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LETTER

Spectral evidence for stepwise ligand substitution on 4Fe4S clusters

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In some iron–sulfur proteins such as aconitase, the four iron atoms of the 4Fe4S core are not exactly equivalent and the core has one labile iron [1]. Holm and co-workers synthesized tridentate type 4Fe4S clusters and studied subsite reactions [2]. It is also known that the original ligands of 4Fe4S clusters can be easily changed by a more acidic thiol ligand [3]. However, when a thiol is used in the anion form, the original ligand in the cluster can be substituted by a more basic thiolate. Thus this interesting phenomenon may allow us to prepare many kinds of 4Fe4S derivatives from a simple cluster. In this work, we show the spectroscopic behavior of stepwise formations of mixed-ligand type 4Fe4S clusters via a reaction with NaCp (Cp: cyclopentadienyl).

Experimental

All operations were carried out under pure nitrogen. FeS clusters used as starting materials were synthesized according to the literature [4]. DMF and DMSO were stored over molecular sieves 4 Å and then distilled from CaH_2. THF was distilled from CaH_2 and then $LiAlH_4$ before use. The chemicals and deuterated solvents in this research were used as purchased.

Proton NMR spectra were obtained on a Brucker AC-200 instrument with Me_4Si as the internal standard, and UV–Vis spectra were obtained on a Hitachi U-3200 spectrophotometer.

NMR study

To a 0.7 ml DMSO-d_6 solution of $(Et_4N)_2[Fe_4S_4(SPh)_4]$ (**1**) (20 μmol) were added 10 μl of 2.0 M THF solution of NaCp under pure nitrogen. After stirring for 15 min, one molar equivalent of MeI (10 μl of 2.0 M degassed dry THF solution) was added to the solution and the reaction mixture was stirred for 15 min. 10 μl of 2.0 M THF solution of thiol (t-BuSH or EtSH) were then added. The reaction mixture of each reaction step was then transferred into a NMR tube via canule.

UV–Vis titration study

10 μmol of cluster **1** were dissolved in 50 ml of degassed dry DMF in a quartz cell. 5 μl of 2.0 M THF solution of NaCP were added to the solution, which was stirred for 15 min at room temperature under nitrogen. To the reaction mixture one molar equivalent of MeI (5 μl of 2.0 M degassed by THF solution) was added and the reaction mixture was stirred for 30 min. 5 μl of 2.0 M THF solution of EtSH were then added. The same operations were carried out with the same solution 5 times.

Results and discussion

Figure 1 shows the ^1H NMR spectral change of 4Fe4S clusters caused by the ligand substitution reaction. On adding an equivalent mole of NaCp into the degassed dry DMSO solution of cluster **1** under pure nitrogen, an equimolar PhS^- was liberated (exp. ii). At the same time, the signals of the *m*, *o* and *p* protons of the remaining three phenyl groups in the new cluster shifted

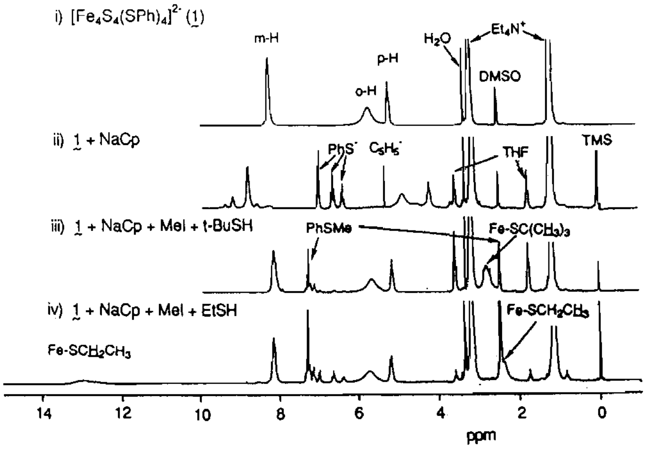

Fig. 1. ^1H NMR spectra of 4Fe4S clusters formed by stepwise ligand substitution reactions in DMSO-d_6.

