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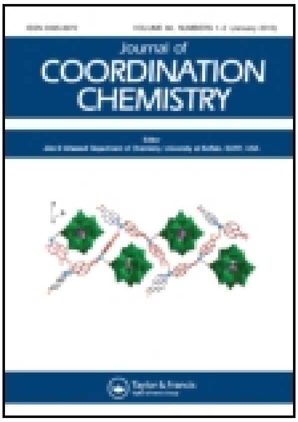

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Synthesis, crystal structures, and fluorescent properties of zinc and cadmium(II) complexes with tridentate Schiff bases

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Synthesis, crystal structures, and fluorescent properties of zinc and cadmium(II) complexes with tridentate Schiff bases

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A new dinuclear zinc(II) complex, $[Zn_2(L^1)_2(N_3)_2]$ (**1**), and a new polynuclear cadmium(II) complex, $[Cd_2(L^2)_2(NO_3)(\mu_2\text{-dca})]_n$ (**2**), where L^1 and L^2 are deprotonated forms of 2-[(2-ethylaminoethylimino)methyl]-6-methylphenol and 2-[(2-ethylaminoethylimino)methyl]-4-methoxyphenol, respectively, have been prepared and characterized by elemental analysis, IR spectra, and single crystal X-ray diffraction. The thermal stability and fluorescence of the complexes were also investigated.

Keywords: Crystal structure; Schiff base; Cadmium; Zinc; Fluorescence; Thermal stability

1. Introduction

Polynuclear complexes containing bridging ligands have received considerable attention because of their interesting molecular topologies and specific functionalities [1–3]. Among pseudohalogens, azide and dicyanamide are versatile bridging ligands [4–6]. Luminescent compounds attract interest because of their applications as organic light emitting devices and sensors [7, 8]. Zinc and cadmium complexes with Schiff bases usually possess various fluorescent properties [9, 10]. Schiff bases derived from salicylaldehyde with *N*-substituted-1,2-diamine represent important ligands in coordination chemistry [11–14], however, during the search of literature, we found no complexes reported for the Schiff bases 2-[(2-ethylaminoethylimino)methyl]-6-methylphenol (HL^1) and 2-[(2ethylaminoethylimino)methyl]-4-methoxyphenol (HL^2; scheme 1). In the present paper, a new dinuclear zinc(II) complex, $[Zn_2(L^1)_2(N_3)_2]$ (**1**), and a new polynuclear cadmium(II) complex, $[Cd_2(L^2)_2(NO_3)(\mu_2\text{-dca})]_n$ (**2**), have been prepared and investigated for their thermal stabilities and fluorescence properties.

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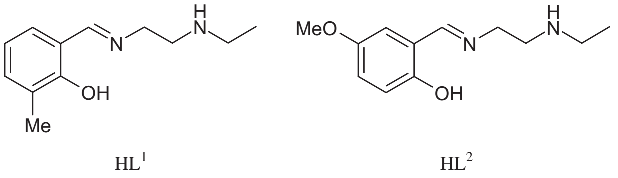

Scheme 1. The Schiff base ligands.

2. Experimental

2.1. *Materials and measurements*

3-Methylsalicylaldehyde, 5-methoxysalicylaldehyde, and *N*-ethylethane-1,2-diamine were purchased from Aldrich Chemical Company Inc. and used as received. All other reagents were of analytical grade. Elemental analyzes (C, H, and N) were performed using a Perkin–Elmer 240 elemental analyzer. IR spectra were recorded on a JASCO FT/IR-480 PLUS Fourier transform spectrophotometer with pressed KBr pellets from 200 to 4000 cm^{-1}. Luminescence spectra were reported on a JASCO FP-6500 spectrofluorometer (solid) from 200–850 nm. Thermal stability analyzes were performed on a Perkin–Elmer Pyris Diamond TG–DTA thermal analysis system.

Caution: Sodium azide is potentially explosive; only small quantity should be used and handled with great care.

