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Chelating N,N′-(bis(pyridin-2-yl)alkylidene)propane-1,3-diamine pseudohalide copper(II) and cadmium(II) coordination compounds: Synthesis, structure and luminescence properties of [M(bpap)(X)]ClO_4 and [M(bpap)$(X)_2$] [M = Cu, Cd; X = N_3^-, NCS^-]

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Abstract

Copper perchlorate hexahydrate on reaction with the chelating ligands, *N,N′*-(bis(pyridin-2-yl)alkylidene)propane-1,3-diamine (bpap) [(py)(R)C=N–$(CH_2)_3$–N=C(R)(py) where py = pyridine; R = H, (bpfp); R = Me, (bpmp); R = C_6H_5, (bpbp)] and NaN_3/NH_4NCS in a 1:1:1 mole ratio forms the complexes [Cu(bpap)(N_3/NCS)]ClO_4 (**1a**–**3b**), while cadmium perchlorate hexahydrate/cadmium nitrate tetrahydrate in a 1:1:2 mole ratio produces [Cd(bpap)$(N_3/NCS)_2$] (**4a**–**6b**). Elemental, spectral, electrochemical and other physicochemical results characterize the complexes. Single crystal X-ray diffraction studies confirm the structure of two representative members, [Cu(bpbp)(N_3)]ClO_4 (**3a**) and [Cd(bpbp)$(NCS)_2$] (**6b**). The complexes of **1a**–**3b** are reduced to [Cu$(bpbp)_2$]ClO_4 by ascorbic acid. However, air oxidation of [Cu$(bpbp)_2$]ClO_4 in the presence of N_3/NCS produces Cu(bpap)(N_3/NCS)]ClO_4. All the complexes display intraligand $^1(\pi–\pi^*)$ fluorescence and intraligand $^3(\pi–\pi^*)$ phosphorescence in glassy solutions (MeOH at 77 K).

Keywords: Copper(II)/cadmium(II); Schiff base chelator; Cu(II)–Cu(I) interconversion; X-ray structure; Luminescence spectra

1. Introduction

Significant contemporary interests in inorganic–organic hybrid materials [1] reflect their potential applications in areas such as catalysis, molecular electronics, magnetism and photochemistry [2–5]. Schiff bases [6,7] are useful chelators because of their preparational accessibilities, structural varieties and varied denticities. We are also interested in this field through variation of metal ions like nickel(II), copper(II), zinc(II) and cadmium(II), coordination environment, organic ligands and suitable bridging units [8–11]. Pseudohalides [8–12], especially the azide and thiocyanate, have long been known for their versatile coordination modes to give monomeric, dimeric and polymeric complexes. Copper complexes are of considerable interest mainly due to their variety in coordination geometry, exquisite colours, technical application, dependant molecular structures and spectroscopic properties, and their biochemical significance [9,13]. Cadmium is well suited [11,14,15] to this study as its d^{10} configuration permits a wide range of symmetries and coordination numbers. Reports on just a few copper(II) and cadmium(II)

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complexes with the Schiff bases formed from propane-1,3-diamine and different pyridine carboxyaldehyde or -ketones [16,17] have prompted us to develop new coordination compounds using azide and thiocyanate ligands. Successfully, we have prepared 12 mononuclear complexes of the type [Cu(bpap)(N_3/NCS)]ClO_4 (**1a**–**3b**) and [Cd(bpap)(N_3/NCS)$_2$] (**4a**–**6b**), characterized on the basis of microanalytical, spectroscopic and other physicochemical properties. X-ray crystallographic studies of [Cu(bpbp)(N_3)]ClO_4 (**3a**) and [Cd(bpbp)(NCS)$_2$] (**6b**) were made to define the coordination sphere. The details of synthesis, structure and luminescence behaviour are described below.

2. Experimental

2.1. Materials

High purity pyridine-2-carboxyaldehyde (Lancaster, UK), 2-acetylpyridine (Lancaster, UK), 2-benzoylpyridine (Lancaster, UK), propane-1,3-diamine (Lancaster, UK), sodium azide (Aldrich, USA), ammoniumthiocyanate (Aldrich, USA) potassium hexafluorophosphate (Fluka, Germany), copper nitrate tetrahydrate (E. Merck, India) and cadmium nitrate tetrahydrate (E. Merck, India) were purchased from their respective concerns and used as received. Copper perchlorate hexahydrate and cadmium perchlorate hexahydrate were prepared by treatment of copper carbonate and cadmium carbonate (E. Merck, India) with perchloric acid (E. Merck, India), respectively, followed by slow evaporation on a steam-bath, filtration through a fine glass-frit, and preservation in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent use. Purification of MeOH (E. Merck, India) and preparation of the supporting electrolyte ([Et_4N]-[ClO_4]) for electrochemical work were executed following a reported method [18]. All other chemicals and solvents were AR grade and were used as received.

