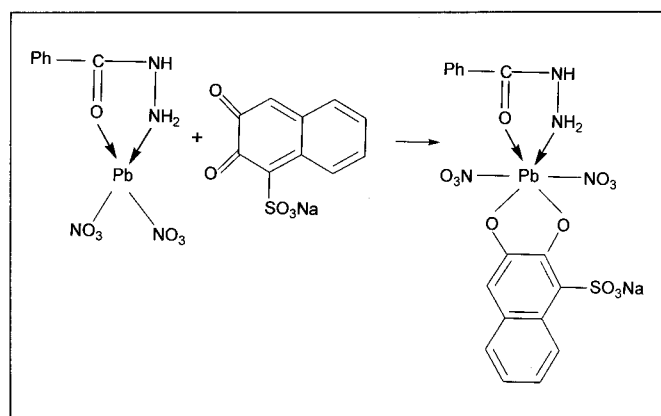
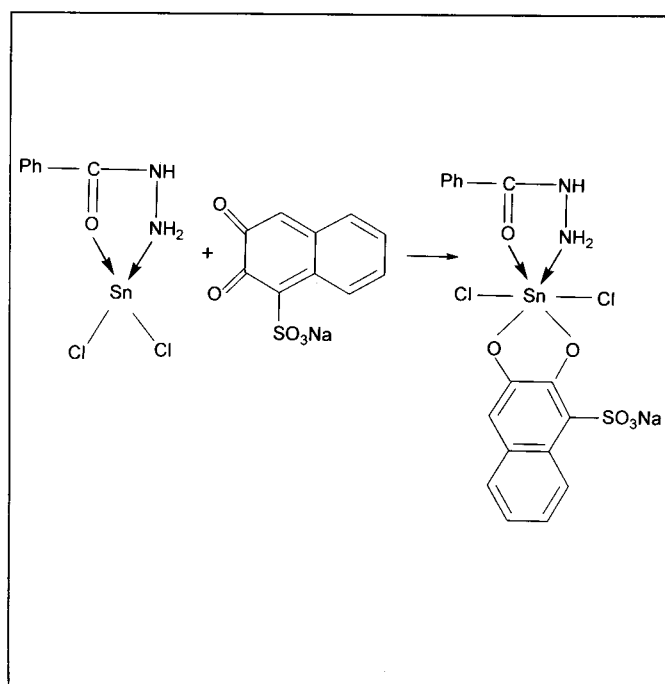
In a similar way, Sn(II) derivatives of hydrazides, hydrazones and Pb(II) derivatives of benzhydrazide react smoothly at room temperature with naphthoquinone to form Sn(IV) and Pb(IV) complexes (reactions 5). The orange colour of the



ketone disappears during the addition to the complexes.<sup>(16-19)</sup> <sup>1</sup>H-nmr and <sup>13</sup>C-nmr were carried out to prove this oxidative addition reactions.

### Spectroscopic Results

The identification of the (BH)SnCl<sub>2</sub>, (BBH)SnCl<sub>2</sub>; (BH)



Pb(NO<sub>3</sub>)<sub>2</sub> compounds, and of their derivatives, depend on both analytical and spectroscopic evidence (Tables I-III). The IR spectra of hydrazide and hydrazone show a characteristics bands for  $\nu$  NH<sub>2</sub> and  $\nu$  NH in the range 3180-3350 cm<sup>-1</sup>. The chelated Sn(II), Pb(II) and Sn(IV) complexes show a signals for the carbonyl group (C=O) at 1700 ± 20 cm<sup>-1</sup> indicating the formation of the keto-form chelate complexes corresponding to the coordinated carbonyl groups.

A comparison of the IR spectra of benzhydrazide, (BH) and (BH)SnCl<sub>2</sub> complexes bring the light to the following facts: (i) the bands due to  $\nu$  (NH<sub>2</sub>), in the ligand spectrum is strongly shifted (30cm<sup>-1</sup>) to lower wave number indicating coordination to the metal ions.

In the adducts with phenanthroline the characteristic IR spectrum of these compounds are observed. With the product of the reaction of (BH)SnCl<sub>2</sub> and (BBH)SnCl<sub>2</sub> with *o*-O<sub>2</sub>C<sub>6</sub>X<sub>4</sub> (X=Cl, Br), the most important observation is that  $\nu$  (C=O) of the *o*-quinone, at *ca.*1700 cm<sup>-1</sup> is absent in every case, being replaced by bands at 1440 and 1240 cm<sup>-1</sup> in the  $\nu$  (C-O) manifold: similar results have been observed in the [Sn(O<sub>2</sub>R)-*o*-O<sub>2</sub>C<sub>6</sub>X<sub>4</sub>], (X =Cl or Br),<sup>(18)</sup> [SnX-*o*-O<sub>2</sub>C<sub>6</sub>Br<sub>4</sub>],<sup>(19)</sup> [InX-*o*-O<sub>2</sub>C<sub>6</sub>Br<sub>4</sub>],<sup>(16)</sup> [(TBSQ)In(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>)]<sup>(20)</sup> and [(O<sub>2</sub>C<sub>6</sub>Br<sub>4</sub>)SnCl(PTS)]<sup>(40)</sup> systems. The IR spectra of tin(IV) compounds show bands at 450 and 360 cm<sup>-1</sup> due to  $\nu$  (Sn-O) and  $\nu$  (Sn-N). The dichlorotin derivatives show  $\nu_{as}$  and  $\nu_s$  Sn-Cl at 310 and 290 cm<sup>-1</sup> respectively.<sup>(6)</sup>

