Spectroscopic Investigation of the Multidentate Coordination Equilibrium among Conformational Isomers of Tris(2,2',2''-terpyridyl)europium(III) Perchlorate in Acetonitrile

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A conformational equilibrium of the ligands in tris(2,2',2''-terpyridyl)europium(III) is observed in acetonitrile solution and in the precipitated solid material as usually synthesized. Terpyridine (tpy) in these complexes can assume approximate geometries of cis,cis or cis,trans or trans,trans, as judged by their fluorescence emission and excitation spectra. The complexes $Eu(tpy)_3^{3+}$ are therefore 9-, 8-, or 7-coordinate, in terpyridine nitrogens. The relative concentrations at 0.01 M $Eu(tpy)_3(ClO_4)_3$ are 8-coordinate > 9-coordinate >> 7-coordinate. Evidence, in the form of ^1H NMR spectra and of high-resolution laser-excited species-selective excitation of fluorescence, is also presented to show the existence of the isomeric species. Previous studies of this complex did not account for this lability toward a thermodynamically appreciable isomerization.

Introduction

Recently developed techniques based on selective laser excitation of tripositive lanthanide ions have allowed characterizations of chemical systems incorporating these ions. Examples include bulk inorganic solids and biomolecules in solution.[3-7] As part of a program to extend such techniques to the analysis of surface-adsorbed molecules, the spectroscopy of tris(2,2',2''-terpyridine)europium(III) perchlorate has been studied. The coordination of this molecule in the solid state and in acetonitrile solution is the subject of this report.

Transition-metal and lanthanide complexes of the tridentate ligand 2,2',2''-terpyridine (tpy) have been studied,[8,9] because of the utility of the terpyridine ligand as an analytical reagent for certain metals[10,11] and because of the advantage, with respect to its chelate effect, of a 3-nitrogen tridentate ligand.

The changes in coordination chemistry during the dissociation and subsequent aquation of bis(terpyridyl)iron complexes have been studied,[12,13] but the conformational isomerism of the dissociating ligand has not been described. The observation of several spectroscopic properties of the europium–terpyridine system reported herein allows the characterization of such behavior. These properties are luminescence from the ligand and the metal as well as the ^1H NMR chemical shifts induced by the paramagnetic lanthanide ion. All of these measurements have been used to provide structural information. These studies have allowed a semiquantitative characterization of the species present in the moderately labile europium–ter-

pyridine system in acetonitrile solvent.

The fluorescence spectrum of solid $Eu(tpy)_3(ClO_4)_3$ was described in an earlier report.[14] Those data were on the undiluted solid compound (where dynamic isomerism is suppressed), and the resolution and sensitivity were insufficient to discern more than the predominant species. With use of high-resolution laser-excited fluorescence spectroscopy, at least two components have been identified in solution as well as in the precipitated solid prepared according to the literature synthesis.[14] The presence of these species in solution is corroborated by ^1H NMR spectroscopic measurements of the system, which has not been studied previously.

Experimental Section

Synthesis. $Eu(tpy)_3(ClO_4)_3$ was synthesized by the literature method[14] using 2,2',2''-terpyridine from G. F. Smith Chemical Co., recrystallized from *n*-pentane, and europium perchlorate, which was synthesized from 99.9% Eu_2O_3 (also from G. F. Smith Chemical Co.). Elemental analyses were performed by Galbraith Laboratories. Anal. Calcd for $C_{45}H_{33}N_9Eu(ClO_4)_3$: C, 46.99; H, 2.89; N, 10.96; Eu, 13.21. Found: C, 46.19; H, 3.13; N, 10.72; Eu, 14.13.

Low-Resolution Fluorescence Spectroscopy. Conventional (corrected) fluorescence spectra, including excitation spectra of all emissions, were recorded on a Perkin-Elmer Model MFP-44B spectrofluorimeter in 1.00-cm square quartz cuvettes or in a triangular cuvette (1-cm sides) positioned to observe emission from the front-face intercept with the excitation beam. Solution concentrations were 1 × 10⁻⁴ M in distilled-in-glass Burdick and Jackson acetonitrile.

High-Resolution Fluorescence Spectroscopy. The high-resolution selective excitation and time resolution experiments were conducted with the following spectrometer system. The excitation source was a nitrogen laser or a nitrogen-laser-pumped tunable dye laser (Dyescan 2100 from EG&G Princeton Applied Research) with a line width specification of 0.08 nm (fwhm) and a power of 30 μJ/pulse (1 ns/pulse). Pulse repetition rates were in the range of 10–41 Hz. Laser dyes were obtained from the Exiton Co., and the following dye solutions were used to obtain specific fluorescence excitations: terpyridine (UV), 7 mM PBD in toluene; europium ($^7F_0 \rightarrow {}^5D_2$), 7.5 mM LD-466 in 3:5 ethanol–dioxane; europium ($^7F_0 \rightarrow {}^5D_1$), 10 mM coumarin-485 in ethanol; europium ($^7F_0 \rightarrow {}^5D_0$), 5 mM rhodamine-590 chloride in ethanol.

Emissions were detected with a thermoelectrically cooled RCA C31034A photomultiplier tube and a Spex Model 1269 1.26-m scanning Czerny-Turner monochromator. Entrance and exit slit widths were varied as appropriate for the desired resolution and optical throughput. Spectral slit widths for emission spectra were always much less than the recorded line widths. Excitation specta were obtained by scanning the dye laser. The reported laser line width is much less than any recorded excitation line widths. Recorded spectra were obtained by employing an EG&G PAR Model 162 boxcar

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(3) (a) Venikouas, G. E.; Powell, R. C. *Phys. Rev. B: Solid State* **1978**, *17*, 3456–3461. (b) Gang, X.; Boulon, G.; Powell, R. C. *J. Chem. Phys.* **1983**, *78*, 4674–4678.

