A Fe^{III}/Oxo Cubane Contained in an Octanuclear Complex of *T* Symmetry That Is Stable Over Five Oxidation States[**]

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Thermodynamic stability is a desired property of materials prepared for commercial applications, but, at the same time, chemical versatility is required for the manifestation of interesting properties such as catalytic activity. A reconciliation of these opposite characteristics is typically achieved by the coating of large surfaces or particles with inert substances on a macroscopic and microscopic scale. Nature applies similar techniques at the macromolecular level when metal active centers are protected inside the organic part of metalloproteins. We propose that a molecular-level analogue of this principle, placing redox-active metal clusters in a chemically inert shell, will result in ideal building blocks for the construction of durable supercluster assemblies with electron transfer properties.

Pyrazolates are convenient bridging ligands for the synthesis of polynuclear complexes in which, owing to the aromatic character of the ligand, the chemical activity is restricted to the metal centers.[1] Here we present the characterization and initial studies of $[Fe_8(\mu^4\text{-O})_4(\mu\text{-pz})_{12}Cl_4]$ (**1**: pz = pyrazolate anion, $C_3H_3N_2^-$), a Fe^{III} complex of *T* symmetry that is assembled in a one-pot reaction from simple starting materials and is stable over five oxidation states. Complex **1** contains a redox-active Fe_4O_4 core protected inside a Fe–pyrazolate coat.

The X-ray crystallographic characterization of **1** showed the whole complex and one-half of an interstitial hexane molecule per asymmetric unit. The core of this octanuclear complex consists of a Fe_4O_4 cubane with distorted octahedral *fac*-O_3N_3-Fe units. Four trigonal-bipyramidal ON_3Cl-Fe units are coordinated around the core. Each of the four outer Fe atoms is connected to three of the inner Fe atoms through μ-pz bridges, and each inner Fe atom is likewise connected to three outer Fe atoms (Figure 1). To connect the equatorial positions of each outer Fe atom to the *fac* sites of three inner Fe atoms, the twelve pyrazolate bridges adopt a propellerlike rotation in the same direction around each of the four C_3 axes of **1**.

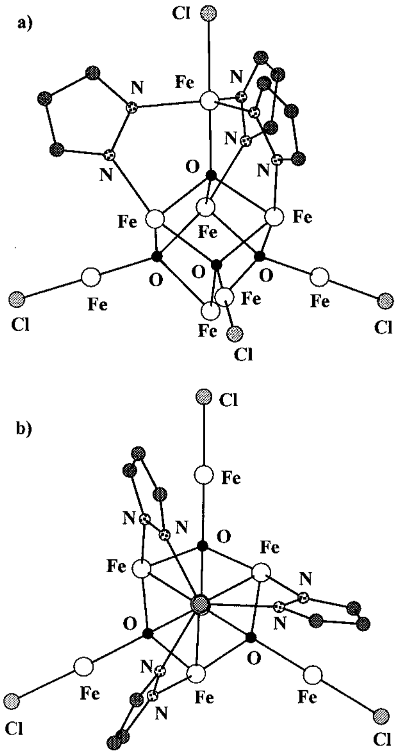

Figure 1. Crystal structure of **1**. Shown is the $Fe_8O_4Cl_4$ moiety plus three of the twelve pyrazolato groups. Selected bond lengths [Å] and angles [°]: for the Fe_4O_4 cube: Fe–O 2.022(4) – 2.056(4), Fe···Fe 3.059(1) – 3.088(1), Fe–N 2.048(5) – 2.070(5); Fe-O-Fe 97.1(2) – 98.7(2), O-Fe-O 81.1(2) – 82.4(1); for the outer Fe atoms: Fe–O 1.944(4) – 1.963(4), Fe–Cl 2.267(2) – 2.276(2), Fe–N 2.007(5) – 2.025(5); N-Fe-N 114.2(2) – 124.6(2), Fe-N-N 119.1(4) – 121.6(4). a) Side view, b) view down a C_3 axis.

