Abstract: The geometry and the electronic structure of chiral lanthanide(III) complexes are traditionally probed by electronic methods, such as circularly polarised luminescence (CPL) and electronic circular dichroism (ECD) spectroscopy. The vibrational phenomena are much weaker. In the present study, however, significant enhancements of vibrational circular dichroism (VCD) and Raman optical activity (ROA) spectral intensities were observed during the formation of a chiral bipyridine–EuIII complex. The ten-fold enhancement of the vibrational absorption and VCD intensities was explained by a charge-transfer process and the dominant effect of the nitrate ion on the spectra. A much larger enhancement of the ROA and Raman intensities and a hundred-fold increase of the circular intensity difference (CID) ratio were explained by the resonance of the $\lambda=532$ nm laser light with the $^{7}F_{0} \rightarrow ^{5}D_{0}$ transitions. This phenomenon is combined with a chirality transfer, and mixing of the Raman and luminescence effects involving low-energy $^{7}F$ states of europium. The results thus indicate that the vibrational optical activity (VOA) may be a very sensitive tool for chirality detection and probing of the electronic structure of EuIII and other coordination compounds.

Introduction

Coordination chemistry of chiral lanthanide complexes constantly attracts interest because of the many applications in chemistry and material science, including chiral NMR shift agents, enantioselective catalysts, reagents, molecular magnets and labels for chemical imaging.[1–6] Unique spectroscopic properties of trivalent lanthanides ions are, given by their electronic structure, supporting many low-energy electronic levels and various spin polarisations.[5,6] Chiral spectroscopic methods are thus natural tools casting light on the structure of these compounds. Elucidation of the electronic structure, geometry and internal energy transfer are important for rational design of luminescent molecular probes.[7]

In the present study, we report an unusually large vibrational optical activity of a bipyridine–EuIII complex. The results suggest that similar enhancement can be generally useful in chiroptical studies of other coordination compounds as well. They also reveal fundamentally different properties of various kinds of optical activity.

Chiroptical spectroscopic methods are based on interaction of the sample with left- and right-circularly polarised light.[8] The electronic circular dichroism (ECD, often referred to as ultraviolet (UV) CD) monitors the absorption difference. It is currently the most frequently applied technique. It usually detects transition from the electronic ground state to an electronic excited state. However, the ECD dissymmetry factor ($g$) defined as the ratio of ECD over the total absorption is rather small; for lanthanide complexes $g$ is approximately $10^{-3}$.[9]

An analogous technique, circularly polarised luminescence (CPL), detects transitions from the excited states. For lanthanide(III) compounds CPL appears more convenient than ECD, because of the high values of the dissymmetry factor (ratio of CPL and the total emission in this case). For a tetrakis((−)-3-heptafuorobutyl)lyrylcamphorato)EuIII complex with an encapsulated CsI ion comprising Cs–FC (fluorocarbon) interactions, for example, Kaizaki and co-workers reported a $g$ value as large as 1.38.[10] However, in the UV spectral region, the number of resolved transitions is rather small and the spectral bands are broad because of the inhomogeneous broadening.

Spectra of the vibrational optical activity (VOA) usually provide more and better resolved spectral bands than the electronic methods.[11] Vibrational circular dichroism (VCD) has been traditionally used to detect the conformation of biopolymers, such as proteins and nucleic acids.[12–15] During the last decade, VCD applications for coordination compounds have
been reported as well, and brought about interesting information about the structure of many complexes.\textsuperscript{\cite{30–34}} For example, VCD shapes of tetrakis(\textpm)-3-heptfluorobutylyryl(camphorato)Ln\textsuperscript{III} complexes were found sensitive to alteration of encapsulated alkali metal ions.\textsuperscript{\cite{31}} A study on Cs\textsuperscript{I} ion-containing Ln\textsuperscript{III} complexes linked the VCD intensities with the parity of the total orbital angular momentum (L).\textsuperscript{\cite{22}} Lanthanide ions also sometimes cause an enhancement of the VCD intensities, whereas the positions and relative magnitudes of the bands are conserved.\textsuperscript{\cite{24}} In the case of the bipyridine complex described in the present study, however, we observe both VCD enhancement and intensity distortion. Rather surprising was the strong participation of the nitrate ions in the spectra, including induced VCD.

