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Synthesis and Characterization of Mercury(II) Complex with Dissymmetric Tetradentate Schiff Base

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Synthesis of a new mercury(II) complex with a dissymmetric Schiff base ligand is described. The ligand which was prepared from aminothioether pyridine and a salicylaldehyde derivative was characterized by ^{1}H, ^{13}C NMR, FTIR and elemental analysis. The complex of this ligand was synthesized by treating an ethanolic solution of ligand with equimolar amount of $HgCl_2$ and methanolic NaOH or alternatively by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. The complex was characterized by elemental analysis, FTIR, electronic spectra and molar conductivity.

Key Words: Synthesis, Dissymmetric tetradentate, Schiff base, Mercury(II) complex.

INTRODUCTION

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde. The resultant functional group, $R^1HC=N-R^2$, is called an imine and is particularly for binding metal ions *via* the N atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocycles. (Ketones, of course, will also form imines of the type $R^1R^2C = N-R^3$, but the reactions tend to occur less readily than with aldehydes.) These compounds have important applications in stabilizing high oxidation states of metals, an obligatory requirement for certain transition metal and main group metal ion catalysts, or producing charge neutral complexes of lower oxidation states such as Fe(II). Salen type ligands, one of the oldest classes of ligands in coordination chemistry, have been used extensively to complex transition and main group metals[1]. Schiff base complexes containing different metal

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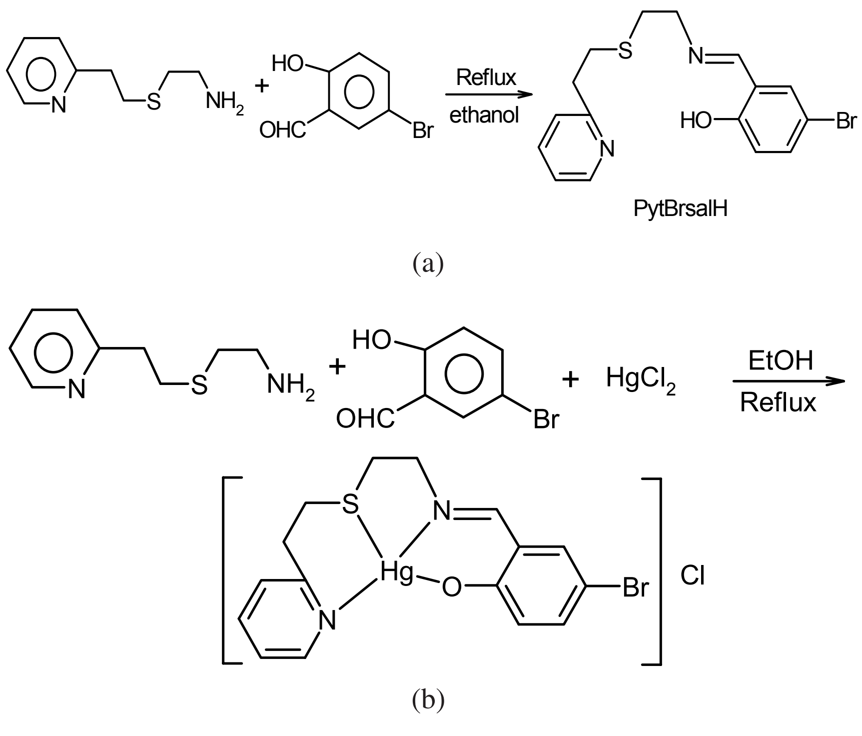
ions such as Ni and Cu have been studied in great details for their various crystallographic feature, structure-/redox relationships and enzymatic reactions, mesogenic characteristics and catalytic properties[2-6]. Recent interest in the design, synthesis and characterization of dissymmetrical Schiff base ligands derived from appropriate amines for transition metal ion complexes has come from the realization that the coordinated ligands around central metal ions in natural systems are unsymmetric[7]. Dissymmetrical Schiff base ligands can clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of metal ion binding sites in metalloproteins and selectivity of natural systems with synthetic materials[8]. Dissymmetric Schiff base complexes as chiral analogues become more effective and prevalent in asymmetric catalysis; an inexpensive, large-scale production of these materials would be highly desirable[7-13]. The synthesis of transition metal complexes containing thiolate coordination is an important area of study with implications in bioinorganic chemistry, catalysis and medicinal chemistry[14]. We describe here, a new mercury(II) complex and its spectroscopic characterizations as shown in **Scheme-I**.



