

Synthesis and Characterisation of Chiral Lanthanide Complexes: Tetraethylammonium Tetrakis [(-)cyclic O,O'-1(R), 2(R)-Dimethylethylene Dithiophosphato] Lanthanide(III), $\{(C_2H_5)_4N\}\{Ln[(-)S_2PO_2C_4H_8]_4\}$, (Ln = Nd, Eu)

PAOLO BISCARINI

Istituto di Chimica Fisica e Spettroscopia, Viale Risorgimento 4, 40136 Bologna, Italy

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The chiral cyclic (-)O,O'-1R,2R dimethylethylene dithiophosphate ligand ion, $[(-)bdtp]^-$, the achiral ion, and the corresponding tetrakis lanthanide(III) complexes, $\{NEt_4\}\{Ln[(-)bdtp]_4\}$, (Ln = Nd, Eu) have been prepared. The characterisation, structure and spectral properties of the compounds are discussed.

The electronic, MCD and CD spectra have been examined for methylecyanide solutions in the spectral range 14000–50000 cm^{-1} . The energies, oscillator, dipole and rotational strengths of the bands have been measured and the assignments to the electronic transitions of intraligand, $4f-4f$ and charge-transfer type performed. With the neodymium complex a broad Cotton effect at 38450 cm^{-1} has been assigned to a charge-transfer transition. With the europium complex hypersensitive ${}^7F_0 \rightarrow {}^5D_2$ (21350 cm^{-1}) and CD sensitive ${}^7F_1, {}^5F_0 \rightarrow {}^5D_1$ (18990, 19050 cm^{-1}) bands have been identified from the comparison between absorbance, MCD and CD spectra.

Introduction

Chiroptical spectroscopy is a sensitive probe for detecting electronic and stereochemical structural aspects of transition metal complexes. Measurements of the oscillator strengths of lanthanide and transition metal complexes, the rotational strengths of chiral, and the Faraday terms of achiral transition metal complexes, have been obtained to test the application of the ligand polarization model to these spectroscopic measurements [1].

The ligand polarization model has been found appropriate for treatment of d-d and f-f transition probabilities in various complexes of known structure [2].

To date, not many optically active lanthanide complexes with known structures have been synthe-

sized for study by chiroptical spectroscopy. Some examples of CD/absorption spectra of Ln(III) amino-acids complexes and other chiral ligands in aqueous solution have been reported [3–5]. Circularly-polarized luminescence spectra of Ln(III) complexes with chiral ligands have also been studied [6]. CD/absorption spectra of the configurational chiral complexes $Na_3[Ln(OCOCH_2OCH_2OCO)_3] \cdot 2NaClO_4 \cdot 6H_2O$ have been reported [7, 8]. Recent attempts have been made to calculate the rotational strengths for this complex [9]. Magnetic circular dichroism (MCD) of some Ln(III) complexes was measured [10].

The aim of the present work is to synthesize new Ln(III) complexes with chiral sulphurated ligands, as models for Ln-S interaction, e.g. in biological systems. In addition, we attempted to characterise these complexes by chiroptical spectroscopy, examining CD and MCD spectra to identify term to term transitions to use as chiroptical probes and/or, measuring the intensities of the transitions, to test the ligand polarization model. The intensities of the f-f transitions, determined by electronic spectra in Ln(III) complexes with sulphur atoms coordinated with the metal ion, are relatively large, yet at times barely observable [11–13]. CD and MCD spectra could contribute to the knowledge of the spectral properties of chiral and achiral Ln(III) complexes containing an LnS₈ chromophoric group.

The synthesis of the O,O'-diethyl dithiophosphates, (ddtp), and diethyldithiocarbamates, (ddtc), ligands and corresponding lanthanide(III) complexes has been reported [11–14].

We synthesized a structurally rigid chelate ligand cyclic, O,O'-1,2-dimethylethylene dithiophosphate ion, (bdtp)⁻, in the chiral, (-)1R,2R, and racemic and meso forms, to obtain the $[Ln(bdtp)_4]^-$ ion complexes and measure the electronic, MCD and CD spectra.

Experimental

Anhydrous lanthanoid(III) chlorides were prepared from the commercial oxides (Fluka), concentrated hydrochloric acid, and ammonium chloride following a reported method [15].

Hydrated lanthanoid(III) chlorides, tetraethylammonium chloride, D(-)-2,3 butandiol (Fluka) and 2,3 butandiol (C. Erba), were used without further purification. Solvents were purified by standard methods. Crystallization and filtration were realized in a nitrogen atmosphere. Analyses were obtained by handling and weighing the samples in inert gas.

Spectroscopic Measurements

Infrared spectra, IR, were obtained on a Perkin-Elmer 225 instrument in CsI discs or nujol and hexachlorobutadiene mulls between 4000 and 200 cm^{-1} , using NaCl and CsI as windows.

Ultraviolet and visible spectra (Vis-UV), were measured with Cary 14 and Cary 17 spectrometers in CH_3CN solution between 11000 and 50000 cm^{-1} .

Circular dichroism (CD) spectra were obtained in freshly-prepared CH_3CN solution between 700 and 200 nm on a Jasco J-500A spectropolarimeter equipped with a Jasco Data Processor, repeating the scanning 32 times when necessary and averaging the accumulated data.

Magnetic circular dichroism, MCD, spectra in CH_3CN solution were obtained on a Jasco J-500 A spectropolarimeter equipped with an electromagnet working at 15600G. The calibration was obtained with a $\sim 1 M$ solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and using the data reported [16].

^1H NMR spectra were obtained in CD_3CN solutions with internal TMS.

The ^{31}P NMR spectra were registered from CD_3CN solutions using a capillary of 85% H_3PO_4 as an external reference to establish the chemical shifts relative to a standard reference peak.

All the NMR spectra were recorded on a Bruker WM 250 NMR spectrometer. The proton spectra were recorded at 250 MHz, the ^{31}P spectra at 36.4 MHz with broadband proton decoupling.

The spectra were recorded using quadrature detection and *ca.* 500–4000 scans for the ^{31}P spectra and *ca.* 8–40 scans for the ^1H spectra.

Preparation of the Compounds

Potassium (-) cyclic O,O'-1(R),2(R)-dimethylethylene Dithiophosphate, (-)bdtpK, (I)

In a nitrogen atmosphere 5 g (5.5 mmol) of (-) 2,3 butandiol was added with magnetic stirring to 6 g (27.0 mmol) of phosphorus pentasulphide. The reaction was completed by heating the flask gently on a sand bath. When the phosphorus pentasulphide had dissolved completely (2–3 h), to the clear

acidic solution was added an excess of potassium carbonate anhydrous. The stirring and heating was continued until complete neutralization of the mixture, followed by the addition of 100 ml of absolute ethanol. The boiling solution was filtered to separate the unreacted potassium carbonate. With cooling and slow evaporation under vacuum of the solvent a white product separated; this was filtered, washed with anhydrous ethyl ether, and recrystallized from ethanol: 5.3 g (yield 43%), identified as (I). *Anal.* Found: C, 21.3; H, 4.0. $\text{C}_4\text{H}_8\text{O}_2\text{PS}_2\text{K}$ requires: C, 21.6; H, 3.6%. The ^1H NMR spectrum in CD_3CN shows two multiplets at 3.98 ppm (2H, m, 2CH) and 1.27 ppm (6H, m, 2 CH_3). The ^{31}P NMR spectrum shows a sharp singlet at 126.3 ppm. The IR spectrum (nujol mull) shows strong bands at 2992, 2976, 2923, 1447, 1437, 1385, 1326, 1285, 1107, 1040 (P–O asym), 982, 925 (P–O sym), 870, 850, 798, 770, 714, 623 (P–S asym), 570, 540 (P–S sym), 433, 419, 374, 316, 250, 222 cm^{-1} .

