of $Co(NH_3)_5X^{2+}$ complexes, especially in mixed-solvent media.[3] Data in Figure 1, however, clearly militate against this possibility for $Co(NH_2CH_3)_5Br^{2+}$. Thus, unlike the behavior of the ammine family, the qualitative features of the quantum yield profile in water are retained in both 80% acetonitrile and 50% glycerol solutions. In particular, there is no evidence for the development of photodissociative character (i.e. a continuous rise in $\Phi_{Co^{2+}}$ toward unity) at high excitation energies in these mixed solvents. It should be noted that the values of $\Phi_{Co^{2+}}$ at a specific wavelength vary with solvent in the order 80% acetonitrile > water > 50% glycerol. This trend tracks solution viscosities (η in Table II) and suggests that solvent influences the photoredox behavior of $Co(NH_2CH_3)_5Br^{2+}$ primarily through its effect upon the separation/recombination kinetics of primary (solvent caged) and secondary (solvent separated) radical-pair photoproducts.[16,17]

We have found that members of the $Co(NH_2R)_5Cl^{2+}$ family undergo photoredox chemistry in mixed-solvent media very similar to that just described for $Co(NH_2CH_3)_5Br^{2+}$. Quite generally, then, it appears that the replacement of NH_3 by NH_2R in the first coordination sphere of cobalt enhances the importance of intramolecular photodecomposition (eqs 3a,b) relative to the intermolecular pathway involving photooxidation of solvent (eq 3c). Such behavior cannot be attributed to the ability of the peripheral alkyl groups to shield the complex from the solvent, since comparable solvatochromatic shifts occur for the Br → Co CT band in $Co(NH_3)_5Br^{2+}$ and $Co(NH_2CH_3)_5Br^{2+}$ (note ΔE values in Table I). We would expect diminished solvent sensitivity of this band for the methylamine complex if such shielding were important.[18] A more attractive explanation is that the LMCT excited states in alkylamine complexes possess weaker Co–N bonds than their ammine analogues. While both types of complex experience photoinduced bond labilizations in their LMCT states resulting from the population of σ-antibonding orbitals, it is quite likely that additional bond weakening occurs in the alkylamine systems owing to nonbonding repulsions between the bulky alkyl groups.[19] Weaker bonding should favor intramolecular decomposition from the initially populated LMCT state over crossing to the potential energy surface of the solvent → Co CT state.

Finally, let us return to the question posed at the outset concerning the role of solvent in the LMCT photochemistry of metal complexes. The present results, in conjunction with earlier work,[3] suggest the following answer: solvent may participate chemically in the reactions of LMCT excited states, but such behavior is not universal. In retrospect, this should not be surprising, since the reactivity of LMCT states undoubtedly is determined by several factors (metal, ligand type, excitation wavelength, nature of solvent), the relative importance of which will vary from system to system.

Summary

The solvatochromism exhibited by the LMCT absorption bands of $Co(NH_3)_5Br^{2+}$ and $Co(NH_2CH_3)_5Br^{2+}$ can be understood in terms of conventional solvent polarity and hydrogen-bonding interactions. Unlike their ammine counterparts, complexes belonging to the $Co(NH_2R)_5X^{2+}$ family undergo redox chemistry from LMCT excited states without accompanying oxidation of the solvent. This disparity has been ascribed to weaker Co–N bonding in the LMCT states of the alkylamine complexes.

Acknowledgment. We thank the U.S. National Science Foundation (Grant DMR-8715635) and the IBM Corp. for financial support.

(16) Scandola, F.; Bartocci, C.; Scandola, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 7898.
(17) Harris, A. L.; Brown, J. K.; Harris, C. B. *Annu. Rev. Phys. Chem.* **1988**, *39*, 341.
(18) Examples of pendant group shielding effects on metal-to-ligand CT excited states: (a) Reitz, G. A.; Demas, J. N.; DeGraff, B. A.; Stephens, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 5051. (b) Sacksteder, L.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1989**, *28*, 1787.
(19) (a) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 1790. (b) Foxman, B. M. *J. Chem. Soc., Chem. Commun.* **1972**, 515. (c) Swaddle, T. W. *Can. J. Chem.* **1977**, *55*, 3166. (d) Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932.