2.2. *Synthesis of HL^1*

To a methanol solution (20 mL) of 3-methylsalicylaldehyde (1.0 mM, 136.2 mg) was added a methanol solution (10 mL) of *N*-ethylethane-1,2-diamine (1.0 mM, 88.2 mg) with stirring. The mixture was stirred for 30 min at room temperature to give a clear yellow solution, concentrated by distillation to give a gummy product of HL^1. Anal. calcd. for $C_{12}H_{18}N_2O$: C, 69.9; H, 8.8; N, 13.6. Found: C, 69.7; H, 8.9; N, 13.5%.

2.3. *Synthesis of HL^2*

The Schiff base HL^2 was prepared by the same method as for HL^1, with 3-methylsalicylaldehyde replaced by 5-methoxysalicylaldehyde (1.0 mM, 152.1 mg). Anal. calcd. for $C_{12}H_{18}N_2O_2$: C, 64.8; H, 8.2; N, 12.6. Found: C, 64.9; H, 8.2; N, 12.5%.

2.4. *Synthesis of [Zn$_2$(L^1)$_2$(N$_3$)$_2$] (1)*

To a methanol solution (10 mL) of HL^1 (0.1 mM, 20.6 mg) and sodium azide (0.1 mM, 6.5 mg) was added a methanol solution (10 mL) of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.1 mM, 22.0 mg) with stirring. The mixture was stirred for 30 min at room temperature to give a clear colorless solution. Upon keeping the solution exposed to air for six days, colorless block-shaped crystals of the complex, suitable for X-ray diffraction, were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated by filtration, washed three times with cold methanol, and dried in air. Yield: 62% on the basis of HL[1]. Anal. calcd. for $C_{24}H_{34}N_{10}O_2Zn_2$: C, 46.1; H, 5.5; N, 22.4. Found: C, 45.9; H, 5.4; N, 22.4%. IR data (cm^{-1}): 3234 (w, sh), 2089 (vs), 1633 (s), 1457 (m), 1406 (m), 1347 (w), 1275 (s), 1223 (m), 1069 (w), 853 (w), 762 (w), 716 (w), 631 (w), 545 (w), and 487 (w).

2.5. *Synthesis of [$Cd_2(L^2)_2(NO_3)(\mu_2$-dca)]$_n$ (2)*

To a methanol solution (10 mL) of HL^2 (0.1 mM, 22.2 mg) and sodium dicyanamide (0.1 mM, 8.9 mg) was added a methanol solution (10 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 mM, 30.8 mg), with stirring. The mixture was stirred for 30 min at room temperature to give a clear colorless solution. Upon keeping the solution exposed to air for three days, colorless block-shaped crystals of the complex, suitable for X-ray diffraction, were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated by filtration, washed three times with cold methanol, and dried in air. Yield: 45% on the basis of HL^2. Anal. calcd. for $C_{26}H_{34}Cd_2N_8O_7$: C, 39.3; H, 4.3; N, 14.1. Found: C, 39.2; H, 4.4; N, 14.2%. IR data (cm^{-1}): 3267 (w, sh), 2177 (s), 2164 (s), 1636 (s), 1551 (w), 1473 (m), 1381 (s), 1336 (w), 1277 (m), 1225 (w), 1160 (m), 1035 (w), 826 (w), 794 (w), and 507 (w).

2.6. *X-ray data collection and structure determination*

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker APEX II CCD area-detector with MoKα radiation ($\lambda = 0.71073$ Å). The collected data were reduced using SAINT [15] and empirical absorption corrections were performed using

Table 1. Crystallographic data for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{24}H_{34}N_{10}O_2Zn_2$	$C_{26}H_{34}Cd_2N_8O_7$
Formula weight	625.3	795.4
Temperature/K	298(2)	298(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a/Å	22.8485(11)	10.1086(9)
b/Å	10.3732(5)	9.9364(9)
c/Å	15.4237(14)	31.377(3)
β/°	126.781(1)	91.387(2)
V/Å^3	2927.9(3)	3150.7(5)
Z	4	4
μ/mm^{-1}	1.677	1.405
D_c/g cm^{-3}	1.419	1.677
Reflections collected	15,456	17,328
Unique reflections	3007	6525
Observed reflections [$I \geqslant 2\sigma(I)$]	2686	5335
Parameters	178	392
Restraints	1	0
F(000)	1296	1592
R_{int}	0.0188	0.0249
R_1 [$I \geqslant 2\sigma(I)$]	0.0248	0.0327
wR_2 [$I \geqslant 2\sigma(I)$]	0.0655	0.0685
R_1 (all data)	0.0292	0.0453
wR_2 (all data)	0.0687	0.0685

