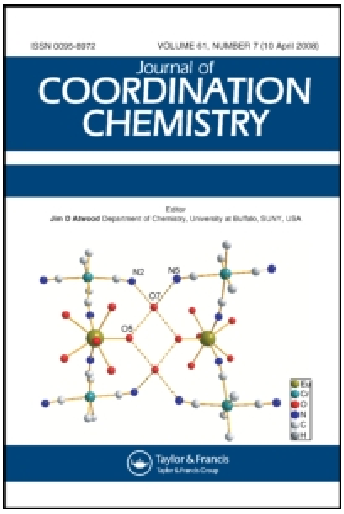

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Cadmium(II) complexes containing 2,2'-dimethyl-4,4'-bithiazole ligand: synthesis, characterization, and crystal structure

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Cadmium(II) complexes containing 2,2′-dimethyl-4,4′-bithiazole ligand: synthesis, characterization, and crystal structure

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Mononuclear and coordination polymer compounds of 2,2′-dimethyl-4,4′-bithiazole (dm4bt) ligand have been prepared by metallation of dm4bt with $Cd(NO_3)_2 \cdot 4H_2O$ and $CdCl_2 \cdot H_2O$. The compounds were characterized by IR, ^{1}H NMR, UV–Vis spectroscopy, and X-ray crystallography. The structural study of $[Cd(dm4bt)_2(NO_3)_2] \cdot H_2O$ (**1**) shows that the complex is a monomeric seven-coordinate (CdN_4O_3) cadmium(II)-bithiazole system with two bidentate dm4bt and mono and bidentate nitrates. The structure of $[Cd(dm4bt)Cl_2]_n$ (**2**) is a distorted octahedral environment around the cadmium(II) (CdN_2Cl_4) forming a 1-D coordination polymer as a result of bridging by two chlorides and 2-D structure from π–π stacking interactions.

Keywords: Cadmium; 2,2′-Dimethyl-4,4′-bithiazole; One-dimensional coordination polymer; π–π stacking; X-ray crystal structure

1. Introduction

Bleomycins (BLMs) are well-known antibiotics related to the glycopeptide family with strong antitumor activity and are currently used clinically in the treatment of skin, head, neck, and testicular cancers [1–3]. The bithiazole moiety is one domain of bleomycin, which was shown to interact with DNA [4, 5]. However, the bithiazole ligands are of interest not only to design biological models of BLM [6, 7] but also for their extensive applications in material [8, 9] and polymer science [10, 11]. Many researchers have designed bithiazole derivatives to tune their coordination ability and biological activity [12–14].

Cadmium and mercury are extremely toxic and known as carcinogens in humans and animals [15]. Although the exact mechanism of cadmium's toxicity is still uncertain, it is suggested to interfere in biological processes of zinc(II) enzymes and its complex with metallothionein remains in kidney, liver, etc. [15]. Thus, competition/comparison

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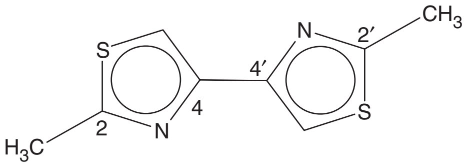

Scheme 1. The structure and numbering scheme of 2,2′-dimethyl-4,4′-bithiazole (dm4bt).

between zinc, cadmium, and mercury in coordination to anticancer moieties such as bithiazole can be useful for synthesis of new drugs. There are only a few reports on coordination of cadmium(II) with 2,2′-diamino-5,5′-dimethyl-4,4′-bithiazole (DADMBTz) [16] and 2,2′-diamino-4,4′-bithiazole [17, 18]. We are interested in designing new bithiazole ligands and examining their coordination chemistry.

We recently introduced the coordination chemistry of 2,2′-dimethyl-4,4′-bithiazole (dm4bt) (scheme 1) with zinc(II) and mercury(II) [19] and report here the synthesis and characterization of two cadmium complexes with dm4bt. One contains the first seven-coordinate Cd(II)-bithiazole system and the other a coordination polymer.

