

Syntheses and crystal structures of neodymium(III) and europium(III) complexes bearing dimethyl-, pyrrolidine-, or *S*-prolinol- dithiocarbamate ligands and their natural and magnetic circular dichroism spectra

Abdallah Yakubu,¹ Takayoshi Suzuki,^{*,1,2} Masakazu Kita³

¹ Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan.

² Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan.

³ Faculty of Education, Okayama University, 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan.

* Corresponding author: E-mail: suzuki@okayama-u.ac.jp.

Abstract

A series of Nd^{III} and Eu^{III} complexes containing achiral or chiral dithiocarbamate (dtc) ligands, [Ln(Xdtc)₃(NN)] {Ln = Nd or Eu; X = dimethyl- (Me₂), pyrrolidine- (pyr), or (*S*)-prolinol- (*S*-proOH); NN = 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy)}, were prepared and their crystal structures and spectroscopic properties, in particular the natural circular dichroism (CD) and magnetic circular dichroism (MCD), were investigated. The crystal structures of the complexes analyzed by the X-ray diffraction method showed an 8-coordinate geometry around the Ln^{III} center with comparable structural parameters to one another and to the related complexes reported previously. These complexes exhibited similar spectral patterns in their absorption, natural CD and MCD spectra in solution. Weak but characteristic sharp f–f transition bands were observed in the absorption and MCD spectra, but no CD signals associated with these transitions were observed even in the *S*-proOHdtc complexes. The MCD spectral pattern of the Eu^{III} complexes revealed a local C_{2v} symmetry around the Ln^{III} center in solution, in contrast to the aqua and the analogous β-diketonato Eu^{III} complexes.

Keywords: Dithiocarbamate, lanthanoid, crystal structures, magnetic circular dichroism, (*S*)-prolinol dithiocarbamate.

1. Introduction

Lanthanoid(III) complexes are currently being investigated extensively for a variety of their functionalities and applications, such as optical probes, medicine, microelectronics, and others [1,2]. Among the complexes widely studied, those of sulfur-donating ligands are still limited to report, owing to the unfavorable bond formation between the ‘hard acid’ lanthanoid ions and ‘soft base’ sulfur-donor ligands [3]. However, it has been well-studied in transition-metal complexes that dithiocarbamates ($RR'dtc^-$) stabilize a wide range of oxidation states of the metal ion, even for hard metal centers at higher oxidation states [4]. In fact, the synthesis and crystallographic studies of several lanthanoid(III) dithiocarbamate complexes have been reported in the last decades [5]. Regulacio et al. described a series of lanthanoid(III) dithiocarbamate complexes as precursors for lanthanoid sulfide materials and nanoparticles [6]. Boncher et al. [7] and Jin et al. [8] also prepared polycrystalline lanthanoid sulfide materials by the thermal decomposition of single-source lanthanoid dithiocarbamate complexes. Lanthanoid(III) complexes of piperidine and pyrrolidine dithiocarbamates have been investigated for their luminescence properties and catalytic activities in cyanohydrin syntheses [9]. Room temperature photoluminescence of Eu^{III} diethyldithiocarbamate and diphenyldithiocarbamate complexes was reported by Faustino et al [1]. Mahato et al. have reported a series of Ln^{III} morpholine 4-dithiocarbamate complexes with their interesting extended structure in the crystals and the spectroscopic properties in solution [2]. Despite of these studies, the chiroptical properties of lanthanoid(III) dithiocarbamate complexes by means of natural circular dichroism (CD) and magnetic circular dichroism (MCD) measurements are rarely investigated. For instance, CD spectroscopic studies for lanthanoid(III) β -diketonato complexes have been reported; Berry et al. observed the solid state CD spectra of the f–f transitions in $Na_3[Eu(ODA)_3]\cdot 2NaClO_4\cdot 6H_2O$ (ODA^- = oxydiacetate) [10]. Shirotani et al.

reported a solution CD spectrum of the f–f transitions in Na[Pr{(+)–hfbc}₄]•CH₃CN (hfbc[–] = 3-heptafluorobutylrylcamphorate) [11]. Circularly polarized luminescence spectra of Ln^{III} complexes with chiral ligands have also been studied [12]. In this study, a series of neodymium(III) and europium(III) complexes with achiral or chiral dithiocarbamate ligands were prepared. In particular, (*S*)-prolinol dithiocarbamate (*S*-proOHdte[–]) complexes are newly synthesized. The crystallographic studies of the complexes as well as their CD and MCD properties are investigated.

2. Experimental section

2.1. Materials and measurements

Sodium dimethyldithiocarbamate dihydrate and ammonium pyrrolidinedithiocarbamate were purchased from Tokyo Chemical Industry Co., Ltd. Hydrated salts of neodymium(III) and europium(III) chloride and 2,2'-bipyridine were obtained from Kanto Chemical Co., Inc., while 1,10-phenanthroline monohydrate was purchased from Nacalai Tesque Inc. (*S*)-Prolinol and carbon disulfide were purchased from Wako Chemical Ltd. All chemicals were of high purity grade and used as received.

The C, H, N and S elemental analysis of the complexes was carried out with a Perkin Elmer Series II CHNS/O Analyzer 2400 at Advanced Science Research Center, Okayama University. FT-IR spectra were recorded on a JASCO FT-001 FT-IR Spectrometer in KBr disk in the range 4000 – 400 cm^{–1}. The absorption spectra were obtained on a JASCO V-550 UV/VIS spectrophotometer. The natural CD and MCD spectra were measured on a JASCO J-1500 CD spectrometer. The magnetic field apparatus used for the MCD measurements was developed in this laboratory and reported previously [13]. All the spectra were recorded at room temperature.

2.2. Synthesis of K(*S*-proOHdte)

The potassium salt of *S*-prolinol dithiocarbamate, K(*S*-proOHdte), was prepared, according to the method described previously [14] with some modifications. An aqueous (3 mL) solution of KOH (0.030 mol) was cooled in an ice bath and diluted with 50 mL of ethanol.

The mixture was stirred for 5 min, and (*S*)-prolinol (0.030 mol) was added slowly with stirring, followed by dropwise addition of an excess amount of CS₂. The mixture was stirred for further 2 h in an ice bath, and the solvents were removed under reduced pressure. The residue was dried in vacuo over P₂O₅. A yellow solid product was formed, and the crude product was dissolved in a minimum amount of ethanol. The filtered solution was layered with diethyl ether to precipitate the dithiocarbamate salt. Yield: 50%. Anal. Calcd.: C, 33.46; H, 4.68; N, 6.50; S, 29.78%. Found: C, 33.07; H, 4.63; N, 6.44; S, 28.56%. FT-IR (cm⁻¹): $\nu(\text{C-N}) = 1399$, $\nu(\text{C-S}) = 966$.

