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Syntheses, X-ray structures and properties of a dinuclear cadmium(II)azido and a polymeric cadmium(II)thiocyanato compounds containing bis(tridentate) congregators

Habibar Chowdhury, Rajarshi Ghosh, Sk. Hafijur Rahaman, Barindra Kumar Ghosh *

Department of Chemistry, The University of Burdwan, Burdwan 713 104, India

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Abstract

One-pot reactions of cadmium(II) perchlorate/nitrate, Schiff bases (pbap/pfap) and pseudohalides (sodium azide/ammonium thiocyanate) in a 2:1:4 molar ratio in MeOH–MeCN solvent mixtures at room temperature result in a dinuclear compound $[Cd_2(pbap)(OH_2)_2(N_3)_4]$ (1) $[pbap = N-(1-pyridin-2-ylbenzylidene)-N-[2-(4-{2-[(1-pyridin-2-ylbenzylidene)amino]ethyl}piperazin-1-yl)ethyl]amine] and a poly$ $meric compound <math>[Cd_2(pfap)(\mu_{1,3}-NCS)(\mu_{1,3}-SCN)(NCS)_2]_n$ (2) $[pfap = N-(1-pyridin-2-ylformylidene)-N-[2-(4-{2-[(1-pyridin-2ylformylid$ $ene)amino]ethyl}piperazin-1-yl)ethyl]-amine]. X-ray crystal structural analyses reveal a bis(tridentate) congregation behaviour of the$ hexadentate blocker (pbap/pfap) encapsulating two metal centers. Each cadmium(II) center in 1 and 2 is in a distorted octahedral geometrywith CdN₅O and CdN₅S chromophores, respectively. In 1, the dinuclear units participate in intermolecular O–H···N hydrogen bonding $between bound water O atoms and terminal azide N atoms, in combination with C–H···<math>\pi$ interactions, resulting in a 3D supramolecular network with an intramolecular Cd···Cd distance of 6.473(2) Å. In the crystal lattice, the covalent 1D chain of 2 is further engaged in face-to-face $\pi \cdots \pi$ interactions from two terminal pyridine rings, which stabilizes the chain with an intradimer Cd···Cd separation of 6.640(5) Å. Both the complexes display intraligand ${}^1(\pi-\pi^*)$ fluorescence and intraligand ${}^3(\pi-\pi^*)$ phosphorescence in glassy solutions. © 2007 Published by Elsevier Ltd.

Keywords: Cadmium(II) azide/thiocyanate; Bis(tridentate) Schiff base; Superstructure; Luminescence

1. Introduction

The construction [1] of metal–organic coordination frameworks has been extensively examined for the preparation of functional materials [2–4] of different shapes and sizes [5] through control and manipulation of metal–ligand covalent bonds [6] with malleable coordination spheres and multiple lateral non-covalent forces like hydrogen bonding [7], $\pi \cdots \pi$ [8] and C–H $\cdots \pi$ [9] interactions. Self-assembly [10] of the building components, such as metal–ion templates, organic blockers and bridging units, is an effective approach to construct such frameworks. We are interested [11,12] in this approach in the construction of functional polymers through variation of ligand backbones and metal-ion coordination environments. Pseudohalides [13] have long been known for their versatile coordination modes. Schiff bases [14] are useful blockers because of their preparative accessibilities, structural varieties and varied denticities. The investigation of polynuclear complexes of cadmium(II) is an important objective because of study of the electronic and optoelectronic properties [15] of this 4d¹⁰ metal ion. This work stems from our interest to prepare different coordination polymers of cadmium(II) in combination with pseudohalides and Schiff bases. In this paper we report the synthesis, characterization, structure

^{*} Corresponding author. Tel.: +91 342 2533913; fax: +91 342 2530452. *E-mail address:* barin_1@yahoo.co.uk (B.K. Ghosh).

