Inorganica Chimica Acta 433 (2015) 72-77

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Mono, di and trinuclear photo-luminescent cadmium(II) complexes with N_2O and N_2O_2 donor salicylidimine Schiff bases: Synthesis, structure and self assembly

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ARTICLE INFO

Article history: Received 9 January 2015 Received in revised form 4 March 2015 Accepted 10 April 2015 Available online 27 April 2015

Keywords: Cadmium(II) Schiff base Crystal structure Photolumiscence

ABSTRACT

Four new octahedral cadmium(II) complexes, $[(Cd)(L^1)(HL^1)](ClO_4)$ (1), $[Cd_2(L^2)_2(SCN)_2(CH_3OH)_2]$ (2), $[(CdL^3)_3(\mu-1,1,1-OH)](ClO_4)_2$ (3) and $[Cd_2(L^4)_2(SCN)(NO_3)]$ (4) have been synthesized using four Schiff bases, HL¹, HL², HL³ and HL⁴, (where HL¹ = 2-(2-(ethylamino)ethyliminomethyl)phenol, HL² = 2-(2-(dimethylamino)ethyliminomethyl)-4-bromophenol, HL³ = 2-(2-(diethylamino)ethyliminomethyl)-6-methoxyphenol and HL⁴ = 2-(2-(ethylamino)ethyliminomethyl)-6-methoxyphenol. All four complexes have been characterized by elemental and spectral analysis and structures have been confirmed by single crystal X-ray diffraction studies. Complex 1 is a mononuclear cationic bis-ligand complex. Complex 2 features a double end-to-end thiocyanate bridged dinuclear cadmium(II) complex. Complex 3 has a partial cubane $[Cd_3O_4]$ core in which three $[CdL^3]$ subunits are interconnected through two types of oxygen bridges afforded by phenoxo oxygen atoms of ligands and a central hydroxo group. Complex 4 has a double phenoxo bridged dinuclear show fluorescence.

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1. Introduction

The chemistry of the metal Schiff base complexes has been paid considerable attention since long and it is still a promising area of research [1–10]. Among different Schiff bases, N₂O donor salicylidimine Schiff bases [11–13], have widely been used by several groups to form different homo and hetero polynuclear complexes with several transition and non-transition metal ions [14-20]. On the other hand, there have been immense interests in studying supra-molecular structures [21]. The molecular and crystalline architectures of the complexes are modulated by hydrogen bonding [22–26] as well as $\pi \cdots \pi$, C–H $\cdots \pi$ and anion $\cdots \pi$ interactions [27-29]. In the present work, we have used four different Schiff bases, produced by the condensation of N-substituted-1,2-diaminoethane and salicylaldehyde or its derivatives, to form cadmium(II) complexes. We have selected cadmium(II) as the metal centre for its ability to exhibit varieties of geometries as a result of its d^{10} electronic configuration with no CFSE in any crystal field, steric requirements of ligands controlling the geometries and coordination numbers [30–32]. Our intension was to examine the changes, if any, in their crystalline and supra-molecular architectures with the change in denticity of Schiff base ligands and with the presence of different co-ligands in the reaction medium. Herein, we would like to report the synthesis, characterization, crystal structures, supramolecular architectures and fluorescence properties of four new cadmium(II) Schiff base complexes.

2. Experimental

All starting materials and solvents were commercially available, reagent grade, and used as purchased from Sigma–Aldrich without further purification.

Caution!!!: Perchlorate salts are potentially explosive. Although no problem was encountered in the present study, only small amounts of the materials should be prepared and they must be handled with care.

2.1. Preparations

2.1.1. Preparation of ligands

2.1.1.1. Synthesis of HL^1 {2-(2-(ethylamino)ethyliminomethyl) phenol}. The tridentate schiff base, HL^1 , was prepared by refluxing N-ethyl-1,2-diaminoethane (1 mmol, 0.105 mL) with salicylalde-hyde (1 mmol, 0.104 mL) in methanol solution (20 mL) for ca.







1 h. Methanol was evaporated under reduced pressure to get HL¹ as yellow oily liquid. It was not purified and used directly for the preparation of complex **1**.

IR (KBr, cm⁻¹): 1636 ($v_{C=N}$), 2968–2846 (v_{CH}), 3308 (v_{OH}).

2.1.1.2. Synthesis of HL^2 {2-(2-(dimethylamino)ethyliminomethyl)-4bromophenol}. The tridentate schiff base, HL^2 , was prepared by refluxing N,N-dimethyl-1,2-diaminoethane (1 mmol, 0.105 mL) with 5-bromosalicylaldehyde (1 mmol, 0.201 g) in methanol solution (20 mL) for ca. 1 h. Methanol was evaporated under reduced pressure to get HL^2 as yellow oily liquid. 1 h. It was not purified and used directly for the preparation of complex **2**.

IR (KBr, cm⁻¹): 1635 $(v_{C=N})$, 2971–2820 (v_{CH}) , 3455 (v_{OH}) .

