CHEMISTRY LETTERS, pp. 919-922, 1992.

Crystal Structure of $(Ph_4As)_2[Fe_4S_4(SAd)_4]$ and Stabilization of $[Fe_4S_4(SAd)_4]^-$ State in Aqueous Media

Hide KAMBAYASHI, Masami NAKAMOTO,† Shie-Ming PENG,†† Hirotaka NAGAO, and Koji TANAKA*
Department of Structural Molecular Science, The Graduate University for Advanced Studies, Institute for Molecular Science, Myodaiji, Okazaki 444
†Osaka Municipal Technical Research Institute, Morinomiya, Joto-ku, Osaka 565
††Department of Chemistry, National Taiwan University, Roosevelt Road Section 4, Taipei, Taiwan 10764, Republic of China

Stability of superoxidized form of $[Fe_4S_4(SAd)_4]^{2-}$ (AdS^-: 1-adamantanethiolate) in DMF, H_2O/DMF, and aqueous poly[2-(dimethylamino)hexanamide] (PDAH) solutions is discussed in connection with the crystal structure of $(Ph_4As)_2[Fe_4S_4(SAd)_4]$.

4Fe-type iron sulfur proteins operate using three oxidation states, $[Fe_4S_4]^+$, $[Fe_4S_4]^{2+}$, and $[Fe_4S_4]^{3+}$ (Eq. 1). Ferredoxins (Fd) and high potential iron-sulfur proteins (Hp) exhibit their redox potentials of the $[Fe_4S_4]^{+/2+}$ and $[Fe_4S_4]^{2+/3+}$ couples around -0.7 and 0 V *vs.* SCE at pH 7.[1)] Most of synthetic Fe_4S_4 clusters show a stable $[Fe_4S_4]^{+/2+}$ redox couple both in organic and aqueous solutions.[2)] On the other hand, the $[Fe_4S_4]^{2+/3+}$ couple of synthetic Fe_4S_4 clusters is observed in less polar solvents such as CH_2Cl_2 and C_6H_5CN,[3)] and the $[Fe_4S_4]^{3+}$ state of those clusters is unstable in polar solvents. For example, $[Fe_4S_4(SPh)_4]^{2-}$ displays a pseudo-reversible (2-/1-) couple at $E_{1/2}$ = -0.32 V in CH_2Cl_2, while it shows only an irreversible oxidation wave in CH_3CN and DMF.[3)] X-Ray structural data suggest that the $[Fe_4S_4]^{3+}$ core of Hp_{ox} is protected from water by hydrophobic protein environments around the Fe_4S_4 core.[1)] In accordance with this, stabilization of the $[Fe_4S_4]^{3+}$ core of synthetic Fe_4S_4 clusters has been achieved by introduction of sterically encumbered ligands such as *t*-butylthiolate,[4)] 2,4,6-tri(*i*-propyl)benzenethiolate,[5)] polypeptide,[5)] 36-membered ring,[6)] and 1-adamantanethiolate[7)] in polar organic solvents. This letter reports the crystal structure of $(Ph_4As)_2[Fe_4S_4(SAd)_4]$ and the first example of the $[Fe_4S_4]^{3+}$ core stabilized in aqueous media.

$$\begin{array}{ccccc} \lbrack Fe_4S_4\rbrack^+ & \rightleftharpoons & \lbrack Fe_4S_4\rbrack^{2+} & \rightleftharpoons & \lbrack Fe_4S_4\rbrack^{3+} \\ Fd_{red} & & Fd_{ox},\ Hp_{red} & & Hp_{ox} \end{array} \qquad (1)$$

