

Syntheses, characterization and the liquid-phase formation enthalpy changes of two new one-dimensional ribbon-like lanthanide supermolecular polymers

Yixia Ren ^{a,b}, Sanping Chen ^a, Shengli Gao ^{a,*}, Qizhen Shi ^a

^a Department of Chemistry, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Shaanxi 710069, PR China

^b Department of Chemistry, Yanan University, Yanan 716000, PR China

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Abstract

Two novel one-dimensional ribbon-like mixed-ligand supermolecular polymers, $[\text{Ln}(5\text{-nip})(\text{phen})(\text{NO}_3)(\text{DMF})]_n$ ($\text{Ln} = \text{Pr}$ (**1**) and Ho (**2**)), assembled into two-dimensional networks by strong π – π stacking interactions, have been synthesized by reactions of lanthanide (III) salts with 5-nitroisophatha acid ($5\text{-H}_2\text{nip}$) and 1,10-phenanthroline (phen) in DMF solvent. They possessed high thermal stabilities and their liquid-phase formation enthalpy changes were determined in DMF solvent at 25.15 °C using an RD496-III type microcalorimeter, which were $\Delta_r H_m^\theta(\mathbf{1}) = -9.21 \text{ kJ mol}^{-1}$, and $\Delta_r H_m^\theta(\mathbf{2}) = -11.02 \text{ kJ mol}^{-1}$, respectively.

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Keywords: Praseodymium; Holmium; 5-Nitroisophatha acid; 1,10-Phenanthroline; Supermolecular polymers

Many interactions including coordination bonding, hydrogen bonding, aromatic π – π stacking interaction and van der Waals force construct a great deal of different coordination molecular architectures with different interesting structural features. Aromatic π – π stacking interaction plays a significant role in assembly of high-dimensional networks as a intermolecular force, as hydrogen bonding does [1]. It was reported that these interplanar distances were about 3.3–3.8 Å [2] with a calculated energy of about 2 kJ mol^{−1} [3] for a typical aromatic–aromatic π -stacking interaction. In the context of the metal compounds of mixed 2,2'-bipyridyl-like and carboxylate ligands, 2,2'-bipyridyl-like ligands such as bpy, phen, are able to engender the π – π stacking interactions which enhances the stability of the compounds both in solution and solid states [4]. In contrast to transition-metal compounds, most of the lanthanide coordination polymers are reported with high-dimension structures for

their high coordination number [5]. However, owing to large radii, high and variable coordination numbers, lanthanide coordination polymers have attracted considerable interest. In order to decrease the dimension of lanthanide coordination polymers, 5-nitroisophathic acid is selected as a rigid ligand with two kinds of function groups. In the self-assemble process, the carboxyl can provide the probability of the diversified coordinated modes, and the phenyl rigid skeleton can be a brace for the framework. Although several transitional metals compounds with 5-nitroisophthalic acid have been reported [6], its lanthanide compounds are rarely studied. Additionally, 1,10-phenanthroline as a heteroatoms cycle ligand is apt to form low-dimension coordination polymers, while the potential π -stacking interaction can enhance the stability of the polymers. Here we prepared two new mixed-ligand lanthanide coordination polymers from 5-nitroisophathic acid and 1,10-phenanthroline in DMF solvent. As we have predicted, they are one-dimension ribbons structures and further build two-dimension wavelike layers via strong offset face-to-face π – π stacking interactions.

* Corresponding author. Tel.: +86 29 88302604; fax: +86 29 88303798.
E-mail address: gaoshi@nwu.edu.cn (S. Gao).

