Oxygenation of a Co-ordinated Tetra-azamacrocycle: The *X*-ray Structure Determination of μ-Oxo-bis{17,18,19,20-tetrahydro-18,19-dioxotribenzo-[*e*,*i*,*m*][1,4,8,11]tetra-azacyclotetradecinato(2−)iron(III)}

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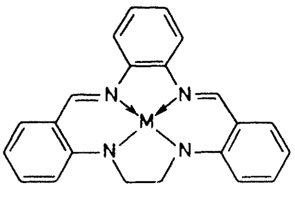
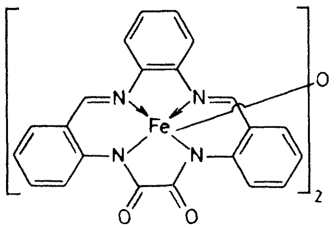
Summary The $-N-CH_2-CH_2-N-$ bridge in the neutral macrocyclic iron(III) complex (**1a**) is readily oxygenated to give a μ-oxo complex of the corresponding oxamido ligand.

During our studies[1] of tetra-aza macrocyclic ligands and their metal complexes, we have prepared the iron(III) complex (**1a**). When (**1a**) was dissolved in dimethylformamide and held at 80 °C for 6 h, the solution slowly deposited black



(1)

a; M = Fe–OAc
b; M = Cu
c; M = Co



(2)

needles. These were examined by *X*-ray analysis† and shown to be the *NN*-dimethylformamide (DMF) solvate of the μ-oxo dimer (**2**) in which oxygenation of the ethane bridge between the anilino nitrogens has occurred. This reaction was unexpected; in certain cases related Co^{II}, Ni^{II}, and Cu^{II} complexes with a trimethylene bridge have been observed[2] to undergo dehydrogenation in the presence of O_2, but oxygenation has not previously been reported.

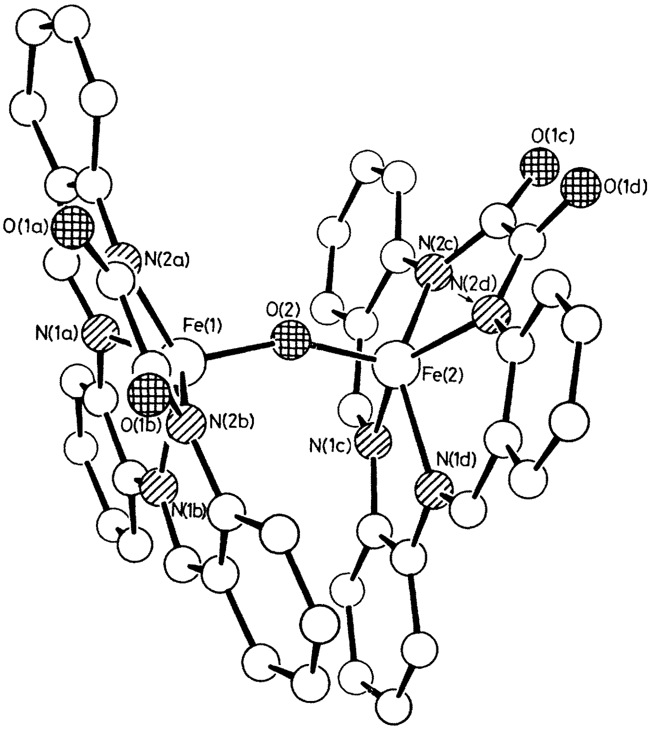
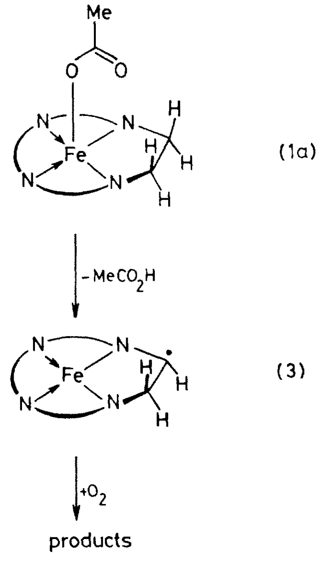


FIGURE. The structure of (**2**). Bond lengths Fe(1)–N(1a), 2·06(1); Fe(1)–N(1b), 2·11(1); Fe(1)–N(2a), 2·01(1); Fe(1)–N(2b), 1·98(1); Fe(1)–O(2), 1·777(8); Fe(2)–N(1c), 2·10(1); Fe(2)–N(1d), 2·07(1); Fe(2)–N(2c), 2·00(1); Fe(2)–N(2d), 1·99(1); Fe(2)–O(2), 1·758(9) Å.

