Synthesis and characterization of Fe_4S_4 clusters with a crown ether skeleton*

Takenori Tomohiro and Hiroaki (Yohmei) Okuno**
National Chemical Laboratory for Industry (NCLI), Tsukuba, Ibaraki 305 (Japan)

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Abstract

Tetrathiol ligands attached to a 36-membered crown ether (**7**) have been prepared by reactions of 4,7,13,16,22,25,31,34-octaoxo-1,10,19,28-tetraazacyclohexatriacontane (**5**) and acylchlorides bearing a thiol function. By ligand exchange reaction of $(Ph_4As)_2[Fe_4S_4(S^tBu)_4]$ (**4c**) and these tetrathiol ligands, Fe_4S_4 clusters with a crown ether type ring were synthesized as black powders (**3**). These clusters showed relatively good solubility and improved stability toward molecular oxygen as compared with the corresponding small thiolate Fe_4S_4 clusters (**4**). In addition, these clusters exhibited their redox potentials of a $[Fe_4S_4]^{1+/2+}$ couple in a polar solvent, whose potentials appeared in the region between those of the corresponding thiolate clusters with a methylene (**1**) or cyclophane (**2**) type ring and of the unclad clusters. This suggested that a hydrophobic environment is important in stabilizing the oxidized core.

Introduction

High potential iron–sulfur proteins (HiPIPs) exhibit their redox potentials as positive from +50 to 450 mV (versus NHE at pH 7.0 in water) for $[Fe_4S_4]^{2+/3+}$ core oxidation levels [1–3]. The preference of the $[Fe_4S_4]^{3+}$ oxidation level in HiPIPs is probably due to the position or cores which are located deep in an area away from the protein surface, in contrast to a location near the surface in low-potential ferredoxins (Fds) as well as the narrow angle of Fe–S–C (increase of ionic bonding character on the Fe–S bond) and number of hydrogen bondings [4–6].

We previously synthesized and characterized a new series of Fe_4S_4 clusters with large methylene (**1**, 28-, 32-, 36-, 40- and 44-membered) or cyclophane (**2**, 38-membered) type rings (Fig. 1), and suggested that the hydrophobic environment makes an important contribution to stabilizing the cores of HiPIPs [7–17]. These macrocycles actually provided a hydrophobic environment around the core and stabilized the core toward molecular oxygen [10, 17]. In addition, all redox potentials of these synthetic clusters shifted to a positive region compared with corresponding thiolate Fe_4S_4 clusters without macrocycles [9–14]. The potentials of $[Fe_4S_4]^{2+/3+}$ couples of the t-butanethiolato type clusters (**1c**) exhibited around +0.24 V (versus SCE in DMSO), which was the most positive values among the Fe_4S_4 clusters synthesized so far and the closest HiPIPs [10]. However, these macrocyclic Fe_4S_4 clusters exhibited low solubility in ordinal organic solvents. From our extensive work on iron–sulfur protein analogues, we report herein the synthesis and properties of Fe_4S_4 clusters with a crown ether type ring which has resulted in great increase of solubility of the new clusters (**3**). The half-wave potentials for $[Fe_4S_4]^{1+/2+}$ core oxidation levels appeared at a more negative field than those of the clusters with methylene or cyclophane type rings, which suggested a relatively weak hydrophobic environment produced by a crown ether ring around the core.

Experimental

General method

Flash chromatographic separations were carried out on Merck 230–400 mesh Kieselgel 60 or Wakogel C-300. THF and diethyl ether were distilled from sodium benzophenone ketyl; DMF, CH_2Cl_2, CH_3CN, benzene and n-hexane were distilled from calcium hydride. EtOAc and acetone were purified by distillation. Other materials were purchased from appropriate sources and used as received. Absorption spectra were recorded on a Hitachi U-3200 spectrophotometer. IR spectra were obtained with a JASCO IRA-2. The NMR spectra were

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**Author to whom correspondence should be addressed.

