(90%, mp 179–180°) which on reduction (NaBH₄, isopropyl alcohol, 25°) and dehydration[16] produced crystalline lactone 22 (mp 150–151°; ν_{max} 1768 cm⁻¹; nmr δ 5.18, s, 1 H, 6.64, t, 1 H). Introduction of the remaining tertiary alcohol and epoxide functions and elaboration of the second lactone ring in dihydropicrotoxinin are under investigation.

(16) Dehydration could be carried out with p-TsCl in pyridine at room temperature or with 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate in CHCl₃ at room temperature for 2 days.

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Effect of Ligand Substituents on the "d–d" Luminescence of Iridium(III) and Rhodium(III) Complexes of 1,10-Phenanthroline

Sir:

The effects of ligand substituents on the visible charge-transfer emission of several 1,10-phenanthroline complexes of Ru(II) and Ir(III) have recently been reported.[1-3] Certain ligand substituents on 1,10-phenanthroline significantly alter both the radiative and radiationless decay rates of the emitting states of these d⁶ complexes, although only minor effects on the energies of the emitting states are observed. We wish to report that observations of the near-infrared emission from the low-lying d–d states of a series of Ir(III) complexes reveal surprisingly large ligand substituent effects. However, such effects are small in a corresponding series of Rh(III) complexes.

Complexes of the type [H-Xphen][IrCl₄(Xphen)] and (H-Xphen)[RhCl₄(Xphen)], where Xphen represents a substituted 1,10-phenanthroline and H-Xphen the corresponding phenanthrolinium ion, were prepared by the method of Broomhead and Grumley.[4] Studies of the complex [H-phen][IrCl₄(phen)] have shown that this complex displays a blue fluorescence in fluid solution characteristic of the phenanthrolinium ion.[5] A blue-green phosphorescence characteristic of the phenanthrolinium ion is also found to occur from the solids at 77°K. Due to these interfering effects, phenanthrolinium ions are unsatisfactory counterions for studies of the complex emission. The phenanthrolinium salts were converted to the potassium salts by stirring the complexes with 5 M potassium acetate in the dark for 3 hr. The absence of both the blue

fluorescence and the blue-green phosphorescence in the products provided evidence that the metathesis was complete. All emission spectra were measured on solid samples of the potassium salts in liquid nitrogen and were corrected for distortions introduced by the wavelength dependence of the instrumental response. The basic components of the emission apparatus were similar to those described by Demas.[6] For lifetime measurements the potassium salts of the complex ions were excited at 337 nm with an Avco C950 pulsed nitrogen laser. In several instances lifetime measurements on the phenanthrolinium salts were also made with the laser. The emission was detected with an Amperex 56TVP photomultiplier, and decay curves were displayed on a Tektronix type 549 oscilloscope.

The emission spectrum of K[IrCl₄(phen)] has been reported, and both the low energy and the broad, Gaussian shape of the spectrum indicate that the emission is due to a d–d transition.[7] Although no previous measurement of the luminescence lifetime of this complex has been reported, the Avco C950 nitrogen laser provides a 10-nanosec pulse of sufficient intensity to measure a lifetime of 0.63 ± 0.05 μsec for this solid at 77°K. The emission of K[RhCl₄(phen)] also occurs in the near-infrared region and has a broad Gaussian shape. The luminescence lifetime of this complex could not be measured accurately due to its low intensity, but could be estimated to be about 0.1–0.2 μsec. This information, coupled with a previous assignment of the [RhCl₂(phen)₂]Cl emission as a d–d transition,[8-10] leaves little doubt that the K[RhCl₄(phen)] emission is also due to a d–d transition. The energies for the various substituted-phenanthroline complexes of Ir(III) and Rh(III) are reported in Table I. In all cases broad, Gaussian emissions are observed, and like the parent phenanthroline complexes are assigned as d–d transitions.

In view of the relatively small substituent-induced shifts (<1 kK) in the energy of charge-transfer emissions of Ir(III) and Ru(II) complexes of 1,10-phenanthroline,[1] it is surprising to find that the d–d emissions of the Ir(III) complexes in Table I are shifted by as much as 2.6 kK. Equally surprising are the facts that the emissions are blue shifted by electron-withdrawing substituents and red shifted by electron-donating substituents in the case of Ir(III). A similar trend occurs for the Rh(III) analogs, but it is less pronounced.

Simple considerations of the effect of an electron-withdrawing substituent on 1,10-phenanthroline suggest that this should decrease the basicity of the ligand and bring about a decrease in its σ-bonding ability. Studies of various substituted phenanthrolines show, for example, that their pK_a values are decreased by, electron-withdrawing substituents.[11,12] Such a decrease would be expected to decrease the value of the crystal field parameter Δ for an octahedral complex.

