



# Synthesis, crystal structure and spectroscopic properties of some cadmium(II) complexes with three polyamine and corresponding macrocyclic Schiff base ligands

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## ABSTRACT

Three Cd(II) macrocyclic Schiff base complexes [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] (**4**), [CdL<sup>5</sup>(NO<sub>3</sub>)<sub>2</sub>] (**5**), [CdL<sup>6</sup>(NO<sub>3</sub>)<sub>2</sub>] (**6**) were prepared by template condensation of 2-pyridinecarboxaldehyde with N1-(2-nitrobenzyl)-N1-(2-aminoethyl)ethane-1,2-diamine (L<sup>1</sup>), N1-(2-nitrobenzyl)-N1-(2-aminoethyl)propane-1,3-diamine (L<sup>2</sup>) or N1-(2-nitrobenzyl)-N1-(3-aminopropyl)propane-1,3-diamine (L<sup>3</sup>), in the presence of cadmium metal ion, respectively. Three Cd(II) complexes with L<sup>1</sup>, L<sup>2</sup> and L<sup>3</sup> were also synthesized. All complexes have been studied with IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, DEPT, COSY, HMQC and microanalysis. Two of these complexes, [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] (**4**) and [CdL<sup>1</sup>(NO<sub>3</sub>)<sub>2</sub>] (**1**) have been characterized through X-ray crystallography. In complex **4**, the Cd is in a six-coordinate environment comprised of the ligand N<sub>4</sub>-donor set and two oxygen atoms of two nitrate groups. In the polyamine complexes (**1**, **2** and **3**) Cd and ligand are in a ratio of 1:1. Supporting ab initio HF-MO calculations have been undertaken using the standard 3-21G<sup>+</sup> and 6-31G<sup>+</sup> basis sets.

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## 1. Introduction

Schiff base complexes have been amongst the most widely studied coordination compounds in the past few years [1–8]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning the metal centred electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalysts [9–14]. They are also becoming increasingly important as biochemical, analytical and antimicrobial reagents [15]. The environment around the metal centre “as coordination geometry, number of coordinated ligands and their donor group” is the key factor for metalloproteins to carry out specific physiological functions [16]. We have been interested in the design and synthesis of a range of amines, polyamine complexes and Schiff base macrocyclic and macroacyclic complexes [17–20]. The variety of possible Schiff base metal complexes with a wide choice of ligands, and coordination environments, has prompted us to undertake research in this area. We wish to report the results of our investigations on the cadmium ion ability to act as a template in synthesizing macroacyclic complexes. Furthermore, to study the effect of existence of a 2-nitrobenzyl pendant arm on

the formation of polyamine complexes, three cadmium(II) complexes were also synthesized.

## 2. Experimental

### 2.1. Starting materials

All solvents were of reagent grade quality and purchased commercially. N1-(2-nitrobenzyl)-N1-(2-aminoethyl)ethane-1,2-diaminetrishydrochloride (I), N1-(2-nitrobenzyl)-N1-(2-aminoethyl)propane-1,3-diaminetrishydrochloride (II), N1-(2-nitrobenzyl)-N1-(3-aminopropyl)propane-1,3-diaminetrishydrochloride (III) were synthesized according to the literature method [21].

### 2.2. Instrumentation

NMR spectra were obtained using a Bruker A V 300 MHz spectrometer. Infrared spectra were recorded in KBr pellets using BIO-RAD FTS-40A spectrophotometer (4000–400 cm<sup>-1</sup>).

### 2.3. X-ray crystal structure determination

X-ray data for [CdL<sup>1</sup>(NO<sub>3</sub>)<sub>2</sub>] were measured on a STOE IPDS-II two circle diffractometer at 150 °C, using graphite monochromated

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Mo K $\alpha$  X-ray radiation ( $\lambda = 0.71073$  nm). X-ray data for [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] were also measured on a Bruker SMART-1000 diffractometer. Other crystallographic data are summarized in Table 1.

#### 2.4. Ab initio molecular-orbital calculations

A full minimization of the structure of each macrocyclic complex was performed at the ab initio HF level of theory using gradient techniques with the GAUSSIAN-98 set of programs [22], on a Pentium-PC computer with a 3000 MHz processor. The effective

**Table 1**  
Crystal data and structure refinement for [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] and [CdL<sup>1</sup>(NO<sub>3</sub>)<sub>2</sub>]