(4) (a) Wright, J. C.; Gustafson, F. J.; Porter, L. C. In "New Applications of Laser to Chemistry"; G. M. Hieftje, Ed.; American Chemical Society: Washington, DC, 1978; pp 1–11. (b) Hamers, R. J.; Wietfeldt, J. R.; Wright, J. C. *J. Chem. Phys.* **1982**, *77*, 683–692.

(5) Evesque, P.; Kliava, J.; Duran, J. *J. Lumin.* **1979**, *18/19*, 646–650.

(6) Horrocks, W. DeW., Jr.; Sudnick, D. R. *Science (Washington, D.C.)* **1979**, *206*, 1194–1196.

(7) Dexpert-Ghys, J.; Faucher, M.; Caro, P. *J. Solid State Chem.* **1982**, *41*, 27–38.

(8) Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341–350.

(9) Sinha, S. P. *Z. Naturforsch., A* **1965**, *20A*, 164, 165, 552–560, 835–837, 1661–1664.

(10) Smith, G. F. *Anal. Chem.* **1954**, *26*, 1534–1538.

(11) Fink, D. W.; Pivnichny, J. V.; Ohnesorge, W. E. *Anal. Chem.* **1969**, *41*, 833–834.

(12) Burgess, J.; Twigg, M. V. *J. Chem. Soc., Dalton Trans.* **1974**, 2032–2036.

(13) Walters, W. S.; Gillard, R. D.; Williams, P. A. *Aust. J. Chem.* **1978**, *31*, 1959–1964.

(14) (a) Durham, D. A.; Frost, G. H.; Hart, F. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 833–838. (b) Frost, G. H.; Hart, F. A.; Heath, C.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1969**, 1421–1422.
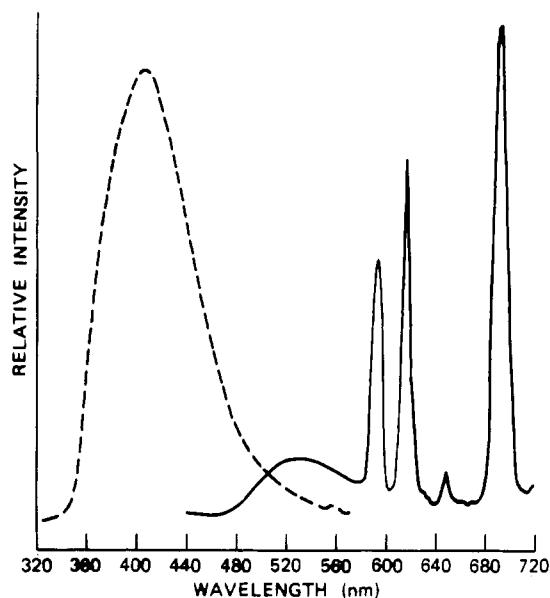
Figure 1. Composite low-resolution fluorescence emission spectra of 10^{-4} M Eu(tpy)$_3$(ClO$_4$)$_3$ in acetonitrile: solid curve, λ_{exc} = 370 nm; dashed curve, λ_{exc} = 302 nm. Note that the Eu(III) transitions at λ > 570 nm were also seen in the dashed spectrum but were left out for clarity.

averager with a Model 164 gated integrator. Delay times and aperture durations were set as appropriate for the desired time resolution. In most cases these were chosen to maximize the observed signal.

Solution samples were 10^{-4} or 10^{-2} M Eu(tpy)$_3$(ClO$_4$)$_3$ in acetonitrile in a 1.00-cm square quartz cuvette, monitored by front-face emission of the fluorescence. Solid samples were studied in a 5-mm borosilicate glass NMR tube. No emission was observed for the sample tube.

NMR Spectroscopy. NMR studies were carried out on a Varian XL-100 spectrometer operating at 100 MHz for ^{1}H. Sample solutions in CD$_3$CN (Stohler Isotope Chemicals) were studied in a concentration range of 0.001–0.050 M Eu(tpy)$_3$(ClO$_4$)$_3$, although the most detailed study was at 0.010 M. Residual protons of CHD$_2$CN, assumed as δ 1.93, were used as a reference.

Results

Low-resolution emission spectra from a 10^{-4} M Eu(tpy)$_3$-(ClO$_4$)$_3$ solution are shown in Figure 1. Two obvious terpyridine emissions are observed. One of these peaks is at 404 nm and the other at 530 nm. Their relative intensity depends on excitation wavelength. In addition, emission from the f–f transitions of europium is observed. None of these emissions corresponds to that previously found for free terpyridine.[15]

Figure 2a shows the UV excitation spectrum of the europium ^{5}D$_0$ → ^{7}F$_4$ emission. The same excitation spectrum is seen for all europium emissions. This spectrum corresponds to the absorption spectrum of the Eu(tpy)$_3$$^{3+}$ complex and is the same as reported for the π → π^* absorption spectrum of H$_2$tpy^{2+} and other metal–terpyridine complexes.[16]

The excitation spectrum of the 404-nm ligand fluorescence (Figure 2a) looks similar to that of the europium (i.e., the absorption spectrum of the complex), but it is distinctly and reproducibly different, most bands being blue shifted between 4 and 8 nm.

