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Registry No. Cu(qo)$_2$, 61721-88-8; 3Cu(qo)$_2$·2KI, 106400-05-9; 3Cu(qo)$_2$·2NH$_4$I·C$_2$H$_5$OH, 106297-49-8; Cu(qo)$_2$·MeOH, 106297-47-6; Cu(qo)$_2$·2Bu$_4$NI, 106297-51-2; Cu(qo)$_2$·Bu$_4$NCl, 106297-53-4; Cu(qo)$_2$·Bu$_4$NBr, 106297-55-6; K(qo)·$^1/_2$H$_2$O, 106319-53-3.

Supplementary Material Available: Tables of calculated atomic coordinates for hydrogen atoms, torsion angles, and anisotropic thermal parameters (3 pages); a listing of observed and calculated moduli of structure factors (20 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Polyaza Cavity Shaped Molecules. 11. Ruthenium Complexes of Annelated 2,2′-Biquinoline and 2,2′-Bi-1,8-naphthyridine

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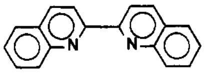
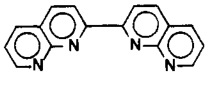
Ruthenium(II) complexes of the type RuL$_3$(PF$_6$)$_2$ and Ru(bpy)$_2$L(PF$_6$)$_2$ have been prepared, where bpy = 2,2′-bipyridine and L is a 3,3′-polymethylene-bridged derivative of 2,2′-biquinoline or 2,2′-bi-1,8-naphthyridine. Effects associated with steric crowding and nonplanarity of the bridged ligands are reflected in the coordination geometry of the RuL$_3^{2+}$ complexes. These effects can be partially evaluated by consideration of NMR shielding effects and interpretation of ^{1}H spin–spin couplings along the polymethylene bridge. The energies of the long-wavelength MLCT absorption are sensitive to the delocalizing ability of the ligand as well as the effectiveness of coordination as dictated by steric effects. Varying the dihedral angle of the 1,4-bidentate chelating moiety affects the intensity more than the energy of charge transfer to the ligands. The oxidation potentials for the tris(biquinoline) complexes are more positive than for Ru(bpy)$_3^{2+}$ while those of the tris(binaphthyridine) complexes are more negative.

Introduction

Ruthenium complexes of 2,2′-bipyridine (bpy) and related compounds have recently been the subject of intensive investigation.[1] Interest in these systems stems partly from their potential photocatalytic activity in the solar conversion of water into its elements.[2] Although the properties of the parent system, Ru(bpy)$_3^{2+}$, have been extensively studied, there have been relatively few attempts to vary the nature of the bipyridyl ligands in a regular fashion to evaluate the impact of steric and electronic factors on the complex.[3] We have undertaken such a study and herein report our initial results involving ruthenium complexes of annelated derivatives of 2,2′-biquinoline (**1**, biq) and 2,2′-bi-1,8-naphthyridine (**2**, binap).



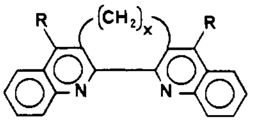
1 (biq)



2 (binap)

We have chosen to prepare and study complexes of azabiaryl systems in which three variables are altered in a regular fashion so as to allow an evaluation of their relative importance in determining the properties of the system. The coordinating azaaryl nucleus has been varied from pyridine to quinoline to 1,8-naphthyridine. The two polynuclear biaryl systems are expected to differ from bipyridine with respect to steric bulk as well as electron delocalization and electronegativity. Second, we have varied the conformation of the biaryl system by connecting the 3- and 3′-positions with a polymethylene bridge. Third, we have examined complexes of the type RuL$_3^{2+}$, where three identical ligands are coordinated to the metal, and mixed-ligand complexes of the type Ru(bpy)$_2$L^{2+}, where one biq- or binap-type ligand is coordinated along with two bipyridines. In this report we will carefully examine the effect of ligand conformation on complexation as well as the complementary effect of coordination on ligand conformation.

In 1976, Klassen first reported preparation of the Ru(biq)$_3^{2+}$ complex and noted a significant red shift in the energy of its lowest lying triplet state.[4] Belser and von Zelewsky have prepared ruthenium complexes of a series of 4,4′-disubstituted 3,3′-annelated biquinolines (**3**) where the annelating bridge contained one to three methylene units and R was methyl or phenyl.[3c] In a subsequent study, they elucidated the photophysical and electron-transfer properties of Ru(bpy)$_{3-n}$(DMCH)$_{n+2}$, where n = 0–3 and DMCH was **3** (x = 2, R = CH$_3$).[5] Their results indicated that this complex where n = 1 is expected to be a more efficient mediator than Ru(bpy)$_3^{2+}$ in the water-splitting reaction. Uhlemann and co-workers have studied the spectroscopic properties and stability of copper(I) complexes of ligands of the type **3**.[6] Thomas and Rehorek have extended this work to include copper(II).[7]



3 (x = 1–3, R = CH$_3$, C$_6$H$_5$)

Although ruthenium complexes of 1,8-naphthyridine and substituted derivatives are known, no complexes have been reported for 2,2′-bi-1,8-naphthyridine (**2**).[8] Kaska and co-workers, however, have prepared a tris complex of the 3,3′-dimethylene-bridged derivative **5a**, for which they observe spectral and photophysical

---

(1) See for example: (a) Angel, S. M.; DeArmond, M. K.; Donohoe, R. J.; Hanck, K. W.; Wertz, D. W. *J. Am. Chem. Soc.* **1984**, *106*, 3688. (b) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *Ibid.* **1984**, *106*, 2172. (c) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *Ibid.* **1982**, *104*, 4803. (d) Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *Ibid.* **1982**, *104*, 3618 and references cited therein.

