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Crystal structure of a one-dimensional coordination polymer of gadolinium dibromoacetate with 4,4'-bipyridine

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ABSTRACT

A new gadolinium(III) complex with 4,4'-bipyridine (4-bpy) and dibromoacetate ligand of general formula $[\text{Gd}(4\text{-bpy})(\text{CBr}_2\text{HCOO})_3(\text{H}_2\text{O})]_n$, has been synthesized, crystallized and characterized by a single-crystal X-ray diffraction analysis. The gadolinium atom has an unsymmetrical eight-coordinate geometry, being coordinated by six oxygen atoms of dibromoacetate anions, one nitrogen atom of 4-bpy and one water molecule. The complex is a one-dimensional polymer as a result of dibromoacetate ligand bridging with the repeating monomeric units. There are $\pi\cdots\pi$ stacking interactions between the 4-bpy rings as well as O-H \cdots O and O-H \cdots N hydrogen bonds. Crystal Data for $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{GdN}_2\text{O}_7$ ($M_w = 981.99$ g/mol): triclinic, space group $P-1$ (no. 2), $a = 9.7368(4)$ Å, $b = 11.5416(4)$ Å, $c = 11.7634(4)$ Å, $\alpha = 104.2750(10)^\circ$, $\beta = 94.060(2)^\circ$, $\gamma = 92.6900(10)^\circ$, $V = 1275.08(8)$ Å³, $Z = 2$, $T = 90$ K, $\mu(\text{CuK}\alpha) = 28.190$ mm⁻¹, $D_{\text{calc}} = 2.558$ g/cm³, 8399 reflections measured ($7.782^\circ \leq 2\theta \leq 133.18^\circ$), 4006 unique ($R_{\text{int}} = 0.0409$, $R_{\text{sigma}} = 0.0639$) which were used in all calculations. The final R_1 was 0.0527 ($I > 2\sigma(I)$) and wR_2 was 0.1396 (all data).

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1. Introduction

Nowadays, coordination polymers gain more and more interest due to their unique and interesting properties. A number of papers have recently been released proving, that this field of study is especially attractive. Coordination polymers may be exploited in various areas of life and science [1]. They find application in catalysis and absorption [2-6]. Some of coordination polymers are gas absorbents [7,8]. The polymers are used also as sensors [9].

In our research as ligands we used 4,4'-bipyridine (4-bpy) and dibromoacetates. Both of them are interesting because of their structure. 4,4'-Bipyridine may be one or two donor ligand, which gives different possibilities of coordination. Two nitrogen atoms opposing themselves and two independent pyridine rings with ability to rotation along C-C bond give chance to create coordination polymers [10-14]. The structure will depend on the size and coordination number of metal ion as well as the presence of other ligands. In the case of carboxylate ligands, the possibility of various coordination with the central ion also gives the possibility of forming polymeric compounds. When coordination polymers are formed, not only ligands, but also central ions play a very

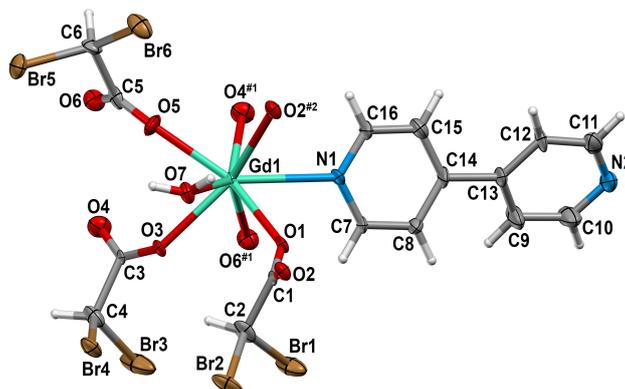
important role. The greater coordination number of the metal, the greater possibility of polymer formation. Due to this feature, lanthanides are good central atoms. In the literature there is little information about similar types of compounds we have studied [15-18]. In our earlier papers we described very similar complexes [19,20]. In this paper we present synthesis and structure of new coordination polymer with general formulae $[\text{Gd}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CBr}_2\text{HCOO})_3(\text{H}_2\text{O})]_n$.

2. Experimental

A solution of gadolinium(III) dibromoacetate as hydrated product was prepared by dissolving freshly precipitated hydroxide in 2 mol/L CBr_2HCOOH in stoichiometric quantities (pH \cong 5.0). The content of Gd(III) ions in obtained solution of dibromoacetate was complexometrically (EDTA) determined. The mixed-ligand complex was prepared by mixing 12.4 mmol of 4-bpy in 96% v:v ethanol (31.25 mL) with the freshly obtained solution of 6.2 mmol metal dibromoacetate in 8.75 mL of water at room temperature. The obtained solid compound was filtered off; washed with 40% ethanol and then with ethanol and diethyl ether mixture (1:1, v:v), air dried at room temperature and described in [21].

Table 1. Crystal data and details of the structure refinement.

