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Six-coordinate cadmium(II) complex containing a bridging dithiolate ligand: synthesis, crystal structure and antifungal activity study

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ABSTRACT
A mixed-ligand polymeric metal complex of Cd(II) has been prepared by reactions of Cd(NO₃)₂·4H₂O with 1,3-diaminopropane (tn) and potassium salt of 1,1-dicyanoethylene-2,2-dithiolate and characterized on the basis of spectroscopy and single-crystal X-ray diffraction analysis. Single-crystal X-ray diffraction analysis reveals that the Cd(II) complex crystallizes in monoclinic space group P2₁/n with distorted octahedral coordination geometry. The Cd(II) complex was screened in vitro against fungal pathogens such as Synchytrium endobioticum, Pyricularia oryzae, Helminthosporium oryzae, Candida albicans (ATCC10231), and Trichophyton mentagrophytes by the disk diffusion method. The biological testing data of the primary ligand K₂i-MNT·H₂O and [Cd(tn)(i-MNT)]ₙ indicate that the complex exhibits fungistatic antifungal activity, whereas K₂i-MNT·H₂O has no activity. The fungicidal properties of [Cd(tn)(i-MNT)]ₙ showed that the cadmium complex was more bioactive than the parent ligand.

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1. Introduction
Coordination polymers of Cd(II) are of interest due to their structures and prospective applications in catalysis, adsorption, magnetism, luminescence, etc. [1]. Both inorganic and organic components...
permit incorporation of useful properties within a single complex, making it possible to create multifunctional materials. With the help of appropriate metal ions and organic linkers, coordination polymers with various architectures, such as 1-D chains, ladders [2], 2-D grids [3], and 3-D networks [4a], can be obtained. For coordination polymers, Cd$^{2+}$ ions are attractive due to their “softness” and opportunity to obtain Cd(II) compounds with the coordination numbers 4, 5, and 6. Although Cd(II) is a d$^{10}$ ion, different coordination geometries are observed, including coordination numbers from 2 to 8. Owing to the larger size, Cd(II) shows coordination number six more easily than Zn(II) [4b].

Cadmium demands special attention due to industrial uses of its compounds and also to inherent toxicity and health effects [5, 6]. Cd$^{2+}$ is able to substitute Zn$^{2+}$ in the active site of Zn-enzymes and affect with the metabolism of Ca$^{2+}$. Cadmium shows resistance to corrosion, excellent electric conductivity, and low-melting point even though its discharge in the environment can cause ecological and health effects [7]. Notable uses of cadmium are Ni–Cd batteries (about 70% of total produced Cd), pigments in ceramics, glasses, paper, plastics, artists colors (13%), coatings on steel, aluminum, and other nonferrous metals (8%) and stabilizers for polyvinyl chloride, related polymers (7%), and specialized alloys (2%) [8].

Proper linkers are crucial in building coordination polymers. Chelating ligands containing N and S donors have different ways in which they are bonded to metal ions. There has been much interest in coordination compounds of unsaturated sulfur chelating ligands, 1,1-dicyanoethylene-2,2-dithiolate, and related molecules owing to interesting chemical properties and possible applications [9a–c]. 1,1-Dicyanoethylene-2,2-dithiolate is a versatile ligand which can chelate as well as bridge various compounds to construct discrete and extended structures, depending on the metal ion and secondary ligand. Due to its flexibility, it displays variable coordination modes resulting from geometry restrictions and twisted conformations, leading to different structures [9d–e]. The molecule is a powerful candidate for creating coordination polymers with novel structures. Biologically active ligands are attractive for uses in medicine, food industry, catalysis, etc. [10]. Hence, transition metal complexes containing 1,1-dicyanoethylene-2,2-dithiolate ligands attract research owing to their rich coordination chemistry and established and potential applications.

