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Synthesis and Characterization of Novel Lead (II) Complexes with Schiff Base Iminopyridine Ligand

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Abstract

First, Schiff base iminopyridine ligand has been prepared by the condensation between primary amine, dimethylaniline and active carbonyl group of pyridine carboxaldehyde, then related complexes were synthesized in methanol solution. The ligand and metal complexes have been characterized by elemental analysis, UV, IR, ^{1}H NMR and ^{13}CNMR spectroscopy. The spectroscopic data of metal complexes indicated that the metal ions are complex with azomethine group and pyridine nitrogen atoms. The ligand acts as bidentate with two N sites and can coordinate with metal ion.

Key words: *Schiff base, Primary amines, Carbonyl group, Metal complex.*

Introduction

Compounds with an azomethine group, Or C=N, are known as Schiff bases, which are usually synthesized from the condensation of primary amines and active carbonyl groups [1].

Recently, a large number of binuclear Schiff base metal complexes have been synthesized and characterized [2]. Schiff base ligand played central role in transition metal coordination chemistry [3, 4]. The tetra dentate Schiff base metal complexes 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 several animal tumors, and some metals have shown good antitumor activity against animal tumors [11, 12]. Recently, Shores et al. have been prepared and characterized a series of divalent iminopyridine Schiff base complexes

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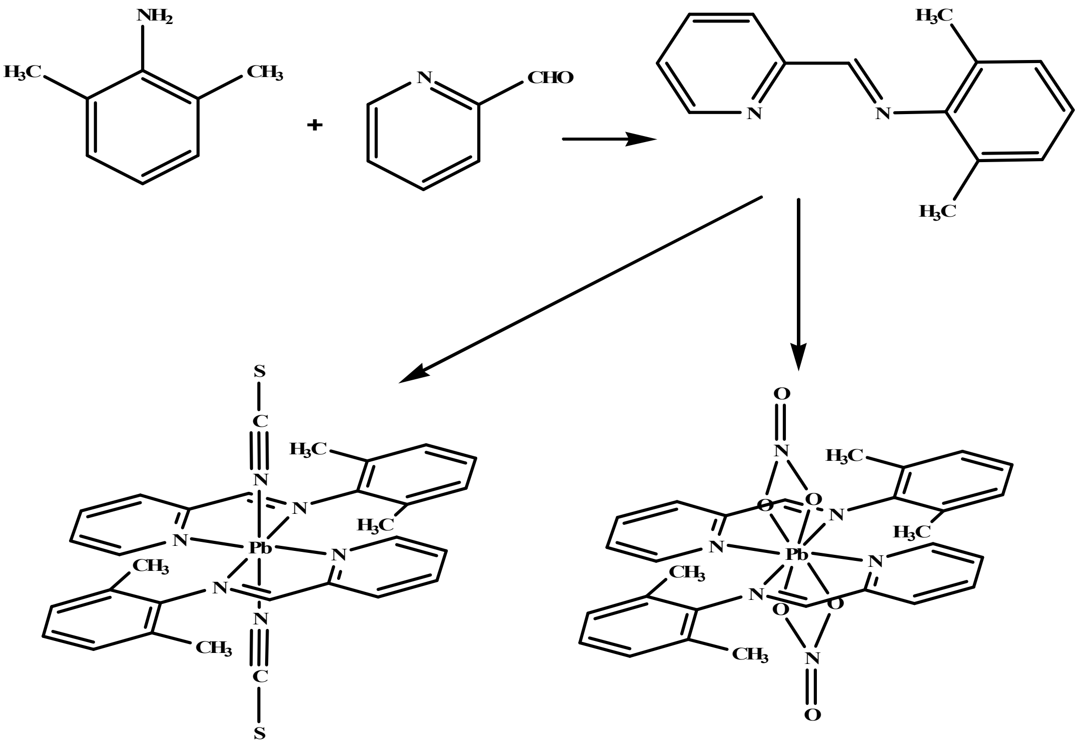
of first row transition metal complexes. The coordination chemistry of Pb (II) with N- and O-donor ligands has been investigated in the past decade and frequently discussed in regard of the stereochemical activity of the lone pair of electrons [13]. In this study, the iminopyridine ligand and related novel complexes derived from Pb(II) containing nitrate, thiocyanate and iminopyridine ligands were synthesized (Scheme 1) and characterized by elemental analysis, ^{1}H NMR and IR and UV–Vis spectroscopy



Scheme 1. Synthesis of 2-[2,6-dimethylphenyl) iminomethyl]-pyridine ligand and related lead complexes.

