N,N-Dialkylcarbamato Oligonuclear Complexes of Iron(II), Including [{$Fe_4(\mu_4\text{-}O)(O_2CNPr^i{}_2)_6$}$_2$], the First Crystallographically Established Uncharged μ-Oxo Complex of Iron(II)

Daniela Belli Dell'Amico,[a] **Fausto Calderazzo,***[a] **Luca Labella,**[a] **Cäcilia Maichle-Mössmer**[b] **and Joachim Strähle***[b]

[a] *Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganics, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy*

[b] *Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany*

The $FeCl_2$–R_2NH–CO_2 synthetic route yielded *N,N*-dialkylcarbamato complexes of iron(II), [{$Fe(O_2CNR_2)_2$}$_m$] (m = 6, R = Et); controlled hydrolysis of the isopropyl derivative under an inert atmosphere led to the title compound, the first member of the crystallographically new class of uncharged iron(II) complexes containing the bridging oxide ligand.

Many iron(III) μ-oxo derivatives have been reported in the literature,[1] and specific interest has been devoted to iron(II) hydroxo-bridged compounds[2] as spectroscopic and magnetic models of the respiratory protein haemerythrin and related proteins, and to mixed-valence Fe^{II}–Fe^{III} systems. On the other hand, the paucity of data about stable iron(II) μ-oxo or hydroxo compounds has been noted.[1e,3] The pentaoxoferrate(II) anion $[Fe_2O_5]^{6-}$, a system containing a μ-O ligand, was recently reported to be obtained by the high-temperature reduction of the oxo-iron(III) precursors on the walls of iron cylinders.[4]

N,N-Dialkylcarbamates of transition and non-transition elements, of general formula [{$M(O_2CNR_2)_n$}$_m$], belong to a relatively new class of compounds whose nuclearity m depends on the nature of both the alkyl group R and the metal, and on the oxidation state of the metal. Nuclearities ranging from one (Hf^{IV}, Si^{II}, Pd^{II})[5] to six (Co^{II}, Mn^{II})[6] were established crystallographically for the homoleptic compounds. Moreover, controlled hydrolysis in organic solvents leads to μ-oxo derivatives of well-defined nuclearity.[7] We therefore reasoned that *N,N*-dialkylcarbamates of iron(II) could lead to *molecular* iron(II) μ-oxo derivatives by a hydrolytic process under anaerobic conditions.

We now report the preparation of the hexanuclear ethyl derivative $[Fe_6(O_2CNEt_2)_{12}]$, **1**. Furthermore, the hydrolysis of the isopropyl derivative [{$Fe(O_2CNPr^i{}_2)_2$}$_m$] gives [{$Fe_4(\mu_4\text{-}O)(O_2CNPr^i{}_2)_6$}$_2$] **2** which, to the best of our knowledge, represents the first example of an uncharged μ-oxo derivative of iron(II).[8]†

Treatment of anhydrous iron(II) chloride with NHR_2/CO_2 (R = Et, Pr^i) in toluene at atmospheric pressure and room temperature yielded, after the usual work-up,[5,6] the colourless [{$Fe(O_2CNR_2)_2$}$_m$] (R = Et, **1a**, R = Pr^i, **1b**) in good yields. The IR spectrum of the ethyl derivative in the 1700–1350 cm^{-1}

