October 2006 Volume 1 Issue 3

Trade Science Inc.

Inorganic CHEMISTRY
An Indian Journal

Full Paper

ICAIJ, 1(3), 2006 [39-46]

Study On The Coordination Behaviour Of Bidentate Schiff Bases Towards Zinc(II) Pseudohalides: X-Ray Structure Of $[Zn(pbba)_2(N_3)_2]$(pbba=N-((pyridin-2-yl)benzylidene)benzylamine)

Barindra Kumar Ghosh
Department of Chemistry,
The University of Burdwan,
Burdwan 713104, INDIA
Tel.: +91-342-2553913; Fax: +91-342-2530452
E-mail: barin_1@yahoo.co.uk

Habibar Chowdhury[1], Jaya Banerjee[1], Rajarshi Ghosh[1], Sk Hafijur Rahaman[1], Hoong-Kun Fun[2]
[1]Department of Chemistry, The University of Burdwan,
Burdwan 713104, INDIA
[2]X-ray Crystallography Unit, School of Physics,Universiti Sains Malaysia,
11800 USM, Penang (MALAYSIA)

Received: 30th April, 2006
Accepted: 29th May, 2006

Web Publication Date : 14th November, 2006

ABSTRACT

Two new Schiff bases, N-((pyridin-2-yl)formylidene)benzylamine (pfba) and N-((pyridin-2-yl)benzylidene)benzylamine (pbba) have been prepared. Two series of hexacoordinated zinc(II)pseudohalide complexes of type $[Zn(L)_2(X)_2]$ (L: pfba; $X=N_3^-$, **(1a)**; $X=NCS^-$, **(1b)**; $X=NCO^-$, **(1c)** and L: pbba; $X=N_3^-$, **(2a)**; $X=NCS^-$, **(2b)**; $X=NCO^-$, **(2c)** have been developed using these two Schiff bases. Elemental, spectral and other physicochemical results characterise the complexes. Structure of $[Zn(pbba)_2(N_3)_2]$ **(2a)** is solved by X-ray diffraction measurements. **(2a)** crystallizes in the orthorhombic space group P21/c with a=16.6671(2) Å, b=44.4722(8) Å, c=8.9687(1) Å, $\alpha=90.00°$, $\beta=90.00°$, Z=8. Structural analyses reveal that each zinc(II) in **(2a)**, has an distorted octahedral geometry with ZnN_6 chromophore coordinated through four N atoms of two bidentate pbba units and two N atoms of terminal azide in1 mutual *cis* orientation. The mononuclear units are engaged intermolecular C-H…N hydrogen bonding resulting 1D molecular chain. All the complexes display intraligand[1](π-π^*) fluorescence and intraligand[3](π-π^*) phosphorescence in glassy solutions (MeOH at 77 K).

KEYWORDS

Zinc(II);
Pseudohalides;
Bidentate schiff base;
Luminescence.

INTRODUCTION

Self-assembly[1] of organic and inorganic molecules in the solid state extends the range of new solid with desirable physical and chemical properties. The range and variety of self-assembled inorganic structure that can be constructed relies on suitable metal-ligand interactions and various types of polymeric structures include 1D, 2D and 3D networks. Synthesis of mono- and polynuclear coordination compounds of group 12 metals ions[2-5] continues unabated for the preparation of functional materials[6-8]. Exploiting the veracity of coordination geometry around metal ion templates different networks can be accessed using varied organic blockers. We are also interested in this field[9,10] through variation of metal ion coordination environments using 3d/4d metal ion templates, organic ligands and suitable bridging units. Zinc(II) is well suited[2] to this study as its d[10] configuration permits a wide range of symmetries and coordination numbers and has significant role in bioinorganic chemistry. Schiff bases[11] are useful blockers because of their preparational accessibilities, structural varieties and varied denticities. Pseudohalides[12-14] are efficient intermediaries, which forms various networks with different transition and non-transition metal ions in combination with organic spacers of varied denticity. In an effort, we have been exploring the coordination behaviour of two different bidentate Schiff base ligands towards zinc(II) in combination with pseudohalides. Successfully we have isolated and studied six hexacoordinated mononuclear complex of the type $[Zn(L)_2(X)_2]$ (L: N-((pyridin-2-yl) formylidene)benzylamine (pfba); $X=N_3^-$, **(1a)**; $X=NCS^-$, **(1b)**; $X=NCO^-$, **(1c)** and L: N-((pyridin-2-yl) benzylidene) benzylamine (pbba); $X=N_3^-$, **(2a)**; $X=NCS^-$, **(2b)**; $X=NCO^-$, **(2c)**) using a one-pot reaction. X-ray structure determination of $[Zn(pbba)_2(N_3)_2]$ **(2a)** reveal that the metal centre is in a distorted octahedral environment and 1D molecular chain formed by C-H…N hydrogen bonding in **(2a)**. The details are described here.

