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Synthesis, spectroscopic characterization and semi-empirical calculations for a low spin carbonyl, pyridine(α-iminooxime)iron(II) macrocyclic complex

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Abstract

Synthetic route and detailed characterization of the macrocyclic complex [Fe^{II}(dohpn)(py)(CO)](ClO$_4$) (dohpn = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundecane-1,3,8,10-tetraen-11-ol-1-olate and py = pyridine) based on analytical, spectrometric and spectroscopic methods are herein reported. The corresponding vibrational and electronic features are discussed and a consistent assignment is proposed on the basis of semi-empirical theoretical calculations.
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1. Introduction

Chemical modelling of heme-proteins has been a central focus of bioinorganic chemistry [1]. The structure and re-activity of iron-porphyrin species are strongly dependent on the nature of the axial ligand. The reversible binding of oxygen and carbon monoxide play a central role in studies of heme-protein structure and function [2–4]. In contrast to the natural porphyrin systems, which present complicated electronic spectra dominated by intense π–π* transitions and provide little information concerning metal–ligand interactions, synthetic FeN$_4$ models have been providing important information concerning the nature of metal–ligand bonding [5–8]. Modelling the bonding capacity of heme-proteins toward carbon monoxide still remains a challenge to inorganic chemists.

In this work we describe the synthesis of Fe^{II}(dohpn)-(py)(CO)](ClO$_4$) (dohpn = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundecane-1,3,8,10-tetraen-11-ol-1-olate and py = pyridine) and its characterization by means of elemental analysis, FAB$^+$ mass spectrometry, FTIR, ^{1}H- and ^{13}C-NMR, Mössbauer, and UV–vis spectroscopies as well as by ZINDO/S and PM3 theoretical calculations.

2. Experimental

2.1. Physical measurements and instrumentation

Mass spectrum (FAB$^+$ technique) was recorded on a VG Autospec spectrometer (Fisons Instruments) equipped with a CsI gun at 25 kV in 3-nitrobenzyl alcohol as the matrix.

Infrared spectra were obtained with a Bomen Hartmann & Braun MB series spectrophotometer in the region 4000–400 cm^{-1} as nujol mulls spread on KBr windows.

^{1}H- and ^{13}C-NMR spectra were taken in acetone-d$_6$ solution using a Jeol Lambda 400 spectrometer.

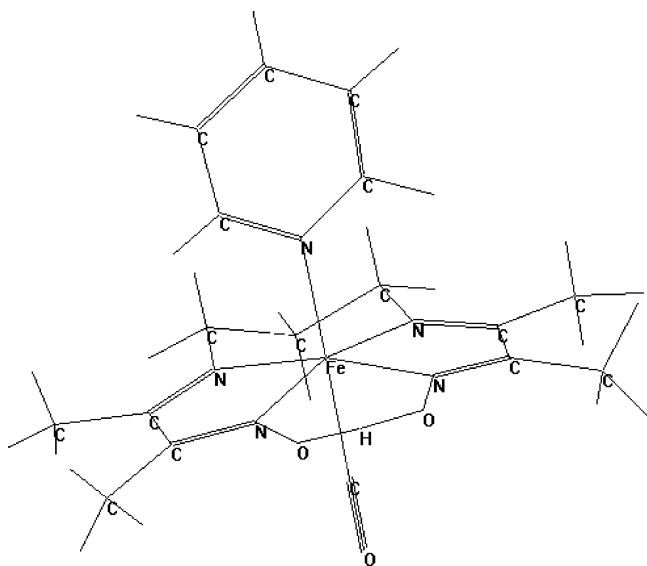Mössbauer data were recorded from frozen MeOH/H$_2$O (75:25%) solutions at 77 K using an ES-Technology MS105

Fig. 1. Molecular mechanics (MM+) optimized configuration for the [Fe^{II}(dohpn)(py)(CO)]$^+$ complex.

spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix. Spectra were referenced against iron foil at 298 K and parameters obtained by fitting the spectrum with Lorentzian lines.

Electronic spectra in the UV–vis range (190–820 nm) were obtained on a Hewlett-Packard Model 8452A diode-array spectrophotometer in methanol solutions.

