

A Mixed Valence μ -Oxo Iron(III)–Iron(II) Complex: a Polynuclear Iron–Sodium–Oxo Aggregate from the Chemical Reduction of a μ -Oxo Di-iron(III) Complex

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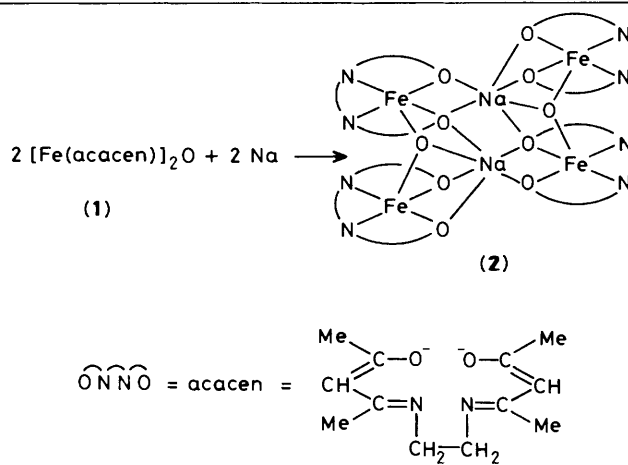
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Reduction of $\{[\text{Fe}(\text{acacen})]_2\text{O}\}$ {acacen = $[\text{MeC}(\text{O}^-)\text{CH}=\text{CMe}=\text{NCH}_2]_2$ } [Fe–O, 1.77(1) Å; Fe–O–Fe, 150.7(13)°] with sodium metal to give an iron–sodium–oxo aggregate $\{[\text{Fe}(\text{acacen})]_2\text{ONa}\}_2$, containing the monoanionic μ -oxo iron(II)–iron(III) moiety, $[\text{Fe}–\text{O}–\text{Fe}]^-$ occurs with a significant lengthening of the Fe–O bonds, and contraction of the Fe–O–Fe angle [Fe–O, 1.999(6) and 2.069(6) Å; Fe–O–Fe, 134.9(4)°], as shown by a crystal structure determination.

μ -Oxo di-iron(III) complexes have excited interest because of their distinctive magnetic and spectroscopic properties¹ and relevance to di-iron non-heme proteins.² In this context the redox properties of the Fe–O–Fe fragment are important, since electron transfer processes can occur between iron in different oxidation states through the bridging oxo ligand.^{3,4} Electrochemical reductions have been carried out on μ -oxo di-iron(III) complexes containing as supporting ligand polydentate Schiff bases⁵ or macrocycles.⁴ While these studies suggest that the reduction is feasible, the $[\text{Fe}–\text{O}–\text{Fe}]^-$ unit was found to have a very limited stability.^{4–6} In contrast to this, we found that the chemical reduction of $\{[\text{Fe}(\text{acacen})]_2\text{O}\}$ (1)⁷ {acacen = $[\text{MeC}(\text{O}^-)\text{CH}=\text{CMe}=\text{NCH}_2]_2$ } affords a stable μ -oxo iron(II)–iron(III) complex, which can be fully characterized.

Reduction of (1) with sodium metal in tetrahydrofuran (thf) is a very slow reaction producing a solution from which (2)