### NMR

The <sup>1</sup>H nmr spectra have been noted in the experimental part and are tabulated in Table II. The <sup>1</sup>H nmr spectra complemented the infrared spectra by confirming the presence of the donor ligands in the appropriate region of the spectra. Significant changes occur in the <sup>1</sup>H nmr resonance spectrum of neutral adduct upon coordination with Sn(II) complex.<sup>(17-21)</sup>

The  $^{13}\text{C}$  nmr spectra of the products that are sufficiently soluble for such measurements are summarized in Table III. The  $^{13}\text{C}$  nmr spectra on the other hand also showed the significant shift of the resonance observed at  $\sim 170.068$  ppm and assigned to  $\nu(\text{C}=\text{O})$  in the parent benzhydrazide, to  $171.264$  ppm, assignable to coordinated carbonyl group in the lead complex.<sup>(21,22)</sup>

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Compound	Colour	% Calc.				% found			
		C	H	M	Halogen	C	H	M	Halogen
[(BH)Sn.2H <sub>2</sub> O]Cl <sub>2</sub> .C <sub>2</sub> H <sub>5</sub> OH	white	26.51	4.4	29.1	17.3	26.6	4.0	29.0	17.4
[(BH)Sn.phen]Cl <sub>2</sub> .4H <sub>2</sub> O	Yellow	39.48	4.2	20.5	12.3	39.2	4.8	20.3	12.0
[(BH)Sn.I <sub>2</sub> ]Cl <sub>2</sub> .2H <sub>2</sub> O.C <sub>2</sub> H <sub>5</sub> OH	brown	16.3	2.7	17.94	49.1	16.1	3.0	18.1	48.9
[(BH)SnTCQ]Cl <sub>2</sub> .C <sub>2</sub> H <sub>5</sub> OH.H <sub>2</sub> O	green	28.3	2.54	18.6	----	28.2	2.8	18.4	----
[(BH)SnTBQ]Cl <sub>2</sub> .H <sub>2</sub> O	deep green	20.3	1.3	15.46	----	20.6	1.5	15.6	----
[(BH)(Sn)Naph.Q.] Cl <sub>2</sub> .4H <sub>2</sub> O	green	31.0	3.2	18.04	10.8	31.2	3.4	17.9	10.2
[(BH)(Pb)](NO <sub>3</sub> ) <sub>2</sub> .C <sub>2</sub> H <sub>5</sub> OH	white	21.05	2.7	40.4	-	20.8	2.2	40.5	-
[(BH)(Pb)(phen)](NO <sub>3</sub> ) <sub>2</sub> .2H <sub>2</sub> O	yellow	33.4	2.95	30.3	-	33.9	3.1	30.5	-
[(BH)(Pb)(bipy)](NO <sub>3</sub> ) <sub>2</sub> .C <sub>2</sub> H <sub>5</sub> OH	yellow	34.1	3.15	30.9	-	34.3	3.2	30.7	-
[(BH)(Pb)(ph <sub>3</sub> P)(NO <sub>3</sub> )]	piage	44.97	3.45	31.0	-	44.8	3.3	31.1	-
[(BBH)(Sn).2H <sub>2</sub> O]Cl <sub>2</sub> .C <sub>2</sub> H <sub>5</sub> OH	yellow	38.75	4.47	26.3	14.3	38.3	4.3	26.1	14.4
[(BBH)(Sn).I <sub>2</sub> ]Cl <sub>2</sub> .2H <sub>2</sub> O	brown	23.9	2.3	16.9	48.6	24.1	2.1	17.2	48.3
[(BBH)(Sn).phen]Cl <sub>2</sub> .2H <sub>2</sub> O	brown	49.5	3.84	18.84	11.25	49.7	4.1	19.1	11.0
[(BBH)(Sn)TCQ]Cl <sub>2</sub> .H <sub>2</sub> O	deep green	35.4	2.1	17.52	10.46	35.1	1.9	17.1	10.4
[(BBH)(Sn)Naph.Q.]Cl <sub>2</sub> .2H <sub>2</sub> O	deep green	40.6	3.00	16.7	9.98	40.7	2.8	16.5	10.2

Table 1: Elemental analysis for Sn(II), Sn(IV) and Pb(II) complexes for Benzhydrazide (BH) and Benzyl Benzhydrazone (BBH) derivatives.

**Table II.**  $^1\text{H}$ -nmr spectra of Sn(II) derivatives of Benzhydrazide and its phenanthroline adduct ( ppm, relative to  $\text{Me}_4\text{Si}$  )

Compound	Chemical shift	Assignment
1,10-Phenanthroline	9.2 (m,2H)	C2,C9 (phen)
	8,4 (m,2H)	C3,C8
	7,7 (m,2H)	C4,C7
	7.9 (m,2H)	C5,C6
(BH)Sn(phen)Cl <sub>2</sub>	9.39 (m,1H)	C2
	9.47 (m,1H)	C9
	8.19 (m,1H)	C3
	8.36 (m,1H)	C8
	9.06 (m,1H)	C4
	9.19 (m,1H)	C7
	8.60 (m,1H)	C5
8.70 (m,1H)	C6	

**Table III.**  $^{13}\text{C}$ nmr spectra of Benzhydrazide and Pb(II) Benzhydrazide Complex.( ppm, relative to  $\text{Me}_4\text{Si}$  )

Compound	Solvent	Chemical shift	Assignment
Benzhydrazide	DMSO	170.068	(carbonyl)
		137.4	(C2)
		132.4	(C3,C7)
		131.062	(C4,C6)
		135.2	(C5)
Pb(BH)(NO <sub>3</sub> ) <sub>2</sub>	DMSO	171.264	(carbonyl)
		136.75	(C2)
		132.687	(C3,C7)
		131.335	(C4,C6)
		135.778	(C5)