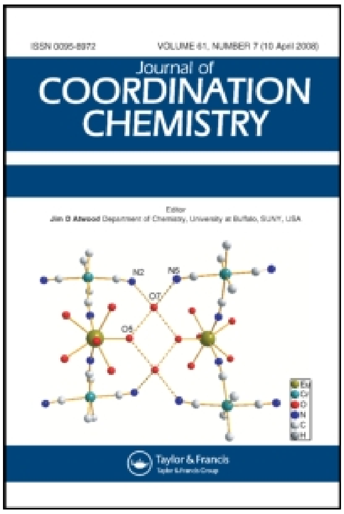

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Solution Phase Chemistry of Lanthanide Complexes. 12. 1:1 and 1:2 Lanthanide Complexes with *s*-Carboxymethoxysuccinic Acid

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To cite this Article Brittain, Harry G. , Kelty, Stephen P. and Peters, Joop A.(1991) 'Solution Phase Chemistry of Lanthanide Complexes. 12. 1:1 and 1:2 Lanthanide Complexes with *s*-Carboxymethoxysuccinic Acid', Journal of Coordination Chemistry, 23: 1, 21 — 32

To link to this Article: DOI: 10.1080/00958979109408239

URL: http://dx.doi.org/10.1080/00958979109408239

J. Coord. Chem. 1991, Vol. 23. pp. 21-32
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SOLUTION PHASE CHEMISTRY OF LANTHANIDE COMPLEXES.
12. 1:1 AND 1:2 LANTHANIDE COMPLEXES WITH *S*-CARBOXYMETHOXYSUCCINIC ACID

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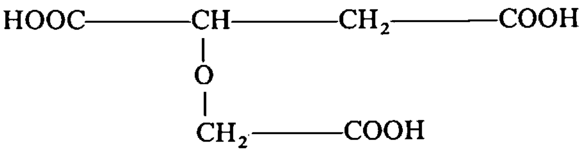
(Received March 29, 1990)

The solution phase coordination chemistry associated with 1:1 and 1:2 complexes of lanthanide ions with *S*-carboxymethoxysuccinic acid (CMOS) has been studied by spectroscopic means. The Tb(III) luminescence intensities and lifetimes were found to be sensitive towards the solution phase properties, as were the circularly polarized luminescence spectra of these complexes. It was found that below pH 6, Ln(CMOS) complexes were monomeric in nature and contained an average of 6 molecules of coordinated water. Above neutral pH, the $\mathrm{Ln(CMOS)_2}$ complexes became self-associated into hydroxy-bridged, oligomeric species. The $\mathrm{Ln(CMOS)_2}$ complexes were found to be oligomeric at all pH values, with ligand bridging taking place below neutral pH and hydroxy bridging taking place above neutral pH.

Keywords: lanthanide, *S*-carboxymethoxysuccinic acid, complexes, luminescence, oligomerization

INTRODUCTION

Due to the variety of complexing agents available, the solution phase coordination chemistry associated with the lanthanide ion complexes of hydroxycarboxylic acids is an interesting area of investigation. *S*-carboxymethoxy succinic acid {CMOS, or *S*-2-oxabutane-1,3,4-tricarboxylic acid} is a potentially tetradentate ligand, containing one ether and three carboxylate binding sites:



$$\begin{array}{lllllll} \mathrm{HOOC} & — & \mathrm{CH} & — & \mathrm{CH_2} & — & \mathrm{COOH} \\ & & | & & & & \\ & & \mathrm{O} & & & & \\ & & | & & & & \\ & & \mathrm{CH_2{—}COOH} & & & & \end{array}$$

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Three acid ionization constants for the CMOS ligand have been obtained, with $pK_1 = 2.52$, $pK_2 = 3.77$, and $pK_3 = 5.00$.[1] It is known that CMOS is capable of forming compounds having either 1:1 or 1:2 metal–ligand stoichiometry,[1,2] with the ligand acting largely as a tetradentate ligand. For the Eu(III)–CMOS system, the two formation constants have been estimated as $\log \beta_1 \approx 6$ and $\log \beta_2 \approx 10^3$.

The lanthanide complexes of CMOS have been studied by ^1H, ^{13}C, ^{17}O and ^{139}La nuclear magnetic resonance, with the aim of understanding more about the analogous Ca(II) complexes.[4] In this latter investigation, the tetradentate binding of lanthanide ions by CMOS was established by means of changes in the vicinal proton–proton coupling constants observed upon complexation.

