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A Cube in a Tetrahedron: Microwave-Assisted Synthesis of an Octametallic Fe^{III} Cluster

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The microwave-assisted reaction of $Fe(O_2CMe)_2$ with salicylaldoxime ($saoH_2$) in pyridine produces an octametallic cluster in crystalline form in 2 min. The core describes a cube encapsulated in a tetrahedron, while sao^{2-} exhibits a novel coordination mode.

Coordination chemists attempting to make large polymetallic clusters of paramagnetic transition metals rarely perform syntheses in conditions other than ambient temperature and pressure. The reason is simple: it is not necessary because the overwhelming majority of polynuclear complexes have been made via simple benchtop methods.[1] Only when making complexes of inert ions such as Cr^{3+} have alternative techniques been pursued.[2] Indeed, the use of solvothermal synthesis has only recently become “standard practice” for metal clusters of, for example, Fe, Ni, and Mn.[3] There is no reason why synthetic inorganic chemists should confine their experiments to a limited temperature and pressure regime, whether that be for the purposes of making completely new complexes or known species in higher yields and in faster reaction times. Given our recent success in the solvothermal synthesis of large metal clusters,[4] we decided to examine whether microwave heating could be used for a similar purpose. Microwaves are now used routinely in many areas of chemistry ranging from analytical chemistry and liquid-phase organic syntheses to solid-state reactions,[5,6] but surprisingly reactions involving liquid-phase inorganic syntheses have received no attention. In our experience, microwave heating not only provides an alternative synthetic tool but also may help to improve the yield and reproducibility of large polymetallic complexes. Moreover, it may also lead to novel products, by permitting access to alternative kinetic pathways. This is especially possible when it effects exceptionally rapid heating of the reaction components.[5] Irrespective of the nature of the product, the reduction of the reaction times through microwave heating permits a larger number of reaction conditions to be explored more quickly, making exploratory synthetic programs more efficient. Here we report the microwave-assisted synthesis of an $\{Fe^{III}_8\}$ cluster that cannot be synthesized under ambient reaction conditions.

The ligand used for the preparation of the $\{Fe^{III}_8\}$ cluster is salicylaldoxime (IUPAC name: 2-hydroxybenzaldehyde oxime, $saoH_2$). This ligand belongs to the family of phenolic oximes.[7] While their classical mode of coordination via deprotonation of the phenol to bind to a metal center as a monoanionic bidentate ligand is frequently observed, a literature survey reveals a plethora of less common coordination modes that can be attained via deprotonation of both the phenolic and oximic groups, resulting in the formation of tridentate ligands and polynuclear metal complexes.[7−9]

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The formation of such polynuclear complexes (clusters) at lightly oxidized metal surfaces also accounts for the efficacy of saoH$_2$ derivatives as corrosion inhibitors.[10] Another point of interest in the coordination chemistry of saoH$_2$ is its activation by 3d metal centers toward further reactions,[11] which seems to be an emergent area of synthetic chemistry.[12]

Fe(O$_2$CMe)$_2$ (229 mg, 1.32 mmol), saoH$_2$ (179 mg, 1.32 mmol), and pyridine (6 mL) were placed in a sealed glass tube, which was then inserted into the cavity of a microwave reactor. The reaction mixture was maintained at $T = 120$ °C, power = 200 W, and pressure = 130 psi for a total of 2 min. After cooling (ca. 1 min), the solution was filtered and allowed to stand. Large red-brown needlelike crystals of [Fe$^{III}_8$O$_4$(sao)$_8$(py)$_4$]·4py (**1**·4py) started to form immediately.

The complex crystallizes in the tetragonal space group *I*41/*a*.[13] The core of the complex (Figure 1) contains a central [Fe$^{III}_4$O$_4$]$^{4+}$ cubane, with each of the four distorted tetrahedral μ_4-O^{2-} ions further bridged to a peripheral Fe^{III} ion (Fe2 and symmetry equivalent). The peripheral metal ions themselves form a tetrahedron, encapsulating the cube such that each face of the tetrahedron is capped (Figure 2). The eight sao^{2-} ligands bridge in two ways: four in a η^2:η^1:η^1:μ_3 fashion along one complete edge of the tetrahedron, with the phenolate O atom bridging one Fe ion of the cube and one Fe ion of the tetrahedron, and four in a η^1:η^1:η^1:μ fashion along half an edge, between an Fe ion in the tetrahedron and a face-capping Fe ion of the central cube. The observed η^2:η^1:η^1:μ_3 coordination mode is unique among the structurally characterized metal complexes containing the sao^{2-} ligand.[7,8] A μ_3 behavior has been observed in sao^{2-} complexes, but with the oximate O providing the bridge between metal ions. The coordination sphere of each of the four Fe ions in the outer tetrahedron is completed by a terminal pyridine molecule. Each Fe ion is in a distorted octahedral geometry, with the Fe ions of the cubane [cis, 73.95(7)−113.22(7)°; trans, 147.88(7)−163.93(7)°] more distorted than those in the outer tetrahedron [cis, 77.56(7)−96.47(7)°; trans, 170.09(7)−174.51(7)°]. Within the [Fe$_4$O$_4$]$^{4+}$ cubane, there are two small (93.55° and 95.68°) and one large Fe−O−Fe [105.66(7)°] angles, suggesting a rather "twisted" metal cubane.

