in fact, the distance is shorter than most of the W–Cl distances recently reported.[28-32] The smaller trans influence of Cl may be responsible for the shortness of the bond distance.[24] As crystallographic analysis of monomeric W(III) complexes is rare,[33] comparison of the W–Cl bond distance in W(III) complexes is difficult. The P–W–P angles are almost the same as those in other $W(dpe)_2$ type complexes. The W–Cl vector slightly bends toward P1 and P2, making P1–W–Cl, and P2–W–Cl angles smaller than 90°.

The structure determination of **10** suggests that the reaction product of $[W(N_2)_2(dpe)_2]$ and $HFeCo_3(CO)_{12}$, (**6**), in dichloromethane is also a dichloro complex and not an alternative such as $[WH(dpe)_2][FeCo_3(CO)_{12}]\cdot CH_2Cl_2$, which we had suspected before the X-ray structure determination.

Formation of no hydrazido(2–) complexes in the aprotic solvents in the present study makes a marked contrast with the very facile formation of alkoxide hydrazido(2–) complexes in alcohols[5] or a hydrazido(2–) hydroxo complex in an aqueous solvent. Although the exact sequence of the reaction is still not clear, the coordination of an oxygen ligand ROH or H_2O to the tungsten center probably makes the metal electron rich and this electron flow is transmitted to the reaction center of dinitrogen that is to be protonated. Thus, the influence of electron-donating ligands upon the protonation[4b,34] seems crucial. In the case of simpler acids HX, coordinated X plays the role of electron donor to the metal but an oxygen ligand from alcohols or water is necessary for the present reaction using the cluster acid incapable of coordinating to the tungsten.

Acknowledgment. We thank Dr. Y. Fukuda for the measurements of magnetic susceptibilities.

Supplementary Material Available: Listings of structure factors, anisotropic thermal factors (Table V), and nonessential bond distances and angles (Table VI) (25 pages). Ordering information is given on any current masthead page.

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Trinucleation of Arylazo Oxime Ensembles: Structure and Reactions of Novel Linear $Fe^{II}Fe^{III}Fe^{II}$ Species

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The reaction of phenylazo aldoximes, RC(=NOH)N=NPh (HRL; R = Me, Ph), with iron(II) perchlorate hexahydrate in ethanol affords $[Fe_3(RL)_6]ClO_4$ (**1**) crystallizing with or without solvent molecules. The structure of one solvate, viz., $[Fe_3(PhL)_6]ClO_4\cdot 2CHCl_3$, has been determined X-ray crystallographically. The compound forms monoclinic crystals in the space group $P2_1/n$ with $Z = 2$ and unit cell dimensions $a = 15.521$ (4) Å, $b = 12.743$ (5) Å, $c = 21.788$ (5) Å, $\beta = 104.35$ (2)°, and $V = 4175$ (2) Å^3. The structure was refined to $R = 0.0881$ and $R_w = 0.1281$. The trinuclear cation $Fe_3(PhL)_6^+$ sits on a crystallographic center of symmetry. The central iron(III) atom is surrounded by an octahedron of six oximato oxygen atoms. Each of the two terminal iron(II) atoms is held in the facial tris chelate environment of azo and oxime nitrogen atoms. The FeN_6 coordination sphere is trigonal antiprismatic. Each oximato function acts as a bridge between iron(III) and iron(II) atoms. Both the ClO_4^- anion and the $CHCl_3$ molecules are disordered in the crystal. The reaction of iron(III) chloride with HRL furnishes $[Fe_3(RL)_6]FeCl_4$ (**2**). The iron(III) and iron(II) atoms of $Fe_3(RL)_6^+$ are high spin ($S = {}^5/_2$) and low spin ($S = 0$), respectively. Subtle rhombic distortion of the $Fe^{III}O_6$ sphere in $Fe_3(RL)_6^+$ is revealed by strong EPR lines near $g = 4$ in both **1** and **2**. The observation of intervalence band(s) in **1** and **2** has been vitiated by the strong visible and near-UV bands localized on the FeN_6 chromophore. Hydroxide ions selectively and quantitatively extrude iron(III) from both **1** and **2**, liberating the green anion $Fe(RL)_3^-$ (isolated as Na^+ and Ph_4As^+ salts), which retains the facial stereochemistry characteristic of the parent aggregate. Reaction with iron(III) salts causes reaggregation into $Fe_3(RL)_6^+$. The $Fe(RL)_3^-$ anion is electrochemically oxidized to axially symmetric (EPR data) low-spin $Fe(RL)_3$, the $Fe^{III}N_6/Fe^{II}N_6$ formal potential being in the range 0.2–0.4 V vs. SCE. In $Fe_3(RL)_6^+$, the couple $Fe^{III}O_6/Fe^{II}O_6$ due to the central iron atom occurs near 0.0 V but the terminal $Fe^{III}N_6/Fe^{II}N_6$ couple is shifted to potentials above 1.5 V and is not directly observable. In the case of **2** the $FeCl_4^-/FeCl_4^{2-}$ couple is exactly superposed on the $Fe^{III}O_6/Fe^{II}O_6$ couple of the cation. These redox patterns have been used to rationalize the formation of **1** and **2** by the chelative redox reactions of iron salts with HRL. The possible role of $Fe(RL)_3^-$ as a translocator of metal ions via the reaggregation–extrusion sequence and its similarity to ferroverdin, the green pigment of a *Streptomyces* species, are noted.

Introduction

The binding of iron by nitrogen and oxygen donors is of widespread chemical interest. Unsaturated nitrogenous groups are good donors for low-spin iron(II). Anionic oxygen functions, on the other hand, commonly display pronounced affinity toward high-spin iron(III). The α-diimines[2] and β-diketones[3] are good examples of these simple rules that find elegant expression in the binding of iron in nature.[4]

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Table I. Some Characterization Data

compd	molar conductivity[a] Λ_M, Ω^{-1} cm^2 M^{-1}	IR data,[b] cm^{-1}		bulk suscepti-bility (298 K)	UV-vis data[a] λ, nm (ε, M^{-1} cm^{-1})
		ν_{NO}	$\nu_{Fe^{III}O}$	μ_{eff}, μ_B	
$[Fe(Fe(PhL)_3)_2]ClO_4$[c]	121	1245	400	5.90	585 (15 300), 455 (26 800), 260 (92 500)
$[Fe(Fe(PhL)_3)_2]ClO_4 \cdot 2CHCl_3$[c]	122	1240	410	5.91	585 (15 500), 460 (27 400), 260 (94 000)
$[Fe(Fe(MeL)_3)_2]ClO_4 \cdot 2H_2O$[c,d]	133	1240	400	5.92	565 (12 500), 415 (36 700), 280 sh (30 500)
$[Fe(Fe(MeL)_3)_2]PF_6 \cdot 2H_2O$[d,e]	140	1240	405	5.89	570 (11 500), 420 (37 100), 280 sh (31 500)
$[Fe(Fe(PhL)_3)_2]FeCl_4$[f]	140	1250	400	8.32[g]	585 (14 000), 430 (25 400), 260 (96 700)
$[Fe(Fe(MeL)_3)_2]FeCl_4$[f]	145	1250	405	8.26[g]	570 (12 800), 415 (40 200), 280 sh (36 500)
$[Ph_4As][Fe(MeL)_3] \cdot H_2O$[d]	85	1240			930 (650), 640 (4500), 395 (16 900), 290 sh (20 900), 260 (26 000)

[a] Solvent is acetonitrile. [b] In KBr disks (4000-300 cm^{-1}). Characteristics are as follows: ν_{NO}, broad and strong; $\nu_{Fe^{III}O}$, broad and weak. [c] ν_{ClO_4}: ~1100 cm^{-1}, broad and strong; ~620 cm^{-1}, sharp and strong. [d] ν_{OH}: ~3400 cm^{-1}, broad and strong. [e] ν_{PF_6}: 840 cm^{-1}, very strong. [f] $\nu_{Fe^{III}Cl}$: 370 cm^{-1}, broad and strong. [g] If both the cation and the anion have $S = {}^5/_2$, the calculated spin-only moment is $70^{1/2} = 8.37\ \mu_B$.

