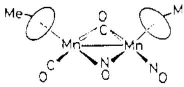
reported by Crease and Legzdins.[9] Higher frequency shifts of the terminal carbonyl and the bridging carbonyl stretches for carbonyl groups not coordinated to Cp_3Sm were especially sensitive to Cp_3 concentration. The terminal NO stretch at 1715 cm^{-1} due to parent compound disappeared for Cp_3Sm to V ratios greater than 1.5:1, while the bridging carbonyl stretch for the bridging carbonyl not coordinated to Cp_3Sm was still detected for Cp_3Sm to V ratios greater than 10:1. A medium-intensity peak clearly appeared at 1705 cm^{-1} for Cp_3Sm to V ratio greater than 7:1. An attempt to locate unambiguously the peak due to bridging NO stretch for the >NO–Sm bond was unsuccessful. Injection of diethylamine into this solution regenerated the original spectrum in the ν(CO) and ν(NO) region. General spectral changes upon the addition of Cp_3Sm indicate that Cp_3Sm interacts preferentially with terminal nitrosyl and bridging carbonyl rather than bridging nitrosyl.[9]

The medium-intensity peak at 1705 cm^{-1} observed for a Cp_3Sm to V ratio greater than 7:1 is assigned to terminal NO stretch in the –NO–Sm bonded 1:2 adduct, where Cp_3Sm interacts with both bridging CO and terminal NO. This assignment is substantiated by the investigation of the peak at 1740 cm^{-1} due to bridging carbonyl stretch in the >CO–Sm bond; the peak possesses a shoulder on the higher frequency side and this shoulder could result from the shift of a bridging carbonyl stretch in the >CO–Sm bond when Cp_3Sm forms a 1:2 adduct via bridging CO and terminal NO. The fact that a weak peak due to bridging carbonyl stretch shifted to higher frequency was detected even for 10:1 reaction suggests that there still exists a small amount of the 1:1 adduct in solution, where the bridging carbonyl is directed in the same direction as those of two methylcyclopentadienyl rings as illustrated in (h). In this cis configuration, approach of bulky Cp_3Sm to bridging carbonyl should be somewhat deterred. From these experimental results, it is concluded that at higher concentrations of Cp_3Sm, three types of adducts, 1:1 with terminal NO, 1:1 with bridging CO, and 1:2 with both terminal NO and bridging CO, coexist in the CH_2Cl_2 solution. However, it is difficult to get any detailed insight into the influence of Lewis acid on the cis–trans equilibrium of V in solutions other than those described above, because compound V and its adduct are devoid of terminal carbonyl stretches characteristic of cis isomers, and attempts to get a proton NMR spectrum in suitable solvents have been unsuccessful.



(h)

Conclusion

In the present work, the Lewis basicity of the nitric oxide ligand has been demonstrated to be a general phenomenon for terminal, two-metal bridge NO, and three-metal bridged NO. The order of the Lewis basicity of NO for these ligation modes with respect to Cp_3Sm is somewhat different from that of carbonyl ligands with respect to group 3 Lewis acids.[8] The order is terminal NO ($\gtrsim$bridging CO) $\gtrsim$ two-metal bridged NO $\sim$ three-metal bridged NO. The low Lewis basicity of bridging NO is presumably responsible for the formation of only 1:1 adducts for $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$. The observed increase in the proportion of the cis-bridged isomer upon adding Cp_3Sm to the nitrosyl bridged system, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, is analogous to the increase in the proportion of cis isomer when AlR_3 is added to the isoelectronic metal carbonyl, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Registry No. I, 36312-04-6; II, 52124-51-3; III, 66795-25-3; IV, 36607-01-9; V, 73636-54-1; Cp_3Sm, 1298-55-1.

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Circularly Polarized Luminescence Studies of Mixed-Ligand Lanthanide Complexes Having the General Formula Tb(pyridine-2,6-dicarboxylic acid)$_m$(L-malic acid)$_n$, Where m = 0–3 and n = 0–2

HARRY G. BRITTAIN

Received January 8, 1980

Circularly polarized luminescence (CPL) spectroscopy has been used to study the mixed-ligand complexes formed between Tb(III), dipicolinic acid (DPA), and L-malic acid (MAL). Complexes having the general formula of $Tb(DPA)_m(MAL)_n$ were prepared, where m = 0–3 and n = 0–2. At low pH, the observed CPL was found to arise from bidentate MAL coordination, but a drastic change in CPL line shape near pH 7 was interpreted to imply terdentate MAL bonding to Tb(III) above this pH. The complexes are mononuclear at all pH values, thus enabling certain conclusions to be drawn regarding relations between the observed CPL spectra and plausible solution structures.

