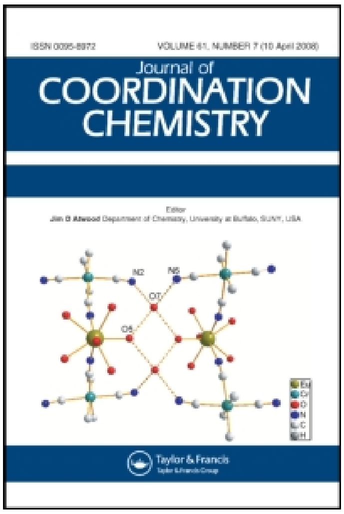

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Synthesis, characterization, and fluorescence properties of dinuclear cadmium(II) complexes

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Synthesis, characterization, and fluorescence properties of dinuclear cadmium(II) complexes

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Four dinuclear cadmium(II) complexes, $[Cd_2(L^1)(\mu_2\text{-}Cl)Cl_2]$ (**1**), $[Cd_2(L^2)(\mu_2\text{-}Cl)Cl_2]$ (**2**), $[Cd_2(L^3)(\mu_2\text{-}Cl)Cl_2]$ (**3**), and $[Cd_2(L^4)_3ClO_4]$ (**4**), where HL^1 = 4-methyl-2,6-*bis*(1-(2-piperidinoethyl)iminomethyl)-phenol, HL^2 = 4-methyl-2,6-*bis*(1-(2-pyrrolidinoethyl)iminomethyl)-phenol, HL^3 = 4-methyl-2,6-*bis*(1-(2-morpholinoethyl)iminomethyl)-phenol and HL^4 = 4-methyl-2,6-*bis*(cyclohexylmethyl)iminomethyl)-phenol, were synthesized. They were characterized by elemental analysis, FT-IR, UV–Vis, fluorescence and electronspray ionization mass spectroscopy. Complexes **1** and **4** were also characterized by single crystal X-ray analysis. The cadmiums atoms in **1** are linked by μ_2-chloride in a distorted square pyramidal geometry, whereas cadmium atom in **4** is in a distorted octahedral environment. The complexes show emission bands around 500 nm with excitation at 395 nm.

Keywords: Cadmium(II) complex; Schiff-base ligand; Crystal structure; Fluorescence

1. Introduction

Metallo-organic frameworks of different architectures of varied metals have been extensively studied for their interesting properties in catalysis, gas storage, etc. [1, 2]. Choice of ligands, bridging ligands, different metal ions, metal-to-ligand ratio, and experimental conditions can tune a mononuclear species into a multinuclear system [3–5]. Cadmium(II) has penta-, hexa- [6–9], and hepta-coordination [10–14]. Polynuclear d^{10} metal complexes attract attention due to their photoluminescence and structural diversity [15–19]. Schiff-bases form complexes with unusual coordination, high thermodynamic stability, and kinetic inertness. Binucleating ligands are widely used to form dinuclear and multinuclear complexes. Our group has recently explored binucleating ligands prepared by reaction between 4-methyl-2,6-diformylphenol and respective amine to form multinuclear metal complexes [20–22].

The synthesis, characterization, and fluorescence of four dinuclear Cd(II) complexes with Schiff-base ligands are reported here. Complexes **1** $\{[Cd_2(L^1)(\mu_2\text{-}Cl)Cl_2]\}$, **2** $\{[Cd_2(L^2)(\mu_2\text{-}Cl)Cl_2]\}$ and **3** $\{[Cd_2(L^3)(\mu_2\text{-}Cl)Cl_2]\}$ were synthesized with the N_4O donor

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Schiff-base ligand [23], whereas **4** $\{[Cd_2(L^4)_3ClO_4]\}$ was synthesized by using a N_2O donor Schiff-base ligand. The complexes were characterized by elemental analysis, FT-IR, UV–Vis, fluorescence and electronspray ionization mass spectra. The structures of **1** and **4** were determined by X-ray single crystal diffraction.