Contribution from the Department of Chemistry, University of Houston, Houston, Texas 77204-5641

An Unsymmetrical Binuclear Ruthenium(II) Complex of Tris(2-pyridyl)-1,3,5-triazine and Its Identification by ^1H NMR Spectroscopy

Sara Chirayil, Vidyadhar Hegde, Yurngdong Jahng, and Randolph P. Thummel*

Received August 9, 1990

Introduction

The past several years have seen an explosive growth in the field of ruthenium polypyridine chemistry. These complexes are of interest because of photochemical and electrochemical properties that predicate their utility in a variety of photoredox applications.[1] Since many of these applications require the transfer of more than one electron, there has been considerable recent interest in the design of polynuclear ruthenium complexes that might satisfy this requirement. These complexes typically involve a bridging ligand (BL) which has two or more bidentate sites into which are incorporated $Ru(bpy)_2^{2+}$ subunits, where bpy = 2,2′-bipyridine.[2-6] Nearly all of these bridging ligands are symmetrical, so that the ruthenium atoms occupy identical, chemically equivalent binding sites. For systems designed to investigate mixed-valence states, binding of two different metals, or sites with different auxiliary ligands, unsymmetrical bridging ligands might prove useful.

In this work we describe how tris(2-pyridyl)-1,3,5-triazine (TPT) can be used as a bridging ligand that incorporates two ruthenium(II) atoms in nonequivalent sites such that one Ru is bound in a bidentate fashion and the other is bound in a tridentate fashion. The same ligand has previously been used to form a dicobalt[7] or dimercury[8] complex using both a bidentate and a tridentate site. There has also been a recent report of TPT binding two $Ru(CO)_2Cl_2$ moieties in a symmetric fashion utilizing two equivalent bidentate sites.[9] It is, in fact, possible that TPT could bind three metals using three equivalent bidentate sites.

A principal problem associated with the preparation of unsymmetrical binuclear polypyridyl complexes is their characterization by ^1H NMR spectroscopy due to the complexity found in the aromatic region of their spectra. Detailed analysis is often impossible even with the assistance of a variety of sophisticated techniques. We recently demonstrated the utility of bpy-d_8 as an auxiliary ligand in the formation and characterization of an unsymmetrical mononuclear ruthenium(II) complex.[10] In this paper we extend the technique to include the perdeuterio analogue of 2,2′;6′,2″-terpyridine (tpy) and demonstrate its utility in the characterization of a binuclear complex of TPT.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a General Electric QE-300 spectrometer in CD_3CN or $CDCl_3$ with chemical shifts reported in parts per million downfield from $(CH_3)_4Si$. FAB mass spectra were obtained on a VG 70-SEQ mass spectrometer using *m*-nitrobenzyl alcohol as a matrix. Tris(2-pyridyl)-1,3,5-triazine was pur-

(1) For an excellent review see: Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. See also: Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. Krause, R. A. *Struct. Bonding (Berlin)* **1987**, *67*, 1.
(2) (a) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691. (b) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857.
(3) Thummel, R. P.; Chirayil, S. *Inorg. Chim. Acta* **1988**, *154*, 77.
(4) (a) Barigelletti, F.; De Cola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1989**, *28*, 4344. (b) Hage, R.; Dijkhuis, A. H. J.; Haasnoot, J. G.; Prins, R.; Reedijk, J.; Buchanan, B. E.; Vos, J. G. *Inorg. Chem.* **1988**, *27*, 2185.
(5) Sahai, R.; Baucom, D. A.; Rillema, D. P. *Inorg. Chem.* **1986**, *25*, 3843.
(6) Ernst, S. D.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 1520.
(7) Vagg, R. S.; Warrener, R. N.; Watton, E. C. *Aust. J. Chem.* **1969**, *22*, 141.
(8) Halfpenny, J.; Small, R. W. H. *Acta Crystallogr.* **1982**, *B38*, 939.
(9) Thomas, N. C.; Foley, B. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3426.
(10) Chirayil, S.; Thummel, R. P. *Inorg. Chem.* **1989**, *28*, 813.

