Mixed-ligand complexes of zinc(II) with 1,1-dicyanoethylene-2,2-dithiolate and N-donor ligands: A combined experimental and theoretical study

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The fascinating structural chemistry of zinc(II) with 1,1-dicyanoethylene-2,2-dithiolate [i-MNT2 = \(\{S_2C:C(CN)_2\}_2\)] ligand is presented. To elaborate, the reactivity of zinc(II) salt towards potassium salt of 1,1-dicyanoethylene-2,2-dithiolate (K2i-MNT) and 1,3-diaminopropane (dap) was studied in the presence of two distinct N-donor ligands, \(\alpha\)-picoline (2-Methylpyridine) and \(\gamma\)-picoline (4-Methylpyridine), respectively. As a result, two different Zn(II) coordination complexes of formula \([\text{Zn}_2(\text{dap})_2(i-MNT)_2] \) (1) and \([\text{Zn}(\text{dap})(i-MNT)(4-MePy)] \cdot 2\text{H}_2\text{O}]_n \) (2) were obtained. They were isolated as stable crystalline solids and fully characterized, including by single crystal X-ray diffraction. Complex 1 is a discrete 0D dimer, whereas 2 is a 1D coordination polymer. Although \(\alpha\)-picoline was used during the synthesis of 1, it is not involved in the metal coordination. Aiming at rationalizing the influence of the different noncovalent interactions, such as H-bonding, unconventional N–H...π and anion–π, on the crystal packing of 1 and 2, DFT calculations (M06-2X/def2-TZVP) were performed. Moreover, luminescence property of the complex 2 was investigated. Finally, in vitro antifungal activity of complex 2 was also screened against five fungi viz. Synchitrium endobioticum, Pyricularia oryzae, Helminthosporium oryzae, Candida albicans (ATCC10231) and Trichophyton mentagrophytes by the disc diffusion method and found to be effective when compared to K2i-MNT.H2O.

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1. Introduction

Dithiolate ligands display enthralling chemistry with the occurrence of two sulfur atoms that could execute as the ligating atoms in the molecule and transition metal-dithiolate complexes have been extensively studied owing to their rich structural varieties, versatile optical and semiconducting properties, biological significance and industrial applications [1]. In particular, several zinc-dithiolates have been synthesized and investigated as precursors for the preparation of metal sulides by metal organic chemical vapor deposition [2]. The transition metal thiolates mainly exhibit thiolate-bridged oligomers and polymers [3]. The ubiquitous dithiolate ligands can coordinate to a metal through sulfur donor atoms or nitrogen atoms, most commonly in a symmetrical or asymmetrical bidentate, bidentate-bridging and less commonly in a monodentate fashion.

The zinc(II) metal ion is second most abundant transition...
element in biological systems after iron to be found in the body and it plays significant roles in nature, industry and medicine due to its vast assortment of functions [4–7]. Zinc-thiolate reactivity, such as cysteine S-alkylation, plays a major role in the function of proteins such as cobalamin-independent/dependent methionine synthase, Ada repair protein and farnesyl transferase [8]. Zinc(II) metal ion is a borderline hard Lewis acid which can accommodate a variety of hard and soft donors such as nitrogen, oxygen and sulfur [9]. The capability to hold various ligand types, numbers and geometries makes the zinc ion ideal for metal exchange reactivity. Zinc(II) thiolate complexes have been studied as models for thiolate metalloproteins such as metallothionein, which are situated in the kidney and liver in a wide range of animals, including man [10]. These proteins attach a variety of metallic cations such as zinc, cadmium, mercury and copper through thiolate ligands and control the levels of these heavy metals in the organism [11]. Dithiolate ligands show affinity for metals such as zinc which is indicated by the fact that the ligands can be engaged as scavengers for this element in biological media. The dithiolate family consists of a variety of ligands such as dithiocarbamates, dithiocarboxylates, phosphor-1,1-dithiolenes, dithioarsinates, xanthates, i-MNT2 etc. Among them i-MNT2 is well-known flexible ligand which can chelate as well as bridge a variety of compounds to construct discrete and extended structures, depending on the metal ion and secondary ligand and also imparting interesting properties and has applications in materials and separation science [12]. But the literature involving dithiolate containing complexes still remains limited.

