Journal of Molecular Structure 1058 (2014) 213-220



Contents lists available at ScienceDirect

Journal of Molecular Structure

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



Syntheses, crystal structure, spectroscopic and photoluminescence studies of mononuclear copper(II), manganese(II), cadmium(II), and a 1D polymeric Cu(II) complexes with a pyrimidine derived Schiff base ligand



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HIGHLIGHTS

• Pyrimidine derived Schiff base ligand has been prepared.

• Wide structural variety of complexes by the ligand was prepared.

• IR, UV-Vis spectra support structural moiety.

• Cd(II) complex is fluorescence active rather than other.

ARTICLE INFO

Article history: Received 13 May 2013 Received in revised form 1 November 2013 Accepted 4 November 2013 Available online 9 November 2013

Keywords: Manganese(II), cadmium(II) and copper(II) complexes Pyrimidine derived Schiff base ligand X-ray crystal structures Photoluminescence properties

ABSTRACT

The complexation behaviour of Schiff base ligand 2-((2-(4,6-dimethylpyrimidin-2-yl)hydrazono)methyl)phenol [HL] towards different metal centres is reported by the syntheses and characterization of three mononuclear Cu(II), Mn(II) and Cd(II) complexes, $[Cu(L)(H_2O)_2](NO_3)(H_2O)$ (1), $[Mn(L)_2](CH_3OH)$ (2), $[Cd(L)_2](CH_3OH)$ (3) and a 1D polymeric Cu(II) complex, $[Cu(L)(ClO_4)(C_2N_2O_2H)]_n(CH_3OH)$ (4) respectively. In the complexes **1–4** the deprotonated uninegative tridentate ligand serves as NNO donor where one pyrimidine ring N, the azomethine N and the salicyl hydroxyl oxygen atoms are coordinatively active. The complex **1** has almost square pyramidal geometry [$\tau = 0.2081$] whereas the metal centres maintain distorted octahedral geometry in the remaining three complexes **2–4**. All the complexes are characterized by X-ray crystallography. The Cd(II) complex has considerable fluorescence while the rest of the complexes and the ligand molecule are fluorescent silent.

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1. Introduction

The coordination behaviour of Schiff bases [1,2] has been drawing an immense interest since long back because of their preparative accessibilities, structural variety, varied denticity and subtle steric and/or electronic control on their frameworks leading to the formation of complexes of not only different coordination numbers but also of different nuclearities those possess interesting molecular and crystalline architectures [3–6] and related properties [7,8]. Pyrimidine derived metal ion complexes are being extensively studied in recent years owing to their great variety of

biological activity ranging from antimalarial, antibacterial, antitumoral, antiviral activities, etc. [9,10] which have often been related to their chelating ability with trace metal ions. The higher $\langle pi \rangle$ acidity of pyrimidine and presence of more than one hetero atom in the same ring play an important role in its coordination chemistry compared to that of pyridine bases for which the former serves as better model for biological systems [11-13]. A part of our research program is directed towards synthesis and structural characterization of transition metal ion complexes of pyrazole and pyrimidine derived Schiff base ligands [14–17]. In the present study, attempts have been made to prepare Cu(II), Mn(II), and Cd(II) complexes of the Schiff base ligand 2-((2-(4,6-dimethylpyrimidin-2-yl)hydrazono)methyl)phenol [HL], a 1:1 condensation product of 2-hydrazino-4,6-dimethyl pyrimidine and

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^{0022-2860/\$ -} see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molstruc.2013.11.004



Scheme 1. Schematic representation of ligand (HL) and their complexes.

Table 1

Experimental data for crystallographic analysis of 1, 2, 3 and 4.