Empirical formula	(C ₁₆ H ₁₃ Br ₆ GdN ₂ O ₇) _n
Formula weight	981.99
Temperature (K)	90
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> , (Å)	9.7368(4)
<i>b</i> , (Å)	11.5416(4)
<i>c</i> , (Å)	11.7634(4)
α, (°)	104.2750(10)
β, (°)	94.060(2)
γ, (°)	92.6900(10)
Volume (Å ³)	1275.08(8)
<i>Z</i>	2
ρ _{calc} (g/cm ³)	2.558
μ (mm ⁻¹)	28.190
F(000)	906
Crystal size (mm ³)	0.08 × 0.10 × 0.10
Radiation	CuKα (λ = 1.54178 Å)
2θ range for data collection (°)	7.78 to 133.18
Index ranges	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -13 ≤ <i>l</i> ≤ 9
Reflections collected	8399
Independent reflections	4006 [R _{int} = 0.041, R _{sigma} = 0.064]
Data/restraints/parameters	4006/0/278
Goodness-of-fit on F ²	1.096
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0527, wR ₂ = 0.0539
Final R indexes [all data]	R ₁ = 0.1386, wR ₂ = 0.1396
Largest diff. peak/hole (e Å ⁻³)	0.22/-2.68

**Figure 1.** ORTEP drawing of independent fragment of the compound with the atom numbering scheme. Atomic displacement ellipsoids are drawn at 50% probability level.

A new coordination polymer of gadolinium(III) of general formula [Gd(4-bpy)(CBr₂HCOO)₃(H₂O)]_n, has been obtained by slow crystallization from mother solution after separation of the solid complex Gd(4-bpy)(CBr₂HCOO)₃·3H₂O [21] and characterized by single-crystal X-ray diffraction.

2.1. Instrumentation

Single crystal X-ray diffraction data were collected at 90 K by the ω-scan technique using a Bruker AXS Smart APEX-II CCD [22] diffractometer with MonoCap capillary and 30W Incoatec Microfocus Source IμS with Montel optics and CuKα radiation (λ = 1.54178 Å). Absorption correction was based on symmetry equivalent reflections using the SADABS program [23]. The structure was solved by direct methods with SHELXT-2018/2 [24] and followed by successive Fourier and difference Fourier syntheses and refined by full-matrix least-squares on F² using the SHELXL-2018/3 program [25]. All non-hydrogen atoms in the complex were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and refined isotropically with a riding model except for those bound to water molecules, which were initially located in a difference (Table 1). Software used

to molecular graphics: Mercury [26]. Software used to geometry calculations: PLATON [27].

3. Results and discussion

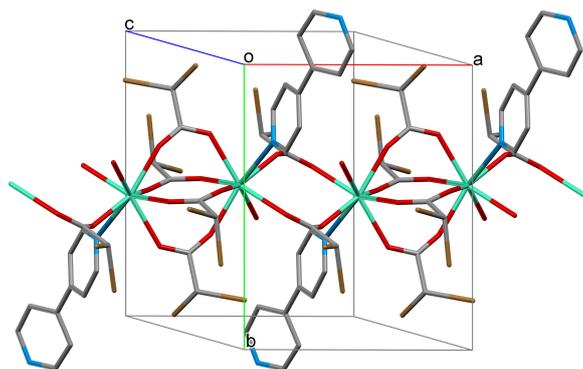
The single crystal X-ray diffraction study at 90 K revealed that the compound crystallizes in the centrosymmetric triclinic space group *P*-1 as of general formula [Gd(4-bpy)(CBr₂HCOO)₃(H₂O)]_n and forms a complex polymer of gadolinium(III) with eight-coordinated Gd^{III} atom by six oxygen atoms from six dibromoacetate anions, one oxygen atom of water molecule and one nitrogen atom from 4-bpy ligand. The crystal structure consists of two crystallographically independent formula units in the unit cell. A perspective view of the title compound structure, occupying the asymmetric unit of the unit cell, together with the atom numbering scheme is shown in Figure 1. The selected bond lengths and angles are listed in Table 2.

The dibromoacetate groups coordinate the gadolinium ion in only a bridged bidentate mode. The crystal structure is built of chains of alternating bridges formed by two or four carboxylato groups of dibromoacetates that join the two neighboring Gd^{III} centers, with metal separation distances of 5.2762(7) and 4.5366(7) Å, respectively.

Table 2. Selected bond distances and bond angles for the title compound.

