FULL PAPER

Hydrothermal Syntheses, Structures, and Properties of First Examples of Lanthanide(III) 2,3-Pyrazinedicarboxylates with Three-Dimensional Framework

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Lanthanide 2,3-pyrazinedicarboxylate complexes with three-dimensional frameworks, $[Ln_2(pzdc)_3(H_2O)]_x \cdot 2xH_2O$ [Ln = Pr (**2**), Nd (**3**), and Eu (**4**)], were obtained by hydrothermal reactions of 2,3-pyrazinedicarboxylic acid (H_2pzdc) and the lanthanide(III) chlorides, while $[La_2(pzdc)_3(H_2O)]_x \cdot 2xH_2O$ (**1**) was obtained by hydro(solvo)thermal reaction of $LaCl_3 \cdot 7H_2O$ and 2,3-pyrazinedicarboxylic acid. They are isomorphous and exhibit complicated 3-D structures based on $[Ln_2(pzdc)_3(H_2O)]$ building blocks. In the asymmetric unit, the two Ln^{3+} ions are both nine-coordinate, but with different coordination environments. The ligand pzdc coordinates to the central Ln^{3+} ions in a tetradentate, hexadentate, or

heptadentate manner. Utilizing the characteristic of Eu^{3+} ion to act as a conformational probe, we determined the high-resolution spectra of **4**, which show that there are two Eu^{3+} ion sites in the coordination polymer. This is also in agreement with the results of the X-ray single-crystal diffraction study. It was concluded that there are two La^{3+}, two Pr^{3+} and two Nd^{3+} ion sites in polymers **1**, **2**, and **3**, respectively. The thermogravimetric analyses of these complexes show that all coordinated and uncoordinated water molecules were lost at the first weight loss above 240 °C.

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Introduction

The field of coordination polymers has undergone an explosive growth since numerous one-, two-, and three-dimensional structures have been obtained.[1−8] Much attention in this area has been focussed on coordination polymers with multifunctional ligands as the presence of different functional groups allows for the incorporation of interesting properties into the resulting coordination networks. Such polymeric structures are generally neutral, which simplifies the ability to control their structures and increases the chances of obtaining porous solids.[6] 2,3-Pyrazinedicarboxylic acid is a commonly used multifunctional ligand. Its complexes with d-block transition metals have been synthesized and their structures have been obtained.[9−16] However, the lanthanide complexes of this ligand are relatively unexplored. Up to now, no structural characterization of the lanthanide complexes of 2,3-pyrazinedicarboxylic acid has been reported. In light of the fact that lanthanide and d-block transition metal ions differ in their coordination number, pzdc may coordinate with them in a different man-

ner, resulting in a characteristic structure. As these complexes have potential applications as new materials, we synthesized the lanthanide coordination polymers of pzdc by hydrothermal and hydro(solvo)thermal syntheses. Here, we report on their crystal structures and their properties.

Results and Discussion

Crystal Structures

The three coordination polymers are isomorphous. Only the structure of **4** will be described in detail. The asymmetric unit of **4** consists of two europium(III) ions, three 2,3-pyrazinedicarboxylate groups, one coordinated water and two lattice water molecules (Figure 1). There are three coordination modes for the three bridging 2,3-pyrazinedicarboxylate groups, as shown in Scheme 1. The three pyrazine rings are oriented differently in the crystal. The dihedral angles between the pyrazine rings are 70.8, 76.3, and 14.4°, owing to the steric effects in the formation of lanthanide coordination polymers. Although Eu1 and Eu2 are both nine-coordinate, the coordination environments around them are different. A hexadentate and a tetradentate pzdc ligand coordinate to Eu1 in a bidentate chelating mode through a nitrogen atom N(2A) of the pyrazinyl group and an oxygen atom O(4A) of an adjacent carboxylate group, and through N(3) and O(5).

In addition, Eu1 is coordinated to two oxygen atoms [O(1), O(2)] from a μ_2,η^3-carboxylate group of a hexadent-

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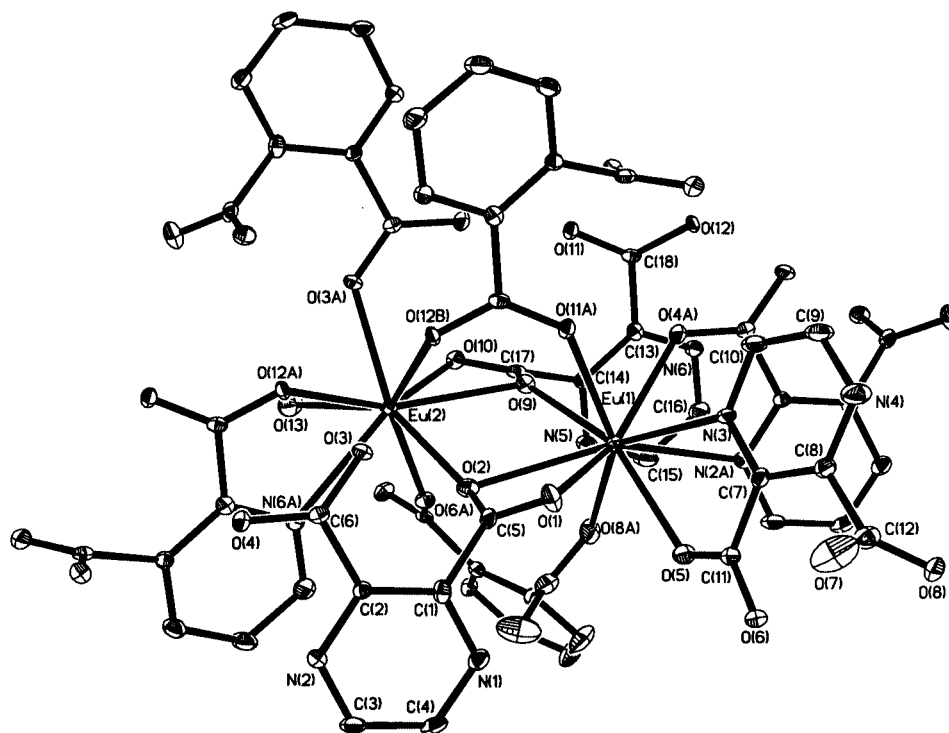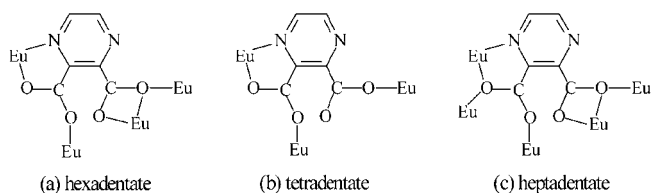Changchun 130021, P. R. China