2. Experimental

2.1. *Materials*

Anhydrous cadmium(II) chloride, cadmium(II) perchlorate hydrate, 1-(2-aminoethyl)-piperidine, 1-(2-aminoethyl)-pyrrolidine, 4-(2-aminoethyl)-morpholine, and cyclohexylmethylamine were purchased from Sigma Aldrich and were used as received. 4-Methyl-2,6-diformylphenol was synthesized starting from *p*-cresol following a published procedure [24]. All other reagents were of analytical reagent grade. Solvents used for spectroscopic studies were purified and dried by standard procedures before use [25].

2.2. *Physical methods*

FT-IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer as KBr pellets. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin–Elmer, Norwalk, CT. Absorption and luminescence spectra were carried out on a Shimadzu UV2100 UV–Vis recording spectrophotometer and a Perkin–Elmer LS 55 luminescence spectrometer, respectively. The ESI-MS was recorded on a Qt of Micro YA263 mass spectrometer.

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amount of material should be handled with care.*

2.3. *Synthesis of* $[Cd_2(L^1)(\mu_2\text{-}Cl)Cl_2]$ *(1)*

To a solution of 4-methyl-2,6-diformylphenol (0.082 g, 0.5 mmol) in 10 mL of acetonitrile was added 1-(2-aminoethyl)-piperidine (0.128 g, 1.0 mmol) in 5 mL acetonitrile. The reaction mixture was refluxed for 4 h and then cooled. Anhydrous cadmium(II) chloride (0.183 g, 1.0 mmol) in 5 mL acetonitrile was added, the mixture was stirred for 30 min, refluxed for another hour, cooled, and filtered. Needle-shaped single crystals of **1** suitable for X-ray crystallography were obtained on slow evaporation of the filtrate at ambient temperature within 2 days (Yield: 75%). Anal. Calcd for $C_{23}H_{35}N_4OCl_3Cd_2$: C, 38.65; H, 4.94; N, 7.84. Found: C, 38.58; H, 4.89; N, 7.87%.

2.4. *Synthesis of* $[Cd_2(L^2)(\mu_2\text{-}Cl)Cl_2]$ *(2)*

Complex **2** was synthesized in a similar process as for **1**. Here 1-(2-aminoethyl)-pyrrolidine is used instead of 1-(2-aminoethyl)-piperidine. Unfortunately, it was not possible to grow single crystals of X-ray diffraction quality after several attempts

(Yield: 65%). Anal. Calcd for $C_{21}H_{31}N_4OCl_3Cd_2$: C, 36.73; H, 4.55; N, 8.16. Found: C, 36.68; H, 4.50; N, 8.07%.

2.5. *Synthesis of [$Cd_2(L^3)(\mu_2\text{-}Cl)Cl_2$] (3)*

Complex **3** was synthesized similarly to **1** with 1-(2-aminoethyl)-morpholine instead of 1-(2-aminoethyl)-piperidine. Unfortunately, it was not possible to grow single crystals suitable for X-ray diffraction analysis after several attempts (Yield: 70%). Anal. Calcd for $C_{21}H_{31}N_4O_3Cl_3Cd_2$: C, 35.10; H, 4.35; N, 7.80. Found: C, 35.02; H, 4.30; N, 7.85%.

2.6. *Synthesis of [$Cd_2(L^4)_3ClO_4$] (4)*

Cyclohexylmethylamine (0.170 g, 1.5 mmol) in 5 mL of acetonitrile was added to a 10 mL acetonitrile solution of 4-methyl-2,6-diformylphenol (0.123 g, 0.75 mmol). The reaction mixture was refluxed for 2 h and cooled. Cadmium(II) perchlorate hydrate (0.311 g, 1.0 mmol) was added to the mixture followed by the addition of sodium acetate (0.123 g, 1.5 mmol). The mixture was stirred for 30 min, refluxed for another hour, cooled and filtered. Prismatic single crystals for X-ray diffraction were obtained from the filtrate at room temperature after 2 days (Yield 80%). Anal. Calcd for $C_{69}H_{97}Cd_2ClN_6O_7$: C, 59.93; H, 7.07; N, 7.09. Found: C, 59.86; H, 7.01; N, 7.15%.

