

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Structural and solution studies of new cadmium(II) complexes with 2,2'-diamino-4,4'-bithiazole

Mohammad Kazem Rofouei^a; Mahmood Payehghadr^b; Ali Morsali^c; Zohreh Rashidi Ranjbar^c; Mojtaba Shamsipur^d

^a Faculty of Chemistry, Tarbiat Moalem University, Iran, Tehran ^b Department of Chemistry, Payame Noor University, Karaj, Iran ^c Department of Chemistry, Tabiat Modares University, Tehran, Iran ^d Department of Chemistry, Razi University, Kermanshah, Iran

Online publication date: 07 April 2010

To cite this Article Kazem Rofouei, Mohammad , Payehghadr, Mahmood , Morsali, Ali , Rashidi Ranjbar, Zohreh and Shamsipur, Mojtaba(2010) 'Structural and solution studies of new cadmium(II) complexes with 2,2'-diamino-4,4'-bithiazole', *Journal of Coordination Chemistry*, 63: 6, 1052 – 1062

To link to this Article: DOI: 10.1080/00958971003698499

URL: <http://dx.doi.org/10.1080/00958971003698499>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Structural and solution studies of new cadmium(II) complexes with 2,2'-diamino-4,4'-bithiazole

MOHAMMAD KAZEM ROFOUEI†,
MAHMOOD PAYEHGHADR‡, ALI MORSALI*§,
ZOHREH RASHIDI RANJBAR§ and MOJTABA SHAMSIPUR¶

†Faculty of Chemistry, Tarbiat Moalem University, Iran, Tehran

‡Department of Chemistry, Payame Noor University, Karaj, Iran

§Department of Chemistry, Tabiat Modares University, Tehran, Iran

¶Department of Chemistry, Razi University, Kermanshah, Iran

(Received 25 June 2009; in final form 10 November 2009)

Two new Cd(II) complexes, [Cd(DABT)(CH₃COO)₂] (**1**) and [Cd(DABT)(NO₃)₂] (**2**), DABT = 2,2'-diamino-4,4'-bithiazole, have been synthesized and characterized by single crystal X-ray crystallography. In **1**, each cadmium is chelated by two nitrogens of one DABT and four oxygens of acetate, whereas **2** is a dinuclear complex and there are two Cd's with eight and six coordination: Cd₁O₆N₂ and Cd₂O₄N₂ units. The counter ion effect of the complex formation reaction between cadmium(II) nitrate and acetate with DABT has been studied by spectroscopy. The formation constants of the 1:1 and 1:2 (metal ion to ligand) complexes were evaluated by computer fitting of the absorbance–mole ratio data.

Keywords: Formation constants; 2,2'-Diamino-4,4'-bithiazole; X-ray crystal structure

1. Introduction

The first 2,2'-bithiazoles and 4,4'-bithiazoles were synthesized by Erlenmeyer and Ueberwasser [1, 2]; other bithiazole derivatives have been synthesized by Erlenmeyer and coworkers [3]. Bithiazole derivatives have been used for the synthesis of magnetic polymers [4, 5], electroluminescence equipment such as optical diodes [6] and medical sciences [7, 8]. Bleomycins (BLM) are antitumor agents [9], and the effect of bithiazoles for binding of BLM to DNA has caused the design and synthesis of different compounds of these ligands. The 1:1 and 1:2 (metal ion to ligand) complexes of Zn²⁺, Cd²⁺ with 4,4'-bithiazole derivatives [10] and Hg²⁺ [11] have been reported. Incorporation of bithiazole groups with amine groups in 2,2'-diamino-4,4'-bithiazole for the preparation of complexes allows both the electronic and steric control of the

*Corresponding author. Email: morsali_a@modares.ac.ir

properties of metal complexes. A five-membered heterocycle like bithiazole and a group like $-\text{NH}_2$ in a single system cause electronic communication between these two heterocycles to be avoided.

The complexation of transition metal complexes with multidentate noncyclic and macrocyclic ligands in nonaqueous and mixed solvents has been reported [12]. As the nature of the solvent may strongly influence the stoichiometry of transition metal complexes in solution, we pursued spectrophotometric studies of the stoichiometry of complexation between DABT (figure 1) and cadmium(II) acetate, as well as cadmium(II) nitrate in acetonitrile (AN). This ligand formed ML and ML_2 complexes with acetate and nitrate salts, respectively. In this regard, the crystal structures of $[\text{Cd}(\text{DABT})(\text{CH}_3\text{COO})_2]$ (**1**) and $[\text{Cd}(\text{DABT})(\text{NO}_3)_2]$ (**2**) are reported.

2. Experimental

2.1. Physical measurements

The IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. The melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

2.2. Preparation of 2,2'-diamino-4,4'-bithiazole (DABT)

The 2,2'-diamino-4,4'-bithiazole (DABT) ligand was prepared from 1,4-dibromobutane-2,3-dione and thiourea by the method of Erlenmeyer and Ueberwasser [1].

