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**Journal of Chemical and Pharmaceutical Research, 2014, 6(7):1895-1902**

**Research Article**

**ISSN : 0975-7384**
**CODEN(USA) : JCPRC5**

# Synthesis and characterization of some new phenyl hydrazinium rare earth(III) dipicolinates hydrates: Crystal and molecular structure of lanthanum complex

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## ABSTRACT

*Several new phenyl hydrazinium Ln(III) pyridine-2,6-dicarboxylate hydrates have been synthesized in aqueous medium and characterized by metal and elemental analyses, UV-visible and infrared spectra, thermal analyses, X-ray powder diffraction and X-ray single crystal techniques. The* $La^{III}N_3O_6$ *part in the complex anion has a nine-coordinated structure in which the nine coordinated atoms (three N and six O) from three pyridine-1,6-dicarboxylate ions are coordinated to the central rare earth metal ion directly. The crystal of the lanthanum complex belongs to the trigonal crystal packing system with p-3 space group. The crystal data are: a=16.4870(3) Å, b=16.4870(3) Å, c=9.2900(2) Å,* $\alpha=\beta=90^o$ *and* $\gamma=120^o$*, V=2186.90(7)* $Å^3$*. The final R and Rw are 0.0338 and 0.0799 for reflection 2581 with [I> 2σ (I)]. The volume and calculated density of the crystal are 2186.90(7) Å and 1.562* $mg/m^3$*.*

**Keywords:** Phenyl hydrazinium, pyridine-2,6-dicarboxylate(PDC), molecular structure, TG-DTA.

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## INTRODUCTION

Lanthanide coordination chemistry has been a resurgence of interest over the past two decades is due to the rich functionality of the ground and excited states of lanthanide complexes. The properties of these coordination complexes in aqueous solutions which are of great importance not only scientifically but also biologically and medically and hence commercially too. Lanthanides both in crystalline complexes as well as in solutions, show variable secondary valencies (6 to 12) in which coordination number 9 is the most predominant and several geometries are thus observed, leading to limiting success in the design of molecular architecture with predetermined structure[1]. General observations reveal that the complexations in aqueous medium are regarded as the partial replacement of water molecules from the coordination sphere by a strong N,O-containing chelating ligands. The extent of substitution depends on several factors like pH, composition and chemical environment. Hence, most of the complexes isolated in aqueous solutions were found to be hydrated and these water molecules present in 1st, 2nd and 3rd coordination spheres of the lanthanum(III) ions. Indeed water of hydration and Ln-$OH_2$ bond length play a dominant role in binding of Ln(III) ions to the biomolecules which are the ultimate factors deciding their potential as drug materials. The inherent strong oxyphilicity of lanthanide causes the interaction binding sites being COOH, OH (phenolic, hydroxylic), O (carbonyl), N (amino, imino, imido) and S (sulphydryl).

Antioxidants are excellent substances used as drugs for the treatment of degenerative diseases. Tocopherol, ascorbates and a number of other organic compounds are considered as components of such drugs due to their antioxidant property shown towards ROS (Reactive Oxygen Species) induced degenerative diseases[2]. Lanthanides are considered as high potentials because of their inherent antioxidant properties. The lanthanide inhibiting ROS involves strong oxyphilicity inherent in lanthanides, because of the availability of oxygen sites on these free radicals, makes them excellent targets for Ln(III) coordination. This causes lanthanide to play the role of scavenger of ROS, therefore presenting good potential for lanthanide as a future drug for a number of degenerative diseases due to ROS. The involvement of lanthanide in ROS is quite different from that by organic compounds like ascorbic acid. Most of the organic oxidants scavenge free radicals by single electron exchange with radicals and thus transform themselves into radicals, hence acting as 'pro-oxidants'. $Ln^{3+}$ very easily interacts with either free radicals or peroxides but is not transformed as radicals. However, the mechanistic understanding about the role of Ln(III) as scavenger of oxidants is very meager.

