

^1H NMR 測定による DMF-水 溶媒中でのシス-ジクロロビス
(1,10-フェナントロリン)イリジウム(III)クロライドとその
関連錯体の溶媒誘起分子変形の研究

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A Study of the Solvent-Induced Molecular Deformations
of cis-Dichlorobis (1, 10-phenanthroline) Iridium(III)
Chloride and Related Complexes in DMF-Water Binary
Solvents by ^1H NMR Measurements

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INTRODUCTION

It is an important problem to control characters of the lowest electronic excited states of metal complexes, because metal complexes have various electronic excited states exhibiting different chemical reactivities. Many emission studies have revealed that excited characters of bis (phenanthroline) iridium (III) complexes are sensitive to solvent properties and temperature.¹

The author has reported that these complexes show an especially complicated solvent dependence of the emission lifetimes and spectra by varying compositions of DMF-water binary solvents.² A change of the complex structure with a variation of the solvent character has not examined in detail. The present paper reports a ^1H NMR study of cis-[IrCl₂L₂]Cl (L = phenanthroline (phen), 4, 7-dimethylphenanthroline (Mephen) and 5, 6-Mephen) in an attempt to analyse the conformational properties of these complexes in DMF-d₇-D₂O binary solvents.

EXPERIMENTAL

Materials

Cis-dichlorobis (1, 10-phenanthroline) iridium (III) chloride trihydrate (1)³ and cis-dichlorobis (5, 6-dimethyl-1, 10-phenanthroline) iridium (III) chloride trihydrate (2)^{1c} were prepared following the procedures of the literature.

Cis-dichlorobis (4, 7-dimethyl-1, 10-phenanthroline) iridium (III) chloride pentahydrate (3) was synthesized in an analogous manner to that of the complex of 5,

6-Mephen. N, N-Dimethylformamide-d₇ and D₂O were obtained from Merck Co. (99% deuterated for DMF and 99.75% deuterated for D₂O).

Measurements

The ¹H NMR measurements were carried out for the complex solutions of $3 \times 10^{-3} \sim 10^{-2}$ mole/l on a JEOL JNM-GX400 spectrometer at 20°C. TSP (deuterated sodium 3-trimethyl-silypropionate-2, 2, 3, 3-d₄) was used as an internal calibrant for the solvents with 0, 0.024 and 0.007 of mole fraction of DMF (χ_{DMF}) and TMS was an internal calibrant for the solvents with 0.09 and 0.41 of χ_{DMF} and for pure DMF-d₇. DMF signals were deleted by the method of water eliminated Fourier transformation. Resolution of the chemical shifts is 0.0008 ppm.

RESULTS AND DISCUSSION

Assignment of NMR spectrum

Fig. 1 shows the observed proton spectrum of the complex 1 in D₂O and the numbering of the protons. The spectrum is composed of eight signals corresponding to the eight symmetrically independent protons. Two quartets can be assigned to H-3 and H-8 with two ortho-site protons. The spectra of the complexes 2 and 3 are analogous to that of the complex 1 lacking in the corresponding signals of methyl substituted proton pairs, (H-5, H-6) and (H-4, H-7), respectively. From the results, the six doublet signals of the complex 1 are divided into three groups of proton pairs. The largest effect separating the paired signals is an anisotropic magnetic field induced by the π electrons of the neighbor ligand.

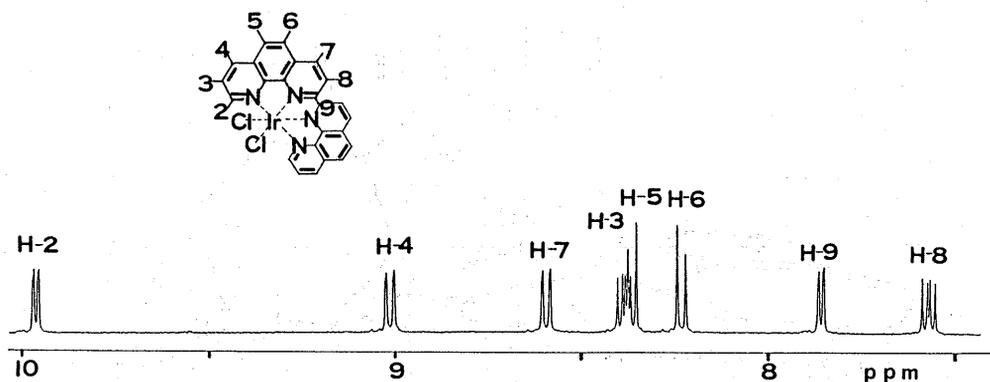


Figure 1. Molecular structure and 400 MHz ¹H NMR spectrum of complex 1 in D₂O at 20 °C.

