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Coordination complexes and polymers from the initial application of phenyl-2-pyridyl ketone azine in mercury chemistry

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ABSTRACT

A series of new mercury(II) azine Schiff base complexes have been synthesized and characterized from the initial use of phenyl-2-pyridyl ketone azine in Hg^{II} chemistry. The synthetic/crystallization technique utilized involved the use of a branched tube, where temperature differential allowed for the slow crystallization of the products. The synthesized compounds are the mononuclear $[Hg(L)Cl_2]$ (**1**), $[Hg(L)Br_2]$ (**2**), $[Hg(L)(NO_2)_2]$ (**3**), and the dinuclear $[Hg_2(\mu\text{-}L)(SCN)_4]$ (**4**) coordination compounds, as well as a 1D coordination polymer $[Hg(L)(\mu\text{-}I)_2HgI_2]_n$ (**5**) (L = phenyl-2-pyridyl ketone azine). From the X-ray data, it is evident that this versatile ligand functions as a bi- or tridentate chelate, and is also able to bridge two Hg^{II} centers. The crystal structures of **1** and **2** are similar, both containing two crystallographically independent Hg^{II} molecules, one tetrahedrally coordinated and one exhibiting trigonal bipyramidal geometry. The heptacoordinated Hg^{II} center in **3** adopts a distorted capped trigonal prismatic coordination sphere, while in the dinuclear complex **4**, the metal ions are bridged via the bis(bidentate) L and each center is also bound to two S-bonded thiocyanate units. The one-dimensional coordination polymer in **5** consists of a tetrahedral HgI_4 and a trigonal bipyramidal HgN_3I_2 chromophore unit, bridged by $\mu\text{-}I^-$ bridges. The thermal stability of the crystal lattice in **1**–**5** follows the pattern **3** > **1** > **2** > **5** > **4**, as studied by TG/DTA, while the TG data of **1**, **2**, and **5** are similar, but different than the respective ones for **3** and **4**, between which important similarities are observed. In the solid state, the ligand and compounds **1**–**5** exhibit intraligand $\pi \rightarrow \pi^*$ fluorescence at room temperature.

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1. Introduction

Mercury and its compounds [1–8] are of immense importance in chemistry and related disciplines due to their potential applications in the paper industry and as preservatives, paints, cosmetics, fluorescent lamps, sensors and mercury batteries [9–12]. Exploiting the diversity in coordination geometries around this $5d^{10}$ ion, different coordination frameworks may be accessed using a variety of organic ligands along with different inorganic/organic bridging units [1,13,14]. The coordination behavior of azines as organic spacers has spawned great interest in recent years due to the ease of their syntheses, their chelating abilities, and the various denticities; additionally, subtle steric and/or electronic control on their frameworks has proven to lead to different monometallic and homo- or heterobimetallic complexes with interesting properties [15–17]. Halides [1,14b,14c,18,19], thiocyanates, ambidentate pseudohalides [13a,14a,20,21], and nitrites [22] are suitable terminal/bridging groups in mercury chemistry, and in combination with organic ligands often result in different molecular frameworks and crystalline networks through their versatile ligation modes and different non-covalent forces [23,24].

The ligand of choice for this work was phenyl-2-pyridyl ketone azine (L; Scheme 1). This ligand has previously afforded a small suite of products, including mono and/or dinuclear Cu, Ag, Ni, Zn, Co (all 3d metals) and Ag (4d metal) complexes [25]; however, there is no report of 5d metal complexes with L. Thus, we ventured to study the coordination behavior of this ligand in Hg^{II}, and explore its coordination chemistry with a 5d metal ion. This work also focuses on the metal ion and its coordination geometry; along these lines we were particularly interested to investigate the synthesis of various complexes, and also structurally characterize the resulting products. Subtle changes to these geometries were also to

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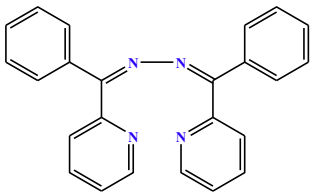

Scheme 1. The chemical structure of phenyl-2-pyridyl ketone azine (L).

be probed in this systematic study, and as such we varied the anionic terminal/bridging ancillary ligands (halides, pseudohalides, etc.). Finally, the chromophore qualities of the resulting systems were of interest, and as such we were able to investigate the fluorescence properties of the resulting compounds. Therefore, herein we report the successful syntheses, X-ray crystallography, thermal behavior, and luminescence properties of three mononuclear compounds $[Hg(L)Cl_2]$ (**1**), $[Hg(L)Br_2]$ (**2**) and $[Hg(L)(NO_2)_2]$ (**3**), one dinuclear compound $[Hg_2(\mu\text{-}L)(SCN)_4]$ (**4**) and one 1D coordination polymer $[Hg(L)(\mu\text{-}I_2)HgI_2]_n$ (**5**), all incorporating the aforementioned phenyl-2-pyridyl ketone azine ligand.

2. Experimental

2.1. Materials and measurements

The Schiff base, phenyl-2-pyridyl ketone azine (L) was prepared following the reported method as described elsewhere [15] and used without further purification. All other reagents and solvents used for the syntheses and analyses were commercially available and used as received. FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Microanalyses were performed using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The respective IR, CHN, and melting point data for complexes **1**–**5** are tabulated in Table 1. The thermal studies were carried out with a NetzschSTA490C. Solid state fluorescence measurements were done using a PerkinElmer LS55 Spectrofluorometer.

