Table III. Exchange Rate Constants and Activation Parameters for Water Exchange of $Pt(H_2O)_4^{2+}$ and $Pd(H_2O)_4^{2+}$

complex	$k_{ex,298}/s^{-1}$	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta V^\ddagger$/cm^3 mol^{-1}	ref
$Pt(H_2O)_4^{2+}$	$(3.9 \pm 0.3) \times 10^4$	89.7 ± 2.4	-9 ± 8	-4.6 ± 0.2^b	this work
$Pt(H_2O)_4^{2+}$	$(5.8 \pm 0.6) \times 10^{-4\,a}$	100 ± 10	29 ± 30^a		4
$Pd(H_2O)_4^{2+}$	$(5.6 \pm 0.4) \times 10^2$	49.5 ± 1.9	-26 ± 6	-2.2 ± 0.2^c	15

[a] Values from ref 4 recalculated to exchange of a particular water molecule of $Pt(H_2O)_4^{2+}$. [b] 297.2 K. [c] 324 K.

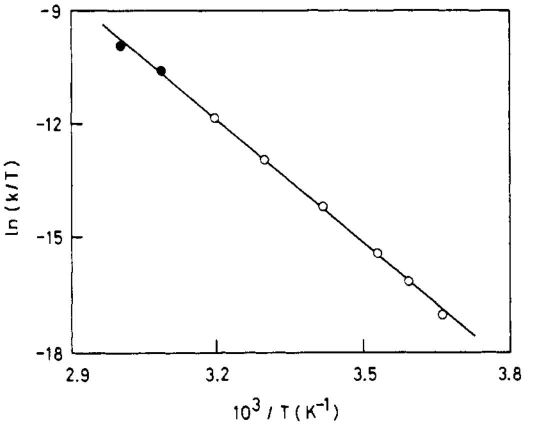

Figure 4. Eyring plot for the water-exchange rate constants k_{ex} of $Pt(H_2O)_4^{2+}$ in 1.5 *m* $HClO_4$: ●, fast injection.

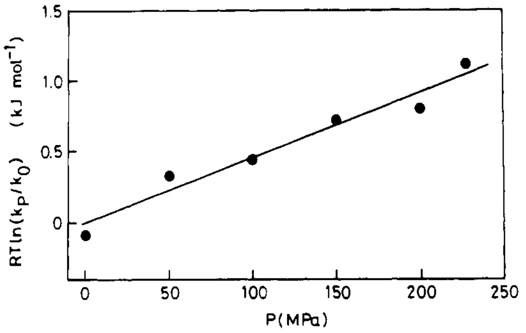

Figure 5. Effect of pressure on the water-exchange rate constant k_{ex} of $Pt(H_2O)_4^{2+}$ in 1.5 *m* $HClO_4$ at 297.2 K.

in isotopic equilibrium, as in Figure 2. The parameters adjusted were the height h_b, the quadrupolar relaxation rate $1/T_{2Q}$, and the coupling constant $^1J_{^{17}O-^{195}Pt}$. Figure 3 shows a typical example of a plot of the height of the NMR signal from coordinated oxygen-17 water vs. time. The water-exchange rate constants listed in Tables I and II were obtained directly from such plots.

Figures 4 and 5 show the temperature and pressure dependencies of the observed exchange rate constants. Activation parameters calculated from those plots are given in Table III. The temperatures of the present experiments could be varied over a wide interval (273–334 K), which gives a much more accurate entropy of activation than that calculated previously.[4]

Negative entropies and negative volumes of activation for solvent-exchange reactions support associative activation, i.e. an A or I_a mechanism. This is well established for octahedral complexes.[13] Although the effect of pressure on many substitution reactions of square-planar complexes has been studied,[14] only a very few activation volumes for symmetric exchange reactions of such complexes are available so far. More detailed mechanistic conclusions based on the present parameters might better be postponed, until more data for solvent exchange have been recorded. It is for example not possible at this stage to use these parameters to discriminate between an associative interchange I_a and a limiting associative A mechanism. However, the slightly negative values for ΔS^* and ΔV^* given in Table III do not support the I_d mechanism for water exchange of $Pt(H_2O)_4^{2+}$ suggested recently.[4]

We have just completed a study of the water exchange of the analogous tetraaquapalladium(II) ion.[15] Table III includes the exchange parameters for this complex also. The palladium complex reacts 1.4×10^6 times faster than that of platinum, and entropies and volumes of activation are negative in this case also.

