# Spectroscopic Characterization of Complexes of Ruthenium(II) and Iridium(III) with 4,4′-Diphenyl-2,2′-bipyridine and 4,7-Diphenyl-1,10-phenanthroline[1]

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**Abstract:** The preparations and spectroscopic characterizations of the tris(4,4′-diphenyl-2,2′-bipyridine) and tris(4,7-diphenyl-1,10-phenanthroline) complex ions of ruthenium(II) and several of the bis complex ions of these ligands with iridium(III) are reported. The transitions which give rise to the visible–ultraviolet absorption spectra and emission spectra of the complexes at 77°K are orbitally assigned, with the exception of the emission from *cis*-dichlorobis(4,7-diphenyl-1,10-phenanthroline)iridium(III) chloride, which displays an anomalous luminescence spectrum. The design of complexes with desired optical properties is discussed.

Since the first synthesis of 2,2′-bipyridine and 1,10-phenanthroline by Blau[2-4] and his subsequent discovery of the highly colored complexes which they form with the ferrous ion, these ligands have been widely used for the spectrophotometric determination of iron. They are now known to form complexes with a number of the transition metals, and the study of the absorption and emission spectra of these complexes is an area of active interest.

The phenyl-substituted ligands, 4,4′-diphenyl-2,2′-bipyridine (diphenylbipy) and 4,7-diphenyl-1,10-phenanthroline (diphenylphen), first synthesized by Case[5,6] were found to provide an even more sensitive spectrophotometric test for iron than the unsubstituted ligands.[7,8] The improved sensitivity is due to a large increase in the extinction coefficients of the intense charge-transfer (CT) bands in the absorption spectra of the iron complexes of the phenyl-substituted ligands relative to the intensities of the CT bands present in the complexes of the parent ligands.

In this paper we report a spectroscopic study of the tris(diphenylbipy) and tris(diphenylphen) complexes of ruthenium(II) and several of the bis complexes of these ligands with iridium(III). The effect of the phenyl substituents on the visible–ultraviolet absorption and emission spectra of the molecules is detailed. Preparation and purification methods are included.

## Experimental Section

**Preparation and Purification of Complexes. Tris(4,4′-diphenyl-2,2′-bipyridine)ruthenium(II) Chloride Pentahydrate: [Ru(diphenylbipy)$_3$]Cl$_2$.** $RuCl_3$ (60 mg) and 4,4′-diphenyl-2,2′-bipyridine (330 mg) were dissolved in 15 ml of absolute ethanol. To this was added a solution of hydroxylamine hydrochloride (70 mg) and sodium acetate (272 mg) in 10 ml of water. This mixture was then refluxed with stirring for 24 hr. After cooling, the product was extracted from the reaction mixture with a small amount of isoamyl alcohol and washed several times with water. The isoamyl alcohol was removed by flash evaporation; the red product was dissolved in acetonitrile and chromatographed on a 9 mm × 400 mm column of activated aluminum oxide. Pure acetonitrile followed by mixtures of acetonitrile and absolute ethanol were used for elution. The fraction containing the brilliant red product was collected and evaporated to dryness; the residue was taken up in 400 ml of boiling water. Upon addition of NaCl (20 g), the chloride salt of the complex precipitated. The above procedure was repeated to ensure complete conversion to the chloride salt. After the complex was dried for 4 hr at 60° *in vacuo*, its purity was tested by thin-layer chromatography on an aluminum oxide plate eluted with acetonitrile. Owing to the presence of a deep purple impurity, the chromatographic purification procedure was repeated to yield a product which showed only one spot on the thin-layer plate. The final product was dried for 12 hr *in vacuo* at 40° to yield 50 mg of a deep red, amorphous substance.

*Anal.* Calcd for $[Ru(C_{22}H_{16}N_2)_3]Cl_2 \cdot 5H_2O$: C, 66.77; H, 4.92; Cl, 5.97; N, 7.07. Found: C, 66.71; H, 4.40; Cl, 5.37; N, 7.36.

**Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) Chloride Pentahydrate: [Ru(diphenylphen)$_3$]Cl$_2$.** $RuCl_3$ (208 mg) and 4,7-diphenyl-1,10-phenanthroline (1.330 g) were mixed with 25 ml of absolute ethanol. To this mixture was added a solution of hydroxylamine hydrochloride (140 mg) in 10 ml of water. Although the diphenylphen was only sparingly soluble in this mixture at room temperature, dissolution of the ligand occurred upon heating. During a refluxing period of 48 hr, a deep red color appeared. Formation of the product was also evidenced by a brilliant pink emission from the reaction mixture upon irradiation with a black light.

The reaction mixture was evaporated to near dryness with a flash evaporator, the residue was dissolved in isoamyl alcohol, the solution was filtered, and the filtrate was washed with an aqueous solution of sodium chloride. The isoamyl alcohol was removed by flash evaporation, and a small amount of acetonitrile was added to the resulting residue. A white, crystalline material, thought to be the free ligand, was evident in the solution of the red product at this point. The mixture was set aside for 8 hr to allow complete crystallization of the white material and was then filtered. The filtrate was placed on a 9 mm × 400 mm column of activated aluminum oxide which was eluted with acetonitrile–ethanol mixtures. The red-orange fraction containing the product was collected and evaporated to near dryness, and the residue was dissolved in a minimum volume of hot 50% water–ethanol. When sodium chloride was added, precipitation of the chloride salt of the complex resulted. This precipitate was collected on a fritted glass filter, washed with water, and recrystallized from an equal-volume mixture of water, acetonitrile, and ethanol. A thin-layer chromatogram of the product on silica gel, with acetonitrile for elution, revealed the presence of two components. Therefore, the product was dissolved in acetonitrile and passed through a 9 mm × 300 mm activated silica gel column eluted with acetonitrile–ethanol mixtures. The product was recrystallized from a 50% water–ethanol mixture and dried in a desiccator at atmospheric pressure to yield 80 mg of the amorphous red-orange solid.

*Anal.* Calcd for $[Ru(C_{24}H_{16}N_2)_3]Cl_2 \cdot 5H_2O$: C, 68.67; H, 4.64; Cl, 5.63; N, 6.67. Found: C, 68.22; H, 4.33; Cl, 5.79; N, 6.80.

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(1) Research supported by AFOSR(NC)-OAR, USAF Grant No. 68-1342.

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***cis*-Dichlorobis(4,4′-diphenyl-2,2′-bipyridine)iridium(III) Chloride Trihydrate: [IrCl$_2$(diphenylbipy)$_2$]Cl.** $K_3[IrCl_6]$ (0.5 g) and 4,4′-diphenyl-2,2′-bipyridine (1.0 g) were intimately mixed with a mortar and pestle, sealed under vacuum in a Pyrex tube, and subsequently held at 220° for 4 hr. The reaction mixture was washed on a fritted glass filter with hot benzene until an olive-green residue remained. This residue was dissolved in chloroform and filtered. Slow reduction of the solvent volume caused precipitation of the complex, which was collected on a fritted glass filter, washed with carbon tetrachloride, and dried. The product was dissolved in methanol and chromatographed on a 21 mm × 950 mm column of Sephadex LH-20 eluted with methanol. A yield of 180 mg of the amorphous yellow complex was recrystallized from chloroform.

*Anal.* Calcd for $[IrCl_2(C_{22}H_{16}N_2)_2]Cl\cdot 3H_2O$: C, 54.51; H, 3.95; Cl, 10.97; N, 5.77. Found: C, 54.09; H, 3.90; Cl, 11.17; N, 5.89.

***cis*-Dichlorobis(4,7-diphenyl-1,10-phenanthroline)iridium(III) Chloride Dihydrate: [IrCl$_2$(diphenylphen)$_2$]Cl.** $K_3[IrCl_6]$ (0.5 g) and 4,7-diphenyl-1,10-phenanthroline (1.0 g) were intimately mixed with a mortar and pestle and sealed under vacuum in a Pyrex tube. The product, which formed upon heating the mixture at 220° for 12 hr, was obtained by extraction with absolute ethanol. The ethanol solution was filtered, the solvent was removed by flash evaporation, and the product was washed with hot benzene on a fritted glass filter. The olive-green residue was dissolved in methanol and chromatographed on a 21 mm × 900 mm column of Sephadex LH-20 eluted with methanol. This procedure was repeated until impurities could no longer be seen during the chromatographic purification of the product. The methanol was then removed by flash evaporation, and the product was washed with benzene and dried to yield 90 mg of the amorphous golden yellow solid.

