GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 9, NO. 3, JUNE 2003: 351 - 357
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SYNTHESES AND SPECTROSCOPIC PROPERTIES OF MERCURY(II) AND NICKEL(II) COMPLEXES OF BIS(N-PHENYL THIOUREA)

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(Received 17 October 2002; Revision accepted 17 March, 2003).

ABSTRACT

Mercury(II) complex, [Hg_2(BPTU-2H)Cl_2] and nickel(II) complex, [Ni(BPTU-H)$_2$] were prepared by reacting Bis(N-phenylthiourea), BPTU, with mercury(II) chloride and nickel(II) acetate respectively. The complexes were characterized by IR, diffuse reflectance, ^{1}H NMR spectra and elemental analysis. BPTU acts as monoanionic bidentate chelating agent in nickel(II) complex, coordinating through thiolato sulphur and hydrazinic nitrogen atoms. Its coordination nature differs in mercury(II) complex, where it acts as dianionic bis(bidentiate) chelating agent, coordinating through thiolato sulphur and hydrazinic nitrogen atoms to two mercury(II) ions simultaneously. On the basis of analysis and spectral properties, Ni(BPTU-H)$_2$ has been tentatively assigned square planar geometry. The [Hg_2(BPTU-2H)Cl_2] appears to have binuclear structure having triangular coordination centres around mercury(II) cations.

Key Words: Bis(N-phenylthiourea), mercury(II) complex, nickel(II) complex, IR, ^{1}H NMR, electronic spectra.

INTRODUCTION

Nickel and its function in the environment, in aquatic systems, in plants, as well as its metabolism in man and animal have been reviewed by Sigel and Sigel (1988). Nickel (II) complexes of 2-acetyl pyridine ^{4}N-diethyl- and ^{4}N –dipropyl thiosemicarbazones show less activity against *Aspergillus niger* than the free thiosemicarbones. However, against *paecilomyces variotii* the nickel (II) complexes possess comparable activity at high concentrations and more active at lower concentrations (West et al. 1990). Nickel(II) complexes of thiosemicarbazide (Jayasooriya and powell, 1982) and thiosemicarbazones (West et al. 1993, Sreekala and Yusuff, 1994) have been investigated in detail, but scanty information is available on complexes with substituted thiosemicarbazides (Leovac et al, 1989). The x-ray crystallographic studies on nickel(II) complexes with thiosemicarbazide (Hazell, 1972,) and thiosemicarbazones (Leovac et al, 1989, Akinchan et al, 1992, Akinchan and Abram 2000) have been the active area of research in recent times. The synthetic, spectroscopic and x-ray crystallographic report on mercury(II) complexes with thiosemicarbazide (Chieh, 1977) and thiosemicarbazones (Macias et al, 1989, Zukerman-Schpector et al, 1991, Akinchan et al, 2000) have also been reported. Bis(N-phenyl thiourea) BPTU a 1, 4-disubstituted thiosemicarbazide has attracted much attention in recent years due to its antiviral activity against potato virus X (PVX) (Devarski et al, 1989). It has also been used as an effective collector for recovery of platinum(II), gold(III) and silver(I) ions from sulphide ore by froth floatation process (Lambert, 1993) Recently bis(n-phenyl thiourea) BPTU, has been characterized by means of x-ray crystallographic, IR, Raman, Uv-visible, ^{1}H NMR and FAB mass spectral measurements (Akinchan et al, 2001).There is only one report in literature on nickel(II) complex with bis (N-phinylthiourea), BPTU and it was prepared using nickel (II) bromide (Furlani and Tarantelli, 1973). We report here the syntheses and spectroscopic properties of nickel(II) and mercury(II) complexes with bis(N-Phenyl thiourea), BPTU.

MATERIALS AND METHODS

Materials:

Mercury(II) chloride (Acs ereagent) nickel(II) acetate tetrahydrate (LR), phenyl isothiocyanate (LR) and hydrazine hydrate (LR) were obtained from Aldrich Chemical company and were used as received. The other chemicals were chemically pure laboratory reagents.