Since the luminescence properties of lanthanide ions are known to be extremely useful in deducing details of the solution phase coordination chemistry, detailed spectral studies of the influence of solution pH on the Ln(CMOS) and $Ln(CMOS)_2$ complexes were performed. The possible oligomerization of the complexes was investigated using the energy transfer method,[5] and the number of bound solvent molecules established using the method of Horrocks.[6] Further characterization of the complexes was obtained through systematic investigations of the Tb(III) luminescence intensities and lifetimes. Since CMOS is a chiral ligand, additional characterization was available through studies of chiroptical spectra obtained for the Tb(III) complexes.

EXPERIMENTAL

S-carboxymethoxysuccinic acid was prepared and purified as described,[1] while hydrated $TbCl_3$ and $EuCl_3$ were used as received from Research Chemicals. Stock solutions were prepared by the dissolution of appropriate quantities of material, and the solutions prepared by mixing stoichiometric amounts of the stock solutions. In all the luminescence experiments, a final Tb(III) concentration of 10 mM was used. The Ln(CMOS) studies were conducted at a ligand concentration of 10 mM, while a ligand concentration of 22 mM was used for the $Ln(CMOS)_2$ studies (the slight excess was to ensure complete formation of the 1:2 complex). During the energy transfer studies, microlitre amounts of 50 mM Eu/CMOS stock solutions (containing the same metal/ligand ratio as the Tb/CMOS solution) were added to a Tb/CMOS solution. The ionic strength of the solutions was not controlled. The emission intensity and lifetime was determined after each addition.

The pH of each solution was varied between pH 2.5 and 11.5, with the required photophysical measurements being obtained at each pH value. Variation of the solution pH of each solution was effected by the addition of microlitre amounts of standard NaOH or HCl directly to the cuvette. The pH was measured using a glass microcombination electrode which could be directly inserted into the cuvette. The pH meter was calibrated daily using phosphate buffers.

The Tb(III) luminescence intensity associated with the Tb(CMOS) and $Tb(CMOS)_2$ complexes was measured on a Spex Fluorolog II spectrometer. Luminescence lifetimes of the same solutions were obtained by exciting the samples with the pulsed 337 nm output of a nitrogen laser (model LN-1000, Photochemical Research Associates), and capturing the decay curve on a boxcar averager (model SR-265, Stanford Research Associates). The luminescence decay times and rate constants were obtained by fitting the decay curve to a single exponential function. The circularly polarized luminescence spectra were obtained on a special apparatus, whose operation has been described in detail.[7]

RESULTS AND DISCUSSION

Semi-quantitative potentiometric studies of the lanthanide complexes with CMOS have been reported.[3] The binding of one CMOS ligand to form the 1 : 1 complex, (*1*),

$$Ln^{3+} + CMOS^{3-} \longleftrightarrow Ln(CMOS) \qquad (1)$$

is known to be extremely efficient, with a log β_1 value of approximately 6 being reported. The addition of the second CMOS ligand to form the 1 : 2 complex, (*2*),

$$Ln(CMOS) + CMOS^{3-} \longleftrightarrow Ln(CMOS)_2{}^{3-} \qquad (2)$$

is not as favourable, but a log β_2 value of 10 has been reported. The magnitude of these complex formation constants is such that the Tb(CMOS) complex is formed by the stoichiometric addition of one equivalent of Tb(III) and one equivalent of CMOS, and the $Tb(CMOS)_2$ complex is formed by the addition of slightly more than two equivalents of CMOS per equivalent of Tb(III).

pH Dependence of Tb(III) Emission Intensity

UV excitation of Tb(III) complexes results in reasonably efficient population of the luminescent $^5D_4$ excited state, and in subsequent emissive transitions to the $^7F_6$ (490 nm), $^7F_5$ (545 nm), $^7F_4$ (585 nm), and $^7F_3$ (625 nm) states of the ground manifold. The intensities of the various emission bands are normally found to be a function of the solution pH, and of the complex stoichiometry under investigation. The existence of a stable emission intensity over a defined pH range usually indicates the existence of a well-defined complex. It is also generally noted that the trends associated with the pH-dependence of each emission band system are identical, therefore requiring only results obtained within the $^5D_4 \rightarrow {}^7F_5$ transition (the most intense Tb(III) emission band) needs to be discussed.

