

# Syntheses and Characterization of Two New 4,4'-Bithiazole $d^{10}$ Complexes, Structural Characterization of $M(DABTZ)_2(CH_3COO)](ClO_4) \cdot 2H_2O$ ( $M = Zn, Cd$ )

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New zinc(II) and cadmium(II) complexes of the 2,2'-diamino-4,4'-bithiazole (DABTZ) ligand,  $[M(DABTZ)_2(CH_3COO)](ClO_4)$ , have been synthesized and characterized by elemental analysis, IR,  $^1H$  NMR and  $^{13}C$  NMR spectroscopy. The structural characterization of the  $Cd(DABTZ)_2(CH_3COO)](ClO_4) \cdot 2H_2O$  complex shows the complex to be a monomer and the Cd atom to be coordinated by four nitrogen atoms of the "DABTZ" ligands and two oxygen atoms of the acetate anion. There is an edge-to-edge  $\pi$ - $\pi$  stacking interaction between the parallel aromatic rings.

**Key words:** Zinc, Cadmium, Crystal Structure, 2,2'-Diamino-4,4'-bithiazole

## Introduction

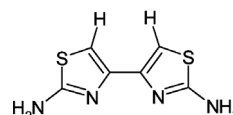
Numerous zinc (II), cadmium (II) and mercury (II) complexes with nitrogen or oxygen donor ligands have been synthesized and studied [1–3]. Some of these complexes are structural models for the active sites in enzymes [2].

In part one of our current study, we reported the preparation and characterization of a series of metal ion complexes of the 4,4'-bithiazole (BTZ) ligand [4–9]. In this paper, we describe two new homoleptic  $d^{10}$  complexes of DABTZ,  $[M(DABTZ)_2(CH_3COO)](ClO_4)$  ( $M = Zn^{2+}$  and  $Cd^{2+}$ ) and the structural characterization of the  $Cd^{2+}$  complex. 2,2'-Diamino-4,4'-bithiazole complexes with different metal ions have been reported [10–12] and some of them have shown ability to inhibit the DNA synthesis of tumour cells [12].

## Results and Discussion

### Syntheses

Reaction between the 2,2'-diamino-4,4'-bithiazole "DABTZ" ligand and mixtures of aqueous cadmium(II) acetate/zinc acetate with sodium perchlorate solutions provided the crystalline material  $[Cd(DABTZ)_2(CH_3COO)](ClO_4) \cdot 2H_2O$  and  $[Zn-$



DABTZ

$(DABT)_2(CCl_3COO)](ClO_4)$ , respectively. The IR spectra of these complexes show  $\nu(ClO_4^-)$  at *ca.* 1090 and 1110  $cm^{-1}$ , respectively. Both complexes exhibit absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1616  $cm^{-1}$  range. The relatively weak bands at around 2960 and 3080  $cm^{-1}$  are assigned to the  $\nu(CH_3)$  mode of the acetate group and the  $\nu(CH)$  mode of the DABTZ aromatic rings, respectively. The broad absorption band for  $\nu(HOH)$  at 3320–3430  $cm^{-1}$  indicates the presence of water molecules in  $[Cd(DABTZ)_2(CH_3COO)](ClO_4) \cdot 2H_2O$ . The broad band is perhaps attributable to  $\nu(O-H \cdots X)$ , indicating the presence of hydrogen bonds, which has been confirmed by the crystal structure determination of this complex. The characteristic bands of the carboxylate group in  $[Cd(DABTZ)_2(CH_3COO)](ClO_4) \cdot 2H_2O$  appear around 1564 for  $\nu_{as}(C-O)$  and 1412 for  $\nu_{sym}(C-O)$ , and in  $[Zn(DABT)_2(CCl_3COO)](ClO_4)$  at around 1560 for  $\nu_{as}(C-O)$  and 1415  $cm^{-1}$  for  $\nu_{sym}(C-O)$ . The  $\Delta \nu$  value ( $\nu_{as} - \nu_{sym}$ ) of 152  $cm^{-1}$  for

Table 1. Crystal data and structure refinement for  $\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$ .