Table II. Selected Distances (Å) and Their Estimated Standard Deviations[a] for $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Fe(1)	Fe(2)	3.484 (2)	O(1)	N(3)	1.32 (2)	N(5)	C(14)	1.389 (15)
Fe(1)	O(1)	2.035 (9)	O(2)	N(6)	1.344 (14)	N(6)	C(14)	1.27 (2)
Fe(1)	O(2)	2.018 (10)	O(3)	N(9)	1.334 (15)	N(7)	N(8)	1.311 (15)
Fe(1)	O(3)	2.010 (9)	N(1)	N(2)	1.27 (2)	N(7)	C(34)	1.42 (2)
Fe(2)	N(1)	1.908 (13)	N(1)	C(8)	1.52 (2)	N(8)	C(27)	1.37 (2)
Fe(2)	N(3)	1.910 (11)	N(2)	C(1)	1.33 (2)	N(9)	C(27)	1.33 (2)
Fe(2)	N(4)	1.940 (11)	N(3)	C(1)	1.30 (2)	C(1)	C(2)	1.51 (2)
Fe(2)	N(6)	1.910 (10)	N(4)	N(5)	1.271 (14)	C(14)	C(15)	1.50 (2)
Fe(2)	N(7)	1.955 (12)	N(4)	C(21)	1.46 (2)	C(27)	C(28)	1.45 (2)
Fe(2)	N(9)	1.909 (13)						

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

This work stems from our interest in mixed-valence systems in which the intramolecular coexistence of both types of iron is supported by ligands[5] possessing both types of binding sites. Herein we examine the case of phenylazo aldoxime,[6-15] RC(=NOH)N=NPh (HRL; R = Me, Ph), as potential supporters of this situation. In HRL the α-diimine-like azo–imine fragment and the oxygen end of the oxime function are potentially good binding sites for low-spin iron(II) and high-spin iron(III), respectively. Very facile formation of mixed iron(II), iron(III) species indeed occurs in the reaction of HRL with iron salts. The structure of one such complex has been revealed by three-dimensional X-ray crystallography. This has helped to rationalize

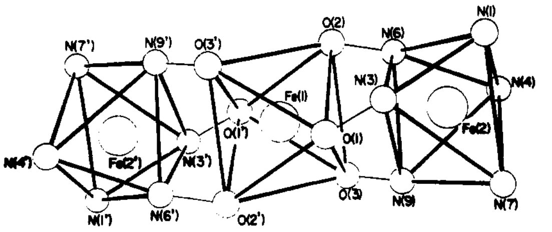

Figure 1. View of the coordination spheres of the three iron atoms in $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$.

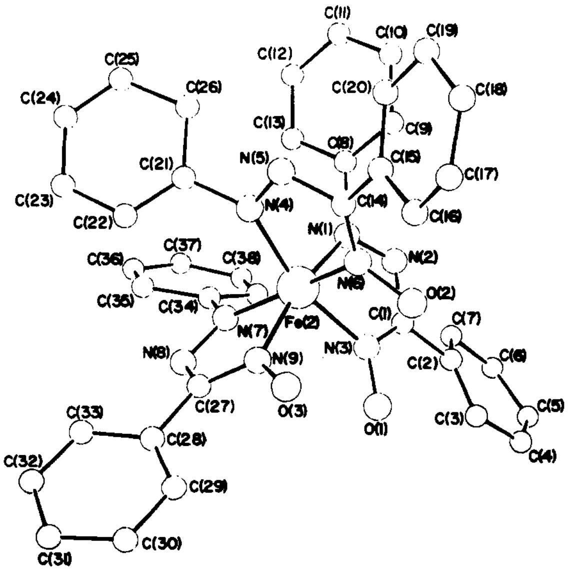

Figure 2. View of one $Fe(PhL)_3$ unit in $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$.

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(5) It is proposed that such ligands which as a single unit or as an ensemble can bring about this situation or the more general situation in which two distinct redox centers are housed adjacently be called *duplex ligands*.

(6) The known transition-metal chemistry of arylazo oximes includes those of cobalt(III),[7] rhodium(III),[8] palladium(II),[8-10] platinum(II),[10-12] copper(I),[13] and ruthenium(II) and -(III).[14,15]

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Table III. Selected Angles (deg) and Their Estimated Standard Deviations[a] for $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$

atom 1	atom2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Fe(2)	Fe(1)	O(1)	54.8 (3)	N(1)	Fe(2)	N(9)	166.6 (5)	Fe(2)	N(4)	C(21)	130.4 (9)
Fe(2)	Fe(1)	O(1′)	125.2 (3)	N(3)	Fe(2)	N(4)	163.1 (5)	N(5)	N(4)	C(21)	113 (1)
Fe(2)	Fe(1)	O(2)	55.1 (3)	N(3)	Fe(2)	N(6)	88.9 (5)	N(4)	N(5)	C(14)	113 (1)
Fe(2)	Fe(1)	O(2′)	124.9 (3)	N(3)	Fe(2)	N(7)	99.1 (4)	Fe(2)	N(6)	O(2)	121.9 (8)
Fe(2)	Fe(1)	O(3)	55.3 (3)	N(3)	Fe(2)	N(9)	90.1 (5)	Fe(2)	N(6)	C(14)	117.7 (9)
Fe(2)	Fe(1)	O(3′)	124.7 (3)	N(4)	Fe(2)	N(6)	77.3 (5)	O(2)	N(6)	C(14)	120 (1)
O(1)	Fe(1)	O(2)	90.7 (4)	N(4)	Fe(2)	N(7)	96.5 (4)	Fe(2)	N(7)	N(8)	117.0 (9)
O(1)	Fe(1)	O(2′)	89.3 (4)	N(4)	Fe(2)	N(9)	99.5 (5)	Fe(2)	N(7)	C(34)	130 (1)
O(1)	Fe(1)	O(3)	90.9 (4)	N(6)	Fe(2)	N(7)	165.2 (5)	N(8)	N(7)	C(34)	113 (1)
O(1)	Fe(1)	O(3′)	89.1 (4)	N(6)	Fe(2)	N(9)	90.1 (5)	N(7)	N(8)	C(27)	113 (1)
O(2)	Fe(1)	O(3)	89.8 (4)	N(7)	Fe(2)	N(9)	77.6 (5)	Fe(2)	N(9)	O(3)	123.2 (9)
O(2)	Fe(1)	O(3′)	90.2 (4)	Fe(1)	O(1)	N(3)	112.9 (7)	Fe(2)	N(9)	C(27)	117 (1)
Fe(1)	Fe(2)	N(1)	118.6 (4)	Fe(1)	O(2)	N(6)	115.9 (7)	O(3)	N(9)	C(27)	119 (1)
Fe(1)	Fe(2)	N(3)	54.1 (3)	Fe(1)	O(3)	N(9)	113.6 (7)	N(2)	C(1)	N(3)	117 (1)
Fe(1)	Fe(2)	N(4)	121.9 (3)	Fe(2)	N(1)	N(2)	119 (1)	N(2)	C(1)	C(2)	118 (2)
Fe(1)	Fe(2)	N(6)	55.5 (3)	Fe(2)	N(1)	C(8)	128 (1)	N(3)	C(1)	C(2)	126 (2)
Fe(1)	Fe(2)	N(7)	120.2 (4)	N(2)	N(1)	C(8)	111 (1)	N(5)	C(14)	N(6)	114 (1)
Fe(1)	Fe(2)	N(9)	54.0 (3)	N(1)	N(2)	C(1)	111 (1)	N(5)	C(14)	C(15)	116 (1)
N(1)	Fe(2)	N(3)	77.1 (5)	Fe(2)	N(3)	O(1)	122.4 (8)	N(6)	C(14)	C(15)	129 (1)
N(1)	Fe(2)	N(4)	93.8 (5)	Fe(2)	N(3)	C(1)	115 (1)	N(8)	C(27)	N(9)	114 (1)
N(1)	Fe(2)	N(6)	93.5 (5)	O(1)	N(3)	C(1)	122 (1)	N(8)	C(27)	C(28)	118 (1)
N(1)	Fe(2)	N(7)	100.3 (5)	Fe(2)	N(4)	N(5)	116.9 (8)	N(9)	C(27)	C(28)	128 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

magnetic properties, redox activity, and synthetic reactions as well as cleavage and reconstitution processes pertaining to the new species.

Results and Discussion

A. Synthesis and Some Properties. The reaction of iron(III) chloride with HRL in hot ethanol furnishes[16–18] a shining black solid of composition $Fe_2(RL)_3Cl_2$ with an average metal formal oxidation number of +2.5. We have thus far failed to grow single crystals of this material, and this has precluded direct determination of its structure. We therefore examined the reactions of HRL with other iron salts. Iron(II) perchlorate was found to undergo facile chelation by HRL in boiling ethanol, affording a solid of empirical formula $[Fe_3(RL)_6]ClO_4$ (**1**) crystallizing with or without solvent molecules (Table I). The X-ray structure of one such complex, $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$, was finally solved.