Table I reports analytical data, colours, optical rotation of this compound and of the achiral one, (II), obtained with the same method.

Tetraethylammonium (-) cyclic O,O'-1(R),2(R)-dimethylethylene Dithiophosphate, (-)bdtpNEt₄, (III)

To a hot ethanolic solution of 1 g (4.5 mmol) of (I), was added an ethanolic solution, 0.75 g (4.5 mmol), of tetraethylammonium chloride. After warming and stirring for two hours the potassium chloride was filtered off and the filtrate concentrated to one-fourth the original volume. Upon addition of a triple volume of ether a white crystalline product separated. Recrystallization from dry acetone and addition of small quantities of anhydrous ethyl ether gave 1.2 g of fine white needles, identified as (III). *Anal.* Found: C, 45.65; H, 9.15; N, 4.5. $\text{C}_{12}\text{H}_{28}\text{NO}_2\text{PS}_2$ requires: C, 46.0; H, 9.0; N, 4.45%. The ^1H NMR spectrum in CD_3CN shows three (four) signals: 3.96 ppm (2H, m, 2CH); 3.23 ppm (8H, q, 4 CH_2); 1.25 ppm (18H, m (and t), 6 CH_3). The ^{31}P NMR spectrum in CD_3CN shows one sharp singlet at 126.52 ppm. The IR spectrum (CsI disc) shows strong bands at 2975, 2930, 2907, 1453, 1400, 1374, 1310, 1185, 1040 (P–O asym), 915 (P–O sym), 830, 750, 665, 620 (P–S asym), 555 (P–S sym), 410, 365, 312 cm^{-1} .

Similar procedures were followed for (IV).

Tetraethylammonium Tetrakis[(-)cyclic O,O'-1(R),2(R)-dimethylethylene dithiophosphato] neodymium(III), [NEt₄]{Nd[(-)bdtp]₄}, (V)

In a three-necked 250 ml flask fitted with a reflux condenser with a calcium chloride guard tube, a dry nitrogen inlet tube and a dropping funnel, were placed and dissolved by slightly heating 1.8 g (8 mmol) of compound (I) in 200 ml of absolute

ethanol. Dissolution was complete using heating to gentle refluxing, when a solution of 0.715 g (2 mmol) of neodymium trichloride hexahydrate in absolute ethanol was dripped in, immediately causing the colour of the solution to pale lilac-sky blue, and also the formation of potassium chloride. After 10 minutes of stirring 0.33 g (2 mmol) of tetraethylammonium chloride was added. After the solution was heated for 2 hours, the nitrogen flow, the heating and the stirring were stopped. The reaction mixture was evaporated UV and the solid residual was solubilized in dry acetone by heating and filtered from the white solid potassium chloride. The addition of successive small quantities of anhydrous ethyl ether to the acetone solution separates two first fractions of a white product, identified as (III) by analyses, IR and ^1H and ^{31}P NMR spectra.

Other small quantities of ethyl ether added to the solution separates 0.8 g of a pale lilac compound. This was crystallized by solution in anhydrous methylene chloride followed by filtration and addition of small quantities of ethyl ether. Slow crystallization yields a pale lilac product, identified as (V). *Anal.* Found: C, 28.75; H, 5.3; N, 1.3. $\text{C}_{24}\text{H}_{52}\text{NO}_8\text{P}_4\text{S}_8\text{Nd}$ requires: C, 28.6; H, 5.2; N, 1.4%.

The ^1H NMR spectrum in CD_3CN shows four signals: 4.126 ppm (8H, s, 8CH); 3.258 (8H, q, 4 CH_2); 1.292 (12H, m, 4 CH_3); 1.05 (24H, d, 8 CH_3).

The IR spectra (nujol mulls) shows the absence of water and strong bands at 2980, 2940, 2920, 2900, 1450, 1445, 1390, 1380, 1320, 1280, 1050 (P–O asym), 930 (P–O sym), 850, 790, 695, 630 (P–S asym), 555 (P–S sym), 250 (M–S) cm^{-1} .

Analogously starting from compound (II) the compound (VI) was synthesized.

Tetraethylammonium Tetrakis[(-)cyclic O,O'-1(R),2(R)-dimethylethylene dithiophosphato]-europium(III), [NEt₄][Eu((-)bdtp)₄], (VIII)

The compound was obtained as for compound (V).

When the solution of europium trichloride hexahydrate in absolute ethanol was dripped into the solution of (-)bdtpK, the solution turned pale orange along with the formation of potassium chloride. After the evaporation under vacuum of the solvent we obtained a red-orange solid, which was purified by crystallization from acetone and anhydrous ethyl ether and finally from anhydrous methylene chloride and small quantities of ethyl ether. Slow crystallization yielded a red-orange product, identified as (VII). *Anal.* Found: C, 28.4; H, 5.4; N, 1.3; P, 12.2. $\text{C}_{24}\text{H}_{52}\text{NO}_8\text{P}_4\text{S}_8\text{Eu}$ requires: C, 28.4; H, 5.15; N, 1.35; P, 12.2%.

The ^1H NMR spectrum in CD_3CN shows four signals: 4.03 ppm (8H, m, 8CH); 3.05 (8H, q, 4 CH_2); 1.71 (24H, m, 8 CH_3); 1.12 (12H, m, 4 CH_3).

The IR spectra (nujol mulls) show the absence of water and strong bands at 2980, 2940, 2920, 1450, 1435, 1375, 1320, 1280, 1040 (P–O asym), 920 (P–O sym), 840, 780, 685, 620 (P–S asym), 550 (P–S sym), 251 (M–S) cm^{-1} .

Tetraethylammonium Tetrakis[cyclic O,O'-1,2-dimethylethylene dithiophosphato]europium(III), [NEt₄][Eu(bdtp)₄], (VIII)

The compound was obtained as (VII), identified as (VIII) by elemental analyses, IR and NMR spectra.

Potassium (O,O'-diethyl dithiophosphate), ddtK, (IX)

The compound was obtained as the described sodium salt [17, 18], using anhydrous K_2CO_3 . Elemental analyses agree with the composition given. The ^1H NMR spectrum in CD_3CN shows two signals: 3.915 (4H, m, 2 CH_2); 1.21 (6H, t, 2 CH_3).

The ^{31}P NMR spectrum shows one singlet at 113.4 ppm.

The IR spectrum (nujol mulls) shows bands at 2983, 2940, 2890, 1470, 1440, 1390, 1015 (P–O asym), 925 (P–O sym), 745, 700, 560, 295, 264 cm^{-1} .