0020-1669/91/1330-2821$02.50/0

Scheme I

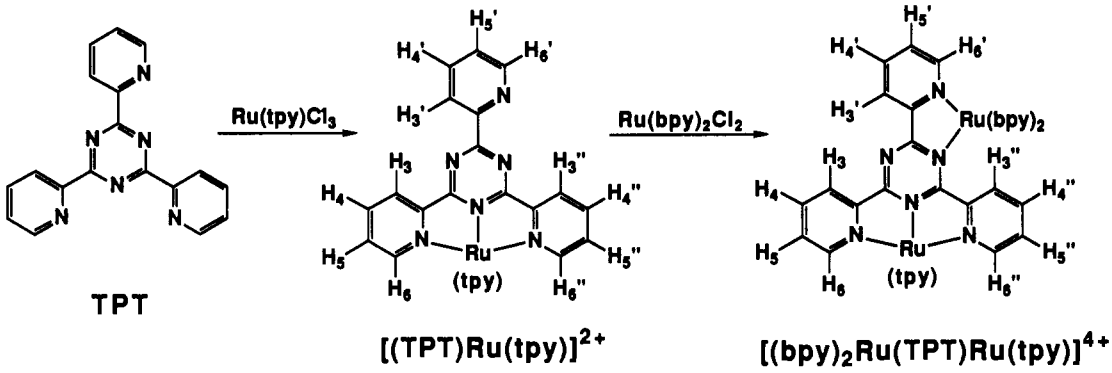

Table I. ^{1}H NMR Chemical Shift Data for Ligands and Ruthenium Complexes[a]

	TPT[b]												tpy[b]					
	H_3	H_4	H_5	H_6	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$	$H_{3''}$	$H_{4''}$	$H_{5''}$	$H_{6''}$	H_3	H_4	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$
tpy[c]													8.46	7.96	8.62	7.86	7.33	8.70
$[Ru(tpy)_2]^{2+}$[c]													8.76	8.42	8.50	7.42	7.17	7.34
TPT	8.91	8.01	7.58	8.98														
$[Ru(TPT)_2]^{2+}$	9.07	8.15	7.42	7.75	9.07	8.28	7.81	9.17										
$[(TPT)Ru(tpy)]^{2+}$	9.10	8.14	7.45	7.61	9.04	8.25	7.78	9.14					8.82	8.50	8.54	7.94	7.13	7.45
$[(tpy\text{-}d_{11})Ru(TPT)Ru(bpy\text{-}d_8)_2]^{4+}$	8.52	7.80	7.07	7.16	8.37	8.09	7.51	7.82	7.43	7.71	7.02	7.02						

[a] Reported in ppm downfield from internal Me_4Si in $CDCl_3$ (ligands) and CD_3CN (complexes). No appreciable solvent shift was observed. [b] The numbering pattern for TPT is given in Scheme I, and tpy is numbered in the usual fashion. [c] Reference 14.

chased from Aldrich Chemical Co. $Ru(bpy)_2Cl_2\cdot 2H_2O$,[11] its perdeuterio analogue,[10] and $Ru(tpy)Cl_3$[12] were prepared according to published procedures.

2,2':6',2''-Terpyridine *N,N',N''*-Trioxide.[13] A solution of (1.0 g, 4.3 mmol) 2,2':6',2''-terpyridine in 5.0 mL of glacial acetic acid and 4.0 mL of 30% hydrogen peroxide was heated for 2 h at 80 °C. After addition of a further 4 mL of 30% hydrogen peroxide, the temperature was raised to 90 °C and maintained for 18 h. The mixture was poured into 50 mL of acetone, and, after several hours of standing, the precipitate was collected and washed with acetone to give 1.0 g (83%) of the trioxide.

