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Crystal Structures, Thermal and Luminescent Properties of Gadolinium(III) *Trans*-1,4-cyclohexanedicarboxylate Metal-Organic Frameworks

Pavel A. Demakov ^{1,*} , Alena A. Vasileva ^{1,2}, Vladimir A. Lazarenko ³, Alexey A. Ryadun ¹ and Vladimir P. Fedin ¹

¹ Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russia; a.vasileva2@g.nsu.ru (A.A.V.); ryadunalexey@mail.ru (A.A.R.); cluster@niic.nsc.ru (V.P.F.)

² Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russia

³ National Research Centre "Kurchatov Institute", 123182 Moscow, Russia; vladimir.a.lazarenko@gmail.com

* Correspondence: demakov@niic.nsc.ru

Abstract: Four new gadolinium(III) metal-organic frameworks containing 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) chelate ligands and *trans*-1,4-cyclohexanedicarboxylate (chdc^{2-}) were synthesized. Their crystal structures were determined by single-crystal X-ray diffraction analysis. All four coordination frameworks are based on the binuclear carboxylate building units. In the compounds $[\text{Gd}_2(\text{bpy})_2(\text{chdc})_3] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Gd}_2(\text{phen})_2(\text{chdc})_3] \cdot 0.5\text{DMF}$ (**2**), the six-connected $\{\text{Ln}_2(\text{L})_2(\text{OOCR})_6\}$ blocks form a 3D network with the primitive cubic (pcu) topology. In the compounds $[\text{Gd}_2(\text{NO}_3)_2(\text{phen})_2(\text{chdc})_2] \cdot 2\text{DMF}$ (**3**) and $[\text{Gd}_2\text{Cl}_2(\text{phen})_2(\text{chdc})_2] \cdot 0.3\text{DMF} \cdot 2.2\text{dioxane}$ (**4**), the four-connected $\{\text{Ln}_2(\text{L})_2(\text{X})_2(\text{OOCR})_4\}$ units (where $\text{X} = \text{NO}_3^-$ for **3** or Cl^- for **4**) form a 2D square-grid (sql) network. The solid-state luminescent properties were investigated for the synthesized frameworks. Bpy-containing compound **1** shows no luminescence, possibly due to the paramagnetic quenching by Gd^{3+} cation. In contrast, the phenanthroline-containing MOFs **2–4** possess yellow emission under visible excitation ($\lambda_{\text{ex}} = 460 \text{ nm}$) with the tuning of the characteristic wavelength by the coordination environment of the metal center.

Keywords: metal-organic frameworks; coordination polymers; rare earth elements; gadolinium; luminescence

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1. Introduction

Metal-organic frameworks (MOFs) are an important class of coordination compounds extensively studied in recent years. Their porosity as well as a wide variability of metal centers and organic ligands unveil a route to design materials with highly tunable adsorption, catalytic, optical and other physico-chemical properties. In particular, lanthanide(III) MOFs deserve a great interest due to the unique f^n electron configuration of the metal center and subsequent applications in magnetic and luminescent materials [1–9].

Gadolinium(III), having a half-filled f^7 sublevel, takes a special place in the lanthanide row. This is a most relevant paramagnetic center in the development of contrast agents for magnetic-resonance tomography and visualization [10–14]. The most intensive electron transitions in Gd^{3+} occur in the ultraviolet region of 290–318 nm with the narrow-banded emission and have been applied in common lasers. Under a soft UV and visible excitation, Gd(III) is a non-emissive center and the luminescence of its coordination compounds is ligand-centered [15–23].

Trans-1,4-cyclohexanedicarboxylate is quite rare, but is still a commercially available example of an aliphatic ligand, which saturated backbone is known to have extremely low UV/vis absorbance and no luminescent activity. Several examples of the distribution of such unusual optical properties to the coordination frameworks using aliphatic ligands have been