Reversible $[Fe_4S_4(SAd)_4]^{2-/3-}$ and $[Fe_4S_4(SAd)_4]^{2-/-}$ redox couples are observed at $E_{1/2}$ = -1.32 and -0.10 V in the cyclic voltammogram (CV) of $(Et_4N)_2[Fe_4S_4(SAd)_4]$ in DMF (Fig. 1a). An irreversible oxidation, however, takes place at potentials of the anodic wave of the $[Fe_4S_4(SAd)_4]^{2-/-}$ couple in the presence of small amount of H_2O (3%) in DMF, while the $[Fe_4S_4(SAd)_4]^{2-/3-}$ couple still remains in the same medium (Fig. 1b),$^{8)}$ suggesting that $[Fe_4S_4(SAd)_4]^-$ is more subject to a hydrolysis reaction than $[Fe_4S_4(SAd)_4]^{2-}$ and $[Fe_4S_4(SAd)_4]^{3-}$. On the other hand, the CV of $(Et_4N)_2[Fe_4S_4(SAd)_4]$ solubilized in aqueous poly[2-(dimethylamino)hexanamide] (PDAH) using an ITO (In_2O_3) disk electrode$^{9)}$ exhibits the redox couples of not only $[Fe_4S_4(SAd)_4]^{2-/3-}$ but also $[Fe_4S_4(SAd)_4]^{2-/-}$ at $E_{1/2}$ = -0.90 and -0.28 V$^{10)}$ (Fig. 1c). In addition, the redox potentials of those $[Fe_4S_4(SAd)_4]^{2-/3-}$ and $[Fe_4S_4(SAd)_4]^{2-/-}$ couples in the aqueous PDAH solutions were shifted by -0.06 V/pH between pH=6 to 11, suggesting that those redox reactions are accompanied by reversible protonation of core and/or terminal sulfur.$^{11)}$ Such a reversible protonation of the cluster suggests that H_2O or H_3O^+ can penetrate into $[Fe_4S_4(SAd)_4]^-$ through PDAH.

The crystal structure of $(Ph_4As)_2[Fe_4S_4(SAd)_4]^{12)}$ was conducted by X-ray analysis in order to estimate hydrophobicity around the Fe_4S_4 core. The core structure of $(Ph_4As)_2[Fe_4S_4(SAd)_4]$ is approximated by D_{2d} symmetry, as shown in Fig. 2. The Fe-S bonds in the Fe_4S_4 core are divided into two sets in bond length: four short Fe-S bonds parallel to the S_4 axis are in the range of 2.237 to 2.268 Å. The

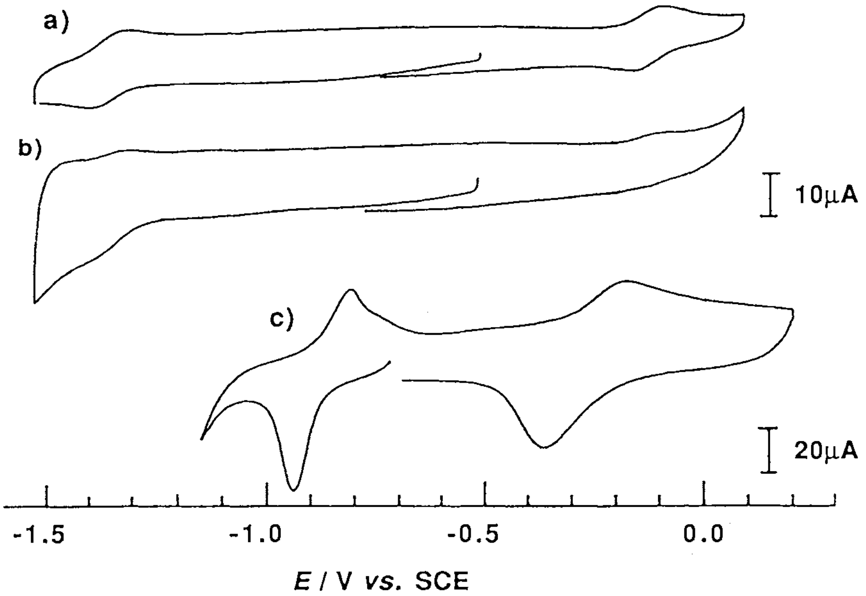
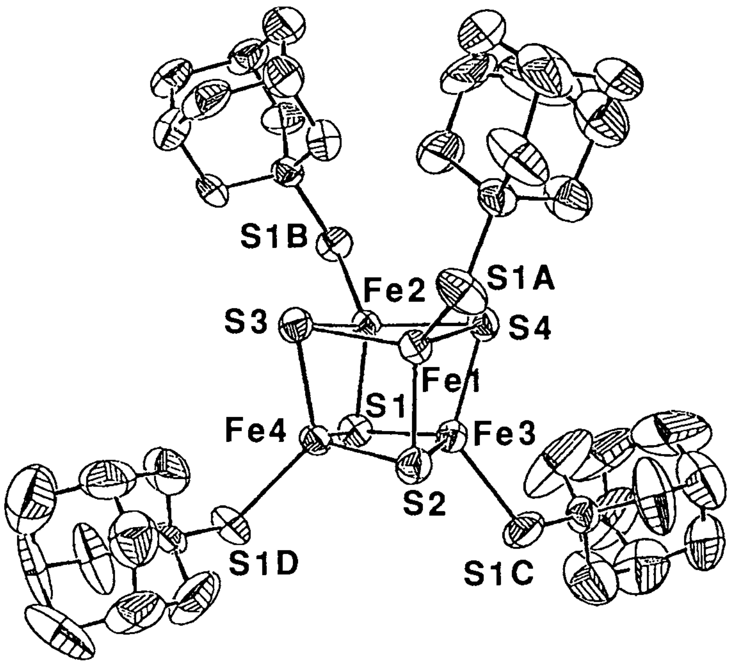