2.1.1.3. Synthesis of HL^3 {2-(2-(diethylamino)ethyliminomethyl)-6methoxyphenol}. The tetradentate schiff base, HL^3 , was prepared by refluxing N,N-diethyl-1,2-diaminoethane (1 mmol, 0.140 mL) with 3-methoxysalicylaldehyde (1 mmol, 0.152 g) in methanol solution (20 mL) for ca. 1 h. Methanol was evaporated under reduced pressure to get HL^1 as yellow oily liquid. It was not purified and used directly for the preparation of complex **3**.

IR (KBr, cm⁻¹): $1632 (v_{C=N})$, 2965–2831 (v_{CH}), 3415 (v_{OH}).

2.1.1.4. Synthesis of HL^4 {2-(2-(ethylamino)ethyliminomethyl)-6methoxyphenol}. It was prepared in a method similar to that for the ligand, HL^1 , except that 3-methoxysalicylaldehyde (0.152 g, 1 mmol) was used instead of salicylaldehyde. Methanol was evaporated under reduced pressure to get HL^4 as yellow oily liquid. It was not purified and used directly for the preparation of complex **4**.

IR (KBr, cm⁻¹): 1635 ($v_{C=N}$), 2964–2838 (v_{CH}), 3471 (v_{OH}).

2.1.1.5. Synthesis of $[(Cd)(L^1)(HL^1)](ClO_4)$ (1). A methanol solution of cadmium(II) perchlorate hexahydrate (0.5 mmol, 0.210 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. X-ray quality single crystals of complex 1 were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.40 g (68%). *Anal.* Calc. for $C_{22}H_{31}CdN_4ClO_6$ (FW 595.37): C, 44.38; H, 5.25; N, 9.41. Found: C, 44.34; H, 5.19; N, 9.48%. IR (KBr, cm⁻¹): 1634 ($\nu_{C=N}$), 3271 (ν_{NH}), 1100 (ν_{ClO4}), 2972–2861 (ν_{CH}). UV–Vis, λ_{max} (nm), [ε_{max} (L mol⁻¹ cm⁻¹)] (DMSO), 263 (1.3 × 10⁴), 326 (8.9 × 10³).

2.1.1.6. Synthesis of $[Cd_2(L^2)_2(\mu-1,3-SCN)_2(CH_3OH)_2]$ (2). A methanol solution of cadmium(II) nitrate tetrahydrate (1 mmol, 0.308 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. A methanol solution of sodium thiocyanate (1 mmol, 0.081 g) was then added to it and refluxed further for ca. 1 h. X-ray quality single crystals of complex **2** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.69 g (73%). Anal. Calc. for $C_{26}H_{36}Br_2Cd_2N_6O_4S_2$ (FW 945.35): C, 33.03; H, 3.84; N, 8.89. Found: C, 32.94; H, 3.77; N, 8.95%. IR (KBr, cm⁻¹): 1633 ($\nu_{C=N}$), 2111, 2076 (ν_{SCN}), 3436 (ν_{OH}), 2998–2840 (ν_{CH}); UV–Vis, λ_{max} (nm), [$\epsilon_{max}(L mol^{-1} cm^{-1})$] (DMSO), 262 (9.3 × 10⁴), 337 (8.2 × 10³).

2.1.1.7. Synthesis of $[(CdL^3)_3(\mu-1,1,1-OH)](ClO_4)_2$ (**3**). A methanol solution of cadmium(II) perchlorate hexahydrate (1 mmol, 0.419 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. X-ray quality single crystals of complex **3** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.81 g (63%). Anal. Calc. for $C_{42}H_{64}Cd_3N_6Cl_2O_{15}$ (FW 1301.12): C, 38.77; H, 4.96; N, 6.46. Found: C, 38.71; H, 4.92; N, 6.53%. IR (KBr, cm⁻¹): 1081 (ν_{CIO4}), 1630 ($\nu_{C=N}$), 3535 (ν_{OH}),

2974–2864 (ν_{CH}); UV–Vis, λ_{max} (nm), [ε_{max} (L mol⁻¹ cm⁻¹)] (DMSO), 264 (1.5 × 10⁴), 332 (3.4 × 10³).

2.1.1.8. Synthesis of $[Cd_2(L^4)_2(SCN)(NO_3)]$ (**4**). A methanol solution of cadmium(II) nitrate tetrahydrate (1 mmol, 0.308 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. A methanol solution of sodium thiocyanate (0.5 mmol, 0.04 g) was then added to it and refluxed further for ca. 1 h. X-ray quality single crystals of complex **4** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.49 g (63%). *Anal.* Calc. for $C_{25}H_{32}Cd_2N_6O_7S$ (FW 785.46): C, 38.23; H, 4.11; N, 10.70. Found: C, 38.17; H, 4.07; N, 10.79%. IR (KBr, cm⁻¹): 1633 ($\nu_{C=N}$), 2074 (ν_{SCN}), 3200 (ν_{NH}), 1451, 1295, 1082 (ν_{NO3}), 2909–2808 (ν_{CH}); UV–Vis, λ_{max} (nm), [ε_{max} (L mol⁻¹ cm⁻¹)] (DMSO), 267 (1.8 × 10⁴), 323 (5.9 × 10³).