reported in the literature to date [24–27]. In this work, four new gadolinium(III) *trans*-1,4-cyclohexanedicarboxylate metal-organic frameworks based on the binuclear carboxylate blocks with the additionally coordinated N-donor chelate ligands were synthesized and characterized. The determined crystallographic formulas of the compounds are $[\text{Gd}_2(\text{bpy})_2(\text{chdc})_3] \cdot \text{H}_2\text{O}$ (**1**, bpy = 2,2'-bipyridyl), $[\text{Gd}_2(\text{phen})_2(\text{chdc})_3] \cdot 0.5\text{DMF}$ (**2**, phen = 1,10-phenanthroline), $[\text{Gd}_2(\text{NO}_3)_2(\text{phen})_2(\text{chdc})_2] \cdot 2\text{DMF}$ (**3**) and $[\text{Gd}_2\text{Cl}_2(\text{phen})_2(\text{chdc})_2] \cdot 0.3\text{DMF} \cdot 2.2\text{dioxane}$ (**4**). A new molecular complex $[\text{Gd}(\text{DMF})_2(\text{phen})]\text{Cl}_3$ (**5**) not containing *trans*-1,4-cyclohexanedicarboxylate bridge (see Figure A1 in Appendix A) was crystallized during this work. The successful synthesis of such a series with a non-photoactive bridging ligand and a non-emissive paramagnetic metal center makes it possible to investigate the impact of the metal ion coordination environment on the N-donor ligand-centered luminescence in the corresponding coordination networks.

2. Materials and Methods

2.1. Materials

Trans-1,4-cyclohexanedicarboxylic acid (H_2chdc , >97.0%), 2,2'-bipyridyl (bpy, >99.0%) and 1,10-phenanthroline monohydrate (phen· H_2O , >98.0%) were received from TCI. $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9% REO) was received from Dalchem. $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (high-purity grade) was received from Krystall. N,N-dimethylformamide (DMF, reagent grade) and dioxane were received from Vekton.

2.2. Instruments

IR spectra in KBr pellets were recorded in the range 4000–400 cm^{-1} on a Bruker Scimitar FTS 2000 spectrometer. Elemental analysis was conducted with a VarioMICROcube analyzer. Powder X-ray diffraction (PXRD) analysis was performed at room temperature on a Shimadzu XRD-7000 diffractometer (Cu- $\text{K}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$, or Co- $\text{K}\alpha$ radiation, $\lambda = 1.78897 \text{ \AA}$). Thermogravimetric analysis was carried out using a Netzsch TG 209 F1 Iris instrument under Ar flow ($30 \text{ cm}^3 \cdot \text{min}^{-1}$) at a $10 \text{ K} \cdot \text{min}^{-1}$ heating rate. Photoluminescence spectra were recorded with a spectrofluorometer Horiba Jobin Yvon Fluorolog 3 equipped with ozone-free Xe-lamp 450W power, cooled photon detector R928/1860 PFR technologies with refrigerated chamber PC177CE-010 and double grating monochromators. The spectra were corrected for source intensity and detector spectral response by standard correction curves. The absolute quantum yield was measured using a G8 (GMP SA, Switzerland) spectralon-coated integrating sphere, which was connected to a Fluorolog 3 spectrofluorometer. Diffraction data for single crystals of **1** were obtained on the ‘Belok’ beamline [28,29] ($\lambda = 0.74539 \text{ \AA}$) of the National Research Center ‘Kurchatov Institute’ (Moscow, Russian Federation) using a Rayonix SX165 CCD detector. The data were indexed, integrated and scaled, and absorption correction was applied using the XDS program package [30]. Diffraction data for single crystals of **2–5** were collected on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$). Integration, absorption correction and determination of unit cell parameters were performed using the CrysAlisPro program package [31]. The structures were solved by the dual-space algorithm (SHELXT [32]) and refined by the full-matrix least squares technique (SHELXL [33]) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Appendix Table A1.

