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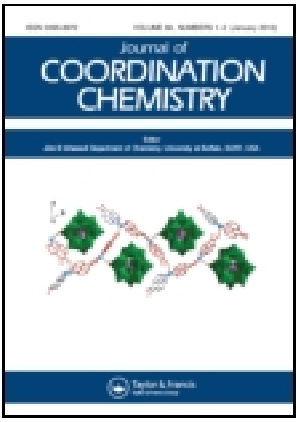

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Synthesis and characterization of two nicotinate-containing cadmium complexes in a tripodal ligand system

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Two nicotinate-containing cadmium(II) complexes were synthesized and structurally characterized. $[Cd(ntb)(nic)]ClO_4 \cdot 0.5CH_3OH$ (**1**) (ntb = tris(2-benzimidazolylmethyl)amine, nic = nicotinate anion) crystallized in the triclinic space group P-1 with $a = 13.9979(17)$ Å, $b = 14.0344(18)$ Å, $c = 17.738(3)$ Å and $\alpha = 104.386(10)^\circ$, $\beta = 93.317(12)^\circ$, $\gamma = 110.081(8)^\circ$. The central Cd(II) is coordinated by four nitrogen atoms of ntb and two oxygen atoms of nicotinate to form a distorted octahedral geometry. $[Cd(tren)(nic)]BPh_4$ (**2**) (tren = tris(2-aminoethyl) amine) crystallized in the monoclinic crystal system, $P2_1/c$ space group with $a = 18.610(6)$ Å, $b = 10.1620(16)$ Å, $c = 20.0085(18)$ Å and $\beta = 111.230(11)^\circ$. The central Cd(II) is coordinated by four nitrogen atoms of tren and one oxygen atom of nicotinate to form a distorted trigonal bipyramidal geometry. A tetramer for **1** and a dimer for **2** are formed through intermolecular hydrogen-bonding.

Keywords: Cadmium(II); Nicotinic acid; Tris(2-benzimidazolylmethyl)amine; Tris(2-aminoethyl)amine; X-ray structure

1. Introduction

Tetradentate tripodal ligands have long been used in coordination, organometallic, and supramolecular chemistry [1–4]. These ligands can differ both in the lengths of the arms and in the nature of the N-donors on each arm (see scheme 1). Tris(2-benzimidazolylmethyl)amine (ntb) contains three aromatic N-donors on its arms, while tris(2-aminoethyl)amine (tren) contains three aliphatic N-donors. These two ligands are widely used to prepare metal complexes. Compared to other metal complexes, cadmium complexes of ntb and tren are fewer. Till now, only five crystallograpically characterized cadmium complexes of ntb containing chloride, nitrate, 4-chlorobenzoate and 4-nitrobenzoate as coligands have been reported [5–9]. Some cadmium complexes of tren have been reported, exhibiting mononuclear [10–12], dinuclear [12, 13], a star-shaped heptanuclear [14], and 2-D structural features [15]. Cadmium(II) complexes of tren and ntb using nicotinate as coligand have never been reported.

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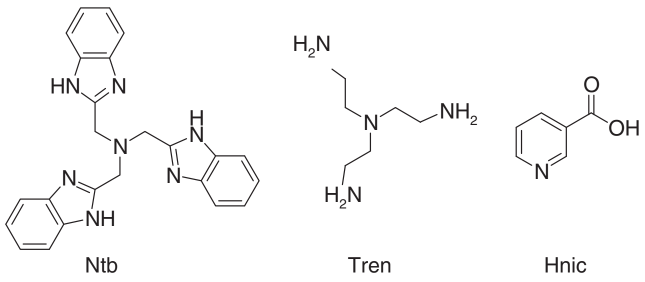


Scheme 1. Chemical diagram of the three principal ligands.

Nicotinic acid has potential coordination sites involving nitrogen of the pyridine ring and carboxlyate oxygen atoms and can coordinate with cadmium *via* one or two oxygen atoms of carboxylate or the pyridine or both. A number of cadmium complexes of nicotinate have been reported and characterized [16–28]. Several cadmium complexes of nicotinate containing azide, dicyanoamide, and ethylenediamine in mixed ligand systems have been characterized *via* X-ray diffraction [24–27]. Most complexes exhibit interesting 1-D, 2-D, and 3-D polymeric structures. Only a few cadmium complexes are mononuclear [10–12].

