

## Local Structure Analysis of Cr Complexes with Distorted Porphyrins

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The low reactivity for ligand substitutions of Cr(III) is improved by the coordination of electron donating ligands. For example, the water exchange rate constant of the Cr(III) tetraphenylporphyrin complex ([Cr(tpp)Cl(H<sub>2</sub>O)]) is larger by ca. 6 orders of magnitude than that of Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, and this is interpreted to be due to the enhanced electron density on Cr(III), which assists the dissociation of coordinating water molecules because of the increased electronic repulsion with donating electrons of water. The improvement of substitution reactivity is much enhanced for the Cr complexes with a deformed porphyrin, but the origin of its enhancement is unclear because the structure of such Cr complex is not resolved and the electronic state of the Cr center is not clarified. In this study, the local structure and the valence state of the Cr center are clarified by the XAFS measurements for the Cr complex of bulky dodecaphenylporphyrin (DPP).

**Experiments**

The XAFS spectra were measured by the conventional method at BL-7C and 9A. The higher order harmonics were removed by the double-mirror system of SiO<sub>2</sub> (3.5 mrad) or Ni-coated SiO<sub>2</sub> (6 mrad) at BL-7C or 9A, respectively. The ionization chambers were used to measure the incident and transmitted X-ray intensities. The first crystal of Si(111) double-crystal monochromator was sagittally focused to get higher X-ray flux at BL-7C.

The XANES and EXAFS spectra of Cr–DPP complex (**1**) was measured together with those of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (**2**) Na[CrO(hmp)<sub>2</sub>] (**3**: hmp = 2-hydroxy-2-methylpropionate), [CrO(tpp)] (**4**: tpp = 5,10,15,20-tetraphenylporphyrin), [CrCl(tpp)(H<sub>2</sub>O)] (**5**). All powder samples were diluted using BN powder.

**Results and Discussion**

The XANES spectrum of the Cr–DPP complex is very similar to that of **5** with the Cr(III) center as shown in Figure 1. The other complexes with the different valence of Cr show a clear and intense pre-edge peak, which is assigned to the transition from 1s to 3d, and the pre-edge peak is shifted to the higher energy with the increasing valence. In the cases of Cr–DPP and **5**, the corresponding pre-edge peak is quite weak and their energies are very similar. It is thus concluded that the valence state of Cr is +3 in the Cr–DPP complex.

The EXAFS spectra were analyzed to determine the local structure parameters around the Cr center in

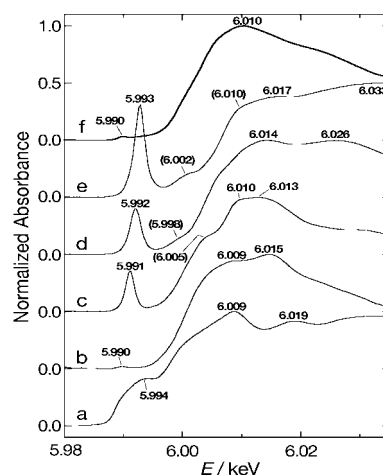
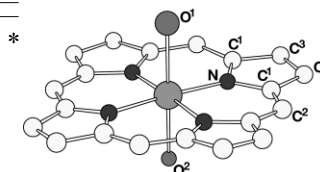


Figure 1: XANES spectra of Cr foil (a), [CrCl(tpp)(H<sub>2</sub>O)] (b), [CrO(tpp)] (c), Na[CrO(hmp)<sub>2</sub>] (d), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (e), and Cr–DPP.

considering all the contributions including multiple scatterings. The number (*N*) and distance (*R*) of some direct interactions are summarized in Table 1 for Cr–DPP and **5**. Two O atoms are found to bind to the Cr center in Cr–DPP. One is assigned to a coordinating water according to its Cr–O<sup>2</sup> distance, and the other (Cr–O<sup>1</sup>) is considered to be the OH group. This coordination environment is consistent with the assignment of Cr(III) on the basis of XANES. The shorter Cr–C interactions of Cr–DPP relative to those of **5** indicate that the porphyrin core is largely deformed in the Cr–DPP complex.

Table 1: Structure parameters

interaction	[CrCl(tpp)(H <sub>2</sub> O)]		Cr–DPP	
	<i>N</i>	<i>R</i> / Å	<i>N</i>	<i>R</i> / Å
Cr–N	4	2.04	4	2.03
Cr–O <sup>1</sup>			1	1.92
Cr–O <sup>2</sup>	1	2.03	1	2.03
Cr–Cl	1	2.32		
Cr–C <sup>1</sup>	8	3.02	8	2.98
Cr–C <sup>2</sup>	4	3.46	4	3.38
Cr–C <sup>3</sup>	8	4.30	8	4.22



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