



Syntheses, spectral and structural characterization of Ni(II) complexes of 4-amino-5-phenyl/3-pyridyl/thiophen-2H-1,2,4-triazole-3-thione



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HIGHLIGHTS

- Ni(II) complexes of 4-amino triazoles containing ethylenediamine (en) are reported.
- The bonding sites of ligands in the complexes are triazole and ethylenediamine nitrogen.
- Complexes contain extended hydrogen bonding which provide supramolecular framework.
- The structures of the complexes are stabilized by intermolecular and intramolecular hydrogen bonding.
- CHCl₃ molecule is lost around 200 °C from complex **2** as shown by TGA.

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ABSTRACT

New mixed ligand complexes [Ni(aptt)₂(en)₂] (**1**), [Ni(apytt)₂(en)₂].CHCl₃ (**2**) and [Ni(athtt)₂(en)₂] (**3**) with 4-amino-5-phenyl-2H-1,2,4-triazole-3-thione (Haptt), 4-amino-5-(pyridin-3-yl)-4,5-dihydro-3H-1,2,4-triazole-3-thione (Hapytt) and 4-amino-5-thiophen-2H-1,2,4-triazole-3-thione (Hathtt) have been prepared containing en as the secondary ligand. The metal complexes have been characterized with the aid of elemental analyses, IR, magnetic susceptibility and single crystal X-ray data. All the complexes are bonded through two nitrogen atoms of two triazole ligands and four nitrogens of two ethylenediamine and the resulting complexes have distorted octahedral geometry. The triazole ligands behave as uninegative monodentate, bonding through triazole nitrogen due to the hard character of the nickel(II). The complexes contain extended hydrogen bonding providing supramolecular framework. The course of the thermal degradation of complex **2** has been investigated by TG-DTA which suggest the loss of CHCl₃ molecule around 200 °C and finally a residue of NiS is left behind.

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1. Introduction

Triazoles and their derivatives show diverse biological activity such as anti-bacterial, anti-fungal, anti-inflammatory, antiviral, analgesic, anticonvulsant, and antidepressant [1–6]. 1,2,4-Triazoles are suitable for further chemical modifications and are synthesized by the intramolecular cyclization of 1,4-disubstituted thiosemicarbazides [7,8]. They are of interest as pharmacologically active ligands in coordination chemistry. It is observed that these compounds are present in thione–thiol tautomeric equilibrium [9–11]. The extensively derived substituted 1,2,4-triazoles have attracted more attention than the unsubstituted one, as they can provide more coordination modes, indicating the formation of new coordinated complexes. In this context, we have designed

and synthesized the Ni(II) complexes of 4-amino-5-phenyl-2H-1,2,4-triazole-3-thione (Haptt), 4-amino-5-(pyridin-3-yl)-4,5-dihydro-3H-1,2,4-triazole-3-thione (Hapytt) and 4-amino-5-thiophen-2H-1,2,4-triazole-3-thione (Hathtt) in the presence of ethylenediamine 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. Benzoic/Nicotinic/Thiophen acid hydrazide (Sigma–Aldrich), CS₂ (S D Fine Chemicals, India) and KOH (Qualigens) were used as received. All the solvents were purchased from Merck and used after purification. The yield calculation is based on the weight of the ligand or the initial starting material where intermediate were not isolated.

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2.2. Physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer as Nujol mulls. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100-FT IR spectrophotometer.

2.3. Synthesis

2.3.1. Preparation of 4-amino-5-phenyl-1,2,4-triazole-3-thione (Haptt), 4-amino-5-(pyridine-3-yl)-4,5-dihydro-3H-1,2,4-triazole-3-thione (Hapytt) and 4-amino-5-thiophen-1,2,4-triazole-3-thione (Hathtt)

The preparation and characterization of 4-amino-5-phenyl-1,2,4-triazole-3-thione (Haptt), 4-amino-5-(pyridine-3-yl)-4,5-dihydro-3H-1,2,4-triazole-3-thione (Hapytt) and 4-amino-5-thiophen-1,2,4-triazole-3-thione (Hathtt) are described elsewhere [12–14].

2.3.2. Preparation of $[\text{Ni}(\text{appt})_2(\text{en})_2]$ (1)

Hot methanolic solutions (20 ml) of $[\text{Ni}(\text{en})_2(\text{NCS})_2]$ (0.460 g, 2 mmol) and Haptt (0.77 g, 4 mmol) were mixed together, stirred well and filtered. The filtrate was kept for 10 days where upon brown crystals of complex **1** suitable for X-ray structural investigation were obtained. Yield: (0.39 g, 70%); m.p.: 548 K. Anal. Found: C, 42.84%; H, 5.35%; N, 30.02%; S, 11.43%. Calc. for $\text{C}_{20}\text{H}_{30}\text{N}_{12}\text{S}_2\text{Ni}$ (561.39): C, 42.75%; H, 5.34%; N, 29.92%; S, 11.40%. IR data (ν cm^{-1} , KBr): (NH) 3263; (C=N) 1597; (N–N) 1008; (C=S) 947; (Ni–N) 518. UV–Vis [λ_{max} , Nujol mulls, cm^{-1}]: 12800, 19415, 31250, 35085.