2.7. *X-ray data collections and structure determinations*

Crystal data of **1** and **4** are summarized in table 1. The diffraction experiments were carried out on a Bruker APEX-2 CCD diffractometer using Mo-Kα radiation at 296 and 150 K, respectively. No crystal decay was observed, so that no decay correction was needed. Data were processed using the Bruker SAINT package. The structure solution and the refinement procedure were carried out using SHELX-97 [26]. The structures were solved by direct methods and refined with the full-matrix least-squares on F^2. All hydrogen atoms were added in calculated positions.

CCDC 696172 and 696173 contain the supplementary crystallographic data of **1** and **4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. *Synthesis and characterization*

Complexes **1**–**3** were synthesized similarly; Schiff-base condensation occurs between one equivalent of 4-methyl-2,6-diformylphenol and two equivalents of amine, and cadmium(II) chloride was added later. During synthesis of **4**, a molar equivalent of sodium acetate was added to the Schiff base for deprotonation.

FT-IR spectra show a number of strong $\nu_{C–H}$ bands at 2800–3000 cm^{-1} [27]. Strong bands in the region of 1600–1650 cm^{-1} for all the complexes may be assigned to C=N of

Table 1. Crystal data for **1** and **4**.

Complex	**1**	**4**
Formula	$C_{23}H_{35}Cd_2Cl_3N_4O$	$C_{69}H_{97}Cd_2ClN_6O_7$
Formula weight	714.70	1382.80
Temperature (K)	296	150
Color	Yellow	Yellow
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcn*	*Pccn*
Units of dimensions (Å, °)		
a	20.477(3)	24.7899(17)
b	12.3372(19)	11.8807(8)
c	11.1467(18)	23.2249(16)
V (Å^3)	2815.9(8)	6840.2(8)
Z	4	4
$F(000)$	1424	2888
D_{Calcd} (g cm^{-3})	1.686	1.343
λ (Mo-Kα) (Å)	0.71073	0.71073
Crystal dimension (mm^3)	0.40 × 0.10 × 0.05	0.40 × 0.20 × 0.10
θ range (°)	2–19	2–23
Reflection collected/unique	1082/810	4818/3687
Absorption correction	Multi-scan	Multi-scan
R_{int}	0.1007	0.0544
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0457$, $wR_2 = 0.1012$	$R_1 = 0.0391$, $wR_2 = 0.1213$
Goodness-of-fit	1.024	0.995

the Schiff-bases. Bands at 1091 and 623 cm^{-1} for **4** are assigned to the stretching and bending frequencies of ClO_4^- [28].

Electronic spectra of **1–4** exhibit an intense band at 310 nm and 390–395 nm, assigned to π–π*/n–π* transitions [29]. A relatively weak transition at around 440–445 nm is assigned to MLCT band [29].

Electronspray ionization mass spectra of **1–4** were performed at room temperature in acetonitrile. Complexes **1–4** show peaks *m*/*z* at 679.24, 651.23, 683.23, and 1224.99, respectively. These peaks can be assigned to $[Cd_2(L^1)Cl_2]^+$, $[Cd_2(L^2)Cl_2]^+$, $[Cd_2(L^3)Cl_2]^+$, and $[Cd_2(L^4)_3]^+$, respectively, since the theoretical isotopic distribution patterns are in excellent agreement with experimental one. The experimental and theoretical isotopic distribution of **1** are shown in figure 1 as a representative case. All complexes retain their dinuclear entity in solution.