Caution! Mercury and its compounds are toxic [26]. Only a small amount of these materials should be prepared and handled with care.

2.2. Synthesis of $[Hg(L)Cl_2]$ (*1*)

Phenyl-2-pyridyl ketone azine (L) (0.181 g, 0.5 mmol) and mercury(II) chloride (0.135 g, 0.5 mmol) were placed in the main arm of a branched tube (Fig. 1). Methanol (25 ml) was carefully added to fill the arms. The tube was sealed and immersed in an oil bath at 60 °C while the branched arm was kept at ambient temperature. After 2 days, yellow crystals of **1** that formed in the cooler arm were filtered off, washed with acetone and ether, and dried in air. The isolated yield was 74%, and the elemental analysis closely matches the crystallographic data, as seen in Table 1.

2.3. Synthesis of $[Hg(L)Br_2]$ (*2*)

In the branched tube apparatus phenyl-2-pyridyl ketone azine (L) (0.181 g, 0.5 mmol) and mercury(II) bromide (0.180 g, 0.5 mmol) were added. Methanol (25 ml) was carefully added to fill the arms. The tube was sealed and immersed in an oil bath at 60 °C while the branched arm was kept at ambient temperature. The yellow crystals of **2**, which formed after a period of 2 days, and were filtered off, washed with acetone and ether, and dried in air. The isolated yield for **2** was 84%.

2.4. Synthesis of $[Hg(L)(NO_2)_2]$ (*3*)

In the main tube of the branched tube apparatus, mercury(II) acetate (0.159 g, 0.5 mmol) and sodium nitrite (0.034 g, 0.5 mmol) were added. Then, a solution of the ligand L (0.181 g, 0.5 mmol) in 25 ml MeOH was carefully transferred to the apparatus, and the reaction tube was sealed, and immersed in an oil bath at 60 °C while the branched arm was kept at ambient temperature. In the cooler arm of the apparatus yellow crystals of **3** formed after a period of 2 days, and they were filtered off, washed with acetone and ether, and dried in air. The isolated yield for **3** was 70%.

2.5. Synthesis of $[Hg_2(\mu\text{-}L)(SCN)_4]$ (*4*)

In the main tube of the branched tube apparatus, mercury(II) thiocyanate (0.158 g, 0.5 mmol) was added, followed by a methanolic solution of L (0.181 g, 0.5 mmol) in 25 ml MeOH. The apparatus was then sealed and immersed in an oil bath at 60 °C for 2 days. During this time, colorless single crystals of **4** formed in the side arm of the apparatus; the crystals were then filtered off, washed with acetone and ether, and dried in air. The isolated yield for **4** was 85%.

2.6. Synthesis of $[Hg(L)(\mu\text{-}I_2)HgI_2]_n$ (*5*)

Phenyl-2-pyridyl ketone azine (L) (0.181 g, 0.5 mmol) and mercury(II) iodide (0.227 g, 0.5 mmol) were placed in the main arm of a branched tube (Fig. 1). Methanol (25 ml) was carefully added to fill the arms. The tube was sealed and immersed in an oil bath at 60 °C while the branched arm was kept at ambient temperature. This synthesis produced yellow single crystals in the apparatus' side arm after 2 days; the crystals were then filtered off, washed with acetone and ether, and dried in air. The isolated yield for **5** was 88%.

Table 1
Some characterization data for **1**–**5**.

Compound (Formula)	Crystal color (Yield)	M.P. (°C)	Microanalyses Found (Calcd.) in%			Representative IR bands (cm^{-1})
			C	H	N	
1 ($C_{24}H_{18}N_4Cl_2Hg$)	Yellow (0.234 g, 74%)	178	45.14 (45.47)	2.75 (2.86)	8.69 (8.84)	693(s), 776(m), 1002(m), 1324(m), 1435(m), 1585(m),1632(w), 3095(w)
2 ($C_{24}H_{18}N_4Br_2Hg$)	Yellow (0.303 g, 84%)	171	39.97 (39.88)	2.29 (39.88)	5.51 (39.88)	574(w), 624(m), 692(vs), 773(m), 1000(m), 1325(s), 1436(s), 1564(s), 1635(w), 3056(w)
3 ($C_{24}H_{18}N_6O_4Hg$)	Yellow (0.150 g, 70%)	182	44.41 (44.01)	2.66 (44.01)	2.66 (44.01)	656(s), 792(m), 849(s) 1031(m), 1171(s), 1236(s), 1271(m), 1317(s), 1433(m), 1467(m), 1572(s), 1648(w), 3061(w)
4 ($C_{28}H_{18}N_8S_4Hg_2$)	Colorless (0.212 g, 85%)	164	34.14 (33.77)	2.05 (33.77)	2.05 (33.77)	452(w), 701(s), 765(m), 1008(m), 1328(m), 1434(m), 1580(m), 1643(w), 2113(vs), 3067(w)
5 ($C_{24}H_{18}N_4I_4Hg_2$)	Yellow (0.224 g, 88%)	167	23.08 (22.68)	1.58 (22.68)	1.58 (22.68)	652(m), 697(vs), 768(s), 956(m), 1006(m), 1252(m), 1427(s), 1560(s), 1628(m), 3062(w)

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