Synthesis and Characterization of the Triazole Derived from Thiosemicarbazide, 4-Amino-5-Phenyl-4H-1,2,4-Triazole-3-Thiol and Their Copper(II) and Nickel(II) Complexes

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ABSRTACT

Triazole N-(3-mercapto-5-phenyl-4H-1,2,4-triazol-4-yl)hydrazinecarbothioamide prepared in good yield via the condensation of 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol and thiosemicarbazide. The copper (II) and nickel (II) complexes of the triazole ligand were also prepared.

Keywords: Triazole, Thiosemicarbazide, ligand, complexes

تحضير وتشخيص مشتق الترايزول من الثايوسيميكاربزايد والامينوفنيل ترايزول ثايول ومعقداتها الانتقالية مع فلزات النحاس والنيكل

الخلاصة

تم تحضير وتشخيص مشتق الترايزول من الثايوسيميكاربزايد والامينوفنيل ترايزول ثايول ومعقداتها الانتقالية مع فلزات النحاس والنيكل.

INTRODUCTION

Triazole derivatives have been reported to have pharmacological, insecticidal, fungicidal, and herbicidal activities. [1], the synthesis of these heterocycles has received considerable attention in recent years [2].

The synthesis and metal complex structures of substituted 1,2,4-triazole ligands have gained considerable attention in recent years [3-7]. 1,2,4-triazole and its

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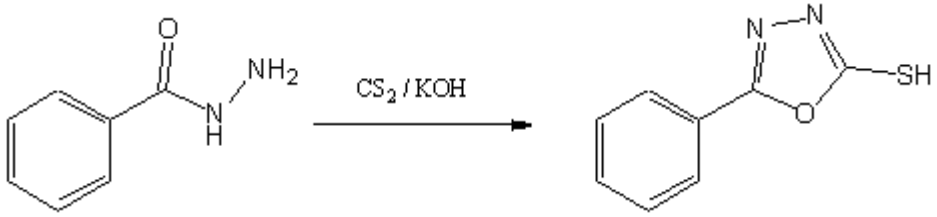
derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. Many transition metal complexes of 1,2,4-triazoles deri- vatives can be synthesized [8]. Triazoles are nitrogen- containing organic compounds, and their metal com- plexes display a broad range of biological activity, acting as antitumor, antibacterial, antifungal and antiviral agents [9]. triazoles nucleus and their derivatives emerge rapidly with the advances of modern heterocyclic chemistry, promising a variety of medical applications such as antibacterial, antifungal, anticancer, antitumor, anticonvulsant, anti-inflammatory, and analgesic properties [10–13]. The incorporation of the 1,2,4-triazole unit into Schiff base macrocycles is of considerable current interest as complexes of 1,2,4-triazoles are being developed for potential use in applications such as magnetic materials and photo chemically driven molecular devices [14].

In the present study we synthesized N-(3-mercapto-5-phenyl-4H-1,2,4-triazol-4-yl)hydrazinecarbothioamide and it Cu (II) and Ni (II) complexes.

EXPERIMENTAL

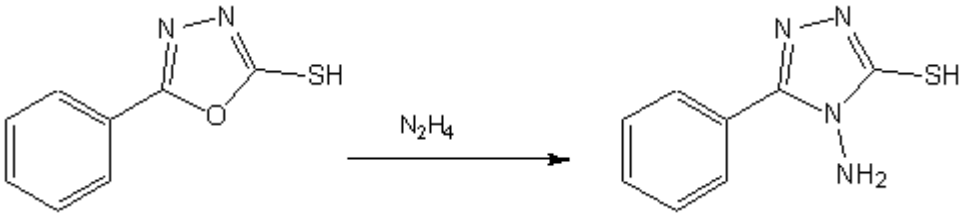
All chemicals used in this work were of reagent grade (supplied by either Sigma-Aldrich or Fluka) and used without farther purifications. The FTIR spectra were recorded in the (4000–200) cm^{-1} range on cesium iodide disks using a Shimadzu FTIR 8300 Spectrophotometer. Proton. The UV-Visible spectra were measured in ethanol using a Shimadzu UV-VIS 160A spectrophotometer in the range (200–1000) nm. Magnetic susceptibility measurement for complexes was obtained at room temperature using a Magnetic Susceptibility Balance Model MSB-MKI. Elemental micro analysis was carried out using a CHN elemental analyzer model 5500-Carlo Erba instrument. A Gallenkamp M.F.B.600.010 F melting point apparatus was used to measure the melting points of ligand and metal complexes.

