ponding to the *d-d* transition. The occurance of the *d-d* transition at such a low wavelength is the characteristic of the intramolecular spectra of conjugated π-molecular radicals.[15] The absorption maxima in solid state are shifted to higher energy at 289, 413, 532 nm. This energy shift may be contributed the increased interactions along TTF⁺ stacks in the solid state.

Cyclic voltammogram was recorded in DMF/0.1 M TEAP from −0.2 to +1.0 V versus on Ag/AgCl electrode. (TTF)₂Cu (hfac)₂·1.5C₂H₅OH exhibited two cathodic (Ep_c) and anodic (Ep_a) peaks at +0.36 (Ep_c), +0.45 V (Ep_a) for the TTF/TTF⁺ couple and at +0.61 (Ep_c), +0.70 V (Ep_a) for the TTF⁺/TTF²⁺ couple. TTF molecule also shows two peaks at nearly the same potential in the same experimental condition. The cyclic voltammograms were scanned several times and there was no change in the potentials, that two couples are reversible. The values of Ep_a/Ep_c are also nearly equal to 1. A redox peak refered to copper couples were not detected in the experimental conditions.

In summary, charge transfer compound, (TTF)₂Cu(hfac)₂· 1.5C₂H₅OH was prepared from the reaction of TTF and Cu (hfac)₂·2H₂O in ethanol solution. The spectroscopic and magnetic properties reveal that charge transfer has occured to the copper ion resulting in diamagnetic Cu(I) state. The odd electrons are delocalized on TTF⁺ radical cations in the stacks. This inter-stack interaction provides the pathway for the electrical conductivity in the stacking direction. The compound exhibited intrinsic semiconductor behavior with low charge carrier activation energy. A considerable interaction between TTF radical cations is also observed by the magnetic properties, although an X-ray structure determination is necessary for further elucidation of the material.

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Solvent Effects on the Chemical Shift of the Bipyridyl 6'-Proton in [Ru(bpy)₂(p-tert-butylpy) (OH₂)]²⁺ Complex

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A novel feature in a series of polypyridyl complexes of ruthenium is the appearance of many oxidation states which are easily accessible over a narrow range. High-oxidation-state [Ru^{IV}=O]²⁺ complexes can be prepared by consecutive proton and electron loss of the corresponding [Ru^{II}-OH₂]²⁺ complexes. Mono-oxo complexes of Ru have been shown as efficient and/or catalytic oxidants toward inorganic and organic substrates and notably as important in understanding the oxidation mechanisms.[1]

X-ray crystallographic and in some instances ESR methods have been successfully utilized for the determination of solid phase molecular and electronic structures of metal complexes.[2] However, question of stereochemistry, fluxional behavior, or substitution dynamics in solutions are best addressed through the application of NMR spectrometry.[3] The chemical shift data for the 2,2'-bipyridyl protons of M(II) and M(III) complexes such as [Ir(bpy)₂Cl₂]⁺, *cis*-[Ru(bpy)₂(OH₂)₂]²⁺, [Ru(bpy)₂(py)₂]²⁺, and [Ru(bpy)₃]²⁺/³⁺, bpy is 2,2'-bipyridine and py is pyridine) were reported by many workers.[4] NMR techniques have also been proved as valuable in unravelling mechanistic pathways related to the Ru(IV)-Oxo complexes.[5]

Because most of Ru oxidants are soluble only in polar solvents, we have been interested in the synthesis of Ru-oxo complexes which are also soluble in organic solvents. Considering the extensive and general reactivity of the Ru(IV) oxidants, we initially tried to understand the details of their electronic structures and spectroscopic properties. While examining NMR spectra of new Ru-aqua complexes, we accidentally found out the migration of the chemical shift of the 6'-bipyridyl proton of the *cis*-[Ru^{II}(bpy)₂(p-tert-butylpy)(OH₂)]²⁺ (p-tert-butylpy is *para-tert*-butylpyridine) complex in various deuteriated solvents. Here we report the initial results of those observations.

Experimental

Materials. RuCl₃·3H₂O, 2,2'-bipyridine and all NMR grade deuterated solvents were purchased from Aldrich Chemical Co. and used without further purification. *Para-tert*-butylpyridine was also obtained from Aldrich and purified according to a literature method.[6]

Preparations. Ru(bpy)₂Cl₂·2H₂O was prepared as described previously.[7] The syntheses of following complexes were modified procedures of [Ru(bpy)₂(py)(O)]²⁺.[8] The spectral data of all of the products were consistent with the literature.

