

## Using a bithiazole Complex as Precursor to Synthesis of CdO-CdS Nanocomposite via Direct Thermal Decomposition

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### Abstract

A new tris-chelate Cd(II) complex,  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$  has been successfully synthesized and characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectroscopy, elemental analysis and single crystal X-ray determination. The thermal behavior, UV-Vis and fluorescence spectra of compound were studied. In reaction with DADMBTZ, Cadmium (II) forms a tris-chelate complex with nearly  $C_3$  symmetry for coordination polyhedron, DADMBTZ acts as a bidentate ligand. In complex the  $\text{ClO}_3^-$  anions are symmetrically different. Complex makes 2-D and 3-D networks via N-H...O and N-H...N hydrogen bonds, respectively. The nanocomposite CdO-CdS have been prepared using  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$  as precursor via thermal decomposition. As-prepared CdO-CdS nanocomposite was characterized By X-ray diffraction measurements (XRD), scanning electron microscopy (SEM).

**Keywords:** Bithiazole, Complex, CdO-CdS, Nanocomposite, Thermal decomposition

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### 1. Introduction

Metal coordination supramolecular compounds have been widely studied as they represent an important interface between synthetic chemistry and materials science. The synthesis of metal coordination supramolecular compounds with different metal ions and ligands have led to a wide range of potential applications as e.g. molecular wires [1-4], electrical conductors [5-7], molecular magnets [8,9], in host-guest chemistry [10-13] and in catalysis [14]. The potential use of supramolecular coordination complexes as materials for nanotechnological applications would seem to be very extensive as nanometer-scaled materials often exhibit the new interesting size-dependent physical and chemical properties that cannot be observed in their bulk analogous.

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Recently, much effort has been devoted to the design and controlled fabrication of nanostructured materials with functional properties. Among these investigations, the nanocomposite materials can not only demonstrate small size effect, surface effect, and quantum–dimension effect, but also combine the advantages of all ingredients. Therefore, the nanocomposite materials have attracted more and more attention due to their tailored properties and potential application in photonic crystal, drug delivery, biological markers, bio-separation, and as catalyst. Various kinds of nanocomposite materials have been successfully fabricated such as metal/metal, metal/semiconductor, semiconductor/ semiconductor, inorganic particle/polymer, and inorganic particle/inorganic particle, showing tailored magnetic optical electrical properties [15,16]. CdS, an important semiconductor with a wide band gap of 2.4 eV at room temperature. It has high potential application in light-emitting diodes, solar cells, optoelectronics and catalysts [17]. There are a variety of methods used to prepare this material. Changes in the photoactivity of CdS can also be achieved by combining the CdS semiconductor with other semiconductors at different energy levels (ZnS, ZnO, TiO<sub>2</sub>...). Modification of CdS by impurity can efficiently adjust its electrical, optical, and magnetic properties. In spite of the absence of studies in literature on the effect of CdO presence on the activity of CdS under visible light, there are interesting results showing the increase in CdS activity for samples mixed with CdO [18,19].

It was found that aromatic heterocyclic polymers containing bithiazole rings are good ligands because the two nitrogen atoms in the bithiazole rings are able to chelate metal ions to form stable five member rings. In addition, transition metal complexes of bithiazole derivative ligands have found increasing application. For instance, Ni and Co complexes of 2,2'-diamino-4,4'-bithiazole have been found to be effective inhibitors of DNA synthesis in tumor cells [20-30] and Fe(II), Fe(III) and Cu(II) complexes have found application in soft magnetic materials [31-33].

The use of bithiazole complexes as precursors for preparing inorganic nano-materials has not yet been investigated thoroughly [34]. In this paper we describe the preparation of Cd(II) complex, [Cd(DADMBTZ)<sub>3</sub>](ClO<sub>3</sub>)<sub>2</sub>, (Scheme 1) and its use for preparation of CdO-CdS nanocomposite via direct thermal decomposition.

