

Synthesis, structure and luminescence behaviour of copper(II)cyanato complexes containing bidentate N-donor Schiff bases

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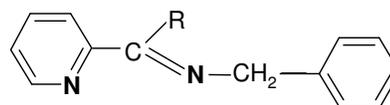
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Two Schiff bases, N-[(pyridin-2-yl)formylidene]benzylamine (pfba) and N-[(pyridin-2-yl)benzylidene]benzylamine (pbba) have been prepared and used to synthesize four pentacoordinated copper(II)cyanato complexes of type [Cu(L)₂(NCO)]X (**1-4**) [L = pfba, X = ClO₄⁻, **1**; L = pfba, X = PF₆⁻, **2**; L = pbba, X = ClO₄⁻, **3**; L = pbba, X = PF₆⁻, **4**]. The complexes have been characterized on the basis of microanalytical, spectroscopic, magnetic, electrochemical and other physicochemical properties. Structure of [Cu(pbba)₂(NCO)]ClO₄ (**3**) has been solved by X-ray diffraction measurement. Structural analysis reveals that the copper(II) centre in **3** has a distorted trigonal bipyramidal geometry with a CuN₅ chromophore coordinated through four N atoms of two bidentate pbba units and one N atom of terminal cyanate. **3** forms a one-dimensional chain through C-H...O hydrogen bond, π...π and C-H...π interactions. The complexes **1-4** exhibit d-d transition and n-π*/π-π* charge transfer transition. Electrochemical electron transfer study reveals copper(II)-copper(I) reduction in methanolic solutions. High-energy intraligand ¹(π-π*) fluorescence at room temperature and intraligand ³(π-π*) phosphorescence in glassy solutions (MeOH at 77 K) and in solid states are seen in all the complexes.

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Construction of self-assembled supramolecular architectures¹ is a current interest due to their intriguing topologies and applications in materials research such as catalysis, molecular electronics, magnetism and photochemistry²⁻⁵. One-pot synthesis⁶ using appropriate ratios of metal ions, organic ligands and bridging units may yield varied networks. Schiff bases⁷ are important organic spacers because of their preparative accessibilities, structural varieties and varied denticities. Pseudohalides⁸ are versatile bridging ligands for the construction of coordination polymers; of them flexidentate cyanate ion⁹ is an important one. Copper(II) chemistry is well documented¹⁰⁻¹⁴ through structural and magneto-structural characterization of different varieties of mono-, di- and polynuclear complexes with different organic ligands of varied denticities and inorganic bridges/organic bridges. Recently, we have reported^{15,16} a number of molecular and crystalline architectures of 3d/4d metal complexes formed by strong covalent bonds and non-covalent weak forces like hydrogen bonding, π...π and C-H...π interactions. In this paper we present synthesis, characterization and properties of four new luminous copper(II)cyanato complexes of type [Cu(L)₂(NCO)]X (**1-4**) [L = N-[(pyridin-2-yl)formylidene]benzylamine (pfba), X = ClO₄⁻, **1**; L = pfba, X = PF₆⁻, **2**; L = N-[(pyridin-2-yl)benzylidene]benzylamine (pbba), X = ClO₄⁻, **3**; L = pbba, X = PF₆⁻, **4**] containing bidentate Schiff bases. X-ray crystallographic study has been done with one representative member (**3**) to define the coordination sphere. In solid state, the molecular units in **3** are engaged in C-H...O, π...π and C-H...π interactions to form a one-dimensional zig-zag supramolecular chain.

lidene]benzylamine (pfba), X = ClO₄⁻, **1**; L = pfba, X = PF₆⁻, **2**; L = N-[(pyridin-2-yl)benzylidene]benzylamine (pbba), X = ClO₄⁻, **3**; L = pbba, X = PF₆⁻, **4**] containing bidentate Schiff bases. X-ray crystallographic study has been done with one representative member (**3**) to define the coordination sphere. In solid state, the molecular units in **3** are engaged in C-H...O, π...π and C-H...π interactions to form a one-dimensional zig-zag supramolecular chain.