2.3. Preparation of $[\text{Cd}(\text{DABT})(\text{CH}_3\text{COO})_2]$ (**1**)

The complex was prepared by dissolving cadmium(II) acetate (0.230 g, 1 mmol) in distilled water (10 mL) and adding an ethanolic solution of DABT (0.198 g, 1 mmol). The resulting solution was stirred for 2 h at room temperature and allowed to stand for 10 days at room temperature (*ca* 25°C). White crystals precipitated were filtered off, washed with acetone and ether, and dried in air (m.p. 220°C). Elemental Anal. $\text{C}_{10}\text{H}_{12}\text{CdN}_4\text{O}_4\text{S}_2$ (%): calculated C: 27.98; H: 2.79; N: 13.06. Found: C: 27.75; H: 2.60;

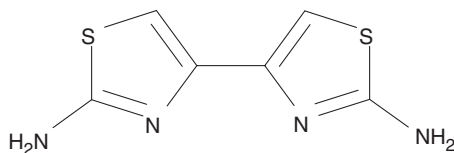


Figure 1. 2,2'-Diamino-4,4'-bithiazole (DABT).

N: 13.50. IR (KBr) selected bonds: $\nu = 710(\text{m}), 974(\text{w}), 1415(\text{vs}), 1560(\text{vs}), 1600(\text{vs}), 2030(\text{s}), 2965(\text{w}), 3080(\text{w}), 3180(\text{br}),$ and $3205(\text{br})\text{cm}^{-1}$.

2.4. Preparation of $[\text{Cd}(\text{DABT})(\text{NO}_3)_2]$ (**2**)

Complex **2** was prepared similarly to **1**. Reactant materials such as DABT and cadmium(II) nitrate (with 2:1 ratio) were used and white crystals (m.p. 215°C) were produced. Elemental Anal. $\text{C}_{12}\text{H}_{12}\text{Cd}_2\text{N}_{12}\text{O}_{12}\text{S}_4$ (%): calculated C: 16.56; H: 1.38; N: 19.32. Found: C: 16.70; H: 1.20; N: 19.50. IR (KBr) selected bonds: $\nu = 713(\text{m}), 973(\text{w}), 1380(\text{vs}), 1415(\text{vs}), 1564(\text{s}), 1605(\text{s}), 2032(\text{s}), 2963(\text{w}), 3082(\text{w}), 3180(\text{br}),$ and $3205(\text{br})\text{cm}^{-1}$.

2.5. X-ray structure determination

Crystallographic measurements were made at $120(2)^\circ\text{C}$ using a Bruker Smart 1000 CCD area detector for **1** and at $100(2)^\circ\text{C}$ using a Bruker SMART APEX2 CCD area detector for **2**. The intensity data were collected using graphite monochromated Mo- $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . Structure solution and refinement was accomplished using SHELXL98 and WinGX [13, 14]. The details of data collection, refinement and crystal data are summarized in table 1.

2.6. Spectrophotometric studies

Reagent grade cadmium(II) nitrate, acetate, and AN from Merck and recently synthesized DABT were of highest purity available and used without purification.

All UV-Vis spectra were recorded on a computerized double-beam Shimadzu 2550 spectrophotometer using two matched 10 mm quartz cells. Absorption measurements were carried out with a single-beam Philips PU8750 spectrophotometer equipped with a Philips cell temperature controller. In a typical experiment, 2.0 mL of ligand solution (5.0×10^{-5} mol) in AN was placed in the spectrophotometer cell and the absorbance of solution was measured. Then, a known amount of concentrated solution of metal ion in AN (1.3×10^{-3} mol) was added in a stepwise manner using a 10 μL Hamilton syringe. The absorbance of the solution was measured after each addition. The metal ion solution was continually added until the desired metal-to-ligand mole ratio was achieved.

The formation constant (K_f) and the molar absorptivity (ϵ) of the resulting 1:2 (metal ion to ligand) complex of cadmium(II) nitrate, as well as 1:1 complex of cadmium(II) acetate with DABT at various temperatures were calculated by fitting the observed absorbance, A_{obs} , at various metal ion/DABT mole ratios to the previously derived equations (equations 1 and 2 for ML and ML_2 , respectively), which express the A_{obs} as a function of the free and complexed metal ions and the formation constant evaluated from a nonlinear least-squares program KINFIT.

