



A new cadmium(II) complex with bridging dithiolate ligand: Synthesis, crystal structure and antifungal activity study



Mahesh Kumar Singh ^a, Sanjit Sutradhar ^a, Bijaya Paul ^a, Suman Adhikari ^b,
Folguni Laskar ^c, Raymond J. Butcher ^d, Sandeep Acharya ^e, Arijit Das ^{f,*}

^a Department of Chemistry, Tripura University, Suryamaninagar 799130, Tripura, India

^b Department of Chemistry, Govt. Degree College, Dharmanagar, Tripura(N), India

^c Advanced Level Institutional Biotech Hub, Karimganj College, Karimganj, Assam, India

^d Department of Inorganic and Structural Chemistry, Howard University, Washington, DC 20059, USA

^e Department of Botany, R.K.Mahavidyalaya, Kailashahar, Unakoti Tripura, Tripura, India

^f Department of Chemistry, Ramthakur College, Agartala, Tripura(W), India

ARTICLE INFO

Article history:

Received 3 November 2016

Received in revised form

15 March 2017

Accepted 19 March 2017

Keywords:

Polymeric complex

Cd(II)

1,1-Dithiolate

X-ray diffraction and antifungal activity study

ABSTRACT

A new polymeric complex of Cd(II) with 1,1-dicyanoethylene-2,2-dithiolate [i -MNT²⁻ = $\{S_2C:C(CN)_2\}^{2-}$] as a bridging ligand 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 six coordinated 1D polymeric in nature. Biological screening effects *in vitro* of the synthesized polymeric complex has been tested against five fungi *Synchytrium endobioticum*, *Pyricularia oryzae*, *Helminthosporium oryzae*, *Candida albicans* (ATCC10231), *Trichophyton mentagrophytes* by the disc diffusion method. *In vitro* antifungal screening indicates that the complex exhibits fungistatic and fungicidal antifungal activity whereas K_2i -MNT.H₂O became silent on *Synchytrium endobioticum*, *Pyricularia oryzae*, *Helminthosporium oryzae*, *Candida albicans* (ATCC10231), *Trichophyton mentagrophytes*.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Construction of new coordination polymeric framework of Cd(II) is of interest due to their fascinating network topologies and their potential application in magnetism, luminescence, adsorption, catalysis, etc [1]. The biological significance of cadmium is based on the fact that its occurrence in a living being can critically alter its metabolism, giving rise to sharp intoxication. Thus it has been classified among the toxic elements [2]. Cadmium can be found in living beings as part of complexes with ligands and its toxic nature is due to coordination disrupting the biological functions of these ligands. Cadmium compounds can cause harm to kidney, central nervous system and are carcinogenic for connective tissue, lungs and liver [3]. Due to human activities cadmium concentration steadily increases leading to development of appropriate chelating ligand for its intoxication [4]. The capability to coordinate *via* sulphur is enhanced for cadmium as compared to zinc. Moreover,

chelating sulphur donors are in fact under study as antidotes in cadmium(II) poisoning [5].

The electronic configuration (d^{10}) and size of cadmium(II) obviously favour its attraction for soft donor atoms as the Cd²⁺ ion is considered a soft Lewis acid. Cd(II) is to exhibit coordination numbers from three to eight. Owing to the larger size, Cd(II) shows coordination number six more easily than Zn(II) [6]. Cadmium complexes seem to be more interesting from a structural point of view because of the ability of these cations to modify both coordination numbers and geometries and also Cd involved in many biological molecules [7].

Systematic design of complexes with novel architectures and desired functionalities with principles of crystal engineering is most demanding subjects in current coordination chemistry. Judicious choice of ligands, bridging ligands, different metal ions, can tune the structure of coordination polymeric frameworks [8]. Sulphur-based 1,1-dithiolate ligands have proved promising when reacted with transition metals to give rise to a different of metal clusters possessing attractive conductive properties. Structural chemistry of dithiolate ligands is extraordinarily diverse and has important advantages over other organic ligands. Dithiolate ligands

* Corresponding author.

E-mail address: arijitdas78chem@gmail.com (A. Das).

are widely engaged in transition metal chemistry, and the flexibility of sulphur as a ligand in transition metal chemistry has been widely recognized [9]. A great deal of interest has been evoked in coordination compounds of unsaturated sulphur chelating ligands, 1,1-dicyanoethylene-2,2-dithiolate, and related molecules owing to interesting chemical properties and possible applications [10]. 1,1-Dicyanoethylene-2,2-dithiolate ion, by virtue of their chelating and bridging behaviours depending on the metal ion leading to various coordination modes and they may connect metal ions in different directions [11]. In spite of this growing range of coordination polymeric complexes, there are still many more coordination polymers which are yet to be synthesized and explored; in particular ligands with sulphur coordination sites have received far less attention.

We have initiated an investigation into the design, synthesis, and characterization of transition metal complexes containing dithiolate ligands and exploring the antifungal activity of the synthesized complex. One of our aims is to study the coordination properties of the N and S donors in $i\text{-MNT}^{2-}$. In our previous study [12], the interaction of dithiolate with different metal ions has been studied. To the best of our knowledge there is no report on polymeric complexes of Cd(II) involving bridging 1,1-dithiolate ligand. As an extension of our previous works we report here on the synthesis, characterization, and antifungal activities of a new polymeric complex of cadmium(II) (**1**) with sulphur donors. We hope the study would offer helpful information about the nature of cadmium(II) complexes with sulphur containing biological ligands.

