# The Importance of Preferential Solvation of the CN Ligands in Electron- and Proton-Transfers Observed for *cis*–[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] Under Ion Bombardment

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Liquid secondary ion mass spectrometry (LSIMS) mass spectra of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] with a strong hydrogen-bonding-induced solvatochromism were measured using 3-nitrobenzyl alcohol (NBA) (oxidizing agent) and glycerol (reducing agent), and mixtures of these solvents. The formation of M<sup>+</sup> (oxidized molecule) correlated closely to the extent of preferential solvation by NBA (preferential solvation-shell) around the cyanide ligands as observed from changes in the energy of the maximum metal-to-ligand charge transfer absorption. (M + H)<sup>+</sup> is caused mainly by the preferential orientation of OH groups with protons in the NBA molecules toward the cyanide ligands in the disrupted region of the solvent structure as observed from the variation in the peak position of the stretching vibration of (OH) in the solvents. Large decreases in  $(M + 2H)^+$  and  $(M + 3H)^+$  (reduced molecules) resulted from the large decrease in the interaction between the cyanide ligands and glycerol owing to the preferential solvation by NBA. The LSIMS mass spectra clearly showed the electron- and proton-transfer processes along with the change in the hydrogen-bonding interaction between the acceptor (NBA and glycerol) and donor (the cyanide ligands), and in the solvent structure of the preferential solvation-shell. These results indicate that the composition of solvent molecules around the cyanide ligands at the surface of the solvents in LSIMS still holds the composition in the preferential solvation around the ligands in the primary solvation-shell. (J Am Soc Mass Spectrom 2002, 13, 1209-1217) © 2002 American Society for Mass Spectrometry

The specific solvent-solute interaction (hydrogenbonds) in the redox and/or electron-transfer of L transition-metal complexes was studied by Sachinidis et al. [1]. The electron-transfer, accompanied by large alterations in the solvent structure, was also observed in short- range solvent structure caused by strong hydrogen-bonds between the coordinated ligands and the surrounding solvent molecules [2, 3]. Recently, electron-transfer accompanying the protontransfer in the metalloenzyme was studied extensively [4]. The most noticeable feature of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] is its strong hydrogen-bonding-induced solvatochromism (solvatochromism is the phenomenon that several compounds change their spectroscopic properties in different solvents within visible and ultraviolet regions), as contrasted with the negligible solvatochromism of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> [5]. The energies of the

maximum metal-to-ligand charge-transfer (MLCT) absorption and the maximum emission of *cis*-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] decrease along with the decrease in the acceptor number (AN) [6] (AN of a liquid is a measure of its readiness to accept electrons from donors and an ability to hydrogen-bond with other molecules by accepting electron pairs from donor [6a]) of the solvents [7]. The cyanide ligands in the interactions behave as electron donors through hydrogen-bonding [8].

The relative proton affinity of cis-[RuX<sub>2</sub>(bpy)<sub>2</sub>] (X = CN, etc.) determined by LSIMS mass spectra correlates with the redox potentials of Ru (3+/2+) and the energy of the maximum absorption derived from the MLCT of the complexes in solution [9]. The chemical species {M<sup>+</sup>, (M + H)<sup>+</sup>, (M + 2H)<sup>+</sup>, and (M + 3H)<sup>+</sup>} observed in the LSIMS mass spectra of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] in thioglycerol (reducing agent) [10] are the same as those used for the measurement of redox potentials [11]. The results of fast atom bombardment (FAB) mass spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in 3-nitrobenzyl alcohol (NBA) (oxidizing agent) [10] are related to the oxidative quenching pro-

Published online August 27, 2002

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cess of the complex in the excited state in nitroaromatic solvents [12].

To elucidate the electron- and proton-transfer processes for metal complexes correlated with the hydrogen-bonding and/or the disruption of the solvent structure, we examined them using the LSIMS mass and MLCT absorption spectra of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] with glycerol (reducing agent) and NBA, and mixtures of these solvents, and using the peak position of the stretching vibration of OH,  $\{\nu(OH)\}\$ , in the solvents.

We found a preferential solvation by NBA around the cyanide ligands of the complex in mixtures of NBA and glycerol. We also found correlations between the changes in the percentages of  $M^+$ ,  $(M + H)^+$ ,  $(M + H)^+$  $(2H)^+$ , and  $(M + 3H)^+$ , and the preferential solvation, and between the changes in the percentages and variations in the solution structure.

