Structure Analyses of Nickel(II) Complexes Bound to Copolymers of 2-Acetyl-5-(4-vinylbenzyloxy)phenol, Acrylamide, and 2,2′-Methylenediacrylamide by EXAFS and XANES

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(Received November 8, 1993)

Synopsis. The coordination of the nickel(II) centers bound to the titled polymers were determined by EXAFS and XANES as being of the octahedral $Ni(avp)_2(H_2O)_2$ type in both template and non-template polymers.

Polymers having negatively charged oxygen donor groups have recently attracted attention, in relation to their selective coordination to certain metal ions.[1—3] We recently found that the titled polymers with the acetylphenol ligand selectively adsorb Pd(II), Cu(II), Ni(II), Co(II), and Zn(II), and that the metal ion-adsorption ability (adsorption pH and velocity) is much higher in the template synthesis polymer than in the non-template one.[4] As an example, the difference for the adsorption velocity of Ni(II) is shown in Fig. 1. In Fig. 2, the proposed structure of the metal complex moiety bound to the polymers is presented. It is essential to study the local structure of the metal binding sites formed in metallo-macromolecules, in order to clarify the template effect described above and, thereby, to design and develop metal-selective polymers with high ability. We have thus investigated the local structure of Ni(II) complexes bound to two polymers which

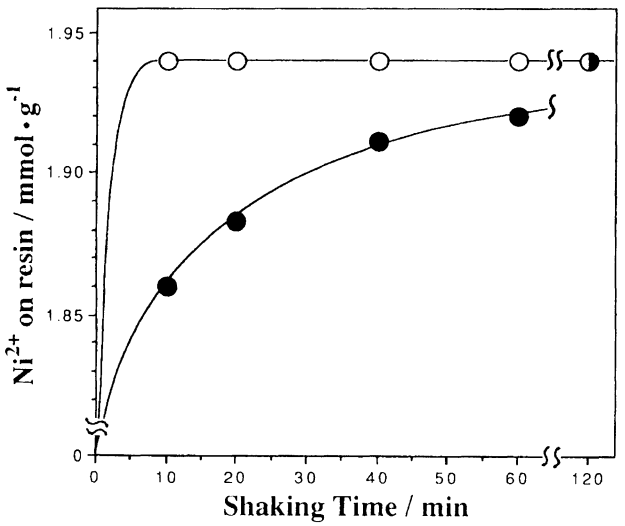

Fig. 1. The difference for adsorption velocity of Ni(II) ion on template (○) and non-template (●) resins. Resin=0.5 g, Volume=50 cm^3, $[NiCl_2]=2.0\times10^{-3}$ mol dm^{-3}, pH=8.5, Temp=25°C.

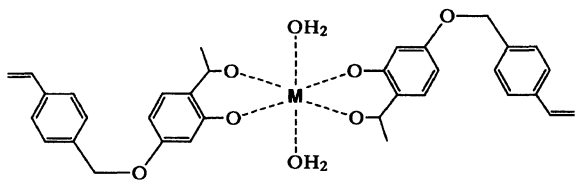

Fig. 2. Proposed structure of the metal complex moiety bound to polymers. The structure illustrates the 1:2 (metal:ligand) complex discussed here, which is bound to polymer chains through the vinyl groups in the end of the avp ligand (see text), where M represents metal cations.

were prepared by different synthetic routes (template and non-template methods) using the X-ray absorption

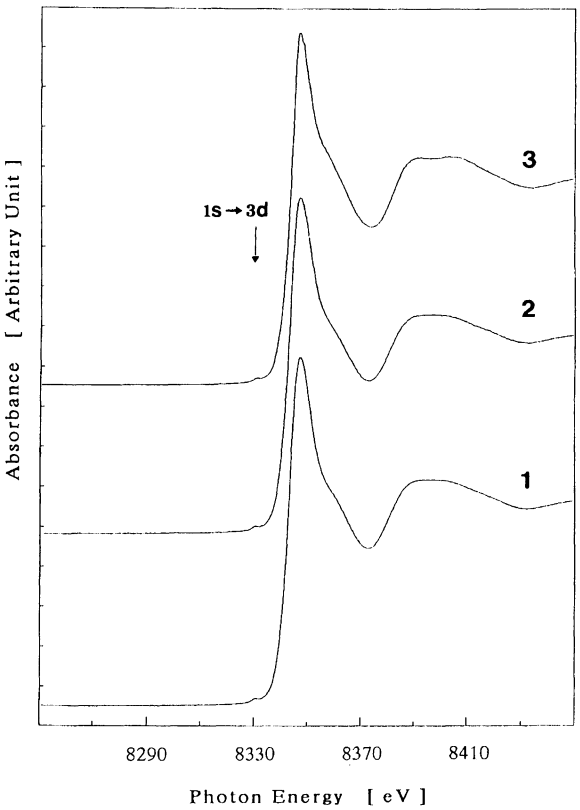

Fig. 3. Ni K-edge XANES spectra for *trans*-[Ni(avp)$_2$(H_2O)$_2$] **1**, Ni(II)-bound template polymer **2**, and Ni(II)-bound non-template polymer **3**.

