  Bull. Chem. Soc. Jpn., 60, 2993—2995 (1987)

Lanthanoid Chirality as a Tool for Assignment of *f*-*f* Transitions. Tb^{3+} and Tm^{3+} Diglycolate

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(Received April 5, 1986)

Although chiral studies have proved to be handy in the assignment of transitions in biological molecules, organic molecules and transition metal complexes, its potentiality for lanthanoid transition needs to be demonstrated. The paper explores the usefulness of CD studies in the assignment of lanthanoid transitions with two specific chiral single crystals-thulium diglycolate (Tm^{3+}-DG) and terbium diglycolate (Tb^{3+}-DG). It has been shown that chirality can distinguish $\Delta J=0, \pm1$ transition from others. The need for studies under higher resolution has been pointed out.

Identification of weak transitions in the presence of a strong one is a challenging problem for spectroscopists. For example, in heterocyclic organic molecules the ^{1}(n, π^*) state often remains undetected as this weak band frequently gets masked by the stronger (π, π^*) transitions. The same is the case with many spin-forbidden transitions. Various techniques, such as, measurement of polarized absorption spectra of single crystals or other orienting medium, measurements of polarized luminescence excitation spectrum by photoselection technique, improving the resolution by using supersonic jet-cooled molecules, application of magnetic or electric field, heavy atom or solvent perturbation, circular dichroism spectroscopy, two-photon spectroscopy etc. have been used to locate hidden transitions. We would like to demonstrate here how chiral studies can help in the assignment of the lanthanoid f^N-f^N transitions in situation where a number of J-states crowd together.

Unlike organic molecules or transition metal complexes, most chiral studies of lanthanoid complexes almost invariably involve chiral centers other than the lanthanoid ion. Although such studies can throw light on the interaction between Ln^{3+}-ion and the chiral center, these systems are hardly appropriate for spectra-environment correlation or assignment of Ln^{3+} transitions. Sen, Bera, and Chowdhury[1] was the first to make detailed study of a system where the chirality is derived from the immediate environment of the Ln^{3+} ion. Since then, extensive studies on three interesting chiral single crystal systems Ln^{3+}-DG (hexagonal; site-symmetry-D_3), lanthanoid double nitrate (Ln^{3+}-DN) (cubic; site symmetry-distorted dodecahedron) and lanthanoid pyrogermanate (Ln^{3+}-PG) (tetragonal; site symmetry-distorted pentagonal bipyramid)—have been made.[2-13] In this paper we would like to report the spectra of chiral single crystals of Tb^{3+}- and Tm^{3+}-DG and discuss the extent they can throw light on the asssignment problem. Crowding of different J-states has caused considerable uncertainty and confusion in the identification of $^1I_6$, $^3P_0$, $^3P_1$ states of Tm^{3+} and those states of Tb^{3+} lying above 25000 cm^{-1}; it is therefore worthwhile to explore the potentiality of other types of spectroscopy.[14-16]

A part of the problem in the case of assignment from one-photon forced electric dipole transition arises from the fact that the selection rules,[17] $\Delta J\leqslant6$, $\Delta L\leqslant6$, $\Delta S=0$ are not always valid due to J-mixing and breakdown of L-S coupling, and even when they are valid, they are not restrictive enough to be useful in the J-assignment of states.[14,15] A more restrictive J-selection rule ($\Delta J\leqslant2$), offered by two-photon transition selection rule, has been used by us and others for assignment of Gd^{3+} and other Ln^{3+} transitions.[18-21] Experimental difficulties, however, have stood in the way of carrying out similar studies on Tm^{3+} and Tb^{3+} crystals. We have therefore tried to exploit $\Delta J=0, \pm1$ selection rule for magnetic dipolar transitions. One way of estimating qualitatively the magnitude of magnetic dipolar transition moment is from the CD/OD strength, as pointed out by us in earlier papers.[6-10] It is expected that the transitions to the $^1I_6$ state of Tm^{3+} and $^5G_{5,6}/^5L_{6,7}$ states of Tb^{3+} will be intense in CD spectrum relative to others, leading to their identification.

Experimental

The single crystals were grown from solution by slow evaporation as described earlier.[10] The optic axis was identified by means of a polarizing microscope and the crystals were thinned by grinding and polishing with diamond paste of different grain sizes. In order to minimize the extent of overlap of transitions (which may cause cancellation of rotation) and identify the crystal-field components, the crystals were cooled to 20 K in an Air-product CS2O2 closed-cycle cryo-cooler. The absorption spectra were taken in a Cary 17D spectrophotometer and the CD spectra in a JASCO 500 spectrophotometer with minimum possible slit. For some of the transitions, the ultimate resolution is limited by the resolving power of the instrument.