# **Experimental**

Cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>]·3H<sub>2</sub>O was prepared by the literature procedure [11]. The mixing of glycerol and NBA, and the transfer of glycerol, the mixtures of these solvents, and NBA to a syringe were performed under an atmosphere of dry N<sub>2</sub> gas. After 100% glycerol, 100% NBA, and the mixtures of these solvents had been put between KBr plates, the intensity of the  $\nu$ (OH) band was measured with a JASCO (Tokyo, Japan) A-202. The peak position of  $\nu(OH)$  was measured with a PERKIN ELMER (Norwalk, CT) FT-1600 (resolving power: 2 cm<sup>-1</sup>) in a nitrogen stream. Intensity of  $\nu$ (OH) band of NBA and glycerol, and the mixtures of NBA and glycerol were obtained from the calculation using the absorbance of the maximum peak of  $\nu(OH)$ . We measured the maximum absorbance with a JASCO A-202, because the reproducibility among several samples was hardly obtained for the same solvent when the measurement of the absorbance repeated with a PERKIN ELMER FT-1600. These outcomes may be the result from the sensibility of FT-IR spectrometer for environment. After measuring the IR spectra, the KBr plate was polished under the nitrogen atmosphere with emery paper with a grain size of 3  $\mu$ m or 1  $\mu$ m until the surface became flat. The electronic spectra of the complex in the solvents were measured with a Hitachi 330 (Tokyo, Japan) spectrophotometer at 25  $\pm$  1 °C. The glycerol used was spectrophotometric grade (purity: 99.94%, GC) from Aldrich Chemical Co. (Milwaukee, WI). The NBA used was special grade (purity: 99.9%, GC) from Wako Pure Chemical Industry, Ltd. (Osaka, Japan) and was kept frozen at 5 °C in a refrigerator. No further purification of the solvents was carried out.

### *Instrumentation LSIMS*

A Hitachi M-2500 double-focusing mass spectrometer equipped with a Hitachi M-0301 computer system was used. The LSIMS mass spectra were recorded with a mass spectrometer using positive ions to desorb the sample. Glycerol and NBA, and the mixtures of these solvents were used as matrices.

The complex in the matrix was placed on a gold sample holder. Xenon was used as the precursor for the primary ion. The primary-ion and the secondary-ion accelerating voltages were each 4 kV. Fifty-four percent of the intensity of m/z 466 in the molecular ions observed in LSIMS mass spectra of [Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] with 100% NBA decreased when the voltage of the deflector of the primary-ion beam was from 2074 to 1788. This indicates that the major part of the first-ion beam of the mass spectrometer used is an ion and is well collimated. The duration of data collection was 3.2 min (25 scans).

## Pattern Analysis

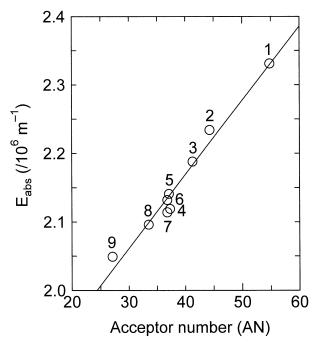
The experimentally measured intensity of each peak in an isotopic cluster observed in LSIMS mass spectra included contributions from the isotopic peaks of molecular ions  $\{M^+, (M + H)^+, (M + 2H)^+, and (M +$ 3H)<sup>+</sup>, etc.}, and from the background [11]. The determination of these different contributions was done by a least-squares method [11]. The molecular ions from the calculation of  $(M - H)^+$  to  $(M + 4H)^+$  have the same patterns of abundances, except that the smallest m/z of each ion is different, because the largest difference in the peaks comprising the isotope pattern of  $(M - H)^+$ and  $(M + 4H)^+$  is 0.0006.

### Results and Discussion

One of the characteristics of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] is its strong hydrogen-bonding-induced solvatochromism. Moreover, the solvatochromism of  $[Ru(CN)_4(bpy)]^{2-}$  is clearly greater than that of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] [7, 13]. These points indicate that the cyanide ligands are a specific solvation site for the solvatochromism [7, 13].

# Metal-to-Ligand Charge Transfer (MLCT) Absorption Spectra

A linear correlation of the energy of the maximum MLCT absorption of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] in H<sub>2</sub>O, glycerol, methanol, 1-propanol, ethanol, 2-propanol, 1-butanol, tert-butanol, and benzyl alcohol, and the AN [6] of each solvent having an OH group was found, as shown in Figure 1. It has been reported that a linear correlation between the energy and AN could be used for the estimation of the acceptor properties of solvents [14]. The coefficient of determination on the regression line obtained was 0.972. Therefore, the AN of NBA calculated from the regression line using the maximum energy in NBA was 42. The maximum absorption of this complex decreased along with the change of the solvent from glycerol (2.234  $\times$  10<sup>6</sup> m<sup>-1</sup>) to NBA (2.187  $\times$  10<sup>6</sup> m<sup>-1</sup>), as shown in Table 1. It was previously reported that electron redistribution is induced from the interaction of the nitrogen atoms in the cyanide ligands of



**Figure 1.** Energy of the maximum absorption derived from the metal-to-ligand charge transfer of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] versus Mayer and Gutmann's acceptor number in alcoholic solvents. The number in parentheses indicates the acceptor number. 1: H<sub>2</sub>O (54.8), 2: glycerol (44.3), 3: methanol (41.3), 4: 1-propanol (37.3), 5: ethanol (37.1), 6: benzylalcohol (36.8), 7: 1-butanol (36.8), 8: 2-propanol (33.5), 9: tert-butanol (27.1).

