Synthesis and spectral characterization of lead(II), silver(I), palladium(II) and dioxouranium(VI) azoimidazole complexes

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A few complexes of Pb(II), Ag(I), Pd(II) and dioxouranium(VI) with arylazoimidazoles have been synthesized and characterized by elemental analyses, IR, UV/Vis, $^1$H NMR and conductance studies. The uranyl complexes are found to be monomeric and ionic in nature whereas Pb(II), Ag(I) and Pd(II) complexes are polymeric.

The incorporation of azo group at C-2 position of the imidazole group gives arylazoimidazoles that may either act as N(3), N(a) or N(1), N(a) chelating molecule; N(a), azo-N to maintain a five-membered chelate structure (1). Besides, N(1) may coordinate singly to soft acids like Ag(I) and may give polymeric backbone through N(3) coordination. Azoimidazoles are N, N chelating ligands and may tune the redox and spectroscopic properties of a metal centre. This property coupled with the biomimetic properties of imidazole lead us to investigate the coordination behaviour with heavy metal ions. Reports on the complexes of arylazoimidazoles are scarce. Therefore, we thought it worthwhile to study the synthesis and characterization of Pb(II), Ag(I), Pd(II) and dioxouranium(VI) complexes.

Experimental

Aromatic amines, imidazole, AgNO$_3$ were obtained from E. Merck. UO$_2$(NO$_3$)$_2$·6H$_2$O; Pb(OAc)$_2$·3H$_2$O were SD's Lab. Chem. chemicals. PdCl$_2$ was obtained from Arrora Mathey. Na$_2$PdCl$_4$ was prepared by usual procedure. All other chemicals and solvents were of reagent grade.

The elemental analyses were carried out on Perkin Elmer 240C elemental analyser. IR spectra were recorded in KBr on a Perkin Elmer 783 and 883 spectrophotometer. The conductances were measured using systronics 304 conductivity meter. The UV-vis spectra were recorded on Schimadzu UV-160A spectrophotometer. The $^1$H NMR spectra were recorded on JEOL, JNM, GX 270, FTNMR spectrophotometer. Lead silver and uranium were estimated by standard procedures.

Synthesis of ligands and complexes

The ligands 2-(arylazo)imidazoles (I) were prepared by reported procedure. The details are given as follows for (Ia). To an aqueous solution (25 ml) of imidazole (3.0 g, 0.044 mol) and Na$_2$CO$_3$ (7.0 g, 0.066 mol) at 5°C was added diazotized solution of aniline (4 g, 0.043 mol) dropwise with continuous stirring. The temperature was controlled at ice cold condition. The orange compound so precipitated was filtered, washed with cold water and extracted with 2N HCl (15 ml x 2). The solution was neutralised with Na$_2$CO$_3$ and pH of the solution was checked at 7. The precipitate was filtered, washed and dried. The yield was 55%; m.p., 190±1°C. The yield of other ligands varied from 50-65%. Their melting points are (Ib), 235±2; (Ie), 240±1°C.

Synthesis of lead(II) (2), silver(I) (3) and palladium(II) (4) compounds

The preparation follows common procedure. To methanolic solution (15 ml) of (Ia) (0.35 g, 2.03 mmol) aqueous solution of Pb(OAc)$_2$·3H$_2$O (0.38 g, 1 mmol)/AgNO$_3$ (0.35 g, 2.06 mmol) Na$_2$PdCl$_4$ (0.3 g, 1.02 mmol) was added dropwise under stirring conditions. Immediately orange or orange-brown precipitate appeared. The solution was stirred for about 1 h and the precipitate filtered, washed and dried over CaCl$_2$. The yield was 80-90%. Other complexes were similarly prepared and the yields found to be same.

Synthesis of uranyl complexes (5a)

To a methanolic solution (20 ml) of 1a (0.35 g, 2.03 mmol), UO$_2$(NO$_3$)$_2$·6H$_2$O (5 g, 1.0 mmol) in
the same solvent was added dropwise and the solution refluxed over steam bath for a period of 3 h. The solution volume was reduced and the precipitate was filtered, washed with MeOH-H2O (1:1 v/v) and dried in vacuo. The yield was 55%. Other complexes were similarly prepared and yield varied from 50-65%.

Results and discussion

The analytical data of the complexes are presented in Table 1. 2-Arylazoimidazoles (1) are N, N chelating ligands and there are two heterocyclic N-centres; pyrrolic N(1) is a soft donor centre while pyridinic N(3) is hard donor centre. A five-membered chelate structure is developed via coordination through heterocyclic-N and azo-N moieties.

The molar conductance measurements suggest that uranyl complexes are 1:2 conductor in DMF. Ag(I) (3) and Pd(II) (4) complexes are almost insoluble even in DMSO, DMF while Pb(II) (2) and dioxouranium(VI) (5) complexes are soluble in these solvents. Due to their insolvability in common organic solvents, the molecular weight measurements could not be performed. Uranyl complexes (5) lose weight at 120-140°C which correspond to two equivalents of water molecules and ligands are released at 350-400°C. The complexes undergo complete decomposition above 600°C to the final residue as their oxides.

The electronic spectral data have been recorded in DMSO. The ligands show two bands in the range 290-300 and 380-400 nm which may be ascribed to intra-ligand charge transfer band \( \pi-\pi^* \) and n-\( \pi^* \) transitions respectively. The complexes of Pd(II), Pb(II) and Ag(I) exhibit these transitions and are blue shifted by 15-20 nm. Only the uranyl complexes show three major transitions; of these first two transitions at shorter wavelength region are ascribed to intraligand charge transfers and the third one at 420-460 nm is due to apical oxygen-\( f^6(U) \) transition.