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and luminescence behaviour of a dinuclear compound of the type $[Cd_2(pbap)(OH_2)_2(N_3)_4]$ (1) [pbap = N-(1-pyri $din-2-ylbenzylidene)-N-[2-(4-{2-[(1-pyridin-2-ylbenzy$ $lidene)amino]ethyl}piperazin-1-yl)ethyl]amine (Scheme$ $1)] and a polymeric compound of the type <math>[Cd_2(pfap)-(\mu_{1,3}-NCS)(\mu_{1,3}-SCN)(NCS)_2]_n$ (2) [pfap = N-(1-pyridin-2 $ylformy-lidene)-N-[2-(4-{2-[(1-pyridin-2ylformy-lid$ $ene)amino]ethyl}piperazin-1-yl)ethyl]amine (Scheme 1)]$ in combination with tailored hexadentate N-donor Schiffbases (pbap/pfap) and azide/thiocyanate.

2. Experimental

2.1. Materials

High purity 2-benzoylpyridine (Fluka, Germany), pyridine-2-carboxaldyde (Fluka, Germany), 2-[4-(2-aminoethyl)piperazin-1-yl]ethylamine (Aldrich, USA), sodium azide (Aldrich, USA), ammonium thiocyanate (E. Merck, India) and cadmium(II) nitrate tetrahydrate (E. Merck, India) were purchased from the respective concerns and were used as received. Cadmium(II) perchlorate hexahydrate was prepared by treatment of cadmium(II) carbonate (E. Merck, India) with perchloric acid (E. Merck, India) followed by slow evaporation on steam-bath, filtration through a fine glass-frit and preservation in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent use. All other chemicals and solvents were AR grade and were used as received.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were measured using a Perkin–Elmer 2400 CHNS/O elemental analyser. 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 DMF was used as the solvent. Thermal analysis was recorded using a Perkin–Elmer Diamond TG/DTA system under a flow of nitrogen (30 ml min⁻¹). The sample was heated at a rate of 10 °C min⁻¹ with inert alumina as a reference. 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. Timeresolved 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.

2.3. Preparation of the Schiff bases

2.3.1. N-(1-Pyridin-2-ylbenzylidene)-N-[2-(4-{2-[(1pyridin-2-ylbenzylidene)amino]ethyl}piperazin-1yl)ethyl]amine (pbap)

2-[4-(2-Aminoethyl)piperazin-1-yl]ethylamine (0.172 g, 1 mmol) with 2-benzoylpyridine (0.366 g, 2 mmol) was refluxed in dehydrated alcohol in a 1:2 molar ratio. After 10 h reflux the reaction solution was evaporated under reduced pressure to a gummy mass, which was dried and stored *in vacuo* over CaCl₂ for subsequent use; yield, 1.928 g (70%). IR (KBr disc, cm⁻¹): v(C=N) 1594. UV–Vis (λ_{max} , nm): 245, 293.

2.3.2. N-(1-Pyridin-2-ylformylidene)-N-[2-(4-{2-[(1pyridin-2ylformylidene)amino]ethyl}pipera-zin-1yl)ethyl]amine (pfap)

2-[4-(2-Aminoethyl)piperazin-1-yl]ethylamine (0.172 g, 1 mmol) and pyridine-2-carboxaldyde (0.214 g, 2 mmol) were mixed together and refluxed in anhydrous ethanol (25 cm³) for 10 h. The yellowish brown solution that resulted was concentrated on a steam bath and dried *in vacuo* over CaCl₂ to a yellowish brown semi-solid for subsequent use. Yield: 1.525 g (75%). IR (KBr disc, cm⁻¹): v(C=N) 1592. UV–Vis (λ_{max} , nm): 242, 290.