2. Experimental

2.1. *Materials and instruments*

All reagents and solvents were purchased and used directly without purification. UV–Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell. ^{1}H NMR spectra were acquired on a Bruker AC-300 MHz spectrometer at ambient temperature in DMSO-d_6 and $CDCl_3$. Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as a 1% dispersion in KBr or CsI pellets using a Shimadzu-470 spectrometer. Elemental analysis was performed using a Heraeus CHN–O Rapid analyzer. Melting points are uncorrected and were obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus.

Caution: Due to the toxic nature of cadmium-containing compounds when inhaled, precautions should be exercised to reduce both contact and inhalation exposure to cadmium salts [15].

2.2. *Synthesis of dm4bt*

2,2′-Dimethyl-4,4′-bithiazole was prepared by the procedure described previously [20]. One gram (4.10 mmol) of 1,4-dibromo-2,3-butandione and 0.62 g (8.20 mmol) of thioacetamide was dissolved in 20 mL of dry methanol. The reaction mixture was refluxed for 3 h. The resulting solution was added to 20 mL water. Neutralization (pH = 7) with Na_2CO_3 solution produces a bright brown solid which was characterized as dm4bt (yield 0.48 g, 60%, m.p. 171–173°C). ^{1}H NMR δH ($CDCl_3$): 7.61 (s, 1H, Ar) and 2.78 (s, 3H, CH_3). ^{13}C NMR δC ($CDCl_3$): 166.46, 150.08, 114.52 (Ar) and 19.45 (CH_3). IR(KBr, cm^{-1}) selected bands: 879 ($\upsilon_{S–C}$), 1184 ($\upsilon_{C–N}$), 1419 ($\upsilon_{C–C}$), 1496 ($\upsilon_{C=N}$), 1558 ($\upsilon_{C=C}$), 3103 ($\upsilon_{C–H}$, Me), and 3434 ($\upsilon_{C–H}$, cycle). UV–Vis

(CH_3OH): λ_{max}: $3.76 \times 10^4 cm^{-1}$. Anal. Calcd for $C_8H_8N_2S_2$ (%): C, 48.90; H, 4.07; N, 14.26. Found: C, 48.71; H, 3.96; N, 14.12.

2.3. *Synthesis of [Cd(dm4bt)$_2$(NO$_3$)$_2$]•H$_2$O (1)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.047 g, 0.152 mmol) was dissolved in methanol (10 mL), mixed with water (2 mL) and reacted with dm4bt (0.06 g, 0.305 mmol) dissolved in 10 mL methanol. The mixture was stirred at 40–45°C for 2 h and the solvent removed in air. The solid was dissolved in acetonitrile at 40°C. After 2 weeks, by slow evaporation of this solution at room temperature, it was beginning to produce pale yellow crystals of **1** which were suitable for X-ray measurements (yield 0.073 g, 72%, m.p. 240–243°C). ^1H NMR δH (DMSO-d_6): 7.75 (s, 1H, Ar) and 2.69 (s, 3H, CH_3). IR(CsI, cm^{-1}) selected bands: {252, 296, 327, 584, 1010, 1028, 1290, 1372, 1440 (br)}(υ_{new}), 890 ($\upsilon_{S–C}$), 1210 ($\upsilon_{C–N}$), 1440 ($\upsilon_{C–C}$), 1519 ($\upsilon_{C=N}$), 1639 ($\upsilon_{C=C}$), 3089 ($\upsilon_{C–H}$, Me), 3477 ($\upsilon_{C–H}$, cycle). UV–Vis (DMSO): λ_{max}: $3.73 \times 10^4 cm^{-1}$. Anal. Calcd for $C_{16}H_{18}Cd_1N_6O_7S_4$ (%): C, 29.67; H, 2.78; N, 12.98. Found: C, 29.54; H, 2.69; N, 12.81.