Acknowledgment. Financial support from the Swiss National Science Foundation and the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. H_2O, 7732-18-5; $Pt(H_2O)_4^{2+}$, 60911-98-0.

Supplementary Material Available: Derivation of eq 2 (4 pages). Ordering information is given on any current masthead page.

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(13) Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479 and references therein.

(14) Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* **1981**, *36*, 89.

(15) Helm, L.; Elding, L. I.; Merbach, A. E. *Helv. Chim. Acta* **1984**, *67*, 1453.

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Circularly Polarized Luminescence from Racemic Terbium(III) Complexes Excited with Circularly Polarized Incident Light

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The use of lanthanide ions as spectroscopic probes in chemical and biochemical systems[1] has resulted in a significant increase in studies concerned with the elucidation of details of the complex solution structure of these species. In particular, emission spectroscopy has proven to be an extremely important experimental tool, since a number of the lanthanides are highly luminescent, often yielding many well-resolved transitions even in solutions at room temperature.[2] In addition, the intensity and polarization of these transitions are, in general, quite sensitive to small changes in the coordination environment.

A substantial amount of research has been devoted to the measurement of circularly polarized luminescence (CPL)[3] from complexes of lanthanide ions. In CPL one measures the difference in emission intensities between left and right circularly polarized light. By far the most widely studied lanthanides for this kind of work are Eu(III) and Tb(III), because of their large quantum yield for luminescence and their spectral accessibility. All of the solution CPL reported to date for lanthanide ions has necessarily involved the complexation of the cation with one or more optically active ligands.[4] This is due to the fact that no one has yet been able to prepare a stable enantiomerically pure complex in solution that is optically active due only to the configuration of ligands, e.g. a lanthanide complex equivalent to the common tris transition-metal species.

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(1) Richardson, F. S. *Chem. Rev.* **1982**, *82*, 541.

(2) See, for example: Horrocks, W. D., Jr.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384.

(3) Richardson, F. S.; Riehl, J. P. *Chem. Rev.* **1977**, *77*, 773.

(4) Brittain, H. G. In "Applications of Luminescence Spectroscopy"; Schulman, S. G., Ed.; Wiley: New York, 1983.

It has been demonstrated in recent years that there are structurally stable terdendate lanthanide species where the configuration of ligands is apparently D_3 or C_{3h} and which are primarily monomeric in solution. These include lanthanide complexes of dipicolinic acid (DPA), oxydiacetic acid (ODA), iminodiacetic acid (IDA), and (methylimino)diacetic acid (MIDA). Considerable work has been reported on the absorption[5] and emission[6] of such systems involving a number of different lanthanide ions. The crystal structures of $Na_3[Ln(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ and $Na_3[Ln(DPA)_3]\cdot 2NaClO_4\cdot 6H_2O$ have been reported,[7,8] and Morley, Saxe, and Richardson[9,10] have measured the CPL in the axial directions from trigonal single crystals of the Eu–ODA and Tb–ODA species.

In this work we report CPL from solutions of $Tb(DPA)_3^{3-}$ and from solutions of racemic malic acid and Tb(III) that were photoprepared in an enantiomerically enriched state by a circularly polarized excitation beam. The former result represents the first example of CPL from a solution of a lanthanide with achiral ligands, and the latter result illustrates the application of this procedure to a considerably more complicated system. This technique[11] holds considerable promise as a structural probe in those studies aimed at some understanding of the complicated solution structure of lanthanide complexes.

