a consequence of the expected smaller internal energy of the AgL_2^+ ion generated from the polymer, given the expenditure of internal energy needed to break its strong intramolecular bonds.

Conclusion

Except for the 1,10-phenanthroline derivative, only one- and two-coordinate silver species are observed in the SIMS analyses; no silver species containing three or four monodentate ligands were obtained. This conspicuous lack of higher molecular weight ions, as previously suggested,[2] attests to the propensity of silver complexes to be linear, two-coordinate species.[8] The rigid nature of the bidentate phenanthroline ligand precludes a two-coordinate linear geometry and so, not surprisingly, is an exception to the general observation, and the presumably four-coordinate $Ag(phen)_2^+$ is observed.

Graphite appears to be the matrix of choice for the SIMS analysis of these complexes in order to generate the most analytically useful spectra. Even under these conditions, though, molecular weight information could be obtained only for those complexes that contained two ligands coordinated to the silver center. Polymeric silver compounds gave no evidence for the complexity of the solid-state geometry in the SIMS spectrum of the analyte. Nonetheless, characteristic spectra were readily obtained for each of the silver(I) complexes studied here.

Our results demonstrate the successful application of SIMS to the analysis of coordination complexes of silver and, furthermore, indicate the potential of this technique in characterizing surface species formed by the chemisorption of carbon, nitrogen, phosphorus, and sulfur ligands on silver-containing surfaces.

Acknowledgment. This work was supported by the NSF-MRL Program, Grant DMR80-20249. We thank Andrew Bell for providing samples of the silver isocyanide complexes.

Registry No. $[Ag(phen)_2]NO_3$, 60939-16-4; $[Ag(bpy)_2]NO_3$, 33971-93-6; $[Ag(PEt_3)_4]NO_3$, 86595-09-7; $[Ag(P\text{-}n\text{-}Pr_3)_4]NO_3$, 86595-11-1; $[Ag(PMe_2Ph)_4]NO_3$, 86550-04-1; $[Ag(PPh_3)_4]ClO_4$, 60185-35-5; $[Ag(SC(NH_2)_2)_2]NO_3$, 33570-47-7; $[Ag(SC(NHMe)_2)_2]NO_3$, 86550-02-9; $[Ag(CNC_6H_{11})_2]ClO_4$, 86550-06-3; $[Ag(CNC_6H_{11})_4]ClO_4$, 86595-13-3; $[Ag(CNCMe_3)_4]ClO_4$, 86631-61-0; $[Ag(bpy)_2]S_2O_8$, 28226-64-4; $[Ag(py)_4]S_2O_8$, 15810-50-1; $[Ag(pyz)]NO_3$, 86550-08-5; $[Ag(pyz)_2]S_2O_8$, 33219-39-5; graphite, 7782-42-5.

Supplementary Material Available: Figures S1–S3, showing the SIMS spectra of $[Ag(PMe_2Ph)_4]NO_3$, $[Ag(CNC_6H_{11})_2]ClO_4$, and $Ag(pyz)NO_3$ (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Seton Hall University, South Orange, New Jersey 07079

Solution Chemistry of Lanthanide Complexes. 6. Circularly Polarized Luminescence Studies on Terbium(III) Mixed-Ligand Complexes Containing Chiral α-Hydroxy Carboxylic Acid Ligands

MARK RANSOM and HARRY G. BRITTAIN*

Received November 2, 1982

The complexation of hydroxy carboxylic acids by Tb(III) in a series of ternary complexes was examined by means of circularly polarized luminescence (CPL) spectroscopy. The chirality induced in the Tb(III) ion by L-mandelic, L-lactic, L-argininic, and L-malic acids was followed by studies of their CPL spectra, and perturbations of these spectra induced by the achiral portion of the complex were examined in detail. A series of complexes having the general formula $Tb(MDL)_2(HXCA)$ (MDL = oxydiacetic, iminodiacetic, or 5-sulfosalicylic acids) and Tb(APC)(HXCA) (APC = hexadentate aminopolycarboxylate ligands) were prepared. The line shapes of the resulting CPL spectra could be used to determine the mode of bonding exhibited by the chiral ligands, and a variety of modes were found to be possible with the L-malic acid ligand. Systematic variation of the concentration of chiral ligand relative to the concentration of either $Tb(MDL)_2$ or Tb(APC) permitted a calculation of the formation constants corresponding to addition of one molecule of chiral ligand, and these values were found to support the trends established from consideration of the CPL band shape data.

