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Solvent Effects on the ESR Spectra of Copper(II) Complexes. A Consideration of the Donicity of Water and Methanol

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Solvent effects on the ESR spectra of bis(2,6-dimethyl-3,5-heptanedionato)copper(II) ([Cu(dibm)$_2$]) and a similar copper(II) complex were investigated in some detail. A clear relationship between the ESR parameters and the donicity of the solvents was confirmed, and this is discussed with the intention of investigating the donicities of water and methanol. The donor number for water in an aqueous solution was estimated to be about 30 from a precise analysis of the ESR spectra of [Cu(dibm)$_2$] in water–methanol mixtures.

The concept of donicity has become increasingly important in the chemistry of non-aqueous solvents, but the donicities of some protic solvents such as water and alcohol still remain open to investigation.[1,2] Solvent effects on various properties of metal complexes have been studied widely for the purpose of determining the donicity of the solvents. Gutmann has found a relationship between the donicity or donor number (DN) of a solvent and the visible absorption band of bis(acetylacetonato)oxovanadium(IV) dissolved in the solvent.[2] Adato and Eliezer[3] have investigated solvent effects on the ESR spectra of bis(acetylacetonato)-copper(II) in connection with the DN of the solvents, but there seems to be some uncertainty in their data, as is described below. In addition, they did not refer at all to the DN of water or methanol.

The purpose of the work reported here is to reinvestigate the relationship between the ESR parameters and the DN of solvents, using some stable planar copper(II) complexes which are soluble in many solvents, and to attempt to estimate the DN of water and methanol.

Experimental

Bis(2,6-dimethyl-3,5-heptanedionato)copper(II) (hereafter abbreviated to [Cu(dibm)$_2$]) and bis(*N*-salicylidenepropylaminato)copper(II) ([Cu(*N*-Pr-sal)$_2$]) were prepared and purified by the usual method.[4,5] For the ligand of the former complex, 2,6-dimethyl-3,5-heptanedione, which was purchased from the Eastman Kodak Company, was used.

Acetonitrile, propylene carbonate, *N,N*-dimethylformamide, and dimethyl sulfoxide were purified according to the methods in the literature.[6–8] The other solvents were purified by the usual method.[9]

ESR spectra of the complexes in solutions (about 10 mM) were measured with a Hitachi 771 X-band ESR spectrometer at 77 K. Mixtures of toluene and the other solvents at various molar fractions were used as solvents.

Results and Discussion

The Relationship between the ESR Parameters and the DN of Solvents. As the first step in this study, it is absolutely necessary to obtain well-defined ESR spectra, and this could be achieved by using mixtures of toluene and the other solvents. Several typical ESR spectra of [Cu(dibm)$_2$] in various solvents at 77 K are shown in Fig. 1. All the spectral line shapes observed in this work were of axial or nearly axial symmetry,[10] and, in addition, the line-widths were rather narrow. Hence, the $g_{//}$ and $|A_{//}|$ values can be accurately determined from these spectra.

The $g_{//}$ and $|A_{//}|$ values of planar copper(II) complexes respectively increase and decrease to a significant extent as the axial ligand field is strengthened by apical coordination of the solvent molecules. Therefore, these values, as well as $g_\perp$, are good parameters for use in the investigation of the donicity of the solvents. The data obtained from the work reported here are given in Table 1, together with the DN and dipole moments (μ) of the solvents, where the DN of toluene was assumed to be approximately zero. Table 1 clearly indicates that $g_{//}$ and $|A_{//}|$ do not correlate with μ, but with DN. A correlation between $g_{//}$ and DN is shown in Fig. 2; the $g_{//}$ value increases with DN, and the order of the solvents is the same as that previously reported with regard to DN.[1] This result, therefore, suggests that the $g_{//}$ value can be used to estimate the DN. Similar results were obtained for [Cu(*N*-Pr-sal)$_2$]; for example, its $g_{//}$ values were 2.225 in pure toluene(T), 2.245 in T–DMF and 2.260 in

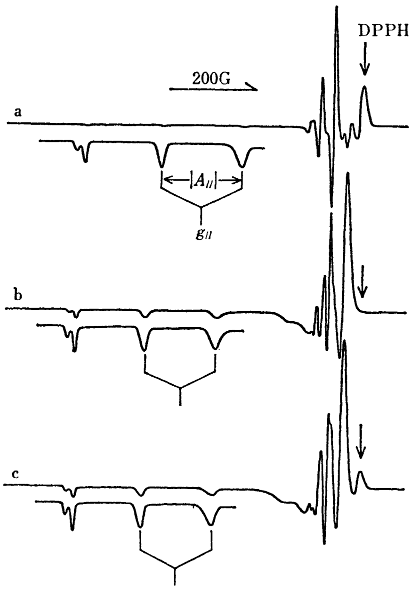

Fig. 1. ESR spectra of [Cu(dibm)$_2$] in pure T (a), T-MeOH (b) and T-DMSO (c).

