calculated kinetic shifts for two measurement approaches. The "conventional" kinetic shift is taken as the energy above E_0 needed to give 1% fragmentation within 10^{-5} s, appropriate to conventional mass spectrometer appearance measurements. The "intrinsic" kinetic shift is taken as the energy needed for 10% fragmentation in competition with radiative relaxation of the excited ion, appropriate to an ion-trap appearance-energy experiment unlimited by ion containment time.

These large kinetic shifts account for the high thresholds obtained even in previous ion-trap work.[1] In the presence of major kinetic shifts, only determination of two or more points on the rate–energy curve (for instance, by photodissociation, PEPICO,[15] or MPI[16]), accompanied by RRKM modeling, leads to useful information about the dissociation activation energy.[14] In the methylnaphthalene case, this leads to a new upper limit on the heat of formation for $C_{11}H_9^+$ of ≤869 ± 20 kJ mol^{-1} (most likely referring to the benzotropylium structure).[17]

Acknowledgment. Support of this work from the National Science Foundation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(14) Only the technique of radical ionization[6] avoids entirely the uncertainty introduced by kinetic shifts, and it may have given a valid measurement of the heat of formation of the methylnaphthylium ion (but no information about the benzotropylium ion).

(15) For instance: Baer, T; Dutuit, O.; Mestdagh, H.; Rolando, C. *J. Phys. Chem.* **1988**, *92*, 5674.

(16) For instance: Neusser, H. J. *J. Phys. Chem.* **1989**, *93*, 3897.

(17) As expected, this is much lower than the previous value of 962 kJ/mol given in the following: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, *Suppl. 1*.

Synthetic $NiFe_3Q_4$ Cubane-Type Clusters ($S = {}^3/_2$) by Reductive Rearrangement of Linear $[Fe_3Q_4(SEt)_4]^{3-}$ (Q = S, Se)

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Heterometal cubane-type clusters MFe_3S_4 containing biological metals such as Co, Ni, and Zn cannot be prepared by assembly reactions analogous to those producing M = V,[1] Mo,[2] W,[2] and Re[3] clusters, owing to the absence of appropriate thiometalate precursors $[MS_4]^{z-}$. However, incubation of proteins having cuboidal Fe_3S_4 clusters with M^{2+} salts affords protein-bound species, which, while structurally undefined, possess electronic properties indicative of the integration of M = Co,[4] Ni,[5] Zn,[6,7] or Cd[7] and Fe_3S_4 into a common, presumably cubane-type, unit. Noting that the linear $[Fe_3S_4(SEt)_4]^{3-}$ (**1**) → cubane $[Fe_4S_4(SEt)_4]^{2-}$ cluster conversion in the system **1**/$FeCl_2$/NaSEt[8] proceeds by an effective two-electron reduction of **1**, we investigated reaction 1 (Q = S, Se) with two trinuclear precursors which differ appreciably in their reducibilities [E_{pc}(**1**) = −1.66, −1.79 V (MeCN); E_{pc}(**2**) = −1.18, −1.24 V (DMF)].[9] Previously unreported $[Fe_3Se_4(SEt)_4]^{3-}$ (**2**) was prepared analogously to **1**[8] (67%) and derivatized (4 equiv of PhSH) to $[Fe_3Se_4(SPh)_4]^{3-}$ (**3**, 68%), which was proven by crystallography to have the linear trinuclear structure (Fe–Fe–Fe, 180°; Fe–Se, 2.321 (1)–2.365 (1) Å; Fe–Fe, 2.781 (1) Å.[10]

