axial compression perturbations are absent (or, if present, are of minor influence) in crystalline $[Co(OMPA)_3](BF_4)_2$.

Consequences of assuming the alternative (first) parameter set to be the correct one, are as follows. This set ($v = 0$, $v' = +100\ \mathrm{cm}^{-1}$) also predicts the correct order of excited states, $E'' < E'$ of $^2E(^2T_1)$, and the ground state is again $E'(\Gamma_4)$ from $^4A_2[^4T_1]$. The polarized crystal spectra implication of $^4A_2$ being the ground state and conclusions reached from the MCD and calculations are all consistent with each other. Obviously it is not now possible to decide unambiguously upon a parameter set. However, the assignment of states remains firm.

The above is a rare, but clear, example of the possibility of assigning the spin–orbit excited states of optically weak, spin-forbidden cobalt(II) transitions using Zeemann or MCD data and ligand field theory. However, the Zeemann experiment is not applicable here, since currently available magnetic field intensities are too low. On the other hand, MCD analysis allows one to identify such transitions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corp., and to the School of Physical and Mathematical Sciences of North Carolina State University for support of this research. R.S.E. held an American Chemical Society–Petroleum Research Fund Fellowship.

Registry No. $[Co(OMPA)_3](BF_4)_2$, 60464-13-3; $[Zn(OMPA)_3](BF_4)_2$, 60428-13-9.

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(7) Optical and MCD spectra were measured with light from a Spex 1400 $^3/_4$-m double monochromator and the $^1/_4\lambda$ modulator and electronics of a JASCO ORD/UV/CD-5 (SS-20 modification). Slit narrowing from 300 μ produced no improvements in the structured region of $^2T_{1g}(P)$.
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(10) v' is likely not to equal zero. However, for previously studied complexes it has been found that the absolute value of v is larger than that of v'.

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Synthesis and Spectroscopic Characterization of Ruthenium and Osmium Complexes with Sterically Hindering Ligands. 2.[1] Tris Complexes with 2-(2′-Pyridyl)quinoline and 2,2′-Biquinoline

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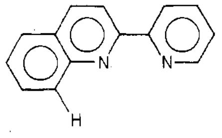
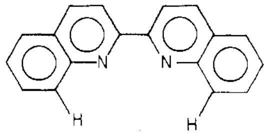
Recently we reported the synthesis and spectroscopic properties of bis(diquinolylpyridine) complexes of ruthenium(II) and osmium(II).[1] Of further interest are the complexes of these metals with the structurally related bidentate ligands 2-(2′-pyridyl)quinoline (pq) (1) and 2,2′-biquinoline (biq) (2).

The steric crowding caused by the hydrogen atoms on the benzo rings markedly changes the metal chelating properties of biq and pq as compared to 2,2′-bipyridine (bpy).[2,3] In particular a single benzo substitution of bpy to form pq changes the tris complex with iron(II) from low spin in $Fe(bpy)_3^{2+}$ to essentially high spin in $Fe(pq)_3^{2+}$, while double benzo substitution to form biq so increases the steric hindrance that the tris complex $Fe(biq)_3^{2+}$ could not be synthesized.[4] We report here the synthesis of the tris(pyridylquinoline) and tris(biquinoline) complexes of ruthenium(II) and osmium(II) and the effect of the benzo substituents on the absorption and emission spectra of the complexes.



1 (pq)



2 (biq)

Experimental Section

Ligands. 2-(2′-Pyridyl)quinoline (pq) was prepared as previously described[4] in 60% yield; mp 99–100°. 2,2′-Biquinoline (biq) was used as purchased from Columbia Organic Chemicals, Co.