Figure 1. Coordination environment of complex **4**; the asymmetric unit and the related coordination atoms are labeled; lattice water molecules and all hydrogen atoms are omitted for clarity; thermal ellipsoids are shown at the 30% probability level

Scheme 1. The coordination modes of the pzdc ligand in complex **4**

ate pzdc ligand, one oxygen atom [O(8A)] from the carboxylate group of a tetradentate ligand, one oxygen atom [O(11A)] from the μ_2,η^2-carboxylate group of a heptadentate pzdc ligand and one oxygen atom [O(9)] from the μ_2,η^3-carboxylate group of another heptadentate pzdc ligand. Compared with Eu1, there is only one heptadentate pzdc ligand that is coordinated to Eu2 through one nitrogen atom [N(6A)] of pyrazinyl group and one carboxylate oxygen atom [O(12A)]. Eu2 is also coordinated to two oxygen atoms [O(9), O(10)] of a carboxylate group from a heptadentate pzdc ligand, four oxygen atoms [O(2), O(3A), O(6A), O(12B)] from the carboxylate groups of two hexadentate, one tetradentate, and another heptadentate pzdc ligands. An oxygen atom [O(13)] from a water molecule coordinates to Eu2 to complete the coordination number of nine. Altogether, there are six pzdc ligands bound to every Eu^{3+} ion. Eu1 is coordinated to two tetradentate, two hexadentate, and two heptadentate pzdc ligands, while Eu2 is coordinated to two hexadentate, one tetradentate, and three heptadentate pzdc ligands, as well as a water molecule. However, their modes of coordination differ, as mentioned above.

The framework structure of **4** is constructed from an Eu$_2$(pzdc)$_3$H$_2$O unit. Firstly, two hexadentate and two heptadentate pzdc ligands link two dieuropium building units to form a parallelogram, the four vertices of which are occupied by four Eu^{3+} ions (Figure 2). The two heptadentate pzdc ligands are located above and below the plane of the parallelogram and link the four Eu^{3+} ions, resulting in a "cage-like" motif. The distances between Eu1 and Eu2, and Eu1 and Eu2B are 4.08 Å and 6.04 Å, respectively, and that between Eu2 and Eu2B is 4.22 Å. Four tetradentate pzdc ligands then link every parallelogram with four adja-
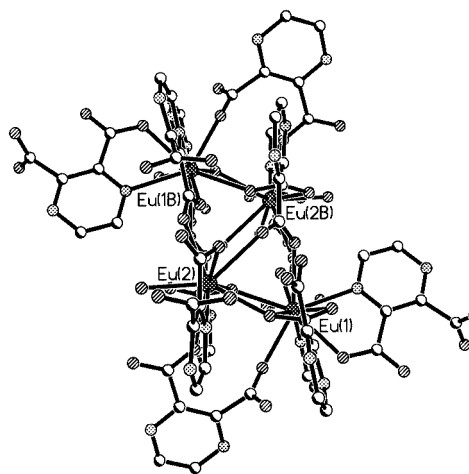

Figure 2. Perspective view of the parallelogram motif along the *a* axis formed by linking two dieuropium building blocks of **4** through tetradentate and hexadentate pzdc ligands

cent parallelograms which are orientated in a different manner. The parallelograms extend infinitely on the plane (100). Simultaneously, along the *a* axis, the parallelograms are linked by the hexadentate and heptadentate pzdc ligands forming a pillar of parallelograms, as shown in Figure 3. Thus, a complicated three-dimensional architecture is built with many cavities along the *a* axis.
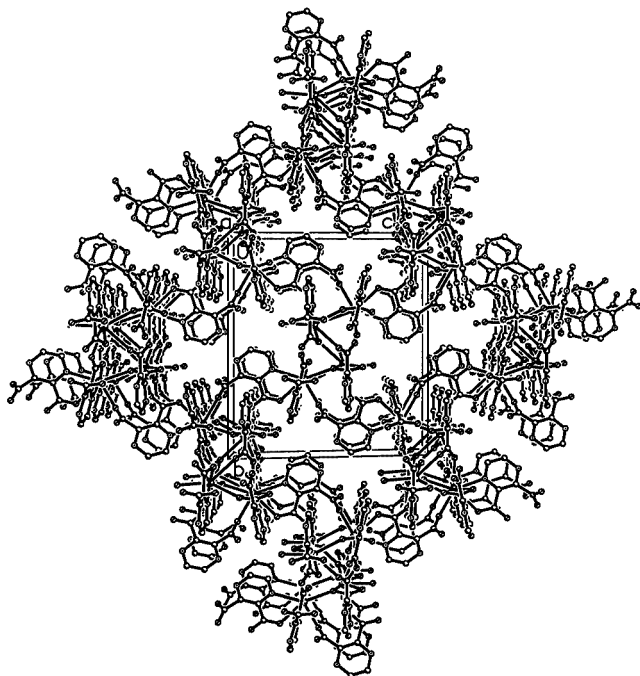

Figure 3. 3-D framework of **4** viewed along the *a* axis; all hydrogen atoms and uncoordinated water molecules are omitted for clarity

Although we have not determined the crystal structure of **3**, we can conclude that **3** has the same 3-D structure as complexes **1**, **2**, and **4** since they have the same components based on elemental analyses; furthermore, complexes **1**, **2**, and **4** are isomorphous and Nd is situated between La, Pr, and Eu in the lanthanide series. The pzdc ligands in **1**, **2**, and **3** have the same bridging modes, as shown in Scheme 1. In the reported binary d-block transition metal complexes with pzdc, there are four bridging modes for pzdc, as shown in Scheme 2. In $[M(pzdc)(H_2O)_2]_x \cdot 2xH_2O$ (M = Co, Ni, Cu),[16] $[Co(pzdc)(H_2O)_2]_x$[17] and $[Cu(pzdc) \cdot HCl]_x$,[13] the pzdc ligands bridge the metal ions through 1,4-diazine links that are supported by forming chelates to both metal ions, as depicted in Scheme 2 (a).