*Anal.* Calcd for $[IrCl_2(C_{24}H_{16}N_2)_2]Cl\cdot 2H_2O$: C, 57.68; H, 3.63; Cl, 10.64; N, 5.60. Found: C, 57.59; H, 3.79; Cl, 9.42; N, 5.90.

***cis*-Dichlorobis(2,2′-bipyridine)iridium(III) Chloride Dihydrate:**[9,10] **[IrCl$_2$(bipy)$_2$]Cl.** $K_3[IrCl_6]$ (2.0 g) and 2,2′-bipyridine (4.0 g) were mixed with mortar and pestle and sealed under vacuum in a Pyrex tube. After 4 hr of heating at 200° the product was extracted from the mixture with 300 ml of water. The water extract was filtered, washed with ether to remove excess 2,2′-bipyridine, and reduced in volume to 50 ml. Addition of sodium chloride precipitated the chloride salt. The latter was washed with ether and dried to yield 1.1 g of the crude product. This was purified by repeated chromatography on a 21 mm × 900 mm column of Sephadex LH-20 eluted with methanol.

*Anal.* Calcd for $[IrCl_2(C_{10}H_8N_2)_2]Cl\cdot 2H_2O$: C, 37.13; H, 3.12; Cl, 16.43; N, 8.66. Found: C, 37.79; H, 3.05; Cl, 15.30; N, 8.87.

Although there has been considerable confusion in the past as to whether the trans isomers of the dichlorobis(2,2′-bipyridine)iridium(III) and the dichlorobis(1,10-phenanthroline)iridium(III) ions have been prepared, recent discussions[9,11] indicate that only the cis isomers are formed in the normal reactions of Ir(III) with these ligands. We feel that it is reasonable to assume that 4,4′-phenyl substitution of 2,2′-bipyridine and 4,7-phenyl substitution of 1,10-phenanthroline do not affect the nature of the isomers formed in these reactions. Therefore, the iridium complexes prepared in this work are presumed to be the cis isomers. The spectroscopic evidence also supports a cis assignment.

**Spectroscopic Measurements.** All absorption spectra were measured on 4:1 (v/v) ethanol–methanol solutions at room temperature with a Cary Model 14 spectrophotometer. Emission spectra were taken in 4:1 (v/v) ethanol–methanol solutions at 77°K. Phosphorescence spectra of the ligands were recorded on a Hitachi Perkin-Elmer Model MPF-2A spectrophotometer which uses a Type R-136 red-sensitive phototube for detection. The emission spectra of the complexes, corrected for the wavelength dependence of the instrumental response, were measured with a red-sensitive apparatus constructed in this laboratory.[12,13] For excitation the 436-nm region of a 1000-W Hanovia 977B-1 compact Hg–Xe lamp was isolated with an American Instrument Co. monochromator using an 11-nm band pass and a filter train consisting of a Corning CS 3-73 and an Optics Technology 450 blue-edge filter.

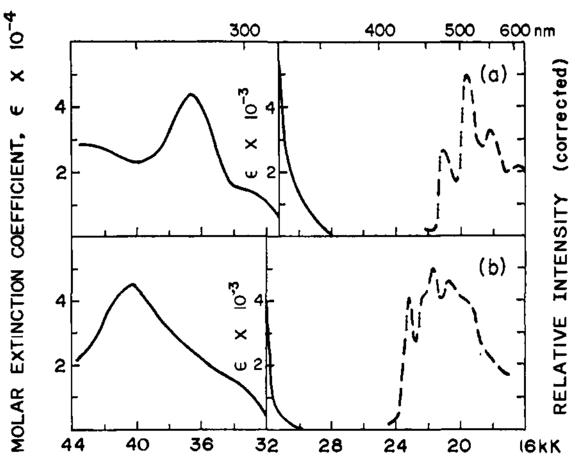

Figure 1. Absorption and phosphorescence spectra of ligands: (a) 4,7-diphenyl-1,10-phenanthroline; (b) 4,4′-diphenyl-2,2′-bipyridine; ———, absorption spectra in ethanol–methanol (4:1, v/v) at room temperature; – – – –, phosphorescence spectra in ethanol–methanol glass (4:1, v/v) at 77°K.