(2) See for example: (a) Abruna, H. D.; Teng, A. Y.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 6745. (b) Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423. (c) Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Isr. J. Chem.* **1982**, *22*, 87. (d) Connolly, J. S. *Photochemical Conversion and Storage of Solar Energy*; Academic: New York, 1981; Chapters 4 and 6 and references therein.

(3) (a) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613. (b) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *Ibid.* **1976**, *98*, 6536. (c) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, *63*, 1675.

(4) Klassen, D. M. *Inorg. Chem.* **1976**, *15*, 3166.

(5) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 2175.

(6) (a) Uhlemann, V. E.; Kurze, P. *J. Prakt. Chem.* **1970**, *312*, 1105. (b) Uhlemann, V. E.; Thomas, P.; Kempter, G. *Ibid.* **1965**, *30*, 273. (c) Uhlemann, V. E.; Thomas, P.; Kempter, G. *Z. Anorg. Allg. Chem.* **1965**, *341*, 11. (d) Uhlemann, V. E.; Thomas, P. *Ibid.* **1965**, *341*, 17.

(7) Rehorek, D.; Thomas, P. *Acta Chim. Acad. Sci. Hung.* **1977**, *93*, 149.

(8) Staniewicz, R. J.; Hendricker, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 6581.

0020-1669/87/1326-0675$01.50/0

Table I. Proton Chemical Shift NMR Data[a] for RuL_3^{2+} Complexes and the Corresponding Ligands

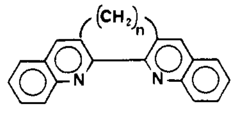
substrate	H_3	H_4	H_5	H_6	H_7	H_8	$-CH_2-$
$Ru(\mathbf{4a})_3^{2+}$		8.66	8.10	7.57	7.02	6.56	4.53
4a		8.26	7.82	7.55	7.74	8.46	4.20
$\Delta\delta$		+0.40	+0.28	+0.02	-0.72	-1.90	+0.33
$Ru(\mathbf{4b})_3^{2+}$		8.17	7.43	7.48	7.00	7.86	3.17/2.90
4b		8.03	7.77	7.52	7.68	8.43	3.20
$\Delta\delta$		+0.14	-0.34	-0.04	-0.68	-0.57	
$Ru(\mathbf{2})_3^{2+}$	8.54	8.54	8.30	7.24	7.47		
2	8.16	8.42	8.42	7.58	9.00		
$\Delta\delta$	+0.38	+0.12	-0.12	-0.34	-1.53		
$Ru(\mathbf{5a})_3^{2+}$		8.26	8.22	7.23	7.53		3.25
5a		8.12	8.18	7.50	9.23		3.31
$\Delta\delta$		+0.14	+0.04	-0.27	-1.70		
$Ru(\mathbf{5b})_3^{2+}$		8.09	8.20	7.30	7.77		2.61/2.42
5b		8.06	8.22	7.44	9.08		2.57/2.06
$\Delta\delta$		+0.03	-0.02	-0.14	-1.31		

[a] Obtained at 300 MHz in CD_3CN and reported in ppm downfield from internal Me_4Si. The numbering pattern is indicated in Table II.

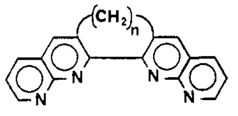
properties similar to those of $Ru(bpy)_3^{2+}$.[9]

Synthesis of Ruthenium Complexes

The ligands to be examined in this study are **1**, **2**, **4**, and **5**, the preparation and properties of which have been reported earlier.[10]



4a, *n* = 1
b, *n* = 2
c, *n* = 3
d, *n* = 4



5a, *n* = 2
b, *n* = 3
c, *n* = 4

The tris complexes of the type RuL_3^{2+} were prepared in the normal fashion by reacting $RuCl_3$ with excess ligand in aqueous ethanol and precipitating the complex by the addition of NH_4PF_6. Purification was effected by chromatography on alumina with toluene/acetonitrile as eluent and crystallization of the complex from the concentrated eluent. The mixed-ligand complexes $Ru(bpy)_2L^{2+}$ were prepared in a similar manner with *cis*-$Ru(bpy)_2Cl_2$ in place of $RuCl_3$.

Although the ligands **4c** and **4d** appeared to react with $Ru(bpy)_2Cl_2$, the resulting complexes decomposed upon attempted purification and could not be isolated.[11] We assumed that the corresponding tris complexes of **4c** and **4d**, being more sterically hindered, would not form and did not attempt their preparation. On the other hand, mixed-ligand complexes could be prepared for all three bridged bi-1,8-naphthyridines but only **5a** and **5b** would form tris complexes.

All the complexes were soluble in CD_3CN and thus were characterized by their 300-MHz ^1H NMR spectra. High symmetry allowed complete assignment of the RuL_3^{2+} complexes (Table I), but the aromatic region of the $Ru(bpy)_2L^{2+}$ systems was often too complex for complete assignment. The 3,3′-bridge protons appeared at higher field and gave the correct integration for the reported stoichiometry. For the tris complexes this integration could allow some ambiguity as to the number of ligands associated with each metal. This question was answered by examining the thermospray ionization interfaced LC–MS spectra of these compounds. Figure 1 illustrates for $Ru(\mathbf{5a})_3(PF_6)_2$ how this convenient technique[12] allowed observation of both the doubly charged (*m/e* 447) and singly charged (*m/e* 953) parent cation as well as the $Ru^IL_2^+$ (*m/e* 669) species and the dissociated ligand (*m/e* 285).

