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Synthesis and Structure of $[Fe_{13}O_4F_{24}(OMe)_{12}]^{5-}$: The First Open-Shell Keggin Ion

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In 1826 Berzelius reported the preparation of the phosphomolybdate ion $[PMo_{12}O_{40}]^{3-}$,[2] but 100 years passed before the structure of the tungsten analogue $[PW_{12}O_{40}]^{3-}$ was determined by Keggin.[3] The Keggin structure, a general name for the large family of complexes having the formula $[XM_{12}O_{40}]^{3-}$ ($X = P^{V}$, Si^{IV}, B^{III}, As^{V}, Co^{II}, Co^{III}, Cu^{I}, Cu^{II}, Fe^{III}, etc; $M = Mo^{VI}$, W^{VI}, V^{V}, Ti^{IV}), comprises four M_3O_4 groups that encapsulate a central heteroatom with a tetrahedral geometry. These bulky spherical anions are part of a larger class of compounds known as polyoxometalates (POMs),[4] which are very useful in diverse disciplines ranging from physics, materials science, and catalysis to biology and medicine.[5−7] In almost all Keggin ions and other POMs, the atoms that form the encapsulating frameworks are early transition metals in their highest oxidation state with a *closed-shell* d^0 configuration. These atoms form strong multiple bonds with terminal oxygen atoms on the surface of the sphere.

Here we report the preparation, structure, and physical properties of the first example of an *open-shell* Keggin ion, $[Fe_{13}O_4F_{24}(OMe)_{12}]^{5-}$ (**1**), which consists of 13 high-spin d^5 iron(III) atoms. Yellow-brown crystals of the pyridinium salt of **1** were obtained in ca. 20% yield, following a reaction between $FeF_3{\cdot}3H_2O$ and pyridine in hot methanol under anaerobic conditions.[8] The anion **1**, which has an ideal α-Keggin structure with 12 surrounding iron atoms and a central tetrahedral $\{FeO_4\}$ core, resides on a crystallographic $\bar{4}3m$ site, manifesting full T_d symmetry (Figure 1).[9] Each oxygen atom in the $\{FeO_4\}$ unit is further bonded to three Fe(III) ions that form triangular $\{Fe_3(\mu\text{-}O)(\mu\text{-}OMe)_3\}$ subunits. These subunits are linked by 12 fluoride ligands to form a sphere that encapsulates the central iron atom. Additionally, each of the 12 iron atoms is coordinated to a terminal fluoride ligand. The Fe(1)−O(1) distance in the central $\{FeO_4\}$ unit in **1**, 1.888(6) Å, is slightly longer than the distance of 1.824(2) Å in a similar tetrahedral $\{Fe^{III}O_4\}$ core within the $\{W_{12}O_{36}\}$ framework of the POM $[FeW_{12}O_{40}]^{5-}$.[10] The (μ_4-O)−Fe(2) distance and Fe(1)−O(1)−Fe(2) bond angle in **1**, 2.093(3) Å and 120.8(1)°, respectively, may be compared with the corresponding values of (μ_4-O)−$W_{surface}$, 2.22 Å, and Fe−O−W, 120.5°, in $[FeW_{12}O_{40}]^{5-}$. The Fe(2)···Fe(2)′ distance within the $\{Fe_3(\mu\text{-}O)(\mu\text{-}OMe)_3\}$ subunits in **1** is 3.1147(8) Å, whereas the iron···iron distance between adjacent units is 3.742(8) Å. The Fe(2)−F(1)$_{bridge}$ distance of 1.979(1) Å is much longer than the Fe(2)−F(2)$_{terminal}$ distance of 1.846(3) Å. The X-ray structural analysis also revealed four pyridinium cations located on crystallographic $3m$ positions. Although charge neutrality would require an overall charge of −4 for **1**, and thus a +4 oxidation state for the central iron atom, the occurrence of a high-valent Fe(IV) atom in the cluster is highly unlikely for the following reasons. Titrations with a standardized $FeSO_4$ solution revealed that **1** does not oxidize any Fe(II) during its decomposition in an acidic aqueous solution. No oxidizing agent was available in the synthesis of **1** from $FeF_3{\cdot}3H_2O$ and pyridine conducted under anaerobic conditions. Multiple elemental analyses clearly indicated the existence of a fifth pyridinium cation, together with one methanol and four water molecules.[11] These molecules must be severely disordered in the crystal lattice and hence undetectable in the difference electron density maps. Finally, the $(PyH)_5{\cdot}\mathbf{1}{\cdot}4H_2O{\cdot}CH_3OH$ formulation is in very good agreement with the density measurements.[12]

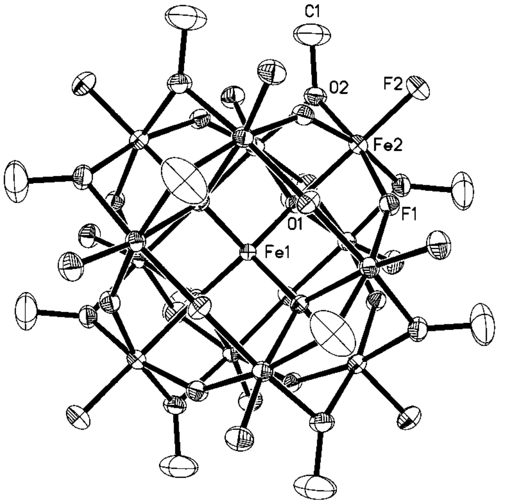

Figure 1. ORTEP diagram of $[Fe_{13}O_4F_{24}(OMe)_{12}]^{5-}$ (**1**) with thermal ellipsoids at 50% probability. Selected interatomic distances (Å) and angles (deg): Fe(1)−O(1), 1.888(6); Fe(2)−O(1), 2.093(3); Fe(2)−F(1), 1.979(1); Fe(2)−F(2), 1.846(3); Fe(2)−O(1), 1.968(2); Fe(1)−O(1)−Fe(2), 120.8(1); Fe(2)−O(1)−Fe(2)′, 96.2(2); Fe(2)−O(2)−Fe(2)′, 104.7(2).

