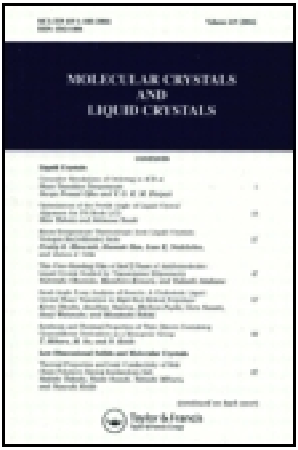

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Synthesis of Novel Iron-Sulfur Complexes with Functional Ligands for Cluster Assembly

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Iron-sulfur clusters containing a variety of ligands, $[Fe_4S_4(SR)_4]^{2-}$ (R = 4-C_6H_4CHO, 4-C_5H_4N, 2-(4-NO_2)C_5H_4N) were prepared as potential constituents for functional assembly. Preparation and structure of a mixed-cluster compound $(Me_4N)_4[Fe(SPh)_4]$ $[Fe_4S_4(SPh)_4]$, involving both rubredoxin and [4Fe-4S] ferredoxin model clusters, are also discussed.

Keywords: iron-sulfur cluster; ligand exchange reaction

INTRODUCTION

Iron-sulfur clusters, including rubredoxin and ferredoxin model complexes (Figure 1), have attracted special attention for their biological significance [1]. A number of metal-sulfur model complexes with allene- and arenethiolato ligands have been synthesized, their properties being investigated extensively by Holm and his co-workers [2]. Recently the clusters have also drawn attention as a constituent of dendrimer complexes [3]. Another interesting aspect of these clusters is the mixed-valent nature of the iron-sulfur core, as we intend to construct electronically functional materials based on mixed valence compounds [4].

We report here the syntheses of novel iron-sulfur clusters with a variety of ligands. For example, incorporating additional coordinating sites into the ligand should lead to a new class of assembled complexes, the electronic functions of which would be of interest. We first discuss the properties of $[Fe_4S_4(SPh)_4]^{2-}$ clusters and then report the preparation of new clusters obtained by ligand exchange reactions.

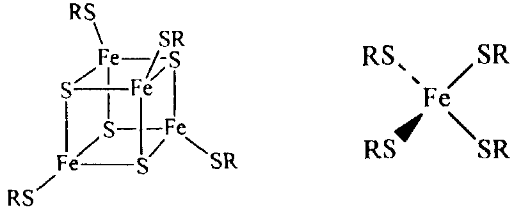

FIGURE 1 The [4Fe-4S] ferredoxin model cluster (left) and the rubredoxin model cluster (right).

EXPERIMENTAL

All operations were performed under a dinitrogen atmosphere by the Schlenk technique. $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$ (**1**) and $(Et_4N)_2\,[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$ (**2**) were prepared by the reported method [5,6]. $(Me_4N)_4[Fe_4S_4(SPh)_4][Fe(SPh)_4]$ (**3**) was obtained as a by-product of $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$. Crystallographic parameters for **3**: Space group P_1 a = 16.627(8)Å , b = 16.982(6)Å , c = 15.610(8)Å, α = 101.09(4)Å , β = 92.88(5)Å , γ = 62.64(3)Å, V = 3838(3)Å^3 , Z = 2 , Final R = 0.097 for 4871 reflections.

$(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}4\text{-}C_6H_4CHO)_4]$ (**4a**). A solution of **1** in acetonitrile was slowly added to a solution of 4,4'-dithiobis (benzaldehyde). Black needle crystals precipitated slowly, yield 73 %. ^{1}H-NMR (DMSO-d_6): δ = 9.80 (br, -CHO) , 8.75 (br, Ar-H) , 6.20 (br, Ar-H).

$(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}C_5H_4N)_4]$ (**4b**). A mixture of **2** and 4-pyridinethiol in acetonitrile was stirred at room temperature for 1 h. The brown precipitate was recrystallized from acetonitrile/diethylether.

^{1}H-NMR (CD_3CN): δ = 9.14 (br, Py-H) , 5.98 (br, Py-H).

$(n\text{-}Bu_4N)_2$ $[Fe_4S_4(S\text{-}2\text{-}(4\text{-}NO_2)C_5H_4N)_4]$ (**4c**). The compound was synthesized by the same procedure as for **4b**, using 2,2'-dithiobis(5-nitropyridine). Black powders were recrystallized from acetonitrile/diethylether. ^{1}H-NMR (CD_3CN): δ = 112 (br, Py-H) , 73.5 (br, Py-H) , 14.3 (br, Py-H). Crystallographic parameters for **4c**: Orthorhombic, Space group *Fddd* a = 27.585(19) Å , b = 29.736(20) Å , c = 12.592(14) Å, V = 10329(15) Å^3, Z = 8.

The X-ray diffraction measurement were performed on a Rigaku AFC-7R four-circle diffractometer using Mo$K\alpha$ radiation. The structure was solved and refined by using the teXsan software package.

RESULTS AND DISCUSSION

1) Structure and Properties of $[Fe_4S_4(SPh)_4]^{2-}$ Cluster Complexes

In order to obtain information on the mixed-valent state of the $(Fe_4S_4)^{2+}$ core, the dielectric response of a representative complex, $(Me_4N)_2[Fe_4S_4(SPh)_4]$ (**1**), was measured. The dielectric constant of the single crystal measured at a frequency of 10 kHz showed only a low value ($\varepsilon < 6$), being temperature independent down to 4.2 K. The absence of dielectric response suggests that the valence state is highly delocalized due to the rapid exchange between Fe(II) and Fe(III) down to low temperatures.

