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Core Chalcogenide Atom Substitution Reactions of $[\text{Fe}_2\text{X}_2(\text{SR})_4]^{2-}$ and $[\text{Fe}_4\text{X}_4(\text{SR})_4]^{2-,3-}$ Clusters (X = S, Se)

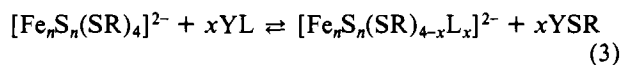
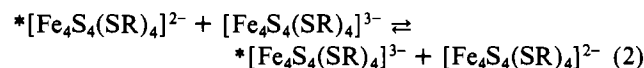
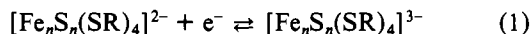
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In initial research directed toward elucidation of core atom reactivity in Fe_nX_n cluster species ($n = 2, 4$; X = S, Se) three reaction systems containing preisolated clusters in acetonitrile solution were examined by ¹H NMR spectroscopy: $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}/[\text{Fe}_2\text{Se}_2(\text{SR})_4]^{2-}$ (A), $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}/[\text{Fe}_4\text{Se}_4(\text{SR})_4]^{2-}$ (B), and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}/[\text{Fe}_4\text{Se}_4(\text{SR})_4]^{3-}$ (C) (R = *p*-tolyl). All three systems exhibited core atom S/Se substitution reactions and afforded at or near equilibrium the mixtures $[\text{Fe}_2\text{S}_{2-n}\text{Se}_n(\text{SR})_4]^{2-}$ ($n = 0-2$, six *m*-H + *p*-Me resonances) and $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{SR})_4]^{2-,3-}$ ($n = 0-4$, 16 *m*-H + *p*-Me resonances). Substitution was most rapid in system C, with all 4 - *n*, *n* species observable in 17 mM solutions at 27 °C after several hours. Hyperfine contact interactions afforded resolution sufficient to assign all *p*-Me signals (and in systems A and C *m*-H signals as well) to specific species. In system C three independent equilibrium constants approach statistical values. Two significant regularities were observed from the contact shifts of all species in each system: (i) relative π -spin densities in phenyl rings are essentially constant irrespective of total spin delocalized; (ii) total spin delocalized is a virtually linear function of core Se atom content and is largest for species with all-Se cores. Reactivity features of tetranuclear clusters in terminal ligand and core atom substitution reactions are summarized, and it is conjectured that Fe atoms may also be subject to substitution by other metals. The core substitution reactions of intact polynuclear species observed here do not appear to be preceded in metal cluster chemistry.

Introduction

In the course of developing the chemistry of the ferredoxin protein active site analogues $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-,2-4}$ $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-,2,3}$ and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-,5-7}$ a number of reactions have been identified that leave intact the Fe_2S_2 and Fe_4S_4 core portions of the cluster structures. These include the simple reversible redox reactions (1)^{2,3} ($n = 2, 4$), the associated



electron self-exchange reactions (2),⁸ and the thiolate substitution reactions (3) ($n = 2, 4$; $x = 1-4$) with the generalized electrophilic reagent YL.^{2,3,9,10} The most familiar example of the latter reaction is substitution of one thiolate ligand by another (L = R'S); other species such as those with L = halide and RCO_2^- may also be generated by, or isolated from, reaction 3.^{9,10}

Having developed means of altering oxidation levels and peripheral substituents of binuclear and tetranuclear Fe-S clusters, we turned our attention to another aspect of the reaction chemistry of these species, viz., that of substituting core iron or sulfur with retention of the rhomboidal- and

cubane-type structures of the original cores. Prior to the initiation of the present work it had been demonstrated that Fe_2Se_2 and Fe_4Se_4 ^{11,12} cores can be assembled from simple reagents and stabilized as their thiolate complexes $[\text{Fe}_n\text{Se}_n(\text{SR})_4]^{2-}$ ($n = 2, 4$) and that the corresponding cores of protein sites result from reconstitution reactions of appropriate apo-proteins with iron and selenium reagents.¹³ Further, the structure of $[\text{Fe}_4\text{Se}_4(\text{SPh})_4]^{2-11}$ exhibits a tetragonally distorted core geometry similar to its sulfur congener, and it and other cluster dianions can be reversibly reduced to $[\text{Fe}_4\text{Se}_4(\text{SR})_4]^{3-11}$. The reduced cluster with R = *p*-tolyl (*p*-tol) has been isolated in pure form as its Me_4N^+ salt.⁸ The collective body of evidence for $[\text{Fe}_n\text{X}_n(\text{SR})_4]^{2-,3-}$ clusters reveals little difference in physicochemical or redox properties between X = S and Se species, a similarity which appears to extend to protein sites as well. This situation, together with the finding that clostridial ferredoxin (Fe_4S_4 sites) undergoes base-catalyzed exchange of iron and sulfur (as sulfide) with radioactive isotopes of these elements,¹⁴ led us to the consideration that cores of synthetic clusters might be reactive with respect to S/Se atom substitution without appreciable degradation. Such behavior has now been demonstrated in the ¹H NMR studies, reported here, of the reactions between the congeneric clusters $[\text{Fe}_2\text{X}_2(\text{SR})_4]^{2-}$, $[\text{Fe}_4\text{X}_4(\text{SR})_4]^{2-}$, and $[\text{Fe}_4\text{X}_4(\text{SR})_4]^{3-}$ (X = S, Se) in acetonitrile solution.