*cis*-[Fe(CN)<sub>2</sub>(phen)<sub>2</sub>] with acceptor solvent molecules [14]. Thus, the major origin of this variation in the maximum energy could arise from the change in the strength of the donor-acceptor interaction (mainly hydrogen-bonds) between the nitrogen atoms in the cyanide ligands in *cis*-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] and OH groups in the acceptor solvents [7, 15].

## Infrared (IR) Spectra

The intensity of the  $\nu(OH)$  band obtained from the measurement of the IR spectra taken in 100% glycerol and 100% NBA, and in mixtures of these solvents, increased with the change of NBA to glycerol. Intensity of  $\nu(OH)$  band of the mixtures of glycerol and 3-nitrobenzyl alcohol (NBA) was calculated using strength 260 observed of 100% glycerol and 74 observed of 100% NBA, and taking the specific gravities  $(d_4^{20})$  of glycerol and NBA as and 1.299, respectively. (cm<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup>) 100% glycerol: observed (260  $\pm$  30), mixture of 0.94 mole glycerol and 0.06 mole NBA: observed (250  $\pm$  10), calculated (250), the mixture of 0.80 mole glycerol and 0.20 mole NBA: obsserved (230  $\pm$  20), calculated (220), the mixture of 0.62 mole glycerol and 0.38 mole NBA: observed (210 ± 10), calculated (190), the mixture of 0.42 mole glycerol and 0.58 mole NBA: observed (170  $\pm$ 20), calculated (150), the mixture of 0.16 mole glycerol and 0.84 mole NBA: observed (96  $\pm$  9), calculated (100), and 100% NBA: observed (74 ± 3). The intensity observed for the mixtures was close to that calculated using the intensities of 100% glycerol and 100% NBA. This result indicates that there is no significant interaction between glycerol and NBA in the mixtures. Therefore, the observed energy of the maximum MLCT absorption for the last section could indicate a net interaction between the cyanide ligands of the complex and the OH group in the solvents.

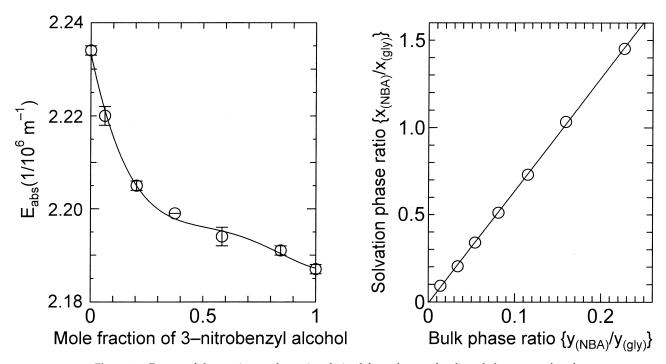
## Preferential Solvation

The plot of the energy of the maximum MLCT absorption of *cis*-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] versus the mole fraction of NBA in the mixtures of glycerol and NBA was nonlinear and showed negative deviation from linearity, as shown in Figure 2 (left figure). This negative deviation

**Table 1.** The energy of the maximum metal-to-ligand charge transfer absorption of cis- $[Ru(CN)_2(bpy)_2]$  in 100% glycerol and 3-nitrobenzyl alcohol (NBA), and the mixtures of these solvents

Mole fraction (wt%)		Concentration of the	Energy ( $10^6 \text{ m}^{-1}$ ) {wave length (nm)}		
Glycerol	NBA	complex in mixtures (mmol g <sup>-1</sup> )	Observed	Calculated*	
1.00		$3.65 \times 10^{-3} \text{ to } 2.69 \times 10^{-2}$	2.234 ± 0.001	2.234	
(100)		(n = 5)	$(447.7 \pm 0.2)$	(447.7)	
0.94	0.06	$8.87 \times 10^{-3} \text{ to } 4.34 \times 10^{-2}$	$2.220\pm0.002$	2.228	
(90)	(10)	(n = 5)	$(450.4 \pm 0.3)$	(448.8)	
0.80	0.20	$3.81 \times 10^{-3} \text{ to } 2.48 \times 10^{-2}$	$2.205 \pm 0.001$	2.220	
(70)	(30)	(n = 4)	$(453.4 \pm 0.1)$	(450.4)	
0.62	0.38	$5.51 \times 10^{-3} \text{ to } 3.98 \times 10^{-2}$	$2.199 \pm 0.000$	2.211	
(50)	(50)	(n = 6)	$(454.7 \pm 0.1)$	(452.3)	
0.42	0.58	$5.51 \times 10^{-3} \text{ to } 4.70 \times 10^{-2}$	$2.194 \pm 0.002$	2.202	
(30)	(70)	(n = 6)	$(455.7 \pm 0.3)$	(454.2)	
0.16	0.84	$8.00  imes 10^{-3}  ext{ to } 4.87  imes 10^{-2}$	$2.191 \pm 0.001$	2.192	
(10)	(90)	(n = 5)	$(456.3 \pm 0.1)$	(456.2)	
	1.00	$5.19 \times 10^{-3} \text{ to } 2.95 \times 10^{-2}$	$2.187 \pm 0.001$	2.187	
	(100)	(n = 4)	$(457.3 \pm 0.1)$	(457.3)	

