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Communication

$[Ln_2(C_2O_4)_2(pyzc)_2(H_2O)_2]_n$ [Ln = Pr (1), Er (2)]: Novel Two-Dimensional Lanthanide Coordination Polymers with 2-Pyrazinecarboxylate and Oxalate

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We report for the first time hydrothermal synthesis of lanthanide–pyzcH polymers, $[Ln_2(C_2O_4)_2(pyzc)_2\ (H_2O)_2]_n$ [Ln = Pr (**1**), Er (**2**)], in which pyzcH was decomposed into $C_2O_4^{2-}$ and thus caused novel two-dimensional hexagonal lattice networks. The magnetic property of polymer **1** has been studied by an approximate treatment being enlightened by McPherson et al. (*Inorg. Chim. Acta* **1988**, *148*, 265), leading to $\Delta = -4.3$ cm^{-1}, $zJ' = -11.73$ cm^{-1}, and $g = 0.79$. Complex **2** displays an intense room-temperature, liquid-state luminescent emission.

As is well-known, lanthanide ions are good choices for building multidimensional coordination polymers because of their tendency to adopt high coordination numbers, which can be employed for the construction of high-dimensional and high-connected frameworks that provide practical materials combining their specific magnetic and optical properties.[1,2] Especially, it is still a challenge to understand the magnetic interactions between lanthanide ions.

On the other hand, 2-pyrazinecarboxylic acid (abbreviated pyzcH) is a good ligand with multifunctional coordination sites providing a high likelihood for the generation of structures with high dimensions. However, most of the work has so far focused on the assembly of the transition metal–pyzcH frameworks,[3] while the analogous chemistry of the lanthanides has received less attention.

In this Communication, we report the structure and magnetism of two lanthanide complexes with 2-pyrazinecarboxylic acid, $[Ln_2(C_2O_4)_2(pyzc)_2(H_2O)_2]_n$ [Ln = Pr (**1**), Er (**2**)]. This is the first example of lanthanide–pyzcH polymers with oxalates.

The hydrothermal reaction of pyzcH, Pr_6O_{11} or Er_2O_3, and $FeCl_3$ in an aqueous solution at 165 °C for 6 days produced prism crystals.[4] Single-crystal X-ray analysis[5] of the two compounds illustrated the presence of an oxalate (ox^{2-}) ligand. Because no oxalate was directly introduced to the starting reaction mixture, we supposed that oxalate might be derived from the decomposition of pyzcH. Similar situations also occurred in other systems.[6]

X-ray crystallography reveals that the two compounds are isomorphous. Here, we choose **1** to represent the detailed structure. As shown in Figure 1, the Pr(III) ion is nine-coordinated with two water molecules, two oxalates, and two pyzc ligands. The coordination polyhedron may be represented as a distorted, tricapped trigonal prism (Figure 2). The Pr–O (within the range from 2.484 to 2.570 Å; mean value 2.534 Å) and Pr–N (2.791 Å) bond lengths are in the normal range for Pr(III) ions.[7] As in the case found in

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(4) The syntheses of complexes $[Ln_2(C_2O_4)_2(pyzc)_2(H_2O)_2]_n$ [Ln = Pr (**1**), Er (**2**)] are as follows: Pr_6O_{11} or Er_2O_3 (0.05 mmol) and pyzcH (1.0 mmol) were dissolved in an aqueous solution (13 mL) at room temperature. After stirring for 30 min, 1 mL of 0.3 mmo1/mL $FeCl_3$ was added dropwise to the initial mixture and reacted at 165 °C for 6 days under hydrothermal conditions. Then small prism crystals of $[Ln(C_2O_4)_2(pyzc)_2(H_2O)_2]_n$ [Ln = Pr (**1**), Er (**2**)] were obtained in approximately 42% (**1**) and 47% (**2**) yield (based on Pr_6O_{11} or Er_2O_3), respectively. Elem anal. Calcd for $C_{14}H_{14}N_4O_{16}Pr_2$ (**1**): C, 21.65; H, 1.80; N, 7.22. Found: C, 21.73; H, 1.87; N, 7.14. Elem anal. Calcd for $C_{14}H_{14}N_4O_{16}Er_2$ (**2**): C, 20.27; H, 1.69; N, 6.76. Found: C, 20.32; H, 1.65; N, 6.79.

(5) Crystal data for **1**: $C_{14}H_{14}N_4O_{16}Pr_2$, $M = 776.11$, triclinic, $P\bar{1}$, $a = 7.9905(1)$ Å, $b = 8.6809(1)$ Å, $c = 8.7788(1)$ Å, $\alpha = 115.540(2)°$, $\beta = 101.868(2)°$, $\gamma = 96.133(2)°$, $V = 524.35(1)$ Å^3, $Z = 1$, $T = 294(2)$ K, $F(000) = 372$, GOF = 1.075, R1 = 0.0259, wR2 = 0.0651. Crystal data for **2**: $C_{14}H_{14}N_4O_{16}Er_2$, $M = 828.81$, triclinic, $P\bar{1}$, $a = 7.967(2)$ Å, $b = 8.670(2)$ Å, $c = 8.763(2)$ Å, $\alpha = 115.521(2)°$, $\beta = 101.985(3)°$, $\gamma = 96.267(3)°$, $V = 520.6(2)$ Å^3, $Z = 1$, $T = 294(2)$ K, $F(000) = 390$, GOF = 1.160, R1 = 0.0270, wR2 = 0.0775. Direct methods with *SHELXS-97* and refinement on F^2 using *SHELXL-97*.

