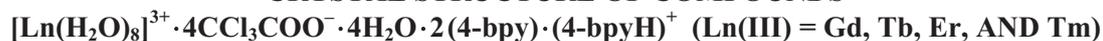


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CRYSTAL STRUCTURE OF COMPOUNDS



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Novel compounds of Gd(III), Tb(III), Er(III), and Tm(III) with 4,4'-bipyridine (4-bpy) and trichloroacetates are prepared. The title compounds are isomorphic and isostructural in the solid state. All atoms in the studied compound lie in general positions of the *Cc* space group. The coordination polyhedra around central atoms can be described as bicapped trigonal prisms slightly disordered towards a square antiprism. All 4-bpy molecules are located in the outer coordination sphere together with four trichloroacetate anions and four water molecules. One of the nitrogen atoms of one 4-bpy is protonated due to stoichiometry.

Keywords: lanthanide compounds, 4,4'-bipyridine, trichloroacetates, crystal structure.

INTRODUCTION

Lanthanide species containing 4-bpy and carboxylate groups are of interest due to not only their structural diversity, but also as new solid microporous materials. Compared with conventional porous materials such as zeolites or activated carbon, these coordination compounds have high microporosity. They have possible various applications in ion exchange, gas storage (CH_4 , H_2 , N_2 , O_2 , CO_2), gas separation, heterogeneous catalysis, etc. [1].

In the lanthanide species, 4,4'-bipyridine, carboxylate groups, and water molecules can be connected as coordinated, non-coordinated, or protonated non-coordinated groups. Moreover, the coordinated ligands are bonded in several fashions [2, 3].

There is scant information about lanthanide complexes with bipyridine isomers and halogenoacetates, both types of ligands are intercoordination sphere entities [4—6].

We isolated compounds of the type $[\text{Ln}(4\text{-bpy})(\text{CCl}_2\text{HCOO})_3\text{H}_2\text{O}]_n$, where Ln(III) = La [7] and Sm [8], in which 4,4'-bipyridine is monodendate and carboxylate groups have different types of coordination: bridging bidendate, bridging tridendate and chelating tridendate. Several lanthanide complexes with trichloroacetates and 2,2'-bipyridine were reported by Rohde et al. [9]. The authors obtained the crystal structure of $[\text{Ln}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_3]$ (Ln(III) = Pr, Nd) and $[\text{Er}(2\text{-bpy})_2(\text{CCl}_3\text{COO})_3 \times \text{H}_2\text{O}]$. In these species, 2,2'-bipyridine and trichloroacetates are coordinated to Ln^{3+} ions. On the other hand, there are species such as $[\text{Gd}_2(2\text{-bpy})_2(\text{CCl}_3\text{COO})_6](\text{H}_2\text{O})_2 \cdot 4(2\text{-bpy})$ [9] and $[\text{Ln}(4\text{-bpy})(\text{CHCl}_2\text{COO})_3(\text{H}_2\text{O})_3] \cdot 0.5(4\text{-bpy})$ (where Ln(III) = Er, Yb, and Lu) [10], containing intercoordination sphere bipyridine isomers and chelating carboxylate groups. Additionally, uncoordinated N-donor molecules exist in these compounds.

This work is a continuation of our studies. Here we present the synthesis and crystal structures of lanthanide(III) complexes containing 4,4'-bipyridine, trichloroacetate ions, and water molecules: $[\text{Ln}(\text{H}_2\text{O})_8]^{3+} \cdot 4\text{CCl}_3\text{COO}^- \cdot 4\text{H}_2\text{O} \cdot 2(4\text{-bpy}) \cdot (4\text{-bpyH})^+$ (Ln(III) = Gd, Tb, Er, and Tm).

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade. Trichloroacetic acid was obtained from Reanal—Budapest; 4,4'-bipyridine, Gd₂O₃, and Er₂O₃ from POCh—Gliwice; Tb₄O₇ and Tm₂O₃ from Aldrich.

Single crystals with the empirical formula $[\text{Ln}(\text{H}_2\text{O})_8]^{3+} \cdot 4\text{CCl}_3\text{COO}^- \cdot 4\text{H}_2\text{O} \cdot 2(4\text{-bpy}) \cdot (4\text{-bpyH})^+$ (Ln(III) = Gd-**1**, Tb-**2**, Er-**3** and Tm-**4**) were obtained by crystallization from the filtrates of $\text{Ln}(4\text{-bpy})_{1.5}(\text{CCl}_3\text{COO})_3 \cdot 3\text{H}_2\text{O}$ (where: Ln(III) = Gd and Tb) [11], $\text{Er}(4\text{-bpy})_2(\text{CCl}_3\text{COO})_3 \cdot \text{H}_2\text{O}$, and $\text{Tm}(4\text{-bpy})_2(\text{CCl}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ [12] solid compounds by the slow evaporation of the solutions. The mixture was undisturbed in the air atmosphere. Over a period of several days new single crystals were formed. All of them are isostructural.