The pH dependence measured for the Tb(III) emission intensity in the Tb(CMOS) and $Tb(CMOS)_2$ complexes is shown in Figure 1. For the Tb(CMOS) complex, the Tb(III) emission intensity increased rapidly up to pH 3 and remained reasonably stable up to pH 6. A second inflection was observed between pH 6 and 8, indicating the formation of another species. The second species remained stable only up to pH 9, where the observed decrease in emission intensity indicated its transformation into yet another complex species.

The pH dependence associated with the $Tb(CMOS)_2$ complex was much simpler than that observed for the Tb(CMOS) complex. The emission intensity increased gradually up to pH 5, and did not change appreciably between pH 5 and 11.

pH Dependence of Tb(III) Emission Lifetime

The mechanisms which lead to alteration in the luminescence lifetime of a Tb(III) species are similar to those which affect the emission intensity. The high-energy, –OH stretching mode of water (around 3500 cm^{-1}) is an efficient promoter for deactivation of the excited $^5D_4$ Tb(III) state, and consequent quenching of the emission lifetime.[8] Most ligands do not contain the required group vibrational frequencies which deactivate the excited state, and therefore are not efficient quenchers of Tb(III) emissive liftetimes. Since the binding of a ligand must result in the expulsion of some of the coordinated water molecules, it follows that the Tb(III) emission lifetime is a good probe for the study of solution chemistry.

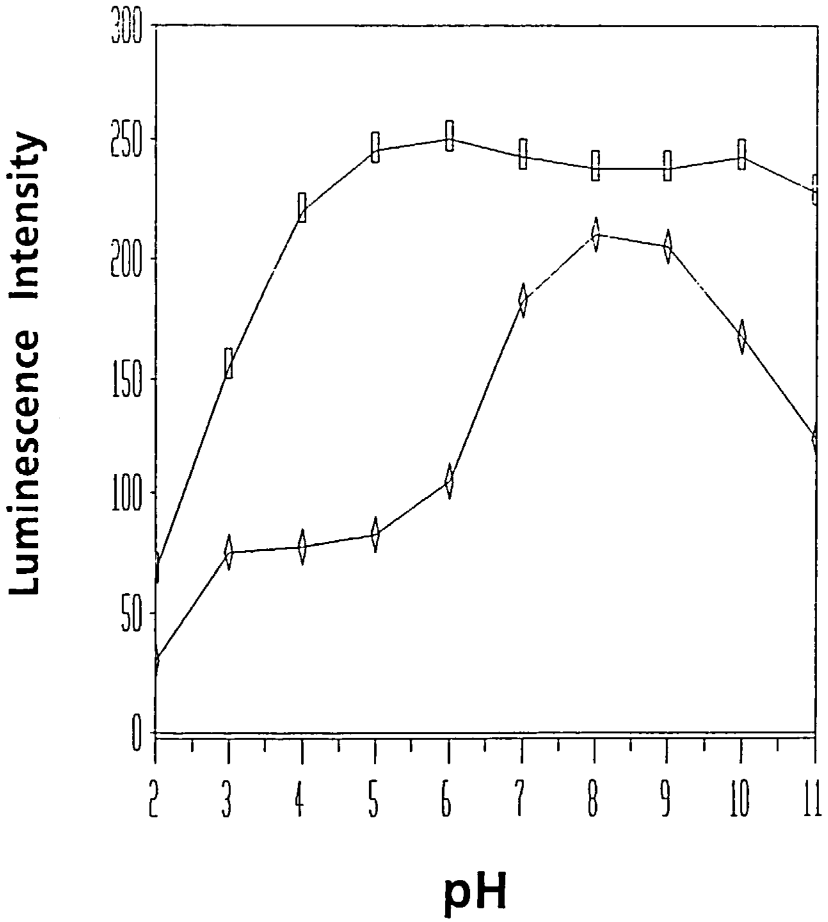

FIGURE 1 pH dependence of Tb(III) luminescence intensities, obtained for Tb(CMOS) {◇} and $Tb(CMOS)_2$ {□} complexes. The data are shown in arbitrary units.