2.3. Synthetic Procedures

Synthesis of $[\text{Gd}_2(\text{bpy})_2(\text{chdc})_3] \cdot \text{H}_2\text{O}$ (**1**): 90.4 mg (0.20 mmol) of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 62.4 mg (0.40 mmol) of bpy, 68.8 mg (0.40 mmol) of H_2chdc and 44.8 mg (0.80 mmol) of KOH were mixed in a 30 mL Teflon-lined stainless-steel autoclave and dispersed in 20 mL of H_2O . The obtained suspension was heated at $180 \text{ }^\circ\text{C}$ for 12 h. After cooling to room temperature, the obtained white precipitate was filtered off, washed with H_2O and dried in air. Yield: 79.2 mg (84%). IR spectrum main bands (KBr, cm^{-1} ; see Figure S5): 3452 (s., br.,

$\nu\text{O}-\text{H}$); 3115 and 3088 (w., $\nu\text{Csp}^2-\text{H}$); 2927 and 2858 (m., $\nu\text{Csp}^3-\text{H}$); 1541 (s., $\nu\text{COO}_{\text{as}}$); 1417 (s., νCOO_{s}). Elemental analysis data, calculated for $[\text{Gd}_2(\text{bpy})_2(\text{chdc})_3]\cdot(\%)$: C, 46.5; H, 4.1; N, 4.9. Found (%): C, 46.4; H, 4.0; N, 4.8. PXRD data: Figure S1.

Synthesis of $[\text{Gd}_2(\text{phen})_2(\text{chdc})_3]\cdot 0.5\text{DMF}$ (**2**): 148.8 mg (0.40 mmol) of $\text{GdCl}_3\cdot 6\text{H}_2\text{O}$, 72.0 mg (0.40 mmol) of $\text{phen}\cdot\text{H}_2\text{O}$ and 137 mg (0.80 mmol) of H_2chdc were mixed in a 20 mL glass vial and dissolved in 10 mL of DMF. The obtained solution was heated at 110 °C for 72 h. After cooling to room temperature, the obtained white precipitate was filtered off, washed with DMF and dried in air. Yield: 90.5 mg (37%). IR spectrum main bands (KBr, cm^{-1}): 3446 (w., br., $\nu\text{O}-\text{H}$); 3078 and 3062 (m., $\nu\text{Csp}^2-\text{H}$); 3010 and 2997 (w., $\nu\text{Csp}^2-\text{H}$); 2927 and 2856 (m., $\nu\text{Csp}^3-\text{H}$); 1685 (m., $\nu\text{CO}_{\text{amide}}$); 1598 and 1587 (s., $\nu\text{COO}_{\text{as}}$); 1409 (s., νCOO_{s}). Elemental analysis data, calculated for $[\text{Gd}_2(\text{phen})_2(\text{chdc})_3]\cdot 0.5\text{DMF}\cdot\text{H}_2\text{O}$ (%): C, 47.9; H, 4.1; N, 5.1. Found (%): C, 47.9; H, 4.1; N, 5.4. TG data: 4% weight loss before 300 °C; calculated for $0.5\text{DMF} + \text{H}_2\text{O}$: 4%. PXRD data: Figure S2.

Synthesis of $[\text{Gd}_2(\text{NO}_3)_2(\text{phen})_2(\text{chdc})_2]\cdot 2\text{DMF}$ (**3**): 45.1 mg (0.10 mmol) of $\text{Gd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, 18.0 mg (0.10 mmol) of $\text{phen}\cdot\text{H}_2\text{O}$ and 17.2 mg (0.10 mmol) of H_2chdc were mixed in a 5 mL glass vial and dissolved in 3.50 mL of DMF. Then, a 10 μL drop of HNO_3 (65%) was added. The obtained solution was heated at 110 °C for 36 h. After cooling to room temperature, the obtained white precipitate was filtered off, washed with DMF and dried in air. Yield: 43.7 mg (96%). IR spectrum main bands (KBr, cm^{-1}): 3420 (w., br., $\nu\text{O}-\text{H}$); 3078 and 3062 (m., $\nu\text{Csp}^2-\text{H}$); 2936 and 2858 (m., $\nu\text{Csp}^3-\text{H}$); 1681 (m., $\nu\text{CO}_{\text{amide}}$); 1587 (s., $\nu\text{COO}_{\text{as}}$); 1426 (s., νCOO_{s}); 1292 (m., νNO). Elemental analysis data, calculated for $[\text{Gd}_2(\text{NO}_3)_2(\text{phen})_2(\text{chdc})_2]\cdot 2\text{DMF}\cdot 2\text{H}_2\text{O}$ (%): C, 41.8; H, 4.1; N, 8.5. Found (%): C, 41.9; H, 4.0; N, 7.6. TG data: 13% weight loss at 120 °C; calculated for $2\text{DMF} + 2\text{H}_2\text{O}$: 14%. PXRD data: Figure S3.

