X-Ray Diffraction Study of the Solvation Structure of the Cobalt(II) Ion in N,N-Dimethylformamide Solution

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

The solvation structure of Co^{2+} in N,N-dimethylformamide (DMF) has been studied by X-ray diffraction measurements on cobalt(II) and magnesium(II) perchlorate solutions of the same concentration, using an isostructural substitution method. The radial distribution function revealed three distinct peaks assigned to the oxygen, amido carbon (C_1), and nitrogen atoms of six planar DMF molecules in the first coordination sphere around the metal atom. The distance from the cobalt atom to each atom (O, C_1, N) is 213, 299, and 423 pm, respectively. This indicates that the Co–O–C_1 bond angle is 122–123° and the metal atom is close to the O–C_1–N plane of the DMF molecule.

Key words: Cobalt; N,N-dimethylformamide; Solvation; X-ray; Structure.

Introduction

Several metal ions in N,N-dimethylformamide (DMF; $HCON(CH_3)_2$) solution have recently been investigated to determine their solvation structure by means of X-ray diffraction and EXAFS (extended X-ray absorption fine structure) measurements [1–7]. In a few cases the coordination distances of the amido carbon and nitrogen atoms around Cu^{2+} [1], Cd^{2+} [2], and Li^+ [6] in the radial distribution functions (RDFs) could be estimated by the X-ray diffraction measurements. However, the detailed solvation structure and the configuration of the DMF molecules were not well-defined because of the presence of many overlapping intra- and intermolecular interactions in the RDFs.

By scattering measurements for two isostructural solutions containing metal ions with different scattering power, the part of the RDF related to the non-metal interactions, which are the same in the two solutions, can be eliminated. The difference procedure leads to a RDF involving only the interactions with the metal ion. Such an isostructural substitution technique was applied to the erbium and yttrium ions in aqueous and dimethyl sulfoxide solutions to determine their coordination structures, and was demonstrated to give useful structural information up to a distance of about 600 pm from the metal ion [8–10]. This technique is applicable for DMF solutions of divalent cobalt and magnesium ions for the following reasons.

Cobalt(II) and magnesium(II) ions coordinate six water molecules in aqueous solution with similar metal-oxygen bond lengths: $r(Co–O) = 210(3)$ pm and $r(Mg–O) = 209(4)$ pm [11]. The isostructural substitution technique has actually been applied for these metal ions in aqueous solutions [12]. The oxygen atom of DMF is a strong electron-pair donor, as indicated by a large Gutmann's donor number (DN = 26.6) [13] and can strongly coordinate to metal ions. The cobalt(II) ion forms a $[Co(dmf)_6]^{2+}$ complex [3, 5]; the magnesium(II) ion exists as an $[Mg(dmf)_6]^{2+}$ complex in the crystal structure of $Mg(ClO_4)_2 \cdot 6\,DMF$ [14].

In the present study, X-ray diffraction measurements were made for DMF solutions of $Co(ClO_4)_2$ and $Mg(ClO_4)_2$ having the same concentration. By regarding these solutions as isostructural, the RDF around the metal ions was obtained and analyzed to determine the distance of the metal ion to each atom

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of the DMF ligands. We will also discuss the structure of the second coordination sphere surrounding the hexa(dmf) complexes.

Experimental

Materials

Warning! Perchlorate salts of the metal complexes prepared in this study are potentially explosive.

All chemicals used were of reagent grade; cobalt(II) and magnesium(II) perchlorate hydrates were purchased from Soekawa Chemical Co. and DMF from Wako Pure Chemical Industries. The DMF solvates of cobalt(II) and magnesium(II) perchlorates were prepared by dissolving the metal perchlorate hydrate in DMF and precipitating with diethyl ether after concentration under reduced pressure, and recrystallized several times from DMF by the same procedure. The crystals thus obtained were dried at room temperature in a vacuum desiccator. The analysis of the metal content by EDTA titration as well as by absorption measurement at $\lambda = 200$ nm for aqueous solutions of about 10^{-5} mol dm^{-3} corresponded to the composition of $Co(ClO_4)_2 \cdot 6DMF$ and $Mg(ClO_4)_2 \cdot 6DMF$. The DMF solvent was dried for several weeks over 5 A molecular sieves. The water content in the DMF was determined to be smaller than 0.02 wt.% by the Karl-Fischer method with an AQ-5 Aquacounter of Hiranuma Sangyo Co.

