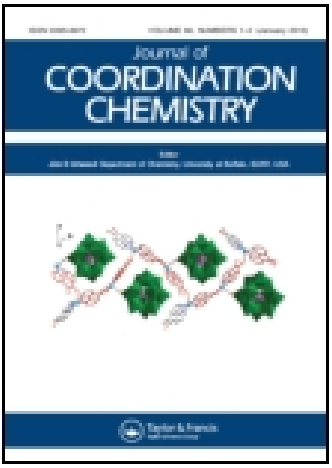

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Synthesis, crystal structure, and antifungal activity of a newly synthesized polymeric mixed ligand complex of Zn(II) with 1,1-dithiolate and nitrogen donors

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Synthesis, crystal structure, and antifungal activity of a newly synthesized polymeric mixed ligand complex of Zn(II) with 1,1-dithiolate and nitrogen donors

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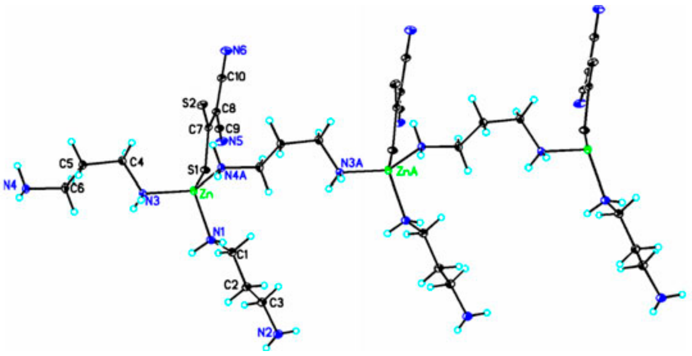

Complex of Zn(II) with 1,1-dicyanoethylene-2,2-dithiolate [i-MNT^{2-} = $\{S_2C{:}C(CN)_2\}^{2-}$] and 1,3-diaminopropane.

A new mixed ligand complex of Zn(II) with 1,1-dicyanoethylene-2,2-dithiolate [i-MNT^{2-} = $\{S_2C{:}C(CN)_2\}^{2-}$] and 1,3-diaminopropane as ligands has been synthesized and characterized on the basis of spectroscopy and single-crystal X-ray diffraction analysis. Spectroscopic studies and single-crystal X-ray diffraction analysis reveal that the zinc(II) complex is tetrahedral and adopts a 1,3-diaminopropane-assisted linear polymeric assembly. The molar conductance data of the complex in DMF solution show non-electrolytic nature. Biological screening effects of the complex *in vitro* have been tested against five fungi *Synchitrium endobioticum*, *Pyricularia oryzae*, *Helminthosporium oryzae*, *Candida albicans* (ATCC10231), and *Trichophyton mentagrophytes* by the disk diffusion method. A comparative study of inhibition zone values of the primary ligand K_2i-MNT·H_2O and its synthesized complex indicates that the complex exhibits a fungistatic antifungal activity whereas K_2i-MNT·H_2O does not affect *P. oryzae*.

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

1. Introduction

Zinc(II) plays dynamic roles in nature, industry, and biological systems such as enzymes, proteins, and medicine [1–3]. It is the second most abundant transition element in biological systems after iron; zinc is indispensable for life. With a closed d-shell, unlike iron and copper, zinc (II) finds biological relevance as a redox-stable element in metalloprotein structures. Zinc also plays a role in the growth and expansion of micro-organisms, plants, and animals [1–3], decisive in structures of enzymes which control growth and development, and also in proteins that aid in the transcription of DNA to RNA [1, 4–7]. Zn(II) does not directly facilitate zinc finger protein binding to the DNA, but is compulsory in order to fold the protein domain into a conformation that is structurally well-matched for DNA interaction. Healthy levels of zinc have been associated with immune system, fertility, skin health, and normal digestion [1–4]. Insufficient zinc in the body of humans results in symptoms such as growth delay, skin damage, and a slowing of sexual maturation [3, 4]. No other metal has as many functions as zinc in living organisms according to Vahrenkamp [8]. The zinc ion is most regularly detected in biological sites which are tetrahedrally ligated to N, S, and O donors of amino acid side chains, small molecules, *etc*.

1,1-Dithiolate ligands form cluster complexes [9]. Among 1,1-dithio ligands, 1,1-dicyanoethylene-2,2-dithiolate (isomaleonitriledithiolate, i-mnt^{2-}) displays exciting coordination properties by virtue of its chelating and bridging behaviors. Our earlier communications [10] include studies on complexes of Ni(II), Cu(II), Zn(II), Cd(II), and Co(II) with 1,1-dicyanoethylene-2,2-dithiolate and some nitrogen bases. Zinc-bound thiolate has been revealed to encourage alkyl group transfer in several zinc enzymes [11]. Zinc complexes have influential antimicrobial activities and are already in use in the medicinal field [12]. The bonding of zinc with complementary amine and thiolate is of interest for new engineered solids in crystal engineering. The study of Zn-thiolates contains a wide range of synthetic models which seek to explain the reactivity of such species. There is no report on mixed ligand complexes of Zn(II) involving 1,1-dithiolate and 1,3-diaminopropane. Here, we report on the formation of a new zinc complex, **1**, with nitrogen and sulfur as donors and its antifungal activity.