Synthesis of $[\text{Gd}_2\text{Cl}_2(\text{phen})_2(\text{chdc})_2]\cdot 0.3\text{DMF}\cdot 2.2\text{dioxane}$ (**4**): 74.3 mg (0.20 mmol) of $\text{GdCl}_3\cdot 6\text{H}_2\text{O}$, 36.0 mg (0.20 mmol) of $\text{phen}\cdot\text{H}_2\text{O}$ and 34.4 mg (0.20 mmol) of H_2chdc were mixed in a 3 mL glass vial and dissolved in the mixture of 1 mL of DMF and 1.50 mL of 1,4-dioxane. Then, 25 μL of HCl (36%) was added. The obtained solution was heated at 100 °C for 36 h. After cooling to room temperature, the obtained white precipitate was filtered off, washed with DMF, then with dioxane, and dried in air. Yield: 54.0 mg (43%). IR spectrum main bands (KBr, cm^{-1}): 3392 (m., br., $\nu\text{O}-\text{H}$); 3080 and 3049 (w., $\nu\text{Csp}^2-\text{H}$); 2935 and 2856 (m., $\nu\text{Csp}^3-\text{H}$); 1654 (w., $\nu\text{CO}_{\text{amide}}$); 1598 and 1587 (s., $\nu\text{COO}_{\text{as}}$); 1425 (s., νCOO_{s}). Elemental analysis data, calculated for $[\text{Gd}_2\text{Cl}_2(\text{phen})_2(\text{chdc})_2]\cdot 0.3\text{DMF}\cdot 3\text{H}_2\text{O}$ (%): C, 42.3; H, 3.8; N, 5.2. Found (%): C, 41.8; H, 3.5; N, 5.4. TG data: 6% weight loss at 130 °C; calculated for $0.3\text{DMF} + 3\text{H}_2\text{O}$: 6%. PXRD data: Figure S4.

3. Results and Discussion

3.1. Synthesis and Crystal Structure Description

Compounds $[\text{Gd}_2(\text{bpy})_2(\text{chdc})_3]\cdot\text{H}_2\text{O}$ (**1**), $[\text{Gd}_2(\text{phen})_2(\text{chdc})_3]\cdot 0.5\text{DMF}$ (**2**) and $[\text{Gd}_2(\text{NO}_3)_2(\text{phen})_2(\text{chdc})_2]\cdot 2\text{DMF}$ (**3**) crystallize in the monoclinic crystal system with $P2_1/n$ space group and are isostructural to the series previously reported by our group: $[\text{Ln}_2(\text{bpy})_2(\text{chdc})_3]\cdot x\text{H}_2\text{O}$ ($x = 0 \dots 1$), $[\text{Ln}_2(\text{phen})_2(\text{chdc})_3]\cdot 0.5\text{DMF}$ [34] and $[\text{Ln}_2(\text{NO}_3)_2(\text{phen})_2(\text{chdc})_2]\cdot 2\text{DMF}$ [35] ($\text{Ln}^{3+} = \text{Y}^{3+}$, Eu^{3+} or Tb^{3+}), respectively. Highly effective luminescence with quantum yields up to 63% was revealed for these structures, including $[\text{Y}_2(\text{bpy})_2(\text{chdc})_3]$ based on the non-emissive and diamagnetic Y^{3+} . Unlike the yttrium(III), Gd^{3+} is paramagnetic but still non-emissive in the soft UV and visible region; therefore, the investigation of isostructural Gd(III)-based compounds **1–3** and the cognate new metal-organic framework **4** could provide significantly new information concerning the luminescent properties of such type series of coordination networks.

