CHEMISTRY LETTERS, pp. 1073-1076, 1988.

Amplitude in EXAFS and Ligand Exchange Reaction of Hydrated 3d Transition Metal Complexes

Takafumi MIYANAGA, Iwao WATANABE, and Shigero IKEDA
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560

EXAFS (Extended X-ray Absorption Fine Structure) spectra are analyzed for a series of hydrated 3d metal complexes in crystal and in aqueous solution. It is found that the peak intensity of the metal-oxygen bond in the Fourier transform of EXAFS being considered to depend on the Debye-Waller factor correlates with the ligand exchange rate constant.

The interatomic distances can be determined with rather high accuracy from EXAFS spectroscopy. However, it is often difficult to determine coordination number from this spectroscopy, since the amplitude of the EXAFS signal correlates not only with the coordination number but with the root-mean-square relative displacement or the Debye-Waller like factor σ . There is little knowledge about the chemistry with regard to the value of σ in EXAFS.

In the recent review,[1)] Sham pointed out that the ligand exchange rate in solution should be closely related to the strength of metal-ligand bond and hence to the bond length and/or σ. He suggested that the large σ values for axial oxygen atoms for Cu^{2+} and Cr^{2+} complexes in aqueous solution arise from fast water exchange on axial sites. In this letter, we report the general correlation between the σ value and the water exchange rate for 3d transition metal complex.

All the K-edge absorption spectra were recorded at BL7C or 10B of the Photon Factory of National Laboratory for High Energy Physics (KEK) in Tsukuba. A Si(111) double crystal monochromator was used. The samples measured are $CrSO_4 \cdot 5H_2O$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Mn(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_2 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$,

$Co(ClO_4)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, and the sulphate or perchlorate solutions of metal complexes (1.0 mol dm^{-3}) containing adequate acids.

Figure 1 shows the Fourier transforms for Cr^{2+}, Cr^{3+}, Fe^{2+}, and Fe^{3+} hexaaqua complexes in solid and in aqueous solution. The corrections of the phase shift and the backscattering amplitudes were performed by use of the values calculated by Teo and Lee.[2)] The k-range for the Fourier transforms is 3.5-13.5 $Å^{-1}$. Owing to the Jahn-Teller effect for Cr^{2+} in which the distance of $Cr-O_{eq}$ is ca. 2.0 Å and that of $Cr-O_{ax}$ is 2.5 Å, the intensty of the peak for Cr^{2+} is smaller than that for Cr^{3+} complex. In the case of Fe complexes, the intensity for Fe^{2+} complex is also smaller than that for Fe^{3+} complex in spite of the absence of the Jahn-Teller distortion in Fe complexes, both of which are octahedrally coordinated by six water molecules. It is also found that the peak intensities are almost the same irrespective of the environments, in crystal or in solution. For the Fe case, the peak for crystal is slightly weaker than that for solution, which should be reversed if the ligand exchange in solution had caused the large σ value. These facts suggest that the intensity of the peak in the Fourier transform is associated with the intrinsic character of the metal-oxygen bond. The lengths r of metal-oxygen bonds and the intensties h of the peaks obtained from the EXAFS measurements for various 3d metals are listed in Table 1.