Experimental Section

CPL measurements were made on a medium-resolution CPL/emission spectrometer constructed along the basic design of Luk and Richardson.[12] Excitation of the solutions was accomplished by directing the 488-nm line of a Coherent Radiation Ar ion laser, oriented at 90° to the direction of emission detection, through a mica quarter-wave retardation plate (Karl Lambrecht) to convert the linearly polarized laser beam to either left or right circular polarization, before entering the cuvette containing the sample of interest. The optical detection system consists of a photoelastic modulator (Hinds International) operating at 50 kHz and linear polarizer (which in combination act as a circular analyzer), 520-nm longpass filter, focusing lens, and monochromator. The emitted light was detected by a cooled EMI9558B photomultiplier tube.

The photomultiplier output is passed through an output resistor and a custom built 50 kHz active filter before entering a lock-in amplifier (PAR 128A) that is referenced to the 50-kHz signal from the PEM. The ac signal is proportional to the differential emission intensity, ΔI, and the dc signal measured on an electrometer yields the total intensity, I. Both signals are appropriately amplified and then input through an 8-bit A/D to a Z-80 microcomputer (Horizon North Star) for the calculation of the dissymmetry ratio, $g_{\text{lum}} = \Delta I/I$, and plotting. A serious problem with the experimental measurement of CPL is artifacts due to the presence of linear polarization. No appreciable linear polarization was detected in the spectra reported here. All spectra were checked by reversing the incident circular polarization and observing the oppositely signed CPL.

DPA, ODA, IDA, racemic malic acid, and $TbCl_3\cdot 6H_2O$ were purchased from Aldrich and used without further purification. DPA and ODA solutions were prepared by first neutralizing to pH 7 with sodium hydroxide and then adding $TbCl_3$ and adjusting the pH to the desired value. Total luminescence (TL) scans were recorded before and after each CPL run to correct for any spatial drift or fluctuation in laser power. Laser intensity changes were less than 2% after 3 h.

Results and Discussion

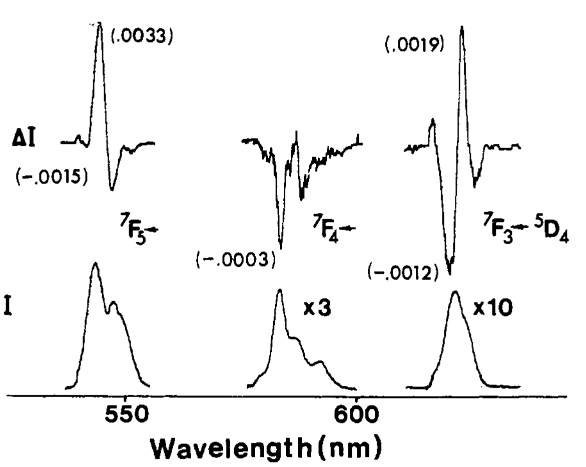

Figure 1. Total luminescence (I) and circularly polarized luminescence (ΔI) for $Tb(DPA)_3^{3-}$ at a pH of 9.2 with circularly polarized 488-nm light as the excitation source. The values in parentheses are the measured luminescence dissymmetry ratios.

In Figure 1 we plot total luminescence and circularly polarized luminescence spectra for a 0.030 M solution of $Tb(DPA)_3^{3-}$ excited by circularly polarized 488-nm light. The Tb:ligand ratio was 1:5, and the pH of the solution was 9.2. No change was observed in the spectra as the pH was adjusted from 7.0 to 10.0. This is consistent with previous results on the nature of this species.[13] Displayed in this figure are the three most intense transitions, i.e. $^7F_5$, $^7F_4$, $^7F_3 \leftarrow {}^5D_4$. Also given in this figure is the luminescence dissymmetry ratio, g_{lum}, which is defined as