The theoretical treatments of the magnetic field induced by the π electrons have been investigated in terms of magnetic dipoles⁴ and ring-currents⁵. A more elaborate treatment, Coupled Hartree-Fock method⁶, was studied, but for large ligands it is very difficult to get accurate molecular wave functions indispensable for the calculation. In the present paper, the ring-current approximation was adopted, because the magnetic

dipole model gives less precise result in a short-range region due to an ambiguity of the dipole position.

The complex structure used is shown in Fig. 2. The metal-N(phen) distance (1.94 Å) and the phenanthroline structure were taken from the reported data of the related *cis*-bis(phen) metal (III) complexes.⁷ The reported coordination angles scarcely differ from an octahedral coordination, so first an octahedral one was assumed, putting N atoms of ligand A at (0, 0, 1.94) and (0, 1.94, 0), and N atoms of ligand B at (1.94, 0, 0) and (0, -1.94, 0) of x, y and z coordinates in Å unit. The reported structures of the pyridine-ring and benzene-ring are almost the same in the phenanthroline ligand, so that for the pyridine and benzene-rings of ligand A the same radius of the circulating ring currents was used as that reported for benzene by Bovey⁵; 1.64 Å is the radius and 1.28 Å is the spacing between two loops representing the two doughnut-like clouds of the π electrons of benzene.

The calculated magnetic field induced by ligand A is displayed as a contour map in Fig. 3, in terms of the chemical shift (in ppm). Fig. 3 (a) shows the magnetic contour-lines on xy plane where ligand B lies and Fig. 3 (b) shows the contourlines on plane A vertical to xy plane through H-9. As is seen in Fig. 3 (a), H-2 ~ H-5 of ligand B are

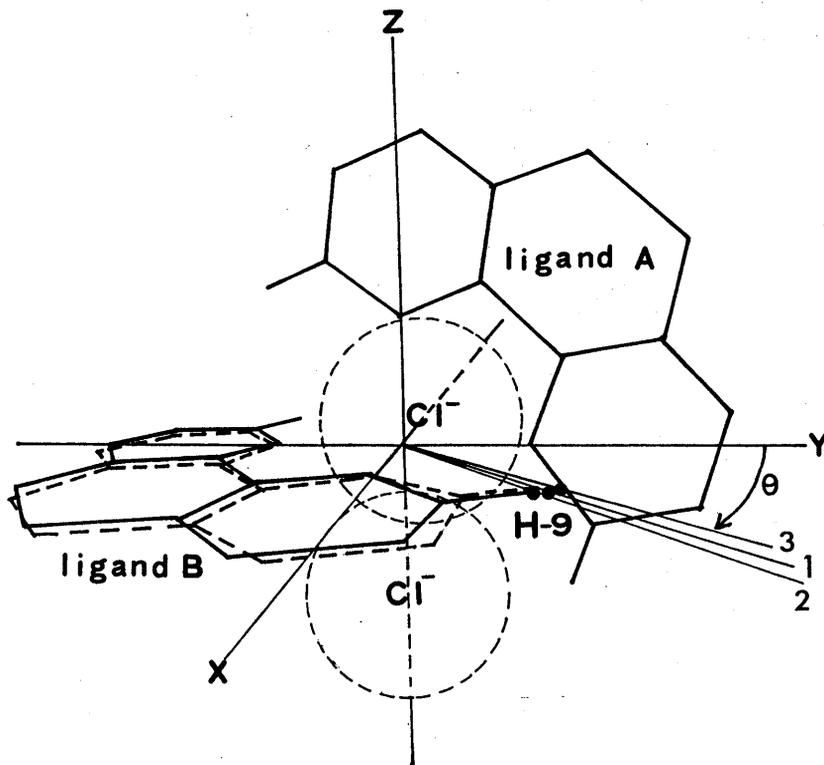


Figure 2. Structure of complex 1. Positions of ligand B proposed by analyses of data in DMF-d₇ (solid line) and in D₂O (dashed line): Ir-(H-9) line in octahedral coordination (1); in DMF-d₇ (2); in D₂O (3).

