Structure of Cobalt(II) Ion and Tri- and Tetrachlorocobaltate(II) Complexes in N,N-Dimethylformamide Determined by the Fluorescent EXAFS Method

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EXAFS (extended X-ray absorption fine structure) spectra were measured for N,N-dimethylformamide (DMF) solutions containing cobalt(II) ion and its chloro complexes of low concentration (20—40 mmol dm^{-3}) by a laboratory EXAFS spectrometer modified for the fluorescence detection. The analysis of the EXAFS data for a cobalt(II) perchlorate DMF solution showed that cobalt(II) ion in DMF has an octahedral structure with six DMF molecules. The Co–O (DMF) bond length within $[Co(dmf)_6]^{2+}$ in DMF is 206(1) pm and is practically the same as that within $[Co(H_2O)_6]^{2+}$ (208 pm) in water within experimental uncertainties. It was also shown that the tri- and tetrachlorocobaltate(II) complexes in DMF have a tetrahedral structure. The Co–O and Co–Cl lengths within $[CoCl_3(dmf)]^-$ in DMF are 202(1) and 227(1) pm, respectively. The Co–Cl distances within $[CoCl_4]^{2-}$ in DMF and in water are the same and 229(1) pm.

Extended X-ray absorption fine structure (EXAFS) spectroscopy has been widely applied to the structure determination of metal complexes in solution. Most of EXAFS measurements of solution samples were performed by the transmission mode. However, this mode can not be used for dilute solutions. It turned out that the fluorescence detection is effective for very dilute systems.[1,2] In fact, EXAFS spectroscopy by the fluorescence detection is indispensable for the structural determination of metal complexes in nonaqueous media, where solubility of metal complexes is usually very low compared with aqueous media.

Complex formation reactions of divalent transition metal with halide ions have been studied in N,N-dimethylformamide (DMF).[3-7] Since metal ions are solvated in solution, solvation structure of metal(II) ions is essential to understand the thermodynamics of complexation. Direct structural information on the solvation structure of copper(II) and cadmium(II) ions in DMF has so far been provided by solution X-ray diffraction.[8,9]

With cobalt(II), a series of mononuclear $[CoCl]^+$, $[CoCl_2]$, $[CoCl_3]^-$, and $[CoCl_4]^{2-}$ complexes are formed in DMF. In particular, the tri- and tetrachloro complexes are extensively formed as the main species at suitable mole ratios of chloride to cobalt(II) ions.[3] However, since the solubility of $((CH_3CH_2)_4N)_2[CoCl_4]$ in DMF is low (less than 20 mmol dm^{-3}), it is difficult to apply the transmission EXAFS method for the structural study. Therefore, in the present study we employed the fluorescent EXAFS method to determine the structure of the solvated cobalt(II) ion and the tri- and tetrachlorocobaltate(II) complexes in DMF. The structure of mono- and dichlorocobalt(II) complexes was not determinable because of their suppressed formation in DMF.

Experimental

Reagents. All chemicals used were of reagent grade. Cobalt(II) perchlorate and cobalt(II) chloride were recrystallized once from water. Cobalt(II) perchlorate DMF solvate was prepared by the same method as described elsewhere.[3] Lithium chloride and tetraethylammonium chloride were used without further purification and dried at 100 °C. N,N-Dimethylformamide was purified as described elsewhere.[5]

Preparation of Solutions. Five sample solutions were prepared for EXAFS measurements. Solution AQ0 is an aqueous cobalt(II) perchlorate solution. Solution AQ4 was prepared by dissolving cobalt(II) chloride in an aqueous 13 mol dm^{-3} lithium chloride solution. The former and latter solutions contain $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ complexes, respectively, of known structure.[10,11] Solution DMF0 is a cobalt(II) perchlorate DMF solution. Solutions DMF3 and DMF4 were prepared by dissolving cobalt(II) perchlorate DMF solvate and tetraethylammonium chloride in DMF at suitable C_{Cl}/C_{Co} mole ratios. The tri- and tetrachlorocobaltate(II) complexes are the main species in solutions DMF3 and DMF4, respectively, according to the stability constants of cobalt(II) chloro complexes in DMF.[3] The compositions of the solutions are given in Table 1.