Given these facts, it was considered worthwhile to undertake the design, synthesis, characterization and investigation of various properties of Zn(II) complexes containing dithiolate ligands. In our previous work [13], we studied the interaction of dithiolate with different metal ions. Earlier, we obtained the crystal structure of Zn(II) with i-MNT2– and dap and demonstrated the linear polymeric nature of the complex where dap acts as a bridging unit [13a]. The motivation for the present contribution was to investigate any effect of the secondary ligand on our earlier established Zn(II)–(i-MNT)2(dap) system. In the present manuscript, we report the synthesis, characterization and X-ray single crystal structures of a dinuclear complex [Zn2(dap)2(i-MNT)2] (1) and a 1D coordination polymer [(Zn(dap)(i-MNT)(4-MePy))2·2H2O]n (2). We also examined the fluorescence and antifungal activities of the synthesized complex 2. The theoretical study of 1 and 2 is devoted to the analysis of the noncovalent interactions in the solid state. The computation of the energetic features of the different noncovalent interactions offers the possibility toward better understanding of the intricate mechanisms that govern the molecular recognition and crystal packing. Moreover, it is of particular interest to assign the discrete energy values for these noncovalent contributions, which may contribute in the development of energy scoring functions for a variety of applications, ranging from crystal engineering and coordination chemistry to catalysis and drug design.

2. Experimental

2.1. Materials and physical measurements

All reactions were performed in the open at ambient temperature. The solvents were purified by standard procedures. All chemicals were obtained from commercial sources and used without purification. Carbon, hydrogen and nitrogen were measured micro-analytically on a Perkin Elmer CHN analyzer (2400 series II). Infrared spectra were recorded in KBr (4000–400 cm−1) on a Bomen DA-8 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DRX 300 FT-NMR spectrophotometer. Fluorescence emission spectra were recorded using a Perkin Elmer spectrofluorometer, model LS55.

2.2. Synthesis of the complexes: [Zn2(dap)2(i-MNT)2] (1) and [(Zn(dap)(i-MNT)(4-MePy))2·2H2O]n (2)

Zn(NO3)2·6H2O (0.005 M) in 50 mL distilled water was added slowly to ligand dap (0.03 M), with constant stirring, resulting in a color change from milky white to colorless and stirring continued for further 40 min. To this mixture, K2-MNT·H2O (0.005 M) in 30 mL water was added with stirring, resulting in a light yellow precipitate and stirring was continued for further 1 h 30 min. The precipitate obtained was filtered, washed with water, alcohol, ether and dried in vacuo over fused CaCl2. The compound (0.005 M) was dissolved in 20 mL of x-picoline slowly with stirring and stirring was continued for further 1 h. Single crystal of complex 1 was grown after 2 weeks from the reaction mixture. In case of complex 2, the compound Zn(dap)·i-MNT (0.005 M) was dissolved in 20 mL of γ-picoline slowly with stirring and stirring was continued for further 1 h. The resulting solution was filtered, no precipitate obtained. Single crystal of complex 2 was grown after 2 weeks from the reaction mixture. A schematic representation of the synthetic method is shown via Scheme 1.

Complex 1: Yield: 63%, 1H NMR (300 MHz, DMso-d6, δ in ppm): 3.601 (br, s, −NH2), 2.80 (d, −CH2), 2.49 (d, −CH2), 1.61 (d, −CH2), FTIR (ν cm−1, KBr): 3460–3142 [ν(N−H), asymmetric and symmetric stretching modes], 2192 [ν(CN) stretching], 1581[ν(N–H), bending scissoring vibration], 1319–1339 [ν(C–C) absorption band], 952 [ν(−CS2) group], 869 [ν(C–S) band], 617–479 [ν(Zn–S) vibrations].

Complex 2: Yield: 72% 1H NMR (300 MHz, DMso-d6, δ in ppm): 9.89 (s, −NH2), 8.02 (br s, 4-MePy ring protons), 6.93 (s, 4-MePy ring protons), 6.21 (d, −CH2), 2.75 (d, −CH2), 2.08 (s, −CH2), 1.76 (br s, −CH2), 1.52 (br s, H2O). FTIR (ν cm−1, KBr): 3419–3136 [ν(N–H), asymmetric and symmetric stretching modes], 2181 [ν(CN) stretching], 1611 [ν(N–H) bending scissoring vibration], 1383–1316 [ν(C–C) absorption band], 977 [ν(−CS2) group], 882 [ν(C–S) band], 618–516 [ν(Zn–S) vibrations].

