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Oxygenation of *meso*-tetrakis(2,4,6-alkoxyphenyl)-porphinato Complexes of Iron(II): Some Unusual Observations

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There is great current interest in synthetic models for hemoglobin and related dioxygen-carrying hemeproteins.[1-4] A major effort has been devoted to preparing iron porphinato compounds resisting irreversible oxidation by virtue of specially designed substituted ligands, two notable examples being the "picket fence" and "capped" complexes described by Collman[1] and Baldwin,[2] respectively.

An apparently universal property of heme-like structures and related ferrous porphyrins in the absence of protein environment is, on exposure to oxygen, to result in μ-oxo dimers, $[-\mathrm{Fe^{III}}(\mathrm{O^{2-}})$-$\mathrm{Fe^{III}}-]$.[5,6] Even the "picket fence" and "capped" complexes,[1,2] after cycles of reversible oxygenation, ultimately seem to yield such ferric derivatives, probably because the steric obstruction is present only on one side of the porphinato plane.

We wish to report some observations on the reactions of molecular oxygen with *meso*-tetrakis-(2,4,6-trimethoxyphenyl)porphinatoiron(II), [Fe(T(MeO)$_3$PP)] **1**,[7] and a related derivative, *meso*-tetrakis(2,4,6-triethoxyphenyl)porphinatoiron(II), [Fe(T(EtO)$_3$PP)] **2**, whose preparation and properties are analogous to those of **1**.[7,8] In these complexes, for which only one isomeric form is possible, the *ortho*-alkoxy substituents are positioned above *and* below the porphinato core.* The rationale behind our syntheses of these symmetrically "fenced" species was to prevent two metal centers from approaching each other closely enough to form a μ-oxo bridge, and thereby possibly produce new types of dioxygen carriers. This objective has only partially been realized, owing to unsuspected complexity of these reactions which, however, have not yielded the commonly observed μ-oxo dimers. The spectral and magnetic data of the reactants and products, and some related complexes (included for comparison) are summarized in the Table.

The reactions of the ferrous compounds **1** and **2** with oxygen (760 mm) in benzene at 25 °C, monitored by visible spectral changes, proceed to completion within 10 min and 24 hr, respectively, the considerably slower conversion of the latter probably reflecting its greater steric obstruction. Preliminary kinetic data suggest that both oxygenations involve two distinct steps: a relatively fast one is followed by a diminished reaction rate. Volumetric oxygen uptake measurements have been somewhat inconclusive. Complex **1** is very slightly soluble, and dilute solutions in benzene or toluene showed no O_2 absorption for several hr, although the color change from red (**1**) to purple (**1a**) was observed, and the electronic spectra indicated that a conversion to the oxygenated product **1a** had taken place. The ethoxy compound **2**, however, whose solubility exceeds *ca.* tenfold that of **1**, showed an oxygen uptake (p_{O_2} = 690 mm, benzene, 10 °C) corresponding to O_2: Fe = 1.0 after 25 hr, but the O_2 absorption continued, resulting in O_2:Fe = 1.6 after 76 hr.

Partial reversibility of these reactions was observed spectrophotometrically. A degassed solution of **1** in toluene was exposed to 1 atm O_2 at 25 °C for 3 min (corresponding to completing the first oxygenation step, see above) followed by three freeze–thaw cycles (–196° to –78 °C) *in vacuo*; warming to room temperature under nitrogen resulted in 70% regeneration of **1**. A second oxygenation–deoxygenation cycle produced 30% of the starting material originally used. The ethoxy derivative **2** showed analogous behavior in benzene solution.

The ferrous complexes react, but very slowly, with molecular oxygen also in the solid state, yielding the same products (**1a**, **2a**) as obtained from solutions. Gravimetric uptake measurements (McBain balance, p_{O_2} = 760 mm, 24 °C) gave these results: **1** + $O_2 \rightarrow$ **1a**, O_2:Fe = 0.98, 9 days; **2** + $O_2 \rightarrow$ **2a**, O_2:Fe = 0.89, 47 days. The oxygenation of the methoxy compound was followed also by intermittent magnetic measurements; a gradual growth of paramagnetism (Table) roughly paralleled the extent

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*According to molecular models,[7] the alkoxy-CH$_3$ hydrogens can approach the central metal atom within 1 - 2 Å. These steric properties seem to account for the unusual observation that the formally four-covalent compounds are *diamagnetic,*[7,8] *i.e.* the possible Fe···H(H$_3$C–) contacts may force a low-spin configuration,[9] in contrast to *meso*-tetraphenylporphinatoiron(II), [Fe(TPP)], which is a high-spin complex.[10]