We are interested in the preparation of cadmium(II) nicotinate complexes containing tren and ntb for the following two reasons. First we would like to see how the structural change of the main ligand with aromatic benzimidazole side arms (ntb) or aliphatic side arms (tren) may influence the coordination behavior of nicotinate as coligand. Second, when the complexes of ntb and tren were formed, the uncoordinated NH groups on the benzimidazole rings of ntb and the coordinated NH_2 group of tren may act as hydrogen donors, the uncoordinated oxygen and nitrogen atoms of nitcotinate, and the counter anions as hydrogen acceptor, intermolecular interactions such as hydrogen bonds and π–π interactions may afford interesting supramolecular coordination assembly. In this article, we report the structures of two new nicotinate-containing cadmium(II) complexes of ntb and tren.

2. Experimental

2.1. *General and physical methods*

The ntb was synthesized by using the published procedure [29]. All other starting materials and solvents were of analytical grade and used without purification. The white solid $Cd(nic)_2 \cdot 4H_2O$ was prepared by reaction of $CdSO_4 \cdot 8H_2O$ and sodium nicotinate at the ratio of 1 : 2 in water.

C, H, and N determinations were performed on an Elemental Vario MICRO CUBE (Germany) elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker TENSOR 27 FT-IR spectrometer. ^1H-NMR spectra of the complexes were recorded on a Varian VNMR-600 MHz spectrometer by using DMSO-d_6 as solvent. The excitation and emission spectra of the solid sample were recorded on an F-4500 Hitachi Fluorescence Spectrophotometer.

2.2. *Syntheses*

2.2.1. Synthesis of [Cd(ntb)(nic)]ClO$_4$·0.5CH$_3$OH (1). To a methanol solution (90 mL) of Cd(ClO$_4$)$_2$ · 6H$_2$O (0.422 g, 1 mmol) was added ntb (0.407 g, 1 mmol) and the mixture was stirred at room temperature. After an hour, a methanol solution (40 mL) of sodium nicotinate (0.145 g, 1 mmol) was added dropwise. Then the solution was stirred at reflux for 4 h and filtered to remove any non-dissolved material. Three weeks later, colorless crystals were obtained. Yield: 727 mg (48%). FT-IR (KBr pellet, cm^{-1}): 3407 s/br, 2915 w, 1596 m, 1471 w 1455 s, 1392 m, 1119 s, 1109 s, 1093 s, 964 w, 853 w, 761 m, 751 m, 691 w, 626 m. Anal. Calcd for $C_{61}H_{54}Cl_2N_{16}Cd_2O_{13}$ (%): C, 48.36; H, 3.59; N, 14.79. Found: C, 48.41; H, 3.66; N, 14.48. ^{1}H-NMR (600 MHz, DMSO-d$_6$) δ (ppm): 13.281 (s, 3H), 9.423 (s, 1H), 8.802–8.813 (s, 1H), 8.578–8.590 (d, 1H), 8.034–8.046 (d, 3H), 7.618-7.640 (q, 1H), 7.547–7.560 (d, 3H), 7.212–7.270 (m, 6H), 4.641 (s, 6H).

2.2.2. Synthesis of [Cd(tren)(nic)]BPh$_4$ (2). A methanol solution (50 mL) of tren (0.146 g, 1 mmol) was added to a methanol solution (120 mL) of Cd(nic)$_2$ · 4H$_2$O (0.429 g, 1 mmol). The mixture was stirred at room temperature for 1 h, then a methanol solution (40 mL) of NaBPh$_4$ (0.342 g, 1 mmol) was added dropwise. After reacting for 4 h, the mixture was filtered. Slow evaporation of the filtrate yielded colorless prism-shaped crystals. Yield: 371 mg (53%). FT-IR (KBr pellet, cm^{-1}): 3302 s, 3055 m, 1595 s, 1551 s, 1480 m, 1427 m, 1314 w, 1150 w, 1063 s, 993 m, 973 w, 883 w, 842 w, 742 s, 716 s, 605 m, 515 w. Anal. Calcd for $C_{36}H_{42}N_5O_2BCd$ (%): C, 61.77; H, 6.05; N, 10.00. Found: C, 61.23; H, 6.01; N, 10.02. ^{1}H-NMR (600 MHz, DMSO-d$_6$) δ (ppm): 9.071 (s, 1H), 8.632–8.642(dd, 1H), 8.199–8.212 (d, 1H), 7.418–7.439 (q, 1H), 7.182 (s, 8H), 6.907–6.938 (m, 8H), 6.786–6.804 (dd, 4H), 3.280–3.333 (m, 6H), 2.705–2.721 (m, 6H), 2.539–2.554 (t, 6H).

2.3. *X-ray crystallography*

Suitable single crystals were selected for diffraction analysis. Data collections were performed on a Bruker P4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature (294 ± 1 K). Data collection and reduction were performed using SMART and SAINT software [30, 31]. An empirical absorption correction (SADABS) was applied to raw intensities. The structures were solved by direct methods and refined by full matrix least squares based on F^2 using the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on calculated positions and refined as riding on their attached atoms. The crystallographic data and refinement details for the complexes are given in table 1.