## Results

The absorption and phosphorescence spectra of 4,4′-diphenyl-2,2′-bipyridine and 4,7-diphenyl-1,10-phenanthroline are presented in Figure 1. The energies of the 0–0 bands of the phosphorescence spectra of these molecules and of the unsubstituted ligands are compiled in Table I. In each instance the energy of the lowest lying ligand triplet state is red shifted by the introduction of phenyl substituents.

The absorption and emission spectra of the ruthenium(II) and iridium(III) complexes are shown in Figures 2 and 3, and the energies of the 0–0 bands of the luminescence spectra of these complexes and of the previously reported unsubstituted complexes are listed in Table I. It is again evident that the emitting states of the complexes of the phenyl-substituted ligands are red shifted with respect to those of the corresponding unsubstituted ligands. In all instances the complexes display a structured luminescence.

The absorption spectra of the ruthenium complexes of the phenyl-substituted ligands display bands in the blue-green region with extinction coefficients of about 30,000–35,000 l. mol$^{-1}$ cm$^{-1}$. The ultraviolet region is dominated by strong bands which are similar to those which occur in the free ligands.

Absorption bands of the iridium complexes of the phenyl-substituted ligands appear in the blue-violet region with extinction coefficients of 7000–8000 l. mol$^{-1}$ cm$^{-1}$. A similar band occurs in the absorption spectrum of $[IrCl_2(bipy)_2]Cl$ with a somewhat smaller extinction coefficient of 2400 l. mol$^{-1}$ cm$^{-1}$. This latter complex also displays a weak, partially resolved band at 22 kK which is unresolved in the complexes of the phenyl-substituted ligands. The ultraviolet absorption spectra of all of the iridium complexes are also dominated by strong bands similar to those observed for the free ligands.

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**Table I.** Energy of the 0–0 Band in the Luminescence of Complexes and Ligands in Ethanol–Methanol Glass at 77°K

| Compound | Energy, kK | Compound | Energy, kK |
|---|---|---|---|
| 1,10-Phenanthroline | 22.2[a] | 4,7-Diphenyl-1,10-phenanthroline | 21.0 |
| 2,2′-Bipyridine | 23.5[a] | 4,4′-Diphenyl-2,2′-bipyridine | 23.2 |
| $[Ru(phen)_3]I_2$[b] | 17.6[c] | $[Ru(diphenylphen)_3]Cl_2$[b] | 16.8 |
| $[Ru(bipy)_3]Cl_2$ | 17.1[c] | $[Ru(diphenylbipy)_3]Cl_2$ | 16.4 |
| $[IrCl_2(phen)_2]Cl$ | 21.1[d] | $[IrCl_2(diphenylphen)_2]Cl$ | 19.5 |
| $[IrCl_2(bipy)_2]Cl$ | 21.1 | $[IrCl_2(diphenylbipy)_2]Cl$ | 20.4 |

[a] See ref 13. [b] Names and formulas for complexes are given in the Experimental Section. [c] See G. A. Crosby, W. G. Perkins, and D. M. Klassen, *J. Chem. Phys.*, **43**, 1498 (1965). For reassignment of the luminescence, see D. M. Klassen and G. A. Crosby, *Chem. Phys. Lett.*, **1**, 127 (1967). [d] See H. J. Clifford, D. H. W. Carstens, and G. A. Crosby, 25th Annual Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970, Abstract No. 170.