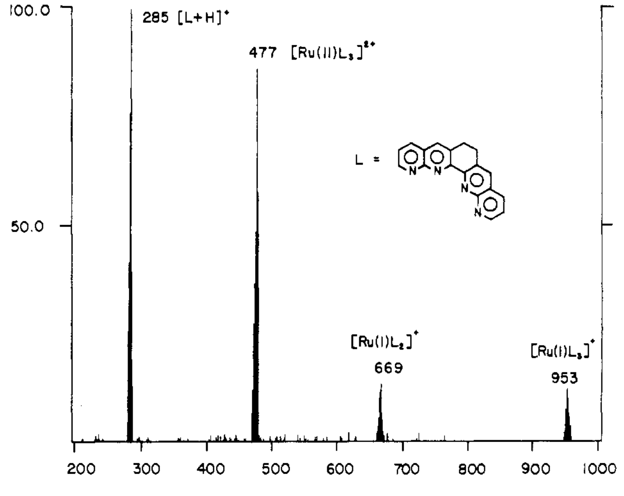


Figure 1. Thermospray ionization interfaced LC–MS of $Ru(\mathbf{5a})_3(PF_6)_2$ in aqueous ammonium acetate.

Properties and Conformational Effects

The inability of certain azabiaryl ligands to coordinate effectively in an octahedral fashion with ruthenium(II) may be explained by invoking two types of steric effects. The first effect involves the relative orientation of the two coordinating nitrogen atoms in a given ligand system while the second effect stems from congestion around the metal atom caused by substituents or additional rings fused to the central bipyridine moiety.

For the bridged biaryl systems under examination, the lowest energy conformation is nonplanar when the 3,3′-bridge contains two or more methylene units. The dihedral angle between the two covalently bonded aromatic rings (Table II) is estimated to be 20° for *n* = 2, 55° for *n* = 3, and 80° for *n* = 4. If effective coordination requires these two rings to become approximately coplanar, the bridging methylene units will experience substantial torsional strain and nonbonded interactions as they are also forced closer to planarity. Some relief of this strain may be achieved by distortion of the 2,2′-bond connecting the aromatic rings in such a way as to bring the two coplanar rings closer to one another. Table II shows estimated distances between the two coordinating nitrogens for the nonplanar uncomplexed ligands and for the same systems where the two aromatic rings are constrained to the same plane. For the cases where *n* = 2, 3, and 4, this N–N distance shortens substantially, by as much as 0.8 Å in the last two cases. It is interesting to note that a monomethylene bridge has the opposite effect and tends to distort the 2,2′-bond in the other direction, pulling the two interior nitrogens further apart. In fact,

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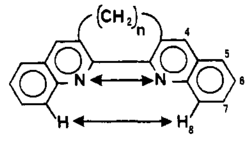
(9) Binamira-Soriaga, E.; Sprouse, S. D.; Watts, R. J.; Kaska, W. C. *Inorg. Chim. Acta* **1984**, *84*, 135.

(10) (a) Thummel, R. P.; Lefoulon, F.; Cantu, D.; Mahadevan, R. *J. Org. Chem.* **1984**, *49*, 2208. (b) Thummel, R. P.; Lefoulon, F. *Ibid.* **1985**, *50*, 3824.

(11) von Zelewsky and Belser have reported preparation of $Ru(bpy)_2(3)(PF_6)_2$, where R = CH_3 and *x* = 3.[3c]

(12) Blakley, C. R.; Vestal, M. L. *Anal. Chem.* **1983**, *55*, 750.

Table II. Estimated[a] Dihedral Angles (±2°) and Key Interatomic Distances (±0.1 Å) for 3,3'-Annelated 2,2'-Biquinolines



ligand	θ	N-N	H-H	N-N[b]	H-H[b]
4a (n = 1)	0	3.2	7.2	3.2	7.2
4b (n = 2)	20	2.85	6.1	2.6	5.7
4c (n = 3)	55	3.1	6.7	2.3	4.8
4d (n = 4)	80	3.2	7.0	2.4	5.1

[a] Measured from Dreiding and Feiser molecular models. [b] Distances for θ(planar ligand) = 0°.

the N-N distances for **4a** and **4d** are very comparable although these two systems differ greatly with regard to dihedral angle.

The second steric effect involves congestion around the central metal atom caused by the benzo or pyrido rings fused at the 5,6- and 5',6'-positions of the central bipyridine moiety. If the biaryl system becomes approximately planar due to coordination, the flattening of the polymethylene bridge and the resulting bending of the 2,2'-bond decreases the size of the ligand cavity. Table II indicates an estimated shortening of the H(8)-H(8') distance by almost 2 Å, where n = 3 and 4. In the RuL_3^{2+} complexes these C(8)-H bonds will be pointing into the face of an orthogonal ligand, causing congestion and inhibiting coordination. On the other hand, the bi[1,8]naphthyridine ligands **5**, which lack a hydrogen at the 8- and 8'-positions, should be able to form tris complexes around ruthenium with less problem of congestion. The possibility that the 8- and 8'-nitrogens might participate in the coordination appears unlikely, particularly in light of a study on the copper(II) complexes of these systems.[13]

Nuclear Magnetic Resonance Spectra

This steric congestion effect may be evaluated by careful consideration of the NMR data presented in Table I. This table lists the ^1H chemical shifts for the free ligands and their corresponding RuL_3^{2+} complexes and indicates the change in chemical shift ($\Delta\delta$) that occurs upon complexation. In each case a large change is observed for the aromatic proton held in closest proximity to the shielding region of an orthogonal ligand: H_8 for the biquinolines and H_7 for the binaphthyridines. With some small exceptions, the effects felt at the more remote positions, H_4, H_5, and H_6, are much less pronounced. The most dramatic shift is observed for $Ru(\mathbf{4a})_3^{2+}$, where H_8 shifts upfield by 1.9 ppm. Since this ligand must be planar, the complex should manifest a very regular octahedral geometry, whereby H_8 points directly into the face of the pyridine portion of an orthogonal ligand. For $Ru(\mathbf{4b})_3^{2+}$ the dimethylene bridge causes some skewing, which may diminish this shielding effect. Another contributing factor might be poor Ru-N overlap found in $Ru(\mathbf{4a})_3^{2+}$ as a result of the large bite angle of **4a**. This poor overlap would result in less ligand to metal charge delocalization and thereby less deshielding of H_8. The possible weakness of the Ru-N bonds in $Ru(\mathbf{4a})_3^{2+}$ is consistent with the unusually low yield (16%) obtained for this complex.

