Reaction of *NN'*-Ethylenebis(thiosalicylideneiminato)iron(II) with Dioxygen. Formation of a μ-Peroxo-intermediate and Isolation of a μ-Oxo-complex with the Unusual $S = \frac{1}{2}$ Spin State

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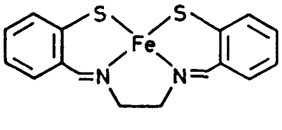
Summary The complex of *NN'*-ethylenebis(thiosalicylideneiminato)iron(II), Fe(Ssalen) (magnetic moment of 1·90 B.M. at 295 K) was treated with dioxygen in pyridine solution at room temperature to yield the μ-oxo-compound [Fe(Ssalen)]$_2$O.pyridine *via* an oxygen complex whose formation could be reversed at higher temperatures (e.s.r. measurements and the stoicheiometry of the oxygen reaction suggest that the latter compound is a peroxo-bridged species); the μ-oxo-complex contains Fe in the unusual $S = \frac{1}{2}$ spin state and displays weak antiferromagnetic coupling.

THE Fe^{II} complex (**1**) was readily prepared by the reaction of ethylenediamine with bis(thiosalicylideneiminato)iron(II) in 2-methoxyethanol, as for the method used in the preparation of the analogous Co^{II} complex.[1] The complex has a magnetic moment of 1·90 B.M. at 295 K compared with the high spin moment of 4·77 B.M. found for the analogous [O$_2$N$_2$] complex, Fe(salen) [salen = *NN'*-ethylenebis(salicylideneiminato)].[2] The Mössbauer spectrum shows a quadrupole doublet with an isomer shift $\delta_{4\cdot2\,K}$ 0·44 mm s^{-1} (relative to Fe), which is compatible with the intermediate $S = 1$ spin state, as has been observed for Fe^{II} phthalocyanins[3] and porphyrins.[4] The magnetic moment of compound (**1**) shows a temperature dependence between 4·2 and 300 K which is consistent with spin-spin coupling occurring within a polymeric solid state structure.



(1)

The passage of dioxygen through a black-green pyridine solution of compound (**1**) at room temperature caused a colour change to black-brown and after a few minutes black crystals of the μ-oxo-complex [Fe(Ssalen)]$_2$O.py (**2**) (py = pyridine) were deposited. Satisfactory elemental analyses for compound (**2**) were obtained; ν (Nujol) 792 cm^{-1} (Fe–O–Fe); μ_{eff} at 295 K 1·89 B.M. (per Fe atom); *g* (pyridine glass, 77 K) 2·161, 2·098, and 1·999; *g* (solid, 77 K), 2·159, 2·105, and 2·005.

The magnetic moment of [Fe(Ssalen)]$_2$O.py is similar to that of the red-orange [O$_2$N$_2$] complex [Fe(salen)]$_2$O[5] and other antiferromagnetically coupled binuclear μ-oxo-species in which each Fe^{III} centre has $S = \frac{5}{2}$.[6] However, the temperature dependence of the magnetic susceptibility of compound (**2**) is quite different from that shown by [Fe(salen)]$_2$O (Figure 1) and indicates only weak interaction between the Fe^{III} atoms. Also, in contrast with most other μ-oxo-species, compound (**2**) shows an e.s.r. spectrum which is characteristic of a rhombically distorted Fe^{III} ion with $S = \frac{1}{2}$. N-Hyperfine splitting occurs on the central line of the pyridine glass spectrum (Figure 2). The observed *g* values are similar to those of an iron(III) complex containing two tridentate *N*-(2-aminoethyl)thiosalicylideneimine ligands, which has been structurally characterized,[7] *g* (solid, 77 K), 2·166, 2·115, and 2·008.

Considerable difficulty was experienced in obtaining crystals of compound (**2**) suitable for *X*-ray diffraction studies. Nevertheless, a crystal structure determination has been carried out[8] which has confirmed the μ-oxo-

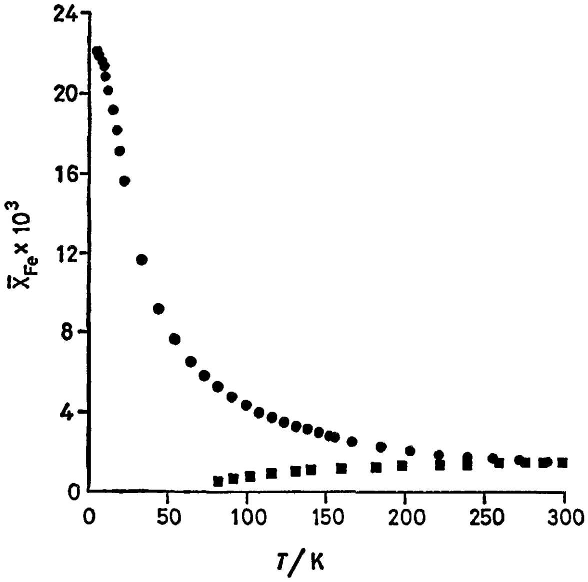


FIGURE 1. The variation of χ_{Fe} with temperature for binuclear μ-oxo-Fe^{III} complexes: ● [Fe(Ssalen)]$_2$O.py, ■ Fe(salen)]$_2$O.

structure and established that distorted square-pyramidal Fe(Ssalen) moeties exist bridged by a non-linear Fe–O–Fe linkage. The pyridine molecule is not co-ordinated to either metal atom.