## State Assignments

Owing to the similarities in the ultraviolet absorption spectra of the complexes and the free ligands, it is apparent that the uv region is dominated primarily by transitions localized on the ligands. In the visible region, however, the large extinction coefficients of the observed bands of the complexes and the absence of such bands in the absorption spectra of the free ligands indicate that charge-transfer transitions are responsible for the absorbances. This assignment of the visible absorption bands in these molecules to CT transitions is analogous to the assignment of the visible bands of $[Ru(bipy)_3]Cl_2$[14–16] and $[Ru(phen)_3]I_2$.[17] The extinction coefficients of these charge-transfer bands are approximately twice as large for the ruthenium(II) complexes of the phenyl-substituted ligands as they are for the complexes of the unsubstituted ligands. This enhancement of intensity is analogous to that observed for the charge-transfer bands in the absorption spectra of the iron(II) complexes of the same ligands.

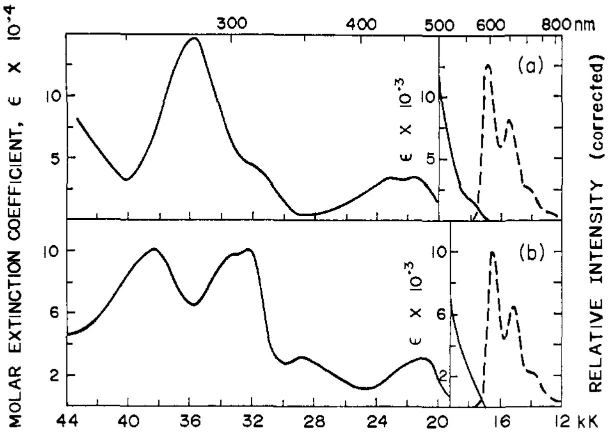

Figure 2. Absorption and luminescence spectra of ruthenium(II) complexes: (a) $[Ru(diphenylphen)_3]Cl_2$; (b) $[Ru(diphenylbipy)_3]Cl_2$; ———, absorption spectra in ethanol–methanol (4:1, v/v) at room temperature; ----, luminescence spectra in ethanol–methanol glass (4:1, v/v) at 77°K.

The partially resolved band at 22 kK in the absorption spectrum of $[IrCl_2(bipy)_2]Cl$ overlaps its emission spectrum. This band is therefore thought to arise from a transition between the ground state and the emissive state. Although the other iridium complexes fail to show a resolved absorption band in this region under the conditions employed, their absorption spectra do overlap their emission spectra significantly. Thus it is likely that the emissive state of each of the iridium complexes is actually seen in absorption but is clearly resolved only in the one case. The maximum extinction coefficients are approximately 500–1000 l. mol$^{-1}$ cm$^{-1}$ in this region, suggestive that the radiative lifetimes of the emitting states are on the order of several microseconds.

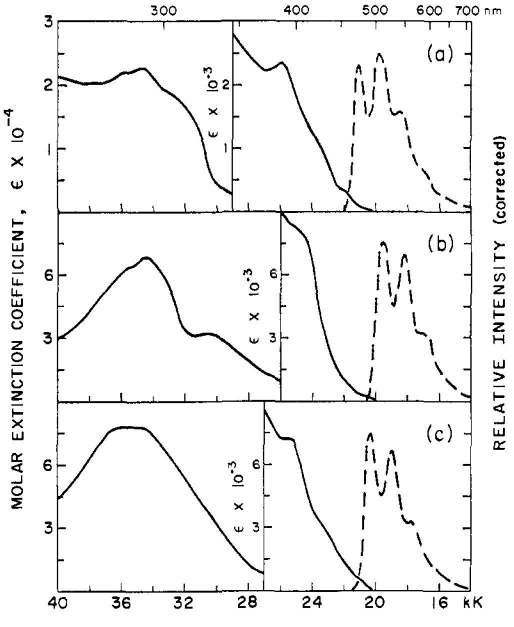

Figure 3. Absorption and luminescence spectra of iridium(III) complexes: (a) $[IrCl_2(bipy)_2]Cl$; (b) $[IrCl_2(diphenylphen)_2]Cl$; (c) $[IrCl_2(diphenylbipy)_2]Cl$; ———, absorption spectra in ethanol–methanol (4:1, v/v) at room temperature; ----, luminescence in ethanol–methanol glass (4:1, v/v) at 77°K.