Fig. 1. Cyclic voltammograms of $(Et_4N)_2[Fe_4S_4(SAd)_4]$ obtained using a) a glassy carbon electrode in DMF, b) added H_2O (3% v/v) to (a), c) an ITO electrode in aq. PDAH soln. at pH 7.3; scan rate 0.1 V s^{-1}.



Selected bond distances (Å)

Fe(1)-S(2) = 2.237(3),
Fe(2)-S(1) = 2.238(3),
Fe(3)-S(4) = 2.264(3),
Fe(4)-S(3) = 2.268(3)
mean = 2.252(16)

Fe(1)-S(3) = 2.320(3),
Fe(1)-S(4) = 2.318(3),
Fe(2)-S(3) = 2.320(3),
Fe(2)-S(4) = 2.331(3)
mean = 2.322(6)
Fe(3)-S(1) = 2.307(3),
Fe(3)-S(2) = 2.316(3),
Fe(4)-S(1) = 2.311(3),
Fe(4)-S(2) = 2.298(3)
mean = 2.308(7)
mean (of last 8)
= 2.315(10)

Fig. 2. Molecular structure of $[Fe_4S_4(SAd)_4]^{2-}$ with selected bond distances.

remaining eight long Fe-S bonds perpendicular to the S_4 axis are in 2.298 to 2.331 Å range. It is worthy to note that the two faces perpendicular to S_4 axis are different in the size; a mean Fe-S bond distance (2.322 Å) in the Fe(1,2)S(3,4) face (Fig. 2) is longer than that in the Fe(3,4)S(1,2) face (2.308 Å). Similar distortion is reported in the crystal structure of $(Et_4N)_2[Fe_4S_4(SCH_2C_6H_5)]$, but the difference in the mean Fe-S bond distance between two faces is 0.01 Å.13) Thus, a relatively large conical distortion of the Fe_4S_4 core is observed in the crystal structure of $[Fe_4S_4(SAd)_4]^{2-}$ compared with other Fe_4S_4 clusters reported so far. However, the structure of $[Fe_4S_4(SAd)_4]^{2-}$ clearly reveals that $[Fe_4S_4(SAd)_4]^{2-}$ has an open space enough for coordination of H_2O to the Fe_4S_4 core. Furthermore, based on the facts that $(Et_4N)_2[Fe_4S_4(SAd)_4]$ was stable in both DMF and aqueous PDAH (pH 7.0) solutions, while it decomposes with liberating a black precipitate in H_2O/DMF (1:9 v/v) in 2 h, PDAH apparently depresses hydrolysis of $[Fe_4S_4(SAd)_4]^{2-}$ in aqueous media. Such stabilization of the cluster in aqueous media is not simply explained by a hydrophobic sphere around the $[Fe_4S_4]^{2+}$ core by PDAH, since a proton participates in the redox reactions of the cluster in the aqueous PDAH solutions. It has been reported that excess of $HOCH_2CH_2SH$ effectively depresses hydrolysis of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ in water.14) We, therefore, propose that stabilization of $[Fe_4S_4(SAd)_4]^-$ as the first model of Hp_{ox} in aqueous media may be attributed to suppression of dissociation of AdS^-

