

# Multinuclear Cd<sub>2</sub>, Cd<sub>3</sub> and 1-D framework structures of Cd(II) Schiff base complexes†

Kyriacos Agapiou,‡ Michelle L. Mejía, Xiaoping Yang and Bradley J. Holliday\*

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Reactions of the “salen” type Schiff bases  $H_2L^1$  and  $H_2L^2$  with  $Cd(OAc)_2 \cdot 2H_2O$  gave complexes with Cd<sub>2</sub> and Cd<sub>3</sub> cores and an extended 1-D framework architecture [ $H_2L^1 = N,N'$ -(1,2-phenylenyl)-bis(5-bromo-2-hydroxy-3-methoxybenzaldimine);  $H_2L^2 = N,N'$ -(propyl)-bis(5-bromo-2-hydroxy-3-methoxybenzaldimine)].

## Introduction

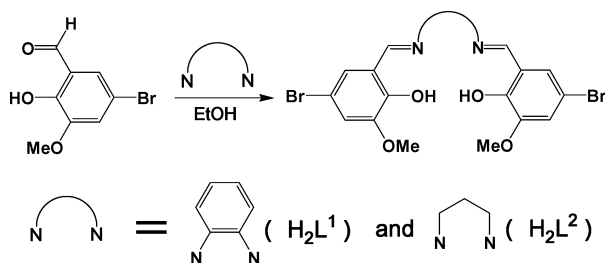
We recently demonstrated that well defined metal complexes which are directly incorporated into the backbones of conducting organic polymers can serve as seed points for the growth of nanocrystalline inorganic materials.<sup>1</sup> Using this method we have, so far, successfully prepared composite hybrid materials comprising polythiophene and nanocrystalline metals as well as the following semiconductors: CdS, CdSe, PbS, Ga<sub>2</sub>S<sub>3</sub>, CuGaS<sub>2</sub> and CuGaSe<sub>2</sub>. These materials may prove to be useful for a new generation of photovoltaic devices and in other key technologies. Initially, in order to assess the feasibility of this approach, we began by selecting ligand systems which are inexpensive, capable of firmly binding a variety of metal ions and which can be modified to incorporate functional groups which would enable subsequent controlled electropolymerizations. Based on our studies of lanthanide Schiff base complexes the “salen” type Schiff base ligand system was chosen as a possible candidate for this purpose.<sup>2</sup> For Cd<sup>2+</sup>, in order to establish data on model compounds, we initially focussed on multidentate Schiff base ligands which do not bear polymerizable groups (Scheme 1). The use of OMe substituted salen type ligands has been previously studied by several groups.<sup>3,4</sup> These substituents can effectively bind

additional metals and we were interested in the effect that this might have on the structures and stoichiometries of complexes with Cd<sup>2+</sup>. The eventual goal here is to investigate the possibility that the ultimate nanocrystal size and morphology can be influenced by the structure and nuclearity of the metallic unit at the very beginning of the nanoparticle growth process. We have investigated the use of two ligands ( $H_2L^1$  and  $H_2L^2$ , Scheme 1) and describe here the synthesis and structures of complexes which have di- and tri-nuclear Cd units and an extended 1-D framework architecture. This work illustrates the fact that structures of metal complexes of this class of ligand can be affected by both the synthetic route employed and by variations in the backbone of the ligand. Future studies will focus on the development of ligand systems bearing polymerizable groups.

## Results and discussion

### Synthesis of $[L^1_2Cd_2(MeOH)_2] \cdot 2H_2O$ (1)

Reaction of  $H_2L^1$  with  $Cd(OAc)_2 \cdot 2H_2O$  (1:1) in EtOH under reflux gave the dinuclear complex  $[L^1_2Cd_2(MeOH)_2] \cdot 2H_2O$  (**1**) in 74% yield. Changing the stoichiometry of the reaction to match the L<sup>1</sup>:Cd ratio found in the product had little or no effect on the yield. The complex is sparingly soluble in polar organic solvents such as CHCl<sub>3</sub>, MeOH and MeCN. Spectroscopic data are consistent with the structure observed in the solid state. Thus the <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN shows peaks assigned to both L<sup>1</sup> and MeOH protons. In order to obtain X-ray quality crystals the compound was successfully crystallized by slow evaporation of the reaction filtrate over several days. Compound **1** crystallizes in the triclinic space group  $P\bar{1}$  with one molecule per unit cell (Fig. 1). The overall molecular framework contains a center of symmetry and features a central Cd<sub>2</sub> core with the Cd atoms coordinated by the N<sub>2</sub>O<sub>2</sub> atoms of the Schiff base ligands and sit out of the N<sub>2</sub>O<sub>2</sub> plane by 0.980 Å. In **1** only one OMe group of each ligand is bound to a metal center. The phenoxide oxygen atom which is located on the same side of the ligand as the bound OMe group adopts a bridging role between the two metals. The Cd...Cd distance is 3.497 Å. Each Cd in **1** is bound to a MeOH group giving a distorted seven coordinate environment. These groups point away from one another on opposite sides of the ligand framework in an *anti* fashion. The average Cd-O(MeOH) distance is 2.441(4) Å. The average Cd-N, Cd-O(phenolic) and Cd-O(methoxy) distances are