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

1			
Zn1–N1	2.0785(15)	Zn1–O1	2.1756(11)
Zn1–N2	2.1927(15)	Zn2–N3	1.9530(16)
Zn2–O1	1.9622(11)		
N1–Zn1–N1A	174.31(8)	N1–Zn1–O1A	92.99(5)
N1–Zn1–O1	82.56(5)	N1–Zn1–O1A	92.99(5)
O1–Zn1–O1A	77.82(6)	N1–Zn1–N2A	103.30(6)
N1–Zn1–N2	80.38(6)	O1–Zn1–N2	159.98(6)
O1–Zn1–N2A	92.66(5)	N1–Zn1–N2A	103.30(6)
O1–Zn1–N2A	92.66(5)	N2–Zn1–N2A	101.37(9)
N3–Zn2–N3A	109.02(10)	N3–Zn2–O1A	110.34(6)
N3–Zn2–O1	119.05(7)	N3–Zn2–O1A	110.34(6)
O1–Zn2–O1A	88.29(7)		
2			
Cd1–O1	2.330(2)	Cd1–O3	2.273(2)
Cd1–N1	2.299(3)	Cd1–N2	2.406(3)
Cd1–N3	2.301(3)	Cd1–N4	2.425(3)
Cd2–O1	2.220(2)	Cd2–O3	2.225(2)
Cd2–O5	2.433(2)	Cd2–O6	2.448(3)
Cd2–N6	2.269(3)	Cd2–N8	2.272(3)
O3–Cd1–N1	113.45(8)	O3–Cd1–N3	79.16(9)
N1–Cd1–N3	167.04(10)	O3–Cd1–O1	76.09(8)
N1–Cd1–O1	77.55(8)	N3–Cd1–O1	103.84(9)
O3–Cd1–N2	92.08(9)	N1–Cd1–N2	74.96(10)
N3–Cd1–N2	108.66(10)	O1–Cd1–N2	142.55(9)
O3–Cd1–N4	150.24(9)	N1–Cd1–N4	93.17(10)
N3–Cd1–N4	73.87(10)	O1–Cd1–N4	98.20(10)
N2–Cd1–N4	108.18(10)	O1–Cd2–O3	79.33(8)
O1–Cd2–N6	97.48(9)	O3–Cd2–N6	93.09(10)
O1–Cd2–N8	99.93(11)	O3–Cd2–N8	171.82(10)
N6–Cd2–N8	95.09(11)	O1–Cd2–O5	105.69(8)
O3–Cd2–O5	85.84(8)	N6–Cd2–O5	156.15(10)
N8–Cd2–O5	86.53(11)	O1–Cd2–O6	157.72(8)
O3–Cd2–O6	94.45(8)	N6–Cd2–O6	104.24(9)
N8–Cd2–O6	83.18(11)	O5–Cd2–O6	52.24(8)

Note: Symmetry transformations used to generate equivalent atoms: (A) – *x*, *y*, 1/2–*z*.

SADABS [16]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using the SHELXTL package [17]. All non-hydrogen atoms were refined anisotropically. The amino hydrogens were located from difference Fourier maps and refined isotropically, with N–H distances restrained to 0.90(1) Å. The remaining hydrogens were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in table 1. Selected bond lengths and angles are summarized in table 2.