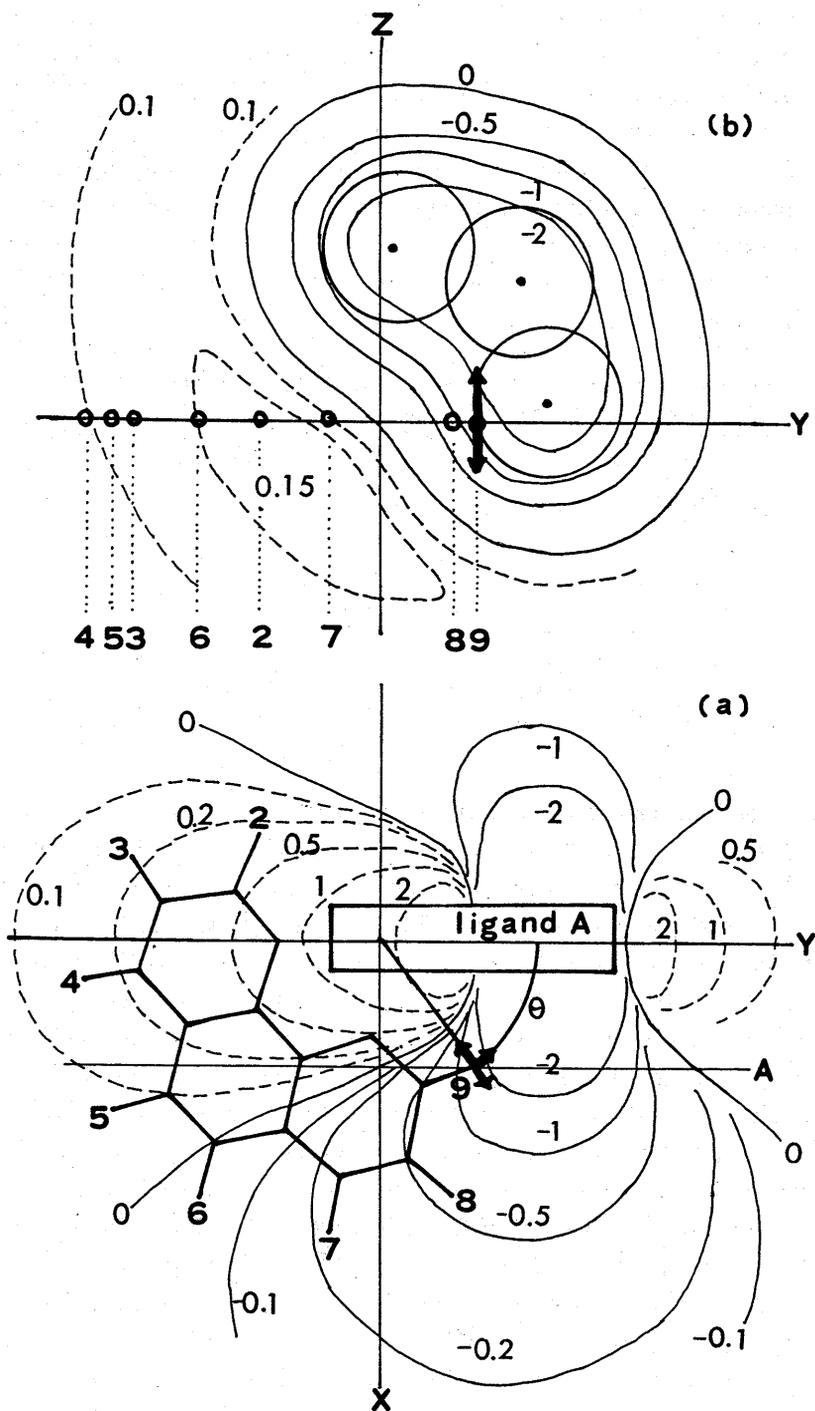


Figure 3. Calculated contourlines of induced magnetic field due to ligand A (in ppm). Highfield (solid) and lowfield (dashed) contourlines ; (a) on xy plane ; (b) on plane A parallel to yz plane, through H-9. Arrows show movements of ligand B (see in text).