The excitation spectrum of the broad 530-nm ligand emission shows a significant shoulder at 365 nm on a spectrum that otherwise looks similar to that obtained monitoring the 404-nm emission. A study of this excitation spectrum as a function of emission wavelength shows that the 530-nm emission is, in fact, correlated only with the 365-nm shoulder. This is presented in Figure 2b where the relative intensity of the 365-nm excitation is seen to increase as the monitored
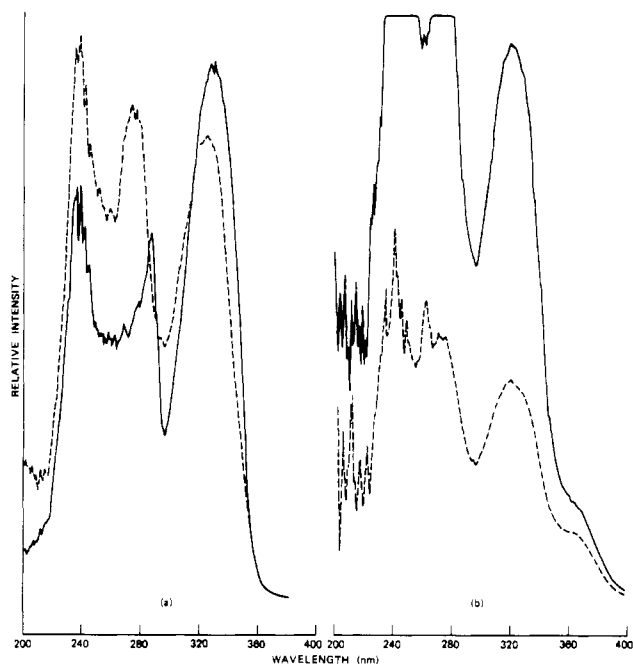

Figure 2. Excitation spectra of 10^{-4} M Eu(tpy)$_3$(ClO$_4$)$_3$ in acetonitrile. (a) Solid curve, λ_{em} = 694 nm (^{5}D$_0$ → ^{7}F$_4$); dashed curve, λ_{em} = 404 nm. (b) Excitation spectra of emission near 530 nm: solid curve, λ_{em} = 508 nm; dashed curve, λ_{em} = 528 nm. The relative intensity of the 365-nm shoulder increases as λ_{em} is shifted to the red.

emission wavelength shifts to the red. An attempt to measure the lifetime of the 530-nm emission using a rotating-bucket chopper on the Perkin-Elmer spectrofluorimeter yielded only an upper limit of 1 ms. Therefore, it is unlikely that this band is due to phosphorescence.

The room-temperature ^{1}H NMR spectrum of 0.01 M Eu-(tpy)$_3$(ClO$_4$)$_3$ in CD$_3$CN is shown in Figure 3. In addition to the most intense resonances, there are smaller peaks that are noticeably shifted from the larger ones but, nevertheless, retain the pattern of multiplicity and relative ordering of the major peaks. An exception is the apparent absence[17] of a smaller companion to the δ 15.35 doublet of the 6,6″ protons of the coordinated terpyridine. There is also some resonance in the region of δ 8–9, corresponding approximately to the chemical shift of free terpyridine.

The energy levels of Eu(III) are well documented. In the present case, the excitations studied are all from the ^{7}F$_0$ ground term to the ^{5}D$_{0,1,2}$ terms. Emission data deal with transitions from the ^{5}D$_0$ term to the ^{7}F$_{0,1,2}$ terms. Transitions to ^{7}F$_{3,4}$ have been observed but are not considered in detail in the present paper.

Figure 4 depicts the high-resolution, time resolved measurements of *two* ^{7}F$_0$ → ^{5}D$_0$ excitations observed in precipitated solid Eu(tpy)$_3$(ClO$_4$)$_3$.[14] The excitation spectrum was measured by monitoring the ^{5}D$_0$ → ^{7}F$_2$ emission at 617.25 nm with a spectral resolution of ~0.5 nm. The use of wide slits allowed a maximum amount of light to be collected without affecting the resolution of the excitation spectrum, which was determined by the fwhm of the laser (0.08 nm). The wide slits also allowed a sampling of the emission from all types of Eu(tpy)$_3$$^{3+}$ complexes (vide infra). The same two transitions have been observed in emission using 337-nm excitation from the N$_2$ laser. The coincidence of excitation (absorption) and emission

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(17) The smaller companion to this major peak has been discovered in a preliminary temperature-dependence study of the ^{1}H NMR of this system, which showed these protons to be involved in appreciably fast exchange with its noncoordinated form. Thus, the fairly broad resonance at δ 9.02 is the signal due to these protons. Further quantitative studies of the thermodynamics and kinetics of these isomerizations are in progress at this laboratory.

