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# EXAFS Amplitudes of Six-Coordinate Aqua and Ammine 3d Transition Metal Complexes in Solids and in Aqueous Solutions

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X-Ray absorption spectra of hexaaqua and hexaammine complexes of some 3d transition metals in solids and in aqueous solutions are measured and analyzed. It is found that the peak intensities in the EXAFS Fourier transforms for aqua complexes correlate with those for ammine complexes.

EXAFS method gives the distance of coordinating atom from central metal ion in complex and the number of coordinating atoms. However, in some cases, it is hard to determine coordination number $N$, since the $N$ and the disorder in bond distance $\sigma$ (Debye-Waller factor) are highly correlated. If a typical value of the $\sigma$ and other parameters contributing to the EXAFS intensity for a pair of atoms are known, the $N$ might be estimated more reliably. In this study, X-ray absorption spectra of many simple six-coordinate 3d transition metal complexes in solids and aqueous solutions are measured in order to study how the EXAFS intensities vary with the kind of central metal ions and ligands.

The powder samples measured are $[Cr(NH_3)_6](NO_3)_3$, $[Co(NH_3)_6]Cl_2$, $[Ni(NH_3)_6]Cl_2$, and $[Cu(NH_3)_6]Cl_2$. The aqueous solution samples of 0.4 mol·dm$^{-3}$ ammine complex of Cr(III) and Ni(II) were prepared by dissolution of above solid samples in 1 mol·dm$^{-3}$ [for Cr(III)] or 2 mol·dm$^{-3}$ [for Ni(II)] ammonia water. Chloride or nitrate complexes and concentrated

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ammonia water were used for 0.4 mol·dm$^{-3}$ Mn(II), Fe(II), and Zn(II) ammine complex solutions, although the coordination number of ammonia for these metals are uncertain. Zn(II) may have ligands of ammonia and water, and it may not be a hexa-coordinate complex. Other samples were previously reported in Ref. 1.

The K-edge X-ray absorption spectra were recorded at the BL7C using a Si(111) double crystal monochromator and 10B using a Si(311) channel-cut crystal monochromator of Photon Factory of National Laboratory for High Energy Physics.

Table 1 lists the bond lengths *r* pertaining to metal-O or -N bonds and intensities *h* of the peaks of the EXAFS Fourier transforms (FT). FT calculations were performed by using the phase shift and back-scattering amplitude parameters tabulated by Teo and Lee,[2)]

Table 1. The bond lengths *r* and the peak intensities *h* in the Fourier transforms for hexaaqua and hexaammine complexes in solids and in aqueous solutions (*h* in arbitrary units).

| Ligand | Metal ion | in solids | | in aqueous solutions | |
|---|---|---|---|---|---|
| | | *r*/Å | *h* | *r*/Å | *h* |
| aqua | Cr(III) | 2.04 | 1.69 | 2.04 | 1.71 |
| | Mn(II) | 2.22 | 0.79 | 2.20 | 0.81 |
| | Fe(II) | 2.18 | 0.81 | 2.19 | 1.00 |
| | Fe(III) | 2.06 | 1.51 | 2.04 | 1.48 |
| | Co(II) | 2.13 | 0.94 | 2.12 | 0.97 |
| | Ni(II) | 2.09 | 1.11 | 2.11 | 1.12 |
| | Cu(II) | 2.04 | 0.95 | 2.03 | 0.90 |
| | Zn(II) | 2.12 | 0.82 | 2.13 | 0.88 |
| ammine | Cr(III) | 2.15 | 1.32 | 2.15 | 1.43 |
| | Mn(II) | — | — | 2.30 | 0.71 |
| | Fe(II) | — | — | 2.25 | 0.69 |
| | Co(II) | 2.23 | 0.71 | — | — |
| | Ni(II) | 2.18 | 0.90 | 2.18 | 0.93 |
| | Cu(II) | 2.09 | 0.77 | — | — |
| | Zn(II) | — | — | (2.10 | 0.90)[a)] |

a)This may not take the six-coordination structure.

and over the $k$-range of 3.5–12.5 Å. Hamming window function was used over the $k$-ranges of 3.5–4.4 Å and 11.6–12.5 Å.

