Journal of

The Chemical Society,

Chemical Communications

NUMBER 7/1976 7 APRIL

A Seven-co-ordinate Dioxygen Adduct of Iron(II) with Spin-triplet Ground State

By VICKIE MCKEE and S. MARTIN NELSON*
(*Department of Chemistry, Queen's University Belfast* BT9 5AG, *N. Ireland*)
and JANE NELSON
(*The Open University, Milton Keynes* MK7 6AA)

Summary Oxygenation of *cis*-$[Fe(bt)_2(NCS)_2]$ (bt = 2,2′-bi-2-thiazoline) in non-aqueous solvents yields a product having properties consistent with a binuclear structure in which seven-co-ordinate iron(II) ions in the triplet ground state are bridged by singlet dioxygen.

RECENT studies[1] of synthetic models for haemoproteins have demonstrated the importance of steric effects on the reversibility of the uptake of dioxygen. In the absence of steric protection of one face of the porphyrin it has been suggested[1,2] that an intermediate in the irreversible autoxidation to iron(III) products may be a binuclear species, as depicted in equation (1), where $[Fe^{II}]$ represents the (five-co-ordinate) iron(II) complex. However, information on such species is lacking. We now report the isolation of a product of oxygenation of a six-co-ordinate iron(II) complex having properties consistent with a dioxygen-bridged binuclear structure.

$$[Fe^{II}] \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} [Fe^{II}\cdot O_2] \xrightarrow{[Fe^{II}]} [Fe^{II}\cdot O_2\cdot Fe^{II}] \rightarrow Fe^{III}\text{-products} \quad (1)$$

The α-di-imine ligand 2,2′-bi-2-thiazoline (bt) reacts with $Fe(ClO_4)_2\cdot 6H_2O$ in ethanol to give the low-spin ($S=0$) complex $[Fe(bt)_3](ClO_4)_2$ (compound A). In the presence of NCS^- ion and in the absence of O_2 the deep blue complex $[Fe(bt)_2(NCS)_2]$ (compound B) is obtained. On the basis of the splitting (2083, 2070 cm^{-1}) of $\nu(C{\equiv}N)$ of the thiocyanate ligand, and of other properties, (B) is assigned a *cis*-octahedral structure. It displays a temperature dependent $^5T \rightleftharpoons {}^1A$ spin equilibrium, the magnetic moment falling from 5·10 B.M. at $T > 184$ K to 1·04 B.M. at 80 K. Mössbauer isomer shifts (δ, relative to natural iron) and quadrupole splittings (ΔE_Q) are 0·96 and 2·73 mm s^{-1} (293 K) and 0·34 and 0·55 mm s^{-1} (77 K). In these properties (B) is similar to analogous complexes of 2,2′-bipyridyl and 1,10-phenanthroline.[3] If the preparation is carried out in the presence of O_2 or if solutions of (B) in dry alcohol or CH_2Cl_2 are exposed to O_2 a microcrystalline blue-black product (compound C) is obtained† which has low solubility in dry organic solvents. Analysis for C, H, O, N, and S indicates the stoicheiometry $Fe(bt)_2(NCS)_2\cdot O$. The same material is obtained from reaction of $Fe(NCS)_3$ with bt in the presence of O_2. Apart from the occurrence of a very much stronger peak at $m/e = 32$ in (C) the mass spectra of (B) and (C) are virtually identical; molecular ion peaks were not observed in either case. The magnetic moment of (C) is 3·61 B.M. per iron atom at 293 K and is virtually temperature independent (3·53 B.M. at 88 K). Mössbauer spectra clearly show the presence of one kind of iron atom only. These consist of a closely spaced quadrupole split doublet with $\delta = 0{\cdot}25$ and 0·35 mm s^{-1} and $\Delta E_Q = 0{\cdot}30$ and 0·31 mm s^{-1}, at 293 and 77 K, respectively.

