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Full Paper

Group Position-Dependent Structurally Diverse Coordination Compounds Based on Isomeric Ligands

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Two isomeric ligands Htzpya and Hpytza (Htzpya = 3-(5-tetrazolyl)pyridine-1-acetic acid, Hpytza = 5-(3-pyridyl) tetrazole-2-acetic acid) have been selected to react with $DyCl_3 \cdot 6H_2O$ or $PrCl_3 \cdot 6H_2O$ under hydrothermal conditions, resulting in the formation of four new coordination compounds, mononuclear $[Dy(tzpya)_2(H_2O)_5]Cl \cdot 4H_2O$ (**1**), dinuclear $[Pr_2(tzpya)_2(H_2O)_{12}]Cl_4 \cdot 2H_2O$ (**2**), and two one-dimensional polymers $[Dy(pytza)_2Cl(H_2O)_2]_n$ (**3**) and $[Pr(pytza)_2Cl(H_2O)_2]_n$ (**4**), whose structures are controlled by the different positions of the carboxylate group. These compounds were characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and single-crystal X-ray diffraction. Compounds **1**–**4** are self-assembled to form three-dimensional network structures by hydrogen bonding interactions. Furthermore, the luminescence properties were also investigated at room temperature in the solid state.

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Introduction

Metal-organic frameworks (MOFs) have attracted much attention for exploration over the past decades, owing to not only their diversity in structure, but also their tunable properties as potentially functional materials in the fields of luminescence,[1] ferroelectric,[2] absorption,[3] and heterogeneous catalysis.[4] Among various ligands, to the best of our knowledge, tetrazole-containing carboxylic acids are outstanding building blocks to construct novel coordination architectures including mono-, bi-, tri-, or multinuclear and one-, two-, or three-dimensional networks.[5] However, it is still a challenge to predict the final supramolecular architectures of the desired crystalline products because of many factors, for example, the coordination ability of the metal centre, the nature of the ligands, and the metal-to-ligand ratio that may have great impacts on the self-assembly process.[6] One of the key factors to obtaining the targeted molecules is via appropriate selection of the ligand; investigations on structurally diverse coordination compounds which are group position dependent have been limited. In this paper, two isomeric tetrazole-containing carboxylic acid ligands, Htzpya and Hpytza, where Htzpya = 3-(5-tetrazolyl)pyridine-1-acetic acid and Hpytza = 5-(3-pyridyl)tetrazole-2-acetic acid (Fig. 1) have been chosen to construct intriguing structures. The two ligands that comprise both nitrogen atoms from the pyridyl and tetrazolyl rings and oxygen atoms from the carboxylate group have high possibilities to display various coordination modes, and the abundant nitrogen and oxygen atoms may participate in hydrogen bonds to stabilize the supramolecular assemblies.[7] Furthermore, the position of the carboxylate group can influence the final structure, leading to unpredictable results and adding to the novelty of existing structures. By reacting Htzpya and Hpytza with $DyCl_3 \cdot 6H_2O$ or $PrCl_3 \cdot 6H_2O$ under hydrothermal conditions, four new coordination complexes, $[Dy(tzpya)_2(H_2O)_5]Cl \cdot 4H_2O$ (**1**), $[Pr_2(tzpya)_2(H_2O)_{12}]Cl_4 \cdot 2H_2O$ (**2**), $[Dy(pytza)_2Cl(H_2O)_2]_n$ (**3**), and $[Pr(pytza)_2Cl(H_2O)_2]_n$ (**4**) were obtained. Herein, we report their synthesis, crystal structure and luminescence properties along with the influence of the different positions of the carboxylate group.

Experimental

Materials and Instrumentations

General chemicals were commercially available reagents of analytical grade used without further purification. The elemental analyses for C, H, and N were performed on an EA1110-CHNS elemental analyzer. The infrared (IR) spectra were obtained on a NICOLET 380 spectrometer using KBr disks in the range of 4000–400 cm^{-1}. Photoluminescence analysis was performed on an F-4600 fluorescence spectrometer.

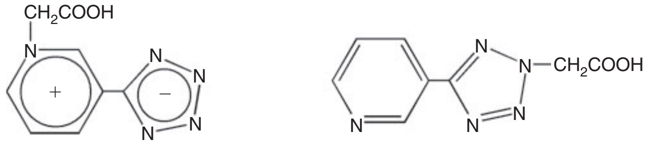
Htzpya Hpytza

Fig. 1. Schematic drawing for Htzpya and Hpytza.

Single-crystal X-ray diffraction was carried out on a Rigaku SCXmini-CCD diffractometer. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA 7 thermogravimetric analyzer; the samples were heated at a rate of 10°C min^{-1} from room temperature to 800°C under nitrogen atmosphere.

Synthesis and Characterization of Htzpya and Hpytza

5-(3-Pyridyl) tetrazole was prepared by [2+3] cycloaddition reactions by treating 3-cyanopyridine with NaN_3 in toluene in the presence of triethylammonium chloride.