It is noteworthy that H_7 for the tris(bi-1,8-naphthyridine) system is highly shielded and shifts upfield while this same proton in the complex $Ru(nap)_4^{2+}$ is deshielded and shifts downfield by 0.73 ppm.[8] The dodecahedral geometry of the latter eight-coordinate complex obviously orients the 1,8-naphthyridine (nap) rings in an array far different from that found in the octahedral six-coordinate system and emphasizes the sensitive nature of these shielding effects as a probe of coordination geometry.

By analysis of the upfield region of the ^1H NMR spectra of **4** and **5** we have previously established that on the NMR time scale the dimethylene- and trimethylene-bridged systems are conformationally mobile while the tetramethylene-bridged ones are rigid. It was of interest to observe how this situation is affected by coordination with ruthenium. Previous workers have examined a series of three ruthenium complexes with DMCH and established that the dimethylene bridge is conformationally rigid.[3a] Their interpretation of the NMR data, however, appears to be somewhat oversimplified. Figure 2 illustrates the aliphatic region for $Ru(\mathbf{4b})_3^{2+}$ at 300 MHz. This deceivingly simple pattern confirms the rigidity of the dimethylene bridge but defies first-order interpretation.[14] Interestingly, in the corresponding tris complex of the dimethylene-bridged binaphthyridine, $Ru(\mathbf{5a})_3^{2+}$, the bridge is conformationally mobile as evidenced by a singlet at 3.25 ppm. Thus it appears that the rigidity of **4b** in $Ru(\mathbf{4b})_3^{2+}$ is the result of congestion due to H_8, which is not present in $Ru(\mathbf{5a})_3^{2+}$.

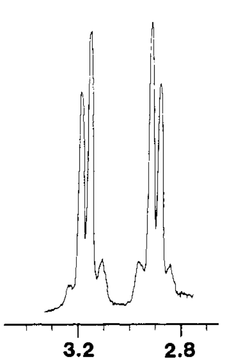
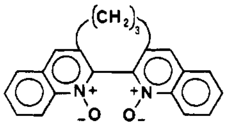


Figure 2. 300-MHz ^1H NMR spectrum of the aliphatic region of $Ru(\mathbf{4b})_3(PF_6)_2$ in CD_3CN.

The effect of coordination itself on the inversion barrier for a bridged ligand becomes clearer when we consider the trimethylene-bridged complexes. For $Ru(bpy)_2(\mathbf{5a})^{2+}$ we observe a singlet for the dimethylene bridge, which is consistent with the results obtained for $Ru(\mathbf{5a})_3^{2+}$. For $Ru(\mathbf{5b})_3^{2+}$ two of the α-methylene protons are shifted upfield to overlap with the β-methylene protons due to shielding by the outer pyridine ring of an orthogonal ligand. This shielding effect is not present in $Ru(bpy)_2(\mathbf{5b})^{2+}$, and the well-resolved pattern illustrated in Figure 3 is observed. We have succeeded in simulation of this pattern as an $(ABC)_2$ system where A and B are the two nonequivalent benzylic protons, one of which is clearly deshielded with respect to the other. The molecule possesses a C_2 axis, causing the non-benzylic methylene protons, designated as C, to be equivalent. Thus we derive the coupling constants shown in Figure 3.

Ideally one might hope to utilize the Karplus relationship between vicinal coupling constants and dihedral angle to gain information about the conformation of the coordinated ligand. It has been established, however, that substituents can have a profound effect on this relationship[16] and thus valid comparisons can be made only between similar systems. For this reason we chose the di-*N*-oxide **6** as an example of a conformationally rigid, noncoordinated, trimethylene-bridged ligand.[10b] Simulation of the aliphatic region of **6** is illustrated in Figure 4 and provides the indicated coupling constants. The fact that we observe a smaller coupling constant, J_{AC}, for **6** than for $Ru(bpy)_2(\mathbf{5b})^{2+}$



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(13) Draux, M.; Bernal, I.; Lefoulon, F.; Thummel, R. P. *Inorg. Chim. Acta* **1985**, *104*, 203.

(14) Simulation for a four-spin system utilizing a Varian SIMEQ program for patterns obtained at both 90 and 300 MHz were unsuccessful. It is not unusual for systems demonstrating chemical equivalence without magnetic equivalence to defy first-order interpretation.[15]

(15) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Oxford, England, 1969; p 147.

(16) Reference 15, p 281.