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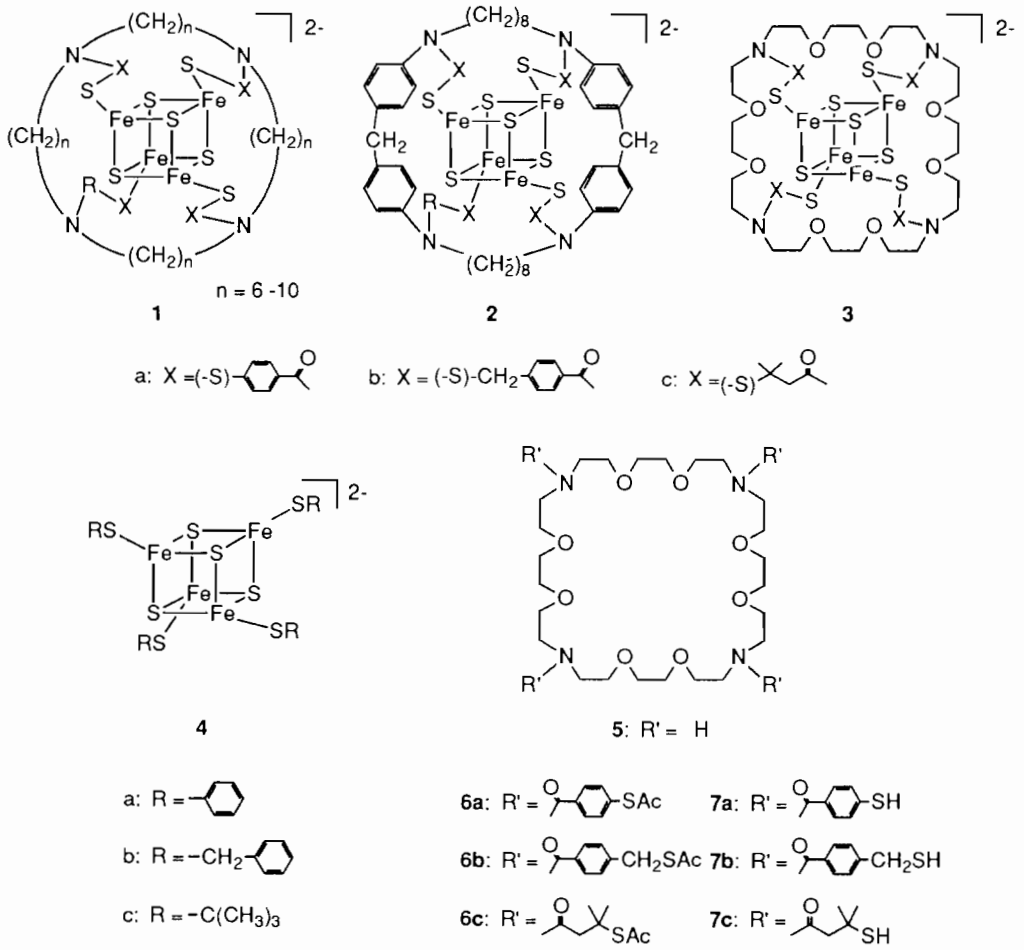

Fig. 1. Structure of clusters and ligands.

determined on a Bruker AC-200 and chemical shifts are relative to TMS as an internal reference. Redox potentials were determined by obtaining cyclic voltammograms with Hokuto Denko instruments (HA-501 potentiostat, HB-104 function generator and HF-201 Coulomb meter).

*4,7,13,16,22,25,31,34-Octaoxo-1,10,19,28-tetra-[4'-(acetylthio)benzoyl]-1,10,19,28-tetraaza-cyclohexatriacontane (**6a**)*

Cyclic tetraamine **5** was prepared according to the literature [18]. To a mixture of **5** (226 mg, 0.43 mmol) and Et_3N (262 mg, 2.6 mmol) in CH_2Cl_2 (15 ml) was gradually added 4-acetylthiobenzoyl chloride [11] (320 mg, 1.5 mmol) in CH_2Cl_2 (7 ml) at 0 °C, and the solution was stirred at room temperature overnight. The mixture was subsequently washed with 1 N HCl, sat. $NaHCO_3$ and brine, and dried ($MgSO_4$). The crude product was then purified by silica gel chromatography eluted with EtOAc–EtOH (6:1) to afford a colorless oil (112 mg, 21%). ^{1}H NMR ($CDCl_3$): 2.42 (s, 12H, $COCH_3$), 3.4–3.7 (br, 32H, NCH_2CH_2O), 3.74 (br s, 16H, OCH_2CH_2O), 7.2–7.4 (s, 16H, arom). ^{13}C NMR ($CDCl_3$): 30.3, 45.5, 49.7, 69.1, 70.4, 127.7, 129.3, 134.2, 137.5, 171.3, 193.2 ppm.

