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Synthesis, X-Ray Analysis, EXAFS, and XANES of $[Ni(SCH_2CH_2S)_2]^{2-}$. An Evidence for the Mononuclear Square Planar $\{Ni(II)S^-_4\}$ Geometry in Nickel/Alkane Thiolate System

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Crystalline $(Ph_3MeP)_2[Ni(edt)_2]$ was isolated and studied by X-ray analysis and X-ray absorption (EXAFS/XANES) methods, which revealed a square planar $\{NiS^-_4\}$ geometry for the chromophore. The results were discussed in terms of the nickel site of hydrogenases.

In the biological nickel systems, hydrogenases[1,2] and CO dehydrogenases[3] are known to have $NiS_{4(3)}$ unit adjacent to the iron-sulfur clusters.[4,5] Any positive evidences for the donation of atoms other than sulfur have been unpublished.[1-3] In the recently developed (motivated by this biological fact or not) synthetic Ni/RS^- systems,[6-10] only two series of mononuclear complexes are known. One is the tetrahedral $[Ni(SR)_4]^{2-}$ (RS^-=allenethiolate),[6,7] which is structurally established. The other is $[Ni(edt)_2]^{2-}$ (H_2edt = ethanedithiol).[8] Although the latter was pointed out to be diamagnetic (namely, square planar), this coordination unit has not been established synthetically and lacked the corroborative evidence for the geometry.[8] Considering the low spin character of the nickel (Ni^{3+}, S=1/2) in hydrogenases,[11] the importance of the precise structural study for $[Ni(edt)_2]^{2-}$ should not be passed over. This letter represents the synthesis, X-ray structural analysis, and the EXAFS/XANES studies on $(Ph_3MeP)_2[Ni(edt)_2]$.

$(Ph_3MeP)_2[Ni(edt)_2]$ has grown up in reddish brown crystals from a greenish aqueous mixture of H_2edt, KOH, $NiCl_2 \cdot 6H_2O$, and $Na_2S \cdot 9H_2O$, (1 : 2 : 0.25 : 1 : 1), when 1 equiv. of Ph_3MePBr was added to the reaction mixture (Yield: 44%. Anal. Data: Found; C 63.07, H 5.54, N 0%. Calcd; C 63.24, H 5.56, N 0%). Only freshly prepared crystals, then coated with epoxy resin and mounted on goniometer head, afforded good reflections. Some crystal data and the experimental condition for the X-ray analysis are as follows: $NiS_4P_2C_{42}H_{44}$=797.70, Monoclinic, a=9.287(1), b=13.263(2), c=15.821(1) Å, β=97.170(9) deg., V=1933.5(7) Å^3, Space group $P2_1/n$, Z=2, D_c=1.37 g cm^{-3}, F(000)=836 electrons, μ(Mo Kα)=8.21 cm^{-1}, A total of 4949 reflections were recorded (θ-2θ scans at 294 K) to $2\theta_{max}$=55.1 degree (graphite-monochromated Mo Kα radiation, λ=0.71069 Å) on a Rigaku AFC 5R diffractometer. No. of observations (I > 3.00(σ(I))) was 2368. R=0.043 (R_w=0.054).

$Ni-S_1$	2.191(1)	$Ni-S_2$	2.198(1)
S_1-C_1	1.801(6)	S_2-C_2	1.786(6)
C_1-C_2	1.345(8)	$S_1-Ni-S_1^*$	180.00
S_1-Ni-S_2	91.31(5)	$S_1-Ni-S_2^*$	88.69(5)
$S_2-Ni-S_2^*$	180.00	C_1-S_1-Ni	103.6(2)
C_2-S_2-Ni	102.7(2)	$C_2-C_1-S_1$	117.2(5)
$C_1-C_2-S_2$	118.7(5)		