In $[M(pzdc)(H_2O)_2]_x \cdot 2xH_2O$ (M = Fe,[9] M = Mn[15]) and $[Zn(pzdc) \cdot 3H_2O]_x$,[18] the pzdc ligands chelate to a metal ion in one chain and bridge two metal ions in the second chain by O−C−O links of a second carboxylate group of the same pzdc ligand, as shown in Scheme 2 (b). While in $[M(pzdc)(H_2O)_3]_x \cdot xH_2O$ (M = Zn,[19] M = Cd[15]), the pzdc ligand links one metal ion forming a chelate and bridges another metal ion with a second carboxylate group in a monodentate fashion, as depicted in Scheme 2 (c). In $[NH_4]_x[Ag(pzdc)]_x$,[14] besides one Ag+ ion coordinated by
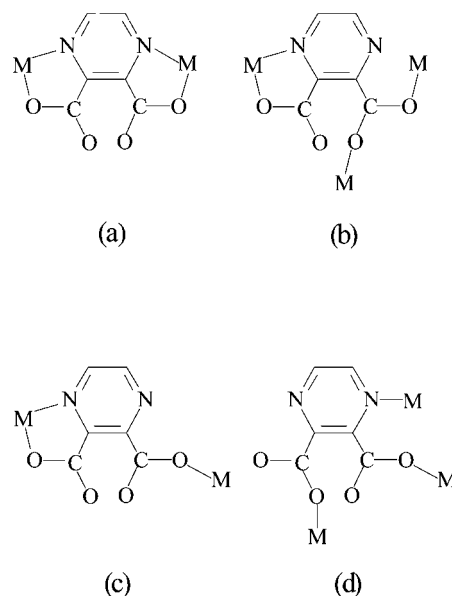
Scheme 2. Coordination modes of the pzdc ligand in the reported binary d-block transition metal complexes

one nitrogen atom of 1,4-diazine, two carboxylate groups of pzdc coordinate to one Ag+ ion in a monodentate fashion, as seen in Scheme 2 (d). Generally speaking, in the above reported d-block transition metal complexes, the pzdc ligand adopts only one bridging mode in every complex. While in the title complexes, pzdc adopts three bridging modes in every complex, and its bridging mode is much more complicated than those in the d-block transition metal complexes (see Scheme 1). This can be attributed to the larger radii and greater positive charge of the LnIII ions, and hence the large coordination number and different coordination modes required by the lanthanide ions.

In addition, two types of hydrogen bonds exist in the crystal. A hydrogen bond forms between the lattice water molecules, and another between the coordinated water molecule and the lattice water molecule. These hydrogen bonds stabilize the crystal.

Photophysical Properties of $[Eu_2(pzdc)_3(H_2O)_x] \cdot 2xH_2O$

Figure 4 illustrates the high-resolution emission spectrum of **4** excited at 355 nm at 77 K, corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0−4) transitions. From Figure 4 it can be seen that the intensity ratio of $^5D_0 \rightarrow {}^7F_2 / {}^5D_0 \rightarrow {}^7F_1$ is 3.2, which indicates that the EuIII ions are not in an inversion center. The number of components of the $^5D_0 \rightarrow {}^7F_1$ transition indicates the presence of more than one chemically different EuIII ion sites. The intensity of the $^5D_0 \rightarrow {}^7F_0$ transition is relatively weak and the emission band is not symmetrical. The non-homogeneous broadening of the $^5D_0 \rightarrow {}^7F_0$ emission band arises from the site to site variation in the local field acting on the ions, and has consequently been studied by selective excitation techniques.

Among the transitions from the lowest emission state $^5D_0$ to the ground state ^7F_J (J = 0−6), the $^5D_0 \rightarrow {}^7F_2$ transition
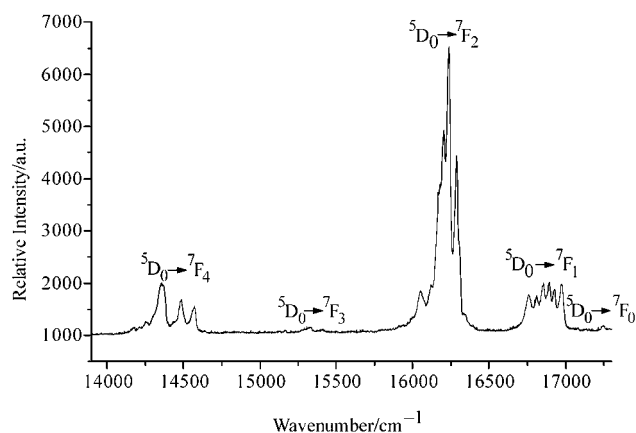
Figure 4. Emission spectrum of **4** corresponding to the $^5D_0\rightarrow{}^7F_J$ ($J = 0-4$) transitions at 77 K, $\lambda_{exc} = 355$ nm

Figure 5. Time-resolved spectra of **4** at 77 K in the range of $16500-15900\,\mathrm{cm}^{-1}$; delay times: 5, 50, 500 µs; $\lambda_{exc} = 355$ nm

is the electronic dipole transition which is hypersensitive, and is greatly affected by the coordination environment. On the other hand, the $^5D_0\rightarrow{}^7F_1$ transition is the magnetic dipole transition and is much less sensitive to the coordination environment. Therefore, the time-resolved spectra of complex **4** in the range of $16500-15900$ cm^{-1} (corresponding to $^5D_0\rightarrow{}^7F_2$ transition) were recorded and are shown in Figure 5. From Figure 5 it can be seen that the relative intensity of the emission peaks change. With a time delay, the peaks marked with "a" decay sharply relative to those marked with "b", which indicates that they arise from the Eu^{III} ion sites with different life-times. However, the less-developed bands show that it is difficult to obtain the exact life-time of each Eu^{III} ion site because they have slightly different chemical environments. Therefore, they may be simultaneously excited, or there may be an energy transfer between the Eu^{III} ion sites when excited, resulting in averaged life-times.