EXAFS Measurements. EXAFS spectra were measured on a laboratory EXAFS spectrometer[12] modified for the fluorescence detection[13] at the Institute for Molecular Science.

A rotating anode X-ray generator (Rigaku RU-200) was

Table 1. The Composition of Sample Solutions

Solution	C_{Co}/ mol dm^{-3}	C_{Cl}/ mol dm^{-3}	C_{Cl}/C_{Co}
AQ0	0.0203	0	0
DMF0	0.0405	0	0
DMF3	0.0413	0.123	2.98
DMF4	0.0192	0.171	8.91
AQ4	0.100	13	130

operated at the voltage of 12 kV and the current of 200 mA. Monochromatized X-rays were obtained by a Johansson cut bent crystal (Ge(220)). Helium bags were placed along the beam path to prevent absorption by air. Sample solutions were held in a 5 mm thick glass cell with a Mylar window.

The incident X-ray intensity I_o and the fluorescence intensity I were simultaneously measured by an ion chamber and an NaI scintillation counter with 2 inches in diameter combined with a filter (iron foil with thickness of 10 μm), respectively, and more than 1×10^6 counts of I were obtained at each data point above the edge. The observed spectra μ ($=I/I_o$) are shown in Fig. 1.

Analysis of EXAFS Data. Background other than that for the K edge of cobalt atom was estimated by least-squares fitting first-order polynomial function to the pre-edge and was subtracted from the raw spectrum by extrapolation. The smooth background μ_o due to an isolated atom was evaluated by fitting a smooth curve to the observed spectrum using an eighth-order polynomial function.

The EXAFS pattern was then extracted and normalized by the following equation;

$$\chi(k) = \{\mu(k) - \mu_o(k)\}/\mu_o\ (k),\qquad(1)$$

where $k(=\{2m(E-E_o)\}^{1/2}/\hbar\,)$ is the photoelectron wave vector. E represents the energy of the incident X-rays and E_o is the threshold energy of a K-shell electron. The E_o value was selected as the position of the half-height of the edge jump in each sample and was set to be 7.722 keV in the present study. The extracted EXAFS spectra weighted by k^3 are depicted in Fig. 2. The $k^3\cdot\chi$ (k) values are converted to the radial structure function $F(r)$ as

$$F(r) = (1/2\,\pi)^{1/2}\int_{k_{min}}^{k_{max}} k^3\cdot\chi(k)\cdot W(k)\cdot\exp\,(-2\,ikr)\mathrm{d}k.\qquad(2)$$

$W(k)$ is the window function of the Hanning type.[14] The $F(r)$ values are shown in Fig. 3.

A curve fitting procedure in the k-space for the refinements of structure parameters was applied to the Fourier filtered $k^3\cdot\chi(k)_{obsd}$ values to minimize the error-square sum U:

$$U = \Sigma\,k^6(\chi(k)_{obsd} - \chi(k)_{calcd})^2.\qquad(3)$$

The model function $\chi(k)_{calcd}$ is given by the single scattering theory as[15-18]

$$\chi(k)_{calcd} = \Sigma\,\{n_j/(k\cdot r_j^2)\}\,\exp\,(-2\,\sigma_j^2 k^2 - 2\,r_j/\lambda)F_j(\pi,k)$$

