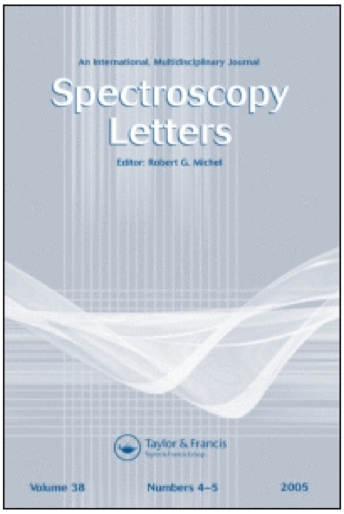

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Synthesis and Spectroscopic Properties of Iron(H) Complex with Sterically Encumbered Thiolate Ligand: 2,4,6-Triphenylbenzenethiolate

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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF IRON(II) COMPLEX WITH STERICALLY ENCUMBERED THIOLATE LIGAND: 2,4,6-TRIPHENYLBENZENETHIOLATE

Key Words: iron(II) complex, 2,4,6-triphenylbenzenethiolate, ^{1}H NMR, electronic spectrum, cyclic voltammogram

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ABSTRACT

Novel iron(II) complex of 2,4,6-triphenylbenzenethiolate (tpbt) was synthesized by ligand exchange reaction of $(Et_4N)_2[Fe^{II}(S\text{-}t\text{-}Bu)_4]$ with tpbt-H. The complex shows absorption maxima at 277 nm (36500 $M^{-1}cm^{-1}$) and 367 nm (22800 $M^{-1}cm^{-1}$), and Fe^{2+}/Fe^{3+} redox potential at -0.78 V vs SCE in acetonitrile. While in tetrahydrofuran solution, the complex is found to be unstable and form a Fe(II) complex with low coordination number.

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INTRODUCTION

Many mononuclear iron-thiolate complexes have been synthesized as model of rubredoxin which is one of the simplest iron-sulfur proteins.[1-4] In such iron-thiolate complexes as well as the active center of the native rubredoxin, the iron ion is surrounded by four sulfur atoms with nearly tetrahedral configuration.[5] We have systematically synthesized the iron(II)/cysteine-thiolate rather than simple alkane- or arene-thiolate complexes.[6-9] Our studies indicate that the aromatic ring plays important roles in controlling the redox potential and stability of Fe(II)/cysteine-containing oligopeptide complexes.[8] Similar aromatic ring of side chain of amino acid residues such as phenylalanine (Phe) and tyrosine (Tyr) also exist near the active site of the rubredoxin, and is considered to be very important in regulating the function of the protein.[10] In order to investigate the influence of aromatic ring on the properties of simple Fe(II) thiolate complex, here we report the synthesis and spectroscopic properties of a novel Fe(II) complex with phenyl ring substituent at ortho, ortho' and para positions of benzenethiolate, *i.e.* 2,4,6-triphenylbenzenethiolate (tpbt) ligand (Figure 1).

Several metal complexes with sterically encumbered thiolate ligand such as SC_6H_2-2,4,6-Ph_3 (tpbt), SC_6H_3-2,6-mes_2 (mes = mesityl), SC_6H_2-2,4,6-*t*-Bu_3 etc. have been reported by Power and co-workers recently.[11-14] The results showed that such thiolate ligands with bulky substituents affect the formation of complex with metal ions, and can form complexes with low coordination numbers.[11-15] Binuclear iron(II)/tpbt complex and 4Fe4S/tpbt cluster have been synthesized,[16, 17] but mononuclear complex with tpbt ligand did not appear yet.

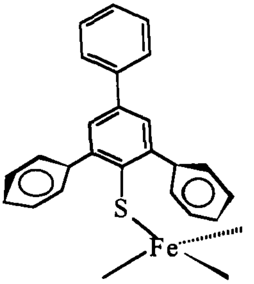

Fig. 1. Schematic structure of Fe(II)/tpbt complex.

EXPERIMENTAL SECTION

The ligand tpbt-H was prepared as reported previously.[17] All solvents were distilled and degassed before use. Synthesis and spectral measurements were carried out under an argon atmosphere.