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(14) G. A. Crosby, W. G. Perkins, and D. M. Klassen, *J. Chem. Phys.*, **43**, 1498 (1965). For reassignment of the luminescence see D. M. Klassen and G. A. Crosby, *Chem. Phys., Lett.*, **1**, 127 (1967).

(15) G. B. Porter and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, **68**, 316 (1964).

(16) J. P. Paris and W. W. Brandt, *J. Amer. Chem. Soc.*, **81**, 5001 (1959).

(17) D. M. Klassen, Ph.D. Dissertation, University of New Mexico, Albuquerque, N. M., 1966.

The luminescence spectra of the ruthenium(II) complexes of the phenyl-substituted ligands are strikingly similar to those of the corresponding complexes of the unsubstituted ligands. A 1.3–1.4-kK vibrational progression is observed in all of them. The phenyl substituents bring about only a small red shift of 0.7–0.8 kK in the energy of the 0–0 bands. The phosphorescence spectra of the solvated free ligands reveal that the first triplet state lies 4.2 kK above the emitting state of $[Ru(diphenylphen)_3]Cl_2$ and 6.8 kK above that of $[Ru(diphenylbipy)_3]Cl_2$. Although the energy of the ligand triplet state in the complex is expected to shift slightly to lower energy from that of the free ligand, this shift is generally no more than about 1 kK.[18] Thus, owing to the similarities in the luminescence spectra of the complexes of the phenyl-substituted and the unsubstituted ligands and to the absence of any low-lying free-ligand triplet states of comparative energies, the emission spectra of both the ruthenium complexes are assigned to charge-transfer $(d-\pi^*) \rightarrow A_1$ transitions.

The luminescence spectrum of $[IrCl_2(bipy)_2]Cl$ shows a vibrational progression of 1.3–1.4 kK which is identical with that observed in the luminescence of $[IrCl_2(phen)_2]Cl$. The latter has been assigned to a CT transition.[18] The energies of the emitting states of these complexes are also found to be identical. Furthermore, the lowest lying free-ligand triplet state lies 2.4 kK above the emitting state of the 2,2′-bipyridine complex of iridium(III). On the basis of these considerations, we assign the luminescence of $[IrCl_2(bipy)_2]Cl$ to a charge-transfer $(d-\pi^*) \rightarrow A_1$ transition also. Therefore, the band at 22 kK in the absorption spectrum of this molecule is assigned to a charge-transfer $A_1 \rightarrow (d-\pi^*)$ transition.

Sinha has recently prepared the aquated complex, $[IrCl(H_2O)(bipy)_2]Cl_2$, and reports a low-energy band at about 21 kK with an extinction coefficient of 320 l. $mol^{-1}$ $cm^{-1}$ in the absorption spectrum.[19] He has assigned this band as a transition to a d–d singlet. It is unlikely that aquation of $[IrCl_2(bipy)_2]Cl$ to form $[IrCl(H_2O)(bipy)_2]Cl_2$ would shift an excited singlet in the d manifold below the low-lying CT state. We suggest, therefore, that the recent assignment of the 21-kK absorption band of $[IrCl(H_2O)(bipy)_2]Cl_2$ as an iridium $A_1 \rightarrow {}^1(d-d)$ transition is questionable and that this band is most likely a charge-transfer $A_1 \rightarrow (d-\pi^*)$ transition. A definitive designation of this band awaits the determination of the emission spectrum of the molecule.

The luminescence spectra of the iridium(III) complexes of the phenyl-substituted ligands are also found to have 1.3–1.4-kK vibrational progressions which are nearly identical with those for the complexes of the unsubstituted ligands. The emitting state of $[IrCl_2(diphenylbipy)_2]Cl$ lies only 0.7 kK lower than that of the unsubstituted ligand, whereas the emitting state of $[IrCl_2(diphenylphen)_2]Cl$ lies 1.6 kK below that of $[IrCl_2(phen)_2]Cl$. Thus, the red shift due to phenyl substitution in the latter case is approximately twice that found for any of the other iridium(III) or ruthenium(II) complexes studied. This suggests to us the occurrence of strong $(d-\pi^*)$–$(\pi-\pi^*)$ configuration interaction.