Results and Discussion

Figure 1 shows the molecular structure of the Ln^{3+}-diglycolate complex. Each lanthanoid metal is coordinated to nine oxygen atoms, comprising a trigonal prism. The upper and lower triangles were made of

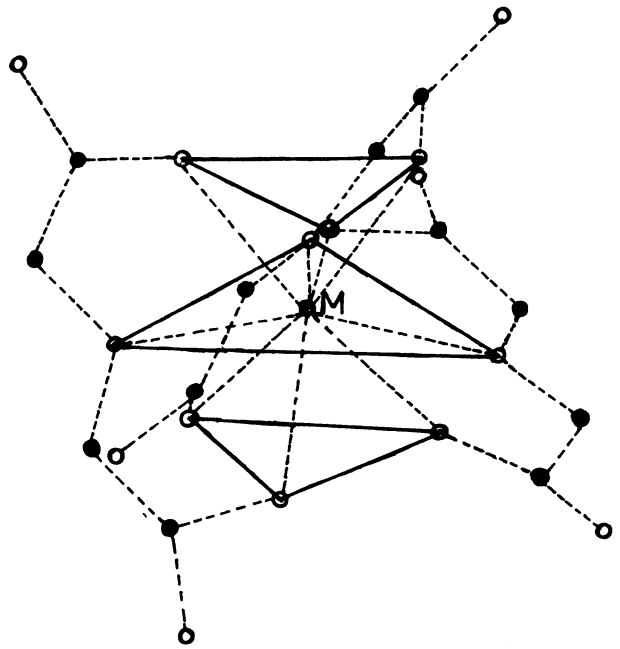

Fig. 1. The molecular structure of $[Ln(OCOCH_2OCH_2OCO)_3]^{3-}$ (Ln^{3+}-DG).

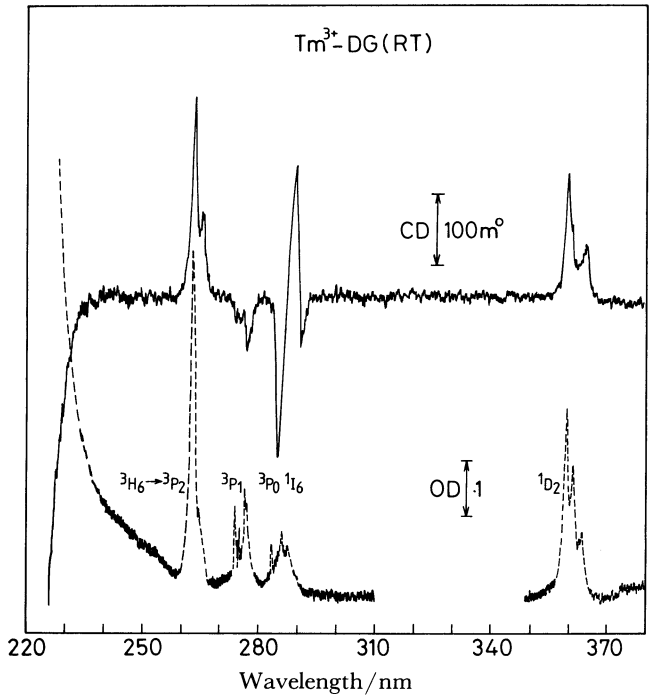

Fig. 2. The low-resolution room temperature absorption (dotted line) and circular dichroism (solid line) spectra of an oriented Tm^{3+}-DG single crystal. Light propagates along the optic axis.

six carboxylate oxygens and they are rotated relative to each other, destroying the plane of symmetry. The middle triangle is formed by the three ethereal oxygens.

Figure 2 shows the CD and absorption spectra of the same single crystal of Tm^{3+}-DG at room temperature. In view of the $\Delta J=0, \pm1$ selection rule for magnetic dipolar transition, and in view of the fact that circular