[(bpy)₂(*p-tert*-butylpy)Ru(Cl)](PF₆)(H₂O). A 3.00 g of Ru(bpy)₂Cl₂·2H₂O was dissolved in approximately 70 m*l* of hot water under a stream of N₂ gas. The blanket of N₂ was necessary to prevent aerial oxidation. To the solution was added a small volume of *p-tert-butylpyridine* sufficient to give 1.2 stoichiometric equivalents with respect to the complex. The resulting solution was heated at reflux for 3 hour. After the solution was cooled to room temperature, 3 g of NaCl and 2 or 3 drops of saturated NH₄PF₆ solution were added to the reaction mixture followed by extraction with methylene chloride. The deep red CH₂Cl₂ layer was removed, several more drops of NH₄PF₆ solution were added, and the extraction was repeated. Solvent was then removed from the combined methylene chloride extracts by rotary evaporation. The crude product could be conveniently purified by absorbing the complex onto a 4 inch length by 1.5 inch diameter column filled with activated alumina and eluting with 5% isopropyl alcohol in CH₂Cl₂. The leading band was collected. After rotary evaporation, the complex was again dissolved in a small amount of methylene chloride. Dropping of this solution into a three-fold excess of diethyl ether resulted in the percipitation of the product. It was filtered and washed with diethyl ether several times. Yields varied but averaged 80% of the theoretical after drying in vacuum.

[(bpy)₂(*p-tert*-butylpy)Ru(OH₂)](ClO₄)₂. 0.67 mmole of above Ru(II)-Cl complex and 1.54 mmole of AgClO₄ were dissolved in 40 m*l* of acetone and 5 m*l* of water and heated at reflux for 1 hr. After the filtration, the volume of the resulting solution was reduced to approximately 5 m*l*. 1 m*l* of saturated silver perchlorate solution was added into the solution. The resulting precipitate was collected on a medium frit, washed with water, and air dried.

[(bpy)₂(*p-tert*-butylpy)Ru(O)](ClO₄)₂. 0.26 mmole of above Ru(II)-OH₂ complex was dissolved in 20 m*l* of warm water. A solution of 2.05 stoichiometric equivalents of (NH₄)₂Ce(NO₃)₆ in 1 M perchloric acid was slowly added while stirring. The light green precipitate which appeared in the brown solution was filtered, washed well with three 1 m*l* portions of iced water, and dried in a vacuum desiccator overnight. (ν(Ru=O), 792 cm⁻¹).

NMR Spectral Experiments. All NMR measurements were performed on a Varian Gemini 200 MHz spectrometer. Chemical shifts were referenced to tetramethylsilane (TMS). The ¹H NMR spectra of Ruᴵᴵ-OH₂²⁺ in the various deuteriated solvents were obtained in two different ways. One method is simply to dissolve Ruᴵᴵ-OH₂²⁺ complex in each D₂O, (CD₃)₂CO, or CD₃CN solvent. The other one is to utilize the reaction of Ruᴵⱽ=O²⁺ complex with the solvent such as CDCl₃, CD₂Cl₂, or d₈-THF. In the each latter reaction, Ruᴵᴵ-aqua complex was obtained as a sole ruthenium product.
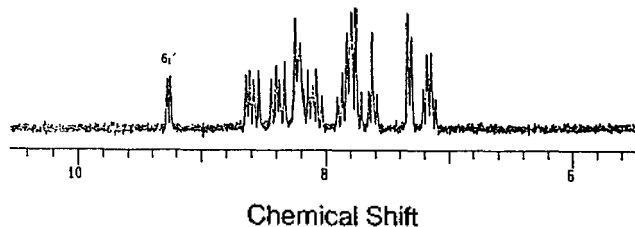
Figure 1. The portion of the ¹H NMR spectrum (200 MHz) of [Ru(bpy)₂(*p-tert*-butylpy)(OH₂)]²⁺ complex in D₂O.