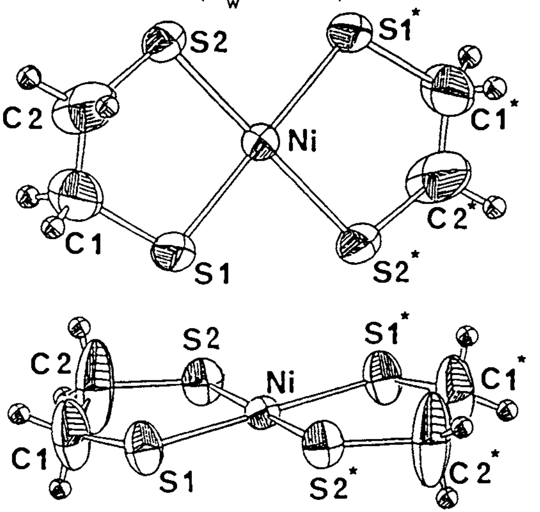

Fig. 1. ORTEP drawings of $[Ni(edt)_2]^{2-}$ and the selected bond distances (Å) and bond angles (deg.).

Figure 1 shows the molecular structure of $[Ni(edt)_2]^{2-}$ together with the important molecular parameters. The first coordination sphere of the molecule adopts a completely flat plane with only two kinds of Ni-S bond distances, and the nickel atom occupying the center of symmetry (Fig. 1). As far as we are aware the compound is the first mononuclear example of having a square planar geometry in nickel complexes with purely alkane thiolate. The mean Ni-S bond length, 2.195(1) Å, is fairly short comparing with 2.292(3) and 2.281(1) Å of $[Ni(PhS)_4]^{2-}$ (Td)[6] and $[Ni(p\text{-}ClC_6H_4S)_4]^{2-}$ (Td),[7] respectively. The reason of this contraction of the coordination sphere in $[Ni(edt)_2]^{2-}$ from those of tetrahedral ones would be the result of the change in spin state from high spin (Td) to low spin (Sq. Pl.), which generally causes the contraction of the ionic radii of central metals. Correlations of terminal bite distance (S-S) and M-S bond distance with the ionic potential per edt^{2-} ligand (Z/rn; Z=oxidation state, r=ionic radius, n=coordination number) was pointed out by R. H. Holm and his co-workers.[9] In the correlation diagram of the literature $[Ni(edt)_2]^{2-}$ situates at a normal point according to M-S bond distance, but at the lowest limit of bite distance (3.09 Å). This, according to the correlation between bite distances and SC-CS torsional dihedral angles mentioned in the literature,[9] means the small SC-CS dihedral angle of $[Ni(edt)_2]^{2-}$. Thus, the flatness of NiSCCS five membered ring in $[Ni(edt)_2]^{2-}$ is far increased from that of free dithiol and the other multinuclear nickel ethanedithiolate, which were already structurally clarified.[8,10] In relation to this problem, it should be pointed out about Fig. 1. The observed C-C bond of $[Ni(edt)_2]^{2-}$ is very short in apparence as if it were doubly bonded. This might misleads to the conclusion that edt^{2-} in $[Ni(edt)_2]^{2-}$ is dithiolen like and that this is the reason for the diamagnetism of the compound. However, the short distance is the result of the puckerring due to disorder as will be seen from the large vertical thermal ellipsoid of the carbon atoms. This, in Fig. 1, is the reason why the Ni-edt ring seems to form a completely flat plane even in the form of involving the two carbon atoms.

