Inorganica Chimica Acta 484 (2019) 394–401

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

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

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ARTICLE INFO

Keywords:
Dithiocarbamate
Lanthanoid
Crystal structures
Magnetic circular dichroism
(*S*)-prolinol dithiocarbamate

ABSTRACT

A series of Nd^{III} and Eu^{III} complexes containing achiral or chiral dithiocarbamato (dtc) ligands, $[Ln(Xdtc)_3(NN)]$ {Ln = Nd or Eu; X = dimethyl- (Me_2), 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.

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) dithiocarbamato complexes have been reported in the last decades [5]. Regulacio et al. described a series of lanthanoid(III) dithiocarbamato 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 dithiocarbamato 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} diethyldithiocarbamato and diphenyldithiocarbamato 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) dithiocarbamato 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 $Na[Pr\{(+)\text{-}hfbc\}_4]\cdot CH_3CN$ ($hfbc^-$ = 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 dithiocarbamato ligands were prepared. In particular, (*S*)-prolinol dithiocarbamato (S-proOHdtc$^-$) complexes are newly synthesized. The crystallographic studies of the complexes as well as their CD and MCD properties are investigated.

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https://doi.org/10.1016/j.ica.2018.09.064
Received 4 June 2018; Received in revised form 3 September 2018; Accepted 20 September 2018
Available online 25 September 2018

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-proOHdtc)

The potassium salt of *S*-prolinol dithiocarbamate, K(*S*-proOHdtc), 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 CS_2. 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 P_2O_5. 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}): ν(C—N) = 1399, ν(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 $LnCl_3{\cdot}6H_2O$ (1.00 mmol) was slowly added to a methanolic solution (10 mL) of Na(Me_2dtc) or NH_4(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(Me_2dtc)$_3$(phen)] **(1a)**

Pale blue crystals. Yield: 47.5%. Calcd for $C_{21}H_{26}N_5NdS_6$: 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}): ν(C—N) = 1374, ν(C—S) = 984.

2.3.2. [Nd(pyrdtc)$_3$(phen)] **(1b)**

Pale blue crystals. Yield: 78.5%. Calcd for $C_{27}H_{32}N_5NdS_6$: 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}): ν(C—N) = 1424, ν(C—S) = 1008.

2.3.3. [Nd(Me_2dtc)$_3$(bpy)] **(1c)**

Pale blue crystals. Yield: 20%. Calcd for $C_{19}H_{26}N_5NdS_6{\cdot}CHCl_3$: 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 $C_{25}H_{32}N_5NdS_6$: 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(Me_2dtc)$_3$(phen)] **(2a)**

Brick-red crystals. Yield: 29%. Calcd for $C_{21}H_{26}N_5EuS_6$: 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 $C_{27}H_{32}N_5EuS_6$: 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(Me_2dtc)$_3$(bpy)] **(2c)**

Brick-red crystals. Yield: 20%. Calcd for $C_{19}H_{26}N_5EuS_6{\cdot}CHCl_3$: 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 $C_{25}H_{32}N_5EuS_6{\cdot}CHCl_3$: 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 $LnCl_3{\cdot}6H_2O$ (1.00 mmol) was added to a methanolic solution (10 mL) of K(*S*-proOHdtc) (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 Et_2O 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 $C_{30}H_{38}N_5O_3NdS_6{\cdot}3H_2O$: 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 $C_{30}H_{38}N_5O_3EuS_6{\cdot}3H_2O$: 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 $C_{28}H_{38}N_5O_3EuS_6{\cdot}C_4H_{10}O$: 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-