Synthesis and Structure of a New Erbium Porous Complex Assembled from 2,3-Pyrazinedicarboxylic Acid and Ammonia

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Research Article

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Abstract

A new erbium porous complex, \((\text{NH}_4)_2[\text{Er}_2(\text{pzdc})_4(\text{H}_2\text{O})_2]\), was synthesized through hydrothermal reaction of 2,3-pyrazinedicarboxylic acid and \(\text{Er(NO}_3)_3\cdot6\text{H}_2\text{O}\) with the pH value adjusted by ammonia. It was characterized by elemental analysis, FT-IR, TGA and further by single-crystal X-ray crystallography. It crystallizes in monoclinic, space group \(P2_1/c\) with \(a = 14.125(3)\,\text{Å},\ b = 15.706(2)\,\text{Å},\ c = 12.726(3)\,\text{Å},\ \beta = 95.714(4)^\circ,\ V = 2809.4(10)\,\text{Å}^3,\ Z = 4,\ D_c = 2.385\,\text{g/cm}^3,\ \mu(\text{MoK}\alpha) = 6.05\,\text{mm}^{-1}\) and \(F(000) = 2056.2056\). 2056 reflections were measured and 6446 independent reflections \((R_{\text{int}} = 0.0695)\) were used in further refinement. The complex exhibits a 3D framework constructed from the \([\text{Er}_2(\text{pzdc})_4(\text{H}_2\text{O})_2]^{2-}\) building blocks. It is scarce that the \(\text{NH}_4^+\) cations are located in the channels and balance the charge of anion framework. Furthermore, the ion exchange property of this complex has also been studied. The \(\text{NH}_4^+\) cations can be replaced by \(\text{Na}^+\) cations, which is an uncommon phenomenon for gadolinium-containing porous complex.

Introduction

The investigation of porous metal–organic frameworks (MOFs) has attracted much interest due to their structural diversity and promising applications for ion exchange, gas storage, separation, and catalysis\(^1\)–\(^5\). The multicarboxylic ligands have been widely used as bridging ligands to construct MOFs with diverse structures.

and topologies\(^6\), owing to their various coordination modes, strong coordination ability, chemical stability and structure rigidity\(^7\)–\(^8\). 2,3-pyrazinedicarboxylic acid \((\text{H}_2\text{pzdc})\) is a commonly used multifunctional ligand\(^9\)–\(^13\). However, much of the work has so far focused on the assembly of the d-block MOFs, while the lanthanon-based MOFs are relatively less developed\(^14\)–\(^15\)\(^16\)–\(^19\). In this paper, we report the syntheses, crystal structures, and ion exchange property of a new Erbium-based MOFs complex, \((\text{NH}_4)_2[\text{Er}_2(\text{pzdc})_4(\text{H}_2\text{O})_2]\), which was assembled from 2,3-pyrazinedicarboxylic acid and ammonia under hydrothermal condition.

Experimental

2.1 Reagents and physical measurements

All reagents and solvents were commercially purchased and used without further purification. Elemental contents of carbon, hydrogen and nitrogen were determined by a German Vario MICRO analyzer. IR spectrum of the complex was recorded on a SpectrumOne FT-IR spectrometer in the 4000–400 cm\(^{-1}\) region using KBr pellets at room temperature. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449C thermal analyzer under air atmosphere with a heating rate of 10°C min\(^{-1}\). Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance X-ray diffractometer using Cu-\(\text{Ka}\) radiation \((\lambda = 1.5418\,\text{Å})\), in which the X-ray tube was operated at 40 kV and 40 mA. The Inductively Coupled Plasma
OES spectrometer (ICP) data were recorded on Ultima2. Working band: 190-800 nm, Wavelength scanning step: 0.001 nm, Detection limit (LD): can be as low as 0.5 ppb.

### 2.2 Synthesis and characterization of the complex

A mixture of Er(NO₃)₃.6H₂O (0.2mmol), H₂pzdc(0.6mmol), H₃BO₃(0.4mmol), H₂O (8mL), was stirred in an ultrasonic equipment for 40 min. Then the solution was adjusted to pH 5 – 6 with 25% ammonia. It was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 120 °C for 72 h, and then slowly cooled to room temperature at a rate of 5 °C./h. A yellow single Prism-shaped crystal was recovered by filtration, washed with distilled water, and dried in air at room temperature. For the complex, Anal. Calc. for

C₂₄H₂₀Er₂N₁₀O₁₈(1071.00): calcd. C 25.99, H 1.81, N 12.52 ; Found: C, 26.91; H, 1.87; N, 13.07 %. Selected IR (KBr pellet, cm⁻¹): 3528(m), 1618(s), 1572(s), 1457(s), 1356(s), 1119(s), 890(m), 840(m), and 549(m). The bands at 3528 cm⁻¹ are N–H stretching vibration modes, and those at 3208 cm⁻¹ are the O–H stretching vibration modes of strong hydrogen bonds. The bands at 1618 and 1572 cm⁻¹ are the C=O stretching vibration modes of carboxylate groups. The band at 1457 cm⁻¹ can be assigned to the distortion vibration of NH₄⁺. At 1119 cm⁻¹, the stretching vibration of C–O is observed, and those at 890, 840 and 549 cm⁻¹ are the stretching vibration modes of C–H.

