Solution Phase Chemistry of Lanthanide Complexes. 9. Mixed Ligand Tb(III) Complexes of Ethylenediamine Tetraacetic Acid and 5-Substituted Salicylic Acids

HARRY G. BRITTAIN* and SANDRA RIVERA

Department of Chemistry, Seton Hall University, South Orange, N.J. 07079, U.S.A.

Received January 9, 1985

Abstract

The solution phase chemistry associated with mixed ligand lanthanide complexes of ethylenediamine tetraacetic and 5-substituted salicylic acids has been studied by means of luminescence spectroscopy. Formation of Tb(EDTA)(ligand) complexes was found to be essentially complete at 1:1:1 mole ratios. The salicylate ligands were found to sensitize Tb(III) emission to various extents, but this process only became important upon ionization of the phenolate proton. Below neutral pH values, the salicylate ligand appeared to bind in a bidentate manner which involved the ionized carboxylate and the unionized phenolate group. In that case, hydrogen bonding of the phenolate group to water molecules coordinated by the Tb(III) ion appears to exist. Deprotonation of these coordinated water molecules was found to lead to large decreases in the Tb(III) emission lifetimes.

Introduction

The ternary complexes formed by lanthanide ions with ethylenediamine tetraacetate (EDTA) and salicylate anions have received a modest amount of interest primarily as a result of possible analytical applications [1]. Tb(III) can be determined at μg/ml levels as the EDTA-sulfosalicylic acid complex [2]. Other workers have contrasted the behavior of this complex with that of other ternary complexes, and have reported that the analytical utility of the salicylate complexes is excellent [3]. In these complexes, the salicylate ligand functions primarily as an energy sensitizer for the Tb(III) ion.

At the same time, other investigators have studied the equilibria associated with the formation of the ternary complexes formed by lanthanides, EDTA, and salicylates. Formation constants for the lanthanide EDTA complexes with 5-sulfosalicylic acid have been obtained [4], while other workers were unable to obtain these constants with different aminopolycarboxylate ligands [5]. The constants which have been obtained are significantly smaller than those reported for the salicylate derivatives of lanthanide aquo ions [6, 7], as would be anticipated.

Surprisingly, the relationship between the luminescence properties of Tb(III) and the salicylate donor ligands has not been investigated systematically. Some spectrophotometric data associated with Ho(III) and Er(III) ternary complexes has been reported [8], but this data was only obtained over a relatively small pH region.

In the present report, we wish to summarize the results of systematic investigations regarding the photophysics associated with Tb(III) ternary complexes containing EDTA and various salicylate anions.

Experimental

All ligands used during the course of the present work were obtained from Aldrich Chemicals, and each was used as received. Stock solutions of Tb(III) were prepared by dissolving the 99.9% oxide (Research Chemicals) in a stoichiometric amount of 70% $HClO_4$, neutralizing to pH 3.5 with NaOH, and then diluting to the desired volume. In all cases, a 1:1 ratio of Tb(III) and EDTA was used, with the large formation constant insuring complete formation of Tb(EDTA). In the usual practice, stoichiometric amounts of Tb(EDTA) and salicylate ligand stock solutions were combined to yield Tb(EDTA)/ligand molar ratios of 1:1 and 1:2.5. The Tb(III) concentration in these studies was normally 15 mM.

The pH of each of these solutions was varied between 3.5 and 11.5, and the required photophysical measurements were made at each pH value. Variation of the solution pH within the solutions was effected by the addition of microliter amounts

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

of standard $HClO_4$ or NaOH directly to the fluorescence cuvette. The pH was obtained using a glass microcombination electrode which could be inserted directly into the cuvette, and read on an Orion 701A pH meter. The system was calibrated daily with phosphate buffers.

The luminescence intensity of the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band (545 nm) was recorded at each pH value on a low-resolution fluorimeter constructed in our laboratory. Samples were excited by the 365 nm output of a 100 W Hg-Xe arc lamp, with this excitation being selected by a combination of UV-transmitting glass filters. The emission was analyzed by the monochromator of a Cary 11 spectrophotometer, and detected by an EMI 9798B photomultiplier tube (S-20 response). All measurements were obtained at an emission bandpass of approximately 5 nm, and under ambient temperature conditions. Daily fluctuations in emission intensities were eliminated by referencing all observed intensities to that of a standard piece of uranyl glass.

