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Synthesis and Characterization of New Mercury (II) Complexes with Bidentate Chelating Schiff Base Iminopyridine Ligand

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Abstract

First, Schiff base iminopyridine ligands has been prepared by the condensation between primary amines, different substituted anilines and active carbonyl group of pyridine carboxaldehyde, then the complexes [diiodo (3-ethylphenyl) pyridine-2-yl methylene amine] mercury(II), complex **a**, [dibromo (2,5-dimethylphenyl) pyridine-2-yl methylene amine] mercury(II) complex **b**, and [dinitrato bis-(2,6-dimethylphenyl) pyridine-2-yl methylene amine] mercury(II) nitrate, complex **c**, synthesized in methanol solution. The ligands and metal complexes have been characterized by elemental analysis, UV, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The spectroscopic data of metal complexes indicated that the metal ions are complexed with azomethine group and pyridine nitrogen atoms. The Schiff base ligand acts as bidentate with two N sites and can coordinate with mercury ion.

Keywords: *Schiff base, iminopyridine, chelate, synthesis, metal complex.*

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Introduction

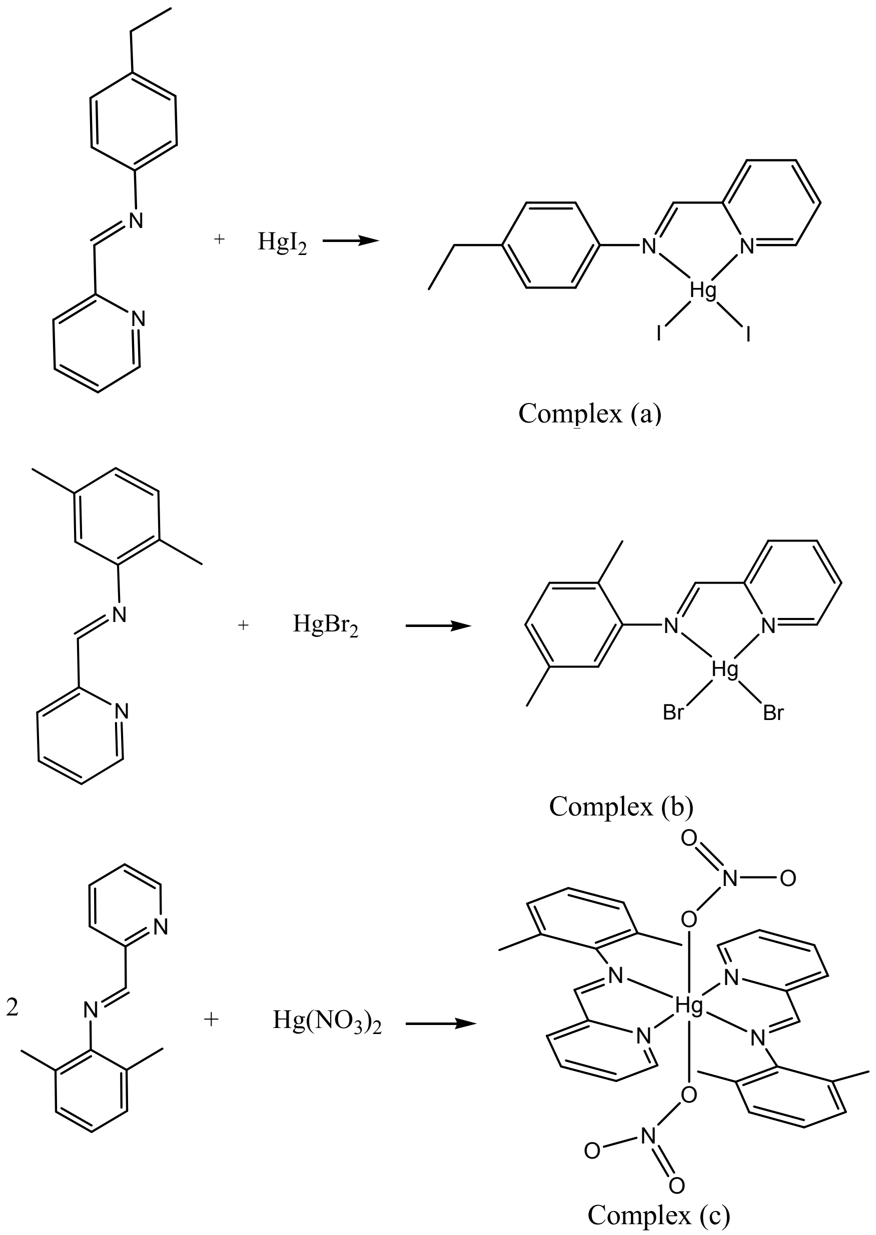
Schiff bases are the compounds containing azomethine group (-HC=N-). They are condensation products of ketones or aldehydes with primary amines which were initially reported by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acids or base catalysis or with heat. The common Schiff bases are crystalline solids, which are weakly basic but at least some form of insoluble salts with strong acids. Schiff bases are used as intermediates for the synthesis of amino acids or as ligands for preparation of metal complexes having a series of different structures which are now regarded as one of the most potential group of chelators for facile preparations of metallo-organic materials [1].