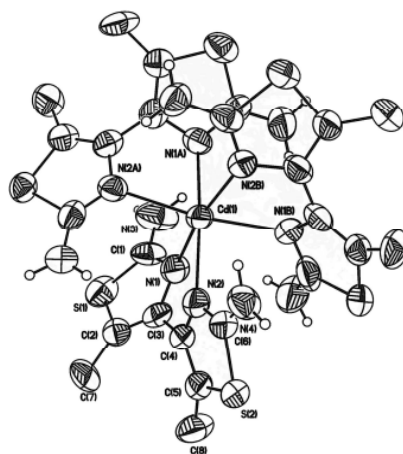


Fig.1. ORTEP drawing of complex showing the atom-labeling scheme and 50% probability level displacement ellipsoids

## 2. Materials and methods

### 2.1. Materials and physical techniques

All reagents and solvents for the synthesis and analysis were commercially available and used as received. Chemical analyses of carbon, hydrogen and nitrogen were performed by micro analytical methods using a Heraeus CHN-O-RAPID apparatus.  $^1\text{H}$  NMR spectra was recorded on a Bruker Avance DRS 500 spectrometer.  $^1\text{H}$  chemical shifts were determined relative to internal TMS. Infrared spectra were recorded on a Shimadzu model IR-60 spectrometer, from KBr pellets in the  $4000 - 370 \text{ cm}^{-1}$  range. The electronic absorption spectra were recorded on a Shimadzu UV-Vis 2100 recording spectrophotometer. Emission and excitation spectra of complexes were determined in DMSO solution using an Shimadzu- RS-5000 fluorescence spectrum photometer at room temperature. The measurements were performed using a PL- STA 1500 Thermal / Sciences in static air atmosphere, with  $\alpha\text{-Al}_2\text{O}_3$  as the reference compound, at a heating rate of  $5 \text{ K/Min}$ . In a ceramic crucible, 200 mg samples were contained. Melting point was measured on an Electrothermal 9100 apparatus.

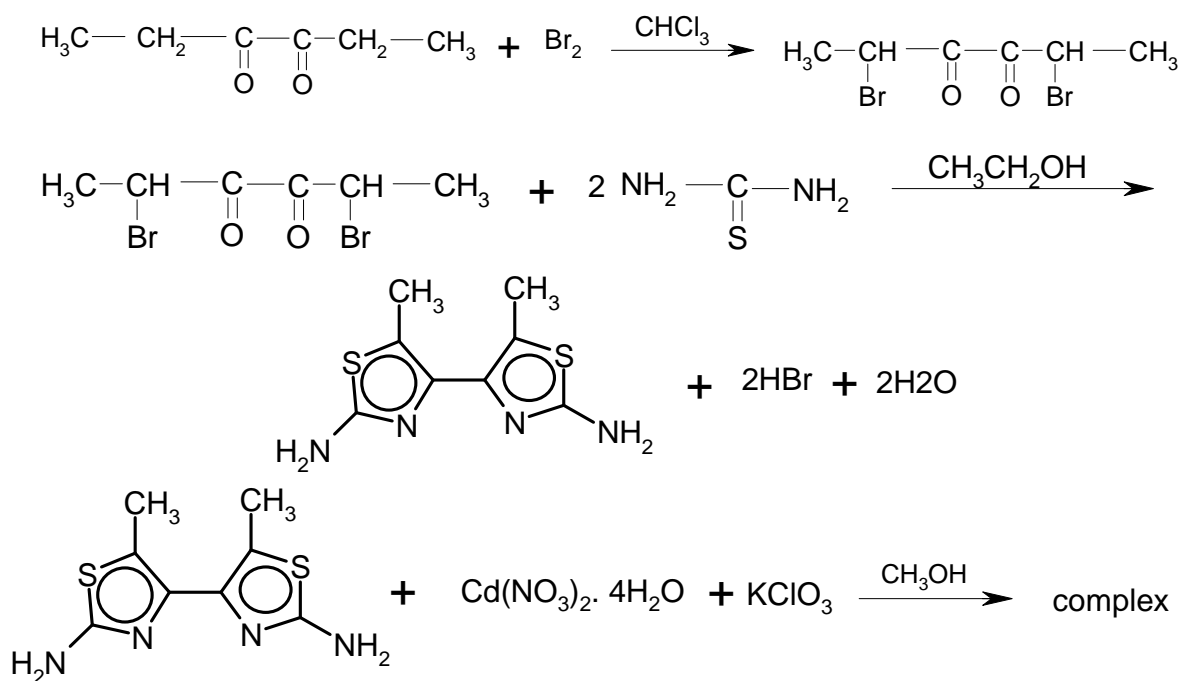
**Table 1.** Crystal data and structure refinement for  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$