Tb(III) excitation spectra were obtained on a Spex Fluorolog instrument, which employed double monochromators at the excitation and emission ends. Corrected spectra were obtained using a reference system based on a standard quantum counter. Absorption spectra were obtained on a Perkin-Elmer 552A UV-Vis spectrophotometer, with the data being processed by the model 3600 data station.

Emission lifetimes were obtained on a separate apparatus. Samples were excited by the 337 nm output of a pulsed nitrogen laser (PRA Associates, model LN-1000). The transient currents developed upon pulsed excitation of the sample were converted into voltages using a 200 K load resistor, and these voltage pulses were captured for viewing on a storage oscilloscope. At the same time, the data were digitized at 4 μsec intervals via a homebuilt analog/digital converter, and the digitized data fed directly into a Commodore PET 4032 microcomputer. The details of the transient digitizer have been described [9]. Our program calculates the baseline from data points taken before the laser pulse, and subtracts the baseline from the decay data. The corrected decay curves were then analyzed using a linear regression analysis of the ln(I) *vs.* time data points. Plots of ln(I) *vs.* time were invariably found to be linear, and thus indicate the presence of only one emitting species.

Results

A. pH Dependence of Tb(III) Emission Intensity

Broad-band UV excitation (using a wavelength centered around 365 nm) of the various Tb(EDTA)(ligand) complexes results in efficient population of the $^5D_4$ excited state, and in the observation of 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 and lifetimes of these bands were found to exhibit dependencies on both the solution pH and on the nature of the particular salicylate ligand used. However it was noted that none of the observed trends depended on the particular band used to obtain the data, and consequently all attention was focused on the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb(III) complexes.

It is well known that the photophysical properties of coordinated Tb(III) are determined primarily by the inner coordination sphere of the complexed ion, and therefore luminescence intensity and lifetime trends can be used to provide information regarding the nature of the Tb(III) complexes. It was noted that the photophysical properties of the Tb(EDTA)(ligand) complexes were essentially identical for the 1:1:1 and 1:1:2.5 ratios, and consequently only data obtained at the 1:1:1 ratio will be used in subsequent discussions. These observations suggest that the ternary Tb(EDTA)(ligand) complexes are fully formed even at the 1:1:1 mole ratios.

In Fig. 1, the pH dependence of Tb(III) emission intensity is illustrated as a function of the identity of the various salicylate ligands. No data have been shown for 5-nitrosalicylic acid, 5-methoxysalicylic acid, 5-bromosalicylic acid, or 5-iodosalicylic acid, since the emission intensities of the Tb(EDTA)(ligand) complexes were identical to those of the parent Tb(EDTA) compound. We attempted to form the ternary complex between Tb(EDTA) and thiosalicylic acid, but no evidence for formation of this ternary complex could be obtained.

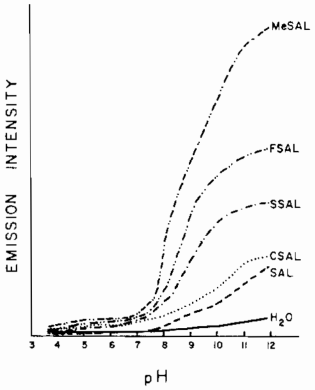

Fig. 1. pH Dependence of the Tb(III) luminescence intensity as a function of the Tb(EDTA)(ligand) complex used. Data are shown for 5-methyl salicylic acid (— — · ·), 5-fluoro salicylic acid (— · ·), 5-sulfo salicylic acid (— · — ·), 5-chloro salicylic acid (· · · · ·), salicylic acid (- - - -), as well as the Tb(EDTA) blank (———). All data were obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band, and are shown in arbitrary units.