Compounds **2** and **3** were obtained in quite similar solvothermal conditions at 110 °C, using N,N-dimethylformamide (DMF) as a solvent. The main difference between their synthetic methods is the starting Gd(III) salt (chloride for **2** or nitrate for **3**) to be used. Thus, it was shown that the anion plays a main structure-forming role in this system, as the presence of NO_3^- leads to the crystallization of nitrate-containing layered MOF **3**. On the contrary,

poorly coordinated Cl^- cannot compete with the carboxylate in such conditions and affords a three-dimensional framework **2**, which contains the only RCOO^- fragments additionally coordinated to the $\{\text{Gd}(\text{phen})\}^{3+}$ moiety. Interestingly, the replacement of pure DMF by the mixture of DMF and dioxane (2:3) leads to the formation of the chloride-containing structure $[\text{Gd}_2\text{Cl}_2(\text{phen})_2(\text{chdc})_2] \cdot 0.3\text{DMF} \cdot 2.2\text{dioxane}$ (**4**) instead of the carboxylate **2**. A significant dilution of DMF by dioxane apparently weakens the solvation of Cl^- and, therefore, strengthens its coordination ability compared to the carboxylate. Thus, the crystallization of two-dimensional framework **4** seems to be anion/solvent-controlled again and suggests a simple route for the synthesis of lanthanide(III) networks with coordinated halogenides, since only one example of the compound containing $\{\text{Ln}_2(\text{Cl})_2(\text{L})_2(\text{OOCR})_4\}$ building units (L = any 2,2'-bipyridyl derivative) has been reported to date [36].

In all the structures **1–3**, Gd(III) adopts a similar capped square-antiprismatic environment consisting of two N atoms of diimine chelate ligand and seven O atoms, which belong to the carboxylic groups in **1** and **2** or to carboxylic groups and terminal nitrate in **3** (Figure 1a–c). The selected coordination bond lengths are listed in Table 1. Two symmetry-equivalent Gd(III) ions form binuclear carboxylate blocks $\{\text{Gd}_2(\text{bpy})_2(\text{RCOO}-\kappa^2)_2(\mu-\text{RCOO}-\kappa^1, \kappa^1)_2(\mu-\text{RCOO}-\kappa^1, \kappa^2)_2\}$ (**1**), $\{\text{Gd}_2(\text{phen})_2(\text{RCOO}-\kappa^2)_2(\mu-\text{RCOO}-\kappa^1, \kappa^1)_2(\mu-\text{RCOO}-\kappa^1, \kappa^2)_2\}$ (**2**) and $\{\text{Gd}_2(\text{phen})_2(\text{ONO}_2-\kappa^2)_2(\mu-\text{RCOO}-\kappa^1, \kappa^1)_2(\mu-\text{RCOO}-\kappa^1, \kappa^2)_2\}$ (**3**). The coordination frameworks in **1** and **2**, consisting of six-connected building units and *trans*-1,4-cyclohexanedicarboxylate bridges, adopt a very distorted three-dimensional primitive cubic topology (pcu) and contain small voids (Figure 2a,b) interconnected by very narrow ($2 \times 2 \text{ \AA}^2$) windows with 5% calculated total void volume. In the coordination framework in **3**, four-connected binuclear blocks are interconnected by cyclohexane moieties into a two-dimensional square-grid network (sql) (Figure 2c). The layers in **3** are packed in a one-layer (AA) manner to form channels with 26% general void volume. These channels are occupied by the localized DMF solvent molecules.

Table 1. Selected bond lengths in the structures **1–4**.

Bond	1	2	3	4
Gd–N, Å	2.566(2), 2.600(3)	2.499(19)–2.59(3)	2.553(2), 2.591(3)	2.564(7), 2.579(5)
Gd–O($\text{COO}_{\text{chelate}}$), Å	2.3482(19)–2.514(2)	2.334(3)–2.539(3)	2.330(2)–2.573(2)	2.294(5)–2.513(5)
Gd–O($\text{COO}_{\text{non-chelate}}$), Å	2.429(2)–2.4800(19)	2.463(3)–2.465(3)	-	-
Gd–O(NO_3 or non-chelate), Å	-	-	2.458(2)–2.529(2)	-

Figure 1. Secondary building units in **1** (a), **2** (b), **3** (c) and **4** (d). Gd atoms are green, N atoms are blue, O atoms are red, Cl atoms are yellow. H atoms are not shown.