We further note the finding of a novel type of mixed-cluster type compound, $(Me_4N)_4[Fe_4S_4(SPh)_4][Fe(SPh)_4]$ (**3**), obtained as a by-product of **1**. The structure is characterized by the unique coexistence of rubredoxin- and ferredoxin-model clusters (1:1), as shown in Figure 2. Judging from the redox potentials, the valence states of each clusters are reasonably attributed to $[Fe_4S_4(SPh)_4]^{2-}$ involving 2Fe(II)+2Fe(III), and $[Fe(SPh)_4]^{2-}$ involving Fe(II). Consistent with this, the intramolecular geometries of each iron-sulfur core are almost the same as those observed for $(Bu_4N)[Fe_4S_4(SPh)_4]$ [7] and $(Et_4N)_2Fe(SPh)_4$ [8], respectively.

Red-black prismatic crystals of **3** were obtained when the addition of ferric chloride to the thiol was performed slowly. The formation of **3** is explained by the reaction path for the formation of the $Fe_4S_4^*$ core, which depends on the amount of thiols [9]; The slow addition of the ferric chloride results in the initial formation of a rubredoxin type $[Fe(S\text{-}Ar)_4]^{2-}$ complex, which leads to the coexistence of both types of cores as seen in the present compound.

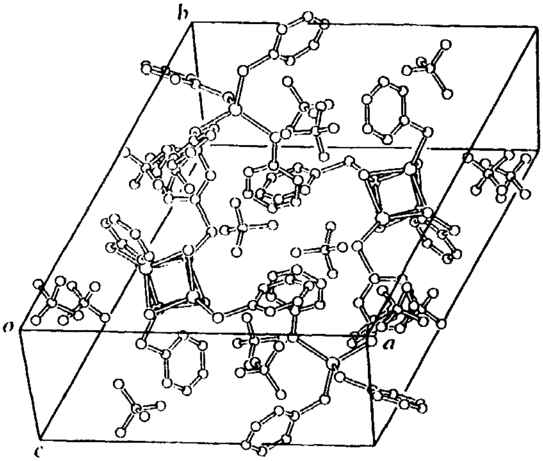

FIGURE 2 X-ray crystal structure of **3**.

2) Introduction of Versatile Ligands into the $Fe_4S_4^*$ core by the Exchange Reactions

We investigated the syntheses of cluster compounds $[Fe_4S_4(SAr)_4]^{2-}$ with the thiolato ligands shown in Figure 3, by applying the ligand exchange reaction using disulfides. The useful exchange reaction was

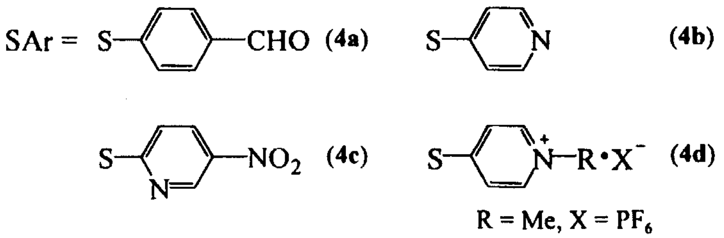

FIGURE 3 Thiolato ligands used for the exchange reactions.

reported by Ueyama *et al.* [10] to construct stabilized complexes by hydrogen bonding of the amide groups.

The preparation of $(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}4\text{-}C_6H_4CHO)_4]$ proceeded quite smoothly, affording black needle-like crystals. The exchange reaction was then applied to pyridinethiols, which have an additional coordination site. The compound $(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}C_5H_4N)_4]$ (**4b**) was prepared using 4-pyridinethiol, which is more reactive than the disulfide, while $(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}2\text{-}(4\text{-}NO_2)C_5H_4N)_4]$ (**4c**) could be prepared efficiently by using the disulfide. The structure of the anion cluster in **4c** is shown in Figure 4 [11]. It is notable that the Fe atoms in the core are coordinated not only by the sulfur atom but also by the nitrogen atom of the ligand; this scheme leads to the unusual slender type of cluster conformation, which has never been observed in compounds with arenethiolato ligands.

We further tried to synthesize a novel type of cluster involving a cationic ligand, $[Fe_4S_4(S\text{-}4\text{-}C_5H_4N^+Me)_4]^{2+}$ (**4d**). The exchange reaction using 4,4'-dithiobis(methylpyridinium) hexafluoroborate immediately afforded black powders, which were virtually insoluble in organic solvents. We expect stabilization of the core by the strong electron withdrawing effect of the ligand. Another advantage of the system is the ease of constructing various derivatives by changing the substituents and counter ions.

Examination of complex formation of **4b** with various metal complexes is underway in this laboratory.

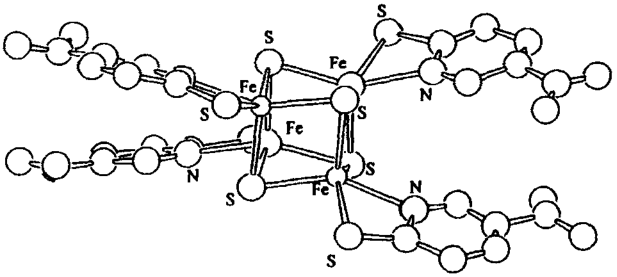

FIGURE 4 X-ray structure of the anion cluster in **4c**.

Acknowledgments

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