Synthesis, Crystal Structures and Photophysical Properties of Novel Tetranuclear Cadmium(II) Schiff-Base Complexes

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The synthesis and structural characterisation of some new tetranuclear cadmium(II) Schiff-base complexes were described. Reaction of the hexadentate Schiff-base ligands (H_2L) with an excess of cadmium(II) acetate, $Cd(OAc)_2$, furnished novel tetracadmium complexes of the general formula $[Cd_4(L)_2(OAc)_4]$, which exhibit an interesting three-dimensional cage-like structure of four ligand-supported cadmium atoms. All of the complexes were fully characterised by spectroscopic (FTIR, NMR and FAB MS) methods and their molecular structures were confirmed by single-crystal X-ray analysis. The X-ray crystal structures of these tetranuclear Schiff-base complexes represent the first structurally characterised examples of this kind for the cadmium triad. These new complexes were found to display rich photophysical properties and they all exhibited low-temperature phosphorescence in the frozen state.

Introduction

Beside supramolecular[1] and bioinorganic studies,[2] cadmium complexes also play an important role in luminescence research.[3] Numerous luminescent polynuclear transition metal complexes of d^{10} transition metals such as Zn^{II}, Cd^{II}, Cu^{I}, Ag^{I}, Au^{I}, and so forth, have been reported.[4] The use of Cd^{II} complexes as luminescence materials has an added advantage because the coordination environment of Cd^{II} is different from other d^{10} transition metals. The coordination number of Zn^{II}, Ag^{I}, Au^{I} and Cu^{I} is usually 4–5 and rarely greater than 6. On the other hand, the coordination number of Cd^{II} lies between 6 and 8, which allows the Cd^{II} complexes to exhibit a special structure and the potential for different structure-related properties, as compared to the other d^{10} metal complexes. Harvesting of the triplet state emission in molecular and polymeric materials has become an important topic nowadays, and metal complexes play an important role in this area. Most of the research is focused on the expensive d-metals (Pt, Ir, Au, etc.) [4,5] and the lanthanide metal complexes.[6] Very recently, phosphorescence has been observed in some Hg^{II} systems.[5d,5e,5f] However, there are relatively few reports on the phosphorescence emission of the analogous cadmium complexes. Schiff-base zinc(II) complexes have been shown to be effective emitters;[7] however, reports on the luminescent properties of Schiff-base cadmium(II) complexes are very rare. In fact, the use of Schiff-base cadmium complexes as potential luminescent materials has great research merits in that they can be prepared on a large scale and are more cost-effective.

Bermejo and co-workers reported the preparation of three-dimensional cage-like Schiff-base Zn complexes by using an electrochemical reaction with hexadentate ligands.[8] In this report, a series of tetranuclear Schiff-base cadmium complexes of the general formula $[Cd_4(L)_2(OAc)_4]$ were prepared by the reaction of the hexadentate Schiff-base ligands H_2L with excess $Cd(OAc)_2$. Under the same reaction conditions, $Zn(OAc)_2$ gave only the mononuclear Schiff-base complexes [ZnL].[9] A possible explanation here is that the coordination number of Zn^{II} ranges normally from 4 to 5, and the inner N_2O_2 cavity of the Schiff-base ligand already provides a tetradentate environment, meaning further extension of the structure from the metal centre is less favourable. On the other hand, the coordination number of Cd^{II} is usually 6–8, and the inner N_2O_2 cavity is only 4, which enables an extension of its structure to the neighbouring complex, forming an interesting tetranuclear cage-like structure.

Results and Discussion

Synthesis and Characterisation

It has been reported that the electrochemical reaction of the cadmium anode with *N*,*N*′-bis(3-hydroxysalicylidene)-ethylene-1,2-diamine (H_4L', L′ = tetraanionic ligand), a potentially hexadentate Schiff base, gave polymeric dinuclear cadmium(II) complexes of the general formula $[Cd_2(L')(H_2O)_2]_n$, whose solid-state structure has not been