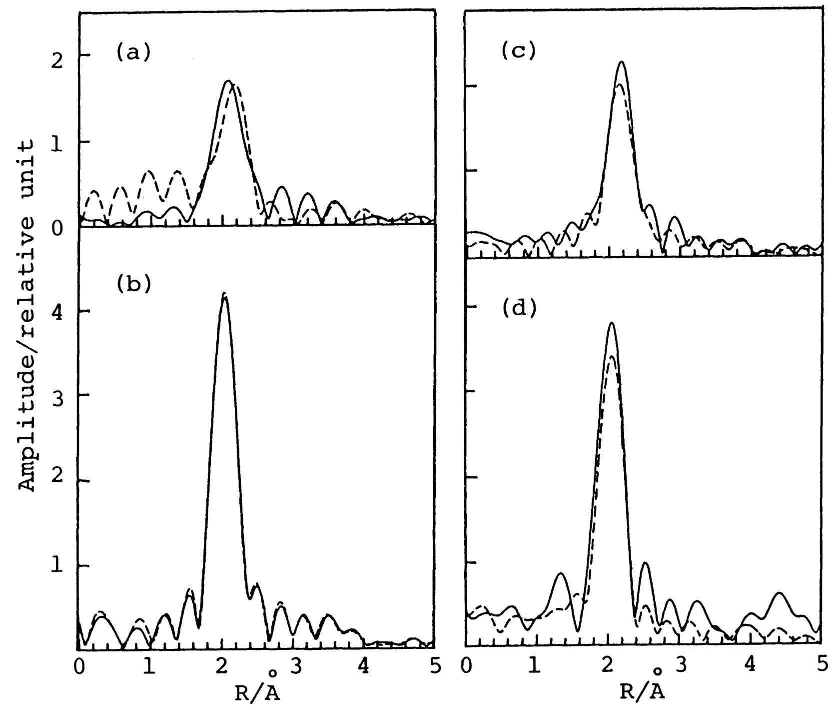

Fig. 1. Fourier transforms for hydrated metal complexes of (a) Cr^{2+}, (b) Cr^{3+}, (c) Fe^{2+}, and (d) Fe^{3+} in solution (——) and crystal (-----).

Table 1. The bond lengths r for metal-oxygen and the peak intensities h in the Fourier transforms and the ligand exchange rate constants k_1 for various 3d metal ions in aqueous solution.
The values in parentheses are for solid samples.

Metal	$r^{a)}$/ Å	h	hr^2	$k_1{}^{b)}$/ s^{-1}
V^{2+}	2.21 (—)	1.08 (—)	5.4 (-)	$Fe^{3+}<V^{2+}<Ni^{2+}$
Cr^{2+}	2.08 (2.12)	0.79 (0.69)	3.4 (3.1)	7×10^9
Cr^{3+}	2.03 (2.03)	1.80 (1.84)	7.4 (7.6)	5×10^{-7}
Mn^{2+}	2.23 (2.20)	0.93 (0.83)	4.6 (4.0)	3×10^7
Fe^{2+}	2.16 (2.14)	0.99 (0.94)	4.6 (4.3)	3×10^6
Fe^{3+}	2.04 (2.05)	1.61 (1.52)	6.7 (6.4)	3×10^3
Co^{2+}	2.10 (2.08)	1.20 (1.21)	5.3 (5.2)	1×10^6
Ni^{2+}	2.09 (2.05)	1.23 (1.23)	5.4 (5.2)	3×10^4
Cu^{2+}	2.00 (2.01)	1.01 (1.00)	4.0 (4.0)	8×10^9
Zn^{2+}	2.13 (2.12)	0.97 (0.98)	4.3 (4.4)	$Mn^{2+}<Zn^{2+}<Cu^{2+}$

a) Uncertainty of the distance is ±0.02 Å.

b) F.Basolo and R.G.Peason, "Mechanism of Inorganic Reaction," Wiley, New York (1967).

The EXAFS signal is derived simply as follows,[3)]

$$\chi(k) = [S(k)N/kr^2]f(\pi,k)\exp[-2r/\lambda(k)]\exp(-2\sigma^2k^2)\sin[2kr+\psi(k)],$$

where N is the number of the coordinating atoms. $f(\pi,k)$ and $\psi(k)$ are the backscattering amplitude and the phase shift, respectively. S(k) is the amplitude reduction factor due to multiple excitations (many-body effects such as shake up and shake off processes) and $\lambda(k)$ is the electron mean free path. Here, we assume that each S(k) or $\lambda(k)$ is the same function of k for all kinds of the central metals. In practice, they are difficult to estimate theoretically. Under the above approximations, Mobilio and Incoccia pointed out that the value of hr^2 is proportional to N/σ if the Fourier transform is performed over the k-range of $0-\infty$.[4)] Therefore, we obtain the Debye-Waller factor as the form of $1/\sigma$ or hr^2 by neglecting the error due to the finite K-range used (3.5-13.5 $Å^{-1}$) and placing N=6 for all of the metal complexes. The values of hr^2 are listed in Table 1. The values scatter considerably and at the first glance one easily notices that the value correlates with the lability of the metal ion. In the table are also included the rate constants k_1 for ligand water exchange reaction. The hr^2 against the logarithm of k_1 is plotted in Fig. 2. There is almost linear correlation between hr^2 or $1/\sigma$ and log k_1. That is, the larger the σ value, the faster the ligand exchange reaction or the smaller activation energy for the reaction. It is more important to note that the σ value for crystal state behaves quite similarly to that for the aqueous solution. This fact indicates that the σ value is not affected by the real exchange motion of the ligand water molecule but reflects the character, strength or hardness, of the chemical bond.