Tris[2-(2′-pyridyl)quinoline]ruthenium(II) Perchlorate, $[Ru(pq)_3](ClO_4)_2$. A blue solution of ruthenium(II) chloride in methanol was prepared by the hydrogen (2 atm) reduction[5] of $RuCl_3 \cdot xH_2O$ (Engelhard Industries). Twenty milliliters of this solution containing 2 mmol of Ru(II) was added slowly under a nitrogen atmosphere to a hot (~80 °C) solution of 1.3 g (6.3 mmol) of pq dissolved in 25 ml of ethylene glycol. After distillation of the methanol solvent the reaction mixture was refluxed for 3 h and then heated for another 5 h while the volume was reduced to 10 ml. The cooled dark red solution was diluted with 20 ml of water and filtered. The filtrate was heated almost to boiling and $NaClO_4$ solution (10%) was added slowly. The reddish brown precipitate which formed was collected, washed with water, and air-dried. The solid was recrystallized from $EtOH–H_2O$ and dried to yield 1.6 g (87% yield). The complex was purified by saturating 10 ml of absolute methanol and passing it through a column (2.8 × 59 cm) of Sephadex LH-20 (Pharmacia Fine Chemicals). The main band was collected and the methanol allowed to evaporate slowly to produce reddish brown crystals which were then vacuum-dried for 24 h over P_2O_5. Anal. Calcd for $[Ru(C_{14}H_{10}N_2)_3](ClO_4)_2$: C, 54.91; H, 3.29; N, 9.15; Cl, 7.72. Found: C, 54.48; H, 3.05; N, 9.08; Cl, 7.80.

Tris(2,2′-biquinoline)ruthenium(II) Perchlorate, $[Ru(biq)_3](ClO_4)_2$. Essentially the same procedure was used for the synthesis of this complex as described above for the $[Ru(pq)_3](ClO_4)_2$ complex. Glycerol was used as the solvent and the reaction mixture was heated for only 1 h. Attempts to purify the product on a Sephadex LH-20 column produced a pale blue decomposition product all the way down the column. The complex was recrystallized twice from methanol to produce a 43% yield of brown crystals. Anal. Calcd for $[Ru(C_{18}H_{12}N_2)_3](ClO_4)_2$: C, 60.68; H, 3.40; N, 7.86. Found: C, 60.48; H, 3.47; N, 7.74.

Tris[2-(2′-pyridyl)quinoline]osmium(II) Perchlorate Hydrate, $[Os(pq)_3](ClO_4)_2 \cdot H_2O$. A mixture of 0.26 g (0.5 mmol) of $K_2OsCl_6 \cdot 2H_2O$ (Research Organic/Inorganic Chemical Corp.) and 0.40 g (1.9 mmol) of pq in 15 ml of glycerol were refluxed for 3 h under a nitrogen atmosphere. The dark solution was cooled, diluted with 20 ml of water, and filtered. Two 5-ml washings of the unreacted ligand were added to the filtrate. The filtrate was heated to 80–90 °C and 8 ml of a 10% solution of $NaClO_4$ added dropwise. The hot solution was cooled overnight in the refrigerator. The black precipitate which formed was collected, washed twice with cold water, and dried to give 0.30 g of product. An additional 0.09 g was obtained by evaporating the filtrate to dryness, dissolving the residue in hot water, and precipitating the product with aqueous sodium perchlorate. The complex was purified on a column (2.8 × 59 cm) of Sephadex LH-20 using methanol as the solvent. The methanol was evaporated and the residue dissolved in hot water and precipitated with $NaClO_4$. The black crystals were collected, washed with cold water, and vacuum-dried for 24 h over P_2O_5 to give 0.25 g (49% yield). Anal. Calcd for $[Os(C_{14}H_{10}N_2)_3](ClO_4)_2 \cdot H_2O$: C, 49.17; H, 3.14; N, 8.19; Cl, 6.91. Found: C, 49.09; H, 2.97; N, 8.10; Cl, 7.34.

Tris(2,2′-biquinoline)osmium(II) Perchlorate Hydrate, $[Os(biq)_3](ClO_4)_2 \cdot H_2O$. The same procedure was used for the synthesis and purification of this complex as described above for the [Os-

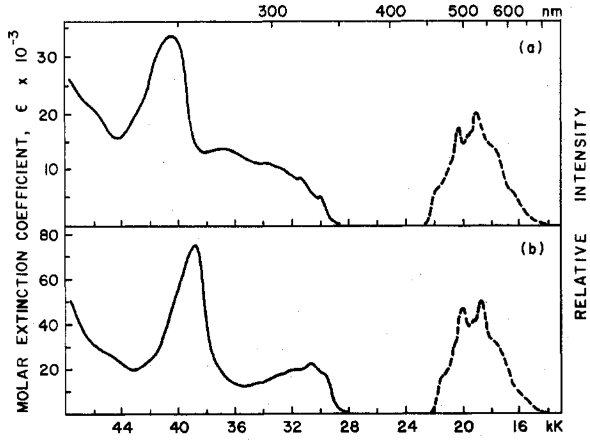


Figure 1. Absorption and phosphorescence spectra of ligands: (a) 2-(2′-pyridyl)quinoline; (b) 2,2′-biquinoline; –, absorption spectra in methanol at room temperature; - - -, phosphorescence spectra in EPA (diethyl ether–isopentane–ethanol, 5:5:2 v/v) at 77 K.