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a PerkinElmer 240C elemental analyzer. Infrared spectra in KBr (4000–400 cm⁻¹) were recorded using a PerkinElmer Spectrum Two FTIR spectrophotometer. Electronic spectra in DMSO (800–200 nm) were recorded on a PerkinElmer Lambda 35 UV–Vis spectrophotometer. Fluorescence spectra in DMSO were obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. Lifetime measurements were recorded using Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBHDAS6 software. The powder XRD data was collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.548$ Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2 θ range of 5–50° using 1-D Lynxeye detector at ambient conditions.

2.3. X-ray crystallography

Single crystals of four complexes having suitable dimensions, were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 293 K. Molecular structures were solved using the SHELX-97 package [33]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, attached to oxygen and nitrogen, were located by difference Fourier maps and were kept at fixed positions. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [34]. A summary of the crystallographic data is given in Table 1.

3. Results and discussion

3.1. Synthesis

Reaction of the Schiff base (HL¹) with cadmium(II) perchlorate hexahydrate produces complex **1**. Use of perchlorate increases the [H⁺] of the medium (0.0158 M) and may be responsible for the non-deprotonation of one of the Schiff bases present in complex **1**. Literature shows that there is only one report of the solid state structure of similar bis-ligand complex of cadmium(II), [Cd(L)(HL)]ClO₄ {HL = 2-(2-(dimethylamino)ethyliminomethyl)phenol} with a similar ligand [12]. This compound was also prepared using cadmium(II) perchlorate. Thiocyante bridged dinuclear complex (**2**) was prepared by the reaction of HL² with cadmium(II) nitrate tetrahydrate. There is only one report of thiocynate bridged dinuclear cadmium complex with similar N₂O donor Schiff base [35]. Reaction of cadmium(II) perchlorate

Table 1	
Crystal data and refinement details of complexes 1-4.	

	1	2	3	4
Formula	$C_{22}H_{31}CdN_4ClO_6$	$C_{26}H_{36}Br_2Cd_2N_6O_4S_2$	C42H64Cd3N6O7Cl2O4	C ₂₅ H ₃₂ Cd ₂ N ₆ O ₇ S
Formula weight	595.37	945.35	1301.12	785.46
Т (К)	293	293	293	293
Crystal system	Orthorhombic	Triclinic	Trigonal	Triclinic
Space group	Pbna	ΡĪ	R-3	$P\bar{1}$
a (Å)	12.9162(3)	8.4198(9)	13.2748(3)	7.1649(2)
b (Å)	18.7636(5)	9.0594(10)	13.2748(3)	11.8337(3)
c (Å)	21.5088(5)	11.9073(14)	53.8944(19)	18.2588(4)
α (°)	(90)	109.818(5)	(90)	79.101(1)
β (°)	(90)	94.169(7)	(90)	87.382(7)
γ (°)	(90)	91.729(6)	(120)	82.122(2)
Ζ	8	1	6	2
D_{calc} (g cm ⁻³)	1.517	1.845	1.576	1.733
$\mu (\mathrm{mm}^{-1})$	0.983	3.761	1.315	1.534
F(000)	2432	464	3936	784
Total reflections	75,054	9254	41,770	22,525
Unique reflections	4985	3262	3510	5730
Observed data[$I > 2\sigma(I)$]	3669	2678	2941	4570
No. of parameters	306	171	207	370
R(int)	0.042	0.039	0.043	0.036
R_1 , wR_2 (all data)	0.0643, 0.1414	0.0669, 0.1452	0.0550, 0.1556	0.0437, 0.0803
$R_1, wR_2 [I > 2\sigma(I)]$	0.0448, 0.1258	0.0529, 0.1348	0.0452, 0.1402	0.0316, 0.0725

hexahydrate with HL³ produces a trinuclear complex, $[(CdL^3)_3 (\mu-1,1,1-OH)](ClO_4)_2$ (**3**). Formation of complex **3** is unique in the sense that solid state characterization of any such partial cubane cadmium(II) complex with N₂O₂ donor salicylidimine Schiff base is not reported in literature.

On the other hand, addition of sodium thiocyanate to the methanol solution of HL^4 and cadmium(II) nitrate tetrahydrate produced a double phenoxo bridged dinuclear complex, $[Cd_2(L^4)_2(SCN)(NO_3)]$ (4), in which nitrate and thiocyanate ions are acting as co-ligands. Formation of complex 4 is also interesting due to the presence of both nitrate and thiocyanate in the complex. All related dinuclear cadmium(II) complexes, reported in literature, contains two molecules of only one co-ligand, without exception [20,36–38].

