

DMF-水 重水素化二成分溶媒におけるジス-[IrCl₂(bpy)₂]Cl の ¹H NMR スペクトルの溶媒依存性解析

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Analysis of Solvent Dependence of ¹H NMR Spectra of cis-[IrCl₂(bpy)₂]Cl in Deuterated DMF-Water Binary Solvents

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INTRODUCTION

Extensive studies have been reported about electrochemical, photochemical and photophysical properties with respect to transition-metal complexes containing 2, 2'-bipyridine (bpy) and 1, 10-phenanthroline (phen) ligands.¹ We have carried out photophysical and ¹H NMR studies of the iridium(III) complexes with bpy and phen ligands using DMF-water binary solvents.² In the present paper, we analysed the solvent dependence of ¹H NMR spectra of [IrCl₂(bpy)₂]Cl in deuterated DMF-water solvents in terms of a model of induced magnetic field due to the aromatic ligands. It was revealed that bipyridine ligand shows a small change of the structure with variation of solvent composition.

EXPERIMENTAL

The preparation of cis-[IrCl₂(bpy)₂]Cl · 2H₂O was described in a previous paper.² ¹H NMR measurements were performed on JEOLGX400 spectrometer at 20°C. TSP (deuterated sodium 3-trimethylsilylpropionate-2, 2, 3, 3-d₄) was used as an internal calibrant for the solvents with 0-0.007 of x_{DMF} (mole fraction of DMF in binary solvent) and TMS for the solvents with more than 0.09 of x_{DMF} .

Induced magnetic field due to π electrons of ligand A on the positions of the ligand-B protons, was calculated by a model of a circulating current proposed by Johnson and Bovey³; the steric conformation of ligands A and B is shown in Figure 1. With respect to a complex structure, we assumed Ir-N distance as 2.10 Å and N-Ir-N angle (angle I in Figure 1) as 78° based on the reported structure of cis-bis (bpy)

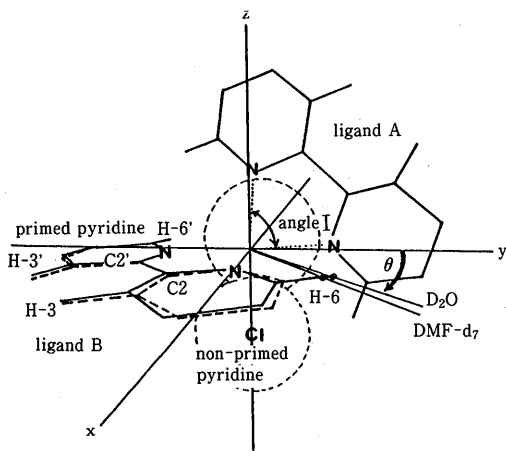


FIG. 1. Structure of $[\text{IrCl}_2(\text{bpy})_2]\text{Cl}$. The solid and dashed structures of ligand B are the estimated positions based on the calculated magnetic field in DMF-d_7 and in D_2O .

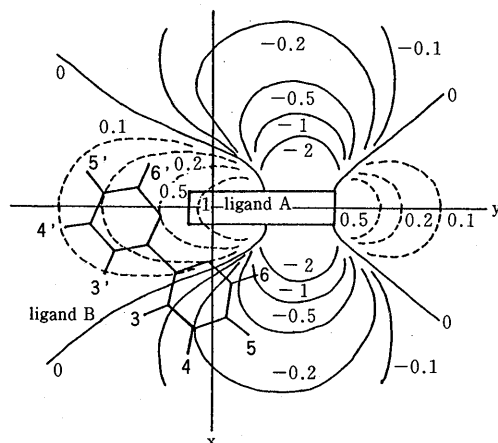


FIG. 2. Calculated lines of induced magnetic field due to ligand A. The solid and dashed lines denote highfield and lowfield shift in ppm.

complex.^{4a} Ligands A and B were put on yz and xy planes such that each symmetric axis of ligand coincides with $y=z$ and $y=-x$, respectively. On the basis of this complex structure, we replaced ligand A by two ring currents with 1.39 Å radius at the centers of the two aromatic rings of ligand A, and calculated the induced magnetic field.

RESULTS AND DISCUSSIONS

Induced Magnetic Field due to Ligand A. Figure 2 shows the calculated lines of magnetic field on xy plane in the vicinity of the ligand-B protons. The numbering of eight protons of bpy is described together. The magnetic field is represented by the chemical shift (δ_{rc}) in ppm, and the solid and dashed lines denote highfield and lowfield shifts induced by ligand A. The primed four protons of ligand B locate in the region of lowfield shift, while the non-primed four protons lie in the region of highfield shift. A large highfield shift for H-6 is noticeable.