2.4. Preparation of the complexes

2.4.1. $[Cd_2(pbap)(OH_2)_2(N_3)_4]$ (1)

Pbap (0.476 g, 1 mmol) dissolved in methanol (20 cm³) was added to an acetonitrile solution (20 cm³) of cadmium perchlorate hexahydrate (0.622 g, 2 mmol) with continuous stirring. To this, a methanolic solution (20 cm³) of sodium azide (0.260 g, 4 mmol) was added. The resulting light yellow solution was filtered and kept for slow evaporation. After 7 days colourless crystals were separated, washed with toluene and dried *in vacuo* over silica gel indicator. Yield: 0.823 g (50%). *Anal.* Calc. for $C_{32}H_{38}N_{18}O_2Cd_2$ (1): C, 41.3; H, 4.0; N, 27.0. Found: C, 41.2; H, 4.1; N, 27.1%. IR (KBr, cm⁻¹): $v(N_3)$ 2070; v(OH) 3300–3500 (broad). UV–Vis (λ , nm) 340. Λ_M (MeOH, Ω^{-1} cm² mol⁻¹): 5.

2.4.2. $[Cd_2(pfap)(\mu_{1,3}-NCS)(\mu_{1,3}-SCN)(NCS)_2]_n$ (2)

An acetonitrile solution (5 cm³) of pfap (0.175 g, 1 mmol) was added dropwise to a solution of Cd(NO₃)₂ · 4H₂O (0.308 g, 2 mmol) in methanol (5 cm³). NH₄NCS (0.152 g, 4 mmol) in methanol (5 cm³) was added slowly to this solution. The resultant solution was filtered and kept for slow evaporation. After 5 days **2** was separated, washed with methanol and dried *in vacuo* over CaCl₂. Yield: 1.570 g (60%). *Anal*. Calc. for C₂₄H₂₆N₁₀S₄Cd₂ (**2**): C, 35.7; H, 3.2;

N, 17.4. Found: C, 35.8; H, 3.3; N, 17.3%. IR (KBr, cm⁻¹): $v_{as}(SCN)$ 2105, 2125. UV–Vis (λ , nm) 312. Λ_M (MeOH, Ω^{-1} cm² mol⁻¹): 5.

2.5. Crystallographic data collection and refinement

Single-crystals suitable for X-ray work were grown by slow evaporation of a methanol–acetonitrile solution of **1** and **2** at 298 K [crystal size: **1**, $0.10 \times 0.10 \times 0.07 \text{ mm}^3$; **2**, $0.12 \times 0.05 \times 0.05 \text{ mm}^3$]. Data were collected on a Siemens SMART CCD area diffractometer equipped with a graphite-monochromator Mo K α radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was employed using the SAINT [16] and SADABS [17] programs for the crystals. Diffraction data for the crystals were measured using the φ - and ω -scan techniques. Systematic absence led to the identification of space groups P2(1)/cfor **1** and C2/c for **2**. A summary of the crystallographic data and structure refinement parameters are given in Table 1.

Table 1

Compound	1	2
Empirical formula	C ₃₂ H ₃₈ N ₁₈ O ₂ Cd ₂	C24H26N10S4Cd2
Formula weight	931.60	807.59
Temperature (K)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P2(1)/c	C2/c
a (Å)	14.7967(13)	27.549(3)
b (Å)	10.4236(9)	7.8073(8)
<i>c</i> (Å)	12.4202(10)	14.6330(15)
β (°)	100.515(2)°	106.758(2)
$V(\text{\AA}^3)$	1883.5(3)	3013.6(5)
Ζ	2	4
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.643	1.780
$\mu (mm^{-1})$	1.186	1.722
<i>F</i> (000)	936	1600
Crystal size (mm)	$0.10\times0.10\times0.07$	$0.12\times0.05\times0.05$
θ Ranges (°)	2.40 to 28.27	2.72 to 26.64
h/k/l	-19,15/-11,13/	-35,35/-10,8/
	-16, 16	-18, 18
Reflections collected	11 344	3523
Independent reflections (R_{int})	4325 (0.0421)	2381 (0.0641)
Completeness to theta	92.6 (28.27°)	91.5 (28.27°)
Data/restraints/ parameters	4325/0/252	2381/0/181
$T_{\rm max}$ and $T_{\rm min}$	1.000 and 0.794	1.000 and 0.805
Goodness-of-fit on F^2	1.011	0.996
Final R indices	$R_1 = 0.0379,$	R = 0.0476,
$[I \ge 2\sigma(I)]$	$wR_2 = 0.0794$	$wR_2 = 0.1003$
R indices (all data)	$R_1 = 0.0510,$	R = 0.0767,
	$wR_2 = 0.0843$	$wR_2 = 0.1107$
Largest peak and hole $(a \mathring{A}^{-3})$	0.934 and -0.355	1.04 and -0.42