3.2. Description of structures

3.2.1. $[(Cd)(L^1)(HL^1)](ClO)_4$ (1)

Complex 1 crystallizes in orthorhombic space group *Pbna*. A perspective view of the complex with selective atom-numbering scheme is shown in Fig. 1. The asymmetric unit consists of a discrete $[(Cd)(L^1)(HL^1)]^+$ cation and one non-coordinated perchlorate



Fig. 1. Perspective view of complex **1** with selective atom-numbering scheme. Perchlorate anion and hydrogen atoms are not shown for clarity. Selected bond lengths (Å): Cd(1)–N(1) 2.391(4), Cd(1)–N(2) 2.271(4), Cd(1)–N(3) 2.381(4), Cd(1)–N(4) 2.285(4), Cd(1)–O(1) 2.314(3), Cd(1)–O(2) 2.330(3).

anion. Cadmium(II) centre is in a hexa-coordinated octahedral environment, being bonded to amine nitrogen atom, N(3), imine nitrogen atom, N(4), and phenoxo oxygen atom, O(1), from one deprotonated Schiff base ligand, $(L^1)^-$, and amine nitrogen atom, N(1), imine nitrogen atom, N(2), and phenol oxygen atom, O(2), of one protonated Schiff base ligand (HL^1) , respectively where both ligands occupy facial positions. Cadmuim(II)-nitrogen bond lengths range from 2.271(4) to 2.391(4) Å, as is also observed in similar systems [12,39]. The saturated five membered chelate rings Cd(1)-N(1)-C(14)-C(15)-N(2) and Cd(1)-N(3)-C(3)-C(4)-N(4)present envelope conformations with puckering parameters q(2) = 0.476(7) Å, $\varphi(2) = 68.8(6)^{\circ}$ and q(2) = 0.473(6) Å, $\varphi(2) = 253.0(5)^{\circ}$ respectively [40]. The hydrogen atom, H(2), attached to phenol oxygen atom, O(2), forms a exceptionally strong hydrogen bond (Fig. S1) with the symmetry related phenoxo oxygen atom, $O(1)^a$, {Symmetry transformation, a = x, 1/2 - y, 1-z of a neighbouring molecule. This is a very strong H bond (Donor···Acceptor distance 2.45 Å) with respect the other reported systems [15,28,47]. Selected bond angles are gathered in Table S1. The details of other supramolecular interactions are described in **Electronic Supplementary Information.**

3.2.2. $[Cd_2(L^2)_2(\mu-1,3-SCN)_2(CH_3OH)_2]$ (2)

Complex **2** crystallizes in triclinic space group $P\overline{1}$. It features a hexa-coordinated double end-to-end thiocyanate bridged dinuclear centrosymmetric cadmium(II) complex, as shown in Fig. 2. The distorted octahedral cadmium(II) centre, Cd(1), is coordinated meridionally by one phenoxo oxygen atom, O(1), one imine nitrogen



Fig. 2. Perspective view of complex **2** with selective atom-numbering scheme. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å): Cd(1)-N(1) 2.430(9), Cd(1)-N(2) 2.273(5), Cd(1)-S(1) 2.797(2), $Cd(1)-N(3)^b$ 2.218(6), Cd(1)-O(1) 2.230(5), Cd(1)-O(2) 2.380(6). Symmetry transformation $^b = 2 - x$, 1 - y, 2 - z.

atom, N(2), one amine nitrogen atom, N(1), from deprotonated Schiff base ligand, $(L^2)^-$, and one sulfur atom, S(1), of coordinated thiocyanate and one oxygen atom, O(2), from a coordinated methanol. The sixth coordination site of the distorted octahedral cadmium(II) is occupied by a symmetry related (2 - x, 1 - y, 2 - z) nitrogen atom, N(3)^b, of an thiocyanate to form a double end-to-end thiocyanate bridged dinuclear cadmium(II) complex. The Cd-O, Cd-S and Cd–N distances fall within the range 2.218(5)–2.797(2) Å, as were also observed in other complexes [35]. The saturated five membered chelate ring Cd(1)-N(1)-C(3)-C(4)-C(5)-N(2) present an envelope conformation, with puckering parameters q(2) = 0.356(11) Å, $\varphi(2) = 257.8(13)^{\circ}$ [40]. The bridging thiocyanates are quasi-linear; the S-C-N angle is 178.6°(7). The Cd...Cd distance within the dinuclear unit is 5.918(9) Å. Selected bond angles are gathered in Table S2. The details of supramolecular interactions are described in Electronic Supplementary Information.