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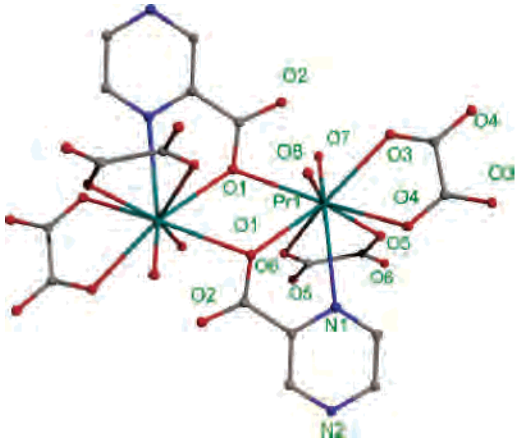

Figure 1. Thermal ellipsoid plots (50% probability) showing the molecular structures of **1** (H atoms omitted for clarity).

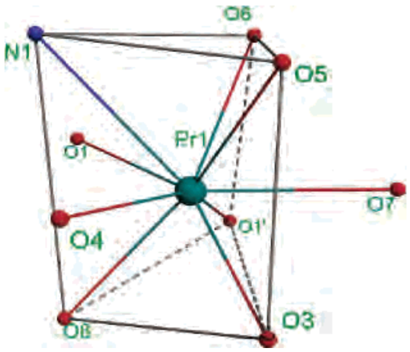

Figure 2. Coordination mode of praseodymium in $[Pr_2(C_2O_4)_2(pyzc)_2(H_2O)_2]_n$ (**1**).

polymer **2**, the Er−O(N) bond lengths (mean value 2.521 Å; 2.780 Å) become shorter with an increase of the atom number of lanthanide because of lanthanide contraction. The oxalates act as bridging ligands to link Pr(III) ions into an infinite zigzag chain (Figure 3a). Neighboring zigzag chains are linked by the pyzc ligands into the two-dimensional layerlike network (Figure 3b). In the cationic layer, each six-Pr(III)-ion unit forms a Pr_6 hexagonal lattice (Figure 3c). Six Pr(III) ions are almost coplanar, and the Pr•••Pr•••Pr angles are within the range from 104.09 to 149.35° while the adjacent Pr(III)•••Pr(III) distances vary from 4.463(4) to 6.499(1) Å. These values for the Ln_6 lattice are similar to that found in the three-dimensional lanthanide polymer $\{[Ln_2(C_2O_4)_3(H_2O)_6]\cdot 3H_2O\cdot 0.5HNO_3\}_n$ [Ln = La(III), Pr(III)],[8] in which six Ln atoms are bridged by six oxalates.

In the synthesis, although $FeCl_3$ was added into the reaction mixture, there were neither chlorine anions nor Fe(III) ions in the products. To confirm the formation of oxalates and investigate the role of $FeCl_3$ in the system, similar reactions were carried out. When we performed the reaction in the absence of $FeCl_3$ or added sodium oxalate directly to the reaction mixture, the same polymers could not be obtained, which indicates that $FeCl_3$ plays a vital role in the formation of the products. We speculate that the presence of $FeCl_3$ in the reaction will take advantage of the degradation of pyzcH and the formation of the title polymers.

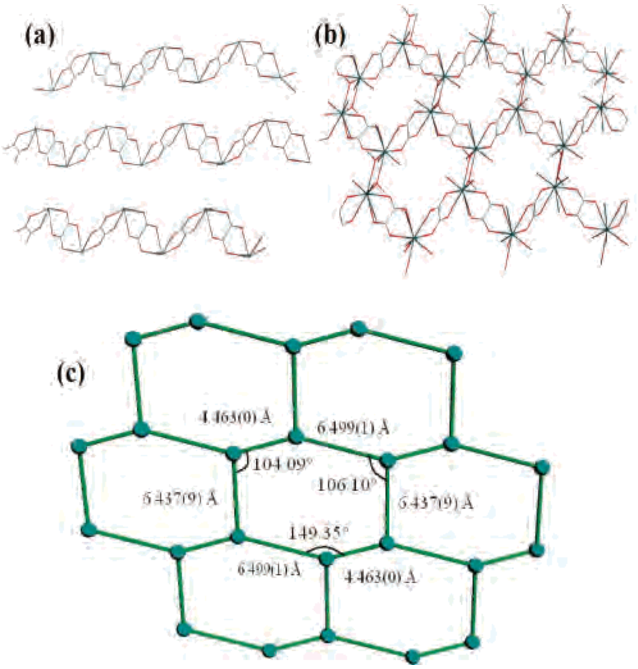

Figure 3. (a) View of the zigzag chain bridged by $C_2O_4^{2-}$ ligands in **1**. (b) Two-dimensional structure formed by Pr−O−Pr bonds, with the pyrazine ring of the $pyzc^-$ ligands omitted for clarity. (c) Schemic drawing representing Pr_6 metallic hexagonal lattices in **1**. Solid balls: Pr. Shorter lines: carboxyl bridges. Longer lines: $C_2O_4^{2-}$ bridges.