mpirical formula C13 H17 Cu N4 03, N 03, H2 0 C26 H26 Cm N8 02, C H4 0 C26 H26 CM N8 02, C H4 0 C16 H13CU Cl N6 09 Formula weight 420.88 569.53 627.00 538.41 Temperature (K) 296 150 071073 071073 Wavelength (Å) 0.71073 0.71073 0.71073 0.71073 Crystal system Monoclinic Triclinic Monoclinic Monoclinic Space group (Z/c P-1 P-1 P21/c Unit cell dimensions (Z/c 10.146(2) 10.1862(16) 7.348(2) b (Å) 9.7867(3) 11.553(2) 11.6560(18) 11.479(3) c (Å) 18.9409(5) 14.146(4) 14.201(3) 26.874(7) c (Å) 100.229(1) 9.725(10) 93.140(8) 98.31(1) γ (°) 90 11.2761(6) 13.817(6) 90 Volume (Å ³) 342.001(77) 1389.66) 1396.4(4) 2243.0(10) z 8 52 1.44 541 Absorption coefficient (mm ⁻¹) <th>Compound</th> <th>1</th> <th>2</th> <th>3</th> <th>4</th>	Compound	1	2	3	4
Temperature (K)296150150150150Wavelength (Å)0.710730.710730.710730.71073Crystal systemMonoclinicTriclinicMonoclinicSpace group $C2/c$ $P-1$ $P-1$ $P21/c$ Unit cell dimensions $riclinic$ $10.146(2)$ $10.1862(16)$ $7.348(2)$ a (Å) $8.7477(5)$ $10.146(2)$ $10.1862(16)$ $7.348(2)$ b (Å) $9.7867(3)$ $11.563(2)$ $11.6560(18)$ $11.479(3)$ c (Å) $8.9409(5)$ $14.146(4)$ $4.201(3)$ $26.874(7)$ a (°) 90 $110.931(10)$ $113.305(8)$ 90 β (°) 90 $112.761(6)$ $13.817(6)$ 90 γ (°) 90 $112.761(6)$ $13.817(6)$ 90 Volume (Å) $3420.01(17)$ $1389.0(6)$ 1.491 1.541 z 8 2 2 4 Density _{cal} (Mg m ⁻³) 1.635 1.622 1.491 1.541 Absorption coefficient (mm ⁻¹) 1.326 0.519 0.825 1.144 $f(000)$ 1736 594 640 1060 e $1.3 \le k \le 13$ $-14 \le k \le 13$ $-15 \le k \le 13$ $rage$ (°) for dat collectin $2.2-30.1$ $1.6-28.5$ $1.6-29.4$ $1.5-25.1$ Index ranges $-26 < h \le 26$ $-13 \le k \le 13$ $-14 \le k \le 13$ $-12 \le k \le 13$ $-13 \le k \ge 126$ $-18 \le i < 18$ $-18 < i < 19$ $-31 < i < 32$ Independent reflections $[R_{int}]$ <t< td=""><td>Empirical formula Formula weight</td><td>C₁₃ H₁₇ Cu N₄ O₃, N O₃, H₂ O 420.88</td><td>C₂₆ H₂₆ Mn N₈ O₂, C H₄ O 569.53</td><td>C₂₆ H₂₆ Cd N₈ O₂, C H₄ O 627.00</td><td>C₁₆ H₁₉CuCl N₆ O₉ 538.41</td></t<>	Empirical formula Formula weight	C ₁₃ H ₁₇ Cu N ₄ O ₃ , N O ₃ , H ₂ O 420.88	C ₂₆ H ₂₆ Mn N ₈ O ₂ , C H ₄ O 569.53	C ₂₆ H ₂₆ Cd N ₈ O ₂ , C H ₄ O 627.00	C ₁₆ H ₁₉ CuCl N ₆ O ₉ 538.41
Wavelength (Å)0.710730.710730.710730.710730.71073Crystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group Z/c $P-1$ $P-1$ $P-1$ $P21/c$ Unit cell dimensions $P-1$ $P-1$ $P21/c$ a (Å)18.7477(5)10.146(2)10.1862(16) $7.348(2)$ b (Å)9.7867(3)11.563(2)11.650(18)11.479(3) c (Å)18.9409(5)14.146(4)14.201(3) $26.874(7)$ c (Å)90110.931(10)113.05(8) 90 β (°)100.229(1) $93.725(10)$ $93.140(8)$ $98.31(1)$ γ (°)90112.761(6)113.817(6) 90 γ (°)90112.761(6)139.64(4)2243.0(10) z 82 2 4 Density _{cal} (Mg m ⁻³)1.6351.3621.4911.541 z 82 2 4 $P(000)$ 17365946401060 θ Range (°) for data collection 230.1 $1.6-28.5$ $1.6-29.4$ $1.5-25.1$ Index ranges $-26 \leqslant h \lesssim 26$ $-13 \leqslant h \leqslant 13$ $-14 \leqslant h \leqslant 12$ $-8 \leqslant h \leqslant 8$ $-3 \leqslant k \leqslant 13$ $-15 \leqslant k \leqslant 15$ $-16 \leqslant k \leqslant 16$ $-12 \leqslant k \leqslant 13$ $-3 \leqslant k \leqslant 13$ $-15 \leqslant k \leqslant 15$ $-16 \leqslant k \leqslant 16$ $-12 \leqslant k \leqslant 13$ $-25 \leqslant 12 \circ 6$ $-18 \leqslant k \leqslant 15$ $-18 \leqslant k \leqslant 10$ $-13 \leqslant k < 13$ $Index ranges$ $-26 \Leftrightarrow h \lesssim 26$ $-18 \leqslant k < 15$ $-16 \leqslant k < 16$ $-12 \leqslant k < $	Temperature (K)	296	150	150	150
Crystal systemMonoclinicTriclinicTriclinicMonoclinicSpace group $C2/c$ $P-1$ $P-1$ $P-1$ $P21/c$ Unit cell dimensions $a(h)$ $8.7477(5)$ $10.146(2)$ $10.1862(16)$ $7.348(2)$ $b(h)$ $9.7867(3)$ $11.563(2)$ $11.650(18)$ $11.479(3)$ $c(h)$ $8.849(5)$ $14.146(4)$ $4.201(3)$ $2.8874(7)$ $a(^{\circ})$ 90 $110.931(10)$ $111.305(8)$ 90 $a(^{\circ})$ 90 $110.931(10)$ $93.140(8)$ $98.31(1)$ $\gamma(^{\circ})$ 90 $112.761(6)$ $113.817(6)$ 90 $\gamma(^{\circ})$ 90 $112.761(6)$ $13.817(6)$ 90 $Volume (Å^3)$ $3420.01(17)$ $1389.0(6)$ $196.4(4)$ $2243.0(10)$ z 8 2 2 4 Density _{cal} (Mg m ⁻³) 1.635 1.362 1.491 1.541 $Absorption coefficient (mm-1)$ 1.26 594 640 1060 h (Mag $e^{\circ})$ for data collection 230.1 $1.6-28.5$ $1.6-29.4$ $1.5-25.1$ Index ranges $-26 \leqslant h \le 26$ $-13 \leqslant h \le 13$ $-14 \leqslant h \le 12$ $-8 \leqslant h \leqslant 8$ $-13 < k < 13$ $-15 < k < 16$ $-12 < k < 13$ $-31 < \lfloor \cdot 32$ $-13 < k < 26$ $-18 < \lfloor \cdot 81$ $-18 < \lfloor \cdot 81$ $-31 < \lfloor \cdot 32$ Index ranges $-26 < h \le 26$ $-18 < \lfloor \cdot 81$ $-18 < \lfloor \cdot 81$ $-31 < \lfloor \cdot 32$ Index ranges $-26 < h \le 26$ $-18 < \lfloor \cdot 81$ $-18 < \lfloor \cdot 81$ $-31 < \lfloor \cdot 32$	Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Space group C/c $P-1$ $P-1$ $P21/c$ Unit cell dimensions a (Å)18.7477(5)10.146(2)10.1862(16)7.348(2) b (Å)9.7867(3)11.563(2)11.6560(18)11.479(3) c (Å)18.9409(5)14.146(4)14.201(3)26.874(7) α (°)90110.931(10)111.305(8)90 β (°)10.0229(1)93.725(10)93.140(8)98.31(1) γ (°)90112.761(6)138.17(6)90Volume (ų)3420.01(7)138.90(6)1396.4(4)2243.0(10) z 8224Density_cal (Mg m ⁻³)1.6351.3621.4911.541Absorption coefficient (mm ⁻¹)1.3260.5190.8251.144 $P(00)$ 17365946401060 θ Range (°) for data collection2.2-30.11.6-28.51.6-29.41.5-25.1Index ranges $-26 \in h \ge 26$ $-13 \leqslant h \le 13$ $-14 \le h \le 12$ $-8 \leqslant h \le 8$ $-13 \leqslant k \le 13$ $-15 \leqslant k \le 15$ $-16 < \leqslant 16$ $-12 < k \le 13$ $-25 < l \le 26$ $-18 < l \le 18$ $-18 < l \le 19$ $-31 < l \le 22$ Independent reflections $[R_{in}]$ 4997 $[R(int) = .032]$ 6877 $[R(int) = .026]$ $Rulti -scan$ Multi-scanMulti-scanAbsorption correctionMulti-scanMulti-scanMulti-scanMulti-scanMulti-scanMulti-scanAbsorption correctionRulti-scanMulti-scanMulti-scanMulti-scanMulti-scanMulti-sca	Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Unit cell dimensionsa (Å)18.7477(5)10.146(2)10.1862(16)7.348(2)b (Å)9.7867(3)11.563(2)11.6560(18)11.479(3)c (Å)18.9409(5)41.146(4)14.201(3)26.874(7) α (°)90110.931(10)111.305(8)90 β (°)10.0229(1)93.725(10)93.140(8)98.31(1) γ (°)90112.761(6)113.817(6)90Volume (Å ³)3420.01(17)1389.0(6)1396.4(4)2243.0(10)z8224Densitycal (Mg m ⁻³)1.6351.3621.4911.541Absorption coefficient (mm ⁻¹)1.3260.5190.8251.144F(000)17365946401060 θ Range (°) for data collection2.2-30.11.6-28.51.6-29.41.5-25.1Index ranges-26 \elep k 266-13 \elep k 515-16 \elep k 516-12 \elep k \ele 13 $-13 \elep k \leq 13$ -15 \elep k \ele 55-16 \elep k \ele 66-12 \ele k \ele 33 $-25 \ele 266$ -18 \ele 18-18 \ele 19-31 \ele 1 \ele 32Independent reflections [R _{int}]4997 [R(int) =.032]6877 [R(int) =.026]7429 [R(int) =.038]3970 [R(int) =.057]Absorption correctionMulti-scanMulti-scanMulti-scanMulti-scanMulti-scanAbsorption correctionFull-matrix least squares on P ² Full-matrix least squares on P ² 3970, 1, 305Absorption correctionMulti-scanMulti-scanMulti-	Space group	C2/c	P-1	P-1	P21/c
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Unit cell dimensions				
	a (Å)	18.7477(5)	10.146(2)	10.1862(16)	7.348(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	b (Å)	9.7867(3)	11.563(2)	11.6560(18)	11.479(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>c</i> (Å)	18.9409(5)	14.146(4)	14.201(3)	26.874(7)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	α (°)	90	110.931(10)	111.305(8)	90
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	β(°)	100.229(1)	93.725(10)	93.140(8)	98.31(1)
Volume (Å3)3420.01(17)1389.0(6)1396.4(4)2243.0(10)z8224Density _{cal} (Mg m ⁻³)1.6351.3621.4911.541Absorption coefficient (mm ⁻¹)1.3260.5190.8251.144 $F(000)$ 17365946401060 θ Range (°) for data collection2.2-30.11.6-28.51.6-29.41.5-25.1Index ranges $-26 \le h \le 26$ $-13 \le h \le 13$ $-14 \le h \le 12$ $-8 \le h \le 8$ $-13 \le k \le 13$ $-15 \le k \le 15$ $-16 \le k \le 16$ $-12 \le k \le 13$ $-25 \le l \le 26$ $-18 \le l \le 18$ $-18 \le l \le 19$ $-31 \le l \le 32$ Independent reflections [R _{int}]4997 [R(int) = .032]6877 [R(int) = .026]7429 [R(int) = .038]3970 [R(int) = .057]Absorption correctionMulti-scanMulti-scanMulti-scanMulti-scanMulti-scanRefinement methodFull-matrix least squares on F^2 Full-matrix least squares on F^2 Full-matrix least squares on F^2 3970, 1, 305	γ (°)	90	112.761(6)	113.817(6)	90
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Volume (Å ³)	3420.01(17)	1389.0(6)	1396.4(4)	2243.0(10)
	Z	8	2	2	4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Density _{cal} (Mg m ⁻³)	1.635	1.362	1.491	1.541
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Absorption coefficient (mm ⁻¹)	1.326	0.519	0.825	1.144
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	F(000)	1736	594	640	1060
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	θ Range (°) for data collection	2.2-30.1	1.6–28.5	1.6–29.4	1.5-25.1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Index ranges	$-26 \leqslant h \leqslant 26$	$-13 \leqslant h \leqslant 13$	$-14 \leqslant h \leqslant 12$	$-8\leqslant h\leqslant 8$
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		$-13 \leqslant k \leqslant 13$	$-15 \leqslant k \leqslant 15$	$-16 \leqslant k \leqslant 16$	$-12 \leqslant k \leqslant 13$
Independent reflections $[R_{int}]$ 4997 $[R(int) = .032]$ 6877 $[R(int) = .026]$ 7429 $[R(int) = .038]$ 3970 $[R(int) = .057]$ Absorption correctionMulti-scanMulti-scanMulti-scanMulti-scanRefinement methodFull-matrix least squares on F^2 Full-matrix least squares on F^2 Full-matrix least squares on F^2 Full-matrix least squares on F^2 Data/restraints/parameters4997, 0, 2616877, 0, 3697429, 0, 3693970, 1, 305		$-25 \leqslant l \leqslant 26$	$-18 \leqslant l \leqslant 18$	$-18 \leqslant l \leqslant 19$	$-31 \leq l \leq 32$
Absorption correctionMulti-scanMulti-scanMulti-scanMulti-scanRefinement methodFull-matrix least squares on F ² Full-matrix least squares on F ² Full-matrix least squares on F ² Full-matrix least squares on F ² Data/restraints/parameters4997, 0, 2616877, 0, 3697429, 0, 3693970, 1, 305	Independent reflections [R _{int}]	4997 [R(int) = .032]	6877 [<i>R</i> (int) = .026]	7429 $[R(int) = .038]$	3970 [<i>R</i> (int) = .057]
Refinement methodFull-matrix least squares on F^2 Full-matrix least squares on F^2 Full-matrix least squares on F^2 Full-matrix least squares on F^2 Data/restraints/parameters4997, 0, 2616877, 0, 3697429, 0, 3693970, 1, 305	Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Data/restraints/parameters 4997, 0, 261 6877, 0, 369 7429, 0, 369 3970, 1, 305	Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F ²
	Data/restraints/parameters	4997, 0, 261	6877, 0, 369	7429, 0, 369	3970, 1, 305

salicylaldehyde (Scheme 1). The ligand behaves as a tridentate uninegative one in all the complexes. In **1** and **4** one ligand molecule takes part in coordination whereas in **2** and **3** two tridentate ligand molecules are engaged to from the octahedral environment around the metal centres. The reaction of HL with Cu(NO₃)₂·6H₂O, Mn(ClO₄)₂·6H₂O and Cd(ClO₄)₂·6H₂O as metal salts taken in 1:1 mol proportion produces mononuclear complexes **1–3**

respectively. By contrast, when the same reaction is carried out with Cu(II) perchlorate in presence of dicyanamide ligand in 1:1:2 molar proportion, the perchlorate ion bridged 1D coordination polymer of **4** is resulted instead of dca bridged product. One interesting feature was observed during the formation of complex **4** in presence of Cu(II) ion one $-C \equiv N$ group of the coordinated dca ligand has been hydrolysed to -COOH group. Our goal is to study