Molecular modelling and quantum mechanical semi-empirical calculations were carried out using the ZINDO/S, PM3 and AM1 methods of HYPERCHEM 6.01 software from Hypercube. The optimized molecular mechanics (MM+) geometry of the [Fe^{II}(dohpn)(py)(CO)]$^+$ complex is given in Fig. 1.

Microanalyses were done under dinitrogen by MEDAC Ltd. Laboratories, Egham, Surrey, UK.

2.2. Materials

2,3-Butanedione monooxime (Aldrich) was used as supplied. Propane-1,3-diamine and pyridine (Merck) were freshly distilled before use, acetonitrile was distilled from CaH$_2$.The macrocyclic ligand dohpn was prepared as described elsewhere [9].

2.3. Synthesis

2.3.1. [Fe(CH$_3$CN)$_6$](ClO$_4$)$_2$

Iron powder (3.0 g, 54 mmol) was mixed with a solution of HClO$_4$ (60%, 24 mL, 0.2 mol) in acetonitrile (130 mL). The system was stirred for 6 days until all the iron was consumed. After evaporation of most of the solvent a light-green product was isolated by filtration, washed with cold acetonitrile and dried under vacuum. Yield was 10 g, 52%.

2.3.2. [Fe^{II}(dohpn)(py)(CO)](ClO$_4$)

This preparation was carried out under dinitrogen atmosphere using Schlenk techniques. [Fe(CH$_3$CN)$_6$](ClO$_4$)$_2$ (4.89 g, 13.7 mmol) and dohpn (3.28 g, 13.7 mmol) were mixed in acetonitrile (100 mL). Pyridine (20 mL) was added resulting in a deep purple solution. Carbon monoxide was bubbled through the solution for 2.5 h, while the color changed to reddish-brown. After 48 h, a red-wine solid was recovered by filtration, washed with ether and vacuum-dried. Yield was 90%. Calc. for C$_{17}$H$_{24}$N$_5$O$_7$ClFe (%): C, 40.7; H, 4.8; N, 14.0. Found: C, 40.0; H, 5.5; N, 14.6.

3. Results and discussion

3.1. Infrared spectrum

Summaries of IR spectra data of [Fe^{II}(dohpn)(py)-(CO)](ClO$_4$) and of dohpn are given in Table 1. The complex has an octahedral geometry around the iron(II) ion with a net 1+ charge balanced by one perchlorate anion. The important features of the IR spectrum are the bands at 2023 (νCO), 1652 (νC=N), 1096 (νClO, δHCC), 977 (νNO) and 534, 493, 465 (νM−N, νM−C) cm^{-1}. The assignment is supported by the theoretical spectra calculated using the PM3 code. Considering the fact that the calculations apply for molecules in the gas phase, the coherence of the frequencies with the experimental data is remarkable. The largest difference relates particularly to the νOH mode, although a better agreement could be obtained using the AM1 method for the dohpn ligand.

3.2. Mass spectrum (FAB$^+$)

The most important features of the spectrum are the peaks at m/z =374 (intensity of 14%) and m/z = 307 (7%) attributed to [Fe(dohpn)(py)]$^+$ and [Fe(dohpn)(CO)]$^+$, respectively, a result that strongly supports the coordination of pyridine and CO. The base peak of the spectrum appears at m/z = 295 (100%) and was assigned to the molecular ion [Fe(dohpn)]$^+$ produced by the dissociation of the axial ligands. Other intense peaks appeared at m/z = 154 (64%) and m/z = 136 (42%); the assignments are shown in Scheme 1.
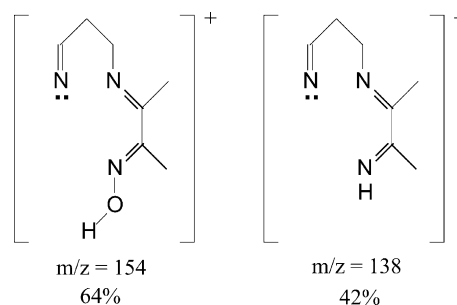
Scheme 1. Assignment of the mass spectrum of [Fe^{II}(dohpn)(py)(CO)]$^+$. See other attributes in the text.