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

2.2. 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 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 the solvent. Ground state absorption and steady-state fluorescence measurements were made with a Shimadzu model UV-1601PC UV–Vis spectrophotometer and Hitachi model F-4500 spectrofluorimeter equipped with polarization accessory and low temperature unit (77 K). The temperature of the solution was kept to within ±0.1 K by circulating water through a HETO HOLTEN system. Room-temperature solid phase magnetic susceptibilities were measured at 298 K with a PAR 155 vibrating sample magnetometer with Hg[Co(SCN)$_4$] as the reference. Mass spectra were obtained with a MAT 8200 (electron ionization, EIMS) instrument. Electrochemical measurements (cyclic voltammetry, CV) were carried out with the use of computer controlled EG & G PARC VersaStat model 270 electrochemical instrument using a platinum disk working electrode as described elsewhere [19]. The solutions were IR compensated and the results were collected at 298 K. The following parameters and relations were used: scan rate (v), 50 mV s^{-1}; formal potential $E^0 = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; ΔE_p is the peak-to-peak separation. The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for junction contributions.

2.3. Preparation of the Schiff bases

The Schiff base chelators, bpfp, bpmp and bpbp, were prepared following a reported [16] procedure with little modification. The details for bpfp are described: Pyridine-2-carboxyaldehyde (0.214 g, 2 mmol) was refluxed with propane-1,3-diamine (0.074 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%)]. Bpmp and bpbp were prepared similarly by refluxing for with 10 h 2-acetyl pyridine (0.242 g, 2 mmol) and 2-benzoylpyridine (0.366 g, 2 mmol), respectively, instead of pyridine-2-carboxyaldehyde, with propane-1,3-diamine (0.088 g, 1 mmol) in a 2:1 molar ratio. Yield: (78–80%). *Anal.* calc. for $C_{15}H_{16}N_4$ (bpfp): C, 71.40; H, 6.39; N, 27.20. Found: C, 71.41; H, 7.40; N, 27.23%. Mass spectrum (EI): *m/z* 252 ($M^+ = L^+$). IR (KBr, cm^{-1}): ν(C=N) 1590. UV–Vis (λ, nm): 240, 370. *Anal.* calc. for $C_{17}H_{20}N_4$(bpmp): C, 77.82; H, 7.19; N, 19.98. Found: C, 77.80; H, 7.20; N, 20.00%. Mass spectrum (EI): *m/z* 280 ($M^+ = L^+$). IR (KBr, cm^{-1}): ν(C=N) 1592 cm^{-1}. UV–Vis (λ, nm): 243, 370. *Anal.* calc. for $C_{27}H_{24}N_4$ (bpbp): C, 81.10; H, 5.98; N, 13.85. Found: C, 80.05; H, 5.91; N, 13.80%. Mass spectrum (EI): *m/z* 404 ($M^+ = L^+$). IR (KBr, cm^{-1}): ν(C=N) 1590. UV–Vis (λ, nm): 245, 372.

2.4. Preparation of the complexes

Complexes **1a**–**3b** were prepared from the perchlorate salts of copper(II) using the same mole ratio (1:1:1) of metal, bpfp/bpmp/bpbp and azide/thiocyanate; these were also isolated using the nitrate salt by finally adding one equivalent sodium perchlorate. **4a**–**6b** were prepared from both cadmium(II) nitrate and/or cadmium(II) perchlorate using a mole ratio of 1:1:2 with bpfp/bpmp/bpbp and azide/thiocyanate. Typical syntheses are described below.

2.4.1. Copper(II)azido complexes

Solid bpfp (0.252 g, 1 mmol) was added pinch by pinch to a solution (10 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g; 1 mmol) in MeOH (15 cm^3) followed by NaN_3 (0.065 g, 1 mmol) with constant stirring. After 30 min the green solution mixture was filtered and the supernatant liquid was kept in air for slow evaporation. After 7 days **1a** was separated, washed with toluene and dried in vacuo over silica gel indicator. Yield: 0.86 g (70%). **2a** and **3a** were prepared by the same procedure using bpmp and bpbp, respectively, instead of bpfp. *Anal.* calc. for $C_{15}H_{16}N_7O_4ClCu$ (**1a**): C, 39.39; H, 3.52; N, 21.44. Found: C, 39.40; H, 3.54; N, 21.46%. IR (KBr, cm^{-1}): ν(C=N) 1637, 1592; $\nu(N_3)$ 2073; $\nu(ClO_4)$ 1080, 622. Mass spectrum (FAB): *m*/*z* 357 ($M^+ = [Cu(bpfp)(N_3)]^+$). Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 130; UV–Vis ($\lambda$, nm): 715, 394. *Anal.* calc. for $C_{17}H_{20}N_7O_4ClCu$ (**2a**): C, 42.06; H, 4.15; N, 20.20. Found: C, 42.08; H, 4.12; N, 20.22%. IR (KBr, cm^{-1}): ν(C=N) 1635, 1592; $\nu(N_3)$ 2072; $\nu(ClO_4)$ 1080, 622. Mass spectrum (FAB): *m*/*z* 385 ($M^+ = [Cu(bpmp)\,(N_3)]^+$). Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 130; UV–Vis ($\lambda$, nm): 717, 395. *Anal.* calc. for $C_{27}H_{24}N_7O_4ClCu$ (**3a**): C, 53.20; H, 3.97; N, 16.08. Found: C, 53.15; H, 4.21; N, 16.05%. IR (KBr, cm^{-1}): ν(C=N) 1637, 1590; $\nu(N_3)$ 2073; $\nu(ClO_4)$ 1080, 622. Mass spectrum (FAB): *m*/*z* 510 ($M^+ = [Cu(bpbp)(N_3)]^+$). Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 120; UV–Vis ($\lambda$, nm): 720, 402.