3.2.3. $[(CdL^3)_3(\mu-1,1,1-OH)](ClO_4)_2$ (**3**)

Complex 3 comprises one cation, $[(CdL^3)_3(\mu-1,1,1-OH)]^{2+}$, which has crystallographic 3-fold symmetry and two non-coordinated perchlorate anions. A perspective view of the complex with selected atom numbering scheme is shown in Fig. 3. The trinuclear cation is comprised of three CdL³ subunits in which each cadmium(II) is coordinated to a deprotonated tetradentate monoanionic ligand $(L^3)^-$. The subunits are held together by two distinct bridging systems: (i) the oxygen atom (O3) of a triply bridging hydroxo group, capping the three cadmium(II) centres and (ii) the bridging phenoxo oxygen atom from a symmetry related adjacent ligand molecule. The three cadmium(II) and the bridging hydroxo group form a flattened trigonal pyramid, with the cadmium(II) falling at the corners of equilateral sides (3.53(8) Å) and angles $(60.00(1)^\circ)$. The face-capping oxygen atom (O3) is located at 1.021 Å above the plane defined by the Cd₃ triangle. The presence of Cd_3OH is confirmed by (a) the location of the hydrogen atom at the expected position in the final difference Fourier map, (b) the electroneutrality of the crystal, and (c) the refined Cd-O(H) distances and Cd-O(H)-Cd angles, which agree well with a roughly tetrahedral or pseudo-tetrahedral sphere of Cd, Cd, Cd, H species around the oxygen atom. The average bond lengths in the octahedral coordination sphere are Cd-N(amine) 2.259 Å. 2.409 Å. Cd–N(imine) Cd-O(phenoxo)2.213 Å. Cd–O(methoxy) 2.613 Å. Cd–O(hvdroxide) 2.284 Å. which are close to those in other related Cd(II) compounds [41]. Selected bond angles are gathered in Table S3. The details of hydrogen bonding interaction is described in Electronic Supplementary Information.



Fig. 3. Perspective view of complex **3** with selective atom-numbering scheme. Only relevant atoms are shown. Hydrogen bonding interaction is shown in dotted line. Selected bond lengths (Å): Cd(1)–N(1) 2.409(5) Cd(1)–N(2) 2.259(7), Cd(1)–O(1) 2.233(4), Cd(1)–O(1)^d 2.194(5), Cd(1)–O(3) 2.284(2), Cd(1)–O(2)^d 2.613(4). Symmetry transformation, $^{d} = 1 - x + y$, 1 - x, z.

3.2.4. $[Cd_2(L^4)_2(SCN)(NO_3)]$ (4)

Complex **4** crystallizes in the triclinic space group $P\overline{1}$. It features a hexa-coordinated phenoxo bridged dinuclear cadmium(II) complex, as shown in Fig. 4. Within the dinuclear unit, each cadmium(II) centre is in a highly distorted pentagonal pyramidal geometry. The amine nitrogen, the imine nitrogen, the phenoxy oygen and the methoxy oxygen of the tetradentate deprotonated Schiff base coordinates equatorially each cadmium(II). A phenoxo oxygen atom from a second molecule of the Schiff base also coordinates cadmium(II) equatorially. The apical position of Cd(1) is occupied by a nitrate nitrogen atom and that of Cd(2) by a thiocyante nitrogen atom. The dinuclear bridging unit Cd₂O₂ describes a rhombohedral plane. The rhombohedral angles are O(2)-Cd(1)-O(1), 74.86(9)°, Cd(1)–O(1)–Cd(2), 102.48(9)°; O(1)–Cd(2)–O(2) 75.34(9)°, Cd(2)–O(2)–Cd(1), 105.2(1)°. The Cd Cd distance within the dinuclear unit is 3.5327(4) Å. The saturated five membered chelate rings Cd(1)-N(1)-C(3)-C(4)-N(2) and Cd(2)-N(3)-C(15)-C(16)-N(4) present a half-chair conformation with puckering parameters q(2) = 0.461(5) Å, $\varphi(2) = 89.9(4)^{\circ}$ and q(2) = 0.546(4) Å, $\varphi(2) = 227.7(4)^{\circ}$ respectively [40]. Selected bond lengths and bond angles are gathered in Table 2 and Table S4, respectively. The details of supramolecular interaction is described in Electronic Supplementary Information.

3.3. Powder X-ray diffraction

The experimental powder XRD patterns of bulk product of all four complexes are in good agreement with simulated XRD patterns from single crystal X-ray diffraction, confirming purity of bulk materials. Simulated patterns were calculated from the single crystal structural data (cif file) using CCDC Mercury software. Fig. 5 shows the experimental and simulated powder XRD patterns of



Fig. 4. Perspective view of complex **4** with selective atom-numbering scheme. Hydrogen atoms are not shown for clarity.

Table 2	
Selected bond lengths	(Å) of complex 4

	4
Cd(1)–N(1)	2.327(4)
Cd(1) - N(2)	2.285(3)
Cd(1) - O(1)	2.315(2)
Cd(1)-O(2)	2.184(2)
Cd(1)-O(3)	2.316(3)
Cd(1)-O(4)	2.691(3)
Cd(2)-O(1)	2.214(2)-
Cd(2)-O(2)	2.264(2)
Cd(2)-N(3)	2.313(4)
Cd(2)-N(4)	2.327(4)
Cd(2)–N(6)	2.250(4)



Fig. 5. Experimental and simulated powder XRD patterns of the complex **1**, confirming the purity of the bulk materials.

complex **1**. The experimental and simulated powder XRD patterns of complexes **2–4** are given in Figs. S7–S9, {Electronic Supplementary Information}.