### 2.2 Structure determination

A colorless crystal of the title compound having approximate dimensions of 0.20mm × 0.20mm × 0.20mm was mounted on the top of a glass fiber. X-ray crystallographic data collection for the complex was performed on a Rigaku-CCD diffractometer equipped with a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by using the ω-scan mode at 293 K. All absorption corrections were applied using the CrystalClear program[20]. The structures were solved by direct methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The organic hydrogen atoms in the pzdca ligands were positioned geometrically, and allowed to ride on their parent C atoms. The hydrogen atoms on the water molecules and the ammonium cations were not located because the data is not good. The structure was refined on F² by full-matrix least-squares using the SHELXTL-97 program package[21,22]. A summary of the crystallographic data of this complex was presented in tables 1 and 2.

**Table 1**: Data collection and handling
Table 2: Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å²×10^3).
| Atom | x       | y       | z       | U       |
|------|---------|---------|---------|---------|
| Er1  | 0.06009 | 0.95301 | -0.18202 | 0.01096 |
| Er2  | 0.44399 | 0.69977 | 0.16235 | 0.01123 |
| O1   | 0.2216  | 0.9600  | -0.1699  | 0.0159  |
| O2   | 0.3623  | 1.0251  | -0.1429  | 0.0213  |
| O3   | 0.4169  | 1.2246  | -0.1560  | 0.0187  |
| O4   | 0.4131  | 1.1764  | 0.0094   | 0.0189  |
| O5   | -0.1266 | 0.7267  | -0.1636  | 0.0225  |
| O6   | -0.0650 | 0.8567  | -0.1785  | 0.0190  |
| O7   | -0.0519 | 0.5843  | -0.0152  | 0.0193  |
| O8   | -0.0417 | 0.5440  | -0.1810  | 0.0250  |
| O9   | 0.0720  | 0.8803  | -0.3387  | 0.0238  |
| O10  | 0.0865  | 0.9733  | 0.1646   | 0.0167  |
| O11  | 0.0855  | 0.9373  | -0.0053  | 0.0168  |
| O12  | 0.2818  | 0.7069  | 0.1407   | 0.0175  |
| O13  | 0.1408  | 0.7711  | 0.1206   | 0.0184  |
| O14  | 0.5694  | 0.6026  | 0.1663   | 0.0196  |
| O15  | 0.6329  | 0.4752  | 0.1408   | 0.0225  |
| O16  | 0.5550  | 0.3166  | 0.0159   | 0.0173  |
| O17  | 0.5474  | 0.2925  | 0.1875   | 0.0207  |
| O18  | 0.4297  | 0.6281  | 0.0232   | 0.0174  |
| N1   | 0.1286  | 1.0966  | -0.1207  | 0.0124  |
| N2   | 0.2173  | 1.2541  | -0.0845  | 0.022   |
| N3   | 0.1122  | 0.7971  | -0.1450  | 0.0138  |
| N4   | 0.1465  | 0.6254  | -0.0986  | 0.0183  |
| N5   | 0.3742  | 0.8481  | 0.1132   | 0.0142  |
| N6   | 0.2838  | 1.0054  | 0.1010   | 0.0170  |
| N7   | 0.3931  | 0.5439  | 0.1246   | 0.0144  |
| N8   | 0.3598  | 0.3694  | 0.0996   | 0.0185  |
| N9   | -0.1940 | 0.9435  | -0.3547  | 0.024   |
| N10  | 0.2964  | 1.1941  | 0.1750   | 0.0168  |
| N11  | 0.2241  | 1.1050  | -0.1205  | 0.013   |
| N12  | 0.2683  | 1.1825  | -0.0980  | 0.0108  |
| N13  | 0.1256  | 1.2445  | -0.0850  | 0.021   |
| N14  | 0.0890  | 1.2919  | -0.0723  | 0.026   |
| N15  | 0.0798  | 1.1665  | -0.1035  | 0.015   |
| N16  | 0.0140  | 1.1634  | -0.1038  | 0.018   |
| N17  | 0.2738  | 1.0238  | -0.1453  | 0.018   |
| N18  | 0.3760  | 1.1950  | -0.0793  | 0.0129  |
| N19  | 0.0399  | 0.7417  | -0.1379  | 0.016   |
| N20  | 0.0587  | 0.6553  | -0.1141  | 0.012   |
| N21  | 0.2174  | 0.6801  | -0.1095  | 0.023   |
| N22  | 0.2797  | 0.6602  | -0.1036  | 0.028   |
| N23  | 0.2000  | 0.7667  | -0.1297  | 0.016   |
| N24  | 0.2512  | 0.8036  | -0.1325  | 0.019   |
| N25  | -0.0584 | 0.7774  | -0.1614  | 0.016   |
| N26  | -0.0204 | 0.5901  | -0.1033  | 0.015   |
| N27  | 0.2791  | 0.8545  | 0.1107   | 0.0123  |
| N28  | 0.2336  | 0.9328  | 0.1000   | 0.014   |
| N29  | 0.3785  | 0.9978  | 0.1041   | 0.020   |
| N30  | 0.4153  | 1.0468  | 0.1037   | 0.023   |
| N31  | 0.4235  | 0.9191  | 0.1077   | 0.016   |
| N32  | 0.4891  | 0.9163  | 0.1063   | 0.020   |
| N33  | 0.2296  | 0.7709  | 0.1234   | 0.017   |
| N34  | 0.1255  | 0.9474  | 0.0861   | 0.014   |
Results And Discussion