The pH dependencies associated with the Tb(III) emission lifetime of Tb(CMOS) and $Tb(CMOS)_2$ are shown in Figure 2, and closely parallel the trends noted for the emission intensities. For the Tb(CMOS) complex, the Tb(III) lifetime was observed not to vary significantly between pH 2 and 6, but did not undergo a substantial increase between pH 6 and 8. The lifetime peaked at pH 9, and then decreased somewhat again beyond pH 9. The $Tb(CMOS)_2$ emission lifetimes were found to increase gradually up to pH 6, and attained a plateau between pH 6 and 8. An increase was noted between pH 8 and 10, followed by a decrease beyond pH 10.

pH Dependence of Coordinated Water Molecules

The existence of a deuterium isotope effect in Tb(III) emission lifetimes has been

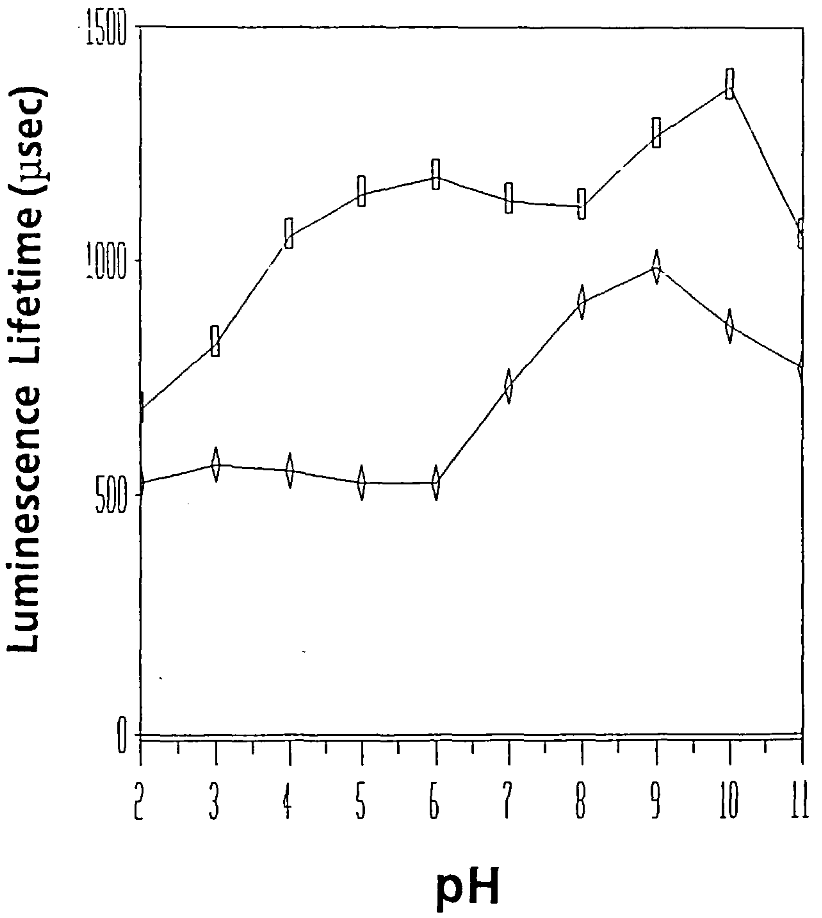

FIGURE 2 pH dependence of Tb(III) luminescence lifetimes, obtained for Tb(CMOS) {◇} and $Tb(CMOS)_2$ {□} complexes. The lifetime data are shown in units of microseconds.

known since the earliest studies of lanthanide ion luminescence.[8] While the –OH stretching mode of coordinated water ($3500\,cm^{-1}$) is effective at quenching the Tb(III) excited $^5D_4$ state, the analogous –OD stretching mode of coordinated deuterium oxide ($2800\,cm^{-1}$) is far less effective. Horrocks and Sudnick[6] have taken advantage of this phenomenon to develop a spectroscopic method suitable for determining the number of water molecules bound at the inner coordination sphere of either Tb(III) or Eu(III). The luminescence lifetime of a given species is measured in both H_2O and D_2O, and the observed rate for luminescence decay obtained in each solvent system. The difference between the rate constants obtained in H_2O and D_2O is directly proportional to the number of coordinated water molecules, which is calculated using the proportionality constants provided by Horrocks and Sudnick.[6]

The pD dependence associated with the Tb(III) emission lifetimes of Tb(CMOS) and $Tb(CMOS)_2$ complexes dissolved in D_2O was obtained in a manner similar to that described above for the same complexes dissolved in H_2O. After correcting the pD values to the pH scale, the rate constants calculated at analogous acidity values were subtracted and the number of coordinated water molecules deduced at selected pH values. These data are plotted in Figure 3.