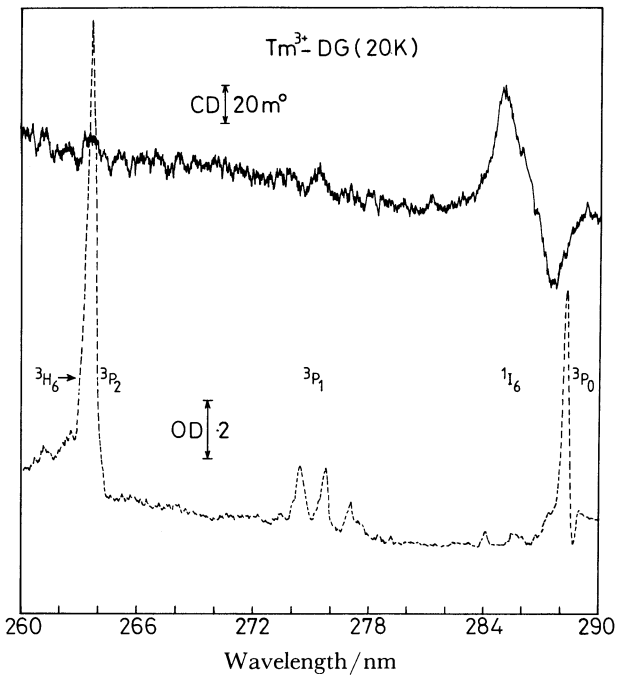

Fig. 3. The resolved absorption (dotted line) and CD (solid line) spectra of Tm^{3+}-DG single crystal at 20 K.

dichroism is a scalar product (imaginary part only) of electric dipolar and magnetic dipolar transition moments while OD depends on the sum of squares (absolute value) of the two moments, the CD/OD ratio is expected to be high for the $^3H_6 \rightarrow {}^1I_6$ transition. The higher CD/OD ratio near 285 nm, the wavelength region for the $^3H_6 \rightarrow {}^1I_6$ transition is apparent from the spectrum. Since the $^3P_0$ state and the components of the $^1I_6$ state overlap, we cooled the crystals to 20 K and carefully scanned the wavelength region 250—300 nm. A phase transition occurs at about 108 K;[7] however, the crystal still remains optically active. In spite of our best effort we have not been able to completely resolve all the components in the commercial CD instruments (Fig. 3). This limitation notwithstanding, the high CD/OD ratio and low OD value leave little doubt that the weak peaks between 283 and 287 nm belong to CF-split components of the $^1I_6$ state. The strong absorption peak at 287.5 nm appears as a weak signal in the slope of the CD band and hence is assigned to the $^3H_6 \rightarrow {}^3P_0$ transition. It is also interesting to note that the $^3P_1$ and $^3P_2$ bands, fairly prominent in absorption spectrum, hardly give any CD signal. Circular dichroism study can therefore be used as a useful tool for identifying the CF components of the spin-forbidden $^3H_6 \rightarrow {}^1I_6$ transition, which are normally masked by spin-allowed $^3H_6 \rightarrow {}^3P_{0,1,2}$ transitions.

In case of Tm^{3+}, neither the crystal field alone nor the spin-orbit coupling alone can cause a mixing, in first order, between the ^3P states and the $^1I_6$ state, although simultaneous application of the two can. It may be expected therefore that $^3P_{0,1,2}$ and $^1I_6$ states will,

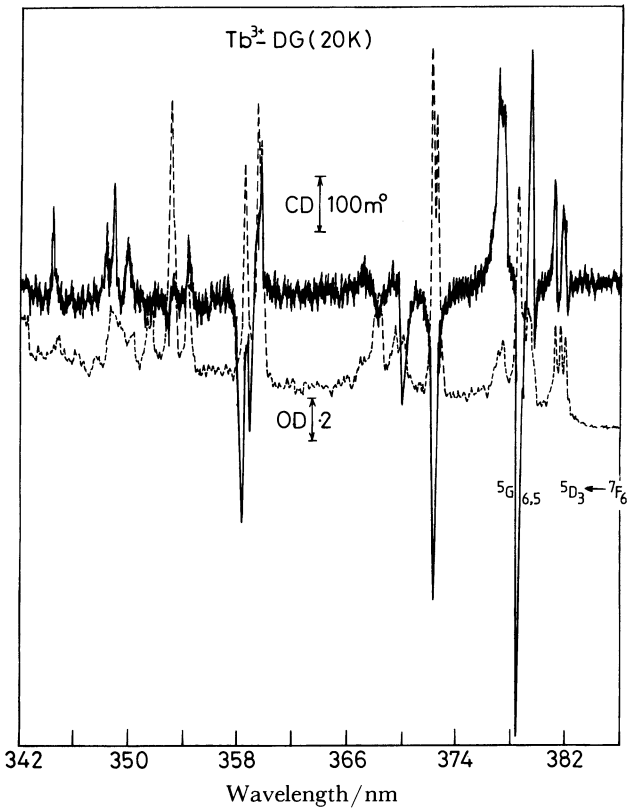

Fig. 4. The absorption (dotted line) and CD (solid line) spectra of a Tb^{3+}-DG single crystal at 20 K.