3. Results and discussion

3.1. *Crystal structures*

Complex **1** was prepared by reacting Cd(ClO$_4$)$_2$ · 6H$_2$O directly with the tripodal ligand ntb and sodium nicotinate in methanol in the ratio of 1 : 1 : 1. Complex **2** was

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

Complex	**1**	**2**
Chemical formula	$C_{61}H_{54}N_{16}O_{13}Cl_2Cd_2$	$C_{36}H_{42}N_5O_2BCd$
Molecular weight	1514.90	699.96
Color/shape	Colorless/prism	Colorless/prism
Crystal size (mm^3)	$0.1 \times 0.1 \times 0.2$	$0.3 \times 0.4 \times 0.4$
Crystal system	Triclinic	Monoclinic
Space group	*P*-1 (No. 2)	$P2_1/c$ (No. 14)
Unit cell dimensions (Å, °)		
a	13.9979(17)	18.610(6)
b	14.0344(18)	10.1620(16)
c	17.738(3)	20.0085(18)
α	104.386(10)	
β	93.317(12)	111.230(11)
γ	110.081(8)	
Volume (Å^3), Z	3130.6(7), 2	3527.1(13), 4
Calculated density (g cm^{-3})	1.607	1.318
$F(000)$	1532	1448
Data collection range	$-1 < h < 16$; $-15 < k < 15$; $-21 < l < 21$	$-1 < h < 22$; $-1 < k < 12$; $-23 < l < 22$
θ range for data collection (°)	2.3–12.6	2.1–12.2
Reflections measured	11,575	7654
Independent reflection	10,892	6205
Max. and min. transmission	0.919 and 0.858	0.821 and 0.757
Data/restraints/parameters	10,892/20/848	6205/0/406
Goodness-of-fit on F^2	0.995	1.045
R_1, wR_2 ($I > 2\sigma(I)$)	0.0574, 0.0906	0.0650, 0.0945
R_1, wR_2 (all data)	0.1649, 0.1200	0.1666, 0.1179
Largest difference peak and hole (e Å^{-3})	−0.564 and 0.535	−0.326 and 0.323

synthesized by the reaction of $Cd(nic)_2 \cdot 4H_2O$ with tren and $NaBPh_4$ as the counter anion. The selected bond lengths and angles of the two complexes are listed in tables 2 and 3.

3.1.1. Crystal structure of 1. The structure of **1** consists of two $[Cd(ntb)(nic)]^+$ cations, two perchlorate anions, and one methanol. The two cations in each lattice are crystallographically independent but chemically identical. The structures of the two cations are shown in figure 1.

The central Cd(II) in each cation is six-coordinate with four nitrogen atoms of ntb and two oxygen atoms of nicotinate. The coordination polyhedron for each Cd(II) is a distorted octahedron. The basal plane is composed of N(2), N(7), O(1), and O(2) with bond lengths 2.633(6) Å for Cd(1)–N(2), 2.272(7) Å for Cd(1)–N(7), 2.426(6) Å for Cd(1)–O(1), and 2.340(6) Å for Cd(1)–O(2). The axial positions are occupied by N(3) and N(5) from imidazoles of ntb with distance of 2.264(6) Å and 2.259(7) Å, respectively. The bond angle N(3)–Cd(1)–N(5) is 119.0(2)°. The degree of distortion from ideal octahedral geometry is reflected in the angles around the Cd(II) in the equatorial plane, ranging from 54.8(2)° [O(2)–Cd(1)–O(1)] to 152.5(2)° [O(1)–Cd(1)–N(2)], while the ideal values should be 90°.

In a similar way to that of other transition metal complexes [32–37], ntb coordinates to Cd(II) through four nitrogen atoms, displaying a tripod-type coordination behavior. Thus the tertiary nitrogen as well as its three benzimidazole arms forms a cone-shaped