Preparation and Analysis of Sample Solutions

The DMF solutions of the cobalt(II) and magnesium(II) perchlorate DMF solvates (solutions CoDMF and MgDMF) were freshly prepared before the X-ray diffraction measurements. Water as a contaminant in the solutions CoDMF and MgDMF was analyzed to be 0.20 wt.% (0.12 mol dm^{-3}) and 0.07 wt.% (0.04 mol dm^{-3}), respectively, and was considered to be negligible. The concentrations of the metal ions were determined by EDTA titration. The values of composition, density (d), and the stoichiometric unit volume (V) containing one metal ion are given in Table 1, together with those for the pure solvent. The density measurements were carried out by using a DA-310 Density/Specific Gravity Meter of Kyoto Electronics Co. or a vibrating-tube SS-D-200 densimeter of the Shibayama Scientific Co.

Table 1. Concentrations (c), densities (d), and stoichiometric unit volumes (V) of solutions at 25 °C.

Solution	c/mol dm^{-3}			d/g cm^{-3}	$V/10^9$ pm^3
	M^{2+}	ClO_4^-	DMF		
CoDMF	0.5004	1.001	12.58	1.051	3.319
MgDMF	0.5009	1.002	12.57	1.031	3.315
DMF	–	–	12.91	0.944	3.234[a]

[a] Volume including the same number of DMF molecules as contained in the stoichiometric unit volume of solution CoDMF.

X-Ray Diffraction Measurements

The X-ray diffraction measurements were made with a Rigaku $\theta - \theta$ diffractometer using Mo $K\alpha$ radiation ($\lambda = 71.07$ pm) and a focusing LiF single-crystal monochromator at 26 ± 1 °C. Intensities were collected for $1.6 < 2\theta < 140°$ (where 2θ is the scattering angle) at intervals in θ of 0.1° for $\theta < 22.5°$ and 0.25° in the remaining region. For each point at least 3×10^5 counts were accumulated, which corresponds to a statistical error of about 0.2%. Divergence slits of 1/6, 1/2, 1, and 2° were used to cover the whole θ range; scattering slits used were 1/2, 1, 2, and 4°, respectively. The liquid surface level was always adjusted to give the maximum intensity at $2\theta = 4-7°$ with the divergence slit of 1/6°; it corresponds to the liquid surface being situated at a distance of 0.027–0.029 cm above the goniometer center. The depth of the container was 2 cm; its bottom was situated below the lowest position on the effective reflection of the divergent X-ray beam at $2\theta = 140°$. Absorption coefficients of solutions were μ/cm^{-1} = 2.36 (CoDMF), 1.18 (MgDMF), and 0.66 (DMF). The absorption correction was made by use of Milberg's equation [15], but partly corrected for the deviation of the liquid surface from the goniometer center. After corrections, the intensity data for the different slits were scaled to a common data set; theoretically the scaling factors for the divergence slit pairs $2° - 1°$, $1° - 1/2°$, and $1/2° - 1/6°$ are 2, 2, and 3, respectively. The actual deviations from these values did not exceed 5%.

The low absorption of the solutions affects the scattering geometry. The true mean value of the scattering angle 2θ is larger than the geometrical angle because of the large volume contributing to the scattering. This effect may give an angle-dependent error which could amount to several pm in the derived interatomic distance, since such an absorption-dependent effect was not corrected in the present study.

Data Treatment and Analysis

The data were treated by a version of the KURVLR program [16] modified for use on an IBM PS/V [8]. After corrections for polarization and incoherent radiation, the observed intensities, $I(s)$, where $s = 4\pi \sin\theta/\lambda$, were normalized to a stoichiometric unit volume (V) without correction for multiple scattering to obtain the reduced intensities, $i(s)$. The normalization procedure was performed by the high-angle method [8–10]. Radial distribution functions, $D(r)$, were calculated according to the standard procedure described previously [8–10], where the modification function, $M(s)$, included the atomic scattering factor (f) of oxygen and a damping factor of 100 pm^2. Spurious peaks below 100 pm in $D(r)$ were removed to correct $i(s)$ for low-frequency additions.