Tetraethylammonium, (O,O'-diethyl dithiophosphate), ddtPNEt₄, (X)

The compound was obtained by adding to a hot ethanolic solution of ddtPNEt₄ a solution of tetraethylammonium chloride. The solvent was evaporated under vacuum and the residual was crystallized from ethylacetate/n-pentane obtaining fine white needles. m.p. 128–30 °C. Identified as (X). *Anal.* Found: C, 45.3; H, 9.7; N, 4.45. $\text{C}_{12}\text{H}_{30}\text{NO}_2\text{PS}_2$ requires: C, 45.7; H, 9.6; N, 4.45%.

The ^1H NMR spectrum in CD_3CN shows four multiplets at 3.89 ppm (4H, m, 2 CH_2); 3.22 (8H, q, 4 CH_2); 1.214 (18H, t + m, 6 CH_3). The ^{31}P NMR spectrum in CD_3CN shows one sharp singlet at 114.2 ppm. The IR spectrum (nujol mulls) shows bands at 3004, 2973, 2930, 2885, 1458, 1440, 1380, 1308, 1180, 1020 (P–O asym), 920 (P–O sym), 760, 720, 680 (P–S asym), 560 (P–S sym) cm^{-1} .

Tetraethylammonium Tetrakis(O,O'-diethyl dithiophosphato)neodymium(III), [NEt₄][Nd(dttp)₄], (XI)

The compound was obtained essentially as reported [13, 14, 19]. Elemental analyses agree with the composition given.

The ^1H NMR spectrum in CD_3CN shows four signals: 3.37 ppm (8H, q, 4 CH_2); 2.32 (16H, s, broad, 8 CH_2); 1.38 (12H, m, 4 CH_3); 0.613 (24H, t, 8 CH_3). The IR spectrum (nujol mull) shows bands at 2980, 2925, 2900, 1460, 1390, 1300, 1155, 1018 (P–O asym), 940 (P–O sym), 770, 722, 682, 650 (P–S asym), 535 (P–S sym), 360, 252 (M–S) cm^{-1} .

TABLE I. Analytical Data for the Compounds.

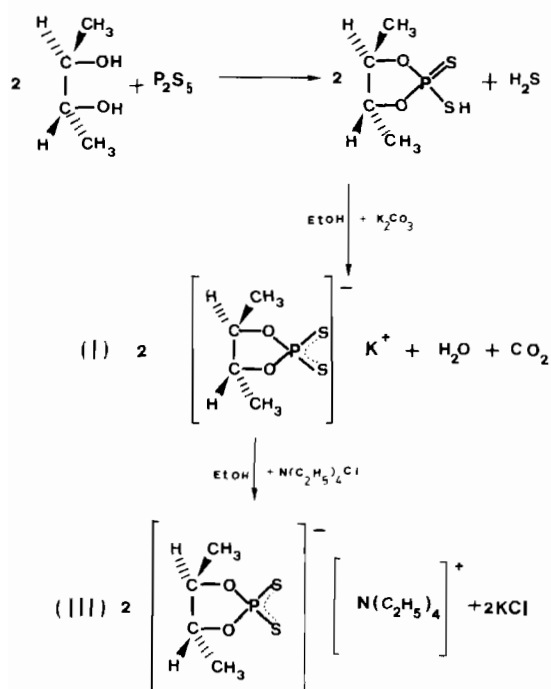
No.	Compound	Colour	M.p.	$[\alpha]_D$ (C%, Solv.)	$[M]_D$
<i>I</i>	$(-)\text{C}_4\text{H}_8\text{O}_2\text{PS}_2\text{K}$	white	288–92	–43.3 (0.6%, CH_3CN)	–96.2
<i>II</i>	$\text{C}_4\text{H}_8\text{O}_2\text{PS}_2\text{K}$	white	288–90		
<i>III</i>	$(-)\text{C}_4\text{H}_8\text{O}_2\text{PS}_2\text{N}(\text{C}_2\text{H}_5)_4$	white	178–82	–44 (1.2%, $(\text{CH}_3)_2\text{CO}$)	–138
<i>IV</i>	$\text{C}_4\text{H}_8\text{O}_2\text{PS}_2\text{N}(\text{C}_2\text{H}_5)_4$	white	170–74		
<i>V</i>	$(-)[\text{Nd}(\text{C}_4\text{H}_8\text{O}_2\text{PS}_2)_4]\text{N}(\text{C}_2\text{H}_5)_4$	pale lilac	234–36	–9.8 (2.8%, CH_3CN)	–98.7
<i>VI</i>	$[\text{Nd}(\text{C}_4\text{H}_8\text{O}_2\text{PS}_2)_4]\text{N}(\text{C}_2\text{H}_5)_4$	pale lilac	232–37		
<i>VII</i>	$(-)[\text{Eu}(\text{C}_4\text{H}_8\text{O}_2\text{PS}_2)_4]\text{N}(\text{C}_2\text{H}_5)_4$	red orange	202–8	–3.9 (1.3%, CH_3CN)	–39.6
<i>VIII</i>	$[\text{Eu}(\text{C}_4\text{H}_8\text{O}_2\text{PS}_2)_4]\text{N}(\text{C}_2\text{H}_5)_4$	red orange	225–28		
<i>IX</i>	$(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2\text{K}$	white	208–12		
<i>X</i>	$(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2\text{N}(\text{C}_2\text{H}_5)_4$	white	128–30		
<i>XI</i>	$\text{Nd}[(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_4\text{N}(\text{C}_2\text{H}_5)_4$	pale lilac	152–55		
<i>XII</i>	$\text{Eu}[(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2]_4\text{N}(\text{C}_2\text{H}_5)_4$	orange	158–62		

Tetraethylammonium Tetrakis(O,O'-diethyl dithiophosphato)europium(III), [NEt₄][Eu(ddtp)₄], (XII)

The compound was obtained as reported [13, 14, 19]. Elemental analyses agree with the composition given.

The ¹H NMR spectrum in CD₃CN shows four signals 5.88 (16H, m, 8CH₂); 3.03 (8H, q, 4CH₂); 1.85 (24H, m, 8CH₃); 1.10 (12H, m, 4CH₃).

The IR spectrum is similar to that of complex (XI).



Results and Discussion

The formation of the $[(-)\text{bdtp}]^-$ ion salts, *I*, *III* (Scheme 1, Table I) differs from the reported synthesis of the achiral sodium salt for the use of ethanol during the reaction [20].

However no change has been ascertained in the composition and optical activity of the dissolved compound, *I*, in an ethanolic solution after boiling for 6 hrs. Chemical analyses, IR and ¹H NMR spectra showed that no ethanolysis takes place on the cyclic dimethylethylene dithiophosphate group, confirming the high stability of the ring in dithiophosphate cyclic compounds [21, 22].

Synthesis of the ddtp^- ion derivatives afforded a particular comparison with the properties of the bdtp^- ion compounds. The two ligand ions fail to absorb under 4000 cm^{-1} and thus it is possible to study the *f*-*f* and charge transfer transitions present at lower frequency values in lanthanide complexes.

