Absolute Configuration Assignment of D_3-Symmetric Lanthanide Complexes Based on Circular Dichroism Induced by Interaction with a Chiral Probe

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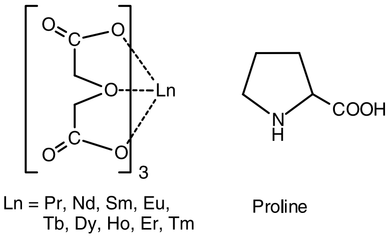
The supramolecular interaction between an achiral chromophoric host and a chiral nonchromophoric guest has proven to be a useful method for probing the chirality of the guest molecule. A number of achiral organic molecules including calixarenes, porphyrins, and resorcinarenes has been developed as molecular hosts, and they have been successfully used as circular dichroism (CD) probes for sensing the chirality of various guest such as amines, amino acids, sugars, glycols, and others.[1] The ability of lanthanides to form highly coordinated complexes has been used for extraction and transport of unprotected amino acids as well as for chirality sensing of amino alcohols by tris(β-diketonato)lanthanide(III) complexes.[2]

While sensing the chirality of the bound guest molecule has been the main focus in host–guest studies, the reverse approach, namely probing the chirality of a host molecule, is in principle also possible. The lanthanide tris complexes with 2,2′-oxydiacetic acid (oda), shown in Scheme 1, are chiral due to the D_3 symmetry arrangement of the three oda ligands around the central metal ion. However, the complexes exist in a racemic equilibrium that is not resolvable by classical methods.[3] Since the oda ligand is achiral, the circular dichroism studies on these lanthanide complexes in solution have not yet been possible. Extensive theoretical studies, as well as CD studies involving single crystals of $[Ln(oda)_3]^{3-}$complexes, shed more light on their optical activity, but the correlation of absolute configuration and the CD properties still remains a difficult issue.[4] This correlation was established only for one member of the series, $[Eu(oda)_3]^{3-}$, after solving the single crystal X-ray structure and recording CD spectra of the fragments of the same crystal.[5] However, for the other ions of the lanthanide series and particularly in solution, the correlation between their absolute configuration and the chiroptical properties, that is, which configuration gives which sign of the CD signal, is still missing.



Scheme 1. Structures of the $[Ln(oda)_3]^{3-}$ complexes (left) and of proline (right).

In this study, nine lanthanide complexes of the $[Ln(oda)_3]^{3-}$ series were examined (Ln = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, or Tm). The complexes are chromophoric but CD silent, due to the presence of equal amounts of Δ and Λ enantiomers in the solution. The chiral L- and D-proline were chosen as a nonchromophoric and CD-silent guest under the conditions employed (> 360 nm). While the addition of racemic DL-proline did not induce any CD signals in $[Pr(oda)_3]^{3-}$, Figure 1 shows that the addition of optically active D- and L-proline induced the CD signals of equal intensity, but of the opposite sign. The same effect was observed for the remaining eight complexes in the $[Ln(oda)_3]^{3-}$ series. The introduction of the optically active probe to a solution containing a kinetically labile racemic lanthanide complex obviously induces a shift in the racemic equilibrium, resulting in the excess of one $[Ln(oda)_3]^{3-}$ enantiomer over the other. This shift in equilibrium is known as the Pfeiffer effect,[6] and has been extensively studied for transition-metal complexes[7] and more recently for lanthanide complexes.[8]

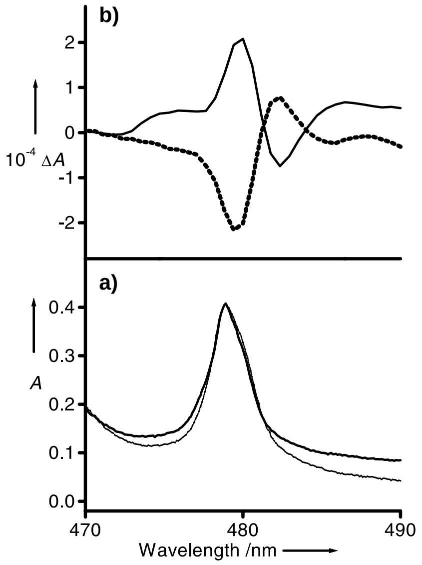


Figure 1. a) Absorption and b) CD spectra of the $^3P_0 \leftarrow {}^3H_4$ transition of $[Pr(oda)_3]^{3-}$ in the presence of L-proline (——) and D-proline (- - - -). In this measurement, the concentration of $[Pr(oda)_3]^{3-}$ was 5×10^{-2} M and that of proline was 2 M.