The prism crystals of the title complexes of Gd(III)-**1**, Tb(III)-**2**, Er(III)-**3**, and Tm(III)-**4** were sealed in glass capillaries and mounted in turn on a KM-4-CCD automatic diffractometer, equipped with a CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 291.0(3) K, with the ω scan mode. A 11 second exposure time was used for each crystal. The unit cells parameters were determined from the least-squares refinement of the setting angles of 14074, 15323, 14807, and 17099 strongest reflections for **1**, **2**, **3**, and **4** respectively. Details concerning the crystal data and refinement are given in Table 1. The examination of reflections on two reference frames monitored after each 20 frames measured showed 100 %, 89.5 %, 100 %, and 66.7 % loss of the intensity for compounds **1**, **2**, **3**, and **4** respectively. During the data reduction Lorentz, polarisation, and numerical absorption [13] corrections were applied. The structures were solved by partial structure expansion procedure. All the non-hydrogen atoms were refined anisotropically using the full-matrix least-squares technique on F^2 . All carbon-bonded hydrogen atoms were placed in calculated positions after four cycles of the anisotropic refinement and refined as riding on the adjacent atom with an individual isotropic displacement factor equal 1.2 times the value of the equivalent displacement factor of the parent carbon atoms. The oxygen- and nitrogen-bonded hydrogen atom could not be reliably located from the difference Fourier syntheses, thus they were not included into the refinement. The positions of carbon-bonded hydrogen atoms were idealised after each cycle of the refinement. The SHELXS97, SHELXL97, and SHELXTL programs [14] were used for all the calculations. Atomic scattering factors were those incorporated in the computer programs. The Flack parameter [15] was refined as a full matrix parameter. Because for all compounds the large decomposition was observed there was an attempt of measuring the crystals at lower temperatures, but during cooling the crystals always broke in a temperature range 238—251 K, even if the pre-cooling technique was used.

RESULTS AND DISCUSSION

Compounds **1**, **2**, **3**, and **4** are isostructural and isomorphous in the solid state. A perspective view of compound **4** used as an example of the structure of all four studied compounds with the general formula $[\text{Ln}(\text{H}_2\text{O})_8]^{3+} \cdot 4\text{CCl}_3\text{COO}^- \cdot 4\text{H}_2\text{O} \cdot 2(4\text{-bpy}) \cdot (4\text{-bpyH})^+$ (Ln(III) = Gd, Tb, Er, and Tm), together with the atom numbering scheme, is shown in Fig. 1. All atoms in the studied compound lie in general positions of the Cc space group. It must be noted that complex cation, anions, water molecules, and two 4-bipy molecules are connected by the non-crystallographic symmetry two-fold axis going through the metal atom, but one 4-bipy molecule has no additional symmetry. Thus, the refinement of the compounds in the higher symmetry minimal non-isomorphous supergroup $C2/c$ leads to disorder of 4-bipy molecules and distinctly worse the refinement parameters compared to those obtained for the refinement in the Cc space group. In general, most atoms show symptoms of disorder exhibited in relatively large displacement ellipsoids. Additionally, some of the bonds show serious deviations from their ideal lengths, but the libration analysis shows typical values of all bond distances and inter-bond angles (including Ln—O bonds for eight coordinated lanthanides). The central atoms are eight coordinated each by eight oxygen atoms of water molecules. The coordination polyhedra around the central atoms can be described as bicapped trigonal prisms slightly disordered towards a square anti-