to a great extent, retain their characteristics regarding magnetic dipolar- or spin-allowedness. The situation is less clear-cut in Tb^{3+}-DG whose spectrum is shown in Fig. 4. In case of Tb^{3+}, the density of levels becomes so high below 348 nm that it becomes virtually impossible to identify the components from the mess of overlapping transitions. However, attempts have been made previously to assign the states in $TbCl_3 \cdot 6H_2O$ and $Tb_2(SO_4)_3 \cdot 6H_2O$. The detailed assignments are given in Dieke's book.[14] In order of increasing energy, the J-states are $^5D_3$, $^5L_{10}$, and $^5G_{5,6}$. In the present case, the first four bands close to 381 nm do not show high CD, although they are more resolved in the CD spectrum than in the normal absorption spectrum. This set of transitions should therefore be ascribed to $^7F_6 \rightarrow {}^5D_3$ transitions. On the other hand, the set of bands between 376 and 381 nm shows very high CD/OD ratio. This agrees with the expected location of the $^5G_{5,6}$ state in this region. However, the resolution of the spectrum is not enough to decide whether only the $^5G_{5,6}$ components appear in the above wavelength region, or there are additional overlapping $^5L_{10}$ components. Other states expected to be CD active are $^5L_{6,7}$. However, they occur at shorter wavelengths where background absorption stands in the way of their identification.

Conclusion

The CD spectrum may be an useful tool for identifying $\Delta J=0, \pm 1$ transitions, specially in situations where J-mixing is expected to be small. However, for unambiguous assignments, all the bands need to be resolved both in absorption and CD spectra. It is also useful for studying the nature of phase transitions.

We thank the National Science Foundation, U.S.A. for supporting the work (Project No. INT 83-19310).

References

1) A. C. Sen, S. C. Bera, and M. Chowdhury, *Chem. Phys. Lett.*, **46**, 594 (1977).
2) A. C. Sen and M. Chowdhury, *Chem. Phys. Lett.*, **79**, 165 (1981).
3) R. W. Schwartz, A. K. Banerjee, A. C. Sen, and M. Chowdhury, *J. Chem. Soc., Faraday Trans. 2*, **76**, 620 (1980).
4) F. S. Richardson, *Inorg. Chem.*, **19**, 2806 (1980).
5) F. S. Richardson and T. R. Faulkner, *J. Chem. Phys.*, **76**, 1595 (1982).
6) A. C. Sen, M. Chowdhury, and R. W. Schwartz, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1293 (1981).
7) R. W. Schwartz, A. K. Banerjee, M. Chowdhury, and R. Kuroda, *J. Chem. Soc., Faraday Trans. 2*, **77**, 557 (1981).
8) P. K. Chatterjee and M. Chowdhury, *J. Chem. Soc., Faraday Trans. 2*, **78**, 429 (1982).
9) P. K. Chatterjee and M. Chowdhury, *Inorg. Chem.*, **21**, 2499 (1982).
10) P. K. Chatterjee, A. Nath, D. Nath, and M. Chowdhury, *Chem. Phys. Lett.*, **110**, 95 (1984).
11) B. Karmakar, P. K. Chatterjee, D. S. Ray, D. Nath, M. Chowdhury, and B. Wanklyn, *Chem. Phys. Lett.*, **107**, 203 (1984).
12) A. Nath, P. K. Chatterjee, and M. Chowdhury, *Chem. Phys. Lett.*, **118**, 427 (1985).
13) B. Karmakar and M. Chowdhury, in Proceedings of the International Conference on Rare Earth Spectroscopy held at Wroclaw, Poland in September, 1984 (World Press publication).
14) G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals," Interscience, New York (1968), and references given therein.
15) B. G. Wybourne, "Spectroscopic Properties of Rare Earth," Wiley Interscience, New York (1965).
16) S. Hufner, "Optical Properties of Transparent Rare Earth Compounds," Academic Press, New York (1978).
17) R. D. Peacock, *Structure and Bonding*, **22**, 83 (1975).
18) B. Karmakar, D. S. Ray, K. Bhattacharyya, A. Samanta, and M. Chowdhury, *Chem. Phys. Lett.*, **97**, 545 (1983).
19) M. Dagenais, M. C. Downer, R. Neumann, and N. Bloembergen, *Phys. Rev. Lett.*, **46**, 561 (1981).
20) M. C. Downer and A. Bivas, *Phys. Rev. B*, **28**, 3677 (1983).
21) C. D. Cordero-Montalvo and N. Bloembergen, *Phys. Rev. B*, **30**, 438 (1984).