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

Identification code	1	2
Empirical formula	C ₁₀ H ₁₂ CdN ₄ O ₄ S ₂	C ₁₂ H ₁₂ Cd ₂ N ₁₂ O ₁₂ S ₄
Formula weight	428.76	869.38
Temperature (K)	120(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>I</i> 2/a	<i>P</i> n
Unit cell dimensions (Å)		
<i>a</i>	13.054(4)	10.2768(6)
<i>b</i>	17.243(3)	7.1844(4)
<i>c</i>	13.270	16.9426(9)
β	104.725(6)°	91.586(5)°
Volume (Å ³), <i>Z</i>	2888.9(12), 8	1250.44(12), 2
Calculated density (g cm ⁻³)	1.972	2.309
Absorption coefficient (Mo-K α) (mm ⁻¹)	1.821	2.121
<i>F</i> (000)	1696	848
Crystal size (mm ³)	0.05 × 0.05 × 0.05	0.32 × 0.20 × 0.14
θ range for data collection (°)	1.98–30.06°	2.20–28.20°
Limiting indices	–18 ≤ <i>h</i> ≤ 18; –24 ≤ <i>k</i> ≤ 24; –18 ≤ <i>l</i> ≤ 18	–14 ≤ <i>h</i> ≤ 13; –9 ≤ <i>k</i> ≤ 9; –20 ≤ <i>l</i> ≤ 9
Reflections collected	16,415	8554
Independent reflection	4204 [<i>R</i> (int) = 0.0331]	5638 [<i>R</i> (int) = 0.0215]
Independent reflections with [<i>I</i> > 2 σ (<i>I</i>)]	3229	5459
Completeness to θ (%)	98.8	99.3
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4204/0/198	5638/2/380
Goodness-of-fit on <i>F</i> ²	0.988	1.052
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	Indices for 3229 reflections	Indices for 5459 reflections
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0267, <i>wR</i> ₂ = 0.0563	<i>R</i> ₁ = 0.0735, <i>wR</i> ₂ = 0.2173
Largest difference peak and hole (e Å ⁻³)	<i>R</i> ₁ = 0.0341, <i>wR</i> ₂ = 0.0573 1.362 and –0.6	<i>R</i> ₁ = 0.0591, <i>wR</i> ₂ = 0.1944 0.716 and –0.592

3. Results and discussion

3.1. Preparation of complexes and crystal structure

Reaction between DABT and cadmium(II) acetate/nitrate provided crystalline materials [Cd(DABT)(CH₃COO)₂] (**1**) and [Cd(DABT)(NO₃)₂] (**2**). The IR spectra exhibit absorption bands resulting from skeletal vibrations of aromatic rings in the 1400–1615 cm⁻¹ range. Relatively weak bands around 2963 and 3082 cm⁻¹ are assigned to the ν (CH₃) of the acetate group in **1** and ν (CH) of the aromatic rings in **1** and **2**. Broad absorptions at 3180 and 3205 cm⁻¹ are assigned to ν (–NH₂). The broad band is attributable to ν (N–H ··· X), indicating the presence of hydrogen bonds, which has been confirmed by the crystal structure determination of this complex. The characteristic bands of the carboxylate in **1** appear around 1560 for $\nu_{\text{as}}(\text{C–O})$ and 1415 for $\nu_{\text{sym}}(\text{C–O})$. The $\Delta\nu$ value ($\nu_{\text{as}} - \nu_{\text{sym}}$) of 145 cm⁻¹, indicating bidentate carboxylate [15–19], was confirmed by the crystal structure. IR active band for $\nu(\text{NO}_3^-)$ in **2** appeared at 1380 cm⁻¹ [20].

The ORTEP diagram and unit cells of **1** and **2** are given in figures 2–5. The selected bond distances and angles around Cd(II) in **1** and **2** are shown in tables 2 and 3. Each cadmium in **1** is octahedrally chelated by two nitrogens of one DABT and four oxygens

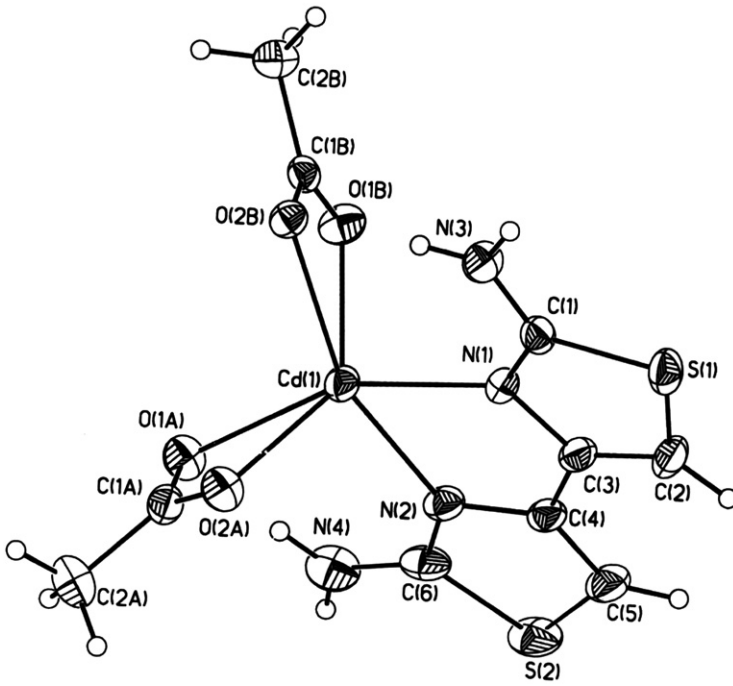


Figure 2. ORTEP diagram of 1.