Table 2				
Selected bond di	istances (Å) a	nd angles (°)	in 1, 2, 3	and 4

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Selected bonds	Value (Å)	Selected angles	(°)
Cui - 01 1.9009(13) 01-Cui - 02 91.82(6) Cui - 02 2.2662(15) 01-Cui - 03 85.95(6) Cui - 03 2.0159(16) 01-Cui - N3 172.62(8) Cui - 03 2.0159(16) 02-Cui - N3 90.93(6) Cui - N3 2.0280(15) 02-Cui - N1 113.19(6) Cui - N3 2.0280(15) 02-Cui - N1 113.53(10) O2-Cui - N3 90.93(6) 03-Cui - N1 152.97(8) O3-Cui - N1 153.54(6) 01-Mni - N1 150.54(6) Mn1-01 2.0858(16) 01-Mni - N1 90.01(5) Mn1-N4 2.2748(16) 01-Mni - N1 90.01(5) Mn1-N4 2.2604(16) 02-Mni - N4 90.01(5) Mn1-N8 2.2604(16) 02-Mni - N4 90.01(5) Mn1-N8 2.2604(16) 02-Mni - N4 90.01(5) Mn1-N8 9.57(5) 01-Cdi - N1 46.34(10) Cdi - 02 2.2262(2) 01-Cdi - N1 46.34(10) Cdi - 02 2.2262(3) 01-Cdi - N1 16.32(1)	Complex 1			
Cu1-01 1.9009(13) 01-Cu1-03 85.95(6) Cu1-02 2.2662(15) 01-Cu1-N3 17.262(6) Cu1-N3 2.0159(16) 01-Cu1-N3 17.262(6) Cu1-N3 2.0280(15) 02-Cu1-N3 99.93(6) O2-Cu1-N3 90.93(6) 03-Cu1-N1 152.97(6) O3-Cu1-N3 100.70(6) N1-Cu1-N3 80.88(6) Cu1-N1 2.02897(15) 01-Mn1-O2 103.38(6) Mn1-O1 2.0858(16) 01-Mn1-N1 150.54(6) Mn1-N4 2.024(17) 01-Mn1-N5 90.01(5) Mn1-N5 2.3376(17) 01-Mn1-N4 80.66(5) Mn1-N5 2.3376(17) 01-Mn1-N5 90.01(5) Mn1-N8 2.2604(16) 02-Mn1-N1 190.72(6) O2-Mn1-N4 100.10(5) 02-Mn1-N8 81.50(5) M1-M8 2.2604(16) 02-Mn1-N8 81.50(5) M1-M8 112.006 N4-Mn1-N5 91.73(8) M1-MN1 2.35(3) 01-Cd1-N1 146.34(10) Cd1-O1 2.218(3) </td <td>1</td> <td></td> <td>01–Cu1–O2</td> <td>91.82(6)</td>	1		01–Cu1–O2	91.82(6)
Cu1-O2 2.2662(15) O1-Cu1-N3 17.4(5) Cu1-O3 2.0159(16) O1-Cu1-N3 17.262(6) Cu1-N3 2.0280(15) O2-Cu1-O3 93.81(6) Cu1-N3 2.0280(15) O2-Cu1-N1 113.19(6) O3-Cu1-N3 90.93(6) O3-Cu1-N3 90.93(6) O3-Cu1-N3 100.70(6) O3-Cu1-N3 80.88(6) Cu1-N1 12.02897(15) O1-Mn1-O2 103.38(6) Mn1-O1 2.0858(16) O1-Mn1-N1 150.54(6) Mn1-N4 2.2748(16) O1-Mn1-N5 90.01(5) Mn1-N5 2.3376(17) O1-Mn1-N4 80.66(5) Mn1-N5 2.3376(17) O1-Mn1-N4 80.61(6) O2-Mn1-N4 100.10(5) O2-Mn1-N4 100.10(5) O2-Mn1-N8 81.50(5) N1-Mn1-N8 117.26(6) N1-Mn1-N8 107.79(6) N1-Mn1-N8 107.79(6) N1-Mn1-N8 100.77(10) Cd1-O2 106.26(10) Cd1-O1 2.218(3) O1-Cd1-N1 146.34(10) Cd1-O2 <	Cu1-01	1.9009(13)	01-Cu1-03	85.95(6)
Cu1-03 2.0159(16) O1-Cu1-N3 172.62(6) Cu1-N1 1.9500(13) O2-Cu1-O3 93.81(6) Cu1-N3 2.0280(15) O2-Cu1-N3 90.93(6) O2-Cu1-N1 152.97(6) O3-Cu1-N1 152.97(6) O3-Cu1-N3 100.70(6) N1-Cu1-N2 113.53(10) Complex 2 Mn1-O1 2.0897(15) O1-Mn1-N1 150.54(6) Mn1-N1 2.3029(17) O1-Mn1-N4 80.66(5) Mn1-N1 96.97(5) Mn1-N4 2.2784(16) O1-Mn1-N5 90.01(5) M0.1-N5 90.97(5) Mn1-N5 2.3376(17) O1-Mn1-N8 96.97(5) M1-N1-N5 90.10(5) Mn1-N5 2.3204(16) O2-Mn1-N8 81.50(5) N1-Mn1-N8 90.99(6) Mn1-N5 2.3264(16) O2-Mn1-N8 81.50(5) N1-Mn1-N8 90.99(6) O2-Mn1-N8 81.50(5) N1-Mn1-N8 90.99(6) N1-Mn1-N8 90.99(6) O2-Mn1-N8 81.50(5) N1-Mn1-N8 112.26(6) N1-Mn1-N8 100.27(6) Cd1-O1	Cu1-02	2.2662(15)	01-Cu1-N1	91.74(5)
Cu1-N1 1.9500(13) O2-Cu1-O3 93.81(6) Cu1-N3 2.0280(15) O2-Cu1-N1 113.19(6) O3-Cu1-N1 152.97(6) O3-Cu1-N3 90.93(6) O3-Cu1-N3 80.88(6) Cu1-N1-U1-N3 80.88(6) Cu1-N1 152.97(6) O3-Cu1-N3 100.70(6) Mn1-O1 2.0897(15) O1-Mn1-O2 103.38(6) Mn1-O2 2.0858(16) O1-Mn1-N1 150.54(6) Mn1-N4 2.2748(16) O1-Mn1-N5 90.01(5) Mn1-N4 2.2748(16) O2-Mn1-N4 80.66(5) Mn1-N5 2.3376(17) O1-Mn1-N8 96.97(5) Mn1-N8 2.2604(16) O2-Mn1-N4 100.10(5) O2-Mn1-N8 81.50(5) N1-Mn1-N8 177.38(5) M1-M1 N5 107.79(6) N4-Mn1-N8 177.38(5) M1-M1 2.362(3) O1-Cd1-N4 79.01(9) Cd1-N1 146.34(10) Cd1-O2 2.222(2) O1-Cd1-N5 88.02(10) Cd1-N4 2.362(3) O2-Cd1-N4 79.01(9)	Cu1-03	2.0159(16)	01-Cu1-N3	172.62(6)
$\begin{array}{cccc} {\rm Cu1-N3} & 2.0280(15) & 02-{\rm Cu1-N1} & 113.19(6) \\ 02-{\rm Cu1-N3} & 90.93(6) \\ 03-{\rm Cu1-N1} & 152.97(6) \\ 03-{\rm Cu1-N3} & 100.70(6) \\ N1-{\rm Cu1-N3} & 100.70(6) \\ N1-{\rm Cu1-N3} & 100.88(6) \\ {\rm Cu1-N1-N2} & 113.53(10) \\ \hline \\ $	Cu1-N1	1.9500(13)	02-Cu1-03	93.81(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu1–N3	2.0280(15)	02-Cu1-N1	113.19(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			02-Cu1-N3	90.93(6)
$\begin{array}{c ccc} & & & & & & & & & & & & & & & & & &$			03-Cu1-N1	152.97(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			03-Cu1-N3	100.70(6)
$\begin{array}{c ccccc} Cu1-N1-N2 & 113.53(10) \\ \hline Cunplex 2 \\ Mn1-O1 & 2.0897(15) & O1-Mn1-O2 & 103.38(6) \\ Mn1-O2 & 2.0858(16) & O1-Mn1-N1 & 150.54(6) \\ Mn1-N1 & 2.3029(17) & O1-Mn1-N4 & 80.66(5) \\ Mn1-N4 & 2.2748(16) & O1-Mn1-N5 & 90.01(5) \\ Mn1-N5 & 2.3376(17) & O1-Mn1-N8 & 96.97(5) \\ Mn1-N8 & 2.2604(16) & O2-Mn1-N1 & 89.61(6) \\ O2-Mn1-N8 & 150.72(6) \\ O2-Mn1-N8 & 81.50(5) \\ N1-Mn1-N8 & 91.12(6) \\ N1-Mn1-N8 & 91.12(6) \\ N1-Mn1-N8 & 111.20(6) \\ N4-Mn1-N8 & 117.38(5) \\ N1-Mn1-N8 & 111.20(6) \\ N4-Mn1-N8 & 117.38(5) \\ N5-Mn1-N8 & 70.99(6) \\ O1-Cd1-O2 & 2.022(2) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O2 & 2.222(2) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O1 & 2.218(3) & O1-Cd1-N1 & 146.34(10) \\ Cd1-N1 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N1 & 2.356(3) & O1-Cd1-N8 & 102.77(10) \\ Cd1-N4 & 2.356(3) & O1-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & O2-Cd1-N1 & 90.34(9) \\ O2-Cd1-N4 & 98.77(9) \\ O2-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 176.88(10) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 176.88(10) \\ N1-Cd1-N8 & 176.88(10) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 109.27(12) \\ O4_{a}-Cu1-N6 & 86.9(2) \\ O1-Cu1-N6 & 86.9(2) \\ O1-N6 & 00, 7(2) \\ O4_{a}-Cu1-N6 & 86.9(2) \\ O1-Cu1-N6 & 86.7(2) \\ O1-Cu1-N6 & 86.$			N1-Cu1-N3	80.88(6)