(15) Fink, D. W.; Ohnesorge, W. E. *J. Phys. Chem.* **1970**, *74*, 72–77.
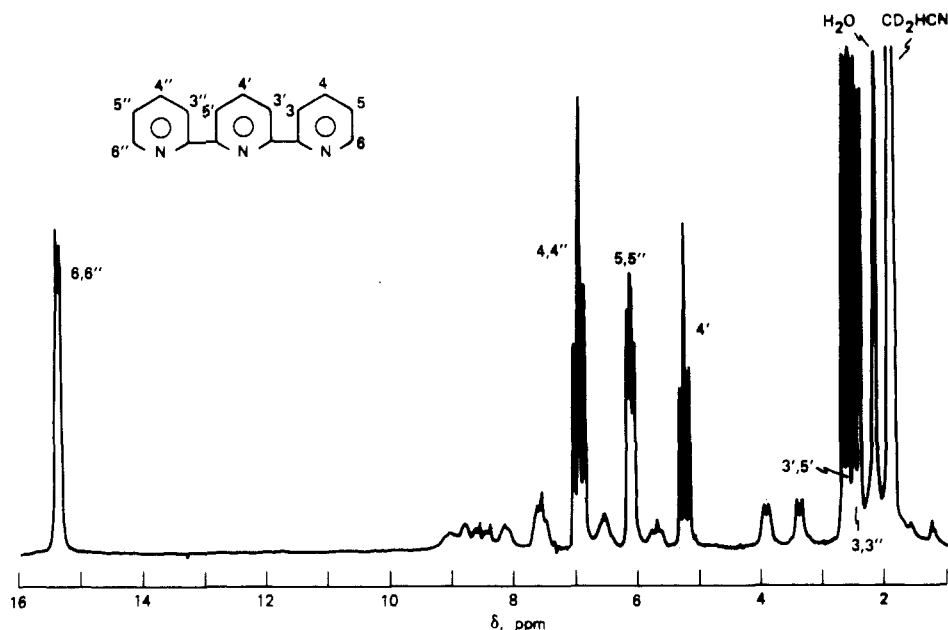(16) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420–1425.

Figure 3. Room-temperature ^1H NMR spectrum of 10^{-2} M $Eu(tpy)_3(ClO_4)_3$ in CD_3CN. Assignments are as shown.

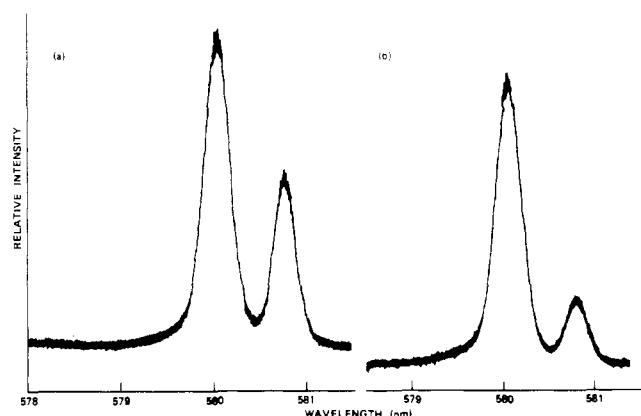**Figure 4.** High-resolution $^7F_0 \rightarrow {}^5D_0$ excitation spectra of solid $Eu(tpy)_3(ClO_4)_3$ (room temperature) monitoring the $^7F_2 \leftarrow {}^5D_0$ emission (50-μs observation window): (a) delay 1.55 ms; (b) delay 0.54 ms.

establishes these transitions as electronic origins associated with the $^7F_0 \leftrightarrow {}^5D_0$ terms.

The species emitting/absorbing at 580.05 nm has a shorter lived excited state than the species emitting/absorbing at 580.80 nm. this is indicated by the relative diminution of the 580.05-nm peak on delaying the emission observation by 1.55 ms as compared to a delay of 0.54 ms. Laser selective excitation of these two transitions gives rise to two different emission spectra in the $^5D_0 \rightarrow {}^7F_2$ region as shown in Figure 5. The broader, less resolved emission has a shorter radiative lifetime than the sharper, narrower emission.

In acetonitrile solution, the behavior is similarly interesting. A major difference is that there is only *one* $^7F_0 \leftrightarrow {}^5D_0$ transition located at 580.03 nm observable in the solution. (A low-intensity emission at 580.62 nm proved to be the $^5D_1 \rightarrow {}^7F_3$ transition by its complete disappearance in the equivalent excitation spectrum.) The $^7F_0 \rightarrow {}^5D_1$ excitation spectrum in solution is shown in Figure 6 (dashed line). These data were collected by monitoring the $^5D_0 \rightarrow {}^7F_2$ emission at 616.7 nm with an ~1.2-nm spectral bandwidth. There are three transitions resolved at 525.70 (shoulder), 526.39, and 527.30 nm. The former two exhibit shorter excited-state lifetime components than the third.

The $^7F_0 \rightarrow {}^5D_1$ excitation spectra were also resolved by varying the monitored emission transition. Figure 6 (solid line)
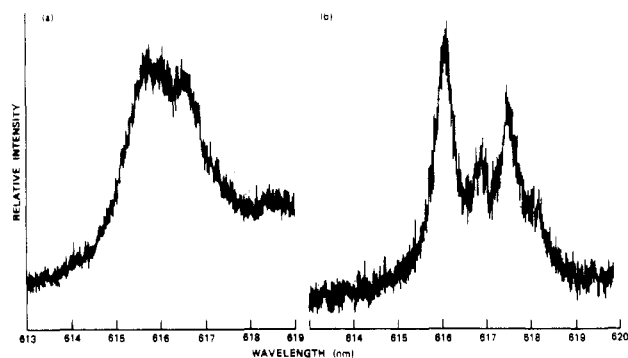