Synthesis of the complexes of Ln(III) where Ln = Nd, Eu (Table I) was performed starting from hydrated chlorides of the trivalent lanthanoids, as well as from anhydrous chlorides, which react in ethanolic solution with bdtp^- to give the complexes *V*–*VIII*, as well as the complexes *XI* and *XII*, from ethyldithiophosphate ddtp^- following reported methods [13, 19].

Preliminary X-ray diffraction studies confirm the composition of the complexes [23]. The structure of $\{\text{NEt}_4\}\{\text{Eu}[(-)\text{bdtp}]_4\}$ complexes, *VII*, shows one Eu^{3+} ion with eight sulphur atoms coordinated, $d(\text{Eu}-\text{S}) = 2.89\text{ \AA}$, and the coordination polyhedral could be described as a dodecahedra very similar to that of $\{\text{Ln}[\text{S}_2\text{P}(\text{OEt})_2]_4\}^-$ and $\{\text{Ln}[\text{S}_2\text{PMe}_2]_4\}^-$ type compounds previously reported [24].

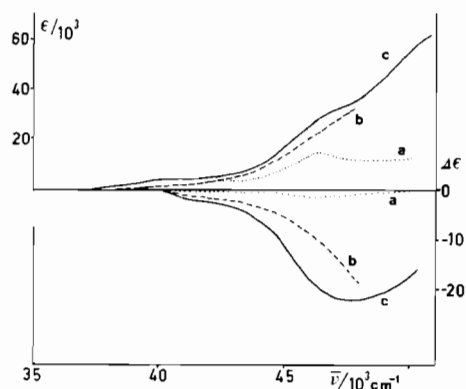


Fig. 1. Absorption and CD spectra in CH_3CN solution of: (-)bdtpNEt₄, a); ----- {NEt₄}{Eu[(-)bdtp]₄}, b); ——— {NEt₄}{Nd[(-)bdtp]₄}, c).

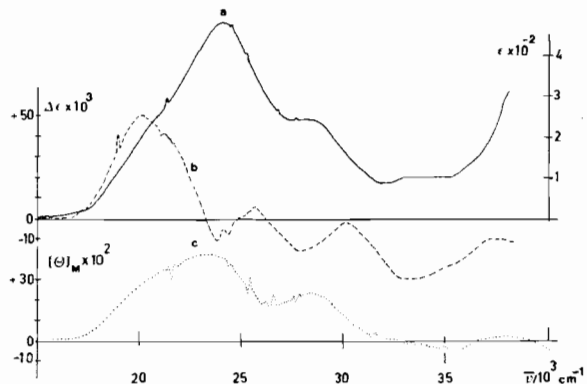


Fig. 3. ——— Absorption; MCD and ----- CD spectra in CH_3CN solution of {NEt₄}{Eu(bdtp)₄} and {NEt₄}{Eu[(-)bdtp]₄}.

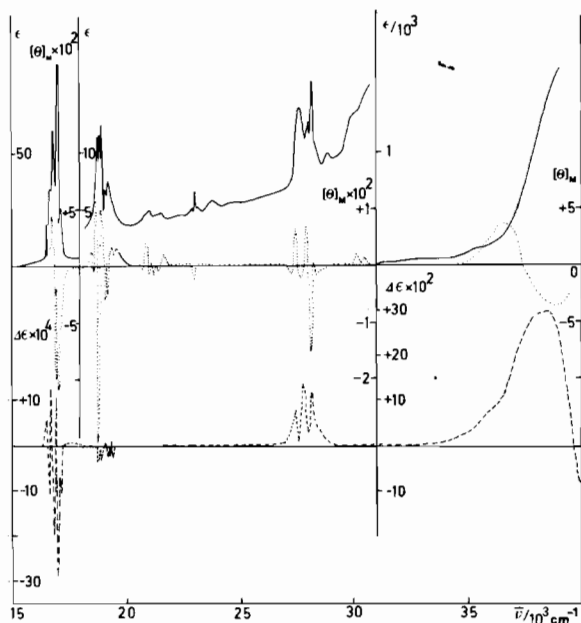


Fig. 2. ——— Absorption; MCD and ----- CD spectra in CH_3CN solution of [NEt₄][Nd(bdtp)₄] and {NEt₄}{Nd[(-)bdtp]₄}.

Only when Ln(III) reacts with 3 mol or less of ligand do we have indication of the formation of neutral tris-(butane dithiophosphato)-complexes of the lanthanoids, but the study of this reaction is still in progress.

Infrared Spectra

The IR spectra of the compounds were measured over the range 4000–200 cm^{-1} as reported in the experimental section. Bearing in mind the structure of the complexes, the assignments are a consequence of a comparison with similar transition-metal com-

plexes, with the free ligands and also the various reported lanthanoid complexes. No differences were registered between chiral and achiral compounds. In all complexes the spectra show a strong band at *ca.* 250 cm^{-1} assigned to the $\nu(\text{M}-\text{S})$ stretching vibration. Similar assignments have been reported for Ln(III) complexes with ddt⁻ ion as ligand [19]. For analogous transition metal complexes a stretching $\nu(\text{M}-\text{S})$ at *ca.* 300 cm^{-1} has been proposed [18, 25]. Other bands characteristic of the ligand structure are assigned by us to $\nu(\text{S}-\text{P}-\text{S})$ sym. and asym. stretching in the regions 530–570 and 620–660 cm^{-1} . The $\nu(\text{O}-\text{P}-\text{O})$ sym. and asym. stretching frequencies were identified between 920–960 and 1014–1042 cm^{-1} respectively. A characteristic spectral pattern in the C–H stretching region, 2850–3000 cm^{-1} , and the bending region 1370–1470 cm^{-1} distinguishes the tetraethylammonium derivatives from those of potassium.

NMR Spectra

The ¹H and ³¹P NMR data are given in the experimental part. The chiral and achiral compounds give signals at the same positions. From these data we observe strong paramagnetic shifts of the ¹H signals in the complexes compared with the corresponding free ligand. These shifts are (0.44 ppm) positive downfield and (–0.22 ppm) negative highfield for CH₃ signals in Eu(III) and Nd(III) complexes respectively. The CH group signals show lower paramagnetic shifts (0.07 and 0.17 ppm). The CH₂ groups of the NEt₄⁺ cation show (–0.18 ppm) highfield paramagnetic shifts for Eu(II) and (0.03 ppm) downfield for Nd(III) complexes. A similar trend of the paramagnetic shifts for Eu(III) and (0.03 ppm) down-group proton signals of [NEt₄][Ln(ddtp)₄] complexes. The nature of these shifts in similar complexes was discussed [26].

TABLE II. Absorbance, MCD and CD Solution (CH₃CN) Spectra for Achiral and Chiral Neodymium(III) Tetrakis(alkyl) dithio-phosphate) Complexes.