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

Cd(1)–N(5)	2.259(7)	Cd(2)–N(11)	2.217(7)
Cd(1)–N(3)	2.264(6)	Cd(2)–N(13)	2.274(6)
Cd(1)–N(7)	2.272(7)	Cd(2)–N(15)	2.282(6)
Cd(1)–O(2)	2.340(6)	Cd(2)–O(4)	2.319(5)
Cd(1)–O(1)	2.426(6)	Cd(2)–O(3)	2.438(5)
Cd(1)–N(2)	2.633(6)	Cd(2)–N(10)	2.663(6)
N(5)–Cd(1)–N(3)	119.0(2)	N(11)–Cd(2)–N(13)	112.4(2)
N(5)–Cd(1)–N(7)	107.6(2)	N(11)–Cd(2)–N(15)	106.3(2)
N(3)–Cd(1)–N(7)	101.5(2)	N(13)–Cd(2)–N(15)	106.2(2)
N(5)–Cd(1)–O(2)	98.3(2)	N(11)–Cd(2)–O(4)	109.6(2)
N(3)–Cd(1)–O(2)	135.5(2)	N(13)–Cd(2)–O(4)	91.3(2)
N(7)–Cd(1)–O(2)	88.1(2)	N(15)–Cd(2)–O(4)	129.8(2)
N(5)–Cd(1)–O(1)	103.0(2)	N(11)–Cd(2)–O(3)	102.0(2)
N(3)–Cd(1)–O(1)	91.6(2)	N(13)–Cd(2)–O(3)	138.6(2)
N(7)–Cd(1)–O(1)	134.8(2)	N(15)–Cd(2)–O(3)	84.5(2)
O(2)–Cd(1)–O(1)	54.8(2)	O(4)–Cd(2)–O(3)	54.72(18)
N(5)–Cd(1)–N(2)	70.7(2)	N(11)–Cd(2)–N(10)	69.7(2)
N(3)–Cd(1)–N(2)	70.2(2)	N(13)–Cd(2)–N(10)	69.2(2)
N(7)–Cd(1)–N(2)	70.9(2)	N(15)–Cd(2)–N(10)	69.3(2)
O(2)–Cd(1)–N(2)	151.0(2)	O(4)–Cd(2)–N(10)	157.3(2)
O(1)–Cd(1)–N(2)	152.5(2)	O(3)–Cd(2)–N(10)	147.90(19)

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

Cd(1)–O(1)	2.198(5)	Cd(1)–N(3)	2.299(5)
Cd(1)–N(2)	2.249(5)	Cd(1)–N(1)	2.462(5)
Cd(1)–N(4)	2.297(6)		
O(1)–Cd(1)–N(2)	128.6(2)	N(4)–Cd(1)–N(3)	118.7(2)
O(1)–Cd(1)–N(4)	95.5(2)	O(1)–Cd(1)–N(1)	154.6(2)
N(2)–Cd(1)–N(4)	119.2(2)	N(2)–Cd(1)–N(1)	75.5(2)
O(1)–Cd(1)–N(3)	90.79(19)	N(4)–Cd(1)–N(1)	75.1(2)
N(2)–Cd(1)–N(3)	102.2(2)	N(3)–Cd(1)–N(1)	74.17(19)

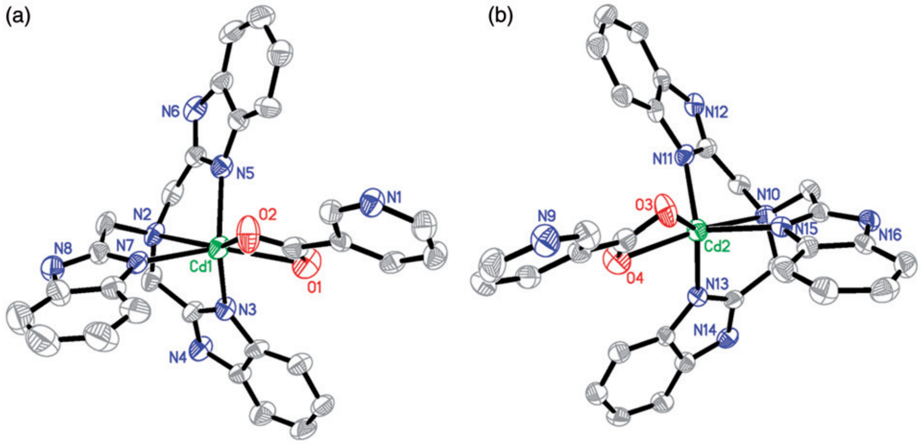
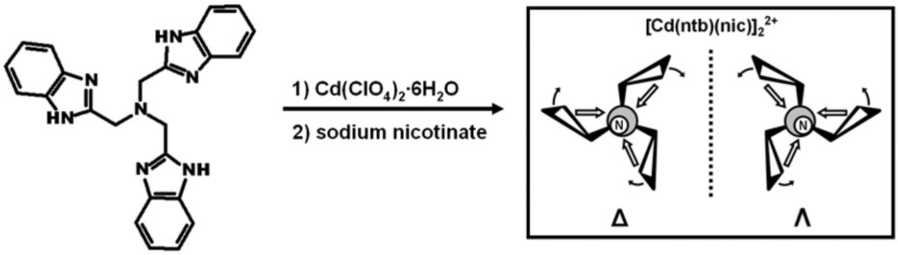


Figure 1. The two cation structures of **1** showing 30% probability displacement ellipsoids: (a) Δ-isomer and (b) Λ-isomer.