Figure 5. Emission of solid $Eu(tpy)_3(ClO_4)_3$ in the $^5D_0 \rightarrow {}^7F_2$ regions showing the result of laser selective excitation: (a) $\lambda_{ex} = 580.05$ nm, delay 0.54 ms; (b) $\lambda_{ex} = 580.80$ nm, delay 1.55 ms.
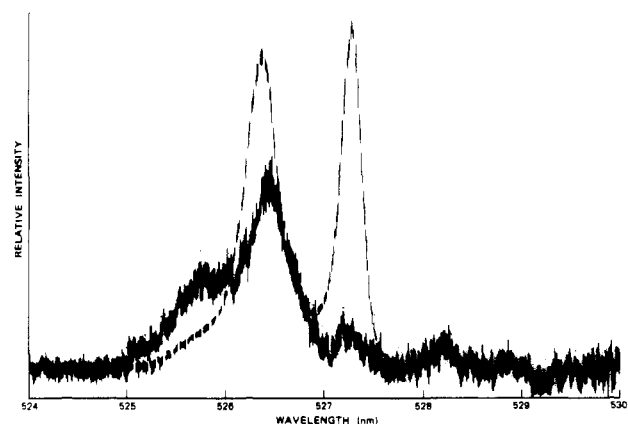

Figure 6. High-resolution $^7F_0 \rightarrow {}^5D_1$ excitation spectra of 10^{-2} M $Eu(tpy)_3(ClO_4)_3$ in acetonitrile: solid curve, $\lambda_{em} = 580.03$ nm $(^5D_0 \rightarrow {}^7F_0)$, delay 0.85 ms; dashed curve, $\lambda_{em} = 616.7$ nm $(^5D_0 \rightarrow {}^7F_2)$, delay 1.8 ms.

also shows the excitation spectrum as a result of monitoring the $^5D_0 \rightarrow {}^7F_0$ emission at 580.03 nm, also with side slits. The spectrum here corresponds to the shorter lived components detected when the $^5D_0 \rightarrow {}^7F_2$ emission is monitored.

Figure 7 depicts the $^5D_0 \rightarrow {}^7F_2$ high-resolution emission spectrum as a function of excited wavelength. With excitation at 527.30 nm, a narrow, partially resolved, doublet is observed. Band maxima are at 616.35 and 617.02 nm. Excitation at
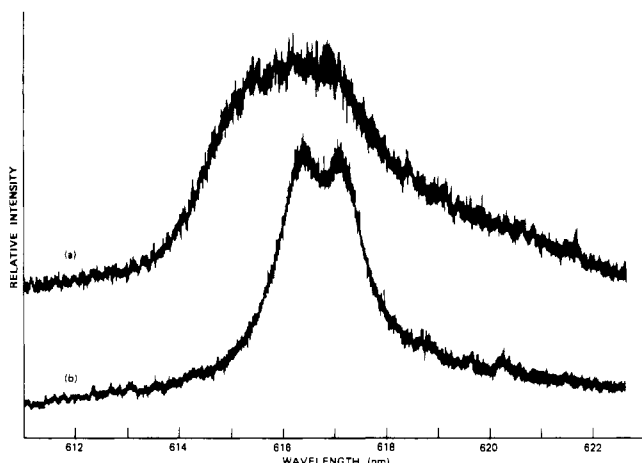
Figure 7. High-resolution $^5D_0 \rightarrow {}^7F_2$ emission spectra of 10^{-2} M Eu(tpy)$_3$(ClO$_4$)$_3$ in acetonitrile: (a) λ_{exc} = 525.70 nm; (b) λ_{exc} = 527.30 nm.

527.30 nm, the most intense band in the $^7F_0 \rightarrow {}^5D_1$ spectrum, produces *no* observable emission in the $^5D_0 \rightarrow {}^7F_0$ region of the spectrum. Excitation into the weak shoulder at 525.70 nm produces a much broader unresolved emission in the $^5D_0 \rightarrow {}^7F_2$ region. Excitation at this wavelength also gives rise to the $^5D_0 \rightarrow {}^7F_0$ emission observed at 580.03 nm.

Discussion

The conformational isomers of terpyridine were previously studied by using UV absorption[16] and luminescence spectroscopy.[15] The latter study showed clear distinctions (with respect to fluorescent emissions) between free base terpyridine and its mono- and diprotonated acid forms. These three forms had been shown[16] to exist in the trans,trans, cis,trans, and cis,cis conformations, respectively, in their ground states.[18]

A broad 520-nm emission from H$_2$tpy^{2+} was postulated[15] to arise from a transition other than the simple $\pi^* \rightarrow \pi$ fluorescence of the stable cis,cis isomer. It was suggested that the emission arose from a $\pi^* \rightarrow \pi$ transition in another isomer formed in fluid solution during the lifetime of the singlet excited state. Reasons for this were the large energy separation from the observed $\pi \rightarrow \pi^*$ absorption, the lack of an afterglow, and the disappearance of the emission upon cooling either with dry ice in a glycerol solution or to 77 K in a rigid acidified ethanol glass.

The present observation of three distinct UV excitation spectra strongly suggests the presence of three types of terpyridine molecules in the Eu(tpy)$_3^{3+}$ complex. On the basis of previous results,[15,16] these three types are postulated to be a tridentate molecule, necessarily in a cis,cis conformation, a bidentate molecule in a cis,trans conformation, and a monodentate molecule, probably in a trans,trans conformation.[18]

The congruence of the absorption spectrum of Eu(tpy)$_3^{3+}$, the UV excitation spectrum of the europium emission, and the reported[16] absorption of cis,cis H$_2$tpy^{2+} indicate that the predominant terpyridine species is the tridentate molecule. This is consistent with the NMR data discussed below. The absence of any terpyridine emission associated with this excitation spectrum and the intensity of the europium emission with UV excitation indicate a very efficient energy transfer between the tridentate species and the europium.