<sup>\*</sup>Calculated using the energies of 100% glycerol and 100% NBA of 2.234  $\times$  10<sup>6</sup> m<sup>-1</sup> and 2.187  $\times$  10<sup>6</sup> m<sup>-1</sup>, and using the specific gravity ( $d_4^{20}$ ) values of 100% glycerol and 100% NBA of 1.261 and 1.299, respectively.



**Figure 2.** Energy of the maximum absorption derived from the metal-to-ligand charge transfer of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] versus mole fraction of 3-nitrobenzyl alcohol (NBA) in 100% glycerol and 100% NBA, and these mixtures of glycerol and NBA (mole fractions of 0.94 glycerol and 0.06 NBA, 0.80 glycerol and 0.20 NBA, 0.62 glycerol and 0.38 NBA, 0.42 glycerol and 0.58 NBA, and 0.16 glycerol and 0.84 NBA) (left figure). Preferential solvation plot {solvation phase ratio  $x_{(NBA)/}/x_{(glycerol)}$  versus bulk phase ratio  $y_{(NBA)/}/y_{(glycerol)}$ } for cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] in the 3-nitrobenzyl alcohol and glycerol system at 25  $\pm$  1 °C (right figure).

indicated preferential solvation by NBA as for the analogous iron complex [16, 17]. Frankel, et al. [18] proposed that solvent molecules are distributed between the bulk and the solvation shell (preferential solvation-shell) of the solute in preferential solvation. A simple relationship between the composition of the bulk solvent and the solvation shell,  $x_A/x_B = K(y_A/y_B)$ , is proposed, where  $x_A$  and  $x_B$  refer to the mole fractions of A and B in the solvation shell, and y<sub>A</sub> and y<sub>B</sub> refer to the bulk solvent. The composition of the solvation shell,  $x_{(\mbox{\scriptsize NBA})/}x_{(\mbox{\scriptsize glycerol})}$  , can be determined from the intercept of the horizontal line with the diagonal straight line from  $y_{(NBA)}=0$  to  $y_{(NBA)}=1$  in Figure 2 (left figure), as in a typical phase diagram procedure [16, 17]. A preferential solvation plot of the solvation phase ratio,  $x_{(NBA)}$  $x_{(glycerol)}$ , versus bulk phase ratio,  $y_{(NBA)}/y_{(glycerol)}$ , for cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] in the glycerol and NBA mixtures is shown in Figure 2 (right figure). The plot is a straight line from NBA mole fractions of 0.096 to 0.61 in the solvation shell, and 0.015 to 0.21 in the bulk solvent. The calculated preferential solvation constant, K [16, 17], is 6.3 (at 25  $\pm$  1 °C). These results indicate that an NBA molecule could approach *cis*-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] smoothly in the solvent on the polymeric structures of glycerol caused by hydrogen-bonds at high glycerol mole fractions, and that a strongly preferential solvation of NBA around the cyanide ligands arises.

## LSIMS Mass Spectra

Raw mass spectra. The raw LSIMS mass spectrum observed with the mixture of 70% glycerol and 30% NBA (the concentration of the complex in the mixture was  $1.78 \times 10^{-2}$  mmol g<sup>-1</sup>) is shown in Figure 3. The spectrum shows good resolution among the peaks in the region of the molecular ions. Identification of the chemical species in the region observed was performed by the least-squares method [11]. The difference between the observed and calculated intensities was small (SD = 0.0035) in the case of spectra with good resolution, as shown in Table 2. In the majority (98 of 101 runs) the standard deviation (SD) was less than 0.01. The SD observed in the run with the best agreement was 0.0018. The SD for the largest difference was 0.0114. Therefore, each chemical species percentage observed can be considered certain because the propagated error calculated by ±1 SD for each chemical species was small, as shown in Table 3.