Introduction

The conformation effects associated with coordinated chelate rings of transition-metal complexes have been of interest for some time,[1,2] and clearly chiroptical techniques are best suited for these studies. Analogous studies on chiral lanthanide complexes have not been carried out in as much detail, a situation which is a consequence of the labile nature of the compounds. Nevertheless, the question is quite important as chiral lanthanide compounds are currently the focus of increasing attention.[3]

The weak f–f absorptions of lanthanide compounds precludes the effective use of circular dichroism in the study of chiral lanthanide complexes, but studies of the circularly polarized luminescence emitted by chiral Tb(III) and Eu(III) compounds can provide the necessary information.[4] In our laboratory, we have been able to simplify solution equilibria through the use of mixed-ligand complexes (containing both chiral and achiral ligands) and have been investigating the optical activity observed in a series of Tb(III)[5–11] and Eu(III)[12] compounds. Related studies have been reported by Das Gupta and Richardson.[13] In the present work, we extend the scope

---

(1) Sargeson, A. M. *Transition Met. Chem. (N.Y.)* **1966**, *3*, 303.
(2) Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* **1971**, *6*, 219.
(3) Brittain, H. G. *Coord. Chem. Rev.*, in press.
(4) Richardson, F. S.; Riehl, J. P. *Chem. Rev.* **1977**, *77*, 773.
(5) Brittain, H. G. *J. Am. Chem. Soc.* **1980**, *102*, 3693.
(6) Brittain, H. G. *Inorg. Chem.* **1980**, *19*, 2136.
(7) Brittain, H. G. *Inorg. Chim. Acta* **1981**, *53*, L7.
(8) Brittain, H. G. *Inorg. Chem.* **1981**, *20*, 959.
(9) Brittain, H. G. *Inorg. Chem.* **1981**, *20*, 4267.
(10) Copeland, R. A.; Brittain, H. G. *Polyhedron* **1982**, *1*, 693.
(11) Brittain, H. G. *Inorg. Chim. Acta*, in press.
(12) Ransom, M.; Brittain, H. G. *Inorg. Chim. Acta* **1982**, *65*, L147.

of these investigations through a study of the perturbations in observed chirality as induced through variations in the achiral ligands contained in the mixed-ligand complexes.

Experimental Details

Most of the experimental procedures required to prepare the mixed-ligand complexes have been adequately summarized.[9] The chiral ligands used in the present work were L-lactic acid (LAC), L-mandelic acid (MAN), L-argininic acid (ARG), and L-malic acid (MAL), and structures of these are also found in the earlier work.[9] The achiral ligands used to complete the mixed-ligand complexes were oxydiacetic acid (ODA, or diglycolic acid), iminodiacetic acid (IDA), 5-sulfosalicylic acid (SSA), ethylenediaminetetraacetic acid (EDTA), (2-hydroxyethyl)ethylenediamminetriacetic acid (HEDTA), and *trans*-1,2-cyclohexanediaminetetraacetic acid (CDTA). All ligands were obtained from commercial sources and were used as received.

All luminescence spectra were obtained on a medium-resolution CPL spectrometer constructed in this laboratory.[5] Generally, the complexes were excited at 365 nm, except with SSA, where excitation at 295 nm was found to yield higher emission intensities. As all work was carried out in aqueous solution at room temperature, an emission band-pass of 1 nm was found to sufficiently resolve all spectral features. The CPL data were obtained exclusively within the $^5D_4 \rightarrow {}^7F_5$ Tb(III) emission band system, as it has been determined[14] that this transition is most suitable for such studies. Since both the total luminescence (I) and CPL (ΔI) are obtained in proportional arbitrary units, we have reported the ratio of these. This quantity is termed the luminescence dissymmetry factor, g_{lum}, and is defined as $2(\Delta I/I$.[4]

Results and Discussion

The mixed-ligand complexes examined in the present study all contain achiral ligands known to bind lanthanide ions with great efficiency, and metal:ligand ratios were chosen so as to restrict the number of chiral ligands that might be bound. For the IDA, SSA, or ODA ligands, a metal:ligand ratio of 1:2 was employed throughout. Thus the equilibrium (where MDL = IDA, SSA, or ODA) within the achiral portion of the Tb(III) coordination sphere is given by

$$\mathrm{Tb}^{3+} + 2\mathrm{MDL}^{2-} \rightleftharpoons \mathrm{Tb(MDL)_2}^- \qquad (1)$$