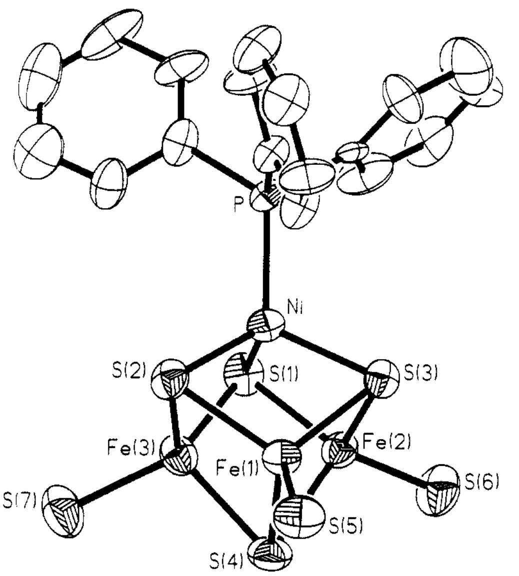
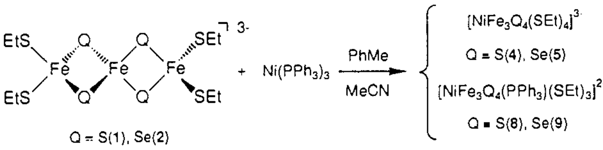


Figure 1. Structure of cluster **8** as its Et_4N^+ salt, showing 30% thermal ellipsoids and the atom-labeling scheme. Mean values of the indicated distance (Å) or angle *type* under idealized C_3 symmetry: Ni–Fe, 2.69 (2); Ni–S, 2.262 (6); Fe(3)–S(2), 2.306 (8); Fe(2)–S(4), 2.297 (8); Fe(3)–S(1), 2.269 (7); Fe(1)–S(5), 2.283 (6); P–Ni–S, 113 (2)°; S–Ni–S, 105.8 (7)°. Also: Ni–P, 2.174 (6) Å; Ni···S(4), 3.824 (7) Å. Esd's of individual distances and angles are 0.004–0.008 Å and 0.1–0.3°, respectively.



(1)

The residue after solvent removal from equimolar reaction 1 (6 h) was treated in two ways.[9] (i) Thorough washing with toluene followed by recrystallization (acetonitrile/ether) gave **4** or **5** (50–60%); **4** contained a 10–15% impurity of $[Fe_4S_4(SEt)_4]^{3-}$ (**6**)[11] which could not be separated. These two clusters were identified by their isotropically shifted ^{1}H NMR spectra:[9] **4**, δ 58.5, 5.80,

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(9) All reactions and measurements were performed under anaerobic conditions. Clusters were isolated as Et_4N^+ salts; purified yields are given. Potentials are referenced to the SCE and isomer shifts to Fe metal at 298 K. ^{1}H NMR spectra were measured in CD_3CN; ethyl group shifts are given in the order CH_2, CH_3 (Fe, Ni). The Ni–SCH_2CH_3 signals of **4** and **5** were obscured by other resonances.

(10) X-ray structures were solved by standard procedures; empirical absorption corrections were applied. Crystallographic data are given as *a*, *b*, *c* (Å); β, space group, *Z*, unique data ($F_o^2 > 3\sigma(F_o^2)$), $R(R_w)$ (%). $(Et_4N)_3$[**3**] (173 K): 27.591 (5), 11.124 (2), 20.961 (3) Å; 118.18 (1)°, *C*2/*c*, 4, 3290, 4.9(5.6). $(Et_4N)_3$[**5**] (203 K): 11.596 (2), 36.768 (6), 11.848 (2) Å; 106.79 (2)°, $P2_1/n$, 4, 3541, 4.5(4.9). $(Et_4N)_3$[**7**] (173 K): 11.639 (4), 36.774 (7), 11.875 (2) Å; 106.79 (2)°, $P2_1/n$, 4, 4255, 6.2(6.3). $(Et_4N)_2$[**8**] (298 K): 13.338 (5), 14.657 (7), 26.627 (9) Å; 100.46 (3)°, $P2_1/n$, 4, 2717 (4σ), 9.5(10.3). $(Et_4N)_2$[**9**] (273 K): 13.467 (3), 14.353 (2), 27.112 (4) Å; 102.20 (1)°, $P2_1/n$, 4, 5257, 5.36(6.22). The structure of **5** was refined with a 25%/75% Ni/Fe site occupancy.

