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A Baker−Figgis Isomer of Conventional Sandwich Polyoxometalates. $H_2Na_{14}[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]$, a Diiron Catalyst for Catalytic H_2O_2-Based Epoxidation

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The Wells−Dawson-derived sandwich-type polyoxometalates (POMs) are a versatile and robust group of compounds with applications in catalysis,[1−5] molecular magnetism,[6,7] and other areas. These compounds (formula $[M_4(H_2O)_2(P_2W_{15}O_{56})]^{n-}$ where M = Co^{II}, Mn^{II}, Cu^{II}, Zn^{II}, and Fe^{III}) are isostructural with a central planar tetrameric M_4 unit bound to two trivacant α-$[P_2W_{15}O_{56}]^{12-}$ units.[8−13] We report here a new type of synthesis which results in a new type of sandwich POM. This complex, $H_2Na_{14}[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]$ (Na**1**), is a structural isomer of the conventional Wells−Dawson and B-Keggin-derived sandwich POMs. It differs in the way the two α-$[P_2W_{15}O_{56}]^{12-}$ units are bound to the central unit in a manner analogous to Baker−Figgis (cap rotation) isomers (e.g., α- versus β-$[XM_{12}O_{40}]^{n-}$ and α- versus β-$[P_2W_{18}O_{62}]^{6-}$), and it contains only two central d-electron metals. This structurally novel diiron POM, unlike previously reported Fe^{III}-containing sandwiches[1,8,14] and $[FePW_{11}O_{39}]$,[15] is an effective catalyst for H_2O_2-based epoxidation, exhibiting selectivity and rates that approach the Neumann/Khenkin systems.

Reaction of α-$[P_2W_{15}O_{56}]^{12-}$ with 2.0 equiv of Fe(II) in aqueous NaCl followed by air oxidation produces Na**1**.[16] The synthesis of **1** requires Fe(II), H_2O, and Na^+. Use of Fe(III) in place of Fe(II) produces only the conventional Wells−Dawson sandwich POM, $[(Fe^{III}OH_2)_2(Fe^{III})_2(P_2W_{15}O_{56})_2]^{12-}$ (**2**). If the Fe(II)/α-$[P_2W_{15}O_{56})_2]^{12-}$ mixture is phase transferred from H_2O to CH_2Cl_2 using tetra-*n*-butylammonium chloride (TBACl) prior to air oxidation, only TBA**2** is formed. In the preparation of **1**, the new dark green air-sensitive complex, $[Fe^{II}_4(P_2W_{15}O_{56})_2]^{16-}$, forms initially (the Fe/P/W ratios are 2/2/15, and the IR spectrum is virtually identical to that of $[Zn^{II}_4(P_2W_{15}O_{56})_2]^{16-}$).[13] During the O_2 oxidation process, the iron atoms with terminal aqua ligands exchange with the sodium atoms in solution. While **2** is stable over the pH range in which Na**1** is prepared (pH 4.5−5), **2** is not observed as an intermediate in the synthesis of **1**.

The X-ray structure[17] reveals that only two d-electron metals reside in the central unit. The other positions in this central unit are occupied by two weakly bound seven-coordinate Na^+ ions.[18] Each sodium ion is ligated by three of the oxygens from each of the trivacant α-$[P_2W_{15}O_{56}]^{12-}$ units and by a weakly bound terminal water molecule. In contrast, four d-block metals (and/or Zn) reside in the central tetrameric unit in all published Wells−Dawson and B-Keggin-derived sandwich POMs.[1,8−14,19−27]

Equally noteworthy, the linkage between each α-$[P_2W_{15}O_{56}]^{12-}$ unit and the central Fe_2Na_2 unit in **1** is rotated 60° relative to that in all known sandwich POMs.[1,8−14,19−27] In all reported sandwich POMs, each of the four edge-sharing MO_6 octahedra of the central tetrameric unit shares corners with a pair of edge-shared WO_6 octahedra at the belt position of the defect