Complex **1** is a 1:1 electrolyte and displays the expected ClO_4^- bands in the IR region. Certain other data (Table I) collected routinely after synthesis could be convincingly rationalized only after structure determination. Thus, the bulk susceptibility of **1** was found to tally with the presence of five unpaired electrons corresponding to one spin-free iron(III) and two spin-paired iron(II) atoms. From a comparative study of the properties, particularly EPR spectra and redox behavior (vide infra), of **1** with those of $Fe_2(RL)_3Cl_2$ it emerged that this enigmatic chloride[16–18] is actually $[Fe_3(RL)_6]FeCl_4$ (**2**), which differs from **1** in the anionic part only ($FeCl_4^-$ instead of ClO_4^-). Complex **2** is indeed a 1:1 electrolyte. Here both the cation and the anion are spin sextuplets. It displays both $\nu_{Fe^{III}O}$ and $\nu_{Fe^{III}Cl}$ bands in the IR spectrum while **1** has only $\nu_{Fe^{III}O}$ (Table I). Salts of $Fe_3(RL)_6^+$ with anions other than ClO_4^- and $FeCl_4^-$ can also be made, e.g., $[Fe_3(MeL)_6]PF_6 \cdot 2H_2O$ (Table I).

B. Structure. a. X-ray Structure of $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$. The lattice consists of discrete trinuclear cations, perchlorate anions, and chloroform molecules. A view of the coordination spheres within the cation $Fe_3(PhL)_6^+$ is shown in Figure 1, and the relative disposition of the three chelate rings around an iron(II) atom, Fe(2), is displayed in Figure 2. Selected bond distances and angles are listed in Tables II and III, respectively.

The trinuclear cation is an iron(III)-mediated aggregate of a pair of $Fe(PhL)_3^-$ units with a Fe(1)···Fe(2) separation of 3.484 (2) Å. The cation sits on a crystallographic center of symmetry, as does the counterion, a disordered perchlorate ion at ($^1/_2$, $^1/_2$, 0). In addition there is a disordered chloroform molecule on a set of general equivalent positions: the two disordered congeners have occupancies of 0.65 and 0.35. The oxygen atoms of the perchlorate ion had not been refined to stable positions, so they were not refined in the final least-squares cycle.

The central iron atom, Fe(1), is surrounded by an octahedron of six oximato oxygen atoms (Figure 1). All angles at the metal between cis oxygen atoms are very close to 90°. The average metal–oxygen distances (2.021 [7] Å)[19] compares favorably with that[20] (1.995 [4] Å) in the alum $CsFe(SO_4)_2 \cdot 12H_2O$ as well as with those[21] in other $Fe^{III}O_6$ species.

The two iron(II) atoms, Fe(2) and Fe(2′), have trigonal-antiprismatic FeN_6 coordination spheres (Figures 1 and 2). Since the chelate bite angle is only ~77°, it is imperative that distortions from the idealized octahedron be severe. The geometry about Fe(2) can be envisaged as the result of a progressive set of distortions from regular octahedral symmetry—a trigonal compression along the line joining Fe(2) and Fe(1), followed by a rhombic distortion of the terminal basal triangular face. Triangular faces of the coordination polyhedra about Fe(1) and Fe(2) abut: however, they are not eclipsed. The average O–Fe(1)–Fe(2)–N(O) torsion angle is −18.9 [8]°. The centrosymmetry of the $Fe_3(PhL)_6^+$ cation requires that the two $Fe(PhL)_3^-$ units have opposite chirality (Δ–Λ) and that the Fe_3 unit be linear (Figure 1).

The three chelate rings on Fe(2) are planar, and their dihedral angles are 88° (between the plane containing N(1) and that containing N(4)), 100° (N(1) and N(7)), and 80° (N(4) and N(7)). The chelate rings are *facially disposed*, bringing all these oximato groups into mutually cis positions crucial for concerted binding of iron(III). The average N=N (1.29 [1] Å) and N—O (1.333 [6] Å) distances as well as other dimensions within the chelate rings are generally comparable with those of other metal

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(16) There are two brief reports[17,18] on iron complexes of arylazo oximes. None of these reveal the nature of the primary reaction products of HRL with iron(III) chloride.

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$$[\sum_{i=1}^{n} \Delta_i^2/n(n-1)]^{1/2}$$

in which Δ_i is the deviation of the *i*th value from the mean of the *n* values.

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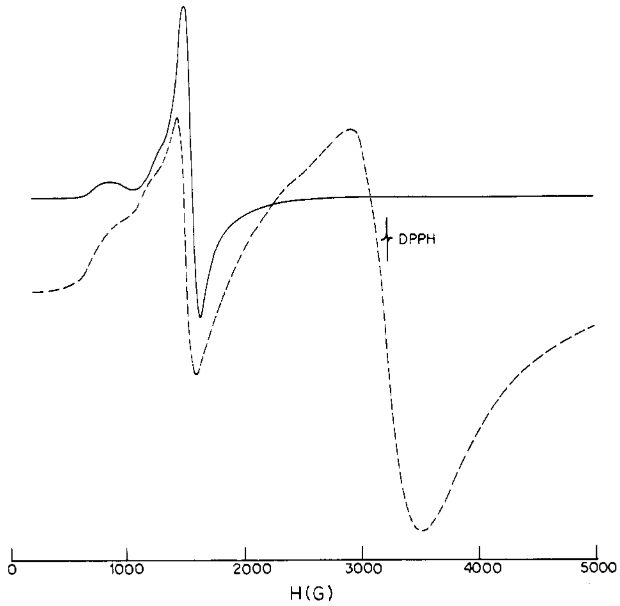

Figure 3. EPR spectra of polycrystalline $[Fe(Fe(PhL)_3)_2]ClO_4 \cdot 2CHCl_3$ (—) and $[Fe(Fe(PhL)_3)_2]FeCl_4$ (---) at 77 K.

Table IV. EPR Spectral Data (77 K)

compd	phase	g			
$[Fe(Fe(PhL)_3)_2]ClO_4 \cdot 2CHCl_3$	powder		4.116	4.986	7.537
	glass[a]		4.242	5.103	7.423
$[Fe(Fe(MeL)_3)_2]ClO_4 \cdot 2H_2O$	powder		4.226	5.316	6.867
	glass[a]		4.414	5.443	7.423
$[Fe(Fe(MeL)_3)_2]PF_6 \cdot 2H_2O$	powder		4.120	5.316	7.165
$[Fe(Fe(PhL)_3)_2]FeCl_4$	powder	2.026	4.265	5.227	7.046
	glass[a]	2.016	4.355	5.268	6.876
$[Fe(Fe(MeL)_3)_2]FeCl_4$	powder	2.016	4.242	5.103	7.423
	glass[a]	2.029	4.414	5.536	7.595

[a] In acetonitrile–toluene (1:1).

arylazo oximates.[10,12,13,15] The average Fe–N distances (Fe–N(O) = 1.910 [1] Å; Fe–N(Ph) = 1.93 [1] Å) are somewhat shorter than that[22] in the α-diimine $Fe^{II}N_6$ system tris(2,2′-bipyridine)iron(2+).

All properties of $Fe_3(MeL)_6^+$ are closely similar to those of $Fe_3(PhL)_6^+$. We therefore assume that the former cation has essentially the same gross structure as that in Figure 1.

b. EPR Spectra. The X-band EPR spectra of **1** and **2** provide further insight into the environment around the iron(III) centers. The most dominating feature in the spectra (77 K) of $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$ in the polycrystalline phase (Figure 3) as well as in a 1:1 acetonitrile–toluene frozen glass is the absorption near $g = 4$ (Table IV) characteristic[23-28] of a rhombic field around iron(III). The completely rhombic field is characterized by $E/D = 1/3$, where D and E are the zero-field parameters related to the splitting of the ^6S ground state of Fe^{3+} due to admixture with quartet excited states such as ^4D. The signal near $g = 4$ arises from the middle Kramers doublet, and in the completely rhombic situation g equals 30/7.

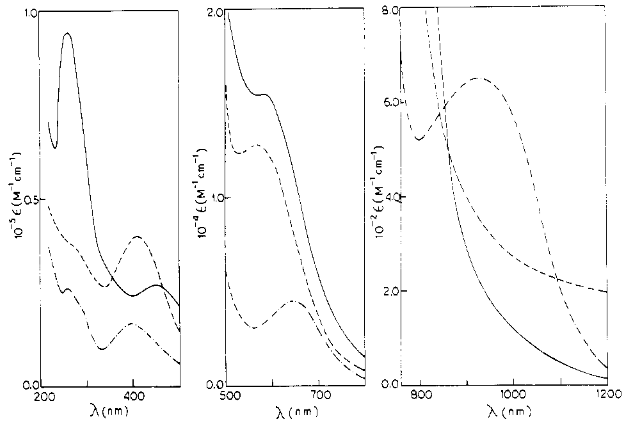

Figure 4. Electronic spectra of $[Fe(Fe(PhL)_3)_2]ClO_4 \cdot 2CHCl_3$ (—), $[Fe(Fe(MeL)_3)_2]FeCl_4$ (---), and $[Ph_4As][Fe(MeL)_3] \cdot H_2O$ (–·–) in acetonitrile.

