Synthesis and characterization of $O,O'$-tris-di-$\alpha$-naphthylidithiophosphate of Iron(III).

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Abstract: $O,O'$-tris -di-$\alpha$-naphthylidithiophosphate of Iron(III) corresponding to [(α-C$_{10}$H$_7$O$_3$)PS$_2$]$_3$Fe, has been synthesized by the reaction of Fe(NO$_3$)$_3$·9H$_2$O in 1:3 molar ratio with sodium salt of $O,O'$-di-$\alpha$-naphthylidithiophosphate in water. This complex has been characterized by elemental analyses, C, H, S, Fe and further characterization by some spectroscopy analyses, namely, IR and ESI mass has been carried out. Monomeric nature of this complex has been confirmed and Iron atom is six coordinate bonded to three bidentate dithiophosphate ligands leading to an octahedral geometry around Iron(III)

1. Introduction

The indispensable role of iron-sulfur cluster proteins in a range of physicochemical processes that influence the electron transfer, catalysis, and gene regulation has been well established [1]. Iron complexes are also active participants in the field of transition metal catalysts and are known to catalyze a variety of reactions [2-3]. Iron sulfur clusters are significant component of nitrogenase, the nitrogen fixing enzyme, and their inorganic models have been investigated rigorously [4-5]. A vast amount of literature is present pertaining to the sulfur donor ligand complexes of Iron(III) [6-9]. Therefore, development of new complexes of iron with sulfur donor ligands, particularly, dithiophosphates is an important field of investigation. Herein, the synthesis and characterization of a complex of iron with a new dithiophosphate ligand corresponding to, $O,O'$-tris-di-$\alpha$-naphthylidithiophosphate of iron(III) has been reported.

2. MATERIALS AND METHODS

Sodium salt of di-$\alpha$-naphthylidithiophosphate was prepared by literature method [10]. Iron was estimated by standard procedure [11]. Elemental analyses (C, H, N, S) were measured with the Elemental Analyser Vario EL-III, their results were found to be in good agreement (±0.3%) with the calculated values. Infrared spectra were recorded in the range of 4000–200 cm$^{-1}$ using pressed KBr pellets on a Perkin Elmer-spectrum RX1 FT-IR spectrophotometer.

Synthesis of [(α-C$_{10}$H$_7$O$_3$)PS$_2$]$_3$Fe

For the synthesis of [(α-C$_{10}$H$_7$O$_3$)PS$_2$]$_3$Fe aqueous solution (30ml) of Fe(NO$_3$)$_3$·9H$_2$O (1.00 g or 2.47 mmol) was taken in a 100 ml round bottom flask. To this solution, added (30ml) aqueous solution of sodium salt of $O,O'$-di-$\alpha$-naphthylidithiophosphate ligand, (α-C$_{10}$H$_7$O$_3$)PS$_2$Na (1.0 g or 2.47 mmol) in a drop wise with constant stirring. Precipitation of black solid complex initiated. The contents were further stirred for 3 hours. The reaction contents were filtered, which yielded black precipitate of [(α-C$_{10}$H$_7$O$_3$)PS$_2$]$_3$Fe as black solid in 89% yield. Anal. Calc. C$_{37}$H$_{40}$O$_7$P$_3$S$_3$Fe: C, 60.05; H, 3.53; Fe, 4.65; S, 16.03; Found: C, 59.85; H, 3.33; Fe, 4.55; S, 15.93; IR (KBr): $v = 1163$, s $[\nu(P)-O-C]$, 979, s $[\nu(P-O-C)]$, 871, s $[\nu(P=S)]$, 583, m $[\nu(P-S)]$, 395, w $[\nu(Pb-S)]$ cm$^{-1}$.

3. Results and discussion

The title complex has been prepared in good yield by the reaction of sodium salt of $O,O'$-di-$\alpha$-naphthylidithiophosphate ligand with Fe(NO$_3$)$_3$·9H$_2$O in 3:1 stoichiometric ratio (Scheme 1).

$$3(\alpha-C_{10}H_7O_3)PS_2Na + Fe(NO_3)_3·9H_2O \xrightarrow{H_2O} -3NaNO_3$$

$$[\alpha-C_{10}H_7O_3(PS_2)_3Fe]$$

Scheme 1: The synthesis of $O,O'$-tris-di-$\alpha$-naphthylidithiophosphate of iron(III).

This complex was obtained as black solid in 89% yield after the separation of sodium chloride. The elemental analyses (C,H,S, Fe) were found in close agreement with the molecular formula of the complexes. It has been further characterized by some other spectroscopic analyses, viz., IR and ESI-Mass.

3.1. Infrared spectroscopic analysis

The IR spectrum for the complex showed characteristic IR peaks which were assigned in
3.2. ESI-Mass Spectroscopic studies

The mass spectra of iron(III) complex represented molecular ion peak [M⁺] at 1200 (m/z). In addition to molecular ion peak several other peaks of different fragments were observed, which were formed after consecutive dismissal of different groups. The occurrence of molecular ion peak in the complex is supporting the monomeric nature of the complex.

4. Structural Features

On the basis of the above observations and the comparison of relevant data from literature[6-10], it can be concluded that the complex has monomeric nature and the metal atom has six coordinate geometry where iron(III) is bonded to three bidentate dithiophosphato ligands leading to an octahedral geometry around the iron atom. The proposed structure has been given in Figure 1.

![Diagram](image.png)

Figure 1: The proposed six coordinate geometry of Fe(III) in the complex [(α-C₆H₅O)₂PS₂]Fe.

5. References