Synthesis of $(Et_4N)_2[Fe(tpbt)_4]$

The titled compound was synthesized by ligand-exchange reaction. A solution of $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$ (52.3 mg, 0.08 mmol) in acetonitrile (CH_3CN) (10 ml) was added to a stirred solution of tpbt-H (202 mg, 0.60 mmol) in tetrahydrofuran (THF) (10 ml). The mixture was stirred for about 30 min at room temperature, and the volatile components (solvents and *t*-BuSH produced) were removed in vacuo. The procedure of addition of CH_3CN and THF (1 : 1) and stirring was repeated to complete the ligand exchange reaction and then the precipitate was washed with diethyl ether twice to give a light brown powder.

Physical measurements

Absorption spectra were measured on a JASCO Ubest-30 spectrophotometer using a 1 mm quartz cell. 400 MHz ^1H NMR spectra were measured in acetonitrile-d_3 using a JEOL GSX400 FT NMR spectrometer. Electrochemical measurements were carried out on a YANACO P-1100 instrument with a three-electrode system: a glassy carbon working electrode, a Pt-wire auxiliary electrode and a saturated calomel electrode (SCE). $[(n\text{-}Bu)_4N][ClO_4]$ (100 mM) was used as a supporting electrolyte. The scan rate was 100 mV/sec. Potentials were determined at room temperature vs SCE as a reference.

RESULTS AND DISCUSSION

^1H NMR spectra

The Fe(II) complex of tpbt was synthesized by ligand exchange reaction which is similar to the synthesis of Fe(II)/cysteine-containing peptide complexes.[6] Complete exchange between S-*t*-Bu ligand and tpbt was confirmed by ^1H NMR spectral measurement. As shown in Figure 2, no signal was observed around 23

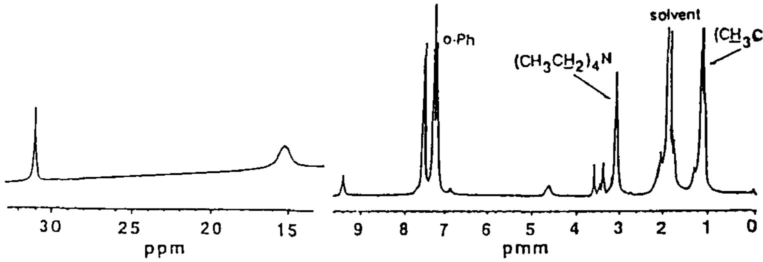

Fig. 2. ^{1}H NMR spectrum of $[Fe(tpbt)_4]^{2-}$ in acetonitrile-d_3 at 30 °C.

ppm in acetonitrile-d_3 at 30 °C which is due to the *t*-Bu protons of the starting complex, $(Et_4N)_2[Fe(S\text{-}t\text{-}Bu)_4]$.[7] Furthermore, the ^{1}H NMR spectral results indicate that the composition of the synthesized complex is $(Et_4N)_2[Fe(tpbt)_4]$.

Two contact shifted signals were observed at 31 and 15 ppm in the ^{1}H NMR spectrum of $[Fe(tpbt)_4]^{2-}$ in acetonitrile-d_3 at 30 °C, and the additional signals appeared in diamagnetic region (7 ~ 8 ppm) (Figure 2). The other small peaks around 9.4, 4.6 ppm *etc.* were considered to be due to artifacts or trace of impurity. Furthermore, the signal of 31 ppm is much sharper than the one of 15 ppm. The sharper signal at 31 ppm was assigned to the meta protons of central phenyl ring of tpbt ligand since the $[Fe(SPh)_4]^{2-}$ presents the meta protons at 22.3 ppm under similar conditions.[18] No signals appeared at the high field in the ^{1}H NMR spectrum of $[Fe(tpbt)_4]^{2-}$. While in the case of the $[Fe(SPh)_4]^{2-}$, the othro and para protons give peaks at -16.8 and -23.5 ppm, respectively.[18] The methyl substituted benzenethiolate/ Fe(II) complexes, *e.g.* $[Fe(SC_6H_4\text{-}o\text{-}CH_3)_4]^{2-}$ and $[Fe(SC_6H_4\text{-}p\text{-}CH_3)_4]^{2-}$, also give methyl proton signal at low field.[18,19] In the ^{1}H NMR spectra of Fe(II) complex of benzenethiolate and its derivatives, only othro proton presents very broad signal. In addition, it is reported that there are Fe---H or Fe---C interactions between iron ion and protons or iron and π-cloud of phenyl rings of *o*-substituent in the sterically encumbered thiolate/Fe(II) complexes.[15]