2.3. Crystallographic data collection and refinement

Single-crystal X-ray diffraction data for complexes [Zn2(dap)2(i-MNT)2] (1) and [(Zn(dap)(i-MNT)(4-MePy))2·2H2O]n (2) were collected using a Agilent Supernova Dual Source diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). The data collection and data reduction were performed with the program CrysAlis Pro [14a]. An empirical absorption correction using spherical harmonics was implemented in ‘SCALE3 ABSPACK’ scaling algorithm. Using Olex2 [14b], the structures were solved by direct methods using SHELXS [14c]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. One of the H-atoms in water molecule in 2 is disordered over two positions with equal occupancy. A summary of the crystallographic data and structure determination parameters for 1 and 2 is given in Table 1. Bond distances and angles for these complexes are listed in Tables S1–S4 (in the Supporting Information).

2.4. Theoretical methods

The calculations of the noncovalent interactions were carried out using the Gaussian-09 [15] and the M06-2X/def2-TZVP level of theory. The aim of this study is not to find the most stable geometry for the interaction of two monomers. Instead we intend to evaluate the interaction of the assemblies as they stand in the solid state in
order to evaluate their relative importance in the solid state, therefore, we have used the crystallographic coordinates. This procedure and level of theory have been successfully used to evaluate similar interactions [16]. The interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique [17].

The molecular electrostatic potential surfaces were computed using the SPARTAN software [18]. The Bader’s “Atoms in molecules” theory [19] has been used to study the interactions discussed herein by means of the AIMall calculation package [20].

2.5. Antifungal activity

The antifungal properties of the ligand K2i-MNT.H2O and its zinc complex 2 were investigated by the disc diffusion method against different plants and animal fungi and compared with standard Griseofulvin (10 μg/disc). The fungal strains were cultured on Sabouraud dextrose agar. In a typical disc diffusion method [21], Tween 80 and the resulting suspension was adjusted to 10⁶ spores/mL. Whatman No.4 filter paper discs (6 mm diameter) were positioned on the inoculated agar surfaces and soaked with 15 μl of stock solutions. Griseofulvin (10 μg/disc) discs 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 moulds. All the readings based on 5 replicates.

3. Results and discussion

3.1. Description of the structures

3.1.1. [Zn2(dap)2(i-MNT)2] (1)

Complex 1 crystallizes in the monoclinic system, space group P21/n. The molecular structure of 1 (Fig. 1) is a dinuclear complex with two bridging i-MNT²⁻ ligands. Each of the Zn(II) centres is further coordinated to one bidentate chelating dap ligand, thereby completing a distorted tetrahedral geometry. The observed bond distances for Zn–S and Zn–N are 2.3216(7) Å [Zn1–S1i; i=1-x,1-y,1-z], 2.3216(7) Å [Zn1–S1i; i=1-x,1-y,1-z], 2.3216(7) Å [Zn1–S1i; i=1-x,1-y,1-z], 2.3216(7) Å [Zn1–S1i; i=1-x,1-y,1-z]. 2.3216(7) Å [Zn1–S1i; i=1-x,1-y,1-z]. The bond angles vary between 95.78(9)° and 127.37(7)°. The distortion of the tetrahedral geometry around Zn(III) can be verified by the calculated value of the structural index parameter ε₄ proposed by Okuniewski et al. [22] to describe the geometry of a four coordinate metal system, which is –0.82 for 1 (for ideal tetrahedron ε₄ = 1).