The other form of VOA, that is, vibrational Raman optical activity (ROA) detects intensity differences in scattering of right- and left-circularly polarised light. Typical ROA applications are similar as for VCD, including induced VCD. enhancement and intensity distortion. Rather surprising was described in the present study, however, we observe both VCD enhancement and intensity distortion. Rather surprising was the strong participation of the nitrate ions in the spectra, including induced VCD.

The experiments take minutes instead of days.

In the present study we report spectra of a bipyridine–Eu complex (Figure 1), which well document the different possibilities of ECD, VCD and ROA spectroscopy for chiral coordination compounds, in particular the possibility to monitor the complexation process by the VOA enhancement. The bipyridine ligand itself has found many applications in coordination chemistry.\textsuperscript{\cite{32–35}} The three techniques well complement each other, with ECD being sensitive to electronic transitions of the bipyridine, but rather insensitive to the changes caused by the complexation. By VCD one can see the vibrational bands of the bipyridine, the relative intensities of which are distorted and enhanced by a factor of ten in the complex. Additionally, the nitrate ion participates both on IR and VCD. Finally, compared to the free ligand, the ROA spectra of the complex are enhanced about hundred times and are dominated by the low-energy electronic circular polarised luminescence induced in the central Eu\textsuperscript{III} ion.

**Results and Discussion**

**UV/Vis and ECD spectra**

Experimental absorption and ECD spectra of the free ligand and the enantiomers of the complex are plotted in Figure 2. The calculated spectra of the monomer and the dimer ligand are presented in Figure 3. No visible absorption or ECD bands were observed above $\lambda = 400$ nm. In the experiment, the bipyridine ligand exhibit an absorption band at $\lambda = 288$ nm, which is assigned to a n–π* transition within the aromatic residues, which is associated with an ECD band at $\lambda = 284$ nm, negative for the $R$ enantiomer. The negative ECD band at $\lambda = 246$ nm and a positive one at $\lambda = 227$ nm are associated with π–π* transitions; the former corresponds to the $\lambda = 247$ nm absorption band. For the latter only a shoulder on the absorption background can be recognised. These characteristics are conserved after the complexation, which causes minor changes in the absorption and ECD spectral shapes only. This is in contrast with a former study concerning the same bipyridine ligand chelating with a Cu\textsuperscript{II} ion.\textsuperscript{\cite{35}} For the copper, its d-orbital electrons contributed a red shift to the π–π* transitions in the bipyridine. The indifference of the spectra of the bipyridine to the presence of europium corresponds to the electronic structure of the lanthanide, where the 4f and 5d electrons are shielded by the 6s shell.
The observed electronic spectra are roughly consistent with the theoretical modelling (Figure 3), as the absorption curves of the monomer and the dimer are similar in shape, differing mostly around $\lambda = 210$ nm. Except of the large negative signal at $\lambda = 329$ nm the calculated ECD spectrum of the dimer does not dramatically differ from that of the monomer. The calculated absorption at $\lambda = 337$ nm is much stronger than the observed one (the corresponding experimental peak is at $\lambda = 288$ nm), most probably because of the error of the time-dependent (TD) DFT method. The differences between the theory and the experiment can also be in part attributed to the simplification used in the modelling, that is, the lack of the metal and the absence of conformational averaging. Note that the adopted geometry was based on an educated guess (X-ray) only. In particular, many orientations of the ligands (e.g., other than those shown in Figure 1) are possible, which would further limit the exciton coupling and the ECD intensity in the complex. We can thus conclude that the ECD signal of the ligand is to be primarily determined internally; by an interaction of the bicyclic system and the pyridine ring system; and that it is not much changed during the complexation process.

**IR and VCD spectra**

Experimental IR and VCD spectra of the ligand (reported previously) and the complex are compared with simulations in Figures 4 and 5, respectively. For the free ligand, the strongest IR and VCD bands around $\tilde{\nu} = 1463$ and 1387 cm$^{-1}$ originate from C–H bending motions; vibrations within the range $\tilde{\nu} = 1700$–1300 cm$^{-1}$ are most connected with the bipyridine ring.