The excitation spectra of **4** (Figure 6) were recorded at 77 K, the analyzing wavenumbers were 16178, 16195, 16216, and 16304cm^{-1}. There are two main peaks located at 579.52 nm and 579.75 nm in every spectrum, which indicates that there are two Eu^{III} ion sites in the complex. This is in agreement with the results of the X-ray single-crystal diffraction study. It is worth noting that the excitation peaks are not narrow enough, and this is possibly a result of the slightly different chemical environments of the Eu^{III} ions in coordination polymers.

Thermogravimetric Analyses

Thermogravimetric analyses of the four complexes were carried out to examine their thermal stabilities. The data of the thermogravimetric analyses for **1**–**4** are listed in Table 1. All four complexes undergo loss of their coordinated and uncoordinated water molecules at the first weight loss.

Their dehydration temperatures range from 240 to 310 °C. They began to decompose beyond 430 °C. Looking at **1** as an example, the TGA curve shows that the first weight
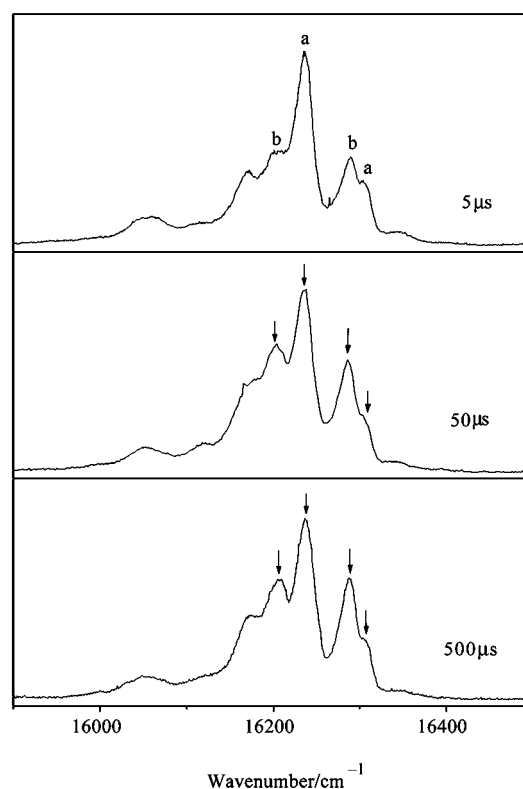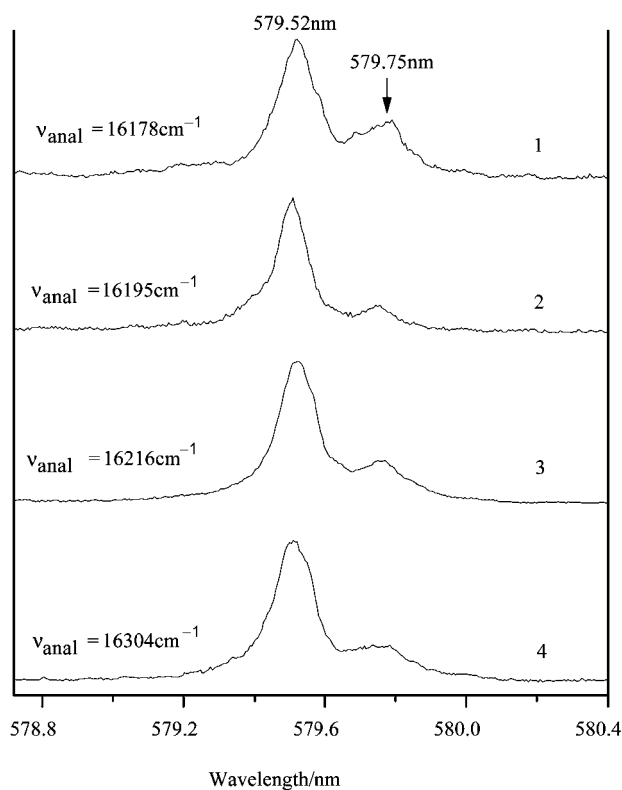

Figure 6. Excitation spectra of **4** at 77 K; analyzing wavenumber: 16178 cm^{-1} (1), 16195 cm^{-1} (2), 16216 cm^{-1} (3), and 16304 cm^{-1} (4)

Table 1. Thermogravimetric analyses of **1−4**

	1	**2**	**3**	**4**
Dehydration temperature [°C]	242.3−277.2	259.5−294.7	263.7−293.1	276.2−309.7
Loss of water:				
Calculated [%]	6.5	6.5	6.4	6.3
Found [%]	6.2	6.4	6.2	5.8
Further decomposition temperature [°C]	443	429.7	432.2	421.2

loss of 6.2%, which occurs between 242.3 and 277.2 °C corresponds to the loss of two uncoordinated water molecules and one coordinated water molecule (calculated: 6.5%). Further decomposition of **1** occurs above 443 °C (see Table 1).

Conclusion

Complexes **1−4** exhibit the same 3-D structures because they are isomorphous. The pzdc ligands in the complexes all adopt tetradentate, hexadentate and heptadentate bridging modes. By utilizing the characteristic of Eu^{3+} to act as a conformational probe, two Eu^{3+} ion sites have been observed in the coordination polymer **4**. In the coordination polymers, the La^{3+}, Pr^{3+}, and Nd^{3+} ions may have similar coordination environments to that of Eu^{3+}. Therefore, a conclusion could be reached that in polymers **1**, **2**, and **3**, there are two La^{3+} ion sites, two Pr^{3+} ion sites, and two Nd^{3+} ion sites, respectively. The four complexes are relatively stable. They all lose their coordinated and lattice water molecules at the first weight loss, above 240 °C.

Experimental Section

General: $LaCl_3 \cdot 7H_2O$, $NdCl_3 \cdot 6H_2O$, and $EuCl_3 \cdot 6H_2O$ were prepared by dissolving their oxides in concentrated hydrochloric acid and the solvents were evaporated to dryness. The stock solution of $PrCl_3$ was prepared by dissolving Pr_6O_{11} in concentrated hydrochloric acid and diluted to 0.49 mol/L. All the other reagents were commercially available and used without further purification. Elemental analyses were performed with an Elementar Vario EL analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique. Thermogravimetric analyses were performed with a ZRY-2P Thermal Analyzer.