The formation constants associated with the addition of these ligands to Tb(III) are all known, with $\log \beta_2 = 9.98$ for ODA, $\log \beta_2 = 12.24$ for IDA, and $\log \beta_2 = 12.86$ for SSA.[15]

With the aminopolycarboxylate ligands, the desired filling of the Tb(III) coordination sphere is accomplished upon binding of only 1 equiv of an HDL ligand (APC = EDTA, HEDTA, or CDTA):

$$\mathrm{Tb}^{3+} + \mathrm{APC}^{4-} \rightleftharpoons \mathrm{Tb(APC)}^- \qquad (2)$$

The equilibria associated with eq 2 are also known to be very favorable: $\log K_1 = 17.92$ for EDTA, $\log K_1 = 15.42$ for HEDTA, and $\log K_1 = 20.20$ for CDTA.[15]

As a family, the hydroxy carboxylic acids (HXCA) bind lanthanide ions to a considerably smaller extent than do the MDL or APC ligands.[15] By restriction of the number of coordination positions on the Tb(III) ion and reduction of the overall positive charge of the complex, the interaction between coordinated Tb(III) and the HXCA ligands is simplified to

$$\mathrm{Tb(MDL)_2}^- + \mathrm{HXCA}^- \rightleftharpoons \mathrm{Tb(MDL)_2(HXCA)}^{2-} \qquad (3)$$

$$\mathrm{Tb(APC)}^- + \mathrm{HXCA}^- \rightleftharpoons \mathrm{Tb(APC)(HXCA)}^{2-} \qquad (4)$$

Clearly, systematic variation of the concentration of the HXCA ligands can be used to evaluate association constants for the addition of these ligands to the coordinated Tb(III) ion. Our computational approach has been outlined for similar studies involving mixed-ligand complexes of L-aspartic acid (L-ASP).[11]

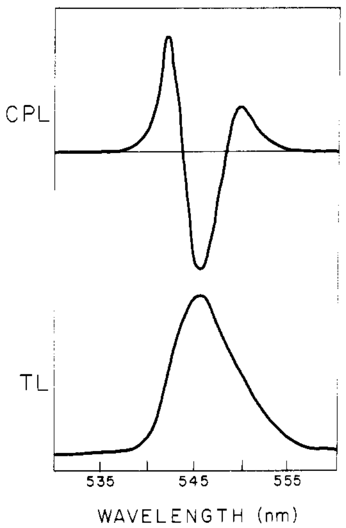

Figure 1. TL (lower) and CPL (upper) spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ emission band system of Tb(ODA)$_2$(L-MAN) at pH 4.5. The Tb(III) concentration was 15 mM, and the Tb:MAN mole ratio was set at 1:3.

L-MAN, L-LAC, and L-ARG are all examples of simple α-hydroxy carboxylic acids capable only of binding lanthanide ions in a bidentate fashion.[16] On the other hand, L-MAL is capable of three bonding modes: (a) bidentate coordination at the α-hydroxycarboxyl functionality, (b) bidentate coordination via the two carboxyl groups, and (c) terdentate coordination using the hydroxy and both carboxyl groups. As the malic acid ligand has been observed to bind as a simple hydroxycarboxylic acid in some instances,[9] it is clear that ionization of the hydroxyl proton is not required for this group to participate in bonding. Full understanding of the nature of the L-MAL bonding can only come after a study of the simple HXCA complexes (bonding mode a) and L-ASP complexes (bonding mode b, discussed elsewhere in detail[11]).

Tb(MDL)$_2$(HXCA) Studies. Addition of any of the chiral HXCA ligands to a Tb(MDL)$_2$ solution invariably led to the observation of strong optical activity, an example of which is shown in Figure 1. The CPL line shape did not vary with the identity of the HXCA ligand, and no essential differences were noted when comparing the results obtained with different MDL systems. Generally, CPL first appeared within the emission spectra between pH 3.0 and 4.0, rapidly increased in magnitude (as measured by the dissymmetry factor) between pH 4.0 and 6.0, and then leveled off above this pH. No change in CPL magnitudes were observed to at least pH 10.0, where apparently the complexes begin to hydrolyze and the CPL decreases in intensity. This final value was found to vary with HXCA concentration, but at sufficiently high HXCA:Tb ratios no further increase could be obtained.