$$\times\,\sin\,(2\,kr_j + \alpha_j(k)),\qquad(4)$$

where F_j (π, k) is the backscattering amplitudes from each of n_j scatterers j at distances r_j from the X-ray absorbing atom.
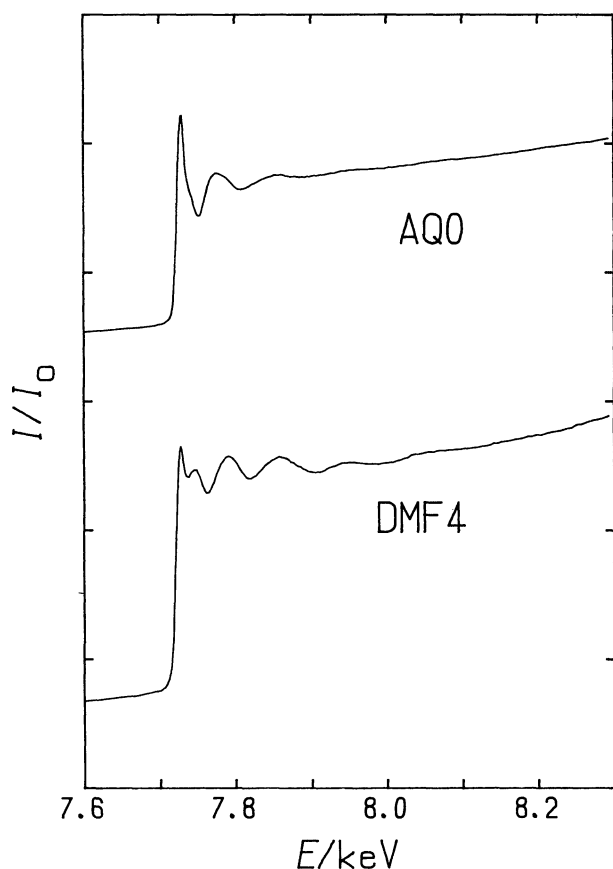

Fig. 1. The raw EXAFS spectra for sample solutions AQ0 and DMF4 of low concentration (ca. 20 mmol dm⁻³) by the fluorescence detection.
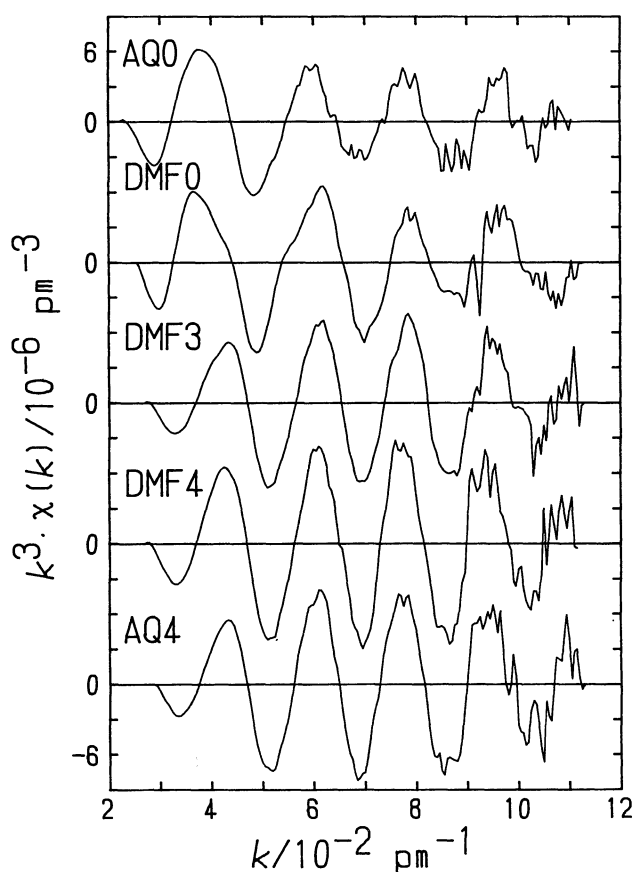

