

In situ cyclodehydration of iminodiacetic acid into 2,5-diketopiperazine-1,4-diacetate in lanthanide-based coordination polymers†

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The reaction of iminodiacetic acid with Ln₂O₃ (Ln = Dy, Ho, Er, Yb) under hydrothermal conditions generate a series of 3D lanthanide-based coordination polymers, in which, the iminodiacetic acid (IDA) was transformed into a 2,5-diketopiperazine-1,4-diacetate.

As a new bridge in both coordination chemistry and organic chemistry, hydrothermal *in situ* ligand synthesis is becoming an important subject in the field of organic synthesis and crystal engineering.^{1–3} Although difficult to design, hydrothermal *in situ* ligand synthesis not only provides the organic compound, which is difficult to obtain through routine synthetic methods,^{3a,3c} but also new types of coordination polymers with potential applications.^{2c} Until now, more than 10 types of hydro(solvo)thermal *in situ* ligand syntheses have been found, such as hydroxylation,⁴ alkylation,⁵ carbon–carbon bond formation,⁶ hydrolysis,⁷ tetrazole and triazole formation,⁸ acylation⁹ and others.¹⁰

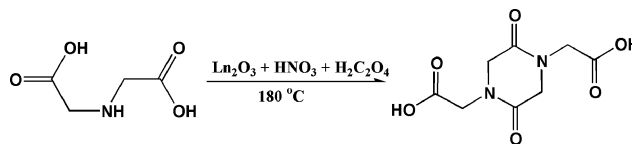
2,5-Diketopiperazine-1,4-diacetic, as one of the smallest cyclic dipeptide derivatives, is considered to be a privileged structure for drug development¹¹ and for peptide chemistry studies.^{12–13} Its structural characteristic also makes it become a potential molecular building block for the assembly of coordination polymers. So far, the dimerization of iminodiacetic acid or its esters remains to be an important method to the preparation of the compound, despite that the yield is rather low.¹⁴ In 2003, Silva and co-workers¹⁵ found that the cyclization of iminodiacetic acid dimethyl ester in the presence of NiCl₂ could generate 2,5-diketopiperazine-1,4-diacetic, but the yield was unclear. Here, we report our observation of *in situ* cyclization of iminodiacetic acid in lanthanide-based coordination polymers, namely, [Ln₂(ox)₂L(H₂O)₂]_n (Ln = Dy (**1**), Ho (**2**), Er (**3**), Yb (**4**); L = 2,5-diketopiperazine-1,4-diacetate, ox = oxalate). An investigation on the factors influencing the formation of the organic ligand shows that oxalic acid plays a key role in the formation of the 2,5-diketopiperazine-1,4-diacetate ligand.

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† Electronic supplementary information (ESI) available: X-Ray crystallographic files in cif format for the four complexes, the electrospray mass spectrum for the reactions of IDA + ox + Ln₂O₃ (Ln = Dy), IDA + HNO₃ + Ln₂O₃ (Ln = Dy), IDA + Ln₂O₃ (Ln = Dy) and IDA + ox + HNO₃ + Ln₂O₃ (Ln = Pr, Eu) (Fig. S1–6), ¹H NMR spectra (Fig. S2) and magnetic properties (Fig. S3) for the four complexes. CCDC reference numbers 708190–708193. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b819792j

The block crystals of **1–4** were obtained by hydrothermal reactions of Ln₂O₃ (Ln = Dy, Ho, Er, Yb), iminodiacetic acid, oxalic acid, HNO₃ and water in a molar ratio of 1 : 4 : 2 : 6 : 550 at 180 °C for 100 h.‡ Interestingly, this reaction results in *in situ* transformation of 2,5-diketopiperazine-1,4-diacetic acid through intermolecular dehydration coupling of iminodiacetic acid (Scheme 1). Single-crystal analysis reveals that complex **1** consists of two Dy(III) cations, one 2,5-diketopiperazine-1,4-diacetate, two ox²⁻ ligands and two water molecules. Each Dy(III) center is located in a square anti-prism geometry and is coordinated by two monodentate carboxylate groups from two 2,5-diketopiperazine-1,4-diacetate ligands, one carboxyl group of 2,5-diketopiperazine-1,4-diacetate ligand, two ox²⁻ ligands in chelate mode and one water molecule as shown in Fig. 1. The bond lengths of Dy–O are in the range from 2.266(2)–2.423(3) Å, very close to those in the complex [Dy₃Cu₆L₆(OH)₆(H₂O)₁₀]·Cl₂·ClO₄·3.5H₂O.¹⁶