3. Results and discussion

To design metal complexes, the ligands used are important. In this paper, we synthesized two new tridentate Schiff base ligands. The yellow gummy products of HL^1 and HL^2 were prepared by condensation of equimolar quantities of *N*-ethylethane-1,2-diamine with 3-methylsalicylaldehyde and 5-methoxysalicylaldehyde, respectively, in methanol. The zinc and cadmium complexes were readily prepared by reaction of the Schiff bases with corresponding metal salts in methanol solutions at room temperature. Single crystals of the complexes are stable in air at room temperature and are soluble in common polar organic solvents, such as DMSO, DMF, methanol, ethanol, and acetonitrile, but insoluble in water. The molar conductance values of **1** and **2** measured in methanol at 10^{-3} M are 43 and 55 Ω^{-1} cm^2 M^{-1}, respectively, indicating partial ionization in solution [18].

3.1. *Crystal structure description of 1*

Figure 1 gives a perspective view of **1** together with the atomic labeling system. The complex, which possesses a crystallographic twofold rotation axis, is a phenolate O-bridged dinuclear zinc complex with Zn···Zn separation of 3.101(1) Å. The Schiff base coordinates Zn through phenolate O, imine N, and amine N. Both Schiff base ligands intersect each other with dihedral angles between the least squares planes of 75.3(3)°. Zn1 is coordinated by two phenolate oxygens, two imine nitrogens, and two amine nitrogens from two Schiff base ligands forming distorted octahedral coordination. The distortion of the octahedral geometry, which is mainly caused by the strain created by four- and five-membered chelate rings, can be observed from the bond angles ranging from 77.8(1)° to 103.3(1)° for *cis* angles and from 160.0(1)° to 174.3(1)° for *trans* angles. The coordinate bond lengths related to Zn1 are 2.078(2)–2.193(2) Å comparable to those observed in Schiff base zinc complexes [11, 19]. Zn2 is coordinated by two phenolate O from two Schiff bases and two terminal N forming a tetrahedral geometry. The tetrahedral coordination is also

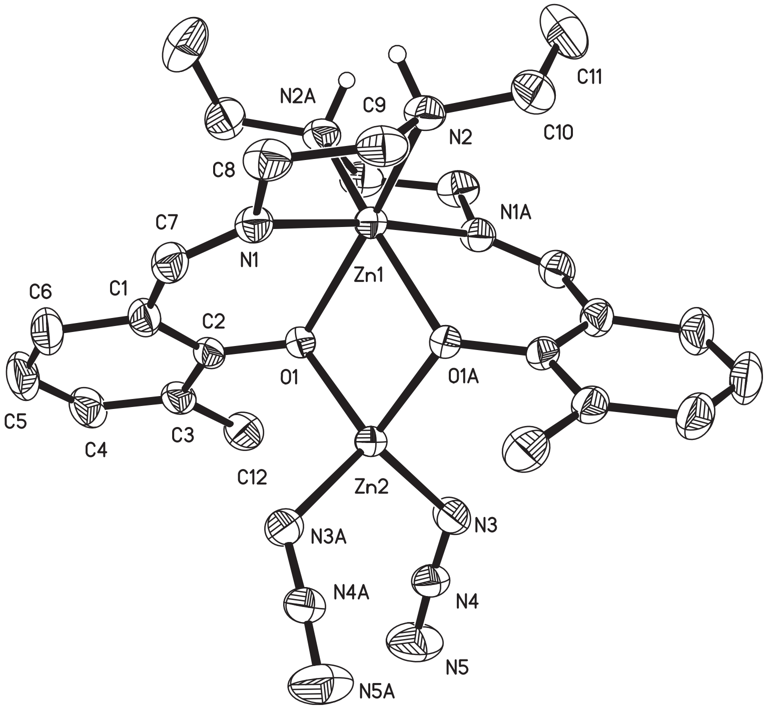

Figure 1. The structure of **1** showing the atom-numbering scheme. Atoms labeled with the suffix A or unlabeled atoms are at the symmetry position –*x*, *y*, 1/2–*z*.