affected by lowfield effects (dashed lines), while H-6 ~ H-9 locate in the region of highfield effects (solid lines). For the proton pairs of (H-2, H-9), (H-3, H-8), (H-4, H-7) and (H-5, H-6), the calculated separations of the chemical shifts are 1.97, 0.80, 0.42 and 0.13 ppm and the corresponding observed values in D₂O are 2.10, 0.82, 0.42 and 0.14 ppm. This good coincidence verifies validity of the ring-current model for an evaluation of an interligand magnetic interaction. The higher-field signal in each pair can be assigned to the proton lying nearer to the neighbor ligand. The assignment is shown in Fig. 1. The observed chemical shifts of the complexes 1-3 in DMF-d₇ and D₂O are summarized in Table 1.

Table 1. Observed chemical shifts (ppm) of phenanthroline protons of the complexes 1-3 in DMF₇ and in D₂O

| | complex 1 | | complex 2 | | complex 3 | |
|-----|--------------------|------------------|--------------------|------------------|--------------------|------------------|
| | DMF-d ₇ | D ₂ O | DMF-d ₇ | D ₂ O | DMF-d ₇ | D ₂ O |
| H-2 | 10.14 | 9.97 | 10.11 | 9.91 | 9.97 | 9.76 |
| H-4 | 9.26 | 9.02 | 9.34 | 9.16 | | |
| H-7 | 8.87 | 8.60 | 8.93 | 8.73 | | |
| H-5 | 8.61 | 8.38 | | | 8.65 | 8.51 |
| H-3 | 8.60 | 8.40 | 8.56 | 8.37 | 8.42 | 8.22 |
| H-6 | 8.49 | 8.24 | | | 8.53 | 8.37 |
| H-9 | 8.39 | 7.87 | 8.29 | 7.76 | 8.22 | 7.64 |
| H-8 | 7.81 | 7.58 | 7.76 | 7.55 | 7.64 | 7.41 |

Temperature and solvent dependence of chemical shift

By using D₂O and DMF-d₇-D₂O with $\chi_{\text{DMF}} = 0.072$ and 0.091 as solvents, the temperature dependence was measured of the proton spectrum of the complex 1 at 20, 40 and 55°C. With increase from 20 to 55°C, the H-9 signal shows 0.10 ppm highfield shift and the H-2 ~ H-8 signals and the proton signals of DMF show a common highfield shift of 0.06 ppm in all the three solvents. Any broadening or intensity changes of the signals suggesting some chemical reactions were not observed.

Varying χ_{DMF} of the DMF-d₇-D₂O binary solvents as 0, 0.0024, 0.007, 0.09, 0.41 and 1, the spectra of the complexes 1-3 at 20°C were measured. The relations between the chemical shift (δ) and the solvent composition (χ_{DMF}) are shown in Fig. 4 and the spectra of the complex 3 in these solvents are compared in Fig. 5. As is seen in Figs. 4(a)-4(c), the H-3 ~ H-8 signals show very similar shifts against χ_{DMF} : the change of δ from $\chi_{\text{DMF}} = 0$ to 1 are lowfield shifts of 0.235 ± 0.035 , 0.20 ± 0.02 and 0.18 ± 0.04 ppm for the complexes 1, 2 and 3. It is noteworthy that the H-9 signal behaves quite differently from these signals; with increase of χ_{DMF} from 0 to 1, it shows a lowfield shift of 0.52-0.58 ppm more than twice compared with the H-3 ~ H-8 signals. The observed results are remarkable in the respect that composition change of the binary solvents brings about a special effect only for H-9 among the eight protons.