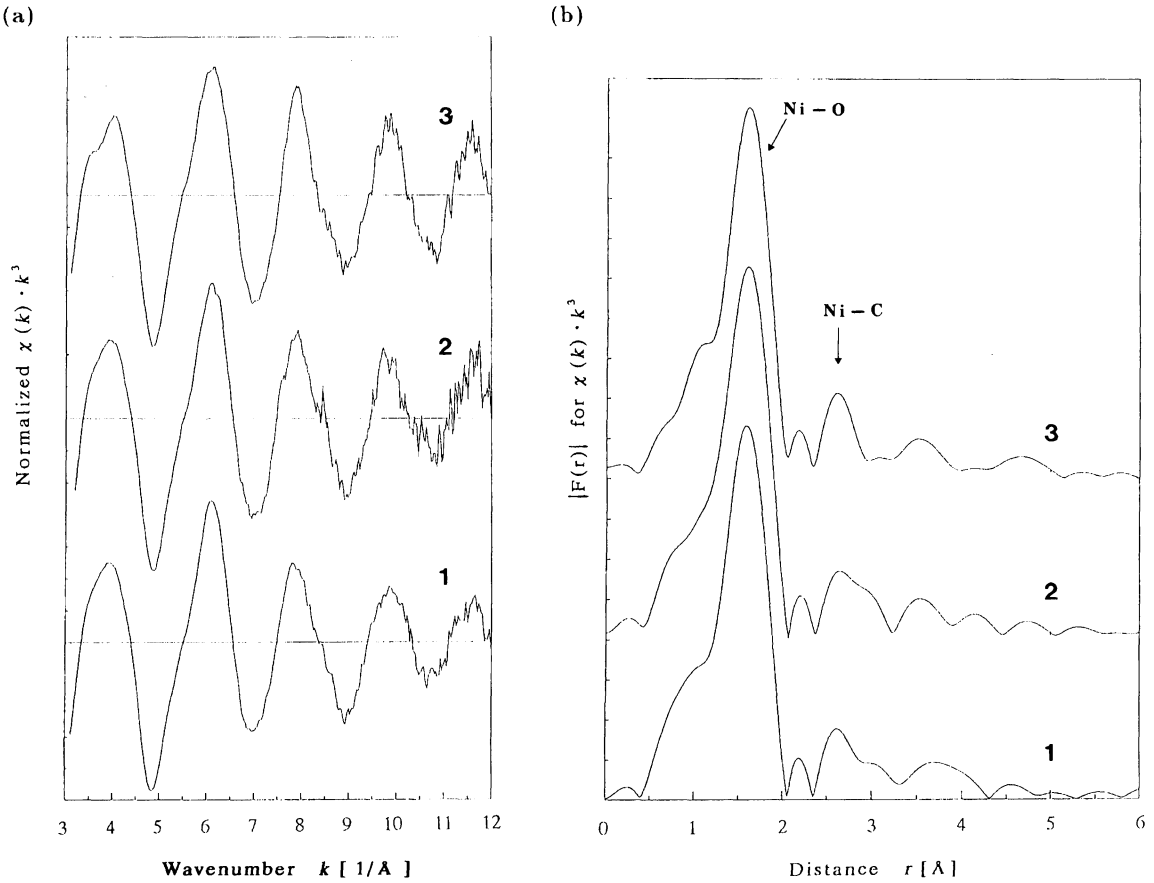

Fig. 4. (a) The k^3-weighted EXAFS spectra for **1**, **2**, and **3**, and (b) the radial structure functions $|F(r)|$ for **1**, **2**, and **3** where the phase shift is not corrected.

spectra (XAS) around the Ni K-edge.

Experimental

Preparation. The template polymer (TP) and non-template one (NTP) were prepared based on the literature.[4] The composition of both polymers is 1 : 5 : 0.5 (avpH: acrylamide: 2,2′-methylenediacrylamide), where avpH represents 2-acetyl-5-(4-vinylbenzyloxy)phenol. Ni(II)-bound polymers were prepared by a reaction of the polymers (1.0 g) with a large excess of $NiCl_2 \cdot 6H_2O$ in methanol–water at pH 5.5. The Ni contents, determined by the atomic absorption method, were 95% (TP) and 90% (NTP) based on the 1 : 2 molar ratio (metal : ligand), respectively.