2.4. *Synthesis of [Cd(dm4bt)Cl$_2$]$_n$ (2)*

$CdCl_2 \cdot H_2O$ (0.071 g, 0.35 mmol) and dm4bt (0.07 g, 0.35 mmol) were dissolved in methanol (10 mL) separately and added together without stirring. A colorless precipitate formed immediately was filtered off. Suitable crystals of **2** were obtained by slow evaporation of a mixed solvent system (DMSO/CH_3OH, 1 : 2) at room temperature (yield 0.038 g, 66%, m.p. > 300°C). ^1H NMR δH (DMSO-d_6): 7.79 (s, 1H, Ar) and 2.71 (s, 3H, CH_3). IR(CsI, cm^{-1}) selected bands: 579 (υ_{new}), 895 ($\upsilon_{S–C}$), 1212 ($\upsilon_{C–N}$), 1437 ($\upsilon_{C–C}$), 1515 ($\upsilon_{C=N}$), 1584 ($\upsilon_{C=C}$), 3106 ($\upsilon_{C–H}$, Me), 3453 ($\upsilon_{C–H}$, cycle). UV–Vis (DMSO): λ_{max}: $3.74 \times 10^4 cm^{-1}$. Anal. Calcd for $C_8H_8Cd_1Cl_2N_2S_2$ (%): C, 25.29; H, 2.11; N, 7.37. Found: C, 25.17; H, 2.02; N, 7.23.

2.5. *Crystal structure determination and refinement*

The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. For $[Cd(dm4bt)_2(NO_3)_2] \cdot H_2O$ (**1**) pale yellow block shape and $[Cd(dm4bt)Cl_2]_n$ (**2**) colorless needle shape crystals were chosen under a polarizing microscope, mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data for **1** and **2**. Data were collected at a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [21] software package. A numerical absorption correction was applied using X-RED [22] and X-SHAPE [23] software. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods [24] and subsequent difference Fourier maps and then refined on F^2 by full-matrix least-squares using anisotropic displacement parameters [25]. All hydrogen atoms were located in a difference Fourier map and then refined isotropically. Subsequent refinement converged with R factors and parameter errors significantly better than for all attempts to model the solvent disorder.

Atomic factors are from International Tables for X-ray crystallography [26]. All refinements were performed using the X-STEP32 crystallographic software package [27]. A summary of crystal data, experimental details, and refinement results is given in table 1.

3. Results and discussion

3.1. *Preparation of 1 and 2*

We previously reported the synthesis and crystal structure of dm4bt and also its zinc and mercury complexes [19]. The synthesis of **1** and **2** were achieved by addition of 2 and 1 molar ratio of dm4bt to methanolic solution of $Cd(NO_3)_2 \cdot 4H_2O$ and $CdCl_2 \cdot H_2O$, respectively, equations (1) and (2). Compound **2** formed without stirring or heating and its melting point was high due to polymer formation. The reaction yields were relatively high and resulting compounds are insoluble in common organic solvents except in DMSO. To the best of our knowledge, all previously reported compounds

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

	1	**2**
Empirical formula	$2(C_{16}H_{18}Cd_1N_6O_7S_4)^a$	$C_8H_8Cd_1Cl_2N_2S_2$
Formula weight	1294.1	379.61
Temperature (K)	298(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size (mm^3)	$0.50 \times 0.50 \times 0.30$	$0.45 \times 0.11 \times 0.04$
Unit cell dimensions (Å, °)		
a	8.614(2)	6.976(2)
b	16.448(4)	9.232(3)
c	17.096(4)	10.371(3)
α	89.139(18)	111.72(2)
β	87.574(18)	104.30(2)
γ	89.015(18)	93.45(2)
V (Å^3)	2419(9)	592.7(3)
Z	4	2
D_{Calcd} ($g\,cm^{-1}$)	1.776	2.127
θ Ranges for data collection (°)	1.71–28.21	2.54–27.91
$F(000)$	1296	368
Absorption coefficient (mm^{-1})	1.298	2.610
Index ranges	$-811 \le h \le 11$	$-9 \le h \le 9$
	$-21 \le k \le 21$	$-12 \le k \le 12$
	$-22 \le l \le 21$	$-13 \le l \le 13$
Data collected	17755	6209
Unique data, (R_{int})	10507, (0.0537)	2790, (0.0268)
Parameters/restraints	637/0	136/0
Final $R_1/wR_2{}^b$ (obsd data)	0.0503/0.1505	0.0185/0.0473
Final $R_1/wR_2{}^b$ (all data)	0.0560/0.1595	0.0196/0.0479
Goodness-of-fit on F^2 (S)	1.076	1.106
Largest difference peak and hole (e Å^{-3})	1.215, −1.362	0.469, −0.626

Notes: $^aZ' = 2$.
$^bR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o2-F_c2)2)/\Sigma w(F_o2)2]^{1/2}$.