2.3. Syntheses of Ln^{III} complexes with achiral dithiocarbamates

The Ln^{III} (Ln = Nd or Eu) complexes were prepared according to the procedure described previously [5] with some modifications. A methanolic solution (10 mL) of LnCl₃•6H₂O (1.00 mmol) was slowly added to a methanolic solution (10 mL) of Na(Me₂dtc) or NH₄(pyrdtc) (3.00 mmol), followed by the addition of a methanolic solution (10 mL) of bpy or phen (1.00 mmol). The mixture was stirred for 1 h, and the resulting precipitate was collected by filtration, washed with portions of methanol and dried in air. The crude product was purified by recrystallization from a chloroform solution by vapor diffusion of diethyl ether. The analytical and FT-IR spectral data are given below.

2.3.1 [Nd(Me₂dtc)₃(phen)] (**1a**): Pale blue crystals. Yield: 47.5%. Calcd for C₂₁H₂₆N₅NdS₆: C, 36.82; H, 3.83; N, 10.22; S, 28.08%. Found: C, 36.35; H, 3.74; N, 10.10; S, 27.55%. FT-IR (cm⁻¹): $\nu(\text{C-N}) = 1374$, $\nu(\text{C-S}) = 984$.

2.3.2 [Nd(pyrdtc)₃(phen)] (**1b**): Pale blue crystals. Yield: 78.5%. Calcd for C₂₇H₃₂N₅NdS₆: C, 42.49; H, 4.23; N, 9.18; S, 25.21%. Found: C, 41.73; H, 4.24; N, 9.00; S, 24.64%. FT-IR (cm⁻¹): $\nu(\text{C-N}) = 1424$, $\nu(\text{C-S}) = 1008$.

2.3.3 **[Nd(Me₂dtc)₃(bpy)] (1c)**: Pale blue crystals. Yield: 20 %. Calcd for C₁₉H₂₆N₅NdS₆•CHCl₃: C, 30.98; H, 3.49; N, 8.97; S, 24.65%. Found: C, 31.20; H, 3.87; N, 9.67; S, 27.45%. FT-IR (cm⁻¹): ν(C–N) = 1374, ν(C–S) = 982.

2.3.4 **[Nd(pyrdtc)₃(bpy)] (1d)**: Pale blue crystals. Yield: 66%. Calcd for C₂₅H₃₂N₅NdS₆: C, 40.62; H, 4.36; N, 9.47; S, 26.03%. Found: C, 40.12; H, 4.32; N, 9.46; S, 25.15%. FT-IR (cm⁻¹): ν(C–N) = 1425, ν(C–S) = 1009.

2.3.5 **[Eu(Me₂dtc)₃(phen)] (2a)**: Brick-red crystals. Yield: 29%. Calcd for C₂₁H₂₆N₅EuS₆: C, 36.40; H, 3.78; N, 10.11; S, 27.77%. Found: C, 36.12; H, 3.66; N, 9.97; S, 27.01%. FT-IR (cm⁻¹): ν(C–N) = 1374, ν(C–S) = 987.

2.3.6 **[Eu(pyrdtc)₃(phen)] (2b)**: Brick-red crystals. Yield: 70%. Calcd for C₂₇H₃₂N₅EuS₆: C, 42.06; H, 4.18; N, 9.09; S, 24.96%. Found: C, 41.75; H, 4.21; N, 8.96; S, 24.74%. FT-IR (cm⁻¹): ν(C–N) = 1424, ν(C–S) = 1010.

2.3.7 **[Eu(Me₂dtc)₃(bpy)] (2c)**: Brick-red crystals. Yield: 20%. Calcd for C₁₉H₂₆N₅EuS₆•CHCl₃: C, 30.48; H, 3.45; N, 8.89; S, 24.41%. Found: C, 29.65; H, 3.71; N, 9.17; S, 25.12%. FT-IR (cm⁻¹): ν(C–N) = 1374, ν(C–S) = 984.

2.3.8 **[Eu(pyrdtc)₃(bpy)] (2d)**: Brick-red crystals. Yield 50%. Calcd for C₂₅H₃₂N₅EuS₆•CHCl₃: C, 36.05; H, 3.84; N, 8.08; S, 22.21%. Found: C, 36.18; H, 4.16; N, 8.37; S, 23.13%. FT-IR (cm⁻¹): ν(C–N) = 1428, ν(C–S) = 1011.

2.4. Syntheses of Ln^{III} complexes with a chiral dithiocarbamate

A methanolic solution (10 mL) of LnCl₃•6H₂O (1.00 mmol) was added to a methanolic solution (10 mL) of K(*S*-proHdtc) (3.00 mmol) with stirring. A white precipitate (KCl) which appeared immediately was filtered off, and a methanolic solution (10 mL) of bpy or phen (1.00 mmol) was added to the filtrate. The mixture was stirred for 1 h, and the solution was

concentrated (to ca. 10 mL) under reduced pressure and filtered to remove the precipitated impurity. The filtrate was layered with diethyl ether to afford crystalline products, which were collected by filtration, washed with portions of Et₂O and dried in air. The analytical and FT-IR spectral data are given below.

2.4.1 [Nd(S-proOHdtc)₃(phen)] (1e): Pale blue crystals. Yield: 49%. Calcd for C₃₀H₃₈N₅O₃NdS₆•3H₂O: C, 39.71; H, 4.89; N, 7.72; S, 21.20%. Found: C, 39.25; H, 4.57; N, 7.74; S, 20.79%. FT-IR (cm⁻¹): ν(C–N) = 1423, ν(C–S) = 972.

2.4.2 [Eu(S-proOHdtc)₃(phen)] (2e): Orange crystals. Yield 52%. Calcd for C₃₀H₃₈N₅O₃EuS₆•3H₂O: C, 39.38; H, 4.85; N, 7.65; S, 21.03%. Found: C, 39.86; H, 4.53; N, 7.60; S, 20.53%. FT-IR (cm⁻¹): ν(C–N) = 1421, ν(C–S) = 972.

2.4.3 [Eu(S-proOHdtc)₃(bpy)] (2f): Yellow powder. Yield 52%. Calcd for C₂₈H₃₈N₅O₃EuS₆•C₄H₁₀O: C, 42.18; H, 5.31; N, 7.69; S, 21.12%. Found: C, 42.03; H, 4.64; N, 7.74; S, 21.03%. FT-IR (cm⁻¹): ν(C–N) = 1419, ν(C–S) = 969.