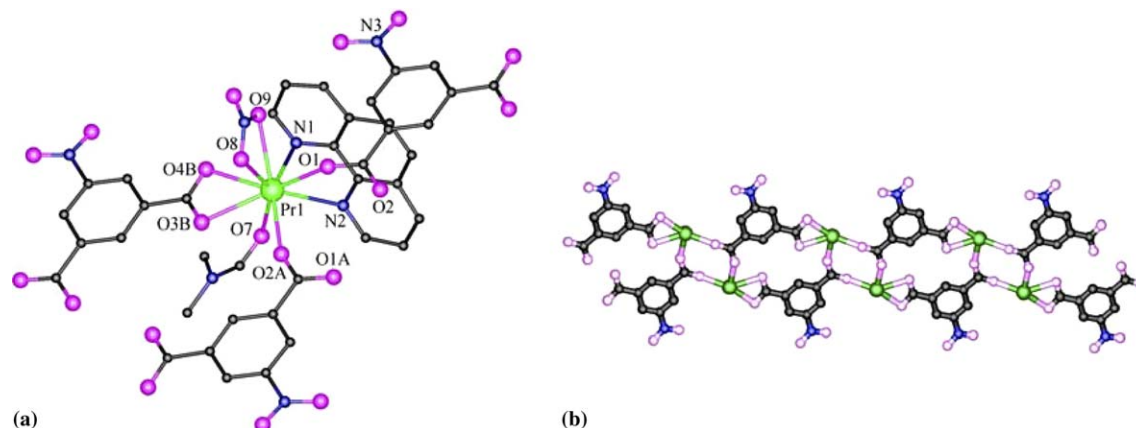
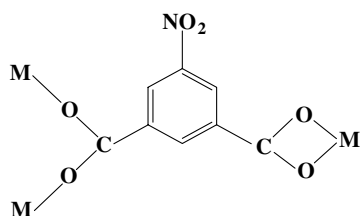


Fig. 1. The Pr(III) coordination environments in compound **1**(a) and the infinite chain in **1** made up of binuclear Pr(III) SBUs (b). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pr(1)–O(2) #1 2.392 (4), Pr(1)–O(1) 2.404 (3), Pr(1)–O(7) 2.469 (4), Pr(1)–O(4) #2 2.522 (4), Pr(1)–O(8) 2.570 (4), Pr(1)–O(3) #2 2.591 (3), Pr(1)–O(9) 2.628 (4), Pr(1)–N(1) 2.629 (4), Pr(1)–N(2) 2.679 (4). Symmetry code : #1 $-x + 1, -y + 1, -z + 2$, #2 $x + 1, y, z$.



Scheme 1. 5-nip²⁻ coordination mode in compounds.

Reaction of the ligands 5-H₂nip and phen with Pr(NO₃)₃ · 6 H₂O gave the one-dimensional ribbon-like coordination polymer **1**, [Pr(5-nip)(phen)(NO₃)(DMF)]_n [7,8], (82% yield based on praseodymium). X-ray single-crystal diffraction of **1** reveals that the Pr(III) ion is located at the center of a distinctly distorted three-capped triangular prism (Pr–O 2.391(4)–2.625 (4) Å; Pr–N 2.627 (5)–2.681 (4) Å), being coordinated by two oxygen atoms from two 1,3-bridged carboxyl groups of 5-nip ligands, two oxygen atoms from one chelating carboxyl groups of 5-nip ligand, two nitrogen atoms from a chelating phen molecule, two oxygen ones from one nitrate group and one oxygen atom from one DMF molecule (Fig. 1(a)). Herein, 5-nip ligand acts in only a chelate-bidentate coordination mode (Scheme 1). Each pair of Pr(III) ions is bridged by a pair

Table 1

Crystal data and structure refinement for compound **1** and compound **2**

| | 1 | 2 |
|---|--|--|
| Empirical formula | C ₂₃ H ₁₈ N ₅ O ₁₀ Pr | C ₂₃ H ₁₈ N ₅ O ₁₀ Ho |
| Formula weight | 665.33 | 689.35 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2(1)/n | P2(1)/n |
| <i>a</i> (Å) | 11.0876 (6) | 10.906 (3) |
| <i>b</i> (Å) | 12.8739 (7) | 12.804 (3) |
| <i>c</i> (Å) | 16.9994 (8) | 16.987 (4) |
| β (°) | 91.193 (4) | 91.400 (5) |
| <i>V</i> (Å ³) | 2426.0 (2) | 2371.4 (10) |
| <i>Z</i> | 4 | 4 |
| <i>F</i> (000) | 1320 | 1352 |
| <i>D</i> _{calc} (Mg/m ³) | 1.822 | 1.931 |
| μ (mm ⁻¹) | 2.077 | 3.407 |
| Reflections collected | 14735 | 14808 |
| Independent reflections | 4322 [<i>R</i> _{int} = 0.0806] | 5772 [<i>R</i> _{int} = 0.0982] |
| Data/restraints/parameters | 4322/0/354 | 5772/0/354 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0740 | <i>R</i> ₁ = 0.0616, <i>wR</i> ₂ = 0.1318 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0739, <i>wR</i> ₂ = 0.0810 | <i>R</i> ₁ = 0.1282, <i>wR</i> ₂ = 0.1574 |