EXPERIMENTAL

Materials and methods

High purity 2-benzoylpyridine (Lancaster, UK), pyridine-2-carboxaldehyde (Lancaster, UK), benzylamine (Lancester, UK), sodium azide (Aldrich, USA), ammonium thiocyanate (Fluka Germany), and sodium cyanate (Aldrich, USA) were purchased from respective concerns and used as received. Zinc(II) perchlorate hexahydrate was 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 AR grade and were used as received.

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

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000-300 cm^{-1}) were recorded using a Perkin Elmer FTIR model RX1 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 Photpmultiplier tube were respectively used as the excitation source and the fluorescence detector.

Preparation of schiff bases

The Schiff bases pfba and pbba were prepared[9a,15] following using reported method with a little modification.

N-((pyridin-2-yl)formylidene)benzylamine (pfba)

Pyridine-2-carboxaldehyde (0.107 g, 1 mmol) was refluxed with benzylamine (0.107 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, 0.157 g (80%). Found: C, 79.51; H, 6.20; N, 14.25; Anal. Calc. for $C_{13}H_{12}N_2$ (pfba): C, 79.56; H, 6.16; N, 14.27%. IR (KBr, cm^{-1}): 1590 ($\nu_{C=N}$). UV-Vis ($\lambda_{max,}$ MeCN): 250, 390 nm.

N-((pyridin-2-yl)benzylidene)benzylamine (pbba)

2-Benzoylpyridine (0.183 g, 1 mmol) was refluxed with benzylamine (0.107 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, 0.218 g (80%). Found: C, 83.77; H, 5.90; N, 10.32; Anal. Calc. for $C_{19}H_{16}N_2$ (pbba): C, 83.80; H, 5.94; N, 10.29%. IR (KBr, cm^{-1}): 1590 ($\nu_{C=N}$). UV-Vis ($\lambda_{max,}$ MeCN): 255, 393 nm.

Preparation of the complexes

All the hexacoordinated zinc(II) complexes were prepared from perchlorate salt of zinc(II) using 1:2:2 mole ratio of the metal, pfba/pbba and azide/thiocyanate/cyanate. Syntheses are given below.

Synthesis of $[Zn(pfba)_2(N_3)_2]$ (1a) and $[Zn(pbba)_2(N_3)_2]$ (2a)

An acetonitrile solution (5 ml) of pfba (0.20 g, 2 mmol) was added dropwise to a solution of $Zn(ClO_4)_2\cdot 6H_2O$ (0.19 g, 1 mmol) in the same solvent (10 ml) followed by aqueous solution (5 ml) of sodium azide (0.076 g, 2 mmol) was mixed slowly. The light yellow solution was filtered and the supernatant liquid was kept in air for slow evaporation. After a few days, the fine yellow coloured compound of **(1a)** that separated out was washed with toluene and dried *in vacuo* over silica gel indicator. **(2a)** was prepared by the same procedure using pbba [0.27 g, 2 mmol] in place of pfba. Yield, 0.19 g (70%). Found: C, 57.65; H, 4.50; N, 25.78; Anal.Calc. for $C_{26}H_{24}N_{10}Zn$ **(1a)**: C, 57.62; H, 4.46; N, 25.85%. IR (KBr, cm^{-1}): 1635, 1595 ($\nu_{C=N}$), 2058, 2042 (ν_{N3}). UV-Vis ($\lambda_{max,}$ nm): 328. Yield, 0.28 g (80%). Found: C, 65.79; H, 4.61; N, 20.20; Anal.Calc. for $C_{38}H_{32}N_{10}S_4Zn$ **(2a)**: C, 65.75; H, 4.65; N, 20.18%. IR (KBr, cm^{-1}): 1595 ($\nu_{C=N}$), 2060, 2038 (ν_{N3}). UV-Vis ($\lambda_{max,}$ nm): 330.

