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## CRYSTAL STRUCTURE OF A LANTHANUM(III) COMPLEX WITH PYRAZINE-2-CARBOXYLATE AND WATER LIGANDS

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The structure of (aqua-*O*)di(pyrazine-2-carboxylate-*N,O-μ-O*)mono(pyrazine-2-carboxylate-*N,O*)lanthanum (III) dihydrate contains La(III) ions, each coordinated by three pyrazine-2-carboxylate (PYR) ligands via their N,O bonding moieties and a water molecule forming an La(PYR)<sub>3</sub>·(H<sub>2</sub>O) structural unit. In addition, each La(III) ion is coordinated by two carboxylate oxygen atoms each belonging to a ligand chelated to a different adjacent metal ion, giving rise to a bridging system. Three bridging paths are observed: one links the structural units into pairs, the others link the pairs into molecular sheets. The carboxylate group of the third ligand coordinates only one carboxylate oxygen atom leaving the second unbonded to the metal ion. The coordination number of the La(III) ion is nine. Solvation and coordinated water molecules participate in a network of hydrogen bonds which also contributes to the stability of the molecular arrangement.

*Keywords:* Lanthanum(III) complexes; Pyrazine-2-carboxylate ligand; X-ray diffraction

### INTRODUCTION

Pyrazine-2-carboxylate (PYR) is known to form monomeric complexes with a number of divalent ions, such as, for example, UO<sub>2</sub><sup>2+</sup> [1], calcium(II) and strontium(II) [2], and 3d transition metal ions [3], exhibiting the coordination modes characteristic for a particular central ion. In all of these complexes the pyrazine-2-carboxylate ligand coordinates its N, O bonding moiety, consisting of the heteroring nitrogen atom and the oxygen atom belonging to the nearest carboxylate group. The second pyrazine ring nitrogen atom does not participate in coordination. No information has been available up to now about the structures of pyrazine-2-carboxylate complexes with 4f trivalent ions. This article describes the structure of such a complex for the first time.

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## EXPERIMENTAL

The title compound was obtained by mixing aqueous solutions of 1 mmol of lanthanum(III) nitrate and 5 mmol of pyrazine-2-carboxylic acid. The pH of the mixture was adjusted to 5 by adding a few drops of 10% hydrazine hydrate. After concentrating the mixture over a water bath to one half of its volume, it was left to crystallize at 5°C. Pale yellow, needle-shaped single crystals separated after a week. Yield 40%. Anal. Found (Calcd.) (%): La 24.02 (24.32); C 30.78 (31.51); H 2.73 (2.80); N 13.97 (14.70). The dimensions of a single crystal used for obtaining X-ray diffraction data are given in Table I.

X-ray reflections were measured at room temperature using a KUMA KM4 four-circle diffractometer operating in  $\omega$ - $2\theta$  mode with two standard reflections monitored every 200 measured reflections. Unit cell dimensions and standard deviations were obtained by a least-squares fit to 35 reflections ( $15^\circ < 2\theta < 30^\circ$ ). Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. An analytical absorption correction was applied. Nonhydrogen ions were located by the Patterson method using the SHELXLS program [4] and hydrogen atoms were then found by successive Fourier syntheses. A final refinement on  $F^2$  by the least-squares

TABLE I Crystal data and structure refinement details for  $\text{La}(\text{PYR})_3(\text{H}_2\text{O}) \cdot 2.5\text{H}_2\text{O}$ 