(cadmium/bithiazole system) contain six-coordinate metal centers [16–18] and only one coordination polymer [28]. We tried to use two equivalents of dm4bt similar to the formation of **1**, but as dm4bt is mixed with solution of cadmium chloride **2** is formed and precipitates at once. Therefore, in solution the limiting reagent is always dm4bt and the smaller chloride could not be displaced.

$$\mathrm{Cd(NO_3)_2 \cdot 4H_2O + 2dm4bt} \underset{40-45^{\circ}\mathrm{C}}{\overset{\mathrm{CH_3OH}}{\longrightarrow}} \left[\mathrm{Cd(dm4bt)_2(NO_3)_2}\right] \cdot \mathrm{H_2O}\ (\mathbf{1}) \tag{1}$$

$$\mathrm{CdCl_2 \cdot H_2O + dm4bt} \underset{\mathrm{r.t}}{\overset{\mathrm{CH_3OH}}{\longrightarrow}} [\mathrm{Cd(dm4bt)Cl_2}]_n\ (\mathbf{2}) \tag{2}$$

3.2. *Spectroscopic characterization*

3.2.1. UV–Vis spectra. Electronic absorption spectra of **1** and **2** were taken in DMSO. A signal was observed for ligand and complexes in the near-UV region ($\sim 3.7 \times 10^4\,\mathrm{cm^{-1}}$) which can be assigned to the ligand-centered π–π^* transitions of bithiazole. Although no significant change in wavelength was observed, it shows the presence of an aromatic ligand in these complexes.

3.2.2. NMR investigation. NMR investigation has importance for study of interaction between bithiazole moiety of BLM with DNA, especially in the absence of structural data [29, 30]. The spectrum of free dm4bt shows a singlet for methyl group at 2.78 ppm and another signal in the aromatic region at 7.61 ppm for C–H similar to different methyl substituted bithiazoles [31]. The spectral patterns of the complexes are almost the same as the free ligand with small change in chemical shifts. In comparison with free dm4bt, an upfield shift for methyl and downfield shift for aromatic proton were observed in **1** and **2**. We encountered the same spectral changes for [Zn(dm4bt)$\mathrm{Cl_2}$] and [Hg(dm4bt)$\mathrm{Cl_2}$] [19] as well for Cu(I) and Ag(I) complexes with bithiazole ligands [32]. For **2**, it is reasonable to think that the polymeric structure does not hold in DMSO and we see spectrum of the monomer.

3.2.3. IR spectroscopy. Infrared spectra for dm4bt and complexes, presented in table 2, show several bands in the range 3400–800 $\mathrm{cm^{-1}}$ corresponding to skeletal vibrations of the aromatic heterocycle [33]. These bands, related to vibrational mode of C–H, C=C, C=N, C–C, C–N, and S–C were observed at higher frequencies in **1** and **2** (table 2). The same trend was observed previously for dm4bt [19] and bipyridine [34] in coordination to metal centers and can be due to conformation change from anti in free ligands to syn in complexes. As shown by X-ray diffraction of **1**, we have two different nitrate groups. One is monodentate and the other is chelating bidentate; each nitrate should have three different vibrational frequencies [35]. These frequencies are related to monodentate [$\upsilon_{\mathrm{a(NO2)}}$, $\upsilon_{\mathrm{s(NO2)}}$, and $\upsilon_{\mathrm{(NO)}}$] and chelating bidentate [$\upsilon_{\mathrm{(N=O)}}$, $\upsilon_{\mathrm{a(NO2)}}$, and $\upsilon_{\mathrm{s(NO2)}}$] (table 2). Compound **1** also shows one and two vibration frequencies for mono and bidentate Cd–$\mathrm{O_{nitrate}}$, respectively, in the range 250–350 $\mathrm{cm^{-1}}$ (table 2) [35]. In addition, these complexes show $\upsilon_{\mathrm{(Cd–N\,thiazole)}}$ at 584 and 579 $\mathrm{cm^{-1}}$ for **1** and **2**,