Experimental Section

Preparation of Compounds. Tetramethylammonium salts of $[\text{Fe}_4\text{S}_4(\text{S-}i>p\text{-tol})_4]^{2-,15}$ $[\text{Fe}_4\text{S}_4(\text{S-}i>p\text{-tol})_4]^{3-,5}$ $[\text{Fe}_4\text{Se}_4(\text{S-}i>p\text{-tol})_4]^{2-,8}$ $[\text{Fe}_4\text{Se}_4(\text{S-}i>p\text{-tol})_4]^{3-,8}$ $[\text{Fe}_2\text{S}_2(\text{S-}i>p\text{-tol})_4]^{2-,4}$ and $[\text{Fe}_2\text{Se}_2(\text{S-}i>p\text{-tol})_4]^{2-,4}$ were prepared as previously described.

Preparation of Samples. Owing to the sensitivity of the compounds to dioxygen all manipulations were performed under an inert atmosphere. Acetonitrile was purified by the procedure given elsewhere.⁸ Solution samples of clusters for ¹H NMR studies were prepared in

- (1) To whom correspondence should be addressed at Harvard University.
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Table I. ^1H NMR Isotropic Shift Data for $[\text{Fe}_2\text{S}_{2-n}\text{Se}_n(\text{S-}p\text{-tol})_4]^{2-}$ and $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{S-}p\text{-tol})_4]^{2-,3-}$ Clusters in CD_3CN Solution at $\sim 27^\circ\text{C}$

2 - n, n or 4 - n, n	<i>p</i> -Me ^a			<i>m</i> -H ^a			<i>p</i> -Me/ <i>m</i> -H
	iso	mean	calcd	iso	mean	calcd	
2,0	-3.72			-2.09			1.78
1,1	-4.04	-4.04	-4.07 ^d	-2.31	-2.31	-2.30 ^e	1.75
0,2	-4.41			-2.50			1.76
4,0 ^b	-5.26 (14) ^j			-3.30 (8)			1.59
3,1 ³	-6.67 (12)	-5.83	-5.81 ^f	-4.10 (5)	-3.59	-3.60 ^g	1.63
3,1 ¹	-3.32 (16)			-2.05 (11)			1.62
2,2	-4.57 (15)	-6.45	-6.36	-2.70 (9)	-3.85	-3.90	1.69
2,2	-8.32 (7)			-5.00 (3)			1.64
1,3 ³	-6.07 (13)	-7.03	-6.91	-3.70 (6)	-4.25	-4.20	1.64
1,3 ¹	-9.92 (2)			-5.90 (1)			1.68
0,4	-7.47 (10)			-4.50 (4)			1.66
4,0 ^c	-1.65						
3,1 ³	-1.79	-1.74	-1.74 ^h				
3,1 ¹	-1.57						
2,2	-1.94	-1.83	-1.83				
2,2	-1.71						
1,3 ³	-1.85	-1.91	-1.92				
1,3 ¹	-2.08						
0,4	-2.01						

^a $(\Delta H/H_0)_{\text{iso}}$, ppm. Observed shifts may be obtained by adding -2.28 (*p*-Me) or -7.10 ppm (*m*-H) to the isotropic shifts. ^b Reduced (3-) species. ^c Oxidized (2-) species. ^d Isotropic shift increment (ppm) per Se atom used to obtain calculated values: 0.35. ^e Isotropic shift increment (ppm) per Se atom used to obtain calculated values: 0.21. ^f Isotropic shift increment (ppm) per Se atom used to obtain calculated values: 0.55. ^g Isotropic shift increment (ppm) per Se atom used to obtain calculated values: 0.30. ^h Isotropic shift increment (ppm) per Se atom used to obtain calculated values: 0.09. ⁱ Chemical shift of incompletely resolved *m*-H signals. Unresolved *o*-H signals are centered at -5.5 ppm. ^j Numbers refer to numbered signals in Figure 2.

either of two ways. (i) Solutions of known concentrations of individual cluster salts (~ 5 – 10 mg) in CD_3CN were prepared in 1-mL volumetric flasks and were mixed in various ratios. (ii) Mixtures of crystalline reduced tetranuclear cluster salts (~ 50 mg) were prepared by weight. A majority portion of a mixture was dissolved in ~ 4 mL of CH_3CN and stirred for 10 days. At the end of this period the solvent was completely removed in vacuo. A sample of this material was dissolved in CD_3CN , and the spectrum of the mixture, which was at equilibrium, was recorded. The mole fraction of each initial component was checked by dissolving the remaining portion of the original solid mixture in CD_3CN , recording the spectrum within 15 min, and integrating the appropriate resonances. Spectra of solutions prepared by either method were also recorded at shorter or longer periods of time in order to examine the time course of the reactions, to elucidate signal assignments (see text), and to establish equilibrium conditions. Reactions of the systems $[\text{Fe}_2\text{X}_2(\text{S-}p\text{-tol})_4]^{2-}$ and $[\text{Fe}_4\text{X}_4(\text{S-}p\text{-tol})_4]^{3-}$ ($\text{X} = \text{S}, \text{Se}$) were conducted at $\sim 27^\circ\text{C}$ with total cluster concentrations of ~ 5 – 10 mM; in the latter systems the mole fraction of the sulfur cluster N_S was varied over the range 0.08–0.85. Reactions of the systems $[\text{Fe}_4\text{X}_4(\text{S-}p\text{-tol})_4]^{2-}$ ($\text{X} = \text{S}, \text{Se}$) were carried out at comparable cluster concentrations and $N_S = 0.3$ – 0.7 , but at 48 – 55°C owing to much slower reaction rates compared to the reduced clusters.

