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Synthesis and Spectroscopic Characterization of Bis[2,6-di(2'-quinolyl)pyridine] Complexes of Ruthenium(II) and Osmium(II)

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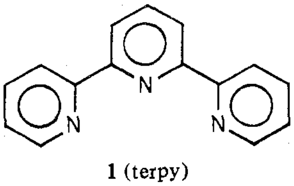
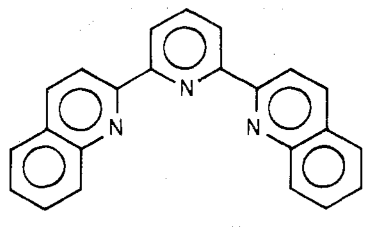
The preparation and spectroscopic characterization of the bis[2,6-di(2'-quinolyl)pyridine] complexes of ruthenium(II) and osmium(II) are reported. In both complexes the charge-transfer absorption bands are broadened and red shifted about 1.5 kK, the emission spectra are red shifted about 2 kK, and the measured luminescence lifetimes are shortened as a result of benzo substitution on the parent terpyridine ligand. The observed luminescence is assigned to a charge-transfer transition.

In 1932 Morgan and Burstall[1] first prepared 2,2',2''-terpyridine (terpy) (**1**) and subsequently showed its ability to form complexes with various metal ions.[2] Since that time terpyridine and many of its derivatives have been studied for possible use in the spectrophotometric determination of iron.[3,4] More recently a benzo-disubstituted terpyridine, 2,6-di(2'-quinolyl)pyridine (dqp) (**2**), and its iron(II) complex have been prepared and studied.[5] Benzo substitution adjacent to the nitrogen atoms leads to such steric crowding that the bischelated ferrous complex is high spin, whereas that of terpy is low spin. Less drastic alterations in the spectral properties of the complexes of the heavier metals are expected.



1 (terpy)



2 (dqp)

In this paper we report a spectroscopic study of the bisdiquinolylpyridine complexes of ruthenium(II) and osmium(II). The effect of the benzo substituents on the visible–ultraviolet absorption and emission spectra of the complexes is presented. Synthesis and purification of the title compounds is detailed.

Experimental Section

Preparations. 2,6-Di(2'-quinolyl)pyridine (dqp) was prepared as described by Harris, Patil, and Sinn.[5] Recrystallization from benzene yielded dqp in 60% yield; mp 227–228°.

Anal. Calcd for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54. Found: C, 82.85; H, 4.46.

Bis[2,6-di(2'-quinolyl)pyridine]ruthenium(II) Perchlorate Monohydrate, $[Ru(dqp)_2](ClO_4)_2 \cdot H_2O$. Procedure A. To 0.20 g (0.53 mmol) of $K_2[RuCl_5(H_2O)]$[6] dissolved in 25 ml of glycerol was added 0.40 g (1.2 mmol) of dqp dissolved in 25 ml of glycerol. The resultant dark purple solution was refluxed for 2 hr, diluted with 40 ml of water, and filtered. The filtrate was heated almost to boiling and sodium perchlorate solution (10%) was added slowly. A dark purple precipitate formed immediately. After cooling in an ice bath the precipitate was collected, washed with cold water, and recrystallized from ethanol to yield 0.15 g (28% yield) of product.

Procedure B. A blue solution of ruthenium(II) chloride in methanol was prepared by the hydrogen (2 atm) reduction of $RuCl_3 \cdot xH_2O$ (Engelhard Industries) catalyzed by platinum black as described by Rose and Wilkinson.[7] Five milliliters of the blue solution containing 0.5 mmol of Ru(II) was added slowly under a nitrogen atmosphere to a hot (70°) solution of 0.40 g (1.2 mmol) of dqp dissolved in 15 ml of ethylene glycol. After distillation of the methanol solvent the