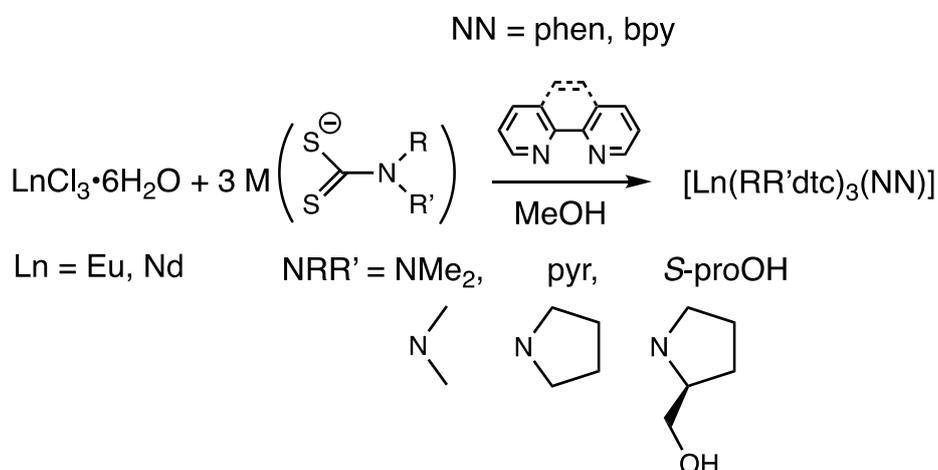
2.5. X-ray diffraction analysis

Single crystals of complexes **1a**, **1b** and **2a–c** were obtained from a mixture of chloroform and diethyl ether, while those of complexes **1c** and **2e** were from dichloromethane/diethyl ether and methanol/diethyl ether, respectively, using a vapor diffusion method. X-ray diffraction intensity data were collected on a Rigaku R-Axis RAPID diffractometer using graphite monochromated Mo-Kα (λ = 0.71075 Å) radiation. The crystal structures were solved and refined using SHELXS and SHELXL Version 2013/1 packages. The structures were solved using the direct method and expanded using Fourier techniques, and refined by full-matrix least-squares methods with anisotropic parameters for all non-hydrogen atoms. Hydrogen atoms were refined using the riding models [15].

3. Results and Discussions

3.1. Preparation and characterization of the complexes

The complexes, $[\text{Ln}(\text{Xdtc})_3(\text{NN})]$ ($\text{Ln} = \text{Nd}$ or Eu ; $\text{X} = \text{Me}_2$, pyr or $S\text{-proOH}$; $\text{NN} = \text{phen}$ or bpy), were prepared by a similar method reported previously [1,3,6] (Scheme 1) and characterized by elemental analysis and spectroscopic methods such as FT-IR and UV-vis absorption spectroscopy. Although, it was difficult to isolate analytically pure sample of the complex $[\text{Nd}(S\text{-proOHdtc})_3(\text{bpy})]$, the reaction product from NdCl_3 , $\text{K}(S\text{-proOHdtc})$ and bpy exhibited similar spectral patterns to those of the phen analogue. The isolated yields of these complexes were varied from 20% to 78%, and exhibited the following tendency of the ligands: $\text{Me}_2\text{dtc} < S\text{-proOHdtc} < \text{pyrdtc}$. Because the cations of these dithiocarbamate used in the preparation were different as $\text{Na}(\text{Me}_2\text{dtc})$, $\text{K}(S\text{-proOHdtc})$ and $\text{NH}_4(\text{pyrdtc})$, the byproducts (i.e., NaCl , KCl and NH_4Cl) were simultaneously formed with the desired Ln^{III} complexes. Thus, the solubility of the chloride salts, as well as the neutral complexes, in methanol gave a large effect in the isolated yields of the complexes.



Scheme 1. Preparation of complexes

In the IR spectrum, the $\nu(\text{C-N})$ stretching band of $\text{Na}(\text{Me}_2\text{dtc})$, $\text{NH}_4(\text{pyrdtc})$ and $\text{K}(S\text{-proOHdtc})$ appeared at 1359, 1413 and 1399 cm^{-1} , respectively, but those of the complexes **1a–2f** were observed in the range of 1374–1428 cm^{-1} . The $\nu(\text{C-S})$ stretching band of $\text{Na}(\text{Me}_2\text{dtc})$, $\text{NH}_4(\text{pyrdtc})$ and $\text{K}(S\text{-proOHdtc})$ appeared at 963, 1001 and 966 cm^{-1} , respectively, but those of the complexes were exhibited in the range of 969–1011 cm^{-1} . These

characteristic bands were similarly observed in the related complexes reported previously [3,16].

In this study the crystal structures of **1a**, **1b**, **1c**•0.5CH₂Cl₂, **2a**, **2b**, **2c** and **2e**•H₂O were determined by the single-crystal X-ray diffraction method, although the crystal structures of **1a** [5], **2c** [3a] and **2d**•3CHCl₃ [8] were reported previously. Crystallographic data and selected bond lengths and angles of the complexes are given in Tables 1 and S1, respectively. The molecular structures of [Nd(pyrdtc)₃(phen)] (**1b**) and [Eu(Me₂dtc)₃(phen)] (**2a**), as examples, are shown in Figures 1 and 2 (and those of the other complexes are in Figure S1), which are very similar to those of the related complexes reported previously with their comparable structural parameters (Table S1) [3,5,6,8]. The Ln^{III} (Nd^{III} or Eu^{III}) center is 8-coordinated by three dithiocarbamato ligands through two S donor atoms and a phenanthroline or bipyridine ligand through two N donor atoms. Interestingly, when the precise coordination geometry around Ln^{III} center is noticed, there are two distinguishable structures observed in this series of complexes. Both bidentate ligands of dithiocarbamato (Xdtc) and diimine (NN) are almost planar, and a set of mutually pseudo *trans*-positioned Xdtc planes is co-planar in all complexes (Figure 1c and 1d). In complexes **1a** and **2a**, the other two ligand planes, i.e., phen and the pseudo *trans*-positioned Me₂dtc plane are nearly co-planar, as their dihedral angles are 13.67(5) and 12.77(9)°, respectively. In the other complexes, in contrast, the NN ligand plane and the pseudo *trans*-positioned Xdtc ligand plane is not coplanar; the dihedral angles are in the range of 39.91(5)–45.21(7)° (Table S1). A similar coordination geometry has been recognized previously, and Regulacio et al. described it as a distorted square antiprism [6], while Pitchaimani et al. [9,14] and Raya et al. [3b] reported it as a distorted dodecahedron. It is also noted that there are no remarkable intermolecular interactions in these crystal structures.