$\begin{array}{c} Complex \ 2 \\ Mn1-O1 & 2.0897(15) & O1-Mn1-O2 & 103.38(6) \\ Mn1-O2 & 2.0858(16) & O1-Mn1-N1 & 150.54(6) \\ Mn1-N1 & 2.3029(17) & O1-Mn1-N4 & 80.66(5) \\ Mn1-N4 & 2.2748(16) & O1-Mn1-N5 & 90.01(5) \\ Mn1-N5 & 2.3376(17) & O1-Mn1-N8 & 96.97(5) \\ Mn1-N8 & 2.2604(16) & O2-Mn1-N1 & 89.61(6) \\ O2-Mn1-N8 & 81.50(5) \\ O2-Mn1-N8 & 81.50(5) \\ O2-Mn1-N8 & 81.50(5) \\ O2-Mn1-N8 & 81.50(5) \\ N1-Mn1-N8 & 111.20(6) \\ N4-Mn1-N5 & 107.79(6) \\ N4-Mn1-N8 & 111.20(6) \\ N4-Mn1-N8 & 111.20(6) \\ N4-Mn1-N8 & 111.20(6) \\ O1-Cd1-O2 & 106.26(10) \\ Complex \ 3 \\ Cd1-O1 & 2.218(3) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O1 & 2.222(2) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O1 & 2.222(2) & O1-Cd1-N3 & 88.02(10) \\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & O1-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & O2-Cd1-N1 & 90.34(9) \\ O2-Cd1-N8 & 73.85(10) \\ O1-Cd1-N8 & 109.27(11) \\ N1-Cd1-N8 & 100.27(2) \\ O4_{a}-Cu1-O6 & 165.7(2) \\ N1-Cu1-N8 & 81.72(19) \\ O6-Cu1-N1 & 81.72(19) \\ O6-Cu1-N5 & 81.72(19) \\ O1-Cu1-O6 & 96.77(19) \\ O1-Cu1-O6 & 96.77(19) \\ O1-Cu1-O6 & 96.77(19) \\ O1-C$			Cu1—N1—N2	113.53(10)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Complex 2			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn1-01	2.0897(15)	01-Mn1-02	103.38(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn1-02	2.0858(16)	01-Mn1-N1	150.54(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn1-N1	2.3029(17)	01-Mn1-N4	80.66(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn1-N4	2.2748(16)	01-Mn1-N5	90.01(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn1-N5	2.3376(17)	01-Mn1-N8	96.97(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn1–N8	2.2604(16)	02-Mn1-N1	89.61(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			02-Mn1-N4	100.10(5)
$\begin{array}{c cccc} 02-Mn1-N8 & 81.50(5)\\ N1-Mn1-N4 & 70.99(6)\\ N1-Mn1-N5 & 91.12(6)\\ N1-Mn1-N8 & 111.20(6)\\ N4-Mn1-N8 & 177.38(5)\\ N5-Mn1-N8 & 70.99(6)\\ 01-Cd1-02 & 106.26(10)\\ \hline \\ Complex 3 \\ Cd1-01 & 2.218(3) & 01-Cd1-N1 & 146.34(10)\\ Cd1-02 & 2.222(2) & 01-Cd1-N4 & 79.01(9)\\ Cd1-N1 & 2.385(3) & 01-Cd1-N5 & 88.02(10)\\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2)\\ Cd1-N5 & 2.362(3) & 01-Cd1-N8 & 102.77(10)\\ Cd1-N8 & 2.369(3) & 02-Cd1-N1 & 90.34(9)\\ 02-Cd1-N5 & 147.05(10)\\ 02-Cd1-N8 & 78.30(9)\\ N1-Cd1-N8 & 109.27(11)\\ N4-Cd1-N8 & 176.88(10)\\ N5-Cd1-N8 & 69.52(11)\\ \hline \\ Complex 4 \\ Cu1-N1 & 1.933(5) & 01-Cu1-04_a & 96.21(18)\\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19)\\ Cu1-N5 & 1.939(6) & 01-Cu1-N1 & 90.24(19)\\ Cu1-01 & 1.919(4) & 01-Cu1-N1 & 86.48(11)\\ N1-Cd1-N5 & 86.9(2)\\ Cu1-04_a & 2.615(5) & 04_a-Cu1-N4 & 86.48(19)\\ 04_a-Cu1-N6 & 69.5(2)\\ U1-06 & 2.725(6) & 04_a-Cu1-N4 & 81.05(19)\\ N1-Cu1-N4 & 81.05(19)\\ N1-Cu1-N5 & 173.7(2)\\ N4-Cu1-N5 & 81.72(19)\\ 06-Cu1-N5 & 81.72(19)\\ 06-Cu1-N5 & 81.72(19)\\ 06-Cu1-N5 & 84.72(19)\\ 06-Cu1-N5 & 86.77(19)\\ \hline \end{array}$			02-Mn1-N5	150.72(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			02-Mn1-N8	81.50(5)
$\begin{array}{c ccc} N1-Mn1-N5 & 91.12(6)\\ N1-Mn1-N8 & 111.20(6)\\ N1-Mn1-N5 & 107.79(6)\\ N4-Mn1-N5 & 107.79(6)\\ N4-Mn1-N8 & 70.99(6)\\ O1-Cd1-O2 & 106.26(10)\\ \hline\\ Cd1-O1 & 2.218(3) & O1-Cd1-N1 & 146.34(10)\\ Cd1-O2 & 2.222(2) & O1-Cd1-N4 & 79.01(9)\\ Cd1-N1 & 2.385(3) & O1-Cd1-N5 & 88.02(10)\\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2)\\ Cd1-N5 & 2.362(3) & O2-Cd1-N1 & 90.34(9)\\ O2-Cd1-N8 & 2.369(3) & O2-Cd1-N1 & 90.34(9)\\ O2-Cd1-N8 & 2.369(3) & O2-Cd1-N8 & 78.30(9)\\ N1-Cd1-N8 & 78.30(9)\\ N1-Cd1-N5 & 93.58(10)\\ N1-Cd1-N5 & 93.58(10)\\ N1-Cd1-N5 & 93.58(10)\\ N1-Cd1-N8 & 109.27(11)\\ N4-Cd1-N5 & 113.24(11)\\ N4-Cd1-N8 & 176.88(10)\\ N5-Cd1-N8 & 109.27(11)\\ N4-Cd1-N8 & 176.88(10)\\ N5-Cd1-N8 & 69.(2)(11)\\ Cu1-O1 & 1.919(4) & O1-Cu1-N4 & 86.44(19)\\ Cu1-O4 & 2.615(5) & O4_{aa}-Cu1-N1 & 84.1(2)\\ Cu1-O6 & 2.725(6) & O4_{aa}-Cu1-N1 & 84.1(2)\\ Cu1-N5 & 1939(6) & O1-Cu1-N5 & 90.7(2)\\ O4_{aa}-Cu1-O6 & 165.7(2)\\ N1-Cu1-N5 & 102.2(2)\\ O6-Cu1-N1 & 101.9(2)\\ O6-Cu1-N4 & 81.72(19)\\ O6-Cu1-N5 & 84.1(2)\\ O1-Cu1-O6 & 96.77(19)\\ \hline\end{array}$			N1-Mn1-N4	70.99(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			N1-Mn1-N5	91.12(6)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			N1-Mn1-N8	111.20(6)
$\begin{array}{c ccc} N4-Mn1-N8 & 177.38(5) \\ N5-Mn1-N8 & 70.99(6) \\ O1-Cd1-O2 & 106.26(10) \\ \hline \\ Cd1-O1 & 2.218(3) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O2 & 2.222(2) & O1-Cd1-N4 & 79.01(9) \\ Cd1-N1 & 2.385(3) & O1-Cd1-N5 & 88.02(10) \\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & O1-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & O2-Cd1-N1 & 90.34(9) \\ O2-Cd1-N4 & 98.77(9) \\ O2-Cd1-N5 & 147.05(10) \\ O2-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N5 & 93.58(10) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 109.27(12) \\ Cu1-O1 & 1.919(4) & O1-Cu1-N4 & 96.21(18) \\ Cu1-O1 & 1.919(4) & O1-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 17.37(2) \\ N4-Cu1-N5 & 102.2(2) \\ O6-Cu1-N1 & 101.9(2) \\ O6-Cu1-N5 & 84.1(2) \\ O1-Cu1-O6 & 96.77(19) \\ \end{array}$			N4—Mn1—N5	107.79(6)
$\begin{array}{c ccc} & N5-Mn1-N8 & 70.99(6) \\ 01-Cd1-O2 & 106.26(10) \\ \hline \\ Complex 3 \\ Cd1-O1 & 2.218(3) & 01-Cd1-N1 & 146.34(10) \\ Cd1-O2 & 2.222(2) & 01-Cd1-N4 & 79.01(9) \\ Cd1-N1 & 2.385(3) & 01-Cd1-N5 & 88.02(10) \\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & 01-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & 02-Cd1-N1 & 90.34(9) \\ 02-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 109.27(11) \\ N1-Cd1-N4 & 81.05(19) \\ N1-Cu1-N5 & 102.2(2) \\ 06-Cu1-N1 & 101.9(2) \\ 06-Cu1-N5 & 84.1(2) \\ 01-Cu1-O6 & 96.77(19) \\ \hline \end{array}$			N4—Mn1—N8	177.38(5)
$\begin{array}{c ccc} Complex \ 3 \\ Cd1-O1 & 2.218(3) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O2 & 2.222(2) & O1-Cd1-N4 & 79.01(9) \\ Cd1-N1 & 2.385(3) & O1-Cd1-N5 & 88.02(10) \\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & O1-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & O2-Cd1-N1 & 90.34(9) \\ & O2-Cd1-N4 & 98.77(9) \\ & O2-Cd1-N5 & 147.05(10) \\ & O2-Cd1-N8 & 78.30(9) \\ & N1-Cd1-N8 & 78.30(9) \\ & N1-Cd1-N8 & 109.27(11) \\ & N1-Cd1-N8 & 109.27(11) \\ & N4-Cd1-N8 & 176.88(10) \\ & N5-Cd1-N8 & 69.52(11) \\ \hline \\ Complex \ 4 \\ Cu1-N1 & 1.933(5) & O1-Cu1-O4_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & O1-Cu1-N1 & 90.24(19) \\ Cu1-O1 & 1.919(4) & O1-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-N5 & 102.2(2) \\ & O4_a-Cu1-N5 & 173.7(2) \\ & N1-Cu1-N4 & 81.05(19) \\ & N1-Cu1-N4 & 81.05(19) \\ & N1-Cu1-N5 & 173.7(2) \\ & N4-Cu1-N5 & 102.2(2) \\ & O6-Cu1-N1 & 101.9(2) \\ & O6-Cu1-N5 & 84.1(2) \\ & O1-Cu1-O6 & 96.77(19) \\ \hline \end{array}$			N5-Mn1-N8	70.99(6)