Table 2. Selected IR[a] frequencies of dm4bt[b] and **1**[c] and **2**[c].

		dm4bt	**1**	**2**
	υ(C–H) cycle	3434	3477	3453
	υ(C–H)Me	3103	3089	3106
	υ(C=C)	1558	1639	1584
	$\upsilon(C_2{=}N)$	1496	1519	1515
	$\upsilon(C_4{-}C_5)$	1419	1440[d]	1437
	$\upsilon(C_4{-}N)$	1184	1210	1212
	υ(S–C)	879	890	895
	υ(Cd–N)	–	584	579
$\upsilon(NO_3)$ Monodentate	$\upsilon a(NO_2)$	–	1440[d]	–
	$\upsilon s(NO_2)$	–	1372	–
	υ(NO)	–	1010	–
$\upsilon(NO_3)$ Bidentate	$\upsilon a(NO_2)$	–	1290	–
	υ(N=O)	–	1440[d]	–
	$\upsilon s(NO_2)$	–	1028	–
	υ(Cd–O)	–	252, 296, 327	–

Notes: [a]In cm^{-1}.
[b]In KBr pellets.
[c]In CsI pellets.
[d]Broad peak.

respectively [16]. As described in the literature, $\upsilon_{(Cd-Cl\,bridge)}$ must appear below 200 cm^{-1} and therefore was not observed [35, 36].

3.3. *Description of the molecular structures of 1 and 2*

Pale yellow block crystals of **1** were obtained by recrystallization of **1** in acetonitrile over 2 weeks. For **2**, colorless needle crystals were grown by slow evaporation of a mixed solvent system (DMSO : CH_3OH, 1 : 2). Crystallographic data and parameters for **1** and **2** are summarized in table 1. The compounds crystallize in the same crystal system and space group (triclinic space group of $P\bar{1}$). Selected bond lengths (Å) and angles (°) with their standard deviations for **1** and **2** are given in tables 3 and 4, respectively.

3.3.1. Structure of $[Cd(dm4bt)_2(NO_3)_2] \cdot H_2O$ (1). The structure of **1** consists of two crystallographically different Cd(II) species in the asymmetric unit, both with similar seven-coordinate cadmium centers coordinated with two bidentate dm4bt, one bidentate, and one monodentate nitrate. An ORTEP of the Cd(II) centers in the asymmetric unit is presented in figure 1(a). A recent publication discusses deviations of Cd coordination polyhedra from octahedral in detail [37]. The coordination polyhedron about cadmium is a distorted pentagonal-bipyramid. One nitrogen from each dm4bt is located in the axial positions and two remaining nitrogens from dm4bt in addition to three oxygens of nitrate occupy the equatorial plane. A perspective view of the Cd(II) environment is shown in figure 1(b). Although, there are several reports on six, seven, and eight-coordinate compounds of cadmium, to the best of our knowledge, all bithiazole-containing compounds are six-coordinate [16–18]; **1** is the first example with seven coordination. The average $Cd{-}N_{thiazole}$ distances are 2.374 and 2.379 Å for Cd1 and Cd2, respectively, similar to the distance found for cadmium/bithiazole systems [9]. These values are between the mean range observed for $[Zn(dm4bt)Cl_2]$ (2.069 Å) and

Table 3. Selected bond lengths (Å) and angles[a] (°) for **1**.