[La₂(pzdc)₃(H₂O)]ₓ·2xH₂O (1): A solution of $LaCl_3 \cdot 7H_2O$ (0.111 g, 0.3 mmol), 2,3-pyrazinedicarboxylic acid (0.077 g, 0.45 mmol), H_2O (6.0 mL), ethanol (1 mL), and aqueous NaOH (1.6 mL, 1.04 mmol) was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 190 °C for 96 h. Colorless crystals of **1** were obtained in a 72.3% yield (0.09 g). $C_{18}H_{12}La_2N_6O_{15}$ (830.16): calcd. C 26.04, H 1.46, N 10.12; found C 25.64, H 1.08, N 9.73. IR data (KBr pellet, $\tilde{\nu}$ [cm^{-1}]): 3501 m, 1618 s, 1558 s, 1448 s, 1366 s, 1119 s, 895 m, 837 m, 443 m.

[Pr₂(pzdc)₃(H₂O)]ₓ·2xH₂O (2): An aqueous solution of $PrCl_3$ (0.61 mL, 0.3 mmol), 2,3-pyrazinedicarboxylic acid (0.077 g, 0.45 mmol), H_2O (6.5 mL), and aqueous NaOH (1.6 mL, 1.04 mmol) was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 190 °C for 62 h. Green crystals of **2** were obtained in a 79.9% yield (0.1 g). $C_{18}H_{12}Pr_2N_6O_{15}$ (834.16): calcd. C 25.92, H 1.45, N 10.07; found C 25.79, H 1.02, N 9.84. IR data (KBr pellet, $\tilde{\nu}$ [cm^{-1}]): 3492 m, 1619 s, 1558 s, 1447 s, 1366 s, 1120 s, 891 m, 843 m, 837 m, 444 m.

[Nd₂(pzdc)₃(H₂O)]ₓ·2xH₂O (3): A solution of $NdCl_3 \cdot 6H_2O$ (0.108 g, 0.3 mmol), 2,3-pyrazinedicarboxylic acid (0.077 g, 0.45 mmol), H_2O (7 mL), and aqueous NaOH (1.46 mL, 0.95 mmol) was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 190 °C for 62 h. Purple crystals of **3** were obtained in a 79.2% yield (0.1 g). $C_{18}H_{12}Nd_2N_6O_{15}$ (840.76): calcd. C 25.71, H 1.44, N 10.00; found C 25.39, H 1.12, N 9.84. IR data (KBr pellet, $\tilde{\nu}$ [cm^{-1}]): 3492 m, 1621 s, 1558 s, 1448 s, 1366 s, 1120 s, 891 m, 837 m, 445 m.

[Eu₂(pzdc)₃(H₂O)]ₓ·2xH₂O (4): A solution of $EuCl_3 \cdot 6H_2O$ (0.11 g, 0.3 mmol), 2,3-pyrazinedicarboxylic acid (0.077 g, 0.45 mmol), H_2O (8.4 mL), and aqueous NaOH (1.4 mL, 0.91 mmol) was sealed in a 25-mL stainless steel reactor with Teflon liner and heated at 190 °C for 88 h. Colorless crystals of **4** were obtained in a 77.8% yield (0.1 g). $C_{18}H_{12}Eu_2N_6O_{15}$ (856.26): calcd. C 25.25, H 1.41, N 9.81; found C 24.78, H 1.10, N 9.43. IR data (KBr pellet, $\tilde{\nu}$ [cm^{-1}]): 3486 m, 1627 s, 1561 s, 1449 s, 1368 s, 1122 s, 898 m, 845 m, 838 m, 449 m.

Measurement of the High-Resolution Luminescence Spectra: The excitation light source was a YAG:Nd laser that emits at 1.064 μm, and the excitation wavelength was 355 nm. The sample was placed in a Dewar bottle and cooled with liquid nitrogen. The fluorescence emitted was collected at right angles through a Spex 1403 monochromator with a photomultiplier tube, then averaged with a Boxcar integrator and finally the data were transferred to a computer.

X-ray Data Collections and Structure Determinations: The X-ray single-crystal data collections for complexes **1**, **2**, and **4** were performed with a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinements. Experimental details for X-ray data collection of **1**, **2**,

Table 2. Crystal data for **1**, **2**, and **4**

	1	**2**	**4**
Empirical formula	$C_{18}H_{12}La_2N_6O_{15}$	$C_{18}H_{12}Pr_2N_6O_{15}$	$C_{18}H_{12}Eu_2N_6O_{15}$
Formula mass	830.16	834.16	856.26
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	9.004(3)	8.945(2)	8.853(3)
b [Å]	17.001(5)	16.924(5)	16.771(5)
c [Å]	15.599(5)	15.482(4)	15.302(4)
α [°]	90	90	90
β [°]	101.739(5)	101.291(5)	100.823(5)
γ [°]	90	90	90
V [Å^3]	2337.9(12)	2298.3(11)	2231.5(11)
Z	4	4	4
T [K]	293(2)	293(2)	293(2)
$\rho_{calcd.}$ [g/cm^3]	2.358	2.411	2.549
μ [mm^{-1}][]	3.699	4.285	5.668
R_1 [a]	0.0221	0.0317	0.0246
wR_2 [a]	0.0489	0.0581	0.0552

[a] The values were calculated for data with [$I > 2\sigma(I)$].