Therefore, we assign the broad signal at 15 ppm observed in the $[Fe(tpbt)_4]^{2-}$ to the partial *o*-phenyl ring protons of tpbt ligand tentatively.

Electronic spectra

The absorption spectra of the synthesized complex in CH_3CN and THF are presented in Figure 3. In acetonitrile solution, the complex exhibits absorption maxima at 277 nm (36500 $M^{-1}cm^{-1}$) and 367 nm (22800 $M^{-1}cm^{-1}$). There are two absorption maxima at 337 nm (16300 $M^{-1}cm^{-1}$) and 390 nm (sh, 2800 $M^{-1}cm^{-1}$) for $[Fe(SPh)_4]^{2-}$ in CH_3CN.[18] The complex $[Fe(SC_6H_4\text{-}o\text{-}Ph)_4]^{2-}$ also shows two intense transitions around 300 and 340 nm (ε: ca 30000 $M^{-1}cm^{-1}$).[21] Such difference of absorption spectra among these Fe(II) complexes was considered to be caused by the phenyl substituent, namely the absorption spectrum of Fe(II)/benzenethiolate complex depends on the phenyl substituent greatly. In tetrahydrofuran solution of $[Fe(tpbt)_4]^{2-}$, the absorption around 277 nm appeared as a shoulder, and a much stronger absorption maximum was observed at 379 nm (37000 $M^{-1}cm^{-1}$). Furthermore, the complex $[Fe(tpbt)_4]^{2-}$ is found to be unstable in the THF solution. Yellow precipitate appeared slowly from the THF solution and can be isolated quantitatively. The ^{1}H NMR spectral data and elemental analysis show that the yellow solid is $(Et_4N)(tpbt)$. It means that the $[Fe(tpbt)_4]^{2-}$ disassociates in the THF solution, *i.e.* the following reaction maybe occur:

$$(Et_4N)_2[Fe(tpbt)_4] \xrightarrow{\text{THF}} (Et_4N)[Fe(tpbt)_3] + \underset{\text{insoluble in THF}}{(Et_4N)(tpbt)}$$

This is also confirmed by ^{1}H NMR spectral measurement of $[Fe(tpbt)_4]^{2-}$ in THF-d_8. No contact shifted signals were observed for $[Fe(tpbt)_4]^{2-}$ in THF-d_8 at 30 °C.

The formation of $[Fe(tpbt)_3]^-$ in THF solution is considered to be due to the sterically encumbered substituents at the othro positions of central phenyl ring of tpbt ligand (Figure 1). Power et al succeeded in synthesis of the first three-

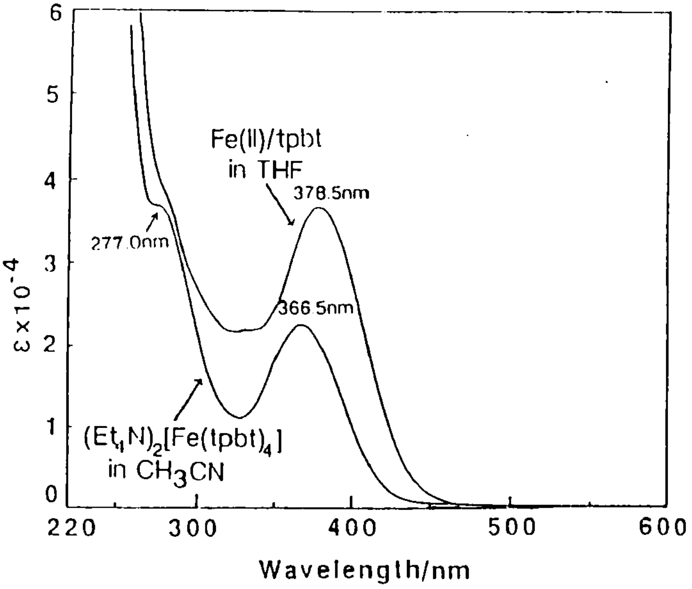

Fig. 3. Absorption spectra of $[Fe(tpbt)_4]^{2-}$ in acetonitrile and tetrahydrofuran.