Scheme 1 Schematic view of hydrothermal *in situ* generation of 2,5-diketopiperazine-1,4-diacetic acid.

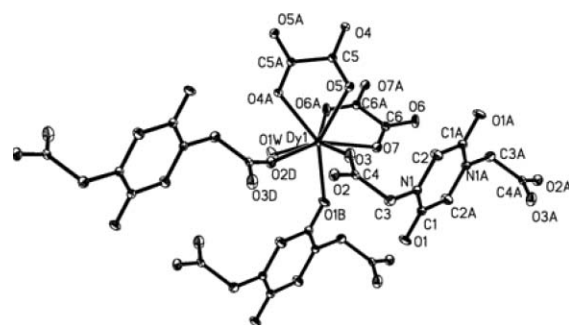


Fig. 1 ORTEP plot showing the coordination environment of the Dy(III) center in **1**. Symmetry transformations: (A) $-x + 1, -y + 2, -z$; (B) $-x + 1, -y + 1, -z + 1$; (D) $-x + 1, -y + 2, -z + 1$.

The structure of **1** can be described as follows: (1) two adjacent Dy(H₂O)³⁺ cations linked by ox²⁻ to form a 1D chain of [Dy(H₂O)(ox)]_n³⁺ as illustrated in Fig. 2; (2) 2,5-diketopiperazine-1,4-diacetate acts as a 4-connected node to link the adjacent 1D chains through each carboxylate and carboxyl group coordinated with one Dy(III) cation from the adjacent 1D chains to generate a 2D layered structure of [Dy₂(ox)₂L(H₂O)₂]_n as shown in

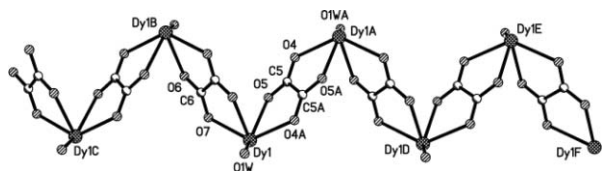


Fig. 2 ORTEP plot showing the 1D chain of $[\text{Dy}(\text{H}_2\text{O})(\text{ox})]_n$ in **1**.

Fig. 3 and (3) two adjacent 2D layers further extend into a 3D structure through the uncoordinated carboxylate group of 2,5-dioxopiperazine-1,4-diacetate from one layer to the Dy(III) cation from adjacent layers as shown in Fig. 4. As a result, each ligand in **1** is coordinated to six Dy(III) ions with four from the same layer and two from the adjacent layers. It was noted that complex **1** is the first 2,5-diketopiperazine-1,4-diacetate metal complex on the basis of a survey of the Cambridge Crystallographic Database.¹⁷

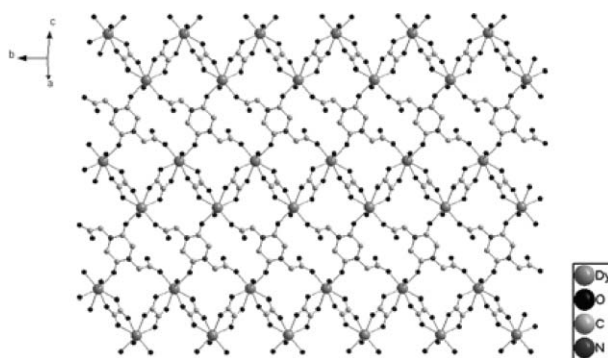


Fig. 3 Stick plot showing the 2D layer in **1**.