R = H; pfba
R = Ph; pbba

Materials and Methods

High purity 2-benzoylpyridine (Lancaster, UK), Pyridine-2-carboxaldehyde (Lancaster, UK), benzylamine (Lancaster, UK), copper(II) nitrate tetrahydrate (E. Merck, India), sodium cyanate (Aldrich, USA) and potassium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and used as received. Copper(II) perchlorate hexahydrate was prepared on treatment of copper

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. Purification of MeOH (E. Merck, India) and preparation of supporting electrolyte ([Et₄N][ClO₄]) for electrochemical work was executed following the reported method¹⁷. All other chemicals and solvents were AR grade and were used as received. The synthetic reactions and work-up were done in open air.

Caution! Perchlorate compounds of transition metal ions are potentially explosive¹⁸ especially in presence of organic ligands and 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, 4000-300 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 photomultiplier tube were used as the excitation source and the fluorescence detector. Room temperature magnetic susceptibilities of powder samples were done on a PAR 155 vibrating sample magnetometer, with Hg[Co(SCN)₄] as the reference. Electrochemical measurements were made with a computer controlled EG&G PARC VersaStat (model 270) electrochemical instrument using a platinum disk-working electrode as described elsewhere¹⁹. The following parameters and relations were used: scan rate (ν), 50 mVs⁻¹; formal potential $E^\circ = 0.5 (E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. The potentials were referenced to a saturated calomel electrode (SCE) and are uncorrected for junction contributions.

Preparation of the Schiff bases

The Schiff bases pfba and pbba were prepared⁷ using reported method with a little modification.

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

Pyridine-2-carboxaldehyde (0.11 g, 1 mmol) was refluxed with benzylamine (0.10 g, 1 mmol) in dehydrated alcohol (20 cm³). After 10 h, the reaction solution was evaporated under reduced pressure to yield a gummy mass, which was dried and stored *in vacuo* over CaCl₂ for subsequent use. Yield, 0.16 g (80%). Found: C, 79.51; H, 6.20; N, 14.25; Calc. C₁₃H₁₂N₂ (pfba): C, 79.56; H, 6.16; N, 14.27%. IR (KBr, cm⁻¹): 1590 ($\nu_{C=N}$). UV-Vis (λ_{max} , MeCN): 250, 390 nm.

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

2-Benzoylpyridine (0.18 g, 1 mmol) was refluxed (10 h) with benzylamine (0.10 g, 1 mmol) in dehydrated alcohol (20 cm³). The reaction solution was evaporated under reduced pressure and processed as in pfba. This was dried and stored *in vacuo* over CaCl₂ for subsequent use. Yield, 0.22 g (80%). Found: C, 83.77; H, 5.90; N, 10.32; Calc. C₁₉H₁₆N₂ (pbba): C, 83.80; H, 5.94; N, 10.29%. IR (KBr, cm⁻¹): 1590 ($\nu_{C=N}$). UV-Vis (λ_{max} , MeCN): 255, 393 nm.

Synthesis of the complexes

1 and **3** were prepared from perchlorate salt of copper(II) using the same molar ratio (1:2:1) of the metal, pfba/pbba and sodium cyanate. **2** and **4** were prepared using a 1:2:1:1 molar ratio of copper(II) nitrate, pfba/pbba, sodium cyanate and potassium hexafluorophosphate; these were also isolated by metathesis of **1** and **3** respectively with potassium hexafluorophosphate. The typical syntheses are given below.

[Cu(pfba)₂(NCO)]ClO₄ (**1**)

An acetonitrile solution (5 cm³) of pfba (0.40 g, 2 mmol) was added dropwise to a solution of Cu(ClO₄)₂·6H₂O (0.37 g, 1 mmol) in the same solvent (10 cm³) followed by the addition of the aqueous solution (5 cm³) of sodium cyanate (0.06 g, 1 mmol). The mixture was stirred magnetically for 15 min. The light green solution was filtered and the supernatant liquid was kept in air for slow evaporation. After three days, green crystals of **1** were deposited which were collected by filtration, washed with MeCN and kept *in vacuo* over CaCl₂. Yield, 0.42 g (70%). Found: C, 54.29; H, 4.07; N, 12.37; Calc. C₂₇H₂₄N₅O₅ClCu (**1**): C, 54.27; H, 4.05; N, 11.42%. IR (KBr, cm⁻¹): $\nu(C=N)$ 1590; $\nu(NCO)$ 2248, 1318; $\nu(ClO_4)$ 1092, 621. UV-Vis (MeOH, λ_{max} , nm): 720, 402. Λ_M (MeOH, $\Omega^{-1}cm^2mol^{-1}$): 130. E°_{298} , V (ΔE_p , mV): 0.11 (100). μ_{eff} (BM): 1.75.