^1H NMR Spectra. All spectra were recorded in CD_3CN solutions at $\sim 27^\circ\text{C}$ and 100 MHz in the FT mode with use of the equipment described elsewhere.⁵ Typical sets of data consisted of 200 acquisitions of 8132 bits digitized as 122.07 Hz/512 bits. Equilibrium constants were evaluated by integrating assigned resonances in Table I with use of the NTCFT routine on Nicolet 1180 computer software (Nicolet Technology Corp., Mountain View, CA). Because of their greater intensities and fewer overlaps with other signals, *p*-CH₃ resonances were integrated. Whenever possible the appropriate peak was integrated, and for species with more than one magnetically inequivalent site (Figure 1) the areas of both resonances were added. If both signals could not be integrated owing to peak overlap, one signal was integrated and statistically weighted to account for magnetic inequivalence. Wherever possible the integrated signal was that of higher intensity. All chemical shifts were measured relative to Me₄Si internal standard. As is conventional with paramagnetic molecules, signals occurring downfield and upfield of the standard are taken as negative and positive, respectively. Isotropic shifts were calculated from the relationship $(\Delta H/H_0)_{\text{iso}} = (\Delta H/H_0)_{\text{obsd}} - (\Delta H/H_0)_{\text{dia}}$, where the diamagnetic shifts are those of the *p*-tolylthiol in CD_3CN .¹⁵

Results and Discussion

To explore the occurrence of core chalcogen atom substitution reactions, we have examined the reaction systems

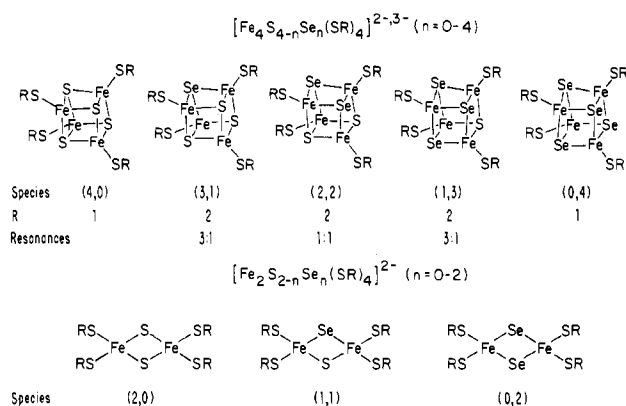


Figure 1. Structures and nomenclature of the species $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{SR})_4]^{2-,3-}$ ($n = 0$ – 4) and $[\text{Fe}_2\text{S}_{2-n}\text{Se}_n(\text{SR})_4]^{2-}$ ($n = 0$ – 2).

$[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}/[\text{Fe}_4\text{Se}_4(\text{SR})_4]^{3-}$, $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}/[\text{Fe}_4\text{Se}_4(\text{SR})_4]^{2-}$, and $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}/[\text{Fe}_2\text{Se}_2(\text{SR})_4]^{2-}$ ($\text{R} = p\text{-tol}$), containing preisolated clusters in acetonitrile solution at and above ambient temperature. The reactions have been monitored by ^1H NMR spectroscopy. Depicted in Figure 1 are the species resulting from all possible permutations of sulfur and selenium atoms in $\text{Fe}_4\text{S}_{4-n}\text{Se}_n$ ($n = 0$ – 4) and $\text{Fe}_2\text{S}_{2-n}\text{Se}_n$ ($n = 0$ – 2) core structures. There are five such tetranuclear cluster species, designated as 4 - n, n, and three 2 - n, n binuclear cluster species. Owing to the tetrahedral coordination of iron atoms, as found in the structure of $[\text{Fe}_2\text{S}_2(\text{S-}p\text{-tol})_4]^{2-}$,¹⁶ all R substituents in each binuclear cluster species are equivalent. However, the 1,3, 2,2, and 3,1 members of the $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{SR})_4]^{2-,3-}$ series necessarily contain inequivalent R groups, the numbers and statistical weights of which are given in Figure 1. These values are based on tetragonal or trigonal (3,1 or 1,3) core structures. Solid-state structures of all $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-,3-}$ clusters thus far determined are tetragonal¹⁶ with one exception, $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{3-}$.¹⁷ Recently it has

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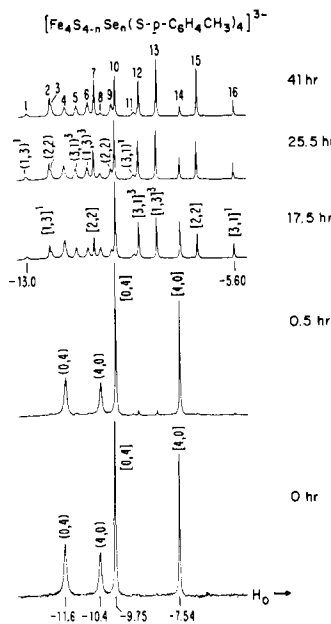


Figure 2. ^1H NMR spectra (100 MHz) depicting the time course of the core atom exchange reactions in the system $[\text{Fe}_4\text{S}_4(\text{S-}i{p}\text{-tol})_4]^{3-}/[\text{Fe}_4\text{Se}_4(\text{S-}i{p}\text{-tol})_4]^{3-}$ at $\sim 27^\circ\text{C}$. The concentration of each initial cluster is ~ 5 mM, and the mole fraction of the initial sulfur cluster is 0.49. Species are designated as in Figure 1. Signal labeling: (*m*-H), [*p*-CH₃].

