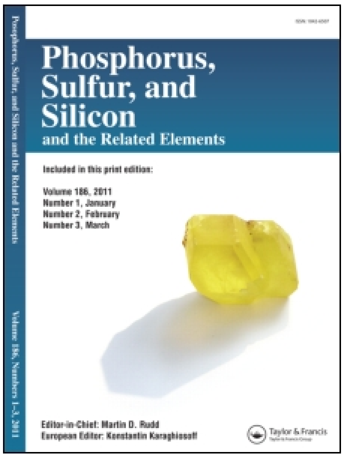

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Norikazu Ueyama[a]; Hiroyuki Oku[a]; Wei-Yin Sun[a]; Akira Nakamura[a]; Keiichi Fukuyama[b]
[a] Department of Macromolecular Science, Faculty of Science, Osaka Unversity, Toyonaka, Osaka [b] Department of Biology, Faculty of Science, Osaka Unversity, Toyonaka, Osaka

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NATURE OF Fe-Se BOND IN $(NR_4)_2[Fe(SePh)_4]$

NORIKAZU UEYAMA, HIROYUKI OKU, WEI-YIN SUN,
AND AKIRA NAKAMURA*
Department of Macromolecular Science, Faculty of Science, Osaka Unversity, Toyonaka, Osaka 560
KEIICHI FUKUYAMA
Department of Biology, Faculty of Science, Osaka Unversity, Toyonaka, Osaka 560

Abstract Crystal parameters obtained by the X-ray analysis of $(NMe_4)_2[Fe(SePh)_4]$ (**1**) were compared with those of $(NEt_4)_2[Fe(SPh)_4]$ (**2**) as in Mn(II), Zn(II), and Cd(II) seleno- or thiophenolate complexes. The Raman bands, e.g. Fe-Se stretching (185 cm^{-1}) were also compared with the bands of **2**, for example, Fe-S stretching (180 cm^{-1}). The difference between the both complexes in the catalytic activity for the oxidation of various alcohols (e.g. benzoin, benzhydrol) with air or *p*-benzoquinone was demonstrated.

INTRODUCTION

The state of coordination of a transition metal ion with selenocysteine-containing proteins has been discussed in biologically important metalloenzymes.[1,2] M-Se (M = metal ion) bond has been considered to be more reactive against air than M-S,[3] although electronegativities of Se and S are almost the same. The difference has been sought in the detailed investigation of their solid state structures. Thus, the crystal structures of $(NMe_4)_2[M(SePh)_4]$ (M = Zn(II),[4] Cd(II),[4] Mn(II)[5]) have been compared with those of $(NMe_4)_2[M(SPh)_4]$ (M = Ni(II), Mn(II), Co(II), Zn(II), Cd(II))[6] which have been known to have a distorted tetrahedral structure. The presence of an interaction in $(NEt_4)_2[Fe(SPh)_4]$ between sulfur and phenyl proton in crystalline state or in acetonitrile was detected by the crystallographic analysis which reveals a considerable delocalization of unpaired electron.[7] Jahn-Teller distortion or the packing effect has been considered not to be significant for the distorted tetrahedral structure of FeS_4 core.

In this paper we synthesized $(NR_4)_2[Fe(SePh)_4]$ (R = Me, Et) independently from the report by McConnachie and Ibers[8] in order to investigate the difference between thiolate and selenolate ligands on the structural, spectroscopic, electrochemical properties and the catalytic activity in oxidation.

RESULTS AND DISCUSSION

Perspective view of the anion part of $(NMe_4)_2[Fe(SePh)_4]$ is shown in Fig. 1. The crystal is monoclinic with a = 12.087(4) Å, b = 14.554(4) Å, c = 10.019(4) Å, β = 90.81(2)°, Z = 2, in space group $P2_1$. A regular tetrahedral geometry of $FeSe_4$ core was similarly found as reported for the structure of $(NEt_4)_2[Fe(SePh)_4]\cdot(CH_3CN)$ by McConnachie and Ibers.[8] The phenyl groups are located in a C_2 structure, different from the pseudo D_{2d} in their structure. The difference comes from a crystal packing effect by the different cation and the concomitant difference in solvation. The differece (0.11Å) between Fe-Se and Fe-S bond distances is almost the same as those for $[M^{II}(QPh)_4]^{2-}$ (M = Zn, Cd; Q = S, Se) while the difference (0.14Å) between Se-C and S-C bond distances is also the same as those listed in Table 1.

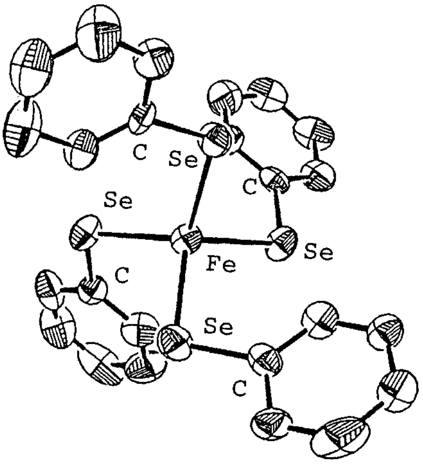

Figure 1. Perspective view for the anion part of $(NMe_4)_2[Fe(SePh)_4]$

Table. 1. Comparison of the average distances of M-Q and Q-C bonds in $[M^{II}(QPh)_4]^{2-}$.