<b>Empirical formula</b>	$\text{C}_{24}\text{H}_{30} \text{ Cd Cl}_2\text{N}_{12}\text{O}_6\text{S}_6$
<b>Formula weight</b>	958.26
<b>Temperature</b>	120(2) K
<b>Wavelength</b>	0.71073
<b>Crystal system</b>	cubic
<b>space group</b>	P -43n
<b>Unit cell dimensions</b>	a = 18.8817(6) Å, $\alpha = 90^\circ$ b = 18.8817(6) Å, $\beta = 90^\circ$ c = 18.8817(6) Å, $\gamma = 90^\circ$
<b>Volume</b>	6731(4) Å <sup>3</sup>
<b>Z</b>	8
<b>Density (calculated)</b>	1.891 Mg/m <sup>3</sup>
<b>Absorption coefficient</b>	1.242 mm <sup>-1</sup>
<b>F (000)</b>	3872
<b>Crystal size</b>	0.30 x 0.24 x 0.21 mm <sup>3</sup>
<b>Theta range for data collection</b>	4.45 to 28.26°
<b>Index ranges</b>	-18 ≤ h ≤ 25, -24 ≤ k ≤ 25, -15 ≤ l ≤ 25
<b>Reflections collected</b>	34751
<b>Final R indices [ with I &gt; 2σ(I) ]</b>	R1 = 0.0585, wR2 = 0.1144 [for 1486 refl]
<b>Completeness to theta</b>	96.9 %
<b>Absorption correction</b>	None
<b>Max. and min. transmission</b>	0.7804 and 0.7069
<b>Refinement method</b>	Full-matrix least-squares on F <sup>2</sup>
<b>Data / restraints / parameters</b>	2710/0/160
<b>Goodness-of-fit on F<sup>2</sup></b>	1.021
<b>R indices (all data)</b>	R1 = 0.1069, WR2 = 0.1286
<b>Largest diff. peak and hole</b>	0.788 and -0.847 e Å <sup>-3</sup>

Crystallographic data of  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$  are given in Table 1. X-ray diffraction measurements were performed at low temperature (120 K) using a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo  $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\varphi$ - $\omega$  scan technique. Empirical absorption corrections were applied using program SADABS. The structure were solved by direct methods and subsequent Fourier differences and refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon and nitrogen atoms were positioned geometrically, with  $U_{\text{iso}}$  values derived  $U_{\text{eq}}$  values of the corresponding carbon and nitrogen atoms. The structures of the title compounds were refined with SHELXL-97[35-37]. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of Xpert company with mono chromatized Cu  $K_\alpha$  radiation. The crystallite sizes of selected samples were estimated using the sherrer method. The samples were characterized with a scanning electron microscope with gold coating.

## 2.2. Preparation of $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$

The reaction of 2,5-dibromo-3,4-hexandion and thiourea leads to compound 2, 2'-diamino-5,5'-dimethyl-4,4'-bithiazolium dibromide monohydrate  $[(\text{C}_4\text{H}_6\text{N}_2\text{S})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$  [38]. This compound was neutralized with NaOH solution (1 M) and gives 2, 2'-diamino-5,5'-dimethyl-4,4'-bithiazole as the ligand then recrystallized from  $\text{CHCl}_3$ . Since the ligand is easily oxidizable in the air, so the following procedures must be in nitrogen atmosphere (Scheme 1).