XAS Measurements. A measurement of X-ray absorption spectra was performed by means of synchrotron radiation employing the EXAFS facilities installed on the Beam Line 6B station at the Photon Factory of the National Laboratory for High Energy Physics (KEK) at Tsukuba. An Si(111) double-crystal monochromator was used to monochromatize white X-rays. All of the XAS data around Ni K-edge (8331.7 eV) were collected in the transmission mode on polyethylene pellets at room temperature, with an integration time of 2 s/point. EXAFS analyses were carried out with the systematic program EXAFS1 using the HITAC M682H computer system at the Computer Center of the University of Tokyo.[5]

Results and Discussion

Measurements and analyses of XAS were carried out on three compounds: *trans*-$[Ni(avp)_2(H_2O)_2]$[4] **1** (the monomer source for the template polymerization), Ni(II)-bound template polymer **2**, and Ni(II)-bound non-template polymer **3**. Figure 3 illustrates the Ni K-edge XANES spectra for **1**, **2**, and **3**. In each spectrum, the weak absorption band, which appears just before the edge jump, can be assigned to the nondipole 1s→3d transition characteristic to octahedral or tetrahedral metal complexes. The two bands close to the jump can be attributed to σ-shape resonances in multiple-scattering theory for metal complexes in octahedral geometry.[6] They suggest the presence of aromatic groups linked to the coordination atoms in the avp ligands. On the other hand, the 1s→4p band, which generally appears in square-planer Ni(II) complexes,[7,8] could not be observed. Thus, it is clear that the geometries of the Ni(II) complexes formed in polymers **2** and **3** are both octahedral on the basis of the similarity among them and the assignment of the bands. These results are consistent with the green color (a characteristic of octahedral Ni(II) complexes) of these polymers and the monomer source **1**.

Figure 4 shows the k^3-weighted EXAFS spectra, cou-

Table 1. Atomic Parameters Determined by Curve Fitting Analysis

Compounds	Shell	Ni–A[a]	C.N.[b]	r/Å[c]	σ/Å	ΔE	R
1 $[Ni(avp)_2(H_2O)_2]$	1st	Ni–O	6.0	2.03	0.055	4.3	0.045
	2nd	Ni–C	4.0	3.01	0.053	12.5	0.071
2 Polymer(TP)	1st	Ni–O	5.6	2.03	0.066	4.3	0.040
	2nd	Ni–C	2.5	3.02	0.052	10.4	0.072
3 Polymer(NTP)	1st	Ni–O	5.5	2.02	0.064	4.3	0.046
	2nd	Ni–C	2.6	3.03	0.057	12.1	0.064

a) Ni is the absorber and A is the back scattering atom, and all back scattering atoms in the first shell are calculated as oxygen. b) The coordination numbers of Ni atoms for polymers **2** and **3** are referenced to the values for the avp complex **1**. c) Estimated errors are ±0.02 Å for the first shell and ±0.01 Å for the second one.

pled with the magnitudes of the Fourier transforms obtained by a Fourier analysis of the EXAFS data. Fourier transforms of $k^3\chi(k)$ were taken over the k range of 3.2—12.0 $Å^{-1}$. A distinguishing resemblance among them can be observed over the wide range of the EXAFS spectra and the radial structure functions, in which the main peaks at 1.6 Å and the sub-peaks at 2.6 Å, respectively, appear before the phase-shift corrections. In order to obtain the bond distance and the coordination number in the first and second shells, the main peaks (0.9—2.4 Å in **R**-space) and the sub-peaks (2.4—3.3 Å) were Fourier filtered into k-space, respectively. The results of curve-fitting analyses are presented in Table 1. The bond distance between Ni–O (2.03 Å) obtained for complex **1** is in good agreement with that from X-ray crystallography of *trans*-$[Ni(sal)_2(H_2O)_2]$,[9] sal=salicylaldehydate anion, which can be regarded as being a suitable model compound for the AVP complex **1**. The reliability of our analyses for macromolecular Ni(II) complexes was thus examined. In each compound, the ΔE and R values of each shell are comparable with thoses of the other compounds, and those of the second shell are significantly larger than those of the first. The coordination number of each Ni(II) complex bound to polymers **2** and **3** was derived based on the respective apparent coordination number (n) by applying the damping factor calculated based on assumption that the coordination number of complex **1** is identical with that of *trans*-$[Ni(sal)_2(H_2O)_2]$. An enlargement of the Debye–Waller-like factors in the first shell shows a tendency to decrease the value of the coordination number; however, the differences between the obtained values are within ca. 10%. On the other hand, the coordination numbers in the second shells of polymers **2** and **3** are small when compared with that of monomer **1**, even though the σ values are almost the same among them. It may be important that the coordination numbers in each shell are equivalent between the two polymers, compared with their structures, because the difference of the Ni(II) contents in both polymers is small.

From these results, it was revealed that the local structures around the Ni centers bound to TP and NTP are almost identical with that of the octahedral *trans*-$[Ni(avp)_2(H_2O)_2]$ complex **1**, indicating that the high metal ion-adsorption ability of TP is not due to the local structure around the metal ions, but to a favourable disposition of the avp ligand for the formation of a 1 : 2 chelate in the template polymer (entropy effect).[10,11] To our knowledge, this paper is the first report to deal with a comparison between the detailed structure around the metal center in the template metallo-macromolecule and that of the non-template one by XAS.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 03650687 from the Ministry of Education, Science and Culture.

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