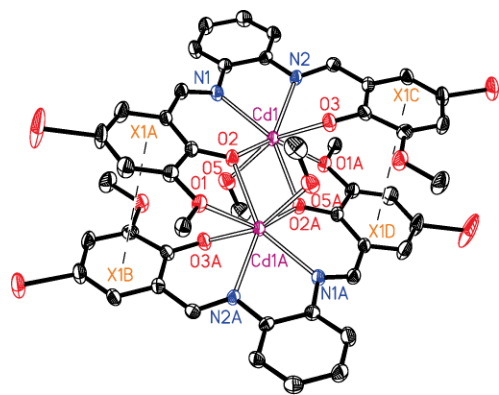


Scheme 1 Ligand synthesis.

Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712-0165. E-mail: bholliday@cm.utexas.edu; Fax: (512) 471-8648; Tel: (512) 471-8491

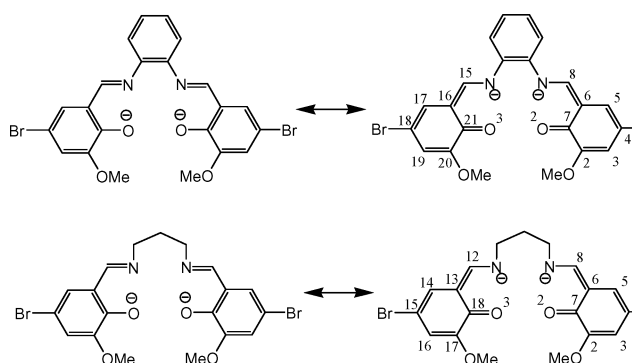
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‡ Present address: eMAT Technology, 8248 Randolph Road NE, Moses Lake, WA, 98837. Fax: (509) 762-5981, Tel: (509) 762-5336, E-mail: kagapiou@emattec.com



**Fig. 1** X-Ray structure of **1**. H atoms have been omitted for clarity. Atoms are shown at the 50% probability level. Symmetry operator  $(1-x, 1-y, 1-z)$  generates equivalent atoms marked with "A". Intramolecular  $\pi$ - $\pi$  stacking interactions: X1A...X1B, X1C...X1D: 3.876 Å.

2.330(4), 2.263(4) and 2.566(4) Å respectively and are comparable to those found in other Schiff base complexes of Cd.<sup>5</sup> The two ligands adopt a planar configuration (dihedral angle between two salicylaldehyde rings of 168.7°), and exhibit an intramolecular  $\pi$ - $\pi$  stacking interaction (Fig 1, X1A-X1B, X1C-X1D: 3.876 Å). For the Schiff base ligand, the rather short distances for C(2)-C(3) (1.364(9) Å), C(4)-C(5) (1.370(9) Å), C(17)-C(18) (1.367(9) Å) and C(19)-C(20) (1.372(9) Å) in comparison with regular aromatic distances are suggestive of a contribution from a quinoid structure (Scheme 2).<sup>6</sup> This is also supported the short distances for C(7)-O(2) (1.302(7) Å), C(21)-O(3) (1.285(7) Å), C(6)-C(8) (1.452(8) Å) and C(15)-C(16) (1.444(8) Å) bonds.<sup>6</sup>