Chemical species observed in LSIMS mass spectra. The majority of chemical species observed with 100% glycerol, two mixtures of glycerol and NBA, (mole fractions of 0.94 glycerol and 0.06 NBA, 0.80 glycerol and 0.20 NBA) were  $M^+$ ,  $(M+H)^+$ ,  $(M+2H)^+$ , and  $(M+3H)^+$ , as shown in Table 3 and Figure 4. The majority species observed with three mixtures (mole fractions of 0.62

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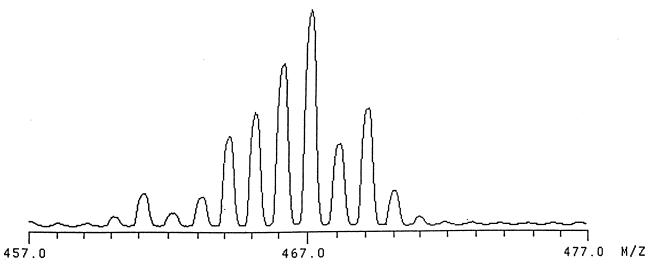


Figure 3. Raw mass spectrum of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] obtained in a mixture of 70% glycerol and 30% 3-nitrobenzyl alcohol. The concentration of the complex in the mixture was  $1.78 \times 10^{-2}$  mmol g<sup>-1</sup>. The multiplier voltage used was 1300V. Gain 400 corresponded to 4 V.

Table 2. Intensities of each peak contained in an overlapping isotope cluster in the region of the molecules observed in LSIMS mass spectra of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>], and of each peak obtained from the least squares

	Inte	ensity		
m/z	Observed	Calculated	Chemical species	Percentage
457	9069			
458	7574			
459	7913			
460	17787	16994		
461	53653	51698		
462	25718	25606		
463	48665	47685		
464	135816	136695	\\\ \> M+*	17.3 ± 0.4**
465	171941	173459		
466	240318	240111	\	$75.4 \pm 0.6$
467	315441	315130	XX	
468	136861	136150	/X	$5.9 \pm 0.4$
469	177189	176954	// X	
470	60098	60686	/// \- (M+3H)+	$1.4 \pm 0.3$
471	17150	18351	////	
472	8358	8940		
473	7818	7539	//	
474	6607	7422		
475	5656			
476	6519			
477	7021			

A matrix containing 70% glycerol and 30% 3-nitrobenzyl alcohol was used. A gold sample holder was used. Concentration of the complex in the matrix was  $1.78 \times 10^{-2}$  mmol g<sup>-1</sup>. Intensity of each peak observed in the LSIMS mass spectrum was the average for 20 scans. Standard deviation was 0.0035, and background obtained from the calculation was 0.0235.

<sup>\*</sup>The mass range of isotopic peaks of more than 0.1% for each chemical species, calculated from the isotopic abundances of all the isotopes in [Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>], was used for calculation by the least-squares method.

<sup>\*\*</sup>The percentage of the value of the propagation of error derived by  $\pm 1$  SD.

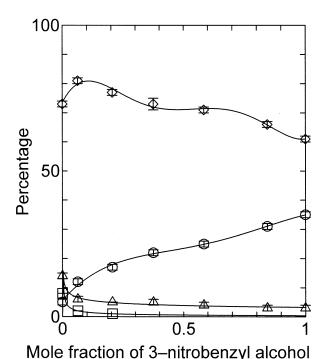
Table 3.	The percentage of each che	emical species in the mass	range corresponding to	molecules of cis-[RuCl <sub>2</sub> (bpy) <sub>2</sub> ] in LSIMS mass
spectra w	vith 100% glycerol and 3-niti	obenzyl alcohol (NBA), a	nd the mixtures of these	solvents

Mole fraction		The concentration range				
Glycerol	NBA	of the complex in the solvents	$M^+$	$(M + H)^{+})$	$(M + 2H)^{+}$	(M + 3H) <sup>+</sup>
1.00		$1.37 \times 10^{-2}$ to $4.44 \times 10^{-2}$ mmol g <sup>-1</sup> (n = 15)	(5 ± 1)* (1 ± 0)**	(73 ± 1) (1 ± 0)	(14 ± 1) (1 ± 0)	(8 ± 0) (1 ± 0)
0.94	0.06	$1.14 \times 10^{-2}$ to $4.67 \times 10^{-2}$	$(12 \pm 1)$	$(81 \pm 1)$	$(6 \pm 1)$	$(2 \pm 0)$
		$mmol g^{-1} (n = 16)$	$(0 \pm 0)$	$(1 \pm 0)$	$(0 \pm 0)$	$(0 \pm 0)$
0.80	0.20	$1.12 \times 10^{-2}$ to $4.13 \times 10^{-2}$	$(17 \pm 1)$	$(77 \pm 1)$	$(5 \pm 0)$	$(1 \pm 0)$
		mmol $g^{-1}$ (n = 12)	$(0 \pm 0)$	$(1 \pm 0)$	$(0 \pm 0)$	$(0 \pm 0)$
0.62	0.38	$1.22 \times 10^{-2}$ to $4.98 \times 10^{-2}$	$(22 \pm 1)$	$(73 \pm 2)$	(5 ± 1)	
		mmol $g^{-1}$ (n = 13)	$(1 \pm 0)$	$(1 \pm 0)$	$(1 \pm 0)$	
0.42	0.58	$1.33  imes 10^{-2}  ext{ to } 4.87  imes 10^{-2}$	$(25 \pm 1)$	$(71 \pm 1)$	$(4 \pm 1)$	
		mmol $g^{-1}$ (n = 16)	$(1 \pm 0)$	$(1 \pm 0)$	$(1 \pm 0)$	
0.16	0.84	$1.16  imes 10^{-2}  ext{ to } 4.78  imes 10^{-2}$	$(31 \pm 1)$	$(66 \pm 1)$	$(3 \pm 1)$	
		mmol $g^{-1}$ (n = 14)	$(0 \pm 0)$	$(1 \pm 0)$	$(0 \pm 0)$	
	1.00	$1.05 \times 10^{-2}$ to $4.60 \times 10^{-2}$	$(35 \pm 1)$	$(61 \pm 1)$	$(3 \pm 1)$	
		mmol $g^{-1}$ (n = 15)	$(0 \pm 0)$	$(0 \pm 0)$	$(0 \pm 0)$	