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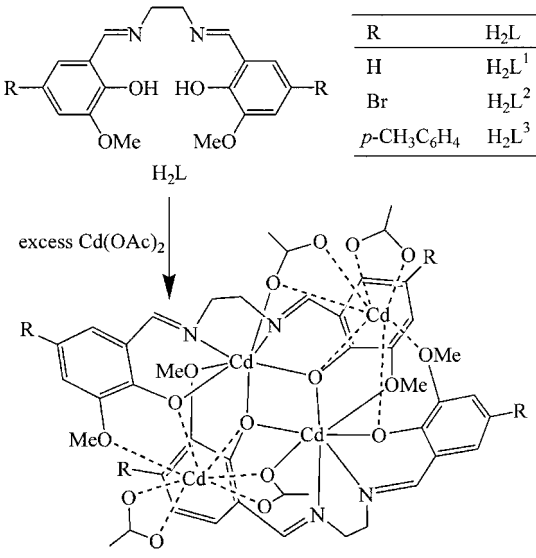
determined.[8b] However, when the corresponding 3-methoxy derivative *N*,*N*′-bis(3-methoxysalicylidene)ethylene-1,2-diamine H_2L (L = dianionic ligand), also a potentially hexadentate Schiff base, was treated with a threefold excess of cadmium(II) acetate in refluxing absolute ethanol overnight, the resultant clear solution, upon workup, gave yellow, air-stable crystalline tetranuclear Schiff-base cadmium(II) complexes of the general formula $[Cd_4(L)_2(OAc)_4]$ [L = L^1 (**1**), L^2 (**2**), L^3 (**3**)] in around 50% yield (Scheme 1). All attempts to isolate other products from the solution mixture have met with little success so far. Compounds **1**–**3** gave satisfactory elemental analyses and collated spectroscopic data (IR, ^{1}H NMR and FABMS) of these complexes are in good agreement with their formulation. Full details are given in the Exp. Sect. In their FAB (positive mode) mass spectrum, all three compounds exhibit a mass peak corresponding to $[M - OAc]^+$ at *m*/*z* = 1277, 1589 and 1637 for **1**, **2** and **3**, respectively, for ^{79}Br and ^{112}Cd. The complexes are soluble in polar organic solvents such as CH_2Cl_2 and $CHCl_3$. All of them exhibit a broad peak in their ^{1}H NMR spectrum at $\delta \approx 8.4$ for their imino protons (–C*H*=N–). Their solid-state IR spectrum also exhibit strong absorption bands corresponding to $\nu_{C=N}$ and $\nu_{C=O}$ at about 1635 and 1460 cm^{-1}, respectively, which are similar to those reported for the 3-hydroxy analogue.[8b] Conductivity measurements showed that complexes **1**–**3** behave as electrolytes in methanol and non-electrolytes in chloroform. This indicates that these complexes dissociate one or more of their coordinated acetate ligands to form cations in methanol and remain neutral and undissociated in chloroform.



R	H_2L	Complex
H	H_2L^1	**1**
Br	H_2L^2	**2**
p-$CH_3C_6H_4$	H_2L^3	**3**

Scheme 1. Synthesis of compounds **1**–**3**.

The molecular structures of **1** and **3** were ascertained by X-ray crystallography and were found to be structurally very similar. Perspective drawings of **1** and **3** are shown in Figures 1 and 2, respectively, and selected bond lengths and bond angles are given in Tables 1 and 2. Structural analysis revealed that all the Cd atoms of such tetranuclear complex are seven-coordinate and are linked together by the hexadentate Schiff-base ligands. The Cd(1) and Cd(2) atoms form a distorted square base with the two phenolic oxygen atoms [O(2) and O(6)] and each of the latter atoms behaves as a μ_3-O ligand coordinating with the other two Cd atoms [Cd(3) and Cd(4)]. The Cd(1) [or Cd(2)] atom is further linked to the Cd(4) [or Cd(3)] atom by a bridging tridentate acetate ligand. Each of the Cd(3) and Cd(4) atoms is further coordinated to a bidentate acetate ligand to give an overall neutral cage-like tetranuclear structure. The distance between each Cd atom falls in the range of 3.555–5.907 Å, which precludes any significant metal–metal interaction. Presumably, aggregation of the four cadmium atoms in the structures of **1** and **3** is triggered by the use of large cadmium atoms that tend to favour high coordination numbers and the multidentate nature of the Schiff-base ligands in our study. The Cd–N bond lengths lie within 2.324(3)–2.356(3) Å for **1** and 2.294(15)–2.354(11) Å for **3**, which are similar to those reported previously.[10] For **1** and **3**, the Cd–O bond lengths of the two complexes span a wide range of 2.248(3)–2.589(3) Å and 2.229(9)–2.552(9) Å, respectively, and this is probably a manifestation of the difference in the nature of the O-donor group in these complexes.