Assignments $^4I_{9/2} \rightarrow J$	[NEt ₄] [Nd(bdtp) ₄]			[NEt ₄] {Nd((-)bdtp) ₄ }	[NEt ₄] [Nd(ddtp) ₄]		
	$\bar{\nu} \times 10^{-3}$ ^a	ϵ ^b	$[\theta]_M \times 10^2$ ^c	$\Delta\epsilon \times 10^4$ ^b	$\bar{\nu} \times 10^{-3}$ ^a	ϵ ^b	$[\theta]_M \times 10^2$ ^c
	16.45			+6.8	16.45	4.7sh	+0.34
	16.55			-10.1			
	16.66	18	+2.3	+12.9	16.68	16.9	+3
	16.75	32	+4.25		16.76	31	+6.4
	16.8	59.2	-9.97	-19	16.83	55.5	-13.8
	16.85			+11			
$^4G_{5/2}$	16.9	88.0	-10.9	-28	16.92	79.4	-14.3
$^2G_{7/2}$	17.06	24.2	-5.9	-10.8	17.1	25	-6.2
	18.46		+0.22		18.47		+0.34
	18.5		-0.06		18.52	3.8	-0.34
	18.7	11.9	+1.14	-3.6	18.64		+1.8
$^2K_{13/2}, ^4G_{7/2}$	18.76	11.9	-3.1		18.73	17.4	-4.5
	18.83	12.3	+1	-3.3	18.8	16.9	-2.3
					18.85	17.9	+1.84
	18.99		-0.6	+0.8	19.0		-1.0
	19.05	6.5		+0.8	19.06	6.5	+0.16
	19.12		-0.5	-2.2	19.12		-0.84
	19.17		+0.3	-1.7	19.19		+0.5
$^4G_{9/2}$	19.2	7.5		+1.4	19.23	7.6	
	19.3		+0.3	-2.7	19.34	5.4	+0.3
	19.57		+0.3				
$^2K_{15/2}$	20.7	3.5	-0.09		20.7		-0.5
	20.85		+0.4		20.88		+0.7
$(^2D_1, ^2P)_{3/2}, ^2G_{9/2}$	20.9	3.7	-0.2		20.98		-0.16
					21.07		+0.16
$^4G_{11/2}$	21.15		-0.2		21.14		+0.16
	21.36		-0.1		21.41		-0.16
	21.5	3.4					
	21.64		+0.2		21.6		+0.25
	22.83	5.1	-0.02		22.78		+0.02
	22.94		-0.3		22.99		-0.5
$^2P_{1/2}$	23.0	6.5		+6.8			
$^2D_{5/2}$	23.8	5.7					
	27.3		-0.2		27.25		-0.27
	27.4		+0.7	+8.2	27.4		+1.1
$^4D_{3/2}$	27.55	14	-0.2		27.55	9.8	-0.4
$^4D_{5/2}$	27.7		-0.4	+13.6	27.62	12.5	-0.8
$^2I_{11/2}$	27.9	12.6	+0.66		27.85		+1.3
$^4D_{1/2}$	28.09	16.4	-1.6	+13.6	28.05	10.9	-2.5
	28.3		-0.2		28.17		+0.2
$^2L_{15/2}$	28.92	9.9			28.98	8.2	+0.17
					29.07		+0.17
$^2I_{B/2}$	30.1		+0.2		30.03		+0.27
	30.5		+0.15		30.4		+0.23
	36.75		+3.9		37.3		+7.3
C.T.	38.45			+2930			
	39.06		-3.5		38.9		-4.3
I.L.	42.5			-28700			
	47.6			-225000			

^a $\bar{\nu}$ expressed in cm⁻¹. ^b ϵ and $\Delta\epsilon$ expressed in dm³ mol⁻¹ cm⁻¹. ^c $[\theta]_M = 3300 \Delta\epsilon$, molar ellipticity expressed in degrees deciliter dm⁻¹ mol⁻¹ per unit gauss.

Electronic Absorbance, MCD and CD Spectra

Vis-UV, MCD and CD solution spectra in the spectral range 14000–40000 cm⁻¹ of achiral and

chiral [NEt₄] [Ln(bdtp)₄] complexes and corresponding ligands are reported in Figs. 1, 2 and 3. The observed energies, the intensities of the bands

TABLE III. Absorbance, MCD and CD Solution (CH₃CN) Spectra for Achiral and Chiral Europium(III) Tetrakis(alkyl dithiophosphate) Complexes.

Assignments	[Eu(bdtp) ₄] ⁻			Eu[(-)bdtp] ₄ ⁻ Δε × 10 ⁻³ b	[Eu(ddtp)] ⁻		
	$\bar{\nu} \times 10^{-3}$ a	ε ^b	[θ] _M × 10 ² c		$\bar{\nu} \times 10^{-3}$ a	ε ^b	[θ] _M × 10 ² c
⁷ F ₁ → ⁵ D ₀	16.95			+2			
⁷ F ₀ → ⁵ D ₀					17.3	5	
⁷ F ₁ , ⁷ F ₀ → ⁵ D ₁	18.99			+10	18.7		+1
	19.05			-6	18.8		-1
C.T.	20.0			+50			
⁷ F ₁ → ⁵ D ₂	21.1			-2			
⁷ F ₀ → ⁵ D ₂	21.35	20					
	21.42			+1	21.4	20	
	21.55		-6		21.5		-7
	21.59			-1			
	23.25		+43		23.5		+51
C.T.	24	480		-11	24.1	580	+1
	24.35		-1		24.3		-1
⁷ F ₁ , ⁷ F ₀ → ⁵ D ₃	24.42			-4			
	24.5		+1		24.45		+1
	25.3		-5		25.3		-3
⁷ F ₁ , ⁷ F ₀ → ⁵ L ₆	25.4		+5		25.4		+5
	25.6			+5			
					26.0		+1
⁷ F ₁ → ⁵ L ₇ , ⁵ G ₅ , ⁵ G ₆	26.2		+1		26.15		-1
	26.3		-1		26.25		+2
					26.4		-1
⁷ F ₀ → ⁵ G ₂ , ⁵ G ₄ , ⁵ G ₆	26.5		+5		26.6		+7
					26.75		-2
	27.5		+2				
⁷ F ₁ , ⁷ F ₀ → ⁵ D ₄ , ⁵ L ₉	27.6		-1		27.65		-5
	27.8		+1		27.75		+2
	27.9			-16	27.8	300	+24
C.T.	28.4	240	+23				
⁷ F ₁ , ⁷ F ₀ → ⁵ H ₄ , ⁵ H ₅ , ⁵ H ₆	31.3		-1		31.3		-3
	31.5		+1		31.45		+3
⁷ F ₁ , ⁷ F ₀ → ⁵ F ₄ , ⁵ I ₄	33.3		+1		33.3		+2
	33.4		-1		33.45		-2
C.T.	33.3	100		-30			
⁷ F ₀ → (⁵ I, ⁵ H) ₆	34.9		+1		34.85		-1
					34.95		+1
	34.5		-4		34.5		-6
C.T.	38.0		+3		38.5		+5

a, b, c See notes of Table IV.

and the assignments of the term to term transitions of the complexes are reported in Tables II and III.

Contemporaneous examination of electronic and chiroptical spectra enables one to determine the energies of intraligand, charge transfer and 4f-4f

transitions and, on the basis of their relative intensities, to establish their character which makes their assignments simpler. In fact the electronic transitions are sometimes observed better in CD spectra, as positive or negative Cotton effects, or in MCD with A, B, C, Faraday terms, than in absorbance spectra.