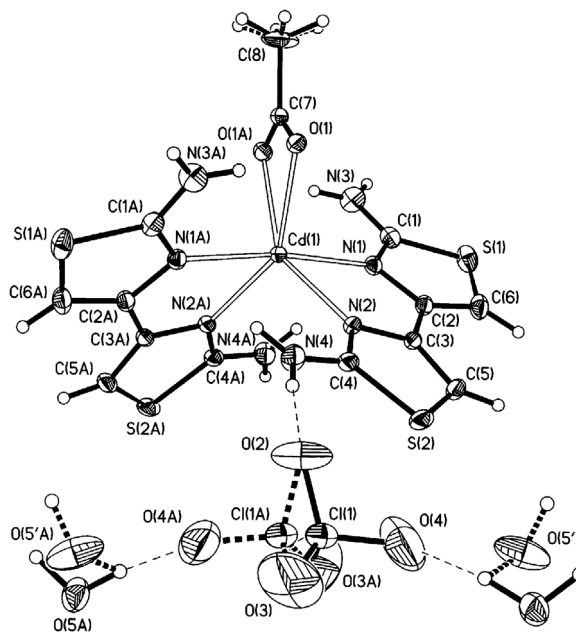
Complex	$\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$
Empirical formula	$\text{C}_{14}\text{H}_{19}\text{CdClN}_8\text{O}_8\text{S}_4$
Molecular weight	703.46
Temperature [K]	120(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
<i>a</i> [Å]	11.3922(9)
<i>b</i> [Å]	8.6090(6)
<i>c</i> [Å]	14.1866(11)
$\beta$ [°]	110.7260(10)
<i>V</i> [Å <sup>3</sup> ]	1301.31(17)
<i>Z</i>	2
<i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.80
$\mu$ [mm <sup>-1</sup> ]	1.32
<i>F</i> (000)	704
Crystal size [mm <sup>3</sup> ]	0.40 × 0.30 × 0.24
$\theta$ Range [°]	1.98 to 30.01
Index ranges	$-14 \leq h \leq 15$ , $-11 \leq k \leq 12$ , $-19 \leq l \leq 19$
Reflections collected	11031
Independent reflections [ <i>R</i> <sub>int</sub> ]	3672 (0.0228)
Reflections observed [ $> 2\sigma$ ]	3511
Absorption correction	Semi-empir. from equivalents
Max. and min. transmissions	0.743 and 0.621
Data / restraints / parameters	3672 / 3 / 183
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.038
<i>R</i> [ $I > 2\sigma(I)$ ]	<i>R</i> 1 = 0.0345, <i>wR</i> 2 = 0.0908
<i>R</i> (all data)	<i>R</i> 1 = 0.0356, <i>wR</i> 2 = 0.0919
Largest diff. peak and hole [e · Å <sup>-3</sup> ]	1.660 and -0.786

Table 2. Bond lengths [Å] and angles [°] for  $\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$ .

Cd1–N1	2.3202(17)	Cd1–N2	2.3213(18)
Cd1–O1	2.3745(16)		
N2–Cd1–N2 <sup>#1</sup>	106.33(9)	N2 <sup>1</sup> –Cd1–N1	101.71(6)
N2–Cd1–N1	73.38(7)	N1–Cd1–N1 <sup>1</sup>	172.04(9)
N2 <sup>1</sup> –Cd1–O1	147.40(6)	N2–Cd1–O1	102.62(6)
N1 <sup>1</sup> –Cd1–O1	86.44(6)	N1–Cd1–O1	100.65(6)
O2–Cd1–O1 <sup>1</sup>	55.56(8)		

<sup>#1</sup>  $-x + 1/2, y, z + 1/2$ .

$\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$  is similar to the value of  $\Delta\nu = 145 \text{ cm}^{-1}$  for  $[\text{Zn}(\text{DABT})_2(\text{CCl}_3\text{COO})](\text{ClO}_4)$ , indicating that the carboxylate group is coordinating with Zn(II) and Cd(II) in the same bidentate manner [13–17], as also unambiguously confirmed by the crystal structure of the Cd complex. The <sup>1</sup>H NMR spectra of DMSO solutions of the two complexes display two distinct absorption bands at 6.50(s, 2H) and 7.25(s, 4H) ppm which have been assigned to the aromatic and amino protons, respectively. The band at 1.77(s, 6H) is assigned to the methyl protons of the acetate anions of both complexes. The