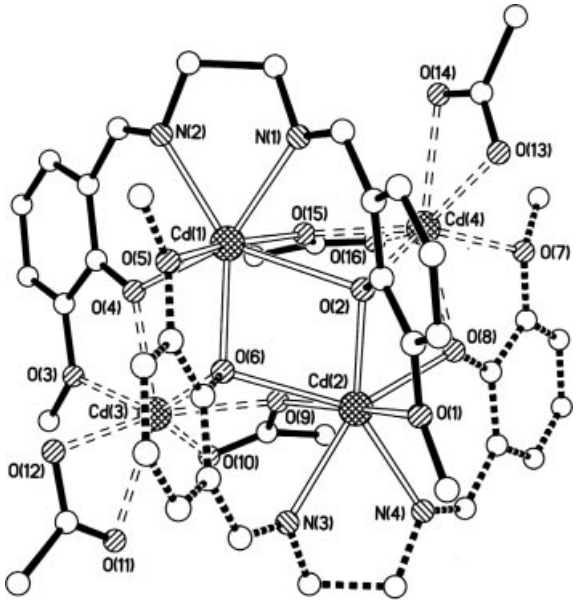


Figure 1. Molecular structure of **1**. Only atoms within the metal coordination core are labelled.

Photophysical Properties

The photophysical properties of **1**–**3** in $CHCl_3$ have been studied and the relevant data are summarised in Table 3. The absorption bands between 240 and 380 nm can be assigned to $\pi \rightarrow \pi^*$ transitions of the Schiff-base ligands. The room-temperature emission of compounds **1**–**3**, with lifetimes (τ) ranging from 0.8 to 1.2 ns and quantum yields (Φ_{em}) of $3.8–5.9 \times 10^{-3}$, can be assigned to the intraligand emission. The absorption, emission and excitation spectra of **1**–**3** are shown in Figures 3, 4 and 5. The room-tempera-

