

Metal Ion Incorporation Reactions of the Cluster $[\text{Fe}_3\text{S}_4(\text{LS}_3)]^{3-}$, Containing the Cuboidal $[\text{Fe}_3\text{S}_4]^0$ Core

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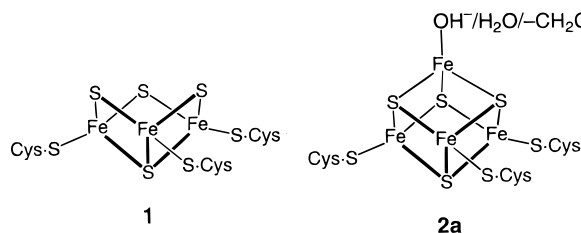
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Abstract: The frequent occurrence of the cuboidal cluster $[\text{Fe}_3\text{S}_4(\text{S}\cdot\text{Cys})_3]$ in a variety of proteins has prompted extensive investigation of its chemical and biological properties. The biological function remains in question, but the cluster is known to sustain two reactions: (i) electron transfer, and (ii) heterometal ion incorporation. The recent preparation of $[\text{Fe}_3\text{S}_4(\text{LS}_3)]^{3-}$ (**3**) [Zhou, J.; Hu, Z.; Münck, E.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 1966] has permitted detailed structural, electronic, and reactivity characterization of the cuboidal $[\text{Fe}_3\text{S}_4]^0$ oxidation state ($\text{LS}_3 = 1,3,5\text{-tris}((4,6\text{-dimethyl-3-mercaptophenylthio})-2,4,6\text{-tris}(p\text{-tolylthio})\text{benzene}(3-))$). Redox properties (i) have been reported previously: here reaction type (ii), resulting in the formation of cubane-type MFe_3S_4 clusters, has been investigated. Reaction of **3** with $[\text{M}(\text{PPh}_3)_4]^{1+}$ affords $[(\text{Ph}_3\text{P})\text{MFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ ($\text{M} = \text{Cu}$ (**6**), Ag (**8**)) while $[(\text{NC})\text{M}(\text{PPh}_3)_3]$ leads to $[(\text{NC})\text{MFe}_3\text{S}_4(\text{LS}_3)]^{3-}$ ($\text{M} = \text{Cu}$ (**7**), Ag (**9**)). Treatment of **3** with $\text{Ti}(\text{O}_3\text{SCF}_3)$ yields $[\text{TiFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ (**10**). The fragment formalism $\{\text{M}^{1+} + [\text{Fe}_3\text{S}_4]^0\}$ applies to **6–10**, which retain the $S = 2$ ground state of **3**. Reaction of **3** with $[\text{M}(\text{PPh}_3)_3\text{Cl}]$ yields $[(\text{Ph}_3\text{P})\text{MFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ ($\text{M} = \text{Co}$ (**12**), Ni (**14**)) in inner-sphere redox reactions. Clusters **12** ($S = 1$) and **14** ($S = 3/2$) are formulated as $\{\text{M}^{2+} + [\text{Fe}_3\text{S}_4]^{1-}\}$; antiferromagnetic coupling of fragment spins gives rise to the indicated spin ground states. The reactions (ii) are metal-ion incorporation processes, a new reaction type in Fe–S chemistry. Previously, all cubane-type MFe_3S_4 clusters had been synthesized by spontaneous self-assembly or reductive rearrangement reactions. Cluster **7** exhibits reversible oxidation and reduction reactions; it is the only cluster that forms a stable oxidized product containing the $[\text{Fe}_3\text{S}_4]^{1+}$ fragment. All other clusters show a reversible reduction and an irreversible or quasireversible oxidation. Potentials of the synthetic clusters are considered intrinsic to the various core units, being less influenced by environmental factors than are those in proteins. At parity of cluster charge and terminal ligation, the potential order is $\text{M} = \text{Fe} < \text{Co} < \text{Ni}$ and $\text{Co} < \text{Ni} < \text{Cu} < \text{Ag} < \text{Ti}$ for the $[\text{MFe}_3\text{S}_4]^{2+,1+}$ and $[\text{MFe}_3\text{S}_4]^{1+,0}$ core redox reactions. These orders are compared with those determined in proteins.

Introduction

The cuboidal $\text{Fe}_3\text{S}_4(\text{S}\cdot\text{Cys})_3$ cluster **1**,¹ with its distinctive spectroscopic^{2–5} and electrochemical^{6,7} features, is now readily recognized and commonly found in proteins.^{8,9} Its structure, as an essentially congruent fragment of the cubane-type $\text{Fe}_4(\mu_3\text{-S})_4$ cluster, has been amply verified by protein crystallography.^{10–13} The occurrence of **1** is now generally

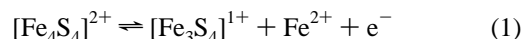
associated with a protein structure that supplies only three cysteinate residues as terminal ligands to a single cluster. In this way, the precursor Fe_4S_4 cluster **2a** contains one iron atom that is ligated by water, hydroxide,¹⁴ or another type of protein ligand such as carboxylate.¹⁵ Oxidation of the $[\text{Fe}_4\text{S}_4]^{2+}$ state



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can result in release of the less tightly bound iron atom under the stoichiometry of minimal reaction 1. A likely intermediate



state is $[\text{Fe}_4\text{S}_4]^{3+}$, which would be prone to lose Fe^{2+} owing to the reduced binding affinity of the sulfur atoms by the mean oxidation state $\text{Fe}^{2.75+}$ and weaker terminal ligation at the unique iron site. Correspondingly, the presence of three Fe^{3+} sites in the product core renders the $\mu_2\text{-S}$ atoms insufficiently basic to retain Fe^{2+} . Under reducing conditions, the trinuclear cluster

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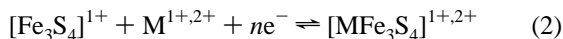
Table 1. Protein-Bound Heterometal Cubane-Type Cores Formed by Metal Ion Incorporation Reactions

core	spin	protein ^a	ref
$[\text{MnFe}_3\text{S}_4]^{1+}$	$S = 0$	<i>Pf</i> Fd	19
$[\text{CoFe}_3\text{S}_4]^{2+}$	$S = 1/2$	<i>Dg</i> Fd II; <i>Pf</i> Fd	17, 18; 19
$[\text{CoFe}_3\text{S}_4]^{1+}$	$S = 1$		
$[\text{NiFe}_3\text{S}_4]^{2+}$	$S = 1^b$	<i>Dg</i> Fd II; <i>Pf</i> Fd	18; 20, 21
$[\text{NiFe}_3\text{S}_4]^{1+}$	$S = 3/2$		
$[\text{ZnFe}_3\text{S}_4]^{2+}$	$S = 2$	<i>Da</i> Fd III; <i>Dg</i> Fd II; <i>Pf</i> Fd	22; 23; 19, 21
$[\text{ZnFe}_3\text{S}_4]^{1+}$	$S = 5/2$		
$[\text{CdFe}_3\text{S}_4]^{2+}$	$S = 2^b$	<i>Da</i> Fd III; <i>Dg</i> Fd II	22; 18
$[\text{CdFe}_3\text{S}_4]^{1+}$	$S = 5/2$		
$[\text{CuFe}_3\text{S}_4]^{2+}$	$S = 1/2$	<i>Da</i> Fd II	24
$[\text{CuFe}_3\text{S}_4]^{1+}$	$S = 2$		
$[\text{TlFe}_3\text{S}_4]^{2+}$	$S = 1/2$	<i>Da</i> Fd III	25, 26
$[\text{TlFe}_3\text{S}_4]^{1+}$	$S = 2$		

^a *Pf* = *Pyrococcus furiosus*, *Dg* = *Desulfovibrio gigas*, *Da* = *Desulfovibrio africanus*. ^b Predicted value (see text).

can be reconstituted to the cubane form by the reverse of reaction 1. In this process, the $[\text{Fe}_3\text{S}_4]^0$ core is doubtless first formed, and is a sufficiently good ligand to bind Fe^{2+} , which is firmly retained in the $[\text{Fe}_4\text{S}_4]^{2+}$ core.

