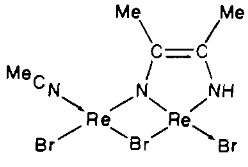

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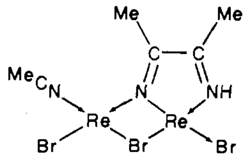

II

if either, is the better description in view of the relatively low precision of the present structure determination. Work is underway to obtain crystals of other derivatives that do not exhibit a disorder between the nitrile and $HN_2C_2R_2$ ligands, so as to permit a more accurate structure determination.

The corresponding 1:2 salts $[Re_2X_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2R_2)(NCR)](PF_6)_2$ can be prepared by oxidizing the green 1:1 salts with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone or $NOPF_6$ in $CH_2Cl_2$.[14] In addition, the red acetonitrile complex $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)](PF_6)_2$ can be isolated from mixtures in acetonitrile of $(n\text{-}Bu_4N)_2Re_2Cl_8$, dppm, and $KPF_6$ that have been refluxed for several days. The $^1H$ NMR spectrum ($CD_2Cl_2$, 25 °C) of this complex is of particular interest. In addition to the resonances associated with the coordinated dppm, there is a broad N–*H* resonance at $\delta = +7.90$ and three methyl resonances at $\delta = +1.74$ (s), +3.02 (s), and +6.05 (s). It is unclear at this time why two of the methyl resonances appear so far downfield, but this may reflect diamagnetic anisotropy effects or some degree of contact shifting.[15] The methyl resonances remain unchanged when this solution is cooled to −50 °C.

The coupling of two acetonitrile molecules by $(Re{\equiv}Re)^{4+}$, as is present in $Re_2X_4(\mu\text{-dppm})_2$, to give I and II, can formally be represented as redox processes that involve oxidation of the dirhenium core to $Re_2^{6+}$ and $Re_2^{8+}$, respectively, depending upon the description of the resulting $Re_2(\mu\text{-}NC(CH_3)C(CH_3)NH)$ dimetallacycle. We can envision the reactions as first giving the dicationic species $[Re_2X_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2R_2)(NCR)]^{2+}$ (these are formally $Re_2^{6+}$ or $Re_2^{8+}$ derivatives depending upon the ligand formulation, i.e. I or II, respectively) that then undergo a one-electron reduction in the reaction mixture to afford the monocations (correspondingly formulated as $Re_2^{5+}$ or $Re_2^{7+}$). The origin of the reductant for the latter step is not known. The structure determination on $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ (Figure 1) has shown the Re–Re distance to be 2.666 (1) Å, a value that does not easily distinguish between a $Re_2^{5+}$ and $Re_2^{7+}$ core in such an edge-sharing bioctahedral structure.[16]

The intramolecular multielectron redox process that gives rise to the nitrile coupling is accompanied by the "protonation" of the terminal nitrogen atom of the coupled ligand. Experiments using $CD_3CN$ in place of $CH_3CN$ show that the source of this hydrogen is the acetonitrile ligand itself. This hydrogen is very labile and exchanges with deuterium when the complex is treated with $CH_3CN/D_2O$. The resulting product has its IR-active $\nu$(N–D) mode at 2493 m $cm^{-1}$.

Along with the bonding mode of the coupled ligand,[17] these reactions have several other important features; viz., they do not require the use of an extraneous reducing agent, the dimetal core remains in the final product, and both alkyl and aryl nitriles have been successfully coupled. Although there are a few examples of the stabilization of reductively coupled nitriles at mononuclear transition-metal centers,[18–22] no systems have shown the combination of features displayed by these dirhenium species, which represent the most versatile reactions of their type to date. An examination of the scope of this chemistry is underway.