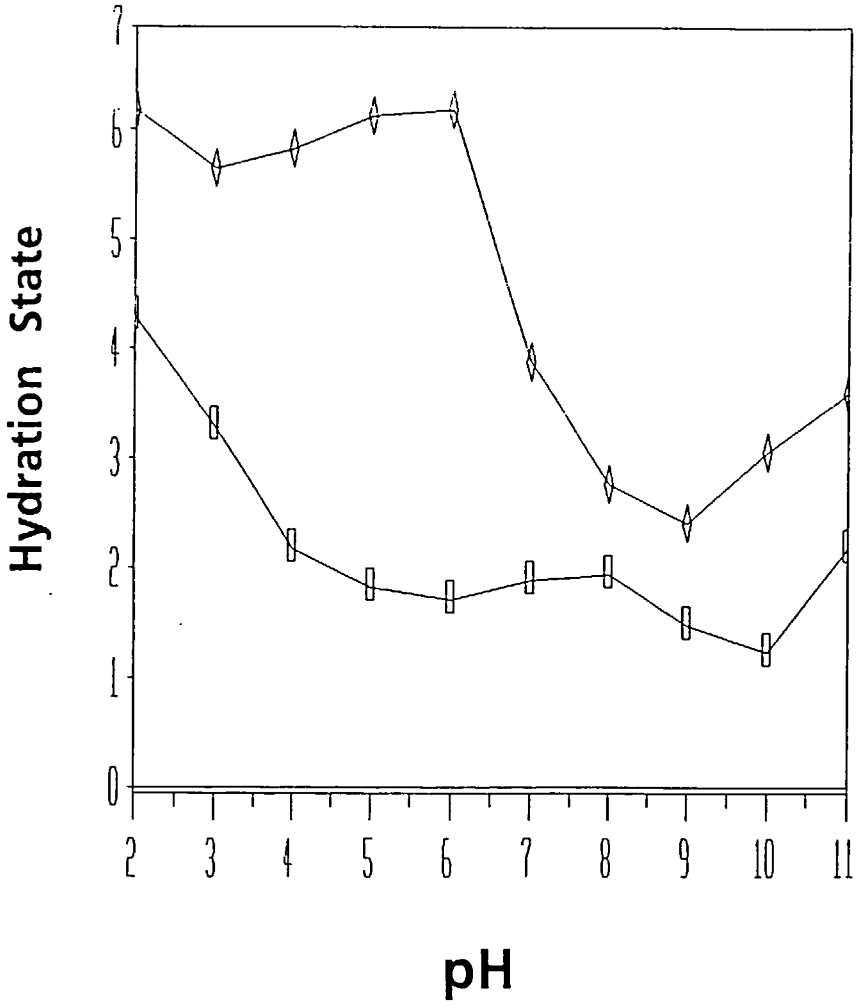

FIGURE 3 pH dependence of the number of water molecules bound at the inner coordination sphere of Tb(III) in the Tb(CMOS) {◇} and $\mathrm{Tb(CMOS)_2}$ {□} complexes.

The hydration state of the Tb(CMOS) complex was found to be very dependent on the solution pH. Between pH 2 and 6, the number of coordinated water molecules remained essentially constant around 6. Between pH 6 and 8, the hydration state decreased rapidly down to approximately 2.75. This low hydration state persisted up to pH 9, whereupon the hydration state was found to increase to approximately 4 by pH 11. These changes in hydration state take place at the same pH values as the alterations previously described for the emission intensities and lifetimes.

Quite different behaviour was noted for the $\mathrm{Tb(CMOS)_2}$ complex. The number of coordinated water molecules decreased gradually up to pH 5, and remained essentially constant at a hydration state of 2 between pH 5 and 8. Between pH 8 and 11, the number of coordinated solvent molecules decreased slightly to 1.2 at pH 10, and rose again to 2 by pH 11.

Energy Transfer Among Lanthanide CMOS Complexes

While the spectroscopic trends described thus far provide insight into the conditions under which Tb(CMOS) and Tb(CMOS)$_2$ complexes exist, full interpretation is not possible unless the oligomerization state of the complexes is determined. A method has been described in which intermolecular energy transfer among lanthanide complexes is used to anlayze the possible self-association of the complexes.[5] A number of cases have now been documented where the observed trends in emission intensity, liftime, or hydration state were not due to a change in the ligand bonding mode, but instead were found to originate with oligomerization of the complexes. In the energy transfer method, the emission intensity and lifetime of a Tb(III) donor complex is monitored as a function of the concentration of added Eu(III) acceptor complex.