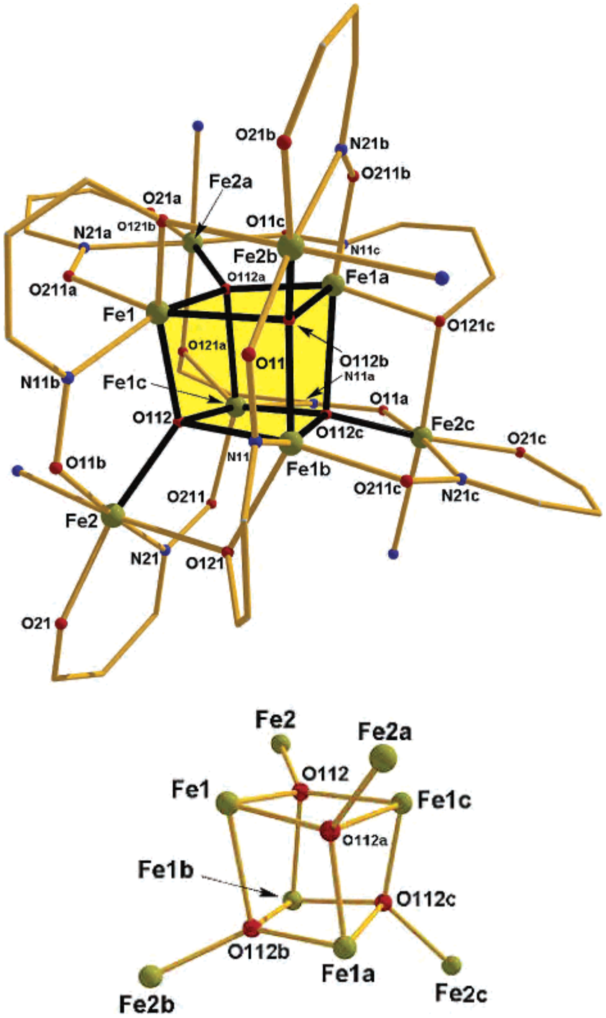

Figure 1. Molecular structure of complex **1** (top) and its metal−oxygen core (bottom). The C atoms of the pyridine rings and most C atoms of the phenyl groups of the oximato ligands have been omitted for clarity.

The [Fe$_8$O$_4$]$^{4+}$ core is uncommon, observed only in one other complex: [Fe$_8$O$_4$(pz)$_{12}$Cl$_4$] (pz = pyrazolate anion, C$_3$H$_3$N$_2^-$) reported in 1999.[14] Similar [M$_8$O$_4$]$^{n+}$ cores have been seen in three other complexes: [VZnO(O$_2$CPh)$_3$(THF)]$_4$, in which the four V^{III} ions form the central cubane and the four Zn^{II} ions the outer tetrahedron;[15] [Co$^{III}_4$Co$^{II}_4$O$_4$(O$_2$CPh)$_{12}$(MeCN)$_3$(H$_2$O)], where the four Co^{III} ions form the cubane;[16] and [Cr$^{III}_8$O$_4$(O$_2$CPh)$_{16}$].[17] The central Fe$^{III}_4$O$_4$ cubane is an extremely rare unit at this oxidation level. Some Fe/O cubanes with Fe^{II} or mixed Fe$^{II/III}$ cores are known, but there are only two Fe$^{III}_4$O$_4$ cubane units (both inside larger clusters) in the literature.[14,18] Complex **1**·4py joins a rather small family of octanuclear Fe^{III} clusters[19] with

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(13) Complex **1** analyzed (C, H, N) as **1**·3py, expected (found): C, 50.94 (51.31); H, 3.52 (3.36); N, 9.79 (9.86). Crystals were kept in contact with a mother liquor to avoid solvent loss and were crystallographically identified as **1**·4py. Diffraction data were collected with Mo Kα X radiation ($\lambda = 0.710\,73$ Å) on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. Crystal data: C$_{96}$H$_{80}$Fe$_8$N$_{16}$O$_{20}$, $M = 2224.56$, red-brown needles, tetragonal, *I*41/*a*, $a = 28.9096(3)$ Å, $b = 28.9096(3)$ Å, $c = 11.1722(3)$ Å, $V = 9337.3(3)$ Å^3, 56 039 reflections collected, of which 5891 were independent ($R_{int} = 0.048$), 316 parameters and 0 restraints, R1 = 0.0384 [based on $F > 4\sigma(F)$], wR2 = 0.0867 (based on F^2 and all data).