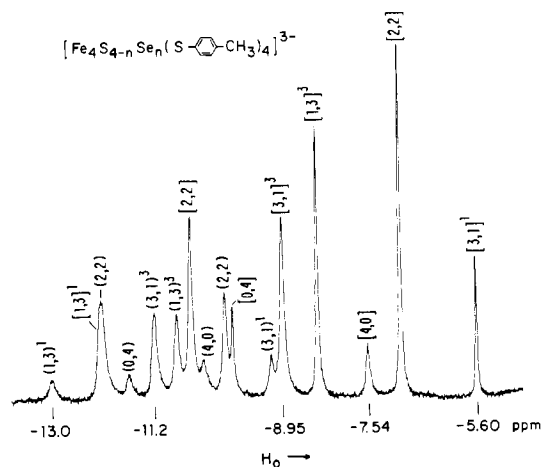


Figure 3. ^1H NMR spectrum (100 MHz) of the system $[\text{Fe}_4\text{S}_4(\text{S-}i{p}\text{-tol})_4]^{3-}/[\text{Fe}_4\text{Se}_4(\text{S-}i{p}\text{-tol})_4]^{3-}$ at $\sim 27^\circ\text{C}$ and at equilibrium. The concentration of each initial cluster is ~ 5 mM, and the mole fraction of the initial sulfur cluster is 0.53; the spectrum was recorded after a 240-h reaction time. Signals are labeled as in Figure 2.

been shown that, on the basis of magnetic and spectroscopic properties, $[\text{Fe}_4\text{S}_4(\text{S-}i{p}\text{-tol})_4]^{3-}$ (as its Me_4N^+ salt) has a core symmetry less than tetragonal in the solid state.⁷ However, both clusters exhibit ^1H NMR spectra indicative of equivalent R groups,⁵ a matter which simplifies signal assignments in complex mixtures (vide infra) and is consistent with other physicochemical evidence demonstrating effective tetragonal structures of reduced clusters in solution.^{6,7}

In the discussion of NMR spectra which follows and in Figures 2–6, *m*-H and *p*-Me signals are enclosed in parentheses and brackets, respectively, and relative intensities of signals for a given species are presented as superscripts. Thus $[3,1]^3$ is the *p*-Me signal of $[\text{Fe}_4\text{S}_3\text{Se}(\text{S-}i{p}\text{-tol})_4]^{2-}$ or $[\text{Fe}_4\text{S}_3\text{Se}(\text{S-}i{p}\text{-tol})_4]^{3-}$ with 3:1 relative intensity; $[3,1]^1$ is the other *p*-Me resonance of that species. Because of their narrower line widths and greater resolution, *p*-Me signals have proven the

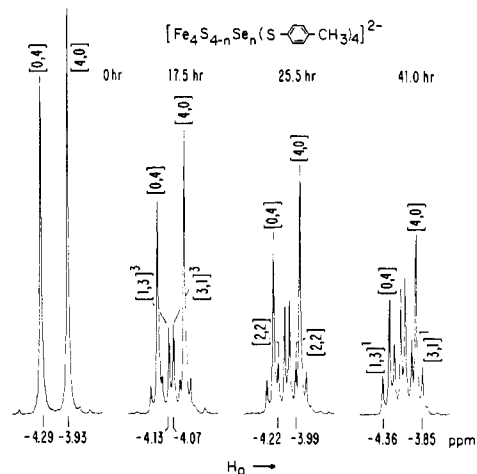


Figure 4. ^1H NMR spectra (100 MHz) depicting the time course of the core atom exchange reactions in the system $[\text{Fe}_4\text{S}_4(\text{S-}i{p}\text{-tol})_4]^{2-}/[\text{Fe}_4\text{Se}_4(\text{S-}i{p}\text{-tol})_4]^{2-}$. Reactions were run at 53°C and spectra recorded at $\sim 27^\circ\text{C}$. The concentration of each initial cluster is ~ 5 mM, and the mole fraction of the initial sulfur cluster is 0.48. Signals are labeled as in Figure 2; only the *p*-CH₃ region of the spectrum is shown.

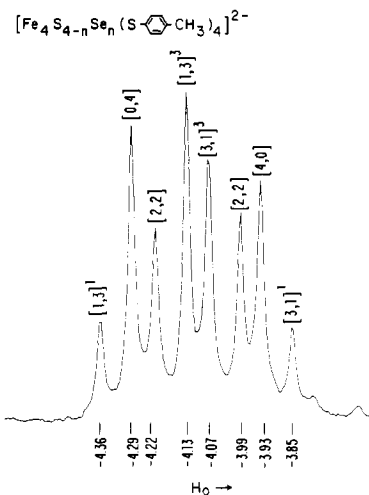


Figure 5. ^1H NMR spectrum (100 MHz) of the system $[\text{Fe}_4\text{S}_4(\text{S-}i{p}\text{-tol})_4]^{2-}/[\text{Fe}_4\text{Se}_4(\text{S-}i{p}\text{-tol})_4]^{2-}$ at $\sim 27^\circ\text{C}$ and at apparent equilibrium. The concentration of each initial cluster is ~ 5 mM, and the mole fraction of the initial sulfur cluster is 0.53; the spectrum was recorded after a 51-day reaction time at 55°C . Signals are labeled as in Figure 2; only the *p*-CH₃ region of the spectrum is shown.

more useful for identification of species and concentration measurements. *o*-H signals are not of value in these respects because of their much larger line widths and attendant poorer resolution. Full spectra of individual clusters employed in the reaction systems above have been presented elsewhere.^{4,5,8,15} Inspection of these spectra reveals significant isotropic contributions to the total chemical shifts of these paramagnetic clusters. As will be seen, the isotropic interactions afford chemical shift resolution of the *m*-H and/or *p*-Me signals of the species in Figure 1, thereby permitting their detection.

