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Polymeric Cd(II), trinuclear and mononuclear Ni(II) complexes of 5-methyl-4-phenyl-1,2,4-triazole-3-thione: Synthesis, structural characterization, thermal behaviour, fluorescence properties and antibacterial activity

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ABSTRACT

Syntheses of a polymeric Cd(II) complex, $[Cd(mptt)_2]_n$ (**1**), a trinuclear Ni(II) complex, $[Ni_3(\mu\text{-}mptt)_4(\mu\text{-}H_2O)_2(H_2O)_2(ttfa)_2]\cdot 3H_2O$ (**2**) and a mononuclear Ni(II) complex $[Ni(mptt)_2(en)_2]$ (**3**) have been performed using the ligand 5-methyl-4-phenyl-1,2,4-triazole-3-thione (Hmptt) and nickel(II)/cadmium(II) salts {ttfa = thenoyltrifluroacetonate). The ligand and the complexes have been characterized by various physicochemical methods in addition to their single crystal X-ray structure. The Cd centre in complex **1** adopts a distorted tetrahedral geometry with one sulfur atom and two mptt ligands provide three nitrogen atoms from three triazole units. The sulfur atom of the ligand binds covalently and overall the ligand acts as uninigative N,S/N,N bidentate moiety. The polymeric structure of complex **1** results from the N atoms of the neighboring triazole units coordinating with the Cd(II) centre. The three Ni(II) centres in the trinuclear Ni(II) complex **2** form a linear arrangement and all have six coordinated arrangements. The middle Ni(II) binds with four deprotonated triazole ring nitrogens and two water molecules form two bridges. The terminal Ni(II) centres bind through two thenoyl oxygens, two triazole nitrogens and water molecules that formed bridges with the middle Ni centre. In complex **3**, the nickel(II) centre is covalently bonded through two deprotonated triazole ring nitrogens from two ligand moieties and other four sites are occupied by four nitrogens from two bidentate en ligands. Thermogravimetric analyses (TGA) of the complexes indicated for NiO as the final residue. The bioefficacy of the ligand and complexes **2** and **3** have been examined against the growth of bacteria to evaluate their anti-microbial potential. Complex **2** showed high antibacterial activity as compared to the ligand and complex **3**. Complexes **1**, **2** and **3** are fluorescent materials with maximum emissions at 425, 421 and 396 nm at an excitation wavelength of 323, 348 and 322 nm, respectively.

1. Introduction

The coordination chemistry of nitrogen-sulfur containing heterocyclic ligands such as 1,2,4-triazoles and their derivatives containing HNCS moiety, is an emerging and rapidly developing area of research [1–3]. Synthesis of 1,2,4-triazoles and their derivatives has attracted considerable attention due to their potential biological activity and agricultural applications [4–8]. These nitrogen-sulfur heterocyclic systems have received considerable interest as ligands in the formation of coordination compounds because they have capacity to form σ bond as well as π bonds in the same system [9]. These compounds have received much attention due to their important pharmacological activities, such as antiviral, analgesic, antimicrobial, antidepressant and antifungal effects [10–12]. 1,2,4-Triazoles may provide multidentate coordination sites and link more than one metal centre which may provide π-π stacking between the rings to generate multi-nuclear complexes [13,14]. Thus,

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1,2,4-triazole and their substituted derivatives are of current interest as bridging ligands between transition metal ions for the preparation of coordination polymers, and a wide variety of polynuclear complexes. Recently, substituted 1,2,4-triazoles have attracted more attention than the unsubstituted one, because of the presence of more complex coordination modes for the formation of new coordination complexes [15]. Some trinuclear complexes of Ni (II), Cu(II) and Fe(II) with similar triazoles have been reported which contain anionic coligands such as thiocynate/perchlorate [16–19] but no such trinuclear complexes of triazole are known which contain thenoyl trifluroacetone as the secondary ligand. A survey of literature shows that a few papers are available on the syntheses and spectral characterization of metal complexes of 1,2,4-triazoles, but scanty of information is available on their mixed ligand or ternary complexes. Therefore, it will be of great interest to investigate the mixed ligand complexes of 1,2,4-triazole ligand and to compare the mode of bonding and structure of the complexes. In view of this, we have prepared and characterized the polymeric Cd(II) complex and trinuclear and mononuclear Ni(II) complexes of 5-methyl-4-phenyl-1,2,4-triazole-3-thione containing ethylenediamine/thenoyltrifluoroacetone as a secondary ligand.

2. Experimental section

2.1. Chemicals and starting materials

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Ethyl acetate, (SD Fine Chemicals), phenyl isothiocyanate (Sigma Aldrich) and NaOH (Qualigens) were used as received. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were dried and distilled before use, following the standard procedure.

2.2. Physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erba 1108. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL300 FT-NMR spectrometer using TMS as internal reference. Electronic spectra were recorded on a SHIMADZU 1700 UV–Vis spectro-photometer. The fluorescent data were collected at room temperature with a Varian CARYECLIPSE spectrophotometer in DMSO solution. Thermogravimetric curves of complexes were recorded using a Perkin Elmer-STA 6000 thermal analyzer, TA Instruments with heating rate of 15 ° $\min^{-1}$ and a platinum sample holder.