Disorder of the unco-ordinated pyridine molecules and the consequent difficulty in locating the atoms has caused the refinement of the structure to converge at R 11%. The Fe–O–Fe bridge angle, 159(3)°, is similar to those in [Fe(salen)]$_2$O derivatives,[6] as are the Fe–O and Fe–Fe distances, 1·78(1) and 3·50(1) Å, respectively. This is perhaps surprising in view of the differences in spin state and degree of exchange coupling observed in the two species. Clearly, the spin state must be primarily determined by the S-donor ligand and pertinent distances are Fe–S, 2·312 and Fe–N, 2·02—2·11(4) Å which are similar to those found in a mononuclear $S = \frac{1}{2}$ iron(III) [S$_2$N$_2$] complex[9] containing a bound NO group. The difference in exchange coupling in the Ssalen and salen complexes is presumably due to different Fe d-orbitals being involved in overlap with the O 2p-orbitals.

The formation of the μ-oxo-complex (**2**) appeared to result from an intermediate oxygen complex whose formation was reversible. The colour of the oxygenated solution was returned to that of the initial Fe(Ssalen) solution when the solution was heated to 40—50 °C and purged with a stream of nitrogen. Any black crystals of compound (**2**) which had precipitated, however, were unaffected by this procedure. It was possible to repeat this oxygenation–deoxygenation cycle several times before conversion of all the sample of Fe(Ssalen) into the μ-oxo-complex was complete.

At 243 K, reaction of compound (**1**) in pyridine solution with dioxygen produced an immediate colour change, but crystals of compound (**2**) were not precipitated, even after several hours of continuous passage of oxygen. The colour change could not be reversed by a stream of nitrogen. When the temperature of the system was raised rapidly to 40—50 °C while nitrogen was passed through the solution a reversal of the colour change occurred, but crystals of the μ-oxo-complex were also precipitated.

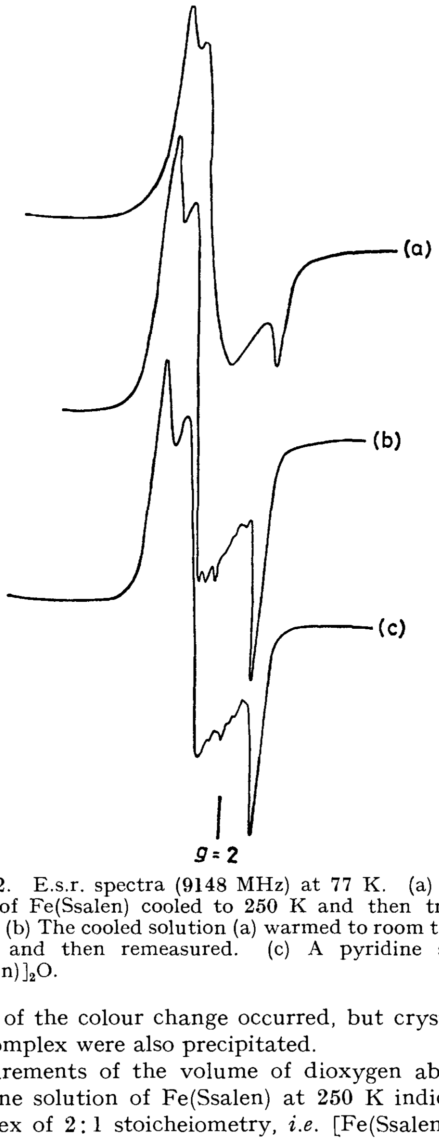


FIGURE 2. E.s.r. spectra (9148 MHz) at 77 K. (a) A pyridine solution of Fe(Ssalen) cooled to 250 K and then treated with oxygen. (b) The cooled solution (a) warmed to room temperature for 1 h and then remeasured. (c) A pyridine solution of [Fe(Ssalen)]$_2$O.

Measurements of the volume of dioxygen absorbed by a pyridine solution of Fe(Ssalen) at 250 K indicated that a complex of 2:1 stoicheiometry, *i.e.* [Fe(Ssalen)]$_2$O$_2$, was formed in solution. The e.s.r. spectrum at 77 K of a pyridine solution of Fe(Ssalen) equilibrated with oxygen at 250 K showed three g values, g 2·156, 2·109, and 2·004. When gradually warmed to room temperature the e.s.r. spectrum of the solution changed and a final spectrum, identical with that given by an authentic sample of [Fe(Ssalen)]$_2$O.py, was observed (Figure 2). These results suggest that the spin states of the Fe atoms in the dioxygen complex are also $S = \frac{1}{2}$ and the complex may be described as a μ-peroxo-species. Its dissociation at higher temperatures in a nitrogen stream is reminiscent of the behaviour of the peroxo-species formed by Co(salen), *viz.* [py.Co(salen)]$_2$O$_2$.

The N$_2$O$_2$ analogue, Fe(salen), was also treated with oxygen in pyridine to yield a μ-oxo-complex, Fe(salen)$_2$O.[10] However, e.s.r. examination of the reaction mixture at 243 K showed only the spectrum of the μ-oxo-complex with no components that might be attributed to a possible μ-peroxo-intermediate. This suggests that any such compound, if formed, reacts rapidly to yield the μ-oxo-complex. The rate of reaction of the [Fe(Ssalen)]$_2$O$_2$ species to yield the oxo-complex is therefore much slower.

These results indicate that an S_2N_2 donor ligand can support the formation of an Fe–O–O–Fe μ-peroxo-linkage, at least in solution.

Previous proposals for the formation of binuclear peroxo-Fe^{III} species have been made following the reaction of dioxygen with Fe^{II} complexes of N_4 donor ligands such as phthalocyanins[11] and porphyrins.[12] Attempts to isolate these peroxo-derivatives, however, resulted in their conversion into the μ-oxo-complexes.[12–14]

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