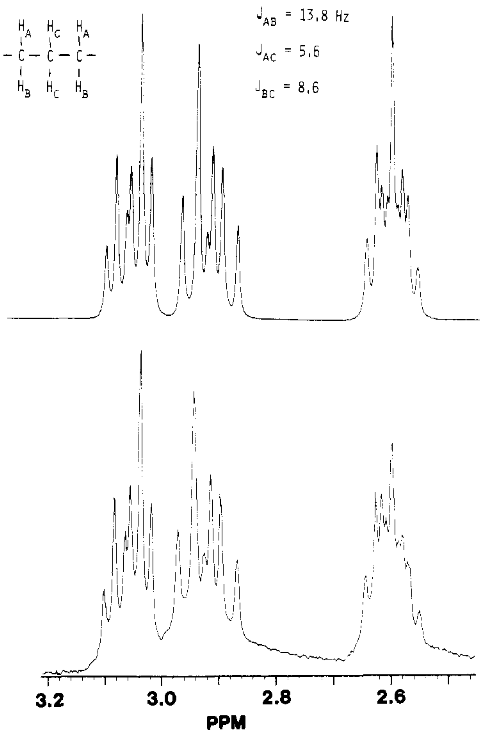

Figure 3. ^{1}H NMR spectra of the aliphatic region of Ru(bpy)$_2$(**5b**)(PF$_6$)$_2$: (bottom) experimental spectrum at 300 MHz in CD$_3$CN; (top) simulated spectrum.

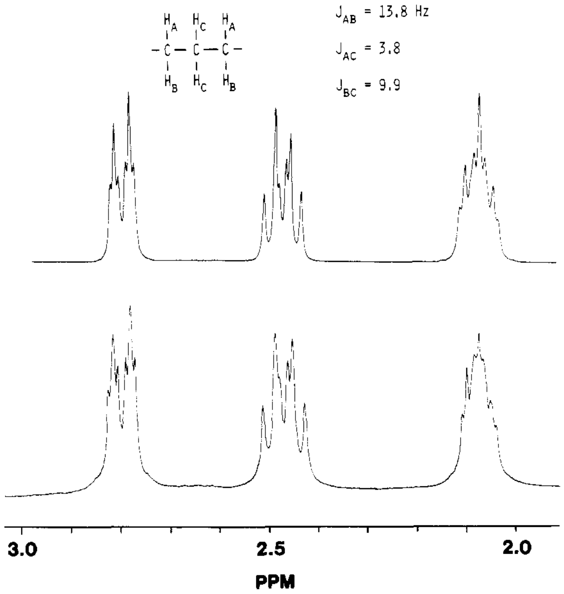

Figure 4. ^{1}H NMR spectrum of the aliphatic region of 3,3′-trimethylene-2,2′-biquinoline di-*N*-oxide (**6**): (bottom) experimental spectrum at 300 MHz in CDCl$_3$; (top) simulated spectrum.

Table III. Electronic Absorption Data for Ruthenium Complexes (nm)

complex	λ_{max}(CH$_3$CN) (ϵ)		
Ru(bpy)$_3^{2+\,a}$	450 (14 000)		284 (80 000) 253 (sh) 243 (25 000)
Ru(**1**)$_3^{2+\,b}$	524 (9000) 485 (6600)		
Ru(**4a**)$_3^{2+}$	512 (7500)	380 (41 000) 358 (28 000) 305 (34 000)	262 (62 000)
Ru(**4b**)$_3^{2+}$	540 (8130) 498 (5800)	396 (33 650) 374 (29 900) 330 (32 700)	266 (65 420)
Ru(**2**)$_3^{2+}$	596 (3920) 572 (4490) 550 (3920)	342 (60 560)	242 (67 290)
Ru(**5a**)$_3^{2+}$	582 (10 300) 560 (7850)	388 (32 700) 358 (56 080)	270 (31 780) 242 (63 550)
Ru(**5b**)$_3^{2+}$	586 (10 280) 540 (7480)	368 (43 980) 343 (54 200)	266 (46 730)
Ru(bpy)$_2$(**1**)$^{2+}$	525 (7290) 420 (7480)	375 (14 950) 320 (26 170)	286 (59 800) 264 (46 730)
Ru(bpy)$_2$(**4a**)$^{2+}$	506 (7420) 422 (13 350)	380 (46 100) 368 (25 500) 358 (29 100)	286 (72 800) 262 (57 000)
Ru(bpy)$_2$(**4b**)$^{2+}$	528 (7100) 440 (6170)	395 (22 430) 373 (14 950)	288 (52 340) 268 (42 990) 255 (33 650)
Ru(bpy)$_2$(**2**)$^{2+}$	574 (10 840) 436 (10 800)	346 (37 380)	286 (78 500) 244 (65 420)
Ru(bpy)$_2$(**5a**)$^{2+}$	576 (9350) 440 (8410)	394 (24 300) 369 (31 780) 316 (20 560)	283 (63 550) 240 (50 470)
Ru(bpy)$_2$(**5b**)$^{2+}$	568 (6840) 441 (9350)	361 (26 170) 325 (22 430)	286 (65 420) 243 (50 470)
Ru(bpy)$_2$(**5c**)$^{2+}$	562 (5600) 443 (10 280)	367 (18 700) 324 (18 700)	286 (56 070) 246 (41 120)

[a] Reference 8. [b] Reference 3c.

indicates that, according to the Karplus equation, the H$_A$–C–C–H$_C$ angle should be smaller for the metal complex than for the di-*N*-oxide, which is consistent with the flattening effect that would be expected upon coordination. As the bridge flattens, one would also expect the inversion barrier for the coordinated ligand **5b** to be lowered. However, in the metal complex, **5b** may be considered as bisannelated with the five-membered chelate ring constituting the second bridge. Apparently this second bridge sufficiently raises the energy barrier for inversion of the binaphthyridine conformation to lock the ligand into a rigid posture.