In the IR spectra of the ligands, \( \nu(N-H) \) 2600 cm\(^{-1}\), \( \nu(N=N) \) 1400-1410 cm\(^{-1}\), \( \nu(C=N) \), 1580-1600 cm\(^{-1}\) and other bands 1500-1300, 790, 775, 700-660 cm\(^{-1}\) corresponding to imidazole moiety are observed. The complexes (2-4) do not exhibit any absorption due to N-H stretching that suggests deprotonation of this functional and pyrrolic N(1)-coordination. In uranyl complexes (5), \( \nu(N-H) \) is red shifted to 2525 cm\(^{-1}\) and a broad medium intense band centred at 3550
cm$^{-1}$ is designated as coordinated water which has been confirmed from thermal studies. The N=N stretching appears at 1340-1360 cm$^{-1}$ and is red shifted by 50-60 cm$^{-1}$ in palladium(II) complexes (4). The uranyl complexes (5) exhibit N=N stretch at 1375-1390 and is red shifted by Pb(II) (2) and Ag(I) (3) complexes. This suggests azo-N coordination in complexes 4 and 5 and maintains a five-membered chelate structure. In Pb(II) and Ag(I) complexes, this remains free. The structural studies of Ag-imidazole system suggests a complex packing of polymeric chains containing linearly coordinated silver atoms bridged by imidazolate ligands. The similar argument may be extended in our case to explain the polymeric behaviour of Pb(II), Ag(I) and Pd(II) complexes. The ionic charges in the complexes (2-4) are satisfied by proton dissociation from N(1)-H and coordination number may be fulfilled by imidazolate bridging from neighbouring molecule and/or azo-N coordination giving a five-membered chelate structure. Selected IR data are collected in Table 1.

The complexes obtained from thermal dehydration are analysed by IR spectra. A sharp stretch at 1360-1370 cm$^{-1}$ is assigned to v$_{as}(\text{NO})$ of the uranyl moiety. A weak stretching $\sim 300-320$ cm$^{-1}$ may be assigned to v(U-N) vibrations.

$$\text{[UO}_2(\text{H}_2\text{O})\text{NO}_3]_2 \rightarrow 120-140^\circ C \rightarrow \text{[UO}_2(\text{NO}_3)]_2\text{NO}_3 + 2\text{H}_2\text{O}$$

(1)

The structures of dioxouranium complexes of 2, 2'-bipyridyl are known. They are of $[\text{UO}_2(\text{bpy})(\text{NO}_3)]_2$. Both nitrate groups act as bidentate chelators. Other complexes of N, N-chelating ligand from five-membered heterocycle imidazole type frame viz. 2,2'-pyrindyl-benzimidazole (PBH), 2, 2'-biimidazole (H$_2$Biim) of dioxouranay are all bis complexes of the formulae $\text{UO}_2L_2(\text{NO}_3)_2$ (L=PBH, H$_2$Biim). In our case the uranyl complexes are all ionic bis complexes $[\text{UO}_2(\text{L})_2(\text{H}_2\text{O})_2]\text{NO}_3]$ (5). The presence of a five-membered ring may provide less steric hindrance and may allow the ligand association to increase coordination number.

The $^1$H NMR spectra of uranium(VI) and lead(II) complexes are recorded in DMSO-d$_6$ and ligands (1) are recorded in CDCl$_3$. Due to sparing solubility of palladium(II) and silver(I) complexes, it did not provide good spectra to analyse. Imidazolic 4- and 5-H protons exhibit overlapping resonance at $\sim 7.36$ for (1), 7.55 for (2) and 7.50 ppm for (5) and may be due to interconversion of protonic positions. The arylazo aromatic protons resonate at two different positions and correspond to symmetrical ABB' multiplet. The downfield signal is assigned to 7- and 11-H and appear at 7.96-8.05 ppm in (1), 7.92-8.02 ppm in (2) and 7.94-8.08 ppm in (5). Another signal is very much sensitive to substituent at 9th position; Me-substitution shifts to upfield while chloro substitution shifts to downfield and is corroborated with their electronic effect. The signal positions are at (1a), 7.40; (1b), 7.16 and (1c) 7.58 ppm. These are assigned to 8- and 10-H [9-H for (1a)] resonances. On complexation, the protons are downfield shifted compared to free ligand and the signal positions are 7.41 (2a), 7.59 (5a); 7.18 (2b), 7.32 (5b) and 7.55 (2c), 7.64 (5c) ppm. The N(1)-H proton signal in free ligands (1) appear at 10.3-10.4 ppm and in complex do not appear even at appreciably high concentration. This may be due to rapid exchange of N(1)-H with DMSO-d$_6$. In Pb(II) complexes (2) imidazolic 4- and 5-H suffer sufficient downfield shifting while aryl protons remain almost unperturbed. This supports our previous position of imidazole coordination while arylazo group remains free.

Thus a comparison has made between the bonding of metal ions to N(1) vs. N(3) centre. The physical and spectroscopic investigation suggest that Pb(II), Ag(I) and Pd(II) preferentially bind pyrrolic N(1) centre and chelate structure maintained in palladium(II) complexes (4) via coordination through N(a)(azo) centre. The polymerisation is continued through N(3) coordination of imidazole fragment to the neighbouring metal centre. The hard acid $\text{UO}_2$(VI) binds N(3) and chelation is achieved through azo-N coordination.

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