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 ($4000\text{--}400\text{ cm}^{-1}$) and in CsI ($600\text{--}50\text{ cm}^{-1}$) on a Bomem DA-8 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DRX 300 FT-NMR spectrophotometer. $\text{K}_2i\text{-MNT}\cdot\text{H}_2\text{O}$ was prepared by a known literature procedure [13]. Crystal data were solved using the direct methods program SHELXS-97 [14a]. All nonsolvent heavy atoms were located using difference Fourier syntheses. The structures were refined against F^2 with SHELXL [14b–c], in which all data collected was used counting negative intensities. All nonsolvent heavy atoms were refined anisotropically.

3. Results and discussion

3.1. Synthesis of the complex **1**

The synthesis of the complex **CP 1** was accomplished as shown in Scheme 1.

$\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.005M) in 50 mL distilled water was added slowly to $\text{K}_2i\text{-MNT}\cdot\text{H}_2\text{O}$ (0.005 M) in 20 mL water with constant stirring for 30 min. The complex $\{\text{Cd}(i\text{MNT})\}$ thus obtained filtered by suction and washed successively with water, alcohol and ether and dried in vacuo. After that $\text{Cd}(i\text{MNT})$ (0.03 M) dissolved in DMF

(50 mL) and 1,3-diaminopropane (tn) (0.03 M) added to it with constant stirring. Stirring was further continued for 2 h. The reaction mixture was kept for 15 days to obtain the yellow crystalline complex **CP 1**.

3.1.1. IR and NMR

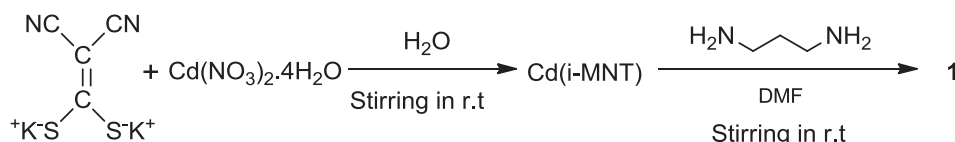
The observations in the IR and ^1H NMR spectra have importance for study of interaction between ligand and metal ion. The infra-red spectra of ligand and its metal complex **1** (**CP 1**) were recorded in the range of $400\text{--}4000\text{ cm}^{-1}$. **CP 1** exhibit a group of broad band in the range $3251\text{--}3316\text{ cm}^{-1}$ attributed to $\nu(\text{N-H})$ (asymmetric and symmetric) stretching modes. In the FT-IR spectrum of the metal complex **1** (**CP 1**) (KBr discs) show strong band at 2200 cm^{-1} due to the ν_{CN} stretching. The N-H bending (scissoring) vibration mode is observed in the range 1632 cm^{-1} for the **CP 1**. The $\nu(\text{C=C})$ absorption band appearing at 1360 cm^{-1} in $\text{K}_2i\text{-MNT}$ is observed in the range $1351\text{--}1377\text{ cm}^{-1}$. The positive shifts of $\sim 17\text{ cm}^{-1}$ in $\nu(\text{C=C})$ suggest that resonance form is more dominant in the isomalononitrile dithiolate complexes. Hence, it can be concluded that the sulphur of the isomalononitrile is involved in metal coordination. In the IR spectrum $\text{K}_2i\text{-MNT}$ a band at 960 cm^{-1} with a shoulder at 985 cm^{-1} is observed due to ($=\text{CS}_2$) group. The corresponding band and shoulder in the mixed ligand complex is shifted to lower frequencies and are found in the 937 regions. This implies coordination of the metal to the thiolate. The $\nu(\text{C-S})$ band occurring in the spectrum of **CP 1** is 870 cm^{-1} is higher than that of $\text{K}_2i\text{-MNT}$ at (860 cm^{-1}). The bands in the region $618\text{--}485\text{ cm}^{-1}$ are assigned to the Cd-S vibrations [15].

The ^1H NMR spectra was carried out in $\text{DMSO-}d_6$ solvent. The complex **CP 1** shows a broad NMR signals at δ 8.07 ppm and 7.78 ppm which suggest the presence of amine protons. The ^1H NMR spectrum of **CP 1** shows a singlet peaks at 3.04 ppm and 2.25 ppm, multiplet at 2.55 ppm and 1.50 ppm, The appearance of these resonances indicates that some unexpected compound formation occurs during the reaction medium. Thus the simple NMR spectrum did not give us a clear answer concerning the structure of the product. To solve the structure, crystal of complex **1** was mounted on a thin glass fiber for the X-ray diffraction analysis.

3.1.2. X-ray crystallography

The bifunctional ligand $i\text{-mnt}^{2-}$ represent supramolecular connectors that can generate infinite networks and metal–organic frameworks. It can coordinate to metal atoms through sulphur and nitrogen atoms only [16], or through both sulphur and nitrogen atoms. The $i\text{-mnt}^{2-}$ may present various coordination modes, leading to the formation of *mono*-nuclear, *di*-nuclear, metal–organic frameworks or coordination polymers. A small yellow crystal of complex **CP 1** was mounted on a thin glass fiber for the X-ray diffraction analysis and the resulting compound crystallizes in the Orthorhombic space group, $P\ c\ c\ n$ (see Table 1). The crystal data, data collection parameters and analysis statistics are listed in Table 1. The crystal structure of **CP 1** shows 1,1-dicyanoethylene-2,2-dithiolate ($i\text{-mnt}^{2-}$) assisted 2-D polymer. The SCHAKAL plot with atom numbering scheme is shown in Fig. 1.

Fig. 1 shows that in the polymeric chain each cadmium cation is hexacoordinated, having the distorted octahedral coordination.



Scheme 1. Synthesis of **1**.

Download English Version:

<https://daneshyari.com/en/article/5161286>

Download Persian Version:

<https://daneshyari.com/article/5161286>

[Daneshyari.com](https://daneshyari.com)