Compound $[\text{Gd}_2\text{Cl}_2(\text{phen})_2(\text{chdc})_2] \cdot 0.3\text{DMF} \cdot 2.2\text{dioxane}$ (**4**) crystallizes in the monoclinic crystal system with the $P2_1/n$ space group. The coordination environment of Gd(III) consists of two N atoms of diimine chelate ligand, five O atoms of the carboxylic groups and one Cl atom. The Gd–N and Gd–O bond lengths are close to those in **1–3** (see Table 1) and the Gd–Cl distance is 2.649(2) Å (Figures 1 and 2). The structure of a binuclear carboxylate block $\{\text{Gd}_2(\text{phen})_2(\text{Cl})_2(\mu\text{-RCOO-}\kappa^1, \kappa^1)_2(\mu\text{-RCOO-}\kappa^1, \kappa^2)_2\}$ in **4** is analogous to the nitrate-containing unit in **3**, except for the reduction of the coordination number to 8 due to the substitution of the bidentate nitrate anion with the larger chloride (Figure 1d), which acts as a monodentate ligand. Four-connected binuclear blocks in **4** are interconnected by cyclohexane moieties (Figure 2d) in a similar AA manner to **3**, with the channels of 32% general void volume. These channels are occupied by solvent molecules. Only one dioxane molecule per formula unit was localized directly, while the non-ordered residual electron density was analyzed by the PLATON/SQUEEZE [37] procedure (69 e[−] in 265 Å³ per formula unit) and assigned to 0.3DMF + 1.2dioxane (69.6 e[−] and ca. 209 Å³ volume estimated from the liquid densities).

Figure 2. Fragments of three-dimensional coordination frameworks in **1** (a) and **2** (b). Coordination layers in **3** (c) and **4** (d), Atom colors are similar to those in Figure 1.

3.2. Thermal Properties

Thermogravimetric analyses for the compounds **1–4** were performed (Figure 3). For **1**, the stepwise decomposition starts at ca. 350 °C. Only 1% weight loss before 300 °C corresponds well to the low content of guest solvent molecules (calculated as 1.5%) deter-

mined by X-ray crystallography, and 33% residual weight at 600 °C matches well to the gadolinium(III) oxide (calculated as 32%).

2 slowly losses solvent molecules at the temperature up to 300 °C, much higher than the boiling points of both DMF and water. Such feature is apparently attributed to the low size of the windows (~ 2 Å) in the coordination framework of **2** and the resulting kinetic hindrance of the guest diffusion. The first step of lattice decomposition occurs in the range 340–440 °C and corresponds well to the loss of phen molecules (66% residue at 440 °C; calculated for $\text{Gd}_2(\text{chdc})_3$: 66.5%). Further weight loss starting at ca. 460 °C corresponds to the decomposition of the bridging ligand and leads to the Gd_2O_3 (34% residue at 600 °C, calculated: 29%) being apparently contaminated by carbon admixture due to the incomplete evaporation of the organic moieties.

Figure 3. TG plots for compounds 1–4.

Compound **3** loses solvents at ca. 120 °C. The first step of coordination lattice decomposition occurs in the range 350–400 °C and corresponds well to the loss of phen molecules (58% residue at 440 °C; calculated for $\text{Gd}_2(\text{NO}_3)_2(\text{chdc})_2$: 59%). Further weight loss, corresponding to the decomposition of the nitrate and chdc^{2-} ligands, starts at ca. 430 °C. The TG profile of **4** is close to **3** and includes solvent loss at ca. 130 °C and two steps of the lattice decomposition occurring in the range 320–410 °C and above 490 °C. In summary, thermal stability characteristics of the coordination framework in **1–4** are high [38–41] and quite similar to each other. However, their stability is limited by the evaporation of the neutral N-donor chelate, occurring below 400 °C.