The overall charge of −5 thus established for **1** requires an all ferric system including the central iron atom. The Mössbauer spectrum of a polycrystalline sample of $(PyH)_5{\cdot}\mathbf{1}{\cdot}4H_2O{\cdot}CH_3OH$ at 4.2 K is broad and featureless, indicative of intermediate electronic relaxation. At 77 K, however, a broad ($\Gamma \cong 0.5$ mm s^{-1}) quadrupole doublet was observed, which was fit with the parameters $\delta = 0.52$ mm s^{-1} and $\Delta E_Q = 0.54$ mm s^{-1} (Figure S1). These values are typical for high-spin iron(III) centers.[13] It was not possible to deconvolute this spectrum into the two quadrupole doublets expected for the two unique iron sites in **1**, owing to the lack of well-resolved spectral features. Preliminary magnetic susceptibility studies indicate strong exchange interactions between the iron atoms. The measured value of $\mu_{eff} = 19.3\ \mu_B$ at 300 K is less than that expected for 13 uncoupled $S = {}^5/_2$ centers having $g = 2$, the calculated spin-only value being $\mu_{eff} = 21.3\ \mu_B$. Upon lowering the temperature, μ_{eff} gradually increases to reach a maximum of 20.9 μ_B at ∼100 K, below which the value drops to

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16.7 μ_B at 4 K (Figure S2). Theoretical models to account for the magnetic coupling interactions, as well as more detailed analysis of the magnetic behavior of $(PyH)_5 \cdot \mathbf{1} \cdot 4H_2O \cdot CH_3OH$, will be reported elsewhere.[14]

It has been suggested that the low affinity of the capping M═O (Mo^{VI}, W^{VI}, V^{V}, Ti^{IV}) units in POMs for adjacent metal centers is the main reason for the formation of discrete polyanions rather than one-, two-, or three-dimensional frameworks.[4] Other metal ions such as Al^{III}, Ga^{III}, or Fe^{III} have similar ionic radii but are poor π-acceptors and do not form M═O bonds. As a result, they are not encountered in POMs. Metal ions having a closed-shell configuration, such as Al^{III} and Ga^{III}, do, however, form Keggin-type structures such as $[M_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, in which water ligands fill the terminal positions on the surface that are normally occupied by oxo groups in POMs.[15] It is noteworthy that the $Al^{III}{}_{13}$ complex adopts the structure of the ϵ- rather than the α-isomer, which occurs almost invariably in Mo^{VI} and W^{VI} Keggin structures. The shorter surface M···M separation in the ϵ-isomer may be rationalized by lower electrostatic repulsions between M^{3+} versus M^{6+} metal ions. Complex **1**, however, adopts the α-isomer with longer M···M separations. Although the different structural isomers observed for Al_{13} and Fe_{13} Keggin ions might be attributed to the larger ionic radius of Fe^{III} (0.785 Å) compared with that of Al^{III} (0.675 Å),[16] the lack of identity of bridging and terminal ligands makes it difficult to draw firm conclusions. Ligands that are isoelectronic with O^{2-}, such as F^-, OH^-, or NH^{2-}, have previously not replaced the terminal oxo ligands in POMs, presumably due to their low propensity to form multiple bonds. Complex **1**, which is an example of a polyfluorometalate, demonstrates for the first time the combination of a transition-metal ion with an *open-shell* configuration and fluoride ligands leading to the formation of a new Keggin-type molecule. The classical *closed-shell* Keggin complexes were the first representatives of a very large and important family of compounds, POMs. The discovery of the first open-shell Keggin ion **1** may lead to a new chemistry of open-shell POM analogues.

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Supporting Information Available: Details of the synthetic procedures, X-ray crystallographic tables, and physical characterization of **1** (PDF) and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The same material can be obtained in comparable yield when reactions are conducted in air.

(9) Crystal data for $(PyH)_5 \cdot \mathbf{1} \cdot 4H_2O \cdot CH_3OH$: $Fe_{13}C_{38}H_{78}F_{24}N_5O_{21}$, M_r = 2123.04, cubic, space-group F43*m* (No. 216), a = 19.4853(7) Å, V (188 K) = 7398(1) Å^3, V (295 K) = 7578(1) Å^3 , Z = 4. For 926 unique observed reflections collected at 188 K with $F^2 > 2\sigma(F^2)$, R = 0.035. UV−vis (MeOH) (λ_{max}, nm; ϵ_M/Fe cm^{-1} M^{-1}) 675; sh 47.

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(11) Anal. Calcd for $Fe_{13}C_{38}H_{78}F_{24}N_5O_{21}$: C, 21.50; H, 3.70; N, 3.30; F, 21.48; Fe, 34.20. Found: C, 21.49; H, 3.54; N, 3.30; F, 21.51; Fe, 34.34.

(12) ρ_{calcd} (295 K) = 1.86 g cm^{-3}, ρ_{exp} (295 K) = 1.86 ± 0.01 g cm^{-3}.

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