3.1  Description of crystal structures

X-ray diffraction studies revealed that the complex with three-dimensional structures. In the complex, there are four fully-deprotonated pyrazine-2,3-dicarboxylic acid ligand (pzdc), two Er ions and two ammonium cations. See Fig. 1. The ligand pzdc have two kinds of coordination motions, which one is a pzdc ligand coordinated with two Er$^{3+}$, the other is one pzdc ligand coordinated with three Er$^{3+}$ See Fig. 2. The Er1 ion is coordinated by five pzdc ligands. Two pzdc ligands, which are in the same asymmetric unit, both chelate the Er1 ion through an -O-C-C-N- loop. Three carboxylate oxygens from different pzdc ligands (O8, O10, O11) are coordinated to Er 1 in the monodentate fashion. Additionally, one aqua ligand (O9) ligates to Er1 to meet the eight-coordination of the Er1 ion. See Fig. 3. Like the Er 1 ion, the Er 2 ion is also coordinated by five pzdc ligands, of which two adopt the -O-C-C-N- loop fashion to chelate the Er2 ions, and the other three pzdc ligands (O3, O16, O17) ligate to the Er2 ion in the monodentate mode through the carboxylate groups. To complete the coordination sphere of the Er2 ion, one water molecule is coordinated to the Er2 ion as a terminal ligand (O18). In the complex, the Er-O distances range from 2.249 (7) to 2.587 (8) Å, the Er-N distances range from 2.546 (8) to 2.583 (8) Å, which are all reasonable.

In the crystal, [Er$_2$(pzdc)$_4$(H$_2$O)$_2$]$^{2-}$ units connect each other through the coordination of carboxylate groups to the Er ions forming a 3D network structures with channels along the a and b axis. (See Fig. 4) The NH$_4^+$ cations are located in the channels. Not only do they balance the charges of anion framework but also they are hydrogen bonded to the carboxylate groups O atoms surrounding them. The anion framework is stabilized by these N–H...O hydrogen Bonds.

3.2.  Thermal behavior

To evaluate the thermal stability of the complexes, their thermal gravimetric analysis (TGA) have been performed and found the complex can be seen that there is no significant mass loss up to about 325°C, and then has one step of continuous mass loss between 325°C and 800°C, corresponding to the decomposition of the complex. The higher decomposition temperature indicates that the framework of the two complexes possesses good thermal stability. The TGA curve of the complex is shown in Fig. 5. It can be seen that the complex is stable up to about 325°C.
3.3. XRD patterns

The X-ray powder diffraction data of the complex was collected. As shown in Fig. 6, the experimental XRD pattern agree well with the simulated pattern generated on the basis of the single-crystal analyses for compound, suggesting the phase purity of the product.

3.3. Ion exchange property

Single-crystal X-ray diffraction shows that the complex exhibit 3D network structure based on the \([\text{Er}_2(\text{pzdc})_4(\text{H}_2\text{O})_2]^{2-}\) building blocks. The \(\text{NH}_4^+\) cations are located in the channels and balance the charge of anion framework. The ion exchange property of the complex in the solid state was investigated at room temperature. The complex was added into the aqueous solution of saturated sodium chloride as ion exchanger. Then stirred for 6 hours and lay up for 3 days at room temperature. The precipitation was filtered and washed with water and ethanol three times, then dried in an oven at 50°C. Then got the content of \(\text{Na}^+\) was 0.79 % by ICP. This is a uncommon experimental phenomenon for gadolinium porous complex. The experiment results show that the \(\text{NH}_4^+\) cations can be replaced by other cations. The further research is still in progress.

Conclusions

A new lanthanide porous complex \((\text{NH}_4)_2[\text{Er}_2(\text{pzdc})_4(\text{H}_2\text{O})_2]\) has been synthesized under hydrothermal conditions and exhibit 3D network structure. The complex has ion exchange property and present better thermal stability before 325°C.

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Declarations

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Author contributions

Y.K. designed, statistically analyzed and wrote the manuscript.

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Supplementary material

“CCDC 760471” contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

Competing interests

The author declares no competing interests.

Figures
Figure 1

The asymmetric unit of complex
Figure 2
The coordinate modes of ligand in complex

Figure 3
The coordinate modes of Er$^{3+}$ in complex
Figure 4

The 3D structure of the complex along a and b axis
Figure 5

TG curve of the complex

Figure 6

The XRD patterns of the complex: (a) simulated; (b) experimental.