Table 3. Selected bond lengths [Å] and bond angles[°] for complex **1**

La(1)−O(6)$^{\#1}$ [a]	2.447(3)	O(13)−La(1)−O(12)$^{\#4}$	126.69(10)	O(8)$^{\#1}$−La(2)−O(10)$^{\#5}$	145.27(9)
La(1)−O(2)$^{\#2}$	2.497(3)	O(3)$^{\#3}$−La(1)−O(12)$^{\#4}$	70.95(8)	O(5)−La(2)−O(10)$^{\#5}$	129.77(9)
La(1)−O(13)	2.528(3)	O(9)−La(1)−O(12)$^{\#4}$	144.24(8)	O(12)$^{\#4}$−La(2)−O(10)$^{\#5}$	69.61(9)
La(1)−O(3)$^{\#3}$	2.530(3)	O(6)$^{\#1}$−La(1)−O(9)$^{\#5}$	139.15(8)	O(1)−La(2)−O(10)$^{\#5}$	69.78(9)
La(1)−O(9)	2.566(3)	O(2)$^{\#2}$−La(1)−O(9)$^{\#5}$	69.31(9)	O(8)$^{\#1}$−La(2)−O(4)$^{\#3}$	102.66(11)
La(1)−O(12)$^{\#4}$	2.589(3)	O(13)−La(1)−O(9)$^{\#5}$	138.98(9)	O(5)−La(2)−O(4)$^{\#3}$	66.27(9)
La(1)−O(9)$^{\#5}$	2.648(3)	O(3)$^{\#3}$−La(1)−O(9)$^{\#5}$	68.86(9)	O(12)$^{\#4}$−La(2)−O(4)$^{\#3}$	114.09(9)
La(1)−O(11)$^{\#4}$	2.726(3)	O(9)−La(1)−O(9)$^{\#5}$	66.88(9)	O(1)−La(2)−O(4)$^{\#3}$	142.06(9)
La(1)−N(5)	2.767(3)	O(12)$^{\#4}$−La(1)−O(9)$^{\#5}$	77.48(8)	O(10)$^{\#5}$−La(2)−O(4)$^{\#3}$	78.62(9)
La(2)−O(8)$^{\#1}$	2.392(3)	O(6)$^{\#1}$−La(1)−O(11)$^{\#4}$	69.37(8)	O(8)$^{\#1}$−La(2)−N(3)	136.73(10)
La(2)−O(5)	2.501(3)	O(2)$^{\#2}$−La(1)−O(11)$^{\#4}$	79.78(8)	O(5)−La(2)−N(3)	61.28(9)
La(2)−O(12)$^{\#4}$	2.509(3)	O(13)−La(1)−O(11)$^{\#4}$	77.92(10)	O(12)$^{\#4}$−La(2)−N(3)	141.04(9)
La(2)−O(1)	2.510(3)	O(3)$^{\#3}$−La(1)−O(11)$^{\#4}$	115.06(8)	O(1)−La(2)−N(3)	74.80(10)
La(2)−O(10)$^{\#5}$	2.568(3)	O(9)−La(1)−O(11)$^{\#4}$	150.41(8)	O(10)$^{\#5}$−La(2)−N(3)	77.91(9)
La(2)−O(4)$^{\#3}$	2.619(3)	O(12)$^{\#4}$−La(1)−O(11)$^{\#4}$	49.10(8)	O(4)$^{\#3}$−La(2)−N(3)	78.58(10)
La(2)−N(3)	2.706(3)	O(9)$^{\#5}$−La(1)−O(11)$^{\#4}$	112.43(8)	O(8)$^{\#1}$−La(2)−O(3)$^{\#3}$	76.21(9)
La(2)−O(3)$^{\#3}$	2.725(3)	O(6)$^{\#1}$−La(1)−N(5)	72.03(9)	O(5)−La(2)−O(3)$^{\#3}$	100.80(8)
La(2)−N(1)	2.737(3)	O(2)$^{\#2}$−La(1)−N(5)	121.73(9)	O(12)$^{\#4}$−La(2)−O(3)$^{\#3}$	69.03(8)
O(6)$^{\#1}$−La(1)−O(2)$^{\#2}$	144.24(9)	O(13)−La(1)−N(5)	70.18(10)	O(1)−La(2)−O(3)$^{\#3}$	138.33(8)
O(6)$^{\#1}$−La(1)−O(13)	81.87(10)	O(3)$^{\#3}$−La(1)−N(5)	78.37(9)	O(10)$^{\#5}$−La(2)−O(3)$^{\#3}$	79.43(8)
O(2)$^{\#2}$−La(1)−O(13)	74.20(10)	O(9)−La(1)−N(5)	60.07(9)	O(4)$^{\#3}$−La(2)−O(3)$^{\#3}$	48.91(9)
O(6)$^{\#1}$−La(1)−O(3)$^{\#3}$	73.84(9)	O(12)$^{\#4}$−La(1)−N(5)	139.96(9)	N(3)−La(2)−O(3)$^{\#3}$	125.84(9)
O(2)$^{\#2}$−La(1)−O(3)$^{\#3}$	138.13(9)	O(9)$^{\#5}$−La(1)−N(5)	114.77(9)	O(8)$^{\#1}$−La(2)−N(1)	73.98(10)
O(13)−La(1)−O(3)$^{\#3}$	144.93(9)	O(11)$^{\#4}$−La(1)−N(5)	132.53(9)	O(5)−La(2)−N(1)	70.87(9)
O(6)$^{\#1}$−La(1)−O(9)	132.00(8)	O(8)$^{\#1}$−La(2)−O(5)	79.40(10)	O(12)$^{\#4}$−La(2)−N(1)	107.49(9)
O(2)$^{\#2}$−La(1)−O(9)	72.38(9)	O(8)$^{\#1}$−La(2)−O(12)$^{\#4}$	78.70(10)	O(1)−La(2)−N(1)	60.74(9)
O(13)−La(1)−O(9)	84.93(10)	O(5)−La(2)−O(12)$^{\#4}$	157.53(8)	O(10)$^{\#5}$−La(2)−N(1)	128.51(9)
O(3)$^{\#3}$−La(1)−O(9)	92.76(8)	O(8)$^{\#1}$−La(2)−O(1)	115.26(11)	O(4)$^{\#3}$−La(2)−N(1)	136.79(10)
O(6)$^{\#1}$−La(1)−O(12)$^{\#4}$	75.11(8)	O(5)−La(2)−O(1)	120.36(9)	N(3)−La(2)−N(1)	76.49(10)
O(2)$^{\#2}$−La(1)−O(12)$^{\#4}$	98.31(9)	O(12)$^{\#4}$−La(2)−O(1)	74.21(9)	O(3)$^{\#3}$−La(2)−N(1)	150.04(9)