Compound	[CdL <sup>4</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	[CdL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]
Empirical formula	C <sub>23</sub> H <sub>24</sub> CdN <sub>8</sub> O <sub>8</sub>	C <sub>11</sub> H <sub>18</sub> CdN <sub>6</sub> O <sub>8</sub>
Formula weight	652.9	474.72
Temperature (K)	150(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P $\bar{1}$
<i>Unit cell dimensions</i>		
a (Å)	16.0337(7)	7.8761(6)
b (Å)	12.1555(5)	8.0679(7)
c (Å)	13.4025(6)	14.5785(12)
$\alpha$ (°)	90	91.649(7)
$\beta$ (°)	104.160(2)	94.098(7)
$\gamma$ (°)	90	115.628(6)
Volume (Å <sup>3</sup> )	2532.75(19)	831.26(12)
Z	4	2
Calculated density (Mg/m <sup>-3</sup> )	1.712	1.897
Absorption coefficient (mm <sup>-1</sup> )	0.928	1.37
F(000)	1320	476
Crystal size (mm)	0.28 × 0.16 × 0.14	0.35 × 0.33 × 0.20
$\theta$ Range for data collection (°)	1.31–27.54	2.81–29.21
Limiting indices	–20 ≤ h ≤ 20, –15 ≤ k ≤ 15, –17 ≤ l ≤ 17	–10 ≤ h ≤ 10, –11 ≤ k ≤ 10, –18 ≤ l ≤ 19
Reflections collected/unique [R(int)]	50012/5835 [0.0351]	9562/4377 [0.0218]
Completeness to $\theta = 25.00^\circ$ (%)	100.0	97.1
Absorption correction	Semi-empirical from equivalents	Numerical
Maximum and minimum transmission	0.8811 and 0.7811	0.750 and 0.625
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	5835/0/361	4377/0/251
Goodness-of-fit on F <sup>2</sup>	1.044	1.08
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0195, wR2 = 0.0470	R1 = 0.0172, wR2 = 0.0428
R indices (all data)	R1 = 0.0229, wR2 = 0.0504	R1 = 0.0180, wR2 = 0.0431
Largest difference peak and hole (e Å <sup>-3</sup> )	0.359 and –0.344	0.415 and –0.520

core potential (ECP) standard basis set LanL2DZ [23], was utilized for cadmium. The full-electron standard basis sets 3-21G\* and 6-31G\* [24] were used for all other atoms. A starting semi-empirical structure for the ab initio calculations was obtained using the HYPERCHEM 5.02 program [25].

#### 2.5. Synthesis

##### 2.5.1. Preparation of complexes

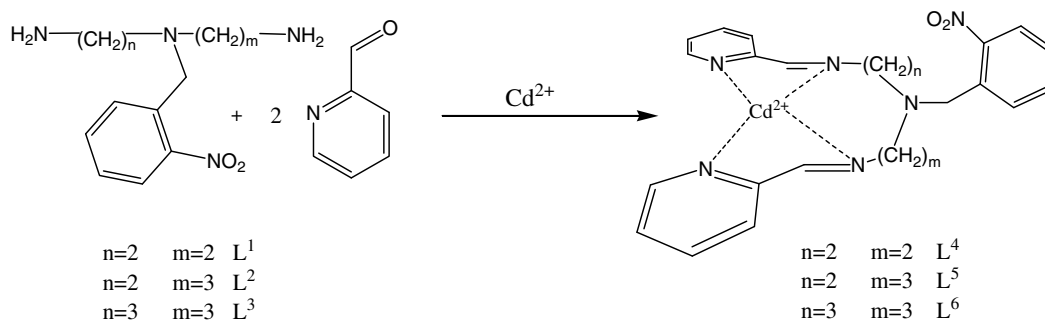
**2.5.1.1. [CdL<sup>1</sup>(NO<sub>3</sub>)<sub>2</sub>] (1).** All syntheses of polyamine complexes were performed under similar conditions. To a solution of (L<sup>1</sup>, L<sup>2</sup> or L<sup>3</sup>), cadmium nitrate (0.5 mmol) was added. The reaction was carried out for 1 h at room temperature a white precipitate formed. This was filtered off and dried *under vacuo*. Yields 82–85%.

Yield (83%). Anal. Calc. for C<sub>11</sub>H<sub>18</sub>CdN<sub>6</sub>O<sub>8</sub>: C, 27.83; H, 3.82; N, 17.20. Found: C, 28.01; H, 4.11; N, 17.43%. IR (KBr) 3273, 3336, 3064, 1604, 1530, 1341 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>, ppm) 2.35 (bt, 4H), 2.67 (bt, 4H), 4.22 (s, 2H), 3.23 (NH<sub>2</sub>, 4H) 7.56–7.93 (Ar, 4H); <sup>13</sup>C NMR  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>, ppm) 36.91, 49.06, 51.13, 124.76, 127.14, 129.97, 132.97, 134.64, 151.91.

