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2-Pyrrolyloximes in High-Nuclearity Transition-Metal Cluster Chemistry: Fe_{10} and Fe_{12}

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Supporting Information

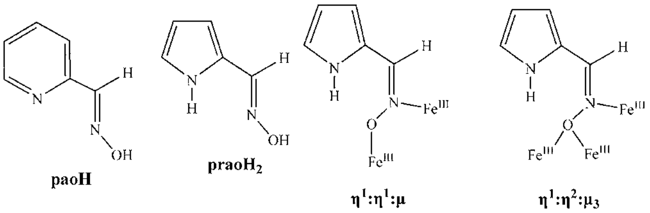
ABSTRACT: The employment of 2-pyrrolyloximes in high-nuclearity transition-metal cluster chemistry has provided access to unprecedented decanuclear and dodecanuclear Fe^{III} cagelike clusters bearing the anion of pyrrole-2-carboxaldehyde oxime ($praoH_2$), the simplest member of this new family of ligands; the identity of the products depends on the nature of the counteranion present in the starting materials.

There are numerous reasons for the continuing interest in the synthesis and study of high-nuclearity 3d molecular metal clusters at moderate-to-high oxidation states. Among these is the search for various nuclearity oxide-bridged metal clusters to model M_x sites in biomolecules, including elucidation of the growth of the core of the ferritin protein and synthesis of the $Mn^{n+}{}_4Ca$ ($n > 3$) site of water oxidation within the photosynthetic apparatus of green plants and cyanobacteria.[1] Moreover, high-nuclearity 3d metal clusters, especially the ones that include Mn^{III}, Fe^{III}, Co^{II}, and Ni^{II}, often display fascinating structures and interesting and occasionally attractive magnetic properties, including high-spin (S) ground-state values and single-molecule-magnetic (SMM) behavior.[2]

A major challenge in the field of polynuclear metal complexes, which undoubtedly supports and enhances the interest of synthetic inorganic chemists, molecular chemists, and magnetochemists, remains the development of new synthetic methods to such molecules through the employment of new chelating/bridging organic ligands. An attractive, and simultaneously effective, approach is to use chelates containing alkoxide[3] or oximate[4] functionalities because these are excellent bridging groups that can foster the formation of polynuclear products with beautiful structures and fascinating magnetic properties.

Our group[5] and others[4,6] have had a long-standing interest in the reactivity of 2-pyridyloxime ligands, (py)C(R)NOH (R = H, Me, Ph, py, CN, NH_2), for the synthesis of structurally novel and magnetically interesting 3d metal clusters. The initial use of the simplest tridentate (N,N,O) 2-pyridyloxime, namely, 2-pyridinealdoxime [(py)C(H)NOH, paoH; Chart 1], in transition-metal cluster chemistry[7] was followed by the logical substitution of the nondonor R (=H) group by other similar groups, albeit more bulky, such as Me and Ph. The resulting anions, $(py)C(Me)NO^-$ and $(py)C(Ph)NO^-$, were employed for isolation of the first triangular Mn^{III} SMMs with $S = 6$ ground-state spin values.[8] In more recent years, several research groups elegantly explored the coordination chemistry of analogous organic molecules in which the nondonor R group was replaced by a donor group, such as py,[9] CN,[10] and NH_2.[11] The resulting tetradentate (N,N,N,O) 2-pyridyloximate ligands have led to molecular species with structural motifs and properties distinctly different from those obtained with 2-pyridyloximes containing nondonor groups.

Chart 1. Structural Formulas and Abbreviations of 2-Pyridinealdoxime and Pyrrole-2-carboxaldehyde Oxime and the Crystallographically Established Coordination Modes of Its Monoanion ($praoH^-$) in Complexes 1 and 2



In all cases, however, the 2-pyridyl moiety has remained unaltered. From one side, that was absolutely reasonable given that the 2-pyridyl functionality would provide what was necessary for the construction of a five-membered chelate ring pyridyl N-donor atom. We have now decided to replace the 2-pyridyl group with the 2-pyrrolyl one and explore the coordination chemistry of the resulting 2-pyrrolyloximes toward isolation of new polynuclear 3d, 4f, and 3d/4f metal complexes with unusual and novel physicochemical properties. Such ligands have shown limited use in coordination chemistry,[12] and we anticipated that the presence of the >N−H functionality would alter the coordination behavior of these ligands (and, hence, the identity of the resultant metal complexes) in comparison with that of the (py)C(R)NOH (R = H, Me, Ph) ligands. Important characteristics that differentiate the pyrrole group are its

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potential for deprotonation, different electronic properties, and hydrogen-bonding effects.