$$g_{\text{lum}} = \Delta I/I = (I_L - I_R)/[(I_L + I_R)/2] \tag{1}$$

I_L and I_R refer respectively to the intensity of left and right circularly polarized emitted light. Calibration of the results reported here was accomplished by comparison with the CPL from $Eu(facam)_3$ (facam = 3-(trifluoroacetyl)-*d*-camphorato) as suggested by Brittain.[14] The calibration values agree with those of Schippers, van den Beukel, and Dekkers.[15] The possibility of measuring CPL from racemic mixtures by using circularly polarized light was first described by Dekkers, Emeis, and Oosterhoff.[16] More recently Schippers and Dekkers[17] have applied the technique to the problem of determining the optical purity of partially resolved systems. A detailed theoretical treatment has been presented by Hilmes and Riehl[11] in which the effects of excited-state racemization, energy transfer, and reorientation have been considered. In the limit that there is no geometry change or intermolecular energy transfer during the lifetime of the excited state, the differential emitted intensity can be related to the absorption dissymmetry ratio, g'_{abs}, and the emission dissymmetry ratio, g'_{lum}, as

$$\Delta I^L = -\tfrac{1}{2} g'_{\text{abs}} g'_{\text{lum}} \tag{2}$$

where ΔI^L is the differential intensity when left circularly excitation is used and g'_{abs} is defined as

$$g'_{\text{abs}} = (\epsilon_L - \epsilon_R)/[(\epsilon_L + \epsilon_R)/2] \tag{3}$$

ϵ_L and ϵ_R denote extinction coefficients for left and right circularly polarized light. The primes in this equation indicate that the dissymmetry ratios are defined for a specific isomer. If the incident light is right circularly polarized, the sign of eq 2 is reversed.

As mentioned previously, the geometry of $Tb(DPA)_3^{3-}$ as determined from the crystal structure indicates that the symmetry of the ligands is D_3. This complex has been shown to be monomeric and to exist in a 3:1 ligand:lanthanide ratio for a wide

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(5) (a) Stephens, E. M.; Schoene, K.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 1641. (b) Salama, S.; Richardson, F. S. *J. Phys. Chem.* **1980**, *84*, 512. (c) Davis, S. A.; Richardson, F. S. *Inorg. Chem.* **1984**, *23*, 184.

(6) (a) Brittain, H. G. *Inorg. Chem.* **1978**, *17*, 2762. (b) Brittain, H. G. *Inorg. Chem.* **1980**, *19*, 2136. (c) Foster, D. R.; Richardson, F. S. *Inorg. Chem.* **1983**, *22*, 3996.

(7) (a) Albertson, J. *Acta Chem. Scand.* **1970**, *24*, 1213. (b) Albertson, J. *Acta Chem. Scand.* **1972**, *26*, 985. (c) Albertson, J. *Acta Chem. Scand.* **1970**, *24*, 1005. (d) Albertson, J. *Acta Chem. Scand.* **1970**, *24*, 1023.

(8) (a) Albertson, J. *Acta Chem. Scand.* **1968**, *22*, 1563. (b) Albertson, J. *Acta Chem. Scand.* **1970**, *24*, 3527.

(9) Morley, J. P.; Saxe, J. D.; Richardson, F. S. *Mol. Phys.* **1982**, *47*, 379.

(10) Saxe, J. D.; Morley, J. P.; Richardson, F. S. *Mol. Phys.* **1982**, *47*, 407.

(11) Hilmes, G. L.; Riehl, J. P. *J. Phys. Chem.* **1983**, *87*, 3300.

(12) Luk, C. K.; Richardson, F. S. *J. Am. Chem. Soc.* **1974**, *96*, 2006.

(13) Desreux, J. F.; Reilley, C. N. *J. Am. Chem. Soc.* **1976**, *98*, 2105.

(14) Brittain, H. G. *J. Am. Chem. Soc.* **1980**, *102*, 3693.