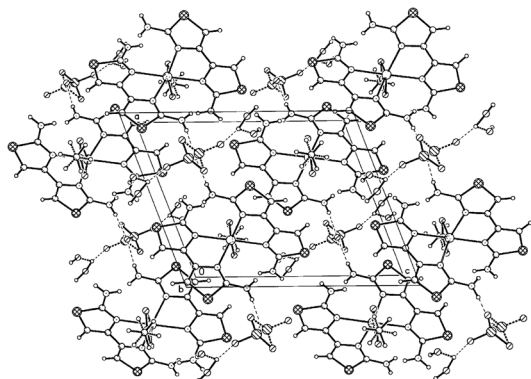
Fig. 1. ORTEP diagram of  $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$  with ellipsoids of 50% probability.

<sup>13</sup>C NMR spectra of the DMSO solutions of the two complexes display three distinct absorption bands at 102.7, 146.1, and 169.5 ppm assigned to the aromatic carbon atoms. Two other resonances at 22.5 (<sup>13</sup>CH<sub>3</sub>-COO) and 179.2 (CH<sub>3</sub>-<sup>13</sup>COO) are assigned to the carbon atoms of acetate anions.

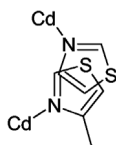
#### Crystal structure of $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$

An ORTEP diagram of the  $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2 \text{H}_2\text{O}$  complex is shown in Fig. 1. The selected bond distances and angles around the Cd(II) ion are given in Table 2. The structure consists of discrete  $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})]^+$  cations and  $\text{ClO}_4^-$  anions. The  $\text{ClO}_4^-$  anions were disordered. Each cadmium atom is octahedrally chelated by four nitrogen atoms of two DABTZ ligands with Cd–N distances of 2.3202(17) and 2.3213(18) Å, and two oxygen atoms of the acetate anion with Cd–O distances of 2.3745(16) Å. The average internal dihedral angle of 7.43° between the thiazole rings of the DABTZ ligand shows a twisted structure of the ligand in the complex. There are two H<sub>2</sub>O molecules per formula unit. It should be noted, that the molecule has crystallographic 2(C<sub>2</sub>) symmetry as required by  $P2_1/n$  and *Z* = 2. The components are linked by hydrogen bonding (Fig. 1

D-H...A	D...A, Å	D-H, Å	H...A, Å	DHA, deg
N(3) – H(3A)···O(1) [ $-x + 1/2, y, -z + 1/2$ ]	2.905(4)	0.88	2.19	139
N(3) – H(3B)···O(5)	2.950(7)	0.88	2.14	153
N(4) – H(4B)···O(2) [ $x - 1, y + 1, z$ ]	3.035(7)	0.88	2.16	175
O(5) – H(5OA)···O(4)	2.495(8)	1.01	1.51	166
O(5) – H(5OA)···Cl(1)	3.792(6)	1.01	2.86	155
O(5) – H(5OB)···O(4) [ $-x + 1, -y, -z$ ]	3.081(8)	1.00	2.27	138
O(5) – H(5OB)···Cl(1) [ $-x + 1, -y, -z$ ]	3.745(6)	1.00	2.80	158
O(5') – H(5OC)···N(3) [ $-x + 1, -y, -z$ ]	3.504(9)	0.97	2.55	169

Table 3. H-Bonds in the structure of  $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$ .Fig. 2. The unit cell of the  $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$ .

and 2). The hydrogen bond parameters are given in Table 3. The distances of two parallel edges, which belong to bithiazole rings of adjacent molecules are only 3.297 Å, indicating major edge-to-edge  $\pi$ - $\pi$  stacking interactions [18], which further stabilize this packing system. Projection of the structure perpendicular to the ring plane shows the overall form of “slipped” stacking [19–20], which can be rationalized qualitatively in terms of optimizing the attraction between atoms of opposite charges (Scheme 1) [21].



Scheme 1.

Thus, two factors, hydrogen bonding and  $\pi$ - $\pi$  stacking control the packing of the complexes.