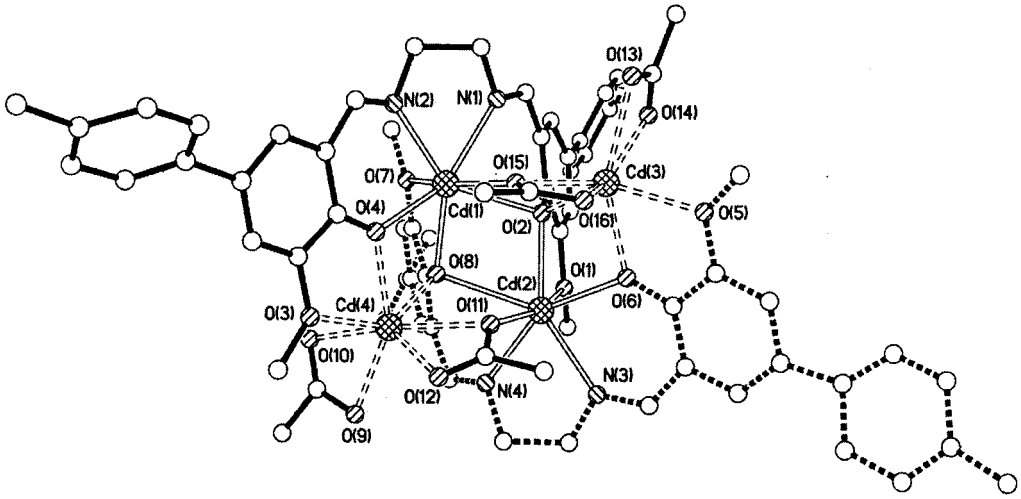


Figure 2. Molecular structure of **3**. Only atoms within the metal coordination core are labelled.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Cd(1)–N(1)	2.356(3)	Cd(1)–N(2)	2.324(3)
Cd(2)–N(3)	2.354(3)	Cd(2)–N(4)	2.349(3)
Cd(1)–O(2)	2.589(3)	Cd(2)–O(1)	2.481(3)
Cd(1)–O(4)	2.296(3)	Cd(2)–O(2)	2.266(3)
Cd(1)–O(5)	2.487(3)	Cd(2)–O(6)	2.545(3)
Cd(1)–O(6)	2.292(3)	Cd(2)–O(8)	2.306(3)
Cd(1)–O(15)	2.279(3)	Cd(2)–O(9)	2.301(3)
Cd(3)–O(3)	2.424(3)	Cd(4)–O(2)	2.407(3)
Cd(3)–O(4)	2.248(3)	Cd(4)–O(7)	2.451(3)
Cd(3)–O(6)	2.400(3)	Cd(4)–O(8)	2.282(3)
Cd(3)–O(9)	2.364(3)	Cd(4)–O(13)	2.258(3)
Cd(3)–O(10)	2.450(3)	Cd(4)–O(14)	2.440(4)
Cd(3)–O(11)	2.376(4)	Cd(4)–O(15)	2.262(3)
Cd(3)–O(12)	2.343(4)	Cd(4)–O(16)	2.514(3)
N(1)–Cd(1)–N(2)	73.49(12)	N(1)–Cd(1)–O(2)	69.61(10)
N(2)–Cd(1)–O(4)	78.54(11)	N(3)–Cd(2)–N(4)	72.58(13)
N(3)–Cd(2)–O(6)	70.76(10)	N(4)–Cd(2)–O(8)	78.07(11)

Table 2. Selected bond distances [Å] and angles [°] for **3**.

Cd(1)–N(1)	2.354(11)	Cd(1)–N(2)	2.312(10)
Cd(2)–N(3)	2.332(15)	Cd(2)–N(4)	2.294(15)
Cd(1)–O(2)	2.552(9)	Cd(2)–O(1)	2.424(10)
Cd(1)–O(4)	2.289(10)	Cd(2)–O(2)	2.276(9)
Cd(1)–O(7)	2.472(10)	Cd(2)–O(6)	2.300(11)
Cd(1)–O(8)	2.298(10)	Cd(2)–O(8)	2.525(10)
Cd(1)–O(15)	2.302(14)	Cd(2)–O(11)	2.246(13)
Cd(3)–O(2)	2.428(11)	Cd(4)–O(3)	2.470(10)
Cd(3)–O(5)	2.424(11)	Cd(4)–O(4)	2.229(9)
Cd(3)–O(6)	2.243(10)	Cd(4)–O(8)	2.320(10)
Cd(3)–O(13)	2.502(12)	Cd(4)–O(9)	2.254(12)
Cd(3)–O(14)	2.256(11)	Cd(4)–O(10)	2.383(17)
Cd(3)–O(15)	2.244(11)	Cd(4)–O(11)	2.338(14)
Cd(3)–O(16)	2.502(14)	Cd(4)–O(12)	2.473(18)
N(1)–Cd(1)–N(2)	73.5(4)	N(1)–Cd(1)–O(2)	70.9(4)
N(2)–Cd(1)–O(4)	78.3(4)	N(3)–Cd(2)–N(4)	73.0(5)
N(3)–Cd(2)–O(6)	77.8(5)	N(4)–Cd(2)–O(8)	70.8(4)

ture excitation spectrum of **3** (monitored at 472 nm) is identical to its 77 K excitation spectrum (monitored at 508 nm), indicating that both the room-temperature and 77 K emission features have the same origin. The absorption, excitation and emission bands are slightly red-shifted upon attachment of a bromide or a *p*-tolyl substituent. Figure 6 depicts the 77 K emission spectra of **1**–**3** in a glassy state. Time-resolved spectra and lifetime measurements showed that both ligand-centred singlet (^{1}LC) and triplet (^{3}LC) emissions coexist at 77 K, with the shoulder being the ^{1}LC fluorescence (τ = 3.4–6.0 ns) and the main peak in the lower energy regime being the ^{3}LC phosphorescence (τ = 10.9–44.2 ms). The ^{3}LC emission was not observed at room temperature even in an oxygen-free solvent system. At room temperature, thermal vibrations, which were minimised at 77 K, can efficiently quench the ^{3}LC transition. Comparing the relative intensity of the ^{1}LC with ^{3}LC emission at 77 K, we observe that the intersystem crossing (ISC) efficiency follows the order **3** > **2** > **1**. On the other hand, the ^{1}LC emission quantum efficiency is in the order **1** > **2** > **3**, which shows that an increase in conjugation or the presence of a heavy bromine substituent can enhance the ISC efficiency, and thus effectively suppress the ^{1}LC emission.