Sch.1. The reaction of 2,5-dibromo-3,4-hexandion and thiourea

Analysis for  $C_8H_{10}N_4S_2$ : C, 42.50 (calcd.: C, 42.47); H, 4.25(4.42); N, 24.70(24.77)%. IR (KBr,  $cm^{-1}$ ):  $\nu(N-H)$  3305 (s)-3420 (m),  $\nu(C-H)_{al}$  2905 (m),  $\nu(C=C)$  1683 (m),  $\nu(C=N)$  1523 (vs),  $\nu(C-S-C)$  753 (m),  $\nu(C=S)$  627 (w).  $^1H-NMR$  ([D6]DMSO, 25°C, TMS)  $\delta$ : 6.5 (4H, 2NH<sub>2</sub>), 2.2 (6H, 2CH<sub>3</sub>).  $^{13}C-NMR$  ([D6]DMSO, 25°C, TMS)  $\delta$ : 164.1, 117.6, 114.1, 11.83. UV- Vis in DMSO ( $\lambda_{max}$ , nm): 229.5.

The complex was prepared by reacting a methanolic solution of  $Cd(NO_3)_2 \cdot 4H_2O$  (0.1542 g, 0.5 mmol) with a methanolic solution of 2,2'-diamino-5,5'-dimethyl-4,4'-bithiazole (0.226 g, 1 mmol) and excess of  $KClO_3$ . After standing 15 days at room temperature, yellow crystals were obtained, filtered and washed with methanol and cold ether and dried in vacuum. The complex is soluble in DMSO and insoluble in water, methanol and  $CHCl_3$ .

Analysis for  $C_{24}H_{30}CdCl_2N_{12}O_6S_6$  (958.26): C, 30.10(Calc. C, 30.05); H, 3.10 (3.13); N, 17.49 (17.53) %. IR data ( $cm^{-1}$ ):  $\nu(N-H)$  3395 (s)-3175 (s),  $\nu(C-H)_{al}$  2895 (m),  $\nu(C=C)$  1610 (s),  $\nu(C=N)$  1510 (s),  $\nu$ (Skeletal vibration) 1418 (w) and 1334 (s),  $\nu(Cl-O)$  962 (s), 930(w),  $\nu(C-S-C)$  747 (w),  $\nu(C=S)$  619 (m),  $\nu(Cd-N)$  480 (w).  $^1H$  NMR ([D6]DMSO, 25°C, TMS)  $\delta$ ppm: 7.0 (4H, 2NH<sub>2</sub>), 2.4 (6H, 2CH<sub>3</sub>).  $^{13}C$  NMR ([D6]DMSO, 25°C, TMS)  $\delta$ ppm: 170.9, 117.1, 114.0, 12.6.  $^{113}Cd$  NMR { $^1H$ } ([D6]DMSO, 25°C)  $\delta$ ppm: 42.3. UV- Vis in DMSO ( $\lambda_{max}$ , nm): 283.

### 2.3. Preparation of CdO-CdS nanocomposite

The  $[Cd(DADMBTZ)_3](ClO_3)_2$  was calcinated at 600°C under air atmosphere for 2h into an alumina boat. The whole organic components were combusted and CdO-CdS nanocomposite was produced.

## 3. Results and discussion

The reaction of  $Cd(NO_3)_2 \cdot 4H_2O$  with DADMBTZ in 1:2 ratio in the presence of an excess amount of potassium chlorate leads to the title complexes (Figure 1).

The IR spectrum of complex shows the bonds at 1418 and 1334  $cm^{-1}$  for skeletal vibration of bithiazole ring suggesting that the coordination has occurred through the ring nitrogen atom of bithiazole [24]. The strong absorption bands at 962, 930  $cm^{-1}$  are assigned to  $\nu(ClO_3^-)$  in complex. The comparison of  $^1H$  NMR in compound free ligand with the ones of the complexes represent a shift for the amine group from 6.5 for the ligand to 7.0 for the complex. A comparison of  $^{13}C$  NMR spectra of complex and the free ligand shows the carbon atoms in the thiazole rings, among the donor nitrogen atom, sulfur atom and amine group, shift to down field from 164.1 ppm in free ligand to 179.9 ppm in complex. The Cd complex shows two singlets in its  $^{113}Cd$  NMR spectrum with a chemical shift at 42.3 ppm, which is very different from our expectation for CdN6 environments. Maybe this is relevant to ligand dissociation in the solution.