Luminescence quenching in fluid solution can proceed *via* two mechanisms, or some combination of these. In **dynamic quenching**, the energy transfer takes place as a result of collisions between the donor and quencher. This nonradiative transfer results in a concomitant decrease in emission intensity and shortening of the emission lifetime. An alternative mechanism is termed **static quenching**, and results when an actual complex is formed between the donor and quencher. Formation of mixed Tb/Eu donor/acceptor species generates non-emissive Tb(III) species, with the only observable emission parameters being associated with Tb/Tb or free Tb species. While static quenching results in a decrease in emission intensity (due to the removal of some emitting Tb species), the emission lifetime is unaffected (since the only detectable species are those which are not quenched).

The intensity data are analyzed according to the Stern–Volmer equation, (*3*),

$$(I_0 - I)/I = K_{sv}^{\varphi}[Q] \qquad (3)$$

where I_0 is the Tb(III) emission intensity in the absence of Eu(III) quencher, I is the emission intensity obtained at a Eu(III) quencher concentration of [Q], and K_{sv}^{φ} is the Stern–Volmer quenching constant for intensity quenching. An analogous equation may be written for lifetime data, (*4*),

$$(\tau_0 - \tau)/\tau = K_{sv}^{\tau}[Q] \qquad (4)$$

where τ_0 is the Tb(III) emission lifetime in the absence of Eu(III) quencher, τ is the emission lifetime obtained at a Eu(III) quencher concentration of [Q], and K_{sv}^{τ} is the Stern–Volmer quenching constant for lifetime quenching.

If the complexes are monomeric in nature, then the energy transfer will take place by the collisional mechanism (dynamic quenching). In that case, the relationship between Stern–Volmer quenching constants will be that given in (*5*).

$$K_{sv}^{\varphi} = K_{sv}^{\tau} \qquad (5)$$

When the complexes undergo self-association into oligomeric species, then the additional contribution from static quenching is observed. The situation usually results in the observation of extremely efficient energy transfer. When the energy transfer is characterized by either pure static or a combination of static and dynamic quenching, the reaction (*6*) is observed.

$$K_{sv}^{\varphi} > K_{sv}^{\tau} \qquad (6)$$

When both static and dynamic mechanisms are possible, then the Stern-Volmer quenching kinetics are described[9] by (*7*),

$$(I_o - I)/I = (K_{sv}^{\tau} + K_c)[Q] + (K_{sv}^{\tau} * K_c)[Q]^2 \qquad (7)$$

where K_c is the intermolecular association constant of the donor and quencher.

TABLE I
Stern–Volmer quenching constants and intermolecular association constants of the Tb(CMOS) complexes.

pH	K_{sv}^{φ}	K_{sv}^{τ}	K_c
2.0	275	160	111
3.0	280	155	121
4.0	365	210	149
5.0	405	225	172
6.0	430	230	191
7.0	1610	210	1344
8.0	2090	180	1845
9.0	1820	145	1628
10.0	1325	120	1177
11.0	900	110	773

TABLE II
Stern–Volmer quenching constants and intermolecular association constants of the $Tb(CMOS)_2$ complexes.

pH	K_{sv}^{φ}	K_{sv}^{τ}	K_c
2.0	635	75	497
3.0	715	80	556
4.0	992	105	740
5.0	1075	125	782
6.0	1100	130	795
7.0	980	150	694
8.0	895	125	653
9.0	1065	110	787
10.0	1435	100	1037
11.0	1740	100	1217

The results of energy transfer studies performed on the Tb(CMOS) complexes are collected in Table I, while analogous results obtained on the $Tb(CMOS)_2$ complexes are given in Table II. The Tb(CMOS) complexes were observed to be essentially monomeric up to pH 6, with only a small degree of oligomerization being observable.

The Tb(CMOS) complexes were found to become strongly associated above pH 6, with the oligomerization reaching a maximum value at pH 8. The polynuclear species apparently dissociate between pH 8 and 11, although the monomeric state is never reached. It is highly likely that the oligomeric species formed within this high pH range represent hydroxy-bridged dimer species, of the type noted by Martin and coworkers[10] during their potentiometric titration work.