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**Supplementary Material Available:** A listing of representative elemental microanalyses, experimental details relating to the crystal structure determination, listings of crystallographic data and data collection parameters (Table S1), atomic positional parameters (Table S2), anisotropic thermal parameters (Table S3), complete bond distances (Table S4), and complete bond angles (Table S5), and a figure showing the full atomic numbering scheme and disorder for the $[Re_2B_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ cation (Figure S1) (24 pages); a table of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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(14) These complexes are not ESR-active and display well-defined NMR spectra. Magnetic moment determinations at room temperature by the Faraday method show a weak paramagnetism after allowance has been made for diamagnetic corrections; e.g., $\chi_g = -0.212 \times 10^{-6}$ cgsu and $\mu_{eff} = 1.20\ \mu_B$ for $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)](PF_6)_2$. They behave as 1:2 electrolytes in acetone and have electrochemical properties in 0.1 M $(n\text{-}Bu_4N)PF_6\text{–}CH_2Cl_2$ that accord with their being the one-electron-oxidized congeners of $[Re_2X_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2R_2)(NCR)]PF_6$; e.g. $E_{1/2}(red) = +0.19$ V and $E_{1/2}(red) = -0.80$ V for X = Cl and R = Me.

(15) Similar features are seen in the $^1H$ NMR spectra of the propionitrile derived complexes. For example, the spectrum of $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Et_2)(NCEt)](PF_6)_2$ (recorded in $CD_2Cl_2$) has resonances at $\delta$ +7.96 (s, N–*H*), −0.05 (t, $CH_3$), +0.44 (t, $CH_3$), +1.56 (t, $CH_3$), +2.07 (q, $CH_2$), +4.20 (q, $CH_2$), and +4.66 (q, $CH_2$).

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# A Novel Hexairon(III) Aggregate Prepared from a Basic Iron(III) Benzoate. Possible Building Blocks in Ferritin Core Formation

*Sir:*

Ferritin is the iron storage protein found in most life forms. Up to 4500 high-spin iron(III) centers can be accommodated in the hollow core of the apoprotein,[1] but few structural details are known about their aggregation and placement. We have been investigating the oligomerization of mononuclear and oxo-bridged binuclear iron(III) units under hydrolytic conditions that might occur during ferritin core formation.[2] Studies of this kind have uncovered a fascinating array of new $Fe_3$,[3] $Fe_4$,[4] $Fe_6$,[5] $Fe_8$,[6] and

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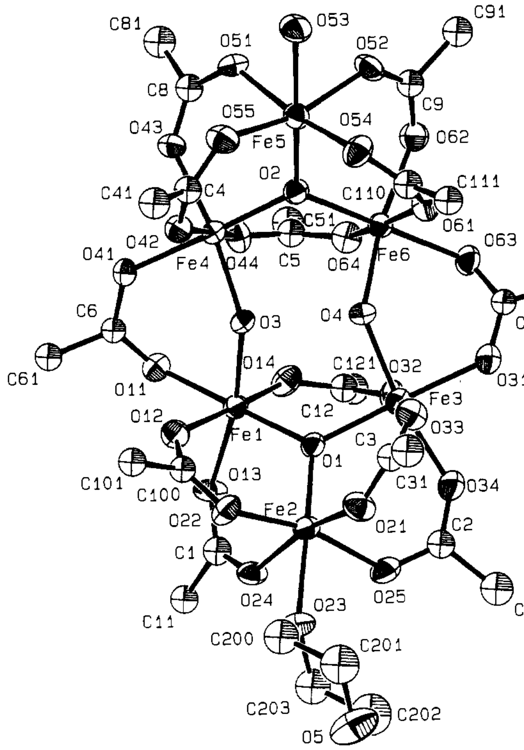


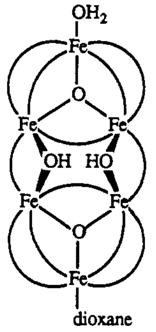
**Figure 1.** ORTEP drawing of **1**, showing the 40% probability thermal ellipsoids and atom labels for the iron atoms, the oxygen atoms, the first two carbon atoms of each benzoate, and the 1,4-dioxane molecule. Selected interatomic distances (Å) and angles (deg) are as follows: Fe1–O1 = 1.943 (8), Fe2–O1 = 1.869 (8), Fe3–O1 = 1.971 (8), Fe4–O2 = 1.950 (8), Fe5–O2 = 1.871 (8), Fe6–O2 = 1.965 (8), Fe1–O3 = 2.000 (8), Fe4–O3 = 2.003 (8), Fe3–O4 = 1.962 (8), Fe6–O4 = 1.985 (8), Fe2–O23 = 2.198 (9), Fe5–O53 = 2.17 (1); Fe1–O1–Fe2 = 118.7 (4), Fe2–O1–Fe3 = 118.9 (4), Fe1–O1–Fe3 = 122.3 (4), Fe4–O2–Fe5 = 119.7 (4), Fe5–O2–Fe6 = 117.9 (4), Fe4–O2–Fe6 = 122.4 (4), Fe1–O3–Fe4 = 129.9 (4), Fe3–O4–Fe6 = 134.4 (5).