It is immediately clear from consideration of Fig. 1 that the photophysical properties of the Tb(EDTA)(ligand) complexes exhibit profound dependencies on the solution pH and on the nature of the salicylate ligand. All complexes exhibited weak Tb(III) luminescence between pH 3.5 and 7.0, but above this pH region rapid increases in emission intensity with increasing pH were noted. No comparable increases could be observed when following the pH dependence of the Tb(EDTA) emission. Both 5-methylsalicylic acid (MeSAL) and 5-fluorosalicylic acid (FSAL) were found to sensitize the Tb(III) emission to a larger extent than the commonly used 5-sulfosalicylic acid (SSAL). An examination of Fig. 1 reveals that the analytical limits of detection for Tb(III) could be lowered by at least a factor of two by using MeSAL instead of SSAL.

For ternary complexes containing SSAL, FSAL, and CSAL, the emission intensity appeared to reach a limiting value at the highest pH values. On the other hand, no such limiting behavior was observed for the ternary complexes containing MeSAL or SAL. Comparison of these observations with the ligand pK data of Table I reveals that when pKa_2 is smaller than 13, a limiting emission intensity may be reached below pH 11.5.

TABLE I. Protonation Constants and Abbreviation Scheme for the 5-Substituted Salicylate Ligands.[a]

Substituent at Position 5	Abbreviation	pK	pK
H	SAL	2.97	13.74
F	FSAL		
Cl	CSAL	2.64	12.95
Br	BSAL	2.64	12.84
I	ISAL		
CH_3	MeSAL	2.88	14.57
OCH_3	OMeSAL		
OSO_3	SSAL	2.84	12.53
NO_2	NSAL	1.87	10.33

[a] All pK data were obtained at 25 °C, at $\mu = 0$, and the values were taken from ref. 10.

B. pH Dependence of Tb(III) Emission Lifetimes

The pH dependence of Tb(III) emission lifetimes as obtained for the ternary complexes proved to be very different from that noted for the emission intensities. The pH trends have been illustrated in Fig. 2 for the Tb(EDTA)(ligand) complexes for which appreciable emission intensities were obtained. With the exception of Tb(EDTA)(SSAL) above pH 8, the emission lifetimes of all Tb(EDTA)(ligand) complexes were lower than those of the parent Tb(EDTA) compound.

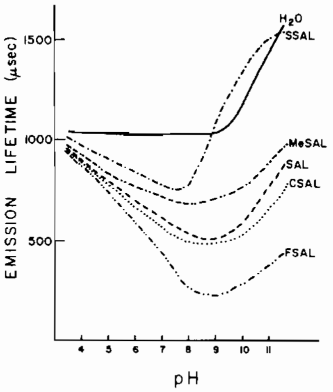

Fig. 2. pH Dependence of the Tb(III) luminescence lifetime as a function of the Tb(EDTA)(ligand) complex used. Data are shown for 5-methyl salicylic acid (— — · ·), 5-fluoro salicylic acid (— · ·), 5-sulfo salicylic acid (— · — ·), 5-chloro salicylic acid (· · · · ·), salicylic acid (-----), as well as the Tb(EDTA) blank (———). All data were obtained within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band.

At low pH values, the lifetime curves appear to extrapolate back to the values which would have been obtained for Tb(EDTA). The intersections associated with such an extrapolation would all be located between pH values of 2.5 and 3.25. Since these salicylate ligands all exhibit carboxylate ionizations characterized by pK values between 2.6 and 2.9, it would appear that the decrease in Tb(III) emission lifetime is associated with the onset of salicylate ligand binding. Continued raising of the solution pH results in further decreases in emission lifetime, until one reaches pH 8 to 9. Above these pH values, one then observes an increase in the emission lifetime. Since none of the ternary complexes exhibits a Tb(III) lifetime greater than the parent Tb(EDTA) compound, it may be concluded that a ligand quenching mechanism exists in the Tb(EDTA) (ligand) solutions.

C. Tb(III) Excitation Spectra in the Tb(EDTA) (Ligand) Complexes

Earlier workers [1–3] have indicated that salicylate ligands efficiently transfer absorbed electronic energy in a non-radiative fashion to a bound Tb(III) ion. We have elected to study the excitation spectra of the various salicylate ligands in greater detail so as to deduce new information about the energy transfer process.

In all cases, the Tb(III) excitation spectra consisted of a single peak located between 340 and 370 nm, the position of which varied with both the identity of the salicylate ligand and with the pH of the solution. Invariably the low pH excitation maxima were located at higher energies than were the maxima observed for the corresponding ternary complexes at high pH. At the same time, the intensity of the

TABLE II. Tb(III) Excitation and Salicylate Absorption Maxima Obtained for 1:1:1 Tb(EDTA) (ligand) Complexes.