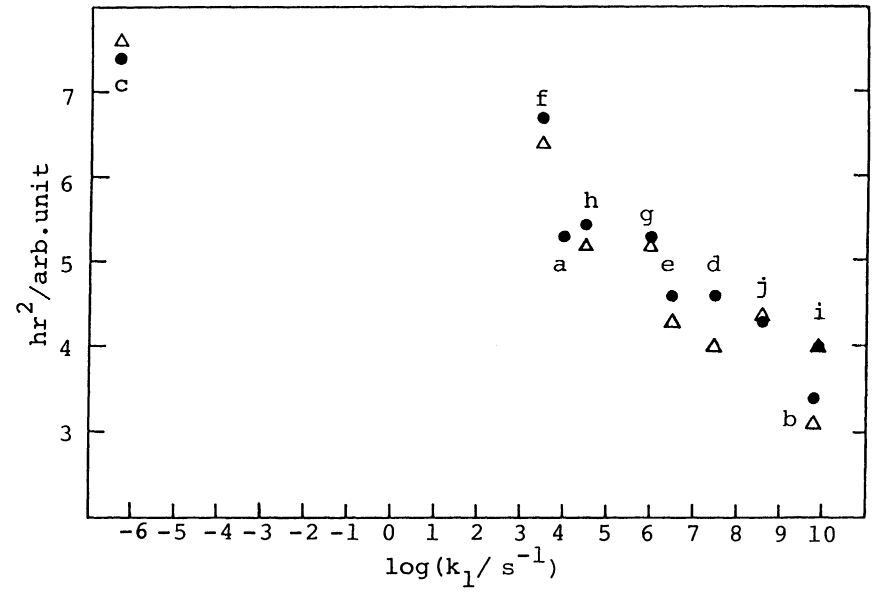

Fig. 2. Correlation of hr^2 with the ligand exchange rate constant for hydrated metal ions of (a) V^{2+}, (b) Cr^{2+}, (c) Cr^{3+}, (d) Mn^{2+}, (e) Fe^{2+}, (f) Fe^{3+}, (g) Co^{2+}, (h) Ni^{2+}, (i) Cu^{2+}, and (j) Zn^{2+}. ● and △ denote those in solution and in crystal, respectively.

Other spectroscopic technique providing similar information to σ in EXAFS is the Raman spectroscopy. Recently the connection between EXAFS and Raman studies has been attempted for the amorphous arsenic.5) More detailed studies on the Debye-Waller factor for each bond in complex would make EXAFS useful to obtain the knowledge of the role of the bond for its chemical reactivity.

The authors thank Drs. Tadashi Matsushita and Masaharu Nomura of National Laboratory for High Energy Physics (KEK) for their help with X-ray absorption measurements. This work was partly supported by the Grant-in-Aid for Special Project Research No.62124039 from the Ministry of Education, Science and Culture.

References

1) T.K.Sham, Acc. Chem. Res., 19, 99 (1986).
2) B.K.Teo and P.A.Lee, J. Am. Chem. Soc., 101, 2815 (1979).
3) B.K.Teo, "EXAFS:Basic Principles and Data Analysis," Springer-Verlag (1985).
4) S.Mobilio and L.Incoccia, Il Nuovo Cimento, 3D, 846 (1984).
5) P.P.Lottici, Phys. Rev. B, 35, 1236 (1987).

(Received April 13, 1988)