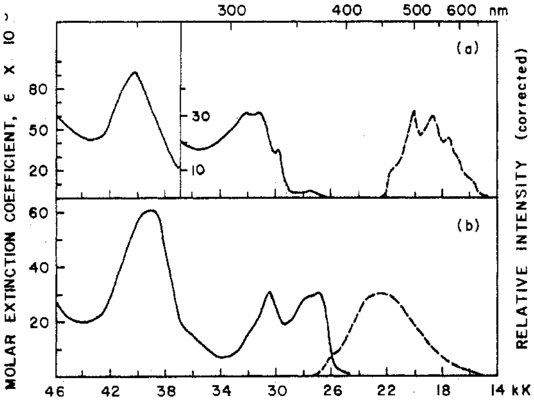


Figure 1. Absorption and emission spectra of 2,6-di(2'-quinolyl)pyridine. (a) ——, absorption spectrum in methanol at room temperature; - - - -, phosphorescence spectrum in EPA (diethyl ether–isopentane–ethanol, 5:5:2, v/v) at 77°K. (b) absorption (——) and emission (- - - -) spectra in 50% H_2SO_4 at room temperature.

reaction mixture was refluxed for 3 hr and worked up as described in procedure A above. After recrystallization from methanol 0.42 g (85% yield) of dark purple crystals was obtained. The product was vacuum-dried over P_2O_5 for 24 hr. Thin-layer chromatograms of the product on silica gel, with methanol or acetonitrile for elution, indicated the presence of only one component.

Anal. Calcd for $[Ru(C_{23}H_{15}N_3)_2](ClO_4)_2 \cdot H_2O$: C, 56.10; H, 3.28; N, 8.53; Cl, 7.20. Found: C, 56.29; H, 2.93; N, 8.38; Cl, 7.08.

Bis[2,6-di(2'-quinolyl)pyridine]osmium(II) Perchlorate, [Os(dqp)$_2$](ClO$_4$)$_2$. To 0.34 g (1 mmol) of dqp dissolved in 15 ml of hot ethylene glycol was added 0.26 g (0.5 mmol) of $K_2OsCl_6 \cdot 2H_2O$ (Research Organic/Inorganic Chemical Corp.). The reaction mixture was then refluxed for 16 hr under a nitrogen atmosphere, diluted with 40 ml of water, and filtered. The filtrate was heated to about 100° and a hot sodium perchlorate solution (10%) was added. The dark purple powder which formed was collected and recrystallized from methanol. Thin-layer chromatography showed the product to be impure. 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). A separation into two lightly colored bands and two dark purple bands was observed. After three extractions of the complex with methanol the remaining samples run through the column did not contain the second dark band. Apparently this product was present in small amounts and was removed early. The dark purple band which was eluted first from the column was collected and combined with the first band from the other sample runs. The methanol was evaporated and the purple crystals were vacuum-dried for 24 hr over P_2O_5. Thin-layer chromatography indicated a pure product.

Anal. Calcd for $[Os(C_{23}H_{15}N_3)_2](ClO_4)_2$: C, 52.33; H, 2.86; N, 7.96; Cl, 6.72. Found: C, 51.80; H, 2.92; N, 7.78; Cl, 6.63.

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 equipped with an emission monochromator grating blazed at 750 nm using both a red-sensitive R446S and a cooled RCA 7102 photomultiplier tube. The emission spectra were recorded on a Hewlett-Packard 7045A X-Y recorder. The complexes were dissolved in methanol–ethanol 1:4 (v/v) solutions (about 10^{-4} *M*) and frozen to rigid glasses in quartz microcells attached to a copper cold-finger. The excitation band pass was 16 nm and the emission band pass was 2.5 nm. Optical Industries cutoff filters 590 and 665 were placed in front of the PM tube for the ruthenium and osmium complexes, respectively. The temperature was measured with a Leeds and Northrup temperature potentiometer using a copper–constantan thermocouple dipping into the solution. The luminescence spectrum of the ruthenium compound was corrected for the wavelength dependence of the instrumental response using a standardized fluorescent solution[8] of 4-dimethylamino-4-nitrostilbene (2 μg/ml in *o*-dichlorobenzene). The osmium emission spectrum is uncorrected.

