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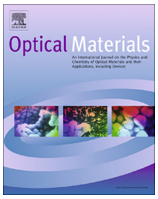

Relations between structure and physicooptical properties of Eu^{3+} and Tb^{3+} tetraphosphonates

Rafał Janicki [a], Maelle Monteil [b], Marc Lecouvey [b], Anna Mondry [a,*]

[a] Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland
[b] Laboratoire de Chimie, Structures, Propriétés de Biomatériaux et d'Agents Thérapeutiques, (CSBAT), CNRS UMR7, Université Paris 13, Sorbonne Paris Cité, F-93017 Bobigny, France

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ABSTRACT

The crystal structure of the Tb^{3+} complex with ethylenediaminetetra(methylenephosphonic acid) (H_8EDTMP) was determined and it was found that the compound is isostructural with the previously studied $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)]\cdot 10H_2O$ crystal. The Eu^{3+} and Tb^{3+} complexes with *trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonic acid) (H_8CDTMP) of known crystal structures were also obtained. As it results from the X-ray analyses both tetraphosphonate ligands (EDTMP and CDTMP) bind the Ln^{3+} ion with 2 nitrogen atoms and 4 oxygen atoms in such a way that only one oxygen atom from each phosphonate group is linked with the central ion. The coordination sphere is completed by two oxygen atoms of the bidendate carbonate anion in the case of Ln^{3+}–EDTMP complexes, whereas two monomeric Ln^{3+}–CDTMP complex anions are connected by two hydroxyl ions and one water molecule. The spectroscopic (FTIR and emission) studies of crystals are presented and discussed with respect to their structures. It was shown that OH oscillators present in the inner-sphere of Eu^{3+} and Tb^{3+} complexes with CDTMP do not quench lanthanide emission. The reasons of that are three very short hydrogen bonds (~2 Å) formed between two hydroxyl groups and a water molecule. The luminescence lifetimes and quantum yields of lanthanide tetraphosphonates were compared with those obtained for Ln^{3+} tetracarboxylates.

1. Introduction

A great interest in lanthanide complexes with polyamino polyphosphonic acids is largely stimulated by their application in medicine [1–4]. The high affinity of polyphosphonate ligands towards bones is a reason that the complex of $^{153}Sm^{3+}$ with EDTMP [H_8EDTMP = ethylenediaminetetrakis(methylenephosphonic acid)], known clinically as QUADRAMET®, is in widespread use to relieve pain from metastatic bone cancer [1,2,5]. The lanthanide complexes with these ligands may be also used as new technology materials [6–10].

Our previous studies on Eu^{3+}–EDTMP crystals of the formulas $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)]\cdot 10H_2O$ [11] (hereinafter **EuI**) and $K_{12}H_8[Eu_4(EDTMP)_4]\cdot 45H_2O$ [12] have shown that these compounds form monomeric and tetrameric structures untypical for lanthanide phosphonates [13]. The structural studies of Ln^{3+} complexes with CDTMP [H_8CDTMP = *trans*-cyclohexane-1,2-diamine-*N*,*N*,*N*′,*N*′-tetrakis(methylenephosphonic acid)] of the formula $[C(NH_2)_3]_6[Ln(CDTMP)(OH)(H_2O)_{1/2}]\cdot 16H_2O$ [14] (hereinafter **EuII**, **TbII**) have revealed that contrary to Eu^{3+} complexes with EDTMP, the OH oscillators are in the inner sphere of Ln^{3+} ion.

The simplified structures of Eu^{3+}–EDTMP and Ln^{3+}–CDTMP (where $Ln^{3+} = Eu^{3+}$ and Tb^{3+}) compounds in the above mentioned crystals are presented in Scheme 1.