Analyses:

Carbon, hydrogen and nitrogen were

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determined by standard micro methods

Physical Measurements:

Infrared spectra were recorded on a Perkin Elmer FTIR 1600, 1800 and 2000 spectrometers using standard KBr pellet technique for middle infrared region and nujol mulls on polyethylene windows for far infrared scanning. Reflectance spectra were recorded on a CARY 500 Scan UV-Vis-NIR sepectrometer. The ^{1}H NMR spectra were obtained as earlier reported (Akinchan et al; 1992).

Synthesis of Bis (N-pHenyl thiourea) BPTU:

The ligand; BPTU, was synthesized as reported earlier (Akinchan et al, 2002)

Synthesis of [Ni(BPTU-H)$_2$]

.BPTU (3.03g, 10mmol) was dissolved in ethanol and refluxed for 30minutes. To this solution was added ethanolic solution of nickel(II) acetate tetrahydrate (1.25g, 5mmol) and the resultant solution was refluxed for another two hours. On concentration cooling at room temperature a light brown product was formed. The product was separated, washed with ethanol and then with diethyl ether, and dried over fused CaCl$_2$. mp 225^{o}C(D) [found Ni 8.79, C. 50.76; N.16.88; H.3.98% Ni($C_{28}H_{26}N_8S_4$) requires Ni 8.87, C.50.84; N.16.94; H.3.96%]

Synthesis of Hg$_2$(BPTU-2H)Cl$_2$

An ethanolic solution of mercury(II) chloride (2.72, 10mmol) was added gradually to ethanolic solution of BPTU (1.51g,5mmol). The solution was stirred for 30minutes then refluxed for 30minutes and left overnight at room temperature. The light yellow microcrystalline product was separated, washed with ethanol and then with diethylether. The complex was dried over fused CaCl$_2$. mp.205^{o}C (D) [Found:] Hg50.82, C.21.66; N.7.20; H.1.61%, $Hg_2C_{14}H_{12}N_4S_2Cl_2$ requires Hg51.93, C.21.77; N.7.25; H.1.56%]

RESULTS AND DISCUSSION

From the elemental analysis the nickel(II) and mercury(II) complexes could be formulated as, Ni(BPTU-H)$_2$ and Hg$_2$ (BPTU-2H)Cl$_2$ respectively. The magnetic susceptibility measurement indicates diamagnetic character and the molar canductance data in dimethyl formamide (10^{-3} molar solution) suggests non-electrolytic nature for the two metal complexes. The coordination nature of bis(N-phenyl thiourea), BPTU, and the possible structures for the two metal complexes will be examined in further discussion.

Infrared spectra:

Table 1 lists infrared spectral bands along with tentative assignments of selected transitions. The recent Fourier-Transform Infrared (FTIR) spectral measurement resulted in better quality spectra, therefore the sets of the observed bands with percentage transmission are presented below.

[Hg$_2$ (BPTU-2H) Cl$_2$] Complex:

The IR Spectra of Bis (N-phenyl thiourea), BPTU and mercury(II) complex are different in the region of V(NH) stretching vibrations. The band at 3113cm^{-1} is assigned to V(NHNH) and at 3212cm^{-1} to V(NHPh) as reported by Akinchan et al (2002). The low energy band representing two NH groups disappears in the spectrum of the mercury(II) complex suggesting double deprotonation of the ligand. The IR band attributable to NH attached to phenyl rings changed to 3238cm^{-1} in the spectrum of the metal complex. The coupled vibration of v(C-N) and v(N-H) is located at 1595cm^{-1} in the spectrum of the ligand and it is found in high energy region at 1618cm^{-1}. Thus the energy of v(C-N) band increased on deprotonation of the ligand before metal chelation, The other coupled vibration of v(C-N) and v(C-S) of thiosemicarbazide moiety observed at 1450 cm^{-1} splits to 1456 and 1394cm^{-1} in the spectrum of mercury(II) complex. The IR band at 780 cm^{-1} appears to be due to v(C=S) vibration and it disappeared in the spectrum of mercury(II) complex. Sreekala et al (1994) have also assigned a band at 780cm^{-1} to vC=S) stretching vibratiom in quinoxaline 2-carboxaldehyde thiosemicarbazone. The central N-N bond stretching vibration coupled with neighboring v(C-N) mode have been located at 1330cm^{-1} in the spectrum of BPTU (Akinchan et al, 2002) and it remained unaffected in the spectrum of the mercury(II) complex. The stretching vibration mode of the C$_{ph}$-N bond is observed at 1248 cm^{-1} and it shifted to 1225cm^{-1} in the spectrum of the complex. The combination mode of 1225cm^{-1} and 621cm^{-1} bands is located at 1836cm^{-1}, on

