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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 endohedral chemistry, that is chemistry within cages, is easy access to host molecules of variable internal diameter.^[1] In this context we have recently reported the tetranuclear adamantanoid Fe^{III} spacer-complex $[\text{Fe}_4\text{L}^1_6]$ **1**.^[1] Complex **1** is endowed with a substantial cavity, which should, in principle, be suitable for the uptake of guest molecules. Our attempts to obtain the spacer-free metallospherand core unit $[\text{Fe}_4\text{L}^2_6]$ in analogous manner have thus far given rise to products which could not be characterized unambiguously.

In contrast, we have obtained for the first time, the tetranuclear, mixed-valence ammonium inclusion complexes $[\text{NH}_4^+\text{Fe}_4\text{L}^2_6]$ **2** and $[\text{NH}_4^+\text{Fe}_4\text{L}^3_6]$ **3** in a one-pot reaction.^[3] Complexes **2** and **3** are formed by spontaneous self-assembly^[1, 4–7] 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

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[++] Electrochemistry.

[+++] Mössbauer spectra.

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chloride. The bis(bidentate), spacer-free bridging ligands L^2 and L^3 are formally obtained by coupling of two dialkyl malonate monoanions with oxalyl chloride to form H_2L^2 and H_2L^3 , respectively, followed by double deprotonation.

The microanalytical data and FAB mass spectra of **2** and **3** gave the first indications that these products might constitute host–guest systems. The molecular- and fragment ion peaks of **2** and **3** are, in each case, 18 mass units greater, as expected for the inclusion of an ammonium ion.

For a definitive characterization of **2** and **3**, we have carried out crystal structure analyses on both complexes.^[8] The results of these show that **2** and **3** are present in the crystal as neutral, tetranuclear, mixed-valence chelate complexes with an endohedrally complexed cation for charge compensation (Fig. 1). The

Fig. 1. Top: Structure of **2** in the crystal (view along the crystallographic C_3 axis; H atoms of the NH_4^+ ion plain, O atoms dotted, C atoms shaded). Bottom: Stereo-view of **2** along the crystallographic C_3 axis. Water of crystallization is not depicted for reasons of clarity.

receptor nucleus of **2** and **3** consists in each case of a regular tetrahedron with corners defined by one Fe^{II} and three Fe^{III} ions. The six edges of the tetrahedron are each formed by the bis(bidentate), doubly negatively charged bridging ligands L^2 or L^3 . Each of the four iron ions is octahedrally coordinated by six oxygen atoms.^[13] In the center of the iron tetrahedron there is an ammonium ion which serves presumably as a template for the formation of **2** and **3**, thereby becoming enclosed during the construction of these systems.

Two pairs of enantiomers [(Δ)-, (Δ)-*fac* and (Δ)-, (Δ)-*mer*] are principally possible for octahedral complexes of type MA_3B_3 [for bidentate ligands: $M(AB)_3$]. The chiral racemic complexes **2** and **3** crystallize in the cubic space group $Fd\bar{3}$. All four iron centers in **2** and **3** are identically coordinated, hence the complexes are present as either (Δ , Δ , Δ , Δ)-*fac* or as (Δ , Δ , Δ , Δ)-*fac* stereoisomers.^[11] With an idealized representation, (the Fe–Fe distances differ from one another in both cases by less than 1.3%), **2** and **3** are shown to have approximately T -molecular symmetry (characterized by three C_2 and four C_3 axes).^[15,15]

This contrasts with the spacer-complex $[Fe_4L_6^I]$ **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 [(Δ , Δ)- and (Δ , Δ)-*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^{II} center: quadrupolar splittings ΔE_Q (4.2 K) = 2.90 (**2**), 2.79 (**3**) $mm\ s^{-1}$, isomeric shifts δ (4.2 K) = 1.29 (**2**), 1.29 (**3**) $mm\ s^{-1}$; three Fe^{III} centers: quadrupolar splittings ΔE_Q (4.2 K) = 0.71 (**2**), 0.84 (**3**) $mm\ s^{-1}$, isomeric shifts δ (4.2 K) = 0.56 (**2**), 0.55 (**3**) $mm\ s^{-1}$] (Fig. 2, left). The observation of distinct Mössbauer

