Inorganica Chimica Acta, 44 (1980) L215–L216

Synthesis and Characterization of a μ-Oxo Dimer formed by the Interaction of Phthalocyanine Iron(II) with Dioxygen

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Received December 20, 1979

We recently examined the kinetics of the interaction of phthalocyanine iron(II) (FePc) with dioxygen in both 96% H_2SO_4 [1] and dimethylsulphoxide (DMSO) [2]. Attempts were also made to obtain solid oxygen-containing derivatives of FePc. It was observed that suspension of FePc in dimethylformamide (DMF), dimethylacetamide (DMA), tetrahydrofuran (THF), or dioxan, kept under stirring in an air atmosphere or in pure oxygen for 12–24 h, gave, reproducibly and quantitatively, a well-defined oxygen-containing species identical to one of the two which can be isolated under similar conditions from DMSO [2]. In a recent communication [3] the same compound (reported as the 'S' form) was formulated as the dioxygen-bridged species $PcFe{\cdot}O_2{\cdot}FePc$, essentially on the basis of the elemental analyses. A brief description of the IR spectrum (specific absorptions in the region 900–800 cm^{-1}) and magnetic behaviour (antiferromagnetic) was given, without interpretation of the data presented. To our knowledge, only two other, not yet fully established, examples of iron(II)–dioxygen complexes have been reported in the literature [4, 5]. Furthermore, well characterized μ-oxo Fe–O–Fe species also show characteristic absorptions in the 900–800 cm^{-1} region and exhibit antiferromagnetic behaviour [6]. The data discussed below clearly indicate that the oxygen-containing derivative of FePc prepared as described above, should be formulated as μ-oxo-bis(phthalocyaninatoiron(III)), *i.e.* PcFe–O–FePc, at variance with the formulation given elsewhere [3].

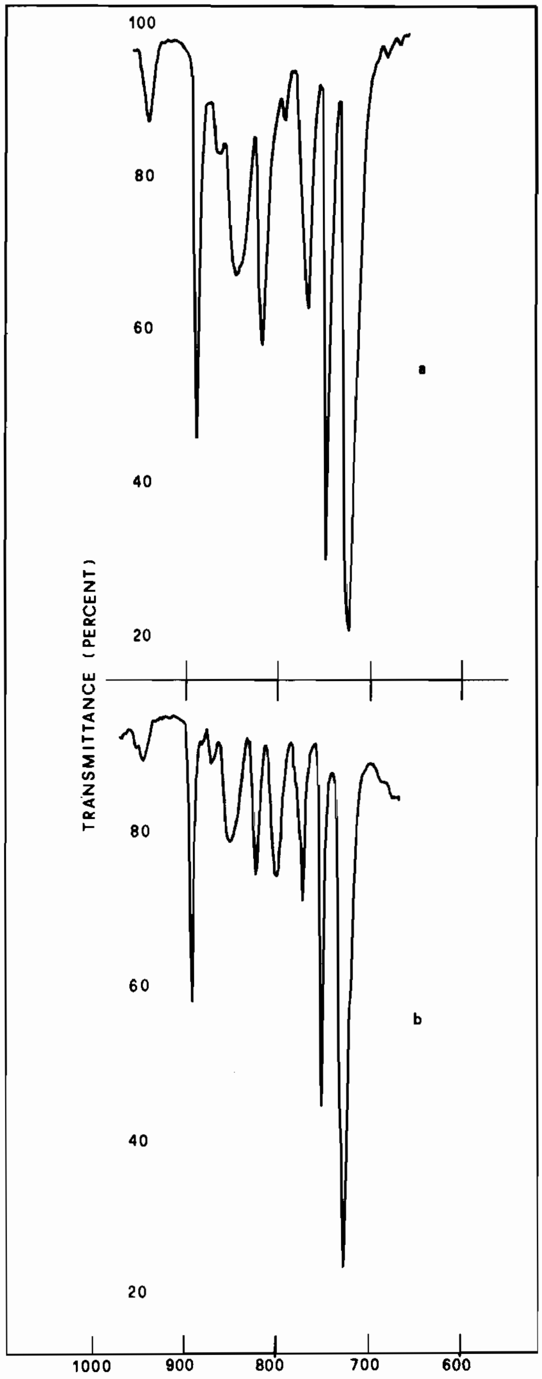

Fig. 1. Nujol mull IR spectra: a) oxygen derivative of FePc prepared by interaction with dioxygen in DMF; b) the same compound prepared similarly by contact with isotopically enriched dioxygen (70.0% ^{18}O).