$[Zn(pjba)_2(NCS)_2]$ (1b) and $[Zn(pbba)_2 (NCS)_2]$ (2b)

To zinc(II) perchlorate hexahydrate (0.19 g, 1 mmol) in acetonitrile solution (10 ml), faint yellow pfba (0.20 g, 2 mmol) in same solvent (5 ml) and NH_4NCS (0.076 g, 2 mmol) in water (5 ml) were added dropwise simultaneously. The final light yellow solution was filtered and left for slow evaporation in air. After a few days fine yellow compound of **(1b)**, which was washed with toluene and dried *in vacuo* over silica gel indicator. Same route was follwed to prepare **(2b)** only using using pbba [0.27 g, 2 mmol] in place of pfba. Yield, 0.19 g (65%). Found: C, 58.55; H, 4.18; N, 14.67; Anal.Calc. for $C_{28}H_{24}N_6S_2Zn$ **(1b)**: C, 58.57; H, 4.21; N, 14.65%. IR (KBr, cm^{-1}): 1595 ($\nu_{C=N}$), 2052, 2072 (ν_{NCS}). UV-Vis ($\lambda_{max,}$ nm): 327. Yield, 0.22 g (60 %). Found: C, 66.20; H,4.41; N, 11.60; Anal.Calc. for $C_{40}H_{32}N_6S_2Zn$ **(2b)**: C, 66.15; H, 4.44; N, 11.57%. IR (KBr, cm^{-1}): 1595 ($\nu_{C=N}$), 2050, 2071 (ν_{NCS}). UV-Vis ($\lambda_{max,}$ nm): 331.

$[Zn(pjba)_2(NCO)_2]$ (1c) and $[Zn(pbba)_2 (NCO)_2]$ (2c)

$Zn(ClO_4)_2.6H_2O$ (0.19 g, 1 mmol) was dissolved in MeCN solution (10 ml). A yellow pfba (0.20 g, 2 mmol) in same solvent (5 ml) was added dropwise followed by addition of sodium cyanate (0.065 g, 2 mmol) in water (5 ml) with constant stirring. The final yellow solution was filtered and left for slow evaporation in air. After a few days yellow coloured compound of **(1c)** was separated out, which was washed with toluene and dried *in vacuo* over silica gel indicator. Same route was follwed to prepare **(2c)** only using pbba in place of pfba. Yield, 0.16 g (60%). Found: C, 62.03; H, 4.46; N, 15.48; Anal. Calc. for $C_{28}H_{24}N_6O_2Zn$ **(1c)**: C, 62.06; H, 4.46; N, 15.51%. IR (KBr, cm^{-1}): 1595 ($\nu_{C=N}$), 2250, 1320 (ν_{NCO}). UV-Vis ($\lambda_{max,}$ nm): 329. Yield, 0.21 g (65 %). Found: C, 69.19; H, 4.67; N, 12.09; Anal.Calc. for $C_{40}H_{32}N_6O_2Zn$

(2c): C, 69.22; H, 4.65; N, 12.11%. IR (KBr, cm^{-1}): 1595 ($\nu_{C=N}$), 2252, 1322 (ν_{NCO}) . UV-Vis ($\lambda_{max,}$ nm): 332.

X-ray diffraction study

A single crystal of **(2a)** was obtained by slow evaporation of MeCN-H_2O solution of the reaction mixture. Yellow coloured crystals suitable for X-ray crystallographic analysis were selected following examination under a microscope. Diffraction data at 293(2) K for **(2a)** was collected on a Siemens SMART CCD diffractometer using MoKα radiation (λ = 0.71073 Å). Systematic absence led to the identification of space groups P21/c for **(2a)**. Of the 8311 unique reflections for the respective complex, 5464 with I>2σ(I) was used for structure solution. The structure was solved by direct methods, and the structure solution and refinement were based on $|F|^2$ using SHELXL-97[16]. All non-hydrogen atoms were refined with anisotropic displacement parameters whereas hydrogen atoms were placed in calculated positions when possible and given isotropic U values 1.2 times that of the atom to which they are bonded. At convergence the final residuals were R1=0.0663; wR2= 0.838 with I>2σ(I), goodness-of-fit=0.968 for the complex. The final differences Fourier map showed the maximum and minimum peak heights at -0.20 and 0.22 eÅ^{-3}. All calculations were carried out using PLATON[17], ORTEP-32[18]. The crystal data and data collection parameters are listed in TABLE 1.