In the present work, we report our first results from the use of the simplest 2-pyrrolyloxime, namely, pyrrole-2-carboxaldehyde oxime (praoH$_2$; Chart 1), in high-nuclearity iron(III) carboxylate chemistry, which has provided access to Fe$_{10}$ and Fe$_{12}$ cagelike clusters, containing the single-deprotonated form of the ligand, praoH$^-$. We believe that these compounds, together with the smaller-nuclearity Fe$^{III}_3$ and Fe$^{III}_6$ clusters, recently reported by Milios et al.,[12] are the prototypes of a rich new area of metal clusters derived from the amalgamation of 2-pyrrolyloximate and carboxylate ligands.

One of the most successful synthetic procedures to polynuclear iron clusters relies on the reaction of triangular [Fe$_3$O(O$_2$CR)$_6$(H$_2$O)$_3$](X) species, where X$^-$ are various counteranions, with a potentially chelating ligand, and this was the route chosen in the present work. In such reactions, the [Fe$_3$O]$^{7+}$ core of the trinuclear iron complex serves as a building block for higher-nuclearity species, but the exact nuclearity and structure of the product depend on several factors. In the present work, we have found that the identity of the counteranion, and specifically its coordination ability (i.e., Cl$^-$) or inability (i.e., ClO$_4$$^-$) with the metal centers, is one of these. The reaction of [Fe$_3$O(O$_2$CBu^t)$_6$(H$_2$O)$_3$](ClO$_4$) and praoH$_2$ in a 1:1 molar ratio in MeCN led to a dark-brown solution, which was allowed to slowly evaporate at room temperature, yielding after 6 days dark-red platelike crystals of [Fe$_{10}$O$_4$(OH)$_4$(O$_2$CBu^t)$_{14}$(praoH)$_4$]·2.2MeCN·1.6H$_2$O (**1**·2.2MeCN·1.6H$_2$O) in 30% yield.[13] The analogous reaction with [Fe$_3$O(O$_2$CBu^t)$_6$(H$_2$O)$_3$](Cl) in place of [Fe$_3$O(O$_2$CBu^t)$_6$(H$_2$O)$_3$](ClO$_4$) gave instead [Fe$_{12}$O$_8$Cl$_2$(O$_2$CBu^t)$_{12}$(praoH)$_6$(H$_2$O)$_2$]·MeCN·0.7H$_2$O (**2**·MeCN·0.7H$_2$O) in 45% yield.[13]

Both complexes **1** and **2** crystallize in triclinic space group $P\bar{1}$ and display crystallographic C_i symmetry. The structure of **1** comprises 10 Fe atoms in a closed, cagelike conformation (Figure 1, top). This can be described as a central Fe$_4$ rectangle (Fe3, Fe3′, Fe5, and Fe5′) whose two edges (Fe3···Fe5 and Fe3′···Fe5′) and two of their apexes (Fe3 and Fe3′) are fused with the edges of four [Fe$_3$(μ_3-O^{2-})] triangular subunits (Fe3, Fe4, Fe5/Fe3′, Fe4′, Fe5′ and Fe1, Fe2, Fe3/Fe1′, Fe2′, Fe3′, respectively). The Fe atoms of the central Fe$_4$ subunit are additionally bridged by two μ-OH$^-$ (O52 and O52′) ions, as well as by the oximate NO$^-$ arms of two praoH$^-$ groups. Two similarly coordinated groups serve to further link the Fe$_4$ unit with two of the extrinsic Fe$_3$ triangles, the edges of which are capped by two μ-OH$^-$ (O51 and O51′) ions. The complex, therefore, contains a [Fe$_{10}$(μ_3-O)$_4$(μ-OH)$_4$(μ-ON)$_4$]$^{14+}$ core (Figure 1, bottom). Peripheral ligation about the core is provided by 2 bidentate chelating and 12 η^1:η^1:μ-Bu^{t}CO$_2$$^-$ groups. All praoH$^-$ groups are single-deprotonated and nonchelating and bind in a η^1:η^2:μ_3 mode (Chart 1), while the pyrrole H atom of each praoH$^-$ group is involved in the formation of a strong intramolecular hydrogen bond with its parent oximate O atom. All Fe atoms are six-coordinate and near-octahedral. The Fe^{III} oxidation states and the degree of protonation of O^{2-} and OH$^-$ groups were confirmed by bond valence sum (BVS) calculations (see Table S1 in the Supporting Information, SI).[14]