3.4. IR, electronic and fluorescence spectra

In IR spectra of all four complexes, distinct bands due to azomethine (C=N) groups within the range of $1630-1634 \text{ cm}^{-1}$ are routinely noticed. Sharp bands at 3271 and 3200 cm⁻¹ in IR spectra of complexes **1** and **4** are assigned as N–H stretching vibrations. End-to-end bridging mode of thiocyanate groups in **2** is confirmed by the splitting of absorption band corresponding to SCN-stretching vibration appearing at 2111 and 2076 cm⁻¹ (indicating S- and N- coordination modes respectively) [42]. In addition, two medium bands are observed at 822 and 794 cm⁻¹ related to v(CS) [43,44].

On the other hand, appearance of strong bands in the range of 1080-1100 cm^{-1} in IR spectra of **1** and **3** indicates the presence of ionic perchlorates. Broad bands at 3436 and $3535\,\mathrm{cm}^{-1}$ are assigned as OH stretching vibrations in IR spectra of complexes 2 and **3** respectively. A distinct band at 2074 cm^{-1} is indicative of the presence of the N-coordinated thiocyanate in the IR spectrum of complex **4**. Monodentate nitrate exhibits three NO stretching bands, $v_{as(NO2)}$ (B2), $v_{s(NO2)}$ (A1) and $v_{(NO)}$ (A1), as expected for its C_{2v} symmetry [45]. In complex **4**, three sharp bands at 1451, 1295 and 1082 cm⁻¹ indicate the presence of unidentate coordination of NO₃ ion, as is also substantiated by the X-ray single crystal structure analysis. The bands in the range of 2998–2840 cm⁻¹ due to alkyl C-H bond stretching vibrations are customarily noticed in the IR spectra of all four complexes. The IR spectra of the complexes have also been compared with those of the free ligands in order to determine the coordination sites that may get involved in chelation. The (C=N) stretching vibration in the free ligands are shifted to lower frequency in the complexes. Theses shifts are



Fig. 6. Lifetime decay profile of complexes 1-4.

due to the reduction of double bond characters of the C=N bonds, caused by the coordination of nitrogen atoms to the cadmium(II) centers and are in agreement with results obtained from other similar complexes described previously [37]. Positions of bands corresponding to C–O stretching vibrations in free ligands also shift towards lower frequency region in complexes due to participation of the oxygen atoms in coordination [46]. At the same time, new bands in the region of 480 cm⁻¹ arise in the complexes indicating cadmium(II)–O vibrations. IR spectra of ligands and complexes are given in Figs. S10–S17, {Electronic Supplementary Information}.

Electronic spectra of complexes and ligands are recorded in DMSO solution in the range 200–800 nm. Absorption spectra of ligands exhibit four bands, of which first two bands around 225 and 260 nm may be attributed to π – π * transitions and the two bands at around 325 and 420 nm may be assinged as n– π * transitions [47]. Although same trends are observed in the complexes, complexation leads to slight shifts in the positions of these bands. Intense absorption bands are observed around 260 and 330 nm for each of four complexes. There is no bands corresponding to d–d electronic transitions as expected for cadmium(II) complexes with d^{10} electronic configurations [41].

All four complexes exhibit luminescence in DMSO medium. On exciting at 326, 337, 332 and 323 nm, emissions are observed at 420, 419, 420 and 416 nm for complexes **1**, **2**, **3** and **4** respectively. Emission of the complexes is tentatively attributed to the intra-ligand transitions modified by metal coordination. Fluorescence lifetimes of complexes are investigated in DMSO solution at room temperature. Lifetimes of **1**, **2**, **3** and **4** are about 8.66, 7.80, 10.50 and 8.16 ns (Table 3) respectively, which are similar to other cadmium(II) complexes [48]. Decay profiles (Fig. 6) were fitted to a multi-exponential model:

$$I(t) = \sum_{i} \alpha_{i} \exp\left(\frac{-t}{\tau_{i}}\right)$$

Tuble 5						
The details data of the	photoluminescence and	time-resolved	photoluminescence	decays of	complexes 1	1-4

Table 3

Complex	λ_{ex} (nm)	$\lambda_{\rm em}$ (nm)	A_1 (%)	τ_1 (ns)	$A_{2}(\%)$	τ_2 (ns)	A ₃ (%)	τ_3 (ns)	τ_{av} (ns)	χ^2
1	326	420	35.23	3.38	47.08	15.67	17.69	0.55	8.66	1.1069
2	337	419	33.30	2.98	44.55	15.16	22.15	0.49	7.80	1.0980
3	332	420	16.75	3.16	74.26	13.35	8.98	0.49	10.50	1.1115
4	323	416	33.42	3.28	48.51	15.64	18.08	0.48	8.16	1.1167

where, tri-exponential functions are used to fit the emission of all complexes with and obtaining χ^2 close to 1. The intensity-averaged life times (τ_{av}) are determined using the following equation:

$$\tau_{av} = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i}$$

where, α_i and τ_i are the pre-exponential factor and excited-state luminescence decay time associated with the *i*-th component, respectively.