Scheme-I. Schematic representation of Schiff base ligand (a) and its complex (b) formation

EXPERIMENTAL

All of the chemicals and solvents were of analytical reagent grade and were obtained commercially from Merck Company with the exception of mercury chloride which was obtained from Aldrich. The solvents were purified by standard methods[15]. 1-(2-pyridyl)-3-thia-5-amino pentane (pyta) were synthesized according to known procedures[16-18] and 2-vinyl pyridine was distilled *in vacuo* before using.

Elemental analyses for CHN were performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared (FTIR) spectra were recorded using KBr discs on a FTIR Unicam 4600. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ on a Bruker Spectrospin Avance 400 MHz ultrashield spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. The electronic spectra in the 200-900 nm range were obtained in acetonitrile on a Perkin-Elmer model Lambda 25 spectrophotometer. The conductivity measurements were carried out in acetonitrile at room temperature using a Hanna conductometer HI 8828N instrument.

Synthesis of Schiff base ligand: The ligand was prepared in a similar manner to other last published Schiff bases (**Scheme-I**)[3-6]. A solution of 1 mmol of pyta in 5 mL absolute ethanol was added to a solution of 1 mmol of the required salicylaldehyde in 5 mL absolute ethanol to give clear yellow or orange solution which was gently refluxed for *ca.* 1 h. Evaporation of the solution in vacuo gave viscous liquid. The ligand 4-Br-2-{[2-(2-pyridin-2-yl-ethylsulfanyl)-ethylimino]-methyl}phenol which will abbreviated as pytBrsal, was obtained as microcrystals. The microcrystals were filtered off, washed with 5 mL of cooled absolute ethanol and then recrystallized from ethanol-chloroform (2:1, v/v). The analytical and physical data of the ligand are: Compound: PytBrsalH- mf.: $C_{16}H_{17}BrN_2OS$, m.w.: 365.293 g mol^{-1}, yield: 83 %, colour: yellow, m.p. = 69 °C, elemental analysis (%): C, 52.50; H, 4.70; N, 7.60. Found: C, 52.60; H, 4.69; N, 7.66. ^{1}H NMR (ppm): 13.20 (br s, 1H, OH), 8.55 (d, 1H, pyridinic), 8.26 (s, 1H, iminic), 7.67 (t, 1H, pyridinic), 7.39- 7.21 (m, 4H, aromatic), 6.85 (d, 1H, aromatic), 3.80 (t, 2H, CH_2 aliphatic), 3.13 (t, 2H, CH_2 aliphatic), 3.00 (t, 2H, CH_2 aliphatic), 2.86 (t, 2H, CH_2 aliphatic). ^{13}C NMR (ppm): (12 C aromatic); 164.61, 160.16, 159.66, 149.32, 136.45, 134.92, 133.46, 123.25, 121.56, 119.96, 119.02, 109.95. (4 C aliphatic); 58.93, 38.36, 32.94, 31.82. Electronic spectra in acetonitrile: PytBrsalH: 225 and 326 nm.

Synthesis of metal complexes: A solution of the ligand was prepared by either dissolving the required amount (1 mmol) of the ligand in absolute ethanol (10 mL). Then 1 mmol of $HgCl_2$ in 5 mL absolute ethanol was added to the ligand solution with stirring and the reaction mixture was stirred under reflux for 25 min. The obtained coloured solution was left at room temperature. The product was removed by filtration, washed with cooled absolute ethanol, recrystallized from acetonitrile or methanol and dried *in vacuo*. The analytical and physical data of the complex are:

m.p. 161.5-163 °C (decomposed). Elemental analysis(%): Calcd. for $C_{16}H_{16}N_2SOBrClHg$: C, 32.01; H, 2.68; N, 4.66. Found: C, 32.2; H, 2.72; N, 4.70. IR (KBr, ν_{max}, cm^{-1}): 3049 (C-H) aromatic, 2860 and 2916 (C-H) aliphatic, 1627 (C=N) imin and 1035 (C-Br). UV/Visible of [Hg (pytBrsal)]Cl: 229 nm, 329 and 384 nm. UV/Visible and ^{1}H NMR were all consistent with the [Hg (pytBrsal)]Cl formula.