Scheme 2. The formation of Δ- and Λ-enantiomers of **1**.

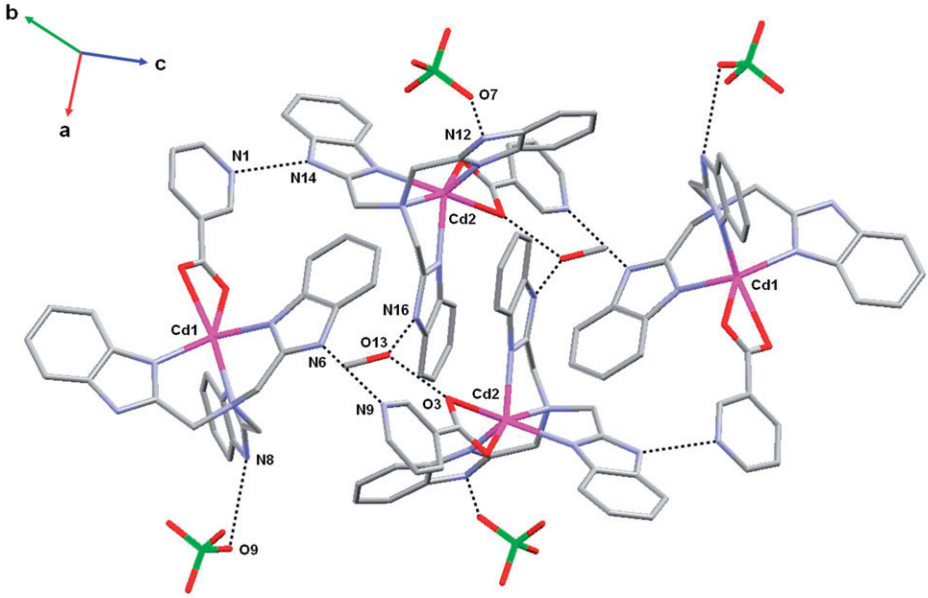


Figure 2. Tetramer formed by intermolecular H-bond and π–π stacking interactions in **1**.

cave with the central Cd(II) lying out of the trigonal plane defined by the three imine nitrogen atoms, and resulting in an elongated bond distance between Cd(II) and the bottom tertiary nitrogen [the bond distance Cd(1)–N(2) is 2.633(6) Å, much longer than Cd(1)–N(3), Cd(1)–N(7), and Cd(1)–N(5), on average 2.265 Å]. This was attributed to the steric requirement of the tripodal tetradentate ligand [8]. The second ligand, nicotinate, coordinates to Cd(II) through its two oxygen atoms, rather than nitrogen.

Viewing from the direction of the tertiary nitrogen of ntb to Cd(II), ntb exhibits right- or left-handed propeller appearance in the two crystallographically independent cations in the same unit cell. This type of helical arrangement is intrinsically chiral and results in a pair of enantiomers [3, 4] (see scheme 2 and figure 1).

Single-crystal X-ray analysis shows that in **1** the cations, perchlorate anions, and methanol molecules are all involved in an extensive hydrogen-bond system to form a tetramer (figure 2), which stacks to form a 3-D structure (figure 3). The hydrogen-bond parameters for **1** are listed in table 4.

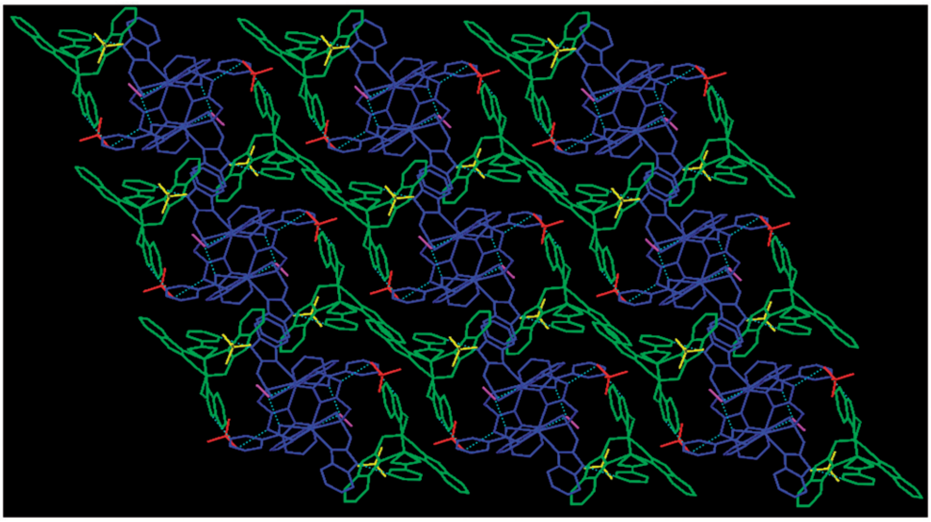


Figure 3. View of the 3-D structure stacked by the tetramer of **1**.