Table I. Energy of the 0-0 Band in the Luminescence of Ligands and Complexes at 77 K

Compd	Energy, cm^{-1}	Compd	Energy, cm^{-1}	Shift, cm^{-1}
bpy^a	23500^b	pq^c	21700 sh^e	1800
		biq^d	21400 sh^e	2100
[Ru(bpy)$_3$]Cl$_2$	17100^f	[Ru(pq)$_3$](ClO$_4$)$_2$	15200	1900
		[Ru(biq)$_3$](ClO$_4$)$_2$	13900	3200
[Os(bpy)$_3$]I$_2$	14100^g	[Os(pq)$_3$](ClO$_4$)$_2$	12200	1900
		[Os(biq)$_3$](ClO$_4$)$_2$	11200	2900

[a] bpy = 2,2′-bipyridine. [b] H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970). [c] pq = 2-(2′-pyridyl)quinoline. [d] biq = 2,2′-biquinoline. [e] Measured in EPA (diethyl ether–isopentane–ethanol, 5:5:2 v/v). [f] See ref 10 and 14. [g] See ref 11 and 14.

$(pq)_3](ClO_4)_2 \cdot H_2O$ complex. The procedure produced 0.24 g (41% yield) of black needle crystals. Anal. Calcd for $[Os(C_{18}H_{12}N_2)_3](ClO_4)_2 \cdot H_2O$: C, 55.15; H, 3.26; N, 7.15. Found: C, 55.65; H, 3.31; N, 6.84.

Spectroscopic Measurements. All absorption spectra were measured using a Cary 14 spectrophotometer with 1-cm quartz cells at room temperature. Emission spectra were measured with an American Instrument Co. Aminco-Bowman spectrophotofluorometer previously described.[1] The complexes were dissolved in methanol–ethanol 1:4 (v/v) solutions (about 10^{-4} M) and frozen to rigid glasses at 77 K by immersion of quartz sample tubes in liquid nitrogen. The excitation band-pass was 22 nm and the emission band-pass was 5.5 nm except for $Ru(pq)_3{}^{2+}$ where an emission band-pass of 1 nm was used. Optical Industries standard color filters OG-550 and RG-630 were placed in front of the PM tube for the pq and biq complexes, respectively. The luminescence spectrum of $Ru(pq)_3{}^{2+}$ was corrected for the wavelength dependence of the instrumental response using a standardized fluorescent solution[6] of 4-dimethylamino-4-nitrostilbene (2 μg/ml in *o*-dichlorobenzene). The relative intensities of the vibrational bands in the emission spectra of the other complexes were adjusted for the spectral response of the RCA 7102 tube using the values for a typical RCA 7102 tube.[7]

The phosphorescence spectra of 2-(2′-pyridyl)quinoline and 2,2′-biquinoline were measured in EPA (diethyl ether–isopentane–ethanol, 5:5:2 v/v) at 77 K. The excitation band-pass was 11 nm and the emission band-pass was 1 nm. An Optical Industries standard color filter GG-435 was placed in front of the PM tube. The spectra were corrected using a standardized fluorescent solution[6] of 3-aminophthalimide (1 μg/ml in 0.05 M H_2SO_4).

Results and Discussion

The absorption and phosphorescence spectra of 2-(2′-pyridyl)quinoline and 2,2′-biquinoline are presented in Figure 1. The energies of the 0–0 bands of the phosphorescence spectra of these molecules and of 2,2′-bipyridine are compiled in Table I. It is apparent that benzo substitution on 2,2′-bipyridine produces a red shift in the energy of the lowest lying triplet state and that the red shift is greater for biq than for pq.