|   |   |
|---|---|
| Empirical formula                                   | $\text{C}_{15}\text{H}_{16}\text{N}_6\text{O}_{9.5}\text{La}$   |
| Formula weight                                      | 571.2   |
| $T$ (K)   | 293   |
| $\lambda$ (Å)                                       | 0.71073   |
| Crystal system                                      | Orthorhombic  |
| Space group   | <i>Pbcn</i>   |
| Unit cell dimensions                                |   |
| $a$ (Å)   | 16.154(3)   |
| $b$ (Å)   | 12.357(2)   |
| $c$ (Å)   | 20.525(4)   |
| $V$ (Å <sup>3</sup> )                               | 4097.0  |
| $Z$   | 8   |
| $D_{\text{calcd}}$ (g cm <sup>-3</sup> )            | 1.852   |
| $\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )          | 2.15  |
| $F(000)$  | 2248.0  |
| Crystal size (mm <sup>3</sup> )                     | 0.07 $\times$ 0.1 $\times$ 0.2                                  |
| Max. $2\theta$ for data collection (°)              | 60.06   |
| Index range   | $-22 \leq h \leq 0$<br>$0 \leq k \leq 17$<br>$0 \leq l \leq 28$ |
| No. of measured reflections                         | 4099  |
| No. of unique reflections with $F_o > 4\sigma(F_o)$ | 3393  |
| $R_{\text{int}}$                                    | 0.0266  |
| Method of structure solution                        | Patterson   |
| Method of structure refinement                      | Full-matrix least-squares on $F^2$                              |
| No. of parameters refined                           | 338   |
| Goodness-of-fit on $F^2$                            | 0.960   |
| Absorption correction                               | Analytical  |
| Min. and max. transmission factors                  | 0.5992, 0.6734  |
| Final $R_1$ [ $F_o > 4\sigma(F_o)$ ]                | 0.0291  |
| Final $wR_2$ index                                  | 0.0887  |
| Largest diff. peak and hole (e Å <sup>-3</sup> )    | 1.52 and -0.87  |
| Weight parameters ( $A, B$ )                        | 0.0544, 11.16   |
| Mean shift/esd                                      | 0.13  |

method was performed on the positional parameters of all atoms, anisotropic temperature factors of all non-H-atoms and isotropic temperature factors of hydrogen atoms. The weighting scheme used was of the form  $w = 1/[\sigma^2(F_o^2) + (A \times P)^2 + (B \times P)]$ , where  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ .  $A$  and  $B$  are the parameters listed in Table I. Calculations were carried out using the SHELXL-97 program [5]. Final atomic coordinates and equivalent isotropic displacements are listed in Table II, and selected bond lengths

TABLE II Fractional atomic coordinates and equivalent isotropic displacements parameters for  $\text{La}(\text{PYR})_3(\text{H}_2\text{O}) \cdot 2.5\text{H}_2\text{O}$