Table 4. Hydrogen-bond parameters for **1** and **2**.

D–H···A	d(H···A) (Å)	∠(DHA) (°)	d(D···A) (Å)	Symmetry codes
Complex **1**				
N(4)–H(4B)···O(8)	2.34	145.0	3.086(9)	$1+x, y, z$
N(6)–H(6A)···N(9)	2.17	137.8	2.862(10)	$x, -1+y, z$
N(8)–H(8A)···O(9)	2.28	139.3	2.984(10)	$1+x, y, z$
N(12)–H(12B)···O(7)	1.97	159.3	2.791(9)	$1+x, 1+y, 1+z$
N(14)–H(14B)···N(1)	2.02	173.9	2.876(9)	$1-x, 1-y, 2-z$
N(16)–H(16A)···O(13)	1.82	173.7	2.678(9)	
O(13)–H(13B)···O(3)	1.92	163.9	2.713(9)	$1-x, 2-y, 2-z$
Complex **2**				
N(4)–H(4B)–N(5)	2.26	162.1	3.130(10)	$-x, 2-y, 2-z$

As shown in figure 2, (i) each $[Cd(ntb)(nic)]^+$ cation is linked to a perchlorate anion by N–H···O intermolecular hydrogen bond [for Δ-enantiomer: N(8)···O(9) 2.984(10) Å, N(8)–H(8A)···O(9) 139.3°; for Λ-enantiomer: N(12)···O(7) 2.791(9) Å, N(12)–H(12B)···O(7) 159.3°]; (ii) each $[Cd(ntb)(nic)]^+$ cation associates with two neighboring ones which are of different chirality by two N–H···N hydrogen bonds, for example, Δ-enantiomer makes two hydrogen bonds with Λ-enantiomer through nitrogen of nicotinate and one NH of ntb. The hydrogen bonds are 2.876(9) Å for N(1)···N(14) and 2.862(10) Å for N(6)···N(9), N(6). In this way, four cations (two Λ-enantiomers and two Δ-enantiomers) link alternatively into a ring; (iii) two Λ-enantiomers are connected by two methanol molecules through two O···H–O [O(13)···O(3) 2.713(9) Å, O(13)–H(13B)···O(3) 163.9°] and two N–H···O [N(16)···O(13) 2.678(9) Å, N(16)–H(16A)···O(13) 173.7°] hydrogen bonds. The tetramer is also stabilized by the π–π stacking interaction from imidazole rings of adjacent

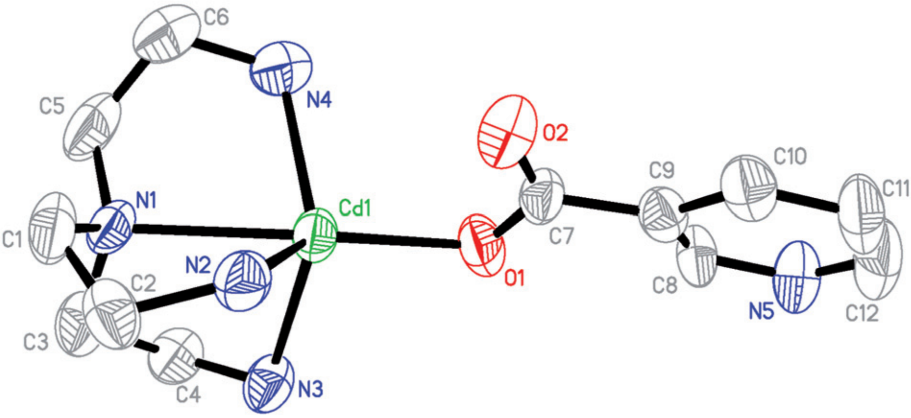


Figure 4. Cation structure of **2** showing 30% probability displacement ellipsoids.

benzimidazoles with centroid-to-centroid distance of 3.671 Å (Cg1 = Cg2 = C54–N15–C55–C56–N16) (see figure 2).

The tetramers further interact by π–π stacking interactions with centroid-to-centroid distances from 3.748 Å (Cg3 = Cg4 = C16–N5–C17–C18–N6) to 3.950 Å (Cg5 = Cg6 = C46–N13–C47–C48–N14). Another π–π stacking interaction is observed from the imidazole ring and the benzene ring of adjacent benzimidazole with centroid-to-centroid distance of 3.530 Å (Cg1 = C39–C40–C41–C42–C43–C44, Cg2 = C38–N11–C39–C40–N12) (see figure 3). The hydrogen-bonding and the π–π stacking interactions play important roles in the stabilization of the final structure.