The distortions from strict O_h symmetry required for observation of rhombic spectra are small,[23] and such spectra in no way contradict the centrosymmetry required by the X-ray data. Indeed, the completely rhombic situation ($E/D = 1/3$) is necessarily centrosymmetric.[23] The main implication of the EPR results is that, within the constraint of centrosymmetry, there are small but genuine differences among individual Fe–O distances. The X-ray results bear some signs of this—e.g., Fe(1)–O(1) is significantly shorter than Fe(1)–O(3) (Table II).

We now consider the spectra of $[Fe_3(PhL)_6]FeCl_4$ (Figure 3, Table IV). The region near $g = 4$ is closely alike to that of the perchlorate. A new feature, absent in the perchlorate, is the strong absorption near $g = 2$ ascribable to[29] tetrahedral $FeCl_4^-$. This observation has been of crucial help in diagnosing the nature of **2**.

The gross behaviors of the R = Me species are essentially similar (Table IV). In all type **1** and **2** complexes examined, there are one or two relatively broad and weak absorptions with g values in the range 5–8 (Figure 3, Table IV). These absorptions, which probably represent[24] deviations from complete rhombicity, have not been specifically assigned. Rhombic iron(III) species can show[24-26] lines near $g \approx 9.7$ arising from the lowest Kramers doublet, but these are not observed in **1** and **2**.

c. Electronic Spectra. The prime purpose of examining the spectra (200–2200 nm) of **1** and **2** was to identify possible intervalence bands—a task in which we did not succeed. Results are shown in Figure 4 and Table I. Even though $Fe_3(RL)_6^+$ has firmly trapped valences, iron(II) and iron(III), in environments of disparate ligand field strengths, a certain amount of valence delocalization may still be expected since the oximato bridge (M–N–O–M) is a known[30] mediator of metal–metal interaction. One may expect at least weak class II character.[31]

The trinuclear cation has no absorption in the region 1000–2200 nm. The absence of low-energy intervalence bands is in line[31,32] with the above discussion and the related fact that the metal redox potentials of the $Fe^{III}O_6$ and $Fe^{II}N_6$ environments differ by more than 1.5 V (vide infra). If such bands actually exist in the visible or near-UV region, their detection is made virtually impossible due to the existence of multiple intense transitions localized within the $Fe^{II}N_6$ units in that region. Thus, in acetonitrile, $Fe(RL)_3^-$ (Na^+ or $AsPh_4^+$ salt, see below) absorbs[33] at 640 nm (presumably due to Fe → azo–imine MLCT excitation) with a shoulder at lower energy. Another intense band occurs near 400 nm. The gross

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(28) Polycrystalline EPR data were also collected at room temperature. The spectral features are essentially similar to those at 77 K except for the improved sharpness at the lower temperature. Thus no drastic changes in molecular dimensions occur on cooling to 77 K.

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(33) An earlier report[18] on the spectrum of $NaFe(PhL)_3 \cdot H_2O$ in chloroform is incomplete and has some errors. The correct band maxima (extinction coefficients) in chloroform are as follows (nm (M^{-1} cm^{-1})): 840 (360), 600 (5630), 410 (13140), 285 (43170).

Table V. Electrochemical Data[a,b] at 298 K

complex	$E°_{298}$, V[c,d]	ΔE_p,[c] mV	n (E, V)[e,f]
$[Fe(Fe(PhL)_3)_2]ClO_4$	0.05	60	1.00 (−0.30)
$[Fe(Fe(PhL)_3)_2]ClO_4\cdot 2CHCl_3$	0.04	60	*g*
$[Fe(Fe(MeL)_3)_2]ClO_4\cdot 2H_2O$	0.00	60	0.93 (−0.30)
$[Fe(Fe(MeL)_3)_2]PF_6\cdot 2H_2O$	0.00	60	*g*
$[Fe(Fe(PhL)_3)_2]FeCl_4$	0.02	100	*g*
$[Fe(Fe(MeL)_3)_2]FeCl_4$	0.00	80	2.25 (−0.35)
$[Et_4N]FeCl_4$	0.01	80	*g*
$NaFe(PhL)_3\cdot H_2O$	0.35	80	0.92 (+0.75)
$NaFe(MeL)_3\cdot H_2O$	0.27	120	1.01 (+0.75)
$[Ph_4As][Fe(MeL)_3]\cdot H_2O$	0.25	60	*g*

[a] Unless otherwise stated, meanings of the symbols used are the same as in the text. [b] The solvent is acetonitrile; the supporting electrolyte is TEAP (0.1 M); the working electrode is platinum. [c] Cyclic voltammetric data: scan rate 50 mV s^{-1}. [d] $E°_{298}$ calculated as the average of anodic and cathodic peak potentials. [e] Constant-potential coulometric data. [f] $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated coulomb count for 1e transfer; E is the constant potential at which electrolysis is performed. [g] Measurement not made.

features[34] of the spectra of $Fe_3(RL)_6^+$ and $Fe(RL)_3^-$ are very similar (Figure 4), and no identifiable signs of intervalence transitions are discernible.

C. Reactions. a. Selective Extrusion of Iron(III). Hydroxide ions selectively extrude iron(III) from brown acetone solutions of **1**, liberating the dark green anionic tris complex $Fe(RL)_3^-$ into solution. In the case of **2**, iron(III) from both the cation and the anion are precipitated by similar treatment. Reactions 1 and 2 proceed quantitatively.

$$\mathbf{1} + 3OH^- \rightarrow Fe(OH)_3 + 2Fe(RL)_3^- + ClO_4^- \qquad (1)$$

$$\mathbf{2} + 6OH^- \rightarrow 2Fe(OH)_3 + 2Fe(RL)_3^- + 4Cl^- \qquad (2)$$

The green anion can be conveniently isolated[35] as the sodium[18] or tetraphenylarsonium salts. The ^1H NMR spectrum of $[Ph_4As][Fe(MeL)_3]\cdot H_2O$ in $CDCl_3$ has a single sharp metal signal[36] down to 223 K, strongly suggesting that the $Fe(MeL)_3^-$ moiety (and by inference $Fe(PhL)_3^-$ retains the facial stereochemistry[37] as in the trinuclear parent (Figure 1) even after iron(III) extrusion.

b. Trinuclear Reaggregation. This is simply achieved by adding Fe^{3+} to $Fe(RL)_3^-$ in the correct mole ratio. Reactions 3 and 4

$$2Fe(RL)_3^- + Fe(ClO_4)_3 \rightarrow \mathbf{1} + 2ClO_4^- \qquad (3)$$

$$2Fe(RL)_3^- + 2FeCl_3 \rightarrow \mathbf{2} + 2Cl^- \qquad (4)$$

$$2Fe(RL)_3^- + M^{n+} \rightarrow M(Fe(RL)_3)_2^{(n-2)+} \qquad n = 2, 3 \qquad (5)$$

are very facile and proceed smoothly in ethanol. The reaggregation reaction is quite versatile (reaction 5), and a variety of bivalent and trivalent ions can be used instead of Fe^{3+}, affording many species of types $M^{II}(Fe(RL)_3)_2$ and $M^{III}(Fe(RL)_3)_2^+$. Their chemistry will be reported separately.[38]

c. Redox Reactions. Voltammetric experiments were performed in acetonitrile solutions at a platinum working electrode. The purpose was to ascertain the redox characteristics of the iron(III) and iron(II) centers. The results (Table V, Figure 5) have helped to rationalize the reactions involved in the synthesis of **1** and **2** and to clarify further the nature of **2**. All potentials are referenced to the SCE, and meanings of symbols are as follows: E_{pa}, anodic peak potential; E_{pc}, cathodic peak potential; $\Delta E_p = E_{pa} - E_{pc}$. The formal potential $E°_{298}$ is taken as the average of E_{pa} and E_{pc}.