The complex exhibits much stronger IR and VCD intensities than the ligand (compare the y scales). The absorption within the range $\tilde{\nu} = 1500$–1300 cm$^{-1}$ was so strong that it inhibited VCD measurement in this region; a lower-concentration experiment was not successful either. The nitrate ions present in the complex seem to be responsible for many of the IR and VCD spectral changes, contributing strongly to the absorption intensities around $\tilde{\nu} = 1486$ and 1464 cm$^{-1}$ ($\nu_1$(NO$_3$), symmetric stretching vibration, calculated at $\tilde{\nu} \approx 1608$ and 1582 cm$^{-1}$), $\tilde{\nu} = 1310$ cm$^{-1}$ ($\nu_4$, symmetric stretching vibration, calculated at $\tilde{\nu} \approx 1364$ and 1354 cm$^{-1}$) and $\tilde{\nu} = 1033$ cm$^{-1}$ ($\nu_2$, symmetric stretching vibration, calculated at $\tilde{\nu} \approx 1078$ cm$^{-1}$).
IR and VCD intensities stemming from the pyridine ring and other vibrations of the ligand are enhanced as well, such as peaks around (in the experiment) $\tilde{v} = 1604, 1589, 1571$ and 1553 cm$^{-1}$. The VCD signal of the complex within the range $\tilde{v} = 1300-950$ cm$^{-1}$ belongs primarily to the pinene moiety.

Both the IR and VCD intensities of the complex are enhanced by approximately 5–10 times if compared with the free ligand; therefore, the average VCD disymmetry factor (≈ 3 $\times$ 10$^{-4}$) stays about the same. However, unlike for the ligands (Figure 4), the simulated VCD spectrum of the complex (Figure 5) lacks the band-to-band correspondence to the experiment, most probably because of the conformational averaging and electronic–vibrational interactions not included in the present model.

The results are consistent with data obtained for other chiral coordination compounds previously.$^{[24, 39–41]}$ The generally accepted mechanism of VCD enhancement through a charge-transfer process and interaction of low-lying electronic states of the metal with the vibrational states of the ligand$^{[20]}$ is quite plausible for the bipyridine–Eu$^3^+$ complex, as the Eu$^{3+}$ ion possesses many low-energy electronic levels comprising the IR region within $\tilde{v} = 3500$–800 cm$^{-1}$.$^{[24, 42, 43]}$ For example, the $^1F_2 \rightarrow ^1F_2$ transition occurs around $\tilde{v} = 1100$ cm$^{-1}$ and has been predicted to produce circular dichroism (ECD) in chiral complexes.$^{[43]}$ Indeed, in our case, the VCD peaks at $\tilde{v} = 996$ and 985 cm$^{-1}$ exhibited both large intensities and disymmetry factors (≈ 10$^{-3}$), more intensive than a previous Eu$^{3+}$ F–F electronic CD band in the region $\tilde{v} = 3500$–3000 cm$^{-1}$.$^{[44]}$

Clearly, also the nitrate ion strongly participated in the IR and VCD spectra of the complex, through a charge-transfer process, chirality induction and direct coupling of nitrate and ligand vibrational modes. An indication of the charge transfer and enhancement of the electron flow by the metal is illustrated in Figure 6, where the magnitude of the polar and axial tensors for each atom is plotted in dependence on the distance from the Eu$^{3+}$ ion. Note that these tensors determine atomic contributions to the IR and VCD intensities. Clearly, the tensor magnitudes significantly increase in the vicinity of europium, in accord with the resultant intensity enhancement observed in Figures 4 and 5.