Concluding Remarks

To the best of our knowledge, complexes **1**–**3** constitute the first examples of tetranuclear Schiff-base cadmium complexes of this type and these compounds can display strong triplet-state emission induced by the heavy-atom effect of cadmium. Structural characterisations of **1** and **3** are particularly interesting and we were able to build up polymetallic Schiff-base complexes assembled through the high-coordinate large cadmium atoms and the multidentate ligands. Work is in progress to enhance such triplet emission by structural modifications of the Schiff-base ligands. Comparative analyses of these Schiff-base cadmium complexes with their lower zinc(II) congeners are worthy of serious investigations and are expected to give equally interesting results in the area of luminescent metallated materials.

Table 3. Photophysical properties of **1**, **2** and **3** in $CHCl_3$.

	Absorption at 298 K λ_{max}/nm [log(ε/dm^3 mol^{-1} cm^{-1})]	Excitation at 298 K λ_{max}/nm	Emission at 298 K λ_{max}/nm (τ, $\Phi_{em} \times 10^{-3}$)	Emission at 77 K λ_{max}/nm (τ)
1	360 (4.10), 277 (4.46), 240 (4.71)	359, 281	455 (1.2 ns, 5.9[a])	484 (29.8 ms), 439 sh[b] (6.0 ns)
2	374 (4.16), 275 sh (4.50), 242 (4.94)	372, 280	472 (1.1 ns, 4.7[a])	507 (10.9 ms), 448 sh[b] (3.4 ns)
3	380 (4.14), 275 (5.06)	374, 288	472 (0.8 ns, 3.8[a])	508 (44.2 ms), 458 sh[b] (3.8 ns)

[a] Quantum yield was measured relative to quinine sulfate in 1.0 N H_2SO_4 (Φ_{em} = 0.55). [b] sh = shoulder.

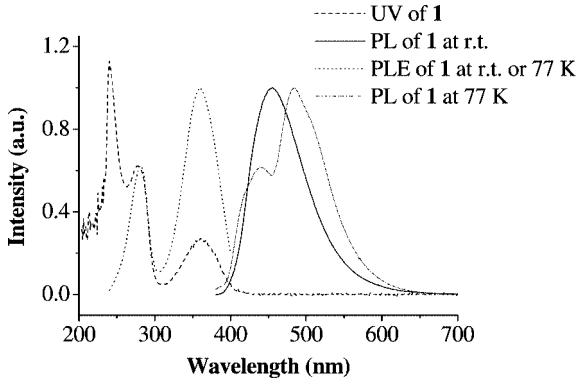


Figure 3. Absorption, photoluminescence excitation (PLE) and photoluminescence (PL) spectra of **1**.

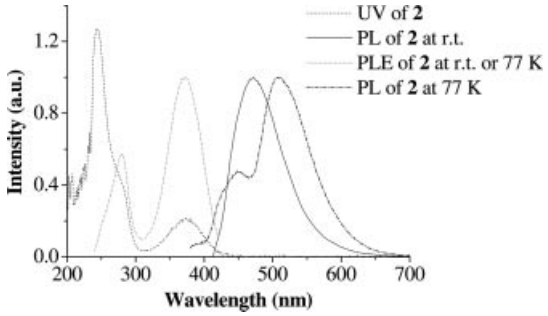


Figure 4. Absorption, photoluminescence excitation (PLE) and photoluminescence (PL) spectra of **2**.

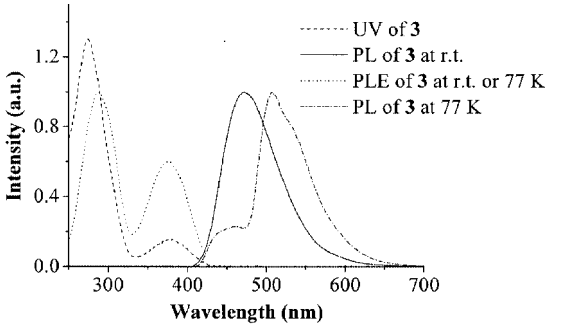


Figure 5. Absorption, photoluminescence excitation (PLE) and photoluminescence (PL) spectra of **3**.