$\begin{array}{c cccc} Complex \ 3 \\ \hline Cd1-O1 & 2.218(3) & O1-Cd1-N1 & 146.34(10) \\ Cd1-O2 & 2.222(2) & O1-Cd1-N4 & 79.01(9) \\ Cd1-N1 & 2.385(3) & O1-Cd1-N5 & 88.02(10) \\ Cd1-N4 & 2.365(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & O1-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & O2-Cd1-N1 & 90.34(9) \\ & O2-Cd1-N4 & 98.77(9) \\ & O2-Cd1-N4 & 98.77(9) \\ & O2-Cd1-N5 & 147.05(10) \\ O2-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 78.30(9) \\ N1-Cd1-N8 & 109.27(11) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N5 & 113.24(11) \\ N4-Cd1-N5 & 113.24(11) \\ N4-Cd1-N8 & 176.88(10) \\ N5-Cd1-N8 & 69.52(11) \\ \hline \\ Complex \ 4 \\ Cu1-N1 & 1.933(5) & O1-Cu1-O4_a & 96.21(18) \\ Cu1-N5 & 1.939(6) & O1-Cu1-N4 & 170.61(19) \\ Cu1-O1 & 1.919(4) & O1-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & O4_a-Cu1-N4 & 86.44(19) \\ O4_a-Cu1-N5 & 102.2(2) \\ O6-Cu1-N1 & 101.9(2) \\ O6-Cu1-N1 & 101.9(2) \\ O6-Cu1-N5 & 84.1(2) \\ O1-Cu1-O6 & 96.77(19) \\ \hline \end{array}$			01-Cd1-02	106.26(10)
$\begin{array}{cccc} Cd1-01 & 2.218(3) & 01-Cd1-N1 & 146.34(10) \\ Cd1-02 & 2.222(2) & 01-Cd1-N4 & 79.01(9) \\ Cd1-N1 & 2.385(3) & 01-Cd1-N5 & 88.02(10) \\ Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & 01-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & 02-Cd1-N1 & 90.34(9) \\ & 02-Cd1-N4 & 98.77(9) \\ & 02-Cd1-N5 & 147.05(10) \\ & 02-Cd1-N5 & 147.05(10) \\ & 02-Cd1-N8 & 78.30(9) \\ & N1-Cd1-N5 & 93.58(10) \\ & N1-Cd1-N5 & 93.58(10) \\ & N1-Cd1-N8 & 109.27(11) \\ & N4-Cd1-N5 & 113.24(11) \\ & N4-Cd1-N5 & 113.24(11) \\ & N4-Cd1-N8 & 176.88(10) \\ & N5-Cd1-N8 & 69.52(11) \\ \hline \\ Cun-N4 & 2.044(5) & 01-Cu1-O4_a & 96.21(18) \\ Cu1-N5 & 1.939(6) & 01-Cu1-N4 & 170.61(19) \\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19) \\ & 04_a-Cu1-N5 & 102.2(2) \\ & 06-Cu1-N1 & 101.9(2) \\ & 06-Cu1-N1 & 101.9(2) \\ & 06-Cu1-N5 & 84.1(2) \\ \hline \\ \end{array}$	Complex 3			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cd1-01	2.218(3)	01-Cd1-N1	146.34(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cd1-02	2.222(2)	01-Cd1-N4	79.01(9)
$\begin{array}{cccc} Cd1-N4 & 2.356(3) & Cd1-N8-N7 & 114.5(2) \\ Cd1-N5 & 2.362(3) & 01-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & 02-Cd1-N1 & 90.34(9) \\ & 02-Cd1-N1 & 98.77(9) \\ & 02-Cd1-N5 & 147.05(10) \\ & 02-Cd1-N5 & 147.05(10) \\ & 02-Cd1-N8 & 78.30(9) \\ & N1-Cd1-N4 & 69.48(11) \\ & N1-Cd1-N5 & 93.58(10) \\ & N1-Cd1-N8 & 109.27(11) \\ & N4-Cd1-N8 & 109.27(11) \\ & N4-Cd1-N8 & 176.88(10) \\ & N5-Cd1-N8 & 69.52(11) \\ \hline \\ \hline \\ Cun-N1 & 1.933(5) & 01-Cu1-O4_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19) \\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N1 & 86.44(19) \\ & 04_a-Cu1-N5 & 102.2(2) \\ & 04_a-Cu1-N5 & 173.7(2) \\ & N1-Cu1-N4 & 81.05(19) \\ & N1-Cu1-N5 & 173.7(2) \\ & N4-Cu1-N5 & 102.2(2) \\ & 06-Cu1-N5 & 84.1(2) \\ & 06-Cu1-N5 & 84.1(2) \\ \hline \\ $	Cd1-N1	2.385(3)	01-Cd1-N5	88.02(10)
$\begin{array}{cccc} Cd1-N5 & 2.362(3) & 01-Cd1-N8 & 102.77(10) \\ Cd1-N8 & 2.369(3) & 02-Cd1-N1 & 90.34(9) \\ & 02-Cd1-N4 & 98.77(9) \\ & 02-Cd1-N5 & 147.05(10) \\ & 02-Cd1-N8 & 78.30(9) \\ & N1-Cd1-N4 & 69.48(11) \\ & N1-Cd1-N5 & 93.58(10) \\ & N1-Cd1-N8 & 109.27(11) \\ & N4-Cd1-N8 & 109.27(11) \\ & N4-Cd1-N8 & 176.88(10) \\ & N5-Cd1-N8 & 69.52(11) \\ \hline \\ Complex \mbox{4} \\ Cu1-N1 & 1.933(5) & 01-Cu1-O4_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19) \\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N1 & 84.4(19) \\ & 04_a-Cu1-N5 & 102.2(2) \\ & 04_a-Cu1-N5 & 173.7(2) \\ & N1-Cu1-N4 & 81.05(19) \\ & N1-Cu1-N5 & 173.7(2) \\ & N4-Cu1-N5 & 102.2(2) \\ & 06-Cu1-N5 & 84.1(2) \\ & 06-Cu1-N5 & 84.1(2) \\ \hline \\ \end{array}$	Cd1—N4	2.356(3)	Cd1—N8—N7	114.5(2)
$\begin{array}{cccc} Cd1-N8 & 2.369(3) & 02-Cd1-N1 & 90.34(9) \\ 02-Cd1-N4 & 98.77(9) \\ 02-Cd1-N5 & 147.05(10) \\ 02-Cd1-N8 & 78.30(9) \\ N1-Cd1-N4 & 69.48(11) \\ N1-Cd1-N4 & 69.48(11) \\ N1-Cd1-N5 & 93.58(10) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 109.27(11) \\ N4-Cd1-N8 & 69.52(11) \\ N4-Cd1-N8 & 69.52(11) \\ N4-Cd1-N8 & 69.52(11) \\ N4-Cd1-N8 & 69.52(11) \\ Cu1-N1 & 1.933(5) & 01-Cu1-O4_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19) \\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19) \\ 04_a-Cu1-N5 & 102.2(2) \\ 04_a-Cu1-N5 & 173.7(2) \\ N1-Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 173.7(2) \\ N4-Cu1-N5 & 102.2(2) \\ 06-Cu1-N1 & 101.9(2) \\ 06-Cu1-N5 & 84.1(2) \\ 01-Cu1-O6 & 96.77(19) \\ \end{array}$	Cd1—N5	2.362(3)	01–Cd1–N8	102.77(10)
$\begin{array}{cccc} 02-Cd1-N4 & 98.77(9) \\ 02-Cd1-N5 & 147.05(10) \\ 02-Cd1-N8 & 78.30(9) \\ N1-Cd1-N4 & 69.48(11) \\ N1-Cd1-N5 & 93.58(10) \\ N1-Cd1-N5 & 193.58(10) \\ N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N5 & 113.24(11) \\ N4-Cd1-N8 & 176.88(10) \\ N5-Cd1-N8 & 69.52(11) \\ Cu1-N1 & 1.933(5) & 01-Cu1-04_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19) \\ Cu1-N5 & 1.939(6) & 01-Cu1-N1 & 90.24(19) \\ Cu1-01 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-04_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-06 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19) \\ 04_a-Cu1-N5 & 102.2(2) \\ 04_a-Cu1-N5 & 173.7(2) \\ N1-Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 102.2(2) \\ 06-Cu1-N1 & 101.9(2) \\ 06-Cu1-N5 & 84.1(2) \\ 01-Cu1-06 & 96.77(19) \\ \end{array}$	Cd1—N8	2.369(3)	02-Cd1-N1	90.34(9)