Currently a direct resonance of the electronic levels of europium with the vibrational ones cannot be modelled theoretically; however, its role seems minor, if favour of the charge transfer, which is included in the modelling, and seems sufficient to explain most of the observed spectral features. The role of the charge transfer in metal complexes for VCD enhancement has also been confirmed by theoretical modelling in previous studies.$^{[41, 45]}$

**Raman and ROA/CPL spectra**

The experimental Raman and ROA spectra of the free ligands are compared to the simulated curves in Figure 7. The simulation reproduces most experimental features, including positions and signs of the ROA bands. For example, the experimental peaks at $\tilde{v} = 1607, 1593$ (shoulder) and 1573 cm$^{-1}$ originate in the aromatic double bonds stretching, and are simulated at $\tilde{v} = 1622, 1604$ and 1580 cm$^{-1}$. Many bands within the range $\tilde{v} = 1239$–1492 cm$^{-1}$ have often contributions from C–H bending and C–C stretching vibrations, coupled with other vibrational modes. A very distinct peak at $\tilde{v} = 997$ cm$^{-1}$ (calculated at $\tilde{v} = 1010$ cm$^{-1}$) is assigned to a pyridine-ring deformation. Interestingly, below $\tilde{v} = 1100$ cm$^{-1}$ most of the other Raman bands are rather weak (compare the inset zoomed spectra in Figure 7), whereas the relative ROA intensities therein are comparable with those in the higher-wavenumber region; the $+/-$ couplet of (5)-bipy at $\tilde{v} = 850$ cm$^{-1}$ even dominates the entire ROA spectrum. The CID ratio of approximately 10$^{-4}$ lies in a range usual for most of organic compounds, and the ROA experiment requires relatively long accumulation time (20 h) and high concentration (0.8 m).

![Figure 6. Dependence of the trace of atomic polar (left, absolute values) and axial (right, local part) tensors on the distance from the europium atom, as calculated for the bipyridine–Eu$^3^+$ complex with (circles) and without (triangles) the europium atom.](image)

![Figure 7. Experimental and calculated Raman (top) and ROA (bottom) spectra of the ligand enantiomers. The experiment was performed in 0.8 m chloroform solutions, the collection time was 20 h, the B3LYP/6-311 + +G(d,p)/CP using CPCM level was used for the calculation.](image)
In comparison with the free ligand, the experimental ROA/CPL and Raman spectra of the bipy–Eu complex presented in Figure 8 are quite different. As observed for similar complexes before,[30,31] the Raman vibrational signal of the ligands is almost invisible as the spectra are dominated by electronic transitions of the europium, with the most intense Raman peak at $\tilde{\nu} = 1928$ cm$^{-1}$. Although empirical models have been proposed,[46] the experimental spectra cannot be reproduced with available software so far. However, based on the crystal field theory and the similarity of Eu$^{3+}$ transitions in different compounds,[47] we can assign the $\tilde{\nu} = 1928$ cm$^{-1}$ band to $^{5}F_{2} \rightarrow ^{5}F_{0}/^{5}F_{1} \rightarrow ^{5}F_{2}$ transitions. This band is accompanied with a strong ROA signal, predominantly positive at $\tilde{\nu} = 1944$ cm$^{-1}$ with a smaller negative lobe at $\tilde{\nu} = 1822$ cm$^{-1}$ for the (R) enantiomer. The maximal CID ratio of about $1.7 \times 10^{-2}$ is also impressive and in combination with the high Raman scattering it enables radically shorter measurement times (down to 16 min) if compared to the free ligand. The electronic europium Raman bands are much broader than slightly interfering solvent vibrational bands (the CHCl$_3$ solvent spectrum is inset at the top of Figure 8).

For somewhat longer accumulation time of two hours, further features are apparent in the Raman and ROA spectra of the complex, as presented in Figure 9. For example, satellite bands at $\tilde{\nu} = 2374, 2252, 2178$ and 1677 cm$^{-1}$ are apparent in the vicinity of the strongest ROA signals at $\tilde{\nu} = 1944$ and 1822 cm$^{-1}$. Within the region $\tilde{\nu} = 600–1000$ cm$^{-1}$ another group of ROA bands (and a Raman band at $\tilde{\nu} = 761$ cm$^{-1}$) appears, which correspond to the $^{5}F_{1} \rightarrow ^{5}F_{2}$ transitions.[42,43] Note that the peak at $\tilde{\nu} = 967$ cm$^{-1}$ is quite close to the VCD band at $\tilde{\nu} = 985$ cm$^{-1}$. The $^{5}F_{2} \rightarrow ^{5}F_{0}$ transition might also contribute to the Raman and ROA spectra around $\tilde{\nu} = 300$ cm$^{-1}$; the signal here is, however, small and obscured by the solvent vibrational bands. Additionally, the spectra suggest that the solvent exhibits a weak ROA signal due to the chirality transfer in this region.