The relative fluorescence quantum yields for all complexes were measured in DMSO using quinine sulfate (in 0.5 (M) H₂SO₄, ϕ = 0.54) as the quantum yield standard [49]. The fluorescence quantum yields of complexes **1**, **2**, **3** and **4** are 0.00274, 0.0330, 0.00549 and 0.00515, respectively.

4. Summary

In the present work, we have synthesized four cadmium(II) Schiff base complexes. N-substituted 1,2-diaminoethane has been used to prepare four Schiff bases with four different aromatic aldehydes. The denticity of the Schiff bases play important role in dictating the structures of the complexes. Complex **1** features a bis-ligand complex. Complex **2** is an example of end-to-end thiocyanate bridged dinuclear complex. Complex **3** contains trinuclear cations with partial cubane [Cd₃O₄] core, in which cadmium(II) centres are bridged by μ -1,1,1-OH. Complex **4** features a phenoxo-bridged dinuclear cadmium(II) complex. Variation in the structures of the complexes is modulated by the change in the denticity of the Schiff bases as well as the presence/absence of suitable coordinated anions (NO₃⁻, SCN⁻, OH⁻) or neutral coordinating molecules (CH₃OH) in the reaction medium. All four complexes show fluorescence with fluorescence lifetime within 8–11 ns.

Acknowledgment

This work was supported by the DST, India, under FAST Track Scheme (Order No. SR/FT/CS-118/2010, dated 15/02/2012).

Crystallographic data were collected at the DST-FIST, Indiafunded Single Crystal Diffractometer Facility at the Department of Chemistry, Jadavpur University.

Appendix A. Supplementary material

CCDC 1034469-1034472 contain the supplementary crystallographic data for complexes **1–4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.ica.2015.04.018.

Reference

- [1] L. Sacconi, I. Bertisi, R. Morassi, Inorg. Chem. 6 (1967) 1548.
- [2] W.N. Wallis, S.C. Cummings, Inorg. Chem. 13 (1975) 991.
- [3] M.G.B. Drew, C.V. Knox, S.M. Nelson, J. Chem. Soc., Dalton Trans. (1980) 942.
- [4] J.P. Costes, Inorg. Chim. Acta 130 (1987) 17.
- [5] P. Bhattacharya, J. Parr, A.T. Ross, A.M.Z. Slawin, J. Chem. Soc., Dalton Trans. (1998) 3149.