The intensity difference function, $s\Delta i(s)$, was obtained as the difference between the normalized $s\,i(s)$ values for solutions CoDMF and MgDMF. The $i(s)$ is expressed as a function of each pair interaction having a partial structure function, $S_{p-q}(s)$, by

$$i(s) = \sum\sum n_p n_q f_p(s) f_q(s)\{S_{p-q}(s) - 1\}, \qquad (1)$$

where n is number of atoms per V, while $\Delta i(s)$ includes only the metal interaction terms as expressed by

$$\begin{aligned}\Delta i(s) = {} & 2 n_{Co} \sum n_q \{f_{Co}(s) - f_{Mg}(s)\} f_q(s) \{S_{Co-q}(s) - 1\} \\ & + n_{Co}^2 \{f_{Co}(s)^2 - f_{Mg}(s)^2\}\{S_{Co-Co}(s) - 1\}, \qquad (2)\end{aligned}$$

where n_{Mg}, $S_{Mg-q}(s)$, and $S_{Mg-Mg}(s)$ were taken to be equal to n_{Co}, $S_{Co-q}(s)$, and $S_{Co-Co}(s)$, respectively. The partial RDF, $D^{Co}(r)$, was calculated by

$$\begin{aligned}D^{Co}(r) = {} & 4\pi r^2 \varrho_0^{Co} \qquad (3) \\ & + 2 r \pi^{-1} \int_0^{s_{max}} s\,\Delta i(s)\, F(s)\, M(s) \sin(rs)\, ds,\end{aligned}$$

$$F(s) \quad = f_{Co}(s) \cdot \{f_{Co}(s) - f_{Mg}(s)\}^{-1}, \qquad (4)$$

where $\varrho_0^{Co} = (\sum n_i Z_i)^2/V$ includes terms involving the cobalt ion only and $F(s)$ is the deconvolution factor for the extraction of partial structure factors [8]. In $D^{Co}(r)$ the non-metal interactions, which are assumed to be the same in solutions CoDMF and MgDMF, are eliminated and only contributions from interactions involving the Co^{2+} ions remain.

The theoretical intensities, $i_{M-q}(r)$, for metal interactions were calculated according to Debye's expression

$$i_{M-q}(s) = 2 n_q f_M(s) f_q(s) \sin(rs)(rs)^{-1} \exp(-l^2 s^2/2), \qquad (5)$$

where l is the root mean square variation in the distance r_{M-q}. The corresponding contribution, $P_{M-q}(r)$, to the RDF was obtained by a Fourier transformation:

$$P_{M-q}(r) = 2 r \pi^{-1} \int_0^{s_{max}} s\, i_{M-q}(s)\, M(s) \sin(rs)\, ds. \qquad (6)$$

The preliminary analysis of $D^{Co}(r)$ was performed by use of $P_{Co-q}(r)$ only, regarding the solutions CoDMF and MgDMF as completely isostructural. The refinement was made by use of the following $P'_{Co-q}(r)$ in stead of $P_{Co-q}(r)$:

$$\begin{aligned}P'_{Co-q}(r) = {} & 2 r \pi^{-1} \qquad (7) \\ & \cdot \int_0^{s_{max}} s\{i_{Co-q}(s) - i_{Mg-q}(s)\}\, F(s)\, M(s) \sin(rs)\, ds,\end{aligned}$$

where a possible minor difference between distances of Co–q and Mg–q interactions was considered in $i_{Co-q}(s) - i_{Mg-q}(s)$, but the difference in the background structure was ignored. When r(Mg–q) was assumed to be 3 pm smaller than r(Co–q), this correction gave a Co–q distance only 1 pm shorter than the apparent peak distance in $D^{Co}(r)$. This is due to the fact that the atomic scattering factor of cobalt is dominant in (7), compared with that of magnesium. Equation (7) was used for the estimation of the error caused from inaccuracies of the isostructural substitution.

