Synthesis and spectral characterization of palladium(II) and silver(I) complexes of antipyrine-azo-imidazoles

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Received 28 October 2005; accepted 22 March 2006

Antipyrine-azo-imidazole (1) and its N(1)-alkyl derivatives (2) are synthesized and characterized spectroscopically. The ligands are N,N'-chelator. Two groups of coordination complexes, Pd(II)Cl₂ (3) and [Ag(2)(HCO₃)] (4) have been synthesized and characterized by spectral (IR, UV-vis., ¹H NMR) data.

IPC Code: Int. Cl. C07F11/10; C07F15/00

Because of various uses of antipyrine, efforts are being made to functionalise this molecule to prepare different other derivatives and to synthesize their metal complexes. We are interested to prepare azoheterocycles by inserting Ar-N=N- group into the N-heterocycle backbone. However, the synthesis of biheterocyclic azo compounds is a tough task. There are a few reports on the biheterocyclic azo compounds: particularly symmetric type, i.e. azo (-N=N-) links two similar heterocycles. We have recently reported pyridyl-azo-imidazole, an antisymmetric biheterocycle azo compound, and its coordination complexes. We have now synthesized antipyrine-azo-imidazoles (1) by diazotisation of antipyrine followed by coupling with imidazole. 1-Alkylation of imidazole unit in this molecule has also been carried out to eliminate bridging ability of imidazole and to synthesise 1-alkyl-2-(antipyrineazo)imidazole (2). Characterisation of the new ligands and their palladium(II) and silver(I) complexes are described here.

Experimental

4-Aminoantipyrine, imidazole, alkyl halides (MeI, EtI, PhCH₂Br (Sisco Research Lab (SRL), Mumbai), PdCl₂ (Arrora Matthey, Kolkata) were used as received. All other chemicals and solvents were obtained from SRL and used without further purification.

Notes

Physical measurements

Microanalytical data (C, H, N) were obtained on Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using Jasco UV-vis-NIR model V 570. For IR spectra (KBr disk, 4000-200 cm⁻¹), FTIR Jasco model 420 was used. ¹H NMR spectra were recorded using Bruker (AC) 300 MHz FTNMR spectrometer. Systronics electrical conductivity meter (model 304) was used for conductivity measurements.

Synthesis of 2-(antipyrineazo)imidazole (1)

To a 3 N HCl solution (40 mL) of 4-aminoantipyrine (2 g, 9.85 mmol), NaNO₂ (0.9 g, 13.04 mmol) in water (10 mL) was added dropwise under ice-cold condition and stirred continuously maintaining temperature (0-5°C). The resulting orange-yellow solution of antipyrine-diazonium salt was then added to an imidazole (0.7 g, 10.30 mmol) solution (25 mL) in NaHCO₃ solution and stirring continued at the low temperature. A Canary yellow precipitate appeared quickly which was then kept at low temperature (5°C) for 8 h. It was then filtered while cold and washed with water. The product was dried under air suction and kept in desiccator. Dry mass was then dissolved in 1N HCl (25 mL) solution and filtered, NaHCO₃ was added in small portion to attain pH 7 (tested by pH paper). Deep yellow precipitate appeared which was then filtered, washed with water and dried under vacuum. Yield: 65% (1.8 g). Anal. Calcd for C₁₅H₁₄N₄O₁ : C, 59.57; H, 4.96; N, 29.79. Found: C, 59.48; H, 5.06; N, 29.64%.

Synthesis of 1-methyl-2-(antipyrineazo)imidazole (2a)

To dry THF solution (30 mL) of 1 (1 g, 3.55 mmol), NaH (50%) (0.2 g) was added gently and stirred for 30 min. Then, MeI (0.55 g, 3.87 mmol) in THF (10 mL) was added through pressure equalizing system for 1 h and then refluxed for additional 2 h. It was then cooled, filtered and the solvent distilled off. The product was then washed with water and extracted with benzene. The solution was chromatographed on a silica gel column prepared in hexane. An orange red band was then eluted by benzene. The solvent was then evaporated in air and dried in desiccator. A tarry gum was isolated. Yield: 64% (0.67 g).
Other ligands 2b and 2c were prepared by identical procedure in 60-70% yield. The compounds were gummy mass.