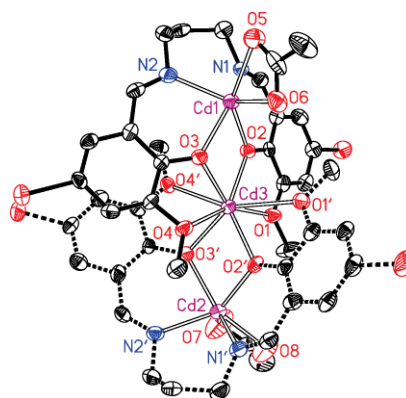


**Scheme 2** Possible tautomeric forms for the Schiff base ligands in **1-3**.

### [L<sup>2</sup><sub>2</sub>Cd<sub>3</sub>(OAc)<sub>2</sub>]-Et<sub>2</sub>O·2MeOH (**2**)

Reaction of **H<sub>2</sub>L<sup>2</sup>**, which features a relatively flexible three carbon backbone relative to the phenylene unit in **H<sub>2</sub>L<sup>1</sup>**, with Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (1:1) in MeOH under reflux gave the trimetallic complex [L<sup>2</sup><sub>2</sub>Cd<sub>3</sub>(OAc)<sub>2</sub>]-Et<sub>2</sub>O·2MeOH (**2**) in 61% yield. As found for **1**, adjusting the stoichiometry of the reaction to match the L<sup>2</sup>:Cd ratio found in the product had little or no effect on the yield. As for **2** the compound is sparingly soluble in polar organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, MeOH and MeCN and spectroscopic data is consistent with the structure observed in the solid state. Thus the <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN shows peaks assigned to both L<sup>2</sup> and OAc protons. X-Ray quality crystals of **2** were

obtained by slow vapor diffusion of Et<sub>2</sub>O into saturated MeOH solutions and the structure described here was obtained with two MeOH and one Et<sub>2</sub>O per Cd<sub>3</sub> unit present in the crystal lattice (Fig. 2). Microanalytical data (C, H, N) for this material were inconsistent and it appears to lose crystallinity when isolated. However, treatment of the reaction mixture with CH<sub>2</sub>Cl<sub>2</sub>/hexane produces a precipitate which gave reproducible C, H and N data consistent with a product of approximate formula L<sup>2</sup>Cd·(C<sub>6</sub>H<sub>14</sub>)<sub>0.5</sub> (see experimental). We have not been able to obtain X-ray structural data on this material. Interestingly, similar treatment of the reaction mixture from the reaction of H<sub>2</sub>L<sup>2</sup> with MeOH/NaH followed by Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O in dichloromethane gave similar microanalytical data (see below for **3**). This suggests that the same product of basic formula L<sup>2</sup>Cd is formed in both cases. Slow crystallization in the presence of excess Cd<sup>2+</sup> and OAc<sup>-</sup> ions or Na<sup>+</sup> and OAc<sup>-</sup> ions then leads to the formation of **2** and **3** respectively. Compound **2** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with four independent molecules per unit cell. The molecular framework contains a central Cd<sub>3</sub> core in which the two terminal Cd atoms are coordinated by the N<sub>2</sub>O<sub>2</sub> atoms of the Schiff base ligands. The Cd<sub>3</sub> core is nearly linear with a Cd(1)-Cd(3)-Cd(2) angle of 171.1° and exhibits similar Cd...Cd distances of 3.580 and 3.576 Å. The terminal Cd atoms are located slightly above the N<sub>2</sub>O<sub>2</sub> plane by 0.898 Å for Cd(1) and 0.895 Å for Cd(2), and are each bonded to a bidentate acetate unit, resulting in a trigonal prismatic configuration. Both OMe groups in **2** from each ligand coordinate to the central Cd atom through their oxygen atoms. The central Cd atom is eight-coordinate being bound by the four phenolic oxygen atoms plus four OMe groups. The average Cd-N, Cd-O (phenolic) and Cd-O (methoxy) distances are 2.280(6), 2.266(4) and 2.635(4) Å respectively and are comparable to those found in other Schiff base complexes of Cd.<sup>5</sup> The average Cd-O (OAc<sup>-</sup>) distance is 2.358(5) Å. With a relatively flexible three carbon backbone, the Schiff base ligands are folded about the central CH<sub>2</sub> group so that they have a V-shaped configuration, and the dihedral angle between two salicylaldehyde rings are 143.5° and 137.1°. The configuration of ligands is such that there is no intramolecular  $\pi$ - $\pi$  stacking interaction between them. As for **1** short distances for C(2)-C(3) (1.376(9) Å), C(4)-C(5) (1.370(9) Å), C(14)-C(15) (1.347(9) Å) and C(16)-C(17) (1.372(9) Å) indicate a quinoid structure contribution for the Schiff base ligand (Scheme 2).<sup>6</sup>



**Fig. 2** Crystal structure of **2**. H atoms have been omitted for clarity. Atoms are shown at the 50% probability level.

