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Ni(1,4,8,11-tetrathiaundecane). Synthesis of a Square Planar $NiS_2S^{-}_2$ Complex in Terms of CO-dehydrogenase

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Ni(1,4,8,11-tetrathiaundecane), the mononuclear nickel complex of 1,4,8,11-tetrathiaundecane, was synthesized, and the molecular structure was studied by X-ray crystallography. The XANES spectrum of the coordination unit, a square planar $NiS_2S^{-}_2$ geometry, was discussed in terms of the nickel in CO-dehydrogenases.

CO-dehydrogenases (CODH) are nickel enzymes which mediate $C_1 \rightleftarrows C_2$ conversion,1,2) as well as the $CO \rightleftarrows CO_2$ conversion.3-5) Scott et al. found that the nickel K-edge EXAFS of *C. thermoaceticum* CODH can be fit by assuming a mixture of N (Ni-N; $\approx$ 1.97 Å) and S (Ni-S; $\approx$ 2.25 Å) atoms.6,7) Based on a comparative study they suggested later a square planar geometry for the nickel in rubredoxin-oxidized and H_2 plus hydrogenase reduced *C. thermoaceticum* CODH. On the other hand, Orme-Johnson et al. has suggested a NiS_4 coordination unit for the Ni-EPR silent CO free form of CODH from *C. thermoaceticum* strain DSM by XAFS experiment.8) Thus, at present, it can possibly be said that CODH adopts a square planar S_xN_{4-x} coordination. In recent papers we have reported the syntheses of square planar $NiS^{-}_2N_2$ compounds.9,10) Here in this paper, we have focused our attension to the square planar NiS_4 units, which will be classified into the following cases (Fig. 1), and synthesized Ni(ttu), where H_2ttu = 1,4,8,11-tetrathiaundecane, as corresponding to case 4 in the figure.

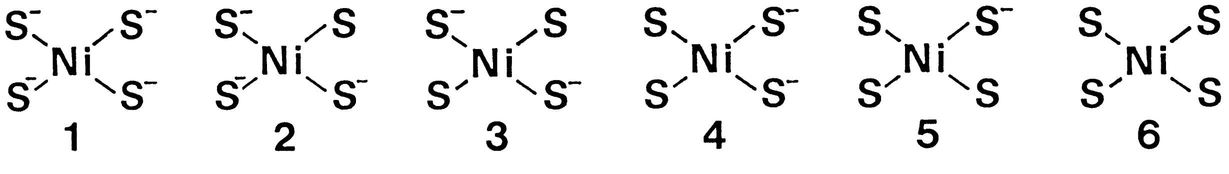


Fig. 1. Possible NiS_4 square planar environments of CO-dehydrogenases.

Ni(ttu) was isolated as black crystals from the aqueous alkaline solution including 1 : 1 H_2ttu[11) and $NiCl_2 \cdot 6H_2O$.[12)

Nickel K-edge XANES spectrum of Ni(ttu),[13) depicted in Fig. 2, shows the basic feature of square planar geometry, giving 1s → $4\pi_u$ absorptions[14,15) (B_1 and B_2 in the figure) and no 1s → 3d transition, which is characteristic to Td and Oh. As we have pointed out previously,[16,17) relative hight/energy plottings for the largest peak C (see Fig. 2) of square planar Ni/S complexes form the area which is clearly distinguishable from the other geometric areas. Ni(ttu) is situated at this area together with the other square planar NiS_4 compounds, [Ni(ttp)]$(BF_4)_2$ (ttp = 1,4,8,11-tetrathiacyclotetradecane)[11) and $[Ni(edt)_2](PPh_4)_2$ (H_2edt = 1,2-ethanedithiol).[17) The XANES spectra for *C. thermoaceticum* CODH published by Scott et al. is also situated in the same area, also showing 1s → $4\pi_u$ absorptions and no 1s → 3d transition.[6)

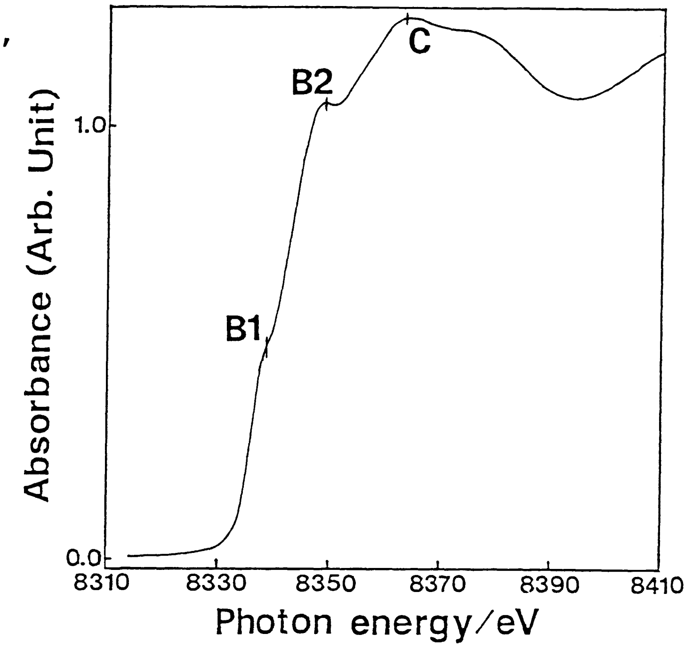
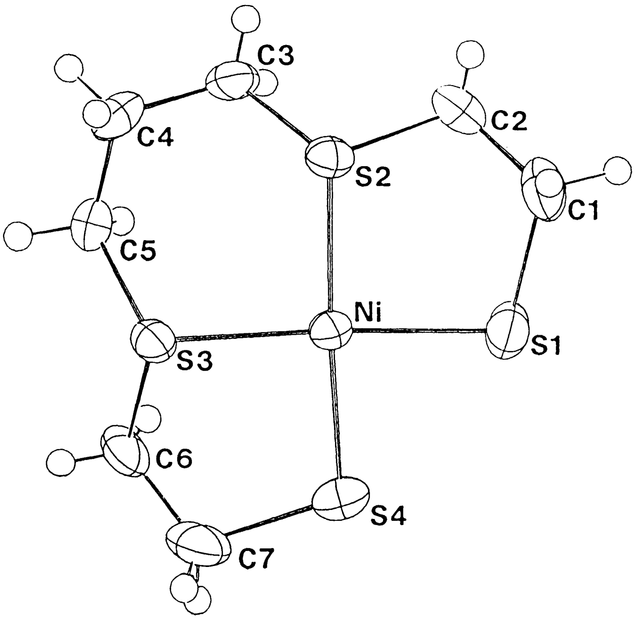