**2.5.1.2. [CdL<sup>2</sup>(NO<sub>3</sub>)<sub>2</sub>] (2).** Yield (80%). Anal. Calc. for C<sub>12</sub>H<sub>20</sub>CdN<sub>6</sub>O<sub>8</sub>: C, 29.49; H, 4.12; N, 17.20. Found: C, 29.21; H, 4.14; N, 17.42%. IR (KBr) 3288, 3349, 3070, 1603, 1530, 1342 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>, ppm) 1.71 (bp, 2H), 2.24 (bt, 2H), 2.49 (bt, 2H), 2.71 (bt, 2H), 2.86 (bt, 4H), 4.26 (s, 2H), 3.4 (NH<sub>2</sub>, 4H), 7.49–7.91 (Ar, 4H); <sup>13</sup>C NMR  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>, ppm) 25.61, 36.72, 43.1, 48.41, 51.66, 54.18, 124.63, 125.7, 130.1, 132.74, 134.64, 152.41.

**2.5.1.3. [CdL<sup>3</sup>(NO<sub>3</sub>)<sub>2</sub>] (3).** Yield (77%). Anal. Calc. for C<sub>13</sub>H<sub>22</sub>CdN<sub>6</sub>O<sub>8</sub>: C, 31.06; H, 4.41; N, 16.72. Found: C, 31.23; H, 4.32; N, 17.02%. IR (KBr) 3264, 3330, 3064, 1604, 1517, 1350 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta_{\text{H}}$  (DMSO-*d*<sub>6</sub>, ppm) 1.59 (bp, 4H), 2.34 (bt, 4H), 3.34 (bt, 4H), 3.76 (s, 2H), 7.65–7.86 (Ar, 4H); <sup>13</sup>C NMR  $\delta_{\text{C}}$  (DMSO-*d*<sub>6</sub>, ppm) 28, 49.05, 51.34, 55.28, 124.52, 128.8, 131.7, 133.18, 134.35, 150.07.

**2.5.1.4. General synthesis (Schiff base macrocyclic complexes).** All syntheses of the Schiff base macrocyclic complexes were performed under similar conditions. A solution of NaOH (1.5 mmol) in methanol (10 cm<sup>3</sup>) was added to a suspension of the appropriate triaminetrihydrochloride (I, II or III) (0.5 mmol) in methanol (10 cm<sup>3</sup>). The mixture was stirred at room temperature for a few minutes then filtered, and the precipitate was washed well with methanol (10 cm<sup>3</sup>). The washings and the filtrate were combined and to this solution (L<sup>1</sup>, L<sup>2</sup> or L<sup>3</sup>) and 2-pyridinecarboxaldehyde (1 mmol) in methanol (50 mL), nitrate cadmium (0.5 mmol) was added. The reaction was carried out for 6 h at room temperature. The solution volume was then reduced to 10 mL by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried *under vacuo*. Yields 69–72%.



**Scheme 1.**

2.5.1.5.  $[\text{CdL}^4(\text{NO}_3)_2]$  (**4**). Yield (72%). Anal. Calc. for  $\text{C}_{23}\text{H}_{24}\text{CdN}_8\text{O}_8$ : C, 42.31; H, 3.71; N, 17.16. Found: C, 42.62; H, 3.75; N, 17.05%. IR (KBr) 3054, 1659, 1591, 1522, 1352  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta_{\text{H}}$  (DMSO- $d_6$ , ppm) 2.83 (bt, 4H), 3.87 (bt, 4H), 4.27 (s, 2H), 7.58–8.46 (Ar, 12H), 8.89 (s, 2H);  $^{13}\text{C}$  NMR  $\delta_{\text{C}}$  (DMSO- $d_6$ , ppm) 51.39, 53.1, 54.6, 124.83, 129.38, 129.54, 133.02, 133.55, 141.29, 147.21, 150.25, 151.23, 163.19.

2.5.1.6.  $[\text{CdL}^5(\text{NO}_3)_2]$  (**5**). Yield (70%). Anal. Calc. for  $\text{C}_{24}\text{H}_{26}\text{CdN}_8\text{O}_8$ : C, 43.22; H, 3.93; N, 16.80. Found: C, 43.63; H, 4.12; N, 16.75%. IR (KBr) 3068, 1652, 1592, 1522, 1353  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta_{\text{H}}$  (DMSO- $d_6$ , ppm) 1.85 (bp, 2H), 2.41 (bt, 2H), 3.00 (bt, 2H), 3.52 (bt, 2H), 3.83 (bp, 2H), 3.90 (s, 2H), 7.54–8.08 (Ar, 12H), 8.68 (s, 1H), 8.70 (s, 1H);  $^{13}\text{C}$  NMR  $\delta_{\text{C}}$  (DMSO- $d_6$ , ppm) 27, 51.82, 52.96, 54.98, 55.44, 56.94, 124.70, 129.48, 129.15, 132.58, 132.7, 133.15, 141.55, 141.77, 149.4, 150.03, 150.61, 162.16, 164.61.