The molecular structure of the [Eu(*S*-proOHdtc)₃(phen)]•H₂O (**2e**•H₂O) complex should be further commented on. It contains a set of unsymmetrical coordination (i.e., the direction of the hydroxymethyl substituent) of the three *S*-proOHdtc⁻ ligands around the Eu^{III} center which gives rise to a variety of possible stereoisomers in the solid state (Scheme 2). This structural feature is observed because of the restricted rotation about the C–N bond in the Xdtc⁻ ligand due to the extended π -electron conjugation over the C–N bond, and the presence of the

asymmetric carbon atom in the prolinol ring. The compound **2e**•H₂O was deposited as orange block crystals from a mixture of methanol and diethyl ether, one of the crystals used for X-ray analysis was revealed to be crystallized in a monoclinic space group *P2* with *Z* = 4. There are two crystallographically independent molecules in the asymmetric unit, and they were found to be diastereoisomers due to the asymmetric coordination of *S*-ProOHdte⁻ ligands: the *PMP* and *PPM* isomers (Figure 2). Interestingly, one of the molecules (*PMP* isomer with Eu1 center) showed a distorted square-antiprism or dodecahedron coordination geometry, likewise to the majority of [Ln(RR'dtc)₃(NN)]-type complexes reported previously. In contrast, the coordination geometry of the other molecule (*PPM* isomer with Eu2 center) was apparently similar to those of **1a** and **2a**; the phen plane and the pseudo *trans*-positioned *S*-proOHdte plane are nearly coplanar (Figure 2 and Table S1). In the crystal structure, these *PMP* and *PPM* isomers are connected by a hydrogen bond between their *S*-proOH moieties, together with the other hydrogen bond between the *PMP* isomers using the *S*-proOH group (Figure S3). Thus, the hydrogen-bonding interaction is one of the reasons why the crystals of **2e**•H₂O contains the *PMP* and *PPM* isomers in a 1:1 ratio. At this stage, however, we cannot deny a possibility that another crystal afforded might contain the other isomers. The IR spectrum of bulk sample of **2e**•H₂O did not exhibit any complicated nature due to the mixture of the diastereoisomers. Also, in the absorption, CD, MCD (*vide infra*) and ¹H NMR spectra (Figure S3), only the averaged structure of the possible diastereoisomers could be observed because of a rapid ligand exchange in solution.

Table 1. Crystal data and structure refinement details

Parameters	1a	1b	1c •0.5CH ₂ Cl ₂	2a
Molecular formula	C ₂₁ H ₂₆ N ₅ NdS ₆	C ₂₇ H ₃₂ N ₅ NdS ₆	C _{19.5} H ₂₇ ClN ₅ NdS ₆	C ₂₁ H ₂₆ N ₅ EuS ₆
Molecular weight	685.07	763.18	703.52	692.79
Crystal system	Triclinic	Triclinic	Tetragonal	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	9.570(2)	10.0851(17)	16.6985(7)	9.5498(6)
<i>b</i> / Å	10.089(2)	10.4426(16)	–	10.0688(4)
<i>c</i> / Å	16.343(4)	17.221(3)	39.7858(17)	16.3618(8)
α / °	93.271(4)	96.922(5)	–	93.292(3)
β / °	103.863(4)	102.713(5)	–	104.420(3)

$\gamma / ^\circ$	113.752(4)	113.109(4)	–	113.678(4)
$V / \text{Å}^3$	1381.2(5)	1583.4(5)	11093.8(8)	1373.28(13)
Z	2	2	8	2
$D_{\text{calc}} / \text{g cm}^{-3}$	1.647	1.601	1.685	1.675
$\mu(\text{Mo K}\alpha) / \text{mm}^{-1}$	23.516	20.605	24.374	27.544
Crystal size / mm^3	0.45 x 0.35 x 0.30	0.25 x 0.10 x 0.10	0.45 x 0.35 x 0.30	0.20 x 0.20 x 0.10
$F(000)$	686.00	770.00	5632.00	692.00
Reflns measured	13706	15739	88013	13580
Unique reflns (R_{int})	6281 (0.0433)	7210 (0.0754)	6340 (0.0478)	6214 (0.0347)
$R1 [I > 2\sigma(I)]$	0.0293	0.0448	0.0415	0.0289
$wR2$ [all reflns]	0.0813	0.1351	0.1142	0.1102
GOF on F^2	1.093	1.186	1.143	1.127
Flack parameter	–	–	–	–

Table 1. (Continued.)

Parameters	2b	2c	2e•H ₂ O
Molecular formula	C ₂₇ H ₃₂ N ₅ EuS ₆	C ₁₉ H ₂₆ N ₅ EuS ₆	C ₃₀ H ₄₀ EuN ₅ O ₄ S ₆
Molecular weight	770.90	668.77	878.98
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$I4_1/a$	$P2$
$a / \text{Å}$	9.9956(12)	16.6431(10)	19.7161(8)
$b / \text{Å}$	10.3900(14)	16.6431	10.7864(5)
$c / \text{Å}$	17.198(3)	39.431(2)	20.2944(10)
$\alpha / ^\circ$	96.603(4)	90	90
$\beta / ^\circ$	102.653(4)	90	115.367(2)
$\gamma / ^\circ$	112.806(4)	90	90
$V / \text{Å}^3$	1566.3(4)	10922.1(15)	3899.8(3)
Z	2	16	4
$D_{\text{calc}} / \text{g cm}^{-3}$	1.634	1.627	1.494
$\mu(\text{Mo K}\alpha) / \text{mm}^{-1}$	2.4243	2.772	1.968
Crystal size / mm^3	0.35 x 0.35 x 0.15	0.35 x 0.30 x 0.25	0.20 x 0.15 x 0.10
$F(000)$	776	5344	1780
Reflns measured	15548	84797	38598
Unique reflns (R_{int})	7108 (0.0286)	6268 (0.0573)	16415 (0.0396)
$R1 [I > 2\sigma(I)]$	0.0248	0.0316	0.0433
$wR2$ [all reflns]	0.0861	0.0737	0.1181
GOF on F^2	1.000	1.087	1.072
Flack parameter	–	–	0.005(5)