Intermolecular N–H···N hydrogen bonding is

### Table 1

Crystalllographic data and structure refinement for 1 and 2.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C₁₄H₂₀N₈S₄Zn₂ (1)</th>
<th>C₁₃H₂₁N₅O₂S₂Zn (2)</th>
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<td>408.84</td>
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<td>Temperature/K</td>
<td>293(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/n</td>
<td>P-1</td>
</tr>
<tr>
<td>a/Å</td>
<td>10.2850(3)</td>
<td>7.6300(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>9.3665(2)</td>
<td>10.5221(10)</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.6670(3)</td>
<td>13.2750(10)</td>
</tr>
<tr>
<td>α°</td>
<td>90.0</td>
<td>68.571(8)</td>
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<tr>
<td>β°</td>
<td>105.244(3)</td>
<td>82.328(8)</td>
</tr>
<tr>
<td>γ°</td>
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<td>70.740(9)</td>
</tr>
<tr>
<td>Volume/A³</td>
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<td>936.46(15)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ρcalc R/cm³</td>
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<td>1.450</td>
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<tr>
<td>μ/mm⁻¹</td>
<td>2.615</td>
<td>1.548</td>
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<td>F(000)</td>
<td>568.0</td>
<td>424.0</td>
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<tr>
<td>Crystal size/mm³</td>
<td>0.25 × 0.22 × 0.20</td>
<td>0.07 × 0.07 × 0.05</td>
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<tr>
<td>Radiation</td>
<td>MoKα (λ = 0.71073)</td>
<td>MoKα (λ = 0.71073)</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
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<td>5.656 to 49.994</td>
</tr>
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<td>Index ranges</td>
<td>–12 ≤ h ≤ 12, –11 ≤ k ≤ 11, –14 ≤ l ≤ 14</td>
<td>–9 ≤ h ≤ 9, –12 ≤ k ≤ 12, –15 ≤ l ≤ 15</td>
</tr>
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<td>Reflections</td>
<td>9182</td>
<td>6510</td>
</tr>
<tr>
<td>Independent reflections</td>
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<td>3307 [R = 0.0537,</td>
</tr>
<tr>
<td></td>
<td>R(sinθ)/λ = 0.0323]</td>
<td>R(sinθ)/λ = 0.0984]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2013/127</td>
<td>3307/12/224</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.076</td>
<td>0.990</td>
</tr>
<tr>
<td>Final R indexes [l ≥ 2σ (I)]</td>
<td>R₁ = 0.0276, wR₂ = 0.0576</td>
<td>R₁ = 0.0578, wR₂ = 0.1035</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0330, wR₂ = 0.0615</td>
<td>R₁ = 0.0903, wR₂ = 0.1220</td>
</tr>
<tr>
<td>Largest. diff. peak/hole/e Å⁻³</td>
<td>0.31/-0.27</td>
<td>0.52/-0.47</td>
</tr>
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foreseen between the molecules which extends to form a sheet-like pattern (Figs. 2 and 3).

The comparison of the molecular structure of 1 with other reported complexes of the same mixed-ligand system is important. Two such related systems, reported from our group, are a 1D coordination polymer [Zn(dap)(i-MNT)]n [13a] and a 2D coordination polymer [Cd(dap)(i-MNT)]n [13c]. In the former complex, N-atoms of i-MNT2− do not coordinate to Zn(II), whereas in the latter, N-atoms of both i-MNT2− and dap coordinate to the Cd(II) centres generating a 2D polymeric structure. Moreover, report of a ionic Cd(II) organic-inorganic hybrid comprising of anionic metal core bridged by i-MNT2− ligands and cationic cyclic...
hexahydropyrimidine motifs (resulting from the reaction between dap and DMF) by our group is also notable [13d]. The difference in the molecular structures of 1 and the complexes mentioned in Refs. [13a] [13c], and [13d] may be attributed to various factors: (a) the different coordination habits of the metal ions, (b) distinct coordination modes of the ligands and (c) also to the different synthetic routes adopted during syntheses.

3.1.2. \([\text{Zn(dap)(i-MNT)(4-MePy)}\cdot2\text{H}_2\text{O}]_n\) \((2)\)