The eight Fe^{III} atoms are located on C_3 axes at positions defining two concentric tetrahedra with average Fe···Fe edges of 3.074(2) and 5.853(4) Å. The μ^4-O atoms, which connect the network of eight Fe atoms, are expected to be efficient mediators of antiferromagnetic coupling and should account for the relatively low effective magnetic moment of 6.52 μ_B of **1**.[2] Within each $(\mu^4\text{-O})Fe_4$ group the O atoms are displaced from the centers towards the bases of the Fe_4 trigonal pyramids. Similar, but asymmetric, $(\mu^4\text{-O})Fe_4$ units have been found in the structures of a hexanuclear Fe^{III}–oxo/alkoxo aggregate and a tetranuclear Fe^{II}–formamidinato complex.[3, 4] The Fe_8O_4 part of **1** resembles the core of the $[Fe_{16}MO_{10}(OH)_{10}(OCOPh)_{20}]$ complexes (M = Mn, Co), which contain $(\mu^4\text{-O})_3(OH)Fe_3M$ cubanes.[5] A mixed-valent $[Co_8O_4(O_2CPh)_{12}(solvent)_4]$ complex as well as a heterometallic $[V_4Zn_4O_4(O_2CPh)_{12}(thf)_4]$ complex bear striking structural resemblance to **1**; their metal and oxygen atoms are arranged as in **1**, but they have carboxylate in place of pyrazolate groups and solvent molecules in place of chlorides.[6, 7] The symmetry of the former is lowered by the coordination of two different solvent molecules to the outer Co centers, while the coincidence of the μ-O_2CPh groups of the latter with the planes of symmetry of the M_8O_4 tetrahedron classifies this complex in the T_d group.

While the $Fe_8O_4Cl_4$ skeleton of **1** is in a tetrahedral arrangement, the propellerlike rotation of the μ-pz groups eliminates the mirror planes of T_d symmetry, reducing the

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overall symmetry of **1** to that of the *T* point group. A consequence of this symmetry is that **1** occurs in two enantiomeric forms, that cocrystallize here as a racemic mixture, the interconversion of which requires the rearrangement of all twelve pyrazolato bridges by simultaneous rotation about the four C_3 axes of **1**. The arrangement of twelve pyrazole rings in the outer part of **1** gives this molecule an approximate appearance of a sphere with a diameter of about 12 Å and provides a hydrophobic surface that is responsible for the high solubility of **1** in nonpolar solvents (Figure 2). A related (μ^4-O)M_4 core supported by pyrazolato bridges has been described in the structure of [$Co_4O(3,5\text{-}Me_2pz)_6$].[8]

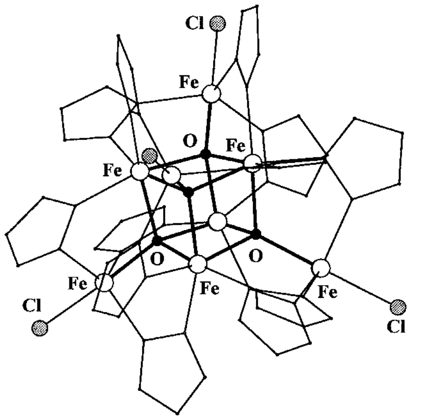

Figure 2. Representation of the structure of **1** in which the Fe–O bonds are emphasized. The Fe, O, and Cl atoms are shown as spheres of arbitrary radii, and the pyrazolate rings as a wireframe. Hydrogen atoms are not shown.

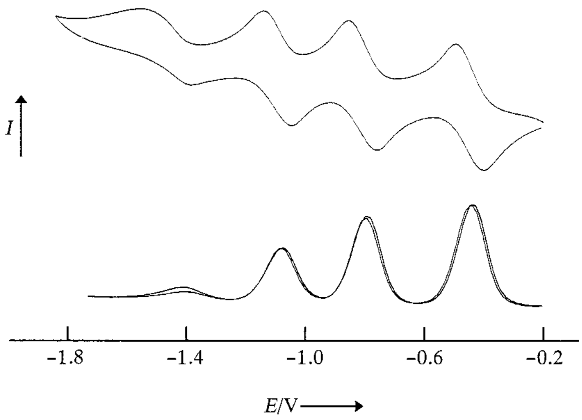

Figure 3. Voltammetry of **1** (in 0.1 M Bu_4NPF_6/PrCN, scan rate 100 mV s^{-1}, $T = 223$ K, Pt-disk working electrode, measured versus Fc/Fc$^+$). Top: Cyclic voltammogram, bottom: cyclic alternating current scan.

