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Distribution Map of the Main Peak of Nickel K-Edge X-Ray Absorption Near Edge Structure. Situations of the Nickels in Hydrogenases in the Map

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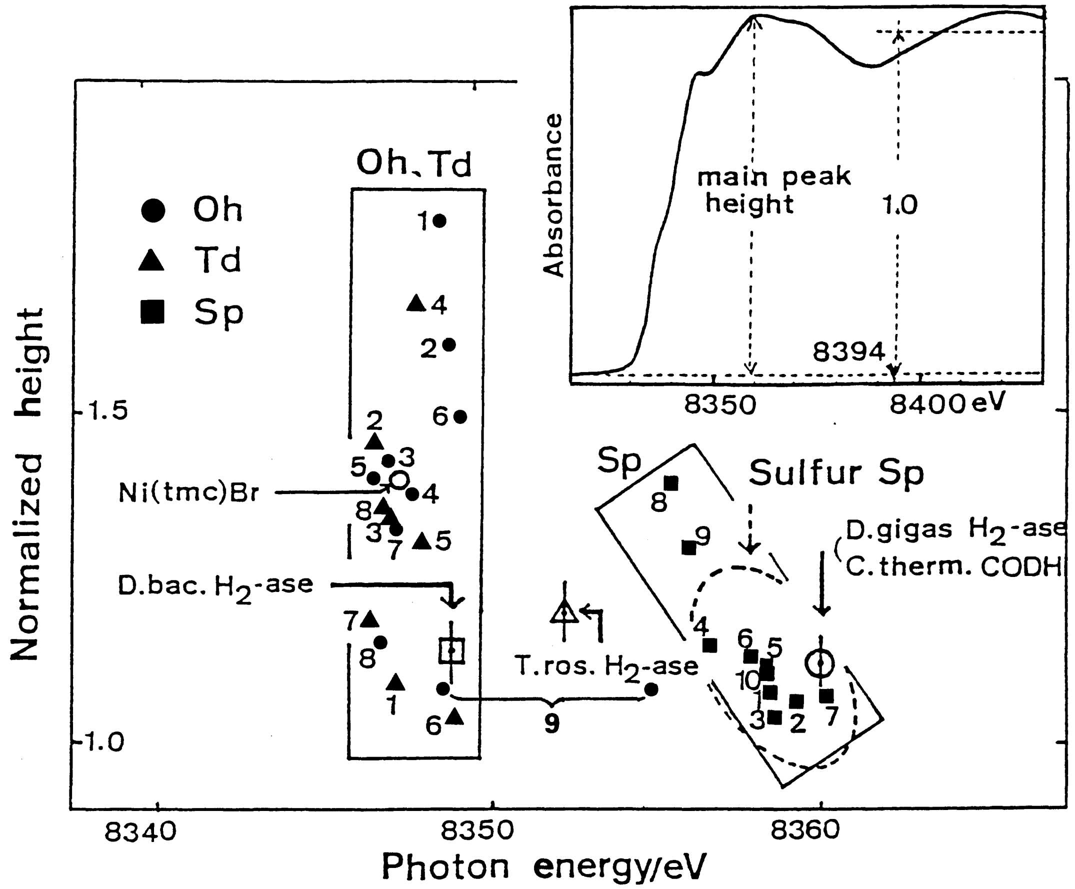
Nickel K edge XANES spectra of 27 compounds were observed. Energy and normalized height mapping of their main peaks has shown a characteristic area for square planar geometry, especially for the cases containing sulfur back scatterer. The coordination geometries of the nickels in hydrogenases and CO dehydrogenases were discussed by using their published data.

XANES (X-ray absorption near edge structure) is known to reflect the metal-ligand covalencies, valence states, and coordination geometries.$^{1)}$ The energy positions and the heights of the satellites such as 1s→3d and 1s→4p have been the objects of molecular orbital calculations,$^{2)}$ while the main peaks were successfully simulated by multiscattering theories.$^{3)}$ However, the latter theory is not generally comprehensive to inorganic chemists and, probably hence, the empirical treatment of the main peaks has almost been overlooked except few cases.$^{1)}$ In this study, we examined the empirical mapping of nickel K-edge main peaks for 27 compounds, in order to correlate the (peak energy, peak height) position to the coordination geometry. The result was applied for the published data about the nickels in hydrogenases (H_2-ase)$^{4-6)}$ and carbon monoxide dehydrogenase (CODH)$^{7)}$ to consider the coordination geometries of the nickel sites.

X-Ray absorption data were recorded on transmission mode at room temperature for the samples sealed in polyethylene pellets. The experiments were carried out on the EXAFS facilities of the beam lines BL-6B, BL-7C and BL-10B of Photon Factory of The National Institute of High Energy Physics at Tsukuba. Edge energies were calibrated with Ni foil (the first inflection point; 8331.6 eV) for every series of experiment. The data were processed by using EXAFS1 program.$^{8)}$The absorption heights of XANES main peaks after extraction were normalized with respect to the EXAFS background absorption at 8394 eV, which is about 60 eV higher than the edge energies, hence, situates at the lower energy boundary of XANES and EXAFS regions. The background absorptions for the enzymes were estimated from the published spectra as sitting on the lines connecting the mid points of the interfering waves (Fig. 1).



