A Tetranuclear Iron(II)–Sodium Complex formed from the Complexation of Sodium Ethoxide by *N,N'*-Ethylenebis(3-hydroxy-1-methylbut-2-enylideneaminato)iron(II)

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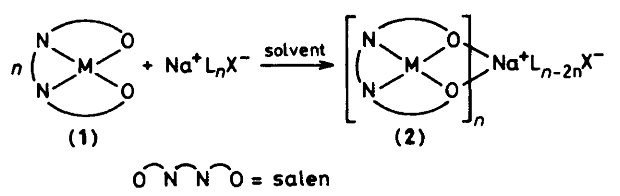
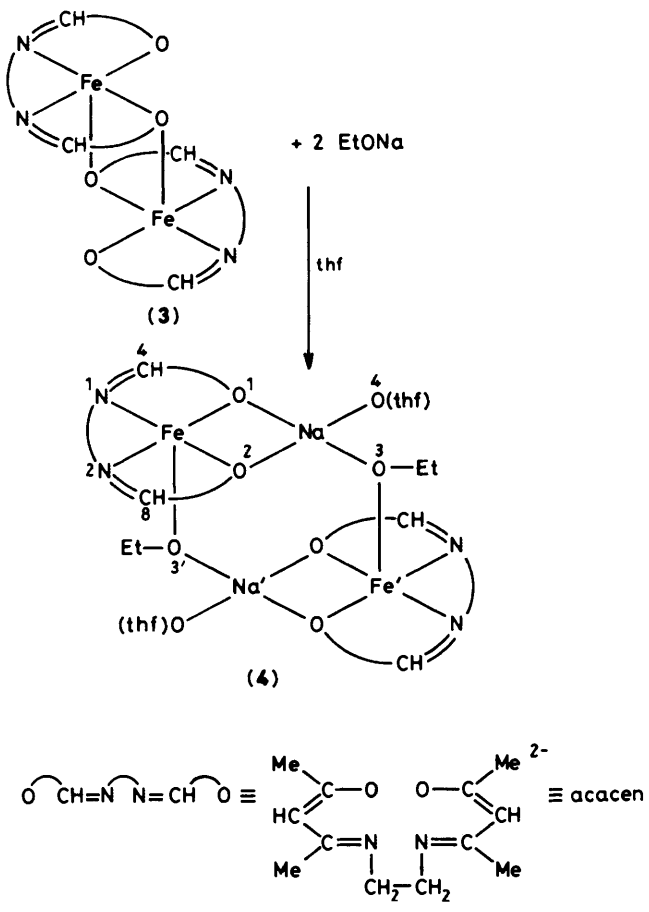
The reaction of *N,N'*-ethylenebis(3-hydroxy-1-methylbut-2-enylideneamine) (H_2acacen) with $FeCl_2$ in the presence of MeONa afforded the iron(II) dimeric complex $[Fe(acacen)]_2$, which reacted with EtONa to form a tetranuclear complex $[Fe(acacen)(NaOEt)]_2$, where the two iron(II) atoms are five-co-ordinate and doubly bridged by the [EtONa] ion pair.

Reaction of alkali metal salts with transition metal Schiff base complexes provides an example of a model reaction for moving from monofunctional to polymetallic, polyfunctional co-ordination chemistry. This can be exemplified by the complexation of an alkali metal cation by M(salen)-type complexes[1] (**1**) [salen = *N,N'*-ethylenebis(salicylideneaminato)dianion] (Scheme 1). The cationic species acts as template bringing together various metal reactive sites in close proximity;[2] it affects the redox potential of the centre M, and it supplies a reactive site different from M in the polyfunctional structure.[3] Moreover polynuclear species like (**2**) can act as electron reservoirs,[4] a peculiarity which along with polyfunctionality has a major role in molecular activation processes.[3,4] Various alkali metal salts have been considered



Scheme 1. M = Co^{II}, Ni^{II}, or Cu^{II}; X^- = BPh_4^-, ClO_4^-, $Co(CO)_4^-$, or NCS^-.



Scheme 2

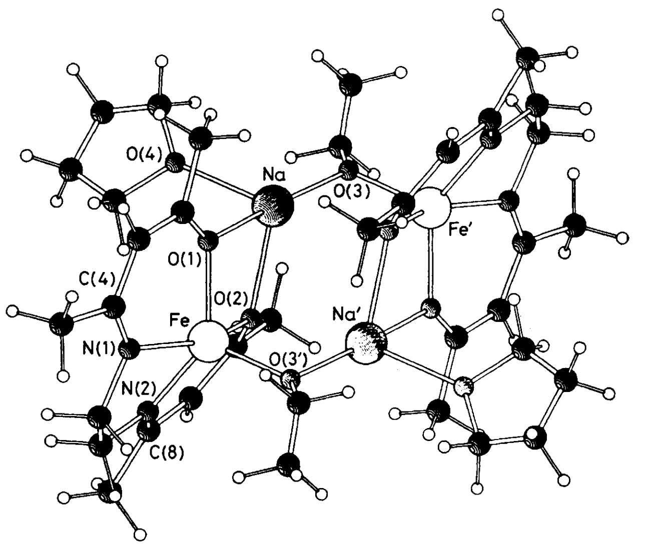


Figure 1. A view of complex (**4**). Bond distances (Å): Fe–O(1) 2.062(11); Fe–O(2) 2.071(9); Fe–N(1) 2.099(14); Fe–N(2) 2.065(14); Fe–O(3) 1.931(11); Na–O(1) 2.355(12); Na–O(2) 2.347(12); Na–O(3) 2.241(12); Na–O(4) 2.369(17); C(4)–N(1) 1.284(28); C(8)–N(2) 1.249(21).