Although cluster **1** has been detected in over 30 proteins, its biological function(s), if other than as an electron storage and transfer center, remains obscure. Indeed, it may be the case that property changes (possibly structural) of a protein molecule attendant to the assembly or disassembly of an Fe_4S_4 center by reaction 1 are implicated in putative non-redox functions of **1**.¹⁶ In any event, the only known non-redox reaction of protein-bound Fe_3S_4 clusters is assembly of Fe_4S_4 clusters by reaction 1, and construction of heterometal cubane-type MFe_3S_4 clusters by reactions with exogenous metal ions. Of the latter, the first such reaction, resulting in the formation of the $[\text{CoFe}_3\text{S}_4]^{2+}$ cluster, was described in 1986.¹⁷ Since that time, trinuclear clusters in three proteins have been reconstituted by generalized reaction 2 ($n = 1, 2$) to afford the cluster cores set out in Table 1.^{17–26} Although there have been no mechanistic studies of this reaction, it is entirely probable that chemical or electrochemical reduction generates the $[\text{Fe}_3\text{S}_4]^0$ state, which then binds the



exogenous metal ion. With divalent metal ions, cluster species

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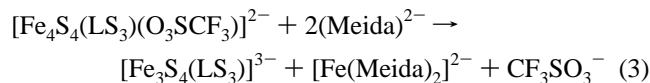
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are formed that contain the $[\text{Fe}_3\text{S}_4]^{1-}$ fragment, which has not yet been independently generated by chemical or direct electrochemical reduction of proteins. In the absence of metal ions, the $[\text{Fe}_3\text{S}_4]^0$ state is reduced in a two-electron proton-coupled process to an all-ferrous core unit.^{6,7,9,22} Consequently, it is likely that in these cases an initial $[\text{MFe}_3\text{S}_4]^{2+}$ cluster is reduced intact to the $[\text{MFe}_3\text{S}_4]^{1+}$ state.

Recently, we have reported the first synthesis of a cuboidal Fe_3S_4 cluster and its crystallographic structure proof.^{27,28} The cluster is readily prepared by the non-redox reaction 3, in which



$\text{Fe}(\text{II})$ is abstracted from the core by the facial tridentate ligand *N*-methylimidodicetate.²⁹ Stability is markedly promoted by use of the semirigid trithiolate ligand LS_3 ,³¹ with the result that the trinuclear cluster is completely stable for at least 1 week in solvents such as acetonitrile and Me_2SO under anaerobic conditions. Clusters with conventional thiolate ligands have lifetimes of several hours or less, and tend to decay mainly to the cubane species $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$. The structure of $[\text{Fe}_3\text{S}_4(\text{LS}_3)]^{3-}$, depicted as **3** in Figure 1, reveals its core to be congruous with any Fe_3S_4 fragment of $[\text{Fe}_4\text{S}_4(\text{LS}_3)\text{Cl}]^{2-}$; thus the cuboidal cluster bears the same geometric relationship to a parent cluster as does protein-bound **1** to **2a**. In turn, $[\text{Fe}_3\text{S}_4(\text{LS}_3)]^{3-}$ and **1** exhibit highly similar core structures. Further, the electronic structures of the native and synthetic clusters, in the $[\text{Fe}_3\text{S}_4]^0$ oxidation state with spin $S = 2$, are practically indistinguishable.²⁸ Access to stable clusters bearing a convincing electronic and geometric relationship to **1** permits scrutiny of metal ion binding propensities of a cuboidal cluster analogous to protein-bound clusters, without whatever complications or benefits protein structure may impose. In this laboratory, we have previously synthesized numerous MFe_3S_4 clusters with a variety of heterometals ($\text{M} = \text{V}, \text{Nb}, \text{Mo}, \text{W}, \text{Re}$). Such clusters are generally prepared in self-assembly systems utilizing tetrathiometalates as the source of the heterometal,³² rather than by direct reaction of the *M* source with a preformed Fe_3S_4 cluster. In this investigation, we have examined the reactions of the cuboidal $[\text{Fe}_3\text{S}_4]^0$ core and a variety of heterometals, with particular interest in binding affinities, relative stabilities of cluster products, and the influence of the heterometal on redox potentials.

Experimental Section²⁹

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere in an inert atmosphere box or standard Schlenk techniques. Solvents were dried and degassed prior to use.

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(29) Abbreviations: $\text{LS}_3 = 1,3,5$ -tris((4,6-dimethyl-3-mercaptophenyl)-thio)-2,4,6-tris(*p*-tolylthio)benzene(3-); Smes, mesitylenethiolate(1-); Meida, *N*-methylimidodiacetate(2-); Stib, 2,4,6-triisopropylbenzenethiolate(1-).

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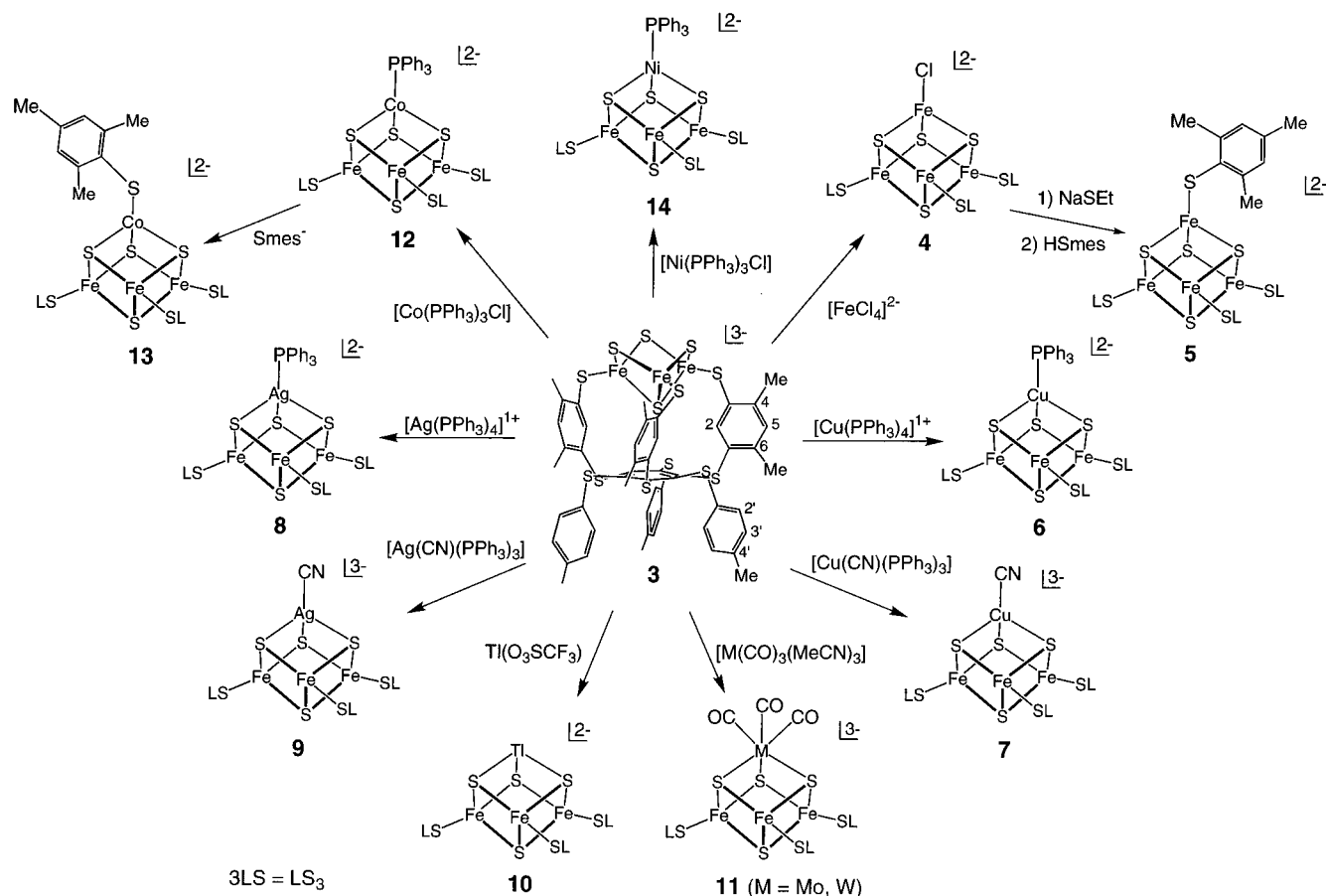
FORMATION OF HETEROMETAL CLUSTERS $[\text{MFe}_3\text{S}_4]$ 

Figure 1. Metal ion incorporation reactions of cuboidal cluster **3** in acetonitrile solution leading to the homo- and heterometal cubane-type clusters **4–14**.