Introduction

Chiroptical techniques enable one to probe the solution stereochemistry of metal complexes, and circular dichroism (CD) of metal d–d transitions has been employed to obtain detailed information regarding the structures of a wide variety of transition-metal complexes in solution.[1] Analogous studies of chiral lanthanide complexes have been attempted,[2] but the results of these investigations are tainted by uncertainities regarding the actual structures of the complexes and low signal-to-noise ratios. The CD is difficult to measure except at high lanthanide ion concentrations owing to the small extinction coefficients of the f–f transitions,[3] and it is usually

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(1) (a) F. S. Richardson, *Chem. Rev.*, **79**, 17 (1979); (b) H. P. Jensen and F. Woldbye, *Coord. Chem. Rev.*, **29**, 213 (1979).

(2) (a) L. I. Katzin, *Inorg. Chem.*, **7**, 1183 (1968); **8**, 1649 (1969); (b) L. I. Katzin and E. Gulyas, *ibid.*, **7**, 2442 (1968); (c) D. L. Caldwell, P. E. Reinbold, and K. H. Pearson, *J. Am. Chem. Soc.*, **92**, 4554 (1970); (d) S. Misumi, T. Isobe, and H. Furuta, *Bull. Chem. Soc. Jpn.* **47**, 421 (1974).

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found that measurable CD is only obtained above neutral pH values.[2] This situation is unfortunate since intermolecular energy-transfer studies of lanthanide complexes in aqueous solution have shown that extensive polynuclear complex formation usually dominates the binding picture above pH 7.[4]

Studies of optically active lanthanide complexes in aqueous solution have also been performed by using circularly polarized luminescence (CPL) as a chiroptical probe, and generally these studies have proved to be somewhat more fruitful than the CD studies.[5] One is able to work at much lower metal ion concentrations due to the sensitivity of the emission technique, and since lanthanide ion luminescence consists of a few sharp, well-resolved bands, little spectral overlap is encountered. Of all the lanthanide ions, Tb(III) and Eu(III) display the largest solution luminescence and are therefore the preferred ions to study. As in the CD studies, the CPL spectra have been richest in detail above neutral pH values, and consequently it has been difficult to draw relations between spectra and structure.

In this laboratory, we have undertaken to prepare lanthanide complexes, which are both chiral and mononuclear, and to then study their CPL spectra. It is known that the lanthanide complexes of pyridine-2,6-dicarboxylic acid (dipicolinic acid or DPA) are mononuclear at all pH values,[6] and in a previous study it was determined that mixed-ligand complexes of Tb(III), DPA, and various L-amino acids are also mononuclear.[7] In the latter study, the first pure vicinal effect found in CPL spectra was reported and it was possible to obtain CPL spectra free of polynuclear complex uncertainities. In the present work, mixed-ligand complexes of Tb(III), DPA, and L-malic acid (MAL) were prepared and their CPL spectra obtained. The complexes were all found to be mononuclear, thus enabling certain conclusions to be reached regarding the nature of the spectral features and plausible modes of complex binding.

Experimental Section

Tb(III) solutions were prepared by dissolving a weighed amount of (99.9% pure, Kerr-McGee) in the miminum amount of 70% $HClO_4$, neutralizing to pH 3, and then diluting to the desired volume. The stock solutions thus prepared were standardized spectrophotometrically with calmagite.[8] Dipicolinic and malic acids were used as received from Eastman; solutions of these ligands were standardized by using potentiometric titrations with standard base.

Tb(III) complexes were prepared by making up solutions that had varying ratios of Tb(III), DPA, and MAL. It was not possible to isolate any of the complexes in solid form; slow evaporation tended to yield material whose composition reflected that of the solution, and attempted heavy-metal precipitation with silver resulted in complex destruction. All solutions were 0.015 M in Tb(III), and the total ligand concentration (DPA plus MAL) was held at 0.045 M. The total ionic strength of all solutions was adjusted to be 0.20 M with $NaClO_4$.

All CPL spectra were obtained on a high-resolution luminescence spectrometer constructed in this laboratory, which has been described previously.[7] An excitation wavelength of 288 nm was used for all complexes (10-nm band-pass), and an emission bandwidth of 10 Å was found to yield the maximum possible resolution. The experiment measures two observables: total luminescent (TL) intensity, given by $I = {}^{1}/_{2}(I_L + I_R)$, and the differential luminescence (CPL) intensity, $\Delta I = I_L - I_R$ (I_L and I_R refer to the emitted intensities of left- and right-circularly polarized light, respectively). Since both I and ΔI are recorded in arbitrary units, an absolute quantity is usually calculated by taking the ratio $\Delta I/I$, and this quantity is termed the luminescence dissymmetry factor, g_{lum}.[5a]