Experimental Section

General Procedures: Solvents and starting materials were purchased commercially and used without further purification unless otherwise stated. The hexadentate Schiff-base ligands H_2L^1, H_2L^2 and H_2L^3 were prepared according to the literature method.[9] Elemental analyses (C, H, N) were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. Electronic absorption spectra in the UV/Vis region were recorded with a Hewlett Packard 8453 UV/Vis spectrophotometer, steady-state visible fluorescence and photoluminescence excitation spectra with a Photon Technology International (PTI) Alphascan spectrofluorimeter, and visible decay spectra with a pico-N_2 laser system (PTI Time Master) with λ_{ex} = 337 nm. Quantum yields of visible emissions were computed according to a literature method[11] using quinine sulfate in 0.1 N H_2SO_4 as the reference standard (Φ = 0.55 in air-equilibrated water).[12] Infrared spectra (KBr pellets) were recorded with a Nicolet Nagna-IR 550 spectrometer and NMR spectra with a JEOL EX270 spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced to internal deuteriated solvents and then recalculated to $SiMe_4$ (δ = 0.00 ppm). Low-resolution mass spectra (LRMS) were obtained with a Finnigan MAT SSQ-710 spectrometer in the positive FAB mode. Conductivity measurements were carried out with a DDS-11 conductivity bridge for 10^{-4} mol dm^{-1} solutions either in CH_3OH or CH_3CN. ***Caution:*** Cadmium complexes are toxic, and all experiments involving these reagents should be carried out in a well-vented hood.

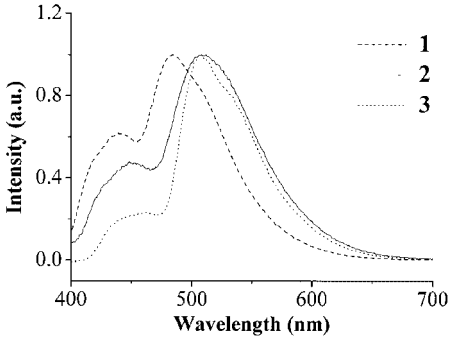


Figure 6. Photoluminescence spectrum of **1**, **2** and **3** at 77 K.

Preparation of $[Cd_4(L^1)_2(OAc)_4]$ (1): Excess $Cd(OAc)_2 \cdot 2H_2O$ (2.80 g, 10.5 mmol) was added to a suspension of H_2L^1 (1.062 g, 3.23 mmol) in absolute ethanol. The resultant reaction mixture was refluxed overnight to give a clear yellow solution. The solution was filtered and the solvents were evaporated to dryness to give a yellow solid. The solid was washed with deionised water, redissolved in a $CHCl_3/CH_3OH$ mixture and the resulting solution was filtered. The filtrate was allowed to concentrate slowly at room temperature to give yellow crystals of $\mathbf{1} \cdot CH_3OH$ in about a week. Yield: 2.214 g (51%). M.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.78 (br. s, 12 H, CH_3COO), 3.73 (m, 4 H, NCH_2), 3.80–3.98 (m, 12 H, OCH_3), 4.35 (m, 4 H, NCH_2), 6.37–6.51 (m, 4 H, Ph-*H*), 6.77–6.80 (m, 8 H, Ph-*H*), 8.41 (m, 4 H, C*H*=N) ppm. IR (KBr): $\tilde{\nu}$ = 3423 s, 1633 s, 1558 s, 1450 s, 1415 s, 1288 m, 1215 s, 1099 m, 970 m, 743 m cm^{-1}. FABMS (positive mode): *m*/*z* = 1277 ([M – OAc]$^+$ for ^{112}Cd). $C_{44}H_{48}Cd_4N_4O_{16} \cdot CH_3OH$ (1370.56): calcd. C 39.44, H 3.82, N 4.09; found C 39.13, H 3.78, N 4.05.