Our focus deals with transition metal complexes containing dithiolate and diamine ligands and exploring the antifungal activity and luminescence property of the synthesized complex. In our previous study [11], the interaction of dithiolate with different metal ions has been studied. There is no report on mixed-ligand complexes of Cd(II) involving 1,1-dithiolate, 1,3-diaminopropane (tn). Here, we report the synthesis, characterization, and antifungal activities of a new mixed-ligand polymeric complex of cadmium(II) [(Cd(tn)i-MNT)$_n$ (1)] with nitrogen and sulfur donors. One of our aims is to study the coordination properties of the N and S donors in i-MNT$^{2-}$.

2. Experimental

2.1. Materials and methods

All chemicals were of E. Merck of GR or equivalent grade and used without purification. Infrared spectra were recorded in KBr (4000–400 cm$^{-1}$) and in CsI (600–50 cm$^{-1}$) on a Bomen DA-8 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DRX 300 FT-NMR spectrophotometer. K$_2$i-MNT·H$_2$O was prepared by a known literature procedure [12]. Crystal data were solved using the direct methods program SHELXS-97 [13a]. All nonsolvent heavy atoms were located using difference Fourier syntheses. The structures were refined against $F^2$ with SHELXL [13b–c], in which all data collected was used counting negative intensities. All nonsolvent heavy atoms were refined anisotropically.

2.2. Synthesis of mixed-ligand polymeric complex 1

Cd(NO$_3$)$_2$·4H$_2$O (0.005 M) in 50 mL distilled water was added slowly to 1,3-diaminopropane (tn) (0.03 M) with constant stirring with change from colorless to milky white. Glacial acetic acid of 1 mL was added dropwise to the reaction mixture to soluble milky white precipitate. Colorless solution was obtained
after adding 1 g ammonium acetate to the reaction mixture. Stirring was further continued for 20 min. To this reaction mixture, K₂i-MNT·H₂O (0.005 M) in 20 ml water was added with stirring resulting in light yellow precipitate. After additional 1.5-h stirring, the reaction mixture was washed with water followed by treatment with ethyl alcohol and diethyl ether and finally kept in a desiccator after drying in air to obtain 1.

C₇H₁₀CdN₄S₂: % of yield: 80%, m.p.: 270, Anal. Calcd: C, 25.73; H, 3.09; Cd, 34.41; N, 17.15; S, 19.63. Anal. found: C, 25.71; H, 3.08; Cd, 34.40; N, 17.14; S, 19.61; 1H NMR (DMSO d₆): δ 3.11 ppm (br, s), δ 2.83 ppm, fT-IR (KBr): 3126–3425, 2198, 1631, 966, 935 cm⁻¹.

3. Results and discussion

From previous work, Zn(NO₃)₂·6H₂O reacted with 1,3-diaminopropane (tn) and K₂i-MNT·H₂O generating the linear 1-D polymeric [Zn(tn)(i-MNT)]ₙ, where 1,3-diaminopropane bridges [11 g]. We now examine the reactions of Cd(NO₃)₂·4H₂O with 1,3-diaminopropane (tn) and K₂i-MNT·H₂O. The complex is nearly insoluble in water and common organic solvents but is soluble in highly coordinating solvents such as DMF and DMSO giving colored solutions. The complex is stable at room temperature. The synthesis of complex 1 (CP 1) was accomplished as shown in Scheme 1.