TABLE 1: Summarised crystallographic data for [Zn(pbba)$_2$(N$_3$)$_2$](2a)

Emperical formula		$C_{40}H_{32}N_{10}Zn$
Formula weight		694.13
Temperature (K)		293(2)
Wavelength (Å)		0.71073
Crystal system		Orthorhombic
Space group		P21/c
D$_{calc}$ (Mgm^{-3})		1.387
Volume (Å^3)		6647.80(16)
Z		8
Unit cell dimensions	a (Å)	16.6671(2)
	b (Å)	44.4722(8)
	c (Å)	8.9687(1)
α(°), β(°), γ(°)		90.00, 90.00, 90.00
F(000)		2880
Nref, Npar		8311, 222
μ(MoKα) (mm^{-1})		0.784
θ range for data collection (°)		1.8 to 38.0
Reflections collected		8311
Independent reflections		5464[R(int) = 0.0251]
Max. and min. transmission		38.00 and 1.83
Refinement method		Full-matrix least-squares on F^2
Unique Data/restraints/ parameters		5464 / 1 / 222
Goodness-of-fit on F^2		0.968
Final R indices [I>2σ(I)]		R1=0.0663, wR2=0.838
Largest diff. Peak and hole (eÅ^{-3})		0.22 and –0.20

RESULTS AND DISCUSSION

Synthesis and formulation

The Schiff bases (pfba and pbba) were synthesized by refluxing benzylamine with pyridine-2-carboxaldehyde and 2-benzoyl pyridine, respectively in 1:1 mole ratio in boiling alcohol. The hexacoordinated mononuclear yellow coloured zinc(II) complexes of the type [Zn(L)$_2$(X)$_2$] (L: pfba; X=N_3^-, **(1a)**; X=NCS$^-$, **(1b)**; X=NCO$^-$, **(1c)** and L: pbba; X=N_3^-, **(2a)**; X=NCS$^-$, **(2b)**; X=NCO$^-$, **(3c)**) were resulted in good yield through reaction of a 1:2:2 molar ratio of the metal perchlorate, organic blockers (L) and pseudohalides (X) – a reactant ratio expected to form a bibridged dinuclear species of the composition [(L)$_2$Zn^{II}(X)$_2$Zn^{II}(L)$_2$](ClO$_4$)$_2$. However, microanalyses show mononuclear unit and in IR spectra, absence of perchlorate band was noticed. The process is summerised below in the equations (1-3).

The complexes were characterized using mi-

$$Zn(ClO_4)_2{\cdot}6H_2O + 2\ pfba/pbba + 2\ NaN_3 \xrightarrow[298\ K]{MeOH} [Zn(pfba/pbba)_2(N_3)_2]\ (1a/1b) + 2\ NaClO_4 + 6\ H_2O \qquad (1)$$

$$Zn(ClO_4)_2{\cdot}6H_2O + 2\ pfba/pbba + 2\ NH_4NCS \xrightarrow[298\ K]{MeOH} [Zn(pfba/pbba)_2(NCS)_2]\ (2a/2b) + 2\ NH_4ClO_4 + 6\ H_2O \qquad (2)$$

$$Zn(ClO_4)_2{\cdot}6H_2O + 2\ pfba/pbba + 2\ NaNCO \xrightarrow[298\ K]{MeOH} [Zn(pfba/pbba)_2(NCO)_2]\ (3a/3b) + 2\ NaClO_4 + 6\ H_2O \qquad (3)$$

croanalytical, spectroscopic and physicochemical results. The air-stable moisture-insensitive complexes are soluble in common solvents like, methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulfoxide but are insoluble in water. In MeCN solution, they behave as non-electrolytes reflecting from Λ_M value (~5 $\Omega^{-1}cm^2mol^{-1}$). All the complexes behave as diamagnet and electro-inactive as expected for $3d^{10}$ configuration of zinc(II). The light yellow solutions of complexes in MeOH exhibit absorption ~330 nm [**1a**: λ, 328; **1b**: λ, 327; **1c**: λ, 326; **2a**: λ, 330; **2b**: λ, 331; **2c**: λ, 332 nm]. Reflectance spectra [**1a**: λ, 329; **1b**: λ, 328; **1c**: λ, 327; **2a**: λ, 332; **2b**: λ, 334; **2c**: λ, 336 nm] in nujol and electronic spectra in MeOH solutions are akin reflecting similar gross structure and electronic structure in solid state and in solution[19].

Spectral studies

In IR spectra, the point of interest for **(1a)** and **(2a)** is the band due to azide in the complexes. The spectra exhibit a very strong and sharp absoption band at 2040-2060 cm^{-1} due to assymmetric stretching vibration[20] of azide. The well resolved peaks attributed to the ν(NCS) are observed for **(1b)** and **(2b)** at ~2070, 2050 cm^{-1}, where the most striking observation is a sharp single intense band of ν(CN) at ~2070 cm^{-1} due to N-coordinated terminal thiocyanate with a weak band at ~2050 cm^{-1} related to ν_{asym}(NCS). IR spectra show characteristic asymmetric and symmetric cyanate stretching vibration at 2250 and 1320 cm^{-1} respectively for **(1c)** and **(2c)**. These are substantially higher than free ion value and are consistent with N-bonding rather O-bonding. The bands found at around 1590-1630 cm^{-1} due to C=N stretching frequency of the Schiff base and weak bands in the range 2980-2900 cm^{-1} are assignable to the aliphetic C-H stretching frequency.

