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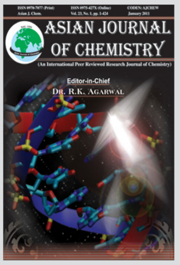

Spectroscopic, Structural and Solution Studies of New Tl(I) Complex with 3-Nitrobenzylidene-4-aminobenzoic Acid

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A new thallium(I) complex with a Schiff base ligand, [Tl(L)](1) [L^- = 3-nitrobenzylidene-4-aminobenzoic acid], has been synthesized and characterized. The carboxylic groups of the ligand 3-nitrobenzylidene-4-aminobenzoic acid in the new Tl(I) complex is chelated *via* oxygen atom of acidic group. The formation and stoichiometry of the Tl^+-L complex in DMF solution was investigated by spectrophotometric and conductometric method. The UV spectra of Tl(I) compelex shows that the thallium-oxygen bonds have considerable covalent character.

Key Words: Thallium(I), Schiff base, Slow evaporation, Solution chemistry, Conductivity.

INTRODUCTION

Polymers are defined as high molecular weight molecules formed by the repetition of monomeric units linked with covalent bonds. The coordination polymers[1] are infinite systems build up with metal ions and organic ligands as main elementary units linked *via* coordination bonds and other weak chemical bonds such as hydrogen bonds, π-π stacking or van der Waals interactions. These compounds are also named metal-organic coordination networks or metal-organic frameworks (MOF) in the case of ordered structures[2].

Metal-organic coordination polymers has attracted much attention because of their potential applications in sorption, electrical conductivity and catalysis[3-7].

Among various ligands, Schiff base polymers are of great intrest due to their especials properties such as high thermal stability[8,9], compelex-forming ability[10,11] and semiconducting qualities[11,12].

Thallium(I) is formally a low-valence *p*-block metal with a closed sub-shell (s^2) and Tl(I) chemistry is very interesting because of the less common properties:(a) thallium salts/complexes are often anhydrous, (b) the lone pair present on thallium may or may not be stereochemically active, (c) high coordination numbers may be present because of the large size of thethallium(I) ion, (d) because of the ease with which Tl(I) complexes form metal-metal bonds and also complexes with aromatic hydrocarbons[13-18].

Tl^+ ion, for example, with an electronic configuration $4f^{14}5d^{10}6s^2$, does exhibit a large variety of unusual coordination geometries caused by the possible presence of stereo-chemically active lone pairs[19,20].

In continuation of our research in this field[21-25], this article describes the synthesis and characterization of a new polymeric Schiff base and its Tl(I) metal complex. In addition to structural studies of compound **1**, solution studies of the Schiff base 4-nitrobenzylidene-4-aminobenzoic acid (HL) are discussed.

EXPERIMENTAL

All chemicals were of reagent grade and were used as commercially obtained without further purification. IR spectra were recorded using Shimadzu 8400S (IR solution) spectrophotometers. ^{1}H NMR spectra were recorded using Broker AVANCE500 spectrophotometers. Melting points were measured on a Barnstead/ElectroThermal (IA9000) apparatus and are uncorrected. All UV-VIS spectra were recorded on a computerized double-beam Shimadzu UV-1700 Pharmaespec spectrophotometer, using two matched 10 mm quartz cells. Conductometric measurements were carried out using a JENWAY 4510 conductometer.

Synthesis of the schiff base ligand HL: 10 mmol (1.37 g) of 4-aminobenzoic acid was dissolved in 20 mL ethanol and then a solution of 10 mmol (1.51 g) of 4-nitro benzaldehyde in 20 mL ethanol was added. The reaction mixture was stirred for 24 h (Fig. 1). A yellow solution was obtained. After filtering it was allowed to evaporate for a few hours to obtain a yellow powder. Yield: 2.54 g (94.07 %), d.p. = 254 °C. IR (selected key bands; in cm^{-1}): 1103 w, 1172 w, 1276 m, 1357 s, 1573 vs, 1598 s, 1691 m, 2948 w, 3488 w, 3402 w. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ: 7.4 [2H, d], 8 [2H, d], 8.22 [2H, m], 8.38 [2H, d], 8.9 [1H, s], 12.9 ppm [1H, br s,OH].