At 70°C, the reaction of 5-(3-pyridyl) tetrazole with chloroacetic acid in methanolic potassium hydroxide solution gave mostly N(pyridine) products 3-(5-tetrazolyl)pyridine-1-acetato potassium salt The reaction of 5-(3-pyridyl) tetrazole with ethyl bromoacetate in methanolic potassium hydroxide solution gave mostly H(tetrazole)-substituted products 5-(3-pyridyl)tetrazole-2-acetato potassium salt.[8] Then, the pH of the solution was adjusted to 2 with HCl (12 M). After cooling to room temperature, the precipitate was filtered off, washed with methanol (2 × 30 mL) and dried, forming the corresponding acid products (Htzpya or Hpytza). Htzpya: a 80 % yield was obtained based on Hpytz consumed. ν_{max} (KBr)/cm^{-1} 3426 (s), 1730 (s), 1570 (s), 1420 (s), 1396 (m), 1257 (m), 1209 (m), 1146 (w), 1064 (m), 1018 (w), 905 (w), 868 (w), 766 (w). Anal. Calc. for $C_8H_7O_2N_5$: C 46.83, H 3.44, N 34.13. Found: C 46.70, H 3.50, N 34.25 %. Hpytza: a 82 % yield was obtained based on Hpytz consumed. ν_{max} (KBr)/cm^{-1} 3261 (s), 3102 (s), 1731 (w), 1544 (m), 1512 (w), 1486 (w), 1457 (m), 1289 (m), 1229 (m), 1176 (w), 1094 (w), 958 (w), 790 (w). Anal. Calc. for $C_8H_7O_2N_5$: C 46.83, H 3.44, N 34.13. Found: C 46.75, H 3.40, N 34.18 %.

*Synthesis of [Dy(tzpya)$_2$(H$_2$O)$_5$]Cl·4H$_2$O (**1**) and [Pr$_2$(tzpya)$_2$(H$_2$O)$_{12}$]Cl$_4$·2H$_2$O (**2**)*

Htzpya (0.0237 g, 0.1 mmol) was dissolved in 0.5 mL distilled water and the pH was adjusted to 5 with KOH, then a mixture of 3 mL ethanol and $LnCl_3 \cdot 6H_2O$ (0.0377 g, 0.1 mmol Ln = Dy (**1**); 0.0355 g, 0.1 mmol Ln = Pr(**2**)) were added. The resulting mixture was sealed in a 25 mL Teflon-lined stainless container and heated at 120°C for 48 h. Colourless block crystals of **1** and light yellow crystals of **2** were acquired. For **1**, a yield of 42 % based on Dy^{3+} consumed was obtained. ν_{max} (KBr)/cm^{-1} 3413 (s), 1740 (w), 1644 (s), 1610 (s), 1520 (w), 1478 (w), 1405 (m), 1308 (w), 1197 (w), 1141 (w), 1047 (w), 984 (w), 942 (w). Anal. Calc. for $C_{16}H_{30}N_{10}O_{13}Dy$: C 26.22, H 4.13, N 19.11. Found: C 26.15, H 4.20, N 19.10 %. For **2**, a yield of 50 % based on Pr^{3+} consumed was obtained. ν_{max} (KBr)/cm^{-1} 3389 (s), 1628 (s),1598 (s),1525 (m),1438 (s),1406 (s),1305 (m),1195 (m),1139 (w), 1022 (w), 930 (w), 829 (w), 730 (m), 700 (m), 621 (m). Anal. Calc. for $C_{16}H_{40}Cl_4N_{10}O_{18}Pr_2$: C 17.72, H 3.72, N 12.92. Found: C 17.69, H 3.75, N 12.96 %.

*Synthesis of [Dy(pytza)$_2$Cl(H$_2$O)$_2$]$_n$ (**3**) and [Pr(pytza)$_2$Cl (H$_2$O)$_2$]$_n$ (**4**)*

Similar methods were adopted to prepare **3** and **4** except that Htzpya was replaced by Hpytza. Colourless crystals of **3** and light yellow crystals of **4** were obtained. For **3**, a yield of 55 % based on Dy^{3+} consumed was obtained. ν_{max} (KBr)/cm^{-1} 3343 (m), 3059 (m), 2963 (w), 1629 (s), 1611 (m), 1576 (s), 1451 (s), 1419 (s), 1394 (w), 1377 (m), 1313 (m), 1196 (m), 1037 (m), 827 (m). Anal. Calc. for $C_{16}H_{16}ClN_{10}O_6Dy$: C 29.92, H 2.51, N 21.81. Found: C 30.02, H 2.60, N 21.67 %. For **4**, a yield of 53 % based on Pr^{3+} consumed was obtained. ν_{max} (KBr)/cm^{-1} 3351 (s), 3058 (w), 3007 (w), 1611 (s), 1567 (s), 1444 (s), 1419 (s), 1393 (m), 1378 (m), 1308 (m), 1197 (w), 1037 (m), 1004 (w), 827 (m). Anal. Calc. for $C_{16}H_{16}ClN_{10}O_6Pr$: C 30.96, H 2.60, N 22.57. Found: C 30.90, H 2.68, N 22.55 %.

X-Ray Crystallography

Suitable single crystals of complexes **1**–**4** were mounted on a Rigaku SCXmini-CCD diffractometer equipped with a graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 291–293 K. All absorption corrections were performed using the *Crystal-Clear* programs. The crystal structures of **1**–**4** were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms.[9] For **1**–**4**, important crystal data and collection and refinement parameters are summarized in Table 1, selected bond lengths and angles are given in Table 2, and hydrogen-bonding geometry are listed in Table 3.

Results and Discussions

*General Characterization of **1**–**4***

Compounds **1**–**4** are stable towards oxygen and moisture. The elemental analysis of **1**–**4** is consistent with their chemical formula. In the IR spectra of **1**–**4**, strong absorptions at 1644–1611 cm^{-1} corresponding to the ν(COO) vibration of the carboxylate group were observed.[10] IR spectra of the products showed typical peaks (1426–1601 cm^{-1}) corresponding to the tetrazole and pyridyl group. Peaks at 3351–3443 cm^{-1} are ascribed to the O-H vibration of water molecules. The identities of **1**–**4** are confirmed by X-ray crystallography.