Weighting Scheme: $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)_2 / \sum w(F_o^2)^2]^{1/2}$, Calc. $w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.0000P]$ for 1 and $w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.0000P]$ for 2 where $P = (F_o^2 + 2F_c^2)/3$.

The structures were solved by direct methods and the structure solution and refinement were based on $|F|^2$. Of the 11344 (1) and 3523 (2) reflections, 4325 and 2381 with $I > 2\sigma(I)$ were used for the structure solution. 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 residual were $R_1 = 0.0379$ (1) and 0.0476 (2); $wR_2 = 0.0794$ (1) and 0.1003 (2) with $I > 2\sigma(I)$, goodnessof-fit = 1.011 (1) and 0.996 (2). The final differences Fourier map showed the maximum and minimum peak heights of 0.934 and -0.355 e Å⁻³ for 1, and 1.04 and -0.42 e Å⁻³ for 2. All crystallographic calculations were conducted with SHELXL-97 [18], ORTEP-32 [19] and PLATON [20] programs.

3. Results and discussion

3.1. Synthesis and formulation

The Schiff bases, *N*-(1-pyridin-2-ylbenzylidene)-*N*-[2-(4-{2-[(1-pyridin-2-ylbenzylidene)amino]ethyl}piperazin-1yl)ethyl]amine (pbap) or *N*-(1-pyridin-2-ylformylidene)-*N*-[2-(4-{2-[(1-pyridin-2-ylformylidene)amino]ethyl}piperazin-1-yl)ethyl]amine (pfap) were synthesized by refluxing 2-[4-(2-aminoethyl)piperazin-1-yl]ethylamine (1 mol) with 2-benzoylpyridine or pyridine-2-carboxaldehyde (2 mol) in dehydrated alcohol. The reaction of cadmium(II) chlorate hexahydrate/cadmium(II) nitrate tetrahydrate, pbap/ pfba and sodium azide/ammonium thiocyanate in a 2:1:4 molar ratio in MeOH–MeCN solvent mixture at room temperature results in a dimeric and a polymeric compound, as shown in Eqs. (1) and (2):

$$2 \operatorname{Cd}(\operatorname{ClO}_{4})_{2.6}\operatorname{H}_{2}\operatorname{O} + \operatorname{pbap} + 4 \operatorname{NaN}_{3} \xrightarrow{\text{MeOH-MeCN}} 298 \operatorname{K} \\ [\operatorname{Cd}_{2}(\operatorname{pbap})(\operatorname{OH}_{2})_{2}(\operatorname{N}_{3})_{4}] + 4 \operatorname{NaClO}_{4} + 10 \operatorname{H}_{2}\operatorname{O} \\ (1) \\ (1) \\ 2n \operatorname{Cd}(\operatorname{NO}_{3})_{2.4}\operatorname{H}_{2}\operatorname{O} + n \operatorname{pfap} + 4n \operatorname{NH}_{4}\operatorname{SCN} \xrightarrow{\text{MeOH-MeCN}} 298 \operatorname{K} \\ \xrightarrow{\text{Col}(\operatorname{NO}_{3})_{2.4}\operatorname{H}_{2}\operatorname{O} + n \operatorname{pfap} + 4n \operatorname{NH}_{4}\operatorname{SCN} \xrightarrow{\text{Col}(\operatorname{NO}_{3})_{2.4}\operatorname{H}_{2}\operatorname{O} + n \operatorname{Pfap} + 4n \operatorname{NH}_{4}\operatorname{NO} \xrightarrow{\text{Col}(\operatorname{NO}_{3})_{2.4}\operatorname{H}_{2}\operatorname{O} + n \operatorname{Pfap} \xrightarrow{\text{Col}(\operatorname{NO}_{3})_{2.4}\operatorname{H}_{2}\operatorname{O} + n \operatorname{Pfap} +$$

$$\label{eq:cd2} \begin{array}{l} [Cd_2(pfap)(\mu_{1,3}\text{-}NCS)(\mu_{1,3}\text{-}SCN)(NCS)_2]_n + 4n \ NH_4NO_3 + 8n \ H_2O \\ (2) \end{array}$$