3.3. Luminescence Spectroscopy

Solid-state luminescence measurements were performed for the synthesized compounds. The bpy-containing **1** appeared to possess no luminescent activity, possibly due to the paramagnetic quenching of the emission by the Gd(III) cation. In contrast, the phen-containing compounds **2–4** demonstrate yellow wide-banded emission under a visible light excitation at $\lambda_{\text{ex}} = 460$ nm. The corresponding emission spectra are shown in Figure 4a. The maxima of the spectra appear at $\lambda = 537$ nm for three-dimensional **2** based on the six-connected carboxylate units, $\lambda = 522$ nm for the nitrate-containing **3** and $\lambda = 556$ nm for the chloride-containing **4**. The observed red-shift of both the maxima and the characteristic wavelengths in the row nitrate < carboxylate < chloride apparently correlates to the electron donor properties of the corresponding ligands. The calculated (x,y) coordinates on the CIE 1931 chromaticity diagram and characteristic wavelength values are shown in Figure 4b and visualize the integral yellow color of the wide-banded emission of **2–4**.

Figure 4. Emission spectra for 2–4 at $\lambda_{\text{ex}} = 460$ nm (a), CIE 1931 chromaticity diagram for 2–4 (b).

4. Conclusions

To summarize, four new gadolinium(III) metal-organic frameworks were synthesized and characterized. Compounds 1 and 2 containing six-connected binuclear metal-carboxylate blocks adopt a distorted primitive cubic topology with narrow pores. A partial substitution of carboxylate by nitrate or chloride in the Gd(III) coordination sphere leads to two-dimensional square-layered networks 3 and 4. Thermal and luminescent properties of the synthesized compounds were investigated. Phenanthroline-based structures 2–4 emit in the yellow region under a visible blue excitation at 460 nm. The observed red-shift in the row of coordinated ligands, nitrate < carboxylate < chloride was attributed to the donor ability of the corresponding ligands.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11111375/s1>: Figure S1: Experimental PXRD pattern for 1 compared to the theoretical one; Figure S2: Experimental PXRD pattern for 2 compared to the theoretical one; Figure S3: Experimental PXRD pattern for 3 compared to the theoretical one; Figure S4: Experimental PXRD pattern for 4 compared to the theoretical one; Figure S5: IR spectra for 1–5.

Author Contributions: P.A.D., original draft preparation, single-crystal XRD, graphing; A.A.V., synthesis, characterization, graphing; V.A.L., synchrotron single-crystal XRD; A.A.R., solid-state luminescence measurements; V.P.F., manuscript review and editing, project administration and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Crystal Structure of a New Complex [Gd(DMF)₂(phen)]Cl₃ (5)

Single crystals of 5 were obtained during the screening syntheses: 37.2 mg (0.10 mmol) of GdCl₃·6H₂O, 18.0 mg (0.10 mmol) of phen·H₂O and 34.4 mg (0.20 mmol) of H₂chdc were mixed in a 3 mL glass vial and dissolved in the mixture of 1 mL of DMF and 1.50 mL of acetone. The obtained solution was heated at 45 °C for 72 h. After cooling to room temperature, the obtained white precipitate was filtered off, washed with DMF and dried in air. IR spectrum main bands (KBr, cm^{−1}): 3375 (s., br., νO–H); 2937 and 2858 (w., νCsp³–H); 1654 (s., νCO_{amide}).

A molecular complex $[\text{Gd}(\text{DMF})_2(\text{phen})]\text{Cl}_3$ (**5**) crystallizes in the triclinic crystal system with the $P\bar{1}$ space group with one independent Gd atom and $Z = 2$. The coordination environment of Gd(III) consists of two N atoms of phenanthroline, two O atoms of the coordinated solvent and three Cl atoms. The Gd–N bond length is 2.584(2) Å, the Gd–O bond lengths are 2.334(2) Å and 2.374(2) Å and the Gd–Cl bond lengths are 2.6408(8) Å, 2.6694(8) Å and 2.6921(7) Å, which are close to the distance in the structure of **4**: 2.649(2) Å.

Figure A1. A molecular complex $[\text{Gd}(\text{DMF})_2(\text{phen})]\text{Cl}_3$. Gd atoms are green, N atoms are blue, O atoms are red, Cl atoms are yellow. H atoms are not shown.

Appendix B. The Crystallographic Data for 1–5

Table A1. Crystallographic data and refinement details for the structures 1–5.