Ni K-edge X-ray absorption (EXAFS and XANES) experiments (290 K) were carried out in transmission mode on polyethylen pellets by using the EXAFS facilities of the beam line BL-7C (2.5 GeV, 180 - 300 mA) of the Photon Factory of National Laboratory of High Energy Physics at Tsukuba. Data processings (subtraction of background, Normalization, EXAFS extraction, Fourier transform, curve fittings) were done with EXAFS 1 program.[12] Figure 2 depicts the Fourier transform of the EXAFS (a), in which the dashed line shows the Fourier window for the EXAFS extraction, and the XANES (b) spectra (Ni foil; 8333 eV) of $(Ph_3MeP)_2[Ni(edt)_2]$. The XANES spectrum of $(NEt_4)_2[Ni(PhS)_4]$ is also depicted in the same figure as representing tetrahedral $\{NiS_4\}$ case (dashed line). The optimized Ni-S bond length (2.19 Å) and the number of the scatterers (n=4.2) calculated by the curve fitting of the EXAFS, which was obtained from the Fourier filtered radial distribution function, Fig. 2a, agree well with the result of the X-ray analysis. As is seen in Fig. 2b, the XANES spectrum of $[Ni(edt)_2]^{2-}$ exhibits four peaks (coaded as B_1, B_2, C, D) around the edge position (0 - 50 eV). The peak assigned to 1s → 3d transition, which is generally coaded A[13-15] and appears for Oh and Td symmetry, is not observed in the pre-edge region. On the other hand, $[Ni(PhS)_4]^{2-}$ shows the small peak A instead of B_1 and B_2 together with C and D (shape resonances[16]). A comparative study for a lot of Ni(II) compounds with Td, Oh, and square planar geometries, and with various kinds of donor atoms (N, O, S, Cl) and their combinations,[17] has revealed that $[Ni(edt)_2]^{2-}$ possesses the general feature of square planar complex (peak energy and relative height for B_1, B_2, C, D).[14] This also agrees to the result of the X-ray analysis mentioned above. B_1 peak, which is assigned to "$1s \rightarrow \pi_u$ + shake down" according to R. A. Bair[14] and N. Kosugi,[15] is located at the low energy limit within several Ni/RS$^-$ compounds with square planar local symmetry, meaning that a very strong LMCT is realized in $[Ni(edt)_2]^{2-}$. It should finally be pointed out that line broadenings of B_1 and B_2 were generally observed for the square planar complexes involving sulfur as the backscatterer.

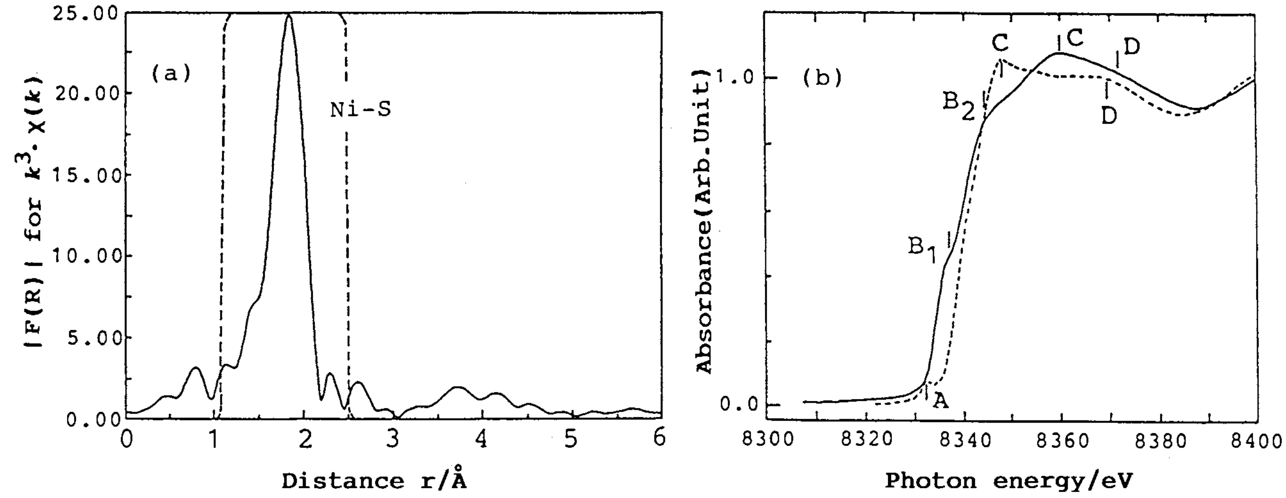

Fig. 2. (a) Fourier transform of the $k^3 \cdot \chi(k)$ vs. k EXAFS spectrum, (b) normalized XANES spectra of $(Ph_3MeP)_2[Ni(edt)_2]$ (——) and $(NEt_4)_2$ $[Ni(PhS)_4]$ (---).