The Fe_4O_4 core of **1** is the first example of an all-Fe^{III} cubane. Consistent with the +3 valence, the Fe–O bonds of **1** (av 2.040(4) Å) are shorter than those of lower valent analogues. Some Fe/O cubanes containing Fe^{II} or mixed Fe$^{II/III}$ cores are known; they contain four- and six-coordinate Fe centers in FeO_4, FeO_4N_2, or FeO_6 environments and $(Fe_4)^{8+}$, $(Fe_4)^{9+}$, or $(Fe_4)^{10+}$ oxidation states.[9–11] The existence of three examples of Fe$_4^{II}$, one each of Fe$_3^{II}$Fe^{III} and Fe$_2^{II}$Fe$_2^{III}$ and now the first example of a Fe$_4^{III}$ cubane, suggests that the remaining permutation, Fe^{II}Fe$_3^{III}$, should be stable with the appropriate set of peripheral ligands. Indeed, all of the above species can be readily generated by stepwise electrochemical reduction of **1**.

The electrochemical study of **1** in the range of −2.60 to +1.60 V shows three reversible reduction processes at −0.43, −0.78, and −1.07 V (versus Fc/Fc$^+$; Fc = ferrocene). A fourth reduction at −1.38 V is irreversible at 285 K, but becomes quasi-reversible in chilled solution (Figure 3). As no oxidation is observed, it is evident that **1** retains its structural integrity, in its neutral or some anionic form, over the 4.20-V window studied here. The complete electrochemical reversibility of the first three reductions, at ambient or low temperature, indicates that no significant structural rearrangement accompanies those electron transfer processes. The unusual stability of **1** over five oxidation states can be accounted for by the encapsulation of the Fe_4O_4 core inside the outer shell of four interlocked Fe(μ-pz)$_3$Cl groups, forcing its structural integrity in a fashion similar to the wrapping of apoferritin around the Fe/O cluster of ferritin.[12] In contrast to the abundant Fe_4S_4 systems,[13] the corresponding Fe_4O_4 cubane units have not been encountered in nature to date. However, the spontaneous assembly from mononuclear precursors, as well as the stability and rich electrochemistry of **1**, anticipate the discovery of an electron transfer protein based on a Fe_4O_4 active center.

The four tetrahedrally arranged chlorine atoms at the outer shell of **1** are readily substituted by anionic or neutral ligands in simple metathesis reactions. This provides a convenient means by which to manipulate the size and solubility of the octanuclear cluster, as well as to connect octanuclear units through bridging ligands into covalent supramolecular assemblies.[14] Preliminary studies show that such derivatives of **1** retain the redox characteristics of their parent compound with minimal variations of the $E_{1/2}$ values, pointing to the Fe_4O_4 core as the site of the redox activity.

Experimental Section

1: To anhydrous $FeCl_3$ (0.180 g, 1.11 mmol) in CH_2Cl_2 (15 mL) is added 3,5-Me_2pzH (0.375 g, 3.90 mmol) under N_2 followed by Kpz (0.355 g, 3.35 mmol). The reaction mixture is exposed to air for several days, and dark red air-stable **1** is precipitated by addition of hexane after reduction of the solvent volume to about 5 mL (yield >30%). M.p. 565 K (determined by differential thermal analysis); elemental analysis found (calcd for **1** · $0.5\,C_6H_{14}$): C 31.14 (31.19), H 2.81 (2.87), N 22.59 (22.39), Cl 9.62 (9.45), Fe 29.43 (29.76); UV/Vis/NIR (CH_2Cl_2): $\lambda_{max} = 359$ nm; IR (KBr disk): $\tilde{\nu} =$ 1490 (m), 1417 (m), 1362 (s), 1268 (s), 1169 (s), 1145 (m), 1078 (w), 1045 (vs), 963 (w), 915 (w), 894 (w), 763 (s), 615 (m), 555 (m), 476 cm^{-1} (s); IR (polyethylene disk): $\tilde{\nu} = 349$ (s), 331 (s), 308 cm^{-1} (s). The strong peak at 476 cm^{-1} is tentatively assigned to a Fe–O stretch. Magnetic moment: $\mu_{eff} = 6.52\,\mu_B$, calculated from a Faraday balance susceptibility measurement at 290 K; FAB-MS (*m/z*): 1457.6 [*M*]$^+$, 1420.6 [*M* − Cl]$^+$, 1388.5 [*M* − pz]$^+$, 1353.6 [*M* − (Cl,pz)]$^+$, 1321.5 [*M* − 2 pz]$^+$, 1286.5 [*M* − (2 pz,Cl)]$^+$. Red, parallelepiped crystals appropriate for X-ray diffraction study grow from a solution of **1** in CH_2Cl_2/hexane.