Complex 2 crystallizes in the triclinic system, space group \(P\overline{1}\). In contrast to 1, the crystal structure of 2 features a 1D coordination polymer driven by the ligand dap spacers with the \(\text{Zn} \cdots \text{Zn}\) separation of 7.630(8) Å. Additionally each \(\text{Zn}(II)\) metal center is stabilized by the terminal bidentate chelating \(\text{i-MNT}^2-/\text{C}_0\) ligand and \(\text{N}\)-atom bound \(4\)-\text{MePy} ligand. The analogous \(\text{Cd}(II)\) complex of formula \([\text{Cd(dap)(i-MNT)(4-MePy)}]4\text{H}_2\text{O}]_n\) was earlier reported by us [13b]. The asymmetric unit of complex 2 is illustrated in Fig. 4 and a packing diagram of complex 2 has been shown in Fig. 5. In 2, the five-coordinate \(\text{Zn}(II)\) atoms adopt a distorted trigonal bipyramidal \((\text{ZnN}_3\text{S}_2)\) geometry, with one of the two \(\text{S}\)-atoms of bidentate chelating \(\text{i-MNT}^2-/\text{C}_0\) ligands and the monodentate \(4\)-\text{MePy} \(\text{N}\)-atom in the apical positions (S2 and N1). The coordination environment around \(\text{Zn}(II)\) atoms can be further verified by the Addison parameter (\(\tau\)) which measures the distortion between a perfect square pyramidal geometry \((\tau = 0)\) and a perfect trigonal bipyramidal geometry \((\tau = 1)\), with the formula: \(\tau = (\beta - \alpha)/60^\circ\), wherein \(\beta\) and \(\alpha\) (in \(^\circ\)) are the two largest coordination angles [23]. The \(\tau\) value of 0.62 in complex 2 confirms severely distorted trigonal bipyramidal geometry for the metal centres in the compound. H-bonding interactions between the lattice water molecules and the \(-\text{NH}_2\) groups lead to the formation of a H-bonded network in complex 2 (Fig. 6).

3.2. Theoretical study

Both complexes 1 and 2 form interesting supramolecular assemblies in the solid state. The theoretical study is devoted to analyze them focusing on the formation of \(\text{N} \cdots \text{H} \cdots \text{N}\) and \(\text{N} \cdots \text{H} \cdots \pi\) noncovalent interactions in complex 1 and anion–\(\pi\) interactions in complex 2. Remarkably, in complex 1 the \(\text{N} \cdots \text{H} \cdots \pi\) interactions involve the \(\pi\)-system of the dianionic \(\text{i-MNT}^2-\) ligand (see Fig. 7).

In Fig. 8a, we represent a supramolecular fragment of the solid state X-ray structure of complex 1. It can be observed that the presence of several hydrogen bonding interactions involving the \(\text{NH}\) and \(\text{CN}\) groups. In addition, two symmetrically related \(\text{N} \cdots \text{H}\) groups of one molecule point to the conjugated \(\pi\)-systems of the \(\text{i-MNT}^2-\) ligands of two neighboring molecules, thus generating an infinite 1D supramolecular chain. To rationalize these interactions in complex 1 we have first computed the molecular electrostatic potential (MEP) surface, which is shown in Fig. 8b. It can be observed that the most negative potential (red color surface) is located, as expected, in the \(\text{i-MNT}^2-\) ligand at the \(\text{N}\) atoms \((-48\ \text{kcal/mol})\). Moreover, the most positive MEP values are located at the \(-\text{NH}_2\) \((+65\ \text{kcal/mol})\) groups due to the enhanced acidity of the hydrogen atoms of the \(-\text{NH}_2\) group upon coordination to the \(\text{Zn}(II)\) metal center. Therefore the \(\text{N} \cdots \text{H} \cdots \text{N}\) (\(\text{i-MNT}^2-\)) H-bonding...
interaction is electrostatically favored. Moreover, the MEP value at the π-system of the i-MNT2 ligand is also negative (−14 kcal/mol) thus it is well suited for establishing X-H⋯π interactions. In order to evaluate energetically both interactions in the solid state of complex 1, we have used a theoretical dimer extracted from the 1D supramolecular chain where both interactions (H-bonding and N⋯H⋯π) are responsible for the formation of this dimer (see Fig. 8c). A close examination reveals that in addition to the conventional N⋯H⋯N interaction (2.41 Å), two longer H-bonding interactions are also established involving the CH2 and NH2 groups (2.82 and 2.94 Å, respectively) resulting in the formation of a trifurcated H-bonding interaction. The binding energy of this assembly is $D_{E1} = -19.8$ kcal/mol, thus confirming its importance in influencing the solid state architecture of complex 1. We have used the Bader’s theory of “atoms in molecules” (AIM) to characterize the interactions in this dimer of complex 1. A bond critical point (CP) and a bond path connecting two atoms is an unambiguous evidence of interaction [19]. The AIM distribution of bond critical points and bond paths is shown in Fig. 8d (the ring and cage critical points are not shown for the sake of clarity). Each individual H-bond of the trifurcated interaction is characterized by a bond CPs (red sphere) and a bond path connecting the N donor atom of the dianion to the corresponding H atom. Interestingly, the unconventional N⋯H⋯π interaction is confirmed and characterized by the presence of two bond CPs (red spheres) and a bond paths connecting the H atom to the conjugated S and C atoms of the ligand.