### [L<sup>2</sup>Cd(OAc)Na·MeOH] (3)

We have also explored the synthesis of Cd Schiff base complexes using alternative routes. Reaction of H<sub>2</sub>L<sup>2</sup> with MeOH/NaH followed by Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O in dichloromethane produces a solution from which material of approximate composition L<sup>2</sup>Cd·(C<sub>6</sub>H<sub>14</sub>)<sub>0.5</sub> can be precipitated by treatment with hexane. Slow crystallization by vapor diffusion of Et<sub>2</sub>O into the filtered reaction mixture provides X-ray quality crystals of [L<sup>2</sup>Cd(OAc)Na·MeOH] (3), which has an interesting 1-D coordination polymeric structure in the solid state. The compound crystallizes in the monoclinic space group *P*2<sub>1</sub> with two independent CdNa moieties in the asymmetric unit (*Z* = 4). The two moieties have similar dimensions and a view of one of them is shown in Fig. 3. The Cd ion sits slightly out of the N<sub>2</sub>O<sub>2</sub> plane of the Schiff base ligand by 1.134 Å while the outer O<sub>2</sub>O<sub>2</sub> binding group coordinates the Na cation which replaces the central Cd ion in 2. Other examples of mixed 3d-alkali metal systems involving similar Schiff base complexes are known. In these cases the Na<sup>+</sup> ion is also bound to the outer O<sub>2</sub>O<sub>2</sub> pocket.<sup>4</sup> The coordination geometry of the Cd ion is completed by a bidentate acetate group resulting in a distorted trigonal prismatic coordination geometry. Interestingly, one oxygen atom of the acetate group coordinates to an Na ion in an adjacent molecule (Na⋯O 2.305(7) Å av.), resulting a 1-D framework structure aligned along the crystallographic *b* axis (Fig. 4). The interaction gives the Na ion a distorted pentagonal pyramidal coordination geometry. In addition to this interaction there is also a short intramolecular hydrogen bonding interaction between the MeOH group on Na and the other O atom of the acetate ligand (O(5)⋯O(7) 2.709 Å, Fig. 4). The Na-O bond distances fall into two regions with relatively short Na-O (phenoxide), Na-O (MeOH) and Na⋯O (acetate) interactions ranging from 2.318(8) to 2.343(7) Å. In contrast, the Na-O (methoxy) distances are significantly longer and range from 2.730(7) to 2.800(7) Å. The average Cd-N and Cd-O (phenolic) distances (2.279(7) and 2.238(6) Å respectively) are comparable to those found in other

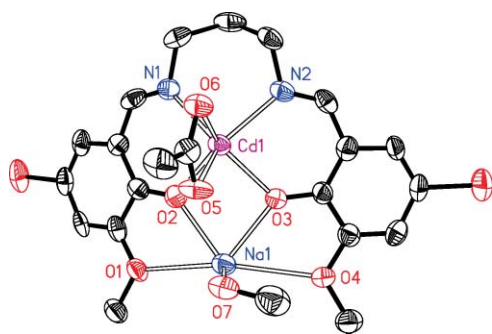


Fig. 3 X-Ray structure of 3. H atoms have been omitted for clarity. Atoms are shown at the 50% probability level.

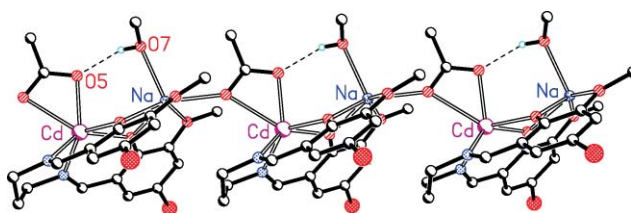


Fig. 4 View of the 1-D framework interactions in the structure of 3.

Schiff base complexes of Cd.<sup>5</sup> As found in 2 the flexible Schiff base ligand also shows a folded V-shaped configuration about the central CH<sub>2</sub> group (fold angle 130.5°). As in 2, the quinoid resonance form of Schiff base ligands also exists in 3 (Scheme 2).

## Experimental

### General

Unless otherwise noted, all reactions and manipulations were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques or in an inert atmosphere glove-box. All solvents were dried prior to use by distillation from CaH<sub>2</sub> (toluene, dichloromethane), magnesium (methanol) or by using an Innovative Technology, Pure Solv solvent purifier with a double purifying column. The following chemicals were used as received: 5-bromo-2-hydroxy-3-methoxybenzaldehyde (Aldrich), 1,3-propanediamine (Aldrich), 1,2-phenylenediamine (TCI), 2,2'-(ethylenedioxy)bis(ethylamine) (Aldrich), Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (OAc = acetate) (Aldrich). NMR spectra were recorded on a Mercury 400 MHz spectrometer and/or Varian 300 Unity Plus spectrometer (<sup>1</sup>H, 300 MHz) at 25 °C. <sup>1</sup>H NMR signals are reported relative to residual solvent peaks. Electrospray ionization (ESI) mass spectra were recorded on a Finnigan MAT TSQ 700. Low-resolution chemical ionization (CI) mass spectra were collected on a Micromass Autospec Ultima mass spectrometer. Infrared spectra were recorded using a Nicolet IR 200 FTIR spectrometer. Microanalytical data were determined by Intertek, NJ. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected.