Sp: 1)NiS^-_4; $[Ni(edt)_2]^{2-}$,**1.**[9] $[Ni(cdt)_2]^{2-}$,**2.**[10] 2)$NiS_2S^-_2$; Ni(ttu),**3.**[11] 3)$NiN_2S^-_2$; Ni(tsalen),**4.**[12] Ni(ebmba),**5.**[13] 4)$NiN^-_2S^-_2$; $[Ni(ebtsa)]^{2-}$,**6.**[14] 5)$NiS^{-1/2}_4$; $[Ni(SEt)_2]_6$,**7.**[15] 6)$NiN^{-1/2}_4$; Ni(tpp),**8.**[16] 7)$NiN_2O^-_2$; Ni(salen),**9.**[17] 8)NiN_4; $[Ni(4\text{-}MePy)_4]^{2+}$,**10.**[18]

Td: 1)NiS^-_4; $[Ni(SPh)_4]^{2-}$, **1.**[19] 2)$NiCl^-_4$; $[NiCl_4]^{2-}$,**2.**[20] 3)$NiBr^-_4$; $[NiBr_4]^{2-}$,**3.**[21] 4)$NiPBr^-_3$; $[Ni(PPh_3)Br_3]^-$,**4.**[22] 5)$NiP_2Cl^-_2$; $Ni(PPh_3)_2Cl_2$,**5.**[23] 6)$NiP_2I^-_2$; $Ni(PPh_3)_2I_2$,**6.**[24] 7)$NiNBr^-_3$; $[Ni(qui)Br_3]^-$,**7.**[25] 8)$NiN_2Br^-_2$; $Ni(qui)_2Br_2$,**8.**[26]

Oh: 1)NiO_6; $[Ni(H_2O)_6]^{2+}$,**1.**[27] 2)$NiS^{-1/3}_6$; NiS,**2.**[28] 3)NiN_6; $[Ni(en)_3]^{2+}$,**3.**[29] $Ni(en)_2(NCS)_2$,**4.**[30] 4)$NiCl^{-1/3}_6$; $RbNiCl_3$,**5.**[31] 5)NiN_4O_2; $Ni(py)_4(ClO_4)_2$,**6.**[32] 6)$NiS_4Cl^-_2$; $Ni(tu)_4Cl_2$,**7.**[33] 8)$NiCl^{-1/3}_6$; $NiCl_2$,**8.**[34] NiS_6; $[Ni(ttn)_2]^{2+}$, **9.**[35]

Fig. 1. The (energy, normalized height) mapping of the Ni K-edge XANES main peaks for 27 compounds, and for *D. gigas*,[4] *D. baculatus*,[5] *T. roseopersicina*[6] H_2-ases and *C. thermoaceticum* CODH.[7] Reading errors are shown by bars. The position of Ni(tmc)Br, a square pyramid compound, was also plotted. (Abb; See Ref. 36).

The result is shown in Fig. 1. The compounds and their structural items (**Sp**; square planar, **Oh**; octahedral, **Td**; tetrahedral) are summarized also in Fig. 1. In the map, we also plotted the (energy, height) coordinates of the oxidized forms of three H_2-ases from *D. gigas*,$^{4)}$ *T. roseopersicina*,$^{6)}$ and *D. baculatus* (includes NiFeSe center),$^{5)}$ as well as that for CODH from *C. thermoaceticum.*, that obeys **Sp** geometry clearly showing 1s→4p absorptions.$^{7)}$ As is seen in Fig. 1, the **Sp** region is obviously distinguishable from those of **Td** and **Oh** ones. The **Sp** cases including sulfur backscatterers form a compact subgroup in **Sp** area. *D. gigas* H_2-ase, as well as the CODH, is located just in the **Sp** area suggesting that the nickel atom is immersed in a **Sp** coordination sphere, although it seems to show no 1s→4p absorptions characteristic to **Sp** geometry, hence, this nickel was proposed to be pseudo **Oh** by Scott et al in Ref. 4).

Oh and **Td** cases are distributed in 8347 - 8350 eV, a narrow range. Our work is still devoid of pentacoordinate cases, but, an example for square pyramid geometry, Ni(tmc)Br,$^{35)}$ was reported in Ref. 4. According to Ref. 5, the compound situates just on this region at ($\approx$8347 eV, $\approx$1.4), showing clear 1s→3d absorption. As for **Oh**, the normalized height seems to diminish with the symmetry drop and the mixing of heavy atom backscatterers. Thus, the position of the nickel in *D. bac.* H_2-ase that it situates at the lowest of the **Oh** area will suggest a distorted **Oh** or square pyramid circumstance, as was proposed in Ref. 5, for the nickel. On the other hand, *T. ros.* H_2-ase$^{6)}$ locates at the interval of **Sp** and **Oh** or **Td** (8352 eV). This energy agrees well with the mean value of the doublet main peaks of $[Ni(ttn)_2]^{2+}$ (8348.5, 8354.8 eV; NiS_6 distorted **Oh**). Although $[Ni(ttn)_2](ClO_4)_2$ presents a sharp 1s→4p like peak on the edge,$^{5)}$ $[Ni(ttn)_2](BF_4)_2$ shows only a small diffused 1s→4p like absorptions. The feature of the former's XANES spectrum is similar to that of *T. ros.* H_2-ase, if the doublet peaks fuse into each other. The nickel in *T. ros.* H_2-ase might be in an elongated pseudo **Oh** circumstance.

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