Considered together the magnetic and Mössbauer evidence appears to be consistent only with the occurrence of iron(II) in the triplet ($S = 1$) ground state. Known examples[3] of $S = 1$ iron(II) compounds have very similar magnetic and Mössbauer properties to those described here. It follows

---

† These are complex reaction systems in which there appears to be competing and/or consecutive reactions yielding other, as yet unidentified, products at relative rates dependent on solute and O_2 concentration, solvent, and temperature.

that (C) is an oxygenation and not an oxidation product of (B). Since (C) contains one atom of oxygen per atom of iron the μ-dioxygen binuclear structure: $[(SCN)_2(bt)_2\text{-}Fe^{II}\text{–}O_2\text{–}Fe^{II}(bt)_2NCS)_2]$, in which the co-ordinated dioxygen is in the singlet state and the metal is seven-co-ordinate is proposed. This stereochemistry would readily account for the triplet ground state [*e.g.*, $(d_{xz},d_{yz})^4$, $(d_{xy})^1$, $(d_{x^2-y^2})^1$]. Approximately pentagonal bipyramidal iron(II) complexes with quintet ground states have recently been described.[4] The alternative formulation of a μ-peroxo-complex of iron(III) in the $S = {}^5/_2$ spin state is untenable; while it is conceivable that there could be antiferromagnetic exchange interaction between the paramagnetic centres (as in μ-oxo dimers) this would require the magnetic moment to be strongly temperature dependent, given that the coupling constant is large enough to reduce the moment to 3·6 B.M. at room temperature.

Supporting evidence for the proposed structure is the occurrence of ν(C≡N) as a single band at 2065 cm^{-1}, *i.e.* in the region characteristic of terminally bonded isothiocyanate. The absence of measurable splitting is suggestive of an approximately *trans*-arrangement of the two NCS^- groups. That both NCS^- ions are co-ordinated is also supported by the observation that no decrease in electrical resistance was observed on exposure to O_2 of a 10^{-3} M solution of the non-electrolyte (B) in 1,2-dichloroethane. The medium intensity ν(C=N) stretch of the co-ordinated bt occurring in (B) at 1568 cm^{-1} is absent in (C) (as in A), an often-noted feature of low-spin Fe^{II} complexes of chelating α-di-imines.[5] Otherwise the i.r. spectra of B and C are similar. No new band attributable to the O=O stretch was observed, a fact consistent with the symmetry of the proposed structure.

The oxygenation of (B) to (C) is partially reversible in that heating (C) *in vacuo* for varying periods within the temperature range 160—200 °C regenerated (B) (identified by i.r. spectra and its unique temperature-dependent Mössbauer spectra) along with a new material (D), with $\delta = 0{\cdot}99$ mm s^{-1} and $\Delta E_Q = 0{\cdot}45$ mm s^{-1} at 293 K, of unknown structure. Loss of *ca.* two-thirds of the dioxygen (identified by mass spectra in separate experiments) between *ca.* 150 and 200 °C was confirmed by thermogravimetric analysis.

Analogous O_2-adducts of iron(II) complexes of the related ligands 5,5′-dimethyl-2,2′-bi-2-thiazoline and 2,2′-bi-2-thiazine have been isolated. The properties and reactions of all these compounds will be reported more fully in due course.

The award of a research grant (to J. N.) by the Open University is gratefully acknowledged.

(*Received*, 31*st December* 1975; *Com.* 1439.)

[1] J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 1973, **95**, 5757; J. P. Collman, R. R. Gagne, T. R. Halbert, J-C.Mardion, and C. C. Reed, *ibid.*, p., 7868.

[2] I. A. Cohen and W. S. Caughey, *Biochemistry*, 1968, **7**, 636; J. M. Pratt in 'Techniques and Topics in Bioinorganic Chemistry,' ed. C. A. McAuliffe, Macmillan, London, 1975.

[3] E. König, *Co-ordination Chem. Rev.*, 1968, **3**, 471.

[4] M. G. B. Drew, A. H. Othman, W. E. Hill, P. D. A. McIlroy, and S. M. Nelson, *Inorg. Chim. Acta*, 1975, **12**, L25; *J.C.S. Dalton*, in the press.

[5] W. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 4834.