Uncharged Mixed-Ligand Clusters with the $[Fe_4S_4]^+$ and $[Fe_4S_4]^{2+}$ Cores. Synthesis, Structural Characterization, and Properties of the $Fe_4S_4X(^tBu_3P)_3$ (X = Cl, Br, I) and $Fe_4S_4(SPh)_2(^tBu_3P)_2$ Cubanes

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Highly reduced Fe/S clusters that formally contain mostly or entirely tetrahedrally coordinated Fe^{II} subsites are not commonly encountered among the non-heme iron−sulfur proteins.[1] In the latter the Fe/S cubane-type sites have been observed in the +3, +2, and +1 oxidation levels that contain the $[Fe_4S_4]^{3+}$, $[Fe_4S_4]^{2+}$, and $[Fe_4S_4]^+$ cores.[2] A unique situation exists in the P-clusters of nitrogenase in which spectroscopic data indicate the presence of super-reduced cubanes that possibly contain $[Fe_4S_4]^\circ$ cores.[3] The presence of two bridged Fe_4S_4 subunits within the octanuclear P-clusters has been revealed in the recently determined structure of the FeMo protein of nitrogenase.[4]

The synthesis of single cubane clusters that contain the $[Fe_4S_4]^\circ$ core has not been realized. However the stabilization of reduced Fe/S clusters by aliphatic phosphines has been demonstrated in the "spontaneous-assembly" synthesis of the $Fe_6S_6(PR_3)_4Cl_2$ "basket" clusters.[5] Our initial attempts to obtain Fe_4S_4 cubanes with aliphatic phosphines as terminal ligands were not successful, and substitution of the chloride ligands in the $[Fe_4S_4(Cl)_4]^{2-}$ cubanes[6] with π-accepting, sterically unencumbered, PR_3 phospine ligands led to the collapse of the Fe_4S_4 unit and formation of the $Fe_6S_6(PR_3)_4Cl_2$ "basket" clusters.[5] In contrast, with sterically hindered PR_3 ligands, the same reaction proceeds with a retention of the Fe_4S_4 core structure.

In this communication we report results of our synthetic studies with sterically hindered phosphines and the synthesis, structural characterization, and spectroscopic properties of the neutral, mixed-ligand Fe_4S_4 cubanes of the type $Fe_4S_4X(P^tBu_3)_3$ (X = Cl, **I**, Br, **II**, and I, **III**). These molecules are the first example of uncharged iron−sulfur cubanes that contain the reduced $[Fe_4S_4]^+$ core. Their synthesis is accomplished upon addition of 4 equiv of P^tBu_3 (in tetrahydrofuran, THF, solution) to an acetonitrile, CH_3CN, solution of the appropriate $(Bu_4N)_2[Fe_4S_4X_4]$ cluster,[6] with the subsequent addition of $NaBPh_4$. After removal of NaX, the compounds are obtained in crystalline form, in ~60% yields, by slow crystallization from CH_3CN after removal of THF *in vacuo*. The crystals of **I**−**III** are obtained as CH_3CN monosolvates.[7] In the syntheses of **I**, **II**, or **III**, the isolation of $^tBu_3P{=}S$[8] as a reaction byproduct indicates that the $^tBu_3P$ reagent abstracts μ_3-S^{2-} from the $[Fe_4S_4X_4]^{2-}$ starting material in a reductive desulfurization process[9] that accounts for the observed core reduction in the final product. In the $Fe_6S_6(PR_3)_4Cl_2$ "basket" clusters,[5] the Fe atoms bound to the PR_3 ligands show a trigonal pyramidal coordination that apparently has considerable stability and may play a significant role in the rearrangement of the reduced Fe_4S_4 clusters and formation of the hexanuclear "basket" structure. The retention of the cubane structure in the synthesis of **I**, **II**, or **III** (with tetrahedral $(\mu\text{-}S)_3Fe(P^tBu_3)$ units) very likely is a direct consequence of steric effects and the fact that trigonal pyramidal coordination for a $(\mu\text{-}S)_3Fe(P^tBu_3)$ unit (a structural feature of the Fe_6S_6 "basket" clusters) is structurally incompatible with the ~180° cone angle[10] of the P^tBu_3 ligand.