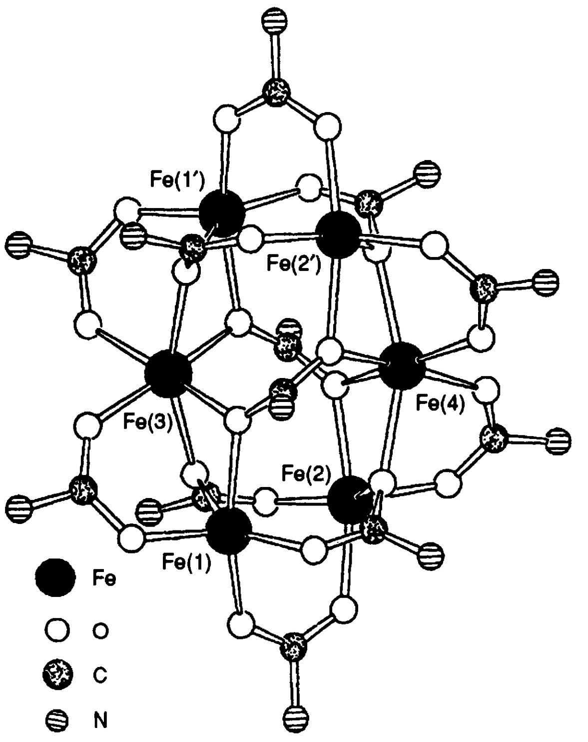

Fig. 1 SCHAKAL plot of $[Fe_6(O_2CNEt_2)_{12}]$. The ethyl groups of the carbamato ligands have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe(1)–O, 1.995(5)–2.169(5), Fe(2)–O, 1.999(5)–2.164(5), Fe(3)–O, 2.043(5)–2.205(5), Fe(4)–O, 2.058(5)–2.218(5); O_{ax}–Fe(1)–O_{ax} 164.0(2), O_{ax}–Fe(1)–O_{eq} 80.2(2)–104.6(2), O_{eq}–Fe(1)–O_{eq} 94.1(2)–140.4(2), O_{ax}–Fe(2)–O_{ax} 164.1(3), O_{ax}–Fe(2)–O_{eq} 80.8(2)–104.8(2), O_{eq}–Fe(2)–O_{eq} 93.7(2)–140.4(2), O–Fe(3)–O_{trans} 158.1(2)–168.7(2), O–Fe(3)–O_{cis} 79.5(2)–107.8(2), O–Fe(4)–O_{trans} 158.5(2)–169.1(2), O–Fe(4)–O_{cis} 79.6(2)–107.5(2).

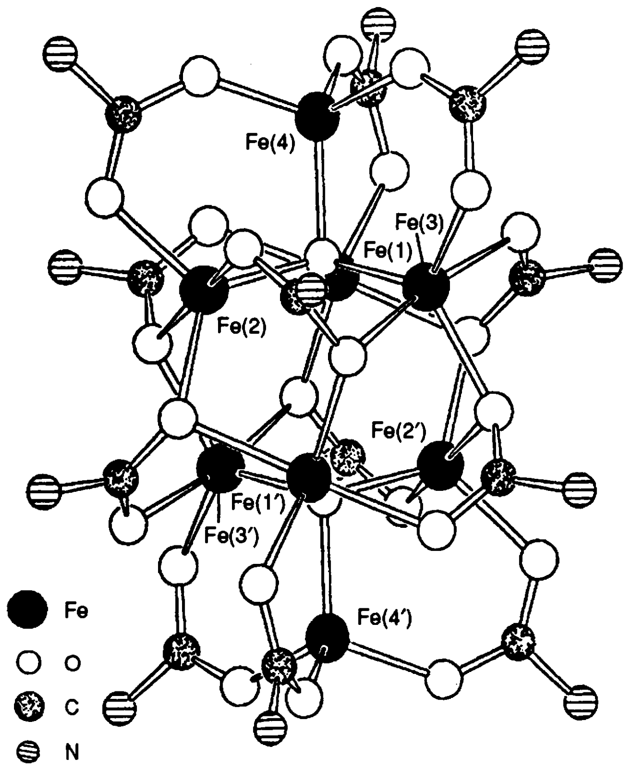

Fig. 2 SCHAKAL plot of [{$Fe_4(\mu_4\text{-}O)(O_2CNPr^i{}_2)_6$}$_2$], **2b**. The isopropyl groups of the carbamato ligands have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe–O_{oxo} 1.955(3)–2.024(4), Fe–$O_{carbamate}$ 1.973(5)–2.206(4); Fe—O_{oxo}–Fe 99.9(2)–117.4(2), O–Fe(1)–O 87.2(2)–172.9(2), O–Fe(2)–O 86.8(2)–172.8(2), O–Fe(3)–O 85.3(3)–171.2(2), O–Fe(4)–O 106.1(2)–114.1(2). Nonbonding distances: Fe···Fe 3.064(2)–3.354(2).

region (PCTFE mull), with intense bands at 1593, 1522, 1485, 1460, 1429, 1375, 1347 and 1314 cm^{-1}, is reminiscent of the IR spectrum of the hexanuclear cobalt(II) ethyl derivative.[6a] The single-crystal X-ray study‡ established the hexanuclear structure of **1a**, with bridging *N,N*-diethylcarbamato groups of three different types. Two of the six iron(II) centres are six-coordinate, the remaining four being five-coordinate, with Fe–O distances ranging from 2.043(5) to 2.218(5) Å in the former coordination set and from 1.995(5) to 2.169(5) Å in the latter. The molecular structure of the hexanuclear iron(II) complex is shown in Fig. 1, with relevant bond distances and angles. Thus, the *N,N*-diethylcarbamato complex of iron(II) has similar structural parameters to the cobalt(II)[6a] and manganese(II)[6b] analogues.