3.2. *Description of crystal structure of 1*

Selected bond distances and angles of **1** are shown in table 2. A perspective view with atom numbering scheme is shown in figure 2. The complex is a discrete dinuclear compound consisting of one N_4O donor binucleating ligand, 4-methyl-2,6-*bis*(1-(2-piperidinoethyl)iminomethyl)-phenolate (L^{1-}), two Zn^{2+}, one μ_2-chloro, and two chlorides. Cd1 is pentacoordinate, connected to one μ_2-phenoxo oxygen O1 and two nitrogens N1 and N2 from L^1, one μ_2-chloro Cl1, and one chloride Cl2. Cd1 is in a distorted square pyramidal geometry, clearly evident from the value of trigonal index, τ of Cd1 is 0.31. The value of τ is defined as the difference between the two largest donor–metal–donor angles divided by 60, a value which is 0 for an ideal square pyramid and 1

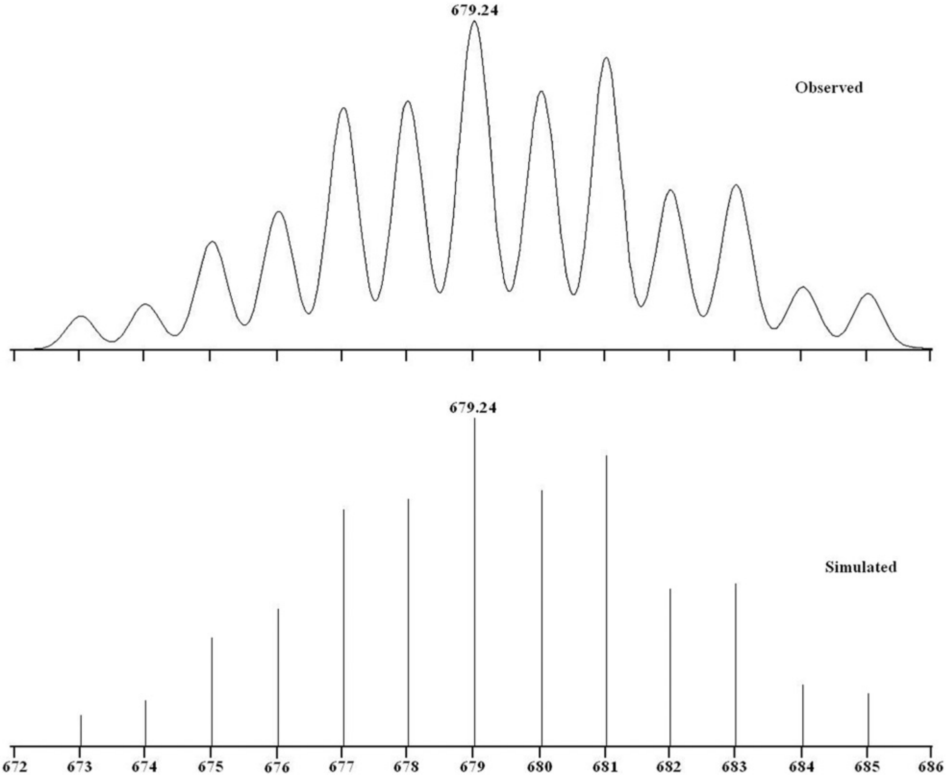

Figure 1. The isotopic distribution of the observed and simulated ESI-MS of **1** in acetonitrile.

Table 2. Selected bond lengths (Å) and angles (°) of **1** and **4**.

1			
Cd1–N2	2.268(12)	Cd1–Cl2	2.396(4)
Cd1–O1	2.296(8)	Cd1–Cl1	2.484(4)
Cd1–N1	2.392(10)		
N2–Cd1–O1	76.9(5)	N2–Cd1–N1	77.5(5)
O1–Cd1–N1	150.9(3)	N2–Cd1–Cl2	113.5(4)
O1–Cd1–Cl2	104.69(14)	N1–Cd1–Cl2	98.2(3)
N2–Cd1–Cl1	132.5(3)	O1–Cd1–Cl1	79.7(3)
N1–Cd1–Cl1	108.1(3)	Cl2–Cd1–Cl1	112.14(19)
4			
Cd1–O1	2.268(3)	Cd1–O2	2.276(3)
Cd1–N3	2.279(4)	Cd1–N1	2.312(4)
Cd1–N2	2.331(3)		
O1–Cd1–O2	75.86(10)	O1–Cd1–N3	145.21(12)
O2–Cd1–N3	102.92(9)	O1–Cd1–N1	79.10(12)
O2–Cd1–N1	152.06(11)	N3–Cd1–N1	104.71(13)
O1–Cd1–N2	103.64(12)	O2–Cd1–N2	76.12(11)
N3–Cd1–N2	109.83(13)	N1–Cd1–N2	98.20(13)