Cd1–N1	2.363(4)	N1–Cd1–N2	71.67(13)
Cd1–N2	2.370(3)	N1–Cd1–N3	82.61(12)
Cd1–N3	2.399(3)	N1–Cd1–N4	109.08(12)
Cd1–N4	2.366(3)	N2–Cd1–N3	110.66(12)
Cd2–N7	2.373(3)	N2–Cd1–O1	96.2(2)
Cd2–N8	2.377(3)	N2–Cd1–O2	105.6(3)
Cd2–N9	2.379(4)	N3–Cd1–O1	71.5(2)
Cd2–N10	2.369(3)	N4–Cd1–N2	176.63(12)
Cd1–O1	2.494(10)	N4–Cd1–N3	72.70(12)
Cd1–O2	2.598(12)	N4–Cd1–O1	84.9(2)
Cd1–O4	2.332(4)	N4–Cd1–O2	73.2(3)
Cd2–O8	2.567(10)	O1–Cd1–O2	42.4(2)
Cd2–O9	2.635(12)	O4–Cd1–O2	91.8(3)
Cd2–O11	2.310(5)	O4–Cd1–N1	79.38(19)
C1–C2	1.500(6)	O4–Cd1–N2	83.98(15)
C2–S1	1.728(4)	O4–Cd1–N3	151.78(16)
C2–N1	1.292(6)	O4–Cd1–N4	92.91(16)
C3–S1	1.698(5)	N7–Cd2–N8	73.27(12)
C3–C4	1.359(6)	N7–Cd2–N9	82.21(12)
C4–N1	1.391(5)	N8–Cd2–N9	112.48(12)
C4–C5	1.449(6)	N8–Cd2–O8	96.1(2)
N5–O1	1.154(8)	N8–Cd2–O9	104.9(3)
N5–O2	1.135(9)	N9–Cd2–O8	72.5(2)
N5–O3	1.152(7)	N10–Cd2–N7	107.49(12)
N6–O4	1.226(6)	N10–Cd2–N8	176.50(13)
N6–O5	1.156(8)	N10–Cd2–N9	71.01(12)
N6–O6	1.224(7)	N10–Cd2–O8	85.1(2)
		N10–Cd2–O9	73.9(3)
Dihedral angles (°)		O8–Cd2–O9	40.7(2)
N1–C4–C5–N2	12.9(5)	O11–Cd2–N7	78.48(19)
N3–C12–C13–N4	14.1(6)	O11–Cd2–N8	82.90(16)
N7–C20–C21–N8	13.3(6)	O11–Cd2–N9	93.7(3)
N9–C28–C29–N10	13.5(5)	O11–Cd2–N10	93.88(10)

Note: [a]Estimated standard deviations are in parentheses.

Table 4. Selected bond lengths (Å) and angles[a] (°) for **2**.

Cd1–N1	2.3507(17)	N1–Cd1–N2	71.62(5)
Cd1–N2	2.4444(16)	N1–Cd1–Cl1	102.87(4)
Cd1–Cl1	2.6274(8)	N1–Cd1–Cl2	158.55(4)
Cd1–Cl2	2.5658(9)	N1–Cd1–Cl1#1	94.47(5)
Cd1–Cl1#1	2.6452(10)	N1–Cd1–Cl2#2	82.75(5)
Cd1–Cl2#2	2.7167(11)	N2–Cd1–Cl1	167.18(4)
Cl1–Cd1#1	2.6452(10)	N2–Cd1–Cl2	93.99(4)
N1–C2	1.309(2)	N2–Cd1–Cl1#1	84.94(4)
N1–C4	1.387(2)	N2–Cd1–Cl2#2	99.56(4)
N2–C7	1.314(2)	Cl2–Cd1–Cl1	94.26(3)
N2–C5	1.385(2)	Cl2–Cd1–Cl1#1	100.13(3)
Cd1–Cd1#2	3.929(10)	Cl1–Cd1–Cl1#1	83.97(3)
Cl1–Cl1#1	3.527(10)	Cl2–Cd1–Cl2#2	84.16(3)
Cl2–Cl2#2	3.543(9)	Cl1–Cd1–Cl2#2	91.02(3)
Dihedral angles (°)		Cl1#1–Cd1–Cl2#2	173.605(14)
N1–C4–C5–N2	4.9(2)	Cd1–Cl1–Cd1#1	96.03(3)
C3–C4–C5–C6	6.3(3)	Cd1–Cl2–Cd1#2	95.84(3)

Notes: [a]Estimated standard deviations are in parentheses; #1 : $2 - x, -y, 1 - z$; #2: $1 - x, -y, 1 - z$.

