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Unusual Differences between the Average Mn-Se and Mn-S Distances and between Se-C and S-C Distances in $(NMe_4)_2[Mn(QPh)_4]$ (Q = Se, S)

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Crystal structures of $(NMe_4)_2[Mn^{II}(SePh)_4]$ and $(NMe_4)_2[Mn^{II}(SPh)_4]$ were determined to compare their structures, properties and catalytic activities. Both complexes have a tetrahedral geometry of $MnSe_4$ or MnS_4 core. An unusual difference (0.22 Å) between Mn-Se and Mn-S distances, and a large difference (0.22 Å) between Se-C and S-C were found, compared with those (0.11 Å and 0.15 Å, respectively) in $(NMe_4)_2[M^{II}(QPh)_4]$ (M = Cd, Zn; Q = Se, S). The differences are ascribed to the stronger Mn-S π-bonding character than those of Cd-S, Zn-S and Fe-S.

Importance of cysteine thiolate coordination in many metalloenzymes is well known. Manganese(II-IV) complexes have been investigated as models of biological redox sites. Unique function of a selenocysteine ligand has been found for some oxidoreductases such as formate dehydrogenase[1)] and hydrogenase.[2)] Biologically relevant redox reaction by Mn(II) complexes having thiolate or selenolate ligands is of interest since dioxygen is available as oxidant in biological systems. Only a few studies using Mn(II) thiolate model complex have concerned with the air oxidation of organic substrates.[3)] We have communicated the catalytic activity of $(NMe_4)_2[Mn^{II}(QPh)_4]$ (Q = Se, S) for the air oxidation of benzoin, benzhydrol and benzaldehyde.[4)]

In this paper, the crystal structures of $(NMe_4)_2[Mn(SePh)_4]$ (**1**)[5)] and $(NMe_4)_2[Mn(SPh)_4]$ (**2**)[6)] are described to compare the nature of Mn-Se and Mn-S bondings. **1** and **2** were synthesized from $MnCl_2 \cdot 4H_2O$ and Me_4NCl, and $Me_3SiSePh$[7)] or thiophenol in methanol as described for the synthesis of $(NMe_4)_2[Zn(QPh)_4]$ and $(NMe_4)_2[Cd(QPh)_4]$ in the previous paper.[8)] Both complexes are air sensitive.

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
Mn	2.564 Å	2.346 Å	0.22 Å
Fe	2.460[a)]	2.353[b)]	0.11
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
Mn	1.903 Å	1.680 Å	0.22 Å
Fe	1.907[a)]	1.767[b)]	0.14
Zn	1.907[c)]	1.760[c)]	0.15
Cd	1.903[c)]	1.755[c)]	0.15

a) Ref. 13. b) Ref. 9. c) Ref. 8.

Generally, a regular tetrahedral geometry of $M^{II}Q_4$ cores was found for these complexes where M(II) = Mn, Fe, Zn, Cd. The crystal structure of **2** is similar to that of $(NEt_4)_2[Mn(SPh)_4]$ already reported.[10,11] Table 1 lists the M-Q bond distances and their differences between Q = S and Se. Interestingly, average Mn-Se distance (2.564 Å) in **1** is longer than average Mn-S distance (2.346 Å) in **2**. The difference between Mn-Se and Mn-S is 0.22 Å which is abnormally large, compared with other $(NMe_4)_2[M(QPh)_4]$ as briefly described in a review.[12] Surprisingly, an unusually small S-C distance (1.680 Å) was found for **2.** The average value of 1.903 Å for **1** is a regular Se-C distance as those in $(NMe_4)_2[M(SePh)_4]$. Thus, the difference (0.22 Å) between Se-C and S-C in both Mn(II) complexes is larger than those (0.15 Å) in the corresponding Zn(II) and Cd(II) complexes. Recently, Ibers and coworker has reported the crystal structure of $(NEt_4)_2[Fe(SePh)_4]\cdot MeCN$ which also has almost the same differences (0.1 Å and 0.14 Å) between the average S-C and Se-C distances and between Fe-Se and Fe-S distances, respectively, compared with the corresponding $(NEt_4)_2[Fe(SPh)_4]$ reported in the literature.[13,14] The unusual Mn-S bond distance is thus ascribed to the stronger donative π-bonding character of Mn-S than those of Zn-S, Cd-S, and Fe-S. This donative bonding reduces the ionicity of Mn-S bonding and thus the Mn-S bond becomes somewhat more covalent than the Mn-Se bond in **1**. The short S-C distance in **2** is also due to larger π-interaction between S *pπ* and phenyl π orbitals. The ionic character of the Mn-Se bond corresponds to the positive-shifted reduction potential for **1** and higher oxidation catalysis of **1** for organic substances as described in the previous paper.[4]