Results and Discussions

All the protons of Ru complexes containing pyridyl derivatives can be assigned using decoupling, relaxation, and isotope exchange methods.[2-4] Connstable and Seddon found out that the 3,3'-positioned protons are slightly more acidic than all the other protons of bipyridyl rings by steric strain in [Ruᴵᴵ(bpy)₃]²⁺ complex.[4b]
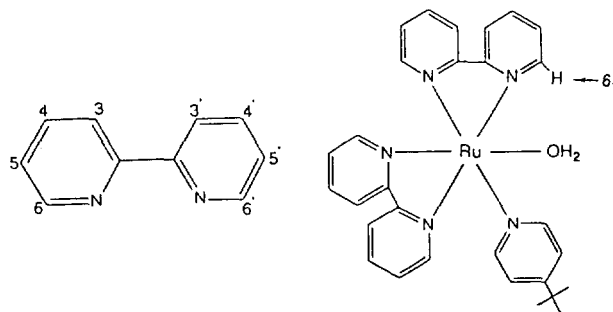
As noted in the above scheme, the primed notation in this case refers to two *trans* configurational pyridyl rings of the bipyridine ligands. Molecular models show that both 6 and 6' protons in one bipyridine ring and one of the 6 and 6' proton in the other bipyridine ring lie in the ring currents of the bipyridine and pyridine ligands. Accordingly, the chemical shifts of those protons are relatively moved to upfield. However, the second 6' proton which is the nearest to the ligand L is out of the ring currents of the pyridyl ligands. This 6'₁ proton is shifted downfield solely as doublet and provides a sensitive diagnostic tool for detecting changes in the ligand L in above complexes of the type [Ruᴵᴵ(bpy)₂(py)(L)]²⁺ and [Ruᴵᴵ(tpy)(bpy)(L)]²⁺ (tpy is 2,2'; 6',2''-terpyridine and L=OH₂, NO, NCCH₃, Cl, DMSO, OPPh₃ etc).[5] Generally the chemical shift of 6'₁ bipyridyl proton is related to the ligand strength of L.

In the ¹H NMR spectrum of cis-[Ruᴵᴵ(bpy)₂(*p-tert*-butylpy)(OH₂)]²⁺ in D₂O shown in Figure 1, 16 nonequivalent proton resonances for the 2,2'-bipyridyl rings as well as 5 protons for *para-tert*-butylpyridyl ring are appeared. All the peaks are assigned by comparision with the spectra of cis-[Ruᴵᴵ(bpy)₂(py-*d₅*)(OH₂)]²⁺ and cis-[Ruᴵᴵ(bpy)₂(py)₂]²⁺. The isolated doublet at downfield can be assigned to the 6'₁ bipyridyl proton.[9] The ¹H NMR spectra of [Ru(bpy)₂(*p-tert*-butylpy)(OH₂)]²⁺ complexes in CD₃CN and acetone-*d₆* were obtained and assigned, too.

[Ruᴵⱽ(bpy)₂(*p-tert*-butylpy)(O)]²⁻ complex was dissolved in solvents like CHCl₃, CH₂Cl₂, or THF. At the same time the Ruᴵⱽ=O²⁺ complex was so unstable that new reactions were incurred in those solvents. We are still investigating their

reaction mechanism(s) using spectroscopic techniques, however, Ru^{II}-OH_2^{2+} complex was surely obtained as a sole ruthenium product in each reaction. The identification of the remaining organic products is still in progress. So far we observed tetrachloroethene, hexachloroethane, and tetrachloroethane products for $CHCl_3$, CH_2Cl_2 oxidation and γ-butyrolactone for THF oxidation. The formation of Ru-aqua complex from the reaction of $Ru^{IV}=O^{2+}$ complex with solvents promptly leads us to study the solvent effects on the chemical shifts of the $6_1'$ bipyridyl proton for the *cis*-[Ru^{II}(bpy)$_2$(*p-tert*-butylpy)(OH$_2$)]$^{2+}$ complex in various deuteriated solvents using NMR spectrometer.

The solvent effects on the chemical shift are defined as the change in the resonance positions of some given proton of the solute between solvents A and B as consequences of intermolecular forces. The chemical force can affect on the electron density of the particular nuclei, which is related to the screening constant. Specifically, the total screening constants(σ_{total}) at the nuclei in the applied magnetic field strength can be split into six contributions as equation (1).[10]

$$\sigma_{total} = \sigma_g + \sigma_b + \sigma_w + \sigma_a + \sigma_r + \sigma_c \quad (1)$$

The subscripted symbols refer to the contribution to the screening of the gaseous molecule (σ_g), bulk susceptibility of the medium (σ_b), van der Waals interaction (σ_w), anisotropy of the susceptibilities of the surrounding molecules (σ_a), reaction field of the medium (σ_r), and specific solute-solvent interaction(σ_c).