2.3.3. Synthesis of $[\text{Ni}(\text{apytt})_2(\text{en})_2]\cdot\text{CHCl}_3$ (2)

A solution of Hapytt (0.386 g, 2 mmol) in MeOH (10 ml) was added to a methanol solution (10 ml) of $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.248 g, 1 mmol) and the reaction mixture was stirred for 3 h at room temperature. The resulting pink precipitate was filtered off, washed thoroughly with methanol and chloroform and methanol solution of en (0.3 ml, 4 mmol) was added to the methanol suspension of the above compound and stirred for 1 h. A red color solution was obtained which was filtered off and kept for crystallization. Red crystals of **2** suitable for X-ray analyses were obtained by slow evaporation of the above solution over a period of 20 days. Yield: (0.35 g 58%); m.p. 547 K; Anal. Found: C, 33.48%; H, 4.12%; N, 28.73%; S, 9.32%. Calc. for $\text{C}_{19}\text{H}_{28}\text{Cl}_3\text{N}_{14}\text{NiS}_2$ (681.73): C, 33.44%; H, 4.10%; N, 28.75%; S, 9.38%. IR (KBr, ν , cm^{-1}): (NH) 3154;

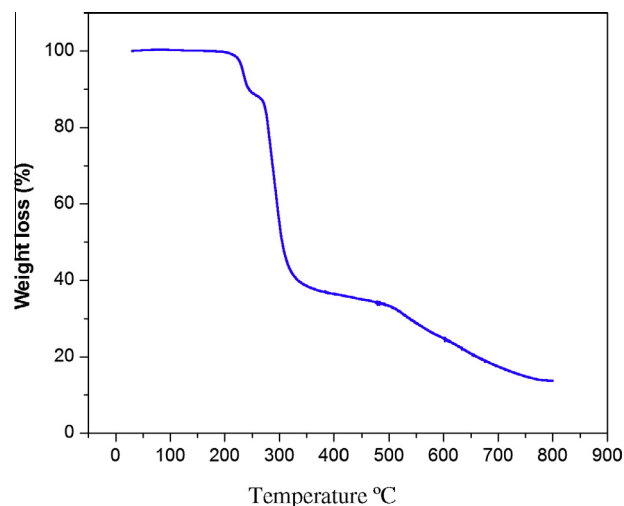


Fig. 1. TGA analysis of $[\text{Ni}(\text{apytt})_2(\text{en})_2]\cdot\text{CHCl}_3$ (2).

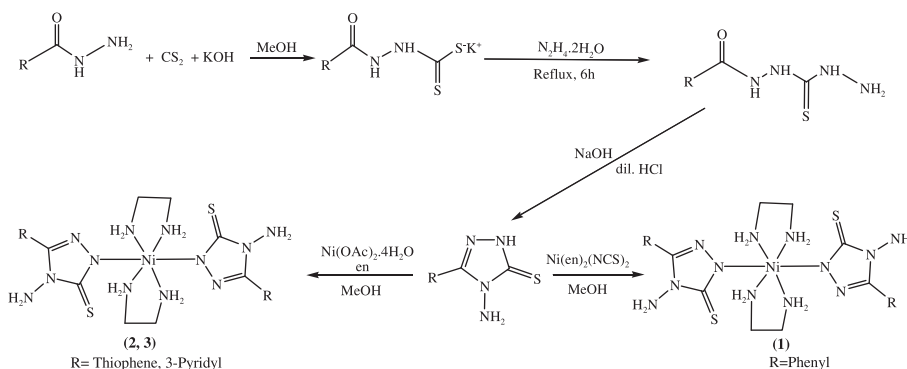
(C=N) 1598; (N–N) 1017; (C=S) 989; (Ni–N) 405. UV–Vis [λ_{max} , DMSO, cm^{-1}]: 13965, 19045, 26315, 29850.

2.3.4. Synthesis of $[\text{Ni}(\text{athtt})_2(\text{en})_2]$ (3)

A solution of Hathtt (0.396 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.266 g, 1 mmol) and the reaction mixture stirred for 3 h at room temperature. The resulting pink precipitate was filtered off and washed with methanol. A methanol solution of en (0.3 ml, 4 mmol) was added to the methanol suspension of the above precipitate and stirred for 1 h. A clear red solution was obtained which was filtered and kept for crystallization. Red crystals of **3** suitable for X-ray analyses were obtained by slow evaporation of the above solution over a period of 20 days. Yield: (0.83 g 58%); m.p. 517 K; Anal. Found: C, 33.55%; H, 4.56%; N, 29.27%; S, 22.36%. Calc. for $\text{C}_{16}\text{H}_{26}\text{N}_{12}\text{NiS}_4$ (573.46): C, 33.48%; H, 4.53%; N, 29.29%; S, 22.32%. IR (KBr, ν , cm^{-1}): (NH) 3233; (C=N) 1614; (N–N) 1053; (C=S) 964; (Ni–N) 511. UV–Vis [λ_{max} , DMSO, cm^{-1}]: 13105, 18515, 29410.

2.3.5. X-ray crystallography

Data were recorded at 293(2) on a Bruker three-circle diffractometer for complex **1** and on an Oxford Diffraction Gemini diffractometer for complexes **2** and **3** equipped with a CrysAlis Pro./SMART 6000 CCD software using a graphite mono-chromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source. The structures were solved by direct methods (SHELXL-2012) and refined against all data by full matrix least-squares on F^2 using anisotropic displacement



Scheme 1. Preparation of complexes **1**, **2** and **3**.

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