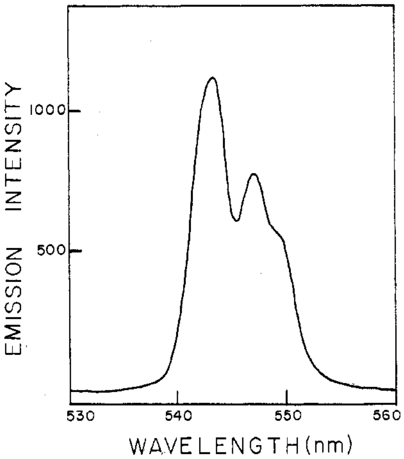

Figure 1. TL spectrum of the $^5D_4 \rightarrow {}^7F_5$ transition of $Tb(DPA)_3^{3-}$ at a pH of 8.58. The intensity scale is in arbitrary units but does allow a comparison with the other spectra.

All studies were carried out in aqueous solution at room temperature. pH adjustment was effected by adding microliter amounts of standard NaOH or $HClO_4$ to a solution of the complex in a spectral cuvette, and the pH readings were obtained by inserting a glass microcombination electrode directly into the cuvette. All readings were taken on an Orion 701A pH meter, which was calibrated daily with phosphate buffers.

Results

It was found that a variety of complexes having the general formula of $Tb(DPA)_n(MAL)_m$ (where m could be varied from 0 to 3 and n from 0 to 2) could be formed by varying the ratios of DPA to MAL in a solution containing Tb(III). The absorption spectra of these did not display large variations with either pH or complex type, but it was found that the intensity of, and the CPL associated with, the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission were quite sensitive to these factors. In general, well-defined CPL was found for all complexes above pH 3.

The CPL associated with all complexes followed a general trend: above pH 3, well-defined CPL appeared, and this CPL persisted in both line shape and intensity up to neutral pH. Around pH 7, the CPL underwent a complete sign inversion, and this new pattern typically persisted to at least pH 9. Above pH 7, the CPL did undergo small changes in g_{lum} with this quantity decreasing as the pH was raised. This latter decrease must be associated with base hydrolysis of the complex and is ultimately responsible for the loss of CPL at high pH.

$Tb(DPA)_3^{3-}$. It has been shown that a 1:3 complex can be formed between Tb(III) and DPA simply by mixing Tb(III) and DPA solutions at the proper mole ratio[6a,10] and that higher ratios of ligand and metal do not yield 1:4 complexes. The pH dependence observed for Tb(III) luminescence in this complex has been published,[6b] and at high resolution the TL spectrum is found to contain several components. The luminescent intensity reaches a limiting value by pH 5 and persists at this value to at least pH 11. A representative example of the Tb(III) emission band shape in the DPA complex is shown in Figure 1; the absolute value of the intensity was not determined, but a relative intensity is valuable in comparison to later data. The two distinct maxima are found to occur at 544 and 547 nm. No CPL was observed for $Tb(DPA)_3^{3-}$ since only racemic material can be prepared during the synthesis. The high degree of lability associated with the complex also precludes the separation of the optical isomers.

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(3) K. B. Yatsimirskii and N. K. Davidenko, *Coord. Chem. Rev.*, **27**, 223 (1979).

(4) H. G. Brittain, *J. Inorg. Nucl. Chem.*, **41**, 561, 567, 721 (1979).

(5) (a) C. K. Luk and F. S. Richardson, *Chem. Phys. Lett.*, **25**, 215 (1974); *J. Am. Chem. Soc.*, **97**, 6666 (1975); (b) H. G. Brittain and F. S. Richardson, *Inorg. Chem.*, **15**, 1507 (1976); *Bioinorg. Chem.*, **7**, 233 (1977).

(6) (a) H. Donato, Jr., and R. B. Martin, *J. Am. Chem. Soc.*, **94**, 4129 (1972); (b) H. G. Brittain, *Inorg. Chem.*, **17**, 2762 (1978).

(7) H. G. Brittain, *J. Am. Chem. Soc.*, **102**, 1207 (1980).

(8) H. G. Brittain, *Anal. Chim. Acta*, **106**, 401 (1979).

(9) D. E. Henrie, R. L. Fellows, and G. R. Choppin, *Coord. Chem. Rev.*, **18**, 199 (1976).

(10) I. Grenthe, *J. Am. Chem. Soc.*, **83**, 360 (1961).