2.4.2. Copper(II)thiocyanato complexes

To copper(II) nitrate tetrahydrate (0.241 g, 1 mmol) in methanolic solution (10 cm^3), faint yellow bpbp (0.406 g, 1 mmol) was added dropwise. An methanolic solution (5 cm^3) of ammoniumthiocyanate (0.076 g, 1 mmol) was added with constant stirring. To this solution one equivalent of sodium perchlorate was added slowly drop by drop. The final deep green solution was filtered and left for slow evaporation in air. After a few days fine green crystals of **3b** were separated out, which were filtered, washed with methanol and dried in *vacuo* over $CaCl_2$. Yield: 0.125 g (74%). **1b** and **2b** were prepared by the same procedure using bpfp and bpmp respectively instead of bpbp. *Anal.* calc. for $C_{28}H_{24}N_5SO_4ClCu$ (**3b**): C, 53.76; H, 3.86; N, 11.19. Found: C, 53.72; H, 3.88; N, 11.14%. IR (KBr, cm^{-1}): ν(C=N) 1637,1592; ν(NCS) 2100, 2095; $\nu(ClO_4)$ 1080, 622. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 130; UV–Vis ($\lambda$, nm): 715, 394. *Anal.* calc. for $C_{16}H_{16}N_5SO_4ClCu$ (**1b**): C, 40.59; H, 3.40; N, 14.79. Found: C, 40.58; H, 3.42; N, 14.77%. IR (KBr, cm^{-1}): ν(C=N) 1635, 1592; ν(NCS) 2092, 2078; $\nu(ClO_4)$ 1080, 622. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 120; UV–Vis ($\lambda$, nm): 717, 395. Anal. Found: C, 43.12; H, 4.01; N, 13.93. Calc. for $C_{18}H_{20}N_5SO_4ClCu$ (**2b**): C, 43.11; H, 4.02; N, 13.96%. IR (KBr, cm^{-1}): ν(C=N) 1637, 1590; ν(NCS) 2098, 2095; $\nu(ClO_4)$ 1080, 622. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 120; UV–Vis ($\lambda$, nm): 720, 402.

2.4.3. Cadmium(II)azido complexes

A methanolic solution (5 cm^3) of bpfp (0.252 g, 1 mmol) was added dropwise to a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.311 g; 1 mmol) in the same solvent (10 cm^3) followed by NaN_3 (0.13 g, 2 mmol) in warm methanol (5 cm^3). The green solution was filtered and the supernatant liquid was kept in air for slow evaporation. After a few days **4a** was separated, washed with toluene and dried in vacuo over silica gel indicator. Yield: 0.113 g (70%). **5a** and **6a** were prepared by same procedure using bpmp and bpbp, respectively, instead of bpfp. *Anal.* calc. for $C_{15}H_{16}N_{10}Cd$ (**4a**): C, 40.18; H, 3.59; N, 31.24. Found: C, 40.14; H, 3.64; N, 31.26%. IR (KBr, cm^{-1}): ν(C=N) 1637,1592; $\nu(N_3)$ 2073, 2040. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5; UV–Vis ($\lambda$, nm): 335. *Anal.* calc. for $C_{17}H_{20}N_{10}Cd$ (**5a**): C, 42.85; H, 4.23; N, 29.40. Found: C, 42.80; H, 4.22; N, 29.42% IR (KBr, cm^{-1}): ν(C=N) 1635, 1592; $\nu(N_3)$ 2072, 2045. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5; UV–Vis ($\lambda$, nm): 336. *Anal.* calc. for $C_{27}H_{24}N_{10}Cd$ (**6a**): C, 53.99; H, 4.02; N, 23.32. Found: C, 53.95; H, 4.06; N, 23.35%. IR (KBr, cm^{-1}): ν(C=N) 1637, 1590; $\nu(N_3)$ 2073, 2040. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5. UV–Vis ($\lambda$, nm): 335.