The tetraphosphonate ligands, similarly as their carboxylic analogues –EDTA [11,15,16] and CDTA [17,18], coordinate to the Ln^{3+} ion through the same donor atoms, namely 2 nitrogen atoms and 4 oxygen atoms. The bidentate carbonate anion (Scheme 1A) or tridendate phosphonic group (Scheme 1B) complete the inner-sphere of the metal ion in the EDTMP crystals, resulting thus in the coordination number of eight for Eu^{3+} cation. In the case of Ln^{3+}–CDTMP crystals, which were obtained at the same experimental conditions as **EuI**, the two neighboring complex anions form a quasi-dimer (Scheme 1C). In addition to 6 donor atoms of the phosphonate ligand, the remaining coordination sites are occupied by a hydroxyl group or by a hydroxyl group and a water molecule. Hence one of the Ln^{3+} cation is 7-coordinate and the other is 8-coordinate. The monomeric complex anion is connected to its symmetry related neighbor through short hydrogen bonds (~2 Å [14]) formed between two OH^- groups and H_2O.

The purpose of this paper is to report relations between structural and photophysical properties of Eu^{3+} and Tb^{3+} complexes in which the phosphonate ligands differ in rigidity, caused by replacement of the ethylene group (EDTMP) by the *trans*-cyclohexyl ring (CDTMP). Such comparative studies can be useful,

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* Corresponding author. Tel./fax: +48 71 375 7370.
E-mail address: anna.mondry@chem.uni.wroc.pl (A. Mondry).

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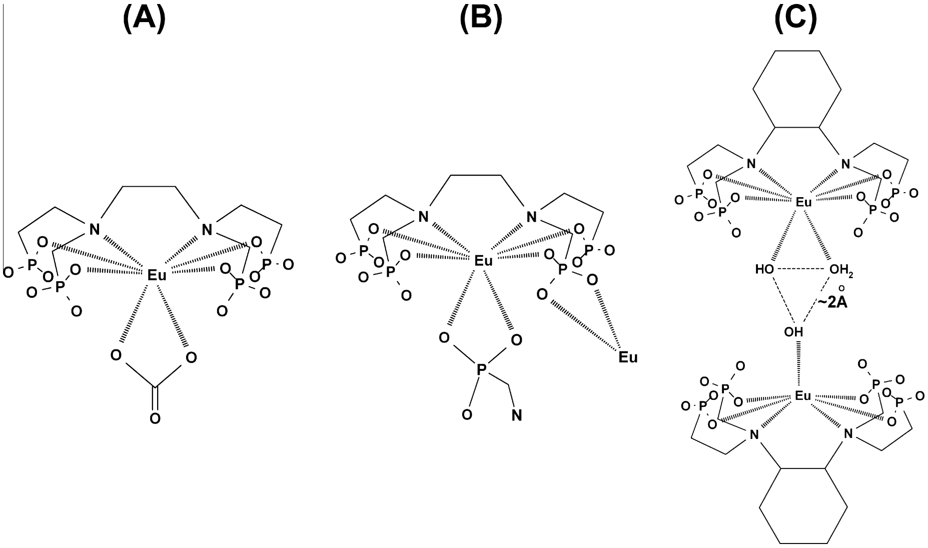

Scheme 1. Structures of anionic complexes in $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)]\cdot10H_2O$ [11] (A); $K_{12}H_8[Eu_4(EDTMP)_4]\cdot45H_2O$ [12] (B); $[C(NH_2)_3]_6[Ln(CDTMP)(OH)(H_2O)_{1/2}]\cdot16H_2O$ [14] (C) compounds.

especially in the case of coordination chemistry of lanthanide phosphonates for which they are rather uncommon. Because the crystal structure of the Tb^{3+}–EDTMP complex was not determined previously, in this paper the crystal data of this compound are also included.

2. Experimental

2.1. Crystal syntheses

Stock solutions of lanthanide perchlorates were prepared from Eu_2O_3 (99.99%, Stanford Materials) or Tb_4O_7 (99.9%, Merck) by dissolving them in hot 2 M perchloric acid. The Ln^{3+} concentrations were determined complexometrically using xylenol orange as an indicator.