Experimental

Reagents and materials

All solvents and chemicals were of analytical grade and the solvents were dried and distilled before use according to a standard procedure [14]. 2,6-dimethylaniline, 2-pyridinecarbaldehyde, were purchased as commercial chemicals from Merckand used without any further purification. 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, UV–Vis spectrophotometer 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}CNMR 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 ligand

To a solution of 2,6-dimethyl aniline (0.121 g, 1mmol) in normal hexane was added to a stirred solution of 2-pyridine carbaldehyde (0.107 g,1mmol) in normal hexane. The resulting light yellow solution was stirred for about 120 minutes (2h), at room temperature and then left to evaporate slowly at 3-5 °C.

After one week, yellow crystals of (2,6-dimethyl phenyl) pyridine-2yl methylene amine was obtained. Yield: 93.38 % (m. p. 324 K).

Elemental analysis: Anal. Calc. for $C_{14}H_{14}N_2$ (210.27): C: 79.97; H: 6.71; N: 13.32. Found: C: 79.85; H; 6.83; N: 13.30%.

Main FT-IR (KBr disk, cm^{-1}); υ (C-H) 2917(m) (alkyl), υ(C=N)1639(s), υ(C=C)1435-1585(m), υ(C-H)(bend.) 774(s) cm^{-1}.

^{1}HNMR (300MHz, DMSO-d_6, δ ppm, 298 k, TMS): 2.48 (group of peaks, DMSO), 2.06 (s, methyl protons, 6H), 7.54 (multiplet, aromatic protons, 3H), 8.28 (s, CH=N, 1H), 6.93-8.70 (group of peaks, pyridine ring protons, 5H).

^{13}CNMR (300MHz, DMSO-d_6, δ ppm, 298 k, TMS): δ17.90 (methyl), 120.77, 123.86, 125.90, 126.17, 127.72, 128.00, 137.16, 149.65, 150.05, 153.75, 163.66(CH=N), UV–Vis: (λ_{max} in Ethanol), 342, 272 nm.

Synthesis of complex a

For the preparation of the complex a, a solution of 2-[(2,6-dimethylphenyl)-iminomethyl]-pyridine (420 mg, 2.00 mmol) in methanol (10 ml) was added slowly to a solution of $Pb(NO_3)_2$ (331 mg, 1.00 mmol) in methanol (10 ml) and the reaction mixture dark yellow solution was stirred for 120 minutes at room temperature. The metal complex was prepared; the resulting product was filtered and dried in room temperature. (Yield: 59.76%, m. p. 430 K).

Main FT-IR (KBr disk, cm^{-1}); υ (C-H) 3437(w) and 2917(m) (alkyl), υ(C=N) 1634(m), υ (N=O) 1588 (s), υ (C=C) 1357-1685 (m), υ (C-H) (bending) 771(s) cm^{-1}.

^{1}HNMR (300MHz, DMSO-d_6, δ ppm, 298 K, TMS): 2.49 (group of peaks, DMSO), 2.05(s, methyl protons, 6H), 6.93-7.06 (multiplet, aromatic protons, 3H), 8.29(s, CH=N, 1H), 7.55-8.70 (group of peaks, pyridine ring protons, 5H).

^{13}CNMR (300MHz, DMSO-d6, δ ppm, 298 K, TMS): δ17.97 (methyl), 121.08, 123.96, 126.50, 126.27, 128.06, 128.00, 137.33, 149.73, 150.08, 153.72, 163.82(CH=N), UV–vis: (λ_{max} in Ethanol), 341, 273 nm.

Synthesis of complex b

For the preparation of the complex b, a mixed solution of 2-[(2,6-dimethylphenyl)-iminomethyl]-pyridine (0.420 g, 2.00 mmol) and KSCN (0.195 g 2.00 mmol) in methanol (10 ml) was added slowly to a solution of $Pb(NO_3)_2$ (331 mg, 1.00 mmol) in methanol (10 ml) and the resulting yellow solution was stirred for 90 min at room temperature and then left to at 3–5°C. After twenty days, the resulting dark yellow solution was obtained. The metal complex was prepared; the resulting product was filtered and dried in room temperature (Yield; 56.76%, m. p. 464 K).