Fig. 2. The extracted EXAFS oscillations multiplied by k^3 for sample solutions. AQ0: $Co(ClO_4)_2$ in water, DMF0: $Co(ClO_4)_2$ in DMF, DMF3: $[CoCl_3]^-$ in DMF, DMF4: $[CoCl_4]^{2-}$ in DMF, and AQ4: $[CoCl_4]^{2-}$ in water.
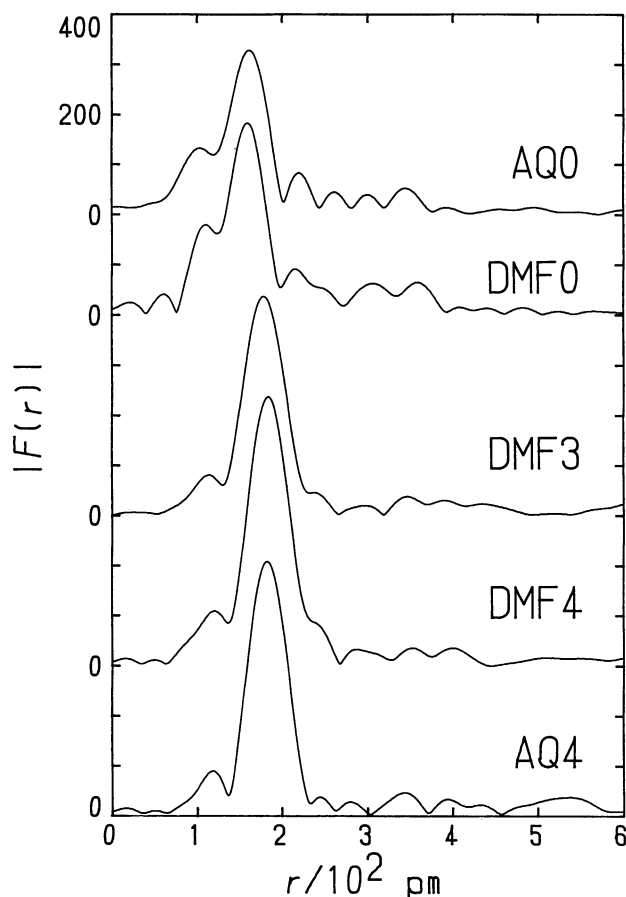
Fig. 3. The Fourier transforms $F(r)$ of the $k^3 \cdot \chi(k)$ curves shown in Fig. 2, phase shift uncorrected.

σ_j^2 is the mean square displacement of the equilibrium distance r_j and λ is the mean free path of the photoelectron. $\alpha_j(k)$ is the total scattering phase shift experienced by the photoelectron. The values of $F_j(\pi, k)$ in Eq. 4 were taken from the tables reported by Teo and Lee.[19] The phase shift $\alpha_j(k)$ was approximated by the function $a_0 + a_1 k + a_2 k^2 + a_3/k^3$,[20] where the a_0, a_1, a_2, and a_3 values were obtained by fitting the function to the phase shift values by Teo and Lee.[19] In the least-squares calculations, the parameters a_0, a_1, and λ were first determined from the standard samples of known structure. The a_2 and a_3 values were fixed at the above values during the refinement. An aqueous cobalt(II) perchlorate solution containing $[Co(H_2O)_6]^{2+}$ (AQ0) and a cobalt(II) chloride in a 13 mol dm^{-3} LiCl solution containing $[CoCl_4]^{2-}$ (AQ4) were used as the standard for the Co–O and Co–Cl atom pairs, respectively.[10,11] The parameters were then used as constants in the course of the structural analysis of unknown samples, while r, σ, and n values were optimized.

Results and Discussion

Figure 2 shows the extracted EXAFS oscillations in the form of $k^3 \cdot \chi$ (k) for solutions AQ0, DMF0, DMF3, DMF4, and AQ4. In Fig. 3, the Fourier transforms of the $k^3 \cdot \chi(k)$ values of the test solutions are depicted. The first intense peaks at 150—180 pm are ascribable to the

bonds between cobalt(II) ion and oxygen atom and/or chloride ion in the first coordination sphere.

