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CRYSTAL STRUCTURE OF $[Et_4N]_2[Fe_4S_4(2,4,6\text{-TRIMETHYLBENZENETHIOLATO})_4]$

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The crystal structure of $[Et_4N]_2[Fe_4S_4$(2,4,6-trimethylbenzenethiolato)$_4]$ was determined by X-ray diffraction. The complex crystallizes in orthorhombic space group (Pcnb). The $Fe_4S_4{}^{2+}$ core of the anion approaches C_2 symmetry. The complex has relatively long Fe-S(Ph) bond lengths and small Fe-S-C angles. The results suggest the prevention of π-overlap between Fe(d)-SPh(p) orbitals by the steric hindrance of two methyl groups at o-positions of phenyl group.

Recently several metal complexes having sterically hindered thiolato ligands have been studied for their unusual properties. For example, the iron(III) state of $[Et_4N]_2[Fe$(2,3,5,6-tetramethylbenzenethiolato)$_4]$ was reported to be relatively stable,[1] although a common iron(III) complex having simple alkane- or arylthiolato ligands is easily reduced with its own thiolato ligands to give an iron(II) form.[2] Our previous paper described the synthesis and the electrochemical property of three ferredoxin model complexes having bulky thiolato ligands.[3] These complexes exhibited the quasi-reversible redox couples of 2-/1- which have not been observed except for extremely purified $[Fe_4S_4(S\text{-}t\text{-}Bu)_4]^{2-}$ complex (1).

A well-known ferredoxin model complex with benzenethiolato ligand, $[Fe_4S_4(S\text{-}Ph)_4]^{2-}$, exhibits a ligand-metal charge transfer (LMCT) absorption maximum at 457 nm (ε: 17700) in N,N-dimethylformamide (DMF), while a ferredoxin model complex having alkanethiolato ligands such as 1 shows an absorption maximum at 417 nm (ε: 16700) in DMF.[4] The difference between these absorptions is considered to be ascribed to the conjugation of a sulfur lone pair orbital with π orbitals of the phenyl ring. Actually, $[Fe_4S_4(S\text{-}p\text{-tol})_4]^{2-}$ (S-p-tol = p-methylbenzenethiolato) and $[Fe_4S_4(S\text{-}o\text{-tol})_4]^{2-}$ were reported to provide absorption maxima at 461 nm (ε: 18600) and at 460 nm (ε: 18300) in DMF, respectively.[5,6] These absorptions are red-shifted from the 457 nm peak by the electron donating methyl group at o,p-positions. $[Et_4N]_2[Fe_4S_4(tmbt)_4]$ (tmbt = 2,4,6-trimethylbenzenethiolato) (2) exhibits a strong LMCT absorption at 409 nm (ε: 29200) in DMF, although the absorption was previously reported to be observed at 412 nm (ε: 22500) in DMF for

Table 1. Crystal data of $[Et_4N]_2[Fe_4S_4(tmbt)_4]$

Formula	$C_{52}H_{84}N_2S_8Fe_4$ a)
Fw	1217.12
Crystal	orthorhombic
Space group	Pcnb
a/Å	20.789(6) (1 Å = 0.1 nm)
b/Å	17.418(6)
c/Å	16.680(6)
V/Å^3	6040(4)
Z	4
D_c/g cm^{-3}	1.35
Radiation	Mo K_α
Unique data	3488 non-zero reflections
R	0.098 b)

a) Found : C, 51.47 ; H, 6.99 ; N, 2.33%. Calcd : C, 51.32 ; H, 6.96 ; N, 2.30%.

b) The R value is still high because of the positional disorder of tetraethylammonium cations.

Table 2. Comparison of Mean Values of Structural Parameters for$[Et_4N]_2[Fe_4S_4(tmbt)_4]$

	$[Fe_4S_4(tmbt)_4]^{2-}$	$[Fe_4S_4(S\text{-}Ph)_4]^{2-}$ a)	$[Fe_4S_4(S\text{-}CH_2\text{-}Ph)_4]^{2-}$ b)
Fe-S	2.273(4) c)[2] d), 2.275(6)[2]	2.263	2.251
Fe-S*	2.266(4)[2], 2.275(4)[2], 2.275(5)[2], 2.293(5)[2], 2.302(4)[2], 2.307(4)[2]	2.267[4], 2.296[8]	2.239[4], 2.310[8]
Fe---Fe	2.743(3)[2], 2.753(5)[1], 2.762(3)[2], 2.796(5)[1]	2.730[2], 2.739[4]	2.732[4], 2.776[2]
S-Fe-S* e)	111.8(2)[2], 112.1(2)[2], 112.9(2)[2], 115.5(2)[2], 116.0(2)[2], 119.8(2)[2]	114.4	115.1
Fe-S*-Fe	mean 74.4(9)[12]	73.5	73.8
S*-Fe-S*	mean 103.8(13)[12]	104.3	104.1
S-C	1.767(14)[2], 1.788(13)[2]	1.771	1.832
Fe-S-C	99.4(7)[2], 100.4(5)[2]	106.1	112.8

a) Data from Ref. 7.

b) Data from Ref. 8.

c) ( ) refers to the estimated standard deviation.

d) [ ] refers to the number of the bond lengths or the bond angles.

e) S* refers to an inorganic sulfur atom.

