## Synthesis and characterization of Mercury (II) complexes of N-Phenyl-N-(2-Pyridyl or 2-benzothiazole) thiourea.

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## Abstract:

Mercury(II) complexes of the type  $[HgX_2(LH)]$  {X= Cl, Br, I, or SCN; LH= N-Phenyl-N-(2-pyridyl)thiourea or N-Phenyl-N-(2-benzothiazole)thiourea were prepared and characterized by elemental analysis and infrared spectra. The complexes were highly insoluble in common organic solvents to be characterize by NMR or conductivity measurements.

#### Keywords: Mercury, Thiourea ligand complexes

#### **Introduction:**

There is a considerable interest in transition metal complexes of thiourea derivatives partially due to their biological activities[1-5]. Thiourea derivative complexes have been screened for various biological actions[6,7]. The Platinum complexes have been used as antitumor agents in chemotherapy for treatment of some types of cancer [8,9].

Recently a series of platinum(II) complexes have been reported for their potentials use as chemotherapeutic agents[8,10]. We have recently reported[11] some palladium(II) and platinum(II) complexes containing the mixed ligands thiourea derivatives and diphosphines. In the present paper we report the synthesis and characterization of mercury(II) complexes of { N-Phenyl-N-(2-Pyridyl or 2-benzothiazol)thiourea}.

Experimental:

#### General

I.R. spectra were recorded on a Shimadzu FI-IR 8400 spectrophotometer in the 200-4000cm<sup>-1</sup> rang using CsI discs. Elemental analyses were carried out on a CHN analyzer type 1106 (Carlo-Erba). Melting points were measured on an electro thermal 9300 melting point apparatus.

#### Starting materials:

The compounds  $HgX_2$  (X=Cl, Br, I, SCN, or OAc), 2aminopyridine, 2-aminobenzothiazol and phenyl isothiosyanate were commercial products and used as supplied, N-phenyl-N-(2-pyridyl)thiourea (AH) was prepared according to literature method[11].

## N-Phenyl-N-(2-benzothiazole)thiourea (BH)

Phenyl isothiosyanate (0.88g, 0.0065mol) was added to a solution of 2-aminobenzothiazol (1.00 g., 0.0065m.) in benzene (10ml). The mixture was heated under reflux for 2h. then cool in an ice bath. The resulting white solid was filtered off washed with benzene and recrystalized from EtOH to give the product as a white needle crystals, (1.3g., 75% yield).

### Preparation of complexes:

The following general procedure has been used to prepare the complexes. A solution of mercuric halide or pseudo halide (0.526m.mol) in EtOH (5ml) was added to a hot solution of the ligand AH or BH (0.526m.mol) in EtOH (5ml). A yellow or white precipitate was formed immediately. The mixture was stirred at room temperature for 2h. The solid was formed, the precipitate was filtered and washed with EtOH, CHCl<sub>3</sub> and then dried at 75°C.





#### **Results and discussion:**

The complexes  $[HgX_2(LH)]$  {X= Cl, Br, I, or SCN; LH= AH or BH} were prepared by reaction of  $HgX_2$  in ethanol with the ligands AH or BH in a mole ratio 1:1. A white or yellow solid formed immediately. The obtained compounds are crystalline solids insoluble in common organic solvents such as ethanol, methanol, chloroform etc. For this reason we were unable to measure <sup>1</sup>H nmr or the conductivity for these complexes. The prepared complexes were characterized by I.R. spectra and elemental analysis. According to the elemental analysis (Table 1), they have a mole ratio M :LH =1:1.

#### Spectroscopic data:

Complexes of the type  $[HgX_2(AH)]$  (Table 2) showed medium to strong bands within the range (350-370 cm<sup>-1</sup>) could probably assigned to v(Hg-S) [12,13]. The spectra also showed strong bands at ((510-518cm<sup>-1</sup>) assigned to v(Hg-N) [14] which indicate that thiourea ligands coordinated to mercury through both nitrogen of the ring and sulfur of thio group. Thioamide band (I) which is mainly due to appeared at (1550-1562cm<sup>-1</sup>), shifted by about 30cm<sup>-1</sup> as compared with the free ligand. Thioamide band (II) which is mainly due to appeared at (1471-1485cm<sup>-1</sup>), shifted to a higher frequency by 50cm<sup>-1</sup>, indicating the coordination of sulfur to metal. Thioamide band (III) appeared at (993-998cm<sup>-1</sup>), except for [HgBr<sub>2</sub>(AH)] which appeared at 920cm<sup>-1</sup>. Thioamide band (IV) appeared at (756-780cm<sup>-1</sup>). The far I.R. spectra