Table 1: Infrared spectral bands[a] (cm^{-1}) of BPTU and its metal complexes

BPTU	Hg_2(BPTU	Ni $(BPTU-H)_2$	Assignments
3212(5.7)	**3238**(39.2)	3217(28.7)	Y (NH)
3113(5..2)	- -	3114(31.4)	Y (NH)
3010(13.3)	- -	-	Y (CH)
2938(9.1)	2922(46.0)	2924(31.1)	Y (CH)
2322(76.7)	2362(28.7)	2322(43.8)	Y (CH)
2322(76.7)	2322(43.8)		Y (CH)
- - -	1836(60.9)		**1225+621=1846**
1595(64.1)	1618(35.4)	1649(33.7)	Y(C=N) + υ (NH)
1547(2.1)		1547(26.6)	
1506(6. 9)	1506(35.7)	1512(28.8)	
1450(39.9)	1456(45.0)		
	1394(49.9)	1394(35.6)	
1330(35.5)	1331(57.2)		υ (C=N)+ υ (C-S)
1248(23.8)	1225(60.4)	1203(50.0)	$(C_{ph}-N)$ mode
1189(4.5)	1167(62.3)	1114(45)	υ (N-H)
1070(47.0)	1070(60.9)		υ (N-H)
1026(60.6)	1026(61.9)		C-H bending
1001(70.8)			υ (C-C) breathing
934(68.9}		907(59.7)	υ (C=S)+ υ (C=N)
780(66.0)			
750(47.7)			
694(8.6)	692(57.4)	694(50.1)	υ (NNCS)
	669(69.3)		
637(23.3)	621(70.6)	633(53.2)	

a - % Transmission in parentheses.

Table 2: ^{1}H NMR Chemical shifts[a] data (ppm Vs TMS) for BPTU and its metal complexes:

^1H	BPTU	$Hg_2(BPTU-2H)Cl_2$	$Ni(BPTU-H)_2$	PTSCH[b]	TTSCH[c]
C(2)H C(6)H	7.55 (d, 4H)	7.57 (d, 4H)	7.52 (d, 4H)	7.65 (d, 2H)	**7.48 (d, 2H)**
C(3)H C(5)H	7.35 (t, 4H)	7.43 (d, 2H) 7.39 (d, 2H)	7.32(t,4H)	7.33 (t, 2H)	**7.09 (d,2H)**
C(4)H	7.18 (t, 2H)	7.22 (t, H) 6.88 (t, H)	7.14 (t, H) 6.93 (t, H)	7.10 (t, H)	- -
Ph NH	9.93 (br, 2H)	8.34 (s,H) 7.22 (s, H)	4.05 (br, 2H)	9.15 (br, H)	9.10 (br, H)
HN-NH	9.73 (br, 2H)	- -	9.60 (br) (,H) 9.68 (br)	- -	- -
NH_2	- -	- -	- -	4.80 (br, 2H)	4.80 (br, 2H)
C(S)NH	- -	- -	- -	9.70 (br, H)	**9.60 (br. H)**

a Measured in DMSO-d_6; the relative resonance integral corresponding **to the appropriate number of protons is given in parentheses, spin multiplicity is given with abbreviations, s=singlet, d=doublet, t=triplet, br=broad**

b. ^{1}H NMR chemical shifts data for phenyl thiosemicarbazide **(measured values in** DMSO - d_6 **during present** investigation).

c. ^{1}H NMR chemical shifts data for 4-tolyl thiosemicarbazide **(Koch, 1988).**