In the past two decades, the synthesis, structure and properties of Schiff base complexes have stimulated much interests in their noteworthy contributions to single molecule-based magnetism, material science [2], catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis [3], etc. In the past recent years, a large number of binuclear Schiff base metal complexes has been synthesized and characterized [2].

Schiff base ligand plays a central role in transition metal coordination chemistry and biochemistry [3, 4]. The Schiff base metal complexes are used as metal enzymes [5], catalyst [6, 7], material chemistry [8], and biomimetic chemistry [9]. The binuclear complexes have greater cleaving efficiency than mononuclear complexes [10]. The Schiff bases are able to inhibit the growth of various animal tumors, while some metals have shown good antitumor activity against animal tumors [11,12]. They are widely used for industrial purposes and have a broad range of applications as antioxidants, too [13].

Recently, Shores et al. have prepared and characterized a series of divalent iminopyridine Schiff base complexes of first row transition metal complexes [14]. The coordination chemistry of Hg (II) has been investigated in the past years. The spherical d^{10} configuration is associated with a flexible coordination environment so that the geometries of these complexes can vary from tetrahedral to octahedral and severe distortions in the ideal polyhedron occur easily [15].

In this paper the iminopyridine ligand and related novel complexes derived from Hg(II) containing iodide, bromide, nitrate and iminopyridine ligands were synthesized (Scheme 1) and characterized by elemental analysis, ^{1}H-NMR and IR and UV–Vis spectroscopy.1



Scheme 1. Synthesis of [diiodo (3-ethylphenyl)pyridine-2-yl methylene amine] mercury(II), complex **a**, [dibromo(2,5-dimethylphenyl) pyridine-2-yl methylene amine] mercury(II), complex **b**, and [dinitrato bis-(2,6-dimethylphenyl) pyridine-2-yl methylene amine] mercury(II), complex **c**.

Experimental

Reagents and materials

All solvents and general chemicals of analytical grade were used without any further purification. 4-ethylaniline, 2,5-dimethylaniline 2,6-dimethylaniline and 2-pyridine carbaldehyde were purchased as commercial chemicals from Merck and were distilled before use according to a standard procedure [16]. 2-pyridinecarbaldehyde was stored at 0 °C to +6 °C.

Physical measurements (apparatus and experimental condition)

Elemental analyses for carbon, hydrogen and nitrogen were performed on Perkin–Elmer Automatic CHNS/O analyzer. Infrared spectra (450–4000 cm^{-1}) were recorded on a FT-IR spectrophotometer Perkin–Elmer spectrum 100 at 298 K using KBr plates; ultraviolet–visible (UV–Vis) spectra were recorded with a BIO-TEK KONTRON spectrum 100, by using a Pyrex cell with a path length of 10 mm.

^{1}H-NMR spectra were obtained on an Avance Bruker 300 MHz NMR spectrometer using DMSO d_6 as solvent. ^{13}C-NMR spectra were acquired on an Avance Bruker 300 MHz NMR spectrometer. Chemical shifts are given in ppm while all coupling constants are reported in Hz. Melting points were recorded on Electrothermal 9200 melting point apparatus.

Synthesis of ligands and its complexes

The ligands (3-ethylphenyl) pyridine-2-yl methylene amine (L_1), (2,5-dimethylphenyl) pyridine-2-yl methylene amine (L_2) and (2,6-dimethylphenyl) pyridine-2-yl methylene amine (L_3) were synthesized and characterized according to the literature [17] with some modifications.

*Synthesis of [diiodo(3-ethylphenyl)pyridine-2-yl methylene amine] mercury(II) complex (**a**)*

For the preparation of the complex **a**, a solution of HgI_2 (45.4 mg, 0.1 mmol) in methanol (5 ml) was added slowly to a solution of 2-[(2,6-dimethylphenyl)-iminomethyl]-pyridine (21.0 mg, 0.1 mmol) in methanol (10 ml). Then the reaction mixture was stirred for 15 minutes at room temperature. The metal complex was prepared by slowly evaporation of solvent and yellow crystals obtained. The resulting product was filtered and dried in room temperature. (Yield: 85%, m. p. 497.8-498.3 K).

Main FT-IR (KBr disk, cm^{-1}); υ (O-H) 3450(w), υ (C-H) (stretching) 2966(m), υ (C=N) 1597(m), υ (C=C) 1444-1563 (m), υ (C-H) (bending) 776-845 (s) cm^{-1}.