Complex 2 is an infinite 1D polymer with a remarkable solid state architecture since it forms a double stranded polymeric ladder governed by a combination of anion−π and H-bonding interactions, as further discussed below. These double stranded polymeric ladders interact with each other by means of H-bonding interactions. We have computed the MEP surface in order to know the most nucleophilic and electrophilic parts of complex 2. It can be observed that the most negative MEP values are located at the N atoms of the i-MNT2 ligand and the most positive MEP values at the −NH2 atoms similarly to complex 1. Interestingly, the π-systems of both Zn(II) ligands (i-MNT2 and 4-MePy) exhibit opposite MEP values. That is, negative at the π-system of i-MNT2 ligand (−38 kcal/mol) and positive at the π-system of 4-MePy ligand (+27 kcal/mol). Therefore, we anticipate that the stacking of both π-systems should be electrostatically very favored. We have computed the interaction energy of two dimers retrieved from the...
Fig. 8. (a) X-ray fragment of complex 1. (b) MEP surface with indication of electrostatic potential values (kcal/mol) at selected points. (c) Theoretical model used to evaluate the noncovalent interactions. Distances in Å. (d) AIM distribution of bond critical points (red spheres) and bond paths for the dimer of complex 1. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 9. (a) X-ray fragment of complex 2. (b) MEP surface with indication of electrostatic potential values (kcal/mol) at selected points. (c,d) Theoretical models used to evaluate the noncovalent interactions. Distances in Å.
crystal structure (see Fig. 9c and d) as representative models of, on one hand, the interaction that govern the formation of the double stranded polymeric ladders and, on the other hand, the interaction that is established between the double strands generating the final 3D architecture of the crystal structure. The binding energy of the dimer shown in Fig. 9c as model of latter assembly, is \( \Delta E_2 = -39.8 \text{ kcal/mol} \) thus confirming the strong interaction. It should be mentioned that we have used a theoretical model (monomer) where the dap ligands have been replaced by methylamine ligands. In this dimer (see Fig. 9c) two symmetrically related NH\( \cdots \)SH-bonds are established. Moreover, this dimer also exhibits an unexpected S\( \cdots \)S chalcogen bonding interaction (distance shorter than the sum of vdW radii \( = 3.60 \text{ Å} \)). The contribution of this S\( \cdots \)S interaction is expected to be energetically unfavourable; since the electrostatic potential at the S atom is negative (MEP value is \(-39 \text{ kcal/mol}\)). It is likely compensated by the electrostatically favored N\( \cdots \)H\( \cdots \)S H-bonds. The binding energy of the other theoretical dimer we have studied (see Fig. 9d) is \( \Delta E_3 = -53.8 \text{ kcal/mol} \). This large binding energy is due to the presence of an intricate combination of interaction that stabilizes this assembly. That is, two symmetrically equivalent and bifurcated N\( \cdots \)H\( \cdots \)N,S H-bonding interactions and two symmetrically equivalent anion–π interactions. This large binding energy obtained for this assembly explains the formation of the remarkable double strand polymeric ladders in the solid state of complex 2.

Finally, we have also used the Bader’s theory of “atoms in molecules” (AIM) to characterize the interactions in the dimers of complex 2 commented above. The AIM distribution of bond critical points and bond paths is shown in Fig. 10. The H-bonding interactions of the dimer shown in Fig. 10a are characterized by two bond CPs (red spheres) and a bond paths connecting the H atom to the S and N atoms. Therefore, the AIM reveals the existence of a long H-bonding interaction (N\( \cdots \)H\( \cdots \)N, 3.03 Å) that further contributes to the formation of the dimer. The AIM analysis also confirms the existence of the S\( \cdots \)S interaction that is characterized by the presence of a bond CP and bond path interconnecting the S atoms. It should be mentioned that the existence of a bond CP and bond path connecting two atoms is simply an indication of interaction (either attractive or repulsive). For the dimer shown in Fig. 10b (responsible of the double strand polymeric ladder), the distribution of bond CPs and bond paths confirms the existence of the aforementioned HBs and reveals the existence of a long HB (N\( \cdots \)H\( \cdots \)N, 2.97 Å) that further contributes to the formation of the assembly. The distribution also shows that the anion–π interaction is characterized by the presence of two bond CPs that connect two carbon atoms of the aromatic ring to two carbon atoms of the i-MNT\(^2\) ligand.