The XANES spectra published for *D. gigas* hydrogenase by I. Moura and her coworkers,[2] do not satisfy the requisit for accurate comparison because of the noise (probably due to the material amount). Nevertheless, they seem to exhibit two interesting features comparing with the ones shown in Fig. 2b and the other sulfur containing nickel complexes. The first point is that the normalized heights of the shape resonances (C) of *D. gigas* hydrogenase (as isolated and reduced) clearly distribute in the group of sulfur containing square planar coordination unit. The second, B_1 and B_2 peaks are not so clearly observed as in the case of $[Ni(edt)_2]^{2-}$. In consequence, it can be concluded that nickel in hydrogenases is immersed in a square planar ligand field. This is consistent with other experimental results (EPR$^{11)}$ and redox potential distribution$^{19)}$) on the Ni(III) in hydrogenases.

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References

1) P. A. Lindahl, N. Kojima, R. P. Hausinger, J. A. Fox, B. K. Teo, C. T. Walsh, and W. H. Orme-Johnson, J. Am. Chem. Soc., 106, 3062(1984).
2) R. A. Scott, S. A. Wallin, M. Czechowski, D. V. Dervartanian, J. LeGall, H. D. Peck. Jr., and I. Moura, J. Am. Chem. Soc., 106, 6864(1984).
3) N. R. Bastian, G. Diekert, E. C. Niederhoffer, B. K. Teo, C. T. Walsh, and W. H. Orme-Johnson, J. Am. Chem. Soc., 110, 5581(1988).
4) S. P. J. Albracht, M. L. Kalkman, and E. C. Slater, Bichim. Biophys. Acta, 724, 309(1983).
5) S. W. Ragsdale, H. G. Wood, and W. E. Antholine, Proc. Natl. Acad. Sci. U.S.A., 82, 6811(1985).
6) D. Swenson, N. C. Baenziger, and D. Coucouvanis, J. Am. Chem. Soc., 100, 1933(1978); T. Yamamura, Chem. Lett., 1985, 269.
7) S. G. Rosenfield, W. H. Armstrong, and P. K. Masharak, Inorg. Chem., 25, 3014(1986).
8) B. S. Snyder, Ch. P. Rao, and R. H. Holm, Aust. J. Chem., 39, 963(1986).
9) Ch. P. Rao, J. R. Dorfman, and R. H. Holm, Inorg. Chem., 25, 428(1986).
10) W. Tremel, M. Kriege, B. Krebs, and G. Henkel, Inorg. Chem., 27, 3886(1988).
11) J. R. Lancaster. Jr., FEBS Lett., 115, 285(1980).
12) N. Kosugi and H. Kuroda, Program EXAFS 1, Research Center for Spectrochemistry, The University of Tokyo(1985).
13) L. S. Kau, D. J. Spira-Solomon, J. E. Penner-Hahn, K. O. Hodgson, and E. L. Solomon, J. Am. Chem. Soc., 109, 6433(1987).
14) R. A. Bair and W. A. Goddard III, Phys. Rew., 22, 2767(1980).
15) N. Kosugi, T. Yokoyama, and H. Kuroda, Chem. Phys., 104, 449(1986).
16) A. Biarconi, M. Dell'Ariccia, P. J. Durham, and J. B. Pendry, Phys. Rew., 26, 6502(1982).
17) N. Nakamura, T. Yamamura, and K. Asakura, 39th Annual Conference on Coordination Chemistry of the Chemical Society of Japan, Mito, September 1989, Abstr., No. 2B03.
18) T. Yamamura, Chem. Lett., 1986, 801.

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