^{1}H-NMR (300MHz, DMSO-d_6, δ ppm, 298 K, TMS): 2.49 (group of peaks, DMSO), 1.23 (t, methyl protons, 3H), 2.57 (q, methylene protons, 2H), 6.27 and 7.49 (two triplet, aromatic protons, 4H), 8.92 (s, CH=N, 1H), 7.77-8.91 (group of peaks, pyridine ring protons, 5H).

^{13}C-NMR (300MHz, DMSO-d_6, δ ppm, 298 K, TMS): 15.52 (methyl), 27.86 (methylene), 122.01, 127.04, 127.65, 128.76, 139.66, 144.26, 145.30, 149.12, 150.50, (aromatic carbons) 157.25, (CH=N). Anal. Calc. for $C_{14}H_{14}HgI_2N_2$: C ۲۵.30, H ۲.۱۲, N ۴.۲۱. Found C ۲۵.۴۷, H 2.19, N, ۴.۳۲%.
UV–Vis: (λ_{max} in Ethanol), 285, 346 nm.

*Synthesis of [dibromo(2,5-dimethylphenyl) pyridine-2-yl methylene amine] mercury (II) complex **(b)***

For the preparation of the complex **b**, a solution of $HgBr_2$ (36.0 mg 0.1 mmol) in methanol (5 ml) was added slowly to a solution of 2-[(2,6-dimethylphenyl)-iminomethyl]-pyridine (21.0 mg, 0.1 mmol) in methanol (10 ml) and the resulting yellow solution was stirred for 15 min at room temperature and then left for two days at the same condition. The metal complex was prepared by slowly evaporation of solvent and yellow crystals obtained. The resulting product was filtered and dried in room temperature (Yield; 82%, decomposed temperature 448.3 - 450.3K).
Main FT-IR (KBr disk, cm^{-1}); υ (O-H) 3426(w), υ (C-H) (stretching) 2916-3089 (w), υ (methyl) 2858 (m), υ (C=N) 1588 (m), υ (C=C) 1500 (m), υ (C-H) (bend) 774 (s).
^{1}H-NMR (300MHz, DMSO-d_6, δ ppm, 298 k, TMS): 2.28 (s, methyl protons, 6H), 6.89-7.14 (s, s and d aromatic protons, 3H), 8.75 (s, CH=N, 1H), 7.78-8.85 (group of peaks, pyridine ring protons, 5H).
^{13}C-NMR (300MHz, DMSO-d_6, δ ppm, 298 K, TMS): 17.55 and 20.52 (two methyl groups), 119.92, 126.66, 127.54, 127.69, 130.32, 135.97, 139.60, 148.39, 148.39, 149.56, 150.29, (aromatic carbons) 159.60 (CH=N), Anal. Calc. for $C_{14}H_{14}Br_2HgN_2$: C ۲۹.۴۷, H ۲.۴۷, N ۴.۹۱. Found C ۲۹.۵۵, H ۲.۴۴, N, ۸۵.۵%.
UV–vis: (λ_{max} in Ethanol), 280, 345 nm.

*Synthesis of bis-[(2,6-dimethylphenyl) pyridine-2-yl methylene amine] dinitrato mercury (II) complex **(c)***

For the preparation of the complex **c**, a solution of $Hg(NO_3)_2$ (32.4 mg, 0.1 mmol) in methanol (10 ml) was added slowly to a solution of 2-[(2,6-dimethylphenyl)-iminomethyl]-pyridine (4.20 mg, 0.2 mmol) in methanol (10 ml) and the resulting yellow solution was stirred for 15 min at room temperature. The metal complex was prepared by slowly evaporation of solvent and yellow crystals obtained after three days. The resulting product was filtered and dried in room temperature (Yield; 86%, m. p. 502 K).

Main FT-IR (KBr disk, cm^{-1}); υ (O-H) 3437(w), υ (C-H) (stretching) 2925(w), υ (C=N) 1634(m), υ (N=O) (nitrate group) (stretching) ۱۳۵۷-۱۳۸۵(vs), υ (C-H) (nitrate group) (bending) 823 (m), cm^{-1}υ (C-H) (bend.) 771 (s), cm^{-1}.

^{1}HNMR (300MHz, DMSO-d$_6$, δ ppm, 298 k, TMS): 2.05 (s, methyl protons, 6H), 6.91-7.03 (multiplet, aromatic protons, 3H), 8.29 (s, CH=N, 1H), 7.54-8.72 (group of peaks, pyridine ring protons, 5H).

