

sure of the relative affinities for Na^+ of the enolate anion and 18-crown-6. The observed temperature dependence of the equilibrium ratios provides some support for this assumption. As the temperature is increased, the concentration of the unassociated *E,E*-1 isomer decreases dramatically. A temperature increase of only 6° lowers the percentage of *E,E*-1 from 30 to 23% (Figures 1a and 1b). In another experiment with the same crown/enolate ratio, the following percentages were observed as a function of temperature²⁰: -46° , 25%; -51° , 32%; -60° , 37%; -65° , 41%. The direction of the temperature effect, to more unequal concentrations as the temperature is increased, points unequivocally to a significant entropy term. Apparently, the entropy requirements for complexation of Na^+ by 18-crown-6 and *Z,Z*-1 differ significantly. Because of its greater flexibility, 18-crown-6 exhibits substantially changed affinity for metal ions as a function of temperature.²¹

(20) These data fit a linear relationship between the logarithm of *N*, the peak ratio (*E,E*-1/*Z,Z*-1), and the reciprocal temperature (correlation coefficient, $r = 0.97$). If we assume an equilibrium of the form $\text{LNa} + \text{C} \rightleftharpoons \text{CNa}^+ + \text{L}^-$, where L^- represents the enolate anion and *C*, the crown ether, the equilibrium constant can be expressed as a function of *N* and *R*, the molar ratio of initial crown ether and sodium enolate concentrations: $K = N^2/(N(R - 1) + R)$. The plot of $\ln K$ vs. $1/T$ exhibited a comparable linearity ($r = 0.97$) since $\ln K$ is proportional to $\ln N$ for these values of *N*, and $R = 1.6$. An accurate determination of entropy and enthalpy as well as the exclusion of other possible equilibria will require more extensive data and is deferred to a subsequent detailed paper.

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A Novel Case of Multiple Emissions from Nonthermally Equilibrated States of a Heterochelated Complex of Iridium(III)

Sir:

Measurements of luminescence decay curves of a vast majority of complexes of d^6 metal ions at 77°K reveal that the decays are simple, first-order processes. This indicates that the emissions are due to transitions from either a single level or a manifold of levels in thermal equilibrium.¹ Several unique heterotrachelated complexes of Rh(III) have recently been reported to show a departure from the normal exponential luminescence decays displayed by other d^6 metal ion complexes.² We wish to report a study of the luminescence decay of two heterobischelated complexes of Ir(III). One of these complexes, *cis*-dichloro-1,10-phenanthroline-2,2'-bipyridineiridium(III) chloride, $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$, displays a nearly normal luminescence decay, which deviates only slightly from exponential behavior. The other, *cis*-dichloro-1,10-phenanthroline-5,6-dimethyl-1,10-phenanthrolineiridium(III) chloride, $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$, is found to have a distinctly non-

exponential luminescence decay. This latter complex represents the first case of multiple emissions from nonthermally equilibrated levels of an Ir(III) complex.

The two heterobischelated iridium(III) complexes were prepared by a modification of the method of Broomhead and Grumley,³ and were characterized by elemental analysis, pmr, and infrared spectroscopy. The synthesis and characterization of the complexes are reported in detail elsewhere.⁴ For this study, further tests for purity were made with thin-layer chromatography on Eastman 6062 Alumina Chromagram Sheet using ethanol for elution. The technique was demonstrated to be capable of resolving samples of the anticipated impurities, $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$, from the $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ complex. No indication of either of these impurities could be detected in a thin-layer chromatogram of the heterobischelated complex, which appeared as a single spot on the plate. In the case of $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$, the primary impurities were expected to be $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$. The thin-layer technique was again found to be capable of resolving samples of these potential impurities from the heterochelated complex, which appeared as a single spot in a chromatogram. In order to check for photochemically induced impurities, aqueous solutions of the two heterochelated complexes were irradiated with a 1000-W Hg-Xe lamp (Hanovia 977B-1). The resulting products could be easily resolved from the starting material by thin-layer chromatography. No traces of these products were found in the complexes before irradiation.

The uv-visible absorption spectra of the two complexes were measured with a Cary 118 spectrophotometer and their corrected luminescence spectra were recorded with a Perkin-Elmer MPF-3 fluorescence spectrophotometer. The results are shown in Figure 1. In absorption, $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ displays a spectrum which has characteristics of both $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$. Similarly, the $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ absorption spectrum has bands found in the absorption of both $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$. Unlike the absorption spectra, the luminescence spectra of the two heterobischelated complexes have characteristics more similar to one of their homobischelated parents. The luminescence spectrum of $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ has its first maximum at 21.1 kK, which is identical with the energy of the first emission maximum in both $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$. The intensity distribution in the emission spectrum of this complex is nearly identical with that in $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$.⁵ The luminescence spectrum of $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ has its first maximum at 20.6 kK compared to a value of 20.5 kK for $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$.⁶

The luminescence lifetimes of the two complexes were measured at 77°K in ethanol-methanol glasses (4:1, v/v). The complexes were excited at 337 nm with an Avco C950 pulsed nitrogen laser. The emission was passed through a Perkin-Elmer Model 98 monochromator equipped with a dense flint prism. Life-

