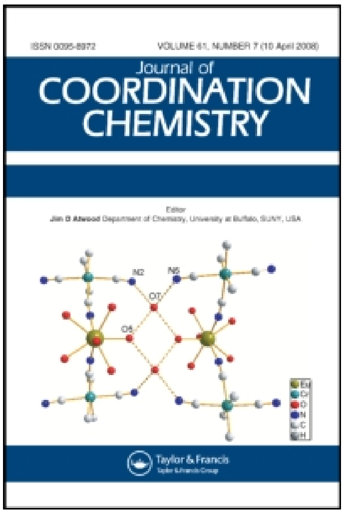

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Synthesis and Crystal Structure of a Cadmium(II) Complex with 2,2'-diamino-4,4'-bis-1,3-thiazole

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SYNTHESIS AND CRYSTAL STRUCTURE OF A CADMIUM(II) COMPLEX WITH 2,2′-DIAMINO-4,4′-BIS-1,3-THIAZOLE

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Crystals of the title complex with diaminobithiazole (DABT) were obtained by a solution diffusion method. X-ray diffraction analysis shows the complex to be monoclinic, space group $P2_1/c$ with cell dimensions $a = 11.684(2)$, $b = 13.625(2)$, $c = 14.859(1)$ Å and $\beta = 109.970(7)^\circ$; $R = 0.026$. The Cd(II) atom lies in a distorted octahedral environment with two DABT and two Cl ligands in a *cis* arrangement. The average internal dihedral angle of 9.3° between thiazole rings of DABT shows the twisted structure of the ligand in the complex. The Cd(II) atom deviates by some −0.570 Å from the mean plane of the thiazole ring containing N(4), but the Cd–N(4) bond is the shortest among four Cd–N bonds in the structure. Intramolecular H-bonds between Cl atoms and amino groups stabilize the *cis*-configuration of the complex.

Keywords: Cadmium(II) complex; Crystal structure; Bithiazole; Electrostatic interaction

INTRODUCTION

Metal complexes with 2,2′-diamino-4,4′-bis-1,3-thiazole (DABT) and its derivatives show interesting properties and have potential application in many fields. For example, several complexes show an ability to recognize and cleave DNA as well as to inhibit the breakage of DNA by BLM [1,2] and multinuclear metal complexes with DABT Schiff bases or amides have been found to be excellent soft magnetic materials [3,4]. Structural investigations of these complexes are helpful for understanding relationships between properties and structure and for designing useful new materials. However, only a few structures of this kind of complex have been reported [5,6]. As a part of a structural investigation of metal complexes with DABT [7], a Cd(II) complex of DABT has been prepared and its structure determined by X-ray diffraction methods.

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EXPERIMENTAL

Synthesis

DABT was prepared according to the literature [8]. Crystals of the complex were obtained by a solution diffusion method using an H-shaped glass tube. $CdCl_2 \cdot 2H_2O$ (0.43 g, 2.0 mmol) was dissolved in 50 cm^3 of anhydrous methanol (solution A) and DABT (0.99 g, 0.5 mmol) was dissolved in 50 cm^3 of hot anhydrous methanol (solution B) under a nitrogen atmosphere. Solutions A and B were introduced into the two branches of the H-shaped tube, respectively. The surfaces of both solutions were about 12 mm below the horizontal pass-through of the tube. Nitrogen gas was bubbled into the solutions for several minutes and air-free methanol was carefully introduced into the tubes and layered above the two solutions as a diffusion medium. The tube was sealed with a piece of Saran wrap and left to stand at room temperature. Dark orange crystals of the complex were obtained after 15 days.

C, H and N contents were analyzed using an Eger 200 instrument. *Anal.* Calcd. for $CdCl_2\ (C_6H_6N_4S_2)_2 \cdot CH_3OH$ (%): C 25.50, H 2.64; N 18.30; Found: C 25.39; H 2.25; N 17.92.

Crystal Structure Determination

X-ray diffraction data were collected on a Rigaku AFC-7S diffractometer with graphite-monochoromated MoKα radiation to a $2\theta_{max}$ of 52°. Among 4576 collected reflections 4358 were unique ($R_{int} = 0.027$). Usual Lp and empirical absorption corrections were applied. The stucture was solved by the Patterson method followed by Fourier syntheses. Non-H atoms were refined anisotropically using 3805 observed reflections [$I > 2\sigma(I)$] with the SHELXL-97 program package [9]. H atoms were located in a difference Fourier map and included in structure factor calculations but were not refined. Scattering factors used were taken from International Tables for X-ray Crystallography [10].