The UV-Vis spectra of compounds in DMSO display intense absorption bands 229.5 for free ligand, 283 nm for complex, respectively (Table 3), indicating that electronic transitions are mostly  $\pi$  to  $\pi^*$ , maybe assigned to interligand charge transfer transitions (Figure 4).

The Cd(II) complex with its metal geometry (being bound to six nitrogen atoms of three equal bidentate bithiazole ligands) is six coordinate (Figure 1). In each ligands the two nitrogen atoms are coordinated to the Cd(II) in center, have very slightly different bond length (2.302(3) Å and

2.303(3) Å). The three ligands in complex act as a bidentate ligand which leads to the five-membered chelate rings, with the same internal angles 72.6(3)° for N-Cd-N.

The most relevant bond lengths and angles are given in Table 2. The ligand DADMBTZ acts as bidentate in complex to form a tris-chelate complex with C<sub>3</sub> symmetry in coordination polyhedron. Unit cell packing of compound represents in Figure 2.

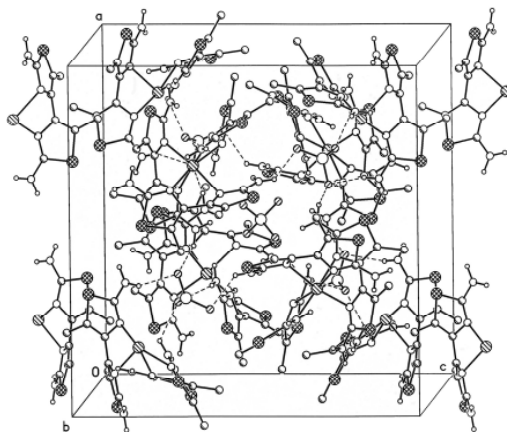


Fig.2. A view of unit cell of complex

There are two ClO<sub>3</sub><sup>-</sup> anions in compound which are symmetrically independent and have some differences in their bond lengths and angles. Both of ClO<sub>3</sub><sup>-</sup> anions are hydrogen bonded to 4 cations in its neighborhood [Cd(DADMBTZ)<sub>3</sub>]<sup>2+</sup> via N(3)-H(3B)...O(1) hydrogen bond (N(3)...O(1) = 2.960 Å), (Figure 3). The other two ClO<sub>3</sub><sup>-</sup> anions have the occupancy factor of 0.5. In complex, N-H...O hydrogen bonds make a 3-D network.

Comparison of free ligand with that in complex represents the effect of coordination. For example the range of C-N in complex is 1.233(5)-1.348(5) Å, is shorter than those in free ligand (1.393(4)-1.399(4) Å), and also C(3)-C(2) = 1.439(5) Å, in complex is shorter than that of free ligand (1.481(4)-1.485(4) Å).

The spatial distances between the two bithiazole nitrogen atoms in free ligands is almost 3.079 Å (two nitrogen atoms are trans with each other) whereas in complex these distances are about 2.725 Å in two DADMBTZ ligands (two nitrogen atoms are cis).

The torsion angle of DADMBTZ in free ligand, ∠N(3)-C(4)-C(4')-N(3'), is about 59.6(4)°, and in complex ∠N(1)-C(3)-C(4)-N(2) = 37.1(4), which shows a deviation from planarity is formed by the two thiazole rings of bithiazoles.