2. Experimental

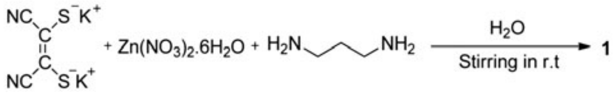
2.1. *Materials and methods*

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 Advance DRX 300 FT-NMR spectrophotometer. K_2i-MNT·H_2O was prepared by a known literature procedure [13]. Crystal data were solved using the direct methods program SHELXS-97 [16] and the structure was refined against F^2 with SHELXL [17].

3. Results and discussion

3.1. *Synthesis of 1*

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



Scheme 1. Synthesis of **1**.

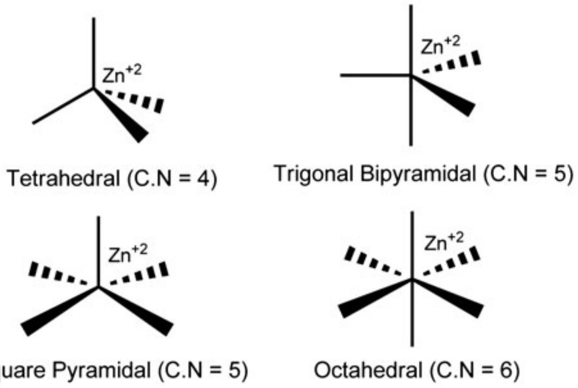
$Zn(NO_3)_2{\cdot}6H_2O$ (0.005 M) in 50 mL distilled water was added slowly to 1,3-diaminopropane (0.03 M), with constant stirring, resulting in a color change from milky white to colorless. To this, K_2iMNT$\cdot H_2O$ (0.005 M) in 20 mL water was added with stirring, resulting in a light yellow precipitate. This was washed with water followed by ethyl alcohol and diethyl ether, and finally kept in a desiccator after drying in open air.

The complex is almost insoluble in water and common organic solvents but is soluble in DMF and DMSO giving colored solutions. The molar conductance data in DMF solution reveal that the complex is non-electrolytic.

Zinc is a borderline hard Lewis acid which can accommodate a variety of both hard and soft donors such as nitrogen, oxygen, and sulfur [1, 4]. Different geometries and capability to bond numerous ligand types makes the zinc ion perfect for ligand exchange reactivity as it has a plastic coordination sphere. Zinc shows extensive coordination possibilities [1, 12, 14, 15]. Figure 1 shows different geometries of zinc with different coordination numbers.

3.2. *IR and NMR*

The results of IR and ^{1}H NMR spectra show that reaction of K_2(i-MNT) with $Zn(NO_3)_2{\cdot}6H_2O$ and 1,3-diaminopropane forms the mixed ligand complex of Zn(II). IR spectra of **1** (KBr discs) show a band at 2190 cm^{-1} corresponding to the stretching modes of the cyano group (νC≡N). Complex **1** has a group of broad bands at 3138–3336 cm^{-1} attributed to νN–H (asymmetric and symmetric) stretching modes. The N–H bending (scissoring) vibration is observed at 1599 cm^{-1} for **1**, lower than free 1,3-diaminopropane (νN–H = 1636 cm^{-1}). These shifts to lower frequency suggest amino nitrogen coordination.


Tetrahedral (C.N = 4)

Trigonal Bipyramidal (C.N = 5)

Square Pyramidal (C.N = 5)

Octahedral (C.N = 6)

Figure 1. Ideal geometries for 4-, 5-, and 6-coordinate zinc.

The band at 1455–1467 cm^{-1} is assigned to an olefinic νC=C stretch. In K$_2$i-MNT, a band at 960 cm^{-1} with a shoulder at 985 cm^{-1} is observed due to (ν=CS$_2$) group. The corresponding band and shoulder in the complexes are found at 933 and 966 cm^{-1} respectively. The νC–S band in **1** is 864 cm^{-1}, nearly the same as K$_2$i-MNT (860 cm^{-1}).

The ^{1}H NMR spectra were carried out in CDCl$_3$. Complex **1** shows NMR signals at δ 7.85 ppm. These downfield shifts clearly suggest the amino nitrogen coordination as indicated by IR spectra. Free amine protons were observed at δ 4.66 ppm. Three methylene protons were observed as separate singlets at δ 2.82, 2.73, and 2.63 ppm in the spectrum of **1**.