$\begin{array}{cccc} 02-Cd1-N5 & 147.05(10)\\ 02-Cd1-N8 & 78.30(9)\\ N1-Cd1-N4 & 69.48(11)\\ N1-Cd1-N5 & 93.58(10)\\ N1-Cd1-N5 & 93.58(10)\\ N1-Cd1-N8 & 109.27(11)\\ N4-Cd1-N5 & 113.24(11)\\ N4-Cd1-N5 & 113.24(11)\\ N4-Cd1-N8 & 176.88(10)\\ N5-Cd1-N8 & 69.52(11)\\ \hline\\ Cu1-N1 & 1.933(5) & 01-Cu1-O4_a & 96.21(18)\\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19)\\ Cu1-N5 & 1.939(6) & 01-Cu1-N4 & 170.61(19)\\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2)\\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2)\\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19)\\ & 04_a-Cu1-N5 & 105.7(2)\\ N1-Cu1-N5 & 173.7(2)\\ N1-Cu1-N5 & 173.7(2)\\ N4-Cu1-N5 & 102.2(2)\\ 06-Cu1-N1 & 101.9(2)\\ 06-Cu1-N5 & 84.1(2)\\ 01-Cu1-O6 & 96.77(19)\\ \hline\end{array}$			02-Cd1-N4	98.77(9)
$\begin{array}{c cccccc} & & & & & & & & & & & & & & & & $			02-Cd1-N5	147.05(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			02-Cd1-N8	78.30(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			N1-Cd1-N4	69.48(11)
$\begin{array}{c cccc} N1-Cd1-N8 & 109.27(11) \\ N4-Cd1-N5 & 113.24(11) \\ N4-Cd1-N8 & 176.88(10) \\ N5-Cd1-N8 & 69.52(11) \\ \hline \\ \hline \\ Cu1-N1 & 1.933(5) & 01-Cu1-O4_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19) \\ Cu1-N5 & 1.939(6) & 01-Cu1-N4 & 170.61(19) \\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19) \\ 04_a-Cu1-N5 & 90.7(2) \\ 04_a-Cu1-N5 & 195.7(2) \\ N1-Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 173.7(2) \\ N4-Cu1-N5 & 102.2(2) \\ 06-Cu1-N1 & 101.9(2) \\ 06-Cu1-N5 & 84.1(2) \\ 01-Cu1-O6 & 96.77(19) \\ \hline \end{array}$			NI-CdI-N5	93.58(10)
$\begin{array}{c cccc} N4-C01-N5 & 113.24(11) \\ N4-C01-N8 & 176.88(10) \\ N5-C01-N8 & 69.52(11) \\ \hline \\ Complex 4 \\ Cu1-N1 & 1.933(5) & 01-Cu1-04_a & 96.21(18) \\ Cu1-N4 & 2.044(5) & 01-Cu1-N1 & 90.24(19) \\ Cu1-N5 & 1.939(6) & 01-Cu1-N4 & 170.61(19) \\ Cu1-01 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-04_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-06 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19) \\ 04_a-Cu1-N5 & 90.7(2) \\ 04_a-Cu1-N5 & 105.7(2) \\ N1-Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 173.7(2) \\ N4-Cu1-N5 & 102.2(2) \\ 06-Cu1-N1 & 101.9(2) \\ 06-Cu1-N5 & 84.1(2) \\ 01-Cu1-06 & 96.77(19) \\ \hline \end{array}$				109.27(11)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			N4-Cd1-N9	113.24(11)
Complex 4 05.32(11) Cu1-N1 1.933(5) 01-Cu1-04_a 96.21(18) Cu1-N4 2.044(5) 01-Cu1-N1 90.24(19) Cu1-N5 1.939(6) 01-Cu1-N4 170.61(19) Cu1-O1 1.919(4) 01-Cu1-N5 86.9(2) Cu1-O4_a 2.615(5) 04_a-Cu1-N1 84.1(2) Cu1-O6 2.725(6) 04_a-Cu1-N4 80.44(19) O4_a-Cu1-N5 90.7(2) 04_a-Cu1-N5 90.7(2) N1-Cu1-N4 81.05(19) N1-Cu1-N5 173.7(2) N1-Cu1-N5 173.7(2) N4-Cu1-N5 102.2(2) O6-Cu1-N1 101.9(2) 06-Cu1-N4 81.72(19) O6-Cu1-N5 84.1(2) 01-Cu1-06 96.77(19)			N4-Cu1-N8	170.00(10) 60.52(11)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			NJ-CuI-No	09.32(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Complex 4			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu1–N1	1.933(5)	01-Cu1-04_a	96.21(18)
$\begin{array}{ccccccc} Cu1-N5 & 1.939(6) & 01-Cu1-N4 & 170.61(19) \\ Cu1-O1 & 1.919(4) & 01-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & 04_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & 04_a-Cu1-N4 & 86.44(19) \\ 04_a_Cu1-N5 & 90.7(2) \\ 04_a_Cu1-N6 & 165.7(2) \\ N1-Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 173.7(2) \\ N4-Cu1-N5 & 102.2(2) \\ 06-Cu1-N1 & 101.9(2) \\ 06-Cu1-N4 & 81.72(19) \\ 06-Cu1-N5 & 84.1(2) \\ 01-Cu1-O6 & 96.77(19) \end{array}$	Cu1–N4	2.044(5)	01–Cu1–N1	90.24(19)
$\begin{array}{ccccc} Cu1-O1 & 1.919(4) & O1-Cu1-N5 & 86.9(2) \\ Cu1-O4_a & 2.615(5) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & O4_a-Cu1-N4 & 86.44(19) \\ O4_a-Cu1-N5 & 90.7(2) \\ O4_a-Cu1-O6 & 165.7(2) \\ N1-Cu1-N4 & 81.05(19) \\ N1-Cu1-N5 & 173.7(2) \\ N4-Cu1-N5 & 102.2(2) \\ O6-Cu1-N1 & 101.9(2) \\ O6-Cu1-N5 & 84.1(2) \\ O1-Cu1-O6 & 96.77(19) \end{array}$	Cu1—N5	1.939(6)	01–Cu1–N4	170.61(19)
$\begin{array}{cccc} Cu1-O4_a & 2.615(5) & O4_a-Cu1-N1 & 84.1(2) \\ Cu1-O6 & 2.725(6) & O4_a-Cu1-N4 & 86.44(19) \\ & O4_a-Cu1-N5 & 90.7(2) \\ & O4_a-Cu1-O6 & 165.7(2) \\ & N1-Cu1-N4 & 81.05(19) \\ & N1-Cu1-N5 & 173.7(2) \\ & N4-Cu1-N5 & 102.2(2) \\ & O6-Cu1-N1 & 101.9(2) \\ & O6-Cu1-N4 & 81.72(19) \\ & O6-Cu1-N5 & 84.1(2) \\ & O1-Cu1-O6 & 96.77(19) \end{array}$	Cu1-01	1.919(4)	01-Cu1-N5	86.9(2)
$\begin{array}{cccc} Cu1-O6 & 2.725(6) & O4_a-Cu1-N4 & 86.44(19) \\ & O4_a-Cu1-N5 & 90.7(2) \\ & 04_a-Cu1-O6 & 165.7(2) \\ & N1-Cu1-N4 & 81.05(19) \\ & N1-Cu1-N5 & 173.7(2) \\ & N4-Cu1-N5 & 102.2(2) \\ & O6-Cu1-N1 & 101.9(2) \\ & O6-Cu1-N4 & 81.72(19) \\ & O6-Cu1-N5 & 84.1(2) \\ & O1-Cu1-O6 & 96.77(19) \end{array}$	Cu1—04_a	2.615(5)	04_a—Cu1—N1	84.1(2)
$\begin{array}{cccc} 04_a-Cu1-Ns & 90.7(2)\\ 04_a-Cu1-O6 & 165.7(2)\\ N1-Cu1-N4 & 81.05(19)\\ N1-Cu1-N5 & 173.7(2)\\ N4-Cu1-N5 & 102.2(2)\\ 06-Cu1-N1 & 101.9(2)\\ 06-Cu1-N4 & 81.72(19)\\ 06-Cu1-N5 & 84.1(2)\\ 01-Cu1-O6 & 96.77(19)\\ \end{array}$	Cu1-06	2.725(6)	04_a—Cu1—N4	86.44(19)
$\begin{array}{cccc} 04_a-Cu1-U6 & 165.7(2)\\ N1-Cu1-N4 & 81.05(19)\\ N1-Cu1-N5 & 173.7(2)\\ N4-Cu1-N5 & 102.2(2)\\ 06-Cu1-N1 & 101.9(2)\\ 06-Cu1-N4 & 81.72(19)\\ 06-Cu1-N5 & 84.1(2)\\ 01-Cu1-O6 & 96.77(19)\\ \end{array}$			04_a-Cu1-N5	90.7(2)
$\begin{array}{cccc} N1-C11-N4 & 81.05(19) \\ N1-C11-N5 & 173.7(2) \\ N4-C11-N5 & 102.2(2) \\ 06-C11-N1 & 101.9(2) \\ 06-C11-N4 & 81.72(19) \\ 06-C11-N5 & 84.1(2) \\ 01-C1-O6 & 96.77(19) \end{array}$			04_a—cu1—Ob	105.7(2)
$\begin{array}{cccc} N1-CU1-N5 & 173.7(2) \\ N4-Cu1-N5 & 102.2(2) \\ O6-Cu1-N1 & 101.9(2) \\ O6-Cu1-N4 & 81.72(19) \\ O6-Cu1-N5 & 84.1(2) \\ O1-Cu1-O6 & 96.77(19) \end{array}$			NI - CUI - N4 NI - CUI - N5	81.05(19)
$\begin{array}{ccc} 102.2(2)\\ 06-Cu1-N1 & 101.9(2)\\ 06-Cu1-N4 & 81.72(19)\\ 06-Cu1-N5 & 84.1(2)\\ 01-Cu1-O6 & 96.77(19) \end{array}$			NI-CUI-NO	1/3./(2)
06–Cu1–N1 81.5(2) 06–Cu1–N4 81.72(19) 06–Cu1–N5 84.1(2) 01–Cu1–O6 96.77(19)			$\Omega_{6} - \Omega_{1} - M_{1}$	102.2(2)
06-Cu1-N5 84.1(2) 01-Cu1-06 96.77(19)			06-Cu1-N4	81 72(19)
01-Cu1-06 $96.77(19)$			06-Cu1-N5	84 1(2)
			01-Cu1-06	96.77(19)