It has been previously noted[16] that the absorption bands of 2,2′,2″-terpyridine do not show an appreciable red shift compared with 2,2′-bipyridine because of the lack of resonance

between the bipyridine portion of the 2,2′,2″-terpyridine and the third pyridine attached to the ortho position of the former. Thus, on the basis of the similarity of the excitation spectrum to the predominant cis,cis isomer, the emission at 404 nm and its attendant excitation spectrum are assigned as $\pi \leftrightarrow \pi^*$ transitions arising from the bidentate cis,trans terpyridine. The 530-nm emission and its associated weak 365-nm excitation are consistent with the n $\rightarrow \pi^*$ transition assignments reported for trans,trans terpyridine.[15] They are, therefore, assigned as arising from the monodentate, trans,trans terpyridine in this work.

The three types of ^{1}H NMR resonances indicate three different environments for the protons involved. The most intense resonance in the NMR spectrum is assigned to protons on the predominant tridentate form of terpyridine (group A). The smaller shifted resonances (group B) in the NMR spectra are assigned to protons in the same positions on pyridine moieties that *are* coordinated to europium in terpyridine molecules that have one or two pyridine nitrogens not coordinated to (detached from) the europium. Such a phenomenon has been observed previously.[19] The ligand exchange of (1,4,7,10-tetraazacyclododecane-N,N',N'',N'''-tetraacetato)-europate(III) (EuDOTA) was studied by using ^{1}H NMR. At -4 °C, where exchange was slow on the NMR time scale, the spectrum showed fairly small and slightly shifted peaks in addition to those from the expected species. The minor component was not identified originally[19] but was later postulated to be an isomeric form.[20] The *partial* coordination of a ligand to a lanthanide also has a precedent in the case of Eu(EDTA)$_2^{5-}$. There,[21] it was assumed that one ligand was bound by only *one* iminodiacetate.

The NMR resonances between 7.2 and 9.5 ppm (group C) that are only slightly shifted from those in free terpyridine in our work are thus assigned to the protons (on pyridine moieties that *are not* nitrogen coordinated to europium) in terpyridine molecules that have one or two pyridine nitrogens coordinated to europium. It is expected that both contact and dipolar contributions to the lanthanide-induced shift (LIS) would be affected by the geometry change of dissociation and isomerization by terpyridine. It seems reasonable that protons in pyridine moieties *not coordinated* to europium should have greatly diminished contact shift contributions and hence have resonances only slightly shifted from those in free terpyridine.

Because of the uncertainty in the NMR integration (3%) and overlap in the free terpyridine region of the spectrum, the uncertainty in the percentage of protons in each environment (A, B, and C) is at least $\pm 5\%$. Integration of the NMR spectrum shows that $\sim 78\%$ of the protons in a 0.01 M Eu(tpy)$_3$(ClO$_4$)$_3$ solution are on tridentate terpyridine molecules (group A). This is equal to the percentage of tridentate terpyridine molecules.

Both bidentate and monodentate terpyridines provide protons to groups B and C. The percentage of protons in each was determined as follows. The total integrated intensity was found for the group B resonances at 3.40, 3.93, 5.68, and 6.55 ppm. These represent respectively two, two, one, and two proton equivalents for a total of seven proton equivalents on an 11-proton-equivalent terpyridine molecule. Dividing by seven gives the integrated intensity for one proton equivalent in group B. The resonance at 7.57 ppm is an overlap of two proton equivalents from group B and an unknown number of proton equivalents from group C. The integrated intensity from the two proton equivalents in group B is subtracted from

(18) It has been found (see footnote 3 of ref 16) that there was a small twist angle about the carbon–carbon bonds connecting the pyridine fragments (<28°). Therefore, the geometries would be better described as cisoid and transoid, rather than cis or trans.

(19) Desreux, J. F. *Inorg. Chem.* **1980**, *19*, 1319–1324.
(20) Albin, M.; Horrocks, W. DeW., Jr.; Liotta, F. J. *Chem. Phys. Lett.* **1982**, *85*, 61–64.
(21) Southwood-Jones, R. V.; Merbach, A. E. *Inorg. Chim. Acta* **1978**, *30*, 77–82.

the measured integrated intensity leaving the contribution from group C. The integrated intensity from all proton equivalents in group C is thus known. The integrated intensity for all proton equivalents in group B is determined by multiplying the integrated intensity for one proton equivalent by 11. Using these integrated intensities and the fact that group B plus group C make up ~22% of the total protons allows the percentage of protons in each group to be determined. These values are ~16% in group B and ~6% in group C with an uncertainty of ±5% in each.

Considering only those protons in groups B and C gives ~75% in group B and ~25% in group C with an uncertainty of ±25%. A calculation of the percentages of protons in these two groups assuming all detached terpyridines are bidentate and no monodentate terpyridines are present gives $^7/_{11}$ = 64% in group B and $^4/_{11}$ = 36% in group C. Thus, the percentage of bidentate terpyridine actually present is ~22% and that of monodentate terpyridine is very small, i.e., on the order of the uncertainty in the data. This is consistent with the failure to observe any emission from 7-coordinate europium (vide infra) and the observation that the emission/excitation assigned to monodentate terpyridine is the weakest observed.

