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Structural and spectral studies of an iron(III) complex [Fe(Pranthas)$_2$][FeCl$_4$] derived from 2-acetylpyridine-*N*(4), *N*(4)-(butane-1, 4-diyl) thiosemicarbazone (HPranthas)

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Abstract

A novel iron(III) complex of 2-acetylpyridine *N*(4), *N*(4)-(butyl-1, 4-diyl) thiosemicarbazone (HPranthas), [Fe(Pranthas)$_2$]FeCl$_4$ was synthesized and physico-chemically characterized by means of partial elemental analysis, magnetic measurements (polycrystalline state), UV–Vis and IR spectroscopies. The presence of spin-paired iron(III) cation with $d_{xz}^2 d_{yz}^2 d_{xy}^1$ ground state is revealed by the EPR and Mössbauer spectral data. Structure of the free ligand HPranthas and the complex [Fe(Pranthas)$_2$]FeCl$_4$ were solved by single crystal X-ray diffraction. The framework of iron(III) complex consists of a discrete monomeric cationic entity containing low spin iron(III) in a slightly distorted octahedral environment. The metal ion is bonded to one sulfur and two nitrogens of each thiosemicarbazone molecule. The tetrachloroferrate(III) ion acts as counterion.

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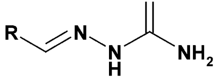
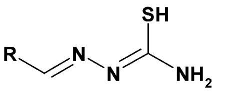
Keywords: Iron(III) complex; Thiosemicarbazone; Single crystal X-ray diffraction; Mössbauer spectrum; EPR spectrum; IR spectrum

1. Introduction

Thiosemicarbazones and their metal complexes have been subject of interest in numerous studies because of their chemical and biological properties [1,2]. Thiosemicarbazones generally exist in the thione form in the solid state but exist as an equilibrium mixture of thione and thioenol forms in solution (A and B) which is essential for their versatile chelating behavior.



A



B

The well documented biological activities of several heterocyclic thiosemicarbazones have been often attributed to a chelation phenomenon with transition metal ions [3]. The success in therapeutic applications of *N*-heterocyclic thiosemicarbazones for removing excess iron from iron-loaded mice through chelation therapy is quite remarkable [4]. 2-Acetylpyridine thiosemicarbazones were the first thiosemicarbazones in which antimalarial activity was detected, and the highest activity is reported when the *N*(4) position is either disubstituted or part of a ring system [5]. There are some reports on the iron(III) complexes of biologically active 2-acetylpyridine thiosemicarbazones [6,7]. Recently we have reported the copper(II) [8] and iron(III) [9] complexes synthesized from 2-benzoylpyridine *N*(4), *N*(4)-(butane-1, 4-diyl)thiosemicarbazone. This paper stems from our interests in the investigation of some biologically active 2-acetylpyridine thiosemicarbazones and their metal complexes. In continuation of our investigations on the thiosemicarbazones and semicarbazones and their metal complexes [10–12], we have synthesized 2-acetylpyridine *N*(4), *N*(4)-(butane-1, 4-diyl)thiosemicarbazone (HPranthas), and its iron(III) complex using ferric chloride.

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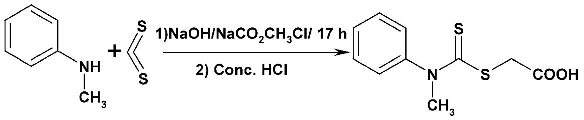
2. Experimental

2.1. General

2-Acetylpyridine (Aldrich), pyrrolidine (SRL), *N*-methylaniline (Merck), thiosemicarbazide (SRL), carbon disulfide (Merck), hydrazine hydrate (99%, SRL) and ferric chloride (Merck) were used as received. All solvents were distilled before use. 2-Acetylpyridine *N*(4), *N*(4)-(butane-1, 4-diyl)thiosemicarbazone (HPranthas) was synthesized (Scheme 1) by the following adoption of a reported procedure [13].

