measured by the composite quantity PD_f (where P is the solution–film partition coefficient and D_f is the film-based diffusion coefficient), systematically decrease with increasing permeant size, and c) permeabilities with films of **1** somewhat exceed those obtained with related electropolymerized materials. For example, the PD_f value for the passage of $[Fe(bpy)_3]^{2+}$ through **1** is $(4 \pm 2) \times 10^{-8}$, but is only $(1.4 \pm 0.2) \times 10^{-8}$ for passage of the related compound $[Os(bpy)_2Cl_2]$ through poly-(orthoamino)tetraphenylporphyrin (or 3.6×10^{-9} for passage through "annealed" polymer films).[5] Other values of PD_f measured with **1** are: $[Fe(CN)_6]^{3-}$: $(1.3 \pm 0.5) \times 10^{-7}$, $[Co(phen)_3]^{2+}$: $(2.4 \pm 1.9) \times 10^{-8}$, $[Fe_2(CN)_{10}(\mu\text{-}4,4\text{-bipyridine})]^{6-}$: $(6.5 \pm 5.0) \times 10^{-9}$. We hope to exploit the sieving characteristics, the tailorability, and the high permeability of thin films of **1** and related compounds in applications-oriented membrane catalysis, sensing, and transport investigations.

Experimental Section

Compound **1** was prepared as described earlier.[1c] $[Fe(bpy)_3](SO_4)$ was purchased from GFS chemicals as a 0.025 M solution. $[Ru(NH_3)_5(4\text{-picoline})](PF_6)_2$, the various $[M(LL)_3](NO_3)_2$ species, $Na_4[Fe_2(CN)_{10}(\mu\text{-}4,4\text{-bipyridine})]$, and $[Fe(bphenSO_3Na)_3](NO_3)_2$ (mix of meta and para sulphonates) were prepared by minor adaptations of literature methods.[6] All other permeants and chemicals were obtained from Aldrich or Mallinckrodt. Films were prepared by the slow evaporation of a drop hanging from a glassy carbon disk electrode spinning at ≈100 rpm. Thicknesses (typically ≈40 nm, but up to 1000 nm) were manipulated by changing the concentration of the casting solution and/or by applying a second coat after a drying time of 10 min; all films were subjected to a final drying of at least 30 min to ensure strong surface adhesion. The casting solutions, which were first filtered through a 0.1 µm polytetrafluoroethylene membrane (Whatman), were: $CHCl_3$ (**1**), 2:1 $CHCl_3$:CH_3CN (**1**·H_2-Py_4P), and 2:1 CH_3Cl:CH_3CH_2OH (**1**·H_2-Py_2P').

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Supramolecular Complexation of Polynuclear Aqua Ions: A Crown Ether Adduct of a μ-Oxo-Bridged Iron(III) Aqua Dimer**

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The hydrolysis and polymerization of iron(III) in aqueous solution has been the subject of intense investigation since before the turn of this century[1, 2] owing to the relevance of iron(III) hydrolytic processes to, for example, aquatic systems, the storage of iron by ferritin, and industrial processes such as alumina production. Although various products were proposed to form in the early stages of polymerization, the constitution and structure of even the simplest oligomers is still open to conjecture. For example, the structure of the binuclear iron(III) aqua ion has proved elusive, and there is considerable debate whether the two metal atoms are linked by two hydroxo bridges, $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(OH_2)_4]^{4+}$, or by a single μ-oxo bridge, $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$.[1–5] The two forms are related by the equilibrium shown in Equation (1). The latter form is favored according to magnetochemical and spectroscopic evidence, but it is noteworthy that a different structural assignment is preferred in two leading textbooks.[4, 5] Moreover, although binuclear Fe^{III} complexes with hydroxo and oxo bridges are both common, with the latter predominant, they provide little insight into the structure of the binuclear aqua ion.

$$[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(OH_2)_4]^{4+} + H_2O \rightleftharpoons [(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+} \quad (1)$$

