

(visible spectrum of **5**, 677, 644, 575, 508, 417 nm; that for ClFe(TPP),¹⁴ 687, 660, 573, 506, 412 nm). However, it appears that the μ -oxo-bridged dimer [T(*o*-MCbMe)P]-Fe^{III}OFe^{III}[T(*o*-MCbMe)P] (**6**) is formed quantitatively by chromatography of **5** on alumina in CHCl₃ in air (compare visible spectrum of **6** (CHCl₃), 650, 565, 420, with that of (TPP)Fe^{III}OFe^{III}(TPP), 612, 571, 408¹⁴).

Treatment of **1c** with piperidine in DMF at 55 °C yields a water-soluble tetrapiperidinium salt, (Pipm)₄H₂T(*o*-MCbMe)P (**1d**) in which the *meso*-CH₂C₂B₁₀H₁₀ Me substituents have been degraded to [-CH₂C₂B₉H₁₀Me]⁻ moieties (visible spectrum in H₂O, 655, 597, 562, 527, 424 nm). This degradation reaction is known to remove one of B atoms on either side of the C-C bond in 1,2-C₂B₁₀H₁₂.¹⁵ Since the borons removed are either enantiotopic or diastereotopic, a multitude of isomeric possibilities other than atropisomerism exist for **1d**. A water insoluble Me₄N⁺ salt of the degraded porphyrin is obtained by quantitative metathesis of **1d** with Me₄NCl. The intensity of the Me₄N⁺ signal (12) relative to the *meso*-CH₂ and β -pyrrole signals (both 2) in the ¹H NMR spectrum of **1e** demonstrates that all four carborane cages have been degraded (the δ values in pyridine-*d*₅ are 1.93, 5.5–6.1, and 9.6–9.8, respectively, with the broad multiplet nature of the latter two resonances reasonably attributable to a mixture of isomers (vide supra)).

The intermediacy of $\alpha,\alpha,\alpha,\alpha$ -*meso*-tetra(*o*-aminophenyl)-porphyrin (**7**)¹⁶ afforded $\alpha,\alpha,\alpha,\alpha$ -H₂T(*o*-CbMeAmP)P (**1f**) atropisomerically pure as evidenced by TLC and ¹H NMR. To obtain **1f**, the aminoporphyrin **7** was treated with a 100% excess of the acid chloride 1-ClC(O)CH₂-1,2-C₂B₁₀H₁₁¹⁷ (**8**) in THF-pyridine at 25 °C followed by hydrolysis of excess **8** and silica gel column chromatography (benzene-ether). The infrared of **1f** (CHCl₃) shows characteristic ν_{BH} at 2600, $\nu_{\text{CO(amide)}}$ at 1705, ν_{NH} at 3445, and $\nu_{\text{CH(carborane)}}$ at 3095 cm⁻¹, respectively; the visible spectrum (CHCl₃) is 418, 512, 543, 572, 652 nm. The ¹H NMR is clean in the β -pyrrole and CH₂ regions unlike those **1b–e** (9.25 (2, β -pyrrole), 8.9 (1, NH), 8.2–7.4 (4, C₆H₄), 4.5 (1, CH carborane), and 2.8 (2, CH₂)).

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Nature of Naked-Metal-Cluster Polyaniions in Solution. Evidence for (Sn_{9-x}Pb_x)⁴⁻ (x = 0–9) and Sn–Sb Clusters

Sir:

Recently, Corbett and his coworkers isolated and determined the crystal structures of several "naked-metal-cluster" polyaniions such as Sb₇³⁻, Pb₅²⁻, Te₃²⁻, Sn₅²⁻, Sn₉⁴⁻, Ge₉²⁻, and Ge₉⁴⁻.¹ Reversion to the alloy phase from which the clusters are derived was prevented by clever use of the bicyclic 2,2,2-crypt ligand² which effectively complexes the alkali metal counterion and thereby precludes electron transfer upon solvent evaporation. Kummer and Diehl³ have found somewhat more limited success in isolating Sn₉⁴⁻ as a solvate with ethylenediamine. Although these crystallographic investigations have defined the geometries of these interesting clusters in the crystalline state, their nature in solution has been the subject of speculation.¹ We report here *prima facie* evidence for the fluxional nature of the Sn₉⁴⁻ cluster in solution, the existence of (Sn_{9-x}Pb_x)⁴⁻ clusters, and the possibility of SbSn₉³⁻ or SbSn₉¹⁻ cluster.