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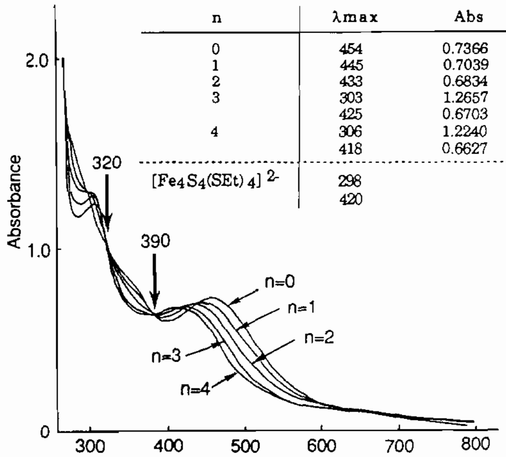
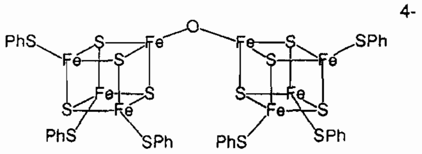
to lower and higher fields, respectively. This indicates that some reactive intermediate was formed concomitant with the liberation of an equimolar PhS$^-$. When cluster **1** was treated with NaCp, MeI and t-BuSH (exp. iii), the liberated PhS$^-$ reacted with MeI to form PhSMe and the intermediate was converted to $[Fe_4S_4(SPh)_3(SBu^t)]^{2-}$ (**2**) via the reaction with t-BuSH. In cluster **2**, chemical shifts of the aromatic protons returned to near the original positions of cluster **1**, and new signals due to t-Bu protons of the ligand appeared (2.8 ppm). Similar results were obtained when EtSH was added instead of t-BuSH (exp. iv), the NMR spectrum being well compatible with the formation of $[Fe_4S_4(SPh)_3(SEt)]^{2-}$ (**3**). In a direct ligand exchange reaction between cluster **1** and NaSEt, three kinds of methylene proton of $-SCH_2CH_3$ were observed around 13 ppm in the ^1H NMR spectrum, which suggested the formation of a mixture of **1**, **3** and $[Fe_4S_4(SPh)_2(SEt)_2]^{2-}$. Figure 2 illustrates the results of a stepwise ligand exchange reaction on cluster **1** in DMF, and each spectrum is observed after the above-mentioned operation ($\mathbf{1}+n$(NaCp + MeI + EtSH), $n = 0$, 1, 2, 3, 4). UV–Vis spectra showed two isosbestic points around 320 and 390 nm. The finally obtained spectrum ($n = 4$) was consistent with that of the authentic $[Fe_4S_4(SEt)_4]^{2-}$ (**4**), which meant that the four PhS$^-$ ligands were substituted stepwise by EtS$^-$. Further operations caused no significant change in the absorption band based on ligand-metal charge transfer (LMCT) around 420 nm [5].

Although the structure of the intermediate formed from complex **1** and an equimolar of NaCp is not clear at present, there may be two candidates. One is $[Fe_4S_4(SPh)_3(Cp)]^{2-}$ (**5**) and the other is the oxo-bridged cluster **6**. When LiFlu (Flu: fluorene) was used instead of NaCp, in fact, the formation of **2** from the cluster **1**/LiFlu/MeI/t-BuSH was similarly confirmed by ^1H NMR. The intermediate in this case, however, was almost the same as that of NaCp, and the fluorene anion changed back to fluorene presumably by the proton from water before addition of the thiol. Cluster **5** was probably very unstable and reacted with water immediately to give the oxo-bridged cluster **6** [6].



n	λmax	Abs	ε x 10^{-3}
0	454	0.7366	17.7
1	445	0.7039	16.9
2	433	0.6834	16.4
3	303	1.2657	30.4
	425	0.6703	16.1
4	306	1.2240	29.4
	418	0.6627	15.9
$[Fe_4S_4(SEt)_4]^{2-}$	298		23.3
	420		17.2

Fig. 2. UV–Vis spectra of 4Fe4S clusters formed by stepwise ligand substitution reactions in DMF: cluster $\mathbf{1}+n$(NaCp + MeI + EtSH).



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In this work, we have given spectral evidence of the stepwise ligand substitution in 4Fe4S clusters using NaCp or LiFlu. We have already developed a series of 4Fe4S clusters with a macrocyclic tetrathiolate ligand [7], and the present evidence may give us a clue to the 4Fe4S↔3Fe4S (or 3Fe3S) conversions with macrocyclic ligands.

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