Solvent Dependence of Observed Chemical Shift. The proton NMR spectra were measured using the deuterated DMF-water solvents with $x_{\text{DMF}} = 0, 0.0024, 0.007, 0.09, 0.41$ and 1. The observed values of chemical shift (δ_{obsd}) in DMF and in D_2O are shown in Table I.

Figure 3 shows solvent shift of δ_{obsd} referred to DMF-d_7 as a function of x_{DMF} . All signals were found to shift to higher shift with decrease of x_{DMF} of the solvent. H-6, H-3 and H-3' show stronger solvent dependence by more than twice compared with the other protons. For the other five protons, the δ_{obsd} values are analogous

Table I. Observed Chemical Shifts (ppm) of Bipyridine Protons of $[\text{IrCl}_2(\text{bpy})_2] \text{Cl}$ in DMF-d_7 and in D_2O

	in DMF-d_7	in D_2O
H-6	8.13	7.75
H-6'	9.82	9.66
H-5	7.62	7.42
H-5'	8.19	8.04
H-4	8.29	8.11
H-4'	8.58	8.44
H-3	8.96	8.55
H-3'	9.05	8.67

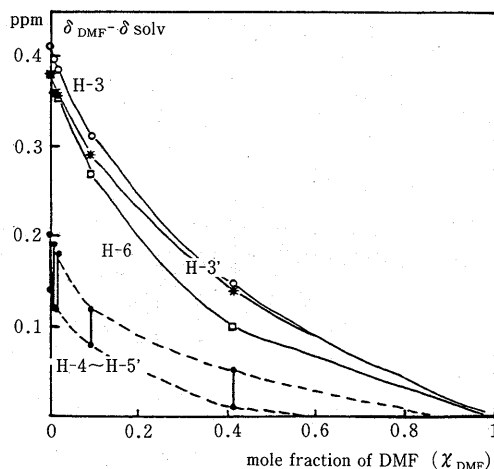


FIG. 3. Solvent shift of δ_{obsd} referred to the value in DMF-d_7 against χ_{DMF} .

and denoted by bars. Their solvent dependence may be considered to represent an uniform portion of solvent effect to all protons. As is shown in Figure 2, H-6 locates in a region where the intensity of the magnetic field changes suddenly, while H-3 and H-3' are in a region of gentle change on the contrary. So the variation of the interligand steric conformation can presumably explain the large solvent shift of δ_{obsd} of H-6 but not the shifts of H-3 and H-3'.

If a steric conformation between two pyridines in one bipyridine molecule changes, the magnetic field on H-3 by the ring current of the primed pyridine varies. X-ray studies of cis-bis(bpy) complexes⁴ revealed that the bond lengths of a bipyridine showed no change but angles determining the relative conformation of the two pyridine halves varied to considerable extent from complex to complex⁴; the N-Ir-N angle (angle I in Figure 1) takes a value of $73^\circ \sim 83^\circ$, the dihedral angle between two pyridine planes (angle II) of $0^\circ \sim 18^\circ$ and the rotation angle about C2-C2' bond of bipyridine (angle III) of $0^\circ \sim 8^\circ$. Then, we calculated the δ_{rc} value of H-3 due to the primed pyridine ring by changing the angles I~III (θ). The results were shown in Figure 4; the changes of θ corresponding to the angles I~III are described as (1), (2) and (3) and the arrows denote the ranges of the reported values by X-ray studies. The δ_{rc} value of H-3 is most sensitive to the N-Ir-N angle and depends scarcely on the dihedral angle.

Figure 3 shows that the δ_{obsd} values of H-3 and H-3' in D_2O shift to highfield from those in DMF-d_7 by 0.2 ppm in addition to the highfield shift of 0.17 ppm due to uniform solvent effect. The shift of 0.2 ppm can be interpreted by the change of the bipyridine structure according to the results described in Figure 4.

The H-6 signal in D_2O showed a 0.2 ppm highfield shift from the value in DMF-d_7

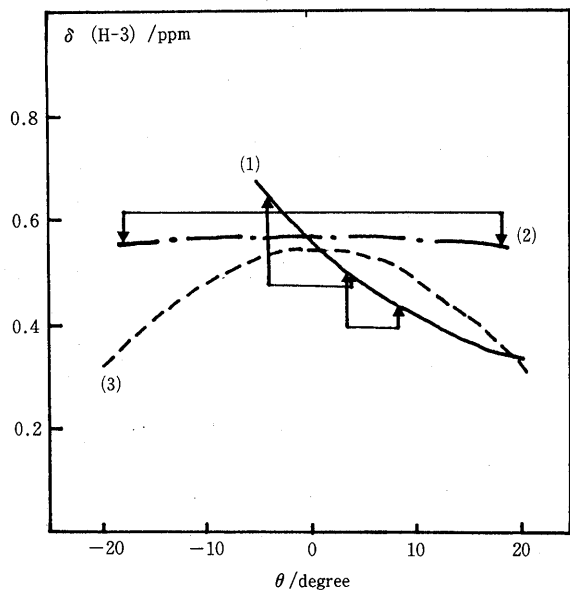


FIG. 4. Calculated magnetic effect on H-3 due to the primed pyridine in ppm for molecular deformations (1), (2) and (3).