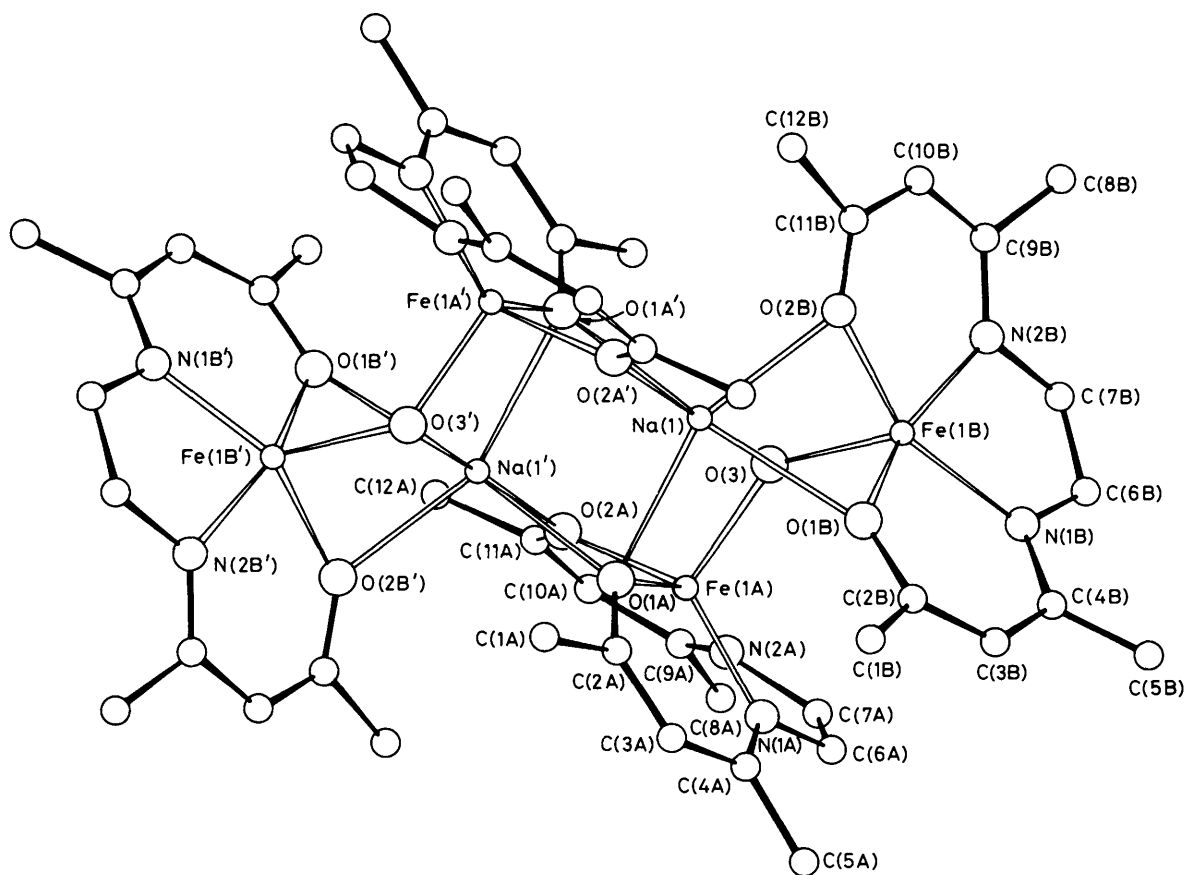


Figure 1. A PLUTO view of the complex (2), $\{[\text{Fe}(\text{acacen})_2]\text{ONa}\}_2$. Bond distances (\AA): Fe(1)–O(3), 1.999(6) [2.069(6)]; Fe(1)–O(1), 2.059(9) [2.043(10)]; Fe(1)–O(2), 2.035(7) [2.016(8)]; Fe(1)–N(1), 2.069(10) [2.030(10)]; Fe(1)–N(2), 2.114(11) [2.081(11)]. Bond angles ($^\circ$): O(1)–Fe(1)–O(2), 91.5(3) [91.4(3)], Fe(1A)–O(3)–Fe(1B), 134.9(4). The values in square brackets refer to the B portion of the complex. Primes indicates the transformation $-x, 1-y, -z$.

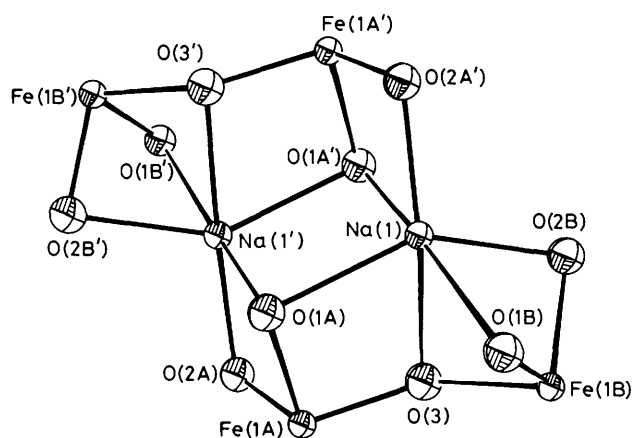


Figure 2. A view of the oxygen core, $\text{Fe}_4\text{Na}_2\text{O}_{10}$, in complex (2). The Na–O distances range from 2.308(10) to 2.577(8) \AA .

crystallized as red-brown crystals (*ca.* 35%) (Scheme 1).[†] Complex (2) is rather air-sensitive. The most interesting spectroscopic changes occurring with the reduction are the lowering of the iron–oxygen band from 840 cm^{-1} in complex (1)⁷ to 780 cm^{-1} in complex (2), and a significant increase in

[†] Complex (2) crystallizes with two molecules of thf. Satisfactory analytical data have been obtained.

the magnetic moment from 1.80 μ_{B} at 290 K [complex (1)]⁷ to 3.64 μ_{B} at 290 K [complex (2)]. Such changes parallel the structural changes of the Fe–O–Fe skeleton.