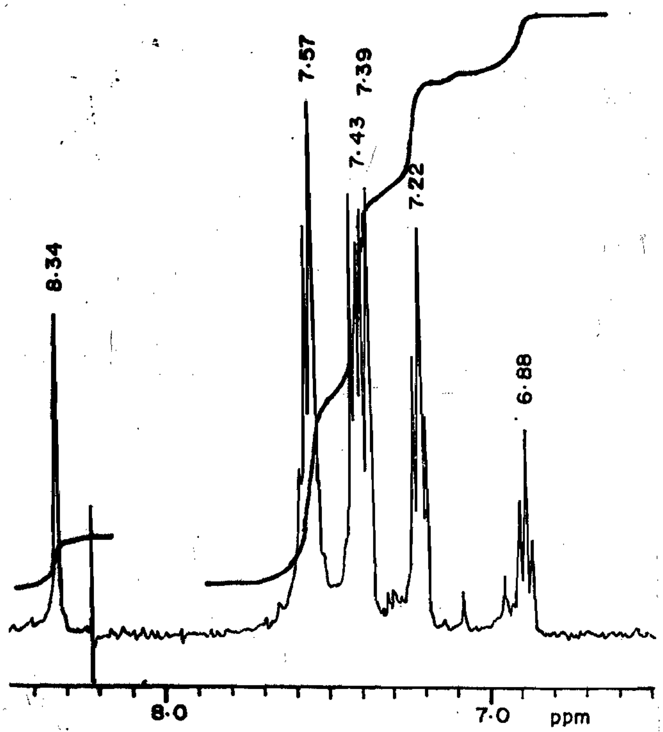

Figure 1: ^{1}H NMR spectrum of Hg_2 (BPTU-2H)Cl_2

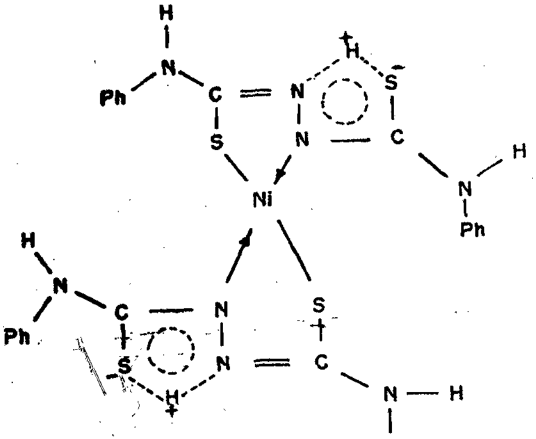

Figure 2: Proposed structure of Ni(BPTU-H)$_2$

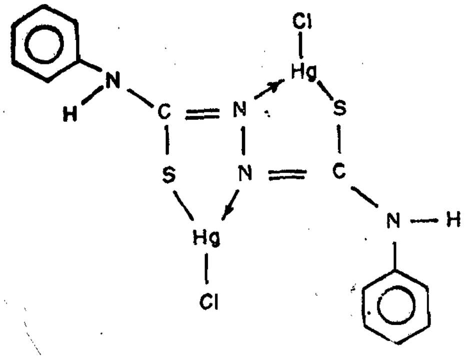

Figure 3: Proposed structure of Hg_2 (BPTU-2H)Cl_2.

metal chelation. All these observations indicate the change in C_{ph}-N bond energy during metal chelation. Absorption bands located in the spectrum of BPTU at 694, and 637cm^{-1} are shifted to 692, 669 and 621cm^{-1} after coordination, suggesting some NNCS mode contribution in these transitions (Ackinchan et al, 2000). In the far IR region, new bands appear after coordination at 318 and 284cm^{-1}. In this region, the v(Hg-S) stretching vibration is proposed. (Akinchan et al, 2000). However, it has been observed that the mercury(II)-sulphur and mercury(II)-chlorine vibrations are of comparable energies and hence the meaningful assignment is v(Hg-S)+v(Hg-Cl). The mercury(II)-nitrogen vibrations are usually at higher energy than those of mecury(II)-sulphur. In the case of Hg_2 (BPTU-2H) Cl_2 the best condidate for this mode is the 457cm^{-1} band. Akinchan et al (2000) reported a band at 427cm^{-1} in the spectrum of dichloro (tolualdehyde thiosemicarbazonate) mercury(II). On the basis of above discussion it is being concluded that BPTU most probably acts as bis(bidentate) chelating agent in dianionic form. The structure of the mercury(II) Complex (Figure 3.) is dimeric, having three coordinate mercury(II) centres. The BPTU coordinates through thiolato sulphur and hydrazino nitrogen to two mercury(II) cations simultaneously.