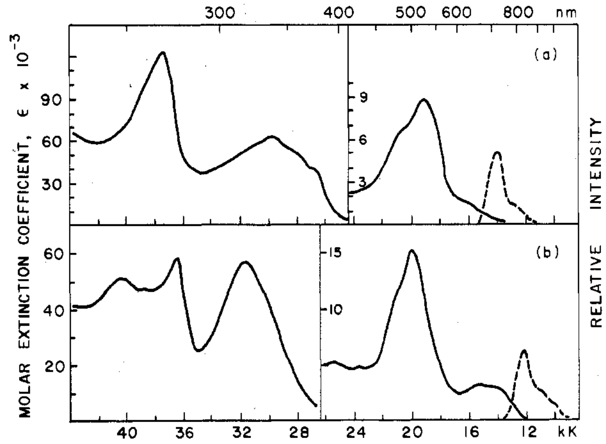


Figure 2. Absorption and luminescence spectra of representative complexes: (a) [Ru(biq)$_3$](ClO$_4$)$_2$; (b) [Os(pq)$_3$](ClO$_4$)$_2$; –, absorption spectra in methanol at room temperature; - - -, luminescence spectra in methanol–ethanol glass (1:4 v/v) at 77 K.

Table II. Energy at the Maximum of the Charge-Transfer Absorption Band of the Complexes^a

Compd^b	Energy, cm^{-1}	Compd^b	Energy, cm^{-1}	Shift, cm^{-1}
[Ru(bpy)$_3$]Cl$_2$	22000	[Ru(pq)$_3$](ClO$_4$)$_2$	20700	1300
		[Ru(biq)$_3$](ClO$_4$)$_2$	19100	2900
[Os(bpy)$_3$]I$_2$	20900	[Os(pq)$_3$](ClO$_4$)$_2$	20000	900
		[Os(biq)$_3$](ClO$_4$)$_2$	18700	2200

[a] Measured at room temperature in methanol. [b] See Table I for meaning of abbreviations.

The absorption and luminescence spectra of the ruthenium(II) biquinoline and the osmium(II) pyridylquinoline complexes are shown in Figure 2 and are representative for all four complexes. The intense absorption bands in the ultraviolet spectra, which are similar to the absorption bands of the protonated ligands recorded in 50% H_2SO_4, can be assigned to intraligand π–π^* transitions with the lowest energy ultraviolet band at a lower energy for the biq complexes (~29 000 cm^{-1}) than for the pq complexes (~32 000 cm^{-1}).

The complexes exhibit broad charge-transfer (CT, t_2–π^*) absorption bands in the visible region which are quite similar to the CT bands of the bpy complexes[8–14] except for the observed red shifts of the band maxima (Table II). This shift is much greater than that observed for 4,4′-dimethyl-2,2′-bipyridine[15–17] and 4,4′-diphenyl-2,2′-bipyridine[17,18] complexes indicating the greater effect of a benzo substitution on the bipyridine ligand. The red shift could result from (a) a decrease of the energy of the π^* level in pq and biq compared to that of bpy, (b) an increase in the energy of the t_2 metal ion orbital in pq and biq complexes, or (c) the combined effects of (a) and (b). A qualitative indication of the causes of the red shift can be obtained in the following way.

The relative energies of the highest occupied π molecular orbitals (HOMO's) of bpy and biq have been determined by HMO calculations[19] (for bpy $E_{HOMO} = -0.756\beta$, for biq $E_{HOMO} = -0.633\beta$). Using $\beta = 25\,800$ cm^{-1} from the first uv absorption band of the free bpy ligand[20] the relative energies of the orbitals can be calculated. Gil et al. have shown by a perturbational molecular orbital calculation that for tris-chelated compounds of bipyridine belonging to D_3 symmetry the last occupied π orbital from the ligand will not be perturbed by bonding to a metal ion[21] so that the energy of the HOMO calculated for the free ligand can be carried over to the complex. The position of the π^* orbital in the complex can

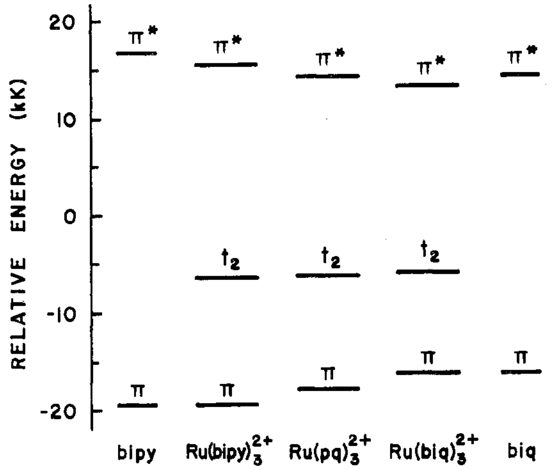


Figure 3. Relative orbital energies of ligands and ruthenium(II) complexes.