The question is, however, which enantiomer of the $[Ln(oda)_3]^{3-}$ has been formed in excess upon addition of L-proline and which upon addition of D-proline? Comparison of

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the solution CD spectrum of the $[Eu(oda)_3]^{3-}$ in the presence of D-proline with the CD spectrum of the single crystal of Δ-$[Eu(oda)_3]^{3-}$, revealed that the CD signal at 526 nm corresponding to $^5D_1 \leftarrow {^7F_0}$ transition has negative sign in both cases.[3] This clearly suggests that addition of D-proline to the racemic mixture of $[Eu(oda)_3]^{3-}$ resulted in excess of Δ-$[Eu(oda)_3]^{3-}$, characterised by the negative CD signal at 526 nm. Thus, the positive CD at the same wavelength, appearing upon addition of L-proline, should correspond to an excess of Λ-$[Eu(oda)_3]^{3-}$. We restricted ourselves here to the analysis of the $^5D_1 \leftarrow {^7F_0}$ transition, rather than analysing the whole CD spectrum, because only the $^5D_1 \leftarrow {^7F_0}$ and the $^5D_2 \leftarrow {^7F_0}$ were treated in detail in ref. [3]. Moreover, the $^5D_2 \leftarrow {^7F_0}$ transition has a g factor which is about three times smaller than that of the $^5D_1 \leftarrow {^7F_0}$, so it is very difficult to obtain a relaible value for the g factor of the latter transition. However, a look at the different CD spectra shows that all the transitions change sign when going from D- to L-proline. As previous studies have shown that the nature of the outer-sphere interactions in nine-coordinate lanthanide complexes is independent on the nature of the lanthanide ion,[9] one can make a general conclusion that addition of D-proline to the racemic mixture of any member of $[Ln(oda)_3]^{3-}$ series results in excess of the Δ-enantiomer, while addition of L-proline results in excess of the Λ-enantiomer of the $[Ln(oda)_3]^{3-}$ complex. Table 1 shows characteristic CD signals of the Λ-enantiomer for the series of $[Ln(oda)_3]^{3-}$ complexes. The transitions shown in Table 1 have the same intensity but the opposite sign in the Δ-enantiomers. Though optical spectra of the lanthanide ions contain several transitions in the visible region, for clarity we only show the CD data of either hypersensitive or well-isolated transitions,[10] for which the sign of the CD signal could be easily determined. Even though the absorption coefficients of f→f transitions are very small ($\varepsilon < 10\,\text{M}^{-1}\,\text{cm}^{-1}$), we show that it is possible to probe the coordination sphere of lanthanide ions under the conditions applied. The excess of proline is not likely to replace tridentate oda ligands from the first coordination sphere of $[Ln(oda)_3]^{3-}$ complexes. This is supported with the observation that various proline esters, which unlike proline are not capable of acting as bidentate ligands to Ln^{3+}, nonetheless induce CD signals of comparable intensity as proline.[11]

Table 1. *Selected CD data of $[Ln(oda)_3]^{3-}$ complexes with L-proline in H_2O.*[a]

Ln	λ [nm]	transition	sign[b]	g_{abs}[c]
Pr	479	$^3P_0 \leftarrow {^3H_4}$	(+)	8.2×10^{-4}
Nd	581	$^4G_{7/2},{^4G_{5/2}} \leftarrow {^4I_{9/2}}$	(−)	6.2×10^{-4}
Sm	404	$^6P_{3/2} \leftarrow {^6H_{5/2}}$	(−)	1.6×10^{-4}
Eu	526	$^5D_1 \leftarrow {^7F_0}$	(+)	2.8×10^{-3}
Tb	362	$^5G_4,{^5D_2},{^5L_9} \leftarrow {^7F_6}$	(−)	2.0×10^{-3}
Dy	453	$^4G_{11/2},{^4I_{15/2}} \leftarrow {^6H_{15/2}}$	(+)	2.5×10^{-2}
Ho	417	$^5G_5 \leftarrow {^5I_8}$	(−)	4.0×10^{-4}
Er	520	$^4G_{11/2} \leftarrow {^4I_{15/2}}$	(+)	1.8×10^{-4}
Tm	794	$^3H_4 \leftarrow {^3H_6}$	(−)	8.6×10^{-4}

[a] Conditions: Concentration $[Ln(oda)_3]^{3-}$ was 0.1 M, L-proline was 4 M, pH 10.0. [b] In the case of a composite CD signal, the sign of the most intense peak is considered. [c] $g_{abs} = \Delta A/A$ (dissymmetry factor; ratio of the CD intensity to the absorbance).

Although the addition of chiral proline clearly results in an equilibrium shift in racemic $[Ln(oda)_3]^{3-}$ complexes, it is not obvious which interactions are responsible for the recognition between the proline and the lanthanide complex. Attempts to observe the equilibrium shift by using other chiral amino acids, such as alanine, lysine, or glutamic acid, did not result in detectable CD signals. Therefore, the electrostatic interactions, which would involve a negatively charged $[Ln(oda)_3]^{3-}$ complex and the positively charged amino part of the amino acid, cannot be solely responsible for the association and some other forces, either hydrogen bonded or hydrophobic in nature, must play an important role. In a study involving the adduct formation between L-proline and terbium tris(2,6-pyridinedicarboxylate), $[Tb(dpa)_3]^{3-}$, Brittain proposed that the hydrogen bonding between L-proline and the dpa π orbitals was responsible for the formation of the adduct.[8c] Furthermore, in order for the Pfeiffer effect to be measured, it was proposed that the chelate rings on the D_3 lanthanide complex must contain aromatic rings. However, we show that $[Ln(oda)_3]^{3-}$ containing nonaromatic oda ligands are also capable of recognizing proline, and that other types of hydrogen bonding, rather than those involving π orbitals on the chelator, could be responsible for the recognition between the lanthanide complex and the chiral probe. Further characterization of the nature of supramolecular interaction is currently under way.