*Crystal Structure of [Dy(tzpya)$_2$(H$_2$O)$_5$]Cl·4H$_2$O (**1**)*

Compound **1** crystallizes in monoclinic space group *C2/c*. As is shown in Fig. 2, each Dy^{III} centre is nine-coordinated by four carboxylate-O from two independent tzpya ligands (O1, O2, O1A, O2A) and five oxygen atoms from five water molecules (O3, O3A, O4, O4A, O5), forming a distorted mono-capped square anti-prism coordination arrangement. Each tzpya adopts a bidentate chelating mode to coordinate with the same Dy^{III} centre, thereby displaying a mononuclear structure. The structure of compound **1** is the same as that of previously reported Y^{III}-tzpya compound,[11] but is different from that of DyAg(oxalate)(2-pzc)$_2$·H$_2$O (2-pzc = pyrazine-2-carboxylate) because 2-pzc acts as a tridentate ligand via its two nitrogen atoms from the pyrazine ring and one carboxylate oxygen atom to form a three-dimensional (3D) network.[12] Internal hydrogen bonds exist to stabilize the molecular assembly. Neighbouring $[Dy(tzpya)_2(H_2O)_5]^+$ cations are further held together via the π–π stacking interactions between the pyridyl and tetrazole rings (3.848 and 4.182 Å) from neighbouring tzpya ligands to generate a two-dimensional (2D) layer. Adjacent layers are linked together via intermolecular hydrogen bonds to form a 3D supramolecular network (Fig. S1, Supplementary Material; Table 3).

*Crystal Structure of [Pr$_2$(tzpya)$_2$(H$_2$O)$_{12}$]Cl$_4$·2H$_2$O (**2**)*

The X-ray analysis reveals that compound **2** crystallizes in monoclinic space group *C2/c* and the asymmetric unit contains only half of $[Pr_2(tzpya)_2(H_2O)_{12}]Cl_4 \cdot 2H_2O$ molecule. As shown in Fig. 3, each Pr^{III} centre in a distorted square anti-prism centre is eight-coordinated by two carboxylate-O atoms from two tzpya ligands (O1, O1A for Pr^{III}1, O2, O2A for Pr^{III}2) and six oxygen atoms from six water molecules (O3, O3A, O4, O4A,

Table 1. Crystallographic data for 1–4

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{16}H_{30}ClN_{10}O_{13}Dy$	$C_{16}H_{40}N_{10}O_{18}Cl_4Pr_2$	$C_{16}H_{16}ClN_{10}O_6Dy$	$C_{16}H_{16}ClN_{10}O_6Pr$
Formula mass	768.45	1084.20	642.34	620.75
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a [Å]	29.083(6)	17.808(4)	23.408(5)	23.702(5)
b [Å]	12.641(3)	14.780(3)	11.131(2)	11.310(2)
c [Å]	7.9236(16)	16.051(3)	8.8964(18)	8.8580(18)
β [°]	100.21(3)	106.78(3)	108.10(3)	107.63(3)
V [Å^3]	2866.9(11)	4044.7(14)	2203.3(8)	2263.0(8)
Z	4	4	4	4
T [K]	291(2)	291(2)	291(2)	291(2)
D_c [g cm^{-3}]	1.780	1.780	1.936	1.822
μ [mm^{-1}]	2.776	2.720	3.570	2.327
Reflections collected	14619	16907	11178	11462
Unique reflections (R_{int})	3295(0.1335)	3555(0.0624)	2527(0.0399)	2590(0.0334)
No. of observations ($I > 2\sigma(I)$)	2382	2965	2418	2489
No. of variables	174	209	157	163
R^A/wR^B	0.0625/0.1082	0.0587/0.1231	0.0210/0.0522	0.0204/0.0469
GOF^C	1.045	1.175	1.027	1.085
Δ/ρ_{max} [e Å^{-3}]	1.491	1.702	0.846	0.564
Δ/ρ_{min} [e Å^{-3}]	−1.781	−0.779	−0.630	0.697

$^A R = \sum(||F_o| - |F_c||)/\sum|F_o|$.
$^B wR = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.
^{C}GOF $= [\sum w((F_o^2 - F_c^2)^2)/(n - P)]^{1/2}$, where n = number of reflections and P = total numbers of parameters refined.

O5, O5A for Pr^{III}1, O6, O6A, O7, O7A, O8, O8A for Pr^{III}2). Compared with **1**, each tzpya acts as a bidentate bridging ligand to connect two Pr^{III} centres via its two carboxylate-O atoms rather than the O,O′ chelating mode, thereby displaying a binuclear structure with Pr···Pr distance of 5.5119 Å. Compound **2** is isostructural to $[Nd_2(tzpya)_2(H_2O)_{12}]Cl_4{\cdot}2H_2O$.[13] However, compared with $[Pr_2(tza)_3(H_2O)_6]_n{\cdot}4nH_2O$ (tza=tetrazole-5-acetato) in which tza ligand acts as pentadentate via one nitrogen atom and the carboxylate group in a $\mu_{1,1,3,3}$-COO bridging mode, only the carboxylate oxygen atoms are coordinated to the Pr^{III} centre, nitrogen atoms being uncoordinated.[14] Therefore, compound **2** is a simple binuclear cluster rather than a 2D layer. Adjacent $[Pr_2(tzpya)_2(H_2O)_{12}]^{4+}$ cations are linked together through six kinds of hydrogen bonding interactions to generate a 2D layer structure. Neighbouring 2D layers are held together through six kinds of hydrogen bonding interactions to form a 3D supramolecular structure (Fig. S2, Supplementary Material; Table 3).