TABLE 1. ESR DATA IN VARIOUS SOLVENTS

Solvent	$g_{//}$[a)]	$\frac{|A_{//}|^{a)}}{10^{-4}\ \mathrm{cm}^{-1}}$	DN	$\frac{\mu}{10^{-18}\ \mathrm{cm\ esu}}$
Toluene (T)	2.251	193	0	0.37
Nitromethane (NM)	2.254	198	2.7	3.54
Nitroethane (NE)	2.259	195	—	3.60
1-Nitropropane (NP)	2.265	190	—	3.59
Acetonitrile (AN)	2.282	181	14.1	3.37
Propylene carbonate (PC)	2.277	185	15.1	5.2
Acetone (AC)	2.284	179	17.0	2.27
Water (W)	2.297[b)]	178[b)]	18.0	1.8
Methanol (MeOH)	2.290 2.289[c)] 2.288[d)] 2.291[e)]	175 176[c)] 175[d)] 177[e)]	19.1	1.66
Tetrahydrofuran (THF)	2.284	181	20.0	1.68
N,*N*-Dimethylformamide (DMF)	2.293	174	26.6	3.86
Dimethyl sulfoxide (DMSO)	2.294	175	29.8	3.9
Pyridine (Py)	2.297	168	33.1	2.20

a) These values were obtained in solvents of various toluene molar fractions at 77 K. No dependency of the data on the molar fraction was found. b) Obtained in an MeOH-water mixture. c) Obtained in an MeOH-NP mixture. d) Obtained in an MeOH-PC mixture. e) Obtained in a pure MeOH.

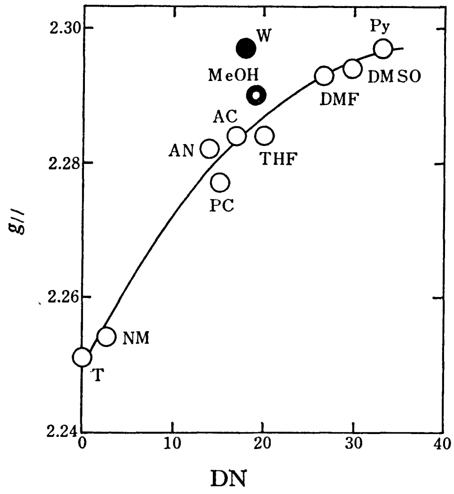

Fig. 2. The relationship between $g_{//}$ value and DN.

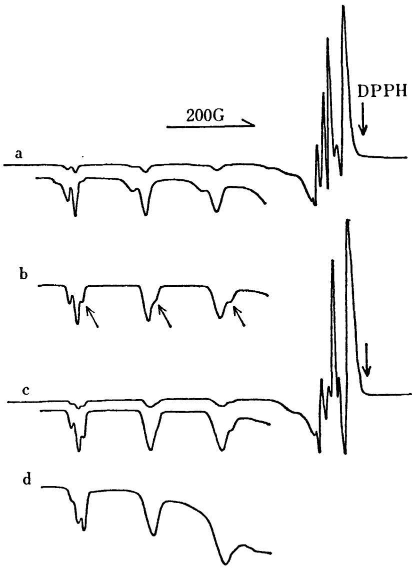

Fig. 3. ESR sepctra of [Cu(dibm)$_2$] in MeOH–water mixture at MeOH molar fractions of 0.31 (a), 0.57 (b), 0.80 (c), and 1.00 (d). The arrows are the absorption line due to MeOH adduct.

T–DMSO. Its $|A_{//}|$ values also decreased for an increase in DN.