X-ray crystal structure analysis of **1**: Rigaku-AFC6S diffractometer, $\lambda(Mo_{K\alpha}) = 0.71069$ Å; space group $P\bar{1}$ (no. 2), $a = 12.367(5)$, $b = 12.508(5)$, $c = 20.794(4)$ Å, $\alpha = 77.45(3)$, $\beta = 80.80(3)$, $\gamma = 70.27(3)^\circ$, $V = 2942(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.694$ g cm^{-3}, $\mu = 21.53$ cm^{-1}; of 8873 unique reflections, 5239 were observed ($I > 3\sigma(I)$), $\omega - 2\theta$ scans, $6 < 2\theta < 50^\circ$, $T = 295$ K. Structure solution: data corrected for Lorentz and polarization effects; an empirical absorption correction based on azimuthal scans was applied. The structure was solved by direct methods (SHELXS-86) followed by Fourier cycles, $R = 0.036$, $R_w = 0.027$ for 712 variable parameters, GOF = 1.73. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101766. 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).

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Organic Nitrates of Isoprene as Atmospheric Trace Compounds**

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Isoprene (2-methyl-1,3-butadiene) is a terpene building block which is emitted preferentially by oaks, but also by other plants, as well as algae.[1] As such, it was examined early on with respect to its broad reaction potential as a butadiene derivative in connection with natural smog formation in the atmosphere.[2] It is by far the single compound biologically emitted in the largest amounts. On a global average, the annual emission of isoprene is an estimated 450 Tg (1 Tg = 1×10^6 tons).[3] After the addition of an OH radical to an isoprene double bond, follow-up reactions with oxygen in the atmosphere lead to the formation of methacrolein ($H_2C{=}C(CH_3)CHO$) and methyl vinyl ketone ($H_2C{=}CHCOCH_3$).[4] Both are also formed in the reaction of isoprene with ozone[5] and were detected in the ambient air; their concentration in the atmosphere shows strong seasonal fluctuations with a maximum in the summer.[4, 6]

According to smog chamber experiments, further products of the reaction of isoprene in the $OH/O_2/NO$ system are 3-methylfuran, hydroxymethyl vinyl ketone, C5-carbonyl compounds, and unspecified organic nitrates.[7] 3-Methylfuran could be detected in forest air.[8] The identification of a peroxyacetyl nitrate analogue of isoprene was the entry of the chemistry of isoprene into the group of "odd nitrogen compounds" (NO_y).[9] Smog chamber experiments on the reaction of isoprene with NO_3 radicals in the dark, simulating night chemistry, led to the known products methacrolein, methyl vinyl ketone, and C5-hydroxycarbonyl compounds as well as C5-aldonitrates such as $O_2NOCH_2C(CH_3){=}CHCHO$ (**13**, **14**), C5-hydroxynitrates such as $O_2NOCH_2C(CH_3){=}CHCH_2OH$ (**5**, **6**), and C5-hydroperoxynitrates such as $O_2NOCH_2C(CH_3){=}CHCH_2OOH$, as shown by atmospheric pressure ionization tandem mass spectrometry (API-MS/MS).[10, 11] This range of products indicates the possibilities of the night chemistry of isoprene in NO_2- and ozone-rich air, in which NO_3 radicals are formed. Such an atmospheric situation usually builds up from traffic emissions when there is a high amount of sunshine during the day (areas of high pressure in temperate zones such as Europe; normal weather conditions in California).

If one considers the reactions that a compound can in principle undergo in the atmosphere, and if the corresponding

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