(2)

The air-stable, moisture-insensitive compounds are powders, soluble in a range of common organic solvents such as methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulfoxide, but insoluble in water. Microanalytical (C, H and N) results and spectroscopic data are useful to formulate the product. In methanolic solution they behave as non-electrolytes, as reflected from their low conductivity values ($\sim 5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). In the IR spectra, **1** shows a strong absorption band at 2070 cm⁻¹, which is assignable to the stretching vibration of the terminal azide $v(N_3)$, and also shows a broad band in the region 3300–3500 cm⁻¹ due to v(O-H), indicating the presence of the coordinated water molecules [21]. Two strong peaks at 2125 and 2105 cm⁻¹, assignable to $v_{as}(SCN)$ stretching vibrations of the thiocyanate [21], are observed for 2. The position ($\geq 2100 \text{ cm}^{-1}$) and number of signals strongly suggest a mutual cis alignment as well as N- and S-coordination of the bound thiocyanates. The solutions are colourless and exhibit absorptions at 340 nm for 1 and 312 nm for 2. Reflectance (in Nujol) and electronic (in MeOH solution) spectra are akin in each complex, reflecting a similar gross structure and electronic structure in the solid state and in solution. The transition may correspond to an intramolecular $n-\pi^*/\pi-\pi^*$ charge transfer [22]. According to the thermal study (TG-DTA), compound 1 upon heating loses two molecule of water at \sim 140 °C, suggesting that the water molecules are involved in coordination and in strong hydrogen bonding interactions.

3.2. X-ray crystal structures

3.2.1. Crystal structure of $[Cd_2(pbap)(OH_2)_2(N_3)_4]$ (1)

The dinucleating hexadentate character or alternatively bis(tridentate) view of the ligand and two pairs of donor set arrangements through the incorporation of the ring within the bridge, is clearly evident and is shown in Fig. 1. Relevant bond distances and bond angles in 1 are listed in Table 2. C–H··· π and O–H···N hydrogen bondings leading to the superstructure formation are shown in Figs. 2–5. The structure of **1** is a centrosymmetric dimer linked by the bis(tridentate) congregator. Cd(1) is surrounded by two terminal azide nitrogen atoms [N(4),N(7)], one coordinated water molecule [O(1)] and three N atoms [N(1), N(2), N(3)] of the new Schiff base ligand (pbap), whereas the neighboring Cd(1A) is ligated to the other three N donor set atoms [N(1A), N(2A), N(3A)] of the same pbap ligand, completing its bis(tridentate) mode, two terminal azides [N(4A), N(7A)] and one water [O(1A)]molecule. The basal dimeric plane consists of a six N-donor set of the congregator and two terminal azide nitrogen atoms, while the axial coordination sites of each cadmium center are occupied by an azide nitrogen [N(4)/N(4A)] and the coordinated water [O(1)/O(1A)]. The cadmium(II) centers are six-coordinate (CdN₅O) with a substantial departure from an ideal octahedral geometry [cisoid angles:



Fig. 1. Thermal ellipsoid plot of the dinuclear $[Cd_2(pbap)(OH_2)_2(N_3)_4](1)$ with the atom labelling scheme and 20% probability ellipsoids for all non-hydrogen atoms.