Note the LS₃ ligand numbering scheme (Figure 1). Certain resonances of Ph₃P-ligated clusters were obscured by the presence of excess phosphine in the preparations.

(Bu₄N)₂[(Smes)Fe₄S₄(LS₃)]. To a solution of 17.5 mg (9.51 μmol) of (Bu₄N)₂[Fe₄S₄(LS₃)(SEt)]³³ in 2 mL of acetonitrile was added a solution of 2.72 μL (17.9 μmol) of mesitylenethiol³⁴ in 0.5 mL of acetonitrile. The resulting solution was stirred for 30 min, and solvent was removed *in vacuo* to leave a black solid. The solid was washed with Et₂O (5 mL) and dried *in vacuo* to afford the desired product in quantitative yield. ¹H NMR (MeCN, anion): δ 8.14 (5-H + *m*-H), 7.11 (2'-H), 6.83 (3'-H), 5.17 (2-H), 3.79 (6-Me), 3.73 (4-Me), 3.40 (*o*-Me), 3.18 (*p*-Me), 2.22 (4'-Me).

(Et₄N)₂[(Ph₃P)CuFe₃S₄(LS₃)]. To a solution of 100 mg (61.2 μmol) of (Et₄N)₃[Fe₃S₄(LS₃)]²⁸ in 25 mL of acetonitrile was added a solution of [Cu(PPh₃)₄](ClO₄)³⁵ formed *in situ* by the addition of 65.0 mg (0.241 mmol) of Ph₃P to a solution of 17.2 mg (0.0603 mmol) of [Cu(MeCN)₄](ClO₄)³⁶ in 5 mL of acetonitrile. The reaction mixture was stirred for 1 h and solvent was removed *in vacuo*, affording a black microcrystalline product. The Ph₃P remaining was not removed owing to its stabilizing effect on the cluster in solution. The ¹H NMR spectrum of the solid revealed that, in addition to Ph₃P, the cluster products consisted of 92% of the desired product and 8% of [Fe₄S₄(LS₃)L']¹⁻ (L' = Ph₃P/solvent). ¹H NMR (MeCN, anion): δ 16.16 (5-H), 13.92 (6-Me), 10.14 (4-Me).

(Et₄N)₃[(NC)CuFe₃S₄(LS₃)]. To a solution of 143 mg (87.6 μmol) of (Et₄N)₃[Fe₃S₄(LS₃)] and 36 mg (88.7 μmol) of (Et₄N)₂(Meida)²⁸ in 50 mL of acetonitrile was added a solution of 115 mg (0.128 mmol)

of [Cu(CN)(PPh₃)₃]³⁷ in 10 mL of dichloromethane. The reaction mixture was stirred for 1 h; its volume was reduced to 5 mL *in vacuo*, causing the separation of a black precipitate. Dichloromethane (5 mL) was added, and the product was collected as 120 mg (80%) of a black solid. ¹H NMR (MeCN, anion): δ 15.82 (5-H), 13.32 (6-Me), 9.49 (4-Me). The NMR spectrum indicated the presence of ca. 5% [(Ph₃P)CuFe₃S₄(LS₃)]²⁻ relative to the desired cluster.

(Et₄N)₂[(Ph₃P)AgFe₃S₄(LS₃)]. To a solution of 100 mg (61.2 μmol) of (Et₄N)₃[Fe₃S₄(LS₃)] was added a solution of [Ag(PPh₃)₄](ClO₄)³⁵ formed *in situ* by the addition of 65 mg (0.241 mmol) of PPh₃ to a solution of 13.8 mg (66.6 μmol) of Ag(ClO₄) in 5 mL of acetonitrile. The reaction mixture was stirred for 1 h, and the solvent was removed *in vacuo*, leaving a black solid. The Ph₃P remaining was not removed owing to its stabilizing effect on the cluster in solution. The ¹H NMR spectrum indicated the presence, in addition to Ph₃P, of ca. equal quantities of the desired product and [Fe₄S₄(LS₃)L']¹⁻ (L' = Ph₃P/solvent). ¹H NMR (MeCN, anion): δ 16.11 (5-H), 13.76 (6-Me), 10.25 (4-Me).

(Et₄N)₃[(NC)AgFe₃S₄(LS₃)]. To a solution of 141 mg (86.3 μmol) of (Et₄N)₃[Fe₃S₄(LS₃)] and 35.0 mg (86.3 μmol) of (Et₄N)₂(Meida) in 30 mL of acetonitrile was added a solution of 119 mg (0.126 mmol) of [Ag(CN)(PPh₃)₃]³⁷ in 5 mL of dichloromethane. The reaction mixture was stirred 30 min and its volume was reduced to 3 mL *in vacuo*. Dichloromethane (5 mL) was slowly added, causing separation of the pure product as 128 mg (84%) of black microcrystalline solid. ¹H NMR (MeCN, anion): δ 15.90 (5-H), 13.29 (6-Me), 9.83 (4-Me).

(Et₄N)₂[(Ti)Fe₃S₄(LS₃)]. A solution of 100 mg (61.2 μmol) of (Et₄N)₃[Fe₃S₄(LS₃)] in 10 mL of DMF was added to a solution of (Et₄N)[Ti(Meida)], prepared by combining solutions of 26.0 mg (73.6 μmol) of Ti(OTf) in 1 mL of Me₂SO and 29.8 mg (73.5 μmol) of (Et₄N)₂(Meida) in 3 mL of acetonitrile. The reaction mixture was stirred for 30 min,

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and 20 mL of ether was added. The resultant black microcrystalline solid was collected as 90 mg (86%) of pure product. 1H NMR (MeCN, anion): δ 16.25 (5-H), 14.10 (6-Me), 10.59 (4-Me), 7.53 (2'-H), 6.36 (3'-H), 2.36 (4'-Me).

$(Et_4N)_2(Ph_3P)CoFe_3S_4(LS_3)$. To a solution of 100 mg (61.2 μ mol) of $(Et_4N)_3[Fe_3S_4(LS_3)]$ in 25 mL of acetonitrile was added a solution of 53.8 mg (59.6 μ mol) of $[Co(Ph_3P)_3Cl]^{38}$ in 5 mL of THF. The reaction mixture was stirred for 30 min, and solvent was removed *in vacuo* to afford a black microcrystalline solid. The Ph_3P remaining was not removed owing to its stabilizing effect on the cluster in solution. 1H NMR (MeCN, anion): δ 12.55 (5-H), 10.12 (*p*-H), 9.56 (6-Me), 9.32 (*o*-H), 7.32 (4-Me), 6.44 (3'-H), 5.75 (*m*-H).

$(Et_4N)_2(Ph_3P)NiFe_3S_4(LS_3)$. To a solution of 100 mg (61.2 μ mol) of $(Et_4N)_3[Fe_3S_4(LS_3)]$ in 25 mL of acetonitrile was added a solution of 54.0 mg (59.9 μ mol) of $[Ni(PPh_3)_3Cl]^{39}$ in 5 mL of THF. The reaction mixture was stirred for 30 min, and the solvent was removed *in vacuo* to give a black microcrystalline solid. The Ph_3P remaining was not removed owing to its stabilizing effect on the cluster in solution. 1H NMR (MeCN, anion): δ 14.50 (5-H), 12.23 (6-Me), 11.22 (*p*-H), 9.63 (*o*-H), 8.80 (4-Me), 6.20 (3'-H), 4.17 (*m*-H), 2.45 (4'-Me).