Previous X-ray structural studies on binuclear aqua ions of Al^{III},[6] Cr^{III},[7] Sc^{III},[8] and Rh^{III},[9] as well as on a heterometallic $Cr^{III}Rh^{III}$ aqua ion,[10] showed that the bis(μ-hydroxo)M_2 core is preferred in all these cases. However, the existence of a μ-oxo-bridged Cr^{III} dimer was proposed on spectroscopic grounds. With the exception of the Al^{III} dimer,[6] aromatic sulfonates were a key factor in the crystallization of these aqua ions. Such anions assist in the assembly of a superlattice in which layers of aqua ions are separated by layers of the anions. The superlattice is stabilized by an extensive hydrogen-bonding network involving the aqua ions, water solvate molecules, and anions, and by interactions between the anion themselves. In a further elaboration of this approach, crown ethers were introduced to modify the hydrogen-bonding array that surrounds these ions in aqueous solution. This led

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recently to the isolation of a novel crown ether adduct of dimeric Cr^{III} mesitylate.[11]

Here the ability of crown ethers to promote the crystallization of the polymerization products of labile metal ions is demonstrated for the first time. We report the X-ray structure and characterization of an [18]crown-6 adduct of the (μ-oxo)Fe^{III} binuclear aqua ion, a product isolated from aqueous solutions of $[Fe(OH_2)_6]^{3+}$. Apart from being the first oxo-bridged binuclear aqua ion to be structurally characterized, the existence of this ion provides strong evidence for its presence in hydrolyzing aqueous solutions of simple iron(III) salts.

Slow evaporation of an aqueous solution of iron(III) nitrate containing [18]crown-6 deposited large orange crystals of a product whose elemental composition and IR spectrum indicated the presence of [18]crown-6 molecules. The X-ray structure confirmed the composition **1**.[12] However, the most exciting feature of the structure was the presence of the hitherto elusive $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$ ion within the crystal lattice (Figure 1).

$[(H_2O)_5Fe(O)Fe(OH_2)_5](NO_3)_4 \cdot 2\,[18]\text{crown-6}$ **1**

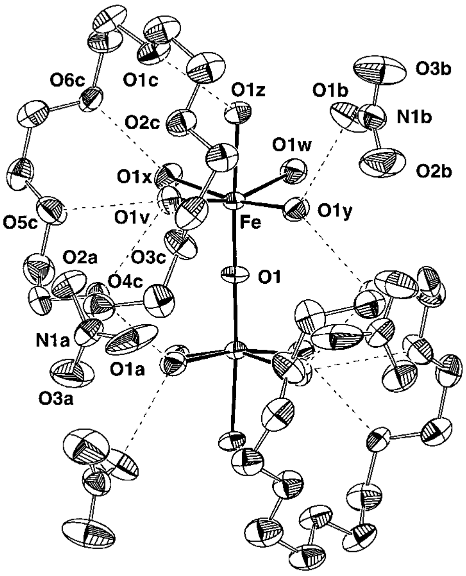

Figure 1. Molecular structure of **1** (20% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Fe–O1 1.784(1), Fe–O1v 2.070(7), Fe–O1w 2.074(8), Fe–O1x 2.049(7), Fe–O1y 2.062(7), Fe–O1z 2.123(6); Fe-O1-Fe 169.6(6), O1-Fe-O1v 101.5(3), O1-Fe-O1w 97.7(3), O1-Fe-O1x 95.9(3), O1-Fe-O1y 94.9(3), O1v-Fe-O1w 160.4(3), O1v-Fe-O1x 85.5(3), O1v-Fe-O1y 93.1(3), O1w-Fe-O1x 88.0(3), O1w-Fe-O1y 93.1(3), O1x-Fe-O1y 168.9(2), O1z-Fe-O1v 81.10, O1z-Fe-O1w 79.94, O1z-Fe-O1x 86.58, O1z-Fe-O1y 82.74, O1z-Fe-O1 176.53; H_2O–[18]crown-6 hydrogen bonds: O1v–O3c 2.752(9), O1v–O4c 2.90(1), O1v–O5c 2.85(1), O1x–O6c 2.710(8), O1y–O4c 2.751(8), O1z–O1c 2.737(8); H_2O–NO_3 hydrogen bonds: O1w–O1a 2.62(1), O1x–O1a 2.58(1), O1w–O3b 2.76(1), O1y–O1b 2.67(1).