Crystal Data

$C_{12}H_{12}CdCl_2N_8S_4 \cdot CH_3OH$, $M = 611.88$, monoclinic, $P2_1/c$, $a = 11.6835(15)$, $b = 13.6248(15)$, $c = 14.8590(13)$ Å, $\beta = 109.970(7)°$, $V = 2223.1(4)$ Å^3, $Z = 4$, $F(000) = 1216$, $D_x = 1.828$ Mg m^{-3}, μ(Mo–Kα) = 1.622 mm^{-1}, $R_1 = 0.0260$, $wR_2 = 0.0812$, GOF = 1.035, No. of variable = 262, $(\Delta\rho)_{max} = 0.40$ e Å^{-3}.

RESULTS AND DISCUSSION

Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table I. Selected bond distances and angles are given in Table II. The molecular structure is illustrated in Fig. 1. The Cd(II) atom lies in a distorted octahedral environment with two Cl and two chelating DABT in a *cis* arrangement. Bond angles around Cd(II) (Table II) confirm the distortion. Four Cd–N distances ranging from 3.337 to 3.454 Å show significant differences. Cd–N(1) and Cd–N(3) located *trans* to Cl atoms are significantly longer than Cd–N(2) and

TABLE I Final coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms

Atom	x/a	y/b	z/c	U_{eq} (Å)^2
Cd	0.28198(2)	0.16102(1)	0.19891(1)	0.0314(1)
Cl(1)	0.11061(6)	0.28051(5)	0.09958(5)	0.0407(2)
Cl(2)	0.42455(7)	0.20332(5)	0.10250(5)	0.0431(2)
S(1)	0.05648(8)	0.02049(8)	0.39200(7)	0.0599(3)
S(2)	0.10119(7)	−0.11785(6)	−0.00711(6)	0.0474(3)
S(3)	0.61853(8)	−0.02236(7)	0.44355(7)	0.0599(3)
S(4)	0.49516(7)	0.43417(6)	0.39416(6)	0.0467(2)
N(1)	0.1582(2)	0.0872(2)	0.2766(2)	0.0369(7)
N(2)	0.1961(2)	0.0186(2)	0.1150(2)	0.0340(7)
N(3)	0.4474(2)	0.0796(2)	0.3255(2)	0.0355(7)
N(4)	0.3842(2)	0.2778(2)	0.3132(2)	0.0353(7)
N(5)	0.1718(3)	0.1954(2)	0.4024(2)	0.0561(10)
N(6)	0.2504(2)	0.0255(2)	−0.0224(2)	0.0474(8)
N(7)	0.4211(3)	−0.0917(2)	0.3043(2)	0.0502(9)
N(8)	0.2730(3)	0.4230(2)	0.2617(2)	0.0549(9)
C(1)	0.1371(3)	0.1105(2)	0.3551(2)	0.0429(9)
C(2)	0.0513(3)	−0.0504(3)	0.2939(3)	0.0547(11)
C(3)	0.1087(3)	−0.0038(2)	0.2410(2)	0.0389(8)
C(4)	0.1220(2)	−0.0370(2)	0.1517(2)	0.0359(8)
C(5)	0.0659(3)	−0.1136(2)	0.0970(2)	0.0456(9)
C(6)	0.1916(2)	−0.0146(2)	0.0309(2)	0.0366(8)
C(7)	0.4829(3)	−0.0110(2)	0.3481(2)	0.0401(8)
C(8)	0.6245(3)	0.1033(3)	0.4538(3)	0.0579(11)
C(9)	0.5273(3)	0.1448(2)	0.3871(2)	0.0395(8)
C(10)	0.4981(3)	0.2496(2)	0.3768(2)	0.0369(8)
C(11)	0.5687(3)	0.3233(2)	0.4254(2)	0.0456(9)
C(12)	0.3720(3)	0.3740(2)	0.3146(2)	0.0377(8)
O(1)	0.7000(3)	0.1241(2)	0.1698(2)	0.0713(10)
C(13)	0.7773(5)	0.1951(4)	0.2275(5)	0.111(2)

U_{eq} is one third of the orthogonalized U_{ij} tensor.

Cd–N(4) located *cis* to Cl atoms. The difference of 0.117 Å between Cd–N(3) and Cd–N(4) bond distances is much larger (0.044 Å) this is found in the Co(II) complex [6].

