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Cd(II) complexation with 1,1-dithiolate and nitrogen donors: synthesis, luminescence, crystal structure, and antifungal activity study

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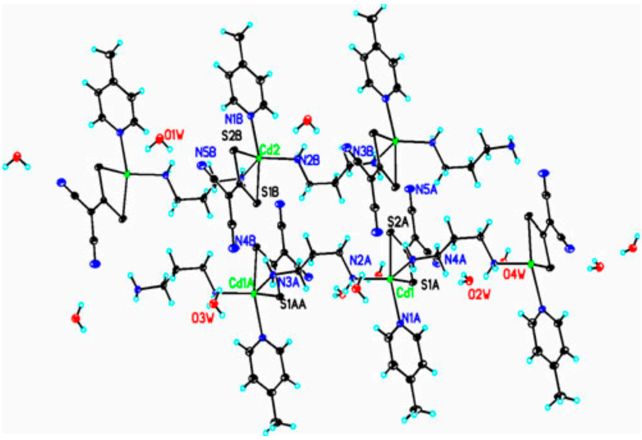

A new luminescent complex of Cd(II) with 1,1-dicyanoethylene-2,2-dithiolate [i-MNT^{2-} = {S_2C:C$(CN)_2$}$^{2-}$] has been synthesized and characterized on the basis of spectroscopy and single-crystal X-ray diffraction analysis. Single-crystal X-ray diffraction analysis reveals that the cadmium(II) complex is five coordinate in a 1-D polymer. Biological screening *in vitro* of the complex has been tested against five fungi *Synchytrium endobioticum*, *Pyricularia oryzae*, *Helminthosporium oryzae*, *Candida albicans* (ATCC10231), and *Trichophyton mentagrophytes* by the disk diffusion method. The antifungal activity of the complex of Cd(II) is significant compared to K_2iMNT on *S. endobioticum*, *P. oryzae*, *H. oryzae*, and *T. mentagrophytes* and proved to be crucial for the growth-inhibitor effect.

A new luminescent complex of Cd(II) with 1,1-dicyanoethylene-2,2-dithiolate [i-MNT^{2-} = {S_2C : C$(CN)_2$}$^{2-}$] with 1,3-diaminopropane (tn) and 4-methyl pyridine (γ-picoline) as secondary ligands has

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been synthesized and characterized on the basis of spectroscopy and single-crystal X-ray diffraction analysis. Single-crystal X-ray diffraction analysis reveals that cadmium(II) is five coordinate in a 1-D polymer. Biological screening effects *in vitro* of the synthesized complex has been tested against five fungi *Synchytrium endobioticum*, *Pyricularia oryzae*, *Helminthosporium oryzae*, *Candida albicans* (ATCC10231), and *Trichophyton mentagrophytes* by the disk diffusion method. A comparative study of inhibition zone values of K_2i-MNT·H_2O and {[Cd(tn)(iMNT)(4-MePy)]·4H_2O}$_n$ (**1**) indicates that the complex exhibits antifungal activity, whereas K_2i-MNT·H_2O became silent on *S. endobioticum*, *P. oryzae*, *H. oryzae*, *C. albicans (ATCC10231),* and *T. mentagrophytes*.

Keywords: Mixed ligand complex; Cd(II); 1,1-Dithiolate; Nitrogen donor; X-ray diffraction; Luminescence; Antifungal activity study

Introduction

Coordination compounds of cadmium are of interest due to industrial uses and also due to their inherent toxicity and health effects [1, 2]. Cadmium is used in many important industrial applications due to its resistance to corrosion, excellent electric conductivity, and low-melting point even though its discharge in the environment can cause ecological and health effects [1–3]. Cd(II) is linked to bone diseases, renal dysfunction, and gastrointestinal problems and cadmium and cadmium compounds are carcinogenic [4]. Cadmium is a catalyst in producing reactive oxygen species. It raises lipid peroxidation and also reduces antioxidants, glutathione, and protein-bound sulfhydryl groups. It stimulates the making of inflammatory cytokines [5, 6]. The foremost uses of cadmium are Ni–Cd batteries, cadmium stabilizers, cadmium pigments, cadmium alloys, cadmium coatings, and cadmium electronic compounds such as cadmium telluride (CdTe) [7]. Ni–Cd batteries which have wide-ranging applications are cost effective appropriate for high power applications, excellent low temperature and high temperature performance relative to other batteries. Cadmium sulfide is used as a yellow pigment. Cadmium is obtained as a byproduct during treatment of zinc, lead, and copper ores.