The lability of lanthanide complexes, strongly oxyphilicity, very fast water exchange reactions (rate constant 5 x $10^7$ $s^{-1}$), non-directionality of lanthanide-ligand bond and varying coordination number, all contribute towards lanthanide interaction with biomolecules.

The complexes of lanthanides are getting more and more applications in cancer therapy and the most important of these are those derive from polyaminocarboxylic acids. The formation constants of these lanthanide chelates with these acids are of the order of $10^{20}$ to $10^{25}$, which enables them to remain intact, while diffusing into extracellular spaces with rapid clearance through kidneys. Due to the high thermodynamic stability and extreme kinetic inertness of these Ln-polyaminocarboxylate chelates, the intact excretion enhances, thereby lowering the body retention of chelated Ln(III) complexes.

Recent investigations on hydrazinium[3-5] and phenyl hydrazinium[6] complexes of lanthanide carboxylates are limited to ethylenediaminetetraacetic acid. Dipicolinic acid with O,N,O chelating mode also capable of coordination with transition metal ions and lanthanide(III) ion has not been studied in detail. Neverthless, recently two transition metal complexes of picolinic acid with phenyl hydrazinium cation has been reported[7,8]. The tridentate coordination with lanthanide ions are expected to yield complexes with coordinated sphere could exclusively occupied by the ligand without water molecules which are scarce and expected only in the presence of cations like $Na^+$, $K^+$,$Li^+$ etc[9]. However, hydrazinium and phenyl hydrazinium cations having dual tendency to act either as coordinating and non-coordinating species leads to unpredictable geometries. However, due to the steric effect, phenyl hydrazinium ion may prefer to stay outside the sphere, still the nine coordinated structure with or without water molecules in the primary sphere is possible. Hence, it is considered interesting to study phenyl hydrazinium complex of lanthanide dipicolinates and the result of their investigations is presented in this paper.

## EXPERIMENTAL SECTION

The chemicals used were of AnalaR or equivalent grade. Phenyl hydrazine, $La_2O_3$, $Pr_6O_{11}$, $Sm_2O_3$, $Dy_2O_3$ and $Yb_2O_3$ were used as received from Sigma Aldrich. The Ln(III) nitrates, ligands and complexes were prepared and analyses were carried out using fresh doubly distilled water and the solvents were distilled before use. The metal contents were determined by complexometric titrations after decomposing the complex with concentrated nitric acid to eliminate the organic part[9]. The C,H and N analyses were carried out using a Perkin-Elmer model 1240 CHN analyzer. The electronic absorption spectra of the complexes in water were recorded on a Systronics Double Beam UV-VIS spectrophotometer model 2202. The infrared spectra of the solid samples in the range 400-4000 $cm^{-1}$ were recorded on a Thermo NICOLET AVATAR 330 FT-IR spectrophotometer using KBr pellets. The TG-DTA curves were recorded on a SWI TG/DTA 6200 thermal analyzer using about 5 mg of the samples with the heating rate of $10^oC$ per min and platinum cups as sample holders. X-ray powder diffraction patterns were recorded on a Druker D8-Focus diffractometer with a scan speed 5 sec/step using Cu-Kα radiation ($\lambda$=1.540598 Å) and scintillation counter as a detector.

### X-ray structure determination

The X-ray intensity data were collected on a Enras 7 - Nonius CAD-4 diffractometer system with graphite monochromated Mo-Kα radiation ($\lambda$=0.71073 Å). The structure was solved by direct methods using SIR92 program and completed using Fourier techniques and refined by applying full matrix least square techniques. Refinement was carried out using SHELXL-97 program[10,11]. Most of the hydrogen atoms could be located in difference

Fourier map. Their positions were constrained at chemically idealized positions wherever geometry permitted. These hydrogen atoms were given riding model refinement. Other hydrogen atoms were isotropically refined.