2.4.4. Cadmium(II)thiocyanato complexes

A methanolic solution (5 cm^3) of bpbp (0.406 g, 1 mmol) was added dropwise to a solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.311 g; 1 mmol) in the same solvent (10 cm^3) followed by NH_4NCS (0.15 g, 2 mmol) in warm methanol (5 cm^3). The green solution was filtered and the supernatant liquid was kept in air for slow evaporation. After a few days **4b** was separated, washed with toluene and dried in vacuo over silica gel indicator. Yield: 0.242 g (72%). **5b** and **6b** were prepared in the same way using bpmp and bpbp. *Anal.* calc. for $C_{17}H_{16}N_6S_2Cd$ (**4b**): C, 42.48; H, 3.35; N, 17.48. Found: C, 42.47; H, 3.39; N, 17.43%. IR (KBr, cm^{-1}): ν(NCS) 2100, 2095; ν(C=N) 1605. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5; UV–Vis (MeOH; λ, nm): 330. *Anal.* calc. for $C_{19}H_{20}N_6S_2Cd$ (**5b**): C, 44.88; H, 3.96; N, 16.53. Found: C, 44.76; H, 3.92; N, 16.57%. IR (KBr, cm^{-1}): ν(C=N) 1635, 1592; ν(NCS) 2100, 2095. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5; UV–Vis ($\lambda$, nm): 335. *Anal.* calc. for $C_{29}H_{24}N_6Cd$ (**6b**): C, 55.06; H, 3.82; N, 13.28. Found: C, 55.08; H, 3.86; N, 13.31%. IR (KBr, cm^{-1}): ν(C=N) 1637, 1590; ν(NCS) 2100, 2095. Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5; UV–Vis ($\lambda$, nm): 332.

2.5. Copper(II)–copper(I) interconversion

2.5.1. [Cu(bpap)(N_3/NCS)]ClO_4 → [Cu(bpap)]ClO_4

To a methanolic suspension (15 cm^3) of the complexes [Cu(bpap)(N_3)]ClO_4 (0.14 g, 0.25 mmol), ascorbic acid (0.045 g, 0.25 mmol) in water (5 cm^3) was added with stirring. The brown suspension quickly changed to deep red-brown and stirring was continued for 30 min, and the precipitated mass was filtered, washed with water and cold methanol. The residue was dried over a $CaCl_2$ desiccator and subjected to column chromatography on a silica gel column prepared in $CHCl_3$. A brownish-red band was eluted by $CHCl_3$–MeOH (4:1, v/v) mixture and dried in air. Crystals were obtained by diffusion of a CH_2Cl_2 solution of the complex to a hexane layer. Yield: 54–57%. The microanalytical data of the complexes are as follows: *Anal.* calc. for [Cu(bpfp)]ClO_4: C, 43.43; H, 3.88; N, 13.50. Found: C, 43.40; H, 3.85; N, 13.49%. *Anal.* calc. for [Cu(bpmp)]ClO_4: C, 46.10; H, 4.55; N, 12.65. Found: C, 46.09; H, 4.54; N, 12.63%. *Anal.* calc. for [Cu(bpbp)]ClO_4: C, 45.48; H, 5.38; N, 12.48. Found: C, 45.47; H, 5.37; N, 12.47%.

2.5.2. [Cu(bpap)]ClO_4 → [Cu(bpap)(N_3/NCS)]ClO_4

To a methanolic suspension of [Cu(bpap)]ClO_4 (0.15 g, 0.25 mmol) an aqueous solution of NaN_3 (0.015 g, 0.25 mmol) was added, air was passed for through the solution for 30 min and from time to time methanol was added to maintain the volume of the solution at 25 ml. The mixture was filtered and kept in a freezer for 4 h. A brown precipitate was filtered and washed with water and cold methanol. The compound was soluble in a mixture of 2-methoxy ethanol and methanol (1:5, v/v) and crystallized by evaporation in air for a week. Yield: 55–60%. The microanalytical data are consistent with complexes **1a**–**3b**.

2.6. X-ray diffraction study

Suitable single crystals of compounds **3a** and **6b** were mounted on a SMART CCD area detector equipped with a graphite monochromotor and Mo Kα(λ = 0.71073) radiation. The intensity data were corrected for Lorentz and polarization effects for all the complexes. Diffraction data for both **3a** and **6b** were measured using the ϕ and ω scan method. The structures were solved by Patterson syntheses using SHELXS-97 [20] and followed by successive Fourier and difference Fourier syntheses. Full-matrix least-squares refinements on F^2 were carried out using SHELXL-97 [21] with anisotropic displacement parameters for all non-hydrogen atoms for the complexes. The hydrogen atoms were fixed geometrically and refined using a riding model. In the final difference Fourier map the residual maxima and minima were 0.395 and −0.262 e $Å^{-3}$ for **3a**, 0.812 and −0.395 e $Å^{-3}$ for **6b**, respectively. All calculations were carried out using PLATON 99 [22] and ORTEP-32 [23]. The crystal data, data collection parameters and the results of analyses of **3a** and **6b** can be found in Table 1.