Chelating ligands containing N, S, and O donors display wide biological activity. The chemistry of cadmium resembles that of zinc and shows multipurpose coordination abilities, giving Cd^{2+} structures ranging from simple complexes to 1-D, 2-D, and 3-D polymeric architectures. Coordination polymers have attracted attention for interesting structures and potential uses in luminescence, magnetism, adsorption, catalysis, etc. [8]. Metal ion complexation enhances biological activities [9]. Interest in coordination chemistry increased by discovery of antibacterial, antifungal, and anticancer activities of several coordination compounds. Biologically active ligand-based metal complexes have potential use in medicine, food industry, catalysis, etc. [10]. Several research groups have studied coordination chemistry of cadmium for synthesis of new compounds of applied interest [11]. The bonding of cadmium with amine and thiolate is of keen interest in the context of its solid-state structure and biological activity. Cd(II) complexes with a CdS_2N_2 core have remained less explored [12]. Our earlier communications include studies on mixed ligand complexes of Ni(II), Cu(II), Zn(II), Cd(II), and Co(II) with 1,1-dicyanoethylene-2,2-dithiolate and some nitrogen bases [13]. There are no reports on mixed ligand complexes of Cd(II) involving 1,1-dithiolate, 1,3-diaminopropane (tn) and 4-methyl pyridine (γ-picoline). Here, we report the synthesis, characterization, luminescence, and antifungal activities of a new mixed ligand polymeric complex of cadmium(II), {[Cd(tn)(iMNT)(4-MePy)]·4H_2O}$_n$ (**1**) with nitrogen and sulfur donors.

Experimental

Materials and methods

All chemicals used 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_2i-MNT·H_2O was prepared by a known procedure [14]. Crystal data were solved using the direct methods program SHELXS-97 and the structure was refined against F^2 with SHELXL.

Results and discussion

Synthesis of {[Cd(tn)(iMNT)(4-MePy)]·4H_2O}$_n$ (1)

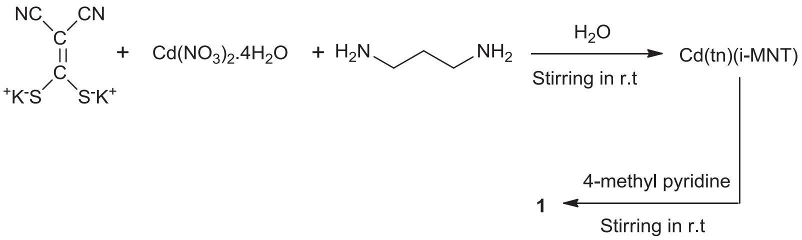
The synthesis of **1** was accomplished as shown in scheme 1.

$Cd(NO_3)_2 \cdot 4H_2O$ (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 (1 mL) was added dropwise to the reaction mixture to dissolve the 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, K_2iMNT·H_2O (0.005 M) in 20 mL water was added with stirring giving light yellow precipitate. After an additional 1.5 h stirring, the reaction mixture was filtered and the product washed with water followed by ethyl alcohol and diethyl ether and finally, kept in a desiccator after drying in open air to obtain Cd(tn)(iMNT), used for further reaction without characterization. To obtain **1**, Cd(tn)(iMNT) (0.8 g) was dissolved in 4-methyl pyridine (γ-picoline) (30 mL) with stirring and stirring was continued for further 40 min. After that the reaction mixture was filtered and the filtrate was allowed to stand at room temperature. Yellow crystals of **1**, stable at room temperature and air, were obtained over a period of 7 days.

The complex is almost insoluble in water and common organic solvents but is soluble in highly coordinating solvents such as DMF giving colored solutions. The molar conductance data in DMF solution reveal that the complex is a nonelectrolyte.

IR and NMR studies of 1

Formation of **1** by reaction of K_2(i-MNT) with $Cd(NO_3)_2 \cdot 4H_2O$, 1,3-diaminopropane and 4-methyl pyridine was indicated by IR and ^1H NMR spectra. Coordination polymer **1**



Scheme 1.

exhibits a group of broadbands at 3153–3454 cm^{-1} attributed to ν(N–H) (asymmetric and symmetric) stretches. The broadness indicates formation of hydrogen bonds. The N–H bending (scissoring) vibration is observed at 1590 cm^{-1} for **1**, lower than free 1,3-diaminopropane (tn) (1636 cm^{-1}). Shift to lower frequency suggests the amino nitrogen of 1,3-diaminopropane (tn) coordinates to cadmium. IR spectra of **1** (KBr disks) show a band at 2187 cm^{-1} corresponding to the stretching modes of cyano. The band at 1439–1457 cm^{-1} is assigned to an olefinic C=C stretch. In the IR spectrum of K_2i-MNT, a band at 960 cm^{-1} with a shoulder at 985 cm^{-1} is observed due to =CS_2. The corresponding band and shoulder are found at 947 and 999 cm^{-1}. The ν(C–S) band for **1** is 880 cm^{-1}, nearly the same as that of K_2i-MNT (860 cm^{-1}).