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−38.6; **6**, δ 36.3, 5.50. Similarly, **5** (δ 62.1, 6.30, −42.4) was differentiated from $[Fe_4Se_4(SEt)_4]^{3-}$ (**7**; δ 50.0, 7.05), formed to a small extent in reaction 1. Cluster **7** was independently synthesized by the reaction of **2** with Zn powder in acetonitrile (79%) and by the reduction of $[Fe_4Se_4(SEt)_4]^{2-}$ with sodium acenaphthylenide in acetonitrile/THF (68%). (ii) Ether addition to an acetone extract afforded **8** (δ 58.6, 4.30) or **9** (δ 63.0, 3.80) in 30–40% yield.

The X-ray structure determination of $(Et_4N)_3[\mathbf{7}]$[10] revealed the familiar cubane-type stereochemistry[12] with a compressed tetragonal $[Fe_4Se_4]^{1+}$ core distortion.[13] $(Et_4N)_3[\mathbf{5}]$ is isomorphous with this compound, and correspondingly, cluster **5** was determined to be a cubane with its $[NiFe_3(\mu_3\text{-}Se)_4]^{1+}$ core and dimensions comparable to those of **7**.[12] Because of disorder, a unique Ni site could not be structurally defined. This is not the case with the isomorphous compounds $(Et_4N)_2[\mathbf{8}]$ and $(Et_4N)_2[\mathbf{9}]$, whose clusters have the cubane configuration. The structure of **8**, which approaches idealized C_3 symmetry, is shown in Figure 1; that of **9** is entirely analogous. These structures are consistent with the NMR spectra, which reveal trigonal cluster symmetry and thus Ni–PPh$_3$ ligation. Important average dimensions of **8** include the Ni–Fe distance of 2.69 (2) Å and the Fe–SEt distance of 2.283 (6) Å, which indicates a mean Fe oxidation state $\lesssim$2.50+.[11,13,14] Substitution of Ni for Fe strongly affects redox potentials in couples of the same charge; e.g., $E_{1/2} = -0.95$ V ($\mathbf{4}^{2-/3-}$) vs −1.26 V ($\mathbf{6}^{2-/3-}$).

The EPR spectrum of cluster **8** (acetonitrile, 3 K) with principal g values at 4.6, 3.3, and 1.95 is suggestive of an $S = {}^3/_2$ ground state, with $D > 0$, and $E/D = 0.12$. Further, the magnetic susceptibilities of **8** and **9** exhibit Curie–Weiss behavior at low temperatures, $\chi^M(\mathbf{8}) = 1.988/(T + 1.74)$ (5–35 K) and $\chi^M(\mathbf{9}) = 1.941/(T + 1.31)$ (5–70 K), and establish an $S = {}^3/_2$ ground state.[15] The zero-field Mössbauer spectra of polycrystalline **8** are significantly broadened by spin–spin interactions at $T < 180$ K. The spectrum at 210 K[9] consists of a single quadrupole doublet (0.32 mm/s line width) with isomer shift $\delta = 0.41$ mm/s and splitting $\Delta E_Q = 0.62$ mm/s. A spectrum taken in a 6.2-T applied field at 1.5 K is shown in Figure 2. With the aid of spectra recorded in weaker fields, three magnetically distinct subsites are discernible. Two have negative, and the third has positive, magnetic hyperfine coupling constants.[16] Thus, local spins of two subsites are aligned parallel to the cluster spin whereas the remaining local spin is aligned antiparallel. Using an $S = {}^3/_2$ spin Hamiltonian, we have simulated the spectra in Figure 2.