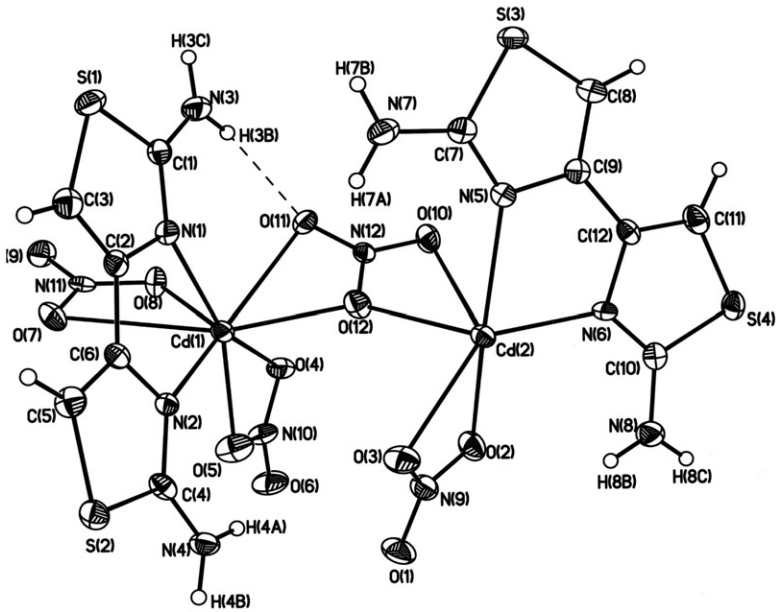


Figure 3. ORTEP diagram of 2.

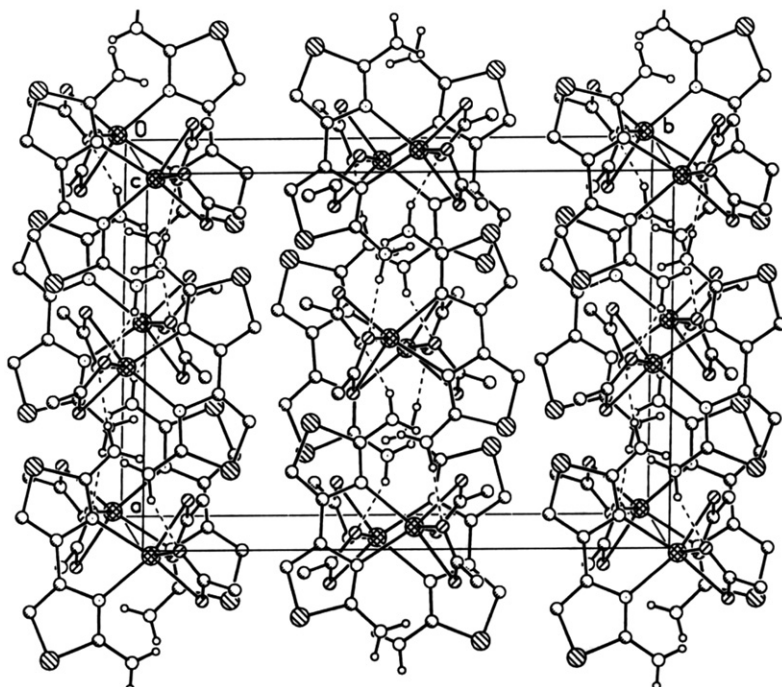


Figure 4. The unit cell and showing 1-D chains of **1**.

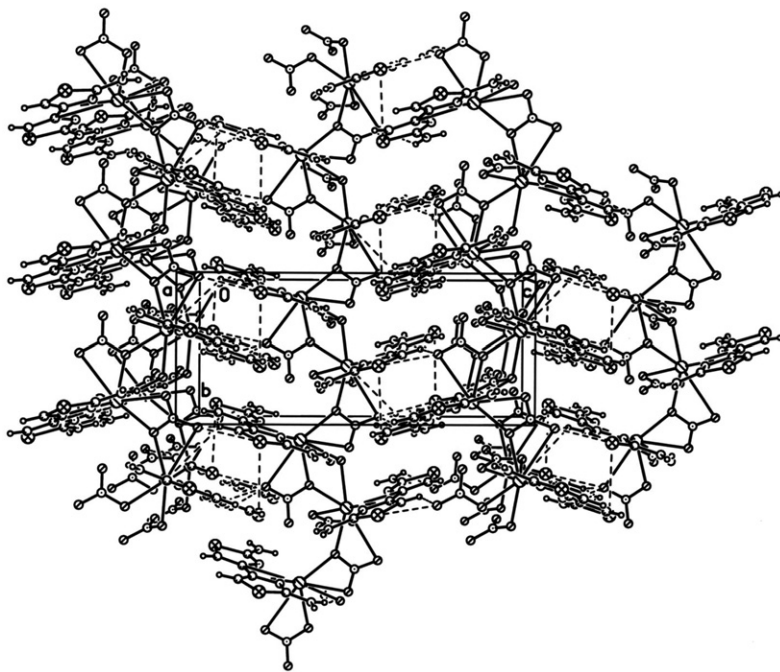


Figure 5. The unit cell and showing 1-D chains of **2**.