The crystal structure of (2) has been determined, and is shown in Figure 1 with some relevant bond distances and angles, while Figure 2 shows the $\text{Fe}_4\text{Na}_2\text{O}_{10}$ core.[‡] Two $\{[\text{Fe}(\text{acacen})_2\text{O}]\}^-$ polyoxo monoanions are bridged by two sodium cations to form a polymetallic aggregate. The ten oxygen atoms from the two $\{[\text{Fe}(\text{acacen})_2\text{O}]\}^-$ units provide a co-ordination cage for the two sodium cations, which achieve hexa-co-ordination with Na–O distances ranging from

[‡] Crystal data for complex (2): $\text{C}_{48}\text{H}_{72}\text{Fe}_4\text{N}_8\text{Na}_2\text{O}_{10} \cdot 2\text{C}_4\text{H}_8\text{O}$, $M = 1334.7$, triclinic, space group $P\bar{1}$, $a = 11.280(2)$, $b = 12.641(2)$, $c = 12.749(2)$ \AA , $\alpha = 102.65(1)$, $\beta = 97.71(1)$, $\gamma = 70.92(1)^\circ$, $U = 1672.5(5)$ \AA^3 , $Z = 1$, $D_c = 1.325$ g cm^{-3} , $F(000) = 702$, $\mu(\text{Cu-K}\alpha) = 74.7$ cm^{-1} . Intensities of 4663 independent reflections were measured in the range $6 < 2\theta < 120^\circ$ using a Siemens AED four-circle diffractometer (Cu– $K\alpha$ radiation, $\lambda = 1.5418$ \AA). 1977 Reflections with $I > 2\sigma(I)$ were used in calculations. The structure, solved by heavy atom methods, was refined with anisotropic thermal parameters to a final $R = 0.068$ ($R_w = 0.072$). An absorption correction was applied.

The two thf molecules of crystallization are disordered. Disorder was solved in terms of partial carbon atoms (no possibility to distinguish between oxygen and carbon) considering the molecule distributed over three positions which were refined isotropically with site occupation factors given in the co-ordinate table.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

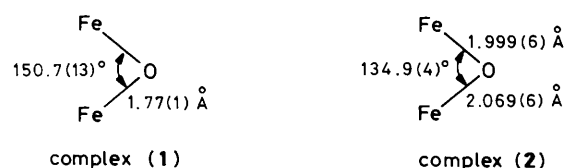


Figure 3. Comparison of bond distances and angles between the [Fe₂O] units in complexes (1) and (2).

2.308(10) to 2.577(8) Å. The co-ordination geometry around iron is a pseudo-square pyramid with the metal out of the basal N₂O₂ plane by 0.491(2) and 0.411(2) Å for the units A and B, respectively. The significant crowding of the structure caused by the sodium complexation may be responsible for some significant differences in the bond distances within the [Fe(acacen)] units for Fe-N, ranging from 2.030(10) to 2.114(11) Å, and Fe-O, ranging from 2.016(8) to 2.059(9) Å.

An important feature is illustrated in Figure 3 which shows the changes occurring in the [Fe-O-Fe] moiety upon reduction to the monoanion [Fe-O-Fe]⁻. The significant lengthening of the Fe-O bonds and the contraction of the Fe-O-Fe angle on going from (1) to (2) occur because of the reduction of the Fe-O double bond character, in agreement with the lowering of the Fe-O i.r. absorption to 780 cm⁻¹. The reduction of the Fe-O bond order probably affects equally the magnetic coupling between the two high-spin centres, the magnetic moment being increased to 3.64 μ_B at 290 K.⁸ Temperature dependent magnetic studies on complex (2) are planned. It has to be pointed out that the presence of Na⁺ cations in the structure can affect to some degree the geometry of the Fe-O-Fe skeleton and at the same time can add significant stability to the μ-oxo iron(II)-iron(III) system, which was found, though the ligands were different from acacen, to be unstable when produced by electrochemical reduction.⁴⁻⁶ The structure of (2), which is reminiscent of that of a polyoxoanion, suggests the use of {[Fe(acacen)]₂O}⁻ as

monoanionic polydentate ligands for building up poly-aggregate structures based on a metal oxide support. Studies on chemical reduction and oxidation of complexes containing the Fe-X-Fe skeleton (X = O or S) are in progress, as well as the use of (2) as ligand for different cations.

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