The Fe$_3$S$_4$ portion of cluster **8** and those of protein-bound $[MFe_3S_4]^{1+}$ (M = Co,[4] Zn,[6,7] and Cd[7]) are isoelectronic. However, as observed by Mössbauer spectroscopy, the delocation patterns within mixed-valence $[Fe_3S_4]^{1-}$ differ. For M = Zn and Cd, the $S = {}^5/_2$ cluster contains a delocalized Fe^{2+}/Fe^{3+} pair ($S = {}^9/_2$) coupled to trapped-valence Fe^{2+} ($S = 2$). $[CoFe_3S_4]^{1+}$ and **8**, on the other hand, lack the distinctive Fe^{2+} site, suggesting a configuration with more delocalized character. Details of the spin coupling need to be worked out, but we conclude that **8** and the NiFe$_3$S$_4$ cluster in *Pyrococcus furiosus* ferredoxin are isoelectronic with an $S = {}^3/_2$ ground state.[17] These results clearly support the concept of a cubane-type structure for protein-bound $[MFe_3S_4]$ units. Nickel EXAFS[20] and EPR line broadening[21] together suggest a Ni–Fe center in CO dehydrogenases (CODH) from several bacteria. The possibility of a NiFe$_3$S$_4$ cluster has been noted.[21d] Access to clusters **4** and **8** now permits the first examination of the reactivity of a Ni site in a proven cubane-type environment. Regiospecific reactions at this site can be accomplished, one example being the complete conversion of **8** to trigonally symmetric $[NiFe_3S_4(t\text{-}BuNC)(SEt)_3]^{2-}$ (δ 59.0, 5.30, 0.90 (t-Bu)) by 4 equiv of t-BuNC in acetonitrile solution. Lastly, the isomer shifts of **4** and **8** (0.47 mm/s) are distinctly smaller than those of isoelectronic protein-bound MFe$_3$S$_4$ clusters (0.53–0.55 mm/s).[4,6,7] The similarity of these shifts to those of the oxidized and reduced Ni–Fe center in *Clostridium thermoaceticum* CODH (0.44 mm/s[22]) renders the synthetic clusters additionally attractive for electronic and reactivity studies as a means of probing the

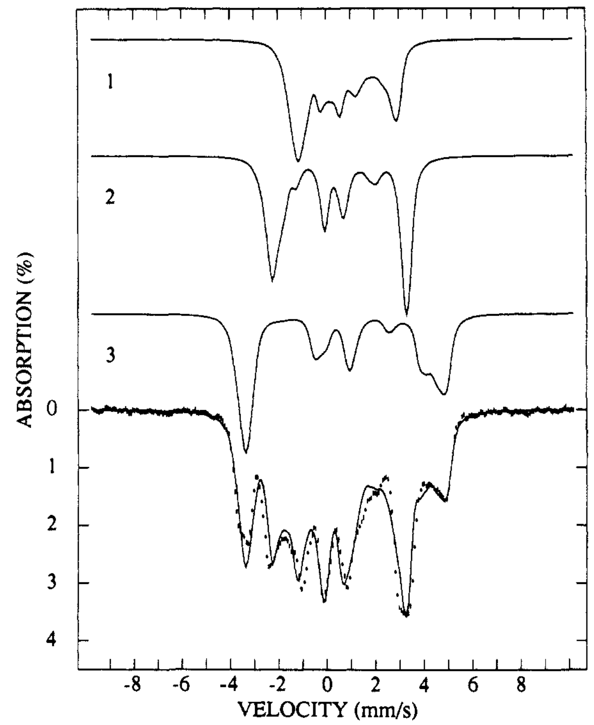

Figure 2. Mössbauer spectra of polycrystalline **8** recorded in a parallel applied field of 6.2 T. The solid lines are theoretical spectra for the three Fe subsites and the sum (bottom), generated from a spin Hamiltonian with $S = {}^3/_2$ cluster spin, the parameters in the text, and the following magnetic hyperfine tensor components (A_x, A_y, A_z, in MHz).[16] Site 1: −10.7, −17.8, −18.5. Site 2: −19.5, −21.7, −23.3. Site 3: +13.4, +18.8, +19.9. For all subsites we used $\delta = 0.47$ mm/s and $\Delta E_Q = -0.90$ mm/s at 4.2 K.