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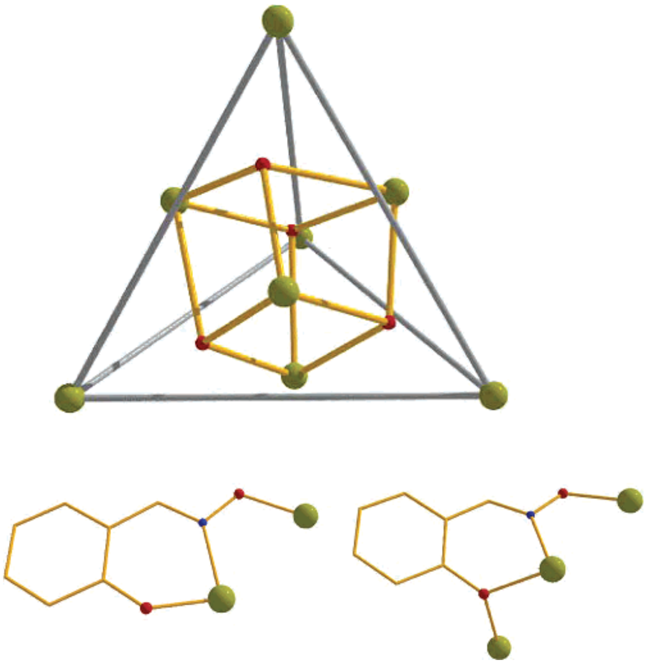

Figure 2. "Metallic skeleton" of complex **1** (top) showing the $\{Fe_4O_4\}$ cubane within the $\{Fe_4\}$ tetrahedron. The bridging modes of the sao^{2-} ligands (bottom).

O and/or N ligation and a handful of structurally characterized $saoH^-$ and/or $sao^{2-}Fe^{III}$ complexes.[8,10−12,20]

Complex **1** cannot be made under ambient reaction conditions or by refluxing of a pyridine solution of $Fe(O_2CMe)_2$ and $saoH_2$. Employing different $Fe^{II/III}$ salts, different solvents or combinations of solvents, and different reaction times also does not produce complex **1**. A microcrystalline powder with an IR spectrum similar to that of complex **1** can be isolated under solvothermal reaction conditions (sealed Teflon container; 120 °C) but requires a minimum heating/cooling period of 24 h and forms in yields of less than ~10%; this equates to an approximately 7-fold decrease in comparison to the microwave reaction. This perhaps suggests that the rapid heating and cooling employed by the microwave plays an important synthetic role.

Variable-temperature dc magnetic susceptibility data were collected on **1** in the temperature range 300−2.0 K in an applied field of 0.1 T. The room-temperature $\chi_M T$ value of approximately 7.3 $cm^3\ K\ mol^{-1}$ is lower than the spin-only ($g = 2$) value expected for a $\{Fe^{III}{}_8\}$ unit consisting of eight noninteracting Fe^{III} atoms (35 $cm^3\ K\ mol^{-1}$). As the temperature is decreased, $\chi_M T$ continually drops to a value of 0.01 $cm^3\ K\ mol^{-1}$ at 2 K. This behavior is indicative of dominant antiferromagnetic interactions, with the $\chi_M T$ value at 2 K suggesting an $S = 0$ spin ground state. Such behavior is expected and probably results from the antiferromagnetic exchange between the peripheral Fe^{III} ions in the tetrahedron and the central Fe^{III} ions in the cubane mediated by the μ_4-bridging O^{2-} ions that display Fe−O−Fe angles in the range 102.9(1)−124.8(1)°.

In conclusion, we have demonstrated that the use of microwave heating is a new appealing approach for the synthesis of large polymetallic transition-metal cluster compounds. In this instance, it has not only led to the isolation of a beautiful and unusual $\{Fe_8\}$ cluster, impossible to produce under ambient reaction conditions, and to a novel coordination mode of the ligand involved but has also greatly improved the reaction rate and enhanced the yield in comparison to solvothermal methods. The use of microwave heating thus has enormous potential for inorganic cluster chemists, and we hope this paper acts as a stimulus for others in the field. A secondary, but also important, chemical message of this preliminary work is that the coordinative flexibility and versatility of the doubly deprotonated salicylaldoximate ligand make it useful for a variety of synthetic objectives in the field of cluster chemistry.

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Supporting Information Available: CIF file, magnetic data, and bond valence sum calculations. The material is available free of charge via the Internet at http://pubs.acs.org.

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