TABLE. Spectral and Magnetic Data for Iron Porphinato Complexes at Room Temperature.[a]

Complex	Electronic Spectrum		μ_{eff}
	λ_{max}, nm[b]		BM[c]
[Fe(T(MeO)$_3$PP)] (**1**)	525	–	diam.
[Fe(T(EtO)$_3$PP)] (**2**)	530	–	diam.
[Fe(TPP)][d]	–	–	4.4
[Fe(T(MeO)$_3$PP)(py)$_2$]	528	–	diam.
[Fe(T(EtO)$_3$PP)(py)$_2$]	526	–	diam.
[Fe(TPP)(py)$_2$]	529	558	diam.
[FeCl(T(MeO)$_3$PP)]	509	579[e]	5.7
[FeCl(T(EtO)$_3$PP)]	511	580	5.7
[FeCl(TPP)]	510	578	5.8
[Fe(T(MeO)$_3$PP)] + O_2 (1a)	505 (sh)	578[f]	5.1
[Fe(T(EtO)$_3$PP)] + O_2 (2a)	505 (sh)	578	4.0
[Fe(TPP)]$_2$O	576	618	1.8[g]
[Fe(O_2)(TPP)(py)][h]	547	583	–

[a] Data from this work, ref. 7 or 8, except where noted otherwise. [b] In C_6H_6. All compounds have a Soret absorbance, 410 - 420 nm. [c] Diam. = diamagnetic; small residual paramagnetism present in some samples. All measurements refer to solid compounds. [d] Ref. 10. [e] In $CHCl_3$. [f] In $C_6H_5CH_3$. [g] Ref. 11. [h] In CH_2Cl_2, –78 °C, ref. 4.

of O_2 uptake. Partial deoxygenation of crystalline **1a** was observed when a sample of **1** was exposed to O_2 for 24 hr (30% conversion to **1a**), and then pumped to regenerate 80% of the starting complex.

The dark purple oxygenated compounds **1a** and **2a** are best prepared by precipitation from their benzene solutions with hexane. The i.r. of the complexes do not show absorbances attributable to the presence of a Fe–O–Fe bridge, in contrast to the well-known μ-oxo dimer, [Fe(TPP)]$_2$O (ν_{FeOFe}= 878, 892 cm^{-1}). Nor are bands evident which could be assigned to vibrations of coordinated dioxygen or Fe–O linkages (some samples of **1a** and **2a** show a weak and broad absorption, of unknown origin, at 1670 cm^{-1}).

The oxygenation of the diamagnetic ferrous complexes (**1**, **2**) produces strongly paramagnetic products (**1a**, **2a**, Table). The moments are somewhat lower than found for the high-spin ferric species with the same porphinato ligands, [FeCl(T(MeO)$_3$PP)] and [FeCl(T(EtO)$_3$PP)] (μ_{eff} = 5.6 - 5.8 BM), but much higher than that observed for the μ-oxo tetraphenylporphinato complex, [Fe(TPP)]$_2$O (1.8 BM). Furthermore, the latter exhibits antiferromagnetic coupling, while the μ_{eff} of **1a** is constant between 298 and 140 °K.

Complexes **1a** and **2a** can readily be reconverted to the diamagnetic Fe(II) compounds (**1**, **2**) by treatment with excess piperidine in chloroform or benzene for a few min at 25 °C. Significantly, the oxo-bridged dimer, [Fe(TPP)]$_2$O, is inert toward piperidine even in boiling solutions. Pyridine (py) also reacts with **1a** (20 hr) and **2a** (5 days) at 25 °C to give [Fe(T(MeO)$_3$PP)(py)$_2$] and [Fe(T(EtO)$_3$PP)(py)$_2$], respectively (identical with those formed directly by reaction of **1** and **2** with py). No molecular oxygen has been detected in these experiments. In summary, the nature of our oxygenated products (**1a**, **2a**) is clearly different from those of μ-oxo compounds[5,6] and the recently reported dioxygen complexes of iron porphyrins[1-4] (see Table).