Synthesis of 5-Phenyl-1,3,4-oxadiazol-2-ylamine. It was synthesized by refluxation of benzoic hydrazide (3 g), Carbon disulfide (10 mL) and 1.3 g of potassium hydroxide in (200 mL) of 250 mL of ethanol for 8 h. After completion of the reaction, excess of ethanol was removed under reduced pressure The mixture was diluted with distilled water (200 mL) and acidified with 4N hydrochloric acid to pH 3. The precipitate was filtered off and washed with cold THF to give white product. Yield 85%; mp 242 °C.



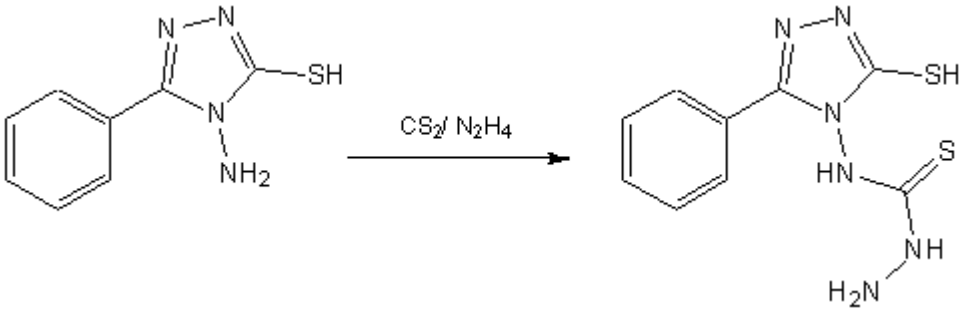
Synthesis of the 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol

5-Phenyl-1,3,4-oxadiazol-2-ylamine (3 g) and 5 mL of hydrazine hydrate in 150 mL of absolute ethanol were refluxed After the completion of the reaction the solvent and excess of hydrazine hydrate were removed under reduced pressure using rotary evaporator. The residue was washed with cold THF and recrystallized from ethanol.

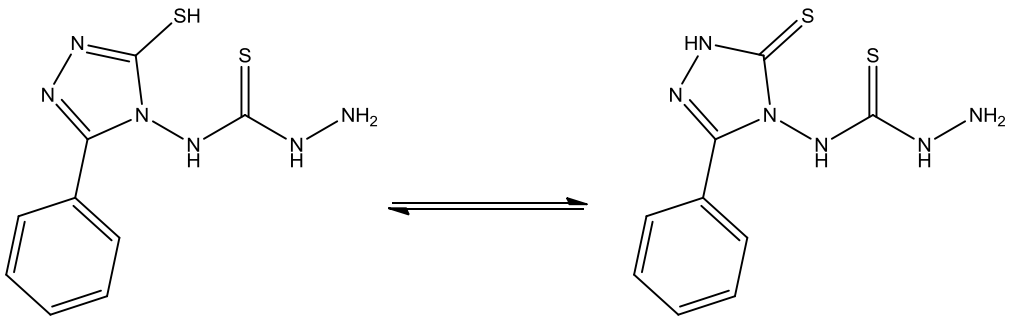


Synthesis of the N-(3-mercapto-5-phenyl-4H-1,2,4-triazol-4-yl)hydrazinecarbothioamide (L).