### Synthesis of $(C_6H_5N_2H_4)_3[Ln(OOC\text{-}C_5H_3N\text{-}COO)_3].6H_2O$

The lanthanide nitrate hydrates were prepared by decomposing their respective lanthanide oxides (La = 1.63 g, Sm = 1.74 g, Pr = 1.72 g, Dy = 1.87 g, Yb = 1.97 g – all metal oxides 10 mmols) in dilute nitric acid and evaporating the resultant solution to dryness. The lanthanide nitrate hydrate thus obtained was dissolved in 20 mL of distilled water and used for the preparation of the complex.

To an aqueous solution (40 mL) of PDCA (3.34 g, 20 mmols), phenylhydrazine (4.325 g, 40 mmols) in 10mL water was added slowly with constant stirring. The resulting contents were mixed with the respective rare earth metal (III) nitrate hydrate (10 mmols) with constant stirring. The resulting precipitate was continuously refluxed in a round bottomed flask. The precipitate was dissolved slowly while refluxing and a clear solution was obtained after 8 h. The clear solution was concentrated to one-third of its original volume and allowed to cool at room temperature. After 24 h to 48 h, the crystals formed were removed, washed several times with ice cold distilled water and dried in air. Analytical data of the complexes are given in table 1.

**Table 1. Percentage composition of elements**

| Complex | Mol. Wt. | Colour | Yield (%) | Found (Calc.) (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | N | Metal |
| La | 1069.77 | dirty white | 75 | 43.74<br>(43.68) | 4.52<br>(4.42) | 11.77<br>(11.68) | 12.98<br>(12.91) |
| Pr | 1071.77 | pale green | 80 | 43.66<br>(43.76) | 4.51<br>(4.40) | 11.75<br>(11.62) | 13.15<br>(13.26) |
| Sm | 1081.22 | dark yellow | 80 | 43.28<br>(43.18) | 4.47<br>(4.52) | 11.65<br>(11.50) | 13.91<br>(13.78) |
| Dy | 1093.37 | Colourless | 70 | 42.80<br>(42.92) | 4.42<br>(4.30) | 11.52<br>(11.44) | 14.87<br>(14.69) |
| Yb | 1103.91 | Colourless | 70 | 42.39<br>(42.33) | 4.38<br>(4.20) | 11.03<br>(11.38) | 15.68<br>(15.50) |

## RESULTS AND DISCUSSION

Phenyl hydrazinium rare earth metal(III) pyridine-2,6-dicarboxylate hydrates, $(C_6H_5N_2H_4)_3[Ln(OOC\text{-}C_5H_3N\text{-}COO)_3].6H_2O$ where Ln = La, Pr, Sm, Dy and Yb were prepared by the aqueous reactions between pyridine-2,6-dicarboxylic acid, phenyl hydrazine and the respective rare earth metal (III) nitrate hydrates. The crystals obtained are stable in air and soluble in water. The compositions of the complexes were determined by metal and micro analyses.

### Electronic Spectra

An aqueous solution of La(III), Dy(III) and Yb(III) complexes show very big absorption band in the visible region as expected since these complexes are nearly colourless. However, Pr(III) and Sm(III) complexes show number of sharp bands in the visible region characteristic of f-block elements.

### Infrared Spectra

All the complexes show several sharp bands in the region 3000-3500 $cm^{-1}$ which are attributed to the presence of N-H stretching of phenyl hydrazinium cation and O-H stretching of water molecules. The N-N stretching of phenyl hydrazinium moiety for the complexes is found at 960 $cm^{-1}$ indicting the ionic nature[12]. The $\nu_{asy}$ and $\nu_{sym}$ stretchings of carboxylate groups are observed in the range 1620 $cm^{-1}$ and 1390 $cm^{-1}$ indicating their monodentate coordination behaviour. In the present cases, $\nu_{asy}$- $\nu_{sym}$ = $\Delta\nu$ is found to be more than 225 $cm^{-1}$ indicating some degree of covalency in the metal-carboxylate bonds[13]. Several other bands are observed between 800 and 1300 $cm^{-1}$, which though are characteristic of complexes and are useful for identification purpose do not show any significant correlations.