TABLE IV. Oscillator, Dipole and Rotational Strengths for the $\text{Nd}^{3+} 4I_{9/2} \rightarrow J$ Transitions in $[\text{NEt}_4]\{\text{Nd}(-)\text{bdtp}\}_4$.

J	Energy range (cm^{-1})	$f \times 10^6$ ^a cgsu	$D \times 10^{40}$ ^b cgsu	$R \times 10^{44}$ ^c cgsu	$\Delta\epsilon/\epsilon = g \times 10^5$
$4G_{5/2}, 2G_{7/2}$	16.2–17.4	101	125	+2.3 –6.2	–3.3
$2K_{13/2}, 4G_{7/2}$	18.4–19.0	17.2	19.2	–0.68	–2.9
$4G_{9/2}$	18.9–20.0	20.6	22.5	+0.24 –0.23	–3.1
$4D_{3/2}, 4D_{5/2},$ $2I_{11/2}, 4D_{1/2},$ $2L_{15/2}, 2I_{13/2}$	27.0–29.0	92	69	+8.05	+9.6

^aOscillator strength calculated as $f_{ba} = 0.476 \times 10^{30} \nu D_{ba}$.

^bDipole strength calculated as $D_{ba} = 91.8 \times 10^{-40} \int (\epsilon/\bar{\nu}) d\bar{\nu}$.

^cRotational strength calculated as $R_{ba} = 23 \times 10^{-40} \int (\Delta\epsilon/\bar{\nu}) d\bar{\nu}$.

TABLE V. Oscillator, Dipole and Rotational Strengths for the Eu^{3+} Transitions in $[\text{NEt}_4]\{\text{Eu}(-)\text{bdtp}\}_4$.

J	Energy range (cm^{-1})	$f \times 10^6$ ^a cgsu	$D \times 10^{40}$ ^b cgsu	$R \times 10^{44}$ ^c cgsu	$\Delta\epsilon/\epsilon = g \times 10^5$
$7F_1 \rightarrow 5D_0$	16.83–17.07			+2.8	
$7F_1, 7F_0 \rightarrow 5D_1$	18.7–19.01 19.01–19.15			+7.6 –4	
$7F_1 \rightarrow 5D_2$	21.0–21.2			–3.2	
$7F_0 \rightarrow 5D_2$	21.25–21.5 21.5–21.6	32.2	31.6	+1.8 –1.5	+3
$7F_0 \rightarrow 5D_3$	24.3–24.65			–4.7	

^{a,b,c}See notes of Table IV.

It is hypothesized that the weak f–f transitions have some magnetic dipole character, and in some cases magnetic dipole transitions have been detected [2].

Whenever possible the oscillator strength, as well as the rotational strength, of each J level have been measured (see Tables IV and V). The measurements of the oscillator strength, f , the intensities of the Faraday terms and the rotational strength R , enable one to determine ‘hypersensitive’ electronic transitions and/or ‘CD sensitive’ transitions characterising the dodecahedral LnS_8 chromophore.

$[\text{Ln}(\text{bdtp})_4]^-$ and $[\text{Ln}(\text{ddtp})_4]^-$ present the same spectral pattern with small shifts of the observed bands indicating that this ligand substitution has only a small effect on the LnS_8 chromophore.

The g factor values have been calculated, as a ratio, $g = \Delta\epsilon/\epsilon$, from the values of anisotropic and isotropic absorbances of the same solution at the same wavelength.

Ligand Transition

The $(-)\text{bdtpNEt}_4$, III, ligand is almost transparent up to 40000 cm^{-1} , $\epsilon \sim 60$. The UV and CD spectra (Fig. 1) exhibit a shoulder at *ca.* 41500 cm^{-1} , $\epsilon = 3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $\Delta\epsilon = -0.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, followed by a large absorption band at 46500 cm^{-1} , $\epsilon = 14300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\delta(-) 1500 \text{ cm}^{-1}$, and a corresponding negative Cotton effect, $\Delta\epsilon = -1.3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, with a g factor, $\Delta\epsilon/\epsilon = -8.9 \times 10^{-5}$. This band could be attributed to a $n - \pi^*$ transition involving the lone pairs of sulphur atoms, similar to that at 44500 cm^{-1} in the ddtp^- spectra assigned to a $3p \rightarrow 4s$ sulphur transition by Jørgensen [27].

Intraligand Transitions

In the same range the Ln(III) complexes electronic spectra show a continuous increasing absorbance with shoulders not clearly resolved at about the same position as the absorption band of the ligand. The CD spectra of the chiral complexes show a blue shift

of the intraligand band at 47500 cm^{-1} for Nd(III) and over 50000 cm^{-1} for Eu(III) complexes, *V* and *VII*. The *g* factor value, -6.6×10^{-4} , indicates a more pronounced magnetic dipole character of this transition in the Nd(III) complex than in the ligand.

Charge Transfer and 4*f*–4*f* Transitions

Neodymium Spectra

In the spectral range $14000\text{--}40000\text{ cm}^{-1}$ the absorbance spectra of Nd(III) complexes, (*V*, *VI*), exhibit some groups of closely adjacent bands in CH_3CN solution (see Fig. 2) at 14.5, 16.9, 18.8, 19.2, 20.9, 23.0, $28.1 \times 10^3\text{ cm}^{-1}$ which are assigned as 4*f*–4*f* transitions from the $^4I_{9/2}$ to the excited J level (Table II) on the basis of a comparison with the assignments reported for $\text{Nd}(\text{aq})^{3+}$ and Nd^{3+} free ion [28].

The MCD spectra of achiral compounds (*VI*) show Faraday terms corresponding to the absorption band groups, but in most cases the transition energies are better detectable owing to the alternate presence of positive or negative terms. Analysis of these terms is under way and in the present work only the energies and intensities of the observed transition are reported (Tables II and IV).

The CD spectrum of the neodymium chiral complex *V* shows a series of Cotton effects, not always corresponding in frequency to the absorption bands (see Fig. 2 and Table II). However, the $^4I_{9/2} \rightarrow ^4G_{5/2}$ transition around 16900 cm^{-1} shows eight sharp lines, the most intense of which, with a *g* value of -3.3×10^{-5} , confirms the pseudo-quadrupolar character of this transition. The corresponding absorbance band has the same extinction coefficient, $\epsilon = 88$, as that in $[\text{NEt}_4][\text{Nd}(\text{ddtp})_4]$, and this confirms its hypersensitivity in that it is 10–15 times more intense than the band in the Nd^{3+} aquo ion [2, 29, 30]. The oscillator strength, $f = 101 \times 10^{-6}$ cgsu, (see Table IV), is also similar to that of $\text{Na}[\text{Nd}(\text{ddtc})_4]$, $f = 105 \times 10^{-6}$ cgsu, and about 3–5 times higher than in Nd^{3+} complexes with oxygenated ligands [13a, 30b].