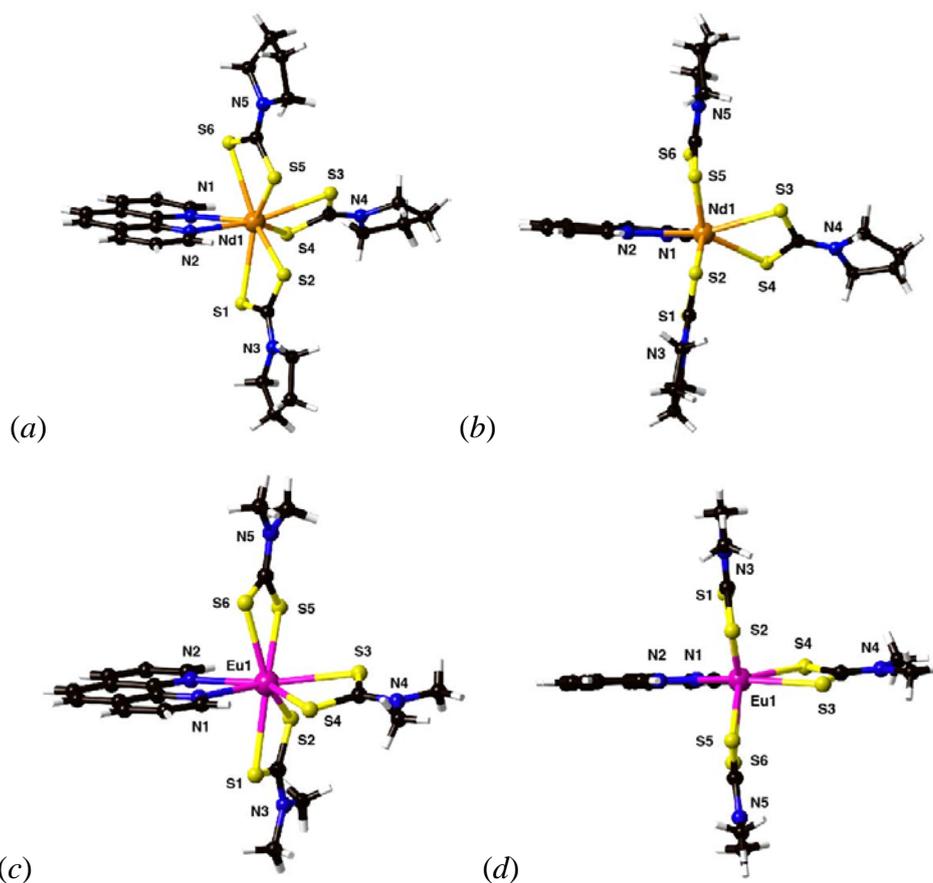


Figure 1. Perspective views of (a and b) $[\text{Nd}(\text{pyrdtc})_3(\text{phen})]$ (**1b**) and (c and d) $[\text{Eu}(\text{Me}_2\text{dtc})_3(\text{phen})]$ (**2a**). The views of (b) and (d) are from the direction that is perpendicular to the phen and two Xdtc planes, showing the difference in the coordination geometry around Ln^{III} center.

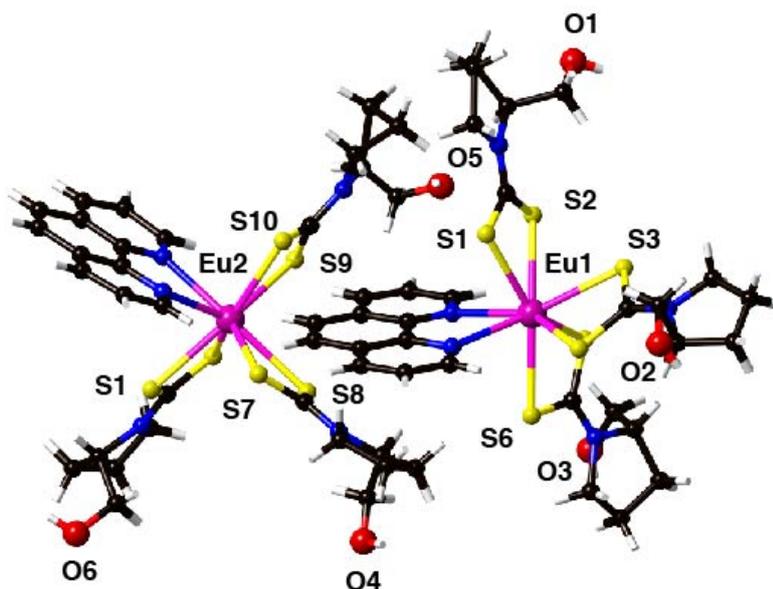
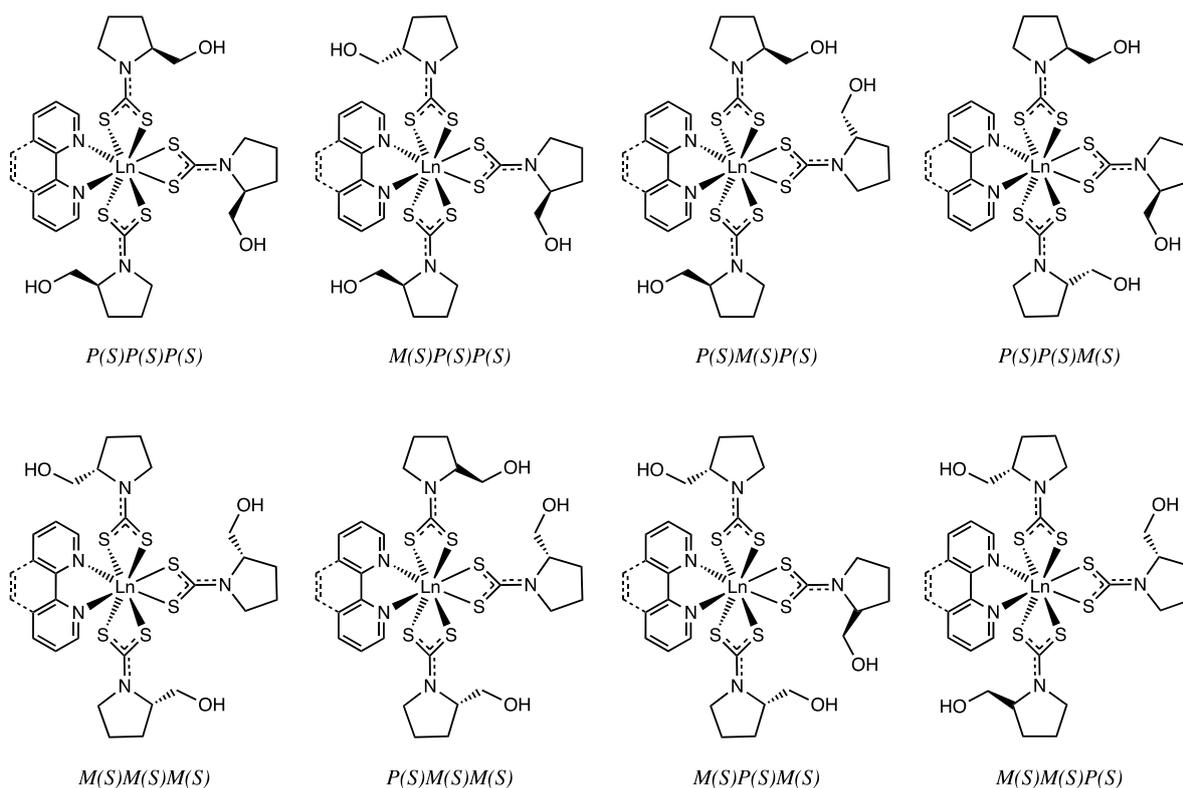


Figure 2. Perspective views of two crystallographically independent $[\text{Eu}(\text{S-proOHdtc})_3(\text{phen})]$ molecules in $2\mathbf{e}\cdot\text{H}_2\text{O}$.