Physical Measurements. 1H NMR spectra were obtained by using a Bruker AM-400 spectrometer. Electrochemical measurements were carried out with a PAR Model 263 potentiostat/galvanostat with a Pt working electrode and 0.1 M $(Bu_4N)(PF_6)$ supporting electrolyte. Potentials were measured at 298 K and are referenced to a SCE.

Results and Discussion

The following clusters **3–14** are of principal interest in this work; of these, **3**, **4**, and **11** have been prepared previously. Schematic structures and methods of preparation of clusters **3–14** are set out in Figure 1.

$[Fe_3S_4(LS_3)]^{3-}$	3 ^{27–29}
$[Fe_4S_4(LS_3)Cl]^{2-}$	4 ³¹
$[Fe_4S_4(LS_3)(Smes)]^{2-}$	5
$[(Ph_3P)CuFe_3S_4(LS_3)]^{2-}$	6
$[(NC)CuFe_3S_4(LS_3)]^{3-}$	7
$[(Ph_3P)AgFe_3S_4(LS_3)]^{2-}$	8
$[(NC)AgFe_3S_4(LS_3)]^{3-}$	9
$[TiFe_3S_4(LS_3)]^{2-}$	10
$[(OC)_3MFe_3S_4(LS_3)]^{3-}$	11 (M = Mo, W) ³⁰
$[(Ph_3P)CoFe_3S_4(LS_3)]^{2-}$	12
$[(Smes)CoFe_3S_4(LS_3)]^{3-}$	13
$[(Ph_3P)NiFe_3S_4(LS_3)]^{2-}$	14

Previously, all MFe_3S_4 cubane-type clusters of synthetic origin have been prepared by the methods of self-assembly or reductive rearrangement. Self-assembly routes, in which simple reactants assemble clusters under thermodynamic control, have proven indispensable in the preparation of clusters with M = V, Nb, Mo, W, and Re.³² However, this method is limited to clusters whose $[MS_4]^{z-}$ precursors are available, a situation that does

not apply to the later transition elements. The method of reductive rearrangement utilizes the linear trinuclear cluster $[Fe_3S_4(SR)_4]^{3-,40}$ whose $[Fe_3(\mu_2-S)_4]^{1+}$ core is isomeric with that of **3**. Reaction of this cluster with complexes containing low-valent metals (Mo(0), W(0), Co(I), Ni(0)) results in reduction and rearrangement of the all-Fe(III) core. In the formation of Mo- and W-containing clusters,^{30,41} a thiolate ligand acts as the reductant. In minimal reactions⁴² and **5**,^{42,43} the metal is the reductant in an inner-sphere process resulting in the capture of the heterometal in a cubane-type core.



MFe_3S_4 Cluster Formation by Metal Ion Incorporation Reactions. (a) **Protein-Bound Clusters.** These clusters are generated by incubating proteins containing $[Fe_3S_4]^{1+}$ clusters **1** with a large excess of heterometal ion and, usually, a reductant (dithionite) in reaction 2 followed by chromatographic purification of the protein. Clusters have been formed in this way from three different proteins and are collected in Table 1; they are depicted in terms of the cubane-type structure **2b** thought to apply to all product clusters. Only the strongly thiophilic metals Cu(I) and Tl(I) form stable complexes with $[Fe_3S_4]^{1+}$. However, the $[TiFe_3S_4]^{2+}$ cluster, with a dissociation constant of 34(10) mM,²⁵ is weakly bound. All other species involve the $[Fe_3S_4]^{0,1-}$ states. Without exception, the indicated spin states can be rationalized in terms of a simple fragment model in which the spin of the $[Fe_3S_4]^0$ ($S = 2$) or $[Fe_3S_4]^{1-}$ ($S = 5/2$) fragment is antiferromagnetically coupled to the high-spin state of the heterometal (Mn(II), Co(II), Ni(II)).^{1,19,42} Indeed, the diamagnetism of the $[MnFe_3S_4]^{1+}$ cluster (presumably arising from the coupling of two $S = 5/2$ components¹⁹) is the strongest evidence of its formation. An extensive tabulation of the fragment formulations and spins of protein-bound clusters is available elsewhere.¹⁹ There is no crystallographic proof of the cubane-type stereochemistry **2b** but, as noted earlier, the cuboidal structure of the precursor **1** is well established. The first demonstration of structure **2b** followed from the close electronic similarity of $[CoFe_3S_4]^{2+}$ and $[NiFe_3S_4]^{1+}$ protein clusters with $[CoFe_3S_4(Smes)_4]^{2-}$ ($S = 1/2$) and $[(Ph_3P)NiFe_3S_4(Smes)_3]^{2-}$ ($S = 3/2$), respectively, whose cubane structures were defined crystallographically.⁴² Currently, mild perturbations of EPR, MCD, and Mössbauer spectroscopic properties upon incorporation of diamagnetic metals and changes in spin state by reaction with paramagnetic metals are established indicators of cubane cluster formation. Direct electrochemistry of proteins⁶ has also proven valuable for detection of MFe_3S_4 cluster formation. Available redox potentials of such clusters are set out in Table 2. However, in nearly all cases the terminal ligation of the heterometal and, therewith, the local cluster charge is undefined. Persuasive spectroscopic evidence for the binding of exogenous cyanide to MFe_3S_4 clusters with M = Co(II), Ni(II), and Zn(II), has been presented.^{19–21}

(b) **Synthetic Clusters.** Our principal goal has been demonstration of metal-ion incorporation reactions of an Fe_3S_4 cuboidal cluster and the influence of the heterometal on certain properties, including redox potentials and isotropic shifts.

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Table 2. Redox Potentials^a for Protein-Bound Clusters

core couple	protein ^b			refs
	Da Fd III ^c	Dg Fd II ^c	Pf Fd ^d	
[Fe ₃ S ₄] ^{1+,0}	-140	-130	-160	22, 18, 19
[MnFe ₃ S ₄] ^{2+,1+}			>-100	19
[Fe ₄ S ₄] ^{2+,1+}	-400	-420	-345	22, 18, 19
[CoFe ₃ S ₄] ^{2+,1+}		-245	-163	18, 19
[NiFe ₃ S ₄] ^{2+,1+}		-360	>-100	18, 19
[ZnFe ₃ S ₄] ^{2+,1+}	-480		-241	22, 19
[CdFe ₃ S ₄] ^{2+,1+}	-580	-495		22, 18
[CuFe ₃ S ₄] ^{2+,1+}	+148			24
[TlFe ₃ S ₄] ^{2+,1+}	+81			25

^a mV vs NHE at 25 °C; uncertainties where quoted are ±(10 to 15) mV. ^b Cf. footnote a, Table 1. ^c Determined by direct electrochemistry. ^d Determined by dye-mediated EPR titrations.

Table 3. Isotopic Shifts of MFe₃S₄ Clusters in MeCN Solutions at 297 K

cluster	-(ΔH/H ₀) _{iso} , ^a ppm		
	4-Me	5-H	6-Me
[Fe ₃ S ₄ (LS ₃)] ³⁻	6.47	8.95	9.60
[(Ph ₃ P)CoFe ₃ S ₄ (LS ₃)] ²⁻ ^b	5.10	5.82	7.22
[(Ph ₃ P)NiFe ₃ S ₄ (LS ₃)] ²⁻ ^c	6.58	7.77	9.95
[(Ph ₃ P)CuFe ₃ S ₄ (LS ₃)] ²⁻	7.92	9.43	11.6
[(NC)CuFe ₃ S ₄ (LS ₃)] ³⁻	7.27	9.09	11.0
[(Ph ₃ P)AgFe ₃ S ₄ (LS ₃)] ²⁻	8.03	9.38	11.5
[(NC)AgFe ₃ S ₄ (LS ₃)] ³⁻	7.61	9.17	11.0
[TlFe ₃ S ₄ (LS ₃)] ²⁻	8.38	9.51	11.8
[(OC) ₃ MoFe ₃ S ₄ (LS ₃)] ³⁻ ^d	6.89	8.69	10.9
[(OC) ₃ WFe ₃ S ₄ (LS ₃)] ³⁻ ^d	6.70	8.56	11.1

^a (ΔH/H₀)_{iso} = (ΔH/H₀)_{dia} - (ΔH/H₀)_{obs}; diamagnetic reference shifts are those of Na₃(LS₃) and Ph₃P in MeCN. ^b Ph₃P isotropic shifts: -1.91 (*o*-H), 1.55 (*m*-H), -2.71 (*p*-H). ^c Ph₃P isotropic shifts: -2.22 (*o*-H), 3.13 (*m*-H), -3.81 (*p*-H). ^d Shifts quoted in Me₂SO due to limited solubility in MeCN (ref 30).

