Synthesis, structure and luminescence behaviour of zinc(II) complexes containing hexadentate N-donor Schiff bases

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Received 29 June 2005; accepted 19 October 2005

Six hexacoordinated zinc(II) complexes of the type [Zn(L)(Y)]₂ [L = N-(1-pyridin-2-yl-formylidene)-N'-[2-[2-(1-pyridin-2-ylformylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pfad), Y = ClO₄ (1a), Y = PF₆ (1b); [L = N-(1-pyridin-2-ylmethylidene)-N'-[2-[2-(1-pyridin-2-ylmethylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pmad), Y = ClO₄ (2a), Y = PF₆ (2b); L = N-(1-pyridin-2-ylbenzylidene)-N'[2-[2-(1-pyridin-2-ylbenzylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pfad), Y = ClO₄ (3a), Y = PF₆ (3b)] have been synthesised and characterized on the basis of microanalytical, spectroscopic and other physicochemical properties. Structural analysis of 3a reveals that zinc(II) adopts a distorted octahedral environment with a ZnN₆ chromophore ligated by two pyridine N atoms (N1, N1'), two imine N atoms (N2, N2') and two amine N atoms (N3, N3') in cis-trans-cis orientation. Spectral properties show that the other complex ions are iso-structural with the dication in 3a.

IPC Code: Int. Cl 7 C07C 251/02; C07F 3/06

Research on design and synthesis of mono- and polynuclear coordination compounds of Group 12 metals ions continues unabated for the preparation of functional materials. Exploiting the veracity of coordination geometry around metal ion templates different networks can be accessed using various organic blockers. Self-assembly is the most efficient approach towards preparation of such materials. We are also interested in this field through variation of metal ion coordination environments using manganese(II), nickel(II), copper(II), zinc(II) and cadmium(II), organic ligands and suitable bridging units. Schiff bases are useful chelators because of their preparational accessibilities, structural varieties and varied denticities. We have isolated six hexacoordinated mononuclear zinc(II) complex of the type [Zn(L)]₂Y₂ [L = N-(1-pyridin-2-ylformylidene)-N'-[2-[2-(1-pyridin-2-ylformylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pfad), Y = ClO₄ (1a), Y = PF₆ (1b); [L = N-(1-pyridin-2-ylmethylidene)-N'-[2-[2-(1-pyridin-2-ylmethylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pmad), Y = ClO₄ (2a), Y = PF₆ (2b); L = N-(1-pyridin-2-ylbenzylidene)-N'[2-[2-(1-pyridin-2-ylbenzylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pfad), Y = ClO₄ (3a), Y = PF₆ (3b)] (Scheme 1). X-ray structure determination of one representative member, 3a shows that the metal centre is in a distorted octahedral environment coordinated by six N atoms of the Schiff base. The details of synthesis, spectra, structure and luminescence behaviour of the complexes are described here.

Materials and Methods

High purity pyridine-2-carboxaldehyde (Lancaster, UK), 2-acetylpyridine (Lancaster, UK), 2-benzoylpyridine (Lancaster, UK), triethylenetetramine (Lancaster, UK), potassium hexafluorophosphate (Fluka, Germany), zinc nitrate tetrahydrate (E. Merck, India) were purchased from respective concerns and used as received. Zinc perchlorate hexahydrate was

Scheme 1
Prepared on treatment of zinc carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on steam-bath, filtration through a fine glass-frit, and was preserved in a desiccator containing concentrated sulphuric acid for subsequent use. All other chemicals and solvents were of AR grade and were used as received.

Caution! Perchlorate compounds of metal ions are potentially explosive especially in presence of organic ligands. Only a small amount of material should be prepared and handled with care.

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000-3000 cm\(^{-1}\)) were recorded using a Jasco FTIR model 420 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01(M) KCl solution and dry MeOH was used as solvent. Ground state absorption and steady-state fluorescence measurements were made with a Jasco model V-530 UV-Vis spectrophotometer and Hitachi model F-4010 spectrofluorimeter, respectively. Time-resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer Edinburgh Instruments, model 199; a hydrogen filled coaxial flash lamp with a pulse width of 1.2 ns at FWHM and a Philips XP-2020Q Photomultiplier tube were respectively used as the excitation source and the fluorescence detector as described elsewhere\(^2\).