3. Results and discussion

3.1. Synthesis and formulation

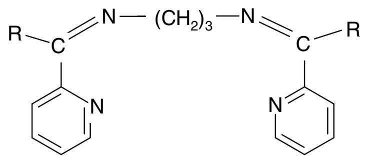
In a one-pot reaction the chelators, the Schiff bases, were prepared by the condensation of one equivalent of propane-1,3-diamine and two equivalents of pyridine-2-carboxyaldehyde/2-acetylpyridine/2-benzoylpyridine in dry alcohol (Scheme 1). The pentacoordinated mononuclear complexes [Cu(bpap)(N_3/NCS)]ClO_4 (**1a**–**3b**) initially formed in an MeOH solution containing a 1:1:2 mixture of $Cu(ClO_4)_2 \cdot 6H_2O$, bpap and NaN_3/NH_4NCS; a reactant ratio expected to yield a mononuclear species of the composition [Cu(pbpa)(N_3/NCS)$_2$]. However, microanalyses showed a 1:1:1 ratio of metal, blocking ligand and the pseudohalide, and in the IR spectra the presence of perchlorate bands was noticed. A reactant ratio corresponding to the product stoichiometry afforded better yields of [Cu(bpap)(N_3/NCS)]ClO_4 (**1a**–**3b**). In an effort to get [Cu(bpap)(N_3/NCS)$_2$], the starting material was changed to $Cu(NO_3)_2 \cdot 4H_2O$, and a 1:1:2 molar ratio of nitrate salt, ligand and the pseudohalide produced a gummy mass of indefinite composition. The hexacoordinated mononuclear complexes (**4a**–**6b)** were obtained starting with a 1:1:2 molar ratio of cadmium perchlorate/metal nitrate, bpap and azide/thiocyanate, and conformed in the IR spectra to the absence of perchlorate and/or nitrate bands. The air-stable moisture-insensitive complex salts are highly soluble in common organic solvents like methanol, ethanol, dichloromethane, acetonitrile and dimethylformamide but are insoluble in water. All the complexes were characterized by elemental analysis, electrical conductivity, IR, UV–Vis and reflectance spectra, luminescence behaviour and also magnetic susceptibility, and electrochemistry for the complexes **1a**–**3b**. The results are consistent with the proposed mononuclear formulation. In methanol solutions **1a**–**3b** behave as 1:1 electrolytes [24] as reflected in their Λ_M values (ca. 130 Ω^{-1} cm^2 mol^{-1}) but **4a**–**6b** behave as non-electrolytes as is evident from their low conductivity values (ca. 5 Ω^{-1} cm^2 mol^{-1}). Room-temperature solid-phase magnetic susceptibility measurements show that the copper(II) complexes have magnetic moments close to the spin-only value (S = 1/2), 1.73 BM, as expected from discrete and magnetically non-coupled mononuclear $3d^9$ ions.

3.2. Spectral studies

In the IR spectra, the point of interest is the band due to the azide and thiocyanate in the complexes.

Table 1
Crystal data and structure refinement parameters for **3a** and **6b**

	3a	**6b**
Empirical formula	$C_{27}H_{24}N_7O_4ClCu$	$C_{29}H_{24}N_6S_2Cd$
Formula weight	609.52	633.06
Temperature (K)	296(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, *Cc*	triclinic, $P\bar{1}$
a (Å)	22.288(2)	7.8480(5)
b (Å)	12.1157(12)	13.7073(8)
c (Å)	10.1279(10)	14.7229(9)
α (°)	90	62.9370(10)
β (°)	102.636(2)	75.9040(10)
γ (°)	90	83.8340(10)
V (Å^3)	2668.6(5)	1367.92(14)
Z	4	2
D_{calc} (Mg m^{-3})	1.517	1.537
μ (mm^{-1})	0.967	0.981
F(000)	1252	640
Crystal size (mm^3)	0.36 × 0.20 × 0.14	0.38 × 0.30 × 0.25
θ ranges (°)	1.87–28.34	1.59–28.27
$h/k/l$	−29.22/−9.16/−11.12	−10.10/−18.18/−18.19
Reflections collected	7742	14194
Independent reflections [R_{int}]	4844 [0.0242]	6395 [0.0310]
Completeness to θ (%)	89.8	94.2
T_{max} and T_{min}	0.8693 and 0.7081	0.783 and 0.709
Data/restraints/parameters	4844/2/361	6395/0/343
Goodness-of-fit on F^2	0.995	1.000
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0555$, $wR_2 = 0.1727$	$R_1 = 0.0295$, $wR_2 = 0.0734$
R indices (all data)	$R_1 = 0.0639$, $wR_2 = 0.1821$	$R_1 = 0.0347$, $wR_2 = 0.0363$
Largest peak and hole (e Å^{-3})	0.395 and −0.262	0.812 and −0.395



R = H, bpfp; R = Me, bpmp; R = Ph, bpbp

Scheme 1.