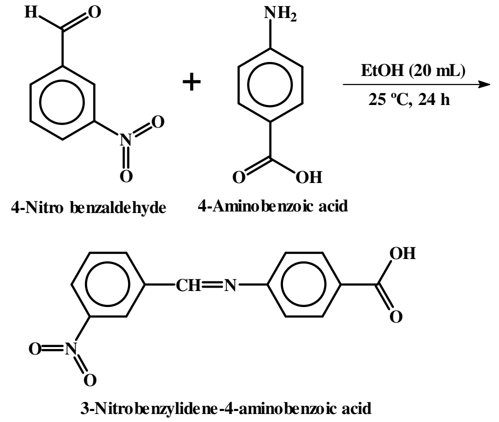

Fig. 1. Reaction of synthesizing of 3-nitrobenzylidene-4-aminobenzoic acid

Synthesis of [Tl(L)] (1): 1 mmol (0.27 g) of the HL ligand was dissolved in 25 mL of methanol and was mixed and stirred with a solution of 1 mmol (0.056 g) of KOH in 5 mL H_2O. Then a solution of 1 mmol (0.266 g) $TlNO_3$ in 2 mL H_2O was added to the mixture and was heated to reflux for 1 h (Fig. 2). After filtering, it was allowed to evaporate for several days to obtain yellow powder. Yield: 0.208 g (44 %), d.p. 282 °C. IR (selected key bands; in cm^{-1}): 696 m, 779 m, 854 s, 1107 w, 1348 vs, 1525 s, 1585 m, 1691 w, 2885 w. ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ: 7.3 [2H, d], 7.92 [2H, d], 8.17 [2H, m], 8.35 [2H, d], 8.8 ppm [1H, s].

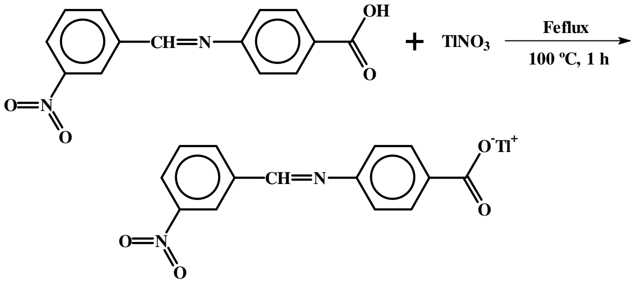

Fig. 2. Reaction of synthesizing of thallium(I)[3-nitrobenzylidene-4-aminobenzoate]

RESULTS AND DISCUSSION

The reaction between 4-nitrobenzylidene-4-aminobenzoic acid (HL) and $TlNO_3$ provided a yellow powder of the general formula [Tl(L)] (**1**). Determination of the structure of this compound by FT-IR spectroscopy showed the aromatic C=C stretch bands (for the carbon-carbon bonds in the aromatic ring) in 1520-1400 cm^{-1} region. The aromatic CH stretch appeared at *ca.* 2890 cm^{-1}. The peak with medium intensity at 1590 cm^{-1} related to stretch band of C=N. The carboxylic acid showed a strong, wide band for the O-H stretch at *ca.* 3600-2400 cm^{-1}. The carbonyl stretch C=O of a carboxylic acid appears as an intense band in 1760-1690 cm^{-1} region. The absorption bonds at 1691 and 1348 cm^{-1} refersed to ν_{ac}(C-O), ν_s(C-O), respectively.

In ^{1}H NMR spectrum of compound **1**, the peak at 13 ppm that relevant to carboxylic group disappeared because the ligand coordinated to the thallium ion.

Solution studies: In a typical procedure, 2.0 mL of ligand solution (5×10^{-5} M) in DMF was placed in the spectrophotometer cell and the absorbance of the solution was measured. Then a known amount of a concentrated solution of thallium(I) nitrate in DMF (1.3×10^{-3} M) was added in a stepwise manner using a 5 μL Hamilton syringe. The absorbance spectrum of the solution was recorded after each addition. The thallium(I) ion solution was continually added until the desired metal to ligand mole ratio was achieved. The electronic absorption spectra of the ligand L in the presence of an increasing concentration of thallium(I) ions in DMF at room temperature are shown in Fig. 3. The strong absorption of ligand at 367 nm increases with increasing concentration of the metal ion. The resulting absorbance (at 367 nm) against [Tl$^+$]/[L] mole ratio plot, shown in the inset of Fig. 3, revealed a distinct inflection point at a metal-to-ligand molar ratio of about 1, emphasizing the formation of a 1:1 complex in solution.