of syn–syn 5-nip carboxylate groups into a dimeric subunit with an intradimer Pr ⋯ Pr distance of 5.669 (1) Å. The different adjacent dimers are doubly interlinked by the

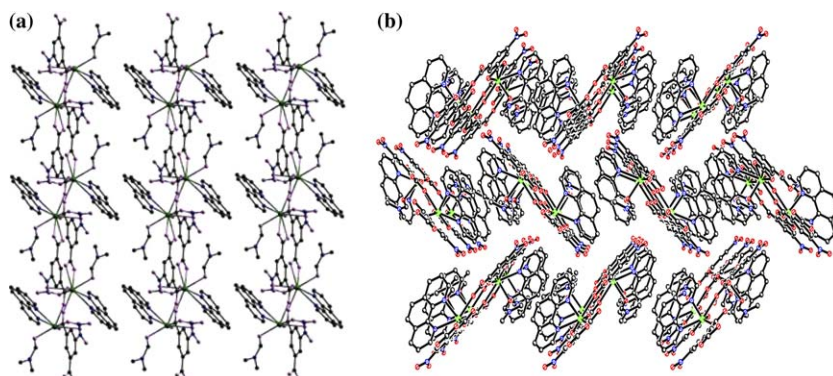


Fig. 2. Perspective views of (a) the two-dimensional networks parallel to the *ab* plane and (b) the three-dimensional ...ABAB... stacking fashion in compound **1**. The NO₃⁻ and hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angle (°) for compounds