2.3. Antibacterial tests

Five human bacterial pathogens *Salmonella typhi* (MTCC 3216), *Shigella flexneri* (ATCC 12022), *Staphylococcus aureus* (ATCC 25323), *Aeromonas hydrophila* (ATCC 7966) and *Enterococcus faecalis* (ATCC 25923) were used to test the antibacterial activity of complexes **2** and **3**. The antibacterial assay was done according to Kirby-Bauer Disk Diffusion the method with some slight modifications [20,21]. The test compounds were dissolved in DMSO to a final concentration of 5 mg/mL. Sterilized Whatman no. 1 filter paper discs (5 mm) were impregnated with different volume (1, 2, 4, 6, 8 and 10 μL) of compounds to get a final concentration of 5, 10, 20, 30, 40 and 50 μg per disc. Sterilized paper disc loaded with the 10 μL of DMSO was taken as a control. The bacterial test pathogens were spread on fresh Mueller Hinton Agar (MHA) plates with the help of cotton swabs to form an even lawn of the test bacteria. The filter paper disc impregnated with the test compound were placed on the surface of the MHA plates seeded with test bacteria and the plates were incubated in a B. O. D. incubator (Caltan-152, Narang Scientific Works, New Delhi, India) for 24 h at 37 ± 2 °C. The inhibition zones around each disc were measured after 24 h of incubation. Commercial antibacterial drugs streptomycin sulphate and neomycin sulphate (Himedia) were used in same concentration of 5–50 μg/disc to compare effectiveness of the test compounds.

2.3.1. Determination of inhibitory concentration (IC_{50})

Inhibitory concentration 50 of compound **2, 3,** $Ni(OAc)_2 \cdot 4H_2O$**,** and $Ni(Cl)_2 \cdot 6H_2O$ were determined using broth dilution method with MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay. The test compounds were dissolved in DMSO to a final concentration of 8 mg/ml. The test compounds were diluted in various concentrations (2, 4, 8, 16, 32, 64, 128 μg/mL) in 5 ml culture tubes containing 4 ml Mueller-Hinton broth. One drop of exponentially growing culture of test bacterium was inoculated in each concentration of compounds and incubated at 37 ± 2 °C for 24 h. A control was prepared using test bacterium and equal volume of the DMSO (64 μl) in Mueller-Hinton broth without test compounds. After incubation period, 400 μL MTT solution (5 mg/ml) prepared in phosphate saline buffer (PBS) was added in each vial and incubated at 37 ± 2 °C for one hour. The absorbance was observed at 600 nm. Minimum concentration of compounds which were able to inhibit growth of half of the test bacterium is considered as IC_{50}.

2.4. Synthesis

2.4.1. Synthesis of 5-methyl-4-phenyl-1,2,4-triazole-3-thione

Acetic acid hydrazide was prepared by the literature method as described earlier [22]. 1-Acetyl-4-phenyl-3-thiosemicarbazide (Hpmt) was prepared by refluxing equimolar amounts of acetic acid hydrazide (0.741 g, 10 mmol) and phenylisothiocyanate (1.35 g, 10 mmol) in ethanol at 70 °C for 3h. The white precipitate obtained on cooling the reaction mixture was filtered off, washed with ethanol followed by water and air dried. Yield: 70%.

5-Methyl-4-phenyl-1,2,4-triazole-3-thione (Hmptt) was synthesized by dissolving the freshly prepared 1-acetyl-4-phenyl-3-thiosemicarbazide (1.06 g, 5 mmol) in an aqueous NaOH (10%, 10 mL) and refluxing the solution for 3 h. The solution was cooled in ice and acidified with conc. HCl. The white precipitate so obtained was filtered, washed with water, air dried and recrystallized from ethanol. Yield: 58%; m.p.220 °C. Anal. Found: C = 56.70, H = 4.85, N = 21.75, S = 16.55 (%) Anal. Calcd for $C_9H_9N_3S$ (191.00) C = 56.54, H = 4.71, N = 21.98, S = 16.75%. IR (ν cm-^{1}, KBr): ν(NH) 3053, ν(C=N) 1580; ν(N–N) 1017s; ν(C=S) 1001. ^{1}H NMR ($CDCl_3$; δ ppm): 12.28 (NH), 7.26–7.57 (m, 5H, phenyl ring), 2.21 (s, CH_3). ^{13}C NMR ($CDCl_3$; δ ppm): 168.16 (C=S), 149.55 (C=N), 127.71–133.37 (phenyl ring carbons), 12.03 (CH_3 carbon).

2.4.2. Synthesis of complex *1*

Complex **1** was synthesized by the reaction of 5-methyl-4-phenyl-1,2,4-triazole-3-thione (0.191 g, 1 mmol) in MeOH–CH_3CN (10 mL) and methanolic solution of $Cd(OAc)_2 \cdot 2H_2O$ (0.130 g, 0.5 mmol). The reaction mixture was stirred for 2 h at room temperature. The resulting brown precipitate was filtered off and washed thoroughly with methanol. The precipitate was dissolved in chloroform-methanol solution (20 mL) of thenoyltrifluroacetone (2.0 mL), yielding a light yellow solution was filtered off and kept for crystallization. The single crystals of complex **1** suitable for X-ray analyses were obtained by slow evaporation of the above solution over a period of 10 days. Yield: 50%; m.p.325 °C. Anal. Found: C = 43.60, H = 3.35, N = 17.20, S = 12.70%. Anal. Calcd for $C_{18}H_{16}CdN_6S_2$ (492.89), C = 43.82, H = 3.24, N = 17.04, S = 12.98%. IR (ν cm-^{1}, KBr): ν(C=N) 1595; ν(C–N) 1541; ν(N–N) 1038s; ν(C=S)