Signal Assignments. A mixture of all five $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{S-}i{p}\text{-tol})_4]^{2-,3-}$ species generates a total of eight *p*-Me and eight *m*-H resonances. All signals were assigned by examination of a large series of spectra with varying mole fractions of initial clusters under nonequilibrium and equilibrium conditions. *p*-Me and *m*-H signals could usually be differentiated on the basis of the narrower widths of the former and relative signal intensities, features evident in the spectra of the reduced clusters in Figure 2. Because of the considerable number of

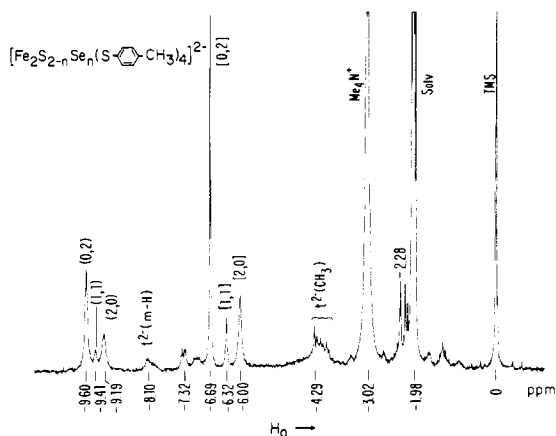


Figure 6. ^1H NMR spectrum (100 MHz) of the system $[\text{Fe}_2\text{S}_2(\text{S-}p\text{-tol})_4]^{2-}/[\text{Fe}_2\text{Se}_2(\text{S-}p\text{-tol})_4]^{2-}$ after a 120-h reaction time at $\sim 27^\circ\text{C}$. The total concentration of initial dimers is ~ 2.5 mM, and the mole fraction of initial sulfur dimer is 0.38. Signals are labeled as in Figure 2; $t^2 = [\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{S-}p\text{-tol})_4]^{2-}$.

spectra required to arrive at final assignments, these spectra are omitted, but the procedure is briefly outlined for the *p*-Me signals in the reduced cluster system with reference to the numbered signals in Table I and Figure 2. In a system with $N_S = 0.76$ and a total cluster concentration of ~ 10 mM, some 33 spectra were recorded over a period of 1350 min. The first new signals to appear were signals 12 and 13. After ~ 200 min it was evident that they were of unequal intensity; consequently both could not be [2,2] nor could both be [1,3] components because of the much higher mole fraction of the initial sulfur cluster. In the same period signal 16 was observed to emerge before signal 15, disallowing their pairing as [2,2]. At ~ 450 min it became even clearer that the former signal was the more intense, and it was observed that it and signal 12 grew in a $\sim 1:3$ intensity ratio. These observations led to the assignments signal 16 = [3,1]¹ and signal 12 = [3,1]³. Of the remaining signals (2, 7, 13, 15), signal 2 appeared last, suggesting that it is the less intense [1,3] component. At longer times signals 13 and 2 appeared in a $\sim 3:1$ intensity ratio, and neither was of the same intensity as signals 7 and 15, whose intensities were approximately equal. As a result the assignments signal 13 = [1,3]³, signal 2 = [1,3]¹, and signals 7 and 15 = [2,2] have been made. These assignments were substantiated by examination of other reaction systems including several with $N_S \approx N_{Se}$ at equilibrium where higher relative proportions of 1,3, 2,2, and 3,1 species permitted more accurate integration of the component signals of each. Similar procedures were employed to assign *m*-H signals and the *p*-Me signals of $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{S-}p\text{-tol})_4]^{2-}$. Final assignments¹⁸ are entered in Table I and Figures 2–6.

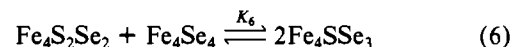
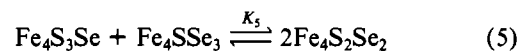
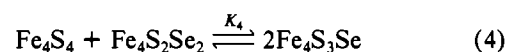
$[\text{Fe}_4\text{X}_4(\text{S-}p\text{-tol})_4]^{2-}$ Reaction System. ^1H NMR spectra showing the time course of the reactions in a system with $N_S = 0.49$ are set out in Figure 2. The *m*-H and *p*-Me signals of the 4,0 and 0,4 species slowly decrease in intensity with time, and a series of new resonances, all of which are observable in the 17.5-h spectrum, appears. At 41 h the system is near equilibrium. The equilibrium spectrum of a system of similar composition ($N_S = 0.53$), recorded after 240-h reaction time, is given in Figure 3. With the exception of signals 2,3 which appear as an asymmetric feature (and which are better resolved at shorter times (Figure 2) or in systems with $N_S \neq N_{Se}$), all signals are well resolved.

Table II. Equilibrium Constants for the Core Atom Exchange Reactions in $[\text{Fe}_4\text{S}_4(\text{S-}p\text{-tol})_4]^{3-}/[\text{Fe}_4\text{Se}_4(\text{S-}p\text{-tol})_4]^{3-}$ Systems in Acetonitrile Solution at $\sim 27^\circ\text{C}$

N_S	K_4	K_5	K_6
0.080	<i>a</i>		2.9 ± 0.8
0.17			2.5 ± 0.6
0.33		2.8 ± 0.8	2.2 ± 0.4
0.42	2.8 ± 0.2	2.5 ± 0.4	2.7 ± 0.4
0.53	2.9 ± 0.1	2.4 ± 0.1	2.7 ± 0.3
0.65	3.1 ± 0.8	2.1 ± 0.4	2.7 ± 0.1
0.85	2.8 ± 0.4		
mean	2.9 ± 0.1	2.4 ± 0.3	2.6 ± 0.3
statistical ^b	2.67	2.25	2.67

^a Low concentrations of certain species prevented meaningful evaluation of equilibrium constant. ^b Mole fractions with $N_S = N_{Se} = 0.5$: 4,0 = 0.4 = 0.0625; 3,1 = 1,3 = 0.2500; (2,2) = 0.3750.