When compared with the spectrum of the $\text{Nd}(\text{aq})^{3+}$ ion, the spectra of the neodymium(III) dimethylethylene dithiophosphate, as well as those of the neodymium diethyl dithiophosphate complexes, show a definite red shift for nearly all the transitions. This nephelauxetic effect, due to a lowering of the interelectronic-repulsion parameters in the complex, may be qualitatively measured through the β mean value of the ratios between the observed baricenters of the corresponding J levels of the complex and the aquo ion for the higher frequency bands in the range $14000\text{--}29000\text{ cm}^{-1}$ [13]. The resulting $\bar{\beta} = 0.981$ value for the bdtp^- ligand in the neodymium(III) complex is similar to those obtained for analogous sulphur ligands [19],

though showing a slightly stronger nephelauxetic effect of bdtp^- compared with ddtp^- , $\beta = 0.985$.

One interesting point in the CD spectrum of the chiral $[\text{NEt}_4][\text{Nd}(\text{bdtp})_4]$ complex (*V*) is the observation of a large Cotton effect at 38450 cm^{-1} , $\Delta\epsilon = +0.29$, with no identifiable corresponding absorbance bands under the continuous increasing absorption line. The *g* factor of these transition is about 10^{-4} or higher. Because of its energy and large half-width, the band could be assigned as electron-transfer transitions from the filled π orbitals of the ligands to the 4*f* orbitals of the metal ion. In some other lanthanoid complexes, which are more reducible than neodymium(III), such transitions occur at lower frequencies outside the spectral region of the intraligand transitions, while the neodymium(III) complex with bromine ion as ligand shows a redox band at $\sim 49000\text{ cm}^{-1}$ [11].

To date no observation of this band has been reported for the known neodymium(III) complexes, perhaps because it is weak and unresolved under the continuous increasing absorbance line. Its magnetic dipole character determines on the contrary the strong Cotton effect in the CD spectrum.

If the 38450 cm^{-1} transition is considered the first electron-transfer band at lower frequencies and the optical electronegativity of the ligand is known, the uncorrected optical electronegativity of the Nd(III) could be calculated from the known Jørgensen relation:

$$\sigma = [\chi_{\text{opt}}(\text{bdtp}^-) - \chi_{\text{uncorr}}(\text{Nd}^{\text{III}})] \times 30000\text{ cm}^{-1}$$

[31]. The optical electronegativity of the bdtp^- ligand $\chi_{\text{opt}}(\text{bdtp}^-) = 2.56$ is obtained from the spectra of Eu^{3+} complexes (see later). Using this value the uncorrected electronegativity of Nd(III) results from the above equation, $\chi_{\text{uncorr}}[\text{Nd}^{\text{III}}] = 1.28$, thus confirming that Nd(III) is less reducible than Eu(III), $\chi_{\text{uncorr}}[\text{Eu}^{\text{III}}] = 1.9$ [31b].

Europium Spectra

In the spectral range $15000\text{--}40000\text{ cm}^{-1}$, and in CH_3CN solution Vis-UV spectra, the Eu(III) complexes exhibit a series of broad and moderate intensity absorption bands at 24000, 28500, 33500 cm^{-1} with unresolved shoulders at lower and higher frequencies, which are however clearly visible at 20000 and 38000 cm^{-1} through CD and MCD spectra (Fig. 3 and Table III). Because of their large half-width, their energy and their moderate intensity, these bands are assigned to the electron-transfer transitions from the filled π orbitals of the ligands to the 4*f* orbitals of the reducible metal ions. These charge transfer bands were identified by Ciampolini through a gaussian analysis of the absorbance spectrum of $[\text{NEt}_4][\text{Eu}(\text{ddtp})_4]$ [13b]. The MCD spectrum of $[\text{Eu}(\text{bdtp})_4]^-$, *VIII*, and $[\text{Eu}(\text{ddtp})_4]^-$,

XII, complexes reveals the presence of the five charge-transfer transition (see Table III), showing in particular a positive Faraday term at 38000 cm^{-1} . The CD spectrum shows the charge-transfer transition at 20000 cm^{-1} as a broad Cotton effect, $\Delta\epsilon = +50 \cdot 10^{-3}$, $g = +2.5 \times 10^{-4}$, due evidently to a magnetic dipole-type transition, together with other broad Cotton effects at 28000 , $\Delta\epsilon = -16 \times 10^{-3}$, $g = -6.6 \times 10^{-5}$, and 33300 cm^{-1} , $\Delta\epsilon = -30 \times 10^{-3}$, $g = -3 \times 10^{-4}$, once again a magnetic dipole-type transition. A small Cotton effect, 23800 cm^{-1} , $\Delta\epsilon = -11 \times 10^{-3}$, $g = -2.5 \times 10^{-5}$, corresponds to the strongest absorption band.

The reducing character of the bdtp^- ligand has been correlated with the optical electronegativity, $\chi_{\text{opt}}(\text{bdtp}^-)$, calculated according to the Jørgensen formula, using the reported value of $\chi_{\text{uncorr}}(\text{Eu}^{\text{III}}) = 1.9$, and the frequency value of the first intense charge-transfer transitions, $\sigma = 20000\text{ cm}^{-1}$. The value of the optical electronegativity so calculated, $\chi_{\text{opt}}(\text{bdtp}^-) = 2.56$, places the bdtp^- ligand in the optical electronegativity series near R_2NCS_2^- , (dtc^-) , and ddtp^- , which shows an analogous strong shoulder at about $20\text{--}21 \times 10^3\text{ cm}^{-1}$ in MCD and absorbance spectra. We may thus consider the reducing character of bdtp^- as being similar to that of ddtp^- and lower than that of the Br^- halogen ion.

The small and narrow bands superposed on the broad electron-transfer bands are assigned to the $4f\text{--}4f$ through comparison with the $\text{Eu}(\text{aq})^{3+}$ ion transitions previously reported [32], and comparison between isotropic and anisotropic absorbance spectra, which enables one to discriminate between electric dipole-and/or magnetic dipole-type, allowed transitions. Similar spectral pattern have been registered for the diethyl-dithiocarbamate europium(III) complex, $\text{Na}[\text{Eu}(\text{ddtc})_4]$ [11, 13a]. These bands are not completely detectable in the absorption spectra. Generally the electric dipole-type transitions are clearly exhibited in absorption and even better in MCD spectra, while the magnetic dipole-type transitions are shown in CD spectra. This seems to establish the presence, and confirm the hypersensitive nature, of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ transition at 21300 cm^{-1} from the relatively strong absorption band and MCD terms, and from the weak Cotton effect at the same frequency in the spectra of achiral and chiral complexes respectively. At the same time the ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$ at 16950 cm^{-1} , the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, at $18990\text{--}19050\text{ cm}^{-1}$ and the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ at 24420 cm^{-1} transitions show their CD sensitive nature with the relatively high Cotton effects exhibited in CD spectra and the small or absent signals in absorbance and MCD spectra. This comparison thus allows one to identify a series of CD sensitive bands to use as chiroptical probes in chiral systems containing Ln-S chromophoric groups, together with the hypersensitive

transition bands detectable in the absorbance and MCD spectra of achiral complexes.

The g factor of the CD sensitive bands of the $\text{Eu}(\text{III})$ complex is not determined on account of the inadequate detection of corresponding absorption bands, but it could be estimated higher than $10^{-3}\text{--}10^{-4}$.