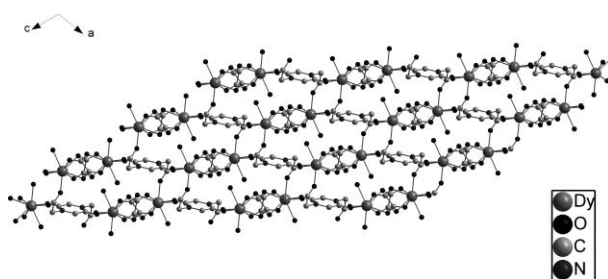


Fig. 4 Stick plot showing the 3D structure of **1**.

The crystal structures of **2**, **3** and **4** are isomorphous with the framework of **1**.§ The bond lengths of Ln–O are 2.249(2)–2.409(2), 2.232(2)–2.392(2) and 2.224(2)–2.390(3) Å for **2**, **3** and **4**, respectively, comparable to those in **1**.

In order to understand the key factor to affect the formation of the organic ligand, we used $\text{IDA} + \text{ox} + \text{Dy}_2\text{O}_3$, $\text{IDA} + \text{HNO}_3 + \text{Dy}_2\text{O}_3$, $\text{IDA} + \text{Dy}_2\text{O}_3$ and $\text{IDA} + \text{ox} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$ ($\text{Ln} = \text{Pr}, \text{Eu}$) to prepare the organic ligand under similar conditions to that of **1**. In these reactions, we could obtain crystals of **1** only in the cases of $\text{IDA} + \text{ox} + \text{Ln}_2\text{O}_3$ ($\text{Ln} = \text{Dy}$) (the yield for the reaction of $\text{IDA} + \text{ox} + \text{Ln}_2\text{O}_3$ is very close to that of $\text{IDA} + \text{ox} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$), and obtained 3D complex $\text{Ln}_2(\text{ox})_3(\text{H}_2\text{O})_6$ ¹⁸ for the reaction of $\text{IDA} + \text{ox} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$ ($\text{Ln} = \text{Pr}, \text{Eu}$), while in the remaining case, we either obtained a clear solution (for the reaction of $\text{IDA} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$) or a suspending solution (for the reaction of $\text{IDA} + \text{Ln}_2\text{O}_3$). However, the electrospray mass spectra show that the residual

solutions of all the reactions contains the 2,5-diketopiperazine-1,4-diacetate ligand (ESI, Fig. S1–6†), and the amount of the 2,5-diketopiperazine-1,4-diacetate ligand in the residual solution of the reaction of $\text{IDA} + \text{ox} + \text{Ln}_2\text{O}_3$ and $\text{IDA} + \text{ox} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$ ($\text{Ln} = \text{Pr}, \text{Eu}$) is significantly higher than that in the reactions of $\text{IDA} + \text{ox} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$, $\text{IDA} + \text{HNO}_3 + \text{Ln}_2\text{O}_3$ and $\text{IDA} + \text{Ln}_2\text{O}_3$. These results indicate that it is oxalic acid, instead of the lanthanide ion and HNO_3 , that plays a key role in the formation of the 2,5-diketopiperazine-1,4-diacetate ligand. Hence, IDA and oxalic acid was used to synthesize the 2,5-diketopiperazine-1,4-diacetate ligand. When the mixture of iminodiacetic acid (0.27 g, 2.0 mmol) and oxalic acid (0.12 g, 2.0 mmol) was sealed in a 25 mL Teflon-lined stainless steel container and heated to 180 °C for 100 h, then cooled to 100 °C at a rate of 3 °C h⁻¹ and held for 16 h, followed by further cooling to 100 °C at a rate of 5 °C h⁻¹, colourless crystals of 2,5-diketopiperazine-1,4-diacetic acid was obtained in a yield of more than 85%. The organic ligand was further confirmed by ¹H NMR spectra (ESI, Fig. S2†) and single-crystal structure analysis.