| <i>Atom</i> | <i>x</i>   | <i>y</i>   | <i>z</i>   | $U_{eq}$ (Å <sup>2</sup> ) |
|-------------|------------|------------|------------|----------------------------|
| La          | 0.82566(2) | 0.45250(2) | 0.55676(1) | 0.01911(8)                 |
| C12         | 0.8525(4)  | 0.4783(4)  | 0.7249(3)  | 0.0385(12)                 |
| C13         | 0.8772(7)  | 0.5195(6)  | 0.7842(4)  | 0.0753(28)                 |
| C15         | 0.8269(6)  | 0.6842(5)  | 0.7539(3)  | 0.0620(20)                 |
| C16         | 0.8071(4)  | 0.6448(5)  | 0.6939(3)  | 0.0404(12)                 |
| C17         | 0.8613(4)  | 0.3582(4)  | 0.7081(2)  | 0.0376(11)                 |
| C22         | 0.9871(3)  | 0.3254(4)  | 0.4692(2)  | 0.0253(8)                  |
| C23         | 1.0393(3)  | 0.2475(4)  | 0.4225(3)  | 0.0355(11)                 |
| C25         | 1.0058(4)  | 0.1322(4)  | 0.5241(3)  | 0.0390(12)                 |
| C26         | 0.9533(3)  | 0.2077(4)  | 0.5506(3)  | 0.0330(10)                 |
| C27         | 0.9784(3)  | 0.4368(3)  | 0.4404(2)  | 0.0239(8)                  |
| C32         | 0.7118(3)  | 0.6243(3)  | 0.4493(2)  | 0.0257(9)                  |
| C33         | 0.6647(3)  | 0.6661(4)  | 0.3999(2)  | 0.0336(11)                 |
| C35         | 0.6460(5)  | 0.4980(5)  | 0.3587(3)  | 0.0479(15)                 |
| C36         | 0.6930(4)  | 0.4556(4)  | 0.4083(3)  | 0.0367(12)                 |
| C37         | 0.7494(3)  | 0.6931(3)  | 0.5023(2)  | 0.0230(8)                  |
| N11         | 0.8195(3)  | 0.5395(3)  | 0.6788(2)  | 0.0306(3)                  |
| N12         | 0.8661(6)  | 0.6247(5)  | 0.7986(3)  | 0.0922(28)                 |
| N21         | 0.9431(2)  | 0.3046(3)  | 0.5291(2)  | 0.0259(8)                  |
| N22         | 1.0480(3)  | 0.1502(4)  | 0.4496(3)  | 0.0422(11)                 |
| N31         | 0.7260(3)  | 0.5170(3)  | 0.4539(2)  | 0.0262(8)                  |
| N32         | 0.6305(3)  | 0.6045(4)  | 0.3534(2)  | 0.0436(11)                 |
| O1          | 0.6771(3)  | 0.4594(4)  | 0.5963(2)  | 0.0469(11)                 |
| O2          | 0.50       | 0.5795(7)  | 0.25       | 0.0789(23)                 |
| O3          | 0.6024(4)  | 0.5837(3)  | 0.6906(3)  | 0.0785(17)                 |
| O4          | 0.8767(4)  | 0.2957(5)  | 0.8911(3)  | 0.0608(14)                 |
| O11         | 0.8464(2)  | 0.3329(3)  | 0.6506(2)  | 0.0348(8)                  |
| O12         | 0.8812(4)  | 0.2944(3)  | 0.7517(2)  | 0.0711(17)                 |
| O21         | 0.9134(2)  | 0.4877(3)  | 0.4552(2)  | 0.0289(7)                  |
| O22         | 0.9641(2)  | 0.5288(3)  | 0.5946(2)  | 0.0289(7)                  |
| O31         | 0.7947(2)  | 0.6474(3)  | 0.5428(2)  | 0.0305(7)                  |
| O32         | 0.7671(2)  | 0.2918(2)  | 0.5018(2)  | 0.0304(7)                  |
| H11         | 0.665(4)   | 0.492(6)   | 0.626(4)   | 0.05(2)                    |
| H12         | 0.638(5)   | 0.440(6)   | 0.581(4)   | 0.05(2)                    |
| H13         | 0.902(9)   | 0.504(11)  | 0.821(6)   | 0.17(6)                    |
| H15         | 0.811(6)   | 0.774(8)   | 0.778(5)   | 0.13(4)                    |
| H16         | 0.782(4)   | 0.689(5)   | 0.658(3)   | 0.04(2)                    |
| H23         | 1.068(3)   | 0.258(4)   | 0.4000(2)  | 0.02(1)                    |
| H25         | 1.017(3)   | 0.076(4)   | 0.545(2)   | 0.02(1)                    |
| H26         | 0.936(6)   | 0.218(8)   | 0.591(5)   | 0.12(4)                    |
| H33         | 0.662(3)   | 0.745(5)   | 0.393(3)   | 0.03(1)                    |
| H35         | 0.624(5)   | 0.459(6)   | 0.334(4)   | 0.07(3)                    |
| H36         | 0.706(5)   | 0.380(6)   | 0.402(4)   | 0.07(2)                    |
| H21         | 0.518      | 0.674      | 0.271      | 0.27(8)                    |
| H31         | 0.595      | 0.513      | 0.704      | 0.10(3)                    |
| H32         | 0.531      | 0.602      | 0.719      | 0.3(1)                     |
| H41         | 0.879      | 0.299      | 0.842      | 0.06(2)                    |
| H42         | 0.903(8)   | 0.327(11)  | 0.902(6)   | 0.15(6)                    |

TABLE III Selected bond lengths (Å) and angles (°) for La(PYR)<sub>3</sub>(H<sub>2</sub>O) · 2.5H<sub>2</sub>O