coordinated mononuclear Fe(II) complex, $[Fe(SC_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_3]^-$.[15] The tpbt ligand can form Fe(II) complex with low coordination number as in the case of $[Fe_2(tpbt)_4]$ in which the Fe(II) ions are also three-coordinated.[16] Recently this binuclear complex was assigned as four coordinate by Evans et al, considered Fe ---C/π-cloud of phenyl rings interactions.[20]

Cyclic voltammetric studies

The different behaviors between the CH_3CN and THF solutions of $[Fe(tpbt)_4]^{2-}$ were also observed in electrochemical measurements. Cyclic voltammograms of $[Fe(tpbt)_4]^{2-}$ are shown in Figure 4. The complex exhibits Fe^{2+}/ Fe^{3+} redox potential at -0.78 V vs SCE in acetonitrile solution. While in the case of THF solution of $[Fe(tpbt)_4]^{2-}$, no obvious oxidation and reduction waves were

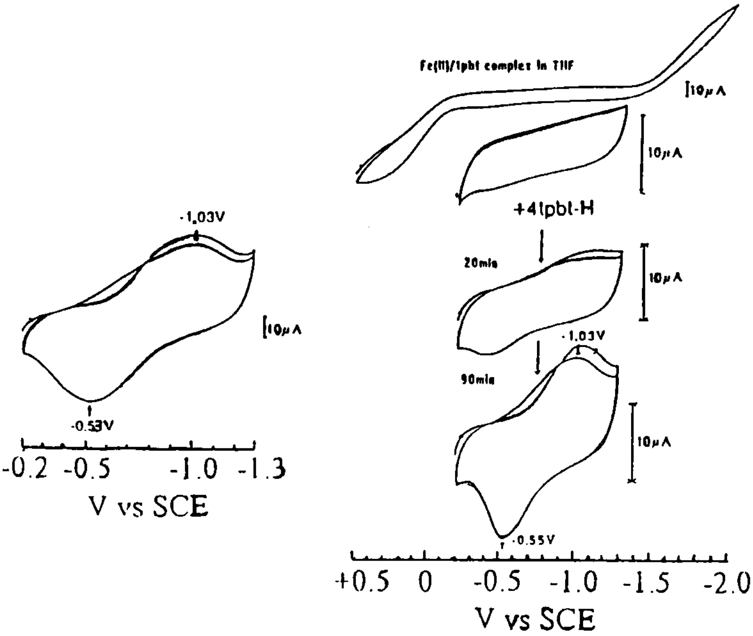

Fig. 4. Cyclic voltammograms of Fe(II)/tpbt complex in acetonitrile (left) and tetrahydrofuran (right).

observed initially. However, when excess tpbt-H ligand was added to the THF solution, the oxidation and reduction waves appeared gradually. As shown in Figure 4, after 90 min of the addition, the oxidation (E_{pa} = -0.55 V) and reduction (E_{pc} = -1.03 V) waves were observed clearly, and the redox potential is -0.79 V vs SCE. The redox potential of $[Fe(tpbt)_4]^{2-}$ shifted to the negative comparing with that of $[Fe(SPh)_4]^{2-}$ (-0.53 V vs SCE in CH_3CN).[18] This means that the electron transfer occurs difficult in the $[Fe(tpbt)_4]^{2-}$ which may be caused by the introduction of phenyl rings at othro and para positions of benzenethiolate ligand.

In conclusion, the results of present study imply that the bulky substituents of the benzenethiolate, especially at othro position, have great influence on the formation and properties of their metal Fe(II) complexes.

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