Solutions AQ0 and DMF0 contain the solvated cobalt(II) ion in water and DMF, respectively. Both solutions show a similar pattern in intensity and phase over the k-range of the measurements (Fig. 2). A slightly different feature in the $k^3 \cdot \chi(k)$ curves between solutions AQ0 and DMF0 at 4.5 and 5.5×10^{-2} pm^{-1}, i.e. two shoulders in the curve of solution DMF0, may be due to the nonbonding Co···C (DMF) interactions. Indeed, similar shoulders due to M···C interactions were observed for the aqueous solutions involving copper(II) bidentate chelate complexes.[21] The first intense peaks around 150 pm in the Fourier transform for both solutions are also practically unchanged in intensity and positions as in Fig. 3. Therefore, the structure of solvated cobalt(II) ion in DMF may be octahedral like the hexaaquacobalt(II) ion in water[10]

According to the species distribution of the cobalt(II) chloro complexes in DMF,[3] the tri- and tetrachlorocobaltate(II) complexes are the predominant species in solutions DMF3 and DMF4, respectively. The relative amounts of the predominant complex in the solutions exceed 90%, on the basis of the molar absorption coefficients of individual cobalt(II) chloro complexes in DMF.[3] Hence, we treated solution DMF3 or DMF4 to contain only tri- or tetrachlorocobaltate(II) complex, respectively.

It has been revealed that a structure change from octahedral to tetrahedral around cobalt(II) ion occurs upon the formation of the dichlorocobalt(II) complex on the basis of the thermodynamic quantities of complexation and the electronic spectra of individual cobalt(II) chloro complexes in DMF.[3]

Very similar $k^3 \cdot \chi(k)$ and $F(r)$ curves were in fact obtained for solutions AQ4 and DMF4 as shown in Figs. 2 and 3. This is expected because the two solutions contain the four-coordinate $[CoCl_4]^{2-}$ complex.

The structure parameters of these complexes were finally determined by a least-squares calculation applied to the Fourier filtered $k^3 \cdot \chi(k)$ values over the range $4.0 < k/10^{-2}$ pm$^{-1} < 10.0$. The Fourier filtering was performed over the r-range including the main peak in the $F(r)$ curve for each sample. The phase function and the λ values were first evaluated for the Co–O and Co–Cl atom pairs from respective solutions AQ0 involving the hexaaquacobalt(II) ion[10] and AQ4 involving the tetrachlorocobaltate(II) complex of known structure.[11] In the fitting procedures, the Co–O and Co–Cl bond distances and the numbers of the relevant interactions were fixed at the interature values,[10,11] while the parameters σ, λ, a_0, and a_1 were optimized as independent variables.

The interatomic distances and Debye–Waller factors for the cobalt(II) complexes in DMF were then refined by adopting the phase function and the λ values in water evaluated above. The coordination numbers were fixed during the calculations at the given values in Table 2

Table 2.   Results of the Least-Squares Refinements of Structure Parameters for Cobalt(II)
Ion and Its Chloro Complexes in N,N-Dimethylformamide[a]

Complex	Solution	Interaction	r/pm	σ/pm	n
$[Co(H_2O)_6]^{2+}$ (in water)	AQ0	Co–O	208[b,c]	7.3(2)	6[b,c]
$[Co(dmf)_6]^{2+}$ (in DMF)	DMF0	Co–O	206(1)	6.2(1)	6[b]
$[CoCl_3(dmf)]^-$ (in DMF)	DMF3	Co–O	202(1)	6.7(6)	1[b]
		Co–Cl	227(1)	5.1(1)	3[b]
$[CoCl_4]^{2-}$ (in DMF)	DMF4	Co–Cl	229(1)	5.0(1)	4[b]
$[CoCl_4]^{2-}$ (in water)	AQ4	Co–Cl	229[b,d]	5.4(1)	4[b,d]