Ligand	Absorption Maximum	Excitation Maximum (pH = 5)	Excitation Maximum (pH = 11)
SAL	297	343	357
FSAL	311	358	370
CSAL	308	353	369
BSAL	308		
ISAL	311		
MeSAL	305	356	368
OMeSAL	318		
SSAL	298	344	354

low pH excitation peak was significantly smaller than that of the corresponding high pH excitation peak. The low and high pH excitation maxima have been collected in Table II. No intense excitation maximum between 340 and 370 nm was detectable for the parent Tb(EDTA) compound at comparable instrumental sensitivities.

Absorption spectra recorded for the same solutions revealed an interesting feature. Since the Tb(EDTA) complex does not exhibit appreciable absorbance in this wavelength region, one may ascribe all strong absorption peaks to the salicylate ligand. All of the salicylate compounds were found to exhibit an absorption maximum at wavelengths shorter than either of the two Tb(III) excitation bands. This behavior has been illustrated in Fig. 3 for the Tb(EDTA)(FSAL) complex. Two observations may be made upon examination of Fig. 3: the excitation and absorption peaks clearly reflect different salicylate transitions, and the absorption band is much broader than either of the Tb(III) excitation peaks.

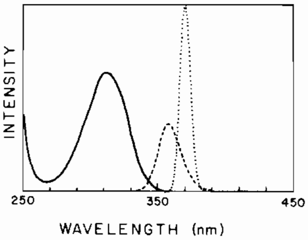

Fig. 3. Absorption spectrum of the 1:1:1 Tb(EDTA)(FSAL) complex (——). Excitation spectra of the same compound taken at pH 5 (-----) and 11 (.....) are also shown. The intensity scales for all spectra are arbitrary.

Discussion

All of the Tb(III) photophysics just described can be explained through consideration of the complex solution chemistry. In that case, the data may then be used to provide additional insight into details of the solution equilibria. Salicylate ligands are known to exhibit two proton ionizations. The carboxylate group is removed at quite low pH values, with pK_1 values ranging from 1.87 to 2.88 having been reported for the 5-substituted salicylates [10]. The phenolate proton is ordinarily removed at much higher pH values, and values of pK_2 ranging from 10.33 to 14.57 have been reported [10]. These ionization data have been collected in Table I for convenience, along with the ligand abbreviation scheme which will be used for the remainder of this report.

The insolubility of most lanthanide salicylate complexes has precluded the determination of formation constants corresponding to the binding of the first salicylate ligand by a Tb(III) ion:

$$Tb^{3+} + SAL^{2-} \rightleftharpoons Tb(SAL)^+$$

The sole exception has been for SSAL, where it was reported that log K = 6.95 [7]. In a kinetic study, the complexation between lanthanide EDTA complexes and SSAL was investigated. No data was obtained for the Tb(EDTA) complex, but for Gd(EDTA) the following reaction was studied:

$$Gd(EDTA)^- + SSAL^{2-} \rightleftharpoons Gd(EDTA)(SSAL)^{3-}$$

These workers deduced a stability constant of pK = 4.40. Thus, it would appear that while the formation constants of the Tb(EDTA)(ligand) complexes are reduced relative to those of the Tb(ligand) complexes, the ligand binding in the ternary complex is still sufficiently strong so as to insure complete formation of the complexes even at 1:1 stoichiometric ratios. This last conclusion is in exact agreement with our photophysical results, since essentially no difference was noted when comparing Tb(EDTA)(ligand) complexes having 1:1:1 or 1:1:2.5 mole ratios. This observation is in agreement with an earlier observation [2].

The pH dependence of Tb(III) emission intensities and lifetimes revealed several general trends. Formation of the ternary complexes began between pH 2.5 and 3.0, and these phenomena clearly accompanied deprotonation of the sole carboxyl group. The salicylate ligands cannot bind in a monodentate fashion, since simple carboxylate binding is known to lead only to feeble complexation [10]. Some sort of bidentate complexation involving the phenolate group (in addition to the carboxylate) must be involved, but consideration of the ligand protonation equilibria reveals that this group cannot be ionized until much higher pH values. It is likely that the phenolate group is hydrogen bonded to one of the water molecules still coordinated by the Tb(III) ion [11], much in the manner of simple hydroxycarboxylic acids [12].