On the other hand, the $Tb(CMOS)_2$ complexes were found to be polymeric at all pH values. The behaviour may be interpreted as implying the presence of ligand-bridged dimers at low pH, and hydroxy-bridged dimers in the high pH region.

These findings indicate that much of the spectral data which can be obtained for the Tb(CMOS) and $Tb(CMOS)_2$ complexes cannot be readily interpreted, due to the uncertain nature of the solution phase species. The sole exception to this trend concerns the Tb(CMOS) complex at low pH, which appears to be monomeric between pH 2 and 6.

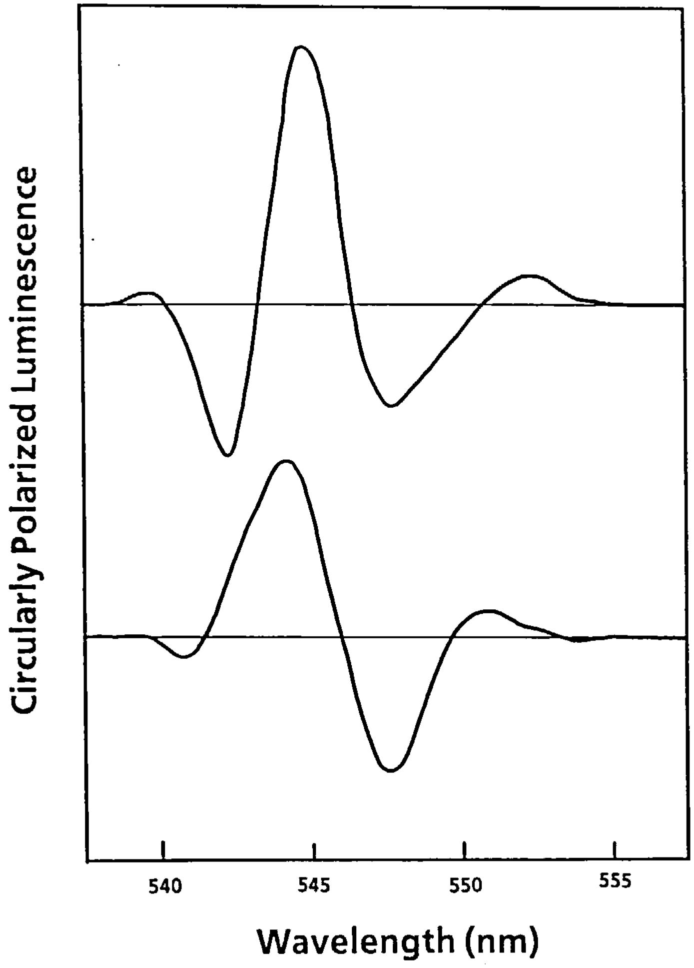

FIGURE 4 Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition of the 1 : 1 Tb(CMOS) complex, at pH 3.9 (lower trace) and pH 8.9 (upper trace).

Circularly Polarized Luminescence Studies of the CMOS complexes with Tb(III)

When a chelating ligand is dissymmetric, chiroptical spectroscopy is a powerful tool for the characterization of these species. It is generally accepted that circularly polarized luminescence (CPL) spectroscopy is the technique of choice for the study of chiral lanthanide compounds,[11,12] since it combines the structural selectivity of chiroptical spectroscopy with the sensitivity of luminescence spectroscopy. Although CPL spectroscopy has proven extremely useful in the characterization of Tb(III) complexes containing α-hydroxycarboxylic acids,[12] its application to the CMOS complexes is somewhat restricted owing to the polynuclear nature of most of the solution phase species.