Synthesis of Pd(2a)Cl₂ (3a)

To MeCN solution (15 mL) of PdCl₂ (0.09 g, 0.51 mmol) was added 2a (0.17 g, 0.57 mmol) in the same solvent (10 mL) and stirred at room temperature for a period of 4 h. Dark precipitate appeared from deep red solution. The solvent was then evaporated to 1/4th of its original volume. The precipitate was then filtered, washed with water and then by MeOH and dried in a desiccator. The compound was purified by column chromatography over silica gel column prepared in benzene. Desired deep red band was eluted by CH₃CN-MeCN (9:1, v/v). The solvent was evaporated in air and the mass was dried in a desiccator. Yield 71% (0.17 g). Anal. Calcd for C₁₀H₁₂N₆Cl₂Pd: C, 45.03; H, 3.40; N, 17.41. Found: C, 45.12; H, 3.49; N, 17.84%.

C₆H₆-MeCN

Synthesis of [Ag(2a)Cl]ClO₄ (4a)

To a dry MeOH solution (25 mL) of AgNO₃ (0.05 g, 0.29 mmol) was added 2a (0.19 g, 0.64 mmol) in the same solvent (15 mL) and stirred continuously for 2 h. The solution colour turned to deep orange. It was then evaporated in air to reduce its volume to half and then filtered. An aqueous solution of NaClO₄ (1 g in 5 mL) was added into the solution. Light brown precipitate appeared quickly which was filtered, washed with water followed by cold MeOH solution. The product was dried in a CaCl₂ desiccator. Dry mass then chromatographed over silica gel column prepared in benzene. MeOH eluted an orange band. The solvent was evaporated in air. The product was dried in vacuum. Yield 68% (0.16 g). Anal. Calcd for C₁₀H₁₂N₆O₂ClAg: C, 45.03; H, 4.00; N, 21.01. Found: C, 45.12; H, 4.07; N, 20.88%.

Synthesis of [Ag(2b)Cl]ClO₄ (4b): C, 46.40; H, 4.35; N, 20.30. Found: C, 46.32; H, 4.27; N, 20.18%.

C₁₂H₁₀N₆O₂ClAg: C, 52.97; H, 4.20; N, 17.66. Found: C, 52.97; H, 4.25; N, 17.58%.

Results and discussion

Synthesis and formulation

The syntheses of ligands are given in Scheme 1. An aqueous solution of antipyrene is diazotised and the diazonium ion is coupled with imidazole at pH 7. Dissolving in 1 N HCl followed by neutralization with NaHCO₃ gave a purified yellow product. The product, 2-(antipyrylazo)imidazole (1), is crystallized from hot methanol solution. Dry compound 1 is then reacted with NaH in dry THF to generate imidazolium ion capable to nucleophilic attack to alkyl halide (RX: Mel, EtI, PhCH₂Br) synthesise 1-alkyl-2-(antipyrylazo)imidazole (2). The purification of 2 has been carried out by chromatographic separation. Evaporation of the solution and drying in a CaCl₂ desiccator isolated a gummy mass. The ligands, 2, may behave as bidentate, N(azo), N(imidazolyl), or tridentate N(azo), Nimidazolyl, O(keto) type system.

Acetonitrile solution of 2 is reacted with PdCl₂ in the same solvent or AgNO₃ in MeOH-H₂O mixture (ligand in MeOH) followed by the addition of NaClO₄ [metal : ligand; 1:1 for palladium(II) complexes and 1:2 for silver(I) complexes] and stirred at room temperature for several hours. Dark coloured complexes are precipitated in both cases. They are filtered, dried and purified by chromatography on a silica gel column. The composition of the complexes are Pd(2)Cl₂ (3) and [Ag(2)Cl]ClO₄ (4).

Microanalytical data support the composition. The solution conductivity suggests that 3 are non-electrolyte and 4 are 1:1 electrolyte (λ = 90-100 Ω⁻¹ cm⁻¹) in methanol.