2.5.1.7.  $[\text{CdL}^6(\text{NO}_3)_2]$  (**6**). Yield (69%). Anal. Calc. for  $\text{C}_{25}\text{H}_{28}\text{CdN}_8\text{O}_8$ : C, 44.10; H, 4.14; N, 16.46. Found: C, 44.21; H, 4.21; N, 16.53%. IR (KBr) 3100, 2928, 2851, 1650, 1593, 1530, 1349  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta_{\text{H}}$  (DMSO- $d_6$ , ppm) 1.7 (pb, 2H), 2.4 (tb, 4H), 3.3 (tb, 4H), 4.01 (s, 2H), 7.04–7.98 (Ar, 12H), 8.67 (s, 2H);  $^{13}\text{C}$  NMR  $\delta_{\text{C}}$  (DMSO- $d_6$ , ppm) 26.61, 51.33, 52.22, 53.11, 161.56, 132.7, 129.15, 129.48, 132.58, 133.15, 141.55, 141.77, 149.4, 150.6.

### 3. Results and discussion

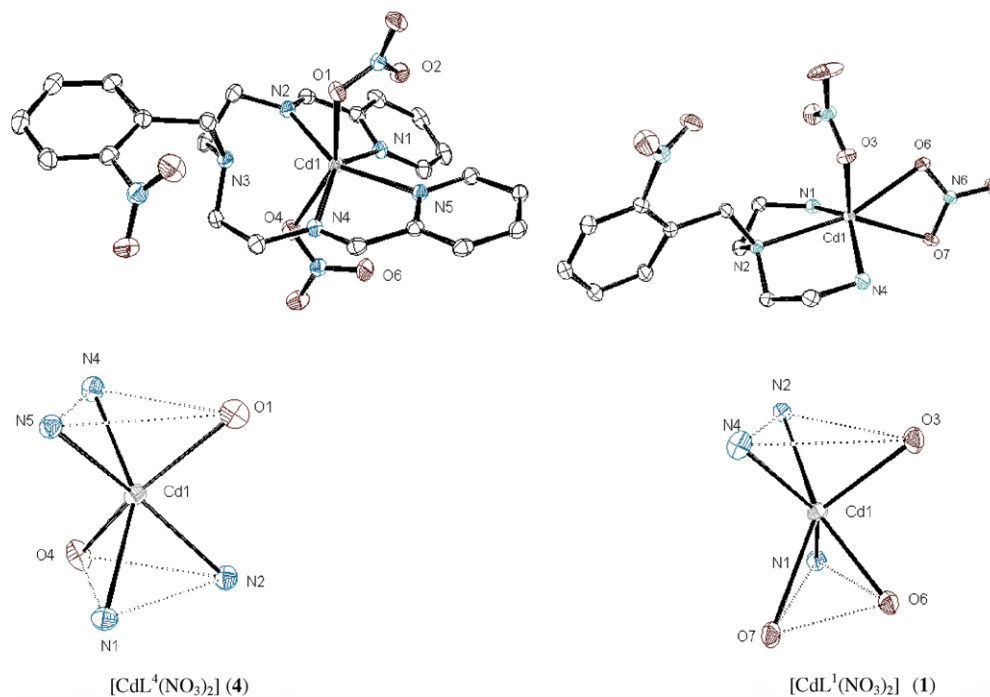
#### 3.1. Synthesis and characterization

The Schiff base condensation of  $\text{L}^1$ ,  $\text{L}^2$  or  $\text{L}^3$  and 2-pyridinecarboxaldehyde in methanol in the presence of cadmium nitrate and in 1:2:1 molar ratio, gave good yields of the analytically pure products  $[\text{CdL}^n(\text{NO}_3)_2]$  ( $n = 4, 5, 6$ ) (Scheme 1). On the other hand, the polyamine complexes (**1–3**) were readily prepared from direct reaction of  $\text{L}^1$ ,  $\text{L}^2$  or  $\text{L}^3$  and cadmium nitrate, respectively. All complexes were characterized by spectroscopic methods and in the case of  $[\text{CdL}^4(\text{NO}_3)_2]$  (**4**) and  $[\text{CdL}^1(\text{NO}_3)_2]$  (**1**) by X-ray crystallogra-

phy. The infrared spectra of the complexes confirm the formation of the macroacyclic compounds by the absence of bands characteristic of carbonyl and primary amine groups of the starting materials and exhibit a Schiff base  $\nu(\text{C}=\text{N})$  vibration in the range of 1652–1659  $\text{cm}^{-1}$ . The complexes exhibit bands at approximately 1522–1530 and 1349–1353  $\text{cm}^{-1}$  associated with a nitro group. In complexes of  $[\text{CdL}^n(\text{NO}_3)_2]$  ( $n = 4, 5, 6$ ) bands about 1595  $\text{cm}^{-1}$  have been seen that attributed to pyridine group. The NMR studies of the cadmium complexes also provides strong evidence for the formation of the macroacyclic complexes.