Raising of the solution pH from 3.0 to 8.0 leads to little or no increase in the luminescence intensities, but does lead to decreases in the emission lifetimes. Such behavior was not noted for the parent Tb(EDTA) compound, for which neither parameter changes over this pH region. The only process likely to occur over this pH region is a partial deprotonation of coordinated water molecules. Since no effect is noted with Tb(EDTA), the effects noted with the salicylate ligands must represent deprotonation of the water molecules involved in hydrogen bonding with the phenolate group. It is entirely plausible that the breakdown of the hydrogen bonding leads to a more labile Tb(EDTA)(ligand) complex, where the salicylates dissociate freely. The lowered emission lifetimes indicate that dissociated salicylate ligands quench the Tb(III) emission.

Raising the solution pH from 8.0 to 11.5 results in a great intensification of the emission intensities, and in a modest increase in the emission lifetimes. These effects appear to level off at the highest pH values, and therefore must be connected with ionization of the phenolate group. Upon deprotonation, this functionality would bind directly to the Tb(III) ion, and such binding would probably result in the expulsion of some of the water molecules coordinated to the Tb(III) ion.

The Tb(III) excitation spectra reveal interesting facets regarding the energy transfer process. The strong absorption bands are certainly due to salicylate $\pi-\pi^*$ transitions, but the excitation spectra reveal that this transition is ineffective for Tb(III) sensitization. One would conclude from this observation that the non-radiative pathway back to the ligand ground state must be a more favorable process than is energy transfer to the Tb(III) ion. The efficient Tb(III) excitation bands are located at lower energies than the $\pi-\pi^*$ absorptions, and are observed to be much sharper in nature. Lowering of the solution pH from 11 to 5 results in protonation of the phenolate group, and also results in a blue shift of the excitation maxima. Such behavior implies that the excitation maxima are actually $n-\pi^*$ in character. The absorption intensity of these $n-\pi^*$ transitions may be far lower than that of the $\pi-\pi^*$ transitions, but the $n-\pi^*$ transition must be strongly coupled to the Tb(III) ion.

The results detailed in the present work clearly demonstrate how luminescence spectroscopy may be used to obtain information on the solution phase chemistry of lanthanide complexes. The sensitivity of lanthanide ion photophysics to details of the metal coordinative environments represents a powerful method for studies detailing this coordination sphere.

Acknowledgement

This work was supported by the Camille and Henry Dreyfus Foundation, through a Teacher-Scholar award to H.G.B.

References

1 P. R. Haddad, *Talanta, 24,* 1 (1977).
2 R. M. Dagnall, R. Smith and T. S. West, *Analyst, 92,* 358 (1967).
3 S. J. Lyle and N. A. Za'tar, *Anal. Chim. Acta, 153,* 229 (1983).
4 C.-G. Ekstrom, L. Nilsson and I. Grenthe, *Inorg. Chim. Acta, 48,* 145 (1981).
5 U. Y. Ozer, *J. Inorg. Nucl. Chem., 32,* 1279 (1970).
6 C. R. Kanekar, N. V. Thakur and S. M. Jogdeo, *Bull. Chem. Soc. Jpn., 41,* 759 (1968).
7 A. Cassol, P. Di Bernardo, R. Portanova and L. Magon, *Gazz. Chim. Ital., 102,* 1118 (1972).
8 T. Taketatsu and S. Yoshida, *J. Inorg. Nucl. Chem., 35,* 881 (1973).
9 R. J. Woods, S. Scypinski, L. J. Cline-Love and H. A. Ashworth, *Anal. Chem., 56,* 1395 (1984).
10 A. E. Martell and R. M. Smith, 'Critical Stability Constants, Vol. 3', Plenum, New York, 1977.
11 J. H. Burns and W. H. Baldwin, *Inorg. Chem., 16,* 289 (1977).
12 T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. J. Randall, *Chem. Rev., 65,* 1 (1965).