

# First hybrid oximehydrazonate phthalocyaninoclathrochelates: The synthesis and properties of lutetium phthalocyanine-capped cage iron(II) complexes

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## Abstract

Ditopic oximehydrazonate iron(II) phthalocyaninoclathrochelates were synthesized by a transmetalation (a capping group exchange) reaction of the initial labile triethylantimony-capped clathrochelate iron(II) oximehydrazonates with lutetium(III) phthalocyanine as a Lewis acid. The complexes obtained were characterized using elemental analysis, PD and MALDI-TOF mass spectrometries, IR, UV-Vis, <sup>57</sup>Fe Mössbauer, and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. An encapsulated iron(II) ion was found to be in a low-spin state. The cyclic voltammograms show oxidation and reduction waves assignable to Fe<sup>2+/3+</sup> couples of macrobicyclic framework and to phthalocyanine macrocycles.

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**Keywords:** Iron complexes; Clathrochelates; Macrocyclic compounds; Phthalocyanines

## 1. Introduction

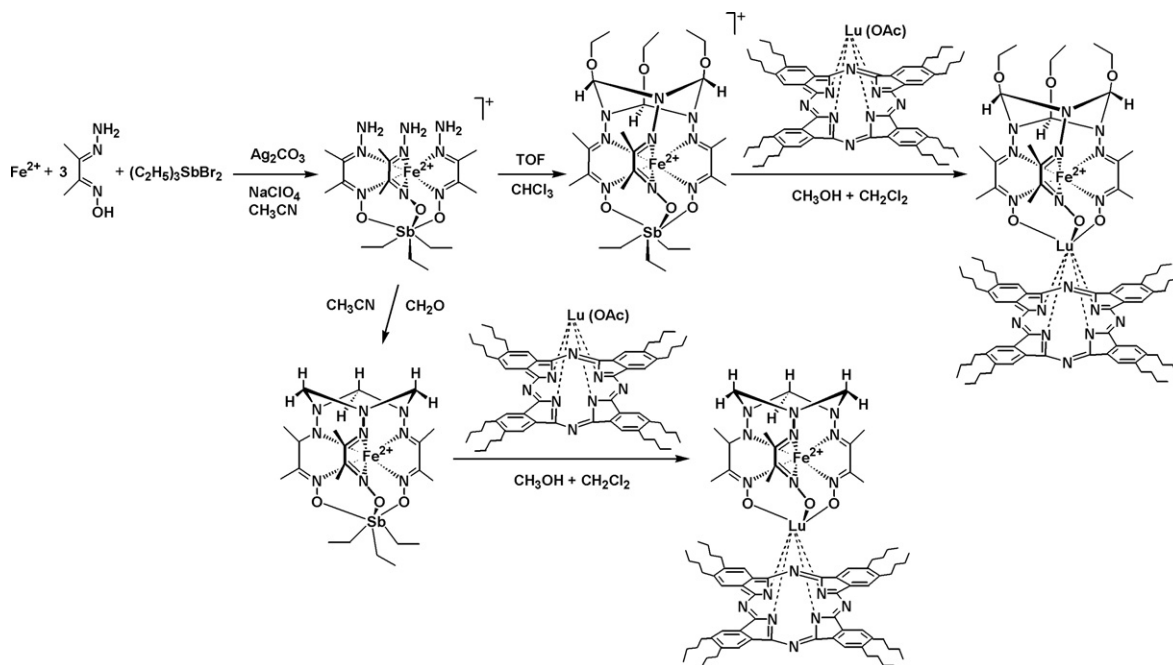
The hybrid polytopic transition metal complexes, which molecules contain the distal and isolated fragments with relatively independent  $\pi$ - and  $\sigma$ -electronic systems, are the most promising precursors for molecular electronic devices [1–6] and the artificial photoexcited long-lived donor–acceptor charge separation systems with photosynthetic properties [7–13]. The recently synthesized trisdioximate iron(II) phthalocyaninoclathrochelates belong to the type of ditopic complexes with highly intensive visible absorption bands of both the macrocyclic (phthalocya-

nine) and macrobicyclic (clathrochelate) fragments of the hybride molecule [14].