Preparation of $[Cd_4(L^2)_2(OAc)_4]$ (2): The synthesis of **2** followed the same procedures as for **1** except that $Cd(OAc)_2 \cdot 2H_2O$ (0.471 g, 1.77 mmol) and H_2L^2 (0.312 g, 0.58 mmol) were used instead. Yel-

low crystals of **2**·CH_3OH were obtained. Yield: 0.481 g (50%). M.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.75 (br. s, 12 H, CH_3COO), 3.70 (m, 4 H, NCH_2), 3.82–3.96 (m, 12 H, OCH_3), 4.28 (m, 4 H, NCH_2), 6.88–6.97 (m, 8 H, Ph-*H*), 8.32 (m, 4 H, C*H*=N) ppm. IR (KBr): $\tilde{\nu}$ = 3423 m, 1635 s, 1542 m, 1456 s, 1401 m, 1286 m, 1233 s, 1211 s, 1094 m, 977 m, 773 m, 688 m cm^{-1}. FABMS (positive mode): *m*/*z* = 1589 ([M – OAc]$^+$ for ^{79}Br and ^{112}Cd). $C_{44}H_{44}Br_4Cd_4N_4O_{16}$·$CH_3OH$ (1686.15): calcd. C 32.05, H 2.87, N 3.32; found 32.53, H 2.85, N 3.45.

Preparation of [$Cd_4(L^3)_2(OAc)_4$] (3): Similarly, a mixture of $Cd(OAc)_2$·$2H_2O$ (0.434 g, 1.78 mmol) and H_2L^3 (0.270 g, 0.53 mmol) was used here to give, after workup, yellow crystals of **3**·$3H_2O$ in 46% yield (0.417 g). M.p. > 300 °C. ^{1}H NMR ($CDCl_3$): δ = 1.81 (br. s, 12 H, CH_3COO), 2.37 (br. s, 12 H, Ph-CH_3), 3.72 (m, 4 H, NCH_2), 3.92–4.06 (m, 12 H, OCH_3), 4.40 (m, 4 H, NCH_2), 6.37–6.51 (m, 4 H, Ph-*H*), 7.03–7.40 (m, 24 H, Ph-*H*), 8.55 (m, 4 H, C*H*=N) ppm. IR (KBr): $\tilde{\nu}$ = 3428 m, 1634 s, 1558 s, 1457 s, 1405 s, 1269 m, 1202 m, 985 m, 815 m, 772 m cm^{-1}. FABMS (positive mode): *m*/*z* = 1637 ([M – OAc]$^+$ for ^{112}Cd). $C_{72}H_{72}Cd_4N_4O_{16}$·$3H_2O$ (1753.07): calcd. C 49.33, H 4.48, N 3.20; found C 49.54, H 4.49, N 3.11.

X-ray Crystallography: Pertinent crystallographic data and other experimental details are summarised in Table 4. Crystals of **1** and **3** suitable for X-ray diffraction studies were grown by slow concentration of a solution of the respective compound in CH_3OH. Intensity data were collected at 293 K with a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT[13] and an absorption correction was applied (SADABS)[14] to the collected reflections. The structures of all compounds were solved by direct methods (SHELXTL)[15] and refined against F^2 by full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically for these structures. Hydrogen atoms were generated in their idealised positions and allowed to ride on their respective parent carbon atoms. CCDC-241608 (**1**) and -241609 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystallographic data for compounds **1** and **3**.

	1·CH_3OH	**3**·$0.5CH_3OH$
Empirical formula	$C_{45}H_{52}Cd_4N_4O_{17}$	$C_{72.5}H_{74}Cd_4N_4O_{16.5}$
Formula mass	1370.51	1714.96
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a [Å]	11.2367(4)	15.9567(17)
b [Å]	16.1250(6)	19.508(2)
c [Å]	27.7456(10)	28.194(3)
β [°]	94.5910(10)	90
V [Å^3]	5011.1(3)	8776.3(16)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.817	1.298
μ(Mo-K_α) [mm^{-1}]	1.748	1.012
F(000)	2712	3444
Reflections collected	24864	44301
Independent reflections	8799	15395
R_{int}	0.0293	0.1611
Observed reflections [$I > 2\sigma(I)$]	7217	6473
Goodness-of-fit on F^2	1.070	0.935
R_1, wR_2 [$I > 2\sigma(I)$]	0.0288, 0.0782	0.0719, 0.1450
R_1, wR_2 [all data]	0.0403, 0.0883	0.2089, 0.1959

Acknowledgments

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