## Experimental Section

### Physical property measurements

IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid ana-

lyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

### Preparation of the 2,2'-diamino-4,4'-bithiazole (DABTZ)

The 2,2'-diamino-4,4'-bithiazole ligand was prepared from 1,4-dibromobutane-2,3-dione and thiourea by the method of Erlenmeyer and Uberwasser [12].

### Preparation of $[\text{Cd}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$

The complex was prepared by dissolving cadmium(II) acetate (0.230 g, 1 mmol) and sodium perchlorate (0.123 g, 1 mmol) in distilled water (10 ml) and adding an ethanolic solution of 2,2'-diamino-4,4'-bithiazole (DABTZ) (0.198 g, 1 mmol). The resulting solution was stirred for 2 h at room temperature and then allowed to stand for 10 d at room temperature (*ca.* 25 °C). White crystals precipitated, which were filtered off, washed with acetone and ether and dried in air (m.p. 200 °C). Yield: 0.316 g, 45%.  $\text{C}_{14}\text{H}_{19}\text{CdClN}_8\text{O}_8\text{S}_4$ : calcd. C 23.88, H 2.70, N 15.92; found C 23.70, H 2.60, N 15.50. – IR (KBr) selected bonds:  $\nu = 719(\text{m}), 974(\text{w}), 1090(\text{vs}), 1412(\text{vs}), 1564(\text{vs}), 1602(\text{vs}), 2035(\text{s}), 2960(\text{w}), 3080(\text{w}), 3250(\text{s})$  and  $3365(\text{s}) \text{ cm}^{-1}$ . – <sup>1</sup>H NMR ( $[\text{D}_6]$ -DMSO):  $\delta = 1.77$  (s, 3H), 6.50 (s, 4H), and 7.25 (s, 8H) ppm. <sup>13</sup>C-<sup>1</sup>H NMR ( $[\text{D}_6]$ -DMSO):  $\delta = ^{13}\text{C}\{-^1\text{H}\}$  NMR (DMSO;  $\delta$ ): 22.60, 102.70, 146.13, 169.52, and 179.25 ppm.

### Preparation of $[\text{Zn}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4)$

The complex  $[\text{Zn}(\text{DABTZ})_2(\text{CH}_3\text{COO})](\text{ClO}_4)$  was prepared similarly. Reactant materials: DABTZ, zinc(II) acetate, sodium perchlorate (2:1:2). White crystals, m.p 210 °C, Yield: 0.341 g, 55%.  $\text{C}_{14}\text{H}_{15}\text{ZnClN}_8\text{O}_6\text{S}_4$ : calcd. C 27.10, H 2.41, N 18.06; found C 26.75, H 2.70, N 17.50. – IR (KBr) selected bonds:  $\nu = 710(\text{m}), 974(\text{w}), 1110(\text{vs}), 1415(\text{vs}), 1560(\text{vs}), 1600(\text{vs}), 2030(\text{s}), 2965(\text{w}), 3080(\text{w}),$  and  $3200(\text{s})$ . – <sup>1</sup>H NMR ( $[\text{D}_6]$ -DMSO):  $\delta = 1.77$  (s, 3H), 6.55 (s, 4H), and 7.25 (s, 8H). <sup>13</sup>C-<sup>1</sup>H NMR ( $[\text{D}_6]$ -DMSO):  $\delta = 22.64, 102.71, 146.12, 169.51,$  and 179.25.

*Determination of the structure of [Cd(DABTZ)<sub>2</sub>(CH<sub>3</sub>COO)]·(ClO<sub>4</sub>)·2H<sub>2</sub>O*

The intensity data were collected at 120(2) K using a Siemens R3m/V diffractometer within the range  $1.98^\circ \leq \theta \leq 30.01^\circ$  using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Accurate unit cell parameters and the orientation matrix for the data collection were obtained from least-squares refinement. The structure has been solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ . The positions of the hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic displacement parameter. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the Sadabs programs were

applied. All structural calculations were carried out with a PDP-11/23+ computer using the SHELXTL v.5.10 program package [23–24].

*Supplementary material*

Complete tables of bond lengths, angles, and atomic parameters for Cd(DABTZ)<sub>2</sub>(CH<sub>3</sub>COO)] (ClO<sub>4</sub>)·2H<sub>2</sub>O have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 257730 for Cd(DABTZ)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·2H<sub>2</sub>O.

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