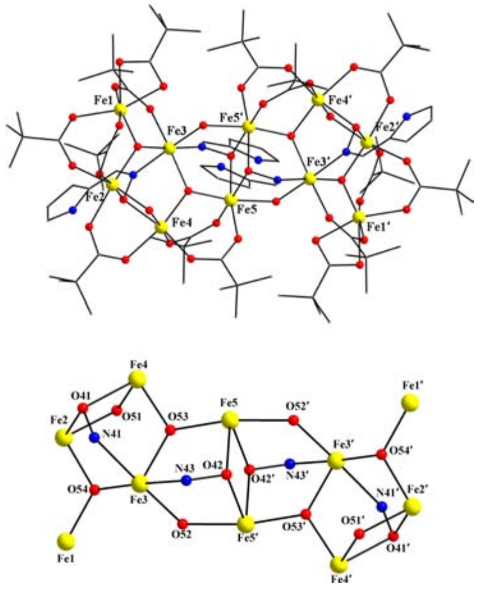

Figure 1. Labeled PovRay representation of complex **1**, with H atoms omitted for clarity (top) and its [Fe$_{10}$(μ_3-O)$_4$(μ-OH)$_4$(μ-ON)$_4$]$^{14+}$ core (bottom). Color scheme: Fe, yellow; O, red; N, blue; C, gray. Primes are used for symmetry-related atoms.

The structure of **2** (Figure 2, left) consists of 12 Fe atoms linked through 8 μ_3-O^{2-} ions (O1X, O2X, O3X, O4X, O1′X, O2′X, O3′X, and O4′X) and the oximate NO$^-$ arms of 6 praoH$^-$ groups. The simplified core of **2** (Figure 2, bottom right) can be described as three adjacent [Fe$_4$(μ_3-O^{2-})$_2$] butterfly units (Fe2′, Fe3, Fe4′, Fe5/Fe4, Fe4′, Fe6, Fe6′/Fe2, Fe3′, Fe4, and Fe5′) fused to (i) each other at common atoms Fe4 and Fe4′ and (ii) two extrinsic [Fe$_3$(μ_3-O^{2-})] triangular subunits (Fe1, Fe5, Fe6/Fe1′, Fe5′, and Fe6′) at common atoms Fe5, Fe5′, Fe6, and Fe6′. Additional ligation between the Fe$_4$···Fe$_4$ and Fe$_4$···Fe$_3$ units is provided by the six NO$^-$ oximate bridges, four of which bridge under the η^1:η^2:μ_3 mode and two in a η^1:η^1:μ fashion (Chart 1). Thus, complex **2** contains an overall [Fe$_{12}$(μ_3-O)$_8$(μ-ON)$_6$]$^{14+}$ core (Figure 2, top right), with peripheral ligation about it provided by 12 η^1:η^1:μ-Bu^{t}CO$_2$$^-$ groups and 2 each of the Cl$^-$ groups and H$_2$O molecules at Fe(6,6′) and Fe(3,3′), respectively. Eight of the Fe atoms (Fe1, Fe1′, Fe2, Fe2′, Fe3, Fe3′, Fe5, and Fe5′) are six-coordinate with distorted octahedral geometries, whereas Fe4, Fe4′, Fe6, and Fe6′ are five-coordinate[15] with very distorted trigonal-bipyramidal geometries (τ = 0.81 and 0.68, where τ is 0 and 1 for perfect square-pyramidal and trigonal-bipyramidal geometries,[15] respectively). BVS calculations have

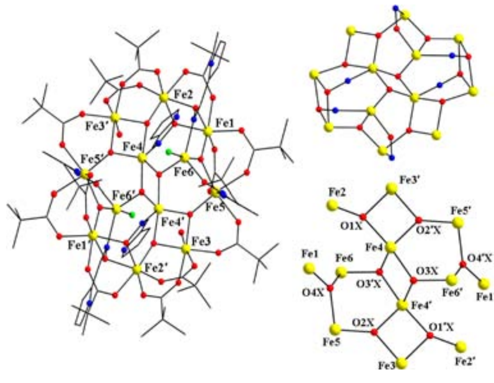

Figure 2. Labeled PovRay representation of complex **2**, with H atoms omitted for clarity (left), and its complete [Fe$_{12}$(μ_3-O)$_8$(μ-ON)$_6$]$^{14+}$ (top, right) and simplified [Fe$_{12}$(μ_3-O)$_8$]$^{20+}$ (bottom, right) core topologies. Color scheme: Fe, yellow; O, red; N, blue; Cl, green; C, gray. Primes are used for symmetry-related atoms.

again confirmed the Fe^{III} oxidation states for all Fe atoms and the degree of protonation of O^{2-} and H_2O groups (see Table S1 in the SI). Strong intramolecular hydrogen bonds are provided by interaction of the pyrrole H atom of each $praoH^-$ group and the corresponding oximate O atom.