### 3.1. IR and NMR data

The IR and ¹H NMR spectra are in agreement with crystal structure of related mixed-ligand complex of Cd(II). The infrared spectra of ligand and 1 were recorded from 400 to 4000 cm⁻¹. In the FT-IR spectrum of 1 (KBr disks), a strong band at 2198 cm⁻¹ is due to the νCN stretch. 1 exhibits a broad band at 3126–3425 cm⁻¹ attributed to ν(N–H) (asymmetric and symmetric) stretches. The N–H bending (scissoring) vibration is observed at 1631 cm⁻¹ for 1, lower than the free 1,3-diaminopropane band (1636 cm⁻¹).
These shifts to lower frequency clearly suggest amino nitrogen coordination to metal ion. In the IR spectrum of K₂i-MNT, a band at 960 cm⁻¹ with a shoulder at 985 cm⁻¹ is observed due to (=CS₂) group. The corresponding band and shoulder in the mixed-ligand complex shifted to lower frequencies, 935 and 966 cm⁻¹. This implies coordination of metal to thiolate. The ν(C–S) band in 1 at 871 cm⁻¹ is higher than that of K₂i-MNT at 860 cm⁻¹. The bands in the region 617–485 cm⁻¹ are assigned to the Cd–S and Cd–N vibrations [14a].

The 1H NMR spectrum was carried out in DMSO d₆. Complex 1 shows a broad NMR signal at δ 3.11 ppm suggesting the presence of amine protons. Three methylene protons were observed at δ 2.83, as a broad singlet, which indicates the formation of metal complex.

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

| Bond                  | Length (Å)   | Angle (°)  |
|-----------------------|--------------|------------|
| Cd–N(4)               | 2.2601 (18)  | N(4)–Cd–N(3) 91.33 (7) |
| Cd–N(3)               | 2.2926 (19)  | N(4)–Cd–S(2)#1 111.93 (5) |
| Cd–S(2)#1             | 2.6129 (5)   | N(3)–Cd–S(2)#1 151.28 (5) |
| Cd–N(1)#2             | 2.7155 (5)   | N(4)–Cd–S(1) 97.37 (5) |
| Cd–S(1)#1             | 2.7246 (19)  | N(3)–Cd–S(1) 100.91 (5) |
| Cd–S(1)#1             | 2.7725 (5)   | S(2)#1–Cd–S(1) 92.846 (16) |
| S(1)–C(1)             | 1.740 (2)    | N(4)–Cd–N(1)#2 78.13 (6) |
| S(1)–Cd#1             | 2.7725 (5)   | N(3)–Cd–N(1)#2 79.61 (6) |
| S(2)–C(1)             | 1.728 (2)    | S(2)#1–Cd–N(1)#2 88.64 (4) |
| S(2)–Cd#1             | 2.6129 (5)   | S(1)–Cd–N(1)#2 175.49 (4) |
| N(1)–C(3)             | 1.151 (3)    | N(4)–Cd–S(1)#1 170.17 (5) |

These shifts to lower frequency clearly suggest amino nitrogen coordination to metal ion. In the IR spectrum of K₂i-MNT, a band at 960 cm⁻¹ with a shoulder at 985 cm⁻¹ is observed due to (=CS₂) group. The corresponding band and shoulder in the mixed-ligand complex shifted to lower frequencies, 935 and 966 cm⁻¹. This implies coordination of metal to thiolate. The ν(C–S) band in 1 at 871 cm⁻¹ is higher than that of K₂i-MNT at 860 cm⁻¹. The bands in the region 617–485 cm⁻¹ are assigned to the Cd–S and Cd–N vibrations [14a].

The ¹H NMR spectrum was carried out in DMSO d₆. Complex 1 shows a broad NMR signal at δ 3.11 ppm suggesting the presence of amine protons. Three methylene protons were observed at δ 2.83, as a broad singlet, which indicates the formation of metal complex.

### 3.2. X-ray crystallography

The i-MNT²⁻ may display various coordination modes, coordinating through sulfur and nitrogen only [14b], or through both sulfur and nitrogen. Therefore, i-MNT²⁻ can be used as a useful building block for new polymeric structures. Interesting physical properties are realized by cadmium complexes. Single crystal of 1 was mounted on a glass fiber for X-ray diffraction analysis; the resulting compound crystallizes in the monoclinic space group, P2₁/n (see Table 1). The crystal data, data collection parameters,
and metric analyses are listed in Table 1. The crystal structure of 1 shows 1,3-diaminopropane and 1,1-dicyanoethylene-2,2-dithiolate (i-MNT$^{2-}$) assisted 2-D polymer. The SCHAKAL plot with atom numbering scheme is shown in Figure 1.