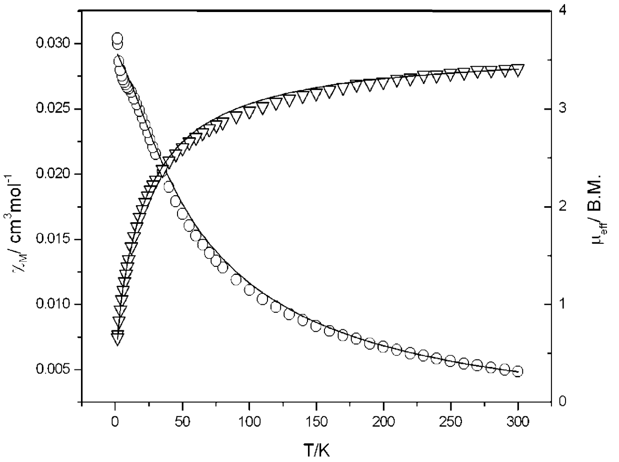

Figure 4. χ_M (○) vs T and μ_{eff} (□) vs T plots for complex **1**. The solid lines represent the theoretical values based on the equations.

The electronic spectra of **1** in an aqueous solution show a typical Pr(III) f−f transition between 400 and 600 nm. Four absorption bands of 190, 482, 442, and 442 nm could be attributed to $^3H_4 \rightarrow {}^1D_2$, $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^3P_1$ and $^3H_4 \rightarrow {}^1I_6$, and $^3H_4 \rightarrow {}^3P_2$.[9] The electronic spectra of **2** in an aqueous solution show a typical Er(III) f−f transition between 400 and 550 nm. Three absorption bands of 444, 488, and 521 nm could be attributed to $^4I_{15/2} \rightarrow {}^4F_{7/2}$ and $^4I_{15/2} \rightarrow {}^2H_{11/2}$.[10]

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The emission spectra of complex **2** at room temperature in an aqueous solution excited at 345 nm exhibited an intense band at 405 nm, which was assigned to the emission of $^2H_{9/2} \rightarrow {}^4I_{15/2}$.[11]

Variable-temperature (1.8−300 K) magnetic susceptibility data at a magnetic field strength of 2 kG were collected for compound **1** (Figure 4). The μ_{eff} value at room temperature was 3.41 μ_B, which is slightly lower than those expected, 3.58 μ_B, per insulated Pr(III) ion in the $^3H_4$ ground state ($g = {}^4/_5$). As far as the existence of a strong spin−orbit coupling for Ln atoms is concerned, the magnetic data were analyzed by the following approximate treatment equations previously derived by McPherson et al.[12]

$$\chi_{\text{Pr}} = \frac{Ng^2\beta^2}{kT}\,\frac{2e^{-\Delta/kT} + 8e^{-4\Delta/kT} + 18e^{-9\Delta/kT} + 32e^{-16\Delta/kT}}{1 + 2e^{-\Delta/kT} + 2e^{-4\Delta/kT} + 2e^{-9\Delta/kT} + 2e^{-16\Delta/kT}}$$

$$\chi_{\text{total}} = \chi_{\text{Pr}}/[1 - \chi_{\text{Pr}}(zJ'/Ng^2\beta^2)]$$

In expressions, Δ is the zero-field-splitting parameter. zJ' is the intermolecular magnetic coupling parameter. A least-squares fit to the data leads to $\Delta = -4.3$ cm^{-1}, $zJ' = -11.73$ cm^{-1}, $g = 0.79$, and $R = \sum(\chi_{\text{obsd}} - \chi'_{\text{calcd}})^2/\sum(\chi_{\text{obsd}})^2 = 4.21 \times 10^{-4}$. The absolute value of zJ' is slightly larger than that reported in the compound $Pr_2L(NO_3)_2(OH)_2$,[12] in which $zJ' = -7$. The negative zJ' suggested the antiferromagnetic interactions between the Pr(III) ions.

In summary, by using the hydrothermal reaction, two Ln(III) coordination polymers containing pyzcH and oxalates have been prepared. X-ray crystallography revealed that the polymers have novel two-dimensional hexagonal lattice networks. The magnetic properties of **1** suggested antiferromagnetic interactions between the Pr(III) ions. Complex **2** displayed an intense room-temperature liquid-state emission. Further experiments are underway to design novel coordination polymers associated with pyzcH and oxalate ligands and better understand the nature of 4f−4f magnetic interaction and the luminescence in these systems.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2**, UV−vis absorption spectra for **1** and **2**, and luminescence emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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