Main FT-IR (KBr disk, cm^{-1}); υ (C-H) 3431(w), υ (C=N) 1634(m), υ (C=C) 1483-1591 (m), υ (C-H) (bend.) 774 (s), υ (C≡N) 2068 (s) (thiocyanate), cm^{-1}.

^{1}HNMR (300MHz, DMSO-d_6, δ ppm, 298 k, TMS): 2.50 (group of peaks, DMSO), 2.05(s, methyl protons, 6H), 6.93-7.05(multiplet, aromatic protons, 3H), 8.32 (s, CH=N, 1H), 7.56-8.72 (group of peaks, pyridine ring protons, 5H).

^{13}CNMR (300MHz, DMSO-d_6, δ ppm, 298 K, TMS): δ18.07 (methyl), 121.58, 124.09, 126.21, 126.42, 128.12, 132.03, 137.53, 149.62, 150.09, 153.64, 164.04 (CH=N), UV–vis: (λ_{max} in Ethanol), 341, 272 nm.

Results and Discussion

All the complexes are insoluble in common solvents such as water, benzene, chloroform, dichloromethane, etc.; they are soluble in 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 are compared with those of the free ligand in order to determine the coordination sites that may involve in chelation. The position and or the intensities of these peaks are expected to be changed upon chelation.

The IR spectra of metal complexes and free ligand were recorded in the range of 450–4000 cm^{-1}. The azomethine nitrogen (C=N) appears around 1644 cm^{-1} which has been shifted to lower wave numbers in the range between 1610 and 1640 cm^{-1}in complexes. The shifts in the frequencies are due to coordination of two imine groups with the metal ions. The strong band around 1350–1550 cm^{-1} could be assigned to the stretching frequency of N=O bands[15]. The strong band around 2069 cm^{-1} could be assigned to the stretching frequency of C≡N bands in thiocyanate [16].

The nitrite ion can 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 B_2 and A_1 modes. The splitting energy provides information regarding the type of coordination and is relatively smaller in the unidentate coordination than in the bidentate coordination in similar complexes. In this complex, the asgined band to nitrite has a large splitting energy where shows its bidentate coordination [17].

Electronic spectral studies

Electronic spectrum of ligand and all the complexes were recorded in ethanol. In electronic spectra of metal complexes the wide range of bands are 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 [18]. The bands observed in 235–265 nm are due to $\pi \rightarrow \pi^*$ transition of C=N group [19]. The bands were shifted to higher range (red shifted), which is due to nitrogen that involved in coordination with metal ion. The absorption bands are observed in the range of 310–370 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), which is due to nitrogen that involved in coordination with metal ion [20].

1H NMR spectra

The structure of ligand was confirmed by ^{1}HNMR and ^{13}CNMR spectra. The spectrum of the ligand shows a singlet at 8.28 ppm corresponding to imine proton and a singlet at 2.06 ppm corresponding to two CH3 groups where the singlet shifts to 8.30 and 8.32 in complex a and complex b respectively. The multiplet at 6.93 ppm and the doublet at 7.06 ppm were was due to aromatic protons and the signals between 7.54 and 8.70 ppm were due to pyridine ring protons in free ligand where they don't show noticeable displacements in the complexes. These slightly displacements, maybe due to main group nature of metal ion.

Conclusion

In the present study, novel Schiff base iminopyridine complexes were prepared and characterized by physico-chemical methods. The metal ions were complexed with nitrogen of the imine groups.

The complex a; [Pb((2,6-dimethylphenyl) pyridine-2ylmethyleneamine)$_2$(NO$_3$)$_2$] have been synthesized and characterized by ^{1}HNMR, ^{13}CNMR, IR and UV–visible spectroscopy.

The Pb^{+2} coordinated by two molecules of 2,6-dimethyl phenyl)pyridine-2yl methylene amine and two molecules of nitrate. The iminopyridines and nitrates coordinated as bidentate ligands. The Pb^{+2} ions are eight-coordinated.

The complex b; [Pb((2,6-dimethylphenyl) pyridine-2ylmethylene amine)$_2$(SCN)$_2$] have been synthesized and characterized by ^{1}HNMR, ^{13}CNMR, IR and UV–visible spectroscopy.

The Pb^{+2} coordinated by two molecules of 2,6-dimethyl phenyl)pyridine-2yl methylene amine and two thiocyanate anions . The Pb^{+2} ions are six-coordinated.

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