In the bithiazole group, bond distances and angles are normal and comparable to those found in free 4,4′-thiazole [11]. The average distance of 1.338 Å for N(5)–C(1), N(6)–C(6), N(7)–C(7) and N(8)–C(12) strongly suggests the existence of electron delocalization between the thiazole and amino groups. Bond distances of 1.459 and 1.464 Å show that both C(3)–C(4) and C(9)–C(10) are single bonds [12], and imply that the thiazole rings may rotate around the C–C bond. In fact, the planarity of both DABT molecules is indeed poor in the structure; dihedral angles between thiazole rings of the same DABT ligand are 10.2° and 8.4°, respectively. Similar twisted bithiazole structures have also been found in Co(II) and Ni(II) complexes, dihedral angles ranging from 7.9 to 11.4° [5,6].

Mean plane calculations (see Table III) show that each thiazole ring is coplanar as expected, but the Cd(II) atom deviates significantly from all of four thiazole mean planes; the maximum deviation (−0.570 Å) is observed in the mean plane involving the N(4) atom. This may imply poor overlap between Cd and N(4) atomic orbitals, and a relatively weaker coordinate bond between N(4) and Cd atoms. However, the distance of 2.337 Å shows that the Cd–N(4) bond is the shortest among the four Cd–N bonds in the structure. Correspondingly, both the minimum deviation (−0.167 Å) of the Cd(II) atom and the longest Cd–N distance (2.454 Å)

TABLE II Selected bond distances (Å) and bond angles (°) for the complex

Cd–Cl(1)	2.6114(8)	Cd–Cl(2)	2.6056(9)
Cd–N(1)	2.361(2)	Cd–N(2)	2.339(2)
Cd–N(3)	2.454(2)	Cd–N(4)	2.337(2)
S(1)–C(1)	1.745(3)	S(1)–C(2)	1.732(4)
S(2)–C(5)	1.733(3)	S(2)–C(6)	1.734(3)
S(3)–C(7)	1.735(3)	S(3)–C(8)	1.718(4)
S(4)–C(11)	1.721(3)	S(4)–C(12)	1.726(3)
O(1)–C(13)	1.399(7)	N(1)–C(1)	1.312(4)
N(1)–C(3)	1.394(4)	N(2)–C(6)	1.314(4)
N(2)–C(4)	1.393(3)	N(3)–C(7)	1.309(4)
N(3)–C(9)	1.384(4)	N(4)–C(12)	1.319(4)
N(4)–C(10)	1.397(4)	N(5)–C(1)	1.342(4)
N(6)–C(6)	1.330(4)	N(7)–C(7)	1.354(4)
N(8)–C(12)	1.334(4)	C(2)–C(3)	1.353(5)
C(3)–C(4)	1.459(4)	C(4)–C(5)	1.348(4)
C(8)–C(9)	1.350(5)	C(9)–C(10)	1.464(4)
C(10)–C(11)	1.343(4)		
Cl(1)–Cd–Cl(2)	93.56(2)	Cl(1)–Cd–N(1)	93.57(6)
Cl(1)–Cd–N(2)	96.28(6)	Cl(1)–Cd–N(3)	165.09(5)
Cl(1)–Cd–N(4)	95.11(6)	Cl(2)–Cd–N(1)	167.50(6)
Cl(2)–Cd–N(2)	97.42(6)	Cl(2)–Cd–N(3)	92.14(6)
Cl(2)–Cd–N(4)	89.15(6)	N(1)–Cd–N(2)	71.58(8)
N(1)–Cd–N(3)	83.48(8)	N(1)–Cd–N(4)	100.43(8)
N(2)–Cd–N(3)	96.64(8)	N(2)–Cd–N(4)	166.46(8)
N(3)–Cd–N(4)	71.19(8)		