for a trigonal bipyramid [30]. The square is formed by O1, N1, N2, and Cl1, whereas Cl2 occupies the apical position. All the donor–Cd bond distances are in agreement with previously reported values [29, 31]. Here the $\text{Cl}_{\text{apical}}$–Cd1 distance is shorter than the $\text{Cl}_{\text{bridged}}$–Cd1 distance. The distance between two cadmiums atoms is 3.659 Å.

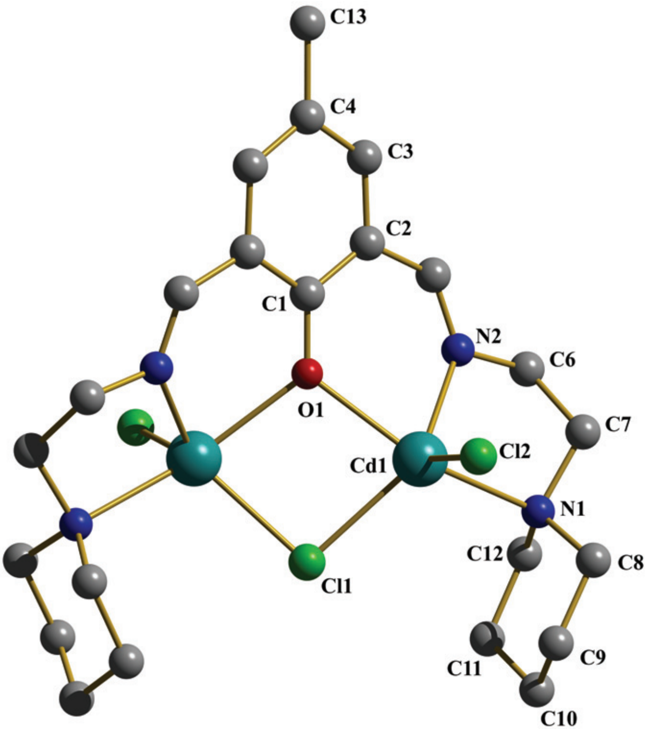

Figure 2. A perspective view of **1** with atom numbering scheme. Hydrogen atoms were omitted for clarity.

3.3. *Description of crystal structure of 4*

Selected bond distances and angles of **4** are shown in table 2. A perspective view of the complex is shown in figure 3. Complex **4** is also a dinuclear complex consisting of three N_2O donor binucleating ligands, two Zn^{2+}, and one perchlorate. Cd1 is hexacoordinate, linked to one μ_2-phenoxo oxygen O1 and one nitrogen, N1, from the ligand; one μ_2-phenoxo oxygen O2 and one nitrogen, N2, from the ligand; and one μ_2-phenoxo oxygen O1 and one nitrogen, N1, from the ligand of another asymmetric unit in a distorted octahedral geometry. The Cd–O and Cd–N bond distances are in agreement with reported values [29, 31]. The distance between the two metals is 3.3192(7) Å.

3.4. *Fluorescence properties*

The fluorescence spectra of **1**–**4** were recorded in solid state at room temperature (figure 4). Complexes **1**–**3** give an emission band in the region 492–505 nm when they are excited at 395 nm (table 3). The emission band at 468 nm for **1**–**3** might be attributed to LMCT (ligand-to-metal charge transfer), which has been observed in other polynuclear d^{10} metal polymers [32]. Complex **1** having the strongest electron-donating moiety, exhibits shorter wavelength at 492 nm [33]. Complex **4** shows emission at 500 nm.