The IR spectrum of this complex shows a moderately strong band at 840 cm^{-1} which is not present in the Raman spectrum and hence can be assigned to the asymmetric vibration of the Fe-O-Fe core.[2, 13] The diffuse reflectance UV/Vis spectrum shows a strong broad band centered at 380 nm consisting of five component peaks between 210 and 430 nm. These bands are rather similar to those reported by Solomon et al.,[14] who carried out a detailed spectral and theoretical analysis on $[(Hedta)Fe(\mu\text{-}O)Fe(Hedta)]^{2-}$ (H_4edta = ethylenediaminetetraacetic acid), a μ-oxo complex first studied by Gray et al.[15] The bands are assigned to oxo (p) ⇒ Fe^{III} (d) ligand-to-metal charge-transfer (LMCT) transitions; the multiple peaks arise from excited state splittings. Further variable-temperature studies on single crystals of **1** are warranted to elucidate the antiferromagnetism of the excited state. A weaker broad band at 799 nm is assigned to the d–d band $^6A_1 \Rightarrow {}^4T_1$, which gains intensity from the low energy LMCT bands and from the covalent Fe-O-Fe bond.[14]

In the molecular structure of **1**, the bridging oxo ligand lies on a twofold rotation axis (Figure 1). The iron centers are octahedrally coordinated by five water molecules (O_w) and the bridging oxo ligand. The μ-O–Fe and O_w–Fe distances of 1.784(1) and 2.049(7)–2.123(6) Å, respectively, are in keeping with the mean values of 1.79(6) (with a range of 1.73–1.82 Å) and 2.09(7) Å for such bond lengths in oxo-bridged iron(III) complexes at room temperature.[17] The fact that the axial O_w–Fe distance (2.123(6) Å) is slightly longer than the equatorial O_w–Fe distances (av 2.064 Å) and the equatorial water molecules are bent away from the oxo ligand (av O-Fe-O_w 97.5°) is indicative of the *trans* influence of the oxo ligand. The Fe-O-Fe angle of 169.6(6)° lies in the range of angles for similar complexes, which vary from 140 to 180° but are generally in the range 170–180°.[17] Significant hydrogen bonding in the structure of **1** (see below) presumably contributes to the deviation of the Fe-O-Fe core from linear geometry. The Fe–Fe distance of 3.552(2) Å is typical for complexes with singly bridged Fe-O-Fe cores, which are usually in the range 3.4–3.6 Å,[2, 17] whereby the longer distances are associated with Fe-O-Fe angles that are linear or close to linearity.[2, 17]

The $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$ cation is stabilized by second-sphere hydrogen-bonding interactions with the [18]crown-6 molecules (Figure 1). In addition, hydrogen bonding occurs between the water ligands (no water of crystallization is present) and nitrate counteranions. The $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$ core forms hydrogen bonds to oxygen atoms of the nitrate counterions. A nitrate group bridges equatorial water molecules on each Fe center, while other nitrate anions form hydrogen bonds to successive $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$ cations and thus link them together into a zigzag polymeric array. The crown ether molecules are involved in hydrogen bonding with the remaining water molecules of $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$, and each crown ether is bound to two water molecules on one Fe^{III} center and one water molecule on the other in an "earmuff" fashion. By forming hydrogen bonds to water ligands of both Fe^{III} centers, the [18]crown-6 macrocycle stabilizes the Fe-O-Fe unit sufficiently to allow the isolation (in the solid state) of the unprecedented $[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+}$ ion. Notably, the protected oxo bridge is not involved in hydrogen bonding, and the crown ether forms no intermolecular hydrogen bonds, in contrast to a dimeric crown ether adduct of Cr^{III}.[11]

The magnetic susceptibility data of **1** (Figure 2) are typical of those observed for Fe^{III}-O-Fe^{III} complexes.[2, 18] The data fit very well to the Heisenberg exchange model ($-2J\,\vec{S}_1 \cdot \vec{S}_2$) for two $S = 5/2$ centers with best-fit parameters of $g = 2.00$ (fixed), $J = -110\ cm^{-1}$, and 0.4% monomer. Weihe and Güdel[19] recently analyzed the dependence of J on the Fe-O-Fe angle ϕ and the average Fe–O distance r by using the angular and radial overlap model. They found that calculated J values increased with decreasing values of r and ϕ. Our values of $r = 1.784(1)$ Å and $\phi = 169.6(6)^\circ$ fit precisely on the $J = -100\ cm^{-1}$ curve in Figure 3 of reference [19], in very good agreement with the observed J value. The model is therefore able to predict J values for new Fe-O-Fe complexes such as **1**. This model ignores contributions from terminal ligands, and it was found that the AOM parameters for the μ-oxo group are in the ratio $e_{p\sigma}:e_{p\pi}:e_{s\sigma} \approx 2.5:1:1$. The earlier "distance-only" model of Gorun and Lippard yields a calculated J value of $-135\ cm^{-1}$, but this model is known not to apply well to singly bridged Fe-O-Fe species.[20] Inclusion of an interdimer interaction parameter θ in the $T-\theta$ term of the susceptibility equation makes very little difference to the fit of the present magnetic data, and this is in agreement with the lack of intermolecular hydrogen-bonded exchange pathways in the crystal structure.