showed a medium intensity band at 320cm<sup>-1</sup> assigned to u(Hg-Cl) [15] for [HgCl<sub>2</sub>(AH)] and a strong band at (2102cm<sup>-1</sup>) assigned to v(NCS) for [Hg(NCS)<sub>2</sub>(AH)]. Infrared spectral data for  $[HgX_2(BH)]$  complexes {X= Cl, Br, I, or SCN}(Table 1) of the complexes [HgX<sub>2</sub>(BH)] shawed a weak band within the rang (365-370 cm<sup>-1</sup>) assigned to  $\upsilon$ (Hg-S)[12,13]. The spectra also showed a weak to medium band within the rang (498-505  $cm^{-1}$ ) assigned to v(Hg-N) [14]. The spectra also showed the three thioamide bands at (1529-1562 cm<sup>-1</sup>) assigned to thioamide band (I) which is shifted to a lower frequency by (7-40cm<sup>-1</sup>) as compared with the spectrum of the free ligand. Thioamide band (II) appeared at (1471-1519cm<sup>-1</sup>) and this is shifted to a lower frequency by 60cm<sup>-1</sup> while Thioamide band (III) appeared at (918-940 cm<sup>-1</sup>) and it is shifted to a lower frequency by 30cm<sup>-1</sup> also the Thioamide band (IV) appeared at (750-757cm<sup>-1</sup>) and this is shifted to a lower frequency by 18cm<sup>-1</sup>.

The  $\upsilon(N-H)$  band at (3175-3440cm<sup>-1</sup>) is shifted to a higher frequency when ligand coordinated to the metal ion. A medium band appeared at (318cm<sup>-1</sup>) assigned to  $\upsilon(Hg-Cl)$  [15] and a strong band appeared at (2104cm<sup>-1</sup>) which is assigned to  $\upsilon(Hg-NCS)$ . From the above I.R. data it can be concluded that the ligands AH and BH coordinated to mercury as chelated ligand through nitrogen atom of the heterocyclic ring and sulfur atom of the thiourea group.

Sea.	Complexes	Color	Yield %	m.p. C <sup>o</sup>	Found(calc)%			
				<u>r</u> · -	С	Н	Ν	
1	[HgCl <sub>2</sub> (AH)]	White	72	222-224	28.7(28.6)	2.4(2.3)	8.4(8.7)	
2	[HgBr <sub>2</sub> (AH)]	White	63	195-197	24.4(24.2)	2.1(2.0)	7.1(6.9)	
3	[HgI <sub>2</sub> (AH)]	White	86	202-204	21.1(21.0)	1.8(1.9)	6.1(6.3)	
4	[Hg(SCN) <sub>2</sub> (AH)]	Black	49	Dec <sup>*</sup>	31.9(32.2)	2.0(2.2)	11.6(11.5)	
5	[HgCl <sub>2</sub> (BH)]	Yellow	62	Dec <sup>*</sup>	30.1(30.2)	2.2(2.4)	7.5(7.2)	
6	[HgBr <sub>2</sub> (BH)]	Yellow	89	163-165	26.0(25.8)	1.9(2.2)	6.5(6.7)	
7	[HgI <sub>2</sub> (BH)]	Yellow	60	177-179	22.7(23.0)	1.6(1.8)	5.7(5.9)	
8	[Hg(SCN) <sub>2</sub> (BH)]	Yellow	61	115-117	31.9(32.0)	2.8(2.2)	11.6(11.6)	

Table 1; color, yield, m.p. and elemental analysis for complexes

\*- Decompose a bove 250 C<sup>o</sup>

 Table 2: I.R. Spectral data<sup>\*</sup> cm<sup>-1</sup> of the ligands and complexes