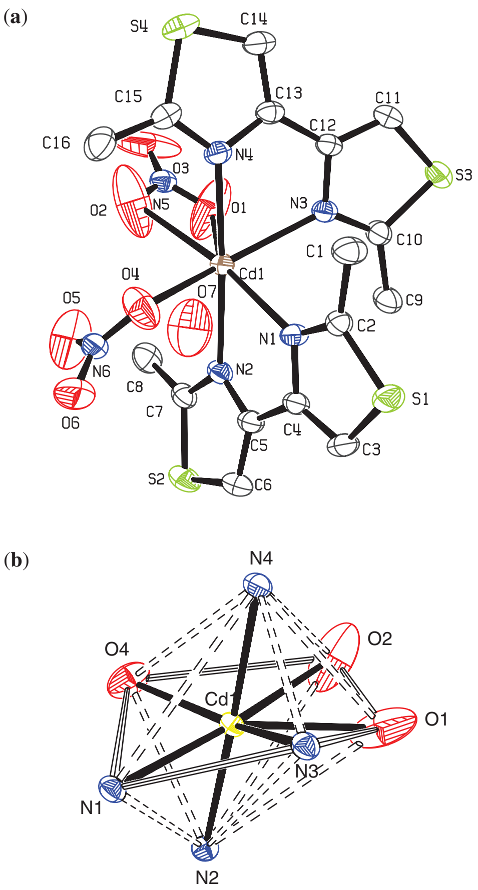

Figure 1. The labeled diagram of (a) structure of **1** (thermal ellipsoids are at 30% probability level) and (b) view of the coordination polyhedron in **1**.

[Hg(dm4bt)Cl_2] (2.397 Å) [19]. The bond lengths and angles for bithiazole moieties are in the normal ranges [19] and the thiazole rings are almost coplanar with dihedral angle between two planes around 12.9–14.1°. This angle in dm4bt was 0° with anti conformation for two thiazole rings [19]. So, the deformation from anti to syn and deviation from planarity provide better coordination to Cd(II) as a bidentate ligand. This dihedral angle was 41.3° in six-coordinate [Cd$(DADMBTz)_3$]$(ClO_4)_2$ [16].

Compound **1** has two nitrate ligands, bonded differently to Cd(II). The bond length in monodentate is smaller than bidentate; bidentate nitrates have two different Cd–O distances [38, 39]. Although, monodentate nitrate in **1** has two free oxygens, there are several reports which show polymer formation via monodentate nitrate [39], so the monomer structure in **1** may result from steric hindrance of methyl groups in dm4bt.

As can be seen from the packing diagram of **1** (figure 2), there is hydrogen bonding in the crystal lattice (table 5) that stabilizes the crystal packing. For this compound the *R* value is slightly high due to disorder of nitrate and water. We tried refining these atoms in two positions with reduced occupancy, but while this model converged satisfactorily,

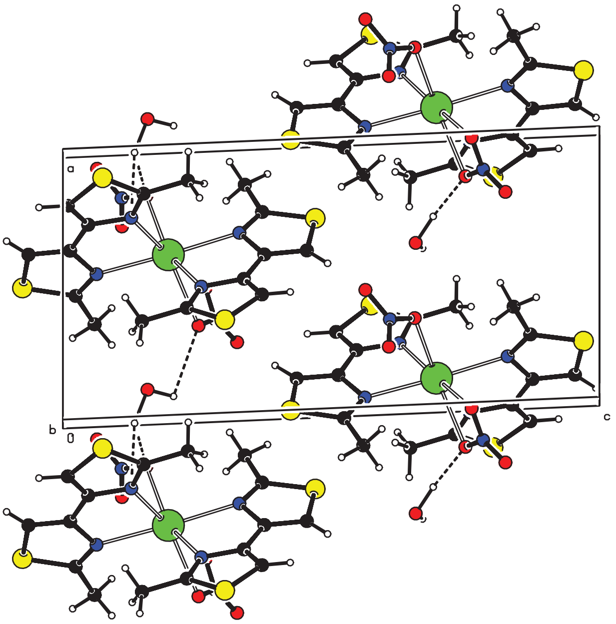

Figure 2. Crystal packing diagram for **1** in the *b* direction showing hydrogen bonding.

Table 5. Hydrogen bonding (Å, °) for **1**.