Table 2	
Selected bond distances (Å) and angles (°) for 1 and 2	

Compound 1		Compound 2	
Bond distances (Å)			
Cd(1)–N(1)	2.414(3)	Cd(1)-N(1)	2.387(5)
Cd(1)-N(2)	2.335(3)	Cd(1)–N(2)	2.250(5)
Cd(1)-N(3)	2.459(2)	Cd(1)–N(3)	2.524(4)
N(4)-N(5)	1.181(4)	Cd(1)–N(4)	2.295(4)
N(5)-N(6)	1.149(5)	Cd(1)–N(5)	2.395(4)
Cd(1)–N(4)	2.335(3)	Cd(1)-S(1)	2.6161(14)
Cd(1)-N(7)	2.243(3)	N(2)-C(2)	1.121(7)
Cd(1)-O(1)	2.317(2)	C(2)–S(2)	1.624(5)
N(7)-N(8)	1.181(4)		
N(8)-N(9)	1.148(4)		
Bond angles (°)			
N(1)-Cd(1)-N(2)	68.88(9)	N(1)-Cd(1)-N(2)	177.80(18)
N(1)-Cd(1)-N(3)	141.95(9)	N(1)-Cd(1)-N(3)	89.13(14)
N(1)-Cd(1)-N(4)	89.73(10)	N(1)-Cd(1)-N(4)	81.86(15)
N(1)-Cd(1)-N(7)	95.24(10)	N(1)-Cd(1)-N(5)	87.39(15)
N(1)-Cd(1)-O(1)	93.14(9)	N(1)-Cd(1)-S(1)	93.77(11)
N(2)-Cd(1)-N(3)	93.14(9)	N(2)-Cd(1)-N(3)	88.70(16)
N(2)-Cd(1)-N(4)	87.95(10)	N(2)-Cd(1)-N(4)	97.85(16)
N(2)-Cd(1)-N(7)	164.12(10)	N(2)-Cd(1)-N(5)	94.57(16)
N(2)-Cd(1)-(O1)	96.42(10)	N(2)-Cd(1)-S(1)	86.78(12)
N(3)-Cd(1)-N(7)	122.47(10)	N(3)-Cd(1)-N(4)	73.24(15)
N(3)-Cd(1)-N(4)	93.38(9)	N(3)-Cd(1)-N(5)	143.66(14)
N(3)-Cd(1)-O(1)	86.56(9)	N(3)-Cd(1)-S(1)	113.82(10)
N(4)-Cd(1)-N(7)	92.14(9)	N(4)-Cd(1)-N(5)	70.45(15)
N(7)-Cd(1)-O(1)	84.05(10)	N(4)-Cd(1)-S(1)	171.78(12)
N(4)-Cd(1)-O(1)	175.42(10)	N(5)-Cd(1)-S(1)	102.51(10)
N(8)–N(7)–Cd(1)	127.5(2)	$N(1)^{*}-C(1)-S(1)$	178.5(5)
N(6)-N(5)-N(4)	178.0(5)	N(2)-C(2)-S(2)	176.4(5)
N(9)-N(8)-N(7)	177.7(4)		

68.88(9)-122.47(10)°; transoid angles: 141.95(9) -175.42(10)°]. Cd-N(pbap) distances are in the range 2.335(3)-2.459(2) Å, and Cd-N(azido) distances are within the range 2.243(3) - 2.335(3) Å. It is worth mentioning that none of the azido anions behave as a bridging ligand; this is an unusual azido coordination mode [15,16]. The intramolecular Cd \cdot ·Cd distance in 1 is quite large [6.473(2) Å]. The azido ligands are quasi-linear with N(4)-N(5)-N(6)and N(7)–N(8)–N(9) angles of $178.0(5)^{\circ}$ and $177.7(4)^{\circ}$; The N4–N5 and N(7)–N(8) bond lengths [1.181(4) Å] are larger than N(5)-N(6) [1.149(5)Å] and N(8)-N(9)[1.148(4) Å], indicating coordination of N(4) and N(7) to the cadmium center.