Results and Discussion

The reduced intensities for the solutions CoDMF and MgDMF are given in Fig. 1 together with that of pure DMF. The corresponding structure-dependent part of the radial distribution functions (RDFs), $D(r) - 4\pi r^2 \varrho_0$, is shown in Figure 2. The difference $\Delta i(s)$ between the reduced intensities of the solutions CoDMF and MgDMF is given in Figure 3. The corresponding RDF, $D^{Co}(r)$, obtained by use of (3), is shown in Figure 4. The peaks in the range up to $r = 550$ pm in $D^{Co}(r)$ are mostly due to the metal ion-ligand atoms of the first-sphere DMF molecules as depicted in Figure 5. The discrete peaks located at about 210 and 300 pm can be assigned to the oxygen and amido carbon (C_1) atoms, respectively; the peak at about

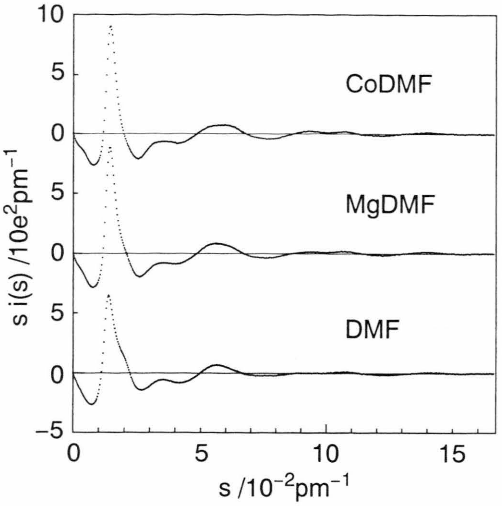

Fig. 1. Reduced intensities multiplied by s for the solutions CoDMF and MgDMF, and pure DMF.

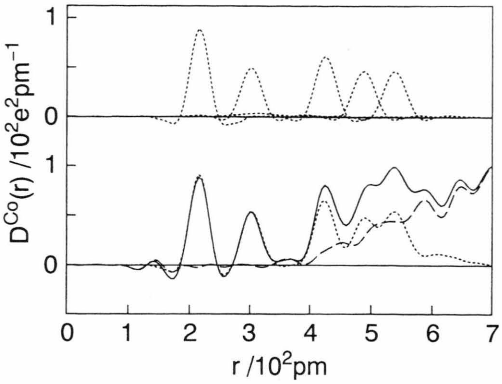

Fig. 4. The experimental partial RDF involving only interactions around the metal atom (solid line), the peak shapes calculated with the structure parameters given in Table 2 (upper dotted lines), the sum of the theoretical curves (lower dotted line), and the difference curve between the experimental and theoretical curves (dashed line).

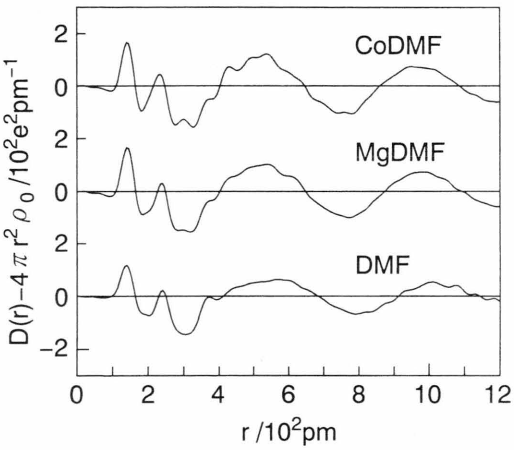

Fig. 2. The structure-dependent part of the RDFs for the solutions CoDMF and MgDMF, and pure DMF.

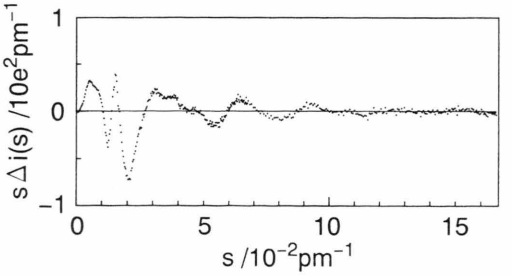

Fig. 3. The differential reduced intensities $\Delta i(s)$ multiplied by s.