Table 2. Solvent effects and expected signal shift

| Interaction | Solvent-induced shift of proton signals |
|--|---|
| (1) Van der Waals interaction between solute and solvent | common shifts for eight protons |
| (2) polarization effect induced by +1 charge of complex | common shifts for eight protons |
| (3) polarization effect induced by dipole moment of complex ^a | dependent on C-H directions but not special for H-9 |
| (4) hydrogen bond between water and Cl anion | H-7 ~ H-9 are affected in a similar extent, since the effect originates in the electronic polarization of pyridine moiety induced by trans-site Cl anion ^b |
| (5) dimer formation between complexes ^c | H-5 = H-6 > H-9 |
| (6) deformation of interligand geometry (see text) | H-9 > H-3 ~ H-8 |
| the observed result | H-9 > H-3 ~ H-8 |

^aRef. 8, ^bRef. 9 reported the shift of the signals induced by the trans-site ligand.

^cRef. 10.

Examination of solvent-solute interaction

In order to discuss the observed solvent dependence, the probable solvent effects and the expected shifts of the signals under the effects are summarized in Table 2. As is described in the table, the interactions (1)-(5) can not explain the special shift of the H-9 signal. A model was, then, proposed that the variation of the solvent causes a deformation of the interligand geometry of the complex (interaction(6) in Table 2). It is evident from the contourlines in Fig. 3(a) that H-9 lying just above the neighbor ligand-plane accepts the largest influence among the eight protons by this deformation.

Analysis of solvent dependence by a ring-current model

A relation between the ligand position and the chemical shifts of H-2 ~ H-9 was examined quantitatively. Fixing ligand A in the position, ligand B was moved along the three orthogonal directions described by the arrows in Figs. 3(a) and 3(b). Each Ir-proton distance was changed within ± 0.2 Å. A ligand as a whole was rotated by θ on xy plane about z axis within $\pm 10^\circ$, and shifted vertically from xy plane within ± 1 Å. As can be grasped from Fig. 3, the rotation θ gives the largest changes for every protons; the magnetic field at the H-9 position varies by about 1 ppm with the θ change of 10° , while the other two movements give changes of less than 0.1 ppm. Therefore, θ is a good parameter, when the effect of the interligand conformation on the chemical shifts is discussed.

In order to compare the observed chemical shifts (δ_{obsd}) with the calculated values, the $\Delta(i-j)$ values for the proton pairs of (2, 9), (3, 8), (4, 7) and (5, 6) were used ;

$$\Delta(i-j) = \delta(H-i) - \delta(H-j)$$

and $\delta(H-i) = \delta_0(H-i) + \delta_\pi(H-i) + \delta_s$

where $\delta(H-i)$ is the chemical shift under solvent interaction, $\delta_0(H-i)$ denotes the chemical shift without the effect of the neighbor ligand, $\delta_\pi(H-i)$ denotes the induced shift by the neighbor ligand and δ_s denotes a common solvent shift. From C_{2v} symmetry of phen, $\delta_0(H-i)$ has the same value for the paired protons, so that $\Delta(i-j)$ depends only on the terms of $\delta_\pi(H-i) - \delta_\pi(H-j)$, which the above calculations can evaluate. In Table 3 the $\Delta(i-j)$ values obtained from the δ_{obsd} values are listed for DMF-d₇ and D₂O ; the $\Delta(2-9)$ values depend much on solvent. Here, the θ value to reproduce the observed $\Delta(i-j)$ values in DMF-d₇ and D₂O was determined. The values of the best coincidence are shown in Table 3 ; θ is 55.5° for DMF-d₇ and 51.7° for D₂O. The structures with the proposed θ are shown in Fig. 1 by the solid-line structure for DMF-d₇ and the dashed-line one for D₂O. Ligand B locates closer to ligand A by about 4 degrees in D₂O than in DMF-d₇.