X-ray crystal structure of $[Zn(pbba)_2(N_3)_2]$ (2a)

In order to define the coordination sphere, single-crystal X-ray diffraction study was made. An ORTEP diagram with atom numbering scheme of the mononuclear unit in **(2a)** is shown figure 1. Selected bond distances and bond angles relevant to the Zn coordination sphere are given in TABLE 2. The zinc(II) center adopts a distorted octahedral geometry with ZnN_6 chromophore ligated by two bidentate pbba units and two terminal azides in *cis* orientation. The coordination includes two pyridine N atoms [N(1), N(1_a)] and two imine N atoms [N(2), N(2_a)] of two different blockers along with two terminal azido N atoms [N(3), N(3_a)]. N(1), N(1_a), N(2) and N(3_a) atoms define the equatorial plane around zinc(II) center, whereas the axial sites are occupied by N(3) and N(2_a). The distortion from ideal octahedral geometry is due to the asymmetric nature of the bound Schiff base and the deviations of the refine angles (90°/180°) formed at the metal center (TABLE 2). The degrees of distorsion from the ideal

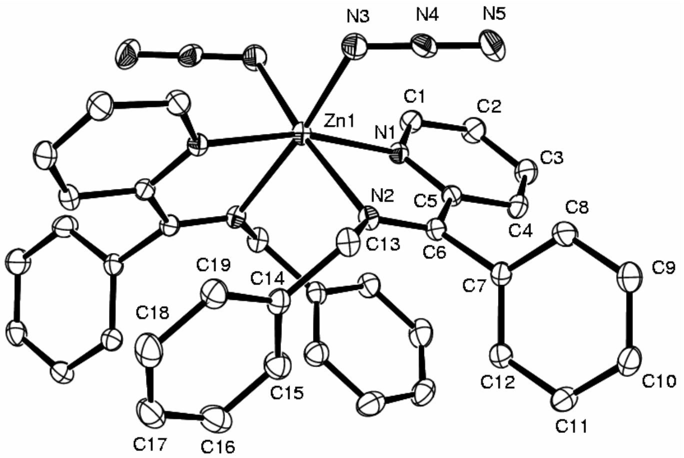

Figure 1: ORTEP representation of $[Zn(pbba)_2(N_3)_2]$ (2a) with atom numbering scheme and 20% probability ellipsoids for all non-hydrogen atoms

TABLE 2: Selected bond distances (Å) and angles (°) for (2a)

Bond distances			
Zn(1)-N(1)	2.1206(9)	Zn(1)-N(2_a)	2.1445(11)
Zn(1)-N(2)	2.2445(11)	Zn(1)-N(3_a)	2.1214(14)
Zn(1)-N(3)	2.1214(14)	N(3)-N(4)	1.1860(19)
Zn(1)-N(1_a)	2.1206(9)	N(4)-N(5)	1.162(2)
Bond angles			
N(1)-Zn(1)-N(2)	75.39(4)	N(1_a)-Zn(1)-N(3)	97.14(5)
N(1)-Zn(1)-N(3)	93.03(5)	N(2_a)-Zn(1)-N(3)	172.45(4)
N(1)-Zn(1)-N(1_a)	165.02(4)	N(3)-Zn(1)-N(3_a)	94.39(6)
N(1)-Zn(1)-N(2_a)	94.51(4)	N(1_a)-Zn(1)-N(2_a)	75.39(4)
N(1)-Zn(1)-N(3_a)	97.14(5)	N(1_a)-Zn(1)-N(3_a)	93.03(5)
N(2)-Zn(1)-N(3)	85.04(5)	N(2_a)-Zn(1)-N(3_a)	85.04(5)
N(1_a)-Zn(1)-N(2)	94.51(4)	Zn(1)-N(3)-N(4)	117.68(11)
N(2)-Zn(1)-N(2_a)	96.51(4)	N(3)-N(4)-N(5)	179.00(17)
N(2)-Zn(1)-N(3_a)	172.45(4)		