3.3. *X-ray crystallography*

Single crystals of **1** were grown by slow evaporation of diethyl ether–ethanol combination and the resulting compound crystallizes in the orthorhombic space group, Pna2$_1$ (see table 1). The crystal data, data collection parameters, and analysis statistics are listed in table 1 (Supplemental material). Crystal data were solved using the direct methods program SHELXS-97 [16]. All non-solvent heavy atoms were located using difference Fourier syntheses. The structures were refined against F^2 with SHELXL [17], in which all the data collected were used counting negative intensities. All non-solvent heavy atoms was refined anisotropically. Crystallization

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

Empirical formula	$C_{10}H_{20}N_6S_2Zn$
Formula weight	353.81
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2$_1$
Unit cell dimensions	a = 14.5064(2) Å; α = 90° b = 7.64640(10) Å; β = 90° c = 14.0872(2) Å; γ = 90°
Volume	1562.58(4) Å^3
Z	4
Density (Calcd)	1.504 Mg/m^3
Absorption coefficient	1.835 mm^{-1}
F (0 0 0)	736
Crystal size	0.8201 × 0.2818 × 0.1846 mm^3
θ Range for data collection	3.01°–41.06°
Index ranges	$-26 \le h \le 26$, $-13 \le k \le 13$, $-25 \le l \le 25$
Reflections collected	76,615
Independent reflections	10,164 [R(int) = 0.0333]
Completeness to θ = 25.50°	99.7%
Absorption correction	Analytical
Max. and min. transmission	0.755 and 0.440
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10,164/1/205
Goodness-of-fit on F^2	1.051
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0205, wR_2 = 0.0432
R indices (all data)	R_1 = 0.0236, wR_2 = 0.0442
Absolute structure parameter	0.001(3)
Extinction coefficient	0.0039(3)
Largest diff. peak and hole	0.357 and −0.290 e Å^{-3}

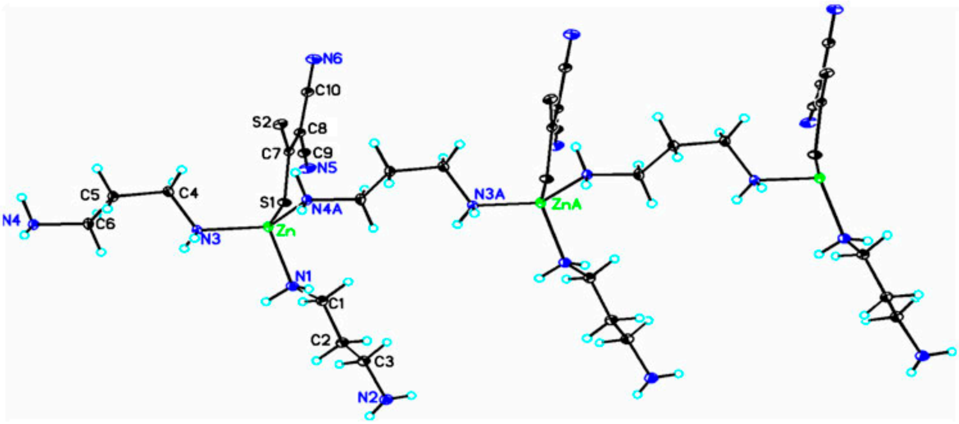


Figure 2. SCHAKAL plot of **1** with atom-numbering scheme.

experiments were conducted in an unmodified atmosphere and solvents were dried by standard methods, prior to use.

The crystal structure of **1** reveals the linear polymeric nature of the complex where 1,3-diaminopropane is a bridging unit. The SCHAKAL plot with atom numbering scheme is shown in figure 2.

Both thiolate S and amine N are involved in coordination with zinc. The Zn(II) is coordinated by three nitrogens (N1, N3, and N4) of 1,3-diaminopropane and S1 of 1,1-dicyano-ethylene-2,2-dithiolate. 1,3-Diaminopropane executes 1,3-diaminopropane-assisted linear polymeric assembly shown in figure 2. The bond distances involving zinc are 2.0500(7), 2.0237(6), 2.0441(7), and 2.2972(2) Å for N1, N3, N4, and S1, respectively. No significant difference for the Zn–S bond distance is observed, compared with $Zn(S_6)(py)_2$ (2.286(1) Å) [18], $Zn(S_6)(N\text{-}Melm)_2$ (2.317(1) Å) [19], $Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_2,(l\text{-}Me\text{-}imid)_2$ (2.301(2)–2.298(2)) [20], and $Zn_2(i\text{-}MNT):(4\text{-}mpy)_4$ (2.317(l) 2.321(1)), respectively. The nitrogens of i-mnt^{2-} do not coordinate with zinc, only nitrogens of 1,3-diaminopropane are coordinated generating a 1-D polymeric structure. Zn(II) ions are linked by 1,3-diaminopropane as a bridging unit to form a linear 1-D polymeric chain. In the 1-D polymeric structure of **1,** the chains are well isolated from each other. The value for the C–N triple bond length for i-mnt in the structure is smaller (1.1558(11) Å) compared with highly symmetrical $C(CN)_3^-$ ion (1.17 Å) [21]. The observed C–S distances (1.6982(7) and 1.7458(7) Å) are smaller than expected for a C–S single bond (1.82 Å) [22]. The bond angles are 117.93(2), 107.88(2), 107.70(3), and 104.69(3) between S1–Zn–N3, S1–Zn–N1, and N3–Zn–N1. Selected bond