Results obtained for **3** in acetonitrile solutions are summarized in Figure 1. The first indication that this cluster might support incorporation came from reaction with [FeCl₄]²⁻ to afford **4** in quantitative yield *in situ*.²⁸ Thereafter, reactions resulting in the incorporation of Cu(I), Ag(I), Tl(I), Co(II), Ni(II), and M⁰(CO)₃ (M = Mo, W)³⁰ have been accomplished. Cluster formation is readily monitored by ¹H NMR spectroscopy owing to the sensitivity of isotropic shifts, presented in Table 3, to the identity of the heterometal. Because of the negative sign of the shifts of substituents on the coordinating arms (4-Me, 5-H, 6-Me), antiparallel ligand → metal spin transfer occurs and contact interactions are dominant at the iron sites.⁴²

Owing to the conformational flexibility of the LS₃ ligand system,⁴⁴ Fe₃S₄ clusters derived from this ligand in general do not crystallize well, thus complicating upon occasion the isolation of highly pure solids and diffraction-quality crystals. In several reaction systems examined here, the homometallic cluster [Fe₃S₄(LS₃)L']¹⁻²⁻ (L' = anion, Ph₃P, solvent) was detected as a minority product. They are detectable by ¹H NMR and/or electrochemistry; the means of formation of such species is unestablished. In the preparation of phosphine-ligated clusters **6**, **8**, **12**, and **14**, the excess phosphine was not separated from the cluster product because of its stabilizing effect on the cluster in solution. In these cases, yields are high but could not be

(44) In Fe₃S₄-LS₃ clusters, the three buttressing *p*-tolylthio legs may be below, or above and below, the central benzene ring in crystalline compounds;^{28,31} Zhou, C.; Holm, R. H. *Inorg. Chem.* In press. Huang, J.; Mukerjee, S.; Segal, B. M.; Akashi, H.; Zhou, J.; Holm, R. H. *J. Am. Chem. Soc.* Submitted for publication. Despite numerous attempts, we have been unable to achieve diffraction-quality crystals of compounds containing clusters **6**–**12** and **14**, a not infrequent result with clusters containing the LS₃ ligand system. However, structures of **3**²⁸ and **4**^{31a} are available.

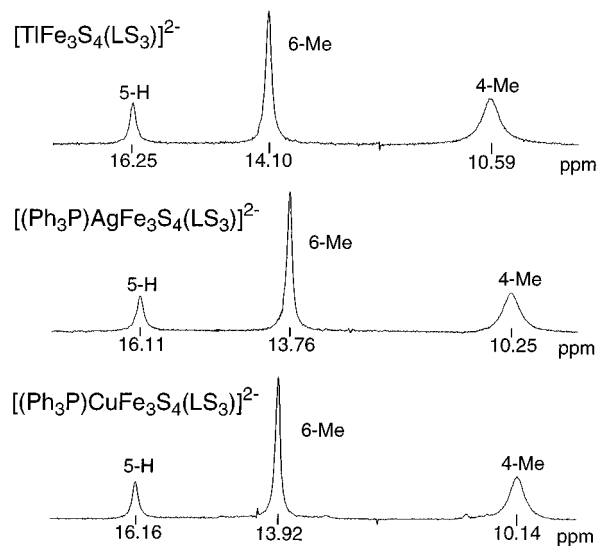
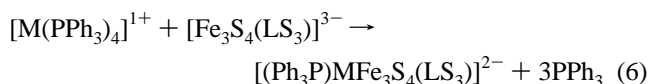


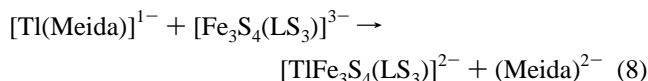
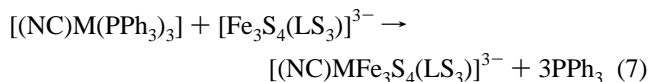
Figure 2. ¹H NMR spectra (downfield region) for [TlFe₃S₄(LS₃)]²⁻ (top), [(Ph₃P)AgFe₃S₄(LS₃)]²⁻ (middle), and [(Ph₃P)CuFe₃S₄(LS₃)]²⁻ (bottom) in acetonitrile solutions at 297 K. Signal assignments are indicated.

quantitated. Consequently, formation and properties of MFe₃S₄ clusters in solution are the matters of principal interest.

As described by reaction 6, treatment of **3** with the tetraphosphine complexes [M(PPh₃)₄]¹⁺ (M = Cu, Ag) results in the rapid formation of the phosphine-supported heterometal cubane-type clusters [(Ph₃P)MFe₃S₄(LS₃)]²⁻ (M = Cu (**6**), Ag (**8**)). These clusters are easily characterized by their distinct,



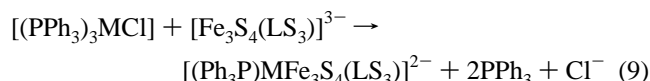
isotropically shifted ¹H NMR spectra. As shown in Figure 2, the chemical shifts of the 5-H signals are quite similar to that of the 5-H signal in the cuboidal [Fe₃S₄]⁰ starting material (15.7 ppm). The same situation holds for cyanide-bound clusters **7** (80%) and **9** (84%) prepared in the indicated yields by reaction 7, and the Tl(I) cluster **10** (86%, Figure 2) obtained by reaction 8. Small amounts of the phosphine-bound clusters **6** and **8**



(≤5%) are inevitable byproducts of reaction 7. The formation of free (Meida)²⁻ in reaction 8 regenerates **3** in reaction 2 from the cubane cluster byproduct, leading to higher yields of **10**. The NMR spectra of **6**–**10** are perturbed versions of the spectrum of **3**, showing the retention of the S = 2 ground state expected upon introduction of a diamagnetic heterometal. All isotropic shifts of this set of clusters are, however, larger than those of **3**. The presence of the heterometal evidently increases the delocalization of spin from the ligand to the [MFe₃S₄]¹⁺ core, leaving a larger spin imbalance on the ligand, and is the type of effect expected (but not previously observed) upon incorporating a closed-shell cation in the core. Further, the shifts are sufficiently sensitive to distinguish Cu(I) and Ag(I) at parity of the terminal ligand, and cyanide and phosphine with the same metal (Table 3).

The $\{\text{M}^{1+} + [\text{Fe}_3\text{S}_4]^0\}$ fragment description of clusters **6–10** is further supported by their Mössbauer spectra, which at 77 K consists of two overlapping doublets with an approximate 1:2 intensity ratio (not shown). For the less intense site, $\delta_1 = 0.37–0.38$ mm/s and $\Delta E_{Q1} = 0.44–0.59$ mm/s. The parameters for the more intense site are $\delta_2 = 0.46–0.48$ mm/s and $\Delta E_{Q2} = 1.04–1.23$ mm/s. These values may be compared with $\delta_1 = 0.35$ mm/s, $\Delta E_{Q1} = 0.5$ mm/s and $\delta_2 = 0.49$ mm/s, $\Delta E_{Q2} = 1.3$ mm/s for **3**, in which site 1 contains Fe^{3+} ($S = 5/2$) and site 2 a double-exchange coupled $\text{Fe}^{3+}/\text{Fe}^{2+}$ delocalized pair ($S = 9/2$).²⁸ Antiparallel spin coupling leads to the $S = 2$ ground state.^{3,45} This description also applies to **6–11** and the spin quintet clusters in Table 1, all of which contain a diamagnetic heterometal.

