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Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Co(II) complexes of 1-phenyl-1H-tetrazole-5-thiol: Synthesis, spectral, structural characterization and thermal studies

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ABSTRACT

The new complexes $[Mn(ptt)_2(en)_2]$ (**1**), $[Ni(ptt)_2(en)_2]$ (**2**), $[Cu(ptt)_2(en)_2]$ (**3**), $[Zn(ptt)_2(en)]$ (**4**), $[Hg(ptt)_2(en)]$ (**5**), $[Cd(ptt)_2(en)_2]$ (**6**), $[Cd_2(\mu\text{-}ptt)_2(ptt)_2(bpy)_2]$ (**7**) and $[Co(phen)_3](ptt)_2$ (**8**) have been synthesized from 1-phenyl-1H-tetrazole-5-thiol (Hptt), containing en/bpy/phen as a co-ligand. The complexes have been characterized by elemental analyses, IR, UV–Vis and single crystal X-ray data. The ligand is covalently bonded through a deprotonated tetrazole ring nitrogen atom in complexes **1**–**4** and *via* a thiolato sulfur atom in complexes **5** and **6**, in which the ligand acts as uninegative monodentate. Complex **7** is dimeric *via* thiolato bridging, in which two terminal ligands act as uninegative monodentate while the other two ligands act as uninegative bridging bidentate. Complex **8** is ionic, in which the cationic part, $[Co(phen)_3]^{2+}$, is held by two tetrazole anions through hydrogen bonding. The structures of the complexes are stabilized through weak intermolecular C–H···S, N–H···S and N–H···N interactions. Complexes **5** and **7** are also stabilized by $\pi\cdots\pi$ interactions. Thermogravimetric analyses of the complexes have been investigated by TG-DTA, which indicate the metal sulfide/oxide as the final residue. All the complexes contain extended hydrogen bonding, providing supramolecular frameworks. The bioefficacy of complexes **1**–**4** and **8** has been examined against the growth of bacteria *in vitro* to evaluate their anti-microbial potential.

1. Introduction

Tetrazoles have received considerable attention because of their potential applications in various fields, such as medicine, explosives, materials science, photography, information recording systems and sweeteners [1–3]. Tetrazole and their derivatives exhibit diverse agricultural, industrial and biological activities, including anti-microbial, sedative, anti-convulsant and anti-inflammatory, and are also employed as precursors to a variety of nitrogen containing heterocycles [4,5]. It is well known that 1-substituted-5-thione tetrazoles have thiol and thione tautomeric forms and their anion, referred to as thionates, can be considered as a 6π-electron ring system, isoelectronic with $C_5H_5^-$. When coordinating to a metal center, mercapto tetrazoles or their anions may act as monodentate ligands through either the sulfur or nitrogen atom, or as a bidentate ligand through both. The common coordination mode reported in similar complexes is monodentate, with most of them involving S coordination. There are only a few metal-mercaptotetrazole and metal-mercaptotetrazolato complexes reported, such as $SnMe_2(phen)(MetzSH)_2$ and $(Ph_3P)_3Cu_4(SCN_4Me)_4$ [6], in which one nitrogen atom or both the sulfur and nitrogen atoms of the mercaptotetrazole or mercaptotetrazolato ligand are involved in coordination. Silver(I) and organotin(IV) complexes of the mercapto tetrazole 1-(4-hydroxyphenyl)-1H-tetrazole-5-thiol exhibit a μ_2-N,S chelating mode [7]. Tetrazoles are known to act as bridging ligands between cations such as Cu(II), Fe(II), Pd(II), Pt(II) and Ru(II) through their nitrogen atoms, forming coordination compounds that are interesting from both magnetic and chemical aspects. This potential metal complexing ligand has interesting properties that arise from the extensive electron delocalization in the tetrazole ring system and the exocyclic sulfur atom [6,8]. In view of the above, it is of great interest to investigate mixed ligand complexes of 1-phenyl-1H-tetrazole-5-thiol and to study the mode of bonding and structure of these complexes.