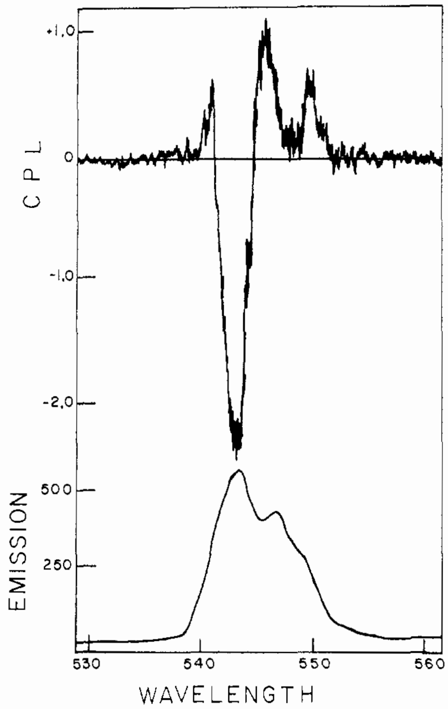

Figure 2. TL (lower) and CPL (upper) spectra of $Tb(DPA)_2(MAL)^{3-}$ at pH 4.98. All spectra are exact tracings of experimental data.

$Tb(DPA)_2(MAL)^{3-}$. A complex of this stoichiometry was prepared by mixing stock solutions that yielded a final mole ratio of 1:2:1 for Tb(III), DPA, and MAL. It is quite reasonable to assume the formation of this complex (even though it was not actually isolated) in solution since the formation constants of all ligands with Tb(III) are quite large. For DPA, Grenthe has determined that $\log K_1 = 8.68$ and $\log K_2 = 7.43$,[10] and other workers have found that for Tb(III), $\log K_1 = 4.77$.[11] A simple distribution diagram reveals that essentially all of the Tb(III) ions would be complexed at the concentrations used in the present work. The TL and CPL magnitudes are also consistent with the stated formula.

The pH behavior of TL for this complex shows some variation in intensity; it increases slowly from pH 3 to pH 6.5, rises sharply from pH 6.5 to pH 7.5, and then rises slowly up to pH 9. It is quite interesting to note that the TL intensity of the $Tb(DPA)_2(MAL)$ complex is approximately two-thirds the TL intensity of the $Tb(DPA)_3$ complex at corresponding pH values, and this behavior is reasonable when one remembers that the excitation energy is being absorbed by the DPA ligand and then subsequently transferred to the Tb(III) ion.

The CPL spectra contain much more information, however, and clearly demonstrate that different modes of MAL binding must exist in low- and high-pH regions. At low pH, the CPL of the 544-nm band is negative, and the CPL of the 547-nm band is positive; when the pH is raised to at least 8, the situation is exactly reversed. The low-pH CPL reaches a maximum intensity (as measured by the g_{lum} value) at pH 5.0 (see Figure 2), and the high-pH CPL is most intense at pH 8.5 (see Figure 3). A most interesting series of CPL spectra can be recorded at mid pH values (as is shown in Figure 4) where one can actually monitor the change in complex bonding. At these pH values, the observed CPL spectrum is found to consist of a superimposition of both types of CPL line shape. This in turn implies that one type of complex bonding is being converted into the other in this pH region. g_{lum} values were calculated at pH 5.0 and 8.5, and these results are located in Table I.

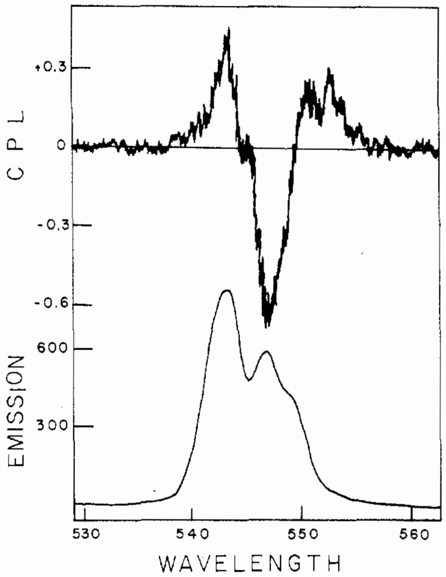

Figure 3. TL (lower) and CPL (upper) spectra of $Tb(DPA)_2(MAL)$ at pH 8.53.

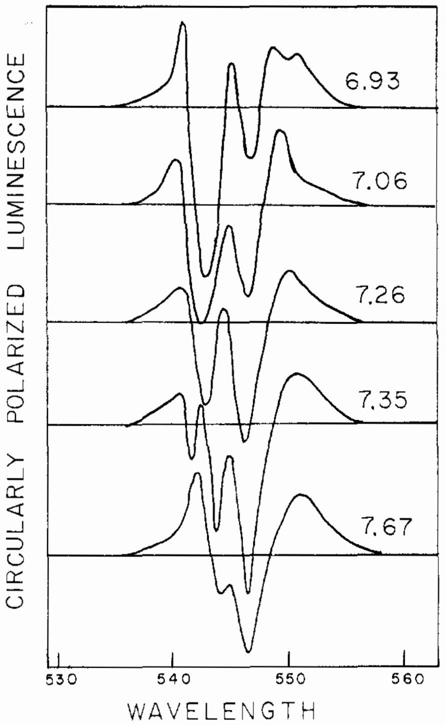

Figure 4. CPL spectra of $Tb(DPA)_2(MAL)$ at pH values of 6.93, 7.06, 7.26, 7.35, and 7.67 which illustrate the conversion from one CPL pattern into the other.