be determined from the first intense absorption band in the uv spectra of the complexes ([Ru(bpy)$_3$]$^{2+}$, 34 930 cm^{-1}; [Ru(biq)$_3$]$^{2+}$, 29 590 cm^{-1}) assuming that this band is due to a jump of an electron from the last occupied π orbital of the ligand to the first empty one, i.e., a π–π^* transition. The position of the metal t_2 orbital can then be determined from the energy of the charge-transfer (t_2–π^*) absorption band observed in the visible region. The results for the ruthenium complexes are plotted in Figure 3. Since HMO calculations are not available for pq, its HOMO is arbitrarily placed between that of bpy and biq and the relative energies of the other orbitals are calculated as for the bpy and biq complexes.

Three observations concerning Figure 3 can be made. First, the energy difference between the π and π^* levels is less for the biq complex than for the bpy complex, a result which is not surprising in view of the expected additional π-electron delocalization in biquinoline. Second, the energy of the t_2 orbital is higher in the biq complex than in the bpy complex, as would be expected if there is a decrease in the ligand field strength as a result of the increased metal–ligand bond distance caused by steric hindrance in the benzo-substituted complex. Presumably the metal e* orbital is lowered by the weaker field but still remains higher than or equal to the π^* orbital since no d–d transitions (t_2–e*) are observed at low energies in the absorption spectra. Third, the red shift in the CT absorption band results from both a lowering of the π^* level and a raising of the t_2 level but appears to result mainly from the downward shift of the π^* orbital. This conclusion is further substantiated by the fact that only slight shifts (100–300 cm^{-1}) of the CT bands are observed in ruthenium and osmium complexes with 6-methyl-2,2′-bipyridine and 6,6′-dimethyl-2,2′-bipyridine,[22] where a comparable amount of steric hindrance is expected.

The luminescence spectra of the pyridylquinoline and biquinoline complexes are very similar to those of the bipyridine complexes[10-13] with a 1200–1300 cm^{-1} vibrational progression observed on the spectra of all of the complexes. The 1900–3200 cm^{-1} red shift in the energy of the 0–0 bands of pq and biq complexes compared to the emission bands of the corresponding bpy complexes (Table I) parallels the red shift of the absorption charge-transfer bands. Again, this is a much larger shift than that observed (500–800 cm^{-1}) in the emission spectra of methyl- and phenyl-substituted bipyridine complexes.[16-18]

As previously described the CT absorption and emission bands of bis(diquinolylpyridine) (dqp) complexes of ruthenium and osmium are red shifted compared to those of the analogous complexes of terpyridine.[1] Considering the complexes of all three ligands, pq, biq, and dqp, the magnitude of the red shift increases in the order pq < dqp < biq. As more quinoline groups are added to the complex, there is a greater decrease in the energy of the π^* level and a greater red shift of the CT absorption and emission bands.

In view of the general interest in Ru(bpy)$_3^{2+}$, Os(bpy)$_3^{2+}$, and Ir(bpy)$_3^{3+}$ as photosensitizers[23] the relatively large shifts in the absorption and emission spectra brought about by benzo substitution of 2,2′-bipyridine may make pq and biq useful ligands for designing luminescent complexes which will further increase the range of available donor energies. It has been suggested that phenyl substitution on bipyridine be used as a "fine-tuning" device for the design of a series of complexes with slightly modified optical properties.[18] Along this line then, benzo substitution could be regarded as a "coarse-tuning" device to produce large shifts in absorption and emission spectra without changing the basic nature of the transitions responsible for the spectra (as would be the case with a "rough-tuning" device[18]). Additional "fine-tuning" could be possible by the use of phenyl- or methyl-substituted pyridylquinolines and biquinolines.

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Registry No. [Ru(pq)$_3$](ClO$_4$)$_2$, 60451-54-9; [Ru(biq)$_3$](ClO$_4$)$_2$, 60451-56-1; [Os(pq)$_3$](ClO$_4$)$_2$, 60451-58-3; [Os(biq)$_3$](ClO$_4$)$_2$, 60451-60-7; pq, 7491-86-3; biq, 119-91-5.

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Convenient Nonphotolytic Route to Substituted Carbonyl Anions of Vanadium, Niobium, and Tantalum

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Substitution of phosphines and other ligands for carbon monoxide in metal carbonyl anions provides substituted carbonyl anions which are often significantly more basic and nucleophilic than the corresponding binary carbonyl anion.[1-3]