Although the results reported in this note have consistently been reproducible, a full interpretation of these reactions is presently not possible, in part, because elemental analyses have not been satisfactory for most of the complexes cited (an observation not unusual for many porphyrin systems; in the present case, the carbon and iron contents have frequently been lower than expected). Considering the total evidence, it seems likely that the first interaction between the ferrous compounds and molecular oxygen involves a reversible formation of dioxygen complexes, eqn.(1) (P = T(MeO)$_3$PP or T(EtO)$_3$PP):

$$[Fe(P)] + O_2 \rightleftarrows [Fe(O_2)(P)] \qquad (1)$$

The latter then seem to decay to some ferric species whose electronic spectra are very similar to those of the five-coordinated high-spin chloro compounds, [FeCl(P)] (see Table). The products (**1a**, **2a**) may represent analogous hydroxo complexes, [Fe(OH)(P)], but no ν_{O-H} has been detected in the i.r. spectra. Another possibility is a *μ-peroxo* dimer, [(P)Fe(O_2)Fe(P)], although molecular models suggest that this structure is not very favorable due to steric hindrance by the alkoxy groups. It is also conceivable that the oxygenation includes a partial oxidation of the alkoxy-phenyl substituents.

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Inorganica Chimica Acta, 14 (1975) L52

Metal Binding at N_1 and N_7 in a Silver Nitrate–9-Methyladenine Complex

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Silver ions bind primarily to the base portion of nucleic acids.[1] On the basis of uv spectra and potentiometric measurements, it was concluded that displacement of an amino hydrogen atom by silver ions takes place in neutral or alkaline solutions. Additional interactions of the metal with ring nitrogen atoms were assumed by Davidson *et al.*[2] in order to explain the polymeric character of the products obtained. On the other hand, chelate formation *via* N_7 and the amino group was postulated for adenosine from solution equilibrium data on slightly acidic solutions.[3]

By reaction of silver nitrate with 9-methyladenine in dilute nitric acid (pH ~ 3), crystal of the 1:1 compound $AgNO_3 \cdot$9-Methyladenine$\cdot H_2O$ were obtained. They belong to space group $P2_1/c$ with the following cell parameters: a = 14.41, b = 7.397, c = 23.36 Å and β = 122.13°. There are eight formula units per cell or two per asymmetric unit. The structure was solved from 2100 unique observed reflections and isotropically refined to a conventional R factor of 0.079. At the moment, the positions of both silver atoms and ligand molecules have been unambiguously determined. The nitrate groups and water molecules appear to be disordered, but that situation does not affect the metal ion and ligand positions.

Figure 1 shows the basic unit (two Ag^+ ions and two ligands) of the infinite cationic chain found in the crystal. Each silver atom is digonally bound to N_1 of one ligand and to N_7 of the following ligand. Each ligand bridges two silver atoms so that N_1 and N_7 are both involved in complexation. The Ag–N distances (2.14 - 2.21 Å) indicate equally strong bonds with both types of nitrogens. Some of the nitrate oxygens are also found around silver. Their exact positions cannot be discussed at the moment because of the disorder, but they appear to interact only very weakly with the metal, as often observed in digonally coordinated Ag(I) and Hg(II) compounds.

From a large number of recent crystallographic studies, N_7 has been identified as the most common complexation site in N_9-substituted adenines. So far, X-ray evidence for simultaneous interactions at N_1 and N_7 has been reported only for $CoCl_2 \cdot$9-Methyladenine,[4] a compound obtained from ethanol solutions. The present structure failed to show interactions with the amino group, but the substitution proposed[1,2] for neutral and alkaline solutions would probably not take place in acidic media, where our compound was isolated. Consequently, the possibility of amino hydrogen substitution at higher pH is not ruled out, but the present work points out that N_1 may be an important reaction site for Ag^+ ions, as in the case of CH_3Hg^+.[5]

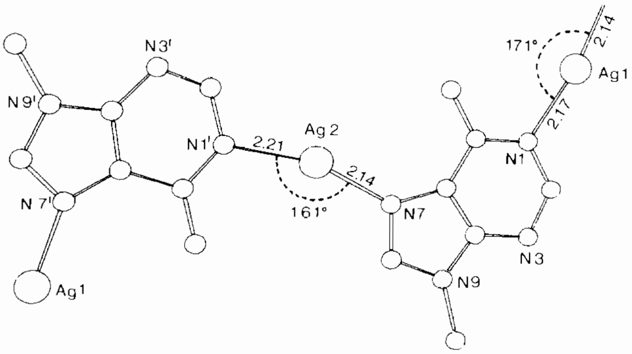

Fig. 1. Basic unit of the polymeric chain $-Ag^+-L-Ag^+-L-Ag^+\cdots$ found in the crystals.

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