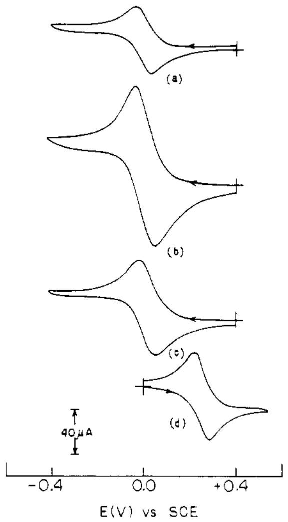

Figure 5. Cyclic voltammograms (scan rate 50 mV s^{-1}) of (a) $[Fe(Fe(ML)_3)_2]ClO_4\cdot 2H_2O$, (b) $[Fe(Fe(MeL)_3)_2]FeCl_4$, (c) $[Et_4N]FeCl_4$, and (d) $[Ph_4As][Fe(MeL)_3]\cdot H_2O$ in acetonitrile (0.1 M TEAP) at a platinum electrode.

Sodium and tetraphenylarsonium salts of $Fe(RL)_3^-$ display a reversible to quasi-reversible (ΔE_p = 60–120 mV) one-electron cyclic response in the potential range 0.2–0.4 V assigned to process 6. In stirred solution facile electrolysis occurs at potentials above

$$Fe^{III}(RL)_3 + e^- \rightleftharpoons Fe^{II}(RL)_3^- \qquad (6)$$

E_{pa} but not at potentials below E_{pc}, confirming that $Fe(RL)_3^-$ undergoes oxidation and not reduction. The one-electron stoichiometry of eq 6 is fully corroborated by coulometric data (Table V). Since Ph is more electron withdrawing than Me, the formal potential of $Fe(PhL)_3^-$ is higher than that of $Fe(MeL)_3^-$. The iron(III)–iron(II) formal potential of anionic $Fe(RL)_3^-$ is much less than that[38] (1.84 V) of the cationic azo–imine complex tris(2-(phenylazo)pyridine)iron(2+). The X-band EPR spectrum ($g_\parallel \approx 2.00$ and $g_\perp \approx 2.13$) of reddish brown $Fe(RL)_3$[39,40] in 1:1 acetonitrile–toluene glass (77 K) is compatible[41,42] with an axially symmetric spin-paired d^5 configuration. Thus both axial symmetry and low-spin characters are conserved in reaction 6.

The trinuclear perchlorate **1** undergoes a one-electron reversible (ΔE_p = 60 mV) reduction near 0.0 V (Figure 5). Coulometry at potentials below E_{pc} produces the green one-electron reductant whose cyclic voltammogram is identical with that of the parent oxidant. The latter can be regenerated from the reductant by coulometry above E_{pa}. These observations are understandable in terms of couple 7, in which the central iron atom alone is redox

$$Fe^{III}[Fe^{II}(RL)_3]_2^+ + e^- \rightleftharpoons Fe^{II}[Fe^{II}(RL)_3]_2 \qquad (7)$$

active. The observed reversibility strongly suggests that the gross stereochemistry of **1** and its reduced congener are the same. The $Fe^{III}O_6$ formal potential in **1** is much higher than that of tris-

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(34) The intensities in $Fe_3(RL)_6^+$ are much higher since the cation has two $Fe(RL)_3^-$ units.

(35) By the respective use of KOH, RbOH, and CsOH in reactions 1 and 2 the K^+, Rb^+, and Cs^+ salts of $Fe(RL)_3^-$ can also be isolated.

(36) The only observable effect of lowering the temperature is a small but systematic increase in δ_{Me} values: 293 K, 2.35; 273 K, 2.40; 253 K, 2.43; 233 K, 2.47; 223 K, 2.49. We have reason to believe that this effect arises from increased cation–anion association and increased anion–solvent hydrogen bonding at lower temperature.

(37) Being the tris chelate of an unsymmetrical bidentate ligand, $Fe(RL)_3^-$ can occur in facial and meridional forms. While $Co(RL)_3$ occurs only in the meridional form,[7] $Rh(RL)_3$ is obtainable in both forms.[8] We now find that $Fe(RL)_3^-$ exists only in the facial form.

(38) Pal, S.; Mukherjee, R.; Chakravorty, A., unpublished results.

(39) The complex is produced in acetonitrile solution by coulometric oxidation[40] of $NaFe(RL)_3\cdot H_2O$. For EPR work the solution is immediately frozen in liquid nitrogen after addition of toluene. The solution of $Fe(RL)_3$ is somewhat unstable at room temperature.

(40) The oxidation of $Fe(RL)_3^-$ by dichlorine in acetonitrile is complex and produces $Fe(RL)_3$, $Fe_3(RL)_6^+$, and $FeCl_4^-$. This is demonstrated by the EPR spectrum of the frozen reaction mixture.

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(42) The reason for the relatively small shift of the *g* values from the free-electron value in the present case is under scrutiny. This phenomenon appears to be a common feature of the EPR spectra of a number of systems with cis placement of two or three oximato groups.

(acetylacetonato)iron(III) (−0.69 V in MeCN)[43] and tris(hydroxamato)iron(III) (~−1 V in MeCN)[44] but is lower than that of $Fe(H_2O)_6^{3+}$ (0.5 V in water).[45]

In **1** the redox process corresponding to couple 6 is not observed up to [46,47] 1.5 V. On binding of $Fe(RL)_3^-$ to cations (eq 5), the oxidation of the iron(II) atom in the former is expected to become more difficult (higher $E°_{298}$). This phenomenon is systematically observed.[38] When the cation is bivalent, the process is still discernible, but for trivalent ions (as in **1**) the formal potential is too high to be identified. We add that the near 0.0-V response (eq 7) is specific for iron(III)-centered **1** and it is not observed[38] in other trinuclear species covered by eq 5.

Preliminary examinations of the stability of coulometrically produced solutions of $Fe^{II}_3(RL)_6$ (eq 7) toward dissociation and oxidation have been made. The R = Ph complex slowly (~5 h) decomposes, forming $Fe(PhL)_3^-$ and other unidentified products. The R = Me complex is stable for at least 24 h. This augmented stability presumably reflects[48] higher (compared to that of the R = Ph case) electron density at the oximato oxygen arising from the electron-donating power of Me. The complexes are quite stable to dioxygen. However, perchloric acid rapidly reoxidizes them to **1**.

The cyclic voltammogram of **2** is virtually identical with that of **1** except that the current heights (and coulomb counts in constant-potential coulometry) are twice as large in the former. This happens because the processes 7 and 8 fortuitously occur at

$$FeCl_4^- + e^- \rightleftharpoons FeCl_4^{2-} \tag{8}$$

the same potential, as confirmed by separately running the voltammogram of $[Et_4N]FeCl_4$ (Figure 5). The voltammogram of a 1:1 mixture of the latter complex and **1** is identical with that of **2** in all respects. The presence of $FeCl_4^-$ in **2** is neatly established by these experiments.

d. Nature of Synthetic Reactions. In the synthesis of $Fe_3(RL)_6^+$ from iron(II) perchlorate and HRL one-third of the iron is oxidized (eq 9) while its formation from iron(III) chloride and HRL involves the reduction of two-thirds of the iron (eq 10). These

$$3Fe^{2+} + 6HRL \rightarrow Fe_3(RL)_6^+ \tag{9}$$

$$3Fe^{3+} + 6HRL \rightarrow Fe_3(RL)_6^+ \tag{10}$$

reactions can now be rationalized in terms of a sequence of primary chelation (eq 11) and subsequent redox transformation (eq 12).

$$2Fe^{x+} \xrightarrow{+6HRL,\ -6H^+} 2Fe(RL)_3^{(x-3)+} \xrightarrow{+Fe^{x+}} Fe_3(RL)_6^{(3x-6)+} \tag{11}$$

$$x = 2:\ Fe_3(RL)_6 \xrightarrow{-e^-} Fe_3(RL)_6^+ \tag{12a}$$

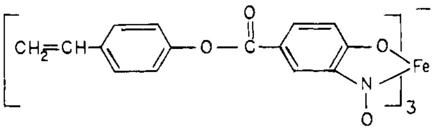
$$x = 3:\ Fe_3(RL)_6^{3+} \xrightarrow{+2e^-} Fe_3(RL)_6^+ \tag{12b}$$

In reaction 9 the formation of the intermediates (eq 11; $x = 2$) is discernible from the initial green color, which rapidly changes to that of $Fe_3(RL)_6^+$. Perchloric acid is known (vide supra) to oxidize $Fe_3(RL)_6$ to $Fe_3(RL)_6^+$. Hence, the perchloric acid liberated (eq 11) during primary chelation of iron(II) perchlorate and HRL is the most plausible oxidant in eq 12a. In the case of reaction 10, the terminal iron(III) atoms in[49] $Fe_3(RL)_6^{3+}$ (eq 11; $x = 3$) are highly oxidizing ($E°_{298} > 1.5$ V, vide supra) and can possibly oxidize, e.g., the solvent (ethanol), resulting in the formation of $Fe_3(RL)_6^+$.