Spectroscopic studies

The IR spectrum of antipyrene shows strong stretch at 3432 and 3328 cm⁻¹ which correspond to v(NH₂) along with v(C=O) at 1648 cm⁻¹; v(=N), 1590 cm⁻¹ and other vibrations. Diazotisation of antipyrene has doubtlessly been confirmed by the absence of v(NH₂) and the presence of a new band of moderate intensity appearing at 1419 cm⁻¹, which may be assigned to v(N=O). In 1, a weak broad band appears centred at 3460 cm⁻¹ and assigned to imidazolyl-NH12 which disappeared on alkylation in 2. The v(C=O) in 1 and 2 appears at 1675-1685 cm⁻¹. In the complexes 3 the significant IR bands are v(N=N), v(C=O) and v(C=N) which appear at 1400-1405, 1680-1690 and 1570-1580 cm⁻¹, respectively. The red shifting of v(N=N) with respect to free ligand suggests coordination of azo-N to Pd(II)³. Besides, two weak bands appear at 310 and 280 cm⁻¹. On comparing with the IR spectra of previously reported Pd(azoimidazole)Cl₂ complexes these two bands may correspond to v(Pd-Cl) of cis-PdCl₂ configuration8⁹. However, v(C=O)
remains almost unaffected in the complexes and may be considered as non-coordinating group. The complexes 4 exhibit high intense sharp band at 1080-1090 cm⁻¹ along with a weak stretch at 625 cm⁻¹. This band refers to ν(ClO₄) and does not exhibit significant coordination to Ag(I)⁹. Besides, the ν(N=N), ν(C=O), and ν(C=N) appear at 1390-1380, 1680-1690 and 1580-1590 cm⁻¹, respectively.

The electronic spectra of the ligands 1 and 2 in MeCN show intense bands (ε~10⁴ mol⁻¹ cm⁻¹) at 250-290 and 360-410 nm. They may be ascribed to ligand centred π→π* and n→π* transitions, respectively. Palladium(II) complexes (3) shift these transitions to longer wavelength by 15-20 nm along with a weak broad transition (ε~10³ mol⁻¹ cm⁻¹) centred at 500 nm. The red shifting of ligand-centred transition in the complexes 3 is in support of bonding interaction between metal and ligand. Besides, weak transition at 500 nm may be ascribed to d(Pd)→π*(ligand) transitions. The ligands possess π-acidic azoimine group and may participate in metal-to-ligand charge transfer transition. [Ag(2h)(ClO₄) (4) exhibit ligand-centred transitions at longer wavelength (5-10 nm) compared to the free ligand data. A weak
transition is also observed at 450 nm, which may be defined to metal-to-ligand charge transfers.10

The proton numbering pattern is shown in the structures in Scheme 1. The NMR spectra of ligands 1 and 2 are taken in CDCl3 (Table 1). Pd(II) and Ag(I) complexes are not sufficiently soluble in CDCl3 and, therefore, their NMR spectra have been recorded in CD2CN. The assignment of individual proton resonance has been made by spin-spin interaction, comparative integration and chemical shift data. Antipyrine-azo-imidazole shows a broad signal at 11.45 ppm which corresponds to δ(N-H) of imidazole. Upon addition of small amount of D2O into the solution, the signal disappears which supports that the signal corresponds to N-H signal. It is due to rapid proton exchange process, 2 N-H + D2O → 2 N-D + H2O. Imidazole protons (4- and 5-H) appear as doublet signal and have been assigned on comparing with the spectra of 2-(arylazo)imidazoles11. Antipyrine protons (6-Me, 7-Me and N-Ph) appear at usual position. In 1-alkyl-2-(antipyrineazo)imidazoles the alkyl group (R) appears as follows: 1-Me in 2a appears as singlet at 4.04 ppm; 1-CH2CH3 in 2b shows quartet (CH2: 4.46 ppm (12 Hz)) and triplet

Table 1—1H NMR data of the ligands1 and the complexes b

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<th>Compound</th>
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<th>5-H</th>
<th>6-Me</th>
<th>7-Me</th>
<th>9, 13-H</th>
<th>10-12-H</th>
<th>1-CH3/CH2</th>
<th>(1-CH2-)CH3</th>
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<td>2a</td>
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1In CDCl3, 2In CD2CN; 3Doublet; 4Triplet; 5Quartet; 6Triplet; 7Singlet; 8(Pre) ppm; 9(Pre) ppm (Data in parentheses represent spin-spin coupling constant J Hz).

by only 0.05 to 0.15 ppm and support of the coordination of N(imidazole) to Pd(II)/Ag(I). Other signals appear as in pattern of their respective ligands but shifted slightly to downfield region.

Acknowledgements

Financial support from CSIR, New Delhi is gratefully acknowledged. We thank Jadavpur University for the research grant.

References