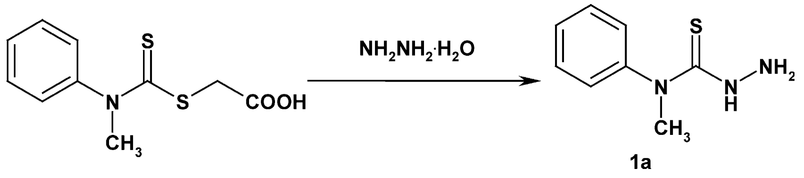
2.2. Synthesis of carboxymethyl N-methyl N-phenyldithiocarbamate

A mixture consisting of 12.0 ml (15.2 g, 0.2 mol) of CS_2 and 21.6 ml *N*-methylaniline was treated with a solution of 8.4 g (0.21 mol) of NaOH in 250 ml water. After stirring at room temperature for 4 h, the organic layer had disappeared. At this point, the straw colored solution was treated with 23.2 g (0.20 mol) of sodium chloroacetate and allowed to stand overnight for 17 h. The solution was acidified with 25 ml of conc. HCl and the solid which separated was collected and dried. This afforded 39.7 g of pale buff colored carboxymethyl *N*-methyl *N*-phenyldithiocarbamate. Mp 197–198 °C.



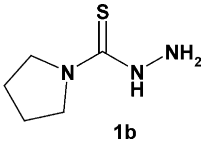
2.3. Synthesis of 4-methyl-4-phenyl-3-thiosemicarbazide (*1a*)

A solution of carboxymethyl *N*-methyl *N*-phenyldithiocarbamate in 20 ml 99% hydrazine hydrate and 10 ml of water was heated on the rings of a steam bath. After 3 min crystals begin to separate. Heating was continued for 22 min. The crystals were collected by filtration, washed well with water and dried under a heat lamp. The crude product was recrystallized from a mixture of 50 ml ethanol and 25 ml of water. This gave 10.8 g of stout colorless rods of 4-methyl-4-phenyl-3-thiosemicarbazide (**1a**). Mp 124–125 °C.



2.4. Pyrrolidine-1-thiocarboxylic acid hydrazide (*1b*)

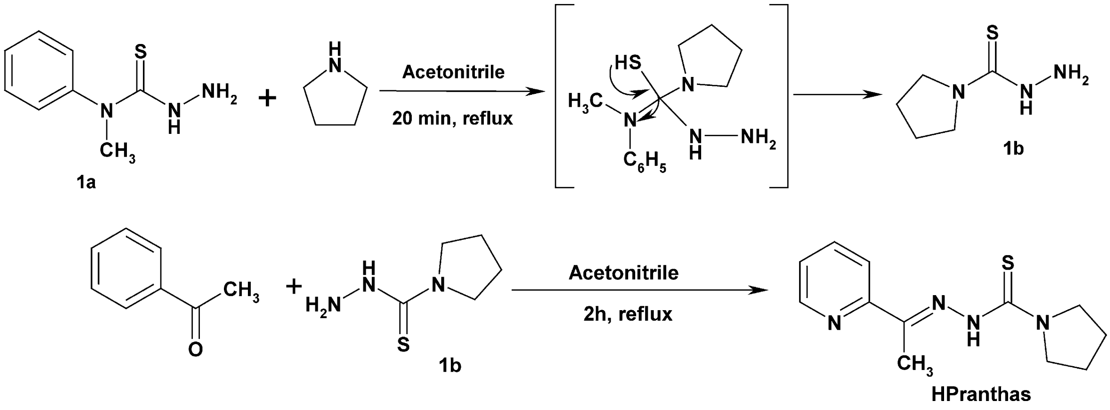
A solution of 1.0 g of **1a** in 5 ml of acetonitrile was treated with 395 mg of pyrrolidine and the solution was heated under reflux for 15 min. The solution was chilled and the microporous off white crystals separated were collected and washed with acetonitrile. This afforded 570 mg of **1b**. Mp 174–175 °C.



1b

2.5. Synthesis of HPranthas

A solution 1 g (2 mmol) of 4-methyl-4-phenyl-3-thiosemicarbazide in 5 ml of acetonitrile was treated with 2 mmol of pyrrolidine-1-thiocarboxylic acid



Scheme 1.

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