$Fe_{11}$[7] iron–oxo aggregates scarcely imagined even a few years ago. In the present communication we report the synthesis and characterization of a novel hexairon(III) complex $[Fe_6O_2(OH)_2(OH_2)(O_2CPh)_{12}(1,4\text{-dioxane})]$ (**1**), obtained in high yield from a trinuclear basic iron(III) benzoate. Compound **1** represents a rare example of the class of structurally characterized $Fe_n$–oxo complexes; with $n > 4$, only three are presently known. This new molecule affords some insight into the process by which fundamental polyiron–oxo building blocks might assemble larger units in ferritin core formation.

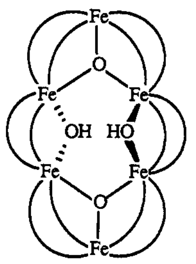
A stirred slurry of 0.5 g (4 mmol) of orange "basic iron(III) benzoate"[8] in a mixture of 20 mL of MeCN and 2 mL of 1,4-dioxane was heated to 80 °C for 1 h. From the final red-brown solution, which was filtered and kept in an open flask at room temperature, orange-brown hexagonal prisms of **1**·1,4-dioxane·2$CH_3CN$ were obtained in 73% yield. The crystals, which lose solvent slowly in air, proved to be suitable for X-ray diffraction studies. A portion of this material was also analyzed for elemental composition and by IR, $^1H$ NMR, UV–vis,[9] and Mössbauer spectroscopic and magnetic measurements.[10]

The molecular structure of **1**[11] is shown in Figure 1. Two ($\mu_3$-oxo)triiron(III) units are linked across one edge via two $\mu_2$-hydroxo and two benzoato ligands. The six iron atoms form a twisted boat conformation with the metal atoms in the plane (Fe1, Fe3, Fe4, Fe6) each bonded to one $\mu_3$-oxo, one $\mu_2$-hydroxo, and four benzoate oxygen atoms. The irons at the apices (Fe2, Fe5) are each bonded to one $\mu_3$-oxo and four benzoate oxygens and one oxygen atom from a water or a 1,4-dioxane molecule, respectively. Interestingly, both hydroxo bridges in **1** point toward the same side of the boat (the concave face), with the O3···O4 separation of 2.46 (1) Å being among the shortest reported.[4b,12–14] Other structural features of **1** include asymmetry within the $\{Fe_3O\}^{7+}$ subunits[15] compared to basic iron(III) carboxylate salts,[16] as well as lengthening of Fe–O bonds trans to the bridging oxo and, to a lesser extent, hydroxo ligands. The latter result reflects the greater structural trans influence[17] of oxo (hydroxo) compared with carboxylato oxygen donor ligands.

The structure of **1** is related to, but fundamentally different from, the only other known hexanuclear iron–oxo complex.[5] In the latter molecule, $[Fe_6O_2(OH)_2(O_2CBu^t)_{12}]$ (**2**), two of the six iron atoms are pentacoordinate. Moreover, the two $\{Fe_3O\}^{7+}$ subunits of **2** are linked by two hydroxo and four carboxylato bridges, and there is no carboxylate bridge along the edges of the two triangular subunits that face one another. In **2**, unlike **1**, the two $\mu_2$-hydroxo ligands are on opposite sides of the mean plane through the six iron atoms. The relationship between the two structures is shown schematically as follows, where the curved lines denote bridging carboxylate ligands.



**1**



**2**

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(9) Anal. ($C_{96}H_{86}N_2O_{33}Fe_6$) C, H, N, O, Fe; IR (KBr, $cm^{-1}$) 3581 ($\nu_s$, OH), 1568, 1543 ($\nu_a$, COO), 1411 ($\nu_s$, COO), 1121 and 875 (1,4-dioxane); $^1H$ NMR (250 MHz, 297 K, 18 mM in $CD_2Cl_2$) $\delta$ 1.96, 4.43, 4.70, 5.11, 6.06, 8.09, 10.55, 10.77, 11.30, 11.52, 11.62; electronic spectrum ($CH_2Cl_2$) [$\lambda_{max}$, nm ($\epsilon_M$/Fe, $cm^{-1}$ $M^{-1}$)] 342 (2700), 410 (sh), 458 (230), 524 (95).

