First Synthesis of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$ and Improved Syntheses of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_n$ (n=1,2)

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$[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$ and $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ were prepared in 81 and 82% yields, respectively, by bulk electrolysis of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ at the requisite potentials according to the results of voltammetric studies. $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$ was prepared and isolated first by electrolysis of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ in acetonitrile at +0.95 V vs. SCE in 83% yield. The electronic spectral data for $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ (n=0, 1+, 2+, 3+) were collected.

The cyclic voltammogram of the iron-sulfur cubane cluster, $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$, shows four reversible redox waves which indicate the existence of five oxidation states. Trinh-Toan et al. reported that the five oxidation states correspond to $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ with n= 1−, 0, 1+, 2+, and 3+.[1] However, recent investigations revealed that the assignment should be corrected to n=0, 1+, 2+, 3+, and 4+.[2-4] On the early assignment that $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ takes the five oxidation states with n=1−, 0, 1+, 2+, and 3+, Trinh-Toan et al. prepared the monocation and the dication of the cluster by bulk electrolysis in 60 and 45% yields, respectively.[1]

In this work, bulk electrolysis of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ was carried out according to the new assignment that the five species are $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ with n=0—4+. The monocation and dication of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ were prepared in better yields than those reported previously.[1] Furthermore, the trication salt of the cluster was also prepared by bulk electrolysis and isolated for the first time. The electronic spectral data of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ (n=0, 1+, 2+, 3+) were collected. Because of the instability of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+}$, the electronic spectral data of this species were found to be obtained accurately only by a spectroelectrochemical measurement.

Experimental

Unless otherwise mentioned all procedures were carried out under a nitrogen atmosphere. Electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer, and NMR measurements were made on a JEOL FX90Q (using acetone-d_6 as solvent).

Materials. $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ was prepared as described in the literature.[5] NH_4PF_6 (Aldrich Chemical Company Inc., 99.5%) was purified by recrystallization from acetonitrile. Tetrabutylammonium tetrafluoroborate (TBAB) (Tokyo Kasei) was recrystallized from ethanol-water mixed solvent. Acetonitrile was distilled from P_2O_5 twice and from CaH_2. Diethyl ether was distilled from sodium.

Preparation of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$. A suspension of 200 mg (0.33 mmol) of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ in 150 cm^3 of an acetonitrile solution containing 0.1 M NH_4PF_6 was oxidized electrochemically while stirring at room temperature.[6] When the potential was applied at +0.17 V vs. SCE and the electrochemical oxidation was continued for 1 h, the current reduced to 1 mA. The coulombic number required for the electrolysis was 40 C (calculated value: 32 C). The solution was filtered and evaporated to dryness and the residue then washed with water to remove excess NH_4PF_6. The crude product was extracted with dichloromethane (80 ml) and the filtered solution evaporated to 5 ml. Upon the addition of diethyl ether, 200 mg of the desired product was obtained as black powder (yield 81%). Found: C, 31.79; H, 2.86%. Calcd for $C_{20}H_{20}F_6Fe_4PS_4$: C, 31.73; H, 2.66%. ^{1}H NMR spectra showed a very broad signal centered at δ=6.15 due to the paramagnetism of the complex.

Preparation of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$. A suspension of 400 mg (0.65 mmol) of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ in 120 cm^3 of acetonitrile solution containing 0.1 M NH_4PF_6 was oxidized electrochemically at +0.5 V vs. SCE. When the electrolysis at +0.5 V vs. SCE was continued for 1 h, the current reduced to 1.5 mA. The coulombic number required for the electrolysis was 132 C (calculated value: 127 C). The solution was filtered and evaporated to dryness and the residue washed with water to remove the electrolyte and then with dichloromethane to remove trace amounts of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$. The procedure gave 486 mg of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ (yield 82%), which was recrystallized from acetonitrile by the addition of diethyl ether. Found: C, 26.47; H, 2.49. Calcd for $C_{20}H_{20}F_{12}Fe_4P_2S_4$: C, 26.63; H, 2.24. ^{1}H NMR δ=6.26.