2,2':6',2''-Terpyridine-d_{11} *N,N',N''*-Trioxide. Sodium (0.58 g, 0.025 mol) was carefully added in small portions to 10 mL of D_2O in a 25-mL three-necked flask under N_2. An appropriate tube was flushed with N_2, and 2,2':6',2''-terpyridine *N,N',N''*-trioxide (1.0 g, 3.6 mmol) was added, followed by the NaOD–D_2O solution. The tube was again flushed with N_2 and sealed. It was heated at 150–160 °C for 60 h. The reaction mixture was cooled, and the precipitate was collected. The filtrate was concentrated and cooled, and a second crop was collected. The combined product was dried to afford 800 mg of material, which was treated with NaOD–D_2O (0.58 g of Na in 10 mL of D_2O) a second time in a similar fashion. After workup, 2,2':6',2''-terpyridine-d_{11} *N,N',N''*-trioxide was collected and dried to afford 700 mg (67%).

2,2':6',2''-Terpyridine-d_{11}. 2,2':6',2''-Terpyridine-d_{11} *N,N',N''*-trioxide (500 mg, 1.71 mmol) was dissolved in 3 mL of PCl_3, and the solution was refluxed for 2 h. After cooling, it was neutralized with 20% aqueous KOH and extracted with ether. The ether layers were washed with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent yielded 2,2'':6',2''-terpyridine-d_{11} (300 mg, 72%). The mass spectrum (*m/e* (relative intensity) 245 (M + 1, 17), 244 (M, 100), 243 (47), 242 (26), 241 (8)) indicates the presence of 58% d_{11}, 26% d_{10}, and 15% d_9, which corresponds to an overall deuterium incorporation of 94.9%.

Ru(tpy-d_{11})Cl$_3$. A mixture of 2,2':6,2''-terpyridine-d_{11} (185 mg, 0.76 mmol) and $RuCl_3\cdot 3H_2O$ (198 mg, 0.76 mmol) was refluxed in 90 mL of absolute EtOH for 2 h. The reaction mixture was cooled, and the precipitate was collected and washed with 3 × 20 mL portions of EtOH, followed by 3 × 20 mL portions of Et_2O, and dried to yield 300 mg (88%) of the desired complex. To evaluate the position of residual ^{1}H, the complex $[Ru(tpy\text{-}d_{11})_2](PF_6)_2$ was prepared in the normal fashion:[14] ^{1}H NMR (300 MHz, CD_3CN) 8.42 (s, $H_{4'}$, 12%), 7.92 (s, H_4, 47%), 7.38 (s, H_6, 24%), 7.17 (s, H_5, 17%).

[(TPT)Ru(tpy)](PF$_6$)$_2$. A mixture of TPT (80 mg, 0.25 mmol) and $Ru(tpy)Cl_3$ (110 mg, 0.25 mmol) was refluxed in 25 mL of 1:1 EtOH/H_2O for 24 h. After cooling, an aqueous solution of NH_4PF_6 (84 mg, 0.52 mmol) was added. The precipitate was collected, dried, and chromatographed on 20 g of alumina by eluting with 1:1 CH_3CN/toluene. The fractions containing the complex were allowed to evaporate slowly to provide dark purple crystals of the complex (170 mg, 72%). Anal. Calcd for $C_{33}H_{23}F_{12}N_9P_2Ru$: C, 42.32; H, 2.48; N, 13.46. Found: C, 42.41; H, 2.69; N, 13.77. The corresponding tpy-d_{11} complex was prepared by an analogous procedure in 51% yield.

[(TPT)Ru(bpy)$_2$](PF$_6$)$_2$. A mixture of TPT (80 mg, 0.25 mmol) and $Ru(bpy)_2Cl_2$ (0.112 g, 0.25 mmol) in 20 mL of 1:1 EtOH/H_2O was refluxed overnight. The reaction mixture was cooled, and an aqueous solution of NH_4PF_6 (84 mg, 0.52 mmol) was added. The precipitated material was collected, dried, and chromographed on 20 g of alumina by eluting with 1:1 CH_3CN/toluene to afford 0.173 g (68%) of $[(TPT)Ru(bpy)_2](PF_6)_2$ as a dark red solid.