3.1.2. Crystal structure of 2. The crystal structure of **2** consists of discrete $[Cd(tren)(nic)]^+$ cations and BPh_4^- anions.

As shown in figure 4, the Cd(II) is five-coordinate with an N_4O donor set in a distorted trigonal bipyramidal geometry. The trigonal equatorial plane is formed by three primary nitrogen atoms of tren with bond lengths 2.249(5) Å for Cd(1)–N(2), 2.299(5) Å for Cd(1)–N(3), and 2.297(6) Å for Cd(1)–N(4). The bond angles are from 102.2(2)° [N(2)–Cd(1)–N(3)] to 119.2(2)° [N(2)–Cd(1)–N(4)]. The Cd(II) is displaced from the mean equatorial plane by 0.594 Å toward O(1). The axial ligands N(1) and O(1) have bond lengths 2.462(5) Å for Cd(1)–N(1) and 2.198(5) Å for Cd(1)–O(1). The Cd(1)–O(2) bond length of 2.722 Å is much longer than the Cd(1)–O(1) bond distance. The bond angle N(1)–Cd(1)–O(1) is 154.6(2)°.

In a similar way to that of **1**, tren is tetradentate N-donor and coordinates to Cd(II) through four nitrogen atoms, also displaying a tripod-type coordination behavior. The distance between N(1) and Cd(II) (2.462(5) Å) is longer than the average distance between the other coordinated nitrogen atoms and the central Cd(II) (2.281 Å). This is attributed to the steric requirement of the tripodal tetradentate ligand [38]. Different than **1**, nicotinate coordinates to Cd(II) through only one carboxylate oxygen, similar to a zinc complex of tren [39].

In **2**, neighboring $[Cd(tren)(nic)]^+$ are linked by two N···H–N hydrogen bonds to form a dinuclear unit [3.130(10) Å for N(4)···N(5), 162.1° for N(4)–H(4B)–N(5)]

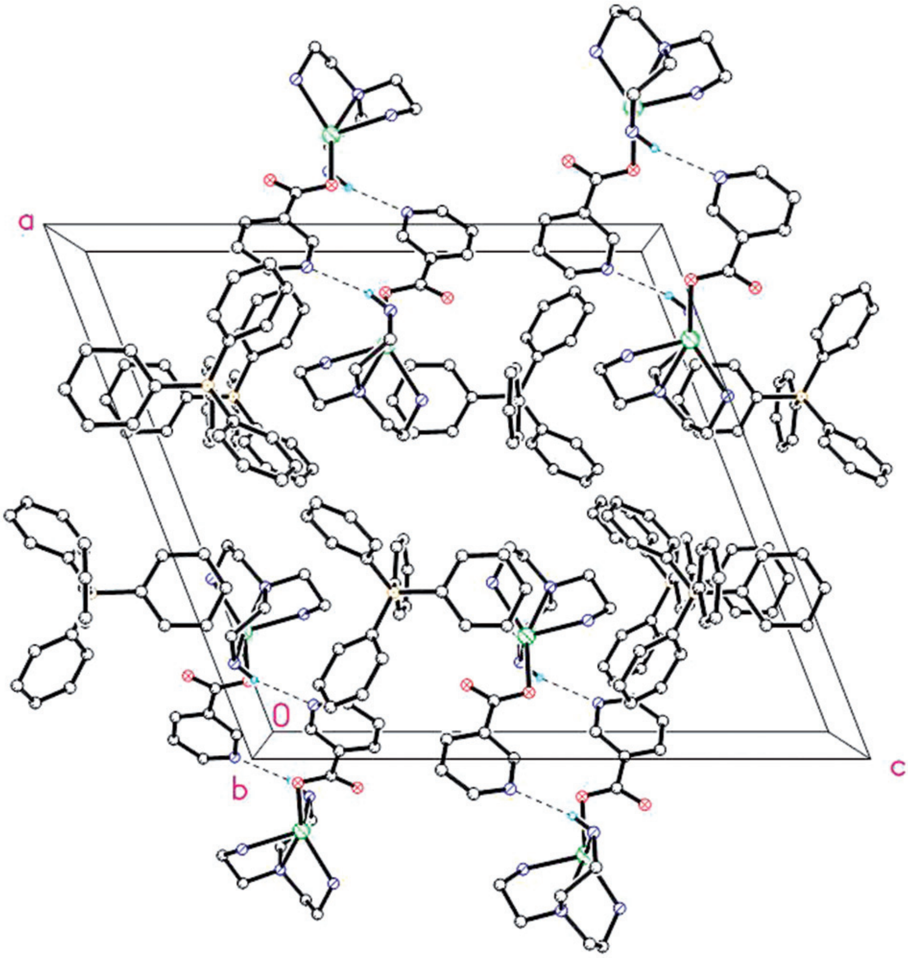


Figure 5. Packing view of **2**.