References

1) J. R. Anderson and L. G. Ljungdall, *J. Bacterial.*, **120**, 6 (1974).
2) M. K. Eidness, R. A. Scott, B. C. Prickril, D. V. DerVartanian, J. LeGall, I. Moura, J. J. G. Moura, and H. D. Peck, Jr., *Proc. Natl. Acad. Sci. U.S.A.*, **86**, 147 (1989).
3) M. Kaneko and A. Yamada, *Makromol. Chem.*, **182**, 101 (1981).
4) A. Kajiwara, N. Ueyama, and A. Nakamura, *Catal. Lett.*, **3**, 25 (1989).
5) Crystallographic data for $(NMe_4)_2[Mn(SePh)_4]$, formula = $C_{32}H_{44}N_2Se_4Mn$: *F*w = 827.47, monoclinic, space group $P2_1$, a = 12.146(1) Å, b = 14.737(1) Å, c = 9.944(1) Å, β = 90.89(1)°, V = 1799(0) Å^3, Z = 2, D_{calc} = 1.558 g/cm^3, No. of used data ($I_o > 3\sigma(I)$) = 2652, R = 0.069, Rw = 0.077.
6) Crystallographic data for $(NMe_4)_2[Mn(SPh)_4]$, formula = $C_{32}H_{44}N_2S_4Mn$: *F*w = 639.91, monoclinic, space group $P2_1$, a = 11.566(7) Å, b = 13.877(4)) Å, c = 9.413(4) Å, β = 91.81(4)°, V = 1510(1) Å^3, Z = 2, D_{calcd} = 1.426 g/cm^3, No. of used data ($I_o > 3\sigma(I)$) = 2180, R = 0.071, Rw = 0.093.
7) M. R. Detty, *Tetrahedron Lett.*, **1978**, 5087 ; N. Miyoshi, H. Ishii, K. Kondo, S. Murai, and N. Sonoda, *Synthesis*, **1979**, 300.
8) N. Ueyama, T. Sugawara, K. Sasaki, A. Nakamura, S. Yamashita, Y. Wakatsuki, H. Yamazaki, and N. Yasuoka, *Inorg. Chem.*, **27**, 741 (1988).
9) D. Coucouvanis, D. Swenson, N. C. Baenziger, C. Murphy, D. G. Holah, N. Sfarnas, A. Simopoulos, and A. Kostikas, *J. Am. Chem. Soc.*, **103**, 3350, (1981).
10) D. G. Holah and D. Coucouvanis, *J. Am. Chem. Soc.*, **97**, 6917 (1975).
11) T. Costa, J. R. Dorfman, K. S. Hagen, and R. H. Holm, *Inorg. Chem.*, **22**, 4091 (1983).
12) A. Nakamura, N. Ueyama, and K. Tatsumi, *Pure Appl. Chem.*, **62**, 1011 (1990).
13) J. M. McConnachie and J. A. Ibers, *Inorg. Chem.*, **30**, 1770 (1991).
14) Recently, we have independently determined the crystal structure of $(NMe_4)_2[Fe(SePh)_4]$ which has almost the same differences (0.11 Å and 0.15 Å) for Fe-Q and Q-C as reported for $(NEt_4)_2[Fe(SePh)_4]$ by McConnachie and Ibers.[13]

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