The phosphorescence spectrum of 2,6-di(2'-quinolyl)pyridine was measured in EPA (diethyl ether–isopentane–ethanol, 5:5:2, v/v) at 77°K by immersion of a quartz sample tube in liquid nitrogen. The excitation band pass was 11 nm and the emission band pass was 1 nm. An Optical Industries GG-435 cutoff filter was placed in front of the PM tube. The spectrum was corrected using a standardized fluorescent solution[8] of 3-aminophthalimide (1 μg/ml in 0.05 *M* H_2SO_4). The emission spectrum of dqp was also measured at room temperature in 50% H_2SO_4 using a 5-nm emission band pass and was corrected using a standardized solution[8] of quinine sulfate (1 μg/ml in 0.05 *M* H_2SO_4).

Table I. Energy of the 0–0 Band in the Luminescence of Ligands and Complexes and Measured Luminescence Lifetimes of the Complexes

Compd	Energy, kK	Lifetime, μsec	Compd	Energy, kK	Lifetime μsec
terpy[a]	23.1[b]		dqp[c]	21.5 sh[d]	
$[Ru(terpy)_2]I_2$	16.6[e]	10.66[h]	$[Ru(dpq)_2](ClO_4)_2$	14.6[g]	4.77[i]
$[Os(terpy)_2]I_2$	14.3[f]	3.88[h]	$[Os(dqp)_2](ClO_4)_2$	12.3[g]	1.22[i]

[a] terpy = 2,2',2''-terpyridine. [b] Measured in methanol–ethanol (1:4, v/v) at 77°K; from D. H. W. Carstens, Ph.D. Dissertation, University of New Mexico, Albuquerque, N.M., 1969. [c] dqp = 2,6-di(2'-quinolyl)pyridine. [d] Measured in EPA (diethyl ether–isopentane–ethanol, 5:5:2, v/v) at 77°K. [e] See ref 10 and 11. [f] See ref 9 and 11. [g] Measured in methanol–ethanol (1:4, v/v) at 82°K. [h] Reference 11. [i] Measured in methanol–ethanol (1:4, v/v) at 77°K; J. N. Demas, private communication.

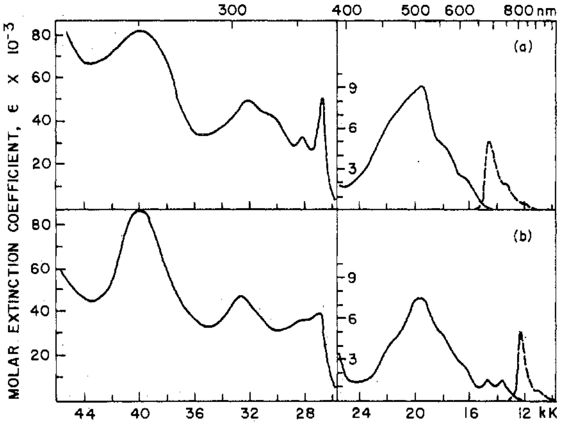


Figure 2. Absorption and luminescence spectra of 2,6-di(2'-quinolyl)pyridine complexes of ruthenium(II) and osmium(II): (a) $[Ru(dqp)_2](ClO_4)_2$; (b) $[Os(dqp)_2](ClO_4)_2$. ——, absorption spectra in methanol at room temperature; - - - -, luminescence spectra in methanol–ethanol glass (1:4, v/v) at 82°K.

Results

The absorption and phosphorescence spectra of 2,6-di(2'-quinolyl)pyridine are shown in Figure 1 and the energies of the 0–0 bands of the phosphorescence spectra of this molecule and of terpyridine are given in Table I. It is apparent that benzo substitution on terpy to produce dqp produces a red shift in the energy of the lowest lying triplet state.