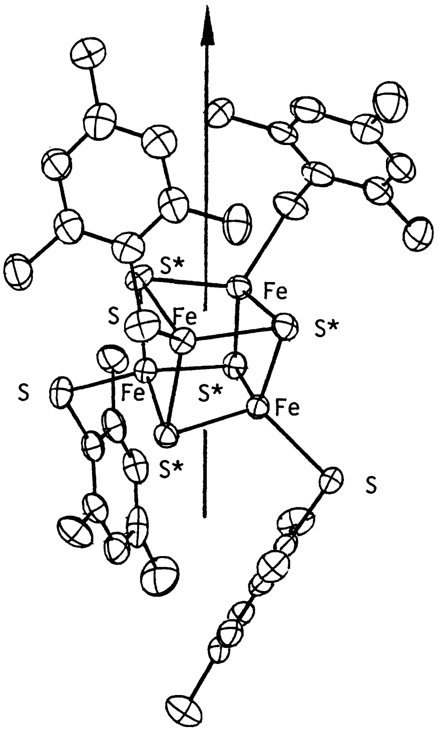

Fig. 1. Perspective view of the anion of $[Et_4N]_2[Fe_4S_4(tmbt)_4]$, showing 50% probability ellipsoids with $\bar{2}$ axis toward C_2 symmetry.

$[(\underline{n}\text{-}Bu)_4N]_2[Fe_4S_4(tmbt)_4]$.[3] Such an absorption is quite different from those of $[Fe_4S_4(S\text{-}\underline{o}\text{-}tol)_4]^{2-}$ and $[Fe_4S_4(S\text{-}\underline{p}\text{-}tol)_4]^{2-}$ described above. Although the methyl substituents at o, p-positions should contribute to an electron donation to phenyl ring and sulfur atom to result in a red shift, the blue shift of LMCT absorption maximum was found for **2**. This paper presents the crystal structure of **2** by X-ray diffraction to solve the above question. The related parameters are listed in Tables 1 and 2. The parameters for $[Fe_4S_4(S\text{-}Ph)_4]^{2-}$,[7] and $[Fe_4S_4(S\text{-}CH_2\text{-}Ph)_4]^{2-}$,[8] were cited for comparison. The perspective view of the anion of **2** is shown in Fig. 1. The results indicate that the structure of $Fe_4S_4^{2+}$ core is similar to the others, but some remarkable differences between **2** and the others were observed in the parameters around benzenethiolato sulfur. The mean Fe-S bond length (2.274 Å) for **2** is longer than those of $[Fe_4S_4(S\text{-}Ph)_4]^{2-}$ and $[Fe_4S_4(S\text{-}CH_2\text{-}Ph)_4]^{2-}$ as listed in Table 2. Furthermore, although the S-C(Ph) bond lengths of **2** and $[Fe_4S_4(S\text{-}Ph)_4]^{2-}$ are almost the same each other, the bond angle (100.4°, 99.4°) of Fe-S-C(Ph) of **2** is smaller than that (106.1°) of $[Fe_4S_4(S\text{-}Ph)_4]^{2-}$.[7] Such parameters indicate that the longer Fe-S(C) bond length of **2** is ascribed to a lack of interaction between pπ orbitals of thiolato sulfur and d orbitals of Fe ion. The lack of the interaction is caused by the steric hindrance of two methyl groups at o-positions. σ-Covalency of the Fe-S(C) bond may lead to the smaller Fe-S-C(Ph) bond angle of **2** because the C-S-H bond angle of methanethiol is close to 96° determined by microwave analysis.[9]

The theoretical calculation of $[Fe_4S_4(S\text{-}CH_3)_4]^{2-}$ suggests the large dependence of $Fe_4S_4^{2+}$ core property on Fe(3d)-S(3p-like) overlap,[10,11] which is probably associated with the orientation of $Fe\text{-}S\text{-}CH_3$. The mean S-C bond length (1.778 Å) of 2 is similar to that of $[Fe_4S_4(S\text{-}Ph)_4]^{2-}$. The interaction between sulfur and phenyl ring is almost the same in both the complexes, because the contribution of electron donating three methyl groups at o,p-positions is cancelled out by the steric hindrance of two methyl groups at o-positions. The blue shift of the LMCT absorption is caused by a decrease of the π-interaction between Fe and sulfur because the two methyl groups cover over the pπ orbitals of thiolato sulfur with the steric groups.

In the case of two other complexes such as $[Fe_4S_4(tipbt)_4]^{2-}$ (tipbt = 2,4,6-triisopropylbenzenethiolato) and $[Fe_4S_4(Z\text{-}cys\text{-}Ile\text{-}Ala\text{-}OMe)_4]^{2-}$,[3] the sterically demanding ligands of these complexes restrict the orientation of S-C bond against the $Fe_4S_4^{2+}$ and a similar blue shift of the LMCT absorption maxima is observed.

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