Bond	Bond length, Å
Gd1-O1	2.353(7)
Gd1-O2 ⁱ	2.383(7)
Gd1-O3	2.389(7)
Gd1-O4 ⁱⁱ	2.349(7)
Gd1-O5	2.301(7)
Gd1-O6 ⁱⁱ	2.374(7)
Gd1-O7	2.420(6)
Gd1-N1	2.657(7)
O1-C1	1.258(11)
O2-C1	1.239(11)
O3-C3	1.218(11)
O4-C3	1.264(11)
O5-C5	1.212(13)
O6-C5	1.250(12)
Bonds	Bond angles, °
O1-Gd1-O2 ⁱ	86.8(2)
O1-Gd1-O3	87.1(2)
O1-Gd1-O4 ⁱⁱ	86.0(2)
O1-Gd1-O5	70.4(2)
O1-Gd1-O6 ⁱⁱ	145.8(2)
O1-Gd1-O7	70.4(2)
O1-Gd1-N1	69.5(2)
O2 ⁱ -Gd1-O3	145.8(2)
O2 ⁱ -Gd1-O4 ⁱⁱ	82.4(2)
O2 ⁱ -Gd1-O5	86.6(3)
O2 ⁱ -Gd1-O6 ⁱⁱ	142.6(2)
O2 ⁱ -Gd1-O7	77.0(2)
O2 ⁱ -Gd1-N1	73.7(2)
O3-Gd1-O4 ⁱⁱ	121.3(2)
O3-Gd1-O5	78.7(3)
O3-Gd1-O6 ⁱⁱ	70.2(2)
O3-Gd1-O7	69.3(2)
O3-Gd1-N1	134.2(3)
O4 ⁱⁱ -Gd1-O5	73.0(3)
O4 ⁱⁱ -Gd1-O6 ⁱⁱ	80.6(3)
O4 ⁱⁱ -Gd1-O7	141.1(3)
O4 ⁱⁱ -Gd1-N1	71.6(3)
O5-Gd1-O6 ⁱⁱ	119.2(3)
O5-Gd1-O7	73.2(3)
O5-Gd1-N1	141.3(3)
O6 ⁱⁱ -Gd1-O7	133.6(2)
O6 ⁱⁱ -Gd1-N1	69.4(3)
O7-Gd1-N1	130.9(2)

Symmetry code: (i) 1-x, 1-y, 1-z; (ii) -x, 1-y, 1-z.

**Figure 2.** A fragment of the polymeric chain of the title compound, extending along the *a* axis. H-atoms have been omitted for clarity.

A resulting polymeric structure extends in a straight line along *a* axis of the unit cell with the Gd1...Gd1'...Gd1'' angle of 165.7° (Figure 2).

The Gd–O_{carboxyl} distances range from 2.301(7) to 2.389(6) Å, with a mean value of 2.358 Å and the Gd–O_{water} bond length is 2.420(6) Å. The 4-bpy ligand coordinates to Gd³⁺ ion through one N1 atom at a distance of 2.657(7) Å. The uncoordinated N2 atom of 4-bpy forms intermolecular hydrogen bond with coordinated water [O7–H72...N2, with *d*(O7...N2) = 2.792(12) Å and angle of O7–H72...N2 = 169°]. The neighboring polymeric chains are interlinked by these H-

bonds leading to the formation of layers extending parallel to the (01-1) plane (Figure 3). The closest distance between adjacent 4-bpy moieties of C8...C11^{1-x,y,-z} = 3.315(4) Å indicates π-π stacking interactions. The pyridyl rings in 4-bpy are not coplanar and the dihedral angle between them is 32.4°. The second hydrogen atom of the water molecule participates in the hydrogen bond with the O1 atom of one of the carboxyl groups [O7–H71...O1, with *d*(O7...O1) = 2.812(9) Å and angle of O7–H71...O1 = 165°]. The crystal is found to be isostructural with catena-(tris(μ₂-2-fluorobenzoato-*O,O'*)-(4-bpy)-aqua-terbium(III)) [28].

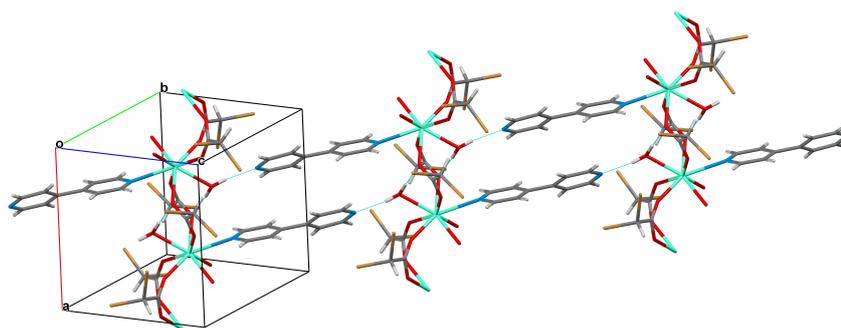


Figure 3. A part of the crystal packing diagram of $[\text{Gd}(4\text{-bpy})(\text{CBr}_2\text{HCOO})_3(\text{H}_2\text{O})]_n$ showing hydrogen bonds joining polymeric chains.

4. Conclusion

The polymeric complex of gadolinium(III) with the 4,4'-bipyridine and dibromoacetate ligands was synthesized and characterized as $[\text{Gd}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{CBr}_2\text{HCOO})_3(\text{H}_2\text{O})]_n$. The structure of the complex was established via single-crystal X-ray diffraction showing eight-coordination geometry of the central Gd^{3+} ion. The crystal is built of chains of alternating bridges formed by two or four chelating dibromoacetate ligands in a bridged bidentate mode. The bridges join the neighboring Gd^{3+} centers, resulting in one-dimensional polymeric structure.

Supporting information

CCDC-1844278 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

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