The two halves of the molecule (Figure) have closely similar structures. The iron atoms Fe(1) and Fe(2) have approximately square-pyramidal co-ordination geometries (lying 0·64 and 0·65 Å above the mean planes of the N_4 donor sets) and are significantly closer to the oxamido nitrogens [2·00(1) Å] than to the other two nitrogens [2·09(1) Å]. The oxamido groups are inclined at 27 and 26° to the N_4 co-ordination planes about Fe(1) and Fe(2), and the iron atoms lie very close to the planes of the oxamido groups. Most of the atoms in the 14-membered inner great ring lie close to the N_4 co-ordination plane. The exceptions are the two carbon atoms attached to a benzene ring which are close (0·05 Å) to the N_4 plane in the macrocycle containing Fe(1) but appreciably below it (0·24 Å) in the other. There are other smaller differences in conformation between the two macrocycles which may be attributed to packing constraints imposed by the solvate molecule whose site was found, by *X*-ray analysis, to have an occupancy of 0·67. The angle and bond lengths of the μ-oxo bridge [157(1)° and 1·777(8) and 1·758(9) Å] fall centrally within the range of values (139—175° and 1·76—1·79 Å) observed[3] in related five-co-ordinate iron(III) complexes.

The mechanism of this facile oxygenation is under investigation, but in the light of recent work[4] on base-induced ligand oxygenations of cobalt(III) complexes, a reasonable proposal (Scheme) for the initial step of the reaction involves the elimination of acetic acid to give an iron(II) complex of the ligand radical shown in (**3**).‡



SCHEME.

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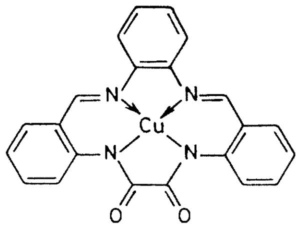
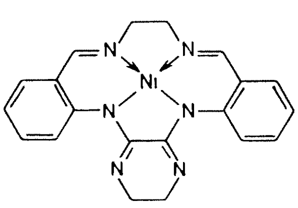
† *Crystal data:* [$C_{44}H_{28}N_8O_5Fe_2$](+0·67 DMF), M = 860·5 (+ 49·0), monoclinic, $P2_1/c$, a = 10·819(3), b = 26·738(7), c = 14·910(4) Å, β = 101·82(8)°, U = 4221·7 Å^3, Z = 4, D_c = 1·43 g cm^{-3}, μ(Mo-K_α) = 6·92 cm^{-1}, R = 0·070 for 1911 data with $I/\sigma(I) > 3·0$ obtained on a Philips PW1100 diffractometer. The structure was solved by Patterson methods and refined using isotropic thermal parameters except for the Fe atoms, with hydrogen atoms set with C–H = 1·08 Å; $0·52 > \Delta\rho > -0·40$ e Å^{-3}. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Certain Ni^{II} and Cu^{II} complexes analogous to (**1**) which contain a trimethylene link between the anilino nitrogen atoms are observed to undergo dehydrogenation (rather than oxygenation) with O_2 in reactions which appear to proceed *via* two-electron transfer followed by proton loss from a methylene group (ref. 2), rather than *via* the mechanism shown in the Scheme.



(4)



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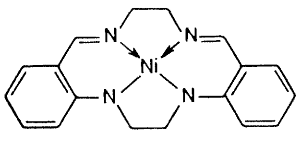

(6)

Preliminary results suggest that other metal complexes of the ligand in (**1**) undergo similar oxygenation reactions, *e.g.* the Cu^{II} compound (**1b**) in DMF (100 °C/18 h) gives (**4**), which has previously[5] been made from ligands in which the oxamido unit has been incorporated[5,6] from a reaction sequence involving oxalyl dichloride. The related Co^{II} compound (**1c**) undergoes a more complex reaction with O$_2$, but i.r. spectra suggest that again an oxamido complex is present in the mixture of products obtained.

It seems likely that the compound (**5**), isolated[7] by Maslen *et al.* during the preparation of (**6**), was formed by oxygenation of (**6**) to give an oxamide which then condensed with the excess of 1,2-diaminoethane which was present.

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