Fig. 2. Left: Mössbauer spectra of a powder sample of **2**, recorded at 4.2 K. The connecting line is the result of a two-doublet adjustment of the Lorentz line. Sub-spectra: Fe^{II} (---), $\Delta E_Q = 2.90\ mm\ s^{-1}$, $\delta = 1.29\ mm\ s^{-1}$, $\Gamma = 0.42\ mm\ s^{-1}$, 24% rel. intensity; Fe^{III} (---), $\Delta E_Q = 0.71\ mm\ s^{-1}$, $\delta = 0.56\ mm\ s^{-1}$, $\Gamma = 0.59\ mm\ s^{-1}$, 76% rel. intensity. Right: Pseudo-thin layer cyclic voltammogram of **2** (—) and **3** (---) in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate, scan rate 2 mVs^{-1} (**2**), 5 mVs^{-1} (**3**). Ordinate scale: one unit corresponds to 0.05 μA (**2**), 0.1 μA (**3**), negative current plotted upwards, potentials vs. ferrocene/ferrocenium (Fe/Fe^+).

subspectra for the Fe^{II} and Fe^{III} 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^{II} and Fe^{III} 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 ($J < 1\ cm^{-1}$) 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

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

		E^I	E^{II}	E^{III}	E^{IV}
2	E_{pc} [a]	-150	-330	-510	-700
	E_{pa} [b]	-130	-310	-470	-640
3	E_{pc} [a]	-240	-450	-660	-910
	E_{pa} [b]	-210	-390	-570	-720

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

the spacer complex **1**, only a very slight electronic interaction exists between the tetrahedrally arranged iron centers of compounds **2** and **3**. In contrast to complex **1**, which shows a one-potential four-electron transfer, a four-potential four-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 coulombic interaction between the metal centers, leading to a splitting of the redox potentials.

All in all, the compounds obtained, **2**^[19] and **3**, 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)₃]e⁻}, and electride {[K⁺⊂[2.2.2]cryptand], e⁻}. Preliminary FAB mass spectrometric results confirm the assumption that inclusion complexes of type [M⊂Fe₄L₆³] (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: Methylolithium solution (1.6 M in diethyl ether, 30 mmol) diluted with dry THF (10 mL) was added dropwise to a solution of the dialkyl malonate (30 mmol) in dry THF (50 mL) (N₂, -78 °C) over 30 min. The mixture was stirred for 1 h at -78 °C and then FeCl₂·4H₂O (5.96 g, 30 mmol) was added. After stirring for 1 h, a cooled (-78 °C) solution of oxalyl chloride (freshly distilled, 0.95 g, 0.65 mL, 7.5 mmol) in dry THF (20 mL) was added dropwise to the suspension, which was then warmed to 20 °C during 18 h and the resulting clear, 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 halide (70 mL, trichloromethane for **2**, dichloromethane for **3**), and the combined organic phases dried over anhydrous sodium sulfate. 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 (R = Me), which, on the basis of Mössbauer spectra (300 K), are shown to have a Fe^{II}/Fe^{III} ratio of 1:1 (Fe^{II}: $\Delta E_0 = 2.69 \text{ mm s}^{-1}$, $\delta = 1.20 \text{ mm s}^{-1}$, Fe^{III}: $\Delta E_0 = 0.55 \text{ mm s}^{-1}$, $\delta = 0.46 \text{ mm s}^{-1}$). Likewise, ruby-red octahedra (R = Et), which, on the basis of Mössbauer spectra (300 K), contain exclusively Fe^{III} ($\Delta E_0 = 0.77 \text{ mm s}^{-1}$, $\delta = 0.44 \text{ mm s}^{-1}$).

2: Ruby-red crystals from chloroform, by diffusion of diethyl ether. Yield: 1.47 g (55%); m.p. > 200 °C (decomp.); IR (KBr): $\tilde{\nu} = 1730 \text{ cm}^{-1}$ (C=O, broad); FAB MS (3-nitrobenzylalcohol matrix): m/z 2138 [NH₄⊂Fe₄L₆³].

3: Ruby-red crystals from dichloromethane, by diffusion of diethyl ether. Yield: 1.23 g (40%); m.p. > 200 °C (decomp.); IR (KBr): $\tilde{\nu} = 1700 \text{ cm}^{-1}$ (C=O, broad). FAB-MS (3-nitrobenzylalcohol matrix): m/z 2475 [NH₄⊂Fe₄L₆³].

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