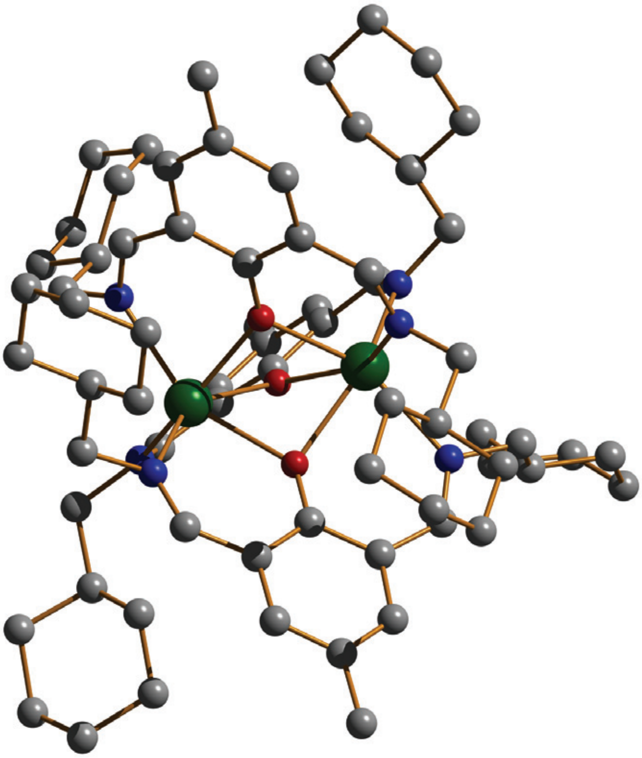

Figure 3. A perspective view of **4**. Hydrogen atoms and perchlorate ion were omitted for clarity. Color code: cadmium (green), nitrogen (blue), oxygen (red), and carbon (grey).

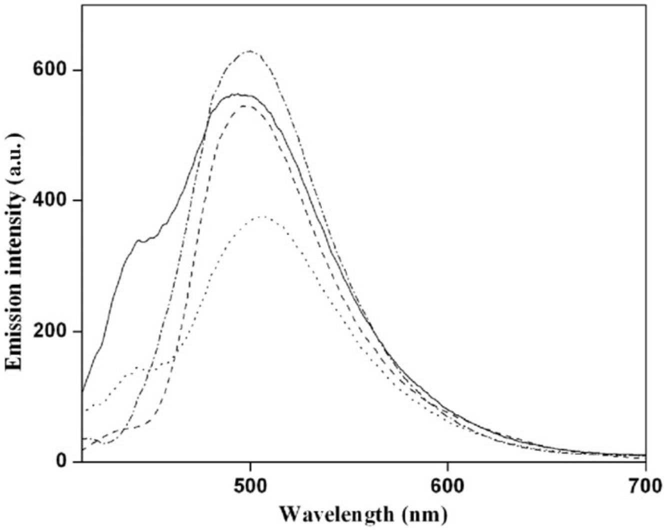

Figure 4. Emission spectra of **1** (solid line), **2** (dashed line), **3** (dotted line), and **4** (dashed-dotted line) in solid state at room temperature (excitation at 395 nm).

Table 3. Emission data for **1**–**4** (excitation 395 nm) at solid state.

Complex	Emission peak (nm)
1	492
2	496
3	505
4	500

4. Conclusion

Four dinuclear cadmium(II) complexes (**1**–**4**) with N_2O and N_4O Schiff-base donor ligands were synthesized, and two (**1** and **4**) are characterized by single crystal X-ray diffraction analysis. Complex **1** has μ_2-chloro bridge between cadmiums. Cd of **1** is pentacoordinate square pyramid geometry, whereas Cd in **4** is in a distorted octahedral geometry. All complexes exhibit emission bands in the region 492–505 nm when they are excited at 395 nm, showing potential as light emitting materials.

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