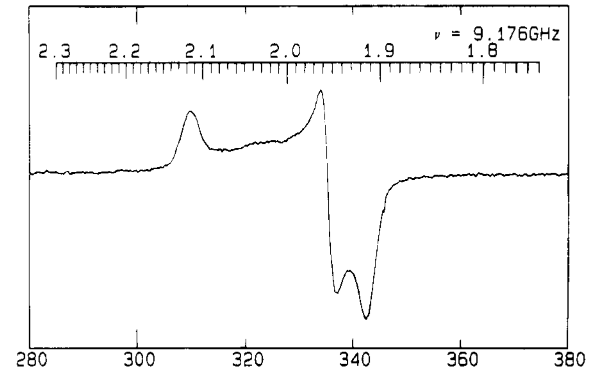

Figure 1. EPR spectrum of the $Fe_4S_4(^tBu_3P)_3Cl$ cluster in frozen CH_2Cl_2 solution at 32 K.

The EPR spectra of frozen CH_2Cl_2 solutions of **I** (Figure 1), **II**, and **III** at 32 K are consistent with a pure $S = {}^1/_2$ ground state, with $g_{av} \approx 2.00$. Magnetic susceptibility measurements of **I**[11] as a function of temperature show antiferromagnetic coupling and the magnetic moment approaches $S = {}^1/_2$ at low temperatures.

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(7) Anal. Calc for $Fe_4S_4ClP_3NC_{36}H_{84}$, **I** (MW = 1035): C, 44.09; H, 8.18; N, 1.35. Found: C, 44.06; H, 7.96; N, 1.25. Anal. Calc for $Fe_4S_4BrP_3NC_{36}H_{84}$, **II** (MW = 1080): C, 42.28; H, 7.84; N, 1.30. Found: C, 42.46; H, 7.62; N, 1.07. Anal. Calc for $Fe_4S_4IP_3NC_{36}H_{84}$, **III** (MW = 1127): C, 40.51; H, 7.52; N, 1.24. Found: C, 39.80; H, 7.52; N, 1.42. Vibrations at 485 (m), 501 (s), 663 (m), 808 (s), 934 (m), 1023 (vs), 1176 (vs), four bands from 1371 to 1483 (vs), and six bands from 2872 to 3012 (vs) cm^{-1} attributable to the P^tBu_3 ligand occur in the mid infrared spectra. Far infrared spectrum of **I**: 349 (s), 367 (s) cm^{-1}. Far infrared spectrum of **II**: 305 (s), 367 (s) cm^{-1}. Far infrared spectrum of **III**: 290 (m), 367 (s) cm^{-1}. The electronic spectra of **I**−**III** (in CH_2Cl_2) are featureless, with a gradual increase in absorption from 700 to 250 nm.

(8) Phosphine sulfide was identified by infrared spectroscopy.

(9) Precedents of alkylphosphines functioning as sulfur receptors from Fe/S clusters include the following: (a) Pohl, S.; Opitz, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 863. (b) Scott, M. J.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 564. (c) Demadis, K. D.; Campana, C. F.; Coucouvanis, D. *J. Am. Chem. Soc.*, in press.

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(11) Magnetic data of **I** were collected on a SQUID magnetometer from 4 K (μ_{eff} = 2.25 μ_B) to 300 K (μ_{eff} = 4.79 μ_B).