Table 1

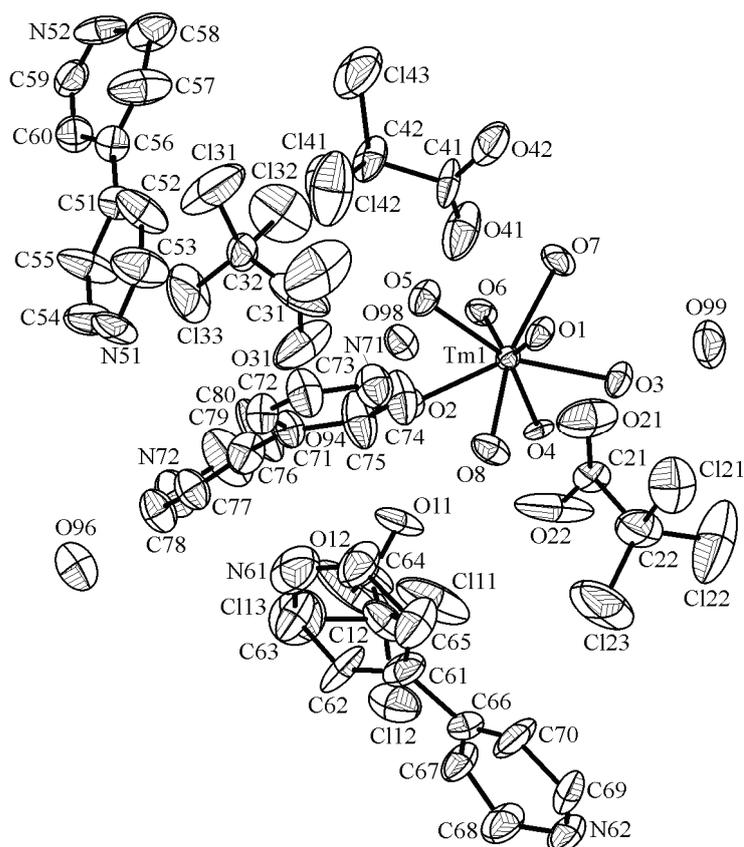
Crystal data and structure refinement details for **1**, **2**, **3** and **4**. Due to low quality of measured data the refinement parameters were not presented for compound **1** and **3**

Compound	1	2	3	4
Empirical formula	C ₃₈ H ₄₉ Cl ₁₂ N ₆ O ₂₀ Gd	C ₃₈ H ₄₉ Cl ₁₂ N ₆ O ₂₀ Tb	C ₃₈ H ₄₉ Cl ₁₂ N ₆ O ₂₀ Er	C ₃₈ H ₄₉ Cl ₁₂ N ₆ O ₂₀ Tm
Formula weight	1492.48	1494.08	1502.49	1504.16
Crystal system; space group; <i>Z</i>	Monoclinic; <i>Cc</i> ; 4			
Unit cell dimensions				
<i>a</i> , Å	26.8697(15)	26.9412(9)	26.5607(18)	26.7305(4)
<i>b</i> , Å	11.8183(11)	11.8461(6)	11.8550(14)	11.7796(1)
<i>c</i> , Å	19.3572(14)	19.4513(11)	19.1171(16)	19.3370(2)
β, deg.	92.841(4)	92.787(4)	92.822(7)	92.851(2)
Volume, Å ³	6139.4(8)	6200.5(5)	6012.2(10)	6081.19(12)
Calculated density, g·cm ⁻³	1.615	1.601	1.660	1.643
Absorption coefficient, mm ⁻¹	1.673	1.727	2.001	2.057
<i>F</i> (000)	2988	2992	3004	3008
Crystal size, mm	0.012×0.010×0.007	0.115×0.087×0.009	0.011×0.010×0.009	0.237×0.176×0.152
θ range for data collection, deg.	1.52—25.00	1.88—36.15	1.59—25.04	1.53—36.25
Index ranges	−31 ≤ <i>h</i> ≤ 31, −11 ≤ <i>k</i> ≤ 14, −23 ≤ <i>l</i> ≤ 23	−39 ≤ <i>h</i> ≤ 43, −14 ≤ <i>k</i> ≤ 19, −30 ≤ <i>l</i> ≤ 31	−32 ≤ <i>h</i> ≤ 31, −15 ≤ <i>k</i> ≤ 14, −23 ≤ <i>l</i> ≤ 24	−44 ≤ <i>h</i> ≤ 37, −19 ≤ <i>k</i> ≤ 16, −32 ≤ <i>l</i> ≤ 28
Reflections collected / unique	19571 / 8279 [<i>R</i> _(int) = 0.1802]	49200 / 19819 [<i>R</i> _(int) = 0.0873]	20451 / 9188 [<i>R</i> _(int) = 0.1605]	50477 / 21253 [<i>R</i> _(int) = 0.0281]
Reflections observed [<i>I</i> > σ(<i>I</i>)]	—	9391	—	17457
Min. and max. transmission	—	0.642 and 0.963	—	0.641 and 0.745
Data / restraints / parameters	—	19819 / 2* / 694	—	21253 / 2* / 694
Flack parameter	—	0.017(15)	—	0.008(10)
Goodness-of-fit on <i>F</i> ²	—	0.941	—	1.024
Final <i>R</i> indices [<i>I</i> > σ(<i>I</i>)]	—	<i>R</i> 1 = 0.070, <i>wR</i> 2 = 0.160	—	<i>R</i> 1 = 0.046, <i>wR</i> 2 = 0.136
<i>R</i> indices (all data)	—	<i>R</i> 1 = 0.180, <i>wR</i> 2 = 0.192	—	<i>R</i> 1 = 0.058, <i>wR</i> 2 = 0.144
Largest diff. peak and hole, e·Å ⁻³	—	1.713 and −1.471	—	1.784 and −1.068

Data common for all structures: measurement temperature 291.0(3) K; measurement wavelength λ(MoK_α) = 0.71073 Å; completeness to 2θ = 50° is 100 %.