Table I. Luminescence Dissymmetry Factors Found for $Tb(DPA)_m(MAL)_n$ Complexes at Various pH Values

pH	g_{lum} 544 nm	g_{lum} 547 nm
	(a) $Tb(DPA)_2(MAL)$	
4.98	−0.0041	0.0021
8.53	0.00088	−0.0012
	(b) $Tb(DPA)(MAL)_2$	
4.70	−0.014	0.0077
7.48	0.0089	−0.014
	(c) $Tb(MAL)_2$	
4.55	−0.036	0.018
7.69	0.11	−0.12

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(11) R. Roulet, J. Feuz, and T. VuDuc, *Helv. Chim. Acta*, **53**, 1876 (1970).

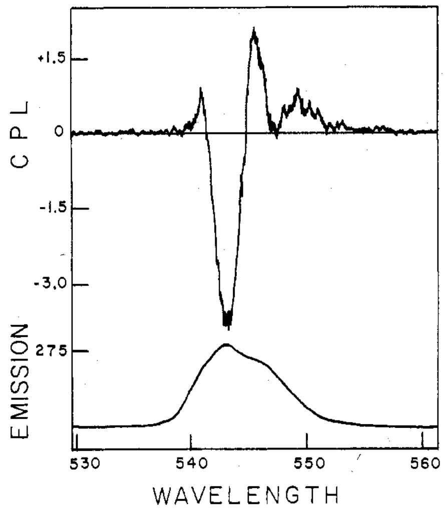

Figure 5. TL (lower) and CPL (upper) spectra of Tb(DPA)(MAL)$_2$ at pH 4.70.

Tb(DPA)(MAL)$_2$$^{3-}$. This complex was prepared by mixing Tb(III), DPA, and MAL in a 1:1:2 mole ratio. Since Tb(III) has been shown to bind a second MAL ligand with log K_2 = 3.26,[11] it should not be unreasonable to assume that the stated complex should be the dominant species in solution. This prediction is supported experimentally, since the TL intensity of the Tb(DPA)(MAL)$_2$ complex is approximately one-third the TL intensity of the Tb(DPA)$_3$ at corresponding pH values (which implies that only one DPA is bound per Tb(III) ion). In addition, the CPL intensities of the Tb(DPA)(MAL)$_2$ complexes are nearly an order of magnitude greater than the CPL intensities of the Tb(DPA)$_2$(MAL) complexes and are also nearly equal to the CPL intensities of the known Tb(MAL)$_2$ complex.

The TL and CPL pH behavior noted in the Tb(DPA)(MAL)$_2$ complex roughly paralleled the situations found for the Tb(DPA)$_2$(MAL) complex, except for the aforementioned differences in TL and CPL intensities. The same general trend in CPL sign patterns was found again, but the pH values at which maxima occurred were all lower for the complexes of the former series. The low-pH CPL pattern reached its maximum value at pH 4.7 (Figure 5) and the high-pH pattern was found to be most intense at pH 7.5 (Figure 6). In addition, the two CPL patterns were found to interconvert at neutral pH (see Figure 7), except that the pH range was somewhat depressed relative to Tb(DPA)$_2$(MAL). Calculated values for g_{lum} are found also in Table I.

Tb(MAL)$_2$$^-$. The pH dependence of CPL obtained at 1:5 mole ratios of Tb(III) and Eu(III) to MAL has been reported previously,[5] but subsequent work on similar solutions using intermolecular energy transfer has shown that above pH 7 (where most of the CPL was found) the MAL complexes were extensively associated.[12] In a subsequent study, Salama and Richardson[13] demonstrated that if one starts with a 1:3 ratio of Tb(III) (70 mM) and MAL (210 mM), only mononuclear complexes were formed. Other workers[11] have demonstrated that at these same ratios, only 1:2 lanthanide–MAL complexes form.

The pH dependence of TL and CPL observed for Tb(MAL)$_2$ tend to resemble that of both previous complexes quite closely. The TL intensities were found to be very low relative to the DPA complexes, but this is to be expected when there is no longer an aromatic group to excite. Direct excitation of the Tb(III) ion at 365 nm was found to be much more effective in promoting luminescence than excitation at the aromatic 295-nm region. The values calculated for g_{lum} are quite close in magnitude to the analogous DPA complex, as may be seen in Table I. The low-pH CPL was found to maximize at pH 4.5 (Figure 8) and the high-pH CPL reached a maximum value at pH 7.4 (Figure 9), and the same type of CPL sign inversion was noted at pH 6.

