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Oligomeric Complexes of Iron(II) with 2-Nitrosophenols (Mono-oximes of *ortho*-Benzoquinones) Containing both Low-spin and High-spin Iron(II) Species

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Although there has been considerable interest in iron complexes of 2-nitrosophenols, there has been little and confusing work carried out on bis-chelate complexes of 2-nitrosophenols with iron(II). A number of workers have reported iron(II) bis-chelates of type $Fe(qo)_2$ (qoH = a 2-nitrosophenol) but gave little evidence to support the proposed formulations [1]. Stukan *et al.* [2] reported the Mössbauer spectrum (Fig. 1a) of a complex formulated as $Fe(1\text{-}nqo)_2$ (1-nqoH = 1-nitroso-2-naphthol), but preparative details and analytical data were not given. This spectrum contained two iron sites, both of which were interpreted as due to iron(II) species. The inner doublet was assigned to a planar form of the complex and the outer to a distorted tetrahedral form. Subsequently, Sano and Takada [3] noted that the interaction of ferrous chloride with 1-nitroso-2-naphthol under oxygen-free conditions leads to a product of indefinite but reproducible composition. The Mössbauer spectrum of this product (Fig. 1b) was interpreted as indicating the presence of both iron(II) and iron(III) species. It was suggested that the spectrum obtained by Stukan *et al.* also reflected a partially oxidised sample. This conclusion has been supported by the Mössbauer parameters reported for $Fe(1\text{-}nqo)_3$ [4].

As a continuation of our studies of complexes of 2-nitrosophenols [4, 5] we have investigated the preparation of the complexes $Fe(1\text{-}nqo)_2$, $Fe(2\text{-}nqo)_2$ (2-nqOH = 2-nitroso-1-naphthol) and $Fe(5\text{-}MeOqo)_2$ (5-MeOqoH = 5-methoxy-2-nitrosophenol) from ferrous ammonium sulphate (1 mol equiv.) and the nitrosophenol (2 mol equiv.) in aqueous ethanol under oxygen-free conditions. In all cases, products of composition $Fe(qo)_2$ resulted.

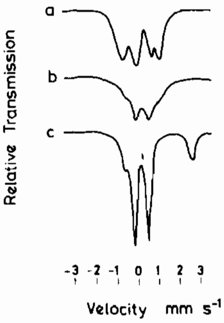
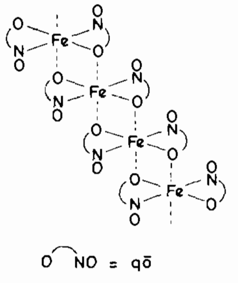


Figure 1. Mössbauer spectra.

The reaction between 1-nitroso-2-naphthol and ferrous ammonium sulphate was carried out several times. In each case the composition of the product corresponded very closely to $Fe(1\text{-}nqo)_2$. The Mössbauer spectra of these products contained two doublets (Fig. 1c) which showed no temperature dependence. The room temperature magnetic moments varied from sample to sample, but each product reacted with pyridine to give the same derivative, the diamagnetic iron(II) complex $Fe(1\text{-}nqo)_2 \cdot 2py$. All samples of the pyridine adduct lost pyridine quantitatively on heating at *ca.* 120 °C/0.1 mm to give residues of composition $Fe(1\text{-}nqo)_2$ which were similar to the products of the reaction between ferrous ammonium sulphate and 1-nitroso-2-naphthol described above. Again the magnetic properties of the residues varied from sample to sample, the Mössbauer spectrum showed two doublets, and each sample reacted readily with pyridine to reform $Fe(1\text{-}nqo)_2 \cdot 2py$. These results clearly indicate that the product of the reaction between ferrous ammonium sulphate (1 mol equiv.) and 1-nitroso-2-naphthol (2 mol equiv.) is not a mixture of different compounds. Similar behaviour was observed for the products arising from the system involving 2-nitroso-1-naphthol or 5-methoxy-2-nitrosophenol.

The results outlined above strongly suggest that the complexes $Fe(qo)_2$ have oligomeric structures.



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Thus the observed magnetic moments and the presence of two doublets in their Mössbauer spectra are in accord with the presence of low-spin, six-coordinate and high-spin, five-coordinate iron(II) species. The variation of the magnetic moments from sample to sample and the broadness of the peaks in the Mössbauer spectra reflect differences in the average chainlength of the oligomer.

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