ligand by PDAH surrounding the Fe_4S_4 cluster rather than hydrophobic spheres around the Fe_4S_4 core.

References

1) C. D. Stout, "Iron-Sulfur Proteins," in "Metal Irons in Biology Vol. 4," ed by T. G. Spiro, John Wiley and Sons, New York (1982), p. 97; C. W. Carter, Jr., "Iron-Sulfur Proteins," ed by W. Lovenberg, Academic Press, New York (1977), Vol. III, p. 157.
2) J. M. Berg and R. H. Holm, "Iron-Sulfur Proteins," in "Metal Irons in Biology Vol. 4," ed by T. G. Spiro, John Wiley and Sons, New York (1982), p. 1; R. H. Holm and J. A. Ibers, "Iron-Sulfur Proteins," ed by W. Lovenberg, Academic Press, New York (1977), Vol. III, p. 205.
3) H. L. Block, O. Kievit, E. K. -H. Roth, J. Jordanov, J. G. M. van der Linden, and J. J. Steggerda, *Inorg. Chem.*, **30**, 3230 (1991).
4) P. K. Mascharak, K. S. Hagen, J. T. Spence, and R. H. Holm, *Inorg. Chim. Acta*, **80**, 157 (1983).
5) N. Ueyama, T. Terakawa, T. Sugawara, M. Fuji, and A. Nakamura, *Chem. Lett.*, **1984**, 1287; T. O'Sallivan and M. M. Millar, *J. Am. Chem. Soc.*, **107**, 4097 (1985).
6) Y. Okuno, K. Uoto, O. Yonemitsu, and T. Tomohiro, *J. Chem. Soc., Chem. Commun.*, **1987**, 1018.
7) M. Nakamoto, K. Tanaka, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1988**, 1422.
8) A similar solvent effect by H_2O has been reported in the $[Fe_4S_4(SPh)_4]^{2-/-}$ couple in CH_2Cl_2; R. Ohno, N. Ueyama, and A. Nakamura, *Chem. Lett.*, **1989**, 399.
9) A glassy carbon electrode is not adequate for the measurements of the redox reaction of the $[Fe_4S_4(SAd)_4]^{-/2-/3-}$ couples in aqueous PDAH solutions because of an adsorption of PDAH on the surface of a glassy carbon electrode.
10) Even in an ITO electrode, PDAH more or less interferes an electron transfer between the ITO and $[Fe_4S_4(SAd)_4]^{2-}$ in aqueous PDAH solutions. So, the peak separations between cathodic and anodic waves of the (2-/3-) and (2-/1-) redox couples in aqueous PDAH solution becomes large compared with those in DMF.
10) M. Nakamoto, K. Tanaka, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **61**, 4099 (1988).
11) We could not get a suitable single crystals of $(Et_4N)_2[Fe_4S_4(SAd)_4]$. Therefore, X-ray analysis was conducted by a use of single crystals of $(Ph_4As)_2[Fe_4S_4(SAd)_4]$; Crystal data for $C_{88}H_{100}S_8As_2Fe_4$, M = 1787.47, orthorhombic, $P2_12_12_1$, a = 14.176(4) Å, b = 22.059(7) Å, c = 26.515(5) Å, Z = 4, D_{calc} = 1.432 g cm^{-3}, R = 0.044 for 4484 independent reflections.
12) B. A. Averill, T. Herskouitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973).
13) C. L. Hill, J. Renaud, R. H. Holm, and L. E. Mortenson, *J. Am. Chem. Soc.*, **99**, 2549 (1977).

(Received February 21, 1992)