Because the experiments were performed in the non-aromatic solution with the internal reference, σ_a, σ_g, and σ_b terms should be excluded.[11] In non-polar and non-aromatic solvents it was generally suggested that the shifts were come from dispersion forces. These forces between molecules in solution perturb the electronic structure of the molecules, and this leads to a change in the nuclear screening constant. The distortion of the electronic environment of the nucleus and departures from the equilibrium solvent configuration lead to a paramagnetic shift. Buckingham and co-workers have been able to obtain an estimate of the shifts in the methane proton resonances due to the van der Waals effect of the solvent.[12] The polyhalogenated solvents produce the largest shifts. Associating with our experiments, the contribution of σ_w is assumed to be related to the whole complex rather than the single $6_1'$ bipyridyl proton.

Larger solvent shifts for polar solutes are also due to the effect of the reaction field (R) arised from polarizing the surrounding medium. The theory of the effect of the reaction field on chemical shifts has been developed from the Onsager model.[13] This model predicts that the solvent shift due to the reaction field should be linear in $(\varepsilon - 1)/(2\varepsilon + n^2)$, where ε is the dielectric constant and n is the refractive index of the pure solute.[14]

Since few molecules approximate to a spherical shape, the Onsager model was considered inadequate to account for the reaction field in complex molecules. Therefore a more sophistigated equation (2) was derived for the reaction field based on an ellipsoidal cavity which takes into account the shape of the solute molecule, *i.e.*

$$\sigma_r = -\chi \ 10^{-12} \frac{3\mu}{abc} \cos\theta \ \xi_a[1+(n^2-1)\xi_a]\frac{\varepsilon-1}{\varepsilon+\beta} \quad (2)$$

Table 1. The chemical shift of the $6_1'$ bipyridyl proton of [Ru (bpy)$_2$(*p-tert*-butylpy)(OH$_2$)]$^{2+}$ complex with the dielectric constant and the dipole moment of various deuterated solvents. (*a*, δ (ppm); *b*, ε (20 ℃); *c*, μ (Debye))

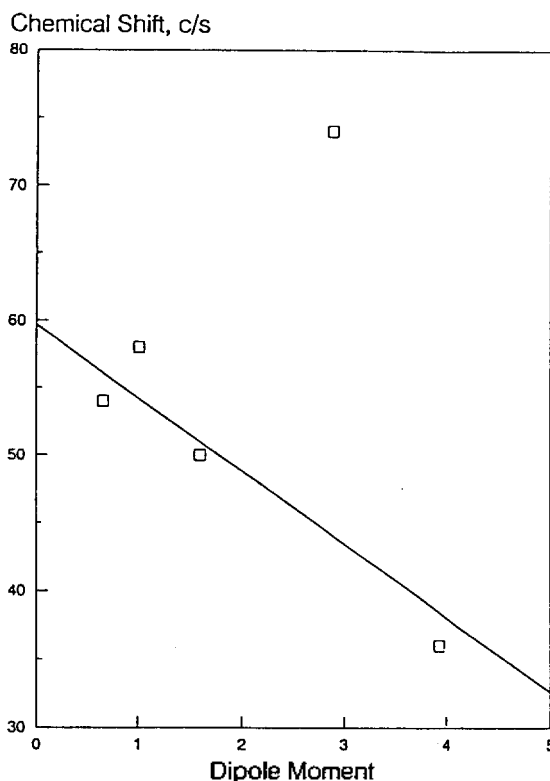| Solvent	Chemical Shift[a]	Dielectric Constant[b]	Dipole Moment[c]
Acetone-d_6	9.62	20.7	2.88
Chloroform-d	9.54	4.81	1.01
Tetrahydrofuran-d_8	9.52	2.95	0.66
Dichloromethane-d_2	9.50	9.08	1.60
Acetonitrile-d_3	9.43	35.1	3.92
Water-d_2	9.25	78.5	1.85

Figure 2. Correlation between the dipole moment and the chemical shift difference of the $6_1'$ bipyridyl proton of [Ru(bpy)$_2$(*p-tert*-butylpy)(OH$_2$)]$^{2+}$ complex against D$_2$O. Data are taken from Table 1.

where $\beta = n^2\xi_a/(1-\xi_a)$, ξ_a is a shape factor and a, b, c are the ellipsoidal semi-axes.[15]