The C-H··· π interaction joins two adjacent molecules and constructs a supramolecular 1D chain (Fig. 2) in the 110 direction (D-H··· π : C(3)-H(3A)···Cg(1), D-H: 0.93(3) Å, H···Cg: 2.88 Å, X···Cg: 3.712(5) Å, < X-



Fig. 2. C–H··· π interactions in 1 forming a 1D chain in the 110 direction.



Fig. 3. $O-H \cdots N$ hydrogen bonding in 1 forming a sheet in the *bc* plane.



Fig. 4. Sheet formation in 1 in the *bc* plane through hydrogen bonding (omitting the ligand frame for clarity).



Fig. 5. $O-H\cdots N$ hydrogen-bonded sheet interwoven by $C-H\cdots \pi$ interactions in **1** forming a 3D network.

H···Cg: 147°, symmetry code: 1 - x, y, 2 - z). Two types of O–H···N hydrogen bonds (O(1)–H(1)···N(4): H···A:2.02(4) Å, D···A: 2.767(4) Å, angle D–H···A: 177(3)°, symmetry code x, 1/2 - y, -1/2 + z and O(1)– H(2)···N(7): H···A: 0.72(4) Å, D···A: 2.840(4) Å, angle D-H···A: 177(4)°, symmetry code 2 - x, y, 2 - z) form a 2D sheet in the *bc* plane (Figs. 3 and 4). These hydrogen bonds and C-H··· π interactions are interwoven to form a 3D network (Fig. 5).

3.2.2. Crystal structure of $[Cd_2(pfap)(\mu_{I,3}-NCS)(\mu_{I,3}-SCN)(NCS)_2]_n$ (2)

A single crystal X-ray diffraction study of 2 shows that the crystal lattice consists of a $[Cd_2(pfap)(\mu_{1,3}-NCS)(\mu_{1,3}-N$ SCN (NCS)₂ unit (Fig. 6). The layer structure for 2, through $\pi \cdots \pi$ interactions, is displayed in Fig. 7. Selected bond distances and bond angles relevant to the metal ion coordination sphere are given in Table 2. The polynuclear unit of 2 contains two symmetry related cadmium(II) centers $[Cd(1), Cd(1^*)]$ connected by a Schiff base acting as a bis(tridentate) ligand, and two end-to-end $(\mu_{1,3-})$ bibridged thiocyanate/isothiocyanate intermediaries and one N-coordinated isothiocyanate are attached to each of the two cadmium(II) centers completing the hexacoordination of the metal ions with a distorted octahedral CdN₅S coordination environment, which propagates forming the 1D polymeric chain. The N-coordination of the terminal NCS⁻ ligands indicates that the three N-atoms of the Schiff base (pfba) and the N-donation of the $\mu_{1,3-}$ bridged NCS⁻ ligand create a hardness in cadmium(II) center that enforces the ambidentate ligand to be bound in such a fashion. Cd(1) is attached by three nitrogen atoms, viz. the piperazine nitrogen [N(3)], the imine nitrogen [N(4)] and the pyridine nitrogen [N(5)], of the Schiff base and two end-to-end $(\mu_{1,3-})$ bi-bridged nitrogen [N(1)] and sulfur [S(1)] atoms and one terminal nitrogen [N(2)] atom of the thiocyanate ligands, whereas the neighbouring symmetry related $Cd(1^*)$ is ligated to the other three N donor set of the same Schiff base, completing its bis(tridentate)mode, and the counter ends $[S(1^*) \text{ and } N(1^*)]$ of two end-to-end $(\mu_{1,3-})$ bi-bridged thiocyanate ligands and the one terminal nitrogen $[N(2^*)]$ of the pseudohalide. Each metal center contains one eight-membered bridging loop and two fivemembered chelate loops. The eight-membered Cd-(SCN)₂-Cd bridging loops adopt a chair confirmation. The equatorial plane of Cd(1) consists of three nitrogen atoms [N(3), N(4), N(5)] of the bis(tridentate) Schiff base and one sulfur atom [S(1)] of a bridging thiocyanate, whereas the axial positions are occupied by a bridging nitrogen atom [N(1)] and a terminal nitrogen atom [N(2)]of the thiocyanate ligands. The maximum deviation of the Cd(1) center from the mean plane is 0.1713 Å. The degrees of distortion from an ideal octahedral geometry are reflected in the cisoid [70.45(15)-113.82(10)°] and transoid [143.66(14)-177.80(18)°] angles. The Cd-N [2.250(5)-2.524(4) Å] bond lengths are shorter than the bridging Cd–S [2.6161(14) Å] distance, as expected, and are consistent [15] with the corresponding values of the cadmium(II) thiocyanato bridging system. The Cd(1)-N(3) [piperazine] distance [2.524(4) Å] is longer than the Cd(1)–N(5) [pyridine] distance [2.395(4) Å] and Cd(1)–N(4) (imine) bond length [2.295(4) Å]. The intradimer Cd···Cd separation