(also see table 4). The binuclear units are dispersed by BPh_4^- anions to form a 2-D structure (figure 5). Weak interactions such as C–H $\cdots \pi$, N–H $\cdots \pi$, and van der Waals interactions are observed between the cations and BPh_4^- anions [39].

3.2. *IR spectra*

3.2.1. IR spectrum of 1. IR spectrum of **1** exhibits several broad bands in the 2900–3400 cm^{-1} region, which could be assigned to hydrogen-bonded ν(O–H) for methanol and ν(N–H) for the benzimidazole ring of ntb. The bands at 1596 cm^{-1} and 1392 cm^{-1} are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$. There is a strong and fairly broad absorption at 1109 cm^{-1}, which can be assigned to non-coordinated perchlorate. In the free ligand, a strong band is found around 1440 cm^{-1} along with a weak band at 1460 cm^{-1}. By analogy with the assigned band of imidazole, the former is attributed to ν(C=N–C=C), while the latter is ν(C=N) [40, 41]. They shift to higher frequency by around 10 cm^{-1} in **1**, which implies direct coordination of all three imine nitrogen atoms to Cd(II). These are the preferred nitrogen atoms for coordination, as found in other metal complexes with benzimidazoles [42].

3.2.2. IR spectrum of 2. The broad band around 3310 cm^{-1} can be attributed to the N–H stretching frequency, indicating the presence of tren in **2**. Bands at 1595 cm^{-1} and 1396 cm^{-1} in **2** are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$; bands at 1551 cm^{-1}, 1479 cm^{-1} and 1427 cm^{-1} together with the bands at 741 cm^{-1} and 714 cm^{-1} imply the presence of BPh_4^-.

3.3. *^{1}H-NMR studies*

^{1}H-NMR spectra of **ntb**, **tren**, **1,** and **2** were measured in DMSO-d$_6$. Both **ntb** and **1** have a signal at 4.45 ppm which belongs to six equivalent methylene (–CH$_2$–) protons. For **ntb**, a symmetrical set of signals can be observed for the aromatic protons (7.21 ppm and 7.59 ppm, AA′BB′) due to the symmetry of the benzimidazole groups. For **1**, two signals are at 7.24 and 7.53 ppm; a third signal for the aromatic proton next to the coordinated nitrogen shifts to lower field from 7.59 to 8.03 ppm. The proton of the "pyrrole" nitrogen has its signal at 12.43 ppm in the ligand and at 13.28 ppm in the complex which is a large shift to lower field.

Both **tren** and **2** have two triplets at 2.54 and 2.71 ppm, which can be attributed to methylene (–CH$_2$–) of **tren**. Protons of the primary amine (–NH$_2$) have a signal at 1.47 ppm for tren and at 3.29 ppm for **2**, also a large shift to lower field.

The chemical shifts of the four protons of nicotinate are 9.4 ppm, 8.8 ppm, 8.5 ppm, 7.6 ppm for **1** and 9.07 ppm, 8.6 ppm, 8.2 ppm, 7.4 ppm for **2**, attributed to the different coordination modes of nicotinate, bidentate chelation in **1** and monodentate in **2**.

3.4. *Fluorescent properties*

The fluorescence spectra of **1** and **2** were measured in the solid state at room temperature. No fluorescent emission can be observed for **1**, different from already reported cadium complexes of ntb [8, 9]. This might be caused by coordination of the second nicotinate. Complex **2** shows a strong broad emission band around 458 nm upon excitation at 389 nm. The emission band of $NaBPh_4$ is at 397 nm when excited at 335 nm. Comparing to $NaBPh_4$, the emission of **2** originates from the BPh_4^-.

4. Conclusion

In this article, two new nicotinate-containing cadmium(II) complexes [Cd(ntb)(nic)]$ClO_4 \cdot 0.5CH_3OH$ (**1**) and [Cd(tren)(nic)]BPh_4 (**2**) with tripodal tetradentate polybenzimidazole and polyamine ligands were synthesized and structurally characterized. Both complexes are mononuclear with nicotinate coordinated to cadmium(II) in a bidentate u-O,O′ chelating mode in **1** and monodentate O coordination in **2**. Since ntb is a ligand with aromatic side arms and tren with aliphatic side arms, the two complexes form different supramolecular structures with different H-bonds and $\pi \cdots \pi$ stacking features.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 705822 for **1** and CCDC No. 705821 for **2**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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