### Thermal Analyses

The simultaneous TG-DTA of complexes in air and nitrogen atmospheres were recorded to understand the number and nature of water molecules present and also to know the degradation patterns and end residues formed during the pyrolysis of ligand. The simultaneous TG-DTA traces of all the five complexes show almost similar patterns. These complexes undergo dehydration in two stages between 60-150°C with approximately 7% weight loss indicating the removal of four water molecules. Both TG and DTA show two stages for this dehydration which is attributed to the difference in hydrogen bonding interaction of three water molecules (removed at lower temperature) from the other three molecules. The mass loss is in well accordance with the calculated weight loss. The anhydrous complexes thus formed undergo decomposition (endothermic) and ligand pyrolysis (exothermic) in multi stages to yield respective oxides as the final residue at 600°C. The final weight loss very well coincides with the theoretical weight loss for the formation of respective oxides. Due to the instability of the intermediates at higher temperatures and continuous decomposition of the anhydrous complexes, we were unable to isolate the intermediates for further characterization. However, the formation of respective rare earth metal oxides was confirmed by heating 1g of the respective powdered complexes at 600°C for about 15 minutes and weighing the final residues formed. The theoretical and experimental weight losses match very well indicating the formation of anticipated oxides.

### X-ray Diffraction Pattern

The X-ray powder diffraction pattern of all the complexes are found to be super imposable and hence expected to possess similarity in structure and bonding. The infra red spectra of these complexes are also super imposable which along with X-ray powder diffraction pattern suggest isomorphism along the series.

### Crystal and Molecular Structure

#### Phenyl hydrazinium lanthanum tris(pyridine-2,6-dicarboxylate) hexahydrate $(C_6H_5N_2H_4)_3[La(OOC\text{-}C_5H_3N\text{-}COO)_3].6H_2O$

The lanthanum complex is nine coordinated and each La(III) ion is surrounded by three pyridine dicarboxylate (PDC) ions which coordinates in a tridentate chelating fashion with one nitrogen and two carboxylate oxygen atoms. This results in the formation of two five membered rings with each PDC ion. Hence, ultimately six such rings are established around the La(III) ion and stabilizes the complex molecule. In the present case, surprisingly water molecules are not coordinated to the central metal ion but present outside the coordination sphere as lattice water. Furthermore, as expected, due to the steric factor, the heavier phenyl hydrazinium ions present as charge neutralizing counter ions and hence present outside the coordination sphere along with water molecules.

In aqueous solutions, lanthanide(III) ions form aqueated complexes with uncertain composition, $[Ln(H_2O)_n]^{3+}$ from which water molecules are replaced by strong chelating ligand containing N and O as donor atoms. Hence, it is expected that the water molecules inside the sphere are usually partially replaced by ligands depending on the ratio of the metal ion to the ligand and some of the water molecules always present inside the coordination sphere as coordinated water. This will largely reduces the overcrowding of chelating ligands around the metal ion. Several hydrazinium complexes studied with variety of carboxylic acids like EDTA, CDTA, DTPA etc., were found to possess one or more coordinated water molecules. However, the present case is the rare occasion without coordinated water molecules. It is also proposed that aqueated species should be $[Ln(H_2O)_9]^{3+}$.

The unit cell has only two complex molecules which are mainly associated through intermolecular hydrogen bonds that play a vital role in stabilizing the crystal structure. It is quite understandable that the intermolecular hydrogen bonding is due to the presence of six lattice water molecules and three phenyl hydrazinium cations which also have a weak impact on the combination. The net structure is formed through the hydrogen bonds and static interactions.

The selected bond distances and bond angles of lanthanum complex are given in Table 3. The ORTEP and crystal packing diagrams are shown in Figs. 1 and 2 respectively.