| <i>Lanthanum(III) coordination</i>    |           |                            |          |
|---------------------------------------|-----------|----------------------------|----------|
| La–O11                                | 2.450(3)  | N11–La–O22                 | 66.8(1)  |
| La–O21                                | 2.557(3)* | O22–La–N21                 | 73.4(1)  |
| La–O31                                | 2.475(3)* | N21–La–O11                 | 72.6(1)  |
| La–O22                                | 2.549(3)* | O11–La–N11                 | 61.4(1)  |
| La–O32                                | 2.472(3)* | O1–La–O31                  | 79.2(1)  |
| La–O1                                 | 2.535(4)  | O31–La–O21                 | 81.5(1)  |
| La–N11                                | 2.728(4)  | O21–La–O32                 | 88.7(1)  |
| La–N21                                | 2.724(4)  | O32–La–O1                  | 79.0(1)  |
| La–N31                                | 2.771(4)  | O1–La–N31                  | 71.6(2)  |
| *Bridging                             |           | O31–La–N31                 | 61.0(1)  |
|                                       |           | O21–La–N31                 | 69.0(1)  |
|                                       |           | O32–La–N31                 | 70.2(1)  |
| <i>Pyrazine-2-carboxylate ligands</i> |           |                            |          |
| N11–C12                               | 1.324(7)  | C16–N11–C12                | 116.5(5) |
| C12–C13                               | 1.377(8)  | N11–C12–C13                | 122.5(5) |
| C13–N12                               | 1.346(9)  | C12–C13–N12                | 120.9(7) |
| N12–C15                               | 1.335(9)  | C13–N12–C15                | 116.4(6) |
| C15–C16                               | 1.362(8)  | N12–C15–C16                | 122.4(6) |
| C16–N11                               | 1.352(6)  | C15–C16–N11                | 121.1(6) |
| C12–C17                               | 1.530(7)  |                            |          |
| C17–O11                               | 1.245(6)  | O11–C17–O12                | 125.3(5) |
| C17–O12                               | 1.236(6)  |                            |          |
| N21–C22                               | 1.338(6)  | C26–N21–C22                | 117.2(4) |
| C22–C23                               | 1.392(6)  | N21–C22–C23                | 120.9(4) |
| C23–N22                               | 1.335(7)  | C22–C23–N22                | 121.6(5) |
| N22–C25                               | 1.330(8)  | C23–N22–C25                | 116.6(5) |
| C25–C26                               | 1.377(7)  | N22–C25–C26                | 122.5(5) |
| C26–N21                               | 1.336(6)  | C25–C26–N21                | 121.2(5) |
| C22–C27                               | 1.504(6)  |                            |          |
| C27–O21                               | 1.262(6)  | O21–C27–O22 <sup>III</sup> | 126.1(4) |
| C27–O22 <sup>III</sup>                | 1.248(5)  |                            |          |
| N31–C32                               | 1.350(5)  | C36–N31–C32                | 116.5(4) |
| C32–C33                               | 1.369(7)  | N31–C32–C33                | 121.1(4) |
| C33–N32                               | 1.340(7)  | C32–C33–N32                | 122.8(5) |
| N32–C35                               | 1.344(8)  | C33–N32–C35                | 115.0(5) |
| C35–C36                               | 1.372(8)  | N32–C35–C36                | 122.5(6) |
| C36–N31                               | 1.319(6)  | C35–C36–N31                | 122.0(5) |
| C32–C37                               | 1.509(6)  |                            |          |
| C37–O31                               | 1.243(5)  | O31–C37–O32 <sup>I</sup>   | 125.1(4) |
| C37–O32 <sup>I</sup>                  | 1.248(5)  |                            |          |
| <i>Coordinated water molecule</i>     |           |                            |          |
| O1–H11                                | 0.75(7)   | H11–O1–H12                 | 106(7)   |
| O1–H12                                | 0.74(8)   |                            |          |
| <i>Hydrogen bonds</i>                 |           |                            |          |
| D–H...A                               | D–A       | H–A                        | D–H–A    |
| O1–H11...O3                           | 2.756(4)  | 2.04(4)                    | 167.5(5) |
| O1–H12...N22 <sup>IV</sup>            | 2.827(4)  | 1.94(4)                    | 173.0(6) |
| O3–H31...O2 <sup>VI</sup>             | 2.873(5)  | 2.13(6)                    | 136.2(6) |
| O3–H32...O12 <sup>I</sup>             | 2.899(5)  | 2.01(6)                    | 137.1(3) |
| O4–H41...O12                          | 2.852(5)  | 1.86(5)                    | 175.2(4) |
| O4–H42...O21 <sup>V</sup>             | 3.050(3)  | 2.44(3)                    | 160.9(4) |

Symmetry code: <sup>I</sup>– $x+3/2, y+1/2, z$ ; <sup>II</sup>– $x+3/2, y-1/2, z$ ; <sup>III</sup>– $x+2, -y+1, -z+1$ ; <sup>IV</sup>– $x-1/2, y+1/2, -z+1$ ; <sup>V</sup>– $x, -y+1, z+1/2$ ; <sup>VI</sup>– $x+1, -y+1, -z+1$ .

and angles in Table III. The observed and calculated structure factors and anisotropic thermal parameters can be obtained from the authors on request. Detailed data on the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre under the code number CCDC 217825.