(10) The sample used for Mössbauer and susceptibility measurements was powdered and dried under vacuum. Elemental analysis showed no residual solvent. Anal. ($C_{88}H_{72}O_{31}Fe$) C, H; magnetic susceptibility, solid state [($T$, K) $\mu_{eff}$/Fe, $\mu_B$] (300) 2.99, (200) 2.50, (100) 1.76, (25) 0.80, (10) 0.39, (2) 0.25, solution (297 K, 4 mM in $CD_2Cl_2$) 2.94 $\mu_B$/Fe.

(11) Crystallographic data for **1**·1,4-dioxane·2$CH_3CN$ ($C_{96}H_{86}N_2O_{33}Fe_6$, fw 2130.8) at 298 K: monoclinic, space group $P2_1/n$ (No. 14); $a = 20.128$ (8) Å, $b = 26.69$ (1) Å, $c = 18.846$ (8) Å, $\beta = 90.09$ (3)°, $V = 10124.4$ Å$^3$, $Z = 4$, $\rho_{obs} = 1.418$ g $cm^{-3}$, $\rho_{calc} = 1.402$ g $cm^{-3}$. With the use of 6472 unique reflections ($F_o > 6\sigma(F_o)$) collected with Mo K$\alpha$ ($\lambda = 0.71069$ Å) radiation between $3° \leq 2\theta < 45°$ on an Enraf-Nonius CAD-4 X-ray diffractometer, the structure was solved by direct methods (SHELXS) and Fourier techniques and refined by least squares using 592 variables to $R = 0.0729$ and $R_w = 0.0862$, respectively ($\mu = 9.43$ $cm^{-1}$, transmission coefficient 0.95–1.00). Only iron and oxygen atoms were refined anisotropically. Full details will be reported elsewhere.

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(15) (a) The Fe2–O1 and Fe5–O2 distances are significantly shorter ($\Delta > 6\sigma$) than the other Fe–$\mu_3$-O bonds. (b) The Fe1···Fe3 and Fe4···Fe6 distances are significantly longer ($\Delta > 12\sigma$) than the remaining Fe···Fe distances in each ($\mu_3$-oxo)triiron(III) subunit.

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Variable-temperature (2-300 K) magnetic susceptibility measurements for solid **1**[10] reveal reduction in the effective magnetic moment from 7.33 to 0.62 $\mu_B$/molecule (2.99 to 0.25 $\mu_B$/iron) with decreasing temperature, indicative of net antiferromagnetic coupling within the $Fe_6$ aggregate. Extrapolation of the $\mu_{eff}$ vs $T$ curve (Figure S1, supplementary material) to 0 K yields a value of $\sim$0.07 $\mu_B$/iron, indicating a diamagnetic ground state having $S_T = 0$. The room-temperature effective moment of 2.94 $\mu_B$/iron,[10] obtained by the Evans method,[18] is consistent with the persistence of the hexanuclear structure in solution. The optical spectrum of the $\{Fe_6O_2(OH)_2\}^{12+}$ unit in **1** has a characteristic maximum at 524 nm not present in its $\{Fe_3O\}^{7+}$ constituents, in further support of the solution integrity of **1**. Zero-field Mössbauer spectra at 80 K can be fit as a symmetric quadrupole doublet with isomer shift $\delta = 0.511$ mm/s (relative to iron metal at room temperature) and quadrupole splitting $\Delta E_Q = 0.575$ mm/s ($\Gamma = 0.370$ mm/s).

Interestingly, hydrolysis of both **1** and "basic iron(III) benzoate" in MeCN, layered with wet THF (0.8% $H_2O$) at room temperature, gives the known molecule $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$[7] in >80% yield, suggesting that **1** might be an intermediate in the formation of the undecairon(III) aggregate or even the ferritin core itself. Use of higher temperatures in the synthesis of polynuclear iron-oxo aggregates thereby seems to favor the assembly of smaller clusters.[5] This limitation in the extent of hydrolysis may be caused by reduced availability of water molecules.