**Table 2**  
Selected bond lengths (Å) and angles ( $^\circ$ ) for  $[\text{CdL}^1(\text{NO}_3)_2]$  (**1**) and  $[\text{CdL}^4(\text{NO}_3)_2]$  (**4**)

<b>4</b>		<b>1</b>	
Bond	Bond length (Å)	Bond	Bond length (Å)
Cd(1)–N(1)	2.4194(14)	Cd(1)–N(1)	2.2085(12)
Cd(1)–N(2)	2.2896(13)	Cd(1)–N(2)	2.5609(11)
Cd(1)–N(4)	2.3417(14)	Cd(1)–N(4)	2.2239(12)
Cd(1)–N(5)	2.3831(12)	Cd(1)–O(3)	2.3401(10)
Cd(1)–O(1)	2.4175(12)	Cd(1)–O(7)	2.5598(11)
Cd(1)–O(2)	2.773	Cd(1)–O(6)	2.3725(10)
Cd(1)–O(4)	2.4923(12)		
Cd(1)–O(6)	2.322(3)		
Bond	Bond angle ( $^\circ$ )	Bond	Bond angle ( $^\circ$ )
N(2)–Cd(1)–N(1)	70.97(5)	N(2)–Cd(1)–N(1)	77.31(4)
N(5)–Cd(1)–N(1)	90.86(4)	O(6)–Cd(1)–N(2)	163.16(3)
N(4)–Cd(1)–N(5)	71.14(5)	N(1)–Cd(1)–O(7)	90.18(4)
N(2)–Cd(1)–N(4)	134.34(5)	N(2)–Cd(1)–N(4)	77.50(4)
N(2)–Cd(1)–O(4)	80.94(4)	N(4)–Cd(1)–O(3)	86.65(4)
N(4)–Cd(1)–O(4)	84.65(5)	O(3)–Cd(1)–O(7)	123.02(4)
N(5)–Cd(1)–O(4)	117.44(4)	N(4)–Cd(1)–O(7)	90.78(4)
N(1)–Cd(1)–O(4)	80.24(4)	N(2)–Cd(1)–O(3)	91.01
O(1)–Cd(1)–O(4)	153.29(4)	N(1)–Cd(1)–O(6)	99.79
N(5)–Cd(1)–O(1)	83.04(4)	O(6)–Cd(1)–O(7)	52.07
O(1)–Cd(1)–N(1)	118.54(4)		
N(2)–Cd(1)–O(1)	87.45(4)		
N(4)–Cd(1)–O(1)	86.51(4)		



**Fig. 1.** ORTEP drawing of the molecular structures of the complexes  $[\text{CdL}^1(\text{NO}_3)_2]$  and  $[\text{CdL}^4(\text{NO}_3)_2]$ .

### 3.2. X-ray crystal structure

The molecular structures of  $[\text{CdL}^1(\text{NO}_3)_2]$  (**1**) and  $[\text{CdL}^4(\text{NO}_3)_2]$  (**4**) are shown in Fig. 1. Selected bond lengths and angles are given in Table 2. In macrocyclic complex **1** the four nitrogen donor atoms of the potentially  $\text{N}_5$  macrocyclic ligand and two oxygen donor atoms of two monodentate nitrate groups are coordinated to the metal ion. The bond length of Cd–N(3) is 2.84 Å. In similar cases where there is no pendant arms, secondary amine can be coordinated [26] while in the presence of 2-nitrobenzyl pendant arm only a weak coordinative bond can be observed. When 2-nitrobenzyl pendant arm is attached to a related macrocyclic complex then the tertiary nitrogen is strongly coordinated to the central cadmium [21]. Two nitrate groups are coordinated to the central cadmium in different manner. In one of Cd–nitrate bonds, in addition to a strong Cd–O(1) bond the other Cd–O(2) linkage is considered to be a relatively weak (2.77 Å). But in the second nitrate group, only one of oxygen atoms, O(4), is strongly coordinated whereas the other one, e.g. Cd–O(6), the

bond length is too long to be considered as a bond (3.26 Å). In complex **1**, the three nitrogen donor of amine and three oxygen donor of two different nitrate groups are coordinated to the metal ion.

In solid complexes previously obtained with Cd(II) nitrate with triamines: dien, 2,3-tri or 3,3-tri of  $\text{CdL}_2$ -type stoichiometry, all six nitrogen atoms take part in the coordination [27] while in this case due to steric hindrance caused by the attachment of an extra 2-nitrobenzyl pendant arm to a secondary amine, only CdL-type stoichiometry are produced

In complex **1**, the tertiary nitrogen atom is coordinated to the metal ion. But in complex **4**, because of displacement of metal ion towards the nitrogen donors of imine and pyridine groups due to back donation, only a weak coordinate bond is formed. The geometry of complex **1** and **4** is best considered as distorted triangular prism structures (Fig. 2). Charge balances for the complexes are provided by two-coordinated nitrate ions producing neutral compounds. There are no solvent molecules in these structures.

