Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 26 (2007) 845–850
POLYHEDRON
www.elsevier.com/locate/poly

Structural and spectroscopic investigations of the Eu^{III}–CDTA system

Rafał Janicki, Anna Mondry, Przemysław Starynowicz *

Wydział Chemii, Uniwersytet Wrocławski, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

Received 20 July 2006; accepted 14 September 2006
Available online 27 September 2006

Abstract

Two crystal structures of Eu^{III} complexes with CDTA (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetate), $[C(NH_2)_3]_3[Eu_2(CDTA)_2(H_2O)_2]ClO_4 \cdot 7H_2O$ (**I**) and $[C(NH_2)_3][Eu(CDTA)(H_2O)] \cdot 2.375H_2O$ (**II**), are presented. Both structures are polymeric and the central metal ions are eight-coordinate. The first coordination sphere of each Eu^{III} cation contains five carboxylate oxygen atoms, two nitrogen ones and a water molecule. For **I**, as well as for water solutions of the Eu^{III}–CDTA complex at various pH values, the spectroscopic (UV–Vis) properties were investigated.

Keywords: Europium(III); CDTA; Structure; UV–Vis spectroscopy

1. Introduction

Lanthanide polyaminopolycarboxylate chelates play an important role both in fundamental investigations and in several areas of practical applications. They are used, among others, as shift reagents in NMR spectroscopy [1], contrast agents in MRI imaging [2], structural probes [3] and luminescent tags in immunoassays [4]. This family of compounds has been epitomized by complexes of Ln^{III} with the ethylenediaminetetraacetate (EDTA) anion, which have been extensively studied both in solution e.g. [5] and in the solid state e.g. [6] and now may serve as a kind of standard when the structure, spectroscopic and/or thermodynamic properties of lanthanide polyaminopolycarboxylates are discussed. It is therefore of interest to find how the properties are altered when the $EDTA^{4-}$ skeleton is modified. In this work we present a study of two Eu^{III} complexes with such a ligand, i.e. *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetate (CDTA). The investigations of Ln^{III}–CDTA complexes carried out so far have been focused to a great part on their properties in aqueous solutions and included thermodynamic as well as spectroscopic aspects. Their stability constants are higher by an order or two of magnitude, depending on the lanthanide, than those of the EDTA complexes [7], and generally saying, they are thermodynamically stable [8]. The spectroscopic studies have revealed that in solutions of Eu^{III}–CDTA complexes an equilibrium exists between two different species, nine- and eight-coordinate, the dissimilarity between them consisting of a different number of coordinated water molecules (three or two) [9]. The average number of these molecules has been found to be 2.3–2.6 and is a little lower than that found in water solutions of the EDTA complexes (2.6–2.8) [5f,5h].

Because of difficulties connected with growing of monocrystals of adequate quality, structural data for Ln^{III}–CDTA complexes are scarce. To the best of the authors' knowledge only three crystal structures of these complexes have been published. Two of them, $NH_4[Ln(CDTA)(H_2O)_2] \cdot 4.5H_2O$ ($Ln = Gd^{III}$, Ho^{III}), are monomeric and isostructural [10,11] whereas in the third one, $Na[Eu(CDTA)(H_2O)] \cdot 4H_2O$ [12], dimeric anions of $[Eu(CDTA)–\mu\text{-}(H_2O)_2–Eu(CDTA)]^{2-}$ are formed. For the last system luminescence properties were also reported. In all these complexes the Ln^{III} ions are eight-coordinate.

In the crystal, the coordination surrounding of Ln^{III} ion is unambiguously defined, therefore the spectra of the

* Corresponding author.
E-mail address: psta@wchuwr.chem.uni.wroc.pl (P. Starynowicz).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.09.031

crystals may be a good starting point for interpretation of spectral data of solution systems. The paucity of such data has motivated us to attempt the preparation of Eu^{III}–CDTA complexes in the crystalline state, to study their crystal structures and spectroscopic properties and to compare the latter with the analogous properties of Eu^{III}–CDTA complexes in solution.