Unlike the clathrochelate tris-dioximate precursor, both capping fragments of which are reasonably labile in the transmetalation reactions [15,16], in case of the oximehydrazonate clathrochelates [16–23] only trioximate capping fragment may undergo transmetalation. However, the intramolecular rearrangements without destruction of the cage framework have been observed for clathrochelates with 1,3,5-triazacyclohexane hydrazonate capping fragment only (in particular, to give a tripodal methine fragment in case of triethyl orthoformate derivatives) [20]. The iron(II) ion has proved to be the most efficient template in the synthesis of such compounds. Moreover, among the synthesized earlier boron-, tin-, germanium- and antimony-capped iron(II) clathrochelates, the triorganylantimony-capped complexes undergo the

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Scheme 1.

transmetallation reactions only. Therefore, we proposed the following strategy for the synthesis of the hybrid oximehydrazonate phthalocyaninoclathrochelates (Scheme 1): the initially obtained triethylantimony-capped clathrochelate iron(II) oximehydrazonates undergo transmetallation reactions with Lewis-acidic rare-earth metal(III) phthalocyanines (in particular, with diamagnetic lutetium(III) phthalocyanines). This allowed us to obtain intracomplex hybrid oximehydrazonate phthalocyaninoclathrochelates (the formal positive 2+ charge of the encapsulated iron(II) ion is compensated by the formal negative 2– charge of the capping  $O_3LuN_4$  fragment). The formation of this intracomplex facilitated the isolation and purification of the resulting hybrid clathrochelate. On the other hand, the nature of this compound increases its solubility in aprotic polar and apolar organic solvents (chloroform, methylene dichloride and benzene). Eight *n*-butyl substituents in the phthalocyanine fragment enhance significantly the solubility of both the initial lutetium(III) phthalocyanine and the target hybrid clathrochelate in these solvents as well. The use of the diamagnetic lutetium(III) ion as a capping one allowed us to control the course of the reactions by  $^1H$  and  $^{13}C$  NMR spectroscopies.

## 2. Experimental

### 2.1. General procedures

The reagents used,  $NaClO_4$ , paraformaldehyde, triethyl orthoformate (TOF),  $CaCO_3$ , sorbents, organic bases, and solvents were obtained commercially (Fluka). Complex  $Fe(CH_3CN)_4Cl_2$  was prepared as described elsewhere [24]. The triethylantimony(V) dibromide and diacetylmono-

oxime hydrazone (HDXO) were synthesized by known procedures [25,26].

Analytical data (C, H, N content) were obtained with a Carlo Erba model 1106 microanalyzer. Iron content was determined spectrophotometrically.

The plasma desorption (PD) mass spectrum of  $[FeDXO_3(HCOC_2H_5)_3(Sb(C_2H_5)_3)](ClO_4)$  complex was recorded in the positive spectral region using a BC MS SELMI time-of-flight mass spectrometer and an accelerating voltage of 20 kV. The ionization was induced by  $^{252}Cf$  spontaneous decay fragments, and typically 20000 decay acts were registered. The sample (approximately 1–2 mg) was applied to a gilded disk.

The MALDI-TOF mass spectra were recorded using a MALDI-TOF-MS Bruker Autoflex mass spectrometer in reflecto-mol mode. The ionization was induced by UV-laser with wavelength 336 nm. The samples were applied to a nickel plate, 2,5-dihydroxybenzoic acid was used as a matrix. The accuracy of measurements was 0.1%.

The IR spectra of solid samples (KBr tablets) in the range of 400–4000  $cm^{-1}$  were recorded with a IR200 Thermo Nicolet FT-spectrophotometer.

The UV–Vis spectra of solutions in methylene dichloride were recorded in the range of 230–900 nm with a Lambda 9 Perkin–Elmer spectrophotometer. The individual Gauss components of these spectra were calculated using the SPECTRA program.

The  $^1H$  and  $^{13}C$  NMR spectra were recorded from  $CD_2Cl_2$ ,  $DMSO-d_6$  and  $CDCl_3$  solutions with a Bruker AC-200 FT-spectrometer.

The  $^{57}Fe$  Mössbauer spectra were obtained with a YGRS-4M spectrometer with a constant acceleration mode. The spectra were collected with a 256-multichannel

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