Careful gas-volumetric measurements were carried out in an appropriate apparatus by suspending FePc in DMF in the presence of pure oxygen at constant temperature and pressure. In all the experiments the volume of gas adsorbed corresponded closely to a Fe/O_2 ratio of 4:1 (in a typical experiment 661.5 mg of FePc adsorbed 7.10 cm^3 of O_2 at 302.3 K and 760 mm corresponding to a Fe/O_2 ratio of 3.94:1). This ratio is twice that expected on the basis of a dioxygen formulation, $Fe{\cdot}O_2{\cdot}Fe$, and suggests, rather, the formation of a μ-oxo dimeric species Fe–O–Fe. Results obtained using either DMA

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or dioxan as a suspension medium were in agreement. Checks of the weight increase of the samples were also made and found to be in keeping with the results of the gas-volumetric measurements.

Vibrational spectra can be used to distinguish between μ-oxo (Fe–P–Fe) and dioxygen ($Fe{\cdot}O_2{\cdot}Fe$) structures provided that (a) absorption bands are observed attributable to vibrations specific for either system and (b) the shift of the IR bands upon ^{18}O substitution is measured. The region 900–800 cm^{-1} appears to be the most interesting one since both the antisymmetric stretch of an approximately linear Fe–O–Fe unit and ν_{O-O} for the dioxygen species have often been found to fall in this region [5, 6]. The IR spectrum of the title compound, taken in the region 4000–650 cm^{-1}, as a nujol mull or KBr disc, differs from that of the starting FePc (crystalline β-form) in that (a) the bands characteristic of the crystalline β-modification (780, 877, 1098, and 1173 cm^{-1}) [7] are no longer present and (b) a new, strong, absorption is observed at 850 cm^{-1} accompanied by two other strong, sharp peaks at 891 and 820 cm^{-1} (Fig. 1a). A sample of the oxygen derivative was prepared in the usual manner by exposing the iron(II) complex to an atmosphere of enriched dioxygen (70.0% of ^{18}O). The IR spectrum recorded is presented in Fig. 1b. A decrease in intensity of the 850 cm^{-1} band is observed (taking the 891 cm^{-1} band as reference) accompanied by the appearance of a new, relatively more intense, band at 801 cm^{-1} (the slight decrease in intensity of the 820 cm^{-1} band is very probably due to the fact that it lies on the 'tail' of the 850 cm^{-1} band). This change of the spectrum appears to be consistent with the presence of a Fe–O–Fe moiety. If this is, indeed, the case, then use of ^{18}O is expected merely to shift the antisymmetric Fe–O–Fe mode to lower frequencies; this is the case. The relative intensities of the original (850 cm^{-1}) and new (801 cm^{-1}) bands are (roughly) in the ratio expected on the basis of the isotopic composition (70.0% ^{18}O). Were a dioxygen structure $Fe{\cdot}O_2{\cdot}Fe$ present, three bands, spread out in a range of 50 cm^{-1}, would be predicted [5], associated with $-^{18}O-^{18}O-$, $-^{16}O-^{16}O-$, and $-^{16}O-^{18}O-$ vibrations and with areas in the ratio α^2: $(1 - \alpha)^2$: $2\alpha(1 - \alpha)$ respectively, α being the atom fraction of ^{18}O (*i.e.* 0.49:0.09:0.42 with $\alpha = 0.70$). Fig. 1b definitely shows that no band is observed between the original 850 cm^{-1} band and the new 801 cm^{-1} band. We conclude that infrared spectra strongly support the μ-oxo binuclear structure, in agreement with the gas-volumetric and gravimetric measurements.

The magnetic behaviour of the compound has also been examined. The room temperature magnetic moment is 2.08 μ_B. On decreasing the temperature, the magnetic moment decreases to 1.10 μ_B at *ca.* 100 K indicating that a strongly antiferromagnetically coupled Fe····Fe system is present. This antiferromagnetic behaviour closely resembles that of other well-characterized μ-oxo compounds [6], and this is consistent with the μ-oxo structure, PcFe–O–FePc, proposed for this compound.

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