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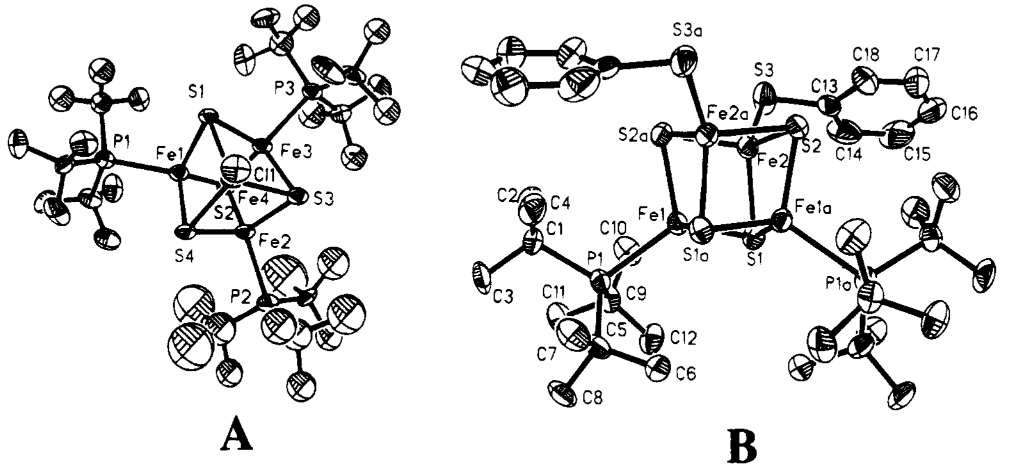

Figure 2. Structures of the $Fe_4S_4(^tBu_3P)_3Cl$ (**A**) and the $Fe_4S_4(SPh)_2(^tBu_3P)_2$ (**B**) clusters, showing the labeling scheme and 40% probability ellipsoids drawn by ORTEP. Mean values of selected interatomic distances (Å) and angles (deg) are reported with the first number in parentheses representing the calculated standard deviation from the mean and the second the number of n independent distances or angles as follows. **A**: Fe••Fe, 2.768(9, 6) (range: 2.737(4)-2.802(5)); Fe–S, 2.297(7, 12) (range: 2.266(7)-2.324(6)); Fe–P, 2.458(7,3) (range: 2.452(7)-2.463(6)); Fe–Cl, 2.244(5, 1); Fe–Fe–Fe, 60.0(2, 12); Fe–S–Fe, 74.1(2, 12); S–Fe–S, 103.9(3, 12); S–Fe–P 115 (1, 9) (range: 112.6(2)-118.6(2)). **B** (located on a crystallographic 2-fold axis): Fe••Fe, 2.740(5, 3) (range: 2.729(2)-2.749(1)); Fe–S, 2.298(2, 2); Fe–S, 2.267(8,4) (range: 2.257(2)-2.287(2)); Fe–SR, 2.257(2), 2.240(3); Fe–P, 2.468(2); Fe–Fe–Fe, 60.0(2, 12); Fe–S–Fe, 74.1(2, 12); S–Fe–S, 103.9(3, 12); S–Fe–P, 115 (1, 9) (range: 109.7(1)-119.5-(1)).

The structure of **I** has been determined.[12] The neutral cluster approaches idealized C_{3v} symmetry when viewed down the Fe–Cl bond (Figure 2A). The Fe_4S_4 core shows the now classical cubane structure with mean Fe–S and Fe–Fe bond lengths of 2.297(7) and 2.768(10) Å, respectively. These values are within 3σ from those previously reported for a plethora of $[Fe_4S_4]^+$ cores[13] and only slightly longer than those of the $[Fe_4S_4]^{2+}$ cores in the oxidized clusters.[2] Unlike the multitude of core distortions (and subsets of Fe–S bonds) found in reduced clusters with terminally coordinated RS^- ligands,[13] the Fe–S bonds in **I** cannot be separated in identifiable, statistically significant, subsets. The mean Fe–P bond length in the distorted tetrahedral $(\mu\text{-}S)_3Fe(P^tBu_3)$ unit at 2.458(7) Å is 0.149 Å longer than that found for the trigonal pyramidal $(\mu\text{-}S)_3Fe(P^nBu_3)$ units in the $Fe_6S_6(P^nBu_3)_4Cl_2$ cluster.[5] The Fe–Cl bond length is only slightly longer than the Fe–Cl bonds found in the oxidized, mixed-ligand cubanes.[14]

The cyclic voltammetry of **I** in 1,2-dichloroethane on a Pt electrode (vs Ag/AgCl) shows a quasi-reversible (q-r.) oxidation at −69 mV (ΔE = 107 mV) and an irreversible reduction at −1200 mV. The Br^- (**II**) and I^- (**III**) analogs display identical patterns.[15] It is worth emphasizing that in **I**–**III**, the $[Fe_4S_4]^{2+}/[Fe_4S_4]^+$ core redox couple occurs at potentials 600–1200 mV less negative than that observed in other synthetic Fe/S cubanes and underscores the stabilization of the reduced state[16] by the P^tBu_3 ligands.