Fig. 6. Thermal ellipsoid plot of the polynuclear $[Cd_2(pfap)(\mu_{1,3}-NCS)(\mu_{1,3}-SCN)(NCS)_2]_n$ (2) with the atom labelling scheme and 30% probability ellipsoids for all non-hydrogen atoms.



Fig. 7. Layer structure in **2** through $\pi \cdots \pi$ interactions.

[6.640(5) Å], through the bis(tridentate) bridge of the Schiff base is larger than the Cd···Cd separation [5.849(5) Å] through the bi-bridged thiocyanates. The angle between the terminal and bridging thiocyanates [S(1)–Cd(1)–N(2)] is 86.78(12)°, reflecting the *cis* alignment of the N- and Scoordination of the bound thiocyanates. N(1) and S(1) from two bridging isothiocyanate and thiocyanate ligands, and N(2) from the terminal isothiocyanate are in the meridional position of the distorted octahedron. The thiocyanates are coordinated in a linear fashion as seen from the N(1*)–C(1)–S(1) and N(2)–C(2)–S(2) angles [178.5(5) and 176.4(5)°]. The N(2)–C(2) length [1.121(7) Å] is shorter than C(2)–S(2) [1.624(5) Å], reflecting N-coordination of the terminal thiocyanate.

In crystal lattice the 1D covalent chain of **2** forms a layer structure with a face-to-face $\pi \cdots \pi$ interaction from two terminal pyridine rings [Ring(4)-ring(4)]: Cg(4)–Cg(4) ^(a) separation: 5.1732(3) Å, vertical displacement of Cg: 4.873 Å; ^(a)1/2 - x, -1/2 + y, 3/2 - z; Cg(4) = N(5)–C(8)–C(9)–C(10)–C(11)–C(12)] (Fig. 7).

3.3. Luminescence spectra

The fluorescence behaviour of **1** and **2** has been examined. The fluorescent emission was measured in MeOH solution at 298 K. Upon photoexcitation at 340 and 312 nm an intense fluorescent band was observed with a maximum at 465 and 410 nm and a lifetime of 2.63 and 2.58 ns for **1** and **2**, respectively. The higher lifetime may be due to the presence of stronger weak interactions, which are mainly responsible [23,24] for fluorescence. In glassy solutions (77 K) a red shift is observable at 535 and 510 nm for **1** and **2**, which is presumably due to ${}^{3}(\pi-\pi^{*})$ phosphorescence.

4. Conclusion

In conclusion, X-ray crystallographic characterization of new dimeric cadmium(II) azido and polymeric cadmium(II) thiocyanato compounds is reported herein. To the best of our knowledge, this the first report of a Schiff base containing polymeric cadmium(II) pseudohalide compound, where the versatility of the tailored hexadentate blocker is realized through its bis(tridentate) congregation behaviour encapsulating two metal ions instead of the classical hexacoordination binding a single metal ion. Again, intermolecular cooperative [25] forces are harnessed to engineer novel crystalline architectures. Both the compounds are examples of good luminous materials.

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5. Supplementary material

CCDC 205911 and 205912 contain the supplementary crystallographic data for 1 and 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallo-graphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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