^{1}H NMR spectrum, which usually provides a good indication of complex formation, was carried out in d6-DMSO. **1** shows NMR signals at δ 8.40 ppm. The large downfield shifts clearly suggest the amino nitrogen of 1,3-diaminopropane coordinates to cadmium as indicated by the IR spectra. 4-Methyl pyridine ring hydrogen shows a single peak as a doublet at δ 7.21 ppm. Three methylene protons of 1,3-diaminopropane were observed as separate singlets at δ 2.82, 2.80, and 2.48 ppm in the spectrum of **1**. The methyl proton of 4-methyl pyridine appears as a sharp singlet at δ 2.29 ppm.

Fluorescence study of 1

The fluorescence characteristics of **1** and its starting compound K_2(i-MNT) were investigated in DMF. The fluorescence spectra reveal that K_2(i-MNT) emission is at 474 nm (figure 1: solid blue line), while **1** shows an emission at 464 nm (figure 1: solid red line) upon excitation at 420 nm. Since cadmium(II) is difficult to oxidize or reduce due to its stable d^{10} configuration, no emission of **1** from metal-centered MLCT/LMCT excited states are expected [15]. Thus, the emission detected in **1** is tentatively allotted to the π–π* intraligand fluorescence. Greater fluorescence intensity of **1** is from chelation of ligand to the metal, chelation enhanced fluorescence intensity. Fluorescence enhancement after complexation is, however, of much curiosity as it opens up the opportunity for photochemical applications of the synthesis of **1** [16].

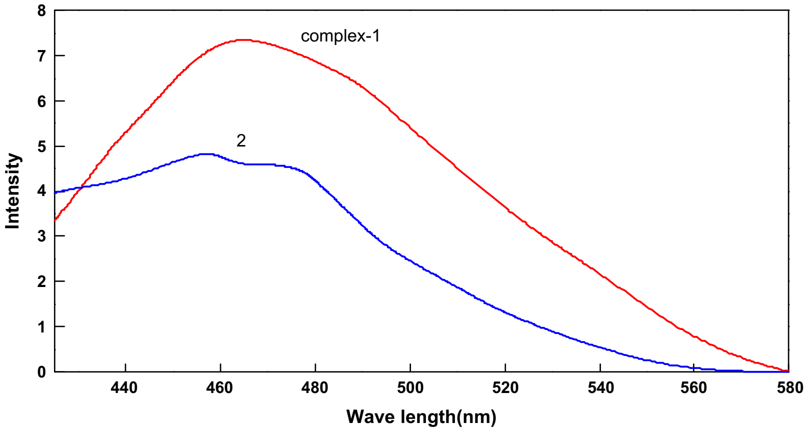


Figure 1. Fluorescence spectra of the coordination polymer **1** and starting compound K_2(i-MNT).

X-ray crystallography

Cadmium shows variable coordination numbers in its complexes and versatile coordination because of its characteristic softness and lack of ligand-field stabilization energy resulting from its d^{10} configuration [17]. Single crystal of **1** was mounted on a glass fiber for X-ray diffraction analysis and the resulting compound crystallizes in the triclinic space group, P-1 (table 1). The crystal data, data collection parameters, and analysis statistics are listed in table 1 (Supplementary material). The crystal structure of **1** has 1,3-diaminopropane assisted 1-D polymer with four lattice waters. The SCHAKAL plot with atom numbering scheme is shown in figure 2.