- [6] S. Basak, S. Sen, S. Banerjee, S. Mitra, G. Rosair, M.T.G. Rodriguez, Polyhedron 26 (2007) 5104.
- [7] S. Mukherjee, P.S. Mukherjee, Cryst. Growth Des. 14 (2014) 4177.
- [8] C. Biswas, M.G.B. Drew, E. Ruiz, M. Estrader, C. Diaz, A. Ghosh, Dalton Trans. 39 (2010) 7474.
- [9] S. Kundu, S. Roy, K. Bhar, R. Ghosh, C.-H. Lin, J. Ribas, B.K. Ghosh, J. Mol. Struct. 1038 (2013) 78.
- [10] P. Chakraborty, A. Guha, S. Das, E. Zangrando, D. Das, Polyhedron 49 (2013) 12.
 [11] A. Bhattacharyya, K. Harms, S. Chattopadhyay, Inorg. Chem. Commun. 48 (2014) 12.
- [12] H.-C. Fang, X.-Y. Yi, Z.-G. Gu, G. Zhao, Q.-Y. Wen, J.-Q. Zhu, A.-W. Xu, Y.-P. Cai, Cryst. Growth Des. 9 (2009) 3776.
- [13] A.A. Hoser, W. Schilf, A.S. Chełmieniecka, B. Kołodziej, B. Kamieński, E. Grech, K. Woźniak, Polyhedron 31 (2012) 241.
- [14] A. Bhattacharyya, P.K. Bhaumik, P.P. Jana, S. Chattopadhyay, Polyhedron 78 (2014) 40.
- [15] S. Jana, B. Shaw, P. Bhowmik, K. Harms, M.G.B. Drew, S. Chattopadhyay, S.K. Saha, Inorg. Chem. 53 (2014) 8723.
- [16] C. Maxim, F. Tuna, A.M. Madalan, N. Avarvari, M. Andruh, Cryst. Growth Des. 12 (2012) 1654.
- [17] P.K. Bhaumik, S. Chattopadhyay, Inorg. Chem. Commun. 22 (2012) 14.
- [18] S. Bag, P.K. Bhaumik, S. Jana, M. Das, P. Bhowmik, S. Chattopadhyay, Polyhedron 65 (2013) 229.
- [19] P. Bhowmik, M. Corbella, N. Aliaga-Alcaldec, V. Gómezd, S. Chattopadhyay, Polyhedron 49 (2013) 269.
- [20] H.-C. Fang, Y.-Y. Ge, Y. Ying, S.-R. Zheng, Q.-G. Zhan, Z.-Y. Zhou, L. Chen, Y.-P. Cai, Cryst. Eng. Comm. 12 (2010) 4012.
- [21] A. Bhattacharyya, P.K. Bhaumik, A. Bauzá, P.P. Jana, A. Frontera, M.G.B. Drew, S. Chattopadhyay, RSC Adv. 4 (2014) 58643.
- [22] C. Biswas, S. Chattopadhyay, M.G.B. Drew, A. Ghosh, Polyhedron 26 (2007) 4411.
- [23] P. Bhowmik, S. Jana, P.P. Jana, K. Harms, S. Chattopadhyay, Inorg. Chim. Acta 39 (2012) 53.
- [24] P.K. Bhaumik, S. Jana, S. Chattopadhyay, Inorg. Chim. Acta 390 (2012) 167.
- [25] M. Das, S. Chattopadhyay, Transition Met. Chem. 38 (2013) 191.
- [26] P.K. Bhaumik, K. Harms, S. Chattopadhyay, Polyhedron 68 (2014) 346.
- [27] M. Das, S. Chattopadhyay, J. Mol. Struct. 1051 (2013) 250.
- [28] M. Das, B.N. Ghosh, A. Valkonen, K. Rissanen, S. Chattopadhyay, Polyhedron 60 (2013) 68.
- [29] S. Jana, P.K. Bhaumik, K. Harms, S. Chattopadhyay, Polyhedron 78 (2014) 94.
 [30] H.-C. Fang, J.-Q. Zhu, L.-J. Zhou, H.-Y. Jia, S.-S. Li, X. Gong, S.-B. Li, Y.-P. Cai, P.K.
- Thallapally, J. Liu, G.J. Exarhos, Cryst. Growth Des. 10 (2010) 3277.
- [31] W.-K. Lo, W.-K. Wong, W.-Y. Wong, J. Guo, Eur. J. Inorg. Chem. (2005) 3950.
 [32] J. Chakraborty, S. Thakurta, B. Samanta, A. Ray, G. Pilet, S.R. Batten, P. Jensen, S. Mitra, Polyhedron 26 (2007) 5139.
- [33] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
- [34] G.M. Sheldrick, SADABS: Software for Empirical Absorption Correction, University of Gottingen, Institute fur Anorganische Chemieder Universitat, Gottingen, Germany, 1999–2003.
- [35] Z.-L. You, H.-L. Zhu, Acta Crystallogr., Sect. C 61 (2005) m397.
- [36] S. Sen, P. Talukder, S.K. Dey, S. Mitra, G. Rosair, D.L. Hughes, G.P.A. Yap, G. Pilet,
- V. Gramlich, T. Matsushita, Dalton Trans. (2006) 1758. [37] C.-H. Dai, F.-L. Mao, Synth. React. Inorg., Met.-Org., Nano-Met. Chem. 42 (2012) 537.
- [38] S.-J. Peng, H.-Y. Hou, Q. Wang, T. Yang, C.-S. Zhou, Synth. React. Inorg., Met.-Org., Nano-Met. Chem. 38 (2008) 746.
- [39] K. Agapiou, M.L. Mejla, X. Yang, B.J. Holliday, Dalton Trans. (2009) 4154.
- [40] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.
- [41] S. Roy, P.K. Bhaumik, K. Harms, S. Chattopadhyay, Polyhedron 75 (2014) 57.
- [42] S. Thakurta, R.J. Butcher, C.J. Gómez-García, E. Garribba, S. Mitra, Inorg. Chim. Acta 363 (2010) 3981.
- [43] M.A.S. Goher, L.A. Al-Shatti, F.A. Mautner, Polyhedron 16 (1997) 889.
- [44] A. Sabtini, I. Bertini, Inorg. Chem. 4 (1965) 959.
- [45] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., Wiley-Interscience, New York, 1978. p. 244.
- [46] S. Shit, D. Saha, D. Saha, T.N.G. Row, C. Rizzoli, Inorg. Chim. Acta 415 (2014) 103
- [47] M.D. Lowther, W.F. Wacholtz, J.T. Mague, J. Chem. Crystallogr. 31 (2001) 395.
- [48] P.K. Bhaumik, S. Roy, K. Harms, S. Chattopadhyay, Polyhedron 81 (2014) 168.
- [49] R.A. Velapoldi, K.D. Mielenz, Standard Reference Materials: A Fluorescence Standard Reference Material: Quinine Sulfate Dihydrate, National Bureau of Standards Special Publication 260–64, National Bureau of Standards, Washington, DC, 1980.