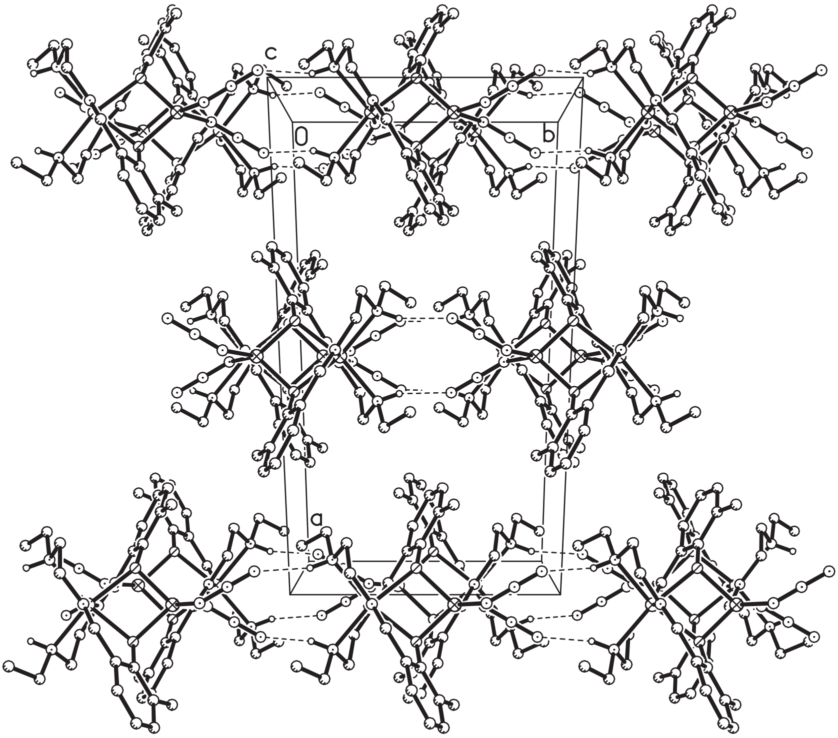

Figure 2. The molecular packing of **1**. Hydrogen bonds are shown as dashed lines.

distorted, as evidenced by bond angles, ranging from 88.3(1)° to 119.0(1)°. This is the first example of a tetrahedral zinc complex with two terminal azides.

Molecules are linked through intermolecular N–H···N hydrogen bonds to form chains running along the *b* axis, as shown in figure 2.

3.2. *Crystal structure description of 2*

Figure 3 gives a perspective view of **2** together with the atom labeling system. The smallest repeated unit of the complex contains a dinuclear $[Cd_2(L^2)_2(NO_3)(\mu_2\text{-dca})]$. The dinuclear moieties are linked through dca ligands forming a polymeric structure. In each dinuclear moiety, the two Cd ions are bridged by two phenolate O with a distance of 3.464(1) Å, which is longer than the Zn···Zn distance in **1**. The Schiff bases coordinate to Cd through phenolate O, imine N, and amine N. The Cd1 is coordinated by two phenolates, two imines, and two amines from two Schiff base ligands forming a distorted octahedral coordination. The distortion of the octahedral geometry, which is caused by the strain created by the four- and five-membered chelate rings, can be observed from the bond angles ranging from 73.9(1)° to 113.4(1)° for *cis* angles and from 142.5(1)° to 167.0(1)° for *trans* angles. The coordinate bond lengths related to Cd1 are 2.273(2)–2.425(2) Å, comparable to those observed in Schiff base cadmium complexes [20, 21]. Cd2 is coordinated by two phenolates from two Schiff bases, two oxygens from a nitrate, and two terminal N from two dca ligands forming a distorted octahedral geometry. The octahedral coordination of Cd2 is also distorted, mainly by the chelating behavior of nitrate, as