Table 3. Calculated and observed values of $\Delta(i-j)$ (ppm) (θ : an angle between y axis and Ir-(H-9) line)

| complex 1 | | | | |
|---------------|-----------------------|---------------------|-----------------------|-----------------------|
| $\Delta(i-j)$ | observed | | calculated | |
| | in DMF-d ₇ | in D ₂ O | $\theta = 55.5^\circ$ | $\theta = 51.7^\circ$ |
| $\Delta(2-9)$ | 1.75 | 2.10 | 1.75 | 2.10 |
| $\Delta(3-8)$ | 0.79 | 0.82 | 0.75 | 0.83 |
| $\Delta(4-7)$ | 0.39 | 0.42 | 0.40 | 0.44 |
| $\Delta(5-6)$ | 0.12 | 0.14 | 0.12 | 0.13 |

For both solvents, the agreements between the observed and calculated $\Delta(i-j)$ values are very good for all the four proton pairs. This fact confirms the model that the solvent-induced conformational change governs the anisotropy of the present solvent dependence.

From the observed $\delta - \chi_{\text{DMF}}$ relations (Figs. 4(a)-(c)), it is expected that the interligand deformation is remarkable in the region of a small χ_{DMF} . The emission lifetimes of the present complexes were reported to exhibit a large solvent dependence in the χ_{DMF} region.² For metal complexes with complicated electronic states, a structure change even small affects the energy transfer rates, so that a conformational change must be taken into consideration to analyse the solvent dependence of the energy

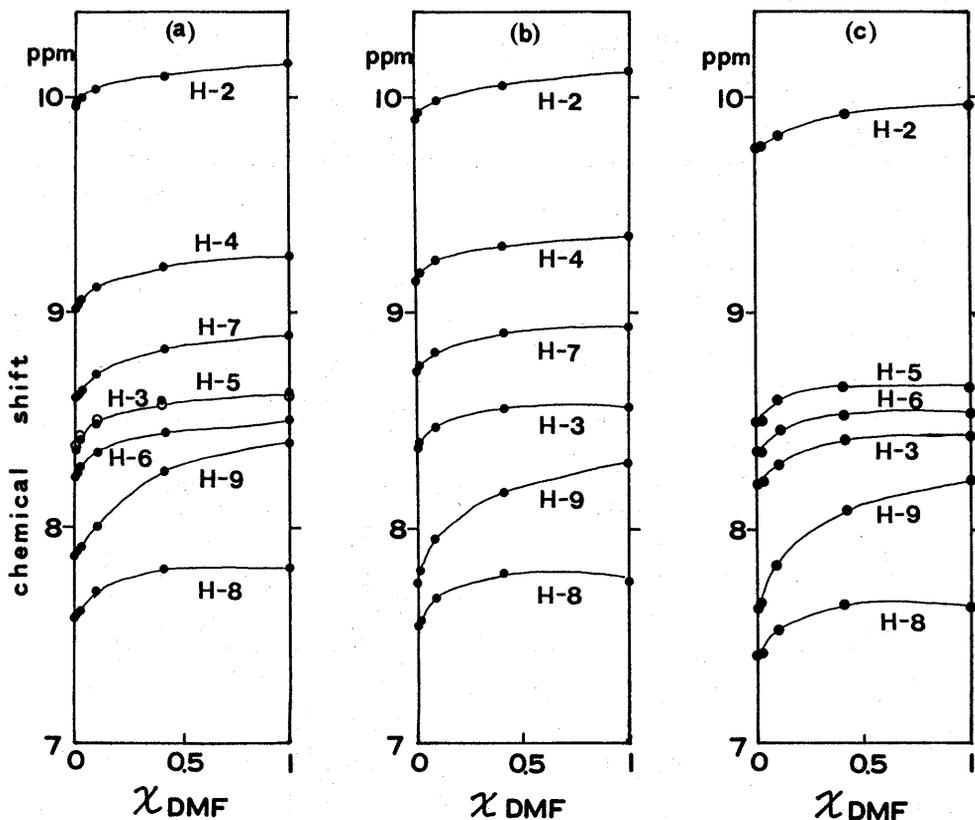


Figure 4. $\delta - \chi_{\text{DMF}}$ relations (a) complex 1, (b) complex 2, and (c) complex 3.

transfer mechanism.

Acknowledgements

This work was carried out under a cooperation with Dr. J. Nakamura in the Institute of Physical and Chemical Research. The authors would like to thank Mrs. T. Chijimatsu in that Institute for the measurements of NMR spectra and Dr. S. Tachiyashiki of Kagawa Nutrition College for the program calculating the magnetic effect.