2. Experimental

2.1. Materials

Solutions for spectroscopic measurements: A stock solution of europium chloride was prepared by dissolving Eu_2O_3 (99.99%; Standford materials) in 2 mol dm^{-3} hydrochloric acid. The Eu^{III} ion concentration was determined complexometrically using xylenol orange as an indicator. The stock solution of H_4CDTA (98%; Lancaster) was prepared by half-neutralization with NaOH. The pH of the 1:1.1 Eu^{III}–CDTA solutions was adjusted by a carbonate-free NaOH water solution.

Crystal preparations: An aqueous solution of equimolar quantities of europium perchlorate and H_4CDTA was heated at ca. 80 °C. Next, solid $[C(NH_2)_3]_2CO_3$ was added until the pH value was 5. Large colourless crystals of $[C(NH_2)_3]_3[Eu_2(CDTA)_2(H_2O)_2]ClO_4 \cdot 7H_2O$ (**I**) were formed during slow evaporation. The other crystals, $[C(NH_2)_3][Eu(CDTA)(H_2O)] \cdot 2.375H_2O$ (**II**), were obtained as follows: a suspension of Eu_2O_3 and H_4CDTA was heated at ca. 80 °C. After dissolution of the substrates, the solution was alkalized with $[C(NH_2)_3]_2CO_3$ to a final pH value of 3, and left for crystallization.

2.2. X-ray study

Appropriate crystals were cut from larger ones and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz and absorption, the last calculated from the crystal habit captured from photo scans. Both crystals turned out to be twinned. The twinning of crystal **I** was pseudo-merohedral; this was brought about by the fact that the unit cells spanned by vectors **a**, **b**, **c**, and **a**, **a**–**b**, **a**–**c** have very similar lattice constants. The fraction of the first twin component found from the refinement was 0.676(1). The twinning matrix in **II** was (−1/2 −1/2 0/ −3/2 1/2 0/ −1/2 1/2 −1) with the result that only reflections with $h + k$ even overlapped. The structure of **I** was solved and refined against all reflections, while that of **II** was solved using one twin component and refined against both. The positions of Eu were found from Patterson maps, the rest of the non-H atoms from difference Fourier

Table 1
Crystal data and structure refinement for both crystals

Crystal	**I**	**II**
Empirical formula	$C_{31}H_{72}ClEu_2N_{13}O_{29}$	$C_{15}H_{30.25}EuN_5O_{11.38}$
Formula weight	1430.39	614.65
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
Unit cell dimensions		
a (Å)	10.652(8)	12.09(9)
b (Å)	16.075(13)	18.83(2)
c (Å)	17.943(14)	23.328(15)
α (°)	69.31(7)	66.82(14)
β (°)	73.24(7)	77.15(12)
γ (°)	70.86(7)	77.47(12)
Volume ($Å^3$)	2663(4)	4712(36)
Z, Calculated density (Mg/m^3)	2, 1.784	8, 1.733
Absorption coefficient (mm^{-1})	2.484	2.727
$F(000)$	1448	2474
Crystal size (mm)	$0.27 \times 0.20 \times 0.15$	$0.27 \times 0.18 \times 0.11$
Theta range for data collection (°)	3.03–28.43	2.25–29.07
Index ranges	$-9 \leqslant h \leqslant 14$, $-21 \leqslant k \leqslant 21$, $-23 \leqslant l \leqslant 23$	$-15 \leqslant h \leqslant 16$, $-25 \leqslant k \leqslant 23$, $-31 \leqslant l \leqslant 31$
Reflections collected/unique (R_{int})	18 077/11 545 (0.0341)	25 498/25 498
Completeness to 2θ	86.0%	69.1%
Absorption correction	analytical, from the shape	analytical, from the crystal shape
Maximum and minimum transmission	0.710 and 0.520	0.768 and 0.529
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	11 545/0/686	25 498/0/1176
Goodness-of-fit on F^2	1.063	0.998
Final R indices $[I > 2\sigma(I)]$	$R(F) = 0.0434$, $Rw(F^2) = 0.1031$	$R(F) = 0.0790$, $Rw(F^2) = 0.1403$
R indices (all data)	$R(F) = 0.0484$, $Rw(F^2) = 0.1059$	$R(F) = 0.1388$, $Rw(F^2) = 0.1620$
Largest differences in peak and hole (e $Å^{-3}$)	2.654 and −2.604	1.800 and −1.616