(15) Schippers, P. H.; van den Beukel, A.; Dekkers, H. P. J. M. *J. Phys. E* **1982**, *15*, 945.

(16) Dekkers, H. P. J. M.; Emeis, C. A.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 4589.

(17) Schippers, P. H.; Dekkers, H. P. J. M. *Tetrahedron* **1982**, *38*, 2809.

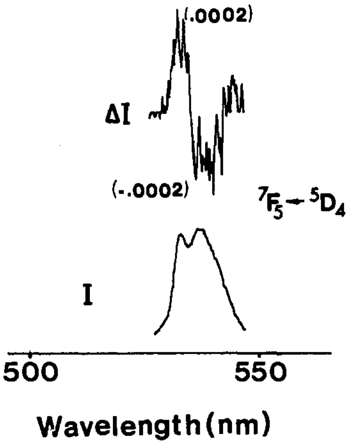

Figure 2. Total luminescence (I) and circularly polarized luminescence (ΔI) for a 1:5 mixture of Tb and racemic malic acid at a pH of 9.4. The values in parentheses are the measured luminescence dissymmetry ratios.

range of pH conditions. The formation constant (K_1)[18] of the complex has been reported to be $\sim 5 \times 10^8$ and is, in fact, the largest value observed for this general type of ligand. The intensity of the luminescence and the sharpness of the observed transitions are consistent with this species being a very tight complex. The observation of CPL from the solution is consistent with D_3 geometry. The other possible nine-coordinate complex, in which the terdentate ligands occupy facial positions on the tricapped prism, has C_{3h} symmetry and, therefore, will exhibit no optical activity.

No CPL was detected from the 3:1 complex of Tb(ODA)$_3^{3-}$. This species also adopts the D_3 geometry in the crystal and has been presumed to have a similar geometry in aqueous solutions.[5,6] The sensitivity of our experimental apparatus under the conditions used here is such that the $|g_{\text{lum}}|$ values for this complex must be less than 1×10^{-4}, considerably smaller than that observed for the Tb–DPA system. The binding constant for Tb–ODA is $\sim 2 \times 10^5$, much smaller than that for Tb–DPA. The absence of measurable differential emission intensity could be due to a small circular dichroism (CD), i.e. g_{abs} at 488 nm, or small values for g_{lum}, or a combination of the two. The measured CPL of the Tb(ODA)$_3^{3-}$ crystals is quite large.[10] It could be that the "looseness" of the complex in solution leads to a flexibility in the ligands that tend to average out the optical activity or the species may exist at least in some percentage as the C_{3h} isomer. Attempts at measuring ΔI using the much weaker 494-nm Ar ion laser line were unsuccessful. Similar attempts at measuring the CPL from solutions of Tb(IDA)$_3^{3-}$ using circularly polarized excitation were also unsuccessful. This species has been suggested to have C_{3h} geometry;[9] thus no CPL would be expected. The upper limit on the $|g_{\text{lum}}|$ value is again $\sim 1 \times 10^{-4}$.

In Figure 2 is plotted the differential emission intensity for a 0.040 M solution of Tb(III) with excess racemic malic acid at a pH of 9.4. This system is an inherently more complicated one, since the optical activity that one observes may be due both to the configuration of the ligands around the central ion and to the chirality of the ligands themselves. In addition, this well-studied system has been shown to be very sensitive to pH, to exist as polymeric species at some pH values, and to include hydroxide ions in the coordination sphere at high pH.[19] Nevertheless, the kinds of results presented here may yield information concerning the optical activity of the emitting species and the nature of the equilibrium mixture that is not easily obtainable by other means.

The measurement of CPL from racemic solutions is a useful experimental probe, since one is able to examine the chiroptical properties of mixtures without having to resolve them. The results reported here indicate that the Tb(DPA)$_3^{3-}$ species probably exists as the D_3 isomer in aqueous solution. It should be possible to apply the theoretical approach of Richardson et al.[20] for the calculation of total and circular emission intensities to this system to see if there is agreement. A more detailed study of the Tb–IDA and Tb–ODA solution equilibrium is under way.