[(bpy)$_2$Ru(TPT)Ru(tpy)](PF$_6$)$_4$. A mixture of $[(TPT)Ru(tpy)](PF_6)_2$ (53 mg, 0.057 mmol) and $Ru(bpy)_2Cl_2$ (32 mg, 0.066 mmol) was dissolved in 15 mL of 1:1 EtOH/H_2O, and the solution was refluxed for 24 h. The mixture was cooled, and NH_4PF_6 (21 mg, 0.13 mmol) was added. The precipitate was collected and chromatographed on 20 g of alumina by eluting with 2:1 CH_3CN/toluene. The fractions containing the complex were allowed to evaporate slowly to provide dark red crystals of the complex (96 mg, 87%). The analogous deuterio complex was prepared by the reaction of $[(TPT)Ru(tpy\text{-}d_{11})](PF_6)_2$ with $Ru(bpy\text{-}d_8)_2Cl_2$ in 70% crude yield (41% after recrystallization).

[Ru(TPT)$_2$](PF$_6$)$_2$. A mixture of TPT (160 mg, 0.5 mmol) and $RuCl_3\cdot 3H_2O$ (65.4 mg, 0.25 mmol) was refluxed in 25 mL of 1:1 EtOH/H_2O for 24 h. After cooling, an aqueous solution of NH_4PF_6 (84 mg, 0.52 mmol) was added. The precipitate was collected, dried, and chromatographed on 20 g of alumina by eluting with 1:1 CH_3CN/toluene. The fractions containing the complex were allowed to evaporate slowly to provide dark red crystals of the complex (192 mg, 74%). Anal. Calcd for $C_{36}H_{24}F_{12}N_{12}P_2Ru$: C, 42.56; H, 2.37; N, 16.55. Found: C, 42.01; H, 2.61; N, 16.22.

Results and Discussion

When $Ru(tpy)Cl_3$ is treated with 1 equiv TPT, the dication $(TPT)Ru(tpy)^{2+}$ is obtained in 72% yield, (see Scheme I). This species possesses a mirror plane so that its 14 nonequivalent aromatic protons are almost completely resolved at 300 MHz, although the exact assignments are not obvious (top, Figure 1). When this complex is subsequently treated with 1 equiv of $Ru(bpy)_2Cl_2\cdot 2H_2O$, a second ruthenium is introduced into a bidentate site and the complex $[(bpy)_2Ru(TPT)Ru(tpy)]^{4+}$ is obtained in 87% yield. This molecule shows no symmetry, and all 39 aromatic protons are nonequivalent, providing the NMR spectrum shown at the top of Figure 2. Very little useful structural information

(11) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
(12) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.
(13) Thummel, R. P.; Jahng, Y. *J. Org. Chem.* **1985**, *50*, 3635.
(14) Thummel, R. P.; Jahng, Y. *Inorg. Chem.* **1986**, *25*, 2527.