Symmetry transformations used to generate equivalent atoms: For complex **4**, a = -1 + x, y, z.

the coordination modes of the ligand towards different metal ions and also to draw a comparative account of the special characterizes in the structures of the metal complexes. Two molecules of the same ligand form the distorted octahedral geometry of MN_4O_2 (M = Mn and Cd) chromophore around the metal centres in **2** and **3**. The **4** is a 1D polymeric Cu(II) complex where the distorted octahedral geometry is maintained around each Cu(II) centre by one



Fig. 1. Structural representation and atom numbering scheme of 1 (H-atoms are omitted for clarity).

ligand molecule, unhydrolysed cyanamide part of one dicyanamide moiety and two μ -bridged propagating perchlorate group. In the complex **1** the ligand utilizes one pyrimidine N, the azomethine N and the salicyl hydroxyl oxygen atoms along with two oxygen atoms of two coordinated water molecules to form square pyramidal geometry. We have also studied the photoluminescence properties of the ligand HL and its metal complexes. Interestingly we have observed that the ligand HL, complexes **1**, **2** and **4** are fluorescence silent where as complex **3** shows chelation enhanced fluorescence.

2. Experimental section

2.1. Materials and physical methods

All chemicals were of reagent grade, purchased from commercial sources and used without further purification.

Caution! Although we have not encountered any problem, it should be kept in mind that perchlorate compounds of metal ions are potentially explosive in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

Elemental analyses (carbon, hydrogen, oxygen and nitrogen) of the ligand and the metal complexes were determined with a Perkin–Elmer CHN analyzer 2400 at the Indian Association for the Cultivation of Science, Kolkata. The electronic spectra of the complexes in methanolic solution were recorded on a Hitachi model U-3501 spectrophotometer. IR spectra (KBr pellet, 400– 4000 cm⁻¹) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. The fluorescence spectra were recorded on a Perkin Elmer LS 50B fluorimeter.

The ligand HL was synthesized using literature method [18].

2.2. Syntheses of complexes

2.2.1. Preparation of complex 1

A methanolic solution (10 ml) of Cu(NO₃)₂·6H₂O (1 mmol, 0.295 g) was added dropwise to a solution of HL (1 mmol, 0.241 g) in the same solvent taken in 1:1 molar ratio with constant stirring. The solution turned yellow and stirring was continued for ca. 2 h. It was left for slow evaporation at room temperature. After 2 weeks X-ray quality crystals of **1** were formed and were collected by usual technique. (Yield: 0.548 g, 65.5%). Anal. Calc. for C₁₃H₁₉ CuN₅O₇: C, 37.10; H, 4.55; N, 16.64; O, 26.61%. Found: C, 35.00; H, 3.44; N, 16.54; O, 23.23%. IR (KBr, cm⁻¹): 1385 (*v* of free NO₃⁻), 1609 (s) ($v_{c=Npym}$), 3346 (*v* of coordinated H₂O). UV–Vis (MeOH): $\lambda_{max}/nm = 385, 605; \varepsilon$ (DMF, M⁻¹ cm⁻¹): 8500.

2.2.2. Preparation of complexes 2 and 3

Complexes **2** and **3** were prepared following the same synthetic procedure as that for **1** using $Mn(ClO_4)_2 \cdot 6H_2O$ and $Cd(ClO_4)_2 \cdot 6H_2O$ as metal salts respectively. The ligand and metal was in 1:2 molar



Fig. 2. Hydrogen bonding interactions in complex 1.

Table 3 Details of hydrogen bond distances (Å) and angles (°) for 1, 2, 3 and 4.

D—H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<(DHA)
Complex 1				
N2-H4···07	0.8600	1.9300	2.771(2)	167.00
02-H1401	0.82(3)	2.05(3)	2.864(2)	173(3)
03-H1605	0.78(3)	2.07(3)	2.846(2)	175(2)
03–H17…04	0.79(3)	2.02(3)	2.801(2)	171(3)
07—H18···06	0.88(3)	2.06(3)	2.904(3)	162(3)
07—H19· · ·07	0.67(5)	2.22(4)	2.859(3)	159(6)
Complex 2				
N3—H3N…O3	0.86(2)	2.01(2)	2.863(3)	174(2)
03–H30···02	0.81(3)	1.96(3)	2.752(3)	166(3)
N7—H7N· · · O1	0.88(2)	1.91(2)	2.794(2)	175.0(18)
Complex 3				
N6-H6···01	0.8800	1.9400	2.775(9)	158.00
N14-H1403	0.8800	1.9000	2.751(11)	162.00
Complex 4				
N2-H2N···07	1.12(9)	2.07(9)	3.027(8)	142(6)
02—H2O…01	1.05(6)	1.82(6)	2.875(7)	177(7)
08—H80···06	1.0500	1.9500	2.998(9)	176.00



Fig. 3. Structural representation and atom numbering scheme of 2 (H-atoms are omitted for clarity).

ratio in each case to afford orange and yellow compounds respectively.

For **2**: (Yield: 0.773 g, 73%). Anal. Calc. for $C_{27}H_{30}MnN_8O_3$: C, 56.94; H, 5.31; N, 19.68; O, 8.43%. Found: C, 55.90; H, 4.56; N, 18.41; O, 6.40%. IR (KBr, cm⁻¹): 1606 (s) ($\nu_{c=Npym}$). UV–Vis (MeOH): $\lambda_{max}/nm = 580$; ε (DMF, M⁻¹ cm⁻¹): 15,000.

For **3**: (Yield: 0.602 g, 67%). Anal. Calc. for C₂₇H₃₀CdN₈O₃: C, 51.72; H, 4.82; N, 17.87; O, 7.66%. Found: C, 51.49; H, 3.63; N, 15.99; O, 6.66%. IR (KBr, cm⁻¹): 1608 (s) ($\nu_{c=Npym}$). UV–Vis (MeOH): $\lambda_{max}/nm = 360$ and 470; ε (DMF, M⁻¹ cm⁻¹): 89,000.

2.2.3. Preparation of complex 4

To a methanolic solution (30 ml) of Cu(ClO₄)₂, 6H₂O (2 mmol, 0.744 g), a solution of the Schiff base HL in the same solvent (2 mmol, 0.482 g) was slowly added, followed by a solution of sodium dicyanamide (4 mmol, 0.356 g) in a minimum volume of aqueous methanol with constant stirring. The stirring was continued for another 2 h and filtered. The light yellow solution was kept in a refrigerator at 10 °C which after 10 days afforded green hexagonal crystals suitable for X-ray diffraction. The crystals were isolated by filtration and made air dried. (Yield: 0.657 g, 61.5%). Anal. Calc. for C₁₆H₁₅ClN₈O₆Cu: C, 37.36; H, 2.94; N, 21.79; O, 18.66%. Found: C, 35.31; H, 2.21; N, 21.51; O, 16.94%. IR (KBr, cm⁻¹): 1100 (ν of coordinated perchlorate), 1610 (s) ($\nu_{c=Npym}$), UV–Vis (MeOH): $\lambda_{max}/nm = 386$, 607; ε (DMF, M⁻¹ cm⁻¹): 10,000.

3. X-ray crystallography

Selected crystal data for **1–4** are given in Table 1 and selected metrical parameters of these complexes are given in Table 2. Diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K (for **1**, **2**, **3** and **4**) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ (Å). Cell parameter refinement and data reduction were carried out using Bruker SMART [19] and Bruker SAINT softwares for **1**, **2**, **3** and **4** [20]. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using the SHELXS-97 and SHELXL-97 programs [21]. An empirical absorption correction for **1**, **2**, **3** and **4** were carried out using the SADABS [22]. One methanol molecule was present as the solvent molecule which was removed using SQUEEZE. Thus four hydrogen atoms, one carbon and one oxygen atom of methanol molecule were added to the chemical formula to adjust the density, molecular mass and F000 value in **3**. A water



Fig. 4. Hydrogen bonding interactions in complex 2.



Fig. 5. Structural representation and atom numbering scheme of 3 (H-atoms are omitted for clarity).

molecule was present as the solvent molecule which was removed using SQUEEZE. Thus two hydrogen atoms and one oxygen atom of water molecule were added to the chemical formula to adjust the density, molecular mass and F000 value in **4**.

4. Result and discussion

4.1. Syntheses

The complexation behaviour of ligand HL towards Cu(II), Mn(II) and Cd(II) salts were investigated. Complexes **1–3** were obtained

by mixing the ligand and respective metal salts taken in 1:1 molar ratio in methanol under appropriate condition, while, complex **4** was isolated from the reaction of the ligand, Cu(II) salt and dicynamide taken in 1:1:2 molar ratio in methanol [Scheme 1]. These complexes were characterized by X-ray crystallography, elemental analyses, UV–Vis, IR spectral studies. The fluorescence behaviour of the ligand and its metal complexes were also studied.

4.2. Structural description

4.2.1. Structural description of complex 1

The perspective view of the asymmetric unit of the complex **1** with atom numbering scheme is shown in Fig. 1. Selected metrical parameters are listed in Table 2. The complex 1 crystallizes in space group *C*2/*c*. The unit cell of **1** comprises of eight molecules. The copper(II) atom maintains five-coordinate environment. The Addison parameter (τ) of the pentacoordinated Cu(II) is 0.2081 suggesting the predominance of square-based pyramidal (SP) geometry. The basal plane is formed by N3 of pyrimidine, N1 of azomethine, O1 of salicyl hydroxyl group and O3 of water molecule and the axial position is occupied by oxygen atom O2 from another water molecule. The Cu-O and Cu-N bond distances are 1.9009(13) Å (Cu1-O1), 2.0159(16) Å (Cu1-O3), 2.2662(15) Å (Cu1-O2) axial, 1.9500(13) Å (Cu1-N1), and 2.0280(15) Å (Cu1-N3) respectively. The copper(II) ion is at 0.196 Å above the basal plane. The complex is stabilized by a network of intermolecular hydrogen bonding. The H4 atom of N2 and O7 atom of water molecule, H14 atom of water molecule and O1 atom of salicyl hydroxyl oxygen and H16 atom of water molecule and O5 atom of nitrate ion, H17 atom of water molecule and O4 atom of nitrate ion, H18 atom of water molecule and O6 atom of nitrate ion and H19 atom of water molecule and O7 atom of water molecule (Fig. 2)



Fig. 6. Hydrogen bonding interactions in complex 3.



