Mixed-Valence, Tetranuclear Iron Chelate Complexes as Endoreceptors: Charge Compensation Through Inclusion of Cations**

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Dedicated to Professor Helmut Ringsdorf on the occasion of his 65th birthday

An essential prerequisite for the rapid development of endo-

eddial, chemistry, that is chemistry within cages, is easy access to

host molecules of variable internal diameter. [12] In this context, we have recently reported the tetranuclear adamantanoid Fe4 II

spacerr complex [Fe4L4]+. [11] Complex I is endowed with a sub-

stantial cavity, which should, in principle, be suitable for the

uptake of guest molecules. Our attempts to obtain the spacer-

free metallospherand core unit [Fe4L4]2 in analogous manner

have thus far given rise to products which could not be charac-

terized unambiguously.

In contrast, we have obtained for the first time, the tetra-

nuclear, mixed-valence ammonium inclusion complexes

[ NH4+ -Fe4L4]2 and [NH4+ -Fe4L4]3 in a one-pot reaction [13]

complexes 2 and 3 are formed by spontaneous self-assembly [14–16] from the reaction of dialkyl malonates with methyl-

lithium/iron(II) chloride and oxalyl chloride at −78 °C in

tetrahydrofuran, followed by workup with aqueous ammonium


[17] Crystal data of 9: [Me2Sn(C5H4)2]2Cl, M = 781.51, orthorhombic, space group Pmn21, a = 2232.2(4), b = 1647.6(8). c = 1312.3(2) pm, V = 4.163(1) nm3, Z = 4, μ = 1.247 gm−1, f(000) = 1640, z = 71.073 pm, T = 130 C, μ(MoKα) = 1.286 nm−1, crystal dimensions: 0.6 x 0.6 x 0.4 mm, 4 < 2θ ≤ 50; of 5491 measured reflections, 5084 were independent and 5080 were used for the refinement of 388 parameters; maximum residual electron density: 1572 e/nm3, R1(F0 > 4σ(F)) = 0.039, wR2 = 0.115 (all data) with R1 = [Σ||obs| - |calcd||Σ||obs|| and wR2 = (Σw(F02 - F̂2)2/Σw(F02))1/2. The data were collected on a Stoe-Huber diffractometer. The intensity measurements were carried out on a rapidly cooled crystal in the oil drop [26] by the ω/θ method. Semiempirical absorption corrections were carried out on all data. The structure was solved by Patterson and Fourier methods (SHELXTL-90) [27] and refined with the least squares method on F2 [28]. The refinement of the inversion twin parameter [29] (λ = 0.002) for x = 0 for the correct absolute structure and x = +1 for the inverted structure) confirmed the absolute structure of 9. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK), on quoting the full journal citation.
[40] G. M. Sheldrick, SHELXL-93, program for crystal structure refinement, Göttingen, 1993.
This contrasts with the spacer-complex \([\text{Fe}_4L_2]^{+}\) 1, which is exactly \(S_4\) symmetric and thus achiral (meso-form). In 1, the ligands \(L^1\) are arranged facially about the four iron centers; however, in this case two of the four iron centers have the same configuration \((A.A)-\) and \((A.A)-fac\).\(^{14}\)

The mixed-valence character of 2 and 3 was established unambiguously from their Mössbauer spectra. Powder samples of complexes 2 and 3 each show, in a temperature range of 4.2–300 K, a virtually temperature independent triplet, arising from the overlap of two quadrupolar doublets [one high-spin Fe\(^{III}\) center: quadrupolar splittings \(\Delta E_Q(4.2 \text{ K}) = 2.90 (2), 2.79 (3) \text{ mm s}^{-1}\), isomeric shifts \(\delta(4.2 \text{ K}) = 1.29 (2), 1.29 (3) \text{ mm s}^{-1}\); three Fe\(^{III}\) centers: quadrupolar splittings \(\Delta E_Q(4.2 \text{ K}) = 0.71 (2), 0.84 (3) \text{ mm s}^{-1}\), isomeric shifts \(\delta(4.2 \text{ K}) = 0.56 (2), 0.55 (3) \text{ mm s}^{-1}\)] (Fig. 2, left). The observation of distinct Mössbauer subspectra for the Fe\(^{III}\) and Fe\(^{II}\) centers in complexes 2 and 3 indicates localized valences, at least on the Mössbauer timescale (ca. 10\(^{-7}\) s). Even at room temperature, no significant line-broadening occurs, which would point to a dynamic valence process. The seemingly contradictory results of the X-ray analyses of 2 and 3, in which there were no apparent differences in the coordination spheres of the Fe\(^{III}\) and Fe\(^{II}\) centers are attributed to a statistical disordering of the Fe\(^{II}\) loci. For complexes 2 and 3, no exchange interactions between the mixed-valence iron centers could be observed from temperature-dependent susceptibility measurements in the range 1.5–300 K. On the basis of the EPR spectroscopic results, it must, however, be assumed that a weak coupling (\(J < 1 \text{ cm}^{-1}\)) between these centers does exist, because only a single, very broad resonance signal at \(g = 2\) is observed.