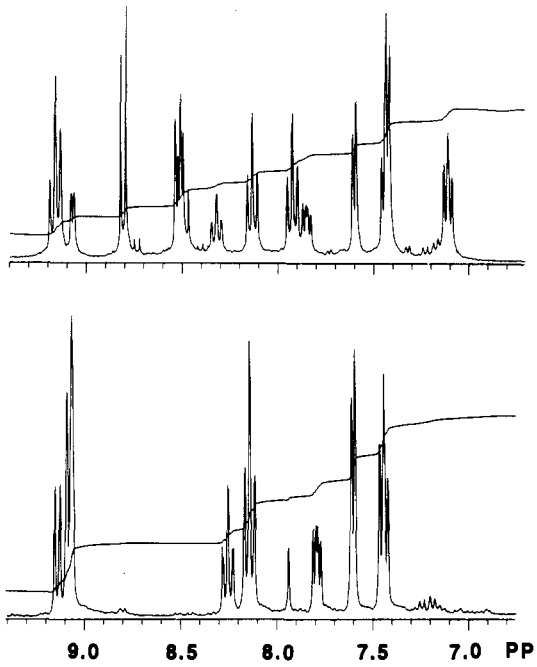

Figure 1. Downfield region of the ^1H NMR spectra of $[(TPT)Ru(tpy)](PF_6)_2$ (top) and $[(TPT)Ru(tpy\text{-}d_{11})](PF_6)_2$ (bottom) recorded at 300 MHz in CD_3CN.

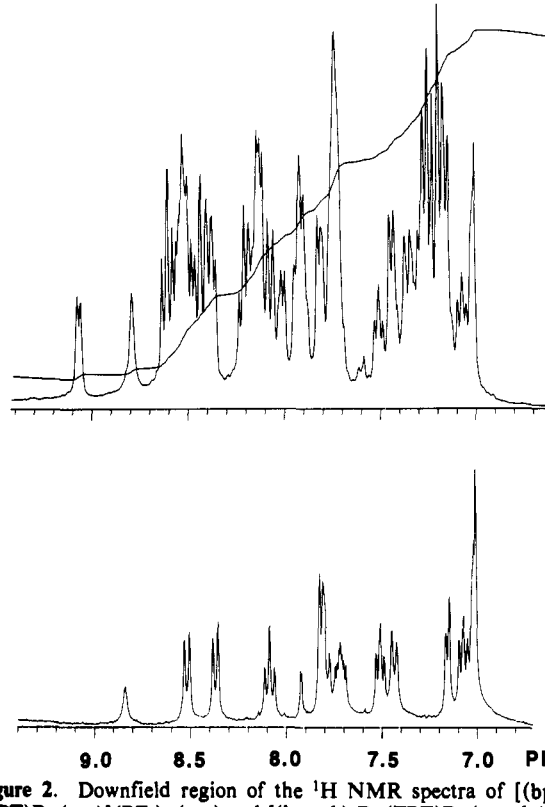

Figure 2. Downfield region of the ^1H NMR spectra of $[(bpy)_2Ru(TPT)Ru(tpy)](PF_6)_4$ (top) and $[(bpy\text{-}d_8)_2Ru(TPT)Ru(tpy\text{-}d_{11})](PF_6)_4$ (bottom) recorded at 300 MHz in CD_3CN. Peaks in the lower spectrum at 7.92 and 8.84 ppm are due to residual protio tpy.

can be derived from this spectrum.

A perdeuterio analogue of tpy can be prepared by a procedure similar to that employed in the preparation of bpy-d_8. The *N*,*N*′,*N*″-trioxide of tpy[13] undergoes H–D exchange upon heating at 150–160 °C in $NaOD/D_2O$. After two such treatments, followed by reduction back to tpy-d_{11}, 95% deuterium incorporation may be realized, with the principal sites of residual proton being H_4, $H_{4''}$ and H_6, $H_{6''}$. Tpy-d_{11} may then be used to prepare the reagent $Ru(tpy\text{-}d_{11})Cl_3$, which can, in turn, be treated with TPT to provide the complex $(TPT)Ru(tpy\text{-}d_{11})^{2+}$. All the tpy