Fig. 2. XANES spectrum of Ni(ttu).



Ni-S1	2.179(2) Å
Ni-S2	2.173(1)
Ni-S3	2.166(2)
Ni-S4	2.177(2)
S1-Ni-S2	90.17(6) deg
S1-Ni-S3	175.85(6)
S1-Ni-S4	87.05(6)
S2-Ni-S3	92.85(5)
S2-Ni-S4	177.02(6)
S3-Ni-S4	89.87(5)

Fig. 3. ORTEP drawing of Ni(ttu) and the significant molecular parameters.

The result for the X-ray crystallography[18)] of this compound is shown in Fig. 3. As was predicted from XANES experiment, nickel in Ni(ttu) is immersed in a (slightly distorted) square planar S_4 environment. Comparing the two types of the nickel-sulfur bond lengths of Ni(ttu), Ni-S (S; neutral, mean 2.170 Å) and $Ni-S^-$ (S^-; anionic, mean 2.177 Å), with the mean Ni-S distance (2.176 Å) of $[Ni(ttp)](BF_4)_2$ (type (1) in Fig. 1) and with the mean $Ni-S^-$ distance (2.195 Å) of $[Ni(edt)_2](PPh_4)_2$ (type (1) in Fig. 1), respectively, we have found that bondings in Ni(ttu) are stronger than those of pure Ni-S and $Ni-S^-$ cases. However, still in this Ni(ttu) case, nickel-sulfur bond distances are longer than that of CODH from *C. thermoaceticum* strain DSM, which was given as 2.16 Å from EXAFS analysis by Orme-Johnson et al.[8)] On the other hand, the best fit for the nickel K-edge EXAFS of *C. thermoaceticum* CODH by Scott et al. gave Ni-S = 2.25 Å and Ni-N = 1.97 Å. This Ni-S length is too long to be compared with Ni(ttu), and compete with that of tetrathiolato nickelate such as $[Ni(edt)_4]^{2-}$.

Cyclic voltammetry of Ni(ttu) in DMSO has shown irreversible cathodic waves at ca. -1.08 V and - 1.70 V (vs. Ag^+/Ag). Since the former wave, which corresponds to $Ni^{2+} \rightarrow Ni^+$, was quenched by introducing CO to the solvent, it is clear that the Ni^+ species of Ni(ttu) interacts with CO. In order to increase the reversibility of Ni^{2+}/Ni^+ redox couple it will be necessary to protect the Ni-S area with bulky groups.

Finally, it should be pointed out that trinuclear ttu complex of nickel was already reported by Roundhill[19)] in relation to semiconductivity, but without X-ray analysis.[20)] Ni(ttu) forms one dimensional column in solid state and changes its colour metallic under I_2.

References

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12) Ni(ttu) Anal Data. Found: C 29.29; H 4.92%. Calcd for $C_7H_{14}S_4Ni$: C 29.28; H 4.95%. ^1H NMR δ(DMSO-d_6): 3.47, 3.10, 2.88. 2.60, 2.24, 2.07, 1.64 (relative intensity; 2 : 2 : 2 : 3 : 2 : 2 : 1). $\lambda_{max}(\varepsilon)$ 812 nm (ε99), 424 nm (ε 431)

13) XAFS experiments on Ni(ttu) were carried out in transmission mode on polyethylene pelletts by using the EXAFS instruments of Photon Factory (BL-7C) at the National Laboratory for High Energy Physics (KEK) at Tsukuba. EXAFS analyses were done by using EXAFS1 programme developed by N. Kosugi and H. Kuroda, Research Center for Spectrochemistry, The University of Tokyo.

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18) Formula $C_7H_{14}NiS_4$, formula weight 285.142, Mo Kα radiation (λ = 0.71069 A), monoclinic, space group $P2_1/n$, a = 9.461(3), b = 8.650(2), c = 13.721(2) Å, β = 92.60(2) deg., V = 1121.7(4) $Å^3$, Dx = 1.688 g cm^{-3}, Z = 2, F(000) = 592, μ(Mo Kα) = 2.40 mm^{-1}. R = 6.43, Rw = 5.31%, Crystal dimensions were ca. 0.4 × 0.3 × 0.2 mm^3.

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20) Thiolato nickelates have a tendency to form higher aggregates such as dinuclear and trinuclear compounds under protic conditions in organic solvents, whereas in aqueous alkaline solution such self assembly is suppressed effectively.

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