^{13}C-NMR (300MHz, DMSO-d$_6$, δ ppm, 298 K, TMS): 17.98 (two methyl groups), 121.03, 123.96, 126.05, 126.27, 128.06, 137.33, 149.73, 150.08, 153.72, 163.02 (CH=N). Anal. Calc. for $C_{28}H_{28}HgN_6O_6$: C 45.13, H 3,79, N 12,88. Found C 45.10, H 3.83, N, 12.27%.

UV–vis: (λ_{max} in Ethanol), 260, 335 nm.

Results and discussion

All the complexes were insoluble in common solvents such as water, benzene, chloroform, dichloromethane, etc.; they were soluble in some solvents like DMF and DMSO. So the single crystal could not be obtained. We tried different methods but unfortunately our obtained crystals were twice.

IR spectral studies

The IR spectrum of ligand and the complexes were compared with those of the free ligand in order to determine the coordination sites that could involve in chelation. The position and the intensities of these peaks were expected change upon chelation.

The IR spectra of metal complexes and free ligands were recorded in the range of 450–4000 cm^{-1}. The azomethine nitrogen (C=N) for ligands L_1, L_2 and L_3 appeared around 1632, 1620 and 1640 cm^{-1} respectively which were shifted to lower wave numbers about 1597, 1588 and 1634 cm^{-1} in the related complexes. The shifts in the frequencies were due to coordination of two imine groups with the metal ions. The strong band around ۱۳۵۷-۱۳۸۵ cm^{-1} could be assigned to the stretching frequency of N=O bands [18].

The nitrite ion could coordinate with the transition metal ion through either one of its oxygen atoms (unidentate) or two of its oxygen atoms (bidentate). This interaction lowers the symmetry of free nitrite ion from the D_{3h} to the C_{2v} point group, therefore the degeneracy of the IR- active E′ modes of free nitrite ion is split into two nondegenerate IR-active A_1 and B_2 modes. The splitting energy provided information regarding the type of coordination and was relatively smaller in the unidentate coordination than in the bidentate coordination in similar complexes. In this complex, the assigned band to nitrite had a small splitting energy which showed its unidentate coordination [19].

Electronic spectral studies

Electronic spectrum of iminopyridine ligands and the related complexes were recorded in ethanol. In electronic spectra of metal complexes, the wide range of bands were due to transition of CH=N, charge transfer results from electrons interaction between the metal and the ligand which involves either a metal to ligand or ligand to metal electron transfer [20]. The bands observed in 258-296 nm were due to $\pi\rightarrow\pi^*$ transition of C=N group [21]. The bands were shifted to a lower range (blue shifted) in complex **a**, and higher range (red shifted) in complexes **b** and **c**, which are due to nitrogen that involved in coordination with metal ion. The absorption bands were observed in the range of 330-390 nm due to $n\rightarrow\pi^*$ transition from imine group corresponding to the ligand or metal complexes. The bands were shifted to higher range (red shifted) in complex **b** and lower range (blue shifted) in complex **b** which is due to nitrogen that involved in coordination with metal ion. In the spectrum of all three complexes there is no d-d transitions observed because the Hg (II) cation has d^{10} electron configuration.

NMR spectra

The structure of ligand was confirmed by ^{1}H-NMR and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of the ligands L_1, L_2 and L_3 shows a singlet at 8.60, 8.44 and 8.28 ppm respectively corresponding to imine proton where they shift to 8.92, 8.75 and 8.29 ppm respectively in complexes **a**, **b** and **c** respectively. The multiplet at around 7 ppm was due to aromatic protons in free ligands where they don’t show noticeable displacements in the complexes. These slightly displacements may be due to d^{10} configuration of metal ion.

Proton chemical shifts of pyridine rings of ligands appear upper than phenyl rings due to nitrogen atom in the aromatic ring. Because of coordination of the N atom of the pyridine ring, related aromatic protons show noticeable displacements in the complexes. The ^{13}C-NMR spectrum of the ligands L_1, L_2 and L_3 shows a singlet at 154.5, 159.59 and 163.67 ppm respectively corresponding to imine proton where they shift to 157.25, 159.60 and 163.02 ppm respectively in complexes **a**, **b** and **c** respectively.

Conclusion

In the present study, three novel Schiff base iminopyridine complexes were prepared and characterized by ^{1}H-NMR, ^{13}C-NMR, IR and UV-visible spectroscopy. These spectroscopic data of metal complexes indicated that in all three complexes, the metal ions are complexed with azomethine group and pyridine nitrogen atoms and the Schiff base ligand acts as bidentate with two N sites. In complex **a** and **b** the Hg^{+2} coordinated by one bidentate iminopyridine ligand and two halide ions and central metal atoms are four-coordinated whereas in complex **c,** the Hg^{+2} ions, surrounded by two chelate ligands and two nitrate anions therefore the Hg^{+2} ions are six-coordinated.

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