The more soluble isopropyl derivative was better suited for the study of the chemical behaviour of these systems towards water. When a solution of the isopropyl complex in toluene was treated with the stoichiometric amount of water (Fe : H_2O = 4) and the solution stirred at room temperature, a pale-yellow solid, **2b**, was obtained in *ca.* 100% yield; this solid had analytical data for iron and carbon dioxide corresponding to CO_2 : Fe = 1.43, close to the expected value of 1.5 for **2b** [eqn. (1)]. The nuclearity of complex **2b** was established by a single-crystal X-ray structure determination.§

The octanuclear compound, Fig. 2, which is structurally analoguous to the octanuclear Zn^{II}–Ni^{II} compound[9] $[\mathrm{Zn_2Ni_6(\mu_4\text{-}O)_2(O_2CNPr^i_2)_{12}}]$, has some peculiar features: (*a*) it is a μ-oxo derivative of iron(II); (*b*) the iron(II) centres are four- and five-coordinated; (*c*) the coordination geometry approximates a tetrahedron for Fe(4) and a trigonal bipyramid for Fe(1), Fe(2) and Fe(3). Within the μ_4-O-Fe core, the Fe···Fe separation is in the range 3.064(2)–3.354(2) Å (Fig. 2), which compares well with a recently reported[10] μ-oxo iron(III) system (3.025–3.239 Å), when the different oxidation state is taken into consideration.

$$8\,[\mathrm{Fe(O_2CNPr^i_2)_2}] + 2\,\mathrm{H_2O} \rightarrow [\{\mathrm{Fe_4(\mu_4\text{-}O)(O_2CNPr^i_2)_6}\}_2] + \mathrm{NHPr^i_2} + 4\,\mathrm{CO_2} \qquad (1)$$

Reactivity and magnetic susceptibility studies of the μ-oxo iron(II) system are in progress.

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Footnotes

† Satisfactory analytical data were obtained for all compounds reported.

‡ *Crystal data* for **1a**, $C_{60}H_{120}Fe_6N_{12}O_{24}$: *M* = 1728.8, colourless, air-sensitive blocks (0.30 × 0.25 × 0.4 mm^3), monoclinic, space group *C2/c*, *a* = 20.939(2), *b* = 25.243(4), *c* = 16.048(1) Å, β = 90.001(7)°, *V* = 8483.05 Å^3, *Z* = 4, *D* = 1.354 g cm^{-3}, μ(Mo-Kα) = 10.689 cm^{-1}. Data collection was carried out with an Enraf-Nonius-CAD4 automatic diffractometer (Mo-Kα radiation, λ = 0.71069 Å, graphite monochromator, T = 213 K), ω-scans, θ = 3–27°, 14221 reflections, 8902 independent, 5798 with $I \geqslant 3\sigma(I)$ considered as observed, solution by direct methods (SHELX86[11]) and refined with SDP (Enraf-Nonius[10]), 462 refined parameters, *R* = 0.072, R_w = 0.074 [$w = 1/\sigma^2(F)$], all non-hydrogen atoms anisotropic, hydrogen atoms calculated at ideal positions. Refinements in the orthorhombic supergroups of the space group *C2/c* were unsuccessful.

§ *Crystal data* for **2b**, $C_{84}H_{168}Fe_8N_{12}O_{26}$: *M* = 2209.1, air-sensitive lozenges, (0.30 × 0.35 × 0.50 mm^3); triclinic, space group $P\bar{1}$, *a* = 15.022(8), *b* = 15.086(4), *c* = 16.861(4) Å, α = 83.74(2), β = 72.40(2), γ = 63.68(2)°, *V* = 3263.1 Å^3, *Z* = 1, D_c = 1.124 g cm^{-3}, μ(Cu-Kα) = 74.356 cm^{-1}. Measurements were carried out with an Enraf-Nonius-CAD4 automatic diffractometer (Cu-Kα radiation, λ = 1.54184 Å, graphite monochromator, T = 213 K), ω-scans, θ = 5–65°, 11557 reflections, 10625 independent, 8108 with $I \geqslant 3\sigma(I)$ considered as observed, solution by direct methods (SHELX86[11]) and refined with SDP (Enraf-Nonius[12]), 587 refined parameters, *R* = 0.070, R_w = 0.095 [$w = 1/\sigma^2(F)$], all non-hydrogen atoms anisotropic, hydrogen atoms calculated at ideal positions.

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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