The C-N bond length in the bithiazole rings in free ligand are at the range 1.393(4)-1.399(4) Å, and the title complex 1.233(3)-1.3524(3) Å, which are shorter than the single bond length of 1.48 Å and longer than the typical C=N distances of 1.28 Å indicating partial double-bond character. This can be interpreted in terms of conjugation in the heterocycle. On the other hand, the bond length range of N(3)-C(1) = 1.291(10) Å, N(4)-C(6) = 1.302(10) Å in complex, is shorter than that

of in normal C-N single bond, which confirms the nitrogen of amido is involved in the delocalization system.



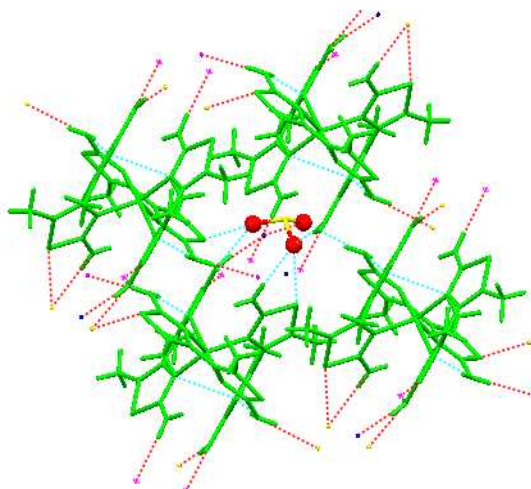


Fig.3. Interaction of one  $\text{ClO}_3^-$  with 4 neighboring  $[\text{Cd}(\text{DADMBTZ})_3]^{2+}$  cations

No emission originating from metal-centered and MLCT or LMCT excited states are expected for the Cd(II) complex, since the Cd(II) ions are difficult to oxidize or reduce due to their  $d^{10}$  configuration. Thus, the emission observed (Table 3) in the complex is tentatively assigned to the  $(\pi-\pi^*)$  interligand fluorescence. The luminescence spectra of the all compounds in DMSO exhibit an emission at 298 K upon excitation at 250 nm (Figure 4).

Table 2. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$

<b>Cd(1)-N(1)</b>	2.302(7)	<b>Cd(1)-N(2)</b>	2.303(8)
<b>Cd(1)-N(1)#1</b>	2.302(7)	<b>Cd(1)-N(2)#1</b>	2.303(8)
<b>Cd(1)-N(1)#2</b>	2.302(7)	<b>Cd(1)-N(2)#2</b>	2.303(8)
<b>N(1)-C(1)</b>	1.314(2)	<b>C(2)-C(3)</b>	1.311(2)
<b>N(1)-C(3)</b>	1.339(2)	<b>C(2)-C(7)</b>	1.453(2)
<b>N(2)-C(6)</b>	1.233(2)	<b>C(4)-C(3)</b>	1.439(2)
<b>N(2)-C(4)</b>	1.410(4)	<b>C(5)-C(8)</b>	1.477(2)
<b>N(3)-C(1)</b>	1.348(9)	<b>N(4)-C(6)</b>	1.302(2)
<b>N(2)#1-Cd(1)-N(2)#2</b>	105.33(2)	<b>N(2)#2-Cd(1)-N(1)</b>	85.0(2)
<b>N(2)#1-Cd(1)-N(2)</b>	105.33(2)	<b>N(2)#2-Cd(1)-N(1)#2</b>	72.6(3)
<b>N(2)#1-Cd(1)-N(1)</b>	169.6(2)	<b>N(2)#1-Cd(1)-N(1)#1</b>	72.6(3)
<b>N(2)#2-Cd(1)-N(2)</b>	105.33(2)	<b>N(2)-Cd(1)-N(1)#2</b>	169.6(2)