*Crystal Structure of $[Dy(pytza)_2Cl(H_2O)_2]_n$ (**3**)*

Compound **3** crystallizes in monoclinic space group *C*2/*c* and the asymmetric unit contains only half of $[Dy(pytza)_2Cl(H_2O)_2]$ molecule. As is shown in Fig. 4, each Dy^{III} centre is seven-coordinated by four carboxylate-O atoms from two independent pytza ligands (O1A, O1C, O2, O2B), two oxygen atoms from two water molecules (O3, O3A) and a chloride anion, forming a distorted pentagonal bipyrimid coordination geometry. Compared with compound **1**, when the carboxylate group transfers from the pyridyl ring to the tetrazolyl ring, each pytza acts as a bidentate ligand with a $\mu_{1,3}$-COO *syn–syn* bridging mode to coordinate to two Dy^{III} centres, displaying a one-dimensional (1D) polymeric chain structure extending along the *c*-axis with Dy···Dy distance of 4.6170 Å and Dy···Dy···Dy bite angle of 118.587° (Fig. 5). Compared with $[Dy_2(tza)_3(H_2O)_6]{\cdot}2H_2O$ (tza = tetrazole-5-acetic acetato) in which tza acts as both tridentate or tetradentate ligands via one nitrogen atom and the carboxylate group in a $\mu_{1,3}$-COO or $\mu_{1,3,3}$-COO bridging mode, compound **3** shows a wave-like chain, whereby only the carboxylate oxygen atoms are coordinated to the Dy^{III} centre.[15] Furthermore, neighbouring 1D chains are linked together by two kinds of hydrogen bonding interactions between the coordinated water and the chloride anion (O3–H3A···Cl1) and between the coordinated water and the nitrogen atom of the pyridyl ring (O3–H3B···N5), forming a 3D supramolecular network (Fig. S3, Supplementary Material; Table 3).

*Crystal Structure of $[Pr(pytza)_2Cl(H_2O)_2]_n$ (**4**)*

The X-ray analysis reveals that compound **4** crystallizes in monoclinic space group *C*2/*c*. As shown in Fig. 6, each Pr^{III} centre is nine-coordinated by six carboxylate-O atoms from two independent pytza ligands (O1, O2, O1B, O2A, O1C, O2C), two oxygen atoms from two water molecules (O3,O3A), and one chloride anion, displaying a distorted mono-capped square antiprism coordination geometry. Two neighbouring Pr^{III} centres are doubly bridged by two carboxylate groups from two pytza ligands forming a 1D polymeric chain structure extending along the *c*-axis with Pr···Pr distance of 4.5684 Å and Pr···Pr···Pr bite angle of 151.624° (Fig. 7). Although Htzpya and Hpytza are isomeric, the structure changes from dinuclear to a 1D polymeric chain. The Pr1–O2 distance of 2.993 Å can be considered as weak coordination bond, therefore pytza is coordinated in an asymmetric chelate and monoatomic bridging mode. Compared with $[Pr(atza)_2(CH_3OH)(H_2O)Cl]$ (atza=5-aminotetrazole-1-acetato) in which atza displays two coordination modes and show a 2D layer network, pytza ligand acts as a bridging ligand via its two carboxylate oxygen atoms, displaying a simple 1D zig-zag chain structure.[16] Furthermore, adjacent 1D chains are held together by three kinds of hydrogen bonding interactions between the coordinated water and the chloride anion