The absorption and luminescence spectra of the diquinolylpyridine complexes of ruthenium(II) and osmium(II) are displayed in Figure 2. The ultraviolet regions of the absorption spectra show several strong bands with extinction coefficients from 40,000 to 90,000 M^{-1} cm^{-1} which are similar to the absorption bands of the protonated ligand. Both complexes exhibit a broad absorption band in the visible region with two shoulders in evidence on the low-energy side and one shoulder on the high-energy side of the main band. The energies, extinction coefficients, bandwidths, and oscillator strengths of these bands and of the analogous bands in the complexes of terpyridine are listed in Table II. The osmium complex exhibits two weaker bands at 734 nm (ε 1390) and 683 nm (ε 1380) which are not observed in the ruthenium compound.

Table II. Electronic Spectral Data of the Charge-Transfer Absorption Bands of the Complexes at Room Temperature

Compd[a]	Solvent	ν, kK	ϵ_{max}[b]	δ,[c] cm^{-1}	f[d]
$[Ru(terpy)_2]I_2$	Water	21.05[e]	15,100[e]	1800	0.13
$[Os(terpy)_2]I_2$	Methanol	21.10[e]	14,900[e]	2400	0.16
$[Ru(dqp)_2](ClO_4)_2$	Methanol	19.53	8,880	2600	0.11
$[Os(dqp)_2](ClO_4)_2$	Methanol	19.68	7,420	3200	0.11

[a] See Table I for meaning of abbreviations. [b] Molar extinction coefficient of the band maximum. [c] Bandwidth at half-height estimated by drawing gaussian curves eliminating shoulders. [d] Oscillator strengths, f, were calculated using the expression $f = 4.60 \times 10^{-9}\epsilon_{max}\delta$, from C. J. Ballhausen, *Prog. Inorg. Chem.*, 2, 251 (1960). [e] Values from D. M. Klassen, Ph.D. Dissertation, University of New Mexico, Albuquerque, N.M., 1966.

The energies of the 0–0 bands of the emission spectra of the diquinolylpyridine complexes are given in Table I along with those of the previously reported[9-11] complexes of terpyridine. It is apparent that the emitting states of the complexes of the benzo-substituted dqp ligand are red shifted with respect to those of the unsubstituted terpy ligand. All of the luminescence spectra exhibit some structure. The luminescence can be produced by irradiation of the complexes in any of the absorption bands in the visible and ultraviolet regions. The emission of the osmium dqp complex can be recorded at room temperature but the ruthenium complex must be cooled to produce the luminescence.

The measured lifetimes of the dqp complexes are presented in Table I. For comparison the previously measured[11] lifetimes of the terpyridine complexes are also listed. The benzo substitution on the terpyridine rings substantially decreases (>50%) the measured luminescence decay times.

Discussion

Because of the similarities in the ultraviolet absorption spectra of the complexes and that of the protonated ligand (in 50% H_2SO_4) the intense bands in the ultraviolet can be assigned to slightly perturbed π–π^* transitions of the ligands. From the previous investigations of the iron,[12] ruthenium,[10] and osmium[11] complexes of terpyridine the intense absorption bands in the visible region of the spectra can be assigned to metal-to-ligand d–π^* charge-transfer (CT) bands for the usual reasons. They are characteristic of the complexes, they are not ligand transitions, and they are too intense to be d–d transitions of the metal. The position of the charge-transfer band maximum is about the same for the ruthenium and osmium complexes of dqp but exhibits a definite red shift compared to the charge-transfer bands of the terpy complexes. It is reasonable to assume that the benzo substitution on terpyridine perturbs the molecule by changing the energy of the π-molecular orbital involved in charge transfer and by changing the energy of the metal d orbitals as well as altering the metal–ligand distance. Krumholz has observed that the main absorption bands of iron(II) complexes of tridentate imine ligands shift toward the blue as the number of aromatic rings in the ligand increases.[12] The red shift in the corresponding bands of ruthenium and osmium complexes of dqp must then be predominantly a result of the addition of the aromatic rings in sterically hindering positions.