The spectra exhibit a very strong and sharp absorption band at 2040–2080 cm^{-1} due to asymmetric stretching vibrations [25] of the terminal azide. The presence of ionic perchlorate bands at 1091 and 621 cm^{-1} is noticed for **1a**–**3b**. The complexes **4a**–**6b** show a characteristic strong transmission at 2098–2105 cm^{-1} along with a weak band at 2090–2093 which correspond to $\nu_{asym}(NCS^-)$. The stretching vibrations of the (C=N) band of the Schiff base are seen at 1629 and 1589 cm^{-1}. All other characteristic ligand vibrations are seen in the range 1600–600 cm^{-1}. The solutions of **1a**–**3b** in MeOH are dark green and exhibit absorptions at ca. 720, 400 nm. The transition >700 nm corresponds to a d–d transition of the copper(II) moiety and the band around 400 nm to intramolecular ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$) charge transfer transitions [26]. The solutions of the complexes **4a**–**6b** in MeOH are colourless and exhibit absorptions at ca. 330 nm. Reflectance spectra in nujol and electronic spectra in MeOH solutions are akin in each complex, reflecting similar gross structure and electronic structure in the solid state and in solution.

3.3. Electrochemical studies for the copper(II) complexes

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

$$[\mathrm{Cu^{II}(L)(N_3)}]^{1+} + \mathrm{e} \rightleftharpoons [\mathrm{Cu^{I}(L)(N_3)}] \qquad (1)$$

The electrode process in the CV is reproducible in the potential range of 0.08 to −0.08 V with no trace of decomposition as reflected in smooth cyclic voltammograms. The one-electron stoichiometry of couple 1 was confirmed by a comparison of the current height with that of a standard [27] copper(II)–copper(I) couple, since attempted coulometry at potentials more cathodic than E_{pc} gave a continuous coulomb count due to some unidentified side reactions [28]. The similar pattern in the electron transfer behaviour of all the complexes at about the same potential once again corroborates a similar structure of the cationic units.

3.4. Luminescence properties

Complexes with bpap shows an intense absorption at ca. 405 nm which is assigned to intraligand π–π* transitions. The emission energy of the complexes in MeOH solutions at 298 K is almost same ($\lambda_{\max} \approx 475$ nm) and is assignable to intraligand fluorescence [11]. The lifetimes of the complexes are in range 2.55–2.63 ns. In glassy solutions (MeOH at 77 K) both fluorescence and ^{3}(π–π*) phosphorescence is observed at 525 nm. In the solid state they show a distinct emission band at 492 nm, differing from their fluorescence spectra in MeOH (Fig. 3).

3.5. X-ray crystal structure

3.5.1. [Cu(bpbp)(N$_3$)]ClO$_4$ (**3a**)

In order to define the coordination sphere, a single-crystal X-ray diffraction study was made in one case, viz **3a**. An ORTEP diagram with the atom numbering scheme of the mononuclear unit in **3a** is shown in Fig. 1. Selected interatomic bond lengths and bond angles are listed in Table 2. The crystal lattice consists of [Cu(bpbd)(N$_3$)]$^+$ cations and ClO$_4^-$ anions. The coordination polyhedron around the metal centre is best described as distorted trigonal bipyramid (tbp) with a CuN$_5$ chromophore. The coordination includes a tetradentate Schiff base (bpbp), a chelating blocker ligated by two pyridine nitrogens (N5, N7) and two imine nitrogens (N4, N6), and one terminal azide nitrogen (N1). The equatorial positions are occupied by one imine nitrogen (N6), one pyridine nitrogen (N7) and the azide nitrogen (N1) while the axial positions are occupied by the remaining imine (N5) and pyridine (N4) nitrogen atoms. The distortion from ideal tbp geometry is due to the asymmetric nature of the Schiff base and the deviations of the refine angles (90°/120°) formed at the metal centre. The propylenic part of the Schiff base N4–C27–C26–C25–N6 is to some extent puckered due to sp^3 hybridization of the saturated portion of the chelating ligand and deviation [114.6(6)°] from the ideal bond C27–C26–C25 angle of 109°28′ (Fig. 1). The equatorial Cu–N distances [2.005(5)–2.101(5) Å] as well as the bond angles [93.2(2)–133.98(19)°] show significant variations. The axial Cu–N distances [Cu–N4 1.978(4) Å, Cu1–N5 1.994(5) Å] are however close and these are the smaller bond distances than the three equatorial bond distances [9]. The three bite angles N4–Cu–N7, N4–Cu–N6 and N6–Cu–N5 are 79.83(19)°, 92.14(19)° and 80.3(2)°, respectively. The larger bite in N4–Cu–N6 arises due to a six-membered puckered loop formed from the propylenic arm and the lower value of the non-bite angle N5–Cu–N7 [100.6(2)°]. The axial bond angle, N4–Cu–N5 [170.0(2)°], deviates from the ideal value (180°). The sum (359.88°) of the equatorial angles N6–Cu–N7 [133.98(19)°], N1–Cu–N6 [132.7(2)°] and N1–Cu–N7 [93.20(2)° are very close to 360.00°; so the atoms N1, N6, N7 and Cu are almost the same plane. In the terminal azide ligand the N1–N2 distance [1.170(9) Å] is longer than the N2–N3 length [1.152(10) Å] which indicates that the nitrogen (N1) atom of N$_3^-$ is coordinated to the copper(II) centre. The N$_3^-$ ion is coordinated in a linear fashion as seen from its N1–N2–N3 angle [179.0(8)°] [8,10b].