in reactions as in Scheme 1, in particular those having anions which can act as ligands for M and can exist in a tight ion-pair form with the alkali metal cation. Moreover, examples of polynuclear complexes like (**2**) are limited to those with M = Co, Ni, and Cu; no report has dealt with an example when M = Fe, in spite of the fact that polynuclear iron(II) species are involved in fundamental redox processes.[4]

The synthesis and structure of bis[*N*,*N*′-ethylenebis(3-hydroxy-1-methylbut-2-enylideneaminato)iron(II)], [Fe-(acacen)]$_2$ (**3**), and its reaction with sodium ethoxide are now reported. Complex (**3**) was synthesised by the reaction of anhydrous $FeCl_2$ with H_2acacen in the presence of MeONa in tetrahydrofuran (thf). Sodium chloride was filtered from the solution and the residue obtained from the evaporation of thf was recrystallized from toluene at −20 °C (*ca.* 45%). Complex (**3**)† has a magnetic moment of 4.84 μ_B at 294 K and a dimeric structure, which was determined unambiguously by an *X*-ray study.[5] There is no previous structural report on iron(II)-Schiff base square-planar complexes having a N_2O_2 set of donor atoms.[6]

A thf suspension of EtONa reacted with (**3**) affording a deep red solution from which complex (**4**) was isolated on cooling (*ca.* 60%) (Scheme 2). Complex (**4**) has a magnetic moment of 4.98 μ_B at 294 K per iron, in agreement with a d^6 high-spin configuration. The structure shown for complex (**4**) in Scheme 2 uses the numbering scheme from the *X*-ray crystal structure analysis (Figure 1). The main characteristic of complex (**4**) is the arrangement of metal ions in a tetranuclear structure, where sodium ethoxide is complexed in the ion-pair form and the alkoxo group acts as a donor ligand for the iron(II) site.

Crystal Data for complex (**4**): $C_{36}H_{62}Fe_2N_4Na_2O_8$, triclinic, $P\bar{1}$, a = 8.821(4), b = 10.205(5), c = 12.173(5) Å, α = 78.66(4), β = 94.87(4), γ = 90.67(3)°, D_c = 1.298 g cm^{-3}, Z = 1. Intensity data were collected with Mo-K_α radiation to θ = 27° (θ–2θ scan mode). Unit cell parameters were obtained from accurate centering of 25 strong reflexions. Intensities of 2416 independent reflexions were measured with an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. No correction for absorbance was applied (μ_{Mo} = 2.9 cm^{-1}). The position of the iron atom was determined by a three-dimensional sharpened Patterson map. A weighted Fourier difference map followed by least-squares refinements and further Fourier difference maps located the remaining atoms. 1055 reflexions with $F_0 > 2\sigma(F_0)$ were measured and used in the anisotropic refinements with unit weights; the final R index was 0.068.‡

The molecule of (**4**), which has $C_i(\bar{1})$ symmetry, is shown in Figure 1 with the most relevant bond distances. The most interesting structural changes occurring in the transformation of (**3**) to (**4**) are the variation of the O–Fe–O angle from 101.2(1)° [complex (**3**)] to 87.7(4)° [complex (**4**)] and of the distance of the iron atom from the least-squares plane defined

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† Satisfactory analytical data have been obtained.

‡ 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.

by the N_2O_2 donor atoms set: 0.293 Å [complex (**3**)] and 0.594 Å [complex (**4**)]. All the other structural parameters are very close to those found for (**3**)[5] and for analogous complexes of iron(III),[7] except for the Fe–O bond distances, which are significantly longer in complex (**4**).

Complex (**3**), unlike [Fe(salen)],[8] is soluble in hydrocarbon solvents and its dimeric structure was established by an *X*-ray analysis.[5] In its reaction with sodium ethoxide, a tetranuclear structure is formed, which can be relevant for redox processes. Moreover, complexation of alkali metal alkoxides, which are important reagents in organic nucleophilic substitutions,[9] is achieved in its ion-pair form. It is difficult to obtain structural information on the complexation of alkali alkoxides by 'inorganic' or 'organic' (*e.g.* crown ethers) ligands.

Complexation of [NaOR] and [NaSR] by iron(II) complexes, and analogous reactions using cobalt(II)–Schiff base compounds are under investigation.

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