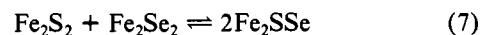
The reaction system involves five species and six equilibria with three independent equilibrium quotients that here have been chosen to correspond to reactions 4–6, written in terms



of core composition. Equilibrium constants evaluated from integrated signal intensities and the assignments in Table I are collected in Table II. It is found that these values are within experimental uncertainty of the statistical equilibrium constants for the three reactions. The latter values are obtained from simple probability considerations given elsewhere.^{19–21}

$[\text{Fe}_4\text{X}_4(\text{S-}p\text{-tol})_4]^{2-}$ Reaction System. Occurrence of core atom substitution in oxidized tetranuclear clusters is demonstrated by the spectra in Figure 4 for a system with $N_S = 0.48$ maintained at 53°C for a 41-h reaction time. Comparison with the spectra at the same times in Figure 2, where reactions were conducted at $\sim 27^\circ\text{C}$, reveals the much slower reaction rates of the oxidized clusters. This behavior is most evident from examination of [4,0] and [0,4] signal intensities relative to those of 3,1, 2,2, and 1,3 species in the two systems. *m*-H signals are poorly resolved and are not shown. A state of apparent equilibrium was achieved in a system with $N_S = 0.53$ after a 51-day reaction time at 55°C . The spectrum of that system is presented in Figure 5. Provided the system is actually at equilibrium the relative band intensities do not correspond to a statistical distribution of species (Table II) and deviate from this behavior in a manner indicative of $K \lesssim K_{\text{stat}}$ for reactions 4–6. This point is also evident upon comparison of Figure 3 and 5. Although signal peaks are all well separated, full line shapes appreciably overlap, precluding meaningful evaluation of equilibrium constants to uncertainties comparable to those in Table II.

$[\text{Fe}_2\text{X}_2(\text{S-}p\text{-tol})_4]^{2-}$ Reaction System. The spectrum of a system with $N_S = 0.38$ after a 120-h reaction time is shown in Figure 6. The occurrence of core atom exchange (reaction 7) is evidenced by the appearance of new signals at -9.41 and



-6.32 ppm, which can only be assigned to (1,1) and [1,1], respectively. The system is complicated by the formation of $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{S-}p\text{-tol})_4]^{2-}$ species at times required to produce appreciable fractions of the binuclear 1,1 complex. Presence

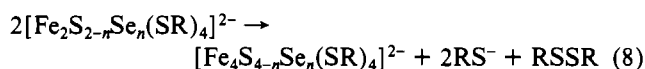
(18) Because of solubility limitations, the more intense and better resolved *p*-Me signals are considered the more securely assigned by the procedure outlined. Because of line width differences peak heights in Figures 2–6 are not necessarily a reliable indication of relative signal intensities.

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of the tetranuclear species is indicated by multiplets near -8.1 and -4.2 ppm, together with *p*-tolyl disulfide/thiolate signals at -7.32 and -2.28 ppm. Reaction 8 ($n = 0$) has been observed



in this laboratory upon allowing solutions of binuclear complexes to stand for hours and is accelerated by the presence of protic molecules.^{22,23} Because of this complication the equilibrium constant for reaction 7 has not been evaluated.

Isotropic Shift Patterns. Previous analyses of the ^1H NMR spectra of $[\text{Fe}_2\text{X}_2(\text{SR})_4]^{2-}$ and $[\text{Fe}_4\text{X}_4(\text{SR})_4]^{2-}$ ^{3-5,8,15} have established that the isotropic shifts of these clusters are dominantly hyperfine contact in origin²⁴ and are effected primarily by $\text{RS}^- \rightarrow \text{Fe}(\text{core})$ antiparallel spin transfer. The simplest manifestations of this behavior are the alternating signs of *o*-, *m*-, and *p*-H shifts and the sign reversals upon H/Me replacement. The negative signs of *m*-H and *p*-Me isotropic shifts of all mixed S/Se clusters (Table I) are indicative of dominant contact shifts also.

Several most interesting regularities emerge from further inspection of the data in Table I. First, the *p*-Me/*m*-H isotropic shift ratios for binuclear and reduced tetranuclear clusters fall in the narrow intervals of 1.75–1.78 and 1.59–1.69, respectively, indicating that within each series relative π -spin densities in each phenyl ring are essentially constant regardless of the total spin delocalized in a given ring. Second, in these two series as well as that comprised of oxidized tetranuclear clusters the weighted mean isotropic shifts of 1,3, 2,2, and 3,1 species change linearly with the number of Se or S atoms in the core. This point is illustrated by the very close agreement between mean shifts and those calculated from linear shift increments obtained from values of the limiting species. This regularity reveals that the total spin delocalized to all four phenyl rings is a virtually linear function of core Se(S) content and is maximized in species with all-Se cores. Because in these systems contact shifts are proportional to magnetic susceptibilities at the same temperature,²⁴ the larger shifts in the latter species are in accord with expectations.²⁶ As a corollary to this regularity it is observed that in $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n(\text{S-}p\text{-tol})_4]^{2-}$ ³⁻⁵ clusters ligands attached to FeS_2Se coordination subunits necessarily are, on the basis of relative signal intensities ($[3,1]^3$, $(3,1)^3$), associated with larger isotropic shifts than the ligand attached to the unique FeS_3 subunit ($[3,1]^1$, $(3,1)^1$ resonances). The reverse situation obtains in 1,3 species where larger isotropic shifts occur in the unique ligand (FeSe_3 subunit) than in the remaining three (FeSSe_2 subunit). On this basis it is proposed that in 2,2 species the larger isotropic shifts are associated with ligands bound to the FeSSe_2 rather than the FeS_2Se coordination subunits.

The foregoing isotropic shift regularities are in no sense required by any element of contact shift theory nor are they necessarily anticipated on the basis of the experimentation with other molecules exhibiting prevalent contact shifts. They are, however, entirely acceptable intuitively and rest on the signal assignments in Table I. The regularities are considered modest arguments in favor of these assignments and the attendant

significance of the equilibrium constants in Table II, but neither was utilized in deducing the assignments.