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

Cd(1)–N(1)	2.2590(19)	N(1)–Cd(1)–C(1B)	101.01(7)
Cd(1)–N(2)	2.2681(19)	N(2)–Cd(1)–C(1B)	136.67(7)
Cd(1)–O(1B)	2.2681(17)	O(1B)–Cd(1)–C(1B)	27.97(6)
Cd(1)–O(2A)	2.2792(17)	O(2A)–Cd(1)–C(1B)	118.15(6)
Cd(1)–O(2B)	2.3726(15)	O(2B)–Cd(1)–C(1B)	28.03(6)
Cd(1)–O(1A)	2.3993(17)	O(1A)–Cd(1)–C(1B)	102.27(6)
		N(1)–Cd(1)–C(1A)	135.64(7)
N(1)–Cd(1)–N(2)	73.52(7)	N(2)–Cd(1)–C(1A)	96.26(7)
N(1)–Cd(1)–O(1B)	103.22(6)	O(1B)–Cd(1)–C(1A)	120.57(7)
N(2)–Cd(1)–O(1B)	109.86(6)	O(2A)–Cd(1)–C(1A)	27.90(6)
N(1)–Cd(1)–O(2A)	111.10(6)	O(2B)–Cd(1)–C(1A)	103.99(6)
N(2)–Cd(1)–O(2A)	103.25(6)	O(1A)–Cd(1)–C(1A)	27.79(6)
O(1B)–Cd(1)–O(2A)	137.63(6)	C(1B)–Cd(1)–C(1A)	114.02(7)
N(1)–Cd(1)–O(2B)	94.19(6)		
N(2)–Cd(1)–O(2B)	159.36(6)		
O(1B)–Cd(1)–O(2B)	55.95(5)		
O(2A)–Cd(1)–O(2B)	96.60(6)		
N(1)–Cd(1)–O(1A)	156.69(6)		
N(2)–Cd(1)–O(1A)	90.23(7)		
O(1B)–Cd(1)–O(1A)	97.92(6)		
O(2A)–Cd(1)–O(1A)	55.63(6)		
O(2B)–Cd(1)–O(1A)	105.82(6)		

of acetate. The average internal dihedral angle of -3.35° between the thiazole rings of DABT shows a twisted structure of the ligand in **1**.

In the structure of **2** is a dinuclear complex with eight and six coordinate Cd: $\text{Cd}_1\text{O}_6\text{N}_2$ and $\text{Cd}_2\text{O}_4\text{N}_2$. One Cd has O_6N_2 donors and the other Cd is O_4N_2 . In the structure of **2**, three nitrates are bidentate and another is both bidentate and bridging between two cadmium centers (a novel behavior of nitrate) (figure 3). The structure of **2** consists of a 1-D polymer with the basic repeating dimeric $[\text{Cd}(\text{DABT})(\text{NO}_3)_2]$, considered a 1-D coordination polymer of cadmium(II) consisting of linear chains formed by bridging nitrate (figure 5). The average internal dihedral angle of 0.6° between the thiazole rings of DABT shows a planar structure of the ligand in **2**. Many new cadmium(II) complexes have recently been reported [21–26]. In these compounds, the structures have been grown in polymeric supramolecular by hydrogen bonds and secondary interactions such as $\text{C}-\text{H}\cdots\text{Cl}$, $\text{N}-\text{H}\cdots\text{Br}$ and $\text{C}-\text{H}\cdots\text{Br}$. In all of these cadmium(II) compounds, the coordination numbers are six or seven, with no complex having coordination number 8. The monomeric **1** and dimeric **2** in the solid state are almost parallel to each other and further linked by $\text{O}\cdots\text{HN}_{\text{amine}}$ hydrogen bonding (tables 4 and 5) growing **1** and **2** into 1- and 2-D polymers, respectively (figures 4 and 5).

3.2. Solution studies

The electronic absorption spectra of DABT and Cd^{2+} (acetate) and Cd^{2+} (nitrate) with increasing concentration of cations were recorded (figure 6) in AN at 25°C . All the resulting complexes have a shift of about 35 nm toward longer wavelength in comparison to the free ligand [27–30]. There is an isobestic point in titration of