420 pm corresponds to the nitrogen atom; the peaks in the region of 450 to 550 pm include the methyl carbon atoms, as explained later.

The metal-oxygen interaction peak can be fitted by a theoretical peak shape, depicted in Fig. 4, calculated with the structure parameter values (Table 2) by use of (7). The best fitting was obtained by assuming a 3 pm-difference for the M−O distance between cobalt and magnesium ($r_{Mg-O} < r_{Co-O}$), suggesting the solutions CoDMF and MgDMF to be practically isostructural. The Co−O bond length, 213 (2) pm, is somewhat longer than 208 (1) pm obtained by the EXAFS measurement [5]. This discrepancy may be partly due to the angle-dependent error in the present study, and partly to the manner of treatment for the standard sample in the EXAFS method, by which the Co−O(H_2O) distance in an aqueous solution was determined as 208 (1) pm [5], slightly shorter than the average distance of 211 (3) pm based on several X-ray diffraction measurements [6]. The estimated Mg−O distance, 210 (5) pm, seems to be somewhat longer than 204.9 (25) pm in the $[Mg(dmf)_6](ClO_4)_2$ crystal [14].

The number of the oxygen atoms, $n = 6.0(2)$, corresponds to hexa (dmf) complexes, and is supported by the same number of the amido carbon atoms (C_1) obtained from the analysis of the second peak; $r(Co-C_1) = 299(2)$ pm and $r(Mg-C_1) = 296(5)$ pm. A preliminary $D^{Co}(r)$ curve obtained by performing the absorption correction with Milberg's original

Table 2. Structural parameters of the Co(II)-DMF interactions in the first coordination sphere.

Interaction	r/pm	l/pm	n
Co–O	213 (2)^a	6 (1)	6.0 (2)
Co–C_1	299 (2)^a	13 (1)	6.0 (5)
Co–H(C_1)	305^b	24^b	6^c
Co–N	423 (2)^a	12 (1)	6^c
Co–C_2^{d}	486 (3)^a	14 (2)	6^c
Co–C_3^{d}	536 (3)^a	14 (2)	6^c

[a] The angle-dependent error due to the absorption-dependent effect (see text) is not included.

[b] Assumed; the C_1–H bond length was regarded as 109 pm [18, 19] and the H–C_1–O angle as 120°.

[c] Fixed.

[d] In the theoretical calculation, the hydrogen atoms of the methyl groups were put at four symmetrical positions around the C_2–N or C_3–N axis, of which two positions were on the O–C_1–N plane, with a weight of 0.75 for each hydrogen atom, assuming $\angle HC_2N = \angle HC_3N = 109.5°$ and $l(M\text{–}H) = 24$ pm.

equation [15] lay somewhat lower in the region of 250 to 400 pm, but the peak positions were the same within 1 pm as in Fig. 4, and the number of C_1 atom estimated was virtually 6. The other peaks due to the interactions in the first coordination sphere were analyzed by assuming six DMF ligands.

Configuration of the DMF Molecules in the First Coordination Sphere

The second and the third peaks in $D^{Co}(r)$, corresponding to the amido carbon (C_1) and nitrogen atoms, are fairly sharp. This suggests that the configuration of each coordinated DMF molecule around the metal atom is uniform with regard to the M–O–C_1 bond angle ($\angle MOC_1$) as well as the dihedral angle between the M–O–C_1 and O–C_1–N planes. The Co–C_1 distance, 299 (2) pm, leads to $\angle CoOC_1 =$ 122–123° by considering the C_1–O bond lengths (125–124 pm) from crystal structures (Table 3). The Co–O–C_1 angle is in agreement with the corresponding M–O–C_1 angles, 123° for the $[Cd(dmf)_6]^{2+}$ complex in solution [2] and 123.2 (20)° (averaged) for the complexes in crystals B and C [17].