[a] Symmetry operation: $^{\#1}$ x, $−y + 1/2$, $z + 1/2$; $^{\#2}$ $−x + 1$, $−y$, $−z + 1$; $^{\#3}$ $x − 1$, y, z; $^{\#4}$ $x + 1$, y, z; $^{\#5}$ $−x$, $−y$,$−z + 1$; $^{\#6}$ x, $−y + 1/2$, $z − 1/2$.

and **4** are presented in Table 2, while selected bond lengths, and angles for **1**, **2**, and **4** are listed in Tables 3, 4, and 5, respectively. CCDC-186337, -186338, and -186339 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Selected bond lengths [Å] and bond angles[°] for complex **2**

Pr(1)−O(11)	2.409(4)	O(13)−Pr(1)−O(7)	126.86(14)	O(10)−Pr(2)−O(6)#1 [a]	146.22(15)
Pr(1)−O(3)#1	2.458(4)	O(2)#2−Pr(1)−O(7)	70.70(13)	O(7)−Pr(2)−O(6)#1	70.36(13)
Pr(1)−O(13)	2.490(5)	O(5)#2−Pr(1)−O(7)	143.75(13)	O(12)#3−Pr(2)−O(6)#1	129.63(14)
Pr(1)−O(2)#2	2.501(4)	O(11)−Pr(1)−O(5)#1	140.26(14)	O(4)−Pr(2)−O(6)#1	68.85(13)
Pr(1)−O(5)#2	2.526(4)	O(3)#1−Pr(1)−O(5)#1	69.34(13)	O(10)−Pr(2)−O(1)#2	103.22(15)
Pr(1)−O(7)	2.542(4)	O(13)−Pr(1)−O(5)#1	138.78(14)	O(7)−Pr(2)−O(1)#2	113.68(13)
Pr(1)−O(5)#1	2.605(4)	O(2)#2−Pr(1)−O(5)#1	69.28(13)	O(12)#3−Pr(2)−O(1)#2	66.35(14)
Pr(1)−O(8)	2.707(4)	O(5)#2−Pr(1)−O(5)#1	66.36(15)	O(4)−Pr(2)−O(1)#2	140.85(14)
Pr(1)−N(3)#2	2.726(5)	O(7)−Pr(1)−O(5)#1	77.47(12)	O(6)#1−Pr(2)−O(1)#2	77.57(14)
Pr(2)−O(10)	2.348(4)	O(11)−Pr(1)−O(8)	69.07(13)	O(10)−Pr(2)−N(6)#3	136.73(15)
Pr(2)−O(7)	2.469(4)	O(3)#1−Pr(1)−O(8)	78.14(12)	O(7)−Pr(2)−N(6)#3	141.24(14)
Pr(2)−O(12)#3	2.471(4)	O(13)−Pr(1)−O(8)	77.46(14)	O(12)#3−Pr(2)−N(6)#3	62.35(14)
Pr(2)−O(4)	2.476(4)	O(2)#2−Pr(1)−O(8)	115.40(13)	O(4)−Pr(2)−N(6)#3	75.64(14)
Pr(2)−O(6)#1	2.532(4)	O(5)#2−Pr(1)−O(8)	149.30(13)	O(6)#1−Pr(2)−N(6)#3	76.90(14)
Pr(2)−O(1)#2	2.583(4)	O(7)−Pr(1)−O(8)	49.76(13)	O(1)#2−Pr(2)−N(6)#3	77.70(14)
Pr(2)−N(6)#3	2.654(5)	O(5)#1−Pr(1)−O(8)	112.58(12)	O(10)−Pr(2)−N(1)	74.62(16)
Pr(2)−N(1)	2.691(5)	O(11)−Pr(1)−N(3)#2	72.07(14)	O(7)−Pr(2)−N(1)	108.26(14)
Pr(2)−O(2)#2	2.694(4)	O(3)#1−Pr(1)−N(3)#2	123.40(14)	O(12)#3−Pr(2)−N(1)	71.10(14)
O(11)−Pr(1)−O(3)#1	142.48(14)	O(13)−Pr(1)−N(3)#2	70.88(15)	O(4)−Pr(2)−N(1)	61.65(14)
O(11)−Pr(1)−O(13)	80.96(15)	O(2)#2−Pr(1)−N(3)#2	77.67(14)	O(6)#1−Pr(2)−N(1)	127.91(14)
O(3)#1−Pr(1)−O(13)	74.42(15)	O(5)#2−Pr(1)−N(3)#2	60.83(13)	O(1)#2−Pr(2)−N(1)	136.77(15)
O(11)−Pr(1)−O(2)#2	74.57(14)	O(7)−Pr(1)−N(3)#2	139.44(13)	N(6)#3−Pr(2)−N(1)	76.28(15)
O(3)#1−Pr(1)−O(2)#2	138.48(14)	O(5)#1−Pr(1)−N(3)#2	114.36(13)	O(10)−Pr(2)−O(2)#2	75.49(14)
O(13)−Pr(1)−O(2)#2	144.81(14)	O(8)−Pr(1)−N(3)#2	132.80(13)	O(7)−Pr(2)−O(2)#2	68.64(13)
O(11)−Pr(1)−O(5)#2	132.88(13)	O(10)−Pr(2)−O(7)	78.91(15)	O(12)#3−Pr(2)−O(2)#2	99.68(13)
O(3)#1−Pr(1)−O(5)#2	72.96(13)	O(10)−Pr(2)−O(12)#3	78.21(15)	O(4)−Pr(2)−O(2)#2	137.50(13)
O(13)−Pr(1)−O(5)#2	84.94(15)	O(7)−Pr(2)−O(12)#3	156.35(13)	O(6)#1−Pr(2)−O(2)#2	80.45(13)
O(2)#2−Pr(1)−O(5)#2	93.41(13)	O(10)−Pr(2)−O(4)	115.85(15)	O(1)#2−Pr(2)−O(2)#2	49.50(14)
O(11)−Pr(1)−O(7)	75.48(13)	O(7)−Pr(2)−O(4)	73.64(13)	N(6)#3−Pr(2)−O(2)#2	125.85(14)
O(3)#1−Pr(1)−O(7)	97.16(13)	O(12)#3−Pr(2)−O(4)	122.42(14)	N(1)−Pr(2)−O(2)#2	149.93(14)

[a] Symmetry operation: #1−x, −y, −z + 1; #2x − 1, y, z; #3x, −y + 1/2, z − 1/2; #4x + 1, y, z; #5x, −y + 1/2, z + 1/2.