D–H···A	D–H	H···A	D···A	∠DHA	Equivalent positions
O(7)–H(7B)···O(1)	1.03(11)	1.91(12)	2.905(12)	160(10)	$-1+x, y, z$
O(14)–H(14B)···O(11)	0.87(7)	2.37(7)	2.901(9)	119(4)	$-1+x, y, z$
O(14)–H(14C) ···O(8)	0.91(5)	2.53(5)	2.856(12)	102(3)	–

there was no decrease in R, and therefore we consider that our original refinement is the best.

3.3.2. Structure of [Cd(dm4bt)Cl$_2$]$_n$ (2). Janiak has reviewed development in the field of coordination polymers [40]. X-ray study of **2** reveals that it forms a 1-D-zigzag-chain coordination polymer. The coordination environment around each Cd(II) is distorted octahedral [37], consisting of one bidentate dm4bt and four chlorides as bridging ligands. Figure 3 illustrates the basic building block of **2**. Many coordination polymers have been reported from cadmium and bridging ligands, such as chloride [36, 41, 42], bromide [36, 41, 42], nitrate [43], thiocyanate [44], azide [45], carboxylate [46], and dicyanamide [47]. Because of similarity to polythiophen, polymeric structures containing bithiazole moiety are of interest and there are several examples of coordination polymers with Mn [48] and Pb [49]. Polymeric structures of Cd(II) complexes with bithiazole ligands are not well documented and only one report exists [28].

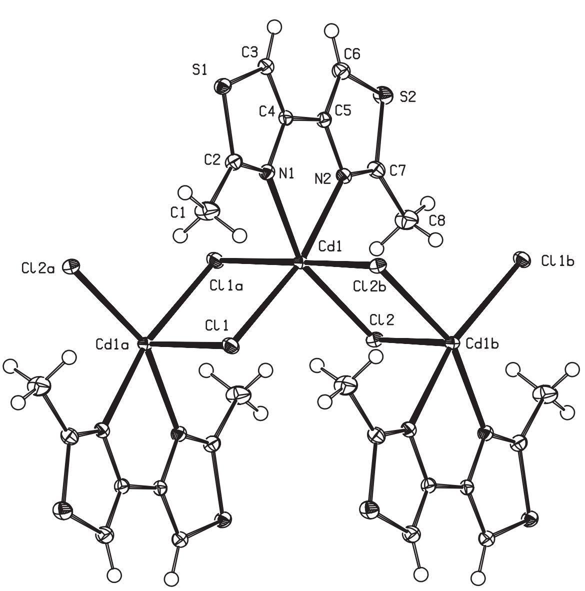

Figure 3. The basic building block of [Cd(dm4bt)Cl_2]*n* (**2**). Thermal ellipsoids are at 30% probability level. Symmetry code: a: 2−X, −Y, 1−Z, b: 1−X, −Y, 1−Z.

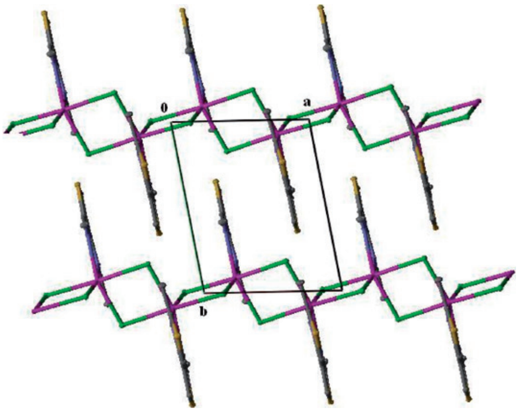

Figure 4. Crystal packing diagram for **2** in the *c* direction. The 2-D structure formed due to π–π interaction between dm4bt ligands.

The crystal structure of **2** shows a 1-D chain (figure 4) extended along *a*. The thiazole rings in **2** are almost planar with a dihedral angle about 4.9(9)°. The average Cd–$N_{bithiazole}$ distance is 2.39(4) Å, similar to a six-coordinate cadmium(II) bithiazole complex [16]. There is a distance of 3.922(6) Å between two cadmium centers in the 1-D chain. Aromatic π–π stacking interactions between two dm4bt ligands in adjacent chains with inter-centroid distances of 3.532(2) and 3.649(3) Å, in accord with a previous report [50], leads to a supramolecular 2-D polymer, as illustrated in figure 4.

Supplementary material

CCDC 665844 and 665845 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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