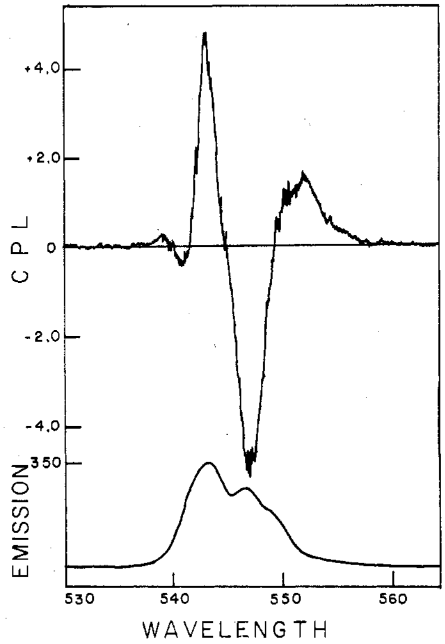

Figure 6. TL (lower) and CPL (upper) spectra of Tb(DPA)(MAL)$_2$ at pH 7.48.

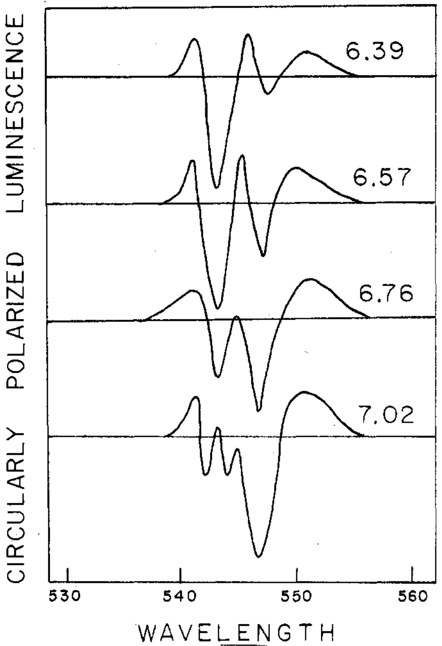

Figure 7. CPL spectra of Tb(DPA)(MAL)$_2$ at pH values of 6.39, 6.57, 6.76, and 7.02.

Discussion

In the case of mononuclear lanthanide ion complexes, the CPL spectra enable one to draw certain conclusions regarding the nature of the bonding existing between metal and ligand in solution. In all cases, we can consider the DPA ligand merely to be an achiral part of the coordination sphere that does not affect the optical activity induced in the Tb(III) f–f transitions when the metal coordinates to the chiral MAL ligand. The close relationships found for the CPL spectra

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(12) H. G. Brittain, *J. Inorg. Nucl. Chem.*, **41**, 721 (1979).
(13) S. Salama and F. S. Richardson, *Inorg. Chem.*, **19**, 629 (1980).

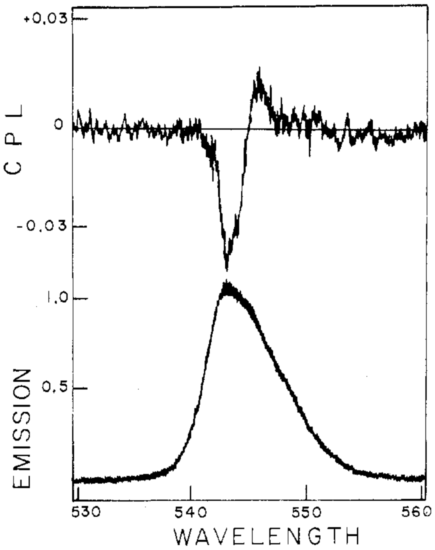

Figure 8. TL (lower) and CPL (upper) spectra of $Tb(MAL)_2$ at pH 4.55.

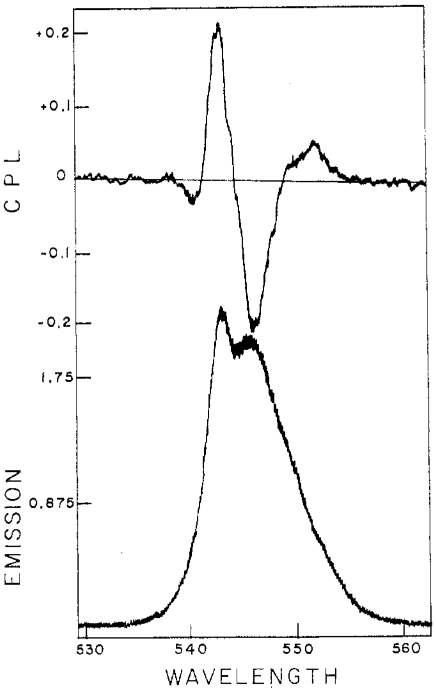

Figure 9. TL (lower) and CPL (upper) spectra of $Tb(MAL)_2$ at pH 7.69.