We had hoped to gain a more quantitative estimate of the inversion barrier of Ru(bpy)$_2$(**5b**)$^{2+}$ by heating this material in the NMR probe and observing coalescence to the simple downfield triplet and upfield quintent characteristic of a mobile trimethylene bridge. Due to its low boiling point, acetonitrile-d_3 was an inappropriate solvent for this experiment. When we instead employed nitrobenzene-d_5 as solvent, the bridge appeared to be mobile by NMR. Mixtures of the two solvents arrived at by dilution in either direction provided intermediate spectra (Figure 5). It appears that a solvent-induced change in chemical shifts caused by nitrobenzene-d_5 has caused accidental equivalence of H$_A$ and H$_B$.[17]

Electronic Absorption Spectra

The electronic absorption spectral data for the ruthenium complexes under discussion are summarized in Table III. Each absorption curve shows three distinct bands, and the data have been organized to emphasize this point.[18] The long-wavelength band is attributed to the metal to ligand charge transfer (MLCT) characteristic of such complexes. The two shorter wavelength bands are principally ligand-centered absorptions and show a good correlation with the spectra of the free ligands.[10]

The MLCT band for the Ru(bpy)$_2$L^{2+} complexes shows two components as is illustrated in Figure 6 for the complexes Ru(bpy)$_3^{2+}$, Ru(bpy)$_2$(**4b**)$^{2+}$, and Ru(bpy)$_2$(**5a**)$^{2+}$. One component, centered at 420–441 nm, is associated with MLCT into the bipyridine ligands. The longer wavelength component is due to charge transfer into the biquinoline or binaphthyridine ligand.

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(17) For a similar analysis of benzylacetone see: Danyluk, S. S. *Can. J. Chem.* **1963**, *41*, 387.

(18) von Zelewsky and Belser[3c] have reported the long-wavelength band of the complexes with **1** and **4b**, and Kaska et al.[9] have reported that for Ru(**5a**)$_3^{2+}$. Their data agree reasonably well with ours.

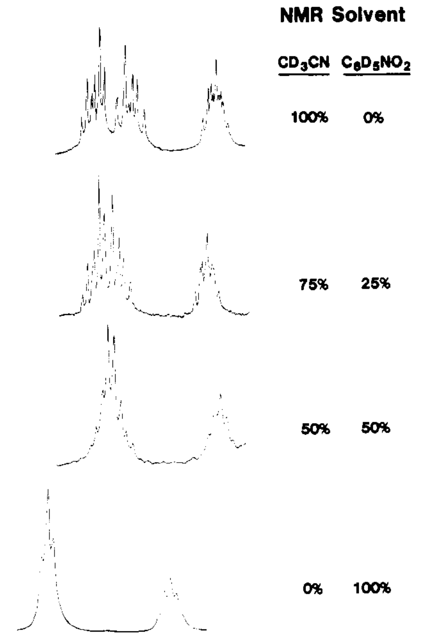

Figure 5. Solvent-dependent variations in the 300-MHz ^{1}H NMR spectrum of the aliphatic region of Ru(bpy)$_2$(**5b**)(PF$_6$)$_2$.

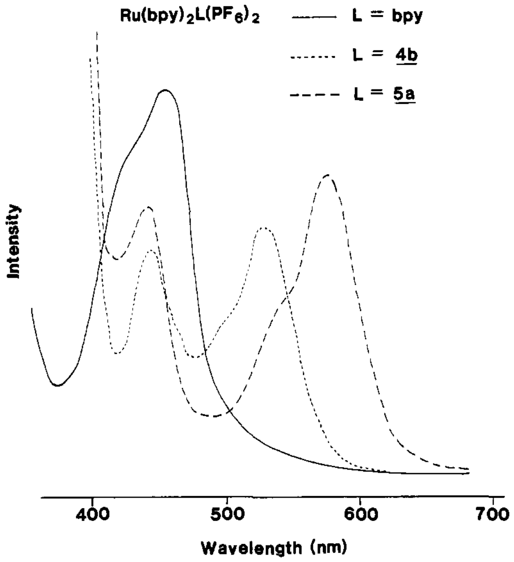

Figure 6. Variation in the electronic absorption spectra of Ru(bpy)$_2$L(PF$_6$)$_2$ as a function of the delocalizing ability of the ligand L (5.35×10^{-5} M in CH$_3$CN).

The observation of localized MLCT states in mixed-ligand ruthenium complexes has been reported for other similar systems and argues strongly for the absence of any significant interligand interactions.[3c,19]

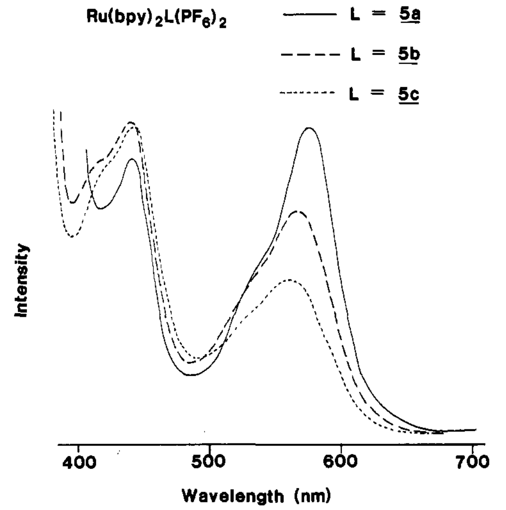

Figure 7. Variation in the electronic absorption spectra of Ru(bpy)$_2$(**5**)(PF$_6$)$_2$ as a function of bridge length (5.35×10^{-5} M in CH$_3$CN).