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

Cd(1)–N(2)	2.272(3)	N(6)–Cd(2)–O(12)	125.22(11)
Cd(1)–N(1)	2.284(4)	O(8)#1–Cd(2)–O(12)	104.46(10)
Cd(1)–O(12)	2.305(3)	N(5)–Cd(2)–O(12)	86.85(11)
Cd(1)–O(5)	2.317(3)	N(6)–Cd(2)–O(3)	133.18(11)
Cd(1)–O(8)	2.331(3)	O(8)#1–Cd(2)–O(3)	76.24(11)
Cd(1)–O(11)	2.718(3)	N(5)–Cd(2)–O(3)	151.89(12)
Cd(2)–N(6)	2.254(3)	N(6)–Cd(2)–O(2)	87.14(11)
Cd(2)–N(5)	2.337(3)	O(8)#1–Cd(2)–O(2)	126.04(10)
Cd(2)–O(12)	2.387(3)	N(5)–Cd(2)–O(2)	146.77(11)
Cd(2)–O(3)	2.407(3)	O(12)–Cd(2)–O(2)	80.92(11)
Cd(2)–O(2)	2.467(3)	O(3)–Cd(2)–O(2)	52.57(10)
		N(6)–Cd(2)–O(4)#1	75.33(11)
N(2)–Cd(1)–N(1)	2.652(3)	O(8)#1–Cd(2)–O(4)#1	68.23(11)
N(2)–Cd(1)–O(12)	2.335(3)	N(5)–Cd(2)–O(4)#1	117.61(10)
N(1)–Cd(1)–O(12)	75.81(12)	O(12)–Cd(2)–O(4)#1	153.03(9)
N(2)–Cd(1)–O(5)	116.69(12)	O(3)–Cd(2)–O(4)#1	76.97(10)
N(1)–Cd(1)–O(5)	102.53(12)	O(2)–Cd(2)–O(4)#1	83.25(10)
O(12)–Cd(1)–O(5)	86.57(11)	N(6)–Cd(2)–N(9)	110.69(11)
N(2)–Cd(1)–O(8)	158.75(12)	O(8)#1–Cd(2)–N(9)	101.23(11)
N(1)–Cd(1)–O(8)	95.92(12)	N(5)–Cd(2)–N(9)	163.50(11)
O(12)–Cd(1)–O(8)	126.59(12)	O(12)–Cd(2)–N(9)	77.26(10)
O(5)–Cd(1)–O(8)	90.23(12)	O(3)–Cd(2)–N(9)	26.27(11)
N(2)–Cd(1)–O(11)	116.64(10)	O(2)–Cd(2)–N(9)	26.30(10)
N(1)–Cd(1)–O(11)	90.86(12)	O(4)#1–Cd(2)–N(9)	78.87(10)
O(12)–Cd(1)–O(11)	157.96(11)		
O(5)–Cd(1)–O(11)	89.15(11)		
O(8)–Cd(1)–O(11)	50.41(9)		
N(2)–Cd(1)–O(4)	110.94(11)		
N(1)–Cd(1)–O(4)	68.42(9)		
O(12)–Cd(1)–O(4)	135.05(10)		
O(5)–Cd(1)–O(4)	147.85(10)		
O(8)–Cd(1)–O(4)	73.82(10)		
O(11)–Cd(1)–O(4)	48.49(9)		
N(2)–Cd(1)–O(7)	64.97(10)		
N(1)–Cd(1)–O(7)	63.51(9)		

Symmetry transformations used to generate equivalent atoms: #1 $x, y+1, z$.Table 4. Hydrogen bonds (Å and °) for **1**.

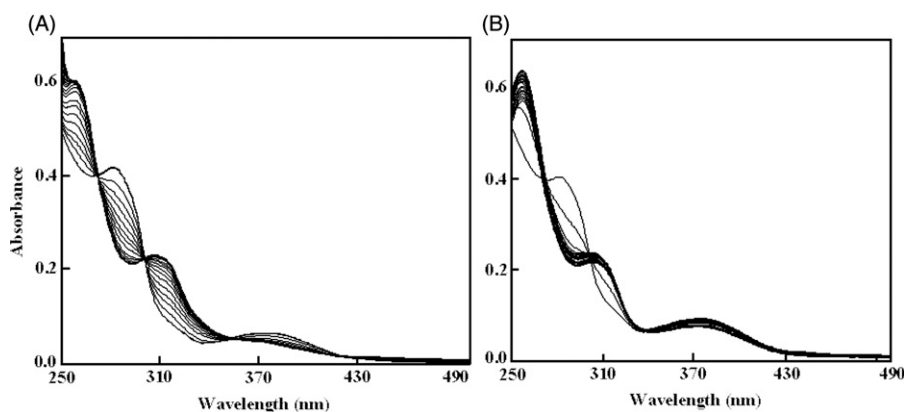
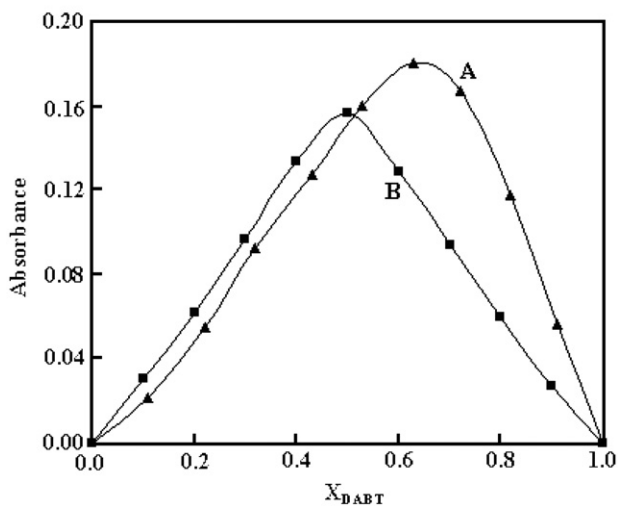
D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
N3–H3B...O1B [$-1/2-x, 2-y, z$]	0.88	2.02	2.774(5)	143.4
N3–H3A...O2B	0.88	2.23	3.056(5)	155.6
N4–H4A...O1A	0.88	2.12	2.935(5)	153.4
N3–H4B...O2A [$-1/2-x, 2-y, z$]	0.88	2.54	2.854(4)	153.1