*4,7,13,16,22,25,31,34-Octaoxo-1,10,19,28-tetra-[4'-(acetylthiomethyl)benzoyl]-1,10,19,28-tetraaza-cyclohexatriacontane (**6b**)*

4-Acetylthiomethylbenzoyl chloride [11] (683 mg, 3.0 mmol) in CH_2Cl_2 (10 ml) was added at 0 °C to a CH_2Cl_2 solution (30 ml) containing **5** (261 mg, 0.50 mmol) and Et_3N (302 mg, 3.0 mmol) over a period of 30 min. The mixture was reacted at room temperature for 1 day. After purification by silica gel column chromatography eluted with EtOAc–EtOH (5:1), **6b** was isolated as a colorless oil (523 mg, 81%). ^{1}H NMR ($CDCl_3$): 2.34 (s, 12H, $COCH_3$), 3.4–3.7 (br, 32H, NCH_2CH_2O), 3.72 (br s, 16H, OCH_2CH_2O), 4.10 (s, 8H, $PhCH_2S$), 7.2–7.4 (m, 16H, arom). ^{13}C NMR ($CDCl_3$): 30.3, 32.9, 45.5, 49.7, 69.2, 70.3, 127.1, 128.8, 135.5, 138.9, 171.7, 194.7 ppm. FAB-MS (*m/z*) 1293 (MH^+). *Anal.* Calc. for $C_{64}H_{84}N_4O_{16}S_4 \cdot 3H_2O$: C, 57.04; H, 6.73; N, 4.16; S, 9.52. Found: C, 56.77; H, 6.31; N, 3.84; S, 9.60%.

*4,7,13,16,22,25,31,34-Octaoxo-1,10,19,28-tetra-(3'-acetylthio-3'-methylbutanoyl)-1,10,19,28-tetra-azacyclohexatriacontane (**6c**)*

To a mixture of **5** (165 mg, 0.31 mmol) and K_2CO_3 (152 mg, 1.1 mmol) in CH_2Cl_2 (10 ml) was added dropwise 3-acetylthio-3-methylbutanoyl chloride [11] (367 mg, 1.9 mmol) in CH_2Cl_2 (5 ml) over a period of 15 min at 0 °C, and the mixture was stirred at room temperature for 4 days. After filtration over celite, the solvent was removed *in vacuo*. The residue was then dissolved in EtOAc, and washed with brine three times. The organic layer was dried over anhydrous $MgSO_4$, and was evaporated to dryness. The residue was purified by silica gel column chromatography eluted with EtOAc–MeOH (10:1) to give a colorless viscous oil (158 mg, 43%). ^{1}H NMR ($CDCl_3$): 1.58 (s, 24H, $C(CH_3)_2$), 2.25 (s, 12H, $COCH_3$), 2.98 (s, 8H, $COCH_2$), 3.0–3.3 (m, 48H, $NCH_2CH_2OCH_2$). ^{13}C NMR ($CDCl_3$): 27.5, 31.3, 41.6, 46.6, 49.1, 49.9, 69.5, 69.6, 69.7, 70.3, 70.5, 70.7, 70.8, 170.4, 197.3 ppm. FAB-MS (*m/z*) 1157 (MH^+); *Anal.* Calc. for $C_{52}H_{92}N_4O_{16}S_4 \cdot H_2O$: C, 53.13; H, 8.06; N, 4.77; S, 10.91. Found: C, 53.21; H, 8.22; N, 4.87; S, 10.99%.

*4,7,13,16,22,25,31,34-Octaoxo-1,10,19,28-tetra-(4'-mercaptobenzoyl)-1,10-19,28-tetraaza-cyclohexatriacontane (**7a**)*

A solution of **6a** (112 mg, 0.015 mmol) in deaerated 1 N HCl/MeOH (25 ml) was heated at 60 °C for 4 h under N_2. After removal of the solvent *in vacuo*, the residue was dissolved in CH_2Cl_2 (100 ml), washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave a pale yellow oil (86 mg, 89%). ^{1}H NMR ($CDCl_3$): 3.50 (br s, 32H, NCH_2CH_2O), 3.60 (s, 4H, SH), 3.71 (br s, 16H, OCH_2CH_2O), 7.1–7.4 (m, 16H, arom). ^{13}C NMR ($CDCl_3$): 45.6, 49.8, 69.1, 70.4, 127.8, 128.7, 133.1, 133.7, 171.6 ppm.