The dissymmetry factors obtained at high HXCA concentrations imply full formation of the Tb(MDL)$_2$(HXCA) complex and permit the calculation of equilibrium constants

$$K_1 = \frac{[\mathrm{Tb(MDL)_2(HXCA)}]}{[\mathrm{Tb(MDL)_2}][\mathrm{HXCA}]} \qquad (5)$$

according to our methods.[11] The limiting dissymmetry factors and association constants obtained for the ODA and SSA complexes are located in Table I. One may note that the constants obtained for SSA are an order of magnitude greater than those found for either ODA or dipicolinic acid (DPA),[9]

---

(13) Das Gupta, A.; Richardson, F. S. *Inorg. Chem.* **1981**, *20*, 2616.

(14) Richardson, F. S. *Inorg. Chem.* **1980**, *19*, 2806.

(15) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1974.

(16) Choppin, G. R.; Friedman, H. G. *Inorg. Chem.* **1976**, *5*, 1599.

Table I. Formation Constants and Limiting Dissymmetry Factors Associated with the Tb(MDL)$_2$(HXCA) Complexes[a]

	MDL			MDL	
	ODA	SSA		ODA	SSA
	(a) Formation Constants				
L-MAN	22	308	L-LAC	18	341
L-ARG	26	325			
	(b) Limiting Dissymmetry Factors[b]				
L-MAN	+0.0654	+0.0874	L-LAC	+0.0604	+0.0784
	−0.0704	−0.0944		−0.0699	−0.0860
L-ARG	+0.0811	+0.101			
	−0.0932	−0.112			

[a] No results are reported for MDL = IDA as precipitation was observed in solutions containing large Tb(III):HXCA ratios. [b] For these HXCA complexes, the positive CPL was noted at 542 nm within the 4-5 band system and the negative CPL was located at 545 nm.

Table II. Formation Constants and Limiting Dissymmetry Factors Associated with the Tb(APC)(HXCA) Complexes

	APC		
	EDTA	HEDTA	CDTA
	(a) Formation Constants		
L-MAN	5.86	5.60	5.51
L-ARG	12.04	14.09	9.25
L-LAC	4.86	5.22	4.57
	(b) Limiting Dissymmetry Factors[a]		
L-MAN	+0.0472	+0.0405	+0.0454
L-ARG	+0.0459	+0.0438	+0.0378
L-LAC	+0.0315	+0.0336	+0.0298

[a] The limiting dissymmetry factors were obtained at the 542-nm component of the 4-5 Tb(III) band system.

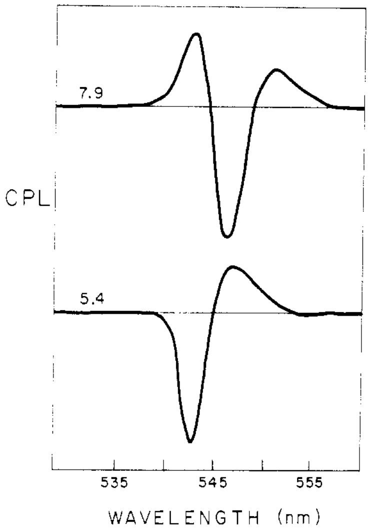

Figure 2. CPL spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ transition of Tb(ODA)$_2$(L-MAL), corresponding to a Tb:MAL ratio of 1:2.5. Spectra are shown for pH 5.4 (lower) and pH 7.9 (upper).

Table III

Formation Constants and Limiting Dissymmetry Factors Associated with the Tb(MDL)$_2$(L-MAL) Complexes at Low pH Values

MDL	K_1	dissymmetry factor (547 nm)
ODA	125	−0.0308
IDA	162	−0.0260
SSA	110	−0.0613

Formation Constants and Limiting Dissymmetry Factors Associated with the Tb(APC)(L-MAL) Complexes

PAC	K_1	dissymmetry factor (542 nm)
EDTA	1403	+0.0402
HEDTA	3583	+0.0332
CDTA	1138	+0.0360

and this observation reflects an increased availability of the Tb(III) ion when the achiral ligand binds only in a bidentate manner (both ODA and DPA bind in a terdentate manner).

Formation of Tb(MDL)$_2$(HXCA) complexes at high concentrations of HXCA was considered in the data analysis. However, the concentrations computed by using such associations were not found to be reasonable, and the formation constants computed in such a calculation were not constant with HXCA concentration. Thus, the formation of the 1:2:2 ternary Tb/MDL/HXCA complexes were not considered further, and all data were interpreted in terms of the 1:2:1 ternary complexes.