The structure of 1 was solved in the space group $P2_1/n$. Figure 1 shows the six-coordinate cadmium center. Selected bond distances and angles are listed in Table 2. The cadmium has a distorted octahedral coordination geometry with the bond angles deviating from 90° to 180° ($N(4)$–Cd–$N(3)$ is 91.33°, $S(1)$–Cd–$N(1)\#2$ is 175.49°). Both thiolate $S$, $N$ and amine $N$ are involved in coordination. Cd(II) is coordinated by three nitrogens ($N3$ and $N4$) of 1,3-diaminopropane ($N1B$) of i-MNT$^{2-}$ and $S1A$ and $S2A$ of i-MNT$^{2-}$. The Cd–$N$ bond distances are Cd–$N(4)$ 2.26, Cd–$N(3)$ 2.29, and Cd–$N(1)\#2$ 2.72 Å, respectively. Nitrogens of 1,3-diaminopropane show comparable Cd–$N$ bond lengths to those reported for cadmium(II) complexes [15]. The cadmium(II) is coordinated by both the nitrogens of 1,3-diaminopropane forming six-membered chelate rings. Dimeric units are linked by Cd–N1 intermolecular bonds. Nitrogens of i-MNT$^{2-}$ executes 1,1-dicyanoethylene-2,2-dithiolate assisted 2-D polymeric assembly as shown in Figure 2.

Cd–$N(1)$ distance is 2.72 Å, significantly longer than reported in the literature [16] which makes distorted octahedral geometry of the cadmium metal complex. The observation may be attributed to the $\pi$ electron delocalization on the i-MNT$^{2-}$ ligand, and the somewhat long $C=C$ bond distance of 1.39 Å.

Figure 2. 2-D layer-like structure of $\{[\text{Cd}(\text{tn})(i-\text{MNT})]_n\}$.

Scheme 1. Synthesis of 1.
Of the two Cd–S distances compared, the i-MNT2− ligand chelated {Cd–S(2)#1} is shorter (2.61 Å) than {Cd–S(1)} (2.71(5) Å). Cd–S bond distances are longer than those of bridging thiolate in [Cd4(μ-SPh)8] (av. 2.538(3) Å) [17], [Cd(SPh)2(tmdp)]n (av. 2.444(5) Å) and [Cd(SC6H4Me4)2(tmdp)]n (av. 2.438 (5) Å) [18].

Previous work on {[Zn(tn)(i-MNT)}n showed that only nitrogens of 1,3-diaminopropane are coordinated with the zinc generating a 1-D polymeric structure. The nitrogens of i-MNT2− do not coordinate with zinc. In the present case, nitrogens of both i-MNT2− and 1,3-diaminopropane coordinate with the cadmium generating a 2-D polymeric structure shown in figure 2. The two adjacent cadmium(II) ions are joined by two bridging sulfurs (S1 and S1A) from different i-MNT2− ligands into a Cd2S2 parallelogram, leading to the dinuclear unit. The Cd–Cd bond distance is 3.79 Å, slightly shorter than normal Cd–Cd single-bond distances (3.90–3.87 Å) [19].

The crystal structure of the complex is stabilized by hydrogen bonds, between 1,3-diaminopropane and i-MNT2− (N(3)–H(3N1)⋯S(2) and N(4)–H(4N1)⋯S(1)#4) owing to strong electron-withdrawing groups.

### 3.3. Antifungal activity study of 1

Qualitative determination of the in vitro antifungal activity of synthesized metal complex was done by the disk diffusion method [20, 21]. The antifungal properties of the ligand and its cadmium complex were investigated against plant and animal fungi, namely Synchytrium endobioticum (wild type), Pyricularia oryzae (wild type), Helminthosporium oryzae (wild type), Candida albicans (ATCC10231), Trichophyton mentagrophytes (clinically isolated), and matched with K2i-MNT and standard sample Griseofulvin (10 μg/disk). In this study, the strains were maintained and verified on Sabouraud Dextrose agar.