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Complex	Emission max[b] ν_{max}, kK	Half-width, $\nu_{1/2}$, kK	Energy of lowest excited state,[c] kK	Lifetime (μsec)
K[IrCl$_4$(phen)]	11.1[d]	3.1	15.1	0.63 ± 0.05
K[RhCl$_4$(phen)]	11.7	3.3	16.0	
K[IrCl$_4$(5-methylphen)]	11.1	3.3	15.4	0.56 ± 0.05
K[RhCl$_4$(5-methylphen)]	11.5	3.3	15.8	
K[IrCl$_4$(5,6-methylphen)]	10.5	3.2	14.7	0.58 ± 0.04
K[RhCl$_4$(5,6-methylphen)]	11.5	2.9	15.3	
K[IrCl$_4$(5-bromophen)]	11.9	3.3	16.2	0.65 ± 0.04
K[RhCl$_4$(5-bromophen)]	11.7	3.4	16.1	
K[IrCl$_4$(5-chlorophen)]	11.9	3.3	16.2	0.61 ± 0.04
K[RhCl$_4$(5-chlorophen)]	12.2	3.0	16.1	
K[IrCl$_4$(5-nitrophen)]	13.7	3.2	17.9	0.094 ± 0.005
K[RhCl$_4$(5-nitrophen)]	11.9	3.3	16.2	
K[IrCl$_4$(4,7-phenylphen)]	13.2	2.8	16.8	2.7 ± 0.15
K[RhCl$_4$(4,7-phenylphen)]	13.5	3.5	18.0	

[a] All measurements were made on solid samples at 77°K. [b] All luminescence spectra were corrected for variations in instrumental response with wavelength in order to determine emission maxima. [c] Calculated by the method of Carstens and Crosby, see ref 7. [d] See ref 6.

On the other hand, an electron-withdrawing group would be expected to increase the π-bonding ability of the 1,10-phenanthroline ligand, which would bring about an increase in Δ. Thus the effect of ligand substituents on Δ will reflect the relative importance of σ- and π-bonding in an octahedral complex.

A complete determination of the effect of ligand substituents on Δ from the emission energies in Table I would require an analysis of electron repulsion parameters, of reduction of symmetry from O_h to C_{2v}, and of spin–orbit coupling terms. However, it is likely that the general increase in the emission energies of the Ir(III) complexes as stronger electron-withdrawing substituents are introduced on the phenanthroline ligand are indicative of an increase in Δ. This would suggest that increases in π-bonding in Ir(III) are far more important than any decrease in σ-bonding. The importance of π-bonding in Ir(III) is also evidenced by the occurrence of low-lying charge-transfer states in complexes of Ir(III) with π acceptor ligands.[1-3] The relative insensitivity of the emission energies of the Rh(III) complexes to ligand substituents suggests that here σ-bonding decreases are more comparable to π-bonding increases than in Ir(III). Studies of the infrared and nmr spectra of Rh(III) complexes have also led to the conclusion that π-bonding is unimportant.[13,14]

The effects of ligand substituents on the lifetimes of the potassium salts of the Ir(III) complexes (see Table I) are also quite surprising. Although nonexponential decay curves were encountered for the phenanthrolinium salts of these complexes due to interfering effects of the cation, rough estimates of lifetimes from the decay curves show the same trends as those shown by the potassium salts. Thus, the lifetime trends appear to be related to intramolecular ligand substituent effects rather than to intermolecular solid state effects due to the counterion. Heavy atoms such as chlorine and

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bromine have very small effects on the lifetimes whereas the nitro and phenyl groups cause large alterations in the lifetimes but in opposing directions. This suggests that in all the Ir(III) complexes, spin–orbit coupling is dominated by the presence of the heavy metal so that heavy-atom ligand substituents have little effect. The increase in the lifetime brought about by the phenyl substituent is consistent with a decrease in the radiationless decay rate with increasing energy.[9] However, the effect of the nitro substituent is anomalous in this respect. Although we cannot determine quantum yields for these solid state emissions, the emission from the nitro-substituted complex is quite bright relative to the parent complex. Coupled with the fact that the measured lifetime is decreased by the nitro substituent, this would indicate a large increase in the radiative decay rate. Although accurate lifetime data for the rhodium(III) complexes could not be obtained, our estimates of the luminescence lifetimes of these complexes suggest that they follow trends which are similar to those discussed for Ir(III).

Further work on the interpretation of these results and the extension of our measurements to include substituent effects on photochemical as well as photophysical processes is currently in progress.
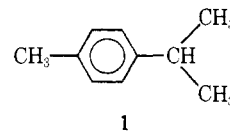
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Ipso Nitration. II.[1] Novel Products and True Positional Selectivities in Nitration of p-Cymene

Sir:

Over a hundred years has passed since nitration of p-cymene (1) first was studied.[2] The reaction has re-

1

ceived much attention in the interim, partly because of the occurrence and/or utility of 1 in commercial processes[3] and partly because of mechanistic questions raised by the presence of p-nitrotoluene in the product mixture.[4] Evidence for direct nitrodeisopropylation (ipso electrophilic attack[5] on the isopropyl-bearing carbon) of 1 was presented in an extensive study of

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