Hence, the authors comment on the data of Adato and Eliezer.³⁾ First, when DMSO, DMF and other solvents were used, the resulting ESR spectra were all broad and not well-defined, and from these spectra it was not possible to obtain data similar to those in Ref. 3. Some of the data in Ref. 3 could be reproduced using solvents without purification. Accordingly, a great deal of this data is considered to be due to bis(acetylacetonato)copper(II) which interacts with impurities in the solvents. Second, it is theoretically reasonable to discuss the $g_\perp$ value of a planar copper(II) complex from the point of view of solvent effects as has been done in the case of the visible absorption spectra of bis(acetylacetonato)oxovanadium(IV).[11)] Generally speaking, however, it is not easy to determine accurately the $g_\perp$ values of copper(II) complexes in solution.[12)] Adato and Eliezer applied an approximate method to estimate $g_\perp$ from the equation, $g_0 = (1/3)(g_{//}+2g_\perp)$, using the experimentally-determined g values in two different states (g_0 for a fluid solution and $g_{//}$ for a rigid or glassy solution). It must be noted, however, that this method is likely to introduce some uncertainty into the results, because the solvent effects are not always the same for the two different states,[13)] and because some complexes exist in solution as two or more configurationally different species in equilibrium.[14)] In order to discuss solvent effects as rigorously as possible, therefore, the authors use only the $g_{//}$ and $|A_{//}|$ values determined in solutions at 77 K throughout this report.

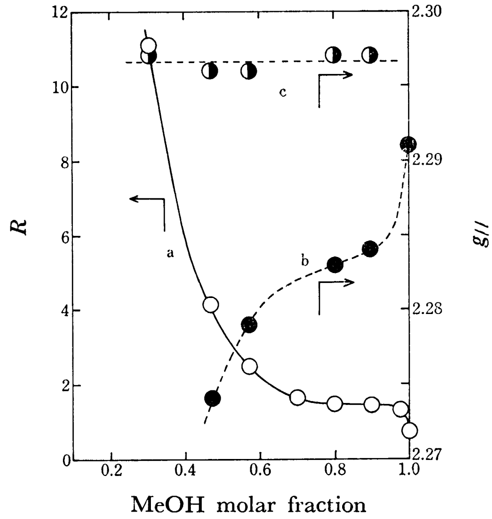

Fig. 4. Plots of R (a) and the $g_{//}$ values of MeOH (b) and water (c) adducts against the molar fraction of MeOH in MeOH–water mixtures.

Donicity of Water and Methanol. As shown in Table 1, the $g_{//}$ values were almost the same in the solvent systems T–MeOH, NP–MeOH and pure MeOH. Furthermore, the $g_{//}$ value in the T–MeOH system did not change with the MeOH molar fraction. This fact indicates that the stereochemical and electronic structures of the MeOH adduct do not depend on environmental changes. Using this $g_{//}$ value and the relationship between DN and $g_{//}$ shown as a solid line in Fig. 2, the DN of MeOH can be estimated to be larger than 19.1 (the generally accepted value[15)]), but smaller than 33.8 (the value estimated by Gutmann from the data of Selbin[2)]).

On the other hand, the ESR behavior in the water–MeOH system was entirely different. Several ESR spectra in water–MeOH mixtures at different MeOH molar fractions are shown in Fig. 3. The ratios (R) of the water adduct to the MeOH adduct in the ESR absorption intensity, which are nearly proportional to the ratios of their concentrations,[16)] were plotted against the MeOH molar fraction, as shown in Fig. 4. Although Fig. 4 indicates that there is a correlation between R and the MeOH molar fraction, its implications appear to be complicated; they should be considered from the standpoint of the preferential solvation of water in this solvent system.

The fact that the $g_{//}$ value of the MeOH adduct in the water–MeOH system varies remarkably with the MeOH molar fraction means that the effects of water in the methanolic solution are significant even at low concentrations. The tendency of the $g_{//}$ value to decrease with an increase in water concentration indicates that the bonding between the complex and the MeOH molecules in the adduct becomes weak, although no definite explanation for this can be offered at the present time. On the other hand, the $g_{//}$ value of the water adduct is constant, as is seen in Fig. 4. This means that water and methanol as solvents have almost the same structural and electronic effects on this water adduct. Using this $g_{//}$ value and the relationship given by a solid line in Fig. 2, the DN of water could be estimated to be about 30, which coincides with the value previously reported by Gutman.[1)]

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