Preparation for mercury complexes [HgX_2SB]

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1. Introduction:

Interest in the metal complexes of acyclic compounds and macrocycles by template reactions developed rapidly due to their biological relevance[1]. The synthesis of cyclic and acyclic organic substrates that preferentially interact with particular metal ions is of fundamental importance to many areas of chemistry[2-3]. The majority of the ligand systems employed in model studies are derived from Schiff bases'. Condensation between dicarbonyls and primary diamines, for example - have played an important role in the development of synthetic acyclic and macrocyclic ligands. However, compounds containing the pyrimidine ring are known to be biologically active[7]. Re-cently, Sonmez and Sekerci[8-9] reported the synthesis and characterisation of heterocyclic complexes obtained from N-aminopyrimidine - 2 - one.

In this paper here the template reactions of N-aminopyrimidine -2 - one with benzyl or glyoxal or 2, 3-butanedione in the presence of HgX_2 (X = Cl, Br, NO_3) in 2:1:1 or 2:1:2 ratio have been done respectively.

2. Experimental

2.1 Preparation of $HgX_2S_13_1$ Complexes:

1 -amino-5-benzoy1-4-pheny1-1-H-pyridine (2 mmol) in methanol was mixed with glyoxal or benzyl or 2, 3 butanedione (1 m mol) HgX_2 (X = Cl, Br, NO3) (l mmol) was mixed in it with stirrering. This mixture solution was refluxed for 3-4 hours and resulting solid solution was washed with dry diethyl ether and dried under vacuo.

2. 2 Preparation of (HgX)SBJ Complexes:

1-amino-5-benzoy1-4-phenyl-1-H-pyridine (2 m mol) in methanol was mixed with glyoxal or benzyl or 2,3 butanedione (l mmol) HgX_2 (X = Cl, Br, NO_3) (2 m mol) was mixed in it with stirring. This mixture solution was refluxed for 3-4 hours and resulting solid solution was washed with dry diethyl ether and dried under vacuo.

3. Result and Discussion:

The template condensation of 1-amino-5-benzoy1-4-pheny1-1-Hpyrimidine-2-one (L'H2) and glyoxal or 2-3 butanedione or benzil (L"02) in the presence of HgX_2 (X = Cl, Br, NO_3) in 2:1:1 or 2:1:2 ratio produced new complexes [HgXSB] and [$(HgX_2)_2.S_{13}$]. All the complexes are non-hygroscopic and stable at room temperature. These complexes are soluble in DMF and DMSO. The molar conductance of the solution of the complexes in DMF are in the 3-25 ohm^{-1} om^2. These values are lower than those expected for an electrolyte. The elemental data and molar conductance are listed in table 1, concluding non-electrolyte nature of all prepared complexes[10]. The infrared spectra of the liand (L'H2 and L"02) and the metal complexes show the absence of the starting materials and the appearance of bands characteristic of the imine group [11-12].

The XpS data of $Hg_4p_{1,1,2}$, Nls and Ols of all the starting materials HgX_2(X = Cl, Br or NO_3) and their metal complexes are listed in table 1. It was observed that the binding energy of $Hg_4p_{1,2}$ is more in the starting material HgX_2 than in their molecular adducts, [HgX_2.SB] or [$(HgX_2)_2$.SB], due to increase of electron density on central metal ion i.e. Hg^{2-} (due to lone pair coordination with mercury).

Preparation of (HgX)SBJ Complexes:

1-amino-5-benzoy1-4-phenyl-1-H-pyridine (2 m mol) in methanol was mixed with glyoxal or benzyl or 2,3 butanedione (l m mol) HgX2 (X = Cl, Br, NO_3) (2mmol) was mixed in it with stirring. This mixture solution was refluxed for 3-4 hours and resulting solid solution was washed with dry diethyl ether and dried under vacuo.

Result and Discussion:

The template condensation of 1-amino-5-benzoy1-4-pheny1-1Hpyrimidine-2-one (L'H2) and glyoxal or 2-3 butanedione or benzil (L"02) in the presence of HgX_2 (X = Cl, Br, NO_3) in 2:1:1 or 2:1:2 ratio produced new complexes [HgXSB] and $[(HgX_2)_2.S_{13}]$. All the complexes are non-hygroscopic and stable at room temperature. These complexes are soluble in DMF and DMSO. The molar conductances of the solution of the complexes in DMF are in the 3-25 ohm^{-1} om^2.

These values are lower than those expected for an electrolyte. The elemental data and molar conductance are listed in table 1, concluding non-electrolyte nature of all prepared complexes[10]. The infrared spectra of the ligand (L'H2 and L"02) and the metal complexes show the absence of the starting materials and the appearance of bands characteristic of the imine group [11-12]. The XpS data of Hg_4p_{112}, Nls and Ols of all the starting materials HgX_2(X = Cl, Br or NO_3) and their metal complexes are listed in table 2. It was observed that the binding energy of $Hg_4p_{1,2}$ is more in the starting material HgX_2 than in their molecular adducts, $[HgX_2.SB]$ or $[(HgX_2)_2.SB]$, due to increase of electron density on central metal ion i.e. Hg^{2-} (due to lone pair coordination with mercury metal ion). The N_1S photoelectron peak of $[HgX_2SB]$ $[(HgX_2)_2.SB]$ have shown two N_1 S photoelectron peaks at 400.8ev and 402.6 eV, suggesting one due to nitrogen from ring and other with higher BE i.e. 402.6eV due to coordinated nitrogen of C=N group nitrogen'. The 01 s photoelectron peak of $[HgX_2 S_{13}]$ have shown two 01S one at 531.6 and other 532.8ev but in $[(HgX_2)_2.S_{13}]$ complexes these two 01S photoelectron peaks are observed at 531.6eV and 533.8eV; suggesting one lower BE Ols photoelectron peak is due to uncoordinated oxygen atom with metal ion and higher BE photoelectron peaks are due to coordinated oxygen with metal ion[13-14]. In case of $[(HgX_2)_2S_{13}]$, the value of Ols due to coordinated oxygen with metal ion is more than in $[HgX_2SB]$ suggesting more than one coordination in $[(HgX_2)_2.S_{13}]$ complexes through one oxygen atom[15].

On the basis of elemental analysis, molar conductance IR and XPS data it is possible to conclude that prepared molecular adducts $[HgX_2SB]$ and $[(HgX_2)_2SB]$ have octahedral and octahedral with tetrahedral geometry.

Table 1: Elemental molar conductivity of [11gX2S13], and $[(HgX_2)_2SBJ$, complexes.

S. No.	Compound			
		C	H	N
1.	$HgCl_2SB_1$	49.2	2.6	9.4
2.	$HgC1_2SB_2$	5.0	3.2	9.0
3.	$HgC1_2SB_3$	56.2	3.0	8.0
4.	$HgBr_2.SB_1$	44.2	2.2	8.4
5.	$HgBr_2.SB_2$	45.6	2.4	8.2

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