Table 2. Selected bond distances [Å] and angles [°] for 1–4

$[Dy(tzpya)_2(H_2O)_5]Cl\cdot 4H_2O$ (**1**)			
Dy1–O4A	2.372(2)	Dy1–O4	2.372(2)
Dy1–O5	2.379(2)	Dy1–O3	2.406(2)
Dy1–O3A	2.406(2)	Dy1–O2	2.420(2)
Dy1–O2A	2.420(2)	Dy1–O1	2.497(5)
Dy1–O1A	2.497(2)	xx	xx
O4–Dy1–O4A	79.57(3)	O4–Dy1–O5	140.23
O4A–Dy1–O5	140.2(11)	O4A–Dy1–O3	74.9
O4–Dy1–O3	139.28(10)	O4–Dy1–O3A	75.0
O5–Dy1–O3	71.10(6)	O3A–Dy1–O3	142.19(11)
O4–Dy1–O2	80.51(7)	O4A–Dy1–O2	126.54(7)
O5–Dy1–O2	73.78(7)	O3A–Dy1–O2	79.82(9)
O3–Dy1–O2	89.73(8)	O4–Dy1–O2A	126.54(7)
O5–Dy1–O2	73.78(7)	O3A–Dy1–O2	79.82(9)
O3–Dy1–O2	89.73(8)	O4–Dy1–O2A	126.54(7)
O4A–Dy1–O2A	80.51(7)	O5–Dy1–O2A	73.68(9)
O3A–Dy1–O2A	89.73(8)	O3–Dy1–O2A	79.82(9)
O2–Dy1–O2A	147.46(10)	O4–Dy1–O1A	126.07(13)
O4A–Dy1–O1A	72.90(12)	O5–Dy1–O1A	111.90(12)
O3A–Dy1–O1A	69.78(13)	O3–Dy1–O1A	126.00(13)
O2–Dy1–O1A	144.15(13)	O2A–Dy1–O1A	53.05(13)
O4–Dy1–O1	72.90(12)	O4A–Dy1–O1	73.72(12)
O5–Dy1–O1	111.9(12)	O3A–Dy1–O1A	126.00(12)
$[Pr_2(tzpya)_2(H_2O)_{12}]Cl_4\cdot 2H_2O$ (**2**)			
Pr1–O1	2.381(6)	Pr1–O7	2.441(2)
Pr1–O6	2.482(2)	Pr1–O8	2.507(2)
Pr2–O2	2.423(2)	Pr2–O3	2.459(2)
Pr2–O4	2.469(2)	Pr2–O5	2.504(2)
O1A–Pr1–O1	90.5(3)	O1A–Pr1–O7	149.67(18)
O1–Pr1–O7	99.19(17)	O7–Pr1–O7A	86.81(12)
O1–Pr1–O6A	71.88(18)	O7A–Pr1–O6A	137.96(10)
O1–Pr1–O6	80.12(19)	O7–Pr1–O6	137.96(10)
O7A–Pr1–O6	75.8	O6A–Pr1–O6	139.90(11)
O1A–Pr1–O8	139.45(18)	O1–Pr1–O8	75.56(17)
O7–Pr1–O8	70.86(6)	O7A–Pr1–O8	78.53(10)
O6A–Pr1–O8	128.2	O6–Pr1–O8	68.31(6)
O8–Pr1–O8A	137.48(11)	O5A–Pr2–O5	73.78(12)
O2–Pr2–O2A	96.73(12)	O2–Pr2–O3A	144.29(6)
O2–Pr2–O3	70.28(7)	O3A–Pr2–O3	138.15(11)
O2–Pr2–O4	84.12(7)	O2A–Pr2–O4	69.47(9)
O3A–Pr2–O4	119.0	O3–Pr2–O4	76.05(7)
O4–Pr2–O4A	140.13(11)	O2–Pr2–O5A	105.70(3)
O3–Pr2–O5A	72.84(9)	O4–Pr2–O5A	141.50(8)
O2–Pr2–O5	142.39(10)	O3–Pr2–O5	73.96(7)
O4–Pr2–O5	76.28(7)		
$[Dy(pytza)_2Cl(H_2O)_2]_n$ (**3**)			
Dy1–O3	2.3481(13)	Dy1–O3A	2.3481(13)
Dy1–O2B	2.355(2)	Dy1–O2C	2.355(2)
Dy1–O1A	2.3920(15)	Dy1–O1	2.3920(15)
O3–Dy1–O3A	70.03(7)	O3–Dy1–O2C	72.22(6)
O3A–Dy1–O2B	129.04(6)	O3–Dy1–O2C	129.04(6)
O3A–Dy1–O2C	72.22(6)	O2B–Dy1–O2C	157.15(11)
O3A–Dy1–O1A	75.16(6)	O3–Dy1–O1	97.28(5)
O3A–Dy1–O4	77.00(3)	O2B–Dy1–O1	75.16(6)
O2C–Dy1–O1	106.25(6)	O1A–Dy1–O1	173.12(6)
O3–Dy1–Cl1	144.98(3)	O3A–Dy1–Cl1	144.98(3)
O2B–Dy1–Cl1	78.57(5)	O2C–Dy1–Cl1	78.57(5)
O1A–Dy1–Cl1	93.44(5)	O1–Dy1–Cl1	93.44(5)
$[Pr(pytza)_2Cl(H_2O)_2]_n$ (**4**)			
Pr1–O3A	2.4543(15)	Pr1–O3	2.4543(15)
Pr1–O1	2.5159(17)	Pr1–O1A	2.5159(17)
Pr1–O2	2.5172(16)	Pr1–O2B	2.5172(16)
Pr1–Cl1	2.7766(2)	Pr1–O2A	2.8113(16)
O3A–Pr1–O3	67.22(7)	O3A–Pr1–O3	76.42(6)
O3–Pr1–O1	92.54(5)	O3A–Pr1–O1A	92.54(5)
O3–Pr1–O1A	76.42(6)	O1–Pr1–O1A	166.86(7)
O3A–Pr1–O2	128.73(19)	O3–Pr1–O2	73.77(5)
O1–Pr1–O2	73.37(6)	O1A–Pr1–O2	109.50(5)
O1A–Pr1–O2C	73.37(5)	O2–Pr1–O2C	156.01(8)
O3A–Pr1–Cl1	146.39(4)	O3–Pr1–Cl1	146.39(4)
O1–Pr1–Cl1	96.57(4)	O1A–Pr1–Cl1	96.57(4)
O2–Pr1–Cl1	78.00(4)	O2C–Pr1–Cl1	78.00(4)
O3–Pr1–O2	73.13(5)	O3–Pr1–O2	130.06(5)
O1–Pr1–O2	48.50(6)	O1A–Pr1–O2	135.33(5)
O2C–Pr1–O2	112.35(5)	O2C–Pr1–O2	62.06(5)
Cl1–Pr1–O2	77.75(3)	O3A–Pr1–O2A	130.06(5)
O3–Pr1–O2A	73.13(5)	O1–Pr1–O2A	135.33(5)
O1A–Pr1–O2A	48.50(5)	O2–Pr1–O2A	62.06(5)
O2C–Pr1–O2A	112.35(5)	Cl1–Pr1–O2A	77.75(3)
O2–Pr1–O2A	155.50(7)		

Symmetry codes.
For **1** – A: $-x, y, 0.5 - z$.
For **2** – A: $1 - x, y, 0.5 - z$.
For **3** – A: $x, 1 - y, -0.5 + z$; B: $1 - x, y, 1.5 - z$; C: $1 - x, 1 - y, 1 - z$.
For **4** – A: $1 - x, -y, 1 - z$; B: $1 - x, y, 0.5 - z$; C: $x, -y, 0.5 + z$.