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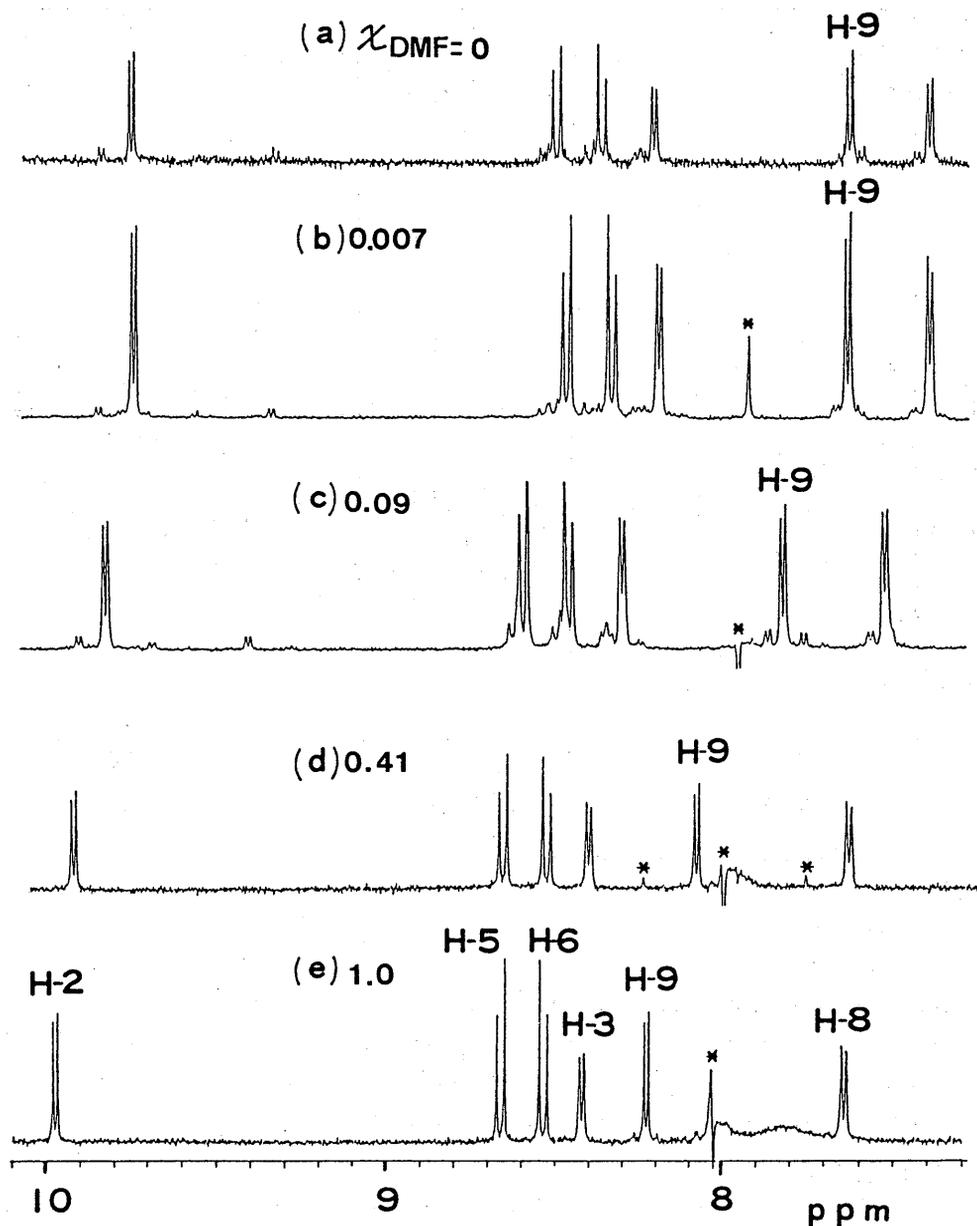


Figure 5. Solvent dependence of 400 MHz ^1H NMR spectra of complex **3**, in DMF- d_7 - D_2O binary solvents. The asterisks denote DMF signals.

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