## CONCLUSION

Novel phenyl hydrazinium Ln(III) pyridine-2,6-dicarboxylate hydrates have been synthesized and their chemical composition were assigned on the basis of elemental and metal analyses. The IR spectra of all the complexes show N-N stretching of phenyl hydrazinium moiety in the range 960 - 965 cm$^{-1}$ indicting the ionic nature.

The simultaneous TG-DTA traces of all the five complexes indicate that they undergo multi stage decomposition to give their respective metal oxides as the final residue. The X-ray powder diffraction pattern of all the complexes are found to be super imposable and hence expected to possess similarity in structure and bonding.

The single crystal X-ray diffraction study reveals that the $La^{III}N_3O_6$ part in the complex anion has a nine-coordinated structure in which the nine coordinated atoms (three N and six O) from three pyridine-2,6-dicarboxylate ions are coordinated to the central rare earth metal ion directly. The crystal of the lanthanum complex belongs to the trigonal crystal packing system with p-3 space group.

**Acknowledgement**
We sincerely acknowledge SAIF, IIT Madras, Chennai for recording single crystal X-ray diffraction data and Dr. Babu Varghese, SAIF, IIT Madras, Chennai for useful suggestions in solving and refining the structures.

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**Supplementary material**

Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition number: CCDC - 915922).

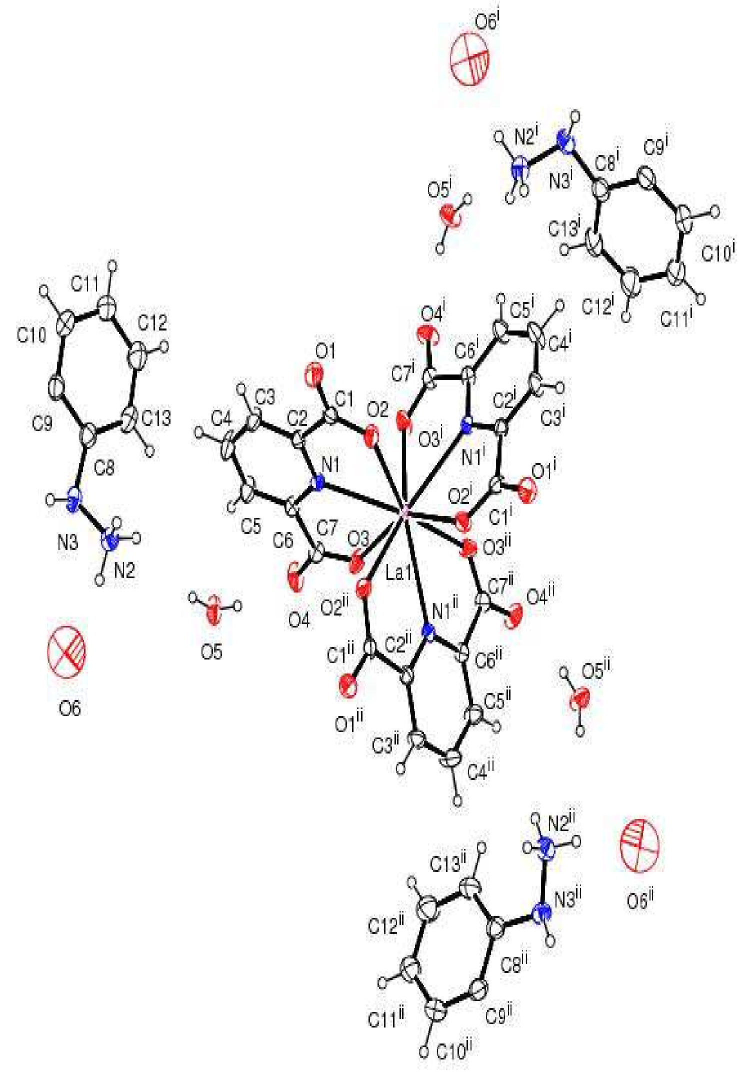

**Fig. 1 ORTEP diagram of lanthanum complex**