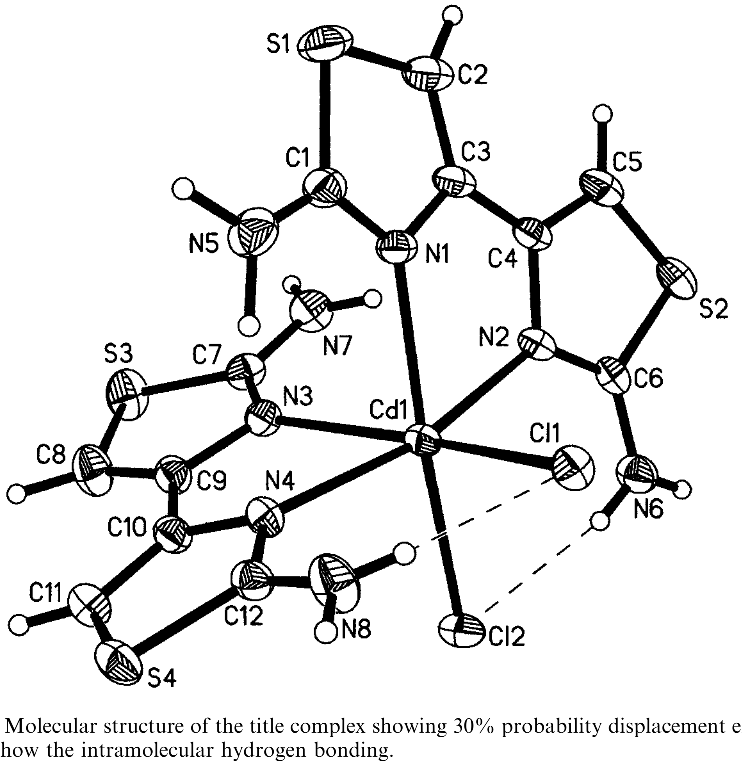

FIGURE 1 Molecular structure of the title complex showing 30% probability displacement ellipsoids. The dashed lines show the intramolecular hydrogen bonding.

TABLE III Mean planes (x, y, z in crystal coordinates) and deviations (Å) from them

The mean plane **1** formed by C(1), C(2), C(3), N(1) and S(1) atoms
$8.3876\,x - 5.9877\,y + 3.8966\,z = 1.8767$
C(1) −0.005, C(2) 0.001, C(3) −0.004, N(1) 0.005, S(1) 0.002/[Cd 0.299]
The mean plane **2** formed by C(4), C(5), C(6), N(2) and S(2) atoms
$7.7941\,x - 8.0209\,y + 2.9901\,z = 1.7108$
C(4) −0.010, C(5) 0.005, C(6) −0.008, N(2) 0.012, S(2) 0.002/[Cd −0.210]
The mean plane **3** formed by C(7), C(8), C(9), N(3) and S(3) atoms
$-9.0786\,x - 0.5951\,y + 12.7126\,z = 0.0396$
C(7) 0.009, C(8) −0.003, C(9) 0.008, N(3) −0.011, S(3) −0.003/[Cd −0.167]
The mean plane **4** formed by C(10), C(11), C(12), N(4) and S(4) atoms
$-7.9763\,x - 1.3665\,y + 13.5725\,z = 0.8001$
C(10) −0.000, C(11) −0.005, C(12) −0.009, N(4) 0.007, S(4) 0.007/[Cd −0.570]

*Dihedral angle: 10.2(2)° between planes **1** and **2**; 8.4(2)° between planes **3** and **4**.

TABLE IV Hydrogen bonding parameters

Donor–H···Acceptor	*D–H*	*H···A*	*D···A*	*D–H–A*
N5−H5···Cl1[a]	0.985	2.305	3.261(3)	163.4
N8−H12···Cl1	0.831	2.361	3.170(3)	164.8
N6−H8···Cl2	0.850	2.462	3.297(3)	167.8
N7−H9···Cl2[c]	0.904	2.467	3.356(3)	167.8
O1−H14···Cl2	0.915	2.351	3.213(4)	157.0
N6−H7···O1[b]	0.861	2.391	3.187(4)	154.0
N8−H11···O1[d]	0.858	2.105	2.902(4)	154.4

Symmetry codes: [a] x, $0.5-y$, $0.5+z$; [b] $1-x$, $-x-y$, $-z$; [c] $1-x$, $-0.5+y$, $1/2-z$; [d] $1-x$, $0.5+y$, $0.5-z$.

are involved in the thiazole molecule containing the N(3) atom. These facts suggest the existence of a more electrostatic interaction between Cd(II) and DABT ligands [13].

Hydrogen bonding parameters are presented in Table IV. Intramolecular hydrogen bonds exist between Cl atoms and amino groups. They stabilize the molecular structure and are considered as a possible reason for forming the *cis*-configuration rather than the *trans*-configuration in the complex. Through intermolecular hydrogen bonding between complex methanol molecules, the crystal shows a three-dimensional network structure.

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Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

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