**Synthesis of N,N'-(1,2-phenylenyl)-bis(5-bromo-2-hydroxy-3-methoxybenzaldimine) (H<sub>2</sub>L<sup>1</sup>).** To a solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.31 g, 10 mmol) in ethanol (125 mL) was added dropwise a solution of 1,2-phenylenediamine (0.540 g, 5 mmol) in ethanol (125 mL). The mixture was stirred at 25 °C for 12 h. The reaction mixture was filtered, to give H<sub>2</sub>L<sup>1</sup> as a reddish orange solid. This solid was washed with cold ethanol and then dried under vacuum. Yield: 2.35 g (88%). m.p. 144–148 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 13.78 (br s, -OH, 2H), 8.49 (s, -CHN-, 2H), 7.32 (d, ArH, 2H, *J* = 5.4 Hz), 7.19 (d, ArH, 2H, *J* = 5.1), 7.04 (s, ArH, 4H), 6.94 (s, ArH, 4H), 6.92 (s, ArH, 4H), 3.79 (s, -OCH<sub>3</sub>, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ 162.6, 151.3, 149.4, 141.5, 128.1, 125.2, 119.9, 119.6, 117.7, 109.7, 56.1; FTIR (Nujol, cm<sup>-1</sup>): 3579 (w), 3051 (m), 2974 (m), 2839 (w), 1613 (m), 1568 (w), 1462 (m), 1437 (m), 1421 (m), 1262 (s), 739 (s), 710 (s). Anal. found: C 49.4; H 3.2; N 5.3. Calc. for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>: C 49.5; H 3.4; N 5.2%.

**Synthesis of N,N'-(propyl)-bis(5-bromo-2-hydroxy-3-methoxybenzaldimine) (H<sub>2</sub>L<sup>2</sup>).** The ligand H<sub>2</sub>L<sup>2</sup> was prepared in a similar manner as described above for H<sub>2</sub>L<sup>1</sup> from 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.31 g, 10 mmol) in ethanol (125 mL) and 1,3-propanediamine (0.371 g, 5 mmol) in ethanol (250 mL). The mixture was stirred at 25 °C for 12 h. After filtering, washing with cold ethanol, and drying under vacuum, H<sub>2</sub>L<sup>2</sup> was isolated as a yellow solid. Yield: 2.27 g (91%). m.p. 126–128 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 13.68 (br s, -OH, 2H), 8.24 (s, -CHN-, 2H), 6.95 (s, ArH, 4H), 3.86 (s, -OCH<sub>3</sub>, 6H), 3.70 (t, -CH<sub>2</sub>-, 4H, *J* = 6.3 Hz), 2.08 (qn, -CH<sub>2</sub>-, 2H, *J* = 6.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR

(100 MHz, CDCl<sub>3</sub>): δ 164.5, 151.5, 149.4, 124.7, 118.9, 116.9, 109.2, 55.8, 38.8, 31.3; FTIR (Nujol, cm<sup>-1</sup>): 3579 (w), 3081 (w), 2933 (m), 2892 (w), 2843 (m), 1634 (s), 1573 (m), 1471 (s), 1442 (s), 1392 (m), 1324 (m), 1294 (s), 759 (m). Anal. found: C 45.5; H 4.1; N 5.6. Calc. for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>: C 45.6; H 4.0; N 5.6%.

**Synthesis of [L<sup>1</sup><sub>2</sub>Cd<sub>2</sub>(MeOH)<sub>2</sub>·2H<sub>2</sub>O (1).** To a solution of ligand H<sub>2</sub>L<sup>1</sup> (0.053 g, 0.1 mmol) in ethanol (10 mL) was added a solution of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) in ethanol (1 mL). The reaction mixture was heated to reflux and stirred for 15 min. After cooling to room temperature, the mixture was filtered. The solid collected upon filtering was taken up in a 1:1 mixture of dichloromethane:methanol (5 mL), and allowed to stand at room temperature in air. Reddish orange crystals of **1** were obtained by slow evaporation. Yield: 0.048 g (74%). dec. 276–280 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 8.44 (s, -CHN-, 2H), 7.25 (m, Ar H, 2H), 7.16 (m, Ar H, 4H), 7.07 (m, Ar H, 2H), 3.69 (s, -OCH<sub>3</sub>, 6H), 3.35 (br s, -CH<sub>3</sub>, 6H), 2.15 (s, -OH, 2H); FTIR (Nujol, cm<sup>-1</sup>): 3052 (m), 2972 (m), 2841 (w), 1613 (m), 1568 (w), 1461 (m), 1437 (m), 1423 (m), 1260 (s), 739 (s), 710 (s); MS (chemical ionization, CH<sub>3</sub>CN) *m/z* 1292 [M<sup>+</sup> - 2 (CH<sub>3</sub>OH)]. Anal. found: C 40.0; H 2.6; N 4.2. Calc. for C<sub>23</sub>H<sub>22</sub>CdN<sub>2</sub>O<sub>6</sub>Br<sub>2</sub>: C 39.8; H 3.2; N 4.0%.