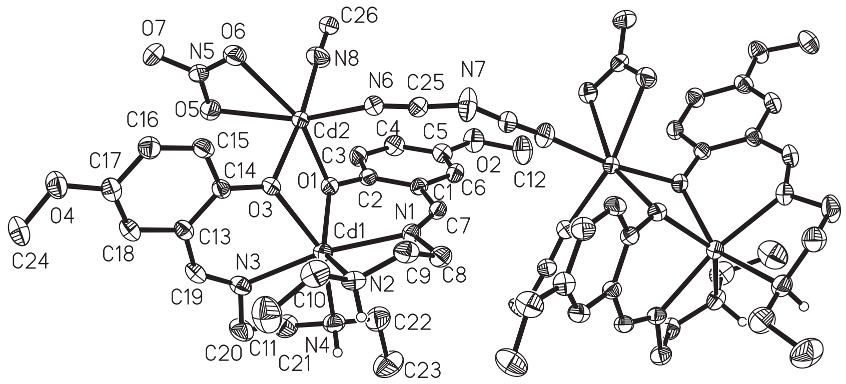

Figure 3. The structure of **2** showing the atom-numbering scheme. Unlabeled atoms are at the symmetry position 1/2–*x*, –1/2 + *y*, 1/2–*z*.

evidenced by bond angles ranging from 52.2(1)° to 105.7(1)° for *cis* angles and from 156.2(1)° to 171.8(1)° for *trans* angles. The Cd–O and Cd–N bonds are also comparable to those observed in similar cadmium complexes of dca [22, 23].

In the crystal structure of the cadmium complex, dinuclear $[Cd_2(L^2)_2(NO_3)(\mu_2\text{-dca})]$ moieties are linked through dca bridges, forming polymeric chains running along the *b* axis, as shown in figure 4.

3.3. *IR spectra*

The IR spectra of the free Schiff bases and the complexes provide information about metal–ligand bonding. The assignments are based on typical group frequencies. Weak and sharp absorptions at 3200–3300 cm^{-1} for the Schiff bases and the complexes can be assigned to ν(N–H). The intense absorption at 2089 cm^{-1} in **1** and those at 2177 and 2164 cm^{-1} in **2** are assigned to the stretching vibrations of azide and dca. Strong absorptions centered at 1645 cm^{-1} in spectra of the free Schiff bases are assigned to azomethine, ν(C=N), which shift to lower wavenumbers in the complexes 1633 cm^{-1} for **1** and 1636 cm^{-1} for **2**. The shift indicates coordination of the azomethine N to metal. In both complexes, the Schiff base ligand coordination to the metal atoms is also substantiated by weak bands at low wavenumbers.

3.4. *Fluorescence character description of the complexes*

The fluorescent properties of **1** and **2** were studied at room temperature (298 K) in the solid state. Supplementary material provides the emission spectra of **1** and **2**. The emission band of **1** is from 380 to 550 nm, with $\lambda_{max} = 465$ nm ($\lambda_{ex} = 365$ nm). Complex **2** exhibits a sharp band at 465–473 nm, with $\lambda_{max} = 467$ nm ($\lambda_{ex} = 300$ nm).

3.5. *Thermal stability*

Differential thermal and thermal gravimetric analyzes were conducted to examine the stability of the complexes (Supplementary material). For **1**, the first step started at 100 °C