3.3. Fluorescence study of complex 2

Fluorescence spectral study of the metal complexes of Zn(II) or Cd(II) is one of the most fascinating subjects as it opens up the new prospect for photochemical applications [24]. The fluorescence study of complex 2 and its starting compound \( K_2(\text{i-MNT}) \) were investigated in dimethyl sulphoxide. The fluorescence spectra reveal that emission for \( K_2(\text{i-MNT}) \) is at 441 nm (Fig. 11, solid blue line), while 2 shows an emission at 372 nm (Fig. 11, solid red line) upon excitation at 331 nm. Since zinc(II) is difficult to oxidize or reduce owing to its stable d\(^{10}\) configuration, no emission of complex 2 from metal-centered MLCT/LMCT excited states are expected [25]. Thus, the emission observed in complex 2 is tentatively allotted to the \( \pi^* \) intra ligand transitions. The greater fluorescence intensity of complex 2 with respect to the free ligand may be ascribed to the CHEF (chelation-enhanced fluorescence) effect of the diamagnetic metal center which effectively increases the rigidity of the ligand and diminishes the loss of energy by
3.4. Antifungal property study of the compound 2

Metal-based complexes containing S-donor atoms represent a novel group of antifungal agents with possible applications for the control of fungal infections. This inspires chemists to explore for new metal complexes and zinc in particular has fascinated the researchers [27]. The synthesized complex 2 and ligand (K2i-MNTH2O) has been tested against five fungi on the basis of its minimum inhibitory concentration (MIC) and the results are accumulated in Table 2. The MIC value of the standard sample Griseofulvin is 0.1 mg/mL. The fungicial activity of complex 2 was found to be significant against Candida albicans and shows no fungicial activity against Pyricularia oryzae and Trichophyton mentagrophytes whereas its ligand (K2i-MNTH2O) showed no effect on any fungi. Usually coordination of an organic ligand to metal ion amplifies its antifungal activities, caused by the increased lipophilicity which enhances the penetration of the complexes into lipid membrane and restricts further multiplicity of the microorganisms [28]. Metal ions are adsorbed on the surface of the cell wall of microorganisms and perturb the respiration process of the cell and thus obstruct the synthesis of the proteins that restricts further growth of the organisms. Thus metal ions are crucial for the growth-inhibitor effect. Due to overlapping of the ligand and metal ion orbitals increases the delocalization of π-electrons over the whole chelate ring and enhances the lipophilicity of the complexes with respect to free ligand [29]. This improved lipophilicity increases the penetration of the complexes into lipid membrane and stops further multiplicity of the microorganisms. The variation in the effectiveness of complex 2 against different fungi depends either on the impermeability of the cells of the microbes or on changes in ribosome of microbial cells.

4. Conclusions

Two new [Zn2(dap)2(i-MNT)2] (1) and {[Zn(dap)[i-MNT][4-MePy]]2H2O}n (2) have been synthesized and characterized by microanalysis and X-ray crystallography and luminescent properties and antifungal activity have been investigated. X-ray crystallography revealed Complex 1 is a discrete 0D dimer, whereas 2 is a 1D coordination polymer. The role of π-picoline in the formation of 1 could not be particularly ascertained, but it may be concluded that it plays a structure directing role because in its absence during the synthesis, a 1D coordination polymer [Zn(dap)[i-MNT]2]n was earlier reported [13a]. We have described the importance of non-covalent interactions (H-bonding, anion–π and unconventional N–H · · · π) in their solid state. The energetic features of these interactions have been studied by means of DFT calculations and further characterized using the AIM analysis. We have shown that the unconventional N–H · · · π interaction with the conjugated π-system of the ligand is important determining the solid state of complex 1 and it is energetically very favourable. Moreover, anion–π interactions are also relevant in the formation of the double stranded polymeric ladder in complex 2. The enhanced fluorescence intensities of complex 2 compared to that of ligand suggests potential as a photocative material. Antifungal activity of 2 is observed with significant activity compared to K2i-MNT on Candida albicans, Helminthosporium oryzae and Synchirium endobioticum and proved to be crucial for the growth-inhibitor effect. Further exploration is in progress in our laboratory.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at 10.1016/j.molstruc.2018.03.073.

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