Measurement of the temperature-dependent magnetic properties of **1**, **2**, **3** and **4** was carried out at an applied magnetic field of 1000 Oe over the temperature range 2–300 K. The temperature dependence of the magnetic susceptibilities in the form of μ_{eff} vs. T for **1**, **2**, **3** and **4** are shown in ESI Fig. S3.† The μ_{eff} value per molecule of **1** is 15.15 μ_B at room temperature, close to the expected value of 15.05 μ_B for two free non-interacting Dy(III) ions. Upon lowering the temperature, μ_{eff} decreases gradually to 15.01 μ_B at 50 K, and then drops rapidly below 50 K to 13.6 μ_B at 2 K. The dramatic decrease of μ_{eff} at low temperature is mainly attributed to the weak antiferromagnetic coupling between the Dy(III) ions, and partially to the splitting of the ligand field of the Ln(III) ion.^{19,20} Similar to **1**, the varieties of the temperature dependence of μ_{eff} can also be found in complexes **2** and **3**. For **4**, the μ_{eff} value at 300 K is 6.16 μ_B , which is close to the expected value for two isolated Yb(III) ions (calculated 6.41 μ_B). However, there is a continuous decrease in μ_{eff} and it reaches 4.35 μ_B at 2 K with the decrease of the temperature, which mainly indicates the feature of single Yb(III).^{19a}

In summary, we have reported the syntheses and crystal structures of four lanthanide-based 3D coordination polymers through hydrothermal reaction of Ln_2O_3 ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$), iminodiacetic acid, oxalic acid and HNO_3 . In these compounds, the iminodiacetic acid was transformed into a 2,5-diketopiperazine-1,4-diacetate. Further investigation shows that oxalic acid plays a key role in the formation of 2,5-diketopiperazine-1,4-diacetic acid. The extension of such a synthetic approach into other kind of cyclic dipeptides is under the way.

Acknowledgements

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Notes and references

‡ Complex **1** was synthesized as follows: iminodiacetic acid (0.27 g, 2.0 mmol), oxalic acid (0.12 g, 2.0 mmol), Dy_2O_3 (0.187 g, 0.5 mmol) and HNO_3 (0.25 mL, 3 mmol), were mixed in 10.0 mL water with stirring at room temperature. The mixture was transferred and sealed in a 25 mL