Fig. 7. Structural representation and atom numbering scheme of 4 (H-atoms are omitted for clarity).



Fig. 8. 3D view of complex 4 with trapped per chlorate molecules within the chains.



Fig. 9. Hydrogen bonding interactions in complex 4.

are involved in the hydrogen bonding. The details of hydrogen bonding are given in Table 3.

4.2.2. Structural description of complexes 2 and 3

The perspective view of the asymmetric units of the complexes **2** and **3** with the atom numbering schemes are shown in Figs. 3 and 5 respectively. Selected metrical parameters are listed in Table 2. The complexes **2** and **3** crystallize in same space group *P*-1. The unit cells of **2** and **3** comprise of two molecules. In all the three complexes, two tridentate ligand molecules are involved in



Fig. 10. Fluorescence emission property of free ligand HL and complexes 1, 2, 3 and 4.

coordination. The central metal ion M [where, M = Mn(II) and Cd(II)] in these complexes attains distorted octahedral geometry with N₄O₂ chromophore. Here the equatorial positions are occupied by the salicyl hydroxyl oxygen atom O1, one pyridmidyl nitrogen atom N1 from one ligand and another salicyl hydroxyl oxygen atom O2, pyridmidyl nitrogen atom N5 from another ligand while the axial positions are occupied by the azomethine nitrogen atom N4 from one ligand and N8 from another ligand. The average M–N1(pym) distance falls in the range 2.3029(17)–2.385(3)Å, 2.3376(17)-2.362(3) Å, M-O1(alkoxy) 2.0897 M-N5(pym)(15)-2.218(3) Å, M-O2(alkoxy) 2.0858(16)-2.222(2) Å, M-N4 (azomethine) 2.2748(16)-2.356(16) Å, M-N8(azomethine) 2.2604 (16)-2.369(3) Å. The average O1-M-O2 bond angle falls in the range 103.38(6)-106.26(10), O2-M-N1 89.61(6)-90.34(9), N1-M-N5 91.12(6)-93.58(10), N5-M-O1 88.02(10)-90.01(5), N8-M-N4 176.88(610)-177.38(5) respectively. The structures 2 and **3** are stabilized by a network of intermolecular hydrogen bonding.(O3 of methanol molecule and H3N of N3. N7H of N7 and O1 of salicyl hydroxyl oxygen, H30 of methanol molecule and O2 of salicyl hydroxyl oxygen) (Fig. 4), O1 of salicyl hydroxy oxygen and H4A of water molecule) and O2 of salicyl hydroxyl oxygen and H3N of N3, O1 of salicyl hydroxyl oxygen and H3O of methanol molecule, O3 of methanol molecule and H7N of N7 (Fig. 6) are involved in hydrogen bonding. The details of H-bonding are presented in Table 3.

4.2.3. Structural description of complex 4

The perspective view with atom numbering scheme is shown in Fig. 7. Selected metrical parameters are given in Table 2. The

complex 4 crystallizes in space group P21/c and its unit cell comprises of six molecules. Each Cu(II) ion is in a distorted octahedral geometry. The equatorial plane is formed by N4 from pyrimidine, N1 from azomethine, N5 from unhydrolysed part of the coordinated dicyanamide ion and O1 from salicyl hydroxyl oxygen atom and the axial positions are occupied by two oxygen atoms O4 and O5 of bridging perchlorate ions. The tetragonally distorted octahedral arrangement around Cu(II) gives the bond distances of Cu1-N1 with 1.937(5) Å, Cu1-N4 2.045(5) Å, Cu1-N5 1.941(6) Å and Cu1–O1 1.921(4) Å, Cu1–O4 2.615(5) Å, Cu1–O5_b 2.727(6) Å. The Cu-O bond distances are within the range of 2.52-2.883 Å reported for a variety of Cu(II) complexes containing co-ordinated per chlorate group [23,24]. The resulting 1D coordination polymeric unit is prolonged along the direction of *b*-axis propagated by the µ-bidentate ligation of perchlorate ions. The 3D view of complex **4** with trapped perchlorate molecules within the chains has been shown (Fig. 8). The crystal structure of this compound can be described as a 2D layer due to intermolecular hydrogen bonding (Fig. 9). H2O of CH₃OH and O1 of salicyl hydroxyl oxygen, O6 of per chlorate and H8O of CH₃OH, H2N of N2 and O7 of perchlorate are involved in hydrogen bonding. The details of hydrogen bonding are given in Table 3.

5. Infrared spectroscopy

A comparative study of the IR spectral data of the reported complexes with that of the uncoordinated ligand gives supportive evidences towards better understanding of the coordinating behaviour of the ligand molecule. The free ligand displays pyridyl C=N stretching frequency at 1528 cm⁻¹. A strong band in the region 1385 cm⁻¹ indicates the presence of nitrate ion in complex **1**. A broad band in the region 3500–3200 cm⁻¹ indicates the presence of lattice water molecules in complex **1** [25]. In **4**, the $v(ClO_4^-)$ observed around 1100 cm⁻¹ splits into three peaks, indicating that the symmetry of the per chlorate ion is lowered from Td to C_{2V} [26]. The strong $v_{C=N}$ bands occurring at 1609, 1606, 1608 and 1610 cm⁻¹ for **1**, **2**, **3** and **4** respectively are shifted considerably towards lower frequencies compared to that of the free Schiff base ligands (1635 cm⁻¹), indicating the coordination of the azomethine nitrogen atom [27].

6. Electronic spectra

The electronic absorption spectrum of the free Schiff base ligand was measured in MeOH solvent. The electronic spectrum of the free ligand shows a band at 345 nm attributed to the $n \rightarrow \pi^*$ transition of the azomethine group. There is a strong band at 280 nm due to a $\pi \rightarrow \pi^*$ transition [28]. The spectra of the Cu(II) complexes (1 and 4) exhibit a strong band at 385 nm and 386 nm which are characterized as the pyrimidine to Cu(II) charge transfer (LMCT) transition [29-33]. The d-d transition has been detected as a relatively broad band with low intensity in the 605 nm and 607 nm for complex **1** and **4** [29–33]. The electronic spectrum of the Mn(II) complex exhibits one band nearly at 580 nm, probably due to a metal-ligand charge transfer transition (MLCT) [34,35]. The electronic spectrum of the Cd(II) complex exhibits intense bands in the range of 360-400 nm. These transitions are assigned as intra ligand $\pi \to \pi^*$ and $n \to \pi^*$ transitions and also the weak band at 450–470 nm is assigned to a MLCT band [36].

7. Emission behaviour

The emission properties of the ligand HL and its complexes were studied at room temperature (298 K) in 1×10^{-5} (M) MeOH solutions (Fig. 10). In general, quenching of fluorescence of a ligand

by the transition metal ions during complexation is a rather common phenomenon which is explained by the process, such as magnetic perturbation, redox activity, and electronic energy transfer [37,38]. Enhancement of fluorescence through complexation is, however, of much interest as it opens up the opportunity for photochemical application of these complexes. The ligand is non fluorescent while its cadmium(II) complex shows emission at 455 nm when it is excited at 360 nm in MeOH. The Mn(II) and Cu(II) complexes are fluorescence silent as like the ligand. The fluorescence behaviour of the Cd(II) complex is suggested to originate from ligand part. The nonfluorescence behaviour of uncomplexed ligand is owing to the presence of free electron pairs on donor centres which become coordinated in the complex suppressing the possible ET quenching mechanism in the complex (i.e. increased luminescence) However, the factor of chelation induced rigidity also plays an important role in inducing the fluorescence behaviour of the ligand part on complexation with metal ion.

8. Conclusion

The complexation behaviour of a pyrimidine derived Schiff base ligand has been studied by syntheses and X-ray crystallographic characterization of three new mononuclear Cu(II), Mn(II), and Cd(II) complexes **1–3** and a 1-D polymeric of copper(II) complex **4**. The ligand behaves as a uninegative tridentate NNO donor in all the complexes. In the complex **4** the expected bridging ligand dca behaves as a monodentate one. In contrast, the very weakly coordinating ClO_4^- acts as unexpected bridging ligand between two Cu(II) centres in the same complex. The ligand HL and three of the metal complexes **1**, **2** and **4** are fluorescent silent, a common observation for transition metal complexes. The Cd complex **3** has considerable fluorescence and probably this has been caused by chelation induced rigidity along with favourable resonance interaction throughout the ligand moieties resulting a red shift emission.

Supplementary material

CCDC 896873, 896874, 896876, 896877 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

Financial support [Sanc. No. 01(2401)/10/EMR-II, dated 05.01.2011] from the Council of Scientific and Industrial Research (CSIR), New Delhi, India, is gratefully acknowledged. S.K. and A.J. thank CSIR for award of SRF. Sangita Ray acknowledges the University Grants Commission (UGC), New Delhi, India [Sanc. No. F. 5-1/2007(BSR)/5-16/2007(BSR), dated 12.02.2006] for a J.R.F. Financial support [Sanc. No. SR/S1/IC-27/2008, dated 13.03.2009] from the Department of Science & Technology (DST), New Delhi, India, is also gratefully acknowledged. X-ray crystallography was performed at the DST funded National Single Crystal Diffractometer facility at the Department of Chemistry, University of Calcutta.

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