Registry No. Tb(DPA)$_3^{3-}$, 38682-37-0; Tb(malate)$_3^{3-}$, 96129-30-5.

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(18) Martell, A. E. "Stability of Metal-Ion Complexes"; Chemical Society: London, 1971.

(19) See, for example: Brittain, H. G.; Richardson, F. S. *Inorg. Chem.* **1976**, *15*, 1507.

(20) Saxe, J. D.; Faulkner, T. R.; Richardson, F. S. *J. Chem. Phys.* **1982**, *76*, 1607.

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Crystal and Molecular Structure of Trimeric Bis(acetylacetonato)manganese(II)[1]

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The molecular structures of anhydrous acetylacetonates of many bivalent first-row transition metals have been determined, and it has been found that the iron,[3,4] cobalt,[5] nickel,[6,7] and zinc[8] chelates are polymeric with structures formed by bridging by the oxygen atoms of the ligands, while the chromium[9] and copper[10] chelates are monomeric with planar structures in the solid phases. However, the structure of the manganese analogue, a well-known compound in the series, has remained undetermined until now. Graddon and Mockler[11] measured its molecular weight in benzene solution at various concentrations and reported that the manganese chelate is trimeric in the solution. They also suggested that the structure was similar to that of the corresponding nickel trimer, where NiO_6 octahedra are fused by sharing triangular faces, though most of the manganese(II) complexes so far studied have been found to be tetrahedral and octahedral for four- and six-coordination, respectively.[12] We now report the crystal and molecular structure of bis(acetylacetonato)manganese(II) and describe the coordination polyhedra of the complexes and the related structure of the acetylacetone ligands in detail.

Experimental Section

Bis(acetylacetonato)manganese(II) dihydrate, $Mn(acac)_2 \cdot 2H_2O$, was prepared by a known procedure.[13] The dihydrate was transferred into a glass tube and heated at 60 °C with phosphorus pentoxide; the anhydrous compound obtained was pale yellow, and crystals (irregular prism) suitable for X-ray work were prepared by repeated sublimation in vacuo, first at 140 °C and then at 190 °C. The complex was stored in vacuo after preparation. Anal. Calcd for $C_{10}H_{14}O_4Mn$: C, 47.45; H, 5.57. Found: C, 47.42; H, 5.63.

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(1) Preliminary report: Shibata, S.; Onuma, S.; Inoue, H. *Chem. Lett.* **1984**, 485.

(2) Present address: Rigaku Denki Co., Matsubaracho, Akishima, Tokyo 196, Japan.

(3) Shibata, S.; Onuma, S.; Iwase, A.; Inoue, H. *Inorg. Chim. Acta* **1977**, *25*, 33.

(4) Cotton, F. A.; Rice, G. W. *Nouv. J. Chim.* **1977**, *1*, 301.

(5) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1965**, *4*, 1145.

(6) Bullen, G. J.; Mason, R.; Pauling, P. *Inorg. Chem.* **1965**, *4*, 456.

(7) Hursthouse, M. B.; Laffey, M. A.; Moore, P. T.; New, D. B.; Raithby, P. R.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 307.

(8) Bennett, M. J.; Cotton, F. A.; Eiss, R. *Acta Crystallogr., Sect. B: Struct. Crsytallogr. Crsyt. Chem.* **1968**, *B24*, 904.

(9) Cotton, F. A.; Rice, C. E.; Rice, G. W. *Inorg. Chim. Acta* **1977**, *24*, 231.

(10) Starikova, Z. A.; Shugam, E. A. *Zh. Strukt. Khim.* **1969**, *10*, 290.

(11) Graddon, D. P.; Mockler, G. M. *Aust. J. Chem.* **1964**, *17*, 1119.

(12) Stephens, F. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3492.

(13) *Inorg. Synth.* **1960**, *6*, 164.