DABT with $\text{Cd}(\text{CH}_3\text{COO})_2$, while in titration with $\text{Cd}(\text{NO}_3)_2$ there is no isobestic point, and it is evident that 1 : 1 complexes are formed with acetate and 1 : 2 (metal to ligand) with nitrate.

The stoichiometry of the complexes in AN was examined by the method of continuous variation [31]. A sample of the resulting plot for Cd^{2+} (nitrate) and Cd^{2+} (acetate) complexes is shown in figure 7, and it is evident that 1 : 1 complexes are formed

Table 5. Hydrogen bonds (\AA and $^\circ$) for **2**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N3-H3A...O11	0.88	2.26	3.101(5)	159
N3-H3C...O6 [1 + x, y, z]	0.88	2.15	3.026(5)	174
N4-H4A...O5	0.88	2.20	2.926(5)	139
N4-H4B...O10 [-1/2 + x, -y, -1/2 + z]	0.88	2.28	2.996(4)	138
N7-H7A...O9 [x, 1 + y, z]	0.88	2.15	3.002(5)	163
N7-H7B...O1 [x, 1 + y, z]	0.88	2.27	3.152(5)	178
N8-H8B...O2	0.88	2.36	3.026(5)	133
N8-H8C...O7 [-1/2 + x, -y, 1/2 + z]	0.88	2.25	2.938(5)	135

Figure 6. Electronic absorption spectra of DABT (5.0×10^{-5} mol) in the presence of increasing concentration of $\text{Cd}(\text{CH}_3\text{COO})_2$ and $\text{Cd}(\text{NO}_3)_2$ at 25°C in AN.Figure 7. Continuous variation plots for Cd^{2+} (nitrate) (A) and Cd^{2+} (acetate) (B) complexes with DABT ligand.

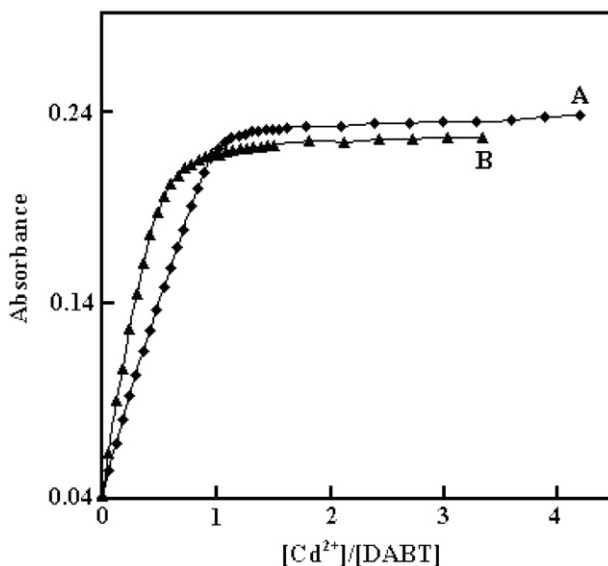


Figure 8. Mole ratio plots of DABT (5.0×10^{-5} mol) with Cd^{2+} (nitrate) and Cd^{2+} (acetate) solution in AN at 25°C .

in acetate solution and 1:2 (metal to ligand) are formed in nitrate solution. The formation of such complexes was further supported by mole ratio method (figure 8). The formation constants of the resulting 1:2 complex between Cd(II) nitrate and DABT ($\log K_f = 10.32 \pm 0.10$) as well as Cd(II) acetate and DABT ($\log K_f = 5.16 \pm 0.01$) were obtained at 25°C by absorbance measurements of solutions in which varying concentrations of metal ion were added to fixed amount (5.0×10^{-5} mol) of ligand solution, at λ_{max} of complexes. All the resulting absorbance–mole ratio data were best fitted to equations (1) (for ML) and (2) (for ML_2), respectively, which further supports the formation of 1:1 complex with acetate and 1:2 complex with nitrate.

$$K_f[\text{L}]^2 + (1 + K_f(C_L - C_M))[\text{L}] - C_L = 0 \quad (1)$$

$$K_1K_2[\text{L}]^3 + K_1(1 + K_2(2C_M - C_L))[\text{L}]^2 + (1 + K_1(C_M - C_L))[\text{L}] + C_L = 0 \quad (2)$$

For evaluation of the formation constants and molar absorptivity coefficients from absorbance *versus* $[\text{M}]/[\text{DABT}]$ mole ratio data, a nonlinear least-squares curve fitting program KINFIT was used. The crystal studies show the formation of 1:1 compounds for **1** and **2** showing that in solution the weak nitrate ligands dissociate and the second DABT can be coordinated.

