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Dimeric and polymeric mercury(II) complexes of 1-methyl-1,2,3,4-tetrazole-5-thiol: Synthesis, crystal structure, spectroscopic characterization, and thermal analyses

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ABSTRACT

Two-dimensional coordination polymer of $[Hg(\mu_3\text{-mmtz})_2]_n$ (**1**) and centrosymmetric dinuclear complexes of $\{[H_2en][Hg_2(mmtz)_4(\mu\text{-}Br)_2]\}$ (**2**) and $\{[H_2en][Hg_2(mmtz)_4(\mu\text{-}I)_2]\}$ (**3**) (where Hmmtz is 1-methyl-1,2,3,4-tetrazole-5-thiol and en is ethylene diamine) were synthesized from the reaction of Hmmtz and en with $HgCl_2$, $HgBr_2$ and HgI_2, respectively, in CH_3OH. Complex **1** was also synthesized from the reaction of Hmmtz and en with HgX_2 (X = OAc and SCN) in CH_3OH. These three complexes were thoroughly characterized by elemental analysis (CHN), thermal gravimetric analysis (TGA), differential thermal analyses (DTA), infrared, UV–vis, ^1H NMR, and luminescence spectroscopy, and their structures were determined by single-crystal X-ray diffraction.

1. Introduction

Synthesis and characterization of 1-methyl-1,2,3,4-tetrazole-5-thiol (Hmmtz) has been reported by Lieber and Ramachandran [1]. Single-crystal structure of this compound has been determined by Sandoval and coworkers by of using X-ray diffraction method [2]. The X-ray structural analysis indicated that this compound is in thione form in the solid state, whereas in the solution tautomerisation between thione form and thiol form is observed (Scheme 1) [2,3]. Hmmtz is a suitable multidentate ligand and can be coordinated to metal centers through three N atoms from tetrazole ring and one S atom from thiol group. In anionic form of this ligand, the tetrazole and thiol group can connect one, two, three, four, five and six metal ions in nine distinct coordination modes (Scheme 2). These multiple coordination modes of $mmtz^-$ anionic ligand may lead to formation of the mononuclear, binuclear, one-dimensional coordination polymers and two-dimensional coordination polymers with topologically interesting structures [4–20]. In this regard, recently we reported preparation and characterization one-dimensional coordination polymer of $[Hg(\mu\text{-mptrz})_2]_n$ and centrosymmetric dinuclear complexes of $\{[H_2en][Hg_2(mptrz)_4(\mu\text{-}Br)_2]\}$ and $\{[H_2en][Hg_2(mptrz)_4(\mu\text{-}I)_2]\}$ [21]. These compounds were synthesized by the reaction of 4-methyl-4H-1,2,4-triazole-3-thiol (Hmptrz) and $HgCl_2$, $HgBr_2$ and HgI_2 in the presence of ethylene diamine in methanol. In continuation of our research works, herein, three new complexes of $[Hg(\mu_3\text{-mmtz})_2]_n$ (**1**), $\{[H_2en][Hg_2(mmtz)_4(\mu\text{-}Br)_2]\}$ (**2**) and $\{[H_2en][Hg_2(mmtz)_4(\mu\text{-}I)_2]\}$ (**3**) have been synthesized in methanol according to the reported synthetic procedure of complexes of $[Hg(\mu\text{-mptrz})_2]_n$, $\{[H_2en][Hg_2(mptrz)_4(\mu\text{-}Br)_2]\}$ and $\{[H_2en][Hg_2(mptrz)_4(\mu\text{-}I)_2]\}$ [21] except instead of 4-methyl-4H-1,2,4-triazole-3-thiol, the 1-methyl-1,2,3,4-tetrazole-5-thiol is used. Compounds **2** and **3** are isostructure with previous reported complexes of $\{[H_2en][Hg_2(mptrz)_4(\mu\text{-}Br)_2]\}$ and $\{[H_2en][Hg_2(mptrz)_4(\mu\text{-}I)_2]\}$, respectively, while the structure of **1** is quite different from the reported homologous one, $[Hg(\mu\text{-mptrz})_2]_n$.