[Cu(pfba)₂(NCO)]PF₆ (2)

To a copper(II) nitrate tetrahydrate (0.26 g, 1 mmol) solution (10 cm³) in MeCN, faint yellow pfba (0.40 g, 2 mmol) in the same solvent (5 cm³) and NaNCO (0.06 g, 1 mmol) in water (3 cm³) and KPF₆ (0.18 g, 1 mmol) in water (3 cm³) were added dropwise. The mixture was stirred magnetically for 15 min. The final light green solution was filtered, left for slow evaporation in air and processed as in **1** to yield pure **2**. Yield, 0.41 g (65%). This was also prepared by metathesis of **1** (0.60 g, 1 mmol) with KPF₆ (0.18 g, 1 mmol) in MeCN-H₂O (2:1) mixture in better yield 0.44 g (68%). Found: C, 50.40; H, 3.79; N, 10.86; Calc. C₂₇H₂₄N₅O₅ClCu (**1**): C, 50.43; H, 3.76; N, 10.89%. IR (KBr, cm⁻¹): ν(C=N) 1590; ν(NCO) 2248, 1318; ν(PF₆) 820, 540. UV-Vis (MeOH, λ_{max}, nm): 718, 404. Λ_M (MeOH, Ω⁻¹cm²mol⁻¹): 130. E^o₂₉₈, V (ΔE_p, mV): 0.11 (100). μ_{eff} (BM): 1.76.

[Cu(pbba)₂(NCO)]ClO₄ (3)

Cu(ClO₄)₂·6H₂O (0.37 g, 1 mmol) was dissolved in MeCN (10 mL); to this pbba (0.54 g, 2 mmol) dissolved in the same solvent (5 cm³) was added dropwise followed by NaNCO (0.06 g, 1 mmol) in water (5 cm³). The mixture was stirred magnetically for 15 min. The resulting green solution was kept undisturbed for slow evaporation. After two days, rectangular green crystals of **3** were deposited and processed as in **1** to yield pure **3**. Yield, 0.56 g (75%). Found: C, 62.51; H, 4.27; N, 9.36; Calc. C₃₉H₃₂N₅O₅ClCu (**3**): C, 62.48; H, 4.30; N, 9.34%. IR (KBr, cm⁻¹): ν(C=N) 1595; ν(NCO) 2250, 1320; ν(ClO₄) 1090, 618. UV-Vis (MeOH, λ_{max}, nm): 720, 406. Λ_M (MeOH, Ω⁻¹cm²mol⁻¹): 130. E^o₂₉₈, V (ΔE_p, mV): 0.11 (110). μ_{eff} (BM): 1.76.

[Cu(pbba)₂(NCO)]PF₆ (4)

4 was prepared using the same procedure and reaction stoichiometry as in **2** except that pbba instead of pfba was used as organic ligand. Yield, 0.52 g (66%). This was also prepared by metathesis of **3** (0.64 g, 1 mmol) with KPF₆ (0.18 g, 1 mmol) in MeCN-H₂O (2:1) mixture in higher yield 0.57 g (70%). Found: C, 62.50; H, 4.27; N, 9.36; Calc. C₂₇H₂₄N₅O₅ClCu (**1**): C, 62.48; H 4.30; N, 9.34%. IR (KBr, cm⁻¹): ν(C=N) 1590; ν(NCO) 2248, 1318; ν(PF₆) 825, 544. UV-Vis (MeOH, λ_{max}, nm): 720, 406. Λ_M (MeOH, Ω⁻¹cm²mol⁻¹): 130. E^o₂₉₈, V (ΔE_p, mV): 0.11 (100). μ_{eff} (BM): 1.77.