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

Zn–N(3)	2.0237(6)	N(3)–Zn–N(4)#1	107.70(3)
Zn–N(4)#1	2.0441(7)	N(3)–Zn–N(1)	104.69(3)
Zn–N(1)	2.0500(7)	N(4)#1–Zn–N(1)	101.66(3)
Zn–S(1)	2.2972(2)	N(3)–Zn–S(1)	117.93(2)
S(1)–C(7)	1.7458(7)	N(4)#1–Zn–S(1)	115.21(2)
S(2)–C(7)	1.6982(7)	N(1)–Zn–S(1)	107.88(2)

distances and angles are given in table 2. A unique feature in **1** is that K_2(i-MNT) reacts with 1,3-diaminopropane (nitrogen base) to form a stable tris(1,3-diaminopropane) adduct (figure 2). The low metal coordination number makes this complex an interesting precursor in reduction chemistry, catalysis, material chemistry, or for mimicking zinc–enzyme processes.

3.4. *Antifungal activity*

1 was screened for its antifungal activity *in vitro* by the disk diffusion method against plant and animal fungi, namely *Synchitrium endobioticum* (wild type), *Pyricularia oryzae* (wild type), *Helminthosporium oryzae* (wild type), *Candida albicans* (ATCC10231), and *Trichophyton mentagrophytes* (clinically isolated), and compared with its primary ligand K_2i-MNT and standard Griseofulvin (10 µg/disk). In this study, the strains were maintained and tested on Sabouraud Dextrose agar.

In disc diffusion method, a 20% (w/v) stock solution of each dry extract (**1** and its primary ligand) 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 discs (6 mm diameter; Whatman No. 4) were placed on the inoculated agar surfaces and impregnated 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 [23]. The results are accumulated in table 3.

The synthesized complex **1** showed fungicidal activity on the basis of its minimum inhibitory concentration (MIC) value against only *P. oryzae* (MIC – 11 mg mL^{-1}); $K_2iMNT{\cdot}H_2O$ showed no effect on any fungi. The MIC value of Griseofulvin is 0.1 mg mL^{-1}. On the surface of the cell wall of microorganisms Zn(II) ions are adsorbed, and thus interrupt the respiration process of the cell and also block the synthesis of the proteins that control extra growth of the organisms. So, Zn(II) ions are indispensable for the growth-inhibitor effect. Activity of **1** can be elucidated on the basis of chelation theory [24, 25] and size of the metal ion. **1** shows higher fungicidal activity than previously reported zinc complexes [26]. The variation in the effectiveness of **1** against different fungi depends either on the impermeability of the cells of the microbes or on the differences in ribosome of microbial cells.

Table 3. Antifungal activity of **1**.

Material (1 mg mL^{-1})	Minimum inhibitory conc. (mg mL^{-1})				
	Pyricularia oryzae	*Helminthosporium oryzae*	*Synchitrium endobioticum*	*Candida albicans*	*Trichophyton mentagrophytes*
Complex **1**	11 (FS)	NE	NE	NE	NE
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, FS = Fungistatic.

4. Conclusion

We have reported the synthesis and structure of a new polymeric complex of Zn(II) with nitrogen and sulfur donors and its antifungal study. We chose nitrogen- and sulfur-based ligands for construction of coordination polymers with d^{10} metal ions and 1,3-diaminopropane-assisted linear type of polymeric assembly was observed. The antifungal activity of the ligand is enhanced upon complexation for *P. oryzae* and proved to be crucial for the growth-inhibitor effect. Fungicidal activity of **1** is higher than previously reported zinc complexes. Further exploration in this direction is in progress in our laboratory.

Supplementary material

CCDC1005138 contains the supplementary crystallographic data for $Zn(tn)_2(i\text{-}MNT)$, obtained from the Cambridge Crystallographic Data Center as supplementary publication CCDC-1005138. 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.code C 44(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/10.1080/00958972.2014.972388].

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