Ni(BPTU-H)$_2$ Complex:

The ligand and the complex spectra appear to be the same in the region of v(N-H) stretching vibrations. It is surprising that after assuming deprotonation of the BPTU, two bands at 3217 and 3114cm^{-1} were observed in the spectrum of the nickel(II) complex. The above observations only supports the presence of NH groups belonging to H-N-N- and Ph-N-H moieties in the nickel(II) coordination sphere. The only difference is observed for the band at 1595 cm^{-1} attributed to coupled v(C=N) and v(NH) vibrations, which shifted to 1649cm^{-1} in the high energy region with decreased absorption intensity. The other two bands in this region at 1547 and 1506cm^{-1} are also affected and located at 1547 and 1512cm^{-1} with decreased absorption intensity. All these observations support the increase in (C=N) bond energy due to deprotonation of thiol group. The other coupled vibrational band at 1450cm^{-1} due to v(C-N) + v(C-S) shifted to 1394cm^{-1} in the spectrum of the

Table 3: Solid state electronic spectra (cm^{-1}) of BPTU, and its metal complexes

BPTU	$Ni(BPTU-H)_2$	$Hg_2(BPTU-2H)CI$	Assignments
42000	41667	41254	∏ - ∏* arom
34700	34790	34860	∏ - ∏* arom
29500	29360	29390	∏ - ∏* Thiosemicarbazone
- -	19849	- -	$dxy \rightarrow dx^2- y^2$
- -	15198	- -	$dxz, dyz \longrightarrow dx^2- y^2$

nickel(II) complex. Furthermore the IR spectral band which has been assigned to v(N-H) + v(C-N) is observed at $1330cm^{-1}$ in the ligand spectrum and it disappeared on metal chelation. The band which appears to be pure v(C=S) mode at 780cm 1 in the ligand spectrum also disappeared on ligand participation in bonding. Thus the above observations provide sufficient evidences to support the coordination of BPTU after deprotonation and the coordination occurs through thiolato sulphur and hydrizino nitrogen atoms. The new bands located at 515 and $396cm^{-1}$ in the far-IR region are assigned to u(Ni-N) and u(Ni-S) stretching vibrations respectively. In earlier report on nickel(II) complex the bands at 460-515 and $380cm^{-1}$ were assigned to u(Ni-N) and u(Ni-S) respectively (Akinchan et al, 1992). Thus the analysis and spectral evidences suggest square planar structure for nickel(II) complex (Figure 2).

^{1}H NMR Spectra:

The ^{1}H NMR spectra of BPTU, Ni($BPTU-H)_2$ and Hg_2 ($BPTU-2H)CL_2$ were recorded in DMSO-d_6 and presented in Table 2. Spectroscopic atom numbering used there and in the following discussion is shown in Figure 1.

Hg_2 ($BPTU-2H)Cl_2$ Complex:

The spectrum of BPTU shows two proton signals in the down field region at 9.93 and 9.73 ppm as broad bands. These signals are exchangeable and disappear on deuteration. The earlier report on x-ray structure of BPTU (Akinchan et al ,2002) support thione tautomeric form and the signal at 9.93ppm is assigned to the two equivalent protons of NH group attached to phenyl rings (Akinchan et al, 2002). The second down field signal at 9.73ppm is assigned to two equivalent protons of H-N-N-H group. The signal at 9.73ppm disappeared in the spectum of the $Hg_2(BPTU-2H)Cl_2$ (Figure 1) and it supports double deprotonation of the ligand molecule. The signal at 9.93ppm shifted to up field and it is located at 8.34 and 7.22ppm in the spectrum of the complex. Now the NH protons attached to phenyl rings are non-equivalent due to the change in electronic structure of the ligand molecule. The aromatic proton signals were found in the range of 7.18 7.55ppm. The signals at 7.35 and 7.18ppm due to C(3)H/C(5)H and C(4)H are split in the spectrum of the complex suggesting change in electronic structure after ligand coordination. The above changes in the ^{1}H NMR spectral bands able to support the ligand deprotonation and the delocalization of electron density from the ligand orbital to metal orbital.