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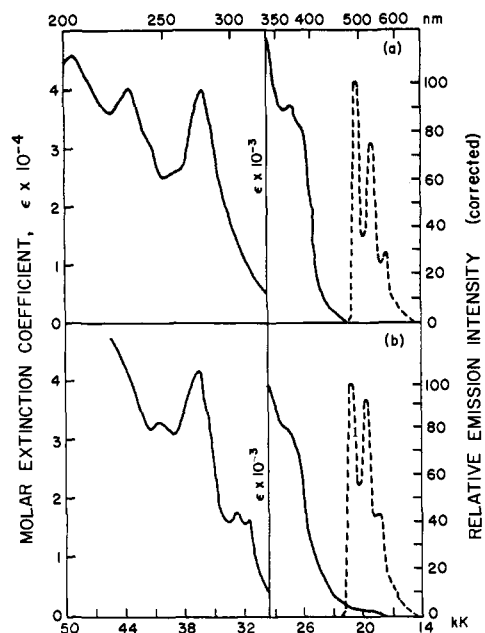


Figure 1. Absorption and luminescence spectra of heterobis-chelated complexes of Ir(III): (a) $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$; (b) $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$; (—) absorption spectra in water at room temperature; (---) luminescence spectra in ethanol-methanol glass (4:1, v/v) at 77°K.

times were measured at the peak of the first three bands in the vibrational progression of the luminescence spectra of each complex (472, 507, and 540 nm for $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ and 486, 523, and 564 nm for $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$). The luminescence decay of $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ was found to be only slightly nonexponential. Lifetimes measured in the first three vibrational bands of the emission spectrum were found to be 6.33 ± 0.05 (473 nm), 6.70 ± 0.06 (507 nm), and 7.13 ± 0.05 μsec (540 nm). Measurements of the lifetimes of $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$ in the vibrational bands of their emission spectra showed that these complexes also have a slight variation in their lifetimes with emission wavelength. However, the variation is only about 50% of that displayed by the $[\text{IrCl}_2(\text{phen})(\text{bipy})]\text{Cl}$ complex. Previous measurements of the lifetimes of $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ ⁷ and $[\text{IrCl}_2(\text{bipy})_2]\text{Cl}$,⁸ which were done under conditions where the entire emission spectrum was monitored, were found to be 6.92 ± 0.05 and 5.94 ± 0.05 μsec , respectively. The luminescence decay curve for $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ was found to be nonexponential and to have a shape which was dependent upon the wavelength at which the emission was monitored. Luminescence decay curves measured at three different wavelengths for this complex are shown in Figure 2. From these curves it is apparent that the decay contains at least two components. From the latter part of the decay curve at 485 nm, the lifetime of the longer-lived component is estimated to be about 70 μsec . Analysis of the initial part of the decay curve at 560 nm yields a lifetime of about 10 μsec . These lifetimes are comparable to the values of 66.3 μsec for $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$ ⁶ and 6.95 μsec for $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$.⁷

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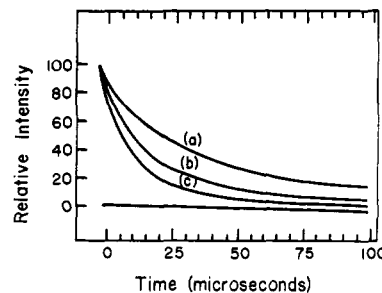


Figure 2. Luminescence decay curves of $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ in ethanol-methanol glass (4:1, v/v) at 77°K excited at 337 nm: (a) luminescence monitored at 486 nm; (b) luminescence monitored at 523 nm; (c) luminescence monitored at 564 nm.

These results indicate that at least two nonthermally equilibrated states are responsible for the luminescence decay of $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$. Due to the dependence of the shape of the decay curves on the emission wavelength, these levels must both emit light. By comparison with previous results reported for $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$ and $[\text{IrCl}_2(5,6\text{-Me}(\text{phen}))_2]\text{Cl}$, it appears likely that the longer lived of these nonthermally equilibrated states has a $\pi\pi^*$ orbital parentage and is localized in the 5,6-Me(phen) part of the complex. The shorter-lived component probably has a $d\pi^*$ orbital parentage and is localized in the region of the complex encompassing the phen ligand and the central metal. We are currently determining the time resolved spectrum of $[\text{IrCl}_2(\text{phen})(5,6\text{-Me}(\text{phen}))]\text{Cl}$ as well as several closely related complexes in order to further elucidate the orbital parentage of the nonequilibrated states responsible for the emission at 77°K. Studies of the photochemical reactions of this novel complex are also in progress and will be reported at a later date.

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Stereochemistry of Olefin Formation in Cyclopentyl Brosylate Solvolysis¹

Sir:

We wish to report a determination of the stereochemistry of the solvolytic elimination of cyclopentyl brosylate based on the observed labeling patterns in the cyclopentene obtained from specifically deuterated starting material.

In earlier papers^{2,3} deuterium isotope effects on the rate of solvolysis and the partial stereochemical results

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