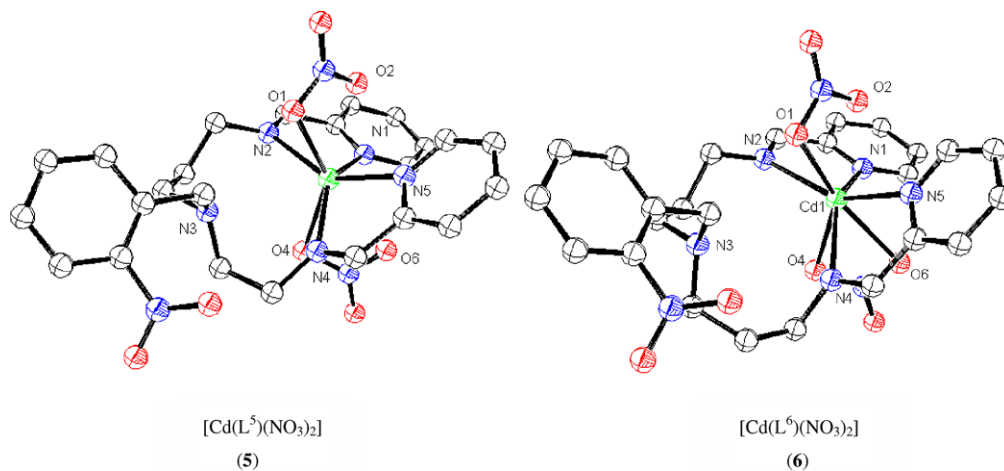


Fig. 2. The ab initio optimized structures of the  $[\text{Cd}(\text{L}^5)(\text{NO}_3)_2]$  and  $[\text{Cd}(\text{L}^6)(\text{NO}_3)_2]$ .

Table 3

Selected calculated bond distances and angles for optimized structures  $[\text{Cd}(\text{L}^4)(\text{NO}_3)_2]$  (**4**),  $[\text{Cd}(\text{L}^5)(\text{NO}_3)_2]$  (**5**) and  $[\text{Cd}(\text{L}^6)(\text{NO}_3)_2]$  (**6**)

$[\text{Cd}(\text{L}^4)(\text{NO}_3)_2]$ ( <b>1</b> ) XRD	( <b>4</b> ) (HF/3-21G <sup>+</sup> )	( <b>4</b> ) (HF/6-31G <sup>+</sup> )	( <b>5</b> ) (HF/3-21G <sup>+</sup> )	( <b>5</b> ) (HF/6-31G <sup>+</sup> )	( <b>6</b> ) (HF/3-21G <sup>+</sup> )	( <b>6</b> ) (HF/6-31G <sup>+</sup> )
<b>Bond length (Å)</b>						
Cd(1)–N(2)	2.2896(13)	2.37	2.5	2.416	2.437	2.418
Cd(1)–N(4)	2.3417(14)	2.413	2.4	2.431	2.431	2.451
Cd(1)–N(5)	2.3831(12)	2.465	2.6	2.48	2.512	2.454
Cd(1)–O(1)	2.4175(12)	2.408	2.4	2.412	2.378	2.415
Cd(1)–O(2)	2.773	2.537	2.4	2.495	2.469	2.465
Cd(1)–N(1)	2.4194(14)	2.56	2.5	2.522	2.593	2.503
Cd(1)–O(4)	2.4923(12)	2.408	2.4	2.391	2.356	2.404
Cd(1)–O(6)	3.23	2.487	2.4	2.469	2.478	2.416
<b>Bond angle (°)</b>						
N(2)–Cd(1)–N(1)	70.97(5)	67.12	67	67.46	66.51	68.17
N(5)–Cd(1)–N(1)	90.86(4)	103.67	112	108.36	104.71	115.31
N(4)–Cd(1)–N(5)	71.14(5)	68.64	65	68.73	67.8	69.19
N(2)–Cd(1)–N(4)	134.34(5)	135.12	131	132.21	137	126.25
O(1)–Cd(1)–N(1)	118.54(4)	116.02	123	122.26	117.65	120.58
N(2)–Cd(1)–O(1)	87.45(4)	76.72	79	78.04	76.64	74.25
N(4)–Cd(1)–O(1)	86.51(4)	97.92	83	90.21	99.28	93.47
N(1)–Cd(1)–O(4)	80.24(4)	74.78	82	79.47	76.93	75.66
O(1)–Cd(1)–O(4)	153.29(4)	149.01	150	142.03	146.06	142.51
N(2)–Cd(1)–O(4)	80.94(4)	82.14	98	84.17	82.96	81.21
N(4)–Cd(1)–O(4)	84.65(5)	81.34	76	77.34	77.64	76.78
N(5)–Cd(1)–O(4)	117.44(4)	123.65	115	126.41	124	129.06

In complex **1**, the angle between planes of the aromatic ring of pendant arm and the plane containing N(4), N(2), N(1) and N(6) is 73.33° whereas in complex **4** the angle between plane of the aromatic ring of pendant arm and the plane containing N(1), N(2), N(4) and N(5) is 17.88°.