The three types of chiral response (ECD, VCD and ROA/CPL) thus allow us to summarise the observed data in a schematic diagram connecting energy levels of the bipyridine–Eu complex with the spectra in Figure 10. The electronic structure of the bipyridine ligand generating the $\pi-\pi^*$ and n–π$^*$ transitions responsible for the ECD/UV spectra, is not much affected by the presence of the Eu$^{3+}$ ion. Therefore, the spectra of the ligand and the complex are very close (compare Figure 2); in addition, the ECD chirality caused by the ligand–ligand interaction in the complex might be eroded by a conformational averaging.

The VCD and IR spectra (Figure 5) are affected more than the ECD/UV spectra because of the similar energies of the electronic $^1F$ states of the europium and the vibrational levels of the ligand. This is also in agreement with the predicted CD sensitivity of the $^1F_1 \rightarrow ^1F_2$ transition of Eu$^{3+}$.[50] Finally, the Raman and ROA spectra exhibit most spectacular and most complicated effects. The excitation laser light ($\lambda = 532$ nm) is in a near resonance with the $^1F_0 \rightarrow ^1D_0$ or $^1F_0 \rightarrow ^1D_1$ Eu$^{3+}$ transitions[47] and causes a significant boost of the scattering cross section. Measured degree of circularity[48] of these transitions (not shown) is close to zero and suggests that the Raman and ROA are significantly mixed with a luminescence, that is, more intermediate electronic Eu$^{3+}$ states, such as $^1D_1$ and $^1D_0$, are involved in the effect. Note that Raman scattering is a two-photon phenomenon,[48,49] whereas for a luminescence a more complicated processes including intramolecular energy transfer can occur (Figure 11).

As indicated in Figure 10, although mostly reflecting by the metal electronic energies, the strong ROA signal arises through a chirality transfer from the ligands to the metal centre.[50]
possible mechanism for similar chirality induction has been proposed in reference [46].

Conclusion

We synthesised a chiral Eu
III complex and compared the performances of the ECD, VCD and ROA spectroscopic methods with respect to their potential to provide insight into the electronic structure and geometry of lanthanide complexes. The ECD spectra were rather indifferent to the binding of the ligand in the complex, whereas the complexation enhanced the vibrational optical activity. Most of the IR and VCD enhancement could be attributed to a charge transfer and the presence of the nitrate ions. An even more dramatic effect caused by the complexation was observed in the Raman and ROA spectra. In the complex, the spectra were dominated by electronic transitions of the europium ion. ROA was induced in the metal by a transfer of chirality from the ligands, and it most probably contains a circular-polarised luminescence component. The enhancement mechanism involving a resonance of laser light with europium \( ^{5}\text{F} \rightarrow ^{5}\text{D} \) transitions provided unusually high CID ratios (\( \approx 10^4 \)), about hundred times larger than the usual values encountered in molecular ROA. Such ROA monitoring of the transitions involving the F states is interesting as their optical activity cannot be measured on CPL spectrometers. The ROA method provides the most sensitive probe of complex chirality where very low concentrations and short measurement times are sufficient.

Experimental Section

All reagents were obtained commercially. \((\text{1R})-\text{and (1S)}-\text{6,6-dimethyl-5,7-methano-2-(2-pyridinyl)-4,5,6,7-tetrahydroquinolino} \) ligands \( (\text{R}^* -\text{and S}^*\text{-bipy}) \) were prepared by a procedure described elsewhere.\[34, 35\] Then each ligand and europium(III) nitrate hydrate (in a 2:1 molar ratio) were suspended in ethanol. The mixture was stirred 2 h at room temperature and concentrated in vacuum. The structure of the products was verified by elemental analysis (calcd for \( \text{C}_9\text{H}_9\text{EuNO}_3 \) (838.67): C 48.89, H 4.33, N 11.69; found: C 48.55, H 4.29, N 11.48) and \( ^1\text{H} \) NMR spectroscopy (\( \delta = 8.48, 7.49, 5.90, 5.69, 4.86, 3.66, 2.81, 2.60, 1.91, 1.67, 1.06 \text{ppm} \)) obtained on a Bruker DRX 400 NMR spectrometer in \( \text{CDCl}_3 \) solutions.