Alloys of compositions near NaSn_{2.25} were dissolved in ethylenediamine (en) to give typical deep-orange-red solutions of Sn₉⁴⁻ which were investigated at both 31.896 and 29.641 MHz by pulse Fourier transform ¹¹⁹Sn NMR.⁴ A sample 85% enriched in ¹¹⁹Sn was used to locate the position of Sn₉⁴⁻. A single resonance was found 1230.0 ppm upfield from tetramethyltin (TMT) with very weak satellites due to a ¹¹⁹Sn–¹¹⁷Sn coupling of 254 Hz. Samples prepared from naturally abundant tin gave a 0.046:0.312:1.000:0.312:0.046 quintet compared with calculated intensities of 0.044:0.311:1.000:0.311:0.044.⁵ The lines were separated by 127 Hz which gives *J*_{119Sn–117Sn} = 254 Hz. The observation of a single resonance indicates that the individual environments of the static C_{4v} structure (monocapped square antiprism)^{1a} are averaged⁶ in some manner (Figure 1). The observation of ¹¹⁹Sn–¹¹⁷Sn spin-spin coupling shows that the averaging process is intramolecular. Other idealized structures such as the D_{3h} tricapped trigonal prism or the C_{4v} monocapped cube also have non-equivalent tin environments and would not be expected to show a single resonance with equivalent ¹¹⁹Sn–¹¹⁷Sn couplings.

The magnitude of *J*_{119Sn–117Sn} is also indicative of a fluxional cluster. The one-bond ¹¹⁹Sn–¹¹⁷Sn coupling constant in a series of hexaorganoditins is known to vary between 4200 and 730 Hz⁷ and two-bond Sn–Sn–Sn couplings have been observed to be even smaller than the latter as expected. The 254-Hz coupling for Sn₉⁴⁻ must be a weighted average of one- and two-bond couplings; however, it will be necessary to observe the limiting spectra of nonfluxional Sn₉⁴⁻ before the magnitudes of ¹*J*_{119Sn–117Sn} and ²*J*_{119Sn–117Sn} are known. We have observed that the spectrum of Sn₉⁴⁻ is the same at –40 °C in NH₃(*l*) and at 30 °C in ethylenediamine. Corbett has estimated a very low barrier between the C_{4v} and D_{3h} structures

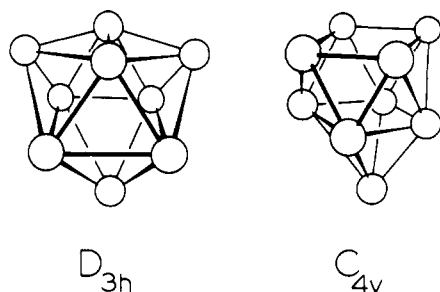


Figure 1. Static structures for Sn_9^{4-} .

of Sn_9^{4-} and has predicted nonrigidity.¹ Our experiments confirm this expectation.

We also have found from ^{119}Sn NMR that the extraction of Na-Sn-Pb and Na-Sn-Sb alloy with en gives solutions containing new clusters in addition to Sn_9^{4-} . The en solutions obtained from the Na-Sn-Pb alloy contain at least six new clusters observable by ^{119}Sn NMR. Each cluster gives a distinct multiplet to the high-field side of Sn_9^{4-} with the displacement of successive multiplets gradually increasing from 42 to 60 ppm. Although the signal-to-noise ratio for these signals is poorer at higher field, our analysis of the multiplet patterns^{5,8} indicates that they arise from $(\text{PbSn}_8)^{4-}$, $(\text{Pb}_2\text{Sn}_7)^{4-}$, $(\text{Pb}_3\text{Sn}_6)^{4-}$, $(\text{Pb}_4\text{Sn}_5)^{4-}$, $(\text{Pb}_5\text{Sn}_4)^{4-}$, and $(\text{Pb}_6\text{Sn}_3)^{4-}$ clusters, respectively. Each multiplet shows ^{119}Sn - ^{117}Sn coupling of ~ 260 Hz and ^{119}Sn - ^{207}Pb coupling of ~ 560 Hz. The ^{207}Pb NMR⁴ at 16.591 MHz shows the clusters $(\text{Pb}_3\text{Sn}_6)^{4-}$, $(\text{Pb}_4\text{Sn}_5)^{4-}$, $(\text{Pb}_5\text{Sn}_4)^{4-}$, $(\text{Pb}_6\text{Sn}_3)^{4-}$, $(\text{Pb}_7\text{Sn}_2)^{4-}$, $(\text{Pb}_8\text{Sn})^{4-}$, and $(\text{Pb}_9)^{4-}$ with the latter at 1190.9 ppm upfield from 1 M $\text{Pb}(\text{NO}_3)_2$ and successive displacements to lower field of ~ 185 ppm/Sn atom.