| 1 | | 2 | |
|-----------------------|-------------|-----------------------|-------------|
| Pr(1)–O(2) #1 | 2.392 (4) | Ho(1)–O(5) | 2.283 (6) |
| Pr(1)–O(1) | 2.404 (3) | Ho(1)–O(4) #1 | 2.312 (5) |
| Pr(1)–O(7) | 2.469 (4) | Ho(1)–O(10) | 2.357 (6) |
| Pr(1)–O(4) #2 | 2.522 (4) | Ho(1)–O(7) #2 | 2.417 (6) |
| Pr(1)–O(8) | 2.570 (4) | Ho(1)–O(1) | 2.445 (7) |
| Pr(1)–O(3) #2 | 2.591 (3) | Ho(1)–N(2) | 2.521 (8) |
| Pr(1)–O(9) | 2.628 (4) | Ho(1)–O(6) #2 | 2.531 (5) |
| Pr(1)–N(1) | 2.629 (4) | Ho(1)–O(2) | 2.533 (7) |
| Pr(1)–N(2) | 2.679 (4) | Ho(1)–N(1) | 2.559 (7) |
| O(2) #1–Pr(1)–O(1) | 86.62 (12) | O(5)–Ho(1)–O(4) #1 | 84.9 (2) |
| O(2) #1–Pr(1)–O(7) | 79.62 (15) | O(5)–Ho(1)–O(10) | 81.1 (2) |
| O(1)–Pr(1)–O(7) | 137.72 (13) | O(4) #1–Ho(1)–O(10) | 138.5 (2) |
| O(2) #1–Pr(1)–O(4) #2 | 122.36 (12) | O(5)–Ho(1)–O(7) #2 | 123.34 (19) |
| O(1)–Pr(1)–O(4) #2 | 143.73 (12) | O(4) #1–Ho(1)–O(7) #2 | 142.7 (2) |
| O(7)–Pr(1)–O(4) #2 | 74.02 (14) | O(10)–Ho(1)–O(7) #2 | 75.0 (2) |
| O(2) #1–Pr(1)–O(8) | 91.88 (14) | O(5)–Ho(1)–O(1) | 90.2 (2) |
| O(1)–Pr(1)–O(8) | 73.71 (12) | O(4) #1–Ho(1)–O(1) | 74.0 (2) |
| O(7)–Pr(1)–O(8) | 145.76 (14) | O(10)–Ho(1)–O(1) | 144.3 (2) |
| O(4) #2–Pr(1)–O(8) | 83.24 (13) | O(7) #2–Ho(1)–O(1) | 81.4 (2) |
| O(2) #1–Pr(1)–O(3) #2 | 72.47 (12) | O(5)–Ho(1)–N(2) | 146.4 (2) |
| O(1)–Pr(1)–O(3) #2 | 139.86 (12) | O(4) #1–Ho(1)–N(2) | 91.0 (2) |
| O(7)–Pr(1)–O(3) #2 | 72.62 (13) | O(10)–Ho(1)–N(2) | 80.2 (2) |
| O(4)–Pr(1)–O(3) #2 | 51.09 (12) | O(7) #2–Ho(1)–N(2) | 77.8 (2) |
| O(8)–Pr(1)–O(3) #2 | 73.19 (13) | O(1)–Ho(1)–N(2) | 120.7 (2) |
| O(2) #1–Pr(1)–O(9) | 138.88 (14) | O(5)–Ho(1)–O(6) #2 | 71.87 (19) |
| O(1)–Pr(1)–O(9) | 71.71 (12) | O(4) #1–Ho(1)–O(6) #2 | 137.7 (2) |
| O(7)–Pr(1)–O(9) | 139.03 (14) | O(10)–Ho(1)–O(6) #2 | 73.0 (2) |
| O(4) #2–Pr(1)–O(9) | 72.02 (13) | O(7) #2–Ho(1)–O(6) #2 | 52.26 (19) |
| O(8)–Pr(1)–O(9) | 49.11 (14) | O(1)–Ho(1)–O(6) #2 | 71.4 (2) |
| O(3) #2–Pr(1)–O(9) | 102.04 (13) | N(2)–Ho(1)–O(6) #2 | 127.5 (2) |
| O(2) #1–Pr(1)–N(1) | 145.43 (14) | O(5)–Ho(1)–O(2) | 138.1 (2) |
| O(1)–Pr(1)–N(1) | 89.41 (13) | O(4) #1–Ho(1)–O(2) | 71.1 (2) |
| O(7)–Pr(1)–N(1) | 80.49 (14) | O(10)–Ho(1)–O(2) | 138.9 (2) |
| O(4) #2–Pr(1)–N(1) | 78.06 (13) | O(7) #2–Ho(1)–O(2) | 71.6 (2) |
| O(8)–Pr(1)–N(1) | 119.81 (14) | O(1)–Ho(1)–O(2) | 50.8 (2) |
| O(3) #2–Pr(1)–N(1) | 126.93 (13) | N(2)–Ho(1)–O(2) | 69.9 (2) |
| O(7)–Pr(1)–N(2) | 70.70 (13) | O(6) #2–Ho(1)–O(2) | 103.5 (2) |
| O(2) #1–Pr(1)–N(2) | 85.12 (13) | O(5)–Ho(1)–N(1) | 83.5 (2) |
| O(1)–Pr(1)–N(2) | 68.57 (13) | O(4) #1–Ho(1)–N(1) | 69.3 (2) |
| O(7)–Pr(1)–N(2) | 70.55 (13) | O(10)–Ho(1)–N(1) | 70.4 (2) |
| O(4) #2–Pr(1)–N(2) | 129.45 (14) | O(7) #2–Ho(1)–N(1) | 131.7 (2) |
| O(8)–Pr(1)–N(2) | 142.27 (13) | O(1)–Ho(1)–N(1) | 143.2 (2) |
| O(3) #2–Pr(1)–N(2) | 139.63 (13) | N(2)–Ho(1)–N(1) | 64.0 (2) |
| O(9)–Pr(1)–N(2) | 116.51 (14) | O(6) #2–Ho(1)–N(1) | 138.4 (2) |
| N(1)–Pr(1)–N(2) | 61.61 (14) | O(2)–Ho(1)–N(1) | 117.0 (2) |

Symmetry transformations used to generate equivalent atoms for compound **1**: #1 $-x+1, -y+1, -z+2$, #2 $x+1, y, z$; for compound **2**: #1 $-x+2, -y+1, -z+1$; #2 $-x+1, -y+1, -z+1$.