D. Concluding Remarks. An ensemble of six arylazo oxime molecules is ideally suited for trinucleation by iron. The mixed-valence $Fe^{II}_2Fe^{III}$ aggregate is spontaneously formed by facile chelative redox transformations. The subtle rhombic nature of the X-ray-characterized centrosymmetric $Fe^{III}O_6$ coordination sphere is reflected in EPR spectra. The redox properties of $Fe^{III}O_6$ ($S = {}^5/_2$) and $Fe^{II}N_6$ ($S = 0$) are disparate. The FeN_6 chromophore richly absorbs in the visible and near-UV regions, and intervalence bands could not be located. It is believed that the $Fe_3(RL)_6^+$ cation belongs to the weak class II category. The trinucleation capabilities of HRL are potentially widespread: first because of the availability of the facile extrusion and reaggregation reactions and second because of the proven existence[38] of new systems based on metals (Mn, Os, and Rh are examples) other than iron. Explorations in these areas are under way.

The extrusion and reaggregation reactions have another significance: $Fe(RL)_3^-$ should be able to act as a shuttle for other metal ions, collecting them under neutral or slightly acidic conditions and depositing them elsewhere under alkaline conditions. Oximes in which the azo function of HRL is replaced by a different donor group would behave like HRL. Isonitroso ketones[50] and 2-nitrosophenols[51] indeed afford facial $Fe^{II}(bidentate)_3^-$, and there are some indications that these can bind other metal ions.[51,52]

This brings us to consider the green pigment called ferroverdin which occurs[53] in the mycelium of a *Streptomyces* species. Isolated as crystalline sodium salts, the anion of ferroverdin is **3**, a facial 2-nitrosophenol complex of iron(II).[54] Hodgkin et al. state that in different ferroverdin preparations sodium ions may be replaced by other ions, even perhaps by additional iron(II) ions, according to the methods of isolation used.[54] The similarity in the behaviors of $Fe(RL)_3^-$ and **3** is striking. The biological function of ferroverdin is not known. We note that **3** should be well-suited for translocation of metal ions.



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Experimental Section

Materials. Arylazo oximes were prepared as before.[7] Iron(II) perchlorate hexahydrate and iron(III) perchlorate hexahydrate were prepared by respectively dissolving iron powder and freshly precipitated $Fe(OH)_3$ in 70% aqueous perchloric acid and crystallizing the salts. The compound $[Et_4N]FeCl_4$ was prepared by a known procedure.[55] Anhydrous $FeCl_3$ was purchased from Sarabhai M. Chemicals, Baroda, India. Tetraphenylarsonium chloride was obtained from Aldrich Chemical Co., Milwaukee, WI. Ammonium hexafluorophosphate was obtained from E. Merck, Darmstadt, West Germany. The purification of acetonitrile and preparation of tetraethylammonium perchlorate (TEAP) were done as described earlier. Solvents used for synthetic experiments and for spectroscopy and other measurements were of analytical grade available commercially.

Measurements. IR spectra were recorded in KBr disks with the help of a Beckman IR-20A spectrometer. Electronic spectra were measured

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(46) Beyond 1.5 V irreversible oxidation currents are observed due to an unidentified oxidation process presumably involving ligand azo groups.[47] In Na^+ and Ph_4As^+ salts of $Fe(RL)_3^-$ a similar response occurs near 1.2 V.

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(48) Significantly, the p*K* of the R = Ph ligand (9.85) is[14] lower than that of the R = Me ligand (10.10).

(49) There is no clear evidence for the formation or even existence of $Fe_3(RL)_6^{3+}$. However, since $Fe(RL)_3$ exists[39] (eq 6), the postulated formation of the trinuclear complex at least as a transient species is tenable.

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with a Hitachi 330 spectrophotometer. X-Band EPR spectra were recorded with a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). The spectra were calibrated with the help of DPPH ($g = 2.0037$). Variable-temperature ^1H NMR data were collected in $CDCl_3$ with the help of a Bruker WH-360 spectrometer. Magnetic susceptibilities were measured with a Gouy balance using $CoHg(SCN)_4$ as the calibrant or PAR vibrating-sample magnetometer (Model 155) fitted with a Walker Scientific magnet (Model L75FBAL). Solution electrical conductivity measurements were made with a Systronics (Baroda, India) 303 or a Philips (Calcutta, India) 9500 conductivity bridge. Electrochemical measurements were done with the help of a PAR Model 370-4 electrochemistry system incorporating the Model 174A polarographic analyzer, the Model 175 universal programmer, the Model RE0074 X-Y recorder, the Model 173 potentiostat, the Model 179 digital coulometer, and the Model 377A cell system. The three-electrode measurements were carried out with use of a planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). For coulometry a platinum-wire-gauze working electrode was used. All experiments were done at 298 K under a dinitrogen atmosphere, and the reported potentials are uncorrected for junction contribution.

Preparation of Complexes. Bis[tris((phenylazo)benzaldoximato)iron(II)]iron(III) Perchlorate, $[Fe(Fe(PhL)_3)_2]ClO_4$. To an ethanolic solution (15 mL) of HPhL (0.45 g, 0.002 mol) was added dropwise an ethanolic solution (5 mL) of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 0.001 mol). A green color developed, which quickly darkened. The mixture was boiled under reflux for 1 h. It was then cooled to 273 K, and a black solid precipitated. The shining crystalline material was collected by filtration. It was washed with water, dried, and finally washed with hexane. The crystals so obtained were dried and stored under vacuum over P_4O_{10}; yield 0.27 g (50%). Anal. Calcd for $Fe_3C_{78}H_{60}N_{18}O_{10}Cl$: Fe, 10.40; C, 58.10; H, 3.72; N, 15.64. Found: Fe, 10.60; C, 57.91; H, 3.85; N, 15.44. The complex $[Fe(Fe(MeL)_3)_2]ClO_4 \cdot 2H_2O$ (yield 40%) was prepared by the same procedure as described above with use of the ligand HMeL in place of HPhL. Anal. Calcd for $Fe_3C_{48}H_{52}N_{18}O_{12}Cl$: Fe, 13.13; C, 45.17; H, 4.11; N, 20.08. Found: Fe, 13.30; C, 44.88; H, 4.29; N, 19.72.

When a solution of $[Fe(Fe(PhL)_3)_2]ClO_4$ (0.025 g, 0.016 mmol) in chloroform (15 mL) was allowed to diffuse slowly into a hexane (15 mL) layer, dark crystals of composition $[Fe(Fe(PhL)_3)_2]ClO_4 \cdot 2CHCl_3$ resulted, which were used for the X-ray work.

Bis[tris((phenylazo)acetaldoximato)iron(II)]iron(III) Hexafluorophosphate Dihydrate, $[Fe(Fe(MeL)_3)_2]PF_6 \cdot 2H_2O$. To a magnetically stirred solution of $[Fe(Fe(MeL)_3)_2]ClO_4 \cdot 2H_2O$ (0.1 g, 0.08 mmol) in acetonitrile (20 mL) was added dropwise a solution of NH_4PF_6 (0.2 g, 1.23 mmol) in a 3:2 acetonitrile–water mixture (20 mL). Stirring was continued for 1 h. After the solution was concentrated to 10 mL, a shining solid separated. It was collected by filtration and washed thoroughly with water. It was dried under vacuum over P_4O_{10}; yield 0.08 g (80%). Anal. Calcd for $Fe_3C_{48}H_{52}N_{18}O_8F_6P$: Fe, 12.69; C, 43.62; H, 3.94; N, 19.08. Found: Fe, 12.65; C, 43.56; H, 3.90; N, 18.87.

Bis[tris((phenylazo)benzaldoximato)iron(II)]iron(III) Tetrachloroferrate(III), $[Fe(Fe(PhL)_3)_2]FeCl_4$. To a solution of 12.2 g (0.05 mol) of HPhL in 40 mL of ethanol was added dropwise an ethanolic solution (70 mL) of 5.8 g (0.36 mol) of anhydrous $FeCl_3$. Immediately the color darkened. The mixture was heated to reflux for 1 h. A black shining solid started separating. The mixture was then cooled to 273 K and filtered. The solid was washed thoroughly with water, dried, and finally washed with hexane. Recrystallization was done from a chloroform–ethanol (2:1) mixture. The shining black solid so obtained was stored under vacuum over P_4O_{10}; yield 6.2 g (40%). Anal. Calcd for $Fe_4C_{78}H_{60}N_{18}O_6Cl_4$: Fe, 13.07; C, 54.75; H, 3.51; N, 14.74. Found: Fe, 13.45; C, 54.44; H, 3.32; N, 14.76.