Preparation of Schiff bases

The Schiff bases pfad, pmad and pbad were prepared\(^1\) following reported method with a little modification. Details with pfad is described: Pyridine-2-carboxaldehyde (0.214 g, 2 mmol) was refluxed with triethylenetetramine (0.146 g, 1 mmol) in dehydrated alcohol. After 10 h, the reaction solution was evaporated under reduced pressure to yield a gummy mass, which was dried and stored in vacuo over CaCl\(_2\), for subsequent use. Yield, 0.212 g (80%). Pmad/pbad was prepared similarly using 1:2 molar ratio of triethylenetetramine (0.146 g, 1 mmol) and 2-acetylpyridine (0.242 g, 2 mmol)/2-benzoylpyridine (0.366 g, 2 mmol) instead of pyridine-2-carboxaldehyde. Found: C 36.49; H, 3.58; N, 14.63; Calc. C\(_{10}\)H\(_{32}\)N\(_6\)O\(_2\)ClZn (1a): C, 36.63; H, 3.45; N, 14.49%. IR (KBr, cm\(^{-1}\)): 1595 (\(\nu_{\text{CN}}\)), 1080, 620 (\(\nu_{\text{CO}}\)). UV-Vis (\(\lambda_{\text{max}}\) nm): 328. Found: C, 39.46; H, 4.82; N, 14.32; Calc. C\(_{20}\)H\(_{26}\)N\(_6\)O\(_2\)ClZn (2a): C, 39.30; H, 4.65; N, 14.00%. IR (KBr, cm\(^{-1}\)): 1590 (\(\nu_{\text{CN}}\)), 1085, 622 (\(\nu_{\text{CO}}\)). UV-Vis (\(\lambda_{\text{max}}\) nm): 330. Found: C, 48.75; H, 4.38; N, 11.76; Calc. C\(_{20}\)H\(_{26}\)N\(_6\)O\(_2\)ClZn (3a): C, 48.60; H, 4.25; N, 11.50%. IR (KBr, cm\(^{-1}\)): 1595 (\(\nu_{\text{CN}}\)), 1082, 620 (\(\nu_{\text{CO}}\)). UV-Vis (\(\lambda_{\text{max}}\) nm): 328.

Synthesis of [Zn(pfad)](PF\(_6\)) (1b)

Zn(NO\(_3\))\(_2\)-4H\(_2\)O (0.24 g, 1 mmol) was dissolved in MeOH (10 ml). To this pfad (0.32 g, 1 mmol) dissolved in same solvent (5 ml) was added slowly followed by KPF\(_6\) (0.36 g, 2 mmol) in H\(_2\)O (5 ml). The final solution was filtered, kept for slow evaporation and processed as in 1a to yield pure 1b; yield, 0.38 g (75%). Using pmad and pbad respectively instead of pfad yielded [Zn(pmad)](PF\(_6\)) (2b) and [Zn(pbaf)](PF\(_6\)) (3b); Yield, (70-75%). 1b, 2b and 3b were prepared in better yield (~80%) by metathesis of 1a, 2a and 3a, respectively using 1 mole of the former and 2 moles of KPF\(_6\) aqueous methanolic solution. Found: C, 52.44; H, 3.81; N, 9.22; Calc. C\(_{30}\)H\(_{32}\)N\(_6\)O\(_6\)Zn (pfad): C, 48.60; H, 4.25; N, 11.50%. IR (KBr, cm\(^{-1}\)): 1590 (\(\nu_{\text{CN}}\)), 1085, 622 (\(\nu_{\text{CO}}\)). UV-Vis (\(\lambda_{\text{max}}\) nm): 328.
10.54; Calc. C30H32N6F12P2Zn (1b): C, 52.30; H, 3.78; N, 10.41%. IR (KBr, cm⁻¹): 1590 (V₁), 540 (V₂). UV-Vis (λmax nm): 328. Found: C, 34.32; H, 4.16; N, 10.92; Calc. C30H32N6F12P2Zn (2b): C, 34.13; H, 3.98; N, 10.34%. IR (KBr, cm⁻¹): 1590 (V₁), 840, 542 (V₂). UV-Vis (λmax nm): 329. Found: C, 43.73; H, 3.87; N, 10.14; Calc. C30H32N6F12P2Zn (3b): C, 43.50; H, 3.89; N, 10.17%. IR (KBr, cm⁻¹): 1592 (V₁), 840, 540 (V₂). UV-Vis (λmax nm): 330.