To a solution of 4-***amino-5*-phenyl-4H-1,2,4-triazole-3-thiol** (2gm)in DMF (10ml) wasadded, sodium hydroxide (0.7g) and carbon disulphide (2. ml). The mixture was stirred at r.t.for 1 hour. Added 5 mL of hydrazine hydrate to the stirred mixture with stirring for another 4 hours at 60oC. The precipitate was separated out and recrystalized from ethanol. Yield 45%, mp= 212 oC.IR (KBr, cm-1) 3351 and 3217.3 cm-1 (NH), 3092.9(C-H aromatic), 1639 (C=N), 1299.1 (C=S).



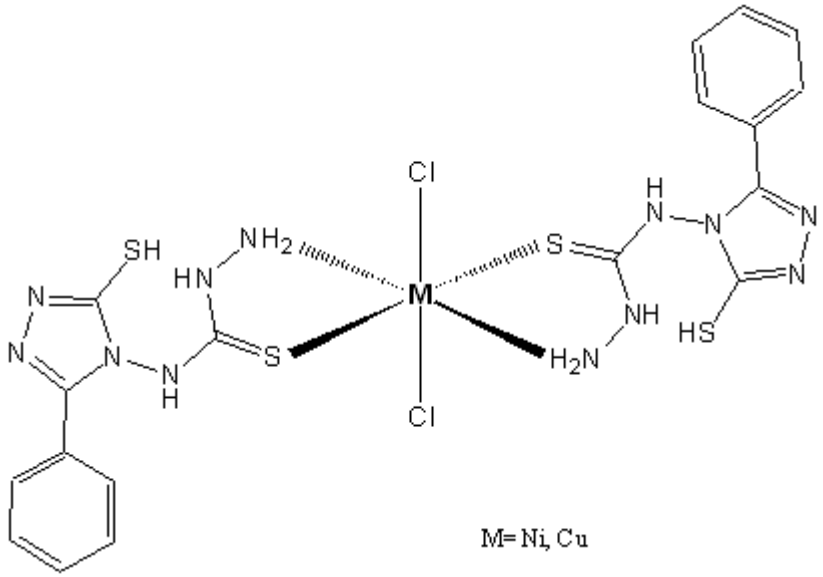
Tautumerization of the ligand



Synthesis of the Complexes

Metal salts ($NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$; 5 mmol) in hot ethanol (20 mL) were mixedwith hot ethanolic solution of the Ligand (1.61 g, 10 mmol) and refluxed for 7 hours. On cooling the contents, the colored complexes were separated out. The products were filtered, washed with cold 50% ethanol.

Ni-complex; yield 70%, mp >300d. Cu-complex; yield 71%, mp 287d.



Results and Discussion

Tow bands were observed for the ligand. The first band at 271 nm which represents the($\pi \rightarrow \pi^*$)transition while the position of the second appeared at 327 nm which represents the ($n \rightarrow \pi^*$) transition. The high spin octahedral Ni(II) complexes exhibit magnetic moment value at 2.51 B. M. Ni(II) complex, have three observed absorptions (2404.6, 28696.2, 40943.8 cm^{-1}) can be attributed to the transitions, $A_2g \rightarrow T_1g$ and $A_2g \rightarrow T_1g$.The Cu(II) exhibit magnetic moment value at 1.68 BM, exhibited a broad absorption centered at 21246.8 cm^{-1}, 32859.3 cm^{-1} and 40114.5 cm^{-1} assigned to $A_2g \rightarrow T_1g$ and $^2Eg \rightarrow {}^2T_2g$ transition suggesting a octahedral geometry

Table (1): Physical data of complexes.

No.	Complexes	Color	ΩM (Ohm cm^2 mol^{-1})	M:L
1	$Ni(C_8H_8N_4S)_2Cl_2$	green	26	1:2
2	$Cu(C_8H_8N_4S)_2Cl_2$	Brown	21	1:2

Table (2): Infrared absorption frequencies (cm^{-1}) of ligand and complexes.

No.	ν (NH)	ν (C=N)	M-N

1	3273, 3237	1644	483
2	3321, 3255	1641	439

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