support this conclusion, and the nearly linear relation that was observed for TL and the number of DPA molecules in a particular complex is additional evidence. The dual purpose of the DPA ligand is then to provide an efficient means of channeling excitation energy into the Tb(III) ion and to provide a coordination sphere "filler" which allows one to interpret CPL spectral line shapes and changes in terms of one (or two) metal–ligand interactions. This set of assumptions will then enable the use of CPL spectra as a direct probe of the bonding existing between metal and ligand in solution; more quantitative interpretations must await further developments in theory. It is not yet possible to assign the emission maxima to particular crystal field components of the $^5D_4 \rightarrow {}^7F_5$ transition.

Below pH 7, MAL can bind to Tb(III) in a bidentate fashion, since both proton dissociation constants are fairly high and metal ion promoted ligand deprotonation is considerable.[11] One would not predict that the observed CPL observed for $Tb(DPA)_2(MAL)$ is due solely to a vicinal effect, since the presence of a chelate ring would require consideration of a conformational effect. Configurational effects are not likely with any of the complexes used in the present work since the number of optically active ligands is never greater than two and the very labile nature of the complexes would interconvert rapidly any isomers. We propose, then, that the observed CPL represents a sum of vicinal and ligand conformational effect. Our previous work with Tb(DPA)(amino acid) complexes[7] demonstrated the extreme weakness of the vicinal effect, so it is quite likely that the observed CPL is due solely to the conformational effect. This effect would be due to a difference in optical activity experienced by the Tb(III) ion as a result of different ring conformations of the chiral ligand, and the observance of CPL then implies that one particular conformation would be more stable and hence dominate the bonding. This CPL can be thought of as being analogous to the CD measured in transition-metal complexes containing one chiral ligand and several achiral ones.[14]

The change in CPL band shape that takes place in all the complexes near neutral pH values is somewhat puzzling. No new ligand ionizations take place in this pH region, and complex hydrolysis does not become important until much higher pH.[11] The complexes remain monomeric,[13] and thus the pH change cannot be ascribed to any type of association. We can only conclude that the hydroxyl group of the MAL ligand becomes involved in bonding with the metal at these neutral pH values. Since no ionizations are observed in potentiometric titration curves that can be assigned to hydroxyl deprotonation,[15] it is possible that the –OH group binds to the metal and remains protonated. Similar conclusions were reached regarding the hydroxyl group of serine and threonine in the $Tb(DPA)_2$(amino acid) studies.[7] One would expect that such a binding change would drastically alter the observed CPL (since the CPL is so dependent on ligand conformation): a 7-membered ring (bidentate MAL coordination) is being exchanged for a set of 5- and 6-membered rings (tridentate MAL coordination). The TL increases that invariably accompany such a transformation must reflect the fact that a water molecule is ejected from the metal's coordination sphere when the –OH binds and a source of luminescence quenching is removed.

It is noteworthy that the CPL line shapes of $Tb(MAL)_2$ and $Tb(DPA)(MAL)_2$ are the same as found for $Tb(DPA)_2(MAL)$. It therefore seems likely that the ligand conformational effects leading to the CPL of $Tb(DPA)_2(MAL)$ are the same as for the other two complexes and that the increase in optical activity (as measured by the g_{lum} values) that takes place when a second MAL ligand is bound represents a reinforcement of the individual contributions. That the CPL intensities are greater than would be expected from a simple sum of vicinal effects implies that the observed CPL contains an additional configurational term.

Some variation in pH behavior is noted when comparing the various complexes and suggests that while the DPA environment does not play a major role in the complex stereochemistry and in the nature of the Tb(III)–MAL interaction, it can influence the results to some extent. It is possible to measure CPL spectra at the pH values where an equal amount of the two (bidentate and tridentate) complexes exists, and these values follow a trend. The pH value at which an equality is noted is found to be 6.3 for $Tb(MAL)_2$, 6.7 for Tb-

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(14) (a) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); (b) B. E. Bryant, H. J. Hu, and W. H. Glaze, *ibid.*, **5**, 1373 (1966); (c) M. Saburi, M. Homma, and S. Yoshikawa, *ibid.*, **8**, 367 (1969); (d) S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).

(15) (a) R. Prados, L. G. Stadtherr, H. Donato, Jr., and R. B. Martin, *J. Inorg. Nucl. Chem.*, **36**, 689 (1974); (b) H. G. Brittain, *Inorg. Chim. Acta*, **40**, 51 (1980).