Table 3. Hydrogen-bonding geometry for 1–4

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
$[Dy(tzpya)_2(H_2O)_5]Cl\cdot 4H_2O]$ (**1**)				
O3—H3B···N3#1	0.85	1.96	2.7735	160
O3—H3C···O6	0.85	2.15	2.8798	144
O4—H4A···N2#2	0.85	2.08	2.7767	139
O4—H4B···N3#2	0.85	2.43	3.2337	158
O4—H4B···Cl1#3	0.85	2.42	3.2206	158
O4—H4B···Cl1#4	0.85	2.31	3.1214	159
O5—H5B···O2#4	0.83	1.93	2.721(3)	160
O6—H6B···O7	0.85	2.05	2.8063	148
O6—H6C···O3#5	0.85	2.23	2.9913	150
O7—H7B···N5#6	0.85	2.12	2.9528	167
O7—H7C···N4#7	0.85	2.26	3.0426	153
C3—H3A···Cl1#4	0.93	2.75	3.606(9)	153
$[Pr_2(tzpya)_2(H_2O)_{12}]Cl_4\cdot 2H_2O$ (**2**)				
O3—H3B···Cl2#1	0.85	2.47	3.0840	130
O3—H3C···N1#2	0.85	1.88	2.7150	167
O3—H3C···N2#2	0.85	2.62	3.3037	138
O6—H5C···Cl3	0.85	2.24	3.0841	172
O6—H6B···Cl1#1	0.85	2.62	3.4626	170
O7—H7B···O9	0.85	2.01	2.8314	163
O6—H6C···Cl1#3	0.85	2.23	3.0540	165
O7—H7C···N3#4	0.85	2.11	2.7431	130
O8—H8A···N3#4	0.85	2.50	3.2821	153
O8—H8A···N4#4	0.85	1.91	2.7502	168
O8—H8B···Cl1#1	0.85	2.30	3.1448	170
O9—H9A···Cl3#5	0.85	2.29	3.036(16)	146
$[Dy(pytza)_2Cl(H_2O)_2]$ (**3**)				
O3—H3A···Cl1#1	0.85	2.42	3.182	143
O3—H3B···N5#2	0.86	1.92(4)	2.7185	154
$[Pr(pytza)_2Cl(H_2O)_2]$ (**4**)				
O3—H3A···Cl1#1	0.852(13)	2.243(13)	3.0948	177(18)
O3—H3B···N5#2	0.85(2)	1.90(2)	2.741(3)	173(2)
C8—H8···O1#3	0.93	2.59	3.376(3)	142

Symmetry codes.
For **1** – #1: $x, -y, -0.5 + z$; #2: $x, -1 + y, z$; #3: $-x, -y, 1 - z$; #4: $x, 1 - y, -0.5 + z$; #5: $1.5 - x, 1 - y, 1 - z$.
For **2** – #1: $x, 1 - y, 0.5 + z$; #2: $1.5 - x, 0.5 - y, 1 - z$; #3: $1 - x, y, 0.5 - z$; #4: $1.5 - x, 1.5 - y, 1 - z$, #5: $1 - x, 1 + y, 0.5 - z$.
For **3** – #1: $1 - x, 1 - y, -z$; #2: $0.5 + x, 0.5 + y, 0.5 + z$.
For **4** – #1: $1 - x, -y, -z$; #2: $0.5 + x, 0.5 - y, 0.5 + z$; #3: $0.5 - x, 0.5 - y, -z$.

(O3–H3A···Cl1), between the coordinated water and the nitrogen atom of the tetrazolyl ring (O3–H3B···N5, and between the C–H group of the pyridyl and the oxygen atom of the carboxylate group (C8–H8···O1), generating a 3D network (Fig. S4, Supplementary Material; Table 3).

Luminescence Properties

The luminescence properties of **1**–**4** and the free ligands were investigated at room temperature in the solid state. As is shown in Fig. 8, the free ligands Htzpya and Kpytza (Kpytza= 5-(3-pyridyl)tetrazole-2-acetato potassium salt) exhibit maximum emissions at 360 and 450 nm upon excitations at 315 and 347 nm, respectively. Compounds **1**–**4** exhibit photoluminescence with maximum intensities at 401, 392, 468, and 508 nm upon excitations at 270, 273, 373, and 371 nm, respectively. These fluorescence emissions could be tentatively assigned to the intraligand fluorescence emissions. The red shift in the maximum intensity may be ascribed to the coordination of the ligand to the metal centre. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the π and π* molecular orbitals of the free ligand, and is related to the extent of π conjugation. In contrast with **1**, a red shift of 67 nm of the peak emission in **3** is found, and is slightly smaller than the shift of the free ligands (90 nm). The difference in maximum intensity of compounds **2** and **4** is 106 nm, demonstrating that the group position difference really has an impact on the luminescence.

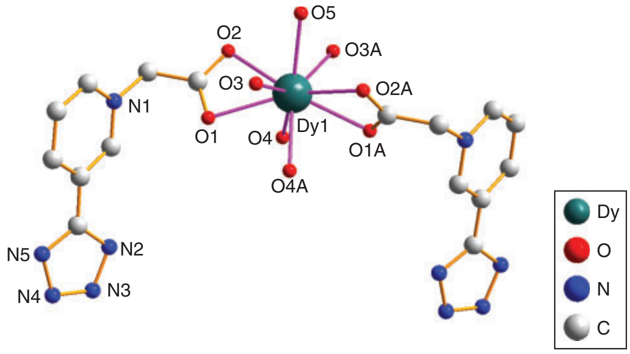

Fig. 2. Coordination environment of Dy^{III} in compound **1**. Hydrogen atoms are omitted for clarity.