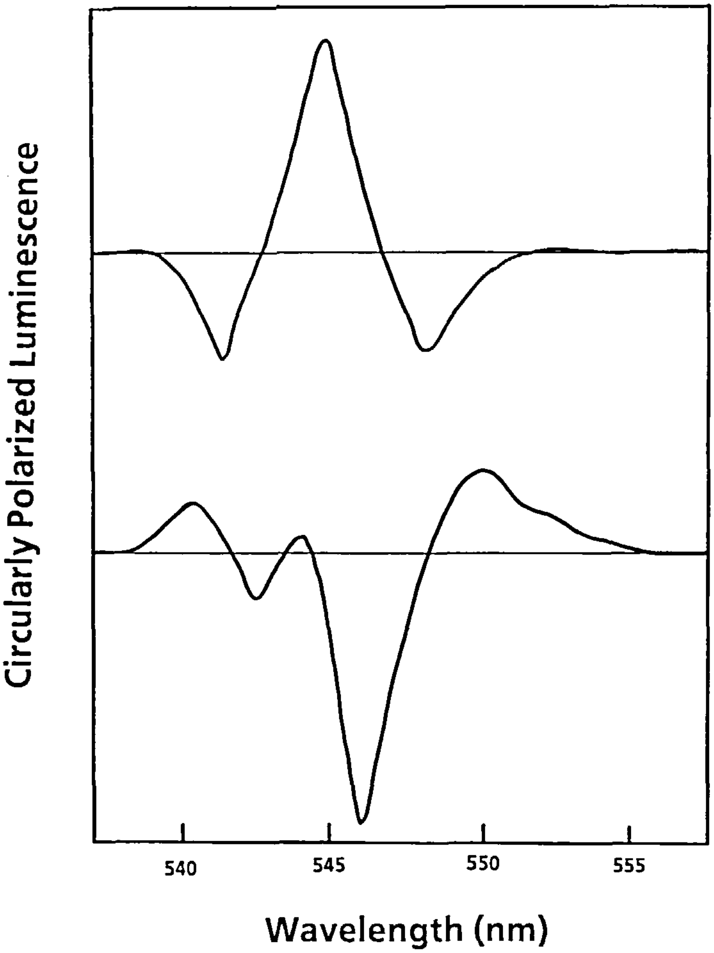

FIGURE 5 Circularly polarized luminescence spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) transition of the 1 : 1 $Tb(CMOS)_2$ complex, at pH 3.0 (lower trace) and pH 7.0 (upper trace).

For the Tb(CMOS) complex, essentially two types of CPL spectra were observed, and representative examples of these are shown in Figure 4. Betwen pH 2 and 6, a common lineshape was observed, with essentially constant intensity over the region.

It is significant to note that this CPL lineshape is identical to that observed for Tb(III) complexes of *S*-malic acid, when this ligand binds in a terdentate mode.[13] Above pH 6, the CPL spectra change to a new pattern, which undergoes further subtle changes up to the highest pH values studied. The observation that a constant lineshape is not reached above pH 6 is further indication of the existence of polynuclear species, which are undergoing rearrangements as the solution pH is changed.

The CPL spectra obtained for the $Tb(CMOS)_2$ complexes were found to be slightly different at all pH values studied (as would be anticipated for polynuclear species), but two main lineshape types were observed. A unique CPL lineshape was noted below pH 5, which is associated with the ligand bridge oligomers. The high pH $Tb(CMOS)_2$ CPL lineshape is very similar to that noted for the high pH Tb(CMOS) species, indicating that the ligand conformations adopted by CMOS in the hydroxy -bridged species must be similar in the complexes having 1:1 and 1:2 stoichiometry.

When examined as a whole, the spectroscopic data provide a good description of the solution phase coordination chemistry of terbium complexes with *S*-carboxymethoxysuccinic acid. The 1:1 Tb(CMOS) complex exists as a monomeric unit up to pH 6, with an average of 6 water molecules making up the remainder of the coordination sphere. Since NMR studies have shown that the CMOS ligand binds in a tetradentate fashion within this pH region, it is concluded that the central Tb(III) ion is 10-coordinate in the monomeric Tb(CMOS) complex. The CPL spectra exhibited by the monomeric Tb(CMOS) complex are equivalent with those exhibited by the Tb(III) complex with *S*-malic acid, indicating that the two ligand conformations must be comparable in the two complexes. Above pH 6, the complexes become self-associated into oligomeric species, which probably are hydroxy-bridged dimers. This process results in a decrease in the number of coordinated solvent molecules, and a fair increase in the Tb(III) emission intensity and lifetime.

The 1:2 $Tb(CMOS)_2$ complexes were found to be associated into polymeric species at all pH values, with ligand bridging taking place at low pH and hydroxy bridging taking place at high pH. The CPL spectra indicate that the ligand conformations in the two types of oligomeric species are not equivalent. However, the nature of the $Tb(CMOS)_2$ hydroxy-bridged species appears to be equivalent to that of the Tb(CMOS) hydroxy-bridged species.

ACKNOWLEDGEMENTS

The authors would like to thank Mrs R. H. Boerstoel for preparing the *S*-CMOS ligand used.

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