Standard deviations are given in parentheses. a) λ_o=630(20) and λ_{Cl}=853(38) pm. b) The values were kept constant
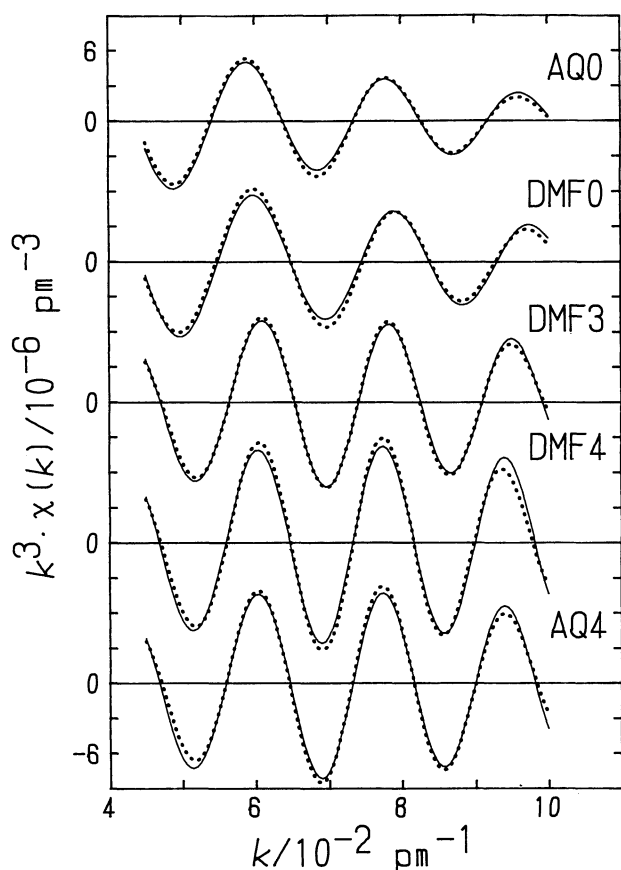during the calculations. c) Ref. 10. d) Ref. 11.

Fig. 4.   The Fourier filtered $k^3 \cdot \chi(k)$ curves of the main
peak depicted in Fig. 3. The observed values are shown
by dots and ones calculated using parameter values in
Table 2 by solid lines.

which are suggested by the spectrophotometric and
calorimetric studies.[3]   This is reasonable because, when
the coordination numbers were also optimized, the
numbers converged to 6.2(2) for the Co–O (DMF) bonds
of the solvated cobalt(II) ion (solution DMF0) and
4.4(2) for the Co–Cl bonds of the tetrachlorocobaltate(II)
complex (solution DMF4), suggesting the six- and four-
coordination structures, respectively.   The final results
are given in Table 2.   The solid curves calculated by
using the parameter values in the table well reproduce the

experimental points, as shown in Fig. 4.

The solvated cobalt(II) ion in DMF has a six-
coordinate octahedral structure and described as
$[Co(dmf)_6]^{2+}$ similar to $[Co(H_2O)_6]^{2+}$ in water.[10]   The
Co–O bond distance within $[Co(dmf)_6]^{2+}$ in DMF is
206(1) pm and is practically the same as that (208 pm)
within $[Co(H_2O)_6]^{2+}$ in water[10] within experimental
uncertainties.

Both tri- and tetrachlorocobaltate(II) complexes in
DMF have a four-coordinate tetrahedral structure.
The Co–Cl bond distances within $[CoCl_4]^{2-}$ in DMF and
in water[11] are the same and 229(1) pm.   The Co–Cl bond
length within $[CoCl_3(dmf)]^-$ in DMF is 227(1) pm and is
practically the same as that within $[CoCl_4]^{2-}$ in DMF
within experimental uncertainties.   On the other hand,
the Co–O bond length within $[CoCl_3(dmf)]^-$ is 202(1) pm
and shorter than that within six-coordinate $[Co(dmf)_6]^{2+}$.
However, the distance is much longer than that (194 pm)
within four-coordinate $[Co(hmpa)_4]^{2+}$ in hexamethyl-
phosphoric triamide (HMPA).[22].

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