Table IV. Polarographic Half-Wave Potentials for Ruthenium(II) Complexes[a,b]

complex	$E_{1/2}$, oxidn Ru^2/Ru^{3+}	$E_{1/2}$, redn Ru^2/Ru$^+$	Ru$^+$/Ru^0	Ru^0/Ru$^-$
Ru(bpy)$_3^{2+\,c}$	+1.24	−1.34	−1.52	−1.75
Ru(**1**)$_3^{2+\,d}$	+1.47	−0.89	−1.25	−1.84
Ru(**4b**)$_3^{2+}$	+1.51	−0.80	−1.08	−1.68
Ru(**2**)$_3^{2+}$	+1.05	−0.80	−1.04	−1.40
Ru(**5a**)$_3^{2+}$	+1.01	−0.82	−1.07	−1.40
Ru(**5b**)$_3^{2+}$	+1.00	−0.89	−1.06	−1.50
Ru(bpy)$_2$(**1**)$^{2+}$	+1.37	−0.89	−1.36	−1.67
Ru(bpy)$_2$(**4a**)$^{2+}$	+1.36	−0.90	−1.43	−1.63
Ru(bpy)$_2$(**4b**)$^{2+}$	+1.34	−0.90	−1.37	−1.66
Ru(bpy)$_2$(**2**)$^{2+}$	+1.42	−0.53	−1.00	−1.60
Ru(bpy)$_2$(**5a**)$^{2+}$	+1.18	−0.76	−1.26	−1.83
Ru(bpy)$_2$(**5b**)$^{2+}$	+1.18	−0.80	−1.26	−1.84
Ru(bpy)$_2$(**5c**)$^{2+}$	+1.33	−0.70	−1.08	−1.70

[a] Potentials are in volts vs. SCE, and all waves were reversible. [b] Solutions were 0.1 M in TBAP; the solvent was acetonitrile; $T = 25 \pm 1$ °C. [c] Reference 9. [d] Reference 3c.

We observe the biquinoline-centered absorptions at 506 and 528 nm while the binaphthyridine ones appear at 562–576 nm. It is now well accepted that these transitions are associated with the promotion of an electron from a ruthenium d orbital to a ligand π^* orbital.[20] The decrease in energy of this transition on progressing from bipyridine to biquinoline to binaphthyridine can thus be correlated with a lowering of the energy of the π^* orbital concomitant with the increasing delocalizing ability of these ligands. It is interesting to note that the MLCT absorption associated with **4b** and **5a** is more intense than the bpy-centered one, although this last species is twice as prevalent in the complex. We are currently investigating Ru(bpy)$_2$L^{2+} complexes where L has an even greater delocalizing ability to see how far this charge-transfer preference can be modified.

The intensity of MLCT absorption is also dependent upon the strength of the coordinative bond. Figure 7 shows that, for the binaphthyridine series Ru(bpy)$_2$(**5**)$^{2+}$, lengthening of the annelating bridge in **5** from two carbons to four significantly diminishes MLCT into the binaphthyridine ligand while the proportional intensity of the bpy-centered band increases. The weakest long-wavelength absorption is thus observed for Ru(bpy)$_2$(**5c**)$^{2+}$, in which the highly distorted **5c**, by formation of the weakest coordinative bonds of this series, is the least efficient charge-transfer acceptor.

In this same series, Ru(bpy)$_2$(**5**)$^{2+}$, there also appears to be a reasonable correlation between the energy of the MLCT absorption and the length of the annelating bridge in **5**. As the bridge is lengthened from two carbons to four, this absorption shifts to shorter wavelengths or higher energy (Figure 7), indicating that as **5** becomes less planar, its ability to delocalize charge diminishes and the energy of its π^* orbital increases. According to this logic one would expect the band for Ru(bpy)$_2$(**4a**)$^{2+}$ at a value of greater than 528 nm while in fact it appears at 506 nm. The higher energy of this MLCT absorption is probably associated with the large bite angle of **4a**, which leads to weaker coordinative bonding. Within certain limitations, therefore, it may be possible to utilize conformational properties of the ligands to control both the position and intensity of MLCT absorptions associated with ruthenium(II) complexes.

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(19) (a) Anderson, S.; Seddon, K. R.; Wright, R. D.; Cocks, A. T. *Chem. Phys. Lett.* **1980**, *71*, 220. (b) Thummel, R. P.; Decloitre, Y. *Inorg. Chim. Acta*, in press.

(20) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: New York, 1984; Chapter 15.

Table V. Yield and Combustion Analysis Data for New Ruthenium Complexes

complex	yield, %	anal. calcd, %			anal. found, %		
		C	H	N	C	H	N
$Ru(\mathbf{2})_3(PF_6)_2 \cdot H_2O$	68	48.69	2.70	14.20	49.24	2.69	13.81
$Ru(\mathbf{4a})_3(PF_6)_2$	16	57.24[a]	3.01	7.03	53.81	2.96	7.02
$Ru(\mathbf{5b})_3(PF_6)_2 \cdot H_2O$	43	52.49	3.38	12.89	52.54	3.29	12.85
$Ru(bpy)_2(\mathbf{2})(PF_6)_2$	68	44.95	2.71	11.65	44.83	2.74	11.44
$Ru(bpy)_2(\mathbf{4a})(PF_6)_2 \cdot H_2O$	96	47.32	3.03	8.50	47.33	3.03	8.90
$Ru(bpy)_2(\mathbf{5a})(PF_6)_2$	82	46.20	2.84	11.35	46.02	2.86	11.33
$Ru(bpy)_2(\mathbf{5b})(PF_6)_2$	80	46.75	3.00	11.19	47.52	3.21	11.25
$Ru(bpy)_2(\mathbf{5c})(PF_6)_2$	89	47.29	3.15	11.03	47.38	3.20	11.51

[a] NMR analysis precludes the presence of any organic impurities; thus if we assume the presence of 6% NH_4PF_6, these calculated values become as follows: C, 53.84; H, 2.98; N, 7.13.