*4,7,13,16,22,25,31,34-Octaoxo-1,10,19,28-tetra-(4'-(mercaptomethyl)benzoyl)-1,10,19,28-tetraaza-cyclohexatriacontane (**7b**)*

Compound **6b** (259 mg, 0.20 mmol) was treated in the same way for 3 h at 60 °C. A pale yellow oil (214 mg, 95%) was obtained. ^{1}H NMR ($CDCl_3$): 1.78 (t, 4H, J = 5.9 Hz, SH), 3.2–4.0 (br, 48H, $NCH_2CH_2OCH_2$), 3.70 (s, 8H, J = 6.1 Hz, $PhCH_2S$), 7.2–7.5 (m, 16H, arom). FAB-MS (*m/z*) 1125 (MH^+).

*4,7,13,16,22,25,31,24-Octaoxo-1,10,19,28-tetra-(3'-mercapto-3'-methylbutanoyl)-1,10,19,28-tetraaza-cyclohexatriacontane (**7c**)*

Compound **6c** (158 mg, 0.015 mmol) was treated in the same way for 2 h at 60 °C and a pale yellow oil (135 mg, quantitative) was obtained. ^{1}H NMR ($CDCl_3$): 1.52 (br s, 24H, $C(CH_3)_2$), 2.70 (s, 12H, $COCH_2$ + SH), 3.4–3.8 (br m, 48H, $NCH_2CH_2OCH_2$). FAB-MS (*m/z*) 989 (MH^+).

*Bis(tetraphenylarsonium)tetra-μ_3-sulfido-[1,10,19,28-tetraaza-4,7,16,22,25,31,34-octaoxocyclohexatriacontane-1,10,19,28-tetrakis(4'-oxomethylbenzenethiolato-SS'S''S''')] = tetrahedro-tetraferrate (**3a**)*

All operations were carried out in a dry pure nitrogen atmosphere using thoroughly degassed solvents and reagents. The Fe_4S_4 clusters without macrocycles were prepared according to procedures in the literature [19].

To a DMF (8 ml) solution of $[Ph_4As]_2[Fe_4S_4(SBu^t)_4]$ (**4c**) (113 mg, 80.4 μmol), **7a** (86 mg, 76.6 μmol) in DMF (7 ml) was added dropwise, the mixture was stirred under dynamic vacuum at 40 °C for 2 h, and DMF (10 ml) was added to dissolve the resulting black oily product. CH_2Cl_2 (20 ml) was then added to the mixture, and this suspension was stirred at 30 °C for 30 min. The black precipitate was collected by filtration, and dissolved in 15 ml of DMF. To the solution was added ether (*c.* 100 ml), which was kept at −80 °C overnight. The black–brown precipitate was collected by filtration, washed with hot CH_2Cl_2 and hot CH_3CN, and dried *in vacuo*. Reprecipitation from DMF–ether afforded a black–brown powder (23 mg, 13%). ^{1}H NMR (DMF-d_7): 2.77 (br s, 8H, NCH_2), 2.94 (br s, 8H, NCH_2), 3.2–4.0 (br s, 32H, skeleton), 5.95 (br s, 8H, arom/*ortho* to S), 7.8–8.1 (m, 40H, arom/cation), and 8.23 (br s, 8H, arom/*meta* to S). λ_{max}(DMF) 451 nm (ε 15 000). $E_{1/2}$ (2^- to 3^-) (versus SCE, DMF) −0.95 V.