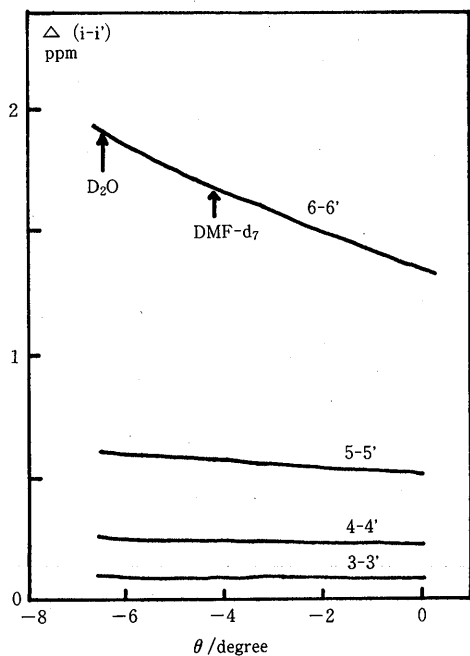


FIG. 5. Calculated $\Delta(i-i')$ values against the rotation angle (θ) of ligand B on xy plane.

Table II. Calculated and Observed Values of $\Delta(i-j)$, Differences between the Chemical Shifts of the H-i Proton and H-j Proton (ppm) (θ : Angle between y Axis and Ir-(H-6) Line)

$\Delta(i'-i)$	observed		calculated	
	in DMF-d ₇	in D ₂ O	$\theta = 50.8^\circ$	$\theta = 48.5^\circ$
$\Delta(6'-6)$	1.69	1.91	1.69	1.91
$\Delta(5'-5)$	0.57	0.62	0.58	0.62
$\Delta(4'-4)$	0.29	0.33	0.26	0.27
$\Delta(3'-3)$	0.09	0.12	0.12	0.13

in addition to uniform solvent effect (Figure 3). We calculated the induced magnetic field on the ligand-B protons due to ligand A by changing the position of ligand B (Figure 1). The δ_{rc} value changes most strongly by the rotation of ligand B on xy plane, compared with the change of the Ir-N distance and the proton movement to upper and lower side of xy plane. Absolute values of δ_{obsd} are influenced by a lot of factors. We can eliminate the factors uniform to protons i and i' , by taking the differences, $\Delta(i-i')$, between the δ_{obsd} values of H- i and H- i' ($i=3, 4, 5$ and 6). The values of the difference may be attributed to a contribution of the induced magnetic field (δ_{rc}) due to ligand A. Figure 5 shows the calculated values of the difference between δ_{rc} 's of H- i and H- i' against the rotation angle (θ) on xy plane. Here, we determined the angle θ so as to reproduce the observed $\Delta(6-6')$ value, since δ_{rc} of H-6 is most sensitive to the ligand-B position. The observed and calculated $\Delta(i-i')$ values listed in Table II show a good coincidence with each other. The positions of ligand B are shown in Figure 1 by the solid (DMF- d_7) and dashed (D_2O) lines. Bipyridine B locates more closely to ligand A in D_2O than in DMF- d_7 .

CONCLUSION

Many discussions have been reported about solvent effect of the emission properties of this complex. In this work, it became clear that the complex structure actually changes with variation of solvent composition, based on an analysis of solvent dependence of 1H NMR spectra. The structural change is small but may play a significant role relating to energy transfer processes.

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Reference

- 1) "Inorganic and Organometallic Photochemistry", M. S. Wrighton, Advances in Chemistry Series 168
- 2) Ohashi, Y. and Nakamura J. : Solvent Effect on Excited States of $[IrCl_2(bpy)_2]Cl$, $[IrCl_2(phen)_2]Cl$ and Related Complexes, Chem. Phys. Lett., 109, 301-305, 1984.
- 3) Johnson, C. E. and Bovey, F. A. : Calculation of Nuclear Magnetic Resonance Spectra of Aromatic Hydrocarbons, J. Chem. Phys., 29, 1012-1014, 1958.
- 4) (a) Bottomley, F., Brooks, W. V. F., Paez, D. E., White, P. S. and Mukaida, M. J. Chem. Soc. Dalton, 186, 2465, 1983.
(b) Belser, P., Zelewsky, A. and Zehnder, M. Inorg. Chem., 20, 3098, 1981.