## RESULTS AND DISCUSSION

The  $\text{La}^{+3}$  ion is coordinated by three pyrazinate (PYR) ligands and a water molecule forming an  $\text{La}(\text{PYR})_3 \cdot (\text{H}_2\text{O})$  structural unit. Each PYR ligand donates one heteroring nitrogen atom N11, N21 or N31 and the nearest carboxylate oxygen atom O11, O21 or O31 forming three bonding N,O moieties. The second heteroring nitrogen atoms of the pyrazine ring N12, N22 and N32 remain unbonded to the metal ion. In addition, the  $\text{La}^{+3}$  ion is coordinated by two carboxylate oxygen atoms O22 and O32, belonging to the pyrazinate ligands chelated to adjacent metal ions. In this way, the latter are bridged by two carboxylate groups via their oxygen atoms. The observed bridging path  $\text{La}-\text{O}21-\text{C}27-\text{O}22^{\text{III}}-\text{La}^{\text{III}}$  links adjacent  $\text{La}(\text{PYR})_3 \cdot (\text{H}_2\text{O})$  units into pairs. Two other paths,  $\text{La}-\text{O}31-\text{C}37-\text{O}32^{\text{I}}-\text{La}^{\text{I}}$  and  $\text{La}-\text{O}32-\text{C}37^{\text{II}}-\text{O}31^{\text{II}}-\text{La}^{\text{II}}$ , link the pairs into molecular sheets (for atom labeling see Fig. 1 and the symmetry code given in Table III). The carboxylate group of the third ligand donates only one carboxylate oxygen atom O11 leaving the second O12 unbonded to the metal ion. Thus the coordination number of the  $\text{La}^{3+}$  ion is nine. The coordination polyhedron can be visualized as a monocapped square antiprism with N31 atom at the apical position (Fig. 3). The atoms O11, O22, N11 and N21, which form the square base of the polyhedron, show maximum displacement from the mean plane amounting to 0.293(2) Å. The maximum deviation from the mean plane formed by the atoms O1, O31, O32 and O21, which form the base of the pyramidal cap, is 0.094(2). The dihedral angle formed by the above planes is 9.4°. The same shape of the coordination polyhedron has been reported in the structures of Nd(III) complex with pyridine-2-carboxylate

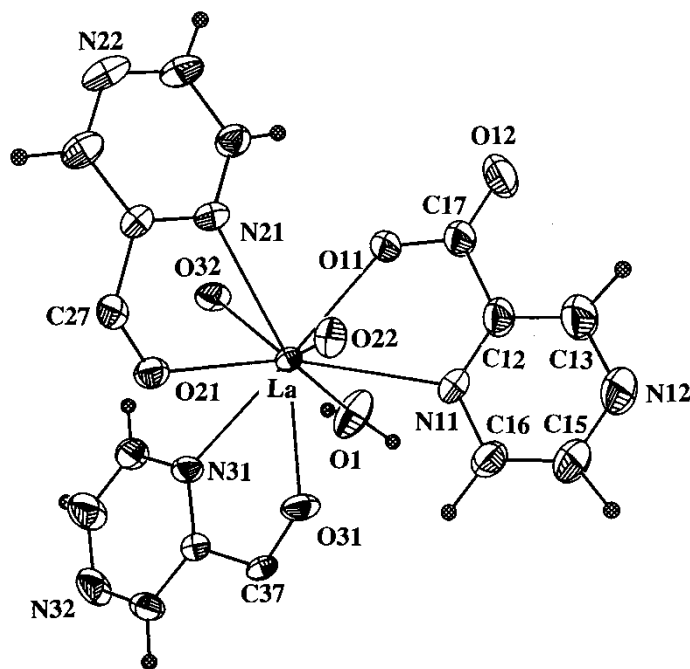


FIGURE 1 The structural unit  $\text{La}(\text{PYR})_3 \cdot (\text{H}_2\text{O})$  with atom labeling scheme. Nonhydrogen atoms are shown as 50% probability ellipsoids. For clarity, labeling of carbon and hydrogen atoms in two pyrazine rings is omitted.