Supplementary material

The crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos

CCDC-616396 for **1** and 616397 for **2**. The copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgment

Support of this investigation by Tarbiat Moalem University is gratefully acknowledged.

References

- [1] H. Erlenmeyer, H. Ueberwasser. *Helv. Chim. Acta*, **23**, 1268 (1940).
- [2] H. Erlenmeyer, H. Ueberwasser. *Helv. Chim. Acta*, **22**, 938 (1939).
- [3] H. Erlenmeyer, E.H. Schmid. *Helv. Chim. Acta*, **22**, 698 (1939).
- [4] J. Weng, L.M. Jiang, W.L. Sun, Z.Q. Shen, S.Q. Liang. *Polymer*, **42**, 5491 (2001).
- [5] Z. Zhou, W. Sun, J. Yang, J. Tang, Z. Shen. *Polymer*, **46**, 9495 (2005).
- [6] J. Park, J.H. Lee, S.I. Ko, T.W. Kim, T. Uemura, Y. Chujo. *Synth. Met.*, **21**, 1689 (2001).
- [7] H. Sosaki. *Tetrahedron Lett.*, **35**, 4401 (1994).
- [8] M.A. Ciufolini, Y.C. Shen. *J. Org. Chem.*, **62**, 3804 (1997).
- [9] Y. Tian, P. Yang, H. Wang, Y.L. Fong, S. Xiong, J.L. Huan. *Polyhedron*, **15**, 2771 (1996).
- [10] A. Morsali, M. Payehghadr, M.R. Poorheravi, F. Jamali. *Z. Anorg. Allg. Chem.*, **629**, 1627 (2003).
- [11] L. Liu, Y.W. Lam, W.Y. Wong. *J. Organomet. Chem.*, **691**, 1092 (2006).
- [12] A. Rouhollahi, M.K. Amini, M. Shamsipur. *Talanta*, **41**, 1465 (1994).
- [13] G. Ferguson, C. Glidewell, E.S. Lavender. *Acta Crystallogr.*, **B55**, 591 (1999).
- [14] G.M. Sheldrick. *SHLXTL-98b V5.10, Bruker AXS*, Madison, Wisconsin, USA (1998).
- [15] V.T. Yilmaz, S. Hamamci, O. Andac, K. Guven. *Z. Anorg. Allg. Chem.*, **629**, 172 (2003).
- [16] S. Sen, S. Mitra, P. Kundu, M.K. Saha, C. Kruger, J. Bruckmann. *Polyhedron*, **16**, 2475 (1997).
- [17] A.V.R. Warriar, R.S. Krishnan. *Spectrochim. Acta*, **24A**, 1243 (1971).
- [18] Y. Fukuda, A. Nakao, K. Hayashi. *J. Chem. Soc., Dalton Trans.*, 527 (2002).
- [19] V.A. Nicely, J.L. Dye. *J. Chem. Educ.*, **49**, 443 (1971).
- [20] T.C. Stamatatos, E. Katsoulakou, V. Nastopoulos, C.P. Raptopoulou, E.M. Zoupa, S.P. Perlepes. *Z. Naturforsch*, **58b**, 1045 (2003).
- [21] J. Gao, K.-J. Wei, J. Ni, J.-Z. Zhang. *J. Coord. Chem.*, **62**, 257 (2009).
- [22] G.-B. Che, J. Wang, B. Liu, X.-Y. Li, C.-B. Liu. *J. Coord. Chem.*, **62**, 302 (2009).
- [23] B. Notash, N. Safari, A. Abedi, V. Amani, H.R. Khavasi. *J. Coord. Chem.*, **62**, 1638 (2009).
- [24] J. Lu, N. Wang, H.-T. Liu. *J. Coord. Chem.*, **62**, 1980 (2009).
- [25] Z.R. Ranjbar, S. Hamidi, F. Heshmatpour, Al. Morsali. *J. Coord. Chem.*, **62**, 2022 (2009).
- [26] Z.-X. Du, J.-Xi. Li, L.-Y. Wang. *J. Coord. Chem.*, **62**, 2411 (2009).
- [27] N. Moloto, N. Revaprasadu, M.J. Moloto, P.O. Brien, M. Helliwell. *Polyhedron*, **29**, 3947 (2007).
- [28] X.J. Zhao, J.L.B. Ding, X.G. Wang, E.C. Yang. *Inorg. Chem. Commun.*, **10**, 605 (2007).
- [29] M. Holt, N.W. Alcock, R.R. Hendrixson, G.D. Malpass Jr, R.G. Ghirardelli, R.A. Palmer. *Acta Crystallogr.*, **21**, 1080 (1981).
- [30] D.R. Feltham. *Pure Appl. Chem.*, **61**, 943 (1989).
- [31] P. Job. *Anal. Chim.*, **9**, 113 (1928).