In conclusion, the reported synthesis, reactions, and structural and physical properties of **1** clearly expand our knowledge of the class of polynuclear iron-oxo complexes. The $Fe_3 \rightarrow Fe_6 \rightarrow Fe_{11}$ conversions observed here provide some indication of the nucleation processes that might be involved in formation of the ferritin core.

**Acknowledgment.** This work was supported by U.S. Public Health Service Grant GM 32134 from the National Institute of General Medical Sciences. W.M. is grateful for a NATO Research Fellowship. We thank G. C. Papaefthymiou and R. B. Frankel of the Francis Bitter National Magnet Laboratory for the magnetic measurements and the Mössbauer spectra and R. L. Rardin and S. G. Bott for assistance with the X-ray structural analysis.

**Supplementary Material Available:** Tables of atomic positional and thermal parameters of **1**·1,4-dioxane·2MeCN and Figure S1, showing temperature-dependent magnetic susceptibility data for compound **1** (10 pages). Ordering information is given on any current masthead page.

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# Articles

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## *nido*-Carborane Building-Block Reagents. 1. Polycyclic Arene $RR'C_2B_4H_6$ Derivatives: Synthesis via Indenyl and Fluorenyl Alkynes and Metal-Promoted Oxidative Fusion

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The preparations of *C*-mono- and *C,C'*-bis(indenylmethyl) and *C*-mono- and *C,C'*-bis(fluorenylmethyl) derivatives of *nido*-2,3-dicarbahexaborane(8) ($C_2B_4H_8$) are described. These carboranes are multifunctional, presenting several aryl and carboranyl sites for metal $\eta^5$ or $\eta^6$ coordination, and are designed as structural modules for use in the construction of multiunit metal sandwich complexes and proposed electron-delocalized solid-state arrays. The carborane syntheses were conducted via the method of Hosmane and Grimes, involving the reaction of alkynes with $B_5H_9$ in the presence of $(C_2H_5)_3N$. However, these preparations required a priori the syntheses of the first known difluorenyl and diindenyl alkynes, as well as an improved synthesis of (9-fluorenylmethyl)acetylene. In the formation of the bis(indenylmethyl)acetylene from 1-lithioindene, an unexpected 1 → 2 rearrangement occurred to give the 2-substituted product exclusively. The new alkynes and carboranes were characterized via multinuclear NMR, IR, and mass spectroscopy, and the properties of the *nido*-$RR'C_2B_4H_6$ carboranes toward bridge deprotonation, complexation with $Fe^{2+}$, and subsequent fusion to generate $R_2R'_2C_4B_8H_8$ products were explored. All of the new $RR'C_2B_4H_6$ species are deprotonated by NaH in THF to give the $RR'C_2B_4H_5^-$ anions, and the monosubstituted anions (R = indenylmethyl, fluorenylmethyl; R' = H) undergo slow $Fe^{2+}$-promoted fusion to form $R_2C_4B_8H_{10}$. However, the disubstituted $R_2C_2B_4H_5^-$ anions do not fuse, owing to steric hindrance by the bulky R groups; the diindenyl species forms a complex of the type $(R_2C_2B_4H_4)Fe(THF)_x$ ($x$ = 2 or 3), which does not react further. Treatment of the neutral diindenyl carborane with $FeCl_2$ gave in low yield an apparent intramolecular sandwich complex in which the iron is proposed to be $\eta^5$-coordinated to the $C_5$ rings of both indenyl groups.

### Introduction

The *nido*-carborane 2,3-$C_2B_4H_8$ and its organosubstituted $RR'C_2B_4H_6$ derivatives are clearly useful to chemists in the boron cluster field, as the starting point in the synthesis of many diverse species including triple-decker sandwiches, large carboranes (e.g. $C_4B_8$ cages), and numerous transition-metal and main-group-metal complexes.[1] Recently, however, it has become apparent that the pyramidal $RR'C_2B_4H_4^{2-}$ and cyclic $RR'C_2B_3H_5^{2-}$ groups (generated from the neutral compounds) are also superb ligands for organometallic synthesis and open the way to construction of new types of complexes and extended $\pi$-systems that would be difficult or impossible to attain with hydrocarbon ligands alone.[2] The open $C_2B_3$ face of the pentagonal-pyramidal $RR'C_2B_4H_4^{2-}$ unit is

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[†] Undergraduate research participant, 1985-1987.

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