Table 5. Selected bond lengths [Å] and bond angles[°] for complex **4**

Eu(1)−O(8)#1 [a]	2.295(4)	O(4)#2−Eu(1)−O(1)	140.23(12)	O(6)#1−Eu(2)−O(12)#5	134.29(11)
Eu(1)−O(9)	2.405(3)	O(5)−Eu(1)−O(1)	66.28(12)	O(3)#4−Eu(2)−O(12)#5	73.11(11)
Eu(1)−O(4)#2	2.420(3)	O(11)#3−Eu(1)−O(1)	76.91(12)	O(13)−Eu(2)−O(12)#5	84.29(12)
Eu(1)−O(5)	2.431(3)	O(8)#1−Eu(1)−N(3)	136.85(13)	O(2)−Eu(2)−O(12)#5	94.83(11)
Eu(1)−O(11)#3	2.460(3)	O(9)−Eu(1)−N(3)	141.65(12)	O(6)#1−Eu(2)−O(9)	76.14(11)
Eu(1)−O(1)	2.538(3)	O(4)#2−Eu(1)−N(3)	76.43(12)	O(3)#4−Eu(2)−O(9)	95.33(11)
Eu(1)−N(3)	2.585(4)	O(5)−Eu(1)−N(3)	63.83(12)	O(13)−Eu(2)−O(9)	127.02(12)
Eu(1)−N(2)#2	2.635(4)	O(11)#3−Eu(1)−N(3)	76.31(12)	O(2)−Eu(2)−O(9)	70.65(11)
Eu(1)−O(2)	2.653(3)	O(1)−Eu(1)−N(3)	77.23(12)	O(12)#5−Eu(2)−O(9)	143.38(11)
Eu(2)−O(6)#1	2.347(3)	O(8)#1−Eu(1)−N(2)#2	74.53(13)	O(6)#1−Eu(2)−O(12)#3	141.86(11)
Eu(2)−O(3)#4	2.396(3)	O(9)−Eu(1)−N(2)#2	108.56(11)	O(3)#4−Eu(2)−O(12)#3	69.46(11)
Eu(2)−O(13)	2.419(4)	O(4)#2−Eu(1)−N(2)#2	62.74(12)	O(13)−Eu(2)−O(12)#3	138.38(12)
Eu(2)−O(2)	2.424(3)	O(5)−Eu(1)−N(2)#2	71.42(12)	O(2)−Eu(2)−O(12)#3	69.40(11)
Eu(2)−O(12)#5	2.458(3)	O(11)#3−Eu(1)−N(2)#2	128.02(12)	O(12)#5−Eu(2)−O(12)#3	65.61(11)
Eu(2)−O(9)	2.476(3)	O(1)−Eu(1)−N(2)#2	136.74(12)	O(9)−Eu(2)−O(12)#3	77.77(10)
Eu(2)−O(12)#3	2.563(3)	N(3)−Eu(1)−N(2)#2	76.49(13)	O(6)#1−Eu(2)−N(6)#5	72.05(12)
Eu(2)−N(6)#5	2.664(4)	O(8)#1−Eu(1)−O(2)	74.88(12)	O(3)#4−Eu(2)−N(6)#5	125.67(12)
Eu(2)−O(10)	2.687(3)	O(9)−Eu(1)−O(2)	67.94(10)	O(13)−Eu(2)−N(6)#5	71.58(13)
O(8)#1−Eu(1)−O(9)	78.58(12)	O(4)#2−Eu(1)−O(2)	136.41(11)	O(2)−Eu(2)−N(6)#5	76.99(12)
O(8)#1−Eu(1)−O(4)#2	115.96(13)	O(5)−Eu(1)−O(2)	98.65(11)	O(12)#5−Eu(2)−N(6)#5	62.27(12)
O(9)−Eu(1)−O(4)#2	73.14(11)	O(11)#3−Eu(1)−O(2)	81.03(11)	O(9)−Eu(2)−N(6)#5	138.99(12)
O(8)#1−Eu(1)−O(5)	76.94(12)	O(1)−Eu(1)−O(2)	50.23(11)	O(12)#3−Eu(2)−N(6)#5	113.62(11)
O(9)−Eu(1)−O(5)	154.50(11)	N(3)−Eu(1)−O(2)	126.25(11)	O(6)#1−Eu(2)−O(10)	68.59(11)
O(4)#2−Eu(1)−O(5)	124.69(11)	N(2)#2−Eu(1)−O(2)	149.25(12)	O(3)#4−Eu(2)−O(10)	75.93(11)
O(8)#1−Eu(1)−O(11)#3	146.65(12)	O(6)#1−Eu(2)−O(3)#4	140.14(11)	O(13)−Eu(2)−O(10)	76.65(12)
O(9)−Eu(1)−O(11)#3	71.11(11)	O(6)#1−Eu(2)−O(13)	79.75(12)	O(2)−Eu(2)−O(10)	116.26(11)
O(4)#2−Eu(1)−O(11)#3	68.26(11)	O(3)#4−Eu(2)−O(13)	74.83(12)	O(12)#5−Eu(2)−O(10)	146.93(11)
O(5)−Eu(1)−O(11)#3	130.04(11)	O(6)#1−Eu(2)−O(2)	75.95(11)	O(9)−Eu(2)−O(10)	50.73(10)
O(8)#1−Eu(1)−O(1)	103.65(13)	O(3)#4−Eu(2)−O(2)	138.47(12)	O(12)#3−Eu(2)−O(10)	113.39(10)
O(9)−Eu(1)−O(1)	113.42(11)	O(13)−Eu(2)−O(2)	144.87(12)	N(6)#5−Eu(2)−O(10)	132.77(11)

[a] Symmetry operation: #1x, −y + 1/2, z − 1/2; #2x − 1, y, z; #3−x, −y, −z; #4−x + 1, −y, −z; #5x + 1, y, z; #6x, −y + 1/2, z + 1/2.

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