The lowest triplet state of diphenylbipy lies 2.8 kK above that of the luminescing state of the iridium(III) complex of this ligand. We feel that this gap is sufficiently large to eliminate any significant configuration interaction between the $(d-\pi^*)$ and $(\pi-\pi^*)$ states. The lowest triplet state of diphenylphen lies only 1.5 kK, however, above the luminescing state of the iridium(III) complex of this ligand. On the basis of these observations we assign the luminescence of $[IrCl_2(diphenylbipy)_2]Cl$ to a normal charge-transfer $(d-\pi^*) \rightarrow A_1$ transition. It is not possible, however, to provide a conclusive assignment of the transition responsible for the luminescence of the diphenylphen complex. We feel that there are undoubtedly both low-lying CT and ligand triplet states in close proximity. Their nearness could lead to a large configuration interaction or possibly even a level inversion. In the former case, the luminescing state would have properties of both a ligand triplet and a CT state and would not fit well into either of these simple classifications. If level inversion occurred, the emission could begin to acquire the characteristics of a normal $\pi^*-\pi$ transition. Preliminary measurements of the luminescence lifetime of this complex yield a value somewhat longer than those found for the other iridium(III) molecules. This result is also indicative of a transition with characteristics intermediate between a CT and $\pi^*-\pi$ emission. Further studies of the luminescence of this complex are currently underway.

## Material Design

The generally small alterations in the absorption and emission spectra of iridium(III) and ruthenium(II) complexes brought about by phenyl substitution of 2,2′-bipyridine and 1,10-phenanthroline may make these ligands useful tools for designing luminescent complexes. We have established that phenyl substituents generally increase the extinction coefficients in the visible absorption spectra and cause a small red shift in the luminescence spectra. This is accomplished without alteration of the types of transitions responsible for the absorption and luminscence in most cases. Phenyl substitution of the ligands does alter the solubility properties of these complexes significantly.

Owing to the types of alterations brought about by phenyl substituents, we suggest that phenyl substitution be described as a "fine-tuning" device for the design of series of complexes with slightly modified optical properties. Along this line of thought one may consider the alteration of the basic nature of the luminescing states of complexes by changes in the central metal ion or the ligands as a "rough-tuning" device. An example of the use of rough tuning would be the replacement of the phen ligands in $[IrCl_2(phen)_2]Cl$, which displays a green CT emission, by four pyridine ligands. The resulting complex shows a red unstructured luminescence which has been assigned to a transition localized within the central metal d orbitals.[18] Thus, a major change in the character of the luminescence is brought about by chemical rough tuning. On the other hand, the fine tuning discussed here is capable of causing small alterations in absorption and emission spectra without grossly changing the basic nature of the transitions responsible for these spectra.

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(18) H. J. Clifford, D. H. W. Carstens, and G. A. Crosby, 25th Annual Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970, Abstract No. 170.

(19) S. P. Sinha, *Indian J. Chem.*, **8**, 82 (1970).

The changes in solubility properties brought about by phenyl substitution of the ligands may also be of importance in the design of complexes with desired properties. For example, the complexes of the phenyl-substituted ligands are significantly more soluble in plastic matrices than those of the unsubstituted ligands. Such matrices are sometimes of practical value in the design of optical devices.[20]

Owing to the large increases brought about in the extinction coefficients of CT transitions in these complexes by phenyl substitution, it is quite probable that the radiative lifetimes for photoluminescence are significantly shortened. Furthermore, in view of the relatively small alterations in the energies of the luminescing states, it is highly probable that radiationless decay rates are unchanged by the phenyl substituents. This set of conditions should lead to an increase in the quantum yields for photoluminescence in the substituted complexes over those of the parent compounds. Thus, it is likely that alterations in the extinction coefficients of these particular systems have far-reaching implications which have not yet been exploited. If these predictions are correct, then this fine-tuning technique could become particularly important for engineering highly efficient luminescent material. Studies are currently underway to measure the effects of ligand substituents on decay rates and quantum efficiencies in these systems.

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(20) R. W. Harrigan, R. J. Watts, and G. A. Crosby, unpublished data, 1970.