	1	2	3	4	5
Chemical formula	$\text{C}_{44}\text{H}_{48}\text{Gd}_2\text{N}_4\text{O}_{13}$	$\text{C}_{49.5}\text{H}_{49.5}\text{Gd}_2\text{N}_{4.5}\text{O}_{12.5}$	$\text{C}_{46}\text{H}_{50}\text{Gd}_2\text{N}_8\text{O}_{16}$	$\text{C}_{47.7}\text{H}_{51.7}\text{Cl}_2\text{Gd}_2\text{N}_{4.3}\text{O}_{11.7}$	$\text{C}_{18}\text{H}_{22}\text{Cl}_3\text{GdN}_4\text{O}_2$
M_r , g/mol	1155.36	1221.93	1285.44	1257.83	589.99
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Temperature, K	100	140	140	140	140
a , Å	10.422(2)	10.4479(4)	12.3986(6)	13.2219(5)	9.2772(4)
b , Å	17.551(4)	17.9554(7)	16.8287(6)	13.3512(7)	9.6641(4)
c , Å	12.294(3)	12.8866(7)	12.7182(5)	15.5831(7)	12.2954(5)
α , °	90	90	90	90	102.460(4)
β , °	103.90(3)	99.104(4)	112.863(5)	109.100(5)	94.032(3)
γ , °	90	90	90	90	92.587(3)
V , Å ³	2183.0(8)	2387.02(19)	2445.20(19)	2599.4(2)	1071.67(8)
Z	2	2	2	2	2
$F(000)$	1144	1212	1276	1247	578
$D(\text{calc.})$, g/cm ³	1.758	1.700	1.746	1.607	1.828
m , mm ^{−1}	3.462	2.82	2.77	2.69	3.49
Crystal size, mm	$0.20 \times 0.04 \times 0.04$	$0.30 \times 0.14 \times 0.10$	$0.30 \times 0.21 \times 0.11$	$0.25 \times 0.17 \times 0.14$	$0.65 \times 0.25 \times 0.20$
θ range for data collection, °	$2.42 \leq \theta \leq 26.68$	$2.3 \leq \theta \leq 25.4$	$2.0 \leq \theta \leq 25.4$	$2.1 \leq \theta \leq 25.4$	$2.2 \leq \theta \leq 25.3$

Table A1. Cont.

	1	2	3	4	5
θ range for data collection, $^{\circ}$	$2.42 \leq \theta \leq 26.68$	$2.3 \leq \theta \leq 25.4$	$2.0 \leq \theta \leq 25.4$	$2.1 \leq \theta \leq 25.4$	$2.2 \leq \theta \leq 25.3$
No. of reflections: measured/independent/observed [$I > 2\sigma(I)$]	14,396/3987/3615	10,535/4383/3520	11,222/4487/3921	11,529/4755/3827	9676/3919/3637
R_{int}	0.0356	0.0249	0.0251	0.0231	0.0368
Index ranges	$-12 \leq h \leq 12$ $-21 \leq k \leq 20$ $-14 \leq l \leq 14$	$-12 \leq h \leq 12$ $-21 \leq k \leq 19$ $-15 \leq l \leq 15$	$-14 \leq h \leq 12$ $-15 \leq k \leq 20$ $-12 \leq l \leq 15$	$-11 \leq h \leq 15$ $-16 \leq k \leq 14$ $-18 \leq l \leq 18$	$-11 \leq h \leq 9$ $-11 \leq k \leq 11$ $-14 \leq l \leq 14$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0205$ $wR_2 = 0.0482$	$R_1 = 0.0286$ $wR_2 = 0.0630$	$R_1 = 0.0227$ $wR_2 = 0.0480$	$R_1 = 0.0475$ $wR_2 = 0.1365$	$R_1 = 0.0231$ $wR_2 = 0.0459$
R indices (all data)	$R_1 = 0.0240$ $wR_2 = 0.0496$	$R_1 = 0.0437$ $wR_2 = 0.0673$	$R_1 = 0.0296$ $wR_2 = 0.0502$	$R_1 = 0.0572$ $wR_2 = 0.1443$	$R_1 = 0.0261$ $wR_2 = 0.0470$
Goodness-of-fit on F^2	1.026	1.043	1.061	1.070	1.049
Largest diff. peak/hole, $e/\text{\AA}^3$	0.525, -0.601	0.73, -0.80	0.66, -0.78	2.36, -0.86	0.63, -0.68

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