The chemical shift values for the magnetically distinct $6_1'$-H nearest to the aqua ligand in complex of [Ru(bpy)$_2$(*p-tert*-butylpy)(OH$_2$)]$^{2+}$ with dielectric constant and dipole moment are shown in Table 1. The plot between the dielectric function $(\varepsilon - 1)/(\varepsilon + 1)$ and the chemical shift of the $6_1'$ bipyridine proton of *cis*-[Ru^{II}(bpy)$_2$(*p-tert*-butylpy)(OH$_2$)]$^{2+}$ in various deuterated solvents shows that a parabolic relationship exists. We also tried to relate for the other dielectric function $(\varepsilon - 1)/(2\varepsilon + 1)$. However same results were obtained. It is not surprising from examining the molecular structure of [Ru^{II}(bpy)$_2$(*p-tert*-butylpy)(OH$_2$)]$^{2+}$ complex. In the quadrupo-

Notes

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lar reaction field of the complex, the positive charge is centered on Ru. All the surrounding atoms can be treated as having the same negative charges and may manifest the equal electric field effects.

The term σ_c has been widely interpreted in terms of a solute-solvent collision complex.[16] The term collision complex is meant to imply a short-lived orientation of the solvent molecule(s) that has been brought about by dipole-induced dipole, dipole-quadrupole, or other weak chemical association, which can be related to the dipole moment. Figure 2 shows the plot for the dipole moment(μ) versus the chemical shift difference of the 6₁ bipyridyl proton for the cis-[Ru^II(bpy)₂(p-tert-butylpy)(OH₂)]²⁺ complex against D₂O solvent(δ). Although there is a deviation for (CD₃)₂CO solvent, linear relationship has been observed. Linearity between molecular dipole moment and solvent shift of the methyl protons has been observed in some organometallic compounds of the type (CH₃)ₙSnX₄₋ₙ (X=Cl, Br, and I).[17]

In conclusion, we find that the change in the nature of the ligand L in the series of cis-[Ru^II(bpy)₂(p-tert-butylpy)(L)]²⁺ complexes can be easily detected from the chemical shift data of 6₁ bipyridyl proton. Those results can be very useful to understand the reaction mechanism(s). The migration of the chemical shift of the 6₁ bipyridyl proton possibly suggests the existence of specific solute-solvent interaction. The formation of Ru^II-OH₂²⁺ complex from the reaction of [Ru^IV(bpy)₂(p-tert-butylpy)(O)]²⁺ complex with solvents like CHCl₃, CH₂Cl₂, or THF indicates that this reaction can be useful as an example of electrocatalytic application.[18] The principle involved is for the case where Ru^IV=O²⁺ is the active oxidant of a substrate S and the products of the redox reaction are the oxidized substrate S_ox and Ru^II-OH₂²⁺. In the electrocatalytic schemes, the catalyst redox couple is oxidatively regenerated at the electrode in a net electrocatalytic shuttle mechanism.[19] Catalytic application of these reactions is now in progress.

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Spectroelectrochemical Study of the Dimerization of Methylviologen Cation Radical in the Diffusion-limited Region

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N,N'-disubstituted-4,4'-bipyridnium ions (vilogens) are very attractive materials for the purpose of electron-transfer reagent[1] in photochemical solar energy conversion,[2] herbicides,[3] and electrochromic display.[4] One of viologens that is encountered most frequently in literatures is N,N'-dimethyl-4-4'-bipyridinum dication (methylviologen, MV²⁺) salt. Most of the reported applications has been focused on methylviologen cation radical (MV·⁺) which can be electrogenerated from the colorless MV²⁺ with equilibrium electrode potential of −0.69 V vs SCE.[15a] MV·⁺ is also known to dimerize in aqueous media as Eq. (1).[1,5-11]

$$2MV^+ \rightleftharpoons (MV^{·+})_2 \qquad (1)$$

$$K_D = [(MV^{·+})_2]/[MV^{·+}]^2 \qquad (2)$$

where K_D is the equilibrium constant for monomer-dimer equilibrium. The formation of dimers should affect further reactions where MV·⁺ participate. Quantitative studies for dimerization were performed by absorption spectroscopy using chemical reduction method.[6,7] There are several reports dealing with dimerization of viologens. Some reports[1,5-9] used 365 and 560 nm bands as those of dimer, which are