[a]Symmetry code: -x, -y, z

octahedral (90°) geometry are reflected in the *cisoid* [75.39(4)-97.14(5)°] and the *transoid* [165.02(4)-172.45(4)°] angles. The axial bond angle of N(3)-Zn(1)-N(2_a) is 172.45(4)°, which deviates from ideal 180°. The sum (360.07°) of the equatorial angles N(1)-Zn(1)-N(2) [75.39(4)°], N(2)-Zn(1)-N(1_a) [94.51(4)°], N(1_a)-Zn(1)-N(3_a) [93.03(5)°] and N(3_a)-Zn(1)-N(1) [97.14(5)°] are very close to 360.00°. So the atoms N(1), N(2), N(1_a), N(3_a) and Zn(1) are almost in a same plane. All the six Zn-N bond lengths lie within a close range [2.1206(9)-2.445(11) Å]. Here Zn-N distances like Zn(1)-N(1) and Zn(1)-N(1_a) are smaller compare to other Zn-N distances due to π-acceptance of imine nitrogen atoms. The azido ligands are almost linear with N-N-N angle of 179.00(17)°, and mutually in *cis* alignment having N(3)-Zn(1)-N(3_a) angles of 94.39(6)°. N(3)-N(4) distances [1.1860(19) Å] are longer than the N(4)-N(5) [1.162(2) Å] reflecting coordination of azide through N(3) atom.

In the crystal lattice, the mononuclear units in **(2a)** are packed with weak C-H…N hydrogen bonding forming 1D chain structure view down along crystallographic *c* axis (Figure 2). The terminal free azide nitrogen (N5) and hydrogen (H11) of aromatic benzene ring of pbba Schiff base are responsible for the formation of such C-H…N hydrogen bonding. The C-H hydrogens of benzene ring are potential proton donor and nitrogens are acceptors [C11-H11…N5 (b): C11-H11: 0.9300 Å; H11…N5: 2.5500 Å;

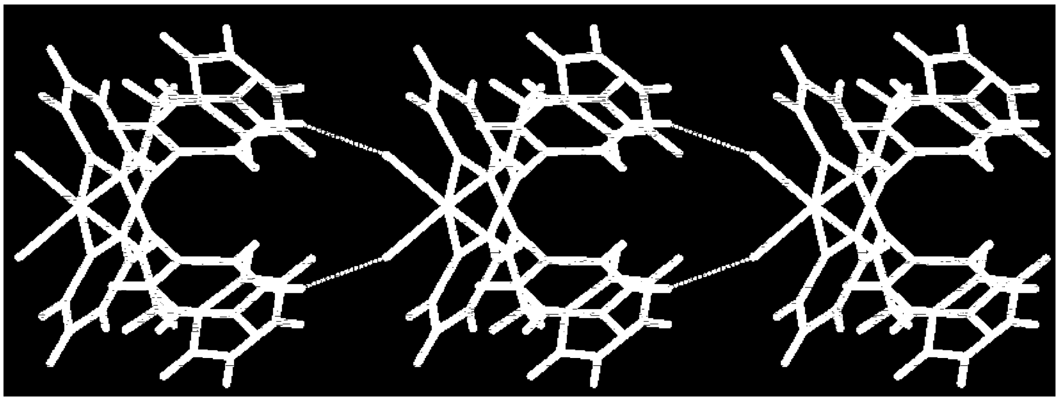

Figure 2: Packing diagram of 1D supramolecular chain formed by C-H…N hydrogen bonding in (2a)

TABLE 3: Hydrogen bond distances (Å) and angles (°) for (2a)

D-H…A	D-H	H…A	D…A	D-H…A
C(11)-H(11)…N(5)(b)	0.9300	2.8600	3.616(3)	139.00

[b]Symmetry code: x, y,1+z

C11…N5: 3.349(2) Å; <C11-H11-N5: 144.00°, (b) symmetry code: x, y, 1+z] to generate 1D chain (TABLE 3).

Luminescence properties

The spectroscopic data in methanol solutions and glasses are listed in TABLE 4. The complexes show emission spectra at around 395 nm at 298 K. These are assignable to intraligand ${}^1(\pi-\pi^*)$ fluorescence[21]. The lifetimes are in the range 2.42-2.46 ns. In glassy solutions (77 K) a red shift is observable at ~470 nm which is presumably due to ${}^3(\pi-\pi^*)$ phosphorescence. A representative diagram for **(2a)** is shown in figure 3.