(DPA)(MAL)$_2$, and 7.3 for Tb(DPA)$_2$(MAL). With the steric bulk of the DPA ligand being considerably larger than that of the MAL ligand, it would appear that it is more difficult for the MAL ligand to bind in a terdentate manner as the steric crowding of the achiral part of the complex becomes appreciable.

The study of optical activity in lanthanide complexes is complicated considerably by the high degree of lability in these complexes, and it is doubtful that the same degree of information can be obtained for these complexes relative to that which has been already collected for inert Co(III) and Cr(III) complexes. Consequently, in lanthanide chemistry one must speak primarily of dominant species in solution and recognize the possibility that other forms may coexist along with the major component. Nevertheless, with careful choice of complex systems (and avoidance of polynuclear complexes), a great deal of information may be obtained from chirooptical techniques and from CPL in particular.

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Registry No. Tb(DPA)$_3^{3-}$, 38682-37-0; Tb(DPA)$_2$(MAL)$^{3-}$, 73663-68-0; Tb(DPA)(MAL)$_2^{3-}$, 73663-69-1; Tb(MAL)$_2^-$, 73663-70-4.

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Ion-Multiplet Formation and the Photoanation of Tris(2,2′-bipyridine)ruthenium(II)

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[Ru(bpy)$_3$]Br$_2$ in dimethylformamide loses one bipyridine upon irradiation at 458 nm, with an overall quantum yield of 3×10^{-4} with 0.017 M Br$^-$ present. The quantum yields of the two photoproducts, [Ru(bpy)$_2$(DMF)Br]$^+$ and [Ru(bpy)$_2$Br$_2$], are linearly dependent on bromide concentration within the range $0.0016 < [\mathrm{Br}^-] < 0.017$ M. The results are consistent with a model based on ion pairs and ion triplets as the photoactive species.

Introduction

For some time [Ru(bpy)$_3$]$^{2+}$ has been used extensively as a triplet sensitizer, in both luminescence and photochemical applications.[2–4] More recently the redox properties of excited state [Ru(bpy)$_3$]$^{2+}$ have come under intense scrutiny,[5–9] in particular because of the suggestion that photocatalytic decomposition of water may be feasible with this or related complexes.[10–13]

Although once thought to be photochemically inert,[2,14] it is now recognized that a permanent substitutional photochemistry does exist for [Ru(bpy)$_3$]$^{2+}$. Demas and Adamson first reported a slight photosensitivity of the chloride salt in water and in 0.05 M H$_2$SO$_4$, detected by a diminished [Ru(bpy)$_3$]$^{2+}$ luminescence intensity.[15] Van Houten and Watts reported the apparent substitution of the chloride salt in 0.1 M HCl at 95 °C, monitoring both changes in the absorption spectrum and the decrease in luminescence intensity.[16] They also observed the release of bipyridine through the appearance of its characteristic fluorescence spectrum, and in addition they concluded that photochemistry and luminescence originate from different excited states.[16] No photoreactivity was observed under the same conditions at room temperature.

At about the same time we observed photosubstitutional behavior for several [Ru(bpy)$_3$]$^{2+}$ salts in some organic solvents at room temperature, with quantum yields on the order of 10^{-3} or less.[17,18] In general the quantum yields were found to increase with anion concentration (except for NO$_3^-$, SO$_4^{2-}$, and ClO$_4^-$, which slowed the reaction), suggesting the involvement of ion pairing in the process. In dimethylformamide (DMF) two, and sometimes more, photoproducts appeared, one of them the [Ru(bpy)$_2$X$_2$] complex, where X$^-$ was the original counterion.

More recently photosubstitutional behavior of the chloride salt in some chlorinated solvents has been noted, with [Ru(bpy)$_2$Cl$_2$] reported as the product.[19] The quantum yield was 0.02, much higher than in DMF or ethanol.[18]

In our earlier work the thiocyanate salt was investigated quantitatively in DMF.[18] Two products were formed, identified as [Ru(bpy)$_2$(DMF)(NCS)]$^+$ and [Ru(bpy)$_2$(NCS)$_2$]. In any single experiment these were formed in nearly constant ratio, as indicated by the presence of isosbestic points in sequential absorption spectra of the photolysate. However, the relative quantum yields of the two products varied with thiocyanate concentration, the dithiocyanato complex being more strongly dependent on [SCN$^-$].

Although it was clear that ion-pair formation was a necessary condition for photolysis to occur, the mechanism by which the products were formed could not be conclusively established. Two possible reaction schemes were proposed.[18] The first involved a classical secondary photolysis, in which one ligand (A$^-$) would coordinate to form the first product,

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