M(II)	M - Se	M - S	difference
Fe	2.460Å	2.353Å b)	0.11Å
Mn	2.564 a)	2.442 b)	0.12
Zn	2.469 c)	2.357 c)	0.11
Cd	2.649 c)	2.541 c)	0.11

M(II)	Se - C	S - C	difference
Fe	1.907Å	1.767Å b)	0.14Å
Mn	1.903 a)	—	—
Zn	1.907 c)	1.760 c)	0.15
Cd	1.903 c)	1.755 c)	0.15

a) Ref. 5. b) Ref. 7. c) Ref. 4.

First we have communicated the short distance for an average Mn-S distance (2.346 Å)[5] in $(NMe_4)_2[Mn(SPh)_4]$ as briefly described in a review.[9] Then an unusually small S-C distance was obtained for $(NMe_4)_2[Mn(SPh)_4]$. However, we are now reexamining the crystal structure again since the observed C-S stretching Raman band in $(NMe_4)_2[Mn(SPh)_4]$ is similar to those of other $(NMe_4)_2[M^{II}(SPh)_4]$ complexes (M = Fe(II), Zn(II), Cd(II)). The difference (0.12 Å) between Mn-Se and Mn-S[7] in both Mn(II) complexes is similar to those (0.11 Å) in the corresponding Fe(II), Zn(II) and Cd(II) complexes.[4,8]

The resonance Raman spectra of both complexes show an intense band at 185 cm^{-1} assignable to ν(Fe-Se) for **1** and at 180 cm^{-1} assignable to ν(Fe-S) for **2**. The redox potentials obtained from the cyclic voltammgrams are -0.60 V vs SCE for **1** and -0.52 V vs SCE for **2** in acetonitrile. This tendency is ascribed to the more ionic character of the Fe-Se bond.

Both complexes, **1** and **2**, exhibit catalytic activity in the oxidation of benzoin or benzhydrol with *p*-benzoquinone or air under mild conditions (1 atm, 25 °C). The reaction is pseudo first order in the concentration of benzoin at the initial stage since a log plot of benzoin consumption against time was linear and the rate constant is proportional to concentration of the catalyst. The observed rates at the initial stage of the benzoin oxidation with *p*-benzoquinone are 98 and 50 $M^{-1}s^{-1}$ for **1** and **2**, respectively, in *N*,*N*-dimethylformamide at 25 °C (reaction conditions: [benzoin], 20 mM; [catalyst]; 1 mM; [*p*-benzoquinone], 40 mM). Thus, a relatively high catalytic reaction rate at the initial stage was observed for **1** which later shows fast decomposition. The results indicate that the ionic Fe-Se bonding in **1** is associated with the better catalytic activity for the electron transfer oxidation. Similarly the somewhat increasing ionic character of the Mn-Se bond leads to the higher oxidation activity by $(NMe_4)_2[Mn(SePh)_4]$ than by $(NMe_4)_2[Mn(SPh)_4]$ for similar organic substances as described in the previous paper.[10]

p-Substitution effect in the catalytic oxidation of benzhydrols was found with a trend of the oxidation rate : *p*-Cl > H > *p*-OMe, which suggests the participation of proton and electron transfer. The reaction proceeds by the same path as the catalytic cycle by $[Fe_4S_4(SR)_4]^{2-}$ (ferredoxin model complexes) in the *p*-benzoquinone oxidation of benzoin.[11] The observed α-deuterium isotope effect in the benzoin oxidation by *p*-benzoquinone also indicates that the methine hydrogen of benzoin and benzhydrol is released as a proton at the rate-determining step with coordination of OH group at Fe(III) center.

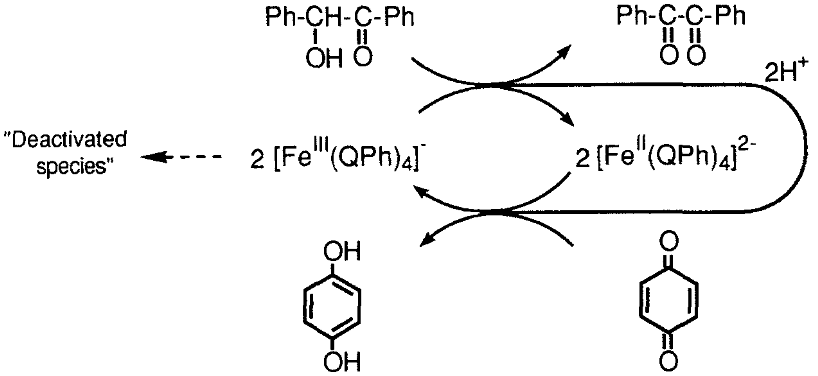

Fig. 2. Oxidation scheme of benzoin by *p*-quinone in the presence of $[Fe^{II}(QPh)_4]^{2-}$

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