The interaction between a host and a guest, where at least one component is chiral, can also produce an induced circular dichroism, in addition to the inherent circular dichroism of the chiral compound. Moreover, it is very difficult to predict the sign of the induced circular dichroism, since it depends very much on the structure in the complex. One could argue that the CD signal which is observed is due to some new chiral "compound" which results upon mixing the complex and proline, and not due to the shift in equilibrium. However, based on findings for transition metal complexes, it has been assumed by Brittain and Riehl,[8] who examined interactions of chiral compounds with analogous $[Ln(dpa)_3]^{3-}$ complexes, that addition of a chiral compound to a kinetically labile racemic mixture of metal complexes may lead to the Pfeiffer effect, namely displacement of the equilibrium existing between the enantiomers of the racemic complex and not to induced circular dichroism. Riehl et al. proved the assumption that the Pfeiffer effect is responsible for the occurrence of CD signals in racemic lanthanide complexes, by measuring CPL spectra of a racemic $[Tb(dpa)_3]^{3-}$ solution in which an optically active excited population was generated by employing a circularly polarized excitation beam.[8f] We believe that one can safely assume that the Pfeiffer effect is also responsible for the detection of optical activity in a solution containing $[Ln(oda)_3]^{3-}$ and proline.

Perturbing the equilibrium in racemic $[Ln(oda)_3]^{3-}$ complexes by adding the chiral probe enabled us to obtain chiroptical information unobtainable by classical methods. Studies on circularly polarized luminescence (CPL) showed that addition of chiral compounds to $[Ln(dpa)_3]^{3-}$ complexes does not perturb the coordination geometry of the lanthanide ion, and that the chiroptical properties of the supramolecular adduct are same to those of the pure enantiomers, even though these enantiomers cannot be resolved by classical methods.[9b] Therefore, the data presented in this work may be used as "fingerprints" for the determination of the absolute configuration for the series of [Ln(oda)$_3$]$^{3-}$ complexes. The novelty of this communication is the utilization of the simple and available circular dichroism method for the detection of the Pfeifer effect in a series of lanthanide complexes, as the rather complicated and not so easily available CPL method, which has been almost exclusively used until now, is limited to only a few luminescent ions in the lanthanide series.

Experimental Section

The [Ln(oda)$_3$]$^{3-}$ complexes were synthesized according to a literature procedure.[3a] The CD spectra were recorded with a circular dichroism spectrometer (AVIV 62DS); the UV/Vis spectra were recorded under the same conditions (Shimadzu UV-3100).

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A Dendritic Antenna for Near-Infrared Emission of Nd^{3+} Ions

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Luminescent materials find an ever expanding number of applications. A particularly interesting class of luminescent compounds is that of lanthanide ions because of their long-lived and linelike emission bands, which cover a spectral range from the near-UV to the visible and the near-IR region.[1] Direct excitation of lanthanide ions, however, is difficult because of the forbidden nature of their electronic transitions.[2] In order to overcome this difficulty, the luminescent lanthanide ions are usually coordinated to ligands containing organic chromophores whose excitation, followed by energy transfer, causes the sensitized luminescence of the metal ion.[3] Another drawback of lanthanide luminescence is the quenching of the emitting excited state by energy loss to high frequency vibrational modes of the solvent,[2] which can be at least in part overcome by enclosing the metal ion in suitably designed ligands.[3, 4] Most of the investigations in the field of luminescent lanthanide complexes have been devoted to europium(III) and terbium(III) compounds, which emit in the visible spectral region,[3] and are used as sensors[5] and as luminescent labels in fluoroimmunoassays and time-resolved microscopy.[6] Currently much work is being devoted to lanthanide compounds emitting in the near infrared (NIR) region for both fundamental reasons and possible applications in long-range optical data transport.[7–9]

In recent years, it has been shown that suitably designed dendrimers can be used as light-harvesting antennas[10, 11] and as ligands for metal ions.[12] Combining these two concepts, we have now designed a dendrimer which is able to play the role of a ligand for lanthanide ions and is also capable of playing the role of antenna for lanthanide luminescence. In this Communication we report the results obtained with the Nd^{3+} ion, which is one of the most interesting NIR luminescent species.[7–9]

The dendrimer **D** used as a light-harvesting ligand for Nd^{3+} luminescence is shown in Scheme 1. It consists[12e] of a benzene

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