The complex $[Fe(Fe(MeL)_3)_2]FeCl_4$ (yield 45%) was prepared similarly. Anal. Calcd for $Fe_4C_{48}H_{48}N_{18}O_6Cl_4$: Fe, 16.70; C, 43.07; H, 3.59; N, 18.84. Found: Fe, 17.10; C, 43.00; H, 3.63; N, 19.65.

Tetraphenylarsonium Tris((phenylazo)acetaldoximato)ferrate(II) Hydrate, $[Ph_4As][Fe(MeL)_3] \cdot H_2O$. To a solution containing $NaFe(MeL)_3 \cdot H_2O$ (0.2 g, 0.34 mmol) in 15 mL of methanol was added dropwise with magnetic stirring a solution of Ph_4AsCl (0.2 g, 0.48 mmol) in 5 mL of water. The green solution was warmed and stirred for 1 h. The solution was then concentrated to 5 mL. The green crystalline precipitate that deposited was filtered, washed with a little ice-cold water, and then dried under vacuum over P_4O_{10}; yield 0.2 g (62%). Anal. Calcd for $FeC_{48}H_{46}N_9O_4As$: Fe, 5.92; C, 61.07; H, 4.88; N, 13.36. Found: Fe, 6.03; C, 60.08; H, 4.82; N, 13.06.

Reaction of $[Fe(Fe(RL)_3)_2]ClO_4$ with Sodium Hydroxide. To a solution of 0.13 g (0.08 mmol) of $[Fe(Fe(PhL)_3)_2]ClO_4$ in 100 mL of acetone was added dropwise an aqueous solution of sodium hydroxide (0.1 mmol in 15 mL of water). The mixture was warmed and stirred for 15 min when it rapidly turned dark green and a brown precipitate of $Fe(OH)_3$ was deposited. The green solution was filtered, and the filtrate was concentrated. Shining green crystals separated. These were collected by filtration and were recrystallized from acetone containing a small amount of aqueous sodium hydroxide. The crystals thus obtained were dried under vacuum over P_4O_{10}. The product was characterized to be $NaFe(PhL)_3 \cdot H_2O$,[18] yield 0.1 g (85%).

Table VI. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$

formula	$[Fe_3(N(O)C(Ph)NN(Ph))_6]ClO_4 \cdot 2CHCl_3$
fw	1851.2 for $Fe_3Cl_7C_{80}N_{18}O_{10}H_{62}$
space group	$P2_1/n$
a, Å	15.521 (4)
b, Å	12.743 (5)
c, Å	21.788 (5)
β, deg	104.35 (2)
V, Å^3	4175 (2)
Z	2
d_{calcd}, g/cm^3	1.48
μ(Mo Kα), cm^{-1}	8.28
data collecn instrument	Enraf-Nonius CAD-4, Syntex $P\bar{1}$ (see text)
radiation	Mo Kα ($\lambda_\alpha = 0.71073$ Å), graphite monochromated
scan method	$2\theta-\omega$
data range, deg	$4 < 2\theta < 48$
no. of unique data, $F_o^2 \geqslant 2\sigma(F_o^2)$	2697
no. of parameters refined	509
R^a	0.0881
$R_w{}^b$	0.1281
quality-of-fit indicator^c	0.974
largest shift/esd, final cycle	0.05

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F|) + (0.125|F|)^2]^{-1}$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

The precipitate of $Fe(OH)_3$ was quantitatively dissolved in 6 N HCl. The iron was estimated volumetrically with standard $K_2Cr_2O_7$ solution with use of standard procedures. The calculated percentage of iron(III) in $[Fe(Fe(PhL)_3)_2]ClO_4$ is 3.47%; that found from deposited $Fe(OH)_3$ is 3.53%.

The complex $[Fe(Fe(MeL)_3)_2]ClO_4 \cdot 2H_2O$ reacted similarly with sodium hydroxide, affording crystalline $NaFe(MeL)_3 \cdot H_2O$.[18] The iron(III) precipitated as $Fe(OH)_3$ was estimated. Anal. Calcd: Fe(III), 4.38. Found: Fe(III), 4.43.

The reactions of sodium hydroxide with $[Fe(Fe(PhL)_3)_2]FeCl_4$ and $[Fe(Fe(MeL)_3)_2]FeCl_4$ produced[18] $NaFe(PhL)_3 \cdot H_2O$ and $NaFe(MeL)_3 \cdot H_2O$, respectively. In each case the iron(III) content estimated as before, was found to be half of the total iron present in the precursor complexes.

Reaction of Sodium Salts of $Fe(RL)_3^-$ with Iron(III) Salts. To a solution containing $NaFe(PhL)_3 \cdot H_2O$ (0.2 g, 0.26 mmol) in ethanol (20 mL) was added $Fe(ClO_4)_3 \cdot 6H_2O$ (0.07 g, 0.15 mmol), and the mixture was heated to reflux for 2 h. The deposited crystalline black solid was filtered, washed thoroughly with water, and dried under vacuum over P_4O_{10}. The product obtained was found to be $[Fe(Fe(PhL)_3)_2]ClO_4$, yield 0.17 g (80%). The reaction between $NaFe(MeL)_3 \cdot H_2O$ and $Fe(ClO_4)_3 \cdot 6H_2O$ was carried out similarly, and the product was identified as $[Fe(Fe(MeL)_3)_2]ClO_4 \cdot 2H_2O$ (yield 80%).

To an ethanolic solution (25 mL) of $NaFe(PhL)_3 \cdot H_2O$ (0.1 g, 0.13 mmol) was added an ethanolic solution (5 mL) of anhydrous iron(III) chloride (0.025 g, 0.15 mmol). The color immediately turned greenish black, and the reaction mixture was heated to reflux for 1 h. The black crystalline solid thus obtained was found to be identical with $[Fe(Fe(PhL)_3)_2]FeCl_4$, yield 0.06 g (55%). The complex $[Fe(Fe(MeL)_3)_2]FeCl_4$ (yield 50%) was obtained similarly by starting from $NaFe(MeL)_3 \cdot H_2O$ and iron(III) chloride.

Crystal Structure Determination. Data Collection and Reduction. Since the data collection procedure was not routine, a summary will be given. Data were gathered from two crystals, each mounted at the end of a glass fiber and covered with a thin layer of epoxy.

The first crystal, with dimensions 0.35 × 0.25 × 0.25 mm, was mounted on a CAD-4F diffractometer. The automatic procedures of the diffractometer were used to locate and to position accurately 25 reflections in the range $20 < 2\theta < 29°$. These were used for the determination of the lattice parameters and orientation matrix, by the usual indexing

Table VII. Atomic Positional Parameters and Isotropic-Equivalent Thermal Parameters[a,b,c] and Their Estimated Standard Deviations[c] for $[Fe_3(PhL)_6]ClO_4 \cdot 2CHCl_3$