5-nip ligands to form an infinite ribbon (Fig. 1(b)). The phen ligands are extended in a parallel fashion on both sides of the 1D ribbon at a face to face distance of 7.504 Å to give a spatial arrangement that is suitable for aromatic intercalation. The nitrate radicals and DMF molecules are decorated between the gaps of phen ligands to occupy two coordinated sites of each Pr(III) ion and prevent a 2D network from forming via coordinated bonds. So the adjacent ribbons interact strongly through π – π stacking interaction between the lateral slanted phen ligands at a offset face-to-face distance of ca. 3.31 Å in offset fashion into 2D wavelike layers. The 2D layers are

arranged in an \cdots ABAB \cdots fashion along c axis into 3D framework (Fig. 2(a) and (b)) (see Tables 1 and 2).

Reaction of the ligands 5-H₂nip and phen with Ho(NO₃)₃·6H₂O gave compound **2**, [Ho(5-nip)(phen)(NO₃)(DMF)]_n [7,8], (78% yield based on holmium), which is isomorphous as compound **1**. The Ho ion is also in a nine-coordinated environment (Ho–O 2.283 (6)–2.533 (7) Å; Ho–N 2.521 (8)–2.559 (7) Å) (the Ho(III) ion coordination environment figure is omitted.) and in the ribbon the intradimer metals distance is 5.572 (1) Å. More interestingly, in the compound **2**, the centroid-plane distance of the packed phen ligands forming offset π – π stacking interaction is

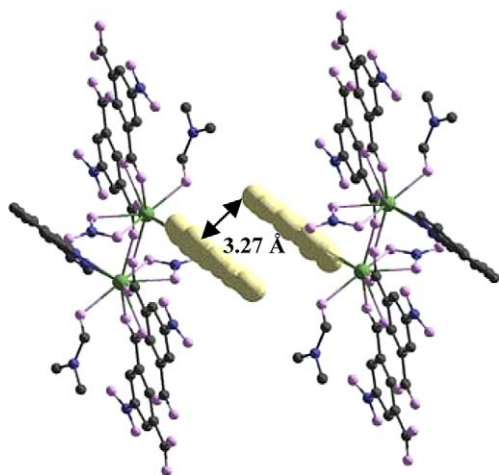


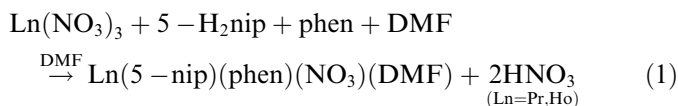
Fig. 3. The strong offset π - π stacking interaction with distance of ca. 3.27 Å existing in Complex **2**. The hydrogen atoms are omitted for clarity.

ca. 3.27 Å (Fig. 3). The π - π stacking interaction is stronger than that of **1** and embodied in the following thermal stabilities of the two coordination polymers. The existences of strong π - π stacking interaction between adjacent ribbons by the phen rings in these compounds are alike as that of some transitional metals compounds[9], such as a shorter distance of π - π stacking in [Cd(mpa)(phen)]_n (the distance is 3.32 Å; mpa = *m*-phthalate) [9a], and in other compounds [Cu(oba)(phen)] (the distance is 3.42 Å; H₂oba = 4,4'-oxybis(benzenecarboxylic acid)) [9b] [Co(oba)(phen)(H₂O)] (the distance is 3.48 Å) [9c]. The interaction in **2** is stronger than that in any other coordination polymers reported. Compared with **1**, the mean distances of Ho–O bonds and Ho–N bonds in **2** are a bit shorter than those of Pr–O bonds and Pr–N bonds in **1**, which could be attributed to the Lanthanide Contraction effect.