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(16) Synthesis of Na**1**: Solid α-$[P_2W_{15}O_{56}]^{12-}$ (5 g, 1.25 mmol) was added slowly with vigorous stirring to $FeCl_2{\cdot}4H_2O$ (0.49 g, 2.46 mmol) in 30 mL of 1 M NaCl. The solution was heated to 60 °C for 5−10 min, filtered hot, and allowed to cool overnight to form green crystals. The crystals, redissolved in 20 mL of H_2O, were allowed to oxidize in air for 2 days, and then 1.5 g of NaCl was added. A brown precipitate was removed on a medium frit, and the yellow filtrate deposited large yellow plates after 2 days (yield = 0.4 g; ~10%). The compound was recrystallized from 0.5 M NaCl. IR (2% in KBr pellet, 1300−400 cm^{-1}): 1088 (s), 1053 (m), 1014 (w), 939 (s), 910 (s, sh), 887 (s), 838 (s), 785 (s, sh), 752 (s), 718 (s), and 523 (m). ^{31}P NMR (9 mM solution in H_2O; D_2O in a capillary insert): −12.9 ppm, $\Delta\nu$ = 200 Hz (equivalent P atoms distal to Fe_2). Anal. Calcd for $H_{132}Fe_2Na_{16}O_{177}P_4W_{30}$: Na, 4.05; Fe, 1.23; P, 1.36; W, 60.72. Found: Na, 4.85; Fe, 1.24; P, 1.24; W, 60.97. TBA**1** was prepared by treating 1.2 g of Na**1** in 30 mL of H_2O with 2.0 g of TBACl followed by extraction with 150 mL of CH_2Cl_2. Addition of Et_2O to the green lower layer produced 1.0 g (~80% yield). IR (2% in KBr pellet, 1300−400 cm^{-1}): 1152 (w), 1089 (s), 1062 (m), 1015 (w), 977 (w, sh), 945 (s), 911 (s), 888 (s), 840 (s), 781 (s), 764 (s, sh), 713 (s), 600 (w), and 525 (m).

(17) Crystal data for $H_2Na_{14}[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]{\cdot}78H_2O$ (Na**1**): Light yellow efflorescent crystal (0.2 × 0.2 × 0.3 mm), triclinic space group $P\bar{1}$ (No. 2), with $a = 12.8027(3)$ Å, $b = 13.9668(3)$ Å, $c = 23.5073(3)$ Å, $\alpha = 79.296(1)°$, $\beta = 78.488(1)°$, $\gamma = 80.365(1)°$, $V = 4009.9(2)$ Å^3, and $Z = 1$. The data were collected on a Bruker SMART system using Mo Kα radiation (λ = 0.71073 Å) and corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 techniques using SHELXTL v5.03 with anisotropic temperature factors for all W, Fe, Na, and P atoms and isotropic temperature factors for the remaining atoms. At final convergence, R_1 = 7.98% and GOF = 1.036 based on 7792 reflections with $F_o > 4\sigma(F_o)$.

(18) Such nonoctahedral coordinating geometries for Na^+ ions in hydrated solids are not uncommon. One example in a POM: Alizadeh, M. H.; Harmalker, S. P.; Jeannin, Y.; Martin-Frère, J.; Pope, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 2662−2669.

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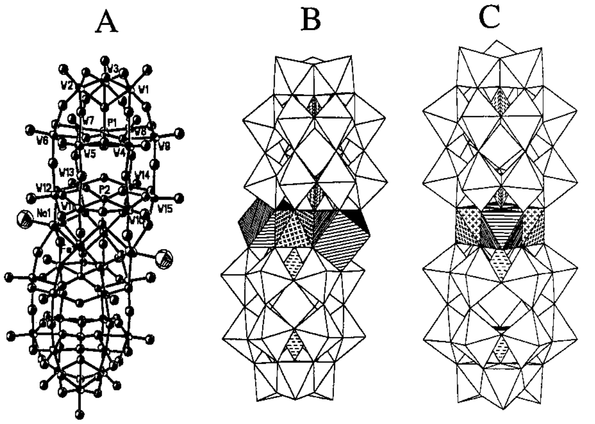


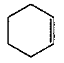
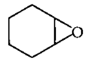
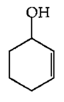
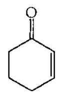
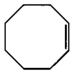
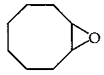
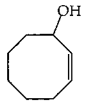
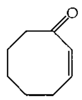
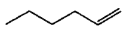
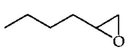
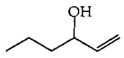
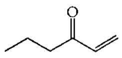
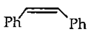
Figure 1. Atom (A) and polyhedral (B) illustrations of $[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$ (**1**) and polyhedral illustration (C) of the conventional trivacant sandwich POM, $[Fe^{III}_2(FeOH_2)_2(P_2W_{15}O_{56})_2]^{12-}$ (**2**). The WO_6, NaO_7, PO_4, and FeO_6 coordination polyhedra in B are designated by clear (unshaded), lined, broken-lined, and crosshatched (small crosses) shading, respectively. Shading in C is the same except the two types of central Fe atoms are distinguished (the end FeO_5OH_2 units have lines; the central FeO_6 units have crosses). The Na−O bond lengths in **1** range from 2.17(3) to 2.89(3) Å. The Na1−OH_2 bond length is 2.41(6) Å, within the range of Na−OH_2 distances in the H_2O-coordinated Na counterions in Na**1** (2.29−2.50(3) Å). The maximum Fe···Fe distance in the Fe_4 unit in **2** (C) is 5.43(1) Å; the Na···Na distance in **1** is 6.48(3) Å.