The presence of three isomeric forms of terpyridine gives rise to at least three possible types of $Eu(tpy)_3^{3+}$ complexes. These are (1) a 9-coordinate complex with three tridentate, cis,cis terpyridine ligands, (2) a complex, 8-coordinate with respect to terpyridine nitrogens, with one bidentate cis,trans and two tridentate cis,cis ligands, and (3) a complex, 7-coordinate with respect to terpyridine nitrogens, with one monodentate trans,trans and two tridentate cis,cis ligands. In addition to these three complexes, there is a second possible type of 7-coordinate complex having one tridentate cis,cis ligand and two bidentate cis,trans ligands. There are also two arrangements that would give rise to 6-coordinate complexes, and so on. Considering the relative amounts of monodentate, bidentate, and tridentate terpyridine ligands, it is reasonable to assume that at least the first three $Eu(tpy)_3^{3+}$ complexes mentioned above are present in solution. Their relative concentrations would have to be 8-coordinate > 9-coordinate >> 7-coordinate. This is consistent with the previous observation that $Eu(tpy)_3(ClO_4)_3$ crystallizes from acetonitrile in two crystal forms.[14b] (The crystal structure[14b] and solid-state luminescence[14a] have been reported previously only for the tris tridentate complex.) The above postulated relative amounts of 7-, 8-, and 9-coordinate species are also consistent with the high-resolution Eu^{3+} luminescence data given above and discussed below. These data provide definitive evidence for the presence of two $Eu(tpy)_3^{3+}$ complexes in solution and in the precipitated solid. Other types of complexes also may be present, but the resolution and sensitivity of our apparatus preclude their detection. The presence of three types of terpyridine requires either that there be at least three complexes or that there be some unusual equlibrium involving complexes with vastly different coordination numbers of europium to terpyridine nitrogens.

The previously reported emission data taken on the solid complex did not show the $^5D_0 \rightarrow {}^7F_0$ transition.[14a] Since those data were recorded by using film methods and without laser excitation, it is probable that this transition, which is much weaker than the $^5D_0 \rightarrow {}^7F_{1,2,4}$ transitions observed, was not intense enough to be detected. It is also uncertain whether the previous data were obtained from a single crystal or from the precipitated (polycrystalline) solid. This makes it impossible to directly compare the present data with that obtained previously.

The present observation of two $^5D_0 \rightarrow {}^7F_0$ transitions (Figure 4) in the excitation/emission of the precipitated solid $Eu(tpy)_3(ClO_4)_3$ clearly shows the presence of at least two types

of complexes. The transition at 580.80 nm is assigned to the 9-coordinate complex while the transition at 580.05 nm is assigned to the 8-coordinate complex. The 9-coordinate complex was reported[14b] to have C_2 symmetry in the solid state. This is a result of second-order site symmetry deviations from the expected D_3 symmetry. These deviations are primarly due to nonplanarity of the terpyridine ligands. These deviations could relax when the complex is in solution and crystal packing forces have been removed. This relaxation and concomitant increase in symmetry from C_2 to D_3 would account for the disappearance of the 580.80-nm, $^5D_0 \rightarrow {}^7F_0$, transition in solution. The 580.05-nm band persists in solution because the 8-coordinate complex retains its low symmetry in solution.

The results of lowering the symmetry from D_3 to C_2 because of second-order effects in the 9-coordinate complex are not expected to be as great as in the 8-coordinate complex, where the deviation from D_3 symmetry is in the first coordination sphere. Thus, the amount of wave function mixing allowed by the lower symmetry would be greater in the 8-coordinate complex than in the 9-coordinate complex. This would explain the longer radiative lifetime (i.e., decreased transition probability) for the transition at 580.80 nm as compared to the transition at 580.05 nm. It is also consistent with the observation that excitation into the 580.80-nm band gives rise to a set of better resolved, longer lived, $^5D_0 \rightarrow {}^7F_2$ emissions than those observed when the 580.05-nm band is excited (Figure 5).

Even though only one $^5D_0 \rightarrow {}^7F_0$ transition is observed for $Eu(tpy)_3^{3+}$ in solution, there is ample evidence for the presence of at least two Eu(III) complexes. Figures 6 and 7 clearly show the presence of one high-symmetry and one low-symmetry complex. The high-symmetry (longer lived) complex shows no $^5D_0 \rightarrow {}^7F_0$ transition, two bands in the $^7F_0 \rightarrow {}^5D_1$ excitation (and in the $^5D_0 \rightarrow {}^7F_1$ emission), and a relatively narrow $^5D_0 \rightarrow {}^7F_2$ emission. These data are consistent with a 9-coordinate D_3 symmetry complex and are so assigned. The very weak shoulder at 525.70 nm seen in the excitation spectrum of the high-symmetry (longer lived) complex (dashed line in Figure 6) is due to some residual intensity from the low-symmetry (shorter lived) complex.

The $^5D_0 \rightarrow {}^7F_0$ transition at 580.03 nm is the same to within 0.02 nm as one observed in the solid. This transition has associated with it shorter lived, broader emissions (and excitations) in the $^5D_0 \rightarrow {}^7F_{1,2}$ and $^7F_0 \rightarrow {}^5D_{1,2}$ regions. These data are consistent with a low-symmetry complex that is assigned as the 8-coordinate one.

Although trivalent lanthanide ions generally are known to be moderately labile with respect to ligand coordination, their complexes with the potential tridentate terpyridine were presumed stable on the basis of the ligand's chelating ability and the observed thermodynamic stability of the tris(terpyridine) complex. It has now been shown that, although $Eu(tpy)_3^{3+}$ *is* easily formed when a poorly coordinating anion (ClO_4^-) is used, the affinity of Eu(III) for the nitrogenous ligand is not so high as to disallow partial dissociation of a terpyridine ligand from the metal ion by means of conformational isomerization. This happens at least in acetonitrile solvent. On the basis of known oxophilicity of trivalent lanthanides, it is expected that potentially coordinating solvents such as alcohols might induce this isomerization to an even greater extent. The coordinative nature of $Eu(tpy)_3^{3+}$ in a solvent such as ethanol would be of interest in this respect.