X-ray diffraction study

Single crystals of **3** were obtained by slow evaporation of MeCN-H₂O solution of the reaction mixture at room temperature (298 K). Diffraction data at 293 K for **3** 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/n for **3**. Of the 137414 unique reflections, 18006 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-97²⁰. 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 = 0.0341; wR₂ = 0.0916 with I > 2σ(I), goodness-of-fit = 1.067 for the complex. The final differences Fourier map showed the maximum and minimum peak heights at 0.71 and -0.63 eÅ⁻³. All calculations were carried out using PLATON²¹, ORTEP-32²². The crystal data and data collection parameters are listed in Table 1.

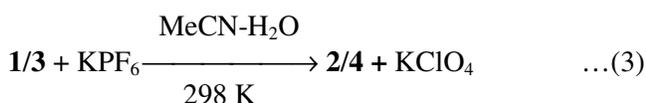
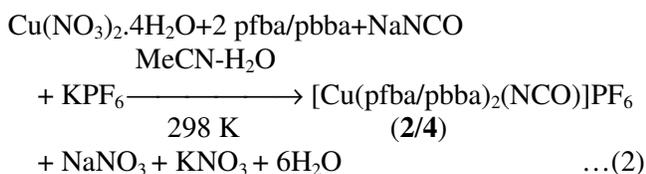
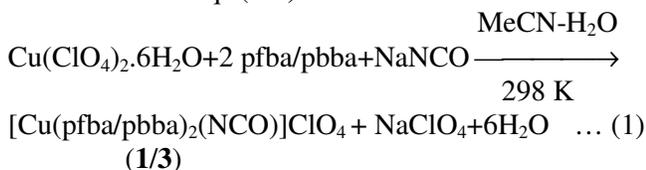
Table 1 — Crystallographic data for [Cu(pbba)₂(NCO)]ClO₄ (**3**)

Empirical formula	C ₃₉ H ₃₂ N ₅ O ₅ ClCu
Formula weight	749.70
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/n
D _{calc} (Mg m ⁻³)	1.451
Volume (Å ³)	3432.65(8)
Z	4
a (Å)	14.0955(2)
b (Å)	17.5593(2)
c (Å)	14.2364(2)
α°, β°, γ°	90, 103.0470(10), 90
F(000)	1548
Crystal size (mm ³)	0.24 × 0.46 × 0.68
μ (mm ⁻¹)	0.768
H / k / l	-24,24/-30,29/-24,24
θ ranges for data collection (°)	1.8 to 37.5
Reflections collected	137414
Independent reflections	18006 [R(int) = 0.029]
Max. and min. transmission	0.5905 and 0.4721
Data/restraints/parameters	18006/0/460
Goodness-of-fit on F ²	1.067
Final R indices [I > 2σ(I)]	R ₁ = 0.0341, wR ₂ = 0.0916
R indices (all data)	R ₁ = 0.0488, wR ₂ = 0.1049
Largest peak and hole (eÅ ⁻³)	0.71 and -0.63
Weighting Scheme: R ₁ = Σ F _o - F _c /Σ F _o , wR ₂ = [Σw(F _o ² - F _c ²) ² /Σw(F _o ²) ²] ^{1/2} , Calc. w = 1/[σ ² (F _o ²) + (0.0525 P) ² + 1.2233 P] where P = (F _o ² + 2F _c ²)/3	

Results and Discussion

Synthesis and formulation

The Schiff base system (pfba/pbba) was prepared by refluxing benzylamine and pyridin-2-carboxaldehyde/2-benzoyl pyridine in 1:1 molar ratio in dehydrated ethanol. The neutral bidentate chelators are N^p, Nⁱ type where N^p and Nⁱ are N(pyridine) and N(imine) donor centers, respectively. Reaction of Cu(ClO₄)₂·6H₂O, pfba/pbba and NaNCO in 1:2:1 molar ratio in aqueous acetonitrile at room temperature resulted in [Cu(pfba/pbba)(NCO)]ClO₄ (**1/3**). Changing the metal salt from Cu(ClO₄)₂·6H₂O to Cu(NO₃)₂·4H₂O and a 1:2:1 molar ratio of metal nitrate, Schiff base and cyanate with addition of 1 equivalent KPF₆ in the reaction mixture, **2** and **4** were obtained. **2** and **4** were also isolated from metathesis of **1** and **3** with KPF₆. Microanalyses and IR spectra confirmed the composition. The reactions are summarized in Eqs (1-3):