The Co–N distance was determined to be 423 (2) pm from the analysis of the third peak in $D^{Co}(r)$. This indicates that the nitrogen atom is situated *trans* to the metal atom in the O–C_1–N plane. Assuming this geometry, we can estimate the Co–N distance as 425 to 429 pm, close to the experimental one by use of the structure parameters of a DMF molecule (Table 3) [14, 17–19] as well as the Co–O and Co–C_1 distances (Table 2).

The two peaks in the region of 450 to 550 pm in $D^{Co}(r)$ are presumed to be attributed to the methyl carbon atoms (C_2 and C_3) of the coordinated DMF molecule, since their peak positions are close to those expected from the planar structure of DMF in the crystalline solvates [17]. If we use the structure parameters of crystals B and C (Table 3) [17] in addition to the structural information obtained in the present study, the Co–C_2 and Co–C_3 distances can be estimated as 482–490 and 534–539 pm, respectively, in good agreement with the experimental peak positions (Table 2).

Consequently, the configuration of the DMF molecules in the first coordination sphere of Co(II) can be depicted as Figure 5. Its structure parameters are summarized in Table 2. The peak shape calculated for each interatomic interaction by (7) is drawn in Fig. 4, together with the sum of the theoretical curves.

The Co(II)-DMF interactions, having a definite configuration in spite of the bulkiness of the DMF molecule and its thermal movement in solution, are

Table 3. Bond lengths (pm) and bond angles (°) within the DMF molecules in the crystal structure of $[Mg(dmf)_6](ClO_4)_2$ (*A*)^a, $[ZnCl_2(dmf)_2]$ (*B*)^b, and $[CuCl_2(dmf)_2]_2$ (*C*)^b and in Liquid DMF^{c,d}.

	In the crystals		In liquid
	A	*B* and *C*^{e}	DMF
O–C_1	123.9 (24)	124.8 (8)	124 (2)
C_1–N	130.8 (22)	131.2 (7)	135 (2)
N–C_2	142.7 (47)	145.7 (7)	145 (2)
N–C_3	143.0 (36)	145.3 (5)	145 (2)
$\angle OC_1N$	124.2 (15)	123.7 (6)	121^c, 130^d
$\angle C_1NC_2$	120.6 (28)	121.2 (5)	116
$\angle C_1NC_3$	121.1 (22)	121.4 (3)	116
$\angle C_2NC_3$	118.0 (10)	117.3 (3)	128^c, 129^d

^{a} [14]. ^{b} [17]. ^{c} [18]. ^{d} [19]. ^{e} Average values in crystals *B* and *C*.

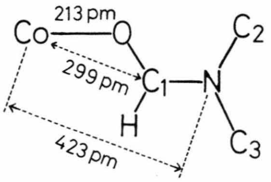

Fig. 5. The structure of the DMF molecule coordinated to the cobalt atom; the methyl hydrogen atoms are excluded.

inferred to be attributed to the fairly strong and directional Co–O bond as well as the fairly rigid and planar structure of DMF. The *trans* form between Co and N atoms is probably due to the steric repulsion with the C_2 methyl group. The value of $l(\text{Co–N})$, which was found to be comparable to $l(\text{Co–C}_1)$ despite the anticipated increase in thermal motion, is based on such a *trans* form. A rotation of the DMF molecule around the Co–O bond axis may be possible, but may be sterically hindered due to the DMF–DMF repulsion. Such a rotation would, however, not much affect the Co–DMF configuration observed.

DMF Molecules in the Second Coordination Sphere

The distribution of molecules in a second coordination sphere, appearing at a distance larger than about 400 pm in $D^{\text{Co}}(r)$, considerably overlaps with the nitrogen and methyl group atoms of the coordinated DMF molecules, as revealed by the difference curve between the experimental and theoretical curves in Figure 4. This indicates that several second-sphere DMF molecules penetrate into the hollows on the surface of the hexa(dmf) complex. The perchlorate ions may rarely penetrate in this region because, from the conductivity measurements of the DMF solutions of $Co(ClO_4)_2$ at 25 °C [20], the ion-association constant was practically zero and the closest distance of approach of ions in the theoretical equations was about 800 pm [21].

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