Thermal gravimetric analyses (TGA) for the two crystal samples were performed from 30 to 700 °C. For compound **1**, the weight loss of 11.18% at the first stage corresponds to the loss of the DMF molecule from 206 °C (ca. 11.13% for one DMF), which is consistent with the absence of the expected 1652 cm⁻¹ for the carbonyl of DMF molecule in IR spectrum of the middle produce at 320 °C. The further weight decrease from 320 °C to 418 °C suggests the stepwise decomposition of the compound and partly decomposition to Pr₂O₃. Finally, the compound is completely converted to Pr₂O₃ of 24.83% (ca. 25.16%) residua rate at 514 °C, and the metal content is analyzed using the EDTA titration with 84.96% (ca. 85.45%). Although the compound **2** is isomorphous as compound **1**, its thermal decomposition process is only divided into two stages. Its first stage from 35 °C includes the lost of DMF molecule and partly decomposition into a middle product, which of the process at 345 °C could be considered as a mixture. And it is proved by IR spectrum, in which the 1670 cm⁻¹ for DMF molecule also disappeared and all the other characterized peaks existed. The mixture is further decomposed to Ho₂O₃ up to 601 °C. Similarly, the metal content in

the final produce was identified by the EDTA titration with 87.06% (ca. 87.30%).

In order to further study the thermal stabilities of the two Lanthanide coordination polymers, we have measured their enthalpy changes of liquid-phase formation reaction in DMF solvent at 25.15 °C using an RD496-III type microcalorimeter [10]. The reaction equation for compounds is showed as:



The experiments were performed for the two compounds according to ref [11]. UV spectrum of the final reaction solutions is identical with that of solution of single crystal sample in DMF. The enthalpy changes of liquid-phase formation reaction for compound **1** is $\Delta_r H_m^\theta(1) = -9.21 \text{ kJ mol}^{-1}$, and $\Delta_r H_m^\theta(2) = -11.02 \text{ kJ mol}^{-1}$ for compound **2**.

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Appendix A. Supplementary data

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC: **1**, 288565; **2**, 288566). These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223336033; E-mail: deposit@ccdc.cam.ac.uk).

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, the IR spectrum are available from the authors on request.

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- [7] Complex **1**: a mixture of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4352 g) and 5- H_2nip (0.2113 g) in 10 ml DMF was stirring at room temperature, to which 5 ml DMF solution of 1,10-phen (0.1980 g) was added, and a clear green solution was obtained. After 6 months placed in air, some green block crystals suitable for single crystal X-ray structural diffraction were recovered in the DMF solution. Anal. Calcd. For $\text{C}_{23}\text{H}_{18}\text{N}_5\text{O}_{10}\text{Pr}$: C, 41.52, H, 2.73 and N, 10.53%. Found: C, 42.05, H, 2.56 and N, 10.33%. Complex **2**: the synthesis process of **2** is similar to that of **1**, with the usage of $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.4588 g), 5- H_2nip (0.2118 g) and 1,10-phen (0.1986 g). The yellow block crystals (78% yield based on holmium) were collected from the DMF solution. Anal. Calcd. For $\text{C}_{23}\text{H}_{18}\text{N}_5\text{O}_{10}\text{Ho}$: C, 40.07, H, 2.13 and N, 10.16%. Found: C, 40.38, H, 2.44 and N, 10.28%.
- [8] Crystal data for Complex **1**: $\text{C}_{23}\text{H}_{18}\text{N}_5\text{O}_{10}\text{Pr}$, $M_r = 665.33$, monoclinic, space group $\text{P}2_1/n$ with $a = 11.0876$ (6) Å, $b = 12.8739$ (7) Å, $c = 16.9994$ (8) Å, $\beta = 91.193(4)^\circ$, $V = 2426.0$ (2) Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.822$ Mg m⁻³, $T = 273(2)$ K, $\mu = 2.077$ mm⁻¹. $R_1 = 0.0382$, $wR_2 = 0.0740$ for 4322 observed reflections with $I > 2\sigma(I)$. Crystal data for Complex **2**: $\text{C}_{23}\text{H}_{18}\text{N}_5\text{O}_{10}\text{Ho}$, $M_r = 689.35$, monoclinic, space group $\text{P}2_1/n$ with $a = 10.906$ (3) Å, $b = 12.804$ (3) Å, $c = 16.987$ (4) Å, $\beta = 91.400$ (5)°, $V = 2371.4$ (10) Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.931$ Mg m⁻³, $T = 273(2)$ K, $\mu = 3.407$ mm⁻¹. $R_1 = 0.0616$, $wR_2 = 0.1318$ for 5772 observed reflections with $I > 2\sigma(I)$.
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