The bandwidths and oscillator strengths for the CT bands listed in Table II are only rough approximations because of the overlapping bands as evidenced by the appearance of the shoulders on the main CT band and the lack of a gaussian shape in the band of the ruthenium complex. However, the oscillator strengths do illustrate that although the extinction coefficients of the CT bands for the dqp complexes are about half as large as they are for the complexes of the unsubstituted terpyridine, the intensities of the CT transitions are similar. The low values of the extinction coefficients in the dqp complexes result, at least in part, from a broadening of the CT band. The increase in the half-width, δ, of the charge-transfer bands of the dqp complexes compared to that of the complexes of terpy can be connected with the increased flexibility of the ligand allowing more vibrational levels in the excited state.[12] It is also possible that the broadening results from an increase in the metal–ligand distance for as Jorgensen has pointed out, even though we cannot estimate the increase of internuclear equilibrium distance, r_L, from δ alone, we may certainly expect a monotonic increase of r_L with increasing δ in a given complex.[13]

The shoulders on the sides of the main charge-transfer bands of both complexes exhibit a regular progression of ca. 1600 cm^{-1}. This progression correlates quite well with an absorption band observed at 1595 cm^{-1} in the infrared spectra of both complexes and supports the assignment of these shoulders to vibrational structure imposed on the main charge-transfer transition. Another equally possible explanation, however, is in terms of the splitting of the threefold degenerate t_{2g} level of the complex into one single and one twofold degenerate level ($b_{2g} + e_g$ in D_{4h} or $b_2 + e$ in D_{2d}) on lowering the symmetry from O_h to D_{4h} or to D_{2d}. Figgins and Busch have concluded that strong π bonding in complexes containing coplanar tridentate ligands should cause appreciable tetragonal distortion producing a D_{4h} microsymmetry around the metal ion.[14] Even in the absence of such a distortion, if the ligands remain planar and all N–M–N angles are 90°, the symmetry about the metal ion, M, is D_{2d}. In either case such a splitting could be responsible for some of the structure on the charge-transfer bands. At the present time it is not possible to determine with certainty the origin of these bands.

The low-energy bands, 13–15 kK, in the absorption spectrum of the osmium(II) complex of dqp are red shifted and have extinction coefficients about half of those of the Os^{II}–terpy complex.[9,11] In this respect these bands parallel the behavior of the main charge-transfer band described above. For this reason and others described in the assignment of analogous bands in the tris(2,2'-bipyridine)osmium(II) complex[15] these low-energy bands are assigned to the principally spin-forbidden singlet–triplet metal-to-ligand charge-transfer absorption.

The luminescence spectra of the diquinolylpyridine complexes are very similar to those of the terpyridine complexes. A 1.2–1.3-kK vibrational progression is observed in both of the ruthenium and osmium complexes. The benzo substitution on the ruthenium and osmium complexes produces a red shift of 2 kK in the energy of the 0–0 bands compared to the emission of the corresponding complexes of the unsubstituted ligand. This is a much larger shift than that observed (0.5–0.8 kK) in the ruthenium complexes of 4,4'-dimethyl-2,2'-bipyridine[15] and 4,4'-diphenyl-2,2'-bipyridine[16] indicating the greater influence of a steric hindering substitution. The red shift parallels that observed in the absorption charge-transfer bands, and therefore in agreement with the assignment of the luminescence of the terpy complexes[10,11] the emission spectra of both the ruthenium and osmium complexes of dqp are assigned to charge-transfer (d–π^*) → A_1 transitions. The measured lifetimes of the luminescence also support the same assignment of the emitting states in the dqp and terpy complexes for they are all on the same order of magnitude (1–10 μsec, Table I). In view of the results of studies on other ruthenium(II) complexes it is possible that the luminescence at 82°K originates from several excited levels in thermal equilibrium[17] and that because of strong spin–orbit coupling in ruthenium and osmium complexes it is not appropriate to give these levels spin labels.[18]

Similarities in the absorption and emission spectra of the dqp complexes of ruthenium and osmium compared to those of terpy allow the conclusion that the dqp complexes are low spin like those of terpy. Thus, benzo substitution cis to the coordinating nitrogen atoms of the ligand and the resulting steric hindrance causes a red shifting of the observed spectra but, in contrast to the effect observed for the iron complex, it is not sufficient to form high-spin complexes with the heavier metals. This result is not surprising in view of the fact that the ligand field strength, Δ, is expected to increase by a factor of 1.45 and 1.75 on passing from metal ions in the first transition series to metals in the second and third transition series, respectively.[19] Further studies of ruthenium and osmium complexes with other sterically hindering ligands is currently under way.