Scheme 2. Possible diastereoisomers for $[\text{Ln}(\text{S-proOHdct})_3(\text{NN})]$

3.2. Spectroscopic Studies

The Nd^{III} and Eu^{III} complexes with different dithiocarbamate ligands exhibited similar spectral patterns, respectively. The absorption, CD and MCD spectra of complexes $[\text{Nd}(\text{pyrdtc})_3(\text{bpy})]$ (**1d**), $[\text{Eu}(\text{pyrdtc})_3(\text{phen})]$ (**2b**), $[\text{Nd}(\text{S-proOHdct})_3(\text{phen})]$ (**1e**) and $[\text{Eu}(\text{S-proOHdct})_3(\text{phen})]$ (**2e**) are presented in Figures 4–7 as representative spectra (and those of the other complexes are given in the Supporting Information: SI).

As shown in Figures 4 and 6, the Nd^{III} complexes exhibited sharp but weak f-f transitions at 19190, 18760, 16860, 13250 and 12350 cm^{-1} , which are assigned to the $^4\text{G}_{9/2}$, $^4\text{G}_{7/2}$, ($^2\text{G}_{7/2}$ and $^4\text{G}_{5/2}$), $^4\text{S}_{3/2}$ and $^4\text{F}_{5/2} \leftarrow ^4\text{I}_{9/2}$ transitions, respectively. These assignments were consistent with the previous report [3a] and comparable with those of an octaqua-neodymium(III) ion [17] and a neodymium-doped fluorozirconate glass [18]. The observed bands for the complexes reported in this study were slightly shifted to lower energies relative to the corresponding absorption bands reported for neodymium(III) acetate complexes [19], but they were in good agreement with the spectra of the related complexes [12, 20, 21]. In the MCD spectra shown

in Figures 4 and 6, the MCD signals corresponding to the bands in the absorption spectra were observed for both Nd^{III} complexes with the achiral (i.e., Me₂dtc⁻ and pyrdtc⁻) and the chiral (*S*-proOHdtc⁻) dithiocarbamato ligands. These signals are characteristic of *C*-terms, except for the signal at 12350 cm⁻¹ which appears as a positive pseudo *A*-term. In Figure 6, no CD signals characteristic of the f–f transitions were observed in the CD spectra of the Nd^{III} complexes of the Me₂dtc, pyrdtc and *S*-proOHdtc ligands. However, a CD band was observed around 368 nm in the *S*-proOHdtc complexes of Nd^{III}. These bands resulted from and are consistent with the bands (spectra not shown) observed in the free *S*-proOHdtc⁻ ligand.

In Figures 5 and 7 (top), the Eu^{III} complexes exhibited a weak f–f transition band at 21460 cm⁻¹ which is assigned to the ⁵D₂ ← ⁷F₀ induced electric dipole transition based on a comparison with the assignment for aqua Eu^{III} ion [17]. The position of this band is in good agreement with that observed in the Eu^{III} oxydiacetato and dipicolinato complexes [22] and is also consistent with the calculated energy levels for a free Eu^{III} ion [23]. In the MCD spectra in Figures 5 and 7 (bottom), an MCD signal characteristic of a negative *B*-term was observed around 21460 cm⁻¹ for the Eu^{III} complexes with the achiral (i.e. Me₂dtc⁻ and pyrdtc⁻) and chiral (i.e. *S*-proOHdtc⁻) dithiocarbamato ligands. As shown in Figure 7 (top), no CD signals characteristic of f–f transitions were observed in the CD spectra of the Eu^{III} complexes with the *S*-proOHdtc ligands. In contrast, an MCD and a CD band were observed around 368 nm in the MCD and CD spectra, respectively, of [Eu(*S*-proOHdtc)₃(phen)] (**2e**). These bands resulted from the intraligand transition, because the spectra of K(*S*-proOHdtc) also exhibited a similar MCD and CD spectra in this region. The non-appearance of the f–f transition bands in CD spectra of the complexes containing the chiral *S*-proOHdtc⁻ ligand suggests the lack of chirality around the Nd^{III} and Eu^{III} centers. It was expected that the chiral *S*-proOHdtc⁻ ligand coordinated to a Nd^{III} or Eu^{III} ion could not induce a chirality at the metal center, because the asymmetric center in the dithiocarbamato ligand is sterically far from the *S,S*-donor atoms to make the coordinated Ln^{III} site chiral, and because the Ln^{III} ions are substitutionally labile in solution.

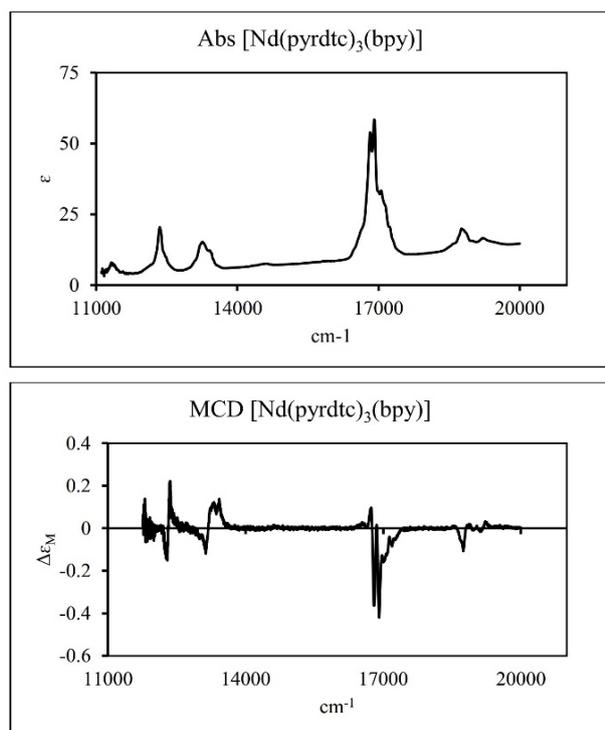


Figure 4. Absorption (top) and MCD (bottom) spectra of $[\text{Nd}(\text{pyrdtc})_3(\text{bpy})]$ (**1d**).