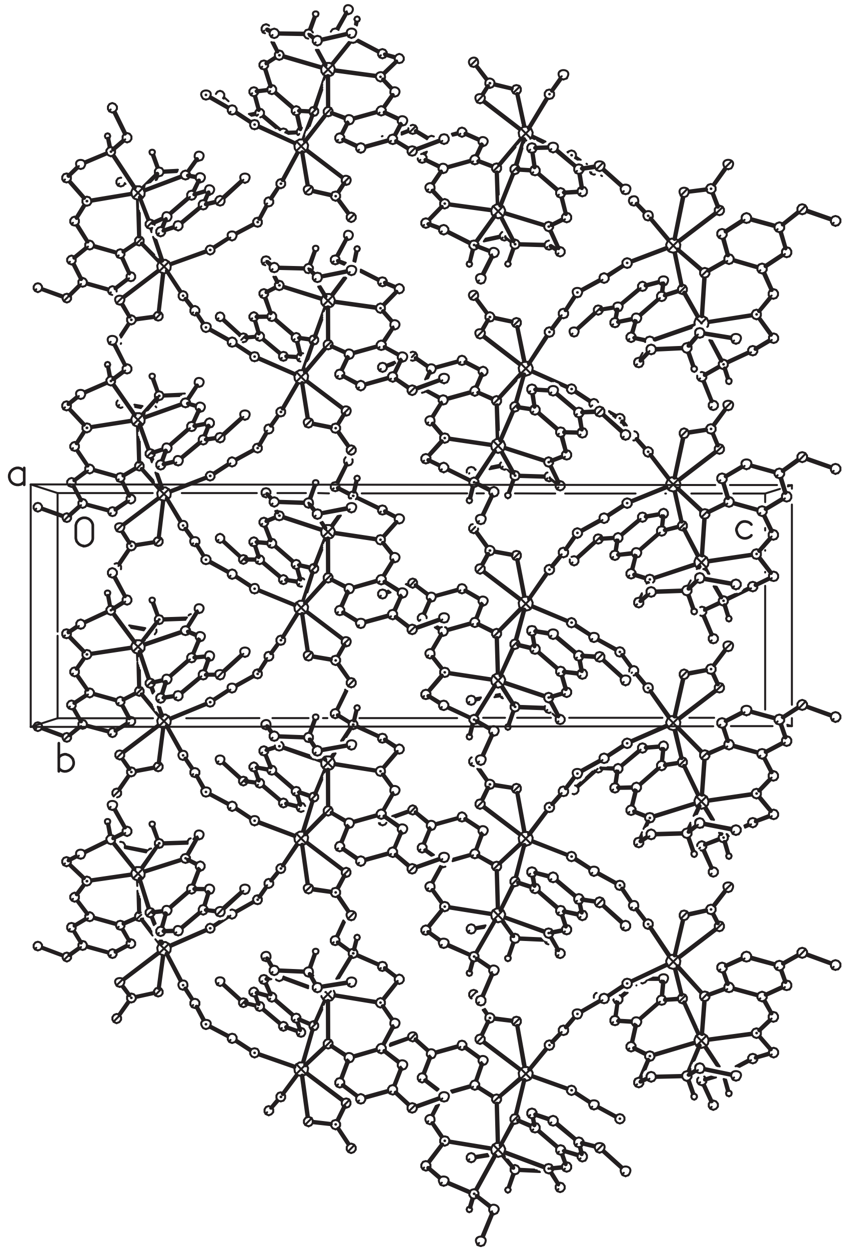

Figure 4. The molecular packing of **2** showing coordination polymers running parallel to the *b* axis.

and finished at 418 °C, corresponding to loss of two azides and the methyl and ethyl of the Schiff base ligands. The observed weight loss of 27.6% is close to the calculated value of 27.5%. The second step, from 418 to 519 °C, corresponds to loss of the remaining parts of the Schiff base ligands and formation of the final product (ZnO). The observed weight loss of 47.1% in this step is close to the calculated value of 46.5%. The total weight loss of 74.7% is in accord with the calculated value of 74.0%. For **2**, the first step started at 250 °C and finished at 426 °C, corresponding to the loss of dca ligands and the methyl and ethyl groups of the Schiff base ligands. The observed weight loss of 27.0% is close to the calculated value of 27.2%. The second step, from 426 to 589 °C, corresponds to loss of the remaining parts of the Schiff base ligands and the formation of final product (CdO). The observed weight loss of 41.3% in this step is close to the calculated value of 40.5%. The total weight loss of 68.3% is in accord with the calculated value of 67.7%.

4. Conclusion

A new dinuclear zinc(II) complex and a new polynuclear cadmium(II) complex were prepared from two tridentate Schiff bases. The complexes have been characterized by elemental analysis, infrared spectra, and single crystal X-ray determination. Thermal stabilities of the complexes were also determined. The fluorescent properties of the complexes indicate that they may be used as interesting materials.

Supplementary material

CCDC-890,796 (**1**) and 890,797 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax:+44(0)1223–336,033 or E-mail: deposit@ccdc.cam.ac.uk.

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