Thiolate S and amine N are involved in coordination with cadmium. Cd(II) is coordinated by three nitrogens, N2 and N3 of 1,3-diaminopropane and N1 of 4-methyl pyridine. S1 and S2 of 1,1-dicyanoethylene-2,2-dithiolate also coordinate with the Cd(II). The amino hydrogen of 1,3-diaminopropane forms a hydrogen bond with S1 and S2 making a 1-D polymeric ladder as shown in figure 2. The Cd–N bond distances are 2.26(15), 2.30(17), and 2.35(17) Å, comparable with the corresponding ones reported in the literature for dinuclear [19] cadmium(II) complexes, but somewhat shorter than mononuclear cadmium complex [20, 21]. Of the two Cd–S distances compared, the 1,1-dicyanoethylene-2,2-dithiolate ligand chelated (Cd–S1A) is shorter {2.58(5)} than (Cd–S2A) {2.71(5)}. Cd–S bond distances are longer than those of bridging thiolate in $[Cd_4(\mu\text{-}SPh)_8]$ {av. 2.538(3) Å} [22], $[Cd(SPh)_2(tmdp)_2]_n$ {av. 2.444(5) Å} and $[Cd(SC_6H_4Me_4)_2(tmdp)_2]_n$ {av. 2.438(5) Å} [23]. In **1**, Cd(II) is five coordinate with two nitrogens of 1,3-diaminopropane, one nitrogen of 4-methyl pyridine,

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

Identification code	SHELXL
Empirical formula	$C_{13}H_{21}CdN_5O_2S_2$
Formula weight	455.87
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 7.8332(2)$ Å, $\alpha = 108.111(3)°$ $b = 13.4646(5)$ Å, $\beta = 96.871(2)°$ $c = 19.4251(6)$ Å, $\gamma = 98.103(2)°$
Volume	1898.53(10) $Å^3$
Z	4
Density (calculated)	1.595 Mg m^{-3}
Absorption coefficient	1.384 mm^{-1}
$F(0\ 0\ 0)$	920
Crystal size	0.5118 × 0.4062 × 0.2194 mm^3
Theta range for data collection	3.09–30.95°
Index ranges	$-11 \le h \le 10, -17 \le k \le 18, -26 \le l \le 27$
Reflections collected	19,757
Independent reflections	10,425 [R(int) = 0.0206]
Completeness to theta = 25.50°	99.7%
Absorption correction	Analytical
Max. and min. transmission	0.812 and 0.669
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10,425/0/481
Goodness-of-fit on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0282$, $wR_2 = 0.0540$
R indices (all data)	$R_1 = 0.0439$, $wR_2 = 0.0613$
Largest diff. peak and hole	0.440 and −0.649 e $Å^{-3}$

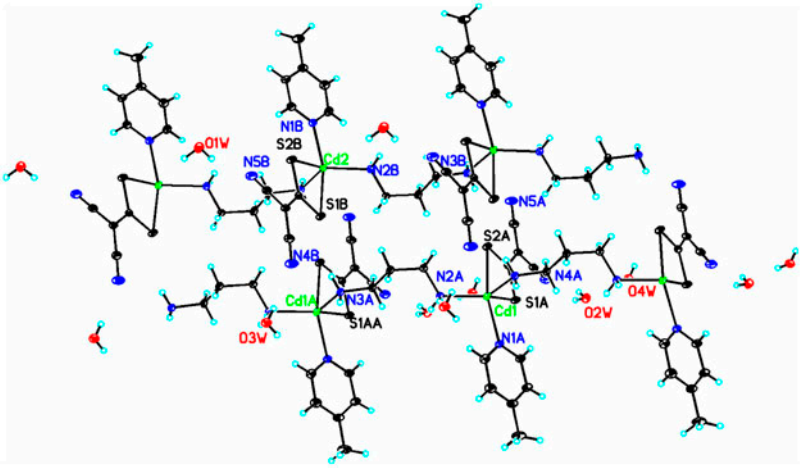


Figure 2. SCHAKAL plot of **1** with atom numbering scheme.

and two sulfurs of 1,1-dicyanoethylene-2,2-dithiolate. Cd(II) has a severely distorted trigonal bipyramidal coordination geometry. This is particularly evident from the intraligand N (1A)–Cd(1)–S(2A), N(2A)–Cd(1)–S(1A) and N(2A)–Cd(1)–N(1A) angles which at 161.02 (4), 142.81(5), and 96.34(6), respectively, are far from the ideal values of 180° and 120°. Selected bond distances and angles are given in table 2.

The crystal structure of **1** is stabilized by hydrogen bonds. Intermolecular N–H–S hydrogen bonds between 1,3-diaminopropane and 1,1-dicyanoethylene-2,2-dithiolate are shown in table 3. There are also lattice water molecules which form hydrogen bonds with nitrogen of 1,1-dicyanoethylene-2,2-dithiolate (figure 3). Formation of intermolecular hydrogen bonds between 1,3-diaminopropane and 1,1-dicyanoethylene-2,2-dithiolate occurs in **1**. However, each macrocycle provides inward pointed free hydrogen bond donors. These cavities can form inclusion complexes of a range of biologically active guest molecules that are both functionally and dimensionally fitted into the macrocyclic cavity [24].