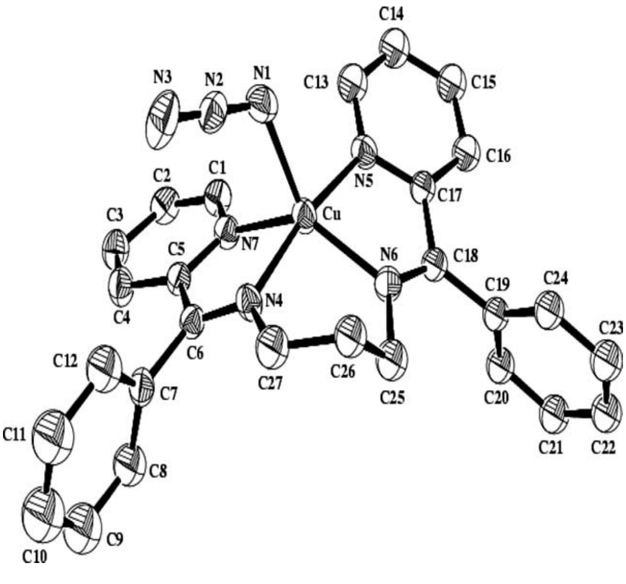


Fig. 1. ORTEP diagram of [Cu(bpbp)(N$_3$)]ClO$_4$ (**3a**) with the atom numbering scheme and 40% probability ellipsoids for all non-hydrogen atoms.

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

Bond distances	
Cu–N(4)	1.978(4)
Cu–N(5)	1.994(5)
Cu–N(7)	2.101(5)
N(2)–N(3)	1.152(10)
Cu–N(6)	2.005(5)
Cu–N(1)	2.077(6)
N(1)–N(2)	1.170(9)
Bond angles	
N(4)–Cu–N(5)	170.0(2)
N(4)–Cu–N(6)	92.14(19)
N(5)–Cu–N(1)	95.8(2)
N(5)–Cu–N(6)	80.3(2)
N(4)–Cu–N(1)	94.1(2)
N(6)–Cu–N(1)	132.7(2)
N(4)–Cu–N(7)	79.83(19)
N(5)–Cu–N(7)	100.6(2)
N(6)–Cu–N(7)	133.98(19)
N(1)–Cu–N(7)	93.2(2)
N(2)–N(1)–Cu	118.1(5)
N(3)–N(2)–N(1)	179.0(8)

3.5.2. [Cd(bpbp)(NCS)$_2$] (**6b**)

An ORTEP view with the atom numbering scheme of the mononuclear unit in **6b** is shown in Fig. 2. Selected bond lengths and angles relevant to the coordination sphere are listed in Table 3. The metal centre is best described as a distorted octahedron with a CdN$_6$ chromophore. Distortion from the ideal octahedral geometry is due to the asymmetric nature of the bound tetradentate Schiff base and the deviations of the refine angles (90°/180°) formed at the metal centre (Table 3). The coordination includes the Schiff base ligated by two pyridine nitrogens (N3, N6) and two imine nitrogens (N4, N5), and two nitrogens (N1, N2) of the thiocyanates. The equatorial positions are occupied by the four nitrogen atoms (N3, N4, N5 and N6) of the tetradentate ligand while the nitrogens (N1, N2) of the isothiocyanato groups are placed at the axial positions. The propylenic part of the Schiff base N5–C17–C16–C5–N4 is to some extent puckered due to sp^3 hybridization of the saturated portion of the chelating ligand and deviation [119.1(2)°] from the ideal C15–C16–C17 bond angle of 109°28′. The four N atoms of the ligand creates hardness in the cadmium(II) centre; so it appears to be a major reason to have preferential N-donation of the ambidentate NCS through its electronegative hard centre. The degrees of distortion from an ideal octahedral (90°) geometry are reflected in the *cisoid* [69.42(6)–119.35(8)°] and the *transoid* angles [141.03(7)–160.23(8)°]. Within the equatorial plane the Cd–N distances are in the range [2.271(2)–2.4486(18) Å], comparable to the corresponding values in similar systems [11]. Axial Cd–N distances [2.301(2)–2.4376(19) Å] indicate stronger coordination of the anionic isothiocyanate over the neutral Schiff base [17]. The angles subtended by the ligand around cadmium in the equatorial plane shows a significant variation [69.42(6)–119.35(8)°] from the ideal 90.00°. The *trans* N2–Cd–N6 angle has a value [160.23(8)°], not close to the ideal value of 180.00°. The angles N1–Cd–N3, N3–Cd–N4 and N4–Cd–N5 in the equatorial plane with values 94.37(8)°, 69.42(6)° and 80.53(6)° are much less than the N1–Cd–N5 angle [119.35(8)°], where N3, N6 belong to the two pyridine ends of the Schiff base. Both the isothiocyanate ligands