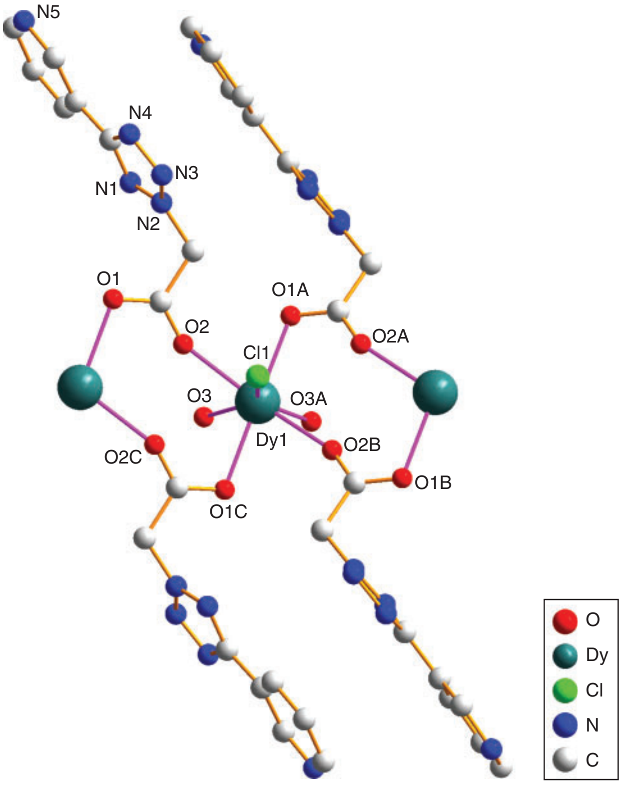

Fig. 4. Coordination environment of Dy^{III} in compound **3**. Hydrogen atoms are omitted for clarity.

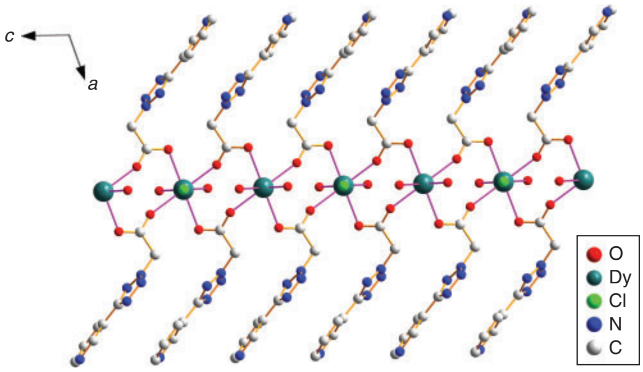

Fig. 5. 1D Chain structure of **3** extending along the *c*-axis.

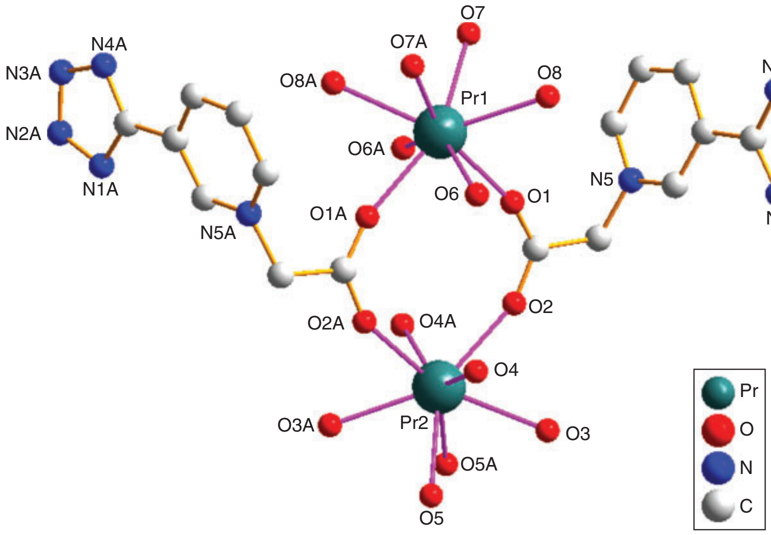

Fig. 3. Coordination mode of Pr^{III} in compound **2**. Hydrogen atoms are omitted for clarity.

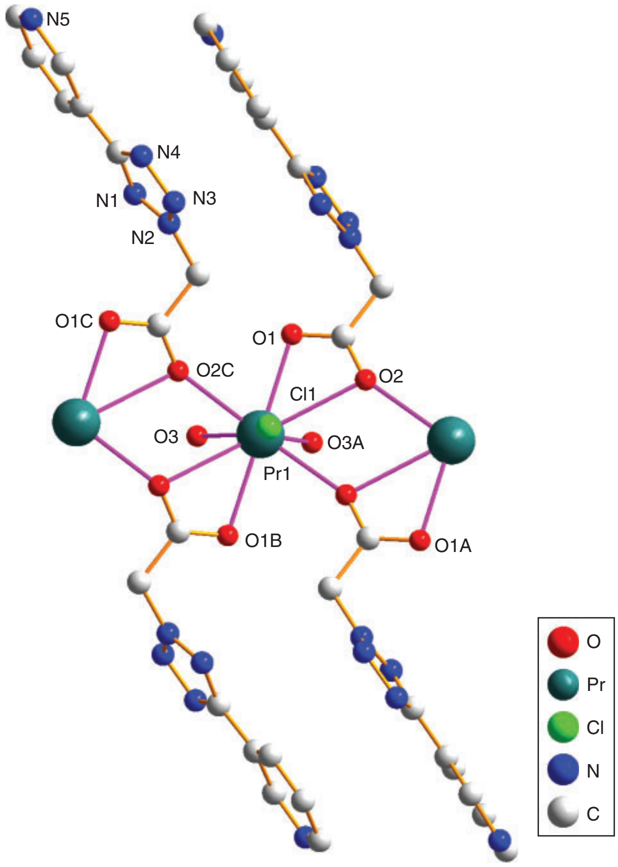

Fig. 6. Coordination mode of Pr^{III} in compound **4**. Hydrogen atoms are omitted for clarity.