*Bis(tetramethylammonium)tetra-μ_3-sulfido-[bis(N,N'-octamethylene-4,4'-diaminodiphenylmethane)-N,N,N',N'-tetrakis(4'-oxomethylphenylmethanethiolato-SS'S''S''')]-tetrahedro-tetraferrate (**3b**)*

In a similar manner, **3b** (256 mg, 63%) was obtained using **4c** (267 mg, 0.18 mmol, 80 ml CH_3CN) and **7b** (214 mg, 0.19 mmol, 30 ml CH_3CN). ^{1}H NMR (DMF-d_7): 2.16 (s, 8H), 2.75 (br s, 8H, NCH_2), 2.92 (br s, 8H, NCH_2), 3.1–4.2 (br s, 32H, skeleton), 7.42 (br s, 16H, arom/ligand), 7.7–8.2 (m, 40H, arom/cation), 13.66 (br s, 8H, $PhCH_2S$). λ_{max} (DMF) 412 nm (ε 13 300). $E_{1/2}$ (2^- to 3^-) (versus SCE, DMF) −1.23 V.

*Bis(tetramethylammonium)tetra-μ_3-sulfido-[bis(N,N'-octamethylene-4,4'-diaminodiphenylmethane)-N,N,N',N'-tetrakis(1',1'-dimethyl-3'-oxopropanethiolato-SS'S''S''')]-tetrahedro-tetraferrate (**3c**)*

3c (85 mg, 31%) was also obtained using **4c** (193 mg, 0.13 mmol, 60 ml CH_3CN) and **7c** (135 mg, 0.14 mmol, 20 ml CH_3CN). ^{1}H NMR (DMF-d_7): 2.75 (br s, 8H, NCH_2), 2.92 (br s, 8H, NCH_2), 3.53 (br s, 64H, skeleton), 7.8–8.1 (m, 40H, arom/cation). λ_{max} (DMF)

415 (ϵ 14 000), 295 nm (ϵ 19 200). $E_{1/2}$ (2^- to 3^-) (versus SCE, DMF) -1.31 V.

Results and discussion

Synthesis of macrocyclic tetrathiol ligands (7a–7c)

We recently developed a convenient method for the preparation of tetraaza macrocycles by a one-pot reaction with two reaction steps [18]. 1,10,19,28-Tetratosyl-4,7,13,16,22,25,31,34-octaoxo-1,10,19,28-tetraazacyclohexatriacontane was obtained in 42% yield by this method. Detosylation into a corresponding free tetraamine (**5**) quantitatively proceeded by $LiAlH_4$ in dry THF under reflux overnight.

Subsequent acylation reactions were carried out by the addition of acyl chlorides to CH_2Cl_2 solutions of **5** in the presence of base; Et_3N for **6a** and **6b**, K_2CO_3 for **6c**. Following deprotection (deacylation) under acidic conditions [11], the macrocyclic tetrathiol ligands **7a–7c** were successfully synthesized. ^1H NMR and ^{13}C NMR spectra of compounds **6a–6c** exhibited the hindered rotation of the amide group; the signals of α-protons to N ($CONCH_2$) appeared broad around δ 3.5 ppm, and α-carbons ($CONCH_2$) were resolved at δ 45.5 and 49.7, 45.5 and 49.7, 46.6 and 49.1 ppm.

Synthesis and physical data of Fe_4S_4 clusters with crown ether type ring (3a–3c)

A slight excess ($\times 1.02$ equiv.) of **6a** in pure degassed DMF was added to a solution of compound **4c**, and the mixture was stirred at 40 °C for 30 min. A rapid color change (brown to reddish brown) was observed following this addition, which suggested fast ligand exchange with the cyclic benzenethiol to form a new material. For the corresponding α-toluenethiol (**6b**) and t-butanethiol (**6c**) derivatives, no marked color change was observed, but the solution turned slightly greenish brown. The ligand substitution reactions were accelerated by removal of t-BuSH from this system under reduced pressure, and then the solvent was removed *in vacuo*. The product was then precipitated by addition of ether, washed with CH_3CN, CH_2Cl_2 and purified by two reprecipitations from DMF–ether. The present clusters showed better solubility than methylene or cyclophane type clusters, which were very soluble in solvents such as DMF, DMSO and PC (propylene carbonate) [9–11].

Relatively strong absorptions due to ligand-metal charge transfer (LMCT) from S to Fe were observed in the visible region, which is similar to other corresponding thiolate type FeS clusters [20]. UV–Vis titration of tetrathiol ligand **6a** into a DMF solution of unclad cluster **4c** was carried out, and a shift of absorption maximum at 417 nm of **4c** to 451 nm of **3a** was clearly observed. Furthermore, an extrusion of the Fe_4S_4 core from the macrocyclic cluster **3c** by the use of excess PhSH resulted in a stoichiometric amount of the unclad benzenethiolate cluster **4a**. This indicated that the Fe_4S_4 core retained its original structure during the ligand exchange reaction.