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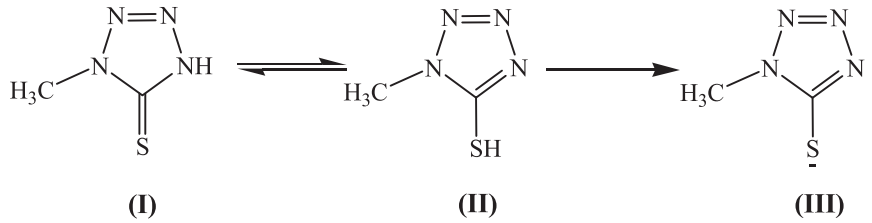
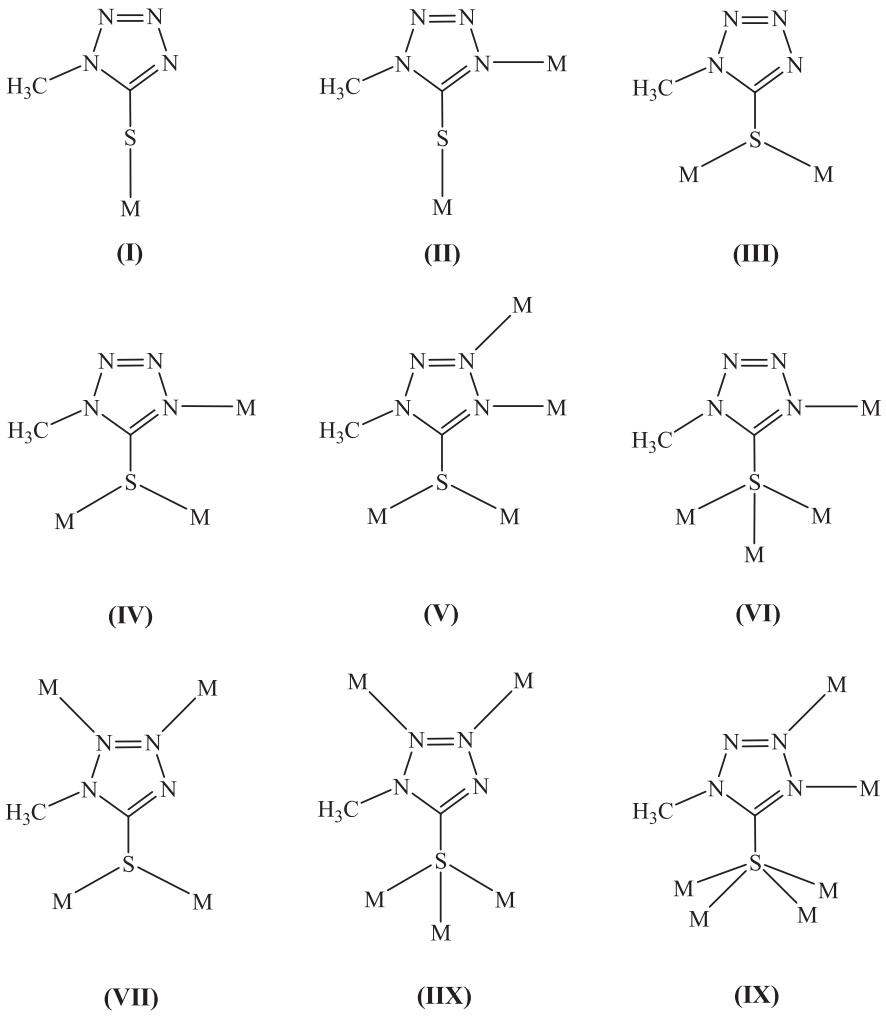


Scheme 1. (I) Thione tautomer, (II) thiol tautomer and (III) anionic form of Hmmtz.



Scheme 2. The possible binding modes of $mmtz^-$ anionic ligand to metal ions.

2. Experimental

2.1. Materials and physical methods

1-Methyl-1,2,3,4-tetrazole-5-thiol was purchased from Aldrich, and used as received. Other materials were purchased from Merck and used without further purification. Infrared spectra (4000–250 cm^{-1}) of solid samples were taken as 1% dispersion in CsI pellets using a Shimadzu-470 spectrometer. NMR spectra were recorded on a Bruker AC-300 spectrometer for protons at 300.13 MHz in DMSO-d_6. Melting points were obtained on a Kofler Heizbank Rechart type 7841 melting point apparatus. Elemental analysis was performed using a Heraeus CHN–O Rapid analyzer. Thermal behavior was measured with a STA 503 Bähr apparatus. UV–vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell in DMSO at room temperature, and luminescence spectra were recorded on a Perkin Elmer LS 45 using a 1 cm path length cell.

2.2. Synthesis of $[Hg(\mu_3\text{-}mmtz)_2]_n$ (**1**)

1-Methyl-1,2,3,4-tetrazole-5-thiol (0.43 g, 3.70 mmol) was dissolved in a mixture of 15 ml methanol and 9.25 ml ethylene diamine (0.2 M in methanol solution, 1.85 mmol). The solution was then stirred for 5 min and added gradually to a solution of mercury(II) chloride (0.51 g, 1.85 mmol) in CH_3OH (15 ml) at room temperature and the resulting white precipitant was dissolved in DMSO. Suitable crystals for X-ray diffraction measurement were