X-ray diffraction study

Single crystals [size: 0.20 × 0.20 × 0.40 mm³] of 3a were obtained by slow evaporation of MeOH solution of the reaction mixture. Colourless crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Diffraction data 296(2) K were collected on a Bruker SMART CCD diffractometer using MoKα radiation (λ = 0.71073 Å). Systematic absence led to the identification of space groups Pccn for 3a. Of the 7895 unique reflections, 3295 with I > 2σ(I) were used for structure solutions. The structure was solved by direct methods, and the structure solution and refinement were based on |F|². All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions when possible and given isotropic values 1.2 times that of the atom to which they are bonded. At convergence, the final residuals were R1 = 0.0676; wR2 = 0.1657 with I > 2σ(I), goodness-of-fit = 1.030. The final differences Fourier map showed the maximum and minimum peak heights at 0.912 and -0.331 eÅ⁻³ with no chemical significance. All calculations were carried out using SHELXL-97, ORTEP-3. The crystal data and data collection parameters are listed in Table 1.

Results and Discussion

The ligands (pfad/pmad/pbad) were synthesised by refluxing triethylenetetramine and pyridine-2-carboxaldehyde/2-acetylpyridine/2-benzoylpyridine in 1:2 mole ratio in boiling alcohol. Colourless powders of the hexacoordinated mononuclear complexes [Zn(L)(Y)₂][L = N-(1-pyridin-2-ylformylidene)-N'-[2-[(1-pyridin-2-ylformylidene)amino]ethyl]amino]ethyl]ethylene-1,2-diamine (pfad), Y = ClO₄ (1a), Y = PF₆ (1b); L = N-(1-pyridin-2-ylmethylidene)-N'-[2-[(1-pyridin-2-ylmethylidene)amino]ethyl]amino]ethyl]ethylene-1,2-diamine (pmad), Y = ClO₄ (2a), Y = PF₆ (2b); L = N-(1-pyridin-2-ylbenzylidene)-N'-[2-[(1-pyridin-2-ylbenzylidene)amino]ethyl]amino]ethyl]ethane-1,2-diamine (pbad), Y = ClO₄ (3a), Y = PF₆ (3b)] resulted in good yield through single-pot reaction of a 1:1 molar ratio of the metal perchlorate and organic blocker for 1a-3a in methanolic solution or a 1:1:2 molar ratio of metal nitrate, L and KPF₆ from methanolic aqueous solutions for 1b-3b. The latter were also isolated by metathesis of 1a, 2a and 3a respectively with potassium hexafluorophosphate. The synthetic procedures are summarised in Eqs (1-3):

\[
\text{MeOH} + \text{Zn}^{2+} + \text{ClO}_4^- + \text{H}_2\text{O} \rightarrow [\text{Zn}^{2+}\text{ClO}_4^-]^{2-} \quad \text{(1)}
\]

\[
\text{MeOH} + \text{Zn}^{2+} + \text{ClO}_4^- + 2\text{PF}_6^- + \text{H}_2\text{O} \rightarrow [\text{Zn}^{2+}\text{ClO}_4^-]^{2-} + 2\text{PF}_6^- \quad \text{(2)}
\]

\[
\text{MeOH} + \text{Zn}^{2+} + \text{ClO}_4^- + \text{PF}_6^- \rightarrow [\text{Zn}^{2+}\text{ClO}_4^-]^{2-} \quad \text{(3)}
\]

The complexes were characterized using microanalytical, spectroscopic and physicochemical results. The air-stable moisture-insensitive complexes...
are soluble in common solvents like methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulfoxide. In methanol solution they behave\(^1\) 1:2 electrolytes as indicated by their conductivity values. The presence of ionic perchlorate bands at ~1090 and ~620 cm\(^{-1}\) for 1a-3a and ionic hexafluorophosphate bands ~840 and ~540 cm\(^{-1}\) for 1b-3b are noticed\(^2\) reflecting counter anionic view with no metal coordinate. The \(v(C=\text{N})\) stretching vibrations of the Schiff base are seen at 1629 and 1589 cm\(^{-1}\). All other characteristic L vibrations are seen in 1600-600 cm\(^{-1}\). The spectra in nujol (e.g. 3a: \(\lambda_c, 328\) nm) and in MeOH (e.g. 3a: \(\lambda_c, 328\) nm) solutions are akin reflecting similar gross structure and electronic structure in solid state and in solution\(^2,\).  