Redox Potentials

The polarographic half-wave potentials for the ruthenium(II) complexes under discussion have been determined by cyclic voltammetry and are summarized in Table IV with the exception of $Ru(\mathbf{4a})_3^{2+}$, which could not be obtained sufficiently pure. In every case, we observe one reversible oxidation wave and three reversible reductions. The usual criteria for reversibility were invoked such that the separation of the anodic and cathodic peaks, ΔE ($E_p^a - E_p^c$), is equal to or less than 60 mV for a one-electron process and that the ratio of anodic to cathodic current, i_p^a/i_p^c, is unity.[21] von Zelewsky and Belser have carried out similar measurements for ruthenium(II) complexes of **1** and **4b**. Their data correlates well with ours with the exception of $Ru(\mathbf{4b})_3^{2+}$, where they find half-wave potentials that are more negative for oxidation and more positive for reduction.[3c] Kaska's data for $Ru(\mathbf{5a})_3^{2+}$ is in good accord with ours.[9]

In a comparison of the oxidation potentials of the RuL_3^{2+}-type systems, the values for the three tris(biquinoline) complexes are 0.21–0.30 V more positive than for $Ru(bpy)_3^{2+}$ while the three tris(binaphthyridine) complexes are 0.21–0.26 V more negative. Since oxidation of $Ru(bpy)_3^{2+}$ involves the removal of an electron from a ruthenium t_{2g} orbital, the observed potential for this process provides evidence for the relative energies of these t_{2g} levels. The tris(biquinoline) complexes, being more difficult to oxidize, have lower lying t_{2g} levels than $Ru(bpy)_3^{2+}$ while the tris(bi-1,8-naphthyridines) have higher lying t_{2g} levels. Earlier efforts to correlate the energies of the MLCT absorptions with the ordering of these orbital energies[9] are not supported by this observation since both the tris(biquinoline) and tris(bi-1,8-naphthyridine) complexes show MLCT bands at substantially longer wavelength than $Ru(bpy)_3^{2+}$ (see Table III). It seems reasonable that the six uncoordinated nitrogen electron pairs present in the $Ru(binap)_3^{2+}$ systems might help to stabilize an RuL_3^{3+} state and thus lower the potential for its formation. Conversely, the lack of such available back-donation combined with weakened metal–ligand interactions due to congestion would contribute to raising the energy required to remove an electron from the tris(biquinoline) complexes. This mediating behavior is further corroborated by the oxidation potential of +1.40 V observed for $Ru(bpy)(\mathbf{1})_2^{2+}$, which is intermediate between the values of 1.47 and 1.37 V observed for $Ru(\mathbf{1})_3^{2+}$ and $Ru(bpy)_2(\mathbf{1})^{2+}$, respectively.[3c] The mixed-ligand bi-1,8-naphthyridine complexes show greater variation in the conformation of the bridged ligands, and the oxidation potentials vary in a less well-defined pattern from 1.18 to 1.42 V. As for the tris complexes, the unbridged system is the most difficult to oxidize.

For the first reduction wave, all the systems examined show potentials that are substantially (0.44–0.81 V) more positive than that of $Ru(bpy)_3^{2+}$, indicating that these complexes are more easily reduced[14a] and implying that their LUMO's are lower in energy. The greater ability of biquinoline and bi-1,8-naphthyridine to delocalize the added electron readily explains this behavior. The lower energy of these LUMO's is also in agreement with the shift of the MLCT band to lower energy, although the potentials for the tris(bi-1,8-naphthyridine) reductions do not differ notably from those of the tris(biquinoline) complexes.

Conclusions

In summary, we can say that effects associated with steric crowding and nonplanarity of bridged azabiaryl ligands are reflected in the coordination geometry of RuL_3^{2+} complexes. These effects can be partially evaluated by consideration of NMR shielding effects and interpretation of ^1H spin–spin couplings along the polymethylene bridge. The energies of the long-wavelength MLCT absorptions are sensitive to the delocalizing ability of the ligand as well as the effectiveness of coordination as dictated by steric effects. Varying the dihedral angle of the 1,4-bidentate chelating moiety affects the efficiency more than the energy of charge transfer to the ligands.

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Nicolet NT-300 WB spectrometer in CD_3CN with chemical shifts reported in parts per million downfield from Me_4Si. Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., New Westminster, BC, Canada. The preparation of the ligands has been previously described.[10] The *cis*-$(bpy)_2RuCl_2 \cdot 2H_2O$ was prepared according to a procedure described by Meyer and co-workers.[22]

Cyclic voltammograms were recorded with a PAR Model 174A polarographic analyzer, a PAR Model 175 universal programmer, and a Houston Instruments Omnigraphic 2000 X-Y recorder. A three-electrode system was employed consisting of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high-purity nitrogen through the solution for 5 min and maintaining a blanket of nitrogen over the solution while making measurements. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc–hexane, dried, and stored in a desiccator.

Preparation of RuL_3^{2+} Complexes. A mixture of 1 equiv of $RuCl_3 \cdot 3H_2O$ and 3.5 equiv of the ligand L in 50% aqueous ethanol was refluxed under nitrogen for periods ranging from 4 to 48 h. After the mixture was cooled, a solution of 2 equiv of NH_4PF_6 in 5 mL of H_2O was added to precipitate the complex, which was collected, dried, and chromatographed on 20–30 g of neutral alumina with 1:1 toluene–acetonitrile as the eluent. Fractions of 20 mL were collected, and those fractions containing the desired complex as indicated by TLC were allowed to stand at room temperature for 2–3 days, during which time the slow evaporation of acetonitrile caused the pure complex to crystallize. The yields and combustion analyses are summarized in Table V.

Preparation of $Ru(bpy)_2L^{2+}$ Complexes. The same procedure was followed as outlined above for RuL_3 with *cis*-$(bpy)_2RuCl_2 \cdot 2H_2O$ and the ligand L in a molar ratio of 1:1.2. The yields and combustion analyses are summarized in Table V.

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