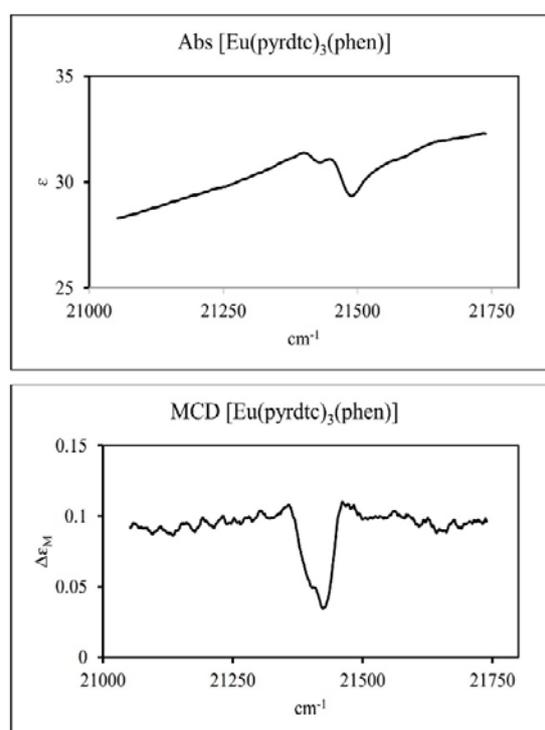


Figure 5. Absorption (top) and MCD (bottom) spectra of $[\text{Eu}(\text{pyrdtc})_3(\text{phen})]$ (**2b**).

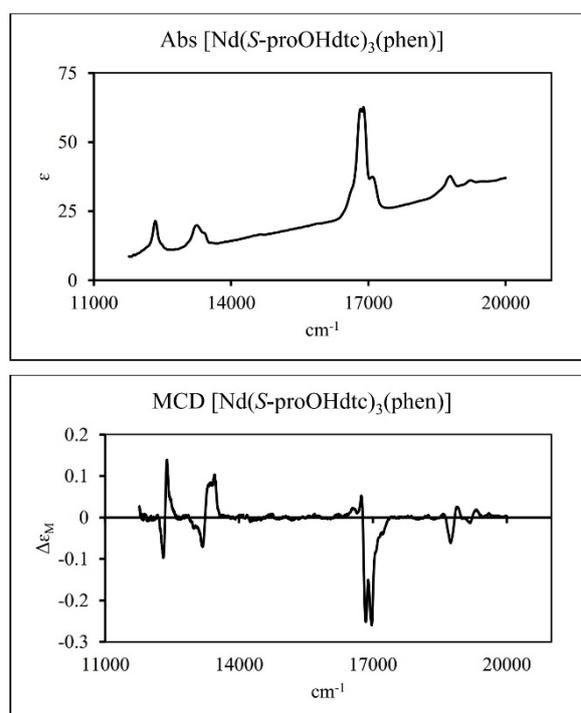
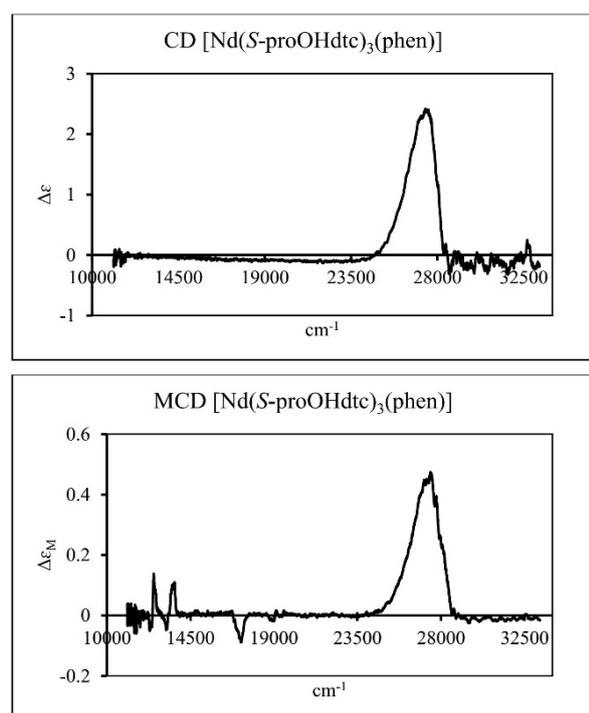


Figure 6. CD (top left), absorption (top right), and MCD (bottom) spectra of $[\text{Nd}(\text{S-proOHdte})_3(\text{phen})]$ (**1e**).