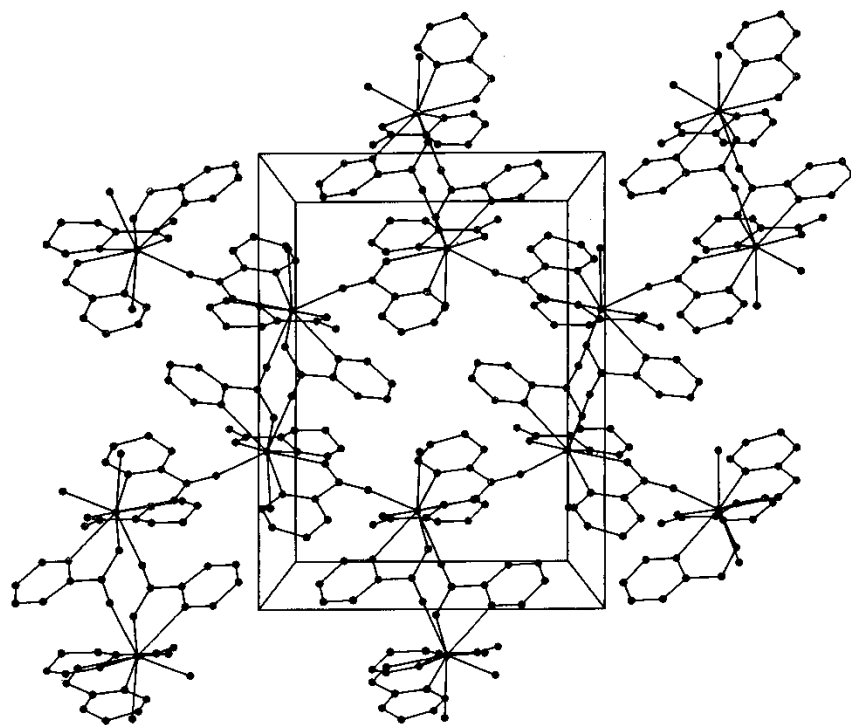
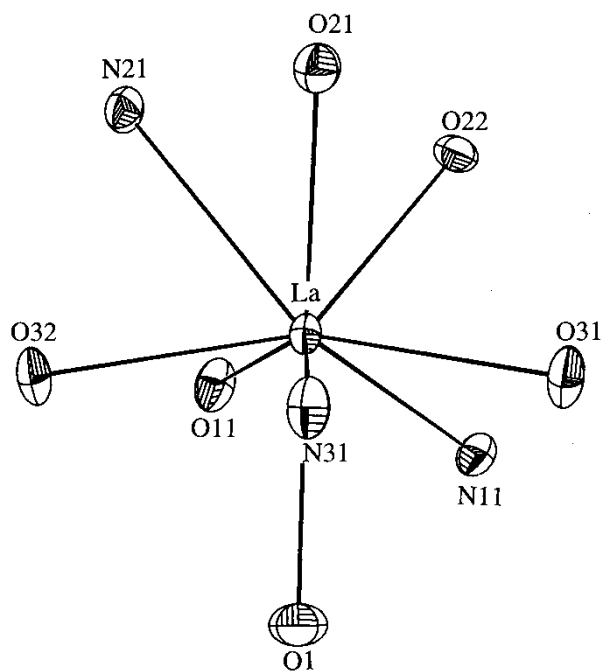
FIGURE 2 Packing diagram of La(PYR)<sub>3</sub>(H<sub>2</sub>O) · 2.5H<sub>2</sub>O.

FIGURE 3 The coordination polyhedron of the La(III) ion viewed along the La–N31 bond.

and water ligands [6] and an isostructural Ho(III) complex [7] as well as in the structure of an La(III) complex with pyridine-2,6-dicarboxylate and water ligands [8]. All of these compounds exhibit polymeric molecular patterns, although the metal ions are bridged by oxygen atoms belonging only to one bidentate carboxylate group and form one bridging path giving rise to a catenated molecular ribbon. The observed La–O and La–N bond distances in the title compound differ slightly from those reported previously [8]: the mean La–O distance is 2.541 Å as compared to 2.501 Å in the title compound. The relevant La–N mean distances are 2.670 and 2.741 Å.

As one solvation water molecule oxygen O2 is situated in a special position (see Table II), there are in fact 2.5 solvation water molecules for each  $\text{La}(\text{PYR})_3 \cdot (\text{H}_2\text{O})$  unit. These solvation water molecules and the coordinated water molecule take part in a network of hydrogen bonds that assures additional stability of the crystal packing. For example, the coordinated water molecule acts as a donor in two moderately strong hydrogen bonds to one of the solvation water molecules and to an unbonded heteroring nitrogen atom in the adjacent  $\text{La}(\text{PYR})_3 \cdot (\text{H}_2\text{O})$  unit. On the other hand, the carboxylate oxygen atoms are acceptors in hydrogen bonds donated by one of the solvation water molecules (for details, see Table III).

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