Cluster Reactivity Features. In the substitution reactions (3) with $\text{R} = \text{CH}_2\text{Ph}$ and $\text{YL} = \text{stoichiometric CH}_3\text{COCl}$ the reactions proceed to completion and afford approximately statistical mixtures of $[\text{Fe}_4\text{S}_4(\text{SR})_{4-x}\text{Cl}_x]^{2-}$ species.⁹ In another case of reaction 3 replacement of thiolate ligands in $[\text{Fe}_4\text{S}_4(\text{S-}t\text{-Bu})_4]^{2-}$ with several cysteinyl peptides yielded multiple apparent equilibrium constants not inconsistent with roughly statistical behavior.²⁷ In the thiolate substitution equilibria involving $[\text{Fe}_4\text{S}_4(\text{S-}t\text{-Bu})_4]^{2-}$ and $[\text{Fe}_4\text{S}_4(\text{S-}p\text{-tol})_4]^{2-}$ the equilibrium constants, which are expressible analogously to those of reactions 4–6, approach (but are slightly less than) their statistical values.²⁸ With the present findings that, for reactions 4–6, $K \lesssim K_{\text{stat}}$ for oxidized clusters and $K \approx K_{\text{stat}}$ for reduced clusters, the following reactivity picture emerges at this stage. Both terminal ligands and core chalcogenide atoms can be substituted by other groups or atoms of the same charge and (for core atoms) of not too dissimilar size²⁹ in reactions which afford roughly statistical product distributions. Given the long distances (6–7 Å) between thiolate sulfur or chloride sites, it is not surprising that statistical behavior obtains upon substitution around a core structure of essentially constant dimensions. It is less obvious, however, that similar behavior would be realized upon substitution of tightly associated core atoms.

The pronouncedly faster core atom substitution reactions of reduced vs. oxidized tetranuclear clusters is presumably a consequence of the longer and weaker bonds in the former species.³⁰ For example, $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ has an elongated tetragonal structure in the solid state with four long (2.354 Å) and eight short (2.286 Å) Fe–S bonds,⁶ whereas $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ has the opposite distortion with four short (2.267 Å) and eight long (2.296 Å) bonds.²⁸ The relatively more facile S/Se core substitution in the reduced clusters is a further indication of a type of structural lability or pliability of their cores. Previous evidence of this property is the existence in the crystalline state of various distortions of cores from tetragonal symmetry^{6,7,17} and the adoption of an elongated tetragonal structure (or at least a shorter range of distortions therefrom) in solution where environmental constraints are minimized.^{6,7} One implication of the present results, to be explored, is that Fe atoms may also be substituted in reduced analogue or protein clusters by other metals (e.g., Co(II), Zn(II)) of the same charge, comparable size,²⁹ and similar stereochemical preference.³¹ Finally, the results reported here demonstrate the occurrence of a type of core substitution reaction of intact polynuclear species which, to our knowledge, has no clear precedent in metal cluster chemistry. At present these results are insufficient for deduction of mechanistic features. However, the seemingly attractive possibility of rupture of long bonds of reduced species following by statistical

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(24) For treatment of contact shifts in antiferromagnetic systems such as these binuclear clusters²⁵ and oxidized⁶ and reduced^{6,7} tetranuclear clusters cf. ref 5 and 15 and G. N. La Mar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 63 (1973).

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(26) Requisite data to support this point are available only for oxidized tetranuclear species in the solid state: $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$, $\chi^M = 1.96 \times 10^{-3}$; $(\text{Me}_4\text{N})_2[\text{Fe}_4\text{Se}_4(\text{SPh})_4]$, $\chi^M = 2.55 \times 10^{-3}$ cgsu¹¹ (~ 300 K).

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(30) This statement assumes that, in their respective systems, 2- and 3- clusters are the reacting species. Both are subject to disproportionation reactions which, however, produce very small concentrations of other oxidation levels. From measured potentials¹¹ K_{eq} values and concentrations of 2- and 4- clusters (10 mM solutions of 3- clusters) for the equilibria $2[\text{Fe}_4\text{X}_4(\text{SPh})_4]^{3-} \rightleftharpoons [\text{Fe}_4\text{X}_4(\text{SPh})_4]^{2-} + [\text{Fe}_4\text{X}_4(\text{SPh})_4]^{4-}$ are the following: X = S, $K_{\text{eq}} = 9.7 \times 10^{-13}$, $\sim 0.1 \mu\text{M}$; X = Se, $K_{\text{eq}} = 4.8 \times 10^{-11}$, $\sim 0.7 \mu\text{M}$ (DMF solution). Corresponding values of 2- cluster reactions cannot be given owing to the absence of 2-/1- potential data.

(31) Such substitutions cannot be attempted analogously to the substitution reactions reported here inasmuch as Co(II) and Zn(II) clusters of the type $[\text{M}_4\text{X}_4(\text{SR})_4]^{4-}$ have not been synthesized.

recombination ($\text{Fe}_2\text{S}_2 + \text{Fe}_2\text{Se}_2 \rightleftharpoons \text{Fe}_4\text{S}_2\text{Se}_2$) does not appear to be the first event of reaction. As may be seen in Figures 2 and 4, as well as in systems with $N_S \neq N_{Se}$, the first new species to appear are 3,1 and 1,3 rather than 2,2.