**Synthesis of [L<sup>2</sup><sub>2</sub>Cd<sub>3</sub>(OAc)<sub>2</sub>·Et<sub>2</sub>O·2MeOH (2).** To a solution of ligand H<sub>2</sub>L<sup>2</sup> (0.050 g, 0.1 mmol) in methanol (10 mL) was added a solution of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.1 mmol) in methanol (1 mL). The reaction mixture was heated to reflux and stirred for 1 h. After cooling to room temperature, the mixture was filtered. The filtrate was subjected to slow vapor diffusion in diethyl-ether to provide **2** as bright yellow crystals. Yield: 0.037 g (61%). dec. 302–306 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.13 (s, -CHN-, 2H), 7.17–6.84 (s, Ar H, 4H), 4.26 (br, CH<sub>3</sub>OH, 2H), 3.80

(s, -OCH<sub>3</sub>, 6H), 3.66 (m, CH<sub>3</sub>OH, 6H), 3.54 (t, -CH<sub>2</sub>-, 4H, *J* = 6.3 Hz), 3.41 (q, -CH<sub>2</sub>CH<sub>3</sub>, 8H, *J* = 7.2 Hz), 1.80 (qn, -CH<sub>2</sub>-, 2H, *J* = 2.5 Hz), 1.26 (s, CO<sub>2</sub>CH<sub>3</sub>, 6H), 1.11 (t, -CH<sub>2</sub>CH<sub>3</sub>-, 6H, *J* = 7.1 Hz); FTIR (Nujol, cm<sup>-1</sup>): 3081 (w), 2932 (s), 2895 (s), 2845 (s), 1633 (s), 1573 (w), 1522 (w), 1516 (w), 1460 (s), 1381 (s), 1303 (m), 1190 (w), 1175 (m), 841 (m), 792 (m), 691 (m); MS (electrospray ionization, CH<sub>3</sub>CN) *m/z* 1392 [M<sup>+</sup> - OAc]. For the precipitate formed by treating the filtered reaction mixture with CH<sub>2</sub>Cl<sub>2</sub>/hexane followed by drying under vacuum. Anal. found: C 42.0; H 3.8; N 4.1. Calc. for L<sup>2</sup>Cd<sub>3</sub>(C<sub>6</sub>H<sub>14</sub>)<sub>0.5</sub> (C<sub>22</sub>H<sub>25</sub>CdN<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>): C 40.4; H 3.9; N 4.3%.

**Synthesis of [L<sup>2</sup>Cd(OAc)Na·MeOH (3).** A solution of NaH (0.007 g, 0.29 mmol) in methanol (5 mL) was added to a solution of H<sub>2</sub>L<sup>2</sup> (0.225 g, 0.3 mmol) in methylene chloride (10 mL) at room temperature. A solution of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.08 g, 0.3 mmol) in methanol (10 mL) was then added and the reaction mixture stirred at room temperature for 8 h. The solvent was removed *in vacuo* to afford a red solid which was dissolved in dichloromethane (8 mL) and filtered through a celite plug. Orange crystals of **3** were obtained by slow vapor diffusion of diethyl ether into the solution at room temperature. Yield: 0.0425 g (87%). m.p. 140–145 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.21(s, -CHN-, 2H), 6.92 (s, Ar H, 4H), 3.84 (s, -OCH<sub>3</sub>, 6H), 3.84 (t, -CH<sub>2</sub>-, 4H, *J* = 6.5 Hz), 2.05 (t, -CH<sub>2</sub>-, 2H, *J* = 6.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 164.78, 151.89, 149.70, 125.00, 119.21, 117.145, 109.42, 56.54, 56.10, 31.63. FTIR (film on KBr disk, cm<sup>-1</sup>): 3600–3200 (s), 1634 (m), 1470 (w), 1250 (w). MS (chemical ionization, CH<sub>3</sub>CN) *m/z* 612 [L<sup>2</sup>Cd<sup>+</sup> + 2H]. For the precipitate formed by treating the filtered reaction mixture with CH<sub>2</sub>Cl<sub>2</sub>/hexane followed by