Characteristic features shown in the ^1H NMR spectra were broad signals and large downfield shifts of α-protons to the ligand sulfur due to the paramagnetic nature of the FeS core [21]. Upfield shifts of *ortho* (δ 6.0) and downfield shifts of *meta* (δ 8.2) protons were also observed for the benzenethiolate derivative **3a**, and the α-protons to S of **3b** were also largely shifted to downfield (δ 13.7). These signals were exhibited at the position of 0.2–0.5 ppm downfield to those of corresponding thiolato type clusters possessing methylene and cyclophane rings.

Stability of macrocyclic Fe_4S_4 clusters towards molecular oxygen

The active sites of the iron–sulfur proteins are known not to be particularly stable towards oxygen. Ordinal clusters of the 2^- state ($[Fe_4S_4(SR)_4]^{2-}$) are easily oxidized by oxygen to the 1^- state. In the macrocyclic Fe_4S_4 clusters, however, the hydrophobic environment may affect the stability of the core towards molecular oxygen [10, 17], since in nature the domain formed by rather hydrophobic peptide chains stabilizes the $1^-/2^-$ couple of the high-potential iron–sulfur proteins in a remarkably positive region. It is particularly of interest that the most stable cluster examined was the complex with the 36-membered ring in a series of methylene types, and that ring-size effect was obvious, viz. both the larger and smaller rings had a less stabilizing effect on the Fe_4S_4 cores [10]. This is one of the reasons we selected a 36-membered ring with an ether type backbone.

The stability of the macrocyclic clusters (**3**, 0.5 mM in DMF) towards molecular oxygen was then evaluated by noting the decrease in absorbance at λ_{max} (due to LMCT). Pseudo-first-order rate constants (k') for decomposition of the clusters were obtained in the form of initial rates (slope $= \Delta A/\Delta t$) from logarithmic plots of the absorbance as a function of time at different oxygen concentrations. Then, the first-order rate constants (k) were determined from plots of k' versus $[O_2]$ by the least-squares method as shown in Fig. 2. The half-life defined as $t_{1/2} = \ln 2/k$ was also computed. These data are summarized in Table 1 together with ratios of the half-life.

Figure 2 clearly shows the notable stabilizing effects of the cyclic ligands on the Fe_4S_4 cubane cores. The ratios in terms of half-life relative to the corresponding unclad clusters were as follows: 251 (**3a**), 428 (**3b**), 319 (**3c**). Benzenethiolato type cluster (**3a**) gave the longest

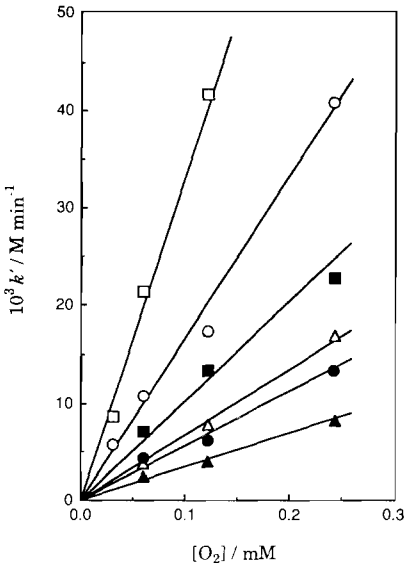

Fig. 2. Plots of pseudo-first-order rate constant (k') as a function of [O_2]. Fe_4S_4 cluster with a crown ether: benzenethiolato type (**3a**, ▲); α-toluenethiolato type (**3b**, ■); t-butanethiolato type (**3c**, ●), $(Ph_4As)_2[Fe_4S_4(SPh)_4]$ (**4a**, △), $(Ph_4As)_2[Fe_4S_4(SCH_2Ph)_4]$ (**4b**, □), $(Ph_4As)_2[Fe_4S_4(SBu^t)_4]$ (**4c**, ○). The total volume of the reaction vessel was 79 cm^3; cluster (0.5 mM) in DMF solution (2 cm^3).