Reaction 9 ($M = \text{Co}, \text{Ni}$) results in the phosphine-ligated clusters **12** and **14**. It should be noted that this procedure affords the $[\text{CoFe}_3\text{S}_4]^{1+}$ oxidation level, one electron more reduced than



that obtained by reductive rearrangement reaction 4.^{42,46} The $[\text{NiFe}_3\text{S}_4]^{1+}$ core is obtained by both reactions 5 and 9. The Mössbauer spectra of the clusters at 77 K (not shown) indicate increased electron density at the iron sites compared to precursor **3** and clusters **6–11**. The spectrum of **12** consists of an essentially symmetric quadrupole doublet with $\delta = 0.51$ mm/s and $\Delta E_Q = 0.97$ mm/s. The spectrum of **14** is best fit with two doublets having the parameters $\delta_1 = 0.50$ mm/s, $\Delta E_{Q1} = 1.24$ mm/s and $\delta_2 = 0.46$ mm/s, $\Delta E_{Q2} = 0.80$ mm/s. The larger isomer shifts indicate a greater extent of reduction, and with **14** an indication that the principal change occurs at site 1. We conclude that these clusters approach the limiting formulation $\{\text{M}^{1+} + [\text{Fe}_3\text{S}_4]^{1-}\}$. The Mössbauer parameters of **14** are nearly identical with those of two other $[(\text{Ph}_3\text{P})\text{NiFe}_3\text{S}_4(\text{SR})_3]^{2-}$ clusters for which the $S = 3/2$ state has been demonstrated.^{42,43} The assignment of $S = 1/2$ for **12** follows from that established for protein-bound $[\text{CoFe}_3\text{S}_4]^{1+}$ clusters (Table 1). The ^1H NMR spectra of these clusters, set out in Figure 3, identify the species and are consistent with these spin states. Isotropic shifts of **14** are larger than those of **12**, and the shifts of both clusters are smaller than those of **6–10**. This is the trend expected for contact-shifted resonances, which are proportional to magnetic susceptibility. Note that the isotropic shifts of the Ph_3P protons—*o*-H and *p*-H negative, *m*-H positive—is the opposite of that expected for the delocalization of positive spin into the phenyl ring π -orbitals. This effect, observed previously,^{42,43} arises because of the antiferromagnetic coupling of the M^{2+} and $[\text{Fe}_3\text{S}_4]^{1-}$ spins to give the system spin. The larger spin is aligned parallel to the magnetic field and results in the creation of parallel (positive) spin on the LS_3 ligand, which is delocalized over the odd-alternate *S*-phenyl component of the ligand arms. At the heterometal site, the spin is oppositely directed, leading to the delocalization of antiparallel (negative) spin in the phenyl rings of Ph_3P ligands.⁴⁷ A qualitative treatment of spin delocalization is given elsewhere.⁴³

From the foregoing results, clusters **12** and **14** must be formed in inner-sphere redox processes in which, presumably, the

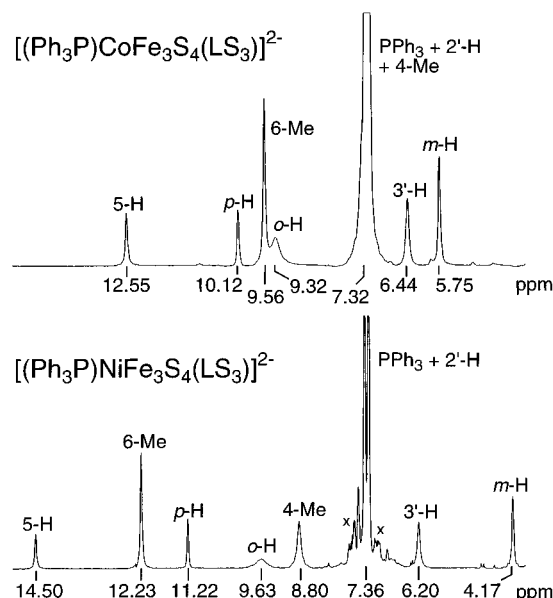


Figure 3. ^1H NMR spectra for $[(\text{Ph}_3\text{P})\text{CoFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ (top) and $[(\text{Ph}_3\text{P})\text{NiFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ (bottom) in acetonitrile solutions at 297 K. Signal assignments are indicated; x = phosphine-containing impurity.

intermediate is structurally similar to the product. Unlike reductive rearrangements, very little structural change of the cuboidal Fe_3S_4 reactant is required in metal ion incorporation reactions. These are new reactions in synthetic iron-sulfur cluster chemistry, having previously been observed only with protein-bound clusters in the presence of large excesses of metal ions (Table 1). The reactions in this work are, or are nearly, stoichiometric and emphasize the concept, introduced earlier,⁴⁸ of cuboidal Fe_3S_4 as a *cluster ligand*. The only comparable reactions are those of cuboidal $[\text{M}_3\text{S}_4]^{4+}$ clusters with a variety of reduced metal sources to afford the cubane-type clusters $[\text{M}'\text{M}_3\text{S}_4]^{2+}$ ($M = \text{Mo},^{49} \text{W}^{50}$). In nearly all these reactions, the clusters must be reduced in order to bind the heterometal, analogous to reaction 9.

Before proceeding to a consideration of redox potentials, we note that not all metals with a demonstrated affinity for sulfur ligation could be incorporated in a cluster core upon reaction with **3**. With tetrahedral $[\text{M}(\text{SPh}_4)]^{2-}$ and $[\text{M}(\text{SET}_4)]^{2-}$, $\text{Hg}(\text{NO}_3)_2$, and Hg_2Cl_2 , only $[\text{Fe}_4\text{S}_4]^{2+}$ cluster products could be identified. Reaction with $[\text{VCl}_3(\text{THF})_3]$, $[\text{MoCl}_3(\text{MeCN})_3]$, $[\text{WCl}_4(\text{MeCN})_2]$, and MCl_2 ($M = \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) resulted in the rapid formation of chloride-ligated **4**, readily identified by its ^1H NMR spectrum.^{31a} Addition of as little as 0.5 equiv of $\text{M}(\text{OSO}_2\text{CF}_3)_2$ ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) yielded only the sulfide-bridged double cubane $\{[\text{Fe}_4\text{S}_4(\text{LS}_3)]_2\text{S}\}^{4-}$, also readily detected by NMR.⁵¹ Additionally, the presence of protic sources as weak and strong acids caused conversion to $[\text{Fe}_4\text{S}_4]^{2+}$ species. We do not know the pathways by which such species are formed in any reaction system. Fortunately, MFe_3S_4 clusters with $M = \text{V}, \text{Mo}$, and W are readily accessible by assembly reactions.^{1,32} The preformed cores $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ obtained in

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(46) In a reaction whose details are unclear to us, the $[\text{CoFe}_3\text{S}_4]^{2+}$ core has also been obtained in the cluster $[\text{CoFe}_3\text{S}_4(\text{Stib})_4]^{2-}$: Roth, E. K. H.; Greneche, J. M.; Jordanov, J. *J. Chem. Soc., Chem. Commun.* **1991**, 105.