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The present paper reports the synthesis, spectral, structural, antibacterial activity and thermal behavior of the metal(II) complexes of 1-phenyl-1H-tetrazole-5-thiol, containing ethylenediamine/phenanthroline/bipyridyl as a co-ligand.

2. Experimental

2.1. Chemicals and starting materials

Commercial reagents were used without further purification and all experiments were carried out in an open atmosphere. 1-Phenyl-1H-tetrazole-5-thiol (Sigma Aldrich) was used as received. The solvents were dried and distilled before use following standard procedures.

2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a CHN Model CE-440 analyzer and on an Elementar Vario EL III Carlo Erba 1108. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant and electronic spectra were recorded on a SHIMADZU 1700 UV–Vis spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. Thermogravimetric analysis of the complexes was done using a Perkin Elmer-STA 6000 thermal analyzer, TA Instrument in a nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

2.3. In vitro antibacterial activity

Five human bacterial pathogens, *Salmonella typhi* (MTCC 3216), *Shigella flexneri* (ATCC 12022), *Staphylococcus aureus* (ATCC 25323), *Aeromonas hydrophila* (ATCC 7966) and *Enterococcus faecalis*, were used to test the antibacterial activity of complexes **1**–**4** and **8**. The antibacterial assay was done according to a reported method, with some slight modifications [9,10]. 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 volumes (1, 2, 4, 6, 8 and 10 μL) of the compounds to get a final concentration of 5, 10, 20, 30, 40 and 50 μg per disc. A sterilized paper disc was loaded with 10 μL of DMSO and 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 was 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. A clearing zone around the disc indicates the inhibitory activity of the test compounds. The commercial antibacterial drugs streptomycin sulfate and neomycin sulfate (Himedia) in the same concentration of 5–50 μg/disc were used to compare the effectiveness of the test compounds.

2.4. Syntheses

2.4.1. Syntheses of complexes *1*–*6*

A solution of Hptt (0.180 g, 1 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of the metal acetate (0.5 mmol)/$HgCl_2$ (for the Hg complex) and stirred for 2 h at room temperature. The resulting precipitates were filtered and washed thoroughly with methanol. A methanol solution (10 ml) of ethylenediamine (0.30 ml, 4 mmol) was added to the methanol suspension of the above compounds and stirred for 1 h at room temperature. The resulting solutions were filtered off and kept for crystallization. Single crystals suitable for X-ray analyses were obtained by slow evaporation of the above solutions over a period of 20–30 days.

$[Mn(ptt)_2(en)_2]$ (1): Yellow, yield: 58%. M.p. 232 °C. *Anal.* Calc. for $C_{18}H_{26}N_{12}S_2Mn$ (529.52): C, 40.79; H, 4.91; N, 31.73; S, 12.09. Found: C, 40.85; H, 4.98; N, 31.82; S, 12.21%. IR (ν cm^{-1}, KBr): ν(NH) 3259, ν(C–N) 1496, ν(N–N) 1063s, ν(C=S) 963, ν(Mn–N) 590.

$[Ni(ptt)_2(en)_2]$ (2): Pink, yield: 67%. M.p. 248 °C. *Anal.* Calc. for $C_{18}H_{26}N_{12}S_2Ni$ (533.34): C, 40.50; H, 4.87; N, 31.49; S, 11.99. Found: C, 40.59; H, 4.97; N, 31.58; S, 12.11%. IR (ν cm^{-1}, KBr): ν(NH) 3240, ν(C–N) 1493, ν(N–N) 1051, ν(C=S) 920, ν(Ni–N) 537.

$[Cu(ptt)_2(en)_2]$ (3): Blue, yield: 56%. M.p. 218 °C. *Anal.* Calc. for $C_{18}H_{26}N_{12}S_2Cu$ (538.17): C, 40.14; H, 4.83; N, 31.22; S, 11.89. Found: C, 40.25; H, 4.88; N, 31.40; S, 11.98%. IR (ν cm^{-1}, KBr): ν(NH) 3262, ν(C–N) 1496, ν(N–N) 1036, ν(C=S) 973, ν(Cu–N) 535.