X-ray crystal structure of \([\text{Zn}(\text{phad})(\text{ClO}_4)](3a)\)

In order to define the coordination sphere conspicuously, single-crystal X-ray diffraction study was made. An ORTEP diagram with atom numbering scheme of the mononuclear unit in 3a is shown Fig. 1. Selected bond distances and bond angles relevant to the Zn coordination sphere are given in Table 2. The crystal lattice of 3a consists of \([\text{Zn}(\text{phad})]^\text{2+}\) cations and \(\text{ClO}_4^{-}\) anions. The coordination polyhedron around zinc is best described as distorted octahedron with ZnN\(_6\) chromophore. The distortion from ideal octahedral geometry is due to the asymmetric nature of the bound hexadentate Schiff base and the deviations of the refine angles formed at the metal center (Table 2). The metal ion is ligated by two pyridine nitrogens (N1, N1\('\)), two imine nitrogens (N2, N2\('\)) and two amine nitrogens (N3, N3\('\)) in \textit{cis-trans-cis} orientation. Two amine nitrogens (N3, N3\('\)) and two pyridine nitrogens (N1, N1\('\)) occupy the equatorial positions of the distorted octahedron, whereas the axial positions are occupied by the two imine nitrogens (N2, N2\('\)). The equatorial Zn-N distances lie within a close range [2.187(4)-2.178(4) Å], but there is a significant variation in the bond angles [100.41(13)-80.66(13)\(^\circ\)] in that plane. The axial Zn-N distances [2.162(3) Å] are found to be smaller than the equatorial ones. Here, tetragonal compression of the octahedral geometry may be raised from the \(\pi\)-acceptance of imine nitrogen atoms. The axial bond angle N2-Zn-N4 [169.76(14)\(^\circ\)]
deviates from the ideal 180°. The sum (373.80°) of the equatorial angles N1-Zn1-N3 (100.41°), N1-Zn1-N1' (92.31°), N1'-Zn1-N3' (100.41°) and N3-Zn1-N3' (80.66°) are very close to 360.00°. So, the atoms N1, N1', N3', N3 and Zn1 are almost in a same plane.

The mononuclear units pack alongside each other through face-to-face π-interactions to give a 2D supramolecular sheet (Fig. 2) in ab plane. The terminal phenyl rings [Ring(7)-Ring(7) and Ring(14)-Ring(14)]; Cg-Cg separation: 4.449(3) and 5.042(4) Å, vertical displacement of Cg: 3.801 and 3.448 Å; dihedral angle 0.03 and 0.0°; symmetry code: 'x,-y,1-z and -x,1-y,-1+z; Cg(7) = C(7)-C(8)-C(9)-C(10)-C(11)-C(12) and Cg(14) = C(22)-C(23)-C(24)-C(25)-C(26)-C(27)] are responsible for this to produce such novel architecture [2.5b].

Luminescence properties

The spectroscopic data in methanol solutions and glasses are listed in Table 3. The complexes show emission spectra at around 395 nm at 298 K. These are assignable to intraligand \((\pi-\pi^*)\) fluorescence. The lifetimes are in the range 2.40-2.46 ns. The reasonably higher lifetime may be due to the presence of stronger π-π interactions (Fig. 2) as is revealed in crystalline state in 3a stabilizing the excimeric structure. In glassy solutions (77 K) a red shift is observable at ~470 nm which is presumably due to \((\pi-\pi^*)\) phosphorescence.

Conclusion

This work reports the synthesis, structure and photophysical behaviour of a set of zinc(II) complexes with hexacoordination environment of the metal centre. The tetraordinated/pentaordinated zinc(II) is well recognised, but hexacoordination of the metal ion is scarce. Under enforced condition the neutral N-donor hexacoordinated Schiff base directs such coordination of this 3d member of Group 12.

### Table 3—Photophysical data

<table>
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<th>Sample</th>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
<th>Fluorescence (ns)</th>
<th>Phosphorescence (ns)</th>
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<td>470</td>
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<td>395</td>
<td>470</td>
<td>2.42</td>
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</table>

*In MeOH at room temperature (298 K)  
*In MeOH at 77 K.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre No. 258488 for 3a. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgement

Financial support from the Department of Science and Technology (DST), Council of Scientific and Industrial Research (CSIR), New Delhi, India is gratefully acknowledged.

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