The Na-Sn-Sb alloy yields a new cluster 108.1 ppm downfield from Sn_9^{4-} with $J_{^{119}\text{Sn}-^{117}\text{Sn}} = 84$ Hz and relative intensities indicative of nine tin atoms in the new cluster. No evidence of ^{119}Sn - ^{121}Sb or ^{119}Sn - ^{123}Sb coupling has been observed. Therefore, NMR cannot establish the number of Sb atoms in the new cluster, and antimony may be exchanging rapidly on the NMR time scale. Isolation is currently being attempted; however, it is interesting to speculate regarding the nature of the cluster. For instance, the PERC⁹ approach would suggest either SbSn_9^{3-} or SbSn_9^- if a single Sb atom per cluster is present. The latter is expected to have a bicapped square antiprism structure, the former a more open structure.

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The Molybdenum-Iron-Sulfur Cluster Complex $[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SC}_2\text{H}_5)_8]^{3-}$. A Synthetic Approach to the Molybdenum Site in Nitrogenase

Sir:

EXAFS (extended x-ray absorption fine structure) spectroscopy of FeMo proteins of nitrogenase¹ and of the FeMo cofactor² (FeMo-co) isolated therefrom³ has demonstrated that the molybdenum coordination sites in these species are distinctly similar, and has implicated molybdenum in a Mo-Fe-S cluster unit as yet undefined in detail. Noting the spontaneous self-assembly of the ferredoxin analogue clusters $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ from simple reagents,⁴ a similar approach to the synthesis of Mo-Fe-S clusters is under investigation by us. Anaerobic reaction of 1 equiv of $(\text{Et}_4\text{N})_2\text{MoS}_4$, 3 equiv of FeCl_3 , and 9 equiv each of ethanethiol and NaOMe in methanol afforded, after unexceptional workup and recrystallization from acetonitrile-THF, black crystals whose composition is consistent with the formulation $(\text{Et}_4\text{N})_3[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SEt})_8]$:⁵ λ_{max} 274 nm (ϵ_M 58 100), 395 (38 000) in DMF.

The compound crystallizes as hexagonal rods in space group $P6_3/m$ with $a = b = 17.230$ (6), $c = 15.999$ (4) Å; $V = 4113$ Å³; and $Z = 2$.⁶ Data collected on a Syntex $P2_1$ diffractometer using graphite monochromatized $\text{Mo K}\alpha$ radiation yielded 800 unique reflections with $F_o^2 > 3\sigma(F_o)^2$ out to 2θ of 50°. The structure (Figure 1) was solved by MULTAN and refined by standard procedures; at the current refinement stage $R = 5.6\%$ and $R_w = 8.6\%$. Two molybdenum atoms, each in a MoFe_3S_4 cubane-type cluster, are bridged by three sulfur atoms across the mirror plane at $z = 1/4$ in $P6_3/m$. All atomic positions except for those of the bridging atoms were readily determined. Fourier and difference Fourier maps of the bridging region revealed electron density elongated in the mirror plane and attributable to sulfur atoms of SEt groups with partial occupancy. This density was satisfactorily refined in terms of the $\text{Mo}(\mu\text{-S})(\mu\text{-SEt})_2\text{Mo}$ unit whose bridging groups are disordered by the crystallographic threefold axis.⁷

The presence of two (but not one or three) $\mu\text{-SEt}$ groups in the 3 anion requires a paramagnetic ground state and is further supported by these observations: (i) $\mu = 4.83 \mu_B$ at 4.2 K and $H_0 = 3.890$ kOe; (ii) magnetic hyperfine ^{57}Fe Mössbauer spectrum at 4.2 K and $H_0 = 60\text{--}80$ kOe (consisting of two superimposed spectra with opposite hyperfine interactions of ca. -210 and $+150$ kOe); (iii) strong EPR spectrum with apparent g values near ~ 10 , 4.0, 1.9, and 1.2 (4.2 K, DMF); (iv) isotropically shifted ^1H NMR spectrum with signals at 54.2 ppm downfield and 3.1 ppm upfield of Me_4Si in a $\sim 3:1$ intensity ratio (CD_3CN , $\sim 25^\circ\text{C}$) (these signals are tentatively assigned to the Fe-SCH₂ and Mo-SCH₂ units, respectively). The Mössbauer spectrum in zero magnetic field consists of a