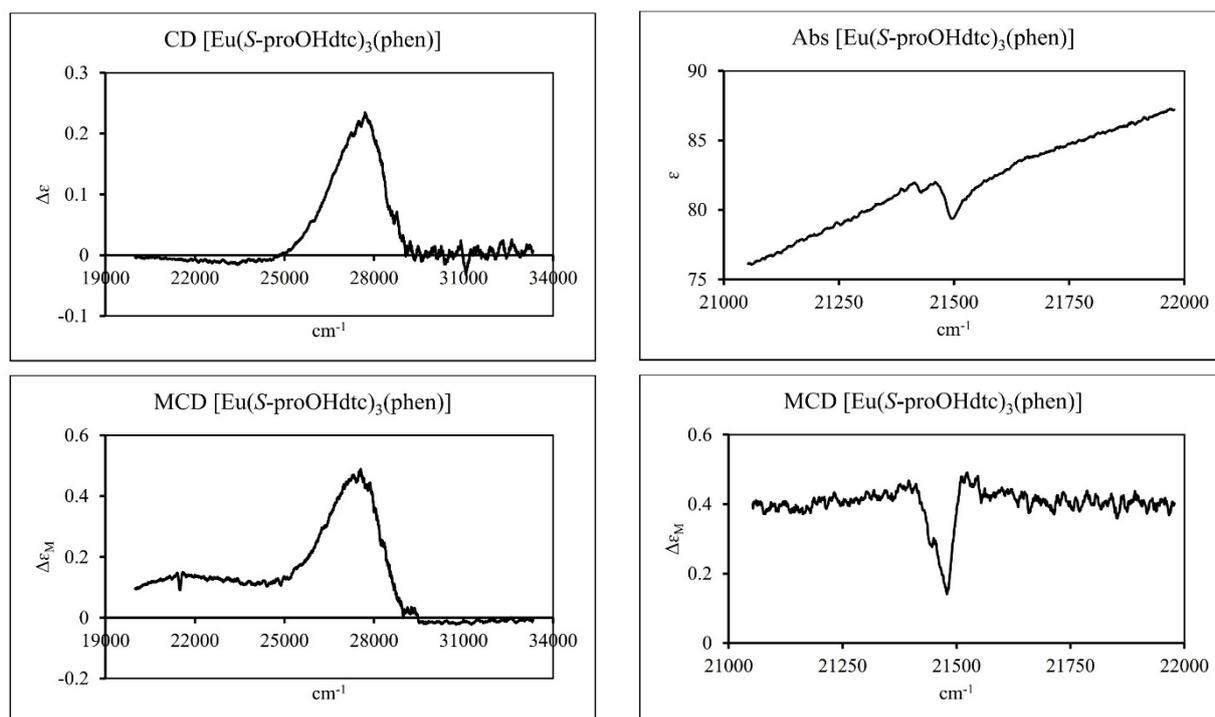


Figure 7. CD (top left), absorption (top right), and MCD (bottom) spectra of $[\text{Eu}(\text{S-proOHdtc})_3(\text{phen})]$ (**2e**).

3.3. Coordination Symmetry of Ln^{III} Dithiocarbamato Complexes

The MCD signal for the induced electric dipole ${}^5\text{D}_2 \leftarrow {}^7\text{F}_0$ transition of the Eu^{III} complexes exhibited a characteristic pattern (Figure 7), as compared to the signals observed in the MCD spectra of $[\text{Eu}(\text{H}_2\text{O})_8]^{3+}$ and $[\text{Eu}(\text{dpp})_3(\text{phen})]$ (dpp = 1,3-diphenyl-1,3-propanedione) (Figure 8). The present dithiocarbamato complexes showed a negative *B*-term MCD signal, while the latter complexes gave a negative *A*-term MCD signal. Based on the suggestion by Görrler-Walrand [24], the MCD spectral pattern of the ${}^5\text{D}_2 \leftarrow {}^7\text{F}_0$ induced electric dipole transition can be a probe of the coordination symmetry of the Eu^{III} complexes. Thus, it is deduced that the present dithiocarbamato complexes have a local C_{2v} symmetry at the Eu^{III} site in solution. In contrast, the β -diketonato complex showing a negative *A*-term MCD signal suggests a local D_{2d} symmetry at the Eu^{III} site. The difference in coordination symmetry indicates that a mixed donor atoms set of O (of β -diketonato) and N (of diimine) in $[\text{Ln}(\text{dpp})_3(\text{phen})]$ did not give a significant difference in the electronic structure of Ln^{III} , but

the S donor atoms of dithiocarbamate showed a significant difference in the electronic structure of the Ln^{III} complexes from that of the N donor atoms of the diimine ligands.

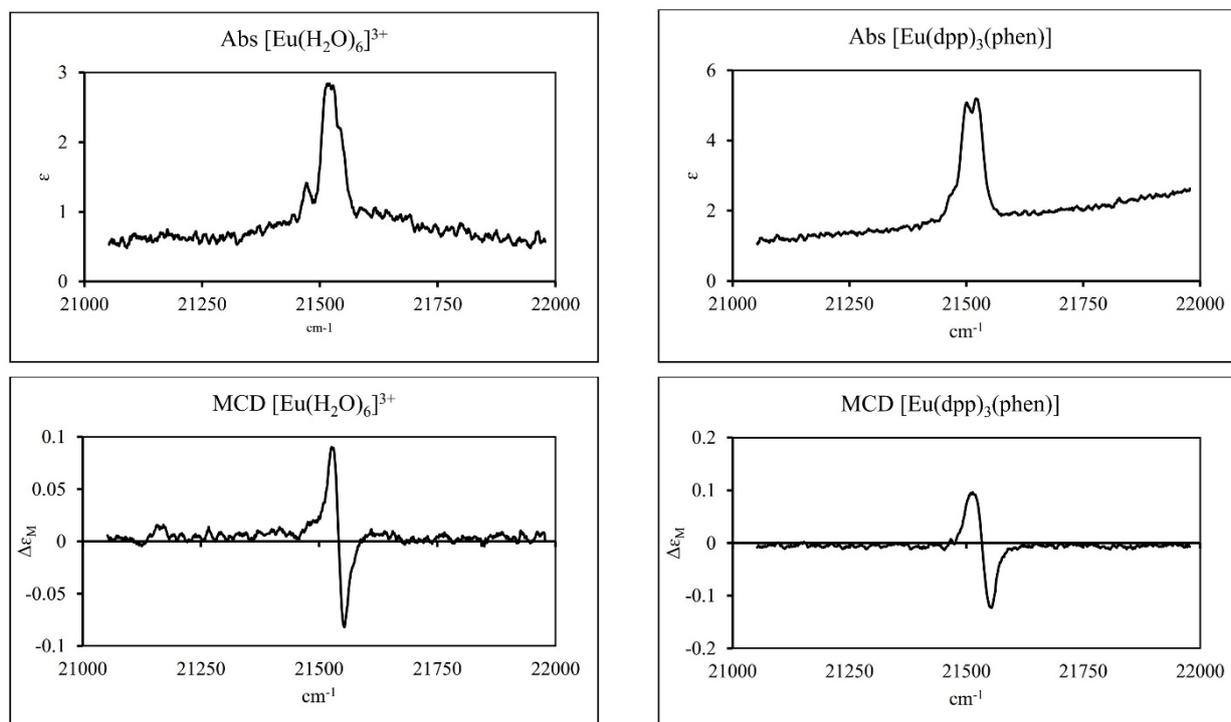


Figure 8. Absorption (top) and MCD (bottom) spectra of aqua (left) and β-diketonato (right) Eu^{III} complexes.

4. Conclusion

A series of lanthanoid(III) dithiocarbamate complexes have been synthesized and characterized through various spectroscopic methods. The molecular structures are all 8-coordinate geometry with insignificant differences in the structural parameters. The complexes showed no CD signals associated with the f–f transitions; however, MCD signals of these transitions were observed in all complexes. The MCD spectral pattern suggests that the dithiocarbamate complexes of lanthanide(III) have a site (coordination) symmetry different from those of the related β-diketonato complexes.

Competing interest

The authors declare no conflict of interest in relation to this work.

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Appendix A. Supplementary data

Details of the crystallographic data, crystal structures, absorption and MCD spectra of the complexes in PDF format. Crystallographic data for compounds **1a–1c**, **2a–2c** and **2e•H₂O** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1845409–1845411 and 1864663–1864666. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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