Preparation of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$. In 120 ml of acetonitrile solution containing 0.1 M NH_4PF_6, was dissolved 170 mg (0.19 mmol) of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$. When the oxidation at +0.95 V vs. SCE was continued for 1 h, the current reduced to 1.5 mA. The coulombic number required for the electrolysis was 22 C (calculated value: 18 C). The solution was evaporated to dryness, and the residue was washed with water and dichloromethane, successively, dried in air, and finally dried by heating at 100 °C under vacuum to remove the acetonitrile which was considered to be solvent of crystallization. The procedure afforded 163 mg of the desired product (83%). Found: C, 23.22; H, 2.03%. Calcd for $C_{20}H_{20}F_{18}Fe_4P_3S_4$: C, 22.95; H, 1.93. ^{1}H NMR spectrum showed a very broad signal centered at δ=6.33 due to the paramagnetism of the complex. ESR spectrum showed signals in acetonitrile at 77 K ($g_\perp$=1.998, $g_{/\!/}$=2.072).

Electrochemical and Spectroelectrochemical Measurements and Equipments. Cyclic voltammetry was made with a model 311 potentiostat (Huso Co.) combined with a Model 321 function generator (Huso Co.). Direct current

polarograms were recorded with a Yanagimoto polarographic Analyzer P-1000. Electrochemical measurements were carried out at room temperature by use of a three electrode system consisting of a working electrode (a platinum rod electrode for cyclic voltammetry and a dropping mercury electrode for DC polarography), a coiled platinum wire as a counter electrode, and an aqueous saturated calomel electrode (SCE) as a reference electrode.

The spectroelectrochemical cell with an optically transparent thin-layer electrode (OTTLE) was constructed according to the direction reported in a literature.[7] The spectroelectrochemical measurements were made at −10 °C with the Model 311 potentiostat and Model 321 function generator.

Bulk electrolysis was carried out by use of a three electrode system consisting of a platinum plate electrode as a working electrode, a carbon rod as a counter electrode, and an aqueous saturated calomel electrode (SCE) as a reference electrode. The potential was applied by a HA-501 potentiostat (Hokuto Denko Ltd.) coupled with a HB-104 function generator (Hokuto Denko Ltd.).

Results and Discussion

Voltammetry of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$. In acetonitrile, $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ shows four reversible one-electron redox waves with $E_{1/2}$=+1.31, +0.85, +0.33, and −0.29 V vs. SCE (Fig. 1). Crucial evidence that $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ takes the five oxidation states assigned as n=0, 1+, 2+, 3+, and 4+, instead of n=1−, 0, 1+, 2+, and 3+, is provided by DC polarography. The polarogram of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ in acetonitrile shows two-step one-electron reduction waves at +0.33 and −0.24 V vs. SCE (Fig. 2). This corresponds to the formation of the monocationic and neutral clusters, respectively.

Syntheses of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ (1+, 2+, 3+). The mono-, di-, and trication of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ were obtained in high yields by electrolysis at +0.17, +0.5, and +0.95 V vs. SCE, respectively. In our previous paper,[2] we reported the synthesis of $[Fe_4(\eta^5\text{-}C_5H_5)_4Se_4]^{3+}$ as the first cubane cluster having 17 skeletal electrons. $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$ obtained in this work is the second example of this sort.

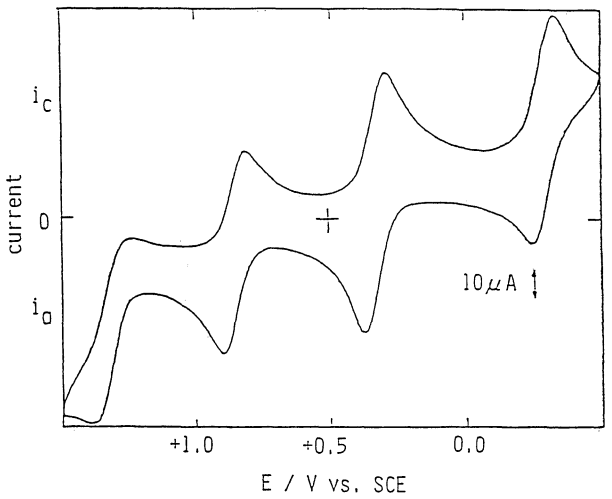

Fig. 1. Cyclic Voltammogram of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ in acetonitrile containing 0.1 M TBAB. [cluster]=0.99×10^{-3} M, scanning speed: 50 mV s^{-1}.