<sup>\*(</sup>Mean ± 1 SD).

glycerol and 0.38 NBA, 0.42 glycerol and 0.58 NBA, 0.16 glycerol and 0.84 NBA), and 100% NBA were  $M^+$ , (M+H) $^+$ , and (M+2H) $^+$ , as shown in Table 3 and Figure 4.

Oxidized molecule (M<sup>+</sup>). The plot of the mean percentage of M<sup>+</sup> against the mole fraction of NBA is shown in Figure 5 (right figure). The relative abundance of M<sup>+</sup>

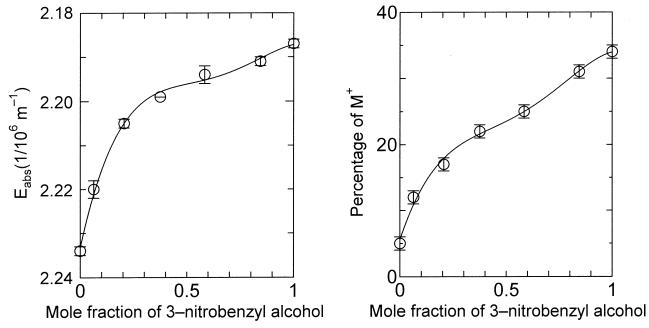


**Figure 4.** Percentages of  $M^+$ ,  $(M + H)^+$ ,  $(M + 2H)^+$ , and  $(M + 3H)^+$  contained in the overlapping isotopic peaks corresponding to the molecules of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] observed in LSIMS mass spectra with 100% glycerol and 3-nitrobenzyl alcohol (NBA), and the mixtures of glycerol and NBA {(mole fractions are the same as those in Figure 2 (left figure)}. Open circle:  $M^+$ , open diamond:  $(M + H)^+$ , open triangle:  $(M + 2H)^+$ , open square:  $(M + 3H)^+$ .

observed with neat glycerol was only 5%, but it increased greatly along with the increase in the fraction of NBA in the matrix, as shown in Figure 5 (right figure) and Table 3. The abundance of M<sup>+</sup> observed with neat NBA was 35%. The energy of the maximum MLCT absorption decreased greatly along with the large decrease in the interaction between the complex and glycerol that was caused by the preferential solvation by NBA surrounding the cyanide ligands, as mentioned above and shown in Figure 2 (left figure). When the left figure in Figure 2 was reversed with reference to an X axis, the mirror image {Figure 5 (left figure)} obtained was very close to the form of M+ in Figure 5 (right figure). The measurement of the electrochemical behavior of this complex indicated that M+ is caused by the removal of one electron from a metal-centered orbital t<sub>20</sub> [19]. NBA is composed of an aromatic ring with an electron-withdrawing group, which increases the electron scavenging capability of the molecule [10], and NBA under bombardment conditions generates the excited nitroaromatic of a powerful oxidative quencher [10]. These results indicate that M<sup>+</sup> is derived mainly from the interaction between the cyanide ligands and the NBA in the preferential solvation-shell at the surface of the solvents in LSIMS.

Protonated molecule  $(M + H)^+$ . The plot of the relative abundance of  $(M + H)^+$  against the mole fraction of NBA is shown in Figure 4. A variation of wave number of  $\nu(OH)$  (ca. 3360 cm<sup>-1</sup>) per NBA mole fraction against the fraction is shown in Table 4 and is plotted at Figure 6 (left figure). A large positive shift in wave number along with the increase in the fraction from 0 to 0.38 indicates that the polymeric structures of neat glycerol caused by intermolecular hydrogen-bonds is disrupted greatly by the addition of NBA. A small positive shift along with an increase in the fraction from 0.38 to 0.58

<sup>\*\*(</sup>Mean  $\pm$  1 SD) of the propagated error calculated using  $\pm$ 1 SD.