TABLE 4: Photophysical data

Sample	Absorption (λ/nm)	Emission (λ/nm)		Lifetime (ns)
		Fluorescence[c]	Phosphorescence[d]	
1a	328	395	470	2.44
1b	327	394	470	2.46
1c	329	396	470	2.42
2a	330	395	470	2.44
2b	331	394	470	2.42
2c	332	396	470	2.42

[c]In MeOH at room temperature (298 K); [d]In MeOH at 77 K

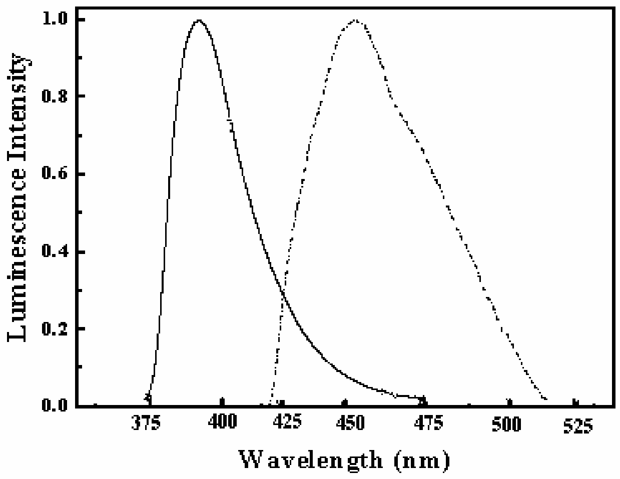

Figure 3: Emission spectra of 2a: Fluorescence in MeOH solution at 298 K (——), phosphorescence in MeOH glassy solution (77 K) (·········)

CONCLUSION

This work reports the synthesis, structure and photophysical behaviour of Zn(II) complexes with hexacoordination environment of the metal centre. The tetracoordinated/pentacoordinated zinc(II) is well recognised[22] but hexacoordination of the metal ion is scarce.

SUPPLEMENTARY INFORMATION

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre No. 286956 for **(2a)**. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

REFERENCES

[1] a) Special issue on Focus on Self-Assembly, Acc. Chem.Res., **32(4)**, **(1999)**.
b) G.F.Swiegers, T.J.Malefestse; Chem.Rev., **100**, 3483 **(2000)**.
c) B.J.Holliday, C.A.Mirkin; Angew.Chem.Int.Ed. Engl., **40**, 2022 **(2001)**.

[2] a) D.Bose, S.H.Rahaman, G.Mostafa, B.R.D.Walsh, M.J.Zaworotko, B.K.Ghosh; Polyhedron, **23**, 545 **(2004)**. and refs therein.
b) J.Banerjee, D.Bose, Sk.H.Rahaman, R.D.Bailey Walsh, M.Zaworotko, B.K.Ghosh; Indian J. Chem., **43A**, 1119 **(2004)**.
c) Sk.H.Rahaman, R.Ghosh, T.H.Lu, B.K.Ghosh; Indian J.Chem, **44A**, 2427 **(2005)**.

[3] a) L.Pan, N.W.Zheng, N.W.Wu, X.Y.Huang; J.Coord. Chem., **47**, 551 **(1999)**.
b) J.K.Nag, P.Santra, C.Sinha, F.L.Liao, T.H.Lu; Polyhedron, **20**, 1253 **(2000)**.
c) B.Chand, U.Ray, P.K.Santra, G.Mostafa, T.H.Lu, C.Sinha; Polyhedron, **23**, 1205 **(2003)**.

[4] a) Y.Diskin-Posner, G.K.Patra, I.Goldberg; Chem

Commun., 1420 **(2002)**.
  b) D.Bose, J.Banerjee, S.H.Rahaman, G.Mostafa, R.D.Bailey Walsh, M.J.Zaworotko, B.K.Ghosh; Polyhedron, **23**, 1045 **(2004)**. and refs therein.
  c) S.H.Rahaman, R.Ghosh, G.Mostafa, B.K.Ghosh; Inorg.Chem.Commun., **8**, 700 **(2005)**.

[5] a) B.Chand, U.Ray, P.K.Santra, G.Mostafa, T.H.Lu, C.Sinha; Polyhedron, **23**, 1205 **(2003)**.
  b) H.Chowdhury, R.Ghosh, S.H.Rahaman, G.M.Rosair, B.K.Ghosh; Indian J.Chem., **44A**, 687 **(2005)**.

[6] a) 'Catalysis from A to Z: A Concise Encyclopedia', Edited by B.Cornils, W.A.Herrmann, R.Schlogl, John Wiley & Sons, New York, **(2000)**.
  b) 'Handbook of Liquid Crystals', Edited by D. Demus, J.W.Goodby, G.W.Gray, H.W.Spiess, V.Vill, Wiley-VCH, Weinheim, **(1998)**.