### 3.3. *Ab initio* modelling studies

We assumed that the same mode that found for [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] had occurred with other cadmium complexes due to the similarity of their IR, NMR spectra and microanalyses, and undertook a full geometry optimization at the HF/3-21G\* and HF/6-31G\* levels of theory, using LanL2DZ basis set for cadmium. The resulting structural diagrams are shown in Fig. 2 and selected calculated bond distances and angles relating to them are shown in Table 3 along with the corresponding values obtained for [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] by X-ray diffraction for comparison. We note that the results of the 3-21G\* calculations for [CdL<sup>4</sup>(NO<sub>3</sub>)<sub>2</sub>] are closer to the experimental data than those of 6-31G\* calculations. There is good agreement between the calculated and observed distances.

### 3.4. NMR studies

The <sup>1</sup>H as well as <sup>13</sup>C{<sup>1</sup>H} NMR data for [CdL<sup>*n*</sup>(NO<sub>3</sub>)<sub>2</sub>] (*n* = 1, 2, 3, 4, 5 and 6) dissolved in DMSO-*d*<sub>6</sub> are shown in Table 4, which uses

the lettering scheme shown in Scheme 2. The <sup>1</sup>H and <sup>13</sup>C signals were assigned using one- and two-dimensional <sup>1</sup>H–<sup>1</sup>H COSY, <sup>1</sup>H–<sup>13</sup>C HMQC and DEPT spectra.

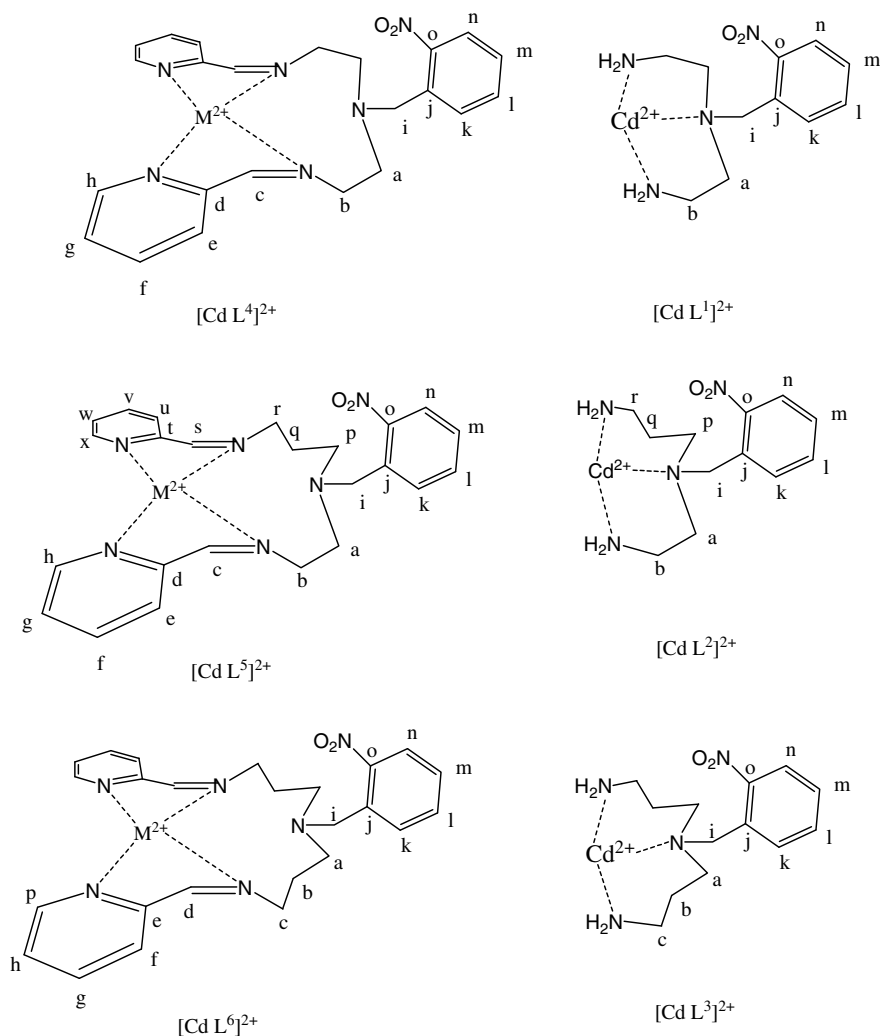
The <sup>1</sup>H NMR spectra of **4**, **5** and **6** show three, six and four distinct signals, respectively, for aliphatic methylene groups. Hi resonance (Scheme 2) for all complexes is appeared as a singlet. The existence of three, six and four different aliphatic methylene group in **4**, **5** and **6**, respectively, was also confirmed by <sup>13</sup>C NMR spectra.