The air-stable, moisture-insensitive compounds are powders, soluble in a range of common organic solvents such as methanol, ethanol, dichloromethane, acetonitrile but are insoluble in water. In MeOH solutions, they behave as 1:1 electrolytes²³ as reflected from their Λ_M (130 Ω⁻¹ cm² mol⁻¹) value. Room-temperature solid phase magnetic susceptibility measurements show that the copper(II) complexes have magnetic moment close to the spin-only value (1.73 BM), as expected from discrete and magnetically non-coupled mononuclear 3d⁹ ion. In IR spectra, characteristic asymmetric and symmetric cyanate stretching vibrations at ~2250 and ~1320 cm⁻¹, respectively are routinely observed in all complexes. The frequency values are substantially higher than that in free ion (2155 cm⁻¹)²⁴ and are

consistent²⁵ with N-bonding rather O-bonding. The presence of ionic perchlorate bands in **1** and **3** was noticed at ~1090 and ~620 cm⁻¹. In **2** and **4**, the bands corresponding to ν(PF₆) vibrations were found at ~840 and 540 cm⁻¹. The ν(C=N) stretching vibrations of metal bound Schiff base are seen at ~1590 cm⁻¹. All the other characteristic ligand vibration is seen in the 1600-600 cm⁻¹ range. The solutions of **1-4** in MeOH are dark green, and exhibit absorption in 400-720 nm range [**1**: λ, 402, 720 nm; **2**: λ, 404, 718 nm; **3**: λ, 406, 720 nm; **4**: λ, 406, 720 nm]. The transition at ~700 nm corresponds to a d-d transition of the copper(II) moiety and band around 400 nm, for intramolecular (n→π*, π→π*) charge transfer transition²⁶. Reflectance spectra [**1**: λ, 400, 715 nm; **2**: λ, 408, 715 nm; **3**: λ, 404, 716 nm; **4**: λ, 410, 722 nm] in nujol and electronic spectra in MeOH solutions are akin reflecting similar gross structure and electronic structure in solid state and in solution.

X-ray crystal structure of [Cu(pbba)₂(NCO)]ClO₄ (**3**)

X-ray structure determination reveals that the crystal lattice of **9c** consists of [Cu(**3b**)₂(NCO)]⁺ cations and ClO₄⁻ anions (Fig. 1). A 1D supramolecular chain results through C-H...O hydrogen bonding, π...π and C-H...π interactions (Figs. 2 and 3). Selected interatomic bond lengths and bond angles are listed in Table 2. Hydrogen bond, π...π and C-H...π interaction parameters are represented in Table 3. The coordination polyhedron around the metal center is best described as a distorted trigonal bipyramid (tbp) with a CuN₅ chromophore. The coordination includes two similar bidentate

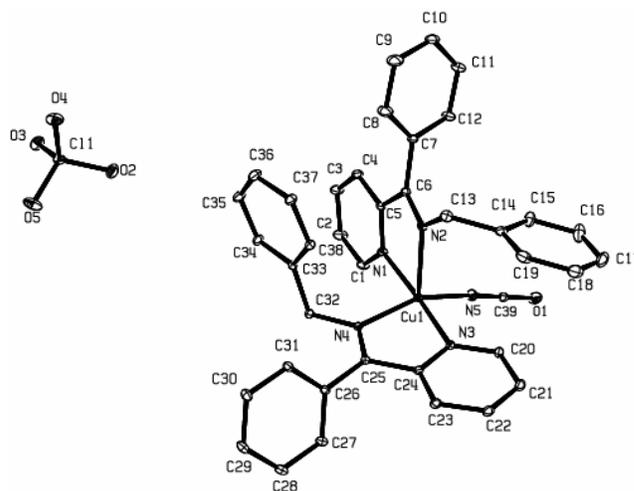


Fig. 1 — Thermal ellipsoid plot of [Cu(pbba)₂(NCO)]ClO₄ (**3**) with atom numbering scheme and 20% probability ellipsoids for all non-hydrogen atoms.