TABLE 1. Rate constants and half-lives of the Fe_4S_4 clusters toward molecular oxygen

Compound	$10^3 \times k$ (min^{-1})[a]	Half-life $t_{1/2}$ (min)[b]
3a	17.7	39.2
3b	50.8	13.7
3c	29.0	23.9
4a	44.4	15.6
4b	217.4	3.2
4c	92.0	7.5

[a]First-order rate constant determined from plots of k' vs. [O_2] using the least-squares method. [b]Defined as $t_{1/2} = \ln 2/k$.

half-life time as well as the largest value of stabilizing effect. This phenomenon was probably caused by the relatively high potential of $2^-/3^-$ couple and the protection of the core from molecular oxygen by a large ring.

Redox potentials of macrocyclic Fe_4S_4 clusters

All redox processes ($[Fe_4S_4] \rightleftharpoons [Fe_4S_4]^{1+} \rightleftharpoons [Fe_4S_4]^{2+} \rightleftharpoons [Fe_4S_4]^{3+}$; core oxidation levels) of certain Fe_4S_4 clusters bearing methylene and cyclophane type ring were observed in a polar solvent, and whose values were shifted to a positive region. It is notable that cyclic voltammograms of these clusters clearly shows a $[Fe_4S_4]^{2+/3+}$ couple in a polar solvent as well as bulky thiolato clusters [5, 6]. The $[Fe_4S_4]^{2+/3+}$ process was not observed in a polar solvent in ordinary clusters, however, in CH_2Cl_2 or an immobile liquid, the $[Fe_4S_4]^{2+/3+}$ process of unclad cluster **4a** was observed [22]. This indicates that the Fe_4S_4 clusters embed in an intramolecular hydrophobic environment provided by macrocyclic tetrathiol ligands. It should also be emphasized that remarkable positive shifts of the $[Fe_4S_4]^{2+/3+}$ couple have been recognized in the t-butanethiolate macrocyclic clusters (around +0.24 V versus SCE in DMSO), since the corresponding potentials of the unclad cluster (**5**) were −0.11 V [23].

The crown ether type clusters (**3a**, **3b**, **3c**) showed only the $[Fe_4S_4]^{1+/2+}$ processes, and no $[Fe_4S_4]^{2+/3+}$ processes were observed. The potentials were higher than those of the corresponding unclad clusters (**4a**, **4b**, **4c**), but lower than those of the corresponding methylene-type clusters. These are summarized in Table 2.

Redox potential is generally affected by molecules or groups having a large dielectric constant; a charged redox center is stabilized by a complex formation with different charged ions and/or solvation [24–26]. These macrocycles probably prevent a counter cation or a solvent from coming near the core. In particular, by the effect of such a hydrophobic environment, these cores are also shielded from electron acceptors which stabilize the 1^- state ($[Fe_4S_4]^{3+}$) [12–14]. The crown ether type ring must have a larger dielectric constant than the methylene or cyclophane type rings and such hydrophobicity is insufficient to give a $[Fe_4S_4]^{2+/3+}$ couple in DMF solution.

In conclusion, the abnormal values of the $1^-/2^-$ redox potentials of the macrocyclic clusters deviate greatly from the normal values of unclad clusters. One reason for the large positive shifts in these potentials could be the effect of a hydrophobic environment surrounding the core. However, it may be difficult to explain these positive shifts by a hydrophobic environ-

TABLE 2. Redox potential of synthetic Fe_4S_4 clusters (vs. SCE)

Redox[a]	Thiolate type	Ring type: Methylene (**1**)[b]	Crown ether (**3**)[c]	Unclad (**4**)[c]
$2^+/3^+$	Bu^t	+0.23		−0.12
	Bzl	−0.35		
	Ph	−0.36		
$1^+/2^+$	Bu^t	−1.29	−1.31	−1.42
	Bzl	−1.12	−1.23	−1.25
	Ph	−0.85	−0.95	−1.04
$0/1^+$	Bu^t			−2.16
	Bzl	−1.86		−1.96
	Ph	−1.70		−1.75

[a]Core $[Fe_4S_4]$ oxidation level. [b]Data of the clusters with 36-membered ring in DMSO. [c]In DMF.

ment effect alone; a steric factor probably has some influence on the potential of the t-butanethiolate ligand.

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