In complex [CdL<sup>5</sup>]<sup>2+</sup> (**5**), there are two signals due to the <sup>1</sup>H imine resonance at ca. 8.68 and 8.70 ppm in <sup>1</sup>H NMR spectrum and two signals (162.16, 164.61 ppm) in <sup>13</sup>C NMR spectrum, demonstrating the non-equivalence of the two imine environments. In the region corresponding to the signals of aromatic rings carbons (124.70, 129.00, 129.48, 132.58, 132.71, 133.15, 141.77, 141.50, 149.40, 150.32 and 150.60 ppm) 11 peaks instead of 16 expected peaks are observed, due to high similarity of head unit and low resolution of instrument. Unfortunately, since the protons do not show scalar-coupling, we were not able to assign explicitly the signals to each of all aromatic systems present in the molecule.

The <sup>1</sup>H NMR spectrum of the complex [CdL<sup>4</sup>]<sup>2+</sup> shows only a single <sup>1</sup>H imine resonance at ca. 8.87 ppm with two satellites (due to coordinated cadmium) and <sup>13</sup>C NMR spectrum shows one imine carbon C<sub>h</sub> (163.19 ppm) that demonstrating the equivalence of the two imine environments. In the region corresponding to the signals of aromatic rings carbons (124.83, 129.38, 129.54, 133.02,

**Table 4**  
<sup>1</sup>H NMR and <sup>13</sup>C NMR{<sup>1</sup>H} spectral assignments for **1–6** recorded in DMSO-*d*<sub>6</sub>

[CdL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]		[CdL <sup>4</sup> (NO <sub>3</sub> ) <sub>2</sub> ]		[CdL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]		[CdL <sup>5</sup> (NO <sub>3</sub> ) <sub>2</sub> ]		[CdL <sup>3</sup> (NO <sub>3</sub> ) <sub>2</sub> ]		[CdL <sup>6</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	
Ha	2.67	Ha	2.87	Hq	1.71	Hq	1.79	Ha	2.53	Ha	2.4
Hb	2.35	Hb	3.87	Hp	2.71	Hp	2.41	Hb	1.59	Hb	1.7
Hi	4.22	Hi	4.27	Ha	2.86	Ha	3	Hc	2.34	Hc	3.3
NH <sub>2</sub>	3.23	H Ar	7.58–8.46	Hr	2.24	Hr	3.5	Hi	3.76	Hi	4
Hn	7.92	Hc	8.87	Hb	2.46	Hb	3.83	NH <sub>2</sub>	3.34	H Ar	7.04–7.98
HI, Cm, Ck	7.56–7.74	Ca	53.1	Hi	4.26	Hi	3.9	Hn	7.85	Hd	8.67
Ca	49.1	Cb	54.6	Hk	7.51	Hc	6.7	HI, Cm	7.65–7.67	Ca	51.33
Cb	36.9	Ci	51.39	HI and Hm	7.61 or 7.72	Hs	6.68	Hk	7.45	Cb	26.61
Ci	51.1	Ck	124.83	Hn	7.9	H Ar	7.54–8.08	Ca	51.3	Cc	53.11
Cj	127	Cd	151.23	NH <sub>2</sub>	3.4	Cq	27	Cb	28.6	Ci	52.22
Ck	124.76	Co, Cj	~133.02	Cq	25.6	Cp	51.82	Cc	49.1	Cd	161.56
Cl, Cm	129.97	Ce, Cf, Cg	129.38, 129.54	Cp	48.41	Ca	52.96	Ci	55.28	Ce, Cj, Co	132.7, 129.15
	132.97	Ch, Cl	133.55, 141.29								129.48, 132.58
		Cm, Cn	147.21, 150.25								133.15, 141.55
Cn	134.64	Cc	163.19	Ca	51.66	Cr	54.98	Cj	128.8	Ck, Cl, Cm, Cf, Cg, Ch, Cp	141.77, 149.4, 150.6
Co	151.91			Cr	36.72	Cb	56.94	Ck	124.52		
				Cb	43.1	Ci	55.44	Cl and Cm	131.7 or 133.18		
				Ci	54.18	Ck	124.7	Cn	134.34		
				Cj	125.7	Cd	150.03	Co	150		
				Ck	125	Ct, Co, Cj	132.7, 129.15				
					130.11	Ck, Cl, Cm, Ce	129.48, 132.58				
				Cl and Cm	or 132.74	Cf, Cg, Ch, Cu	133.15, 141.55				
						Cv, Cw, Cx	141.77, 149.4				
				Cn	134.64	Cn	150.61				
				Co	152	Cs, Cc	162.16, 164.61				



Scheme 2.

133.55, 141.29, 147.21, 150.25 and 151.23 ppm) nine peaks instead of 11 expected peaks are observed, due to high similarity of head unit and low resolution of instrument.

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the complex  $[CdL^6]^{2+}$  is resemble to complex  $[CdL^4]^{2+}$ .

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### Appendix A. Supplementary material

CCDC 649842 and 663127 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](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2008.03.025.

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