$[Zn(ptt)_2(en)]$ (4): Colorless, yield: 45%. M.p. 240 °C. *Anal.* Calc. for $C_{16}H_{18}N_{10}S_2Zn$ (479.93): C, 40.01; H, 3.76; N, 29.17; S, 13.34. Found: C, 40.13; H, 3.80; N, 29.26; S, 13.42%. IR (ν cm^{-1}, KBr): ν(NH) 3235, ν(C–N) 1458, ν(N–N) 1082s, ν(C=S) 994, ν(Zn–N) 508.

$[Hg(ptt)_2(en)]$ (5): Colorless, yield: 64%. M.p. 288 °C. *Anal.* Calc. for $C_{16}H_{18}N_{10}S_2Hg$ (615.11): C, 23.41; H, 2.93; N, 22.76; S, 10.41. Found: C, 23.54; H, 2.99; N, 22.87; S, 10.52%. IR (ν cm^{-1}, KBr): ν(NH) 3237, ν(C=N) 1595, ν(N–N) 1088, ν(C–S) 762, ν(Hg–N) 557, ν(Hg–S) 490.

$[Cd(ptt)_2(en)_2]$ (6): Colorless, yield: 65%. M.p. 216 °C. *Anal.* Calc. for $C_{18}H_{26}N_{12}S_2Cd$ (587.03): C, 36.79; H, 4.43; N, 28.62; S, 10.90. Found: C, 36.86; H, 4.47; N 28.71; S, 11.05%. IR (ν cm^{-1}, KBr): ν(NH) 3267, ν(C=N) 1608, ν(N–N) 1091s, ν(C–S) 774, ν(Cd–N) 566, ν(Cd–S) 416.

2.4.2. Synthesis of $[Cd_2(\mu\text{-}ptt)_2(ptt)_2(bpy)_2]$ (**7**) and $[Co(phen)_3](ptt)_2$ (**8**)

The metal acetate (0.5 mmol) and the ligand Hptt (0.180 g, 1 mmol) were dissolved separately in 15–20 ml methanol, mixed together and stirred for 2 h. The solid which separated was filtered, washed successively with a methanol–water mixture (50:50 v/v) and finally with methanol. A methanol–$CHCl_3$ solution (10 ml) of 2,2′-bipyridyl/1,10-phenanthroline (1 mmol) was added to the methanol suspension of the above compound and stirred for 30 min. A clear solution was obtained which was filtered and kept for crystallization. Colorless and dark brown crystals of complexes **7** and **8** were obtained by slow evaporation of the above solution over a period of 20–25 days.

$[Cd_2(\mu\text{-}ptt)_2(ptt)_2(bpy)_2]$ (7): Colorless, yield: 73%. M.p. 238 °C. *Anal.* Calc. for $C_{48}H_{36}N_{20}S_4Cd_2$ (1246.07): C, 46.23; H, 2.89; N, 22.47; S, 10.27. Found: C, 46.28; H, 2.96; N, 22.61; S, 10.35%. IR (ν cm^{-1}, KBr): ν(C=N) 1596, ν(N–N) 1096, ν(C–S) 742, ν(Cd–N) 541, ν(Cd–S) 498.

$[Co(phen)_3](ptt)_2$ (8): Dark brown, yield: 68%. M.p. 244 °C. *Anal.* Calc. for $C_{50}H_{34}N_{14}S_2Co$ (953.96): C, 62.89; H, 3.56; N, 20.55; S, 6.70. Found: C, 63.02; H, 3.60; N, 20.74; S, 6.91%. IR (ν cm^{-1}, KBr): ν(C=N) 1587, ν(N–N) 1076, ν(C=S) 977, ν(Co–N) 562.

3. Crystal structure determination

Crystals suitable for X-ray analyses of compounds **1**–**8** were grown at room temperature. The crystal data were collected on an Oxford Gemini diffractometer equipped with CrysAlis CCD software, using a graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source at 293 K. A multi scan absorption correction was applied to the X-ray data collection. The structures were solved by direct methods (SHELXL-08) and refined against all data by full matrix least-square on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All of the hydrogen atoms were