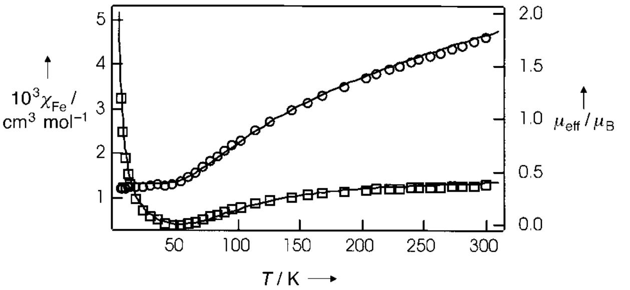

Figure 2. Variation of magnetic susceptibility (□) and magnetic moment per Fe atom (○) for **1**. The solid lines are calculated from the best fit with $g = 2.00$ (fixed), $J = -110\ cm^{-1}$, and 0.4% monomer, with $R = 3.1\%$. The best fit was obtained with $g = 1.85$, $J = -99\ cm^{-1}$, and 0.4% monomer, with $R = 0.7\%$ ($R = S(|X_{obs}| - |X_{calc}|)T/SX_{obs}T$). The low value of g probably reflects errors due to slight contamination with [18]crown-6.

Experimental Section

1: $Fe(NO_3)_3 \cdot 9H_2O$ (0.15 g, 0.38 mmol) and [18]crown-6 (0.10 g, 0.38 mmol) were dissolved in H_2O (5 mL), and the water was allowed to evaporate at room temperature. Large orange crystals of **1** were isolated. Elemental analysis calcd for $C_{24}H_{68}O_{35}N_4Fe_2$: C 26.6, H 6.3, N 5.2; found: C 26.8, H 6.9, N 6.1; IR (KBr disk): $\tilde{\nu} = 3391$ (vs br), 2899 (m), 1638 (s), 1384 (vs), 1285 (w), 1248 (w), 1111 (s), 1032 (w), 964 (s), 861 (w), 840 (s), 432 (m), 261 cm^{-1} (m); selected Raman bands (crystal): $\tilde{\nu} = 2958$ (m), 2919 (m), 1462 (w), 1274 (w), 1074 (w), 1035 (vs), 867 (m), 282 cm^{-1} (m).

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[12] a) X-ray structural analysis of **1**: $C_{24}H_{68}O_{35}N_4Fe_2$, $M_r = 1084.51$, crystal dimensions $0.24 \times 0.32 \times 0.24$ mm; monoclinic, space group $C2/c$ (no. 15), $a = 22.863(3)$, $b = 10.993(1)$, $c = 20.758(4)$ Å, $\beta = 111.02(1)^\circ$, $V = 4870(1)$ Å^3; $\rho_{calcd} = 1.424\ g\,cm^{-3}$, $Z = 4$; $2\theta_{max} = 50^\circ$; $2\theta/\theta$ scan mode; monochromatic $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; $\mu(Mo_{K\alpha}) = 0.7\ mm^{-1}$; 4268 independent reflections; 1839 observed reflections ($I > 3\sigma(I)$) used in large-block least-squares refinement; $T = 295$ K; $F(000)$ 2160; final $R = 0.056$, $R_w = 0.062$ for 294 variables and 1839 unique observed reflections with $I > 3\sigma(I)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and were not refined. Hydrogen atoms on the water molecules were not located. Conventional residuals R, R_w on $|F|$ are quoted; statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\,\sigma^4(I_{diff})$ were used. Neutral atom complex scattering factors were employed, and computation was performed with the XTAL 3.4 program system, implemented by S. R. Hall et al.[12b] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116680. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). b) S. R. Hall, G. S. D. King, J. M. Stewart, Xtal 3.4 User's Manual. University of Western Australia, Lamb, Perth, **1995**.
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