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(12) Bond distance ranges M–M, M–Se, M–SEt (Å): 2.782 (3)–2.842 (3), 2.401 (3)–2.480 (3), 2.287 (4)–2.310 (4) (**7**); 2.751 (2)–2.855 (2), 2.391 (2)–2.456 (2), 2.282 (4)–2.289 (4) (**5**).

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(15) $C = 1.875$ emu K/mol for $S = {}^3/_2$ and $g_e = 2$.

(16) We defer a listing of the complete A_i parameter set until studies on paramagnetically dilute samples are complete. It appears that $D = 2$–3 cm^{-1}; under these circumstances, the 6.2-T spectrum is essentially independent of D and E. The average values $(A_x + A_y + A_z)/3$ are probably accurate to ±5% for all sites.

(17) This state could arise from antiparallel coupling of spins $S = {}^5/_2$ and $S = 1$ (Ni^{2+}). In this sense, Ni(PPh$_3$)$_3$ functions as a two-electron reductant in reaction 1. Also, the increase in isomer shift from 0.23 mm/s ($\mathbf{1}$[18]) to 0.47 mm/s (**4**, **8**) at 4.2 K indicates substantial reduction of the $[Fe_3S_4]^{1+}$ portion of **1**. Rearrangement of linear **1** to a MoFe$_3$S$_4$ cubane-type species upon one-electron reduction has been reported.[19]

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structure and function of the enzymic Ni–Fe center.

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Supplementary Material Available: Tables of positional parameters for the five compounds in footnote 10 (8 pages). Ordering information is given on any current masthead page.

Intramolecular Alkane Dehydrogenation and Functionalization at Niobium Metal Centers

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The last 10 years have seen an explosion of interest in the transition-metal chemistry associated with ancillary aryl oxide ligation.[1-3] A particularly popular ligand is the 2,6-diisopropylphenoxide group due to its steric size as well as its apparent reluctance to undergo cyclometalation chemistry.[4,5] We report here on the facile dehydrogenation[6,7] of the substituent alkyl groups of this ligand at niobium metal centers as well as upon the ensuing reactivity of the resulting metallacyclopropane.

The room temperature reduction of thf solutions of the dichloride $Nb(OC_6H_3Pr^i{}_2\text{-}2,6)_3Cl_2$ (**1**)[8] with sodium amalgam (2 Na/Nb) results in the formation of dark solutions from which the deep-green crystalline complex $Nb(OC_6H_3Pr^i{}_2\text{-}2,6)_2(OC_6H_3Pr^i\text{-}\eta^2\text{-}CMe{=}CH_2)(thf)$ (**2**) can be obtained in high yield (Scheme I). A reasonable pathway for the formation of **2** from **1** involves intramolecular oxidative addition of an isopropyl CH bond (either primary or tertiary) in an intermediate Nb(III) compound $[Nb(OC_6H_3Pr^i{}_2\text{-}2,6)_3]$ followed by elimination of H_2.[9] The new vinyl phenoxide group in **2** is clearly indicated in solution spectra. The $CMeCH_2$ protons appear as a singlet and AB pattern in the ratio of 3:1:1 in the ^1H NMR spectrum. In the ^{13}C NMR spectrum the two carbon atoms coordinated to the metal center resonate at δ 95.9 and 90.1 ppm, the latter appearing as a triplet with $^1J(^{13}C\text{–}^1H) = 140.8$ Hz. A single-crystal X-ray diffraction analysis of **2**[8] clearly shows the new ligand strongly chelated to the metal center (Figure 1). In particular the short Nb–C distances of 2.167 (3) and 2.208 (2) Å and C–C distance of 1.453 (4) Å coupled with the significant bending back of the methylene group protons are more consistent with a metallacyclopropane