In a typical disk diffusion process, a 20% (w/v) stock solution of each dry extract (1 and its primary ligand) was prepared in pure DMSO. For molds, suspensions of mature spores were acquired by gently washing the surface of solid media with a 0.05% (v/v) solution of Tween 80, and the resulting suspension was adjusted to 10⁶ spores ml⁻¹. Whatman No.4 filter paper disks (6 mm diameter) were positioned on the inoculated agar surfaces and soaked with 15 μl of stock solutions. Griseofulvin (10 μg/disk) disks were used as positive controls while pure DMSO (15 μl) was used as a negative control. The plates were observed after 96 h at 25 °C for molds. All tests were performed in triplicate. The results are gathered in Table 3.

Chelating ligands containing N, S, and O donors show broad biological activity. 1 showed fungicidal activity on the basis of its minimum inhibitory concentration (MIC) value against the fungi S. endobioticum, P. oryzae, and H. oryzae, whereas its primary ligand (K2i-MNT-H2O) showed no effect on fungi. The MIC value of the standard sample Griseofulvin is 0.1 mg ml⁻¹. 1 shows highest fungicidal activity against H. oryzae and shows no fungicidal activity against C. albicans and T. mentagrophytes. In our work, {[Zn(tn)(i-MNT)}n showed fungicidal activity [11 g] against the fungi P. oryzae only but 1 showed fungicidal activity against the fungi S. endobioticum, P. oryzae, and H. oryzae. A review of the literature indicates that generally coordination of an organic ligand to metal centers amplifies its antifungal activities [22] due to the greater lipophilic nature of the complex than the ligand [23]. A growth in lipophilicity and therefore improved diffusion in microbial membrane may be a prominent reason for

| Material (1 mg mL⁻¹) | P. oryzae | H. oryzae | S. endobioticum | C. albicans | T. mentagrophytes |
|----------------------|------------|-----------|-----------------|-------------|------------------|
| [Cd(tn)(i-Mnt)]n     | 07 (FC)    | 20        | 12 (FS)         | NE          | NE               |
| K2i-MNT·H2O         | NE         | NE        | NE              | NE          | NE               |
| Control (DMSO)       | NE         | NE        | NE              | NE          | NE               |
| Griseofulvin (10 μg/disk) | 0.1  | 0.1 | 0.3  | 0.2  | 0.4  |

Note: All readings are based on five replicates ± SEM; (NE) = No effect.
this activity improvement. Improved activity of 1 is of significance in medicine. The difference in the efficiency of 1 against different fungi depends either on the impermeability of the cells of the microbes or on changes in ribosome of microbial cells.

4. Conclusion

We report the synthesis and crystal structure of a new complex of Cd(II) with nitrogen and sulfur donors and its antifungal activity. The metal centers remain unchanged during these reactions, and no C–S bond cleavage took place, presumably due to delocalization of $\pi$ electrons in i-MNT$^{2-}$ and the metal complex is six-coordinate adopting a distorted octahedral geometry. Our work also demonstrates that 1,1-dicyanoethylene-2,2-dithiolate [i-MNT$^{2-}$ = {S$_2$C : C(CN)$_2$}] may serve as a building block for creation of new polymers, by utilizing the coordination power of the ligands at both S and N sites, as shown by the structure of [(Cd(tn)(i-MNT))$_n$. Antifungal activity of 1 is observed with significant activity compared to K$_2$i-MNT on S. endobioticum, P. oryzae, and H. oryzae and proved to be crucial for the growth-inhibitor effect. Cadmium complex has higher antifungal activity due to the presence of cadmium. These findings indicate that 1 has practical applications for the development of new antifungal medicine. Further exploration is in progress in our laboratory.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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