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Table 4. Redox Potentials and Electron Transfer Series of [MFe₃S₄] Clusters in Acetonitrile Solutions^a at 297 K

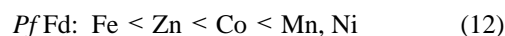
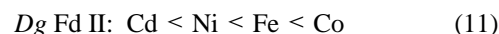
Cluster	Series / Potentials ^b			ref.	
[Fe ₃ S ₄ (LS ₃) ³⁻	[Fe ₃ S ₄] ¹⁺ $\xrightleftharpoons{E_1}$ [Fe ₃ S ₄] ⁰ $\xrightleftharpoons{E_2}$ [Fe ₃ S ₄] ¹⁻	-0.79	-1.72	28	
[Fe ₄ S ₄ (SET) ₄] ²⁻	---	---	-1.29	43	
[Fe ₄ S ₄ (Smes) ₄] ²⁻	---	0.00	-1.20	Ⓞ	
[Fe ₄ S ₄ (LS ₃)(Smes)] ²⁻	---	-0.29 ^d	-1.11	Ⓞ	
[CoFe ₃ S ₄ (Smes) ₄] ²⁻	[CoFe ₃ S ₄] ³⁺ $\xrightleftharpoons{E_1}$ [CoFe ₃ S ₄] ²⁺ $\xrightleftharpoons{E_2}$ [CoFe ₃ S ₄] ¹⁺ $\xrightleftharpoons{E_3}$ [CoFe ₃ S ₄] ⁰	-0.03	-1.02	---	42
[(Smes)CoFe ₃ S ₄ (LS ₃)] ³⁻	---	---	-0.95	---	Ⓞ
[(Ph ₃ P)CoFe ₃ S ₄ (LS ₃)] ²⁻	---	---	-0.57 ^d	-1.57	Ⓞ
[NiFe ₃ S ₄ (SET) ₄] ³⁻	[NiFe ₃ S ₄] ²⁺ $\xrightleftharpoons{E_1}$ [NiFe ₃ S ₄] ¹⁺ $\xrightleftharpoons{E_2}$ [NiFe ₃ S ₄] ⁰	-0.96	---	---	43
[NiFe ₃ S ₄ (Smes) ₄] ³⁻	---	-0.90	---	---	42
[(Ph ₃ P)NiFe ₃ S ₄ (LS ₃)] ²⁻	---	-0.49 ^d	-1.45	---	Ⓞ
[(Ph ₃ P)NiFe ₃ S ₄ (SET) ₃] ²⁻	---	-0.58 ^d	-1.62	---	43
[(Ph ₃ P)NiFe ₃ S ₄ (Smes) ₃] ²⁻	---	-0.50 ^d	-1.55	---	42
[(Ph ₃ P)CuFe ₃ S ₄ (LS ₃)] ²⁻	[CuFe ₃ S ₄] ²⁺ $\xrightleftharpoons{E_1}$ [CuFe ₃ S ₄] ¹⁺ $\xrightleftharpoons{E_2}$ [CuFe ₃ S ₄] ⁰	-0.38 ^d	-1.35	---	Ⓞ
[(NC)CuFe ₃ S ₄ (LS ₃)] ³⁻	---	-0.52	-1.50	---	Ⓞ
[(Ph ₃ P)AgFe ₃ S ₄ (LS ₃)] ²⁻	[AgFe ₃ S ₄] ²⁺ $\xrightleftharpoons{E_1}$ [AgFe ₃ S ₄] ¹⁺ $\xrightleftharpoons{E_2}$ [AgFe ₃ S ₄] ⁰	-0.38 ^d	-1.30	---	Ⓞ
[(NC)AgFe ₃ S ₄ (LS ₃)] ³⁻	---	-0.46 ^d	-1.44	---	Ⓞ
[TiFe ₃ S ₄ (LS ₃)] ²⁻	[TiFe ₃ S ₄] ²⁺ $\xrightleftharpoons{E_1}$ [TiFe ₃ S ₄] ¹⁺ $\xrightleftharpoons{E_2}$ [TiFe ₃ S ₄] ⁰	-0.40 ^d	-1.19	---	Ⓞ

^a 0.1 M TBA(PF₆) supporting electrolyte. ^b V vs SCE. ^c This work. ^d Irreversible wave, $E_{1/2}$ determined by differential pulse voltammetry.

this way can be directly inserted in the LS₃ ligand.⁵² We have also been unable to incorporate divalent metals in systems in which **3** is chemically or electrochemically reduced in their presence. Although we have detected a cluster formulated as [(CF₃SO₃)ZnFe₃S₄(LS₃)]²⁻ in earlier work,²⁷ we have experienced difficulty in obtaining substantially pure solution or solid samples of this species. Consequently, the current set of synthetic heterometal cubanes does not include clusters with M = Mn(II), Zn(II), and Cd(II) analogous to those achieved in proteins, a situation that must be ascribed to an enhanced stabilization of native cluster **1** vs **3** by protein structure.

Electron Transfer Reactions. The influence of heterometal on the redox potentials of protein-bound clusters, collected in Table 2, is difficult to discern because of possible differences in terminal ligation and local protein charge and other environmental effects. Relative to the couple [Fe₄S₄]^{2+,1+}, the irregular potential orders 10–12 emerge for other [MFe₃S₄]^{2+,1+} couples. With the clusters in Figure 1 and others prepared earlier,^{42,43} a more exact comparison of cluster redox potentials

can be made as a function of heterometal. The electron transfer



series and redox potentials for these clusters are presented in Table 4. In most cases, these clusters exhibit a single reversible reduction wave and an irreversible or quasireversible oxidation in acetonitrile solution, with chemical reversibility based upon the criterion that $i_p/i_a \approx 1$. As already noted, oxidation of a cluster reduces the binding affinity of the Fe₃S₄ fragment. The concomitant release of the heterometal ion is therefore anticipated, and the irreversibility of certain oxidative electrochemical processes can be rationalized on this basis.

The cyclic voltammograms of clusters **7** and **10** are shown in Figure 4. That of cluster **7** has two effectively reversible steps. The two weak features at slightly higher potentials are due to a cluster **6** impurity that is present upon preparation of

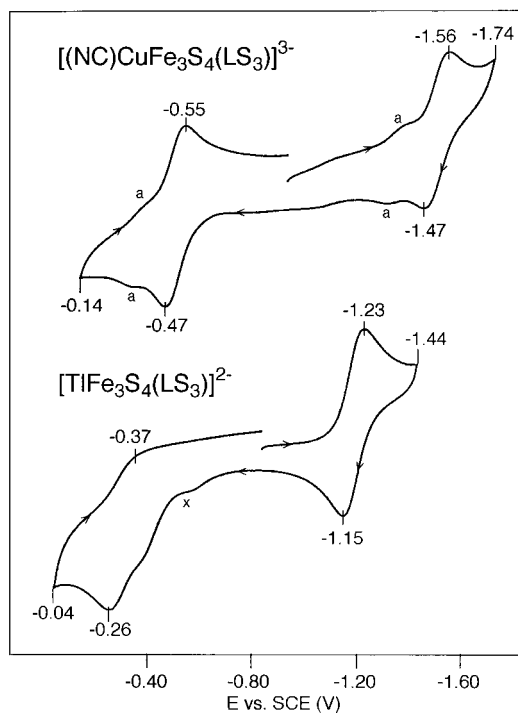


Figure 4. Cyclic voltammograms (100 mV/s) of $[(\text{NC})\text{CuFe}_3\text{S}_4(\text{LS}_3)]^{3-}$ (top) and $[\text{TlFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ (bottom) in acetonitrile solutions. Peak potentials are indicated; a = $[(\text{Ph}_3\text{P})\text{CuFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ as determined by comparison with authentic sample and x = unidentified impurity.

the cyanide cluster. Cluster **7** is the only species cleanly oxidizable to a level containing the $[\text{Fe}_3\text{S}_4]^{1+}$ fragment, as is the case with one protein. These situations must reflect the pronounced thiophilic nature of soft Cu(I). Spectroscopic studies of the protein-bound clusters $[\text{CuFe}_3\text{S}_4]^{2+,1+}$ prove that the heterometal is not involved in the redox process.²⁴ The voltammogram of cluster **10** shows a reversible reduction and irreversible oxidation typical of all other clusters prepared in this work. A minimum basis for comparison of potentials is parity of cluster charge, a matter made evident by the 80–150 mV lower potentials of the E_1 and E_2 steps of **7** and **9** (3–) compared to **6** and **8** (2–) (Table 4), respectively, when core charges are the same. For the pair **7/9**, the order of potentials is $\text{Cu} < \text{Ag}$, and for the set **6/8/10** it is $\text{Cu} < \text{Ag} < \text{Tl}$. The $\text{Cu} - \text{Ag}$ values are in the order of standard potentials in acid solution ($\text{Tl} < \text{Cu} < \text{Ag}$ for $\text{M}^{1+,0}$),⁵³ but the differences here are attenuated to only 50–60 mV by covalent bonding.