Antifungal activity study of 1

The *in vitro* antifungal activity of **1** was done by the disk diffusion method [25, 26] against plants and animal fungi, *Synchytrium endobioticum* (wild type), *Pyricularia oryzae* (wild type), *Helminthosporium oryzae* (wild type), *Candida albicans* (ATCC10231), and *Trichophyton mentagrophytes* (clinically isolated) and compared with K_2i-MNT and

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Cd(1)–N(2A)	2.2682(15)	N(2A)–Cd(1)–N(3A)#1	100.86(6)
Cd(1)–N(3A)#1	2.3033(17)	N(2A)–Cd(1)–N(1A)	96.34(6)
Cd(1)–N(1A)	2.3494(17)	N(3A)#1–Cd(1)–N(1A)	93.11(6)
Cd(1)–S(1A)	2.5879(5)	N(2A)–Cd(1)–S(1A)	142.81(5)
Cd(1)–S(2A)	2.7093(5)	N(3A)#1–Cd(1)–S(1A)	114.51(4)
S(1A)–C(10A)	1.724(2)	N(1B)–Cd(2)–S(1B)	160.63(4)
		N(2A)–Cd(1)–S(2A)	100.89(5)

Table 3. Hydrogen bonds for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(2A)–H(2A1)···O(3W)#1	0.85(2)	2.29(2)	3.125(3)	168.6(19)
N(2A)–H(2A2)···N(4A)#3	0.86(2)	2.68(2)	3.338(2)	134.9(18)
N(2A)–H(2A2)···S(1A)#3	0.86(2)	2.82(2)	3.4982(19)	136.7(17)
N(3A)–H(3A1)···O(2W)#3	0.87(3)	2.43(3)	3.259(3)	159(2)
N(3A)–H(3A2)···S(1B)	0.84(2)	2.89(3)	3.641(2)	151(2)
N(2B)–H(2B1)···O(4W)#4	0.88(2)	2.27(2)	3.137(3)	166.7(18)
N(2B)–H(2B2)···N(5B)#5	0.840(19)	2.72(2)	3.357(2)	133.9(18)
N(2B)–H(2B2)···S(2B)#5	0.840(19)	2.82(2)	3.4786(19)	137.1(16)
N(3B)–H(3B1)···S(2A)	0.84(3)	2.86(3)	3.635(2)	154(2)
N(3B)–H(3B2)···O(1W)#5	0.85(3)	2.41(3)	3.206(3)	156(2)
O(1W)–H(1W1)···O(3W)#6	0.77(2)	2.10(2)	2.840(2)	162(2)
O(1W)–H(1W2)···N(5B)	0.80(2)	2.09(2)	2.871(2)	164(2)
O(2W)–H(2W1)···O(1W)#7	0.82(4)	1.99(4)	2.800(3)	176(4)
O(2W)–H(2W2)···N(4A)	0.72(3)	2.22(3)	2.915(2)	162(3)
O(3W)–H(3W1)···O(4W)#3	0.84(3)	1.94(3)	2.786(3)	177(2)
O(3W)–H(3W2)···N(4B)	0.72(3)	2.18(3)	2.895(3)	175(3)
O(4W)–H(4W2)···N(5A)#8	0.70(2)	2.20(2)	2.894(2)	167(3)
O(4W)–H(4W1)···O(2W)	0.78(3)	1.97(3)	2.746(2)	173(3)

Notes: Symmetry transformations used to generate equivalent atoms: #1 $x - 1, y, z$; #2 $x + 1, y, z$; #3 $-x, -y + 1, -z + 1$; #4 $-x, -y + 2, -z + 1$; #5 $-x + 1, -y + 1, -z$; #6 $-x + 2, -y, -z$; #7 $x - 1, y + 1, z + 1$; #8 $-x - 1, -y + 2, -z + 1$.