α-$[P_2W_{15}O_{56}]^{12-}$. In **1**, by contrast, each of the four edge-sharing polyhedra in the central unit (two FeO_6 octahedra and two distorted NaO_7 heptahedra) shares corners with a pair of corner-shared WO_6 octahedra at the belt position of the defect POM. Figure 1 illustrates **1** (in two notations) and **2**. All Wells−Dawson sandwich POMs have the configuration (junction connectivity) $\alpha\beta\beta\alpha$ for the first cap−belt junction, the first belt−M_4 junction, the second belt−M_4 junction, and the second belt−cap junction, respectively; Na**1** has the configuration αααα. The +3 oxidation state for the two iron atoms in **1** is unambiguous based on bond-valence sum calculations[28] (calcd valence: 2.9(2) per Fe), charge balance, and elemental analysis (ratio of Fe/P/W is 1/2/15).

The spectroscopic and chemical properties indicate that the structure of **1** in aqueous solution is very similar to that in the solid state (Figure 1).[29] First, the ^{31}P NMR shows one singlet for the symmetry-equivalent P atoms distal to the Fe_2 center, while the paramagnetism of the Fe_2 unit renders the signal for the P atoms proximal to the Fe_2 center too broad to observe. Second, treatment of **1** with 2 equiv of $Fe^{3+}(aq)$ rapidly forms the conventional sandwich POM $[Fe_4(H_2O)_2(P_2W_{15}O_{56})]^{12-}$.[8,31]

TBA**1**^{16} is an effective catalyst precursor for H_2O_2-based epoxidation in homogeneous organic media. The selectivities and rates of epoxidation (facile at ambient temperature) approach those in the extremely effective Neumann/Khenkin systems.[2−5] Representative product distributions and reaction conditions are given in Table 1. The selectivities for epoxide in all cases are very high. Within experimental error, the terminal alkene, admittedly at low turnovers, produces no detectable allylic products. These selectivities rule out homolytic mechanisms including Fe-assisted radical-chain breakdown of H_2O_2 and Fenton-type chemistry. Also, in contrast to other Fe-containing POMs except γ-$[Si(FeOH_2)_2W_{10}O_{38}]^{6-}$,[32,33] the organic product yields based on H_2O_2 are high as indicated in Table 1. Analysis of a representative reaction, cyclooctene oxidation, shows an induction period, which is shortened by prereaction incubation with H_2O_2. Finally, like the Neumann sandwich POM catalysts for H_2O_2 oxidation, **1** appears to be stable to H_2O_2 under the reaction conditions: **1** can be reisolated intact after 48 h of incubation with ca. 0.25 M aqueous H_2O_2 based on analysis of the product POM by both IR and ^{31}P NMR.

Table 1. Product Distributions for Ambient Temperature Oxidation of Alkenes by H_2O_2 Catalyzed by TBA1[a]

Substrate	Products Selectivity (Yields Based on H_2O_2) [Turnovers][b]		
			
	99% (99%) [20][b]	0[c]	0[c]
			
	98% (97%) [219][b]	0[c]	2% (2%) [4.1][b]
			
	99% (80%) [5.3][b]	0[c]	0[c]
			PhCHO
	90% (86%) [77][b]	10% (10%) [9][b]	0[c]

[a] Conditions: 25 μL of 30% $H_2O_2(aq)$ was injected into 1 mL of CH_3CN 4 mM in TBA**1**^{16} and 0.9 M in alkene under Ar to initiate the reaction. Organic products as a function of time were quantified by GC and GC/MS. [b] Selectivity = moles of indicated product/moles of all organic products derived from the substrate × 100 (yields based on epoxide = moles of epoxide/moles of H_2O_2 consumed × 100) [turnovers = moles of indicated product/moles of catalyst after 30 h reaction time]. [c] No products within the detection limit (<0.2%).

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Supporting Information Available: Complete listing of structure determination summary, crystal and structure refinement data, atomic coordinates and isotropic displacement coefficients, bond lengths and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) The infrared spectrum of **1** shows the W−O stretching bands characteristic of polytungstophosphates. The υ_3 vibrational mode of the central PO_4 unit is split, indicating a local symmetry lower than T_d,[30] a feature seen in all sandwich POMs including **2**. The UV−visible spectrum of **1** in solution is not structurally informative (the intense oxygen-to-metal charge-transfer bands exhibited by all POMs obscure Fe-centered d−d and possibly intervalence-charge-transfer bands).

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