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Preparation and Properties of Agglomerates Containing Fe_4S_4 Groups Cross-Linked by Meta- or Para-Benzenedithiolate Ligands

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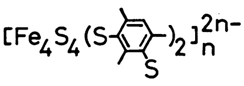
N,N-Dimethylformamide(DMF)-soluble agglomerated $[Fe_4S_4]^{2+}$-clusters (MW ca. 15000 in DMF) multiply bridged with 2,4,6-trimethylbenzene-1,3-dithiolate, benzene-1,3-dithiolate, or benzene-1,4-dithiolate show a redox potential of $[Fe_4S_4]^{2+/+}$ at -1.32 V (vs. SCE), -1.13 V, or -0.95 V, respectively in DMF. These complexes effectively catalyze oxidation of benzoin by quinone.

A magnetic and electronic interaction among the $[Fe_4S_4]^{2+}$ cores of iron-sulfur proteins has been discussed in biologically important redox systems, e.g. an ESR-detectable spin coupled interaction between two $[Fe_4S_4]^{2+}$ clusters in *P. aerogenes* ferredoxin in singly-reduced and doubly-reduced states.$^{1)}$ A series of model complexes, $[Fe_4S_4(S\text{-aryl})_4]^{2-}$ has been reported to show a slight spin distribution on the aromatic rings of *m*- or *p*-substituted benzenethiolate ligands.$^{2)}$

Agglomerated $[Fe_4S_4]^{2+}$ clusters multiply connected by the following *m*- or *p*-benzenedithiolate ligands were synthesized by the ligand exchange reaction$^{3)}$ between $[Me_4N]_2[Fe_4S_4(S\text{-}t\text{-}Bu)_4]$ and the corresponding dithiol with a ratio of 1:2 in DMF under argon atmosphere at room temperature. A DMF-soluble agglomerated $[Fe_4S_4]^{2+}$ polymer, $\{[Fe_4S_4(2,4,6\text{-trimethylbenzene-1,3-dithiolato})_2][NMe_4]_2[HS\text{-}t\text{-}Bu]_{0.3}[DMF]_{1.6}\}_n$ (1),$^{4)}$ exhibits a weight-average molecular weight, 15000 (15 - 20 $Fe_4S_4{}^{2+}$ cubanes), which was determined by the sedimentation equilibrium method using an ultracentrifuge. The results of the viscosity measurement suggest a spherical shape for **1** in DMF. Accumulation of large numbers of the negative charges of the cluster anions seems to limit the molecular weight and the shape. Absorption maxima were observed at 406 nm (ε 17200) for **1**, at 458 nm (ε 15600) for $[Fe_4S_4(\text{benzene-1,3-dithiolato})_2]_n^{2n-}$ (2), and at 481 nm (ε 16800) for $[Fe_4S_4(\text{benzene-1,4-dithiolato})_2]_n^{2n-}$ (3) in DMF. The resonance Raman bands of ν(Fe-S*) of the $[Fe_4S_4]^{2+}$ cores for **1**, **2**, and **3** in solid state were found at 341, 340,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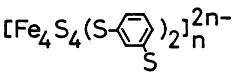
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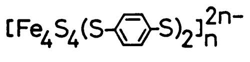
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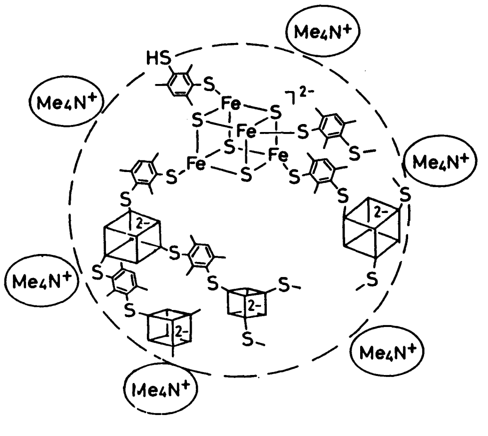
and 350 cm^{-1}, respectively.

The $[Fe_4S_4]^{2+/+}$ redox potentials of **1**, **2**, and **3** in DMF were observed at -1.32 V, -1.13 V, and -0.95 V (vs. SCE), respectively. The most negative redox potential of **1** among them is ascribed to disruption of the S pπ-phenyl interaction by bulky methyl groups at *o*-positions which has been observed for $[Fe_4S_4(2,4,6\text{-trimethylbenzenethiolato})_4]^{2-}$.[5] The magnetic moment of **1** per iron is 1.92 BM (300 K), while that of $[Et_4N]_2[Fe_4S_4(S\text{-}Ph)_4]$ has been reported to be 2.17 BM (300 K).[6]

The presence of noncoordinating *t*-BuS⁻ detected by the ^{1}H-NMR spectrum may be caused by the persistence of protons within the agglomerated cluster, **1**. Addition of sodium tetraphenylborate resulted in formation of *t*-BuSH via ion exchange between sodium cation and proton in the domain of **1**. The tenacious presence of *t*-BuS⁻ before the cation exchange suggests that the synthetic solution of **1** contains $[Me_4N][t\text{-}BuS]$ around the agglomerate and proton inside the agglomerated cluster carrying negative charge (Scheme 1). It is likely that the proton is held in the agglomerate as a counterion instead of bulky tetramethylammonium cation and is ion-exchanged with sodium ion. The steric congestion inside the agglomerate does not seem to allow the existence of tetramethylammonium cation in it.



Scheme 1.

In the case of the oxidation of benzoin by 1,4-benzoquinone, **1**, **2**, and **3** exhibited the considerable yields of benzil based on $[Fe_4S_4]^{2+}$ complexes added, which are 13000, 14000, and 13200%, respectively, ([benzoin], 2.5×10^{-1} M ; [1,4-benzoquinone], 5×10^{-1} M ; $[Fe_4S_4]^{2+}$, 1×10^{-3} M) in DMF for 3 h at 25 °C. The electron transfer among the $[Fe_4S_4]^{2+,+}$ cores in the agglomerated cluster is also manifest in this effective catalysis of benzoin oxidation.

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4) Analytical data : Calcd ; C, 39.49 ; H, 6.02 ; N, 5.18%. Found ; C, 38.93 ; H, 5.98 ; N, 5.28%. Determination of *t*-BuS⁻ and DMF by ^{1}H-NMR spectroscopy also supports the analytical data.

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