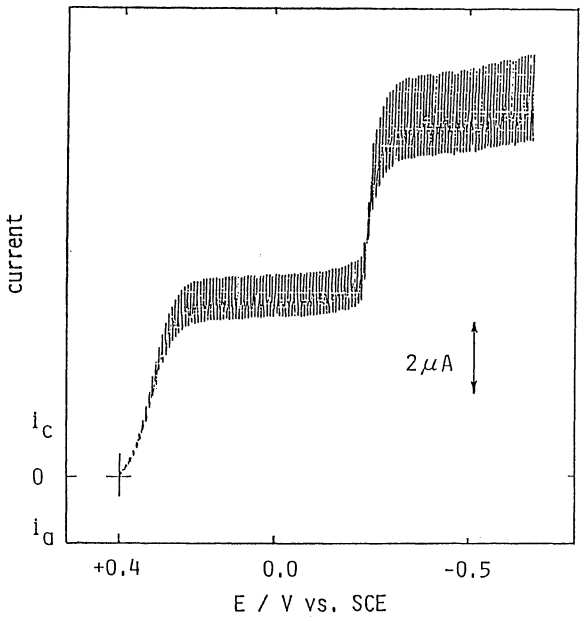

Fig. 2. DC polarogram of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ in acetonitrile containing 0.1 M TBAB. [cluster]= 2.2×10^{-3} M.

Although we obtained crystals of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$, they were not suitable for X-ray structure analysis due to their efflorescent property. Prolonged exposure to various solvents caused the reduction of the cluster to $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ or $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)$. In the case of $[Fe_4(\eta^5\text{-}C_5H_5)_4Se_4](PF_6)_3\cdot CH_3CN$, the crystals effloresce less easily, and no reduction was observed.[2] This may be due to the difference of crystal packing structures and the redox potentials between the selenium and sulfur clusters. Since even the trication is reduced by solvents or impurities in the solvents, the preparation and isolation of the tetracation is likely to be more difficult.

The potentials that Trinh-Toan et al. employed for the preparation of the mono- and dication of the clusters were +0.4 and +1.1 V vs. SCE, respectively.[1] According to our electrochemical results, the dication and trication must be formed at these respective potentials. However, it is not surprizing that they obtained the monocation and the dication at +0.4 and +1.1 V vs. SCE, because, in their preparations, the constant potential electrolysis was interrupted when the coulombic number of the electrolysis reached the requisite value. Therefore, it is considered that the $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{2+}$ formed by the electrolysis at +0.4 V vs. SCE reacts with $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$ in the bulk solution and proportionates to $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^+$. Similarly, it may be understood that electrolysis at +1.1 V vs. SCE gave the dication of the cluster. In fact, $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$ was obtained in this work,

Table 1. Electronic Spectral Data of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ (n=0, 1+, 2+, 3+)

n	Solvent	λ_{max}/nm (log (ε/$M^{-1}cm^{-1}$))			Ref.
0	CH_2Cl_2	468 (3.57),	298 (4.30),	231 (4.33)	This work
	CH_3CN	450 (3.17),	297 (3.88)		1
1+	CH_3CN	440 sh (3.78),	298 (4.53)		This work
	CH_3CN	440 (3.85),	297 (4.55)		1
2+	CH_3CN		293 (4.60),	235 sh (4.63)	This work
	CH_3CN	345 sh (4.26),	295 (4.53)		1
3+	CH_3CN	305 (4.58),	235 (4.66)		This work