**Figure 5**. Mirror image obtained when the plot of the energy of the maximum absorption derived from the metal-to-ligand charge transfer of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] versus mole fraction of 3-nitrobenzyl alcohol (NBA) in the mixtures of glycerol and NBA (left figure in Figure 2) was reversed with reference to an X axis (left figure). Percentage of  $M^+$  contained in the overlapping isotopic peaks corresponding to the molecules of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] observed in LSIMS mass spectra with 100% glycerol and 100% NBA, and these mixtures of glycerol and NBA {mole fractions are the same as those in Figure 2 (left figure)} (right figure).

indicates that the large disruption of the solvent structure continued. A small negative shift along with the increase from 0.58 to 0.84 indicates repair of the hydrogen-bonding structure. A large negative shift along with the increase from 0.84 to 1.0 indicates that a strong hydrogen-bonding network in a nearly neat NBA structure is constructed. The plot of the abundance of (M  $\,\pm$ 

**Table 4.** The wave number of the stretching vibration of (OH)  $\{v\ (OH)\}\$ in 100% glycerol and 3-nitrobenzyl alcohol (NBA), and the mixtures of these solvents, and variation  $\{\Delta\ v\ (OH)\}\$ of the wave number of  $v\ (OH)\$ per NBA mole fraction

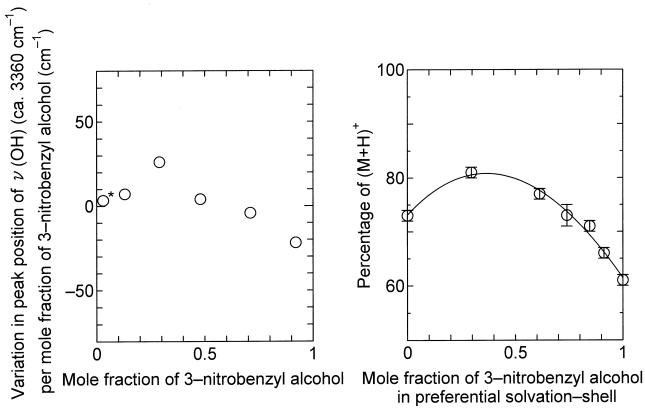
Mole fract	ion	Wave number*,**	۸ (۵۲)	
Glycerol			$\Delta~v~(OH) \ (cm^{-1})$	
1.00		3356.9		
(0.97)	(0.03)***		3.3	
0.94	0.06	3357.1		
(0.87)	(0.13)		7.1	
0.80	0.20	3358.1		
(0.71)	(0.29)		26.1	
0.62	0.38	3362.8		
(0.52)	(0.48)		4.0	
0.42	0.58	$3363.6 \pm 0.3 (n = 3)$		
(0.29)	(0.71)		-4.2	
0.16	0.84	3362.5		
(80.0)	(0.92)		-21.9	
	1.00	3359.0		

<sup>\*</sup>An average of 256 scans.

\*\*\*An average of two mole fractions.

H)<sup>+</sup> against the fraction in the preferential solvationshell in Figure 6 (right figure) is similar to the curve in Figure 6 (left figure). These results indicate that the formation of (M + H)<sup>+</sup> correlates well with the structural disruption of solvents in the solvation-shell. Moreover, the maximum MLCT absorption of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] decreased greatly along with the preferential solvation of NBA up to the fraction of 0.61 in the solvation-shell. These results indicate that the OH groups in NBA molecules in the structurally disrupted region preferentially orient toward the cyanide ligands [3]. The chemical species of molecular and proton adduct molecular ions in the isotopic cluster of glycerol and 2glycerol observed in the LSIMS mass spectra were obtained by the least-squares method. The species in the cluster of glycerol and 2glycerol were {(glycerol + H)<sup>+</sup> and  $(glycerol + 2H)^{+}$ , and  $\{(2glycerol + H)^{+}\}$  and  $(2glycerol + 2H)^{+}$ , and the percentages were  $\{(99 \pm 0)\}$ and  $(1 \pm 0)$ , and  $\{(99 \pm 0) \text{ and } (1 \pm 0)\}$ , (n = 9), respectively. The SD values of glycerol and 2glycerol were very small (0.0009 to 0.0022, n = 9). The chemical species of molecular and proton adduct molecular ions in the cluster of NBA and 2NBA observed in the spectra were  $\{NBA^+, (NBA + H)^+, (NBA + 2H)^+, and (NBA + H)^+\}$  $3H)^{+}$ , and  $\{2NBA^{+}, (2NBA + H)^{+}, (2NBA + 2H)^{+}, and \}$  $(2NBA + 3H)^{+}$ , respectively. The percentage of each species for NBA was  $(8 \pm 1)$ ,  $(79 \pm 0)$ ,  $(12 \pm 0)$ , and  $(2 \pm 0)$ , respectively. The percentage of each species for 2NBA was  $(1 \pm 0)$ ,  $(91 \pm 1)$ ,  $(6 \pm 0)$ , and  $(1 \pm 0)$ , respectively. The SD values of NBA and 2NBA were

<sup>\*\*</sup>An average of two runs except for IR spectra with a mixture of 30% glycerol and 70% NBA. Resolving power: 2 cm<sup>-1</sup>.