Teflon-lined stainless steel container. The container was heated to 180 °C and held at that temperature for 100 hour, then cooled to 100 °C at a rate of 3 °C h⁻¹ and held for 16 h, followed by further cooling to 100 °C at a rate of 5 °C h⁻¹. Colourless crystals of **1** were collected in 170 mg (45% yield based on Dy₂O₃). Compounds **2** (184 mg, 48% yield based on Ho₂O₃), **3** (162 mg, 42% yield based on Er₂O₃) and **4** (204 mg, 52% yield based on Yb₂O₃) were prepared in a similar way as illustrated for **1**. Anal. calcd (found) for C₁₂H₁₂N₂O₁₆Dy₂ (**1**): C 18.83 (19.21), N 3.66 (3.996), H 1.58 (1.59). IR spectra for **1** (KBr) ν/cm^{-1} : 3431 s, 2930 w, 1712 m, 1630 s, 1503 m, 1439 m, 1397 m, 1352 m, 1314 m, 1275 m, 1257 w, 1189 m, 1109 w, 982 w, 944 m, 875 m, 794 s, 697 m, 573 m, 501 m, 408 w. Anal. calcd (found) for C₁₂H₁₂N₂O₁₆Ho₂ (**2**): C 18.72 (18.08), N 3.64 (3.44), H 1.57 (1.41). IR spectra for **2** (KBr) ν/cm^{-1} : 3444 s, 2926 w, 1714 m, 1633 s, 1504 m, 1441 m, 1398 m, 1353 m, 1315 m, 1275 m, 1190 m, 1108 w, 980 w, 960 m, 945 w, 875 w, 795 s, 697 m, 574 m, 501 m, 408 w. Anal. calcd (found) for C₁₂H₁₂N₂O₁₆Er₂ (**3**): C 18.60 (19.26), N 3.62 (3.70), H 1.56 (1.55). IR spectra for **3**, (KBr) ν/cm^{-1} : 3444 s, 2926 w, 1716 w, 1632 s, 1504 m, 1440 m, 1398 m, 1353 m, 1315 m, 1274 m, 1190 w, 1110 w, 960 w, 876 w, 796 m, 696 w, 577 w, 501 w, 408 w. Anal. calcd (found) for C₁₂H₁₂N₂O₁₆Yb₂ (**4**): C 18.33 (18.41), N 3.56 (3.61), H 1.54 (1.37). IR spectra for **4**, (KBr) ν/cm^{-1} : 3443 s, 2928 w, 1718 m, 1636 s, 1504 m, 1442 m, 1400 m, 1353 m, 1315 m, 1274 m, 1191 w, 1108 w, 960 w, 877 w, 797 m, 698 m, 575 m, 501 m, 408 m. § Crystal data for **1**: triclinic, space group P $\bar{1}$ (#2), $a = 6.7426(16)$ Å, $b = 7.8105(18)$ Å, $c = 9.168(2)$ Å, $\alpha = 95.603(4)^\circ$, $\beta = 110.399(4)^\circ$, $\gamma = 93.470(4)^\circ$, $V = 448.06(18)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.836$ g cm⁻³, $M_r = 765.24$, $\mu(\text{MoK}\alpha) = 8.370$ mm⁻¹. Of the 3425 reflections collected, 1725 are independent ($R_{\text{int}} = 0.0177$) and 1705 are observed ($I > 2\sigma(I)$). On the basis of all the data and 145 refined parameters, R_1 (obs.) = 0.0217 and wR_2 (all data) = 0.0511 were obtained. For **2**: triclinic, space group P $\bar{1}$ (#2), $a = 6.6964(15)$ Å, $b = 7.7827(18)$ Å, $c = 9.126(2)$ Å, $\alpha = 95.692(4)^\circ$, $\beta = 110.274(3)^\circ$, $\gamma = 93.543(4)^\circ$, $V = 441.57(17)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.896$ g cm⁻³, $M_r = 770.10$, $\mu(\text{MoK}\alpha) = 8.992$ mm⁻¹. Of the 3329 reflections collected, 1680 are independent ($R_{\text{int}} = 0.0240$) and 1655 are observed ($I > 2\sigma(I)$). On the basis of all the data and 145 refined parameters, R_1 (obs.) = 0.0201 and wR_2 (all data) = 0.0560 were obtained. For **3**: triclinic, space group P $\bar{1}$ (#2), $a = 6.6574(15)$ Å, $b = 7.7517(18)$ Å, $c = 9.066(2)$ Å, $\alpha = 95.676(4)^\circ$, $\beta = 110.170(3)^\circ$, $\gamma = 93.544(4)^\circ$, $V = 434.73(17)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.959$ g cm⁻³, $M_r = 774.76$, $\mu(\text{MoK}\alpha) = 9.685$ mm⁻¹. Of the 3318 reflections collected, 1656 are independent ($R_{\text{int}} = 0.0182$) and 1640 are observed ($I > 2\sigma(I)$). On the basis of all the data and 145 refined parameters, R_1 (obs.) = 0.0186 and wR_2 (all data) = 0.0504 were obtained. For **4**: triclinic, space group P $\bar{1}$ (#2), $a = 6.6649(15)$ Å, $b = 7.7808(17)$ Å, $c = 9.076(2)$ Å, $\alpha = 95.798(3)^\circ$, $\beta = 109.928(3)^\circ$, $\gamma = 93.594(3)^\circ$, $V = 437.83(17)$ Å³, $Z = 1$, $\rho_{\text{calcd}} = 2.982$ g cm⁻³, $M_r = 786.32$, $\mu(\text{MoK}\alpha) = 10.713$ mm⁻¹. Of the 3318 reflections collected, 1664 are independent ($R_{\text{int}} = 0.0219$) and 1659 are observed ($I > 2\sigma(I)$). On the basis of all the data and 145 refined parameters, R_1 (obs.) = 0.0206 and wR_2 (all data) = 0.0539 were obtained.

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