Schiff base (pbba) ligated by two pyridine nitrogens [N(1), N(3)], two imine nitrogens [N(2), N(4)] and one terminal cyanate nitrogen [N(5)]. The equatorial positions are occupied by two imine nitrogen [N(2), N(4)] from two different pbba units and the cyanate

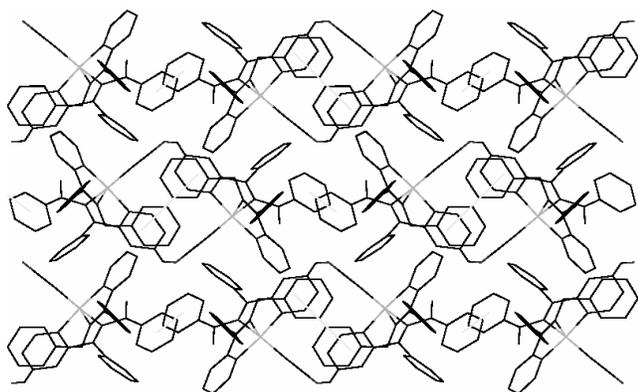


Fig. 2 — The $\pi \dots \pi$ interaction based 1D chain stabilized by C-H...O hydrogen bonding in **3**.

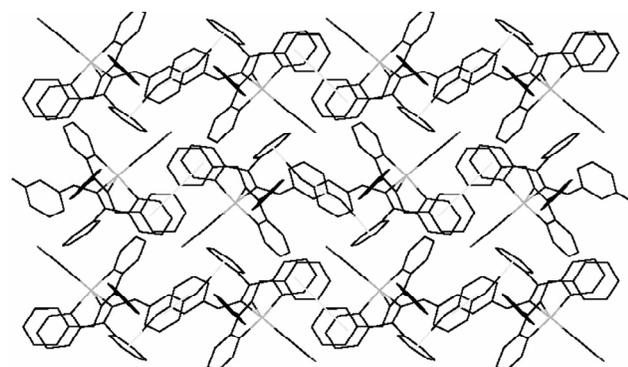


Fig. 3 — The 1D chain through $\pi \dots \pi$ interaction stabilized by C-H... π interaction in **3**.

nitrogen [N(5)] while the axial positions are occupied by two pyridine N atoms [N(1), N(3)]. The distortion from ideal *tbp* geometry is due to the asymmetric nature of the Schiff base and can be seen from the deviations of the refined angles ($90^\circ/120^\circ$) formed at the metal center. The equatorial Cu-N distances [1.9311(10)–2.2761(9) Å] as well as the bond angles [98.85(3)–157.16(4)°] show significant variations. The axial Cu-N distances [Cu(1)–N(1) 2.0319(9) Å, Cu(1)–N(3) 2.0059(8) Å] are however close. The lowest value [1.9311(10) Å] of Cu(1)–N(5) distance indicates stronger coordination of the anionic cyanate over neutral Schiff base. The two bite angles N(1)–Cu(1)–N(2) and N(4)–Cu(1)–N(3) are 76.12(3) and 79.90(3)°, respectively. The axial bond angle, N(1)–Cu(1)–N(3) [175.17(3)°], deviates slightly from the ideal value (180°). The sum (359.97°) of the equatorial angles N(2)–Cu(1)–N(4) [98.85(3)°],