**Table 1** Crystal data and structure refinement for **1–3**

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>46</sub> H <sub>44</sub> Br <sub>4</sub> N <sub>4</sub> O <sub>12</sub> Cd <sub>2</sub>	C <sub>48</sub> H <sub>60</sub> Br <sub>4</sub> N <sub>4</sub> O <sub>15</sub> Cd <sub>3</sub>	C <sub>22</sub> H <sub>25</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>7</sub> CdNa
Fw	1389.26	1589.84	724.65
Crystal syst.	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)
<i>a</i> /Å	9.6620(19)	17.088(3)	13.7004(3)
<i>b</i> /Å	11.470(2)	13.312(3)	7.6677(2)
<i>c</i> /Å	12.405(3)	25.861(5)	25.5552(6)
$\alpha$ /°	70.93(3)	90	90
$\beta$ /°	71.84(2)	103.27(3)	99.4209(9)
$\gamma$ /°	71.28(3)	90	90
<i>V</i> /Å <sup>3</sup>	1197.3(4)	5726(2)	2648.38(11)
<i>Z</i>	1	4	4
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.921	1.844	1.817
<i>T</i> /K	153(1)	153(1)	153(1)
<i>F</i> (000)	676	3120	1424
$\mu$ /mm <sup>-1</sup>	4.292	3.961	3.901
$\theta$ range/°	2.95–25.00	2.96–25.00	1.82–25.00
Reflections measured	6590	18431	8693
Reflections used	4208	10074	8693
Parameters	306	667	632
<i>R</i> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> 1 = 0.0468 <i>wR</i> 2 = 0.1168	<i>R</i> 1 = 0.0483 <i>wR</i> 2 = 0.0958	<i>R</i> 1 = 0.0478 <i>wR</i> 2 = 0.1020
<i>R</i> <sup>a</sup> (all data)	<i>R</i> 1 = 0.0606 <i>wR</i> 2 = 0.1257	<i>R</i> 1 = 0.1056 <i>wR</i> 2 = 0.1147	<i>R</i> 1 = 0.0659 <i>wR</i> 2 = 0.1106
<i>S</i>	1.025	0.974	1.117

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad wR2 = [\sum w[(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}. \quad w = 1/[\sigma^2(F_o^2) + (0.075P)^2], \quad \text{where } P = [\max(F_o^2, 0) + 2F_c^2]/3.$$

drying under vacuum. Anal. found: C 40.7; H 3.4; N 4.8. Calc. for  $L^2Cd(C_6H_{14})_{0.5}(C_{22}H_{25}CdN_2O_4Br_2)$ : C 40.4; H 3.9; N 4.3%.

### X-Ray crystallography

The crystallographic data and structure refinements for complexes **1–3** are listed in Table 1 and selected bond lengths (Å) and angles (°) are given in Tables 2, 3, 4. Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELXL97 program package.<sup>7</sup> The coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.<sup>8</sup>

**Table 2** Selected bond distances (Å) and angles (°) for **1**. Symmetry operator (1 - x, 1 - y, 1 - z) generates equivalent atoms marked with "a"

Cd(1)-O(2)	2.250(4)	O(3)-Cd(1)-N(1)	121.47(17)
Cd(1)-O(3)	2.276(4)	N(2)-Cd(1)-N(1)	70.62(16)
Cd(1)-N(2)	2.318(5)	O(2a)-Cd(1)-N(1)	150.43(15)
Cd(1)-O(2a)	2.328(4)	O(2)-Cd(1)-O(5)	84.93(15)
Cd(1)-N(1)	2.340(5)	O(3)-Cd(1)-O(5)	157.37(15)
Cd(1)-O(5)	2.442(4)	N(2)-Cd(1)-O(5)	119.07(16)
Cd(1)-O(1a)	2.567(4)	O(2a)-Cd(1)-O(5)	76.89(14)
O(2)-Cd(1)-O(3)	90.70(15)	N(1)-Cd(1)-O(5)	79.63(16)
O(2)-Cd(1)-N(2)	136.33(17)	O(2)-Cd(1)-O(1a)	143.92(13)
O(3)-Cd(1)-N(2)	78.78(16)	O(3)-Cd(1)-O(1a)	87.70(15)
O(2)-Cd(1)-O(2a)	80.40(16)	N(2)-Cd(1)-O(1a)	78.52(15)
O(3)-Cd(1)-O(2a)	80.49(15)	O(2a)-Cd(1)-O(1a)	63.78(13)
N(2)-Cd(1)-O(2a)	137.38(15)	N(1)-Cd(1)-O(1a)	130.53(15)
O(2)-Cd(1)-N(1)	79.85(16)	O(5)-Cd(1)-O(1a)	82.97(15)