RESULTS AND DISCUSSION

Previous studies showed that the reaction of pyta with several salicylaldehyde derivatives containing donor, withdrawing and bulky groups in absolute ethanol gave the desired dissymmetric tetradentate Schiff base ligands in good yield and purity (**Scheme-I**)[19,20]. Mononuclear mercury(II) complex was prepared by treating an ethanolic solution of the appropriate ligand with equimolar amount of $HgCl_2$ and methanolic NaOH or alternatively by a more direct route in which the two reactants are added to a solution of the ligand immediately after formation of the ligand and prior to any isolation. Both routes gave identical products but the latter was less time consuming and gave higher yields (**Scheme-I**). The Schiff base ligand and complex were characterized by elemental analysis, molar conductivity, ^{1}H and ^{13}C NMR, FTIR and electronic spectra. The complex is very stable at room temperature in air and is insoluble in water and nonpolar solvents. However, it is soluble in acetonitrile, methanol, DMF and DMSO, completely. Solution conductivity measurements were performed to establish the electrolyte type of the complex. The molar conductivities at 10^{-3} M concentration for the complex in acetonitrile are in the range expected for their formulation as 1:1 electrolytes[19,20]. The ^{1}H and ^{13}C NMR spectra data of the ligand in $CDCl_3$ solvent confirm the proposed structure of the ligand (**Scheme-I**). In the ^{1}H NMR spectrum of ligand, the signal for proton of the NH group was not found and it is suggested that the Schiff base ligand do not undergo keto-enol tautomerism[16,17]. Most of the IR characteristic bands of ligand are: 3447 cm^{-1} ν(O-H), 3050-3015 cm^{-1} ν(C-H) aromatic, 2930-2850 cm^{-1} ν(C-H) aliphatic, 1634 cm^{-1} ν(C=N) iminic. The FTIR spectra of the complex compared with those of the ligand, indicate that the ν(C=N) band at 1634 cm^{-1} is shifted to lower frequency by 7 cm^{-1} in the complex, indicating that the ligand is coordinated to the metal ion through the nitrogen atom of the azomethine group. On the other hand, the disappearance of the OH bands of the free ligand in the complex indicates that the OH group has been deprotonated and bonded to metal ions as O atom. The electronic absorption spectral data for ligand and complex are given in Figs. 1 and 2. The spectra were recorded using CH_3CN as solvent. The broad, slightly intense and poorly resolved bands between 400-320 nm may be assigned to charge transfer LMCT or MLCT[7,23-30].

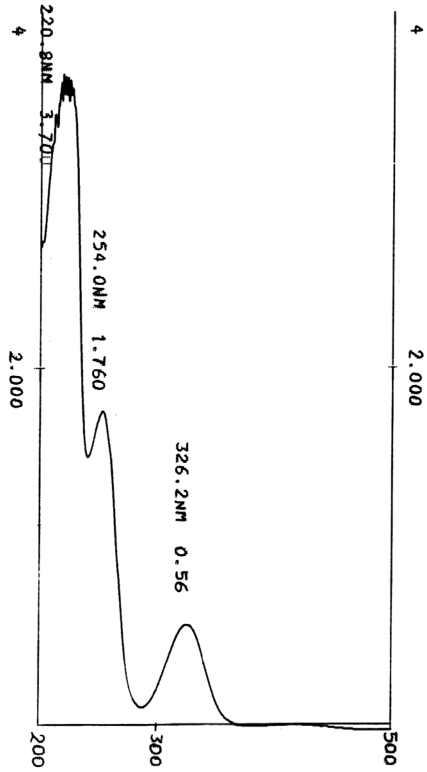


Fig. 1. Electronic spectra of PytBrsalH ligand

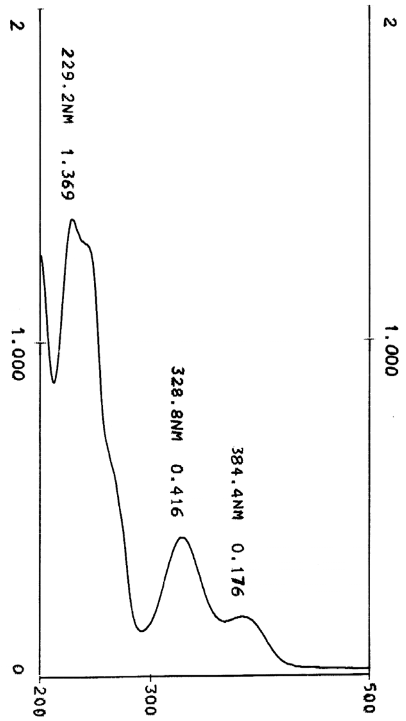


Fig 2. Electronic spectra of [Hg (pytBrsal)]Cl complex

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