Complexes **1** and **2** are the third and fourth structurally characterized coordination compounds to contain any form (neutral or mono- or dianionic) of the pyrrole-2-carboxaldehyde oxime ligand,[12] while **2** together with $[Fe_{12}O_8(OMe)_2(O_2CPh)_{12}(pao)_6]$[16a] and $[Fe_{12}Na_4O_2(OH)_8(sao)(OMe)_6(MeOH)_{10}]$[16b] ($saoH_2$ = salicylaldoxime) are the highest-nuclearity iron oximate clusters reported to date. Note that, despite of the nonchelating trend of the $praoH^-$ groups in complexes **1** and **2**, the oximate bridging arms foster the formation of species with distinctly different topologies than the "ferric wheels" first reported by Taft and Lippard[17] using simple alkoxido (OMe^- or OH^-) bridges.

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data were collected on powered polycrystalline samples of **1** and **2** in a 1 kG (0.1 T) field in the 5.0−300 K range. The obtained data are plotted as $\chi_M T$ versus T in Figure 3: $\chi_M T$ for both complexes steadily decreases with decreasing temperature from 10.59 (for **1**) and 10.22 (for **2**) $cm^3\ K\ mol^{-1}$ at 300 K to 1.75 and 0.19 $cm^3\ K\ mol^{-1}$ at 5 K, respectively, suggesting the presence of strong antiferromagnetic exchange interactions between the metal centers and very small (for **1**) or zero (for **2**) ground-state spin values. In order to determine the ground-state S values for **1** and **2**, we carried out alternating-current (ac) susceptibility studies, a powerful complement to dc studies for determining the S value of a system. The in-phase (χ_M') ac signals for **1** and **2**, shown as $\chi_M'T$ in Figures S3 and S4 in the SI, are both temperature-dependent in the 4−15 K region, indicating the presence of low-lying excited states with S larger than the ground state. For **2**, the plot is clearly heading for $\chi_M'T \sim 0$ at 0 K, suggesting an $S = 0$ ground state, but for **1**, the plot does not appear to be heading for zero, and, in fact, extrapolation of the plot to 0 K gives a $\chi_M'T$ value of ~1.0 $cm^3\ K\ mol^{-1}$, which is consistent with an $S = 1$ ground state and $g \sim 2.0$. We cannot rule out the possibility that it is an $S = 0$ ground state with very low-lying $S > 0$ excited states; theoretical calculations are in progress to rationalize the experimental observations.

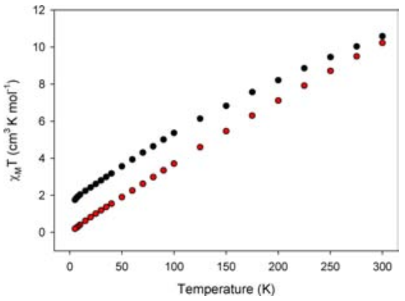

Figure 3. Plot of $\chi_M T$ versus T for complexes **1** (black circles) and **2** (red circles).

In conclusion, the use of pyrrole-2-carboxaldehyde oxime ($praoH_2$), the simplest and most flexible member of 2-pyrrolyloxime ligands, in 3d metal cluster chemistry has afforded two new Fe^{III}_{10} and Fe^{III}_{12} clusters with a closed, cagelike topology. These high-nuclearity products suggest that reactions of this ligand with other paramagnetic metal ions promise to deliver many new and beautiful clusters, and why not with some fascinating magnetic properties.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF format), synthetic details, and structural and magnetism figures for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Anal. Calcd (found) for dried **1** (solvent-free): C, 42.51 (42.75); H, 5.95 (6.13); N, 4.41 (4.26). Calcd (found) for dried **2** (solvent-free): C, 38.98 (38.63); H, 5.16 (5.11); N, 6.06 (6.32). Crystal structure data for $1\cdot2.2MeCN\cdot1.6H_2O$: $C_{94.40}H_{159.80}Fe_{10}N_{10.20}O_{41.60}$, F_w = 2661.82, triclinic, space group $P\bar{1}$ with a = 13.5678(3) Å, b = 15.6628(3) Å, c = 18.6330(3) Å, α = 105.195(1)°, β = 92.884(1)°, γ = 113.185(1)°, V = 3459.66(12) Å^3, T = 160(2) K, Z = 1, R1 [$I > 2\sigma(I)$] = 0.0934, wR2 (F^2, all data) = 0.2449. Crystal structure data for $2\cdot MeCN\cdot0.7H_2O$: $C_{92}H_{146.40}Fe_{12}N_{13}O_{40.70}Cl_2$, F_w = 2826.92, triclinic, space group $P\bar{1}$ with a = 15.4735(2) Å, b = 16.0289(2) Å, c = 16.9333(3) Å, α = 116.870(1)°, β = 105.874(1)°, γ = 98.732(1)°, V = 3412.82(9) Å^3, T = 160(2) K, Z = 1, R1 [$I > 2\sigma(I)$] = 0.0582, wR2 (F^2, all data) = 0.1517. CCDC deposition numbers for **1** and **2**: 906754 and 906755.

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