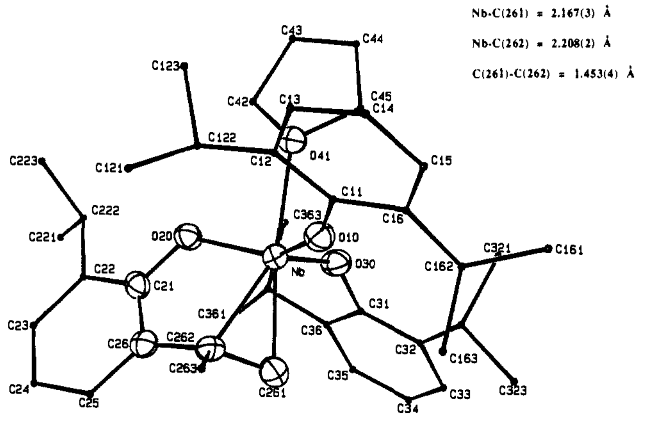

Figure 1. ORTEP view of **2** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg): Nb–O(10), 1.875 (2); Nb–O(20), 1.949 (2); Nb–O(30), 1.967 (2); Nb–O(41), 2.293 (2); Nb–C(261), 2.167 (3); Nb–C(262), 2.208 (2); C(261)–C(262), 1.453 (4); Nb–O(10)–C(11), 157.6 (2); Nb–O(10)–C(21), 120.0 (1); Nb–O-(30)–C(31), 137.7 (2).

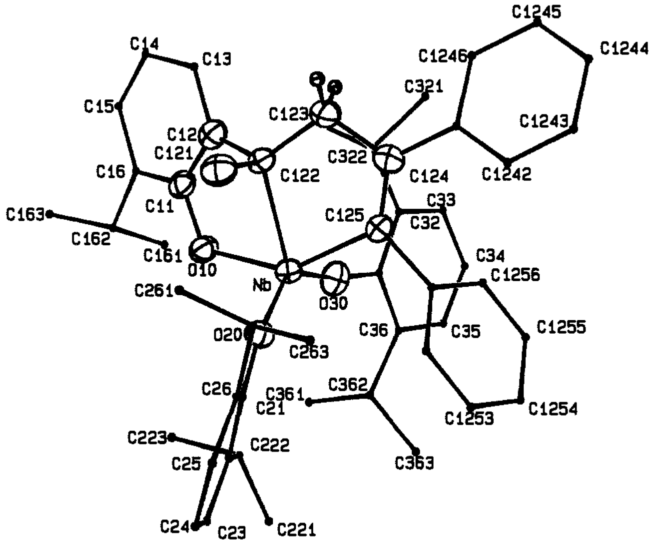

Figure 2. ORTEP view of **3**. Selected bond distances (Å) and angles (deg): Nb–O(10), 1.943 (4); Nb–O(20), 1.873 (4); Nb–O(30), 1.882 (4); Nb–C(122), 2.261 (6); Nb–C(125), 2.125 (6); C(122)–C(123), 1.532 (8); C(123)–C(124), 1.501 (9); C(124)–C(125), 1.349 (8); Nb–O(10)–C(11), 123.0 (4); Nb–C(122)–C(123), 114.0 (4); Nb–C(125)–C(124), 125.1 (5).

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(8) Details of the analytical and spectroscopic data as well as the crystallographic studies are contained in the supplementary material.

(9) Oxidative addition of aliphatic and aromatic CH bonds to M(III) (M = Nb,Ta) metal centers has precedence; see ref 2f and see: (a) Lapointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382. (b) Steffey, B. D.; Chamberlain, L. R.; Chesnut, R. W.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1419.

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