Complexes.	Thioamide bands				Other	υ	υ	υ	υ	υ
	Ι	II	III	IV	υ(N-H)	(Hg-N)	(Hg-S)	(Hg-Cl)	(NCS)	(C-H)
AH	1532 <sub>m</sub>	1427 <sub>m</sub>	959 <sub>w</sub>	772 <sub>s</sub>	$\frac{3218_m}{3174_m}$					3037 <sub>w</sub>
BH	1569 <sub>m</sub>	1446 <sub>m</sub>	948 <sub>m</sub>	730 <sub>m</sub>	3161 <sub>m</sub>					3005 <sub>m</sub>
1	1562 <sub>m</sub>	1477 <sub>m</sub>	995 <sub>w</sub>	780 <sub>s</sub>	3244 <sub>s</sub> 3182 <sub>w</sub>	510 <sub>s</sub>	365 <sub>m</sub>	320 <sub>m</sub>		$3035_{\rm w}$
2	1560 <sub>m</sub>	1477 <sub>m</sub>	920 <sub>m</sub>	775 <sub>s</sub>	3269 <sub>s</sub> 3110 <sub>w</sub>	518 <sub>s</sub>	350 <sub>w</sub>			3031 <sub>w</sub>
3	1558 <sub>s</sub>	$1475_{m}$	$998_{\rm w}$	775 <sub>s</sub>	3298 <sub>s</sub>	516 <sub>s</sub>	360 <sub>s</sub>			$3030_{\rm w}$
4	1550 <sub>s</sub>	1485 <sub>m</sub>	993 <sub>m</sub>	756 <sub>s</sub>	3411 <sub>w</sub> 3312 <sub>w</sub>	510 <sub>s</sub>	363 <sub>m</sub>		2102 <sub>s</sub>	3039 <sub>w</sub>
5	1531 <sub>s</sub>	1481 <sub>w</sub>	915 <sub>w</sub>	752 <sub>s</sub>	3250 <sub>w</sub>	505 <sub>w</sub>	370 <sub>w</sub>	318 <sub>m</sub>		3050 <sub>m</sub>
6	1529 <sub>m</sub>	1487 <sub>m</sub>	918 <sub>m</sub>	$750_{\rm s}$	3413 <sub>m</sub>	$498_{\rm w}$	365 <sub>m</sub>			$3058_{\rm w}$
7	1529 <sub>s</sub>	$1487_{s}$	920 <sub>w</sub>	750 <sub>s</sub>	3415 <sub>m</sub>	503 <sub>w</sub>	368 <sub>w</sub>			3030 <sub>w</sub>
8	1546 <sub>s</sub>	1488s	930 <sub>m</sub>	755 <sub>s</sub>	3440 <sub>w</sub>	501 <sub>m</sub>	370 <sub>w</sub>		2104 <sub>s</sub>	3060 <sub>w</sub>

\*- for I.R. data; w= weak; m= medium; s= strong.

#### **References:**

1- S. Nadeen, M. K. Rawf, S. Ahmed, M. Ebihara, S. A. Tirmizi, S. A. Bashir and A. Badshals, *Transition Met. Chem.*, 34 (2009) 197

2- S. S. Kandil, S. M. A. Matib and N. H. M. Yarkandi, *Transition Met. Chem.*, 32 (2007) 791.

3- L. Fuks, N. S. Sosnowska, K. Samochocka and W. Starosta. J. Moles. Stru., 740(2003)229.

4- G. M. S. El-Bahy, B. A. El- Sayed and A. A. Shabana, Vibrational Spectroscopy, 31 (2003) 101.

5- S. Ahmed, A. A. Isab and H. Perzanowski., *Transition Met. Chem.* 27 (2002) 782.

6- E. R. Fernandez, J. L. Manzano, J. J. Benito, R.Hermosa, E. M. onte and J. J. Criado, *J. Inorg. Biochem.*, 99 (2005)1558.

7- R. delCampo, J. J. Criado, R.Gheorghe, F. J. Gonzalez, M. R. Hermosa, F. Sanz, J.L Mmanzano, E.Monte and E. R. Fernandez., Inorg. Biochem., 98 (2004) 1307.

8- C. Sscht, M.S. Datt, S. Otto and A. Roodt, J. Chem. Soc. Dalton. Trans., (2000) 727.

9- I. Kostova, Recent Patents on Anti-Cancer drug discovery, 1,1 and refrences therein (2006).

10- C. Sscht, and M.S. Datt, *Polyhedron*, 19 (2000) 1347.

11- L. J. AL-Hayaly, B. H. Abdullah, A. A. N. AL-Dulaimi and S. A. AL-Jibori., *Orient. J. Chem.*, 24 (2008) 38.

12- N. Al-Nassiri, *M. Sc. Thesis*, University of Tikrit, IRAQ, (1999).

13- A. S. Al-Janabi, *M. Sc. Thesis*, University of Tikrit, Iraq., (2008).

14- E. J. Baran and V.T.Yilmaz, *Coord. Chem. Rev.*,250(2006)1980.

15- M. R. Chaurasia, and N. K. Sengh, *Chemicals and Petro Chem. J.*, 12 (8) (1981) 3-8.

# تحضير وتشخيص معقدات الزئبق (II) مع N-Phenyl-N-(2-Pyridyl or 2-benzothiazole) thiourea. عدنان عبد النبي حمادة الدليمي

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الملخص

تم تحضير وتشخيص معقدات الزئبق (II) من نوع -X= Cl, Br, I, or SCN; LH= N-Phenyl-N-(2- الزئبق (II) من نوع . pyridyl)thiourea or N-Phenyl-N-(2-benzothiazole)thiourea.

بواسطة التحليل الدقيق للعناصر ومطيافية الاشعة تحت الحمراء. المعقدات عديمة الذوبان بصورة كبيرة في معظم المذيبات العضوية الشائعة لذلك لم يتم التمكن من اجراء قياس التوصيلية الكهربائية وطيف الرنين المغناطيسي (NMR) لهذه المعقدات.