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Registry No. $K_2[RuCl_5(H_2O)]$, 14404-33-2; K_2OsCl_6, 16871-60-6; dqp, 2176-51-4; $[Ru(dqp)_2](ClO_4)_2$, 56258-91-4; $[Os(dqp)_2](ClO_4)_2$, 56258-93-6.

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Isomerization Reactions of Tetracyanodiaquocobaltate(III)

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The thermal and the photochemical isomerization reactions of $Co(CN)_4(H_2O)_2^-$ in aqueous solution are investigated as a function of pH and temperature. Rate constants and quantum yields are reported. The thermal and the photochemical reactions are explained by independent mechanisms. At 2°C and unit ionic strength, the pK_a values are about 9.5 and 11.7 for the cis isomer and 7.7 and 10.4 for the trans isomer.

Recently the formation of the tetracyanodiaquo and -dihydroxo complexes of Co(III) by irradiation of the corresponding pentacyanoaquo and -hydroxo complexes was reported.[1-3] Similar to the pentacyano complexes of Co(III) these tetracyano complexes can undergo thermal as well as photochemical substitution reactions. Either cyanide or H_2O (or OH^-) can eventually be replaced by another ligand. Specific however for the tetracyano complexes is the observation of isomerization reactions. Indeed, at room temperature the cis form is found to be the stable conformation, but under the influence of light a very efficient isomerization reaction yields almost exclusively the trans form.[3] At reduced temperature this trans structure can be preserved for a limited time.

In this paper we will discuss the kinetics of these thermal and photochemical isomerization reactions. These data evidence the importance of the stereospecific excitation, possible in photochemical reactions, and the consequences for the further course of the reaction.

Experimental Section

Preparation of the Different Complexes. The starting material was $K_3Co(CN)_6$ as prepared by Poskozim.[4] A solution of 5×10^{-3} *M* $Co(CN)_6^{3-}$ in 10^{-1} *M* $HClO_4$ was irradiated in a Pyrex vessel with a mercury high-pressure immersion lamp at a temperature of 1°C. The HCN, produced during the irradiation, was continuously removed by means of a stream of nitrogen. After some 10 hr of irradiation, the cold reaction mixture was passed through an anionic-exchange resin. The tetracyanodiaquocobaltate(III) complex is eluted as the trans isomer. The cis isomer is obtained upon standing at room temperature. Solutions containing the aquohydroxo and the dihydroxo complexes were obtained by adding either NaOH, a borax, or a phosphate buffer to the solution of *trans*- and *cis*-diaquo complexes. A detailed discussion of the preparation and the separation of the various tetracyano complexes is to be published elsewhere.[3] In Figures 1 and 2 the spectra of the *cis*- and *trans*-tetracyanodiaquo and -dihydroxo complexes are given. The assignments of the cis and the trans structures were made on the basis of the electronic absorption spectra. Thus the first ligand field absorption band of the trans species is expected to be considerably shifted toward the red as compared to the band of the cis species.[5]

For all the subsequent experiments the ionic strength of the solutions was adjusted to unity by means of $NaClO_4$ (Merck, p.a.).

Thermal Isomerization. The trans form of the tetracyano complexes is not stable and converts thermally into the cis form. At reduced temperature this isomerization can be slowed down enough in order to allow a kinetic investigation.

The reaction was monitored spectrophotometrically using a Unicam SP 700 C recording spectrophotometer. The solutions were thermostated in the sample holder.

In acid medium a clean isomerization reaction is observed and no secondary products can be detected. The two intersections of the spectra represent isosbestic points over the entire course of the isomerization reaction.

In alkaline solutions, isosbestic points are only observed in the beginning of the reaction. This is due to the formation of polynuclear compounds when the reaction proceeds.[6] At any pH the rate of the latter reaction is considerably slower than the rate of the isomerization