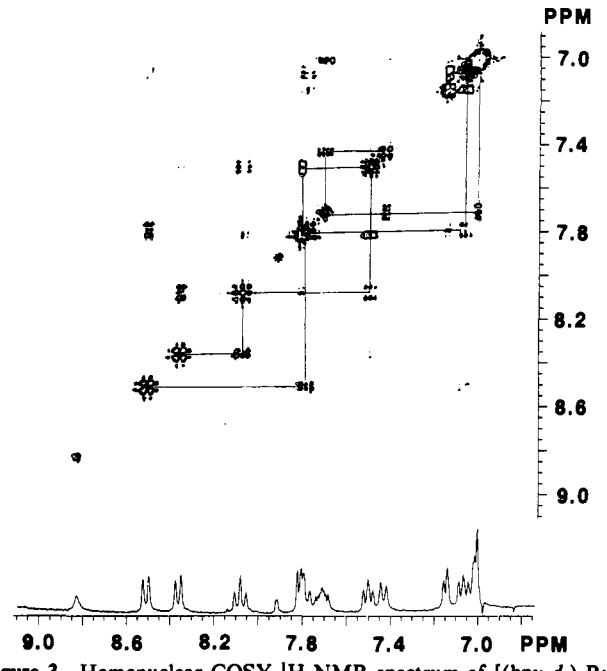

Figure 3. Homonuclear COSY ^1H NMR spectrum of $[(bpy\text{-}d_8)_2Ru(TPT)Ru(tpy\text{-}d_{11})](PF_6)_4$ recorded at 300 MHz in CD_3CN.

resonances have disappeared from the NMR spectrum of this complex, which exhibits only two sets of four proton resonances in a 2:1 ratio for the TPT ligand (bottom, Figure 1). The more abundant peaks are associated with the two equivalently bound pyridyl rings of TPT. It is interesting to note that the protons on the unbound pyridyl ring, $H_{3'}$–$H_{6'}$, have shifted slightly upfield in the complex containing tpy-d_{11}. This shift is most clearly evident for the $H_{4'}$ (8.25) and $H_{5'}$ (7.78) triplets which are found at 0.07 ppm higher field. The $H_{3'}$ and $H_{6'}$ doublets are less clear due to overlap. This shielding is associated with decreased conjugation between the unbound pyridyl ring and the central triazine, probably resulting from a small steric isotope effect due to tpy-d_{11} causing a small increase in the dihedral angle between these two rings.

When $[(TPT)Ru(tpy\text{-}d_{11})](PF_6)_2$ is treated with $Ru(bpy\text{-}d_8)Cl_2\cdot 2H_2O$, a binuclear complex is obtained for which only the 12 nonequivalent TPT protons are observed by ^1H NMR spectroscopy. The lower spectrum in Figure 2 shows these 12 signals with some overlap. To facilitate the assignment of these signals, a 2-dimensional proton-coupled COSY experiment was carried out, and the resulting spectrum is shown in Figure 3. Three separate four-proton spin systems can be identified. The doublets are due to protons in the 3- and 6-positions, and the triplets (or multiplets) are due to protons in the 4- and 5-positions. The four peaks at 8.37, 8.09, 7.51, and 7.82 ppm are assigned to $H_{3'}$–$H_{6'}$ of the pyridyl ring of TPT bound to $Ru(bpy\text{-}d_8)_2^{2+}$ by analogy with $Ru(bpy)_3^{2+}$, which shows similar resonances at 8.53, 8.06, 7.41, and 7.75 ppm.[15] The lowest field doublet at 8.52 ppm is assigned as H_3 on the pyridyl ring most remote from $Ru(bpy\text{-}d_8)_2^{2+}$, thus establishing the identity of H_4–H_6. This leaves the remaining four-proton system as $H_{3''}$–$H_{6''}$. Notice that the chemical shifts of the protons on the two pyridyl rings bound to $Ru(tpy\text{-}d_{11})^{2+}$ are quite similar with the exception of the shifts of H_3 and $H_{3''}$, the latter of which has shifted 1.67 ppm upfield due to shielding by the proximate $Ru(bpy\text{-}d_8)_2^{2+}$ subunit while H_3 only shifts upfield by 0.58 ppm.

Acknowledgment. We are grateful to the Robert A. Welch Foundation and the National Science Foundation (Grant CHE-8607935) for financial support of this work. The NMR spectrometer was partially funded by the NSF (Grant CHE-8616352).

(15) Thummel, R. P.; Lefoulon, F.; Korp, J. *Inorg. Chem.* **1987**, *26*, 2370.