The basic EXAFS formula is[3]

$$\chi(k) = \frac{SN}{kr^2} F(k)\exp\left(\frac{-2r}{\lambda(k)}\right)\exp(-2\sigma^2 k^2)\sin(2kr + \phi(k)), \qquad (1)$$

where $F(k)$ and $\phi(k)$ are the back-scattering amplitude and the phase shift, respectively. $S$ is the amplitude reduction factor due to multiple excitations and $\lambda(k)$ is the electron mean free path due to interactions with the valence electrons. If FT is performed over the $k$-range of 0–∞ and $\lambda(k)$ does not depend on $k$, $r^2$ weighted peak intensity $hr^2$ is derived from Eq. 1 as follows,[1]

$$hr^2 \propto \frac{SN}{\sigma}\exp\left(\frac{-2r}{\lambda}\right). \qquad (2)$$

In Fig. 1, the $hr^2$ values for aqua complexes in aqueous solutions and for ammine complexes in solids and in aqueous solutions are plotted against those for aqua complexes in solids. There are linear correlations among these values. It was pointed out[1] that the $hr^2$ values of aqua complexes have correlation with the logarithm of the ligand exchange rate constants and reflect the character of the coordination bond. Here, $N$ is constantly 6 except for Cu(II) that has the Jahn-Teller distortion, and $S$ and $\lambda$ must be almost the same for all kinds of complexes.

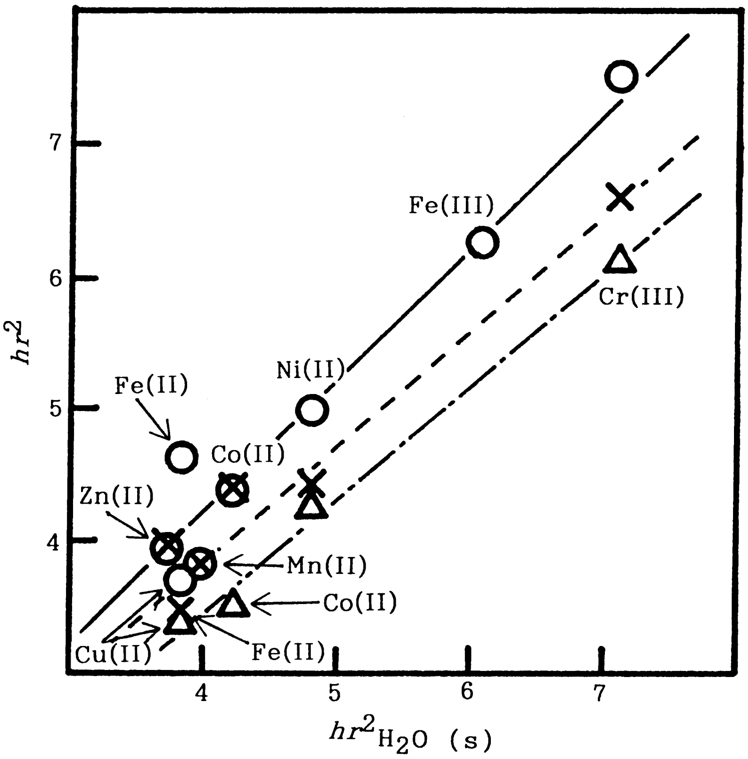

Fig. 1. EXAFS peak intensities $hr^2$ for 3d transition metal complexes. Aqua complexes in aqueous solutions (——○——), ammine complexes in aqueous solutions (· – -×- – ·) and in solids (·——△-·-—). The values for aqua complexes in solids, $hr^2_{H_2O}$ (s), are indicated on the abscissa.

Furthermore, because $\lambda$ is usually more than 5 Å in inorganic materials,[3] the differences in the exponential term of Eq. 2 among the complexes studied here must be less than about 10%. Thus, the result of Fig. 1 indicates that each metal ion has almost intrinsic $\sigma$ value irrespective of its environments and ligands. It should be noted that the position of Cu(II) in Fig. 1 lies on the same line as other ions do, in spite of the fact that Cu(II) complexes have different amounts of distortion among the aqua and the ammine complexes.

The predictions of the characteristic $\sigma$ value of each metal ion and its variation with ligands from the present work would be useful in analyzing EXAFS spectra of simple metal complexes. Curve-fitting calculations on these data and other simple six-coordinate complexes are now in progress.

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