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Fe(1)	0.000	0.000	0.000	3.38 (6)	C(20)	0.266 (1)	−0.345 (1)	0.0587 (8)	7.7 (5)
Fe(2)	0.2098 (1)	0.0400 (1)	0.10075 (8)	2.84 (3)	C(21)	0.3258 (9)	−0.0622 (9)	0.2219 (6)	4.1 (3)
O(1)	0.0710 (6)	0.1356 (6)	0.0072 (4)	3.7 (2)	C(22)	0.291 (1)	−0.022 (1)	0.2680 (7)	6.5 (5)
O(2)	0.1094 (6)	−0.0846 (7)	−0.0012 (4)	4.0 (2)	C(23)	0.343 (2)	−0.019 (2)	0.3295 (8)	10.2 (7)
O(3)	0.0285 (5)	−0.0134 (7)	0.0948 (4)	3.7 (2)	C(24)	0.434 (2)	−0.055 (2)	0.3411 (9)	14.0 (7)
N(1)	0.3078 (7)	0.0643 (7)	0.0643 (5)	4.0 (3)	C(25)	0.466 (1)	−0.100 (2)	0.2974 (9)	10.4 (6)
N(2)	0.2962 (7)	0.1188 (8)	0.0139 (6)	4.8 (3)	C(26)	0.4136 (9)	−0.107 (1)	0.2317 (8)	6.2 (4)
N(3)	0.1578 (6)	0.1204 (7)	0.0269 (4)	2.7 (2)	C(27)	0.0946 (9)	0.102 (1)	0.1734 (5)	3.8 (3)
N(4)	0.2707 (6)	−0.0690 (8)	0.1573 (4)	3.3 (2)	C(28)	0.0219 (9)	0.109 (1)	0.2042 (7)	4.9 (4)
N(5)	0.2692 (7)	−0.1609 (8)	0.1344 (4)	3.3 (2)	C(29)	−0.061 (1)	0.089 (1)	0.1755 (8)	6.9 (5)
N(6)	0.1740 (7)	−0.0850 (8)	0.0528 (4)	3.4 (2)	C(30)	−0.132 (1)	0.090 (2)	0.207 (1)	10.3 (7)
N(7)	0.2285 (6)	0.1523 (7)	0.1638 (5)	3.3 (2)	C(31)	−0.109 (1)	0.121 (2)	0.2733 (9)	9.4 (5)
N(8)	0.1667 (7)	0.1657 (8)	0.1946 (5)	4.0 (3)	C(32)	−0.018 (1)	0.143 (2)	0.3019 (8)	8.3 (5)
N(9)	0.0995 (7)	0.0421 (8)	0.1247 (5)	3.7 (2)	C(33)	0.048 (1)	0.134 (1)	0.2691 (7)	6.0 (4)
C(1)	0.2133 (9)	0.154 (1)	−0.0047 (6)	4.1 (3)	C(34)	0.3016 (9)	0.221 (1)	0.1849 (7)	4.5 (3)
C(2)	0.191 (1)	0.228 (1)	−0.0604 (6)	4.5 (3)	C(35)	0.3339 (9)	0.239 (1)	0.2524 (7)	5.2 (4)
C(3)	0.109 (1)	0.251 (2)	−0.0942 (7)	7.8 (5)	C(36)	0.406 (1)	0.310 (1)	0.2697 (8)	6.2 (4)
C(4)	0.098 (1)	0.319 (2)	−0.1465 (9)	10.3 (6)	C(37)	0.443 (1)	0.358 (1)	0.2268 (9)	6.9 (5)
C(5)	0.167 (2)	0.374 (2)	−0.156 (1)	11.5 (8)	C(38)	0.407 (1)	0.344 (1)	0.1614 (9)	6.9 (5)
C(6)	0.252 (1)	0.372 (2)	−0.1129 (9)	8.9 (6)	C(39)	0.336 (1)	0.273 (1)	0.1409 (7)	5.2 (4)
C(7)	0.269 (1)	0.297 (1)	−0.0614 (8)	7.7 (5)	C(40)	0.671 (2)	0.342 (3)	0.142 (2)	17 (1)*
C(8)	0.3974 (9)	0.008 (1)	0.0790 (7)	5.3 (4)	Cl(1)	0.500	0.500	0.000	11.3 (3)
C(9)	0.406 (1)	−0.077 (1)	0.0430 (8)	7.0 (4)	Cl(2)	0.7812 (9)	0.317 (1)	0.1147 (6)	14.5 (4)*
C(10)	0.491 (1)	−0.126 (1)	0.0563 (9)	11.2 (6)	Cl(3)	0.626 (1)	0.212 (1)	0.1262 (8)	17.1 (5)*
C(11)	0.559 (1)	−0.084 (2)	0.108 (1)	10.0 (7)	Cl(4)	0.709 (1)	0.369 (2)	0.214 (1)	22.4 (8)*
C(12)	0.543 (1)	−0.004 (2)	0.145 (1)	10.4 (7)	Cl(5)	0.651 (2)	0.275 (2)	0.208 (1)	16.6 (9)*
C(13)	0.463 (1)	0.044 (2)	0.134 (1)	9.5 (7)	Cl(6)	0.703 (2)	0.246 (3)	0.086 (2)	22 (1)*
C(14)	0.2101 (8)	−0.1706 (8)	0.0753 (5)	3.0 (3)	Cl(7)	0.778 (2)	0.396 (3)	0.164 (2)	21 (1)*
C(15)	0.1915 (9)	−0.2800 (9)	0.0504 (5)	3.8 (3)	O(4)	0.504 (3)	0.507 (4)	0.061 (2)	18 (1)*
C(16)	0.108 (1)	−0.309 (1)	0.0171 (8)	6.0 (4)	O(5)	0.560 (4)	0.396 (5)	−0.009 (3)	23 (2)*
C(17)	0.091 (1)	−0.414 (1)	−0.0020 (8)	7.5 (5)	O(6)	0.439 (4)	0.480 (6)	−0.036 (3)	23 (2)*
C(18)	0.162 (2)	−0.479 (2)	0.000 (1)	9.8 (6)	O(7)	0.546 (3)	0.577 (4)	−0.023 (2)	18 (1)*
C(19)	0.254 (1)	−0.449 (1)	0.0330 (9)	8.2 (5)					

[a] $B = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac \cos\beta]$. [b] Entries marked with an asterisk correspond to atoms refined isotropically. [c] Numbers in parentheses are estimated standard deviations in the least significant digits.

and least-squares methods. The $2\theta-\omega$ motion was used to scan the bisecting positions of 7579 possible data points in the range $4 \leq 2\theta \leq 48°$, with $\Delta\omega$ calculated as $(0.85 + 0.35 \tan \omega)°$. Three check reflections, measured after every 1 h of X-ray exposure time, showed an average loss of intensity of 23.1% during the 131 h of data collection. An interpolative anisotropic decay correction was applied during data reduction.[56] Azimuthal scans of nine reflections were used as the basis of an empirical absorption correction,[57] but it was found that the intensities varied by only ca. 10% as the crystal was rotated about the scattering vector of each reflection. Axial photographs were used to verify the Laue class ($2/m$) and lattice dimensions of this crystal. Systematic absences from the data unambiguously identified the space group as $P2_1/n$.

The second crystal was mounted on a Syntex $P\bar{1}$ diffractometer. Routine procedures were used to verify the lattice dimensions and to obtain the orientation matrix, which was refined by a least-squares fit to the positions of 15 accurately located reflections in the range $20 < 2\theta < 29°$. Axial photography was used to verify the lattice dimensions, Laue group, and crystal quality. Intensity data were gathered in the range $33 \leq 2\theta \leq 47.5°$, by the $2\theta-\omega$ technique. The intensities of 3 check reflections were measured after every 97 data scans. We observed that these intensities dropped suddenly after about 70 h of X-ray exposure time. We observed further that the crystal and most of its epoxy cover had left their mount, with only the base of the crystal and a small partial shell of epoxy remaining attached to the glass fiber. The cause of this is unknown, but we can speculate that it is related to the process that caused a continuous decay in the check-reflection intensities from the beginning of data collection. The second crystal had given 1114 data scans by the time the data collection was stopped. Routine data reduction included an interpolative decay correction, since the check reflections had lost an average of approximately 25% of their intensities in 71.4 h of beam time.

Data from the two crystals were merged by a least-squares method[58] with a merging *R* factor of 0.0551. There were 2697 unique reflections with $F_o^2 > 2\sigma(F_o^2)$ for use in structure solution and refinement.

Structure Solution and Refinement. The structure was solved by Patterson techniques and developed and refined by an alternating sequence of difference maps and least-squares cycles. In the last least-squares cycle, 509 variable parameters were fitted to 2697 reflections, giving a data-to-parameter ratio of 5.3:1. The weight of each observed reflection was calculated[59] as $[\sigma^2(|F|) + (0.125|F|)^2]^{-1}$, with the constant 0.125 chosen so as to make the least-squares variance approach its theoretical limit. The refinement converged with residuals of $R = 0.0881$ and $R_w = 0.1281$ and a goodness-of-fit indicator of 0.974. These and other crystal parameters and data are summarized in Table VI. The last refinement cycle did not shift any parameter by more than 0.05 times its estimated standard deviation. A difference Fourier map following convergence contained no peak more dense than 0.72 e/Å^3. There was no serious correlation effect in the final refinement. Atomic coordinates and isotropic-equivalent thermal parameters are given in Table VII.

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Registry No. **1** (R = Ph), 94978-78-6; **1**$\cdot 2CHCl_3$ (R = Ph), 94978-79-7; [**1**]ClO_4 (R = Me), 94993-06-3; **2** (R = Ph), 94978-82-2; **2** (R = Me), 94978-83-3; $[Fe_3(MeL)_6]PF_6$, 94978-81-1; $[Ph_4As][Fe(MeL)_3]$, 94978-85-5; $NaFe(PhL)_3$, 70224-24-7; $NaFe(MeL)_3$, 70198-84-4.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table VIII), root-mean-square amplitudes of thermal vibrations (Table IX), bond distances (Table X), bond angles (Table XI), least-squares planes (Table XII), torsion angles (Table XIII), and observed and calculated structure factors (Table XIV) (28 pages). Ordering information is given on any current masthead page.

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(56) Data were processed on the VAX-11/780 computer in the Chemistry Department at Texas A&M University with software from SHELX76 and from the Enraf-Nonius package VAX SDP.

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