Intensities

The oscillator and rotational strengths of the $4f\text{--}4f$ transition bands are reported in Tables IV and V. The oscillator strength is often not detectable owing to the weakness of the bands. The values of the rotational strengths of some CD sensitive bands of the $\text{Eu}(\text{III})$ complex, *VII*, are of the same order of magnitude as those obtained from the chiral $\text{Nd}(\text{III})$ complex, *V*. On the basis of the obtained rotational strengths, we may consider ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, with $R = +7.6 \times 10^{-44}$ and $R = -4.1 \times 10^{-44}$ cgsu, as the best CD sensitive transition of the $\text{Eu}(\text{III})$ complex and ${}^4\text{I}_{9/2} \rightarrow ({}^4\text{D}_{3/2}, {}^4\text{D}_{5/2}, {}^2\text{I}_{11/2}, {}^4\text{D}_{1/2}, {}^2\text{L}_{15/2}, {}^2\text{I}_{13/2})$, with $R = +8 \times 10^{-44}$, as good CD sensitive transitions of the $\text{Nd}(\text{III})$ complex. The purely magnetic dipole character of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ transition was confirmed with absorption and emission spectra of Eu^{3+} doped in $\text{GdAl}_3(\text{BO}_3)_4$ by Peacock, who showed contemporaneously the pseudo quadrupolar character of the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, hypersensitive transition [2].

The values of the oscillator strengths confirm that the term to term transitions, ${}^4\text{I}_{9/2} \rightarrow ({}^4\text{G}_{5/2}, {}^2\text{G}_{7/2})$ with $f = 101 \times 10^{-6}$ cgsu and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ with $f = 32.2 \times 10^{-6}$ cgsu, are the hypersensitive of $\text{Nd}(\text{III})$ and $\text{Eu}(\text{III})$ complexes respectively. The rotatory strengths of the ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ transitions indicate their magnetic dipole character.

Conclusions

The synthesis of chiral rare earths complexes allows us to study their chiroptical properties and use these to complete the knowledge of the electronic transitions in the lanthanoid complexes.

Chiroptical spectroscopy plays a sizeable role in the assignment of $4f\text{--}4f$ and charge transfer transitions. The measurements of rotational strengths, together with the oscillator strengths, enable one to pinpoint the CD-sensitive and the hypersensitive bands of lanthanoid complexes to be used potentially as probes in systems containing analogous LnS_8 chromophoric groups.

It is hoped that the knowledge of the structural data and of the experimental intensities, providing a basis for optical activity calculations, will enable us to test the ligand polarization theory.

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References

- 1 S. F. Mason, *Acc. Chem. Res.*, **12**, 55 (1979); *idem*, Optical Activity and Chiral Discrimination, Reidel, Dordrecht, 161 (1979) and references therein; *idem*, *Structure and Bonding*, **39**, 43 (1980).
- 2 R. D. Peacock, *Structure and Bonding*, **22**, 83 (1975); *idem*, *Chem. Phys. Lett.*, **35**, 420 (1975); *idem*, *Mol. Phys.*, **33**, 1239 (1977); *idem*, *J. Mol. Struct.*, **46**, 203 (1978).
- 3 S. Misumi, S. Kida and T. Isobe, *Spectrochim. Acta*, **24A**, 271 (1968); *idem*, *Bull. Chem. Soc. Jpn.*, **47**, 421 (1974); S. Misumi, S. Kida, T. Isobe, Y. Nishida and H. Furuta, *ibid.*, **42**, 3433 (1969).
- 4 L. I. Katzin, *Inorg. Chem.*, **7**, 1183 (1969); *idem*, *ibidem.*, **8**, 1649 (1969); L. I. Katzin and E. Gulyas, *ibidem.*, **7**, 2442 (1968).
- 5 R. Prados, L. G. Stadtherr, H. Donato Jr. and R. B. Martin, *J. Inorg. Nucl. Chem.*, **36**, 689 (1974).
- 6 a) F. S. Richardson, in *Optical Activity and Chiral Discrimination*, S. F. Mason (ed.), Reidel, Dordrecht, 107 (1979) and references therein.
b) H. G. Brittain and F. S. Richardson, *J. Am. Chem. Soc.*, **99**, 65 (1977).
- 7 B. Norden and I. Grenthe, *Acta Chem. Scand.*, **26**, 407 (1972).
- 8 R. W. Schwartz, A. Banerjee, A. C. Sen and M. Chowdhury, *J. Chem. Soc. Faraday II*, **76**, 620 (1980).
- 9 J. D. Saxe, T. R. Faulkner and F. S. Richardson, *J. Chem. Phys.*, **76**, 1607 (1982).
- 10 Y. Kato and M. Asano, *Bull. Chem. Soc. Jpn.*, **52**, 999 (1979).
- 11 C. K. Jørgensen, *Mol. Phys.*, **5**, 271 (1962).
- 12 T. H. Siddal III and W. E. Stewart, *J. Inorg. Nucl. Chem.*, **32**, 1147 (1970).
- 13 a) M. Ciampolini, N. Nardi, P. Colamarino and P. Orioli, *J. Chem. Soc. Dalton*, 379 (1977);
b) M. Ciampolini and N. Nardi, *J. Chem. Soc. Dalton*, 2121 (1977).
- 14 A. A. Pinkerton, *Inorg. Nucl. Chem. Letters*, **10**, 495 (1974).
- 15 M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).
- 16 A. J. McCaffery, P. J. Stephens and P. N. Schatz, *Inorg. Chem.*, **6**, 1614 (1967).
- 17 D. E. Coldery, W. C. Fernelius and M. Shamma, *Inorg. Synth.*, **6**, 142 (1960).
- 18 R. G. Cavell, W. Byers and E. D. Day, *Inorg. Chem.*, **10**, 2710 (1971).
- 19 A. A. Pinkerton, Y. Meseri and C. Rieder, *J. Chem. Soc. Dalton*, 85, (1978).
- 20 A. N. Pudovik, R. A. Chercasov and R. M. Kondrat'eva, *Zr. Obshch. Khim.*, **38** (2), 307 (1968).
- 21 P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).
- 22 M. W. Wiczorek, *Phosphorus and Sulphur*, **9**, 137 (1980).
- 23 R. Kuroda and P. Biscarini, unpublished results.
- 24 A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc. Dalton*, 1470 (1981); *idem*, *ibidem*, 2464 (1976); S. Spiliadis, A. A. Pinkerton and D. Schwarzenbach, *ibidem.*, 1809 (1982).
- 25 D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 1299 (1968).
- 26 A. A. Pinkerton and W. L. Earl, *J. Chem. Soc. Dalton*, 267 (1978).
- 27 C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).
- 28 W. T. Carnall, P. R. Fields and K. Rajank, *J. Chem. Phys.*, **49**, 4424 (1968).
- 29 G. R. Choppin, D. E. Henrie and K. Buijs, *Inorg. Chem.*, **5**, 1743 (1966).
- 30 a) D. G. Karraker, *Inorg. Chem.*, **7**, 473 (1968);
b) *idem*, *ibidem*, **6**, 1863 (1967).
- 31 a) C. K. Jørgensen, *Oxidation Numbers and Oxidation Dates*, Springer, Verlag, Berlin 1969, p. 362;
b) *idem*, *Progress Inorg. Chem.*, **12**, 101 (1970).
- 32 W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.*, **49**, 4450 (1968).