The redox-active iron centers of the mixed-valence complexes 2 and 3 are located in fairly inaccessible sites within these compounds, and possess very similar electrochemical properties. The cyclic voltammograms of these compounds under aprotic conditions\(^{16}\) show an extreme dependency on the scan rate. Consequently, meaningful spectra of 2 and 3 could only be obtained under pseudo-thin-layer conditions\(^{17}\) with a very slow scan rate. With these preconditions, cyclic voltammograms are observed which display four\(^{18}\) quasi-reversible redox steps (Fig. 2, right). The recorded potentials are listed in Table 1. Notably, 3 is reduced at more negative potentials than 2. As for...
The spacer complex I, only a very slight electronic interaction exists between the tetrahedrally arranged iron centers of compounds 2 and 3. In contrast to complex I, which shows a one-electron, four-ligand transfer, a four-electron-four-ligand electron transfer is observed for 2 and 3. These findings are probably due to the shorter iron–iron distances in 2 and 3 (compared to 1): this gives rise to a stronger covalent interaction between the metal centers, leading to a splitting of the redox potentials.

All in all, the compounds obtained, 2I and 3, are may be viewed as neutral fragments. Species of this type are of considerable interest because of their analogies with the series metal atom [Na], cryptatium [Na^+(bpy)], and electrode ([K = [2.2.2]cryptand], e^-). Preliminary FAB mass spectrometric results confirm the assumption that inclusion complexes of type [M = Fe,L_2]^+ (molecular zeolites, M = Na, K, Rb, Cs) may also be prepared by the method described above. A decisive advantage of the synthetic strategy utilized here is that complex structures with defined architecture and specific properties are accessible by spontaneous self-assembly and without the inconvenience associated with multistep synthesis.

**Experimental Procedure**

General procedure: Methylithium solution (1.6M in diethyl ether, 30 mmol) diluted with dry THF (10 mL) was added dropwise to a solution of the diazil malonate (30 mmol) in dry THF (50 mL) (N_2) over 30 min. The mixture was stirred for 1 h at 78° C and then EtCl_2, 4H_2O (5.6 g, 30 mmol) was added. After stirring for 1 h, a cooled (78° C) solution of oxalyl chloride (freshly distilled, 0.95 g, 6.65 mL, 75 mmol) in dry THF (20 mL) was added dropwise to the suspension, which was then warmed to 20° C during 1 h, and the resulting deep red solution treated with saturated aqueous ammonium chloride solution (100 mL). The two phases were separated, the aqueous layer extracted three times with an alkyl (cyclohexane, EtOAc) solvent. After concentration to small volume (5 mL), the reaction product was crystallized by the addition of diethyl ether/hexane (1:1, 50 mL, 0°C). Occasionally, black-red octahedra are formed (M = Me) which, on the basis of Mössbauer spectra (300 K), are shown to have a Fe^II/Fe^III ratio of 1:1 (Fe^III). \( \Delta E_{Q} = 2.00 \text{ mm}^s^{-1} \), \( \Delta E_{Q} = 0.55 \text{ mm}^s^{-1} \). Likewise, ruby-red octahedra (M = Et), which, on the basis of Mössbauer spectra (300 K), contain exclusively Fe^II (\( \Delta E_{Q} = 0.77 \text{ mm}^s^{-1} \), \( \Delta E_{Q} = 0.44 \text{ mm}^s^{-1} \)).

1. Ruby-red crystals from chloroform, by diffusion of diethyl ether. Yield: 1.47 g (55%), m.p. > 200° C (decomp.), IR (KBr): \( \nu = 1730 \text{ cm}^{-1} \), C=O, broad; FAB MS (3-nitrobenzylalkohol matrix): m/z 239 [NH_4FeCl_2].

2. Ruby-red crystals from chloroform, by diffusion of diethyl ether. Yield: 1.23 g (40%), m.p. > 200° C (decomp.), IR (KBr): \( \nu = 1730 \text{ cm}^{-1} \), C=O, broad; FAB-MS (3-nitrobenzylalkohol matrix): m/z 2475 [NH_4FeCl_2].

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Table 1. Peak potentials for 2 and 3, given in mV against Fe/Fe', derived from thin-layer cyclic voltammograms in acetonitrile 0.1 M tetrabutylammonium hexafluorophosphate with a scan rate of 2 mV s^{-1} (2) or 5 mV s^{-1} (3) (see Fig. 2, right).

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>2</th>
<th>3</th>
</tr>
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<tbody>
<tr>
<td>( E_{pa} )</td>
<td>-150</td>
<td>-240</td>
</tr>
<tr>
<td>( E_{pc} )</td>
<td>-330</td>
<td>-450</td>
</tr>
<tr>
<td>( E_{pa} )</td>
<td>-510</td>
<td>-660</td>
</tr>
<tr>
<td>( E_{pc} )</td>
<td>-700</td>
<td>-910</td>
</tr>
</tbody>
</table>

[a] \( E_{pa} \): cathodic peak potential. [b] \( E_{pc} \): anodic peak potential.