* Floating origin restraints imposed by non-centrosymmetric space group.

Fig. 1. Molecular conformation of the Tm(III) compound with atom numbering, plotted with 50 % probability of displacement ellipsoids. Hydrogen atoms are omitted for clarity



prism (Fig. 2). All 4-bpy molecules are located in the outer coordination sphere together with four trichloroacetate anions and four water molecules. One of the nitrogen atoms of one 4-bpy must be protonated due to stoichiometry, but its exact position cannot be located from the difference Fourier synthesis. However it can be postulated that it is located at the N71 or N72 atom because of the existence of a short N \cdots N contact (2.72 Å), originating most likely from the N—H \cdots N hydrogen bond. Based on the analysis of O_(water) \cdots O_(water/acetate) and O_(water) \cdots N_(4-bpy) short contacts (Fig. 2, b), it can be postulated that molecules and ions are connected by O—H \cdots N and O—H \cdots O hydrogen bonds to the hydrogen-bonded network. However, the lack of water hydrogen atoms (as described in the Experimental section) leads to a defective and ambiguous hydrogen bonding scheme, thus it cannot be definitely determined.

CONCLUSIONS

From this study, the following conclusions may be drawn.

1. New single crystals of $[\text{Ln}(\text{H}_2\text{O})_8]^{3+} \cdot 4\text{CCl}_3\text{COO}^- \cdot 4\text{H}_2\text{O} \cdot 2(4\text{-bpy}) \cdot (4\text{-bpyH})^+$ (Ln(III) = Gd, Tb, Er and Tm) have been prepared. Compared to the typical procedure [11, 12] these compounds have been obtained after the isolation of the solid species of the empirical formula $\text{Ln}(4\text{-bpy})_m \times (\text{CCl}_3\text{COO})_3 \cdot n\text{H}_2\text{O}$.

2. $[\text{Ln}(\text{H}_2\text{O})_8]^{3+} \cdot 4\text{CCl}_3\text{COO}^- \cdot 4\text{H}_2\text{O} \cdot 2(4\text{-bpy}) \cdot (4\text{-bpyH})^+$ are characterized by unusual architectures. All bipyridine moieties (4-bpy and 4-bpyH⁺) are located in the outer coordination sphere together with trichloroacetate anions and four water molecules.

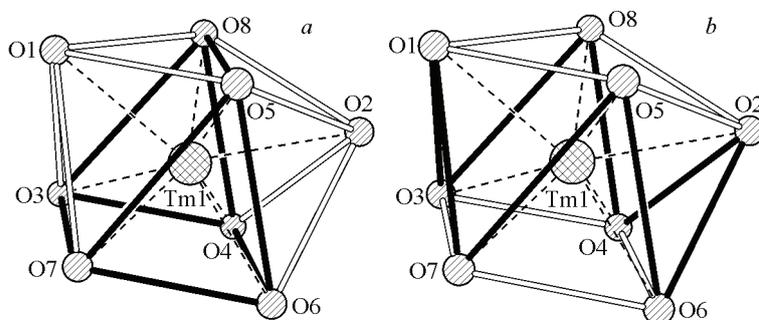


Fig. 2. Thulium coordination polyhedra: (a) bicapped trigonal prism, (b) square antiprism

3. The central atoms of the obtained species are eight-coordinated, as in the case of $[\text{Ln}(4\text{-bpy})(\text{CHCl}_2\text{COO})_3(\text{H}_2\text{O})_3] \cdot 0.5(4\text{-bpy})$ (where $\text{Ln}(\text{III}) = \text{Er}, \text{Yb}, \text{and Lu}$) [10]. On the other hand, in $[\text{Sm}(4\text{-bpy})(\text{CCl}_2\text{HCOO})_3\text{H}_2\text{O}]_n$ [8] it is nine and in $[\text{La}(4\text{-bpy})(\text{CCl}_2\text{HCOO})_3\text{H}_2\text{O}]_n$ [7] it is ten-coordinated.

4. Generally, our research on the molecular structures of lanthanide(III) compounds with chloroacetates and 4,4'-bipyridine shows the different types of the nature of bonds with the ligands.

Supplementary data. Tables of the crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and interbond angles have been deposited with the Cambridge Crystallographic Data Centre under No CCDC797960 and CCDC797961 respectively for compounds **2** and **4**.

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