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Registry No. $[\text{Fe}_2\text{S}_2(\text{S-}p\text{-tol})_4]^{2-}$, 55939-63-4; $[\text{Fe}_2\text{SSe}(\text{S-}p\text{-tol})_4]^{2-}$, 77136-59-5; $[\text{Fe}_2\text{Se}_2(\text{S-}p\text{-tol})_4]^{2-}$, 74752-89-9; $[\text{Fe}_4\text{S}_4(\text{S-}p\text{-tol})_4]^{3-}$, 67724-72-5; $[\text{Fe}_4\text{S}_3\text{Se}(\text{S-}p\text{-tol})_4]^{3-}$, 77305-58-9; $[\text{Fe}_4\text{S}_2\text{Se}_2(\text{S-}p\text{-tol})_4]^{3-}$, 77305-56-7; $[\text{Fe}_4\text{SSe}_3(\text{S-}p\text{-tol})_4]^{3-}$, 77305-54-5; $[\text{Fe}_4\text{Se}_4(\text{S-}p\text{-tol})_4]^{3-}$, 75025-81-9; $[\text{Fe}_4\text{S}_4(\text{S-}p\text{-tol})_4]^{2-}$, 51899-68-4; $[\text{Fe}_4\text{S}_3\text{Se}(\text{S-}p\text{-tol})_4]^{2-}$, 77305-57-8; $[\text{Fe}_4\text{S}_2\text{Se}_2(\text{S-}p\text{-tol})_4]^{2-}$, 77305-55-6; $[\text{Fe}_4\text{SSe}_3(\text{S-}p\text{-tol})_4]^{2-}$, 77305-53-4; $[\text{Fe}_4\text{Se}_4(\text{S-}p\text{-tol})_4]^{2-}$, 75025-82-0.

Contribution from the Chemical Laboratories of the University of California, Santa Barbara, California 93106

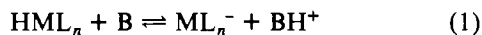
Rate and Equilibrium Data for the Protonation of Vaska's Compound and Analogues

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Equilibrium constants, K_{H^+} , for the addition of a proton, and K_{HCl} , for the addition of HCl, were measured in methanol for a series of analogues of Vaska's compound, $\text{MY}(\text{CO})\text{L}_2$. The constants were nearly equal, showing that chloride and methanol are held about equally well in the product complexes. Rhodium(I) complexes are 10 times less basic than the corresponding iridium(I) complexes. A study of the kinetics of the addition reactions showed that chloride ion or solvent added to the metal first, followed by protonation.

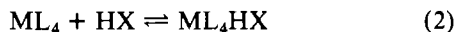
The Brønsted acidity of transition-metal hydrides and the related proton basicity of transition-metal complexes are receiving increased attention.^{1,2} The role of such hydrides in homogeneous catalysis is a major reason for such interest. The general equation is



where both rate and equilibrium constants can be measured in many cases. An additional feature of (1) is that it is an example of reductive elimination in the forward direction and oxidative addition in the reverse direction. The normal oxidation state of the metal is increased by two units upon protonation. Structural changes also occur which show that the oxidation is more than formal.

There is only a modest amount of information available on the effect of changing the metal, M, and the coligands, L, on rates and equilibrium for reaction 1. There is a strong trend for greater basicity in complexes of heavier elements compared to the analogous complexes of the lighter elements. However a recent study of the nucleophilic reactivity of a large number of ML_n showed that no simple pattern existed for rate data.³ Similar irregularities may be expected for proton basicities.

When ML_n is a square-planar complex of a d^8 metal atom, addition of H^+ is usually accompanied by addition of a second group, X (eq 2). The role played by the group X in deter-



mining the rates and equilibria for (2) is not well-known. Pioneering studies by Shaw and Deeming⁴ on addition of HX in benzene to Vaska's compound and its analogues showed that variations did exist (eq 3). For example $\text{X} = \text{Cl}^-$ added more



strongly than $\text{X} = \text{NO}_3^-$. The addition of acetic acid was reversible and allowed equilibria to be measured as a function of Y and L. Other carboxylic acids also added, with the

stronger acids binding to a greater extent.

The complexes $\text{Ir}(\text{cod})\text{L}_2^+$ and $\text{IrCl}(\text{cod})\text{L}$, where cod is 1,5-cyclooctadiene, will add HCl and HBr in methanol, but the proton alone will not add.⁵ Thus $\text{X} = \text{CH}_3\text{OH}$ is ineffective in oxidative addition to these complexes. Somewhat surprisingly, it was found that the mechanism of addition occurred by X^- adding first, followed by the proton.

The present work was undertaken to get more information on the role of changes in the metal, M, and the coligands, L. An early observation was that, unlike the cod complexes above, Vaska's compound would add the proton only. That is, acids such as $\text{CF}_3\text{SO}_3\text{H}$ and FSO_3H would react. As in the related case of reaction with $\text{CF}_3\text{SO}_3\text{CH}_3$, it is likely that the solvent methanol occupies the sixth position.⁶ The kinetics of the addition of H^+ and of HCl were also examined.

Experimental Section

Reagent grade methanol was distilled to remove most of the water present. It was then stored over 3A or 4A molecular sieves under a positive pressure of dry, oxygen-free nitrogen. This was then followed by storage over lumps of calcium hydride, again under a positive pressure of nitrogen.

Reagent grade acetonitrile was predried by stirring with calcium hydride until gas evolution stopped. It was then distilled from P_2O_5 (≤ 5 g/L) in an all-glass apparatus. The first 5% and the last 10% of the distillate were discarded in order to reduce the acrylonitrile content. This was followed by storage under a positive pressure of nitrogen.

Prior to use, the solvents were deoxygenated by bubbling purified nitrogen through them for approximately 1 h. All solvents were handled with use of standard airless techniques (Schlenk tube or serum cap/syringe).

All materials were prepared and stored under prepurified nitrogen. All solutions were prepared and stored under nitrogen in vessels equipped with serum caps to allow for transfer by syringe. Acid and base solutions were freshly prepared prior to each experiment. Trifluoromethanesulfonic acid, HSO_3CF_3 (Aldrich Chemical Co., analytical grade), was used without further purification. Hydrochloric acid and hydrobromic acid (Linde Division, Union Carbide Corp.) solutions were prepared by bubbling gaseous HCl or HBr (anhydrous) through methanol followed by standardization by simple titration.

Tetraethylammonium chloride and bromide (J. T. Baker Chemical Co.), AgNO_3 (Mallinckrodt Chemical Co.), $\text{P}(\text{OMe})_3$ (Ventron

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