uyNi($BPTU-H)_2$ Complex:

On the comparison of ^{1}H NMR spectra of BPTU and Ni($BPTU-H)_2$ complex, (Table 2) it is observed that the monodeprotonated form of the ligand is involved in bond formation. The signals at 9.73ppm due to HN-NH protons shifted to 9.86 and 9.68ppm and it supports the loss of at least one proton from each BPTU molecule. The proton signal at 9.93ppm due to NH group attached to phenyl rings shifted to upfield and it is located at 4.05ppm in the spectrum of nickel(II) complex. This unsusual up field shift could be attributed to greater shielding of NH proton attached to phenyl rings. The upfield proton signal has earlier been reported for the 4-p-tolyl thiosemicarbazide at 4.8ppm due to NH_2 group proton (Koch, 1988) Further, the observed value of proton signal at 4.8ppm for the NH_2 proton of thiosemicarbazide could be cited to support up field proton signal in the nickel(II) complex (Table 2). The aromatic proton signals at 7.55 and 7.35ppm due to C(2)H/C(6)H and C(3)H/C5)H remained almost unchanged but the proton signal due to C(4)H is split to give two separate proton signals at 7.14 and 6.93ppm. Thus the above ^{1}H NMR spectral changes are able to provide some evidences in support of deprotonation of the ligand and the electron density delocalization during metal chelation.

Electronic Spectra:

The reflectance spectra of BPTU,

$Ni(BPTU-H)_2$ and $Hg_2(BPTU-2H)Cl_2$ are presented in Table 3. The bands above $34000 cm^{-1}$ in the spectrum of BPTU are assigned to $\Pi-\Pi^*$ transitions of aromatic ring system and they are located at 42000 and $34700 cm^{-1}$ (Akinchan, et al, 2002). These electronic transitions are changed either to lower or higher energy of the spectrum of the metal complexes. It clearly indicates that none of these electronic transitions seems to be pure and it is attributed to the conjugation of the lone pair of electrons on nitrogen with the Π -bonding orbitals of aromatic rings. A shoulder located at $29500 cm^{-1}$ in the spectrum of BPTU is attributed to a $\Pi-\Pi^*$ electronic transition of thiosemicarbazide moiety (Akinchan et al 2002). On metal chelation this transition shifts to lower energy in the spectra of the metal complexes. This observation is able to support the electron density change due to bonding through nitrogen .The expected d- d electronic transitions in the spectrum of $Ni(BPTU-H)_2$, are observed at 19849 and $15198 cm^{-1}$. Assuming square planar structure for this nickel(II) complex, these transitions are assigned to $dxy \rightarrow dx^2-y^2$ and $dxz, dyz \rightarrow dx^2-y^2$ electronic transitions. (Akinchan et al, 1992)

CONCLUSIONS

The analytical, spectral and other data discussed above indicate two different coordination nature for bis(N-phenyl thiourea), BPTU, It acts as mono anionic bidentate ligand coordinating through thiolato sulphur and hydrazine nitrogen atoms in nickel(II)complex. In $Hg_2(BPTU-2H)Cl_2$ it acts in dianionic form and it coordinates to two mercury(II) cations simultaneously through thiolato sulphur and hydrazine nitrogen atoms. The results presented here suggest a square planar structure (Figure 2) for $Ni(BPTU-H)_2$ and a dinuclear structure for $Hg_2(BPTU-2H)Cl_2$ having three coordinate mercury(II) centers, (Figure 3). However, unambigueous assignment of the structures to these complexes should be based on single crystal structure determinations.

ACKNOWLEDGEMENTS:

We thank the authorities of the Regional Sophisticated Instrumentation centre, Central Drug Research Institute, Luckhow, India for microanalyses and spectral measurements.

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