[7] a) J.R.Farraro, J.M.Williams; 'Introduction to Synthetic Electrical Conductors', Academic Press, New York, **(1987)**.
  b) S.R.Marder; 'Metal Containing Materials for Nonlinear Optics in Inorganic Materials', Edited by D.W.Bruce, D.O'Hare, Wiley, Chichester, **(1996)**.

[8] a) O.Kahn; 'Molecular Magnetism', VCH, New York, **(1993)**.
  b) 'Magnetism: Molecules to Materials III', Edited by J.S.Miller, M.Drillon, Wiley-VCH, Weinheim, **(2002)**.
  c) Special issue on Chemical Sensors, Chem.Rev., **100**, 7 **(2000)**.

[9] a) T.K.Karmakar, S.K.Chandra, J.Ribas, G.Mostafa, T.H.Lu, B.K.Ghosh; Chem.Commun., 2364 **(2002)**.
  b) S.H.Rahaman, D.Bose, H.Chowdhury, G.Mostafa, H.K.Fun, B.K.Ghosh; Polyhedron, **24**, 1837 **(2005)**.

[10] a) S.H.Rahaman, R.Ghosh, D.Bose, H.K.Fun, B.K. Ghosh; Indian J.Chem., **43A**, 1901 **(2004)**.
  b) S.H.Rahaman, D.Bose, R.Ghosh, G.Mostafa, H.K. Fun, B.K.Ghosh; Struct.Chem., in press **(2005)**.

[11] a) V.Alexander; Chem.Rev., **95**, 273 **(1995)**.
  b) A.D.Garnovskii, A.L.Nivorozhkin, V.I.Nivorozhkin; Coord.Chem.Rev., **126**, 1 **(1993)**.

[12] a) A.M.Golub, H.Kohler, V.V.Skopenko; 'Chemistry of Pseudohalides', Elsevier, Amsterdam, **(1986)**.
  b) J.Ribas, A.Escuer, M.Monfot, R.Vicente, R.Cortes, L.Lezama, T.Rojo; Coord.Chem.Rev., **193**, 102 **(1999)**.
  c) T.K.Maji, P.S.Mukherjee, G.Mostafa, T.Mallah, J.Ribas, C.Boquera, N.Ray Chaudhuri; Chem. Commun., 1012 **(2001)**.
  d) J.Lau, X.G.Zhou, S.Geo, L.H.Shao, C.M.Zhang, Y.R.Li, J.Zhang, R.F.Zhang; Polyhedron, **23**, 1243 **(2004)**.

[13] a) J.M.Dou, X.K.Gao, F.Y.Dong, D.C.Dong, D.O.Wang; Dalton Trans, 2918 **(2004)**.
  b) J.M.Shi, Y.M.Sun, Z.Liu, L.D.Liu, W.Shi, P.Cheng; Dalton Trans, 376 **(2006)**.

[14] a) Z.E.Serna, M.K.Urtiaga, M.G.Barandika, R.Cortes, S.Martin, L.Lezama, M.I.Arriortua, T.Rojo; Inorg. Chem., **39**, 4550 **(2000)**.
  b) P.Talukder, A.Datta, S.Mitra, G.Rosair, M.S.E. Fallah, J.Ribas; Dalton Trans, 4161 **(2004)**.
  c) S.H.Rahaman, R.Ghosh, D.Bose, H.K.Fun, B.K. Ghosh; Indian J.Chem., **43A**, 1901 **(2004)**.

[15] S.Deoghoria, S.Sain, M.Soler, W.T.Wong, G.Cristou, S.K.Bera, S.K.Chandra; Polyhedron, **22**, 257 **(2003)**.

[16] G.M.Sheldrick; SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen, Germany, **(1997)**.

[17] A.L.Spek; PLATON 99, Program for Refinement of Crystal Structures, University of Utrecht, The Netherlands, **(2003)**.

[18] L.J.Farrugia; J.Appl.Crystallogr., **30**, 565 **(1997)**.

[19] A.B.P.Lever; 'Inorganic Electronic Spectroscopy', 2nd Edn., Elsevier, New York, **(1984)**.

[20] K.Nakamoto; 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', John Wiley & Sons, New York, 290 **(1986)**.

[21] a) K.Y.Ho, W.Y.Yu, K.K.Cheung, C.M.Che; Chem. Commun., 2101 **(1998)**.
  b) K.Y.Ho, W.Y.Yu, K.K.Cheung, C.M.Che; J.Chem. Soc., Dalton Trans, 1581 **(1999)**.

[22] F.A.Cotton, G.Wilkinson, C.A.Murillo, M.Bochmann; 'Advanced Inorganic Chemistry', 6th Edn., John Wiley & Sons, New York, 598 **(1999)**.