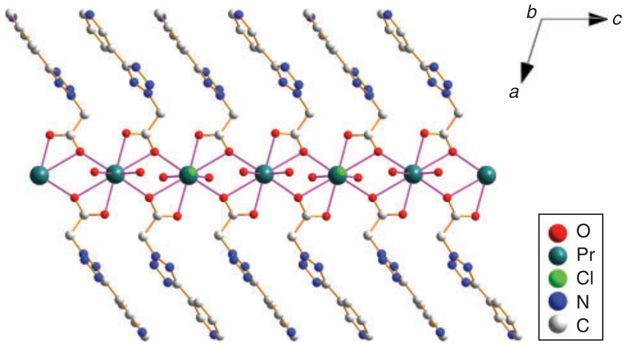

Fig. 7. 1D Chain structure of **4** extending along the *c*-axis.

TGA

In terms of thermal stability, TGA of **1–4** was carried out in the temperature range of 30–800°C under nitrogen atmosphere (Fig. 9). The TG curves show initial weight losses of 20.47 % from 30 to 219°C for **1**, 27.22 % from 30 to 257°C for **2**, 5.60 % from 195 to 259°C for **3**, and 5.65 % from 191 to 233°C for **4** that can be ascribed to the loss of uncoordinated and coordinated water molecules for compounds **1** and **2** (calculated as 20.18 % for **1** and 27.27 % for **2**) and the loss of coordinated water molecules for compounds **3** and **4** (calculated as 5.52 % for **3** and 5.71 % for **4**). Further weight losses beginning at 219°C for **1**, 257°C for **2**, 259°C for **3**, and 233°C for **4** are probably caused by the decomposition of the tzpya ligands for **1** and **2** and the decomposition of pytza ligands for **3** and **4**, leading to the collapse of the framework.

Conclusions

To the best of our knowledge, we are the first to report Dy^{III} and Pr^{III} coordination compounds with Htzpya and Hpytza. Four new coordination compounds were successfully constructed. The different positions of the carboxylate group control the coordination modes of the ligands and further determine the structure of the compounds. The luminescence properties show the intraligand emissions. Our research results indicate that the difference of the carboxylate group really has an impact on the structure of the complexes and further endeavours for exploration of other isomeric ligands are underway in our work group.

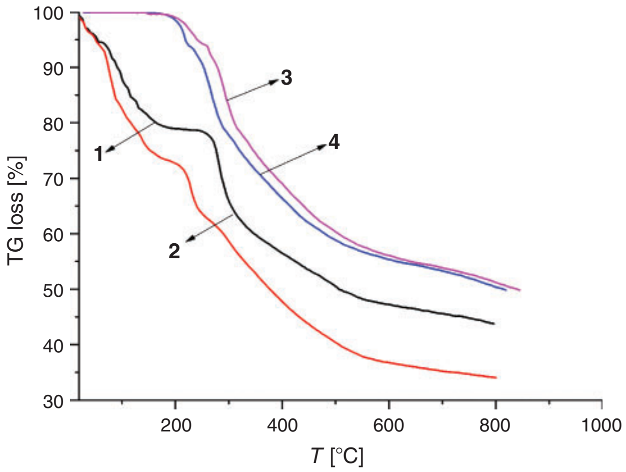

Fig. 9. TG curves of compounds **1**–**4**.

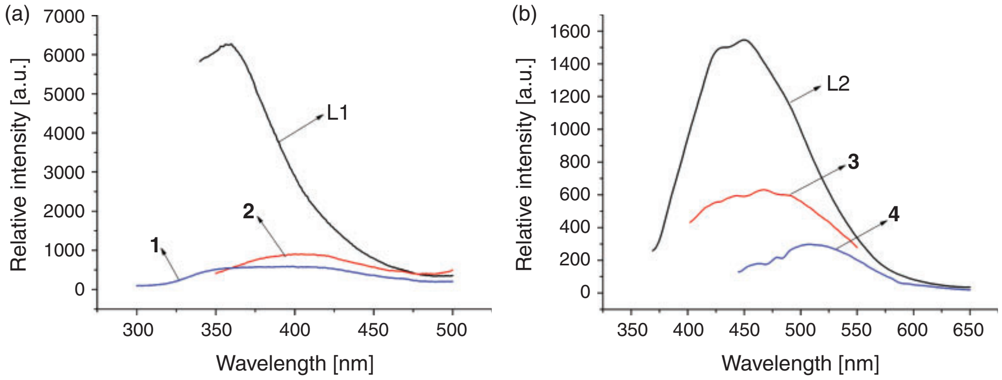

Fig. 8. (a) Emission spectra of **1**, **2**, and ligand **1** (L1) at room temperature in the solid state. (b) Emission spectra of **3**, **4**, and ligand **2** (L2) at room temperature in the solid state.

Supplementary Material

The stacking pictures of compounds **1**–**4** are available on the Journal's website.

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