Inorganica Chimica Acta, 138 (1987) 169–170

Preparation and Characterization of the First Disulphidothionitrato Metalloporphyrin in Complex: Disulphidothionitrato(*meso*-tetraphenylporphinato)-iron(III)

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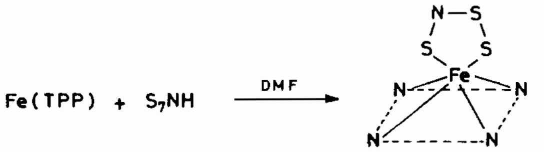
(Received May 26, 1987)

The reactions of the small molecules dioxygen, nitric oxide and carbon monoxide with metalloporphyrins have been intensively investigated [1]. Synthesis, structure and bonding of the transition metal complexes with small sulphur–nitrogen ligands such as NS, NSO^-, SO, NS_2^+ and NS_3^- have been the subject of much current interest [2–4]. However, the complexes of metalloporphyrins with these sulphur–nitrogen ligands have not yet been described. We wish to report here the synthesis of the first complex of a metalloporphyrin complexed by the disulphidothionitrate (S_3N^-) ligand.

Heptasulphurimide reacts with Fe^{II}(TPP) to afford the disulphidothionitrato complex (TPP)-$Fe^{III}(S_3N)$ (1):



In a preparative experiment, a blue solution of S_7NH [5] (1 mmol) in dimethylformamide (DMF) was added to a stirred solution of Fe(TPP) (1 mmol) in DMF under a nitrogen atmosphere. The reaction mixture was further stirred for 6 h. It was filtered and concentrated to 5 ml under reduced pressure. On addition of methanol, bluish black crystals of complex 1 separated out and were centrifuged, washed with methanol and dried under vacuum. It was recrystallized with CH_2Cl_2–CH_3OH (yield 58%). The size of the crystals were too small to be suitable for X-ray crystal structure determination. *Anal.* Calc: C, 67.86; H, 3.62; N, 8.99; S, 12.35. Found: C, 67.62; H, 3.60, N, 8.58; S, 12.52%. It is a high-spin iron(III) complex, as indicated by its magnetic moment [6–8] ($\mu_{eff} = 5.9$ B.M.) determined in the solid state by the Gouy method. The IR spectrum of complex 1 shows absorption bands at 439, 470, 522, 555, 570, 615, 623, 640, 662, 700, 708, 712, 720, 730, 740, 749, 755, 801, 838, 851, 880, 895, 908, 912, 930, 998, 1008, 1075, 1160, 1180, 1201, 1300, 1340, 1440, 1488, 1599 and 1815 cm^{-1}. The bands at 912, 740 and 720 cm^{-1} due to ν(NS) and at 623 cm^{-1} due to ν(S–S) are in close agreement with the values for coordinated bidentate S_3N^- ligands. The ^1H NMR spectrum ($CDCl_3$, Me_4Si, ppm), reveals δ 8.85 (S, 8H), 8.12 (m, 8H), 7.71 (m, 12H) for the porphyrin ring.

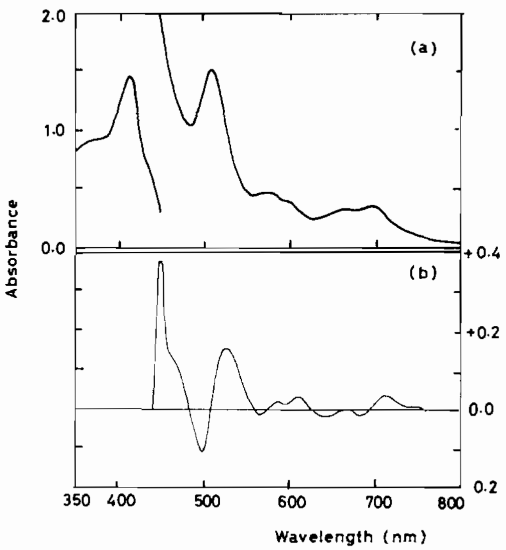


Fig. 1. Electronic spectra of (TPP)Fe(S_3N) in CH_2Cl_2: (a) absorption spectrum; (b) first-derivative spectrum.

The electronic spectrum of (TPP)Fe(S_3N) (Fig. 1) shows peaks at λ_{max} (ϵ_{max}): 693 (2.7×10^3), 658 (2.2×10^3), 600 (2.7×10^3), 573 (3.5×10^3), 510 (1.1×10^4), 447 (1.8×10^4) and 415 nm (7.9×10^4 M^{-1} cm^{-1}). The very high intensity of these bands suggests that they are charge-transfer and not d–d transition bands. All d–d transitions are masked by intense charge-transfer bands. The electronic spectrum of 1 is similar to known high-spin Fe(III) porphyrins [8] except for an additional band at 600 nm which may arise due to charge-transfer or π–π^* transitions of the S_3N^- ligand [9].

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