UV/Vis absorption spectra were measured on a UV-3600 spectrophotometer in the region of \( \lambda = 200–600 \text{ nm} \). ECD spectra were recorded on a Jasco J-815 spectropolarimeter within \( \lambda = 200–600 \text{ nm} \). All experiments were performed at room temperature, 1 mm quartz cell, and methanol solutions; the concentration was 2.5 \( \times 10^{-5} \text{ mol L}^{-1} \) for the complex and 6.67 \( \times 10^{-3} \text{ mol L}^{-1} \) for the ligand.

IR and VCD spectra (in detail reported in a separate study\[36\]) were recorded within the range \( \rho = 1800–800 \text{ cm}^{-1} \) with a IFS 66/S Fourier transform infrared spectrometer equipped with a PMA 37 VCD/IRRAS module (Bruker, Germany).\[18–20\] The PEM was set to \( \rho = 1500 \text{ cm}^{-1} \), the spectral resolution was 4 \( \text{ cm}^{-1} \), and the zero filling factor was four. A demountable cell with 
KBr windows and 0.05 mm Teflon spacer were used. All samples were dissolved in deuterated chloroform. The concentration was 0.4 \( \text{ mol L}^{-1} \) for the complex, and 1.6 \( \text{ mol L}^{-1} \) for the ligand. VCD spectra were collected for 4 h (twelve blocks of 20 min). Baseline correction was done with spectra of 
CCl4, used by the same setup as for the samples. Backscattering Raman and scattered circular polarisation (SCP) ROA spectra were acquired on a BioTools ROA spectrometer operating with a laser excitation at \( \lambda = 532 \text{ nm} \) at a resolution of 7 \( \text{ cm}^{-1} \), equipped with an edge filter (Semrock, frequency cut off at 90 \( \text{ cm}^{-1} \)). An aliquot (100 \( \mu\text{L} \)) of the sample chloroform solution was placed in a fused silica cell; the laser power at the sample was 20–60 mW. The collection time was about 20 h for the free ligand, and 16 min–2 h for various concentrations of the complex. Third-order five-point Savitzky–Golay smoothing was applied to the ROA spectra. The solvent background signal of the ligand was subtracted from the Raman spectra.

IR, VCD, Raman and ROA spectra of ligand were simulated by using the density functional theory (DFT) within the Gaussian 09 software.\[37\] The ligand geometry optimised previously for VCD calculations\[38\] \( \lambda = 532 \text{ nm} \) excitation frequency for ROA and the B3LYP/6-311++(G(d,p) level were employed. The B3LYP/6-311++ (G(d,p) level has been used for the energy levels in the complex.
G(d,p) functional and basis set combination provided previously reliable electronic and vibrational simulated spectra for similar systems. The initial complex geometry was based on analogous X-ray structure and optimised by using the B3LYP functional, 6-311 + + G(d,p) for C, H and N and the MWB28 pseudopotential for Eu.

For the full complex application of the time-dependent density functional theory (TDDFT) is meaningless with currently available functional because of the complicated europium electronic structure. Therefore, UV absorption and ECD spectra were obtained for the dimer composed of the ligands only, that is, the Eu ion was deleted in the calculated structure of the full complex. To estimate the extent of exciton coupling between the ligands in the complex independent of conformational change, spectra of the free ligand were simulated for the same conformation as adopted in the complex, without further optimisation. The f electrons of the Eu ion do not participate in chemical bonding, and the absorption of the metal is very weak, the simplified model thus provides the main effects of the complexation on ligand ECD and absorption spectra.

In all computations, the effect of the solvent was modelled by the conductor-like polarisable continuum solvent model (CPCM).

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