Table 2 — Selected bond distances (Å) and angles (°) for **3**

<i>Bond distances</i>			
Cu(1)–N(1)	2.0319(9)	Cu(1)–N(5)	1.9311(10)
Cu(1)–N(2)	2.2761(9)	N(5)–C(39)	1.1658(15)
Cu(1)–N(3)	2.0059(8)	C(39)–O(1)	1.2061(17)
Cu(1)–N(4)	2.0339(8)		
<i>Bond angles</i>			
N(1)–Cu(1)–N(2)	76.12(3)	N(2)–Cu(1)–N(5)	103.96(4)
N(1)–Cu(1)–N(3)	175.17(3)	N(3)–Cu(1)–N(4)	79.90(3)
N(1)–Cu(1)–N(4)	95.64(3)	N(3)–Cu(1)–N(5)	93.97(4)
N(1)–Cu(1)–N(5)	90.86(4)	N(4)–Cu(1)–N(5)	157.16(4)
N(2)–Cu(1)–N(3)	102.62(3)	Cu(1)–N(5)–C(39)	175.09(10)
N(2)–Cu(1)–N(4)	98.85(3)	O(1)–C(39)–N(5)	178.60(14)

Table 3 — Non-covalent interaction parameters for **3**

Hydrogen bond parameters donor/acceptor scheme (Å, °)

D–H...A	D–H	H...A	D...A	D–H...A
C(1)–H(1)...O(5) ^(c)	0.9300	2.4900	3.2997(15)	146.00

Symmetry code: (c) -x, 1-y, 1-z.

$\pi \dots \pi$ Interactions (Å, °)

Cg–Cg	Cg–Cg distance	Dihedral angle (i,j)	⊥ Distance between baricentres (i,j)
Cg(4)–Cg(4) ^(a)	4.6845(6)	0.03	3.423
Cg(8)–Cg(8) ^(b)	5.3515(7)	0.00	3.374

Symmetry code: (a) -x, -y, 1-z; (b) -x, 1-y, 1-z; Cg(4) = N(3)–C(20)–C(21)–C(22)–C(23)–C(24); Cg(8) = C(33)–C(34)–C(35)–C(36)–C(37)–C(38).

C–H... π Interactions bond donor/acceptor scheme (Å, °)

D–H...A	D–H	H...A	D...A	<D–H...A
C(35)–H(35A)...Cg(7) ^(d)	0.9300	2.80	3.6304(14)	150.00

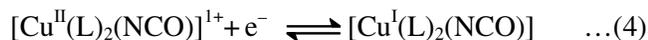
Symmetry code: (d) -x, 1-y, 1-z; Cg(7): C(26)–C(27)–C(28)–C(29)–C(30)–C(31).

N(2)-Cu(1)-N(5) [103.96(4)°] and N(4)-Cu(1)-N(5) [157.16(4)°] are very close to 360.00°; so the atoms N(2), N(4), N(5) and Cu(1) are almost in a same plane. In the terminal cyanate ligand, the N(5)-C(39) distance [1.1658(15) Å] is longer than the C(39)-O(1) length [1.2061(17) Å] which indicates that the nitrogen [N(5)] atom of NCO⁻ is coordinated to copper(II) centre. The NCO⁻ ion is coordinated in a linear fashion as seen from its N(5)-C(39)-O(1) angle [177.6(5)°].

The zero-dimensional (0D) mononuclear units pack alongside each other via $\pi\cdots\pi$ interactions to give 1D supramolecular chains when viewed down the crystallographic *a* axis. Two types of face-to-face $\pi\cdots\pi$ interactions between two terminal pyridine rings and two terminal benzene rings are responsible for the formation of the 1D chain. The chains are stabilized by C-H...O hydrogen bonding. The terminal non-bridged cyanate oxygen [O(5)] and para-hydrogen [H(1)] of aromatic pyridine ring play a vital role in the formation of such C-H...O hydrogen bonding. The C-H hydrogens are potential proton donors and cyanates are acceptors (Fig. 2). C-H... π interactions are also playing an importance role to stabilize 1D chain in crystal packing. The 1D chains created by $\pi\cdots\pi$ interactions are interlinked by C-H... π interactions between meta-hydrogen [H(35a)] of aromatic benzene ring and terminal benzene ring of another unit. The C-H hydrogens are potential proton donors and benzene rings are acceptors where the π -interactions are mainly responsible for the formation of solid state (Fig. 3).