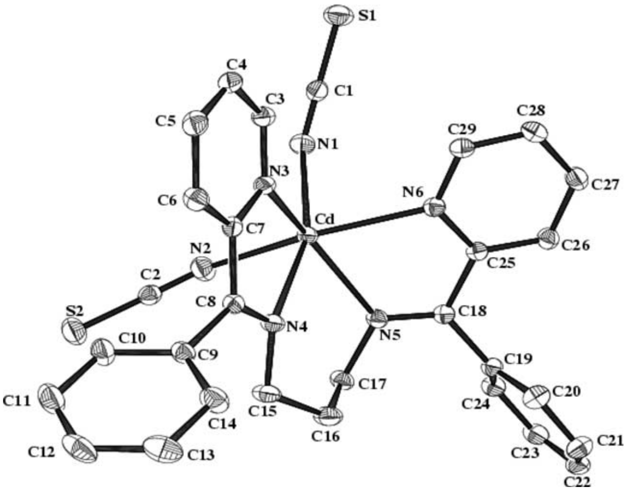


Fig. 2. ORTEP plot of [Cd(bpbp)(NCS)$_2$] (**6b**) with the atom numbering scheme and 40% probability ellipsoids for all non-hydrogen atoms.

Table 3
Selected bond distances (Å) and angles (°) for **6b**

Bond distances	
Cd–N(3)	2.3429(18)
Cd–N(6)	2.4376(19)
Cd–N(1)	2.271(2)
Cd–N(4)	2.4486(18)
S(1)–C(1)	1.620(3)
Cd–N(2)	2.301(2)
Cd–N(5)	2.3157(19)
S(2)–C(2)	1.621(3)
N(1)–C(1)	1.161(3)
N(2)–C(2)	1.158(3)
Bond angles	
N(3)–Cd–N(1)	94.37(8)
N(5)–Cd–N(1)	119.35(8)
N(3)–Cd–N(2)	100.70(8)
N(5)–Cd–N(2)	98.02(8)
N(1)–Cd–N(2)	90.63(9)
N(5)–Cd–N(6)	69.48(6)
N(3)–Cd–N(6)	98.44(6)
N(1)–Cd–N(4)	159.36(8)
N(6)–Cd–N(5)	82.97(7)
N(3)–Cd–N(5)	141.03(7)
N(2)–Cd–N(6)	160.23(8)
N(2)–Cd–N(4)	80.39(8)
N(5)–Cd–N(4)	80.53(6)
N(3)–Cd–N(4)	69.42(6)
N(6)–Cd–N(4)	111.25(6)
N(1)–C(1)–S(1)	179.2(3)
N(2)–C(2)–S(2)	179.2(3)

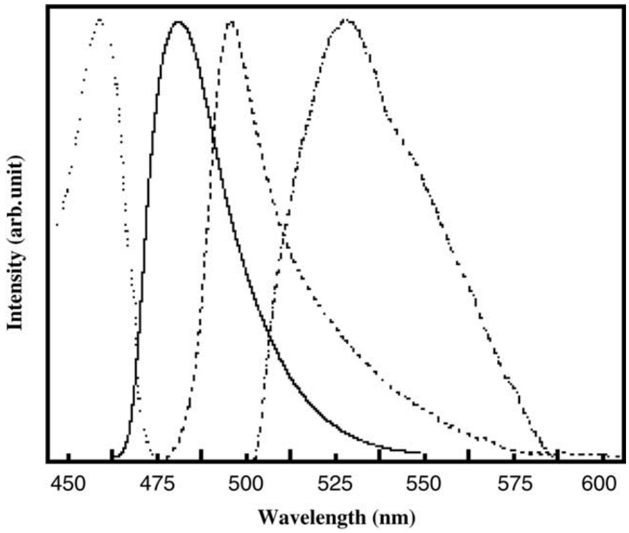


Fig. 3. Emission spectra of **3a**: fluorescence (—), phosphorescence in DMF glassy solution (-·-·-·), solid state at 298 K (-----).

are almost linear with exact 179.2(3)° angles. N–C [1.158(3)–1.161(3) Å] and C–S [1.620(3)–1.621(3) Å] bond lengths are as expected for N-coordination [11]. All the other bond lengths and angles on the ligand network are close to the expected values [6a].

4. Conclusion

Twelve new complexes are prepared in combination with tetradentate Schiff bases as blockers. In all cases a chelation mode of the Schiff bases is noticeable. The compounds are new example of luminous materials. We are now investigating the congregation [8] behaviour of related tetradentate N-donor Schiff bases with tailoring on the propylenic arm as well as acidic proton(s) on the ligand network towards the preparation of coordination polymers and supramers of varied molecular and crystalline architectures, which may behave as better luminous materials.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre Nos. 260089 for **3a** and 260090 for **6b**. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44 1223 336 033; e-mail: deposit @ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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