Although Eu(III) complexes can assume 7- and 8-coordination, it seems probable that the original eighth and ninth coordination sites in $Eu(tpy)_3^{3+}$ are replaced by solvent molecules upon displacement of the terpyridine nitrogens. The ^1H NMR spectrum (Figure 3) shows no discernible ethanol residual from the synthesis. The relatively slight (considerably

less than CHD_2CN) water signal present showed no lanthanide-induced shift as would be expected if water were coordinated to Eu^{3+}. It is surmised, therefore, that such available coordination sites are occupied by acetonitrile solvent. Though acetonitrile is quite weakly coordinating, its complexation to Eu(III) is known.[22] Since it is more strongly coordinating

than perchlorate, vacant sites arising from terpyridine isomerization can become occupied by acetonitrile. This might be ascertained by ^1H NMR with high dynamic range in CH_3CN so that the LIS is apparent.

Registry No. $Eu(tpy)_3^{3+}$, 12579-88-3.

(22) Bünzli, J.-C. G.; Yersin J.-R.; Mabillard, C. *Inorg. Chem.* **1982**, *21*, 1471–1476.

Intramolecular Electron Transfer at Metal Surfaces. 1. Relative Energetics of Some Corresponding Outer- and Inner-Sphere Pathways Involving Halide and Pseudohalide Bridging Ligands

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The electroreduction kinetics of a number of Co(III) ammine and ethylenediamine complexes containing chloride, bromide, and isothiocyanate ligands have been studied at platinum– and gold–aqueous interfaces in order to investigate the effects of attaching simple transition-metal reactants to electrocatalytic metal surfaces upon the electron-transfer energetics. The virtues of evaluating unimolecular rate constants k_{et} (s^{-1}) for comparing the energetics of electrochemical inner- and outer-sphere pathways are pointed out. Values of k_{et} for inner-sphere electron transfer, k_{et}^{is}, were obtained by combining apparent rate constants k_{app} for the overall reaction with measurements of the reactant surface concentration. Estimates of k_{et} for the same reactions occurring via outer-sphere pathways, k_{et}^{os}, were extracted from the measured values of k_{app} at iodide-coated platinum surfaces and from the rate constants obtained by using homogeneous outer-sphere reductants. For halide-bridged reactions, $k_{et}^{is} \gtrsim k_{et}^{os}$, whereas for isothiocyanate-bridged reactions, $k_{et}^{is} \lesssim k_{et}^{os}$. Likely reasons for these greater bridging efficiencies with the halide ligands are sought in terms of electronic coupling effects between the redox center and the metal surface and also in the anticipated differences of reactant orientation between the inner- and outer-sphere transition states.

Introduction

A fundamental question in electrochemical kinetics concerns the various ways in which the chemical nature of the electrode material may influence the energetics of electron transfer. The simplest class of electrode reactions involves redox couples of the form

$$Ox + e^-(electrode) \rightleftharpoons Red \qquad (1)$$
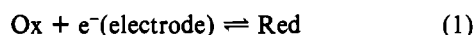
where both the oxidized and reduced forms (Ox and Red, respectively) are solution species, so that the electrode material is not involved in the reaction stoichiometry. Such electrode processes can take place via an "outer-sphere" route where the reactant is excluded from the inner layer of solvent molecules adjacent to the electrode surface. For such pathways the electrode surface may exhibit little specific influence upon the transition-state stability. However, many electrode reactions are thought to proceed via "inner-sphere" mechanisms where the reactant or its coordinated ligands are bound directly to the surface in the transition state for electron transfer. Although the kinetics of such "strong-interaction" pathways will clearly be sensitive to the chemical composition of the electrode, little attention has been devoted to examining the matter and extent to which metal surfaces may perturb the electron-transfer energetics, i.e., act as "electrocatalysts".

Electrochemical,[2,3] as well as homogeneous,[4] electron-transfer reactions can be considered to occur in two steps involving the formation of a precursor intermediate having the appropriate configuration at the interface that subsequently undergoes thermal activation leading to electron transfer. It is useful to distinguish between influences of the metal surface upon the reaction energetics arising from changes in the activation barrier for the elementary electron-transfer step itself and those merely due to variations in the stability of the precursor state, i.e. in the cross-sectional reactant concentration at the electrode surface.[2,3] Such a separation can be made by expressing the "apparent" rate constant for the overall reaction, k_{app}, as[3]

$$k_{app} = K_p k_{et} \qquad (2)$$

where K_p is the equilibrium constant for forming the precursor

(1) Graduate research assistant, Michigan State University, 1977–1981.

(2) (a) Weaver, M. J. *Inorg. Chem.* **1979**, *18*, 402. (b) Weaver, M. J. *Isr. J. Chem.* **1979**, *18*, 35. (c) Guyer, K. L.; Barr, S. W.; Cave, R. J.; Weaver, M. J. "Proceedings of the 3rd Symposium on Electrode Processes"; Bruckenstein, B., McIntyre, J. D. E., Miller, B., Yeager, E., Eds.; Electrochemical Society: Princeton, NJ, 1980; p 390.

(3) (a) Hupp, J. T.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *152*, 1. (b) Weaver, M. J. In "Inorganic Reactions and Methods"; Zuckerman, J. J., Ed.; Verlag Chemie: Weinheim, Germany; in press.

(4) (a) Sutin, N. *Bioinorg. Chem.* **1973**, *2*, Chapter 19. (b) Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264. (c) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. (d) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982**, *No. 198*, 105.