Limiting dissymetry factors could not be obtained for the IDA complexes, as precipitation of Tb(HXCA)$_3$ complexes was noted at high ligand:metal ratios. This strongly binding ligand only can bond in a terdentate manner at high pH (after ionization of the ammonium group), and apparently IDA cannot compete with large amounts of HXCA for access to the Tb(III) ion at pH 6.0–8.0.

Tb(APC)(HXCA) Studies. Addition of any of the HXCA ligands to Tb(EDTA), Tb(HEDTA), or Tb(CDTA) also led to the observation of strong optical activity. The CPL line shapes obtained of this sequence of compounds were found to be absolutely identical with those just shown for the Tb(MDL)$_2$(HXCA) compounds, indicating that the HXCA chelate ring must adopt a very similar conformation in both situations. This observation is in marked contrast to the situation in the L-ASP complexes, where a large conformational change was observed in passing from the Tb(MDL)$_2$ to the Tb(APC) complexes.[11]

In Table II, we have listed the limiting dissymmetry factors obtained for the Tb(APC)(HXCA) compounds, and these are found to be somewhat smaller than those found for the Tb(MDL)$_2$ compounds. This difference indicates that while the chelate conformations are quite similar, they cannot be identical in the two systems. The concentration dependence of the optical activity permitted the computation of formation constants, and these are also located in Table II. The smaller formation constants found for the APC complexes relative to those of the analogous MDL compounds may indicate that the HXCA binding site is less accessible in the APC series. It is also noted that the Tb(HEDTA) complexes display the largest affinity for the HXCA ligands, and this trend probably reflects the existence of a larger binding "pocket" at the Tb(III) ion. In addition, the neutrality of the Tb(HEDTA) compound will make this species a better Lewis acid than the other negatively charged Tb(APC) compounds.

Tb(MDL)$_2$(MAL) Studies. While addition of L-MAL to a solution of any of the Tb(MDL)$_2$ complexes resulted in the observation of optical activity, the lines shapes observed (see Figure 2) were found to be totally different from those found with the simple HXCA ligands. At the same time, the TL spectra of the different systems were essentially superimposable. However, the CPL line shape shown in Figure 2 is not totally new and is found to be identical with that obtained for Tb(MDL)$_2$(ASP).[11] Thus, it may be concluded that for MDL = ODA, IDA, or SSA, the MAL ligand binds to the Tb(III) ion in a bidentate manner between the two ionized carboxylated groups (this is bonding mode b as described earlier). This trend is in marked contrast to our previous work involving DPA complexes: in this study, the MAL ligand bound Tb(III) in exactly the same fashion as did the simple HXCA ligands (bonding mode a).[9]

While the bonding mode may differ, the pH dependence of the CPL intensities follows the trends discussed for the simple

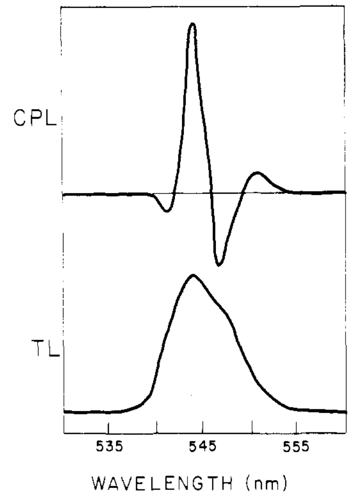

Figure 3. TL (lower) and CPL (upper) spectra obtained within the $^5D_4 \rightarrow {}^7F_5$ band system of Tb(CDTA)(L-MAL). The spectra were obtained at a Tb:MAL ratio of 1:3.3 and at a solution pH of 7.5.

HXCA ligands. Limiting dissymmetry factors and formation constants were calculated in the usual manner, and these may be found in Table III.

Raising the solution pH of the Tb(MDL)$_2$(MAL) complexes above 8.0 was found to result in complete inversion of the CPL spectra, and a new spectral line shape results (also shown in Figure 2). This line shape resembles that of Figure 1, but the wavelengths of the CPL maxima are totally different in the two situations. It is reasonable to assume that this chiroptical change is associated with a transformation of the MAL bonding mode from bidentate to terdentate (bonding mode c). The same CPL inversion was noted at high pH values with Tb(DPA)$_2$(MAL), and the final line shapes were identical with those of the present work.[6] Thus, while the identity of the MDL ligand dictates the bidentate ligand bonding mode, such variability was not observed when MAL bound in a terdentate mode.