Electrochemical study

Electroactivity of the complexes was studied in MeOH solutions using cyclic voltammetry (CV) and coulometry at platinum working electrodes. A one-electron reductive response is observed presumably due to electrode reaction shown in Eq. (4):



A representative cyclic voltammogram is shown in Fig. 4. The one-electron stoichiometry of above couple was confirmed from the comparison of current height with that of standard²⁷ Cu^{III} couple, since attempted coulometry at potentials more cathodic than *E*_{pc} gave continuous coulomb count due to some unidentified side reactions²⁸. The similar pattern in electron transfer behaviour of all the complexes at about same potential once again corroborates closely similar structure of the cationic units.

Luminescence studies

The spectroscopic data are listed in Table 4. Complexes with pfba/pbba feature intense absorption at ~405 nm which are assigned to intramolecular $\pi\rightarrow\pi^*$ transitions. The emission energy of the complexes in MeOH solutions at 298 K is almost same ($\lambda_{\text{max}} \approx 475$ nm) and is assignable to intraligand ¹($\pi\text{-}\pi^*$) fluorescence^{29,30}. The lifetimes of the fluorescence of **1** to **4** are 2.63, 2.61, 2.62 and 2.62 ns, respectively. In glassy solutions (MeOH at 77 K) both fluorescence and ³($\pi\text{-}\pi^*$) phosphorescence are

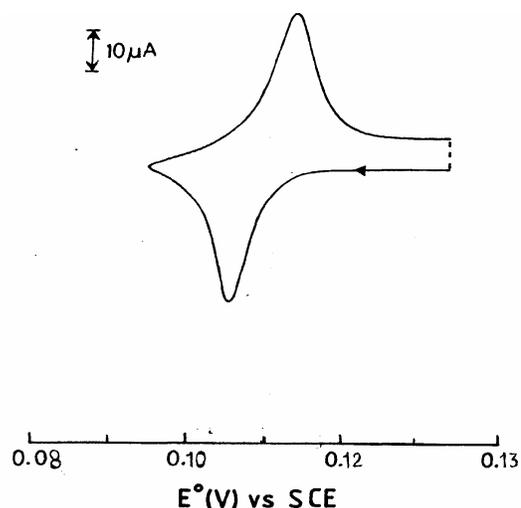


Fig. 4 — Cyclic voltammogram of **3**.

Table 4 — Photophysical data for **1-4**

Sample	Absorption (λ /nm)		Emission (λ /nm)		Life time (ns)
		Fluorescence ^a	Phosphorescence ^b	Solid state ^c	
pfba	370	465	520	485	2.57
pbba	372	466	522	486	2.58
1	406	475	525	492	2.63
2	405	476	524	491	2.61
3	406	475	525	492	2.62
4	404	476	524	491	2.60

^aIn MeOH at room temperature (298 K); ^bIn MeOH at 77 K; ^cAt room temperature (298 K).

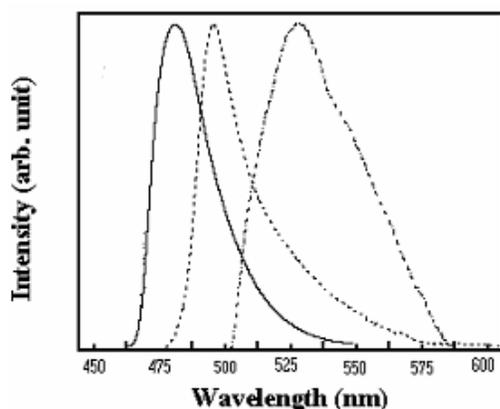


Fig. 5 — Emission spectra of **3**: Fluorescence (—), phosphorescence in MeOH glassy solution (-----) and solid state at 298 K (-----).

observed at 525 nm. In solid state, they show distinct emission bands at ~492 nm differing from fluorescence spectra in MeOH (Fig. 5).

Conclusions

Four pentacoordinated copper(II)cyanato complexes containing bidentate Schiff base have been synthesized using self assembly and also through metathesis. X-ray structure determination of one case shows trigonal bipyramidal geometry around copper(II) centre. This is very important as $\pi\cdots\pi$, C-H... π interactions and weak C-H...O hydrogen bond play an important role for construction of the 1D chains in the crystal structure. The complexes exhibit electronic spectra, metal reduction and luminance behaviour.

Supplementary Data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre Number 607459 (**3**). 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; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) on request quoting the deposition number.

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