#1 y, z, x

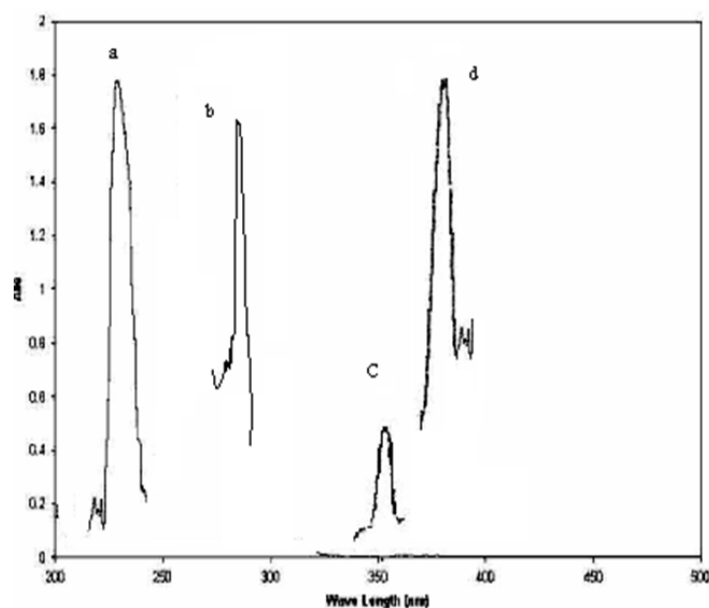
#2 z, x, y

Table 3. Absorption ( $\lambda_{\text{abs}}$ ), emission ( $\lambda_{\text{em}}$ ) band maxima<sup>a</sup> of compound

Compound	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm} (298 \text{ K})$
$[(\text{C}_4\text{H}_6\text{N}_2\text{S})_2]$	229.5	360
$[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$	286	370

<sup>a</sup> Solvent: DMSO.

The thermal stability of complex  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$  was investigated in static air atmosphere from ambient to  $700^\circ\text{C}$  and studied by thermal gravimetric (TG) and differential thermal analysis (DTA) (Figure 5). Compound at  $180^\circ\text{C}$  begins to decompose. Decomposing of chlorate anions takes place at  $191.2^\circ\text{C}$  [weight loss: 17.59, calcd: 19.92 %] with one exothermic effect. The weight loss of 69.1% from  $250^\circ\text{C}$  to  $650^\circ\text{C}$  is equivalent to the loss of three coordinated DADMBTZ molecules [calcd: 70.75 %] with three exothermic effect at  $262.9$ ,  $347$  and  $547^\circ\text{C}$ . The solid residue formed at around  $670^\circ\text{C}$  is suggested to be CdO-CdS nanocomposite. Figure 6 shows the X-ray powder diffraction pattern of CdO-CdS nanocomposite after calcinations of compound  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$ . This pattern is quite the same and in agreement with the typical structure of CdO and hexagonal CdS diffraction (JCPDS 77-2306) and CdO (JCPDS 05-0640). Sharp diffraction peaks indicate good crystallinity of CdO-CdS nanocomposite prepared from compound  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$ . The broadening of the peaks indicated that the composite was of nanometer scale. Estimated from the Scherrer formula ( $D=0.891 \times \lambda/\beta \cos\theta$ ), the average size of the particles were 43 nm for CdO - CdS nano composite after calcination of compound



**Fig.4.** Electronic absorption of ligand DADMBTZ (a), Electronic absorption of complex (b) Absorption:  $c=1.36 \times 10^{-4} \text{ mol l}^{-1}$ , DMSO,  $d=1 \text{ cm}$  for ligand and complex. The fluorescence spectra of ligand (c) and complex (d) in DMSO solution. Room temperature,  $\lambda_{\text{exc}}=250 \text{ nm}$