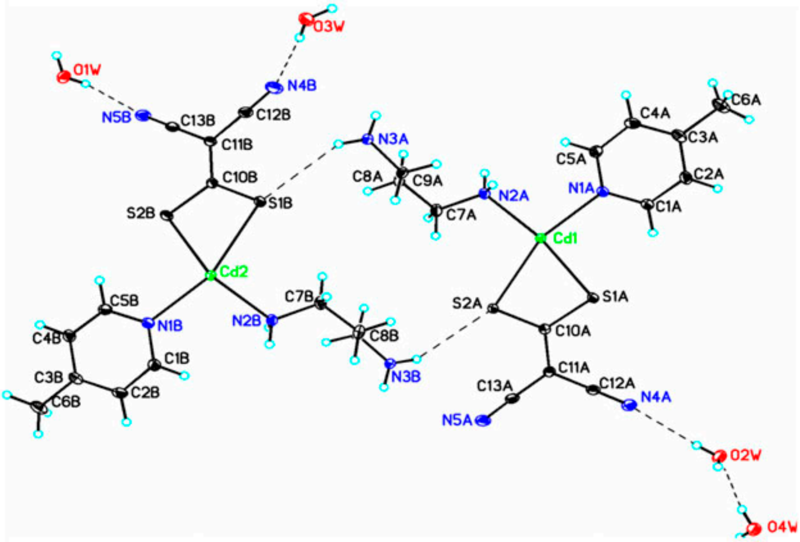


Figure 3. Hydrogen bonding of **1** with atom numbering scheme.

standard Griseofulvin (10 μg/disk). In this study, the strains were maintained and tested on Sabouraud Dextrose agar.

In the disk diffusion method, a 20% (w/v) stock solution of each dry extract (**1** and K_2i-MNT) were prepared in pure DMSO. For molds, suspensions of mature spores were obtained 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 10^6 spores mL^{-1}. Filter paper disks (6 mm diameter; Whatman No. 4) were placed on the inoculated agar surfaces, and impregnated

Table 4. Antifungal activity of **1**.

	Minimum inhibitory conc. (mg/mL)				
Material (1 mg/mL)	*Pyricularia oryzae*	*Helminthosporium oryzae*	*Synchytrium endobioticum*	*Candida albicans*	*Trichophyton mentagrophytes*
1	11	13	10	NE	10
K_2-iMNT·H_2O	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 the readings based on 5 replicates ± SEM, (NE) – No effect.

with 15 μL of stock solutions. Pure DMSO (15 μL) was used as a negative control while Griseofulvin (10 μg/disk) disks were used as positive controls. The plates were observed after 96 h at 25 °C for molds. All tests were performed in triplicate. The results are accumulated in table 4.

There is growing interest in new biologically important coordination compounds as metal binding can change their activity. **1** showed fungicidal activity on the basis of its minimum inhibitory concentration (MIC) value against the fungi *S. endobioticum*, *P. oryzae*, *H. oryzae,* and *T. mentagrophytes,* whereas K_2iMNT·H_2O showed no effect on fungi. The MIC value of Griseofulvin is 0.1 mg/mL. **1** shows highest fungicidal activity against *H. oryzae* and shows no fungicidal activity against *C. albicans*. Sometimes coordination of a ligand intensifies its antifungal activities [27] due to the greater lipophilic nature of the complex than the ligand. Improved activity of **1** can be explained on the basis of chelation theory [28] and size of the metal ion. After chelating, the polarity of the metal will be decreased owing to the overlap of the ligand orbital and partial sharing of positive charge of the metal with donors. Improved activity of **1** is of significance in pharmaceutics. The variation in the effectiveness of **1** against different fungi depends either on the impermeability of the cells of the microbes or on differences in ribosome of microbial cells.

Conclusion

We have reported the synthesis, luminescence, and crystal structure of a new complex of Cd(II) with nitrogen and sulfur donors and its antifungal study. We have developed an efficient synthesis for five coordinate **1**. We have chosen nitrogen- and sulfur-based ligands for construction of hydrogen bonded coordination polymer with d^{10} cadmium. The improved fluorescence intensities of **1** compared to that of ligand indicates potential as a photoactive material. Antifungal activity of **1** is observed with significant activity compared to K_2i-MNT on *S. endobioticum*, *P. oryzae*, *H. oryzae,* and *T. mentagrophytes* and proved to be crucial for the growth-inhibitor effect. Further exploration is in progress in our laboratory.

Supplementary material

CCDC-1016755 contains the supplementary crystallographic data for **1** and can be obtained from the Cambridge Crystallographic Data Centre through email. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data

Centre as supplementary publication CCDC-1016755. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.codeC44(1223) 336 033, E-mail: deposit@ccdc.cam.ac.uk).

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Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1013946].

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