A direct comparison of the cyclic voltammograms of di-negative clusters **12** and **14** is presented in Figure 5. A well-defined reduction and an oxidation bordering on irreversibility are observed. Upon addition of 1 equiv of mesitylenethiolate to an acetonitrile solution of **12**, the feature with $E_{1/2} = -1.57$ V is replaced with a new step at $E_{1/2} = -0.95$ V shown to result from the oxidation of **13**. This potential is very near that of the $[\text{CoFe}_3\text{S}_4(\text{Smes})_4]^{2-,3-}$ couple (-0.95 V⁴²); both processes are the E_2 step in the CoFe_3S_4 redox series. Using the data of Table 4, the potential order 13 is established for the $[\text{MFe}_3\text{S}_4(\text{SR})_4]^{2-,3-}$ ($\text{R} = \text{Et}, \text{mes}$) and $[(\text{Smes})\text{MFe}_3\text{S}_4(\text{LS}_3)]^{2-,3-}$ couples. When results for all $[(\text{Ph}_3\text{P})\text{MFe}_3\text{S}_4(\text{LS}_3)]^{2-,3-}$ couples are considered, the potential order 14 emerges. Iron is tentatively placed in the latter series on the basis of its position in order 13; we lack clusters of comparable ligation for

(53) $\text{Cu}^{2+,1+,0} = 0.16, 0.52$ V; $\text{Ag}^{2+,1+,0} = 1.98, 0.80$ V; $\text{Tl}^{3+,1+,0} = 1.25, -0.34$ V: Bard, A. J.; Parsons, R.; Jordan, J., Eds. *Standard Potentials in Aqueous Solution*; Marcel Dekker, Inc.: New York, 1985. While we offer these comparisons, we cannot insist that standard potentials are the best guide to intrinsic potential orders of these elements when coordinated.

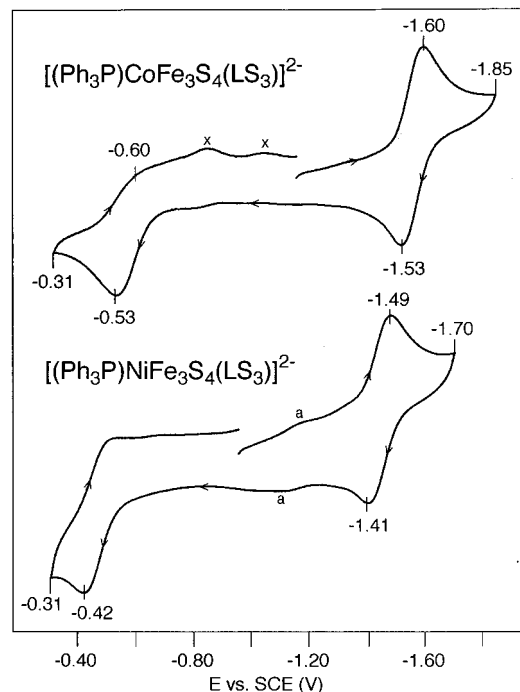


Figure 5. Cyclic voltammograms (100 mV/s) of $[(\text{Ph}_3\text{P})\text{CoFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ (top) and $[(\text{Ph}_3\text{P})\text{NiFe}_3\text{S}_4(\text{LS}_3)]^{2-}$ (bottom) in acetonitrile solutions. Peak potentials are indicated: a = $[(\text{Fe}_4\text{S}_4(\text{LS}_3)\text{L}')^{2-}$ impurity and x = unidentified impurity.

$$\text{Fe} < \text{Co} < \text{Ni} \quad (13)$$

$$(\text{Fe}) < \text{Co} < \text{Ni} < \text{Cu} \lesssim \text{Ag} < \text{Tl} \quad (14)$$

measurement of $[\text{Fe}_4\text{S}_4]^{1+,0}$ redox steps.⁵⁴ These orders are formulated on the basis of invariant ligation (except for Tl cluster **10**) and cluster net charge, conditions which require equality of core charge in redox couples. We consider these to represent the intrinsic effect of heterometals on MFe_3S_4 redox potentials. Inasmuch as the available evidence indicates that the primary locus of electron density change is the Fe_3S_4 fragment rather than the M center in both synthetic and protein-bound clusters,^{1,19,21,32} the potentials represent the perturbations placed on the $[\text{Fe}_3\text{S}_4]^{0,1-}$ and (unknown) $[\text{Fe}_3\text{S}_4]^{1-,2-}$ potentials by metal ion incorporation. With iron and four heterometals in common in the complete set of potentials but not in individual series, none of the protein potential sequences 10–12 can be said to track exactly on orders 13 and 14. However, $\text{Fe} < \text{Co}$ and $\text{Fe} < \text{Co} < \text{Ni}$ are present in sequences 11 and 12, respectively.

Summary. The following are the principal results and conclusions of this investigation:

1. The cuboidal cluster $[\text{Fe}_3\text{S}_4(\text{LS}_3)]^{3-}$ (**3**) sustains two types of metal ion incorporation reactions to yield the cubane-type clusters $[\text{L}'\text{MFe}_3\text{S}_4(\text{LS}_3)]^{2-,3-}$: (a) non-redox binding of the soft, thiophilic metals Cu(I), Ag(I), and Tl(I) with the terminal ligands Ph_3P and CN^- (Cu, Ag) and (b) inner-sphere reactions with Co(I) and Ni(I). Clusters containing Mn(II), Zn(II), and Cd(II) could not be formed or, if formed, prepared in substantially pure form.

2. Type (a) reactions result in retention of the $S = 2$ ground state of **3** in clusters that are formulated as $\{\text{M}^{1+} + [\text{Fe}_3\text{S}_4]^{10}\}$. Type (b) reactions are inner-sphere redox processes leading to clusters formulated as $\{\text{M}^{2+} + [\text{Fe}_3\text{S}_4]^{1-}\}$. Reaction products are readily identified by their isotropically shifted ^1H NMR

(54) Redox reactions involving these oxidation states have recently been demonstrated with the clusters $[\text{Fe}_4\text{S}_4(\text{PR}_3)_4]^{1+}$: Goh, C.; Segal, B. M.; Huang, J.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 11844.

spectra, which for type (a) are perturbed versions of the spectrum of **3** and for type (b) are consistent with the spin states $S = 1$ for $[\text{CoFe}_3\text{S}_4]^{1+}$ and $S = 3/2$ for $[\text{NiFe}_3\text{S}_4]^{1+}$ established by other means.

3. Metal ion incorporation is a new reaction type for synthetic iron–sulfur clusters, all previous MFe_3S_4 clusters having been produced by self-assembly and reductive rearrangement reactions. A type (b) reaction utilizing Co(I) has afforded the $[\text{CoFe}_3\text{S}_4]^{1+}$ oxidation state, not yet isolated from any reductive rearrangement reactions. Protein-bound clusters with some seven heterometals have been produced by reaction of cuboidal cluster **1** with exogenous metal ions; a second oxidation level of each is generally obtainable by chemical or electrochemical redox reactions. Their existence as native clusters and biological function (if any) remain open matters.

4. All synthetic clusters exhibit a reversible one-electron reduction and a quasireversible or irreversible oxidation. Only

$[(\text{NC})\text{CuFe}_3\text{S}_4(\text{LS}_3)]^{3-}$ could be oxidized to a level containing the $[\text{Fe}_3\text{S}_4]^{1+}$ fragment. The potential orders 13 and 14 are taken as representing the intrinsic effect of variant heterometal on the redox potentials of $[\text{MFe}_3\text{S}_4]^{2+,1+}$ and $[\text{MFe}_3\text{S}_4]^{1+,0}$ core oxidation states at parity of ligation and net cluster charge. Sequence orders 10–12 of protein potentials do not closely follow the former orders with respect to iron at the unique metal site and the four heterometals in common (Co, Ni, Cu, Tl).

With the synthesis and redox chemistry of $[\text{L}'\text{MFe}_3\text{S}_4(\text{LS}_3)]^{2-,3-}$ clusters in hand, we are now investigating additional electronic and reactivity properties, including ligand binding at the unique $\text{M} = \text{Fe}$ and heterometal atom sites.

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