**Figure 6.** Variation of the peak position of stretching vibration of (OH) {ca. 3360 cm<sup>-1</sup>} per mole fraction of 3-nitrobenzyl alcohol (NBA) against the NBA mole fraction observed in 100% glycerol and 100% NBA, and these mixtures of glycerol and NBA {(mole fractions are the same as those in Figure 2 (left figure)}, (asterisk is an average of two NBA mole fractions), (left figure). Percentage of (M + H)<sup>+</sup> in preferential solvation–shell observed in LSIMS mass spectra of *cis*-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] with 100% glycerol and 100% 3-nitrobenzyl alcohol (NBA), and these mixtures of glycerol and NBA (right figure).

very small (0.00005 to 0.0012, n = 7). Glycerol holds protons strongly, and the proton affinity of NBA is almost the same as that of glycerol. Moreover, a proton in (NBA + H) $^+$  could attach to the OH group in the NBA molecule because a proton attached to the OH in (glycerol + H) $^+$  was observed in the FAB mass spectra [20]. The proton transfer to the solute from (glycerol + H) $^+$  accounts for the formation of the (solute + H) $^+$  ions [20]. These findings indicate that (M + H) $^+$  results mainly after the OH groups in NBA molecules orient toward the cyanide ligands in the structurally disrupted region caused by the preferential solvation of NBA at the surface of the solvents in LSIMS.

Reduced molecules  $\{(M+2H)^+ \text{ and } (M+3H)^+\}$ . The relative abundance of  $(M+2H)^+$  observed with glycerol was 14%, as shown in Table 3. However, the abundance of  $(M+2H)^+$  observed with NBA was only 3%. The abundance of  $(M+3H)^+$  (a more extensively reduced species ion) observed with neat glycerol was 8%, as shown in Table 3. Moreover,  $(M+3H)^+$  was observed with only two mixtures (2% relative abundance for a mixture of 0.94 mol glycerol and 0.06 mol NBA, and 1% relative abundance for 0.80 mol glycerol and 0.20 mol NBA), and was not observed with other

mixtures, or for 100% NBA. Cyclic voltammetry indicates stable formations of singly-reduced  $(M + 2H)^+$ , and doubly-reduced (M + 3H)<sup>+</sup>, complexes of cis- $[Ru(CN)_2(bpy)_2]$ . The complexes contain one and two bipyridine ligands with one electron, respectively [19]. When particles or ions of keV energy impact the matrices, electrons are produced. Glycerol is unlikely to scavenge electron, but NBA has a great electron scavenging capability [10]. The abundances of  $(M + 2H)^+$ and (M + 3H)<sup>+</sup> decreased greatly with a large increase of NBA around the cyanide ligands resulting from the preferential solvation of NBA when an NBA mole fraction of only 0.063 was added to glycerol. The (M + 3H)<sup>+</sup> did not form in more than 0.7 of the NBA fraction in the solvation-shell. These results indicate that (M + 2H)<sup>+</sup> and (M + 3H)<sup>+</sup> of the reduced molecules are caused mainly by the interaction between the cyanide ligands and glycerol in the preferential solvation-shell at the surface of the solvents in LSIMS.

# Conclusion

A large increase in the abundance of  $M^+$  (oxidized molecule) and large decreases in the abundances of  $(M + 2H)^+$  and  $(M + 3H)^+$  (reduced molecules) ob-

served in the LSIMS mass spectra of cis-[Ru(CN)<sub>2</sub>(bpy)<sub>2</sub>] upon addition of NBA to a mole fraction of only 0.063 with respect to the glycerol were clearly related to the preferential solvation by NBA observed from the large decrease in the energy of the maximum MLCT absorption. The abundance of  $(M + H)^+$  correlated clearly with the preferential orientation of OH groups in NBA molecules toward the cyanide ligands in the structurally disrupted region, which was supported from the large positive shift in wave number of the  $\nu$ (OH).

The mass spectra clearly showed changes in the electron- and proton-transfer processes along with large changes in the hydrogen-bonding interaction between the acceptors (NBA and glycerol) and donors (the cyanide ligands), and in the solvent structure occurring with the preferential solvation of NBA around the cyanide ligands.

The LSIMS mass spectra is a usefulness for the clarification of electron- and proton-transfer processes of the complex occurring in the primary solvation-shell.

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