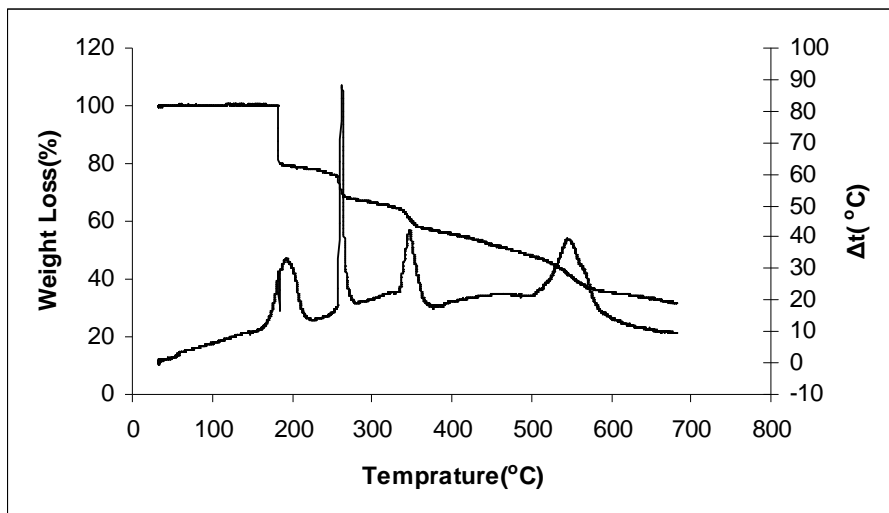


Fig.5. Thermal behavior of complex

$[Cd(DADMBTZ)_3](ClO_3)_2$  in agreement with that observed from SEM images. The X- ray diffraction pattern and SEM picture of heated sample are shown in Figure 6 and Figure 7.

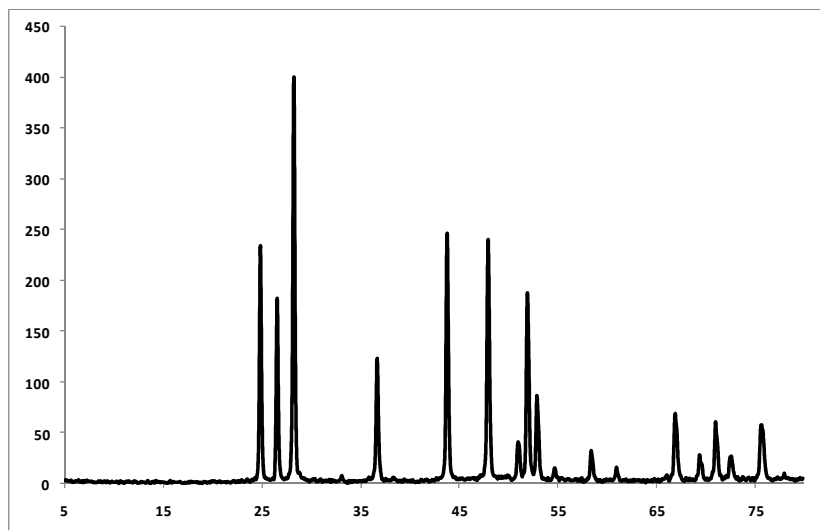
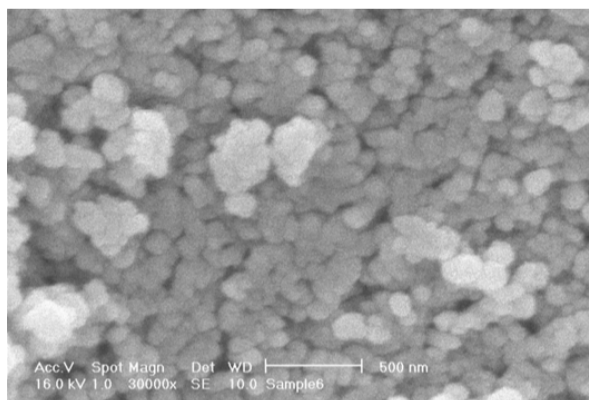


Fig.6. XRD patterns CdO-CdS nanocomposite



**Fig.7.** SEM image of CdO-CdS nanocomposite

#### 4. Conclusion

In summary, new bithiazole Cd(II) complex  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$  has been synthesized. Calcination of this compound produced CdO-CdS nanocomposite. This study demonstrates that bithiazole complexes may be suitable precursors for the preparation of nanoscale composites. Synthesis of nanocomposite of CdO-CdS, making use of this method, is a novel approach in the literature.

#### 5. Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited with the Cambridge Crystallography Data Centre, CCDC Nos. 611091 for  $[\text{Cd}(\text{DADMBTZ})_3](\text{ClO}_3)_2$ . Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@cdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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