**Table 3** Selected bond distances (Å) and angles (°) for **2**

Cd(1)-O(3)	2.246(4)	O(8)-Cd(1)-O(2)	107.57(17)
Cd(1)-O(8)	2.248(5)	N(1)-Cd(1)-O(2)	78.81(17)
Cd(1)-N(1)	2.270(6)	N(2)-Cd(1)-O(2)	124.51(18)
Cd(1)-N(2)	2.271(6)	O(3)-Cd(1)-O(7)	128.16(16)
Cd(1)-O(2)	2.287(4)	O(8)-Cd(1)-O(7)	54.58(17)
Cd(1)-O(7)	2.498(5)	N(1)-Cd(1)-O(7)	89.17(18)
Cd(2)-O(2')	2.238(4)	N(2)-Cd(1)-O(7)	85.70(19)
Cd(2)-N(2')	2.265(6)	O(2)-Cd(1)-O(7)	147.07(16)
Cd(2)-O(3')	2.287(4)	O(2')-Cd(2)-N(2')	131.37(18)
Cd(2)-O(5)	2.316(5)	O(2')-Cd(2)-O(3')	74.26(15)
Cd(2)-N(1')	2.318(6)	N(2')-Cd(2)-O(3')	82.11(18)
Cd(2)-O(6)	2.371(6)	O(2')-Cd(2)-O(5)	124.8(2)
Cd(3)-O(2')	2.244(4)	N(2')-Cd(2)-O(5)	97.2(2)
Cd(3)-O(2)	2.246(4)	O(3')-Cd(2)-O(5)	91.5(2)
Cd(3)-O(3')	2.261(4)	O(2')-Cd(2)-N(1')	81.00(18)
Cd(3)-O(3)	2.274(4)	N(2')-Cd(2)-N(1')	87.4(2)
Cd(3)-O(1')	2.528(4)	O(3')-Cd(2)-N(1')	135.30(17)
O(3)-Cd(1)-O(8)	92.03(17)	O(5)-Cd(2)-N(1')	133.0(2)
O(3)-Cd(1)-N(1)	140.85(18)	O(2')-Cd(2)-O(6)	102.2(2)
O(8)-Cd(1)-N(1)	123.24(19)	N(2')-Cd(2)-O(6)	124.0(2)
O(3)-Cd(1)-N(2)	82.20(19)	O(3')-Cd(2)-O(6)	135.15(19)
O(8)-Cd(1)-N(2)	123.0(2)	O(5)-Cd(2)-O(6)	53.0(2)
N(1)-Cd(1)-N(2)	90.5(2)	N(1')-Cd(2)-O(6)	85.9(2)
O(3)-Cd(1)-O(2)	74.17(15)	O(2')-Cd(3)-O(2)	139.12(16)

**Table 4** Selected bond distances (Å) and angles (°) for **3**

Cd(1)-O(2)	2.230(6)	O(5)-Cd(1)-N(2)	122.8(2)
Cd(1)-O(3)	2.243(6)	O(2)-Cd(1)-N(1)	82.1(2)
Cd(1)-O(5)	2.262(6)	O(3)-Cd(1)-N(1)	138.2(2)
Cd(1)-N(2)	2.272(7)	O(5)-Cd(1)-N(1)	127.6(3)
Cd(1)-N(1)	2.278(6)	N(2)-Cd(1)-N(1)	88.4(2)
Cd(1)-O(6)	2.560(7)	O(2)-Cd(1)-O(6)	127.2(2)
O(2)-Cd(1)-O(3)	78.5(2)	O(3)-Cd(1)-O(6)	132.2(2)
O(2)-Cd(1)-O(5)	93.6(2)	O(5)-Cd(1)-O(6)	53.2(2)
O(3)-Cd(1)-O(5)	90.4(2)	N(2)-Cd(1)-O(6)	92.0(2)
O(2)-Cd(1)-N(2)	139.1(2)	N(1)-Cd(1)-O(6)	88.7(2)
O(3)-Cd(1)-N(2)	82.8(2)		

### Conclusions

In conclusion we have isolated and characterized three multinuclear Schiff base complexes of Cd(II) which exhibit variations in structures and stoichiometries based on ligand design and the synthetic route employed.

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