Crystals of Tb^{3+}–EDTMP, Eu^{3+} and Tb^{3+} with CDTMP complexes were prepared as follows. The ligand solutions of H_8EDTMP (95%, ABCR; 0.48 g, 1.1 mmol) and H_8CDTMP (synthesized as previously described [19]; 0.56 g, 1.1 mmol) were neutralized with $[C(NH_2)_3]_2CO_3$ to pH around 7 and added to an aqueous solution of $Ln(ClO_4)_3$ (1 mmol). Next the resulting solutions were basified with guanidinium carbonate to pH 10.7. Colourless crystals were formed during slow evaporation of solutions. The crystals were checked by the X-ray diffraction and it was found that the Tb^{3+}–EDTMP crystal (**TbI**) is isomorphic with the previously studied $[C(NH_2)_3]_7[Eu(EDTMP)(CO_3)]\cdot10H_2O$ [11], whereas the Ln^{3+}–CDTMP crystals are isomorphic with $[C(NH_2)_3]_6[Ln(CDTMP)(OH)(H_2O)_{1/2}]\cdot16H_2O$ (**EuII**, **TbII**) [14].

2.2. X-ray analysis

An appropriate crystal was cut from a larger one and mounted on a Kuma KM4 diffractometer equipped with a CCD counter. The collected data were corrected for polarization, Lorentz and absorption, the last being calculated from the crystal habit captured from photo scans. The positions of Tb atoms were found from Patterson maps, the rest of the non-H atoms were found from difference Fourier maps. The positions of the C-bonded hydrogen atoms were calculated geometrically. The refinement was full-matrix with all non-H atoms anisotropic. All computations were performed using SHELXS-97 [20] and SHELXL-97 [21] programs. The molecular graphics was prepared with XP–Interactive Molecular Graphics [22].

2.2.1. Selected data for **TbI**

$C_{14}H_{74}TbN_{23}O_{25}P_4$, $M = 1247.76$, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 12.462(3)$, $b = 16.638(3)$, $c = 24.105(4)$ Å, $\beta = 102.24(2)°$, $V = 4884.1(2)$ Å^3, $\mu = 1.680$ mm^{-1}, $D_c = 1.697$ g cm^{-3}, $F(000) = 2576$, crystal size = $0.3 \times 0.25 \times 0.2$ mm, $\theta = 3$–$37°$, index ranges: $-20 \leqslant h \leqslant 16$, $-28 \leqslant k \leqslant 22$, $-39 \leqslant l \leqslant 40$, reflections collected/unique = 76541/22142 ($R_{int} = 0.0362$). Final R indices $[I > 2\sigma(I)]$ $R(F) = 0.0404$, $R_w(F^2) = 0.0831$ and $R(F) = 0.0892$, $R_w(F^2) = 0.0675$ (all data). Data completeness to $2\theta = 30.0°$, 98.5%. Largest diff. peak and hole 1.965 and -1.763e Å^{-3}.

CCDC 939664 contains the supplementary crystallographic data for **TbI**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

2.3. Spectroscopic measurements

The FTIR spectra of the complexes in KBr pellets were recorded in the range 400–4000 cm^{-1} with a Bruker IFS66 spectrometer.

Corrected emission spectra were measured on a SLM Aminco 500 spectrofluorometer at room temperature and 77 K. The luminescence decay curves were detected on Edinburgh Instruments FLS 920 spectrometer.

3. Results and discussion

3.1. Crystal structures

Views of the terbium complex anions, **TbI** and for comparison purposes **TbII**, are shown in Fig. 1. It is worth to stress that in the case of lanthanide complexes with acyclic polyphosphonic ligands the monomeric coordination pattern is rare [7,13]. Moreover, the coordination of a CO_3^{2-} anion to a highly negative lanthanide chelate is also very uncommon. The bidendate coordination mode of the carbonate anion is thus caused by a good fit of this ion to the coordination geometry of the $[Ln(EDTMP)]^{5-}$ unit.

It is therefore interesting to compare Ln–L bond lengths of both compounds. They are presented in Table 1. The data included in