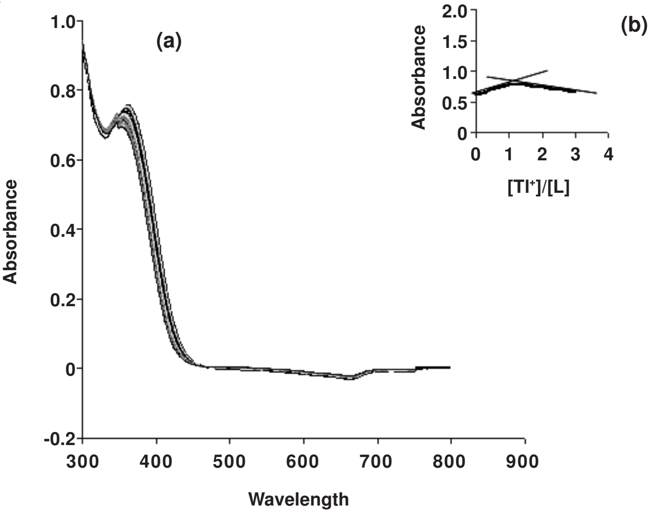

Fig. 3. (a) Electronic absorption spectra of ligand L in DMF (5×10^{-5} M) in the presence of increasing concentration of thallium(I) ion at room temperature. (b) Corresponding mole ratio plot at 367 nm

The formation and stoichiometry of the Tl$^+$-L complex in DMF solution was also investigated by a conductometric method. In a typical experiment, 20.0 mL of thallium(I) nitrate solution (5.0×10^{-5} M) in DMF was placed in a glass cell and the conductance of the solution was measured. Then a known amount of the concentrated solution of ligand in DMF (5.0×10^{-3} M) was added in a stepwise manner using a 5 μL Hamilton syringe. The conductance of the solution was measured after each addition. The ligand solution was added regularly until the desired ligand to metal ion mole ratio was achieved. The conductivity of the 5.0×10^{-5} M of thallium(I) nitrate solution in DMF was monitored as a function of the [L]/[Tl$^+$] mole ratio and the resulting plot is shown in Fig. 4. The initial conductivity is relatively low, probably due to some degree of ion pairing which is common in solvents with a relatively low dielectric constant such as DMF. Addition of the ligand to the metal salt solution does not cause a variation in the solution conductivity possessing a rather distinct inflection point at a molar ratio of about one, again indicating the formation of a 1:1 Tl^+-L complex in solution.

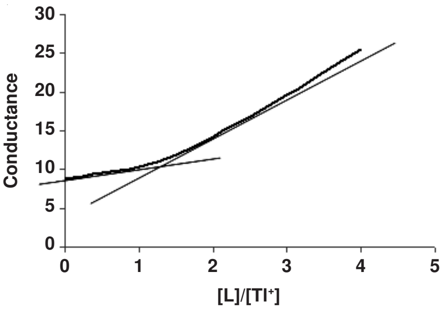

Fig. 4. Conductivity *vs.* [L]/[Tl^+] mole ratio plot DMF solution

Conclusion

A new Tl(I) complex of a Schiff base ligand, [Tl(L)] (**1**) [HL = 3-nitrobenzylidene-4-aminobenzoic acid], was synthesized and characterized. Complex formation studies by spectrophotometric and conductometric analysis in solution show the preferential formation of a 1:1 complexe of L^- and Tl^+. The failure to obtain a 1:1 stoichiometry in the solid state- despite the 1:1 ratio used in the synthesis and the 1:1 ratio preferred in solution-points towards spatial arrangements in the solid state to be the determining factor during complex formation, but with no solid state structure of a 1:1 complex for comparison this has to remain speculation.

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