An attempt to replace the Cl^- ligand in **I** with PhS^- has led to the formation of the oxidized, neutral $[Fe_4S_4(SPh)_2(P^tBu_3)_2]^\circ$ cluster, **IV**, in what appears to be an "all or nothing" low-yield reaction. In the presence of PhSSPh as an oxidizing agent, the reaction of **I** with 1 equiv of NaSPh proceeds to form **IV** in 90% yield.[17] The structure of the EPR silent (32 K) **IV** has been determined[18] (Figure 2B). The $[Fe_4S_4]^{2+}$ core in this mixed-ligand cluster is located on a crystallographic 2-fold axis and shows axial elongation along an idealized 2-fold axis perpenticular to the crystallographic 2-fold axis. The mean values of the structural parameters are unexceptional and similar to those found in numerous other similar clusters. The cyclic voltammetry of **IV** shows a reversible reduction wave at −600 mV.

The new P^tBu_3 cubanes with excellent solubility in nonpolar, noncoordinating solvents are expected to be well suited for the synthesis of new, reduced, Fe/S clusters of possible relevance to the P-clusters of the FeMo proteins of nitrogenase. Studies of the structural, electronic, and reactivity properties of these compounds are currently underway in our laboratory.

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Supporting Information Available: Listings of positional parameters, thermal parameters, selected bond distances and angles, and crystal data (16 pages). Ordering information is given on any current masthead page.

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(12) Crystal and refinement data: Black crystals of **I** are triclinic, space group $P\bar{1}$, with a = 11.476(6) Å, b = 14.54(1) Å, c = 18.186(9) Å, α = 68.14(6)°, β = 86.59(4)°, γ = 68.42(6)°, V = 2608(3) Å^3, and Z = 2. Single-crystal diffraction data for **I** were collected on a Nicolet P3F diffractometer using MoKα radiation at ambient temperature. The solution of the structure was carried out using direct methods and Fourier techniques. The refinement of the structure by full-matrix least-squares methods was based on 6804 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$). Refinement of 415 parameters has converged to R (R_w) = 0.082 (0.092).

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(15) Voltammetry of **II** (Pt working, Ag/AgCl reference, in 1,2-dichloroethane, Bu_4NPF_6 supporting electrolyte): oxidation (q-r.) at −32 mV (ΔE = −144 mV) and a reduction at −1300 mV (irreversible, i.r.). Voltammetry of **III**: oxidation (q-r.) at −80 mV (ΔE = −161 mV) and a reduction at −1350 mV (i.r.) at scan rates of 400 mV/s.

(16) **I** is readily oxidized by $[Fe(Cp)_2]PF_6$. Mid infrared spectrum shows ν(PF) at 559 (s) and 840 (vs) cm^{-1}. Far infrared spectrum: 346 (s), 354 (s), 371 (s), 377 (s) cm^{-1}.

(17) Anal. Calc for $Fe_4S_6P_2C_{36}H_{64}$, **IV** (MW = 974.6): C, 44.37; H, 6.62. Found: C, 44.82; H, 6.70.

(18) Compound **IV** crystallizes in monoclinic space group $C2/c$ with a = 16.598(4) Å, b = 19.472(4) Å, c = 15.060(2) Å, β = 112.36(1)°, and Z = 4. Single-crystal diffraction data for **IV** were collected on a Nicolet P3F diffractometer using Mo Kα radiation at ambient temperature. The solution of the structure was carried out using direct methods and Fourier techniques. The refinement of the structure by full-matrix least-squares methods was based on 4734 unique relections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$). Refinement of 217 parameters converged to R (R_w) = 0.037 (0.036).