Tb(APC)(MAL) Studies. Not unexpectedly, addition of L-MAL to a solution of Tb(APC) led to the observation of optical activity within the Tb(III) luminescence. An example of the CPL line shape is provided in Figure 3, and it may be noted that this line shape has no parallel in any of the HXCA or MAL spectra. However, the line shape is absolutely identical with that we have obtained for Tb(APC)(ASP),[11] and thus we conclude that in the APC compounds the L-MAL ligand again binds in a purely bidentate manner between the two ionized carboxylate groups. Raising the solution pH up to 10.0 resulted in no alteration of the basic line shape, and thus it may be concluded that in the Tb(APC) complexes L-MAL bonds exclusively in the bidentate manner we have classified as mode b.

Unlike the situation in the preceding systems, very small amounts of MAL led to limiting values for the dissymmetry factors. These quantities and association constants computed in the usual fashion are found in Table III. The values indicate that the bonding is considerably stronger than any of the HXCA equilibrium constants previously encountered. As before, the Tb(HEDTA) ligand displays the largest affinity for the L-MAL ligand.

Summary

The work just detailed demonstrates the usefulness of CPL spectroscopy as a means to characterize the nature of ligand bonding in lanthanide complexes. The ligand conformation associated with complexation at an α-hydroxycarboxyl group apparently is not affected by the presence of other achiral ligands. However, bidentate attachment of a succinate-type ligand (bonding mode b) represents the formation of a larger chelate ring, and the variability in CPL spectra demonstrates that the conformational effects provided by such a system may be varied upon changing the achiral ligands in the complex.

Of particular interest is the variability in bonding mode that can be exhibited by the malic acid ligand. As far as the incoming malate ligand is concerned, the Tb(MDL)$_2$ and Tb(APC) complexes would appear to be identical in the charge distribution and number of ligand positions already occupied. However, the size of the available coordination sites would be expected to differ in that two MDL ligands would have much more freedom to exhibit fluxional behavior on the surface of the Tb(III) ion than would a single APC ligand. Thus, one would predict that a greater steric problem would exist for the incoming malate ligand in the Tb(MDL)$_2$ complexes relative to the Tb(APC) complexes and that the ligand would choose to bind in the manner that presents the least amount of constraint. Should the steric problem not exist, then the ligand would bind in the manner dictated by thermodynamic considerations.

Invariably, the formation constants (k_1) associated with the production of the ternary complexes from coordinated Tb(III) are reduced from the analogous k_1 values obtained in the addition of HXCA ligands to the Tb(III) aquo ion. One may attribute this reduction to a combination of electronic and statistical effects: a reduced positive charge on the Tb(III) ion combined with a decreased number of available coordination sites on the Tb(III) ion.

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

Registry No. Tb(ODA)$_2$(L-MAN)$^{2-}$, 86480-68-4; Tb(ODA)$_2$(L-ARG)$^{2-}$, 86480-69-5; Tb(ODA)$_2$(L-LAC)$^{2-}$, 86497-04-3; Tb(SSA)$_2$(L-MAN)$^{2-}$, 86480-70-8; Tb(SSA)$_2$(L-ARG)$^{2-}$, 86480-71-9; Tb(SSA)$_2$(L-LAC)$^{2-}$, 86480-72-0; Tb(EDTA)(L-MAN)$^{2-}$, 86497-05-4; Tb(EDTA)(L-ARG)$^{2-}$, 86480-73-1; Tb(EDTA)(L-LAC)$^{2-}$, 86480-74-2; Tb(HEDTA)(L-MAN)$^-$, 86497-06-5; Tb(HEDTA)(L-ARG)$^-$, 86480-75-3; Tb(HEDTA)(L-LAC)$^-$, 86480-76-4; Tb(CDTA)(L-MAN)$^{2-}$, 86480-77-5; Tb(CDTA)(L-ARG)$^{2-}$, 86480-78-6; Tb(CDTA)(L-LAC)$^{2-}$, 86480-79-7; Tb(ODA)(L-MAL)$^{3-}$, 86480-80-0; Tb(IDA)$_2$(L-MAL)$^{3-}$, 86480-81-1; Tb(SSA)$_2$(L-MAL)$^{3-}$, 86480-82-2; Tb(EDTA)(L-MAL)$^{3-}$, 86480-83-3; Tb(HEDTA)(L-MAL)$^{2-}$, 86480-84-4; Tb(CDTA)(L-MAL)$^{3-}$, 86480-85-5.