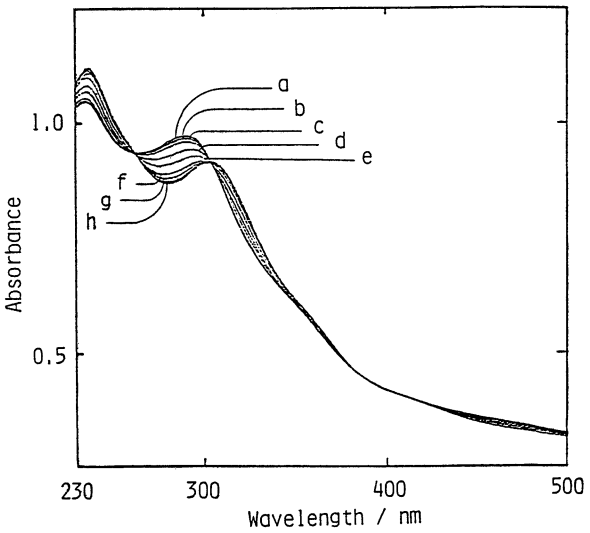

Fig. 3. Spectral change of 0.25×10^{-3} M $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_2$ obtained by spectropotentiostatic measurement. E_{appl}: (a) +0.5—+0.70; (b) +0.75; (c) +0.78; (d) +0.81; (e) +0.83; (f) +0.85; (g) +0.87; (h) +0.89—+0.95 V vs. SCE.

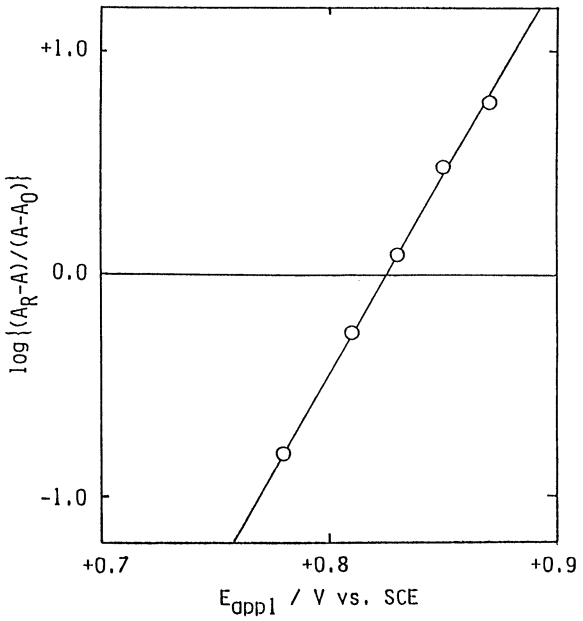

Fig. 4. Nernst plots of $\log\{(A_R-A)/(A-A_O)\}$ vs. applied potentials E_{appl}. Data are taken from Fig. 3.

when the electrolysis was carried out at +0.95 V vs. SCE, which is more negative than +1.1 V vs. SCE.

Electronic Spectral Data of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^n$ (n=0, 1+, 2+, 3+). The electronic spectra of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]$, $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^+$, and $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{2+}$ were measured in CH_2Cl_2 or acetonitrile. The data are summarized in Table 1 along with the reported data.[1] Both data are reasonably in good agreement. As mentioned above, when $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_3$ is dissolved in a solvent, reduction of the cluster is induced. To obtain accurate numerical data for $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+}$, spectropotentiometric measurements were carried out using OTTLE. Spectral change with the change of applied potentials is shown in Fig. 3. Curve (a) corresponds to the spectrum of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{2+}$. The spectral change accompanies isosbestic points at 263, 305, and 400 nm. This suggests strongly that curve (h) obtained at more positive potential than +0.89 V vs. SCE corresponds to the spectrum of the one-electron oxidized species $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+}$. In fact, Nernst plots of $\log\{(A_R-A)/(A-A_O)\}$ vs. the applied potentials E_{appl} give a good linear relation (Fig. 4), where A denotes the absorbance at 280 nm and at any applied potential E_{appl}. A_R and A_O represent the absorbances at 280 nm of the completely reduced species $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{2+}$ and the completely oxidized species $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+}$, respectively. The reciprocal slope of the plots given in Fig. 4 was 56 mV. This indicates that the electrode process for the $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+/2+}$ redox couple is reversible. The potential value of the intercept was +0.82 V vs. SCE, which is in good agreement with the $E_{1/2}$ of the $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+/2+}$ redox couple obtained by the cyclic voltammetric measurements (+0.85 V vs. SCE). In Table 1, the spectral data of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{3+}$ thus obtained is given. When the potential is applied beyond +1.2 V vs. SCE, absorbance decreases over the whole range of wavelengths. This means that $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4](PF_6)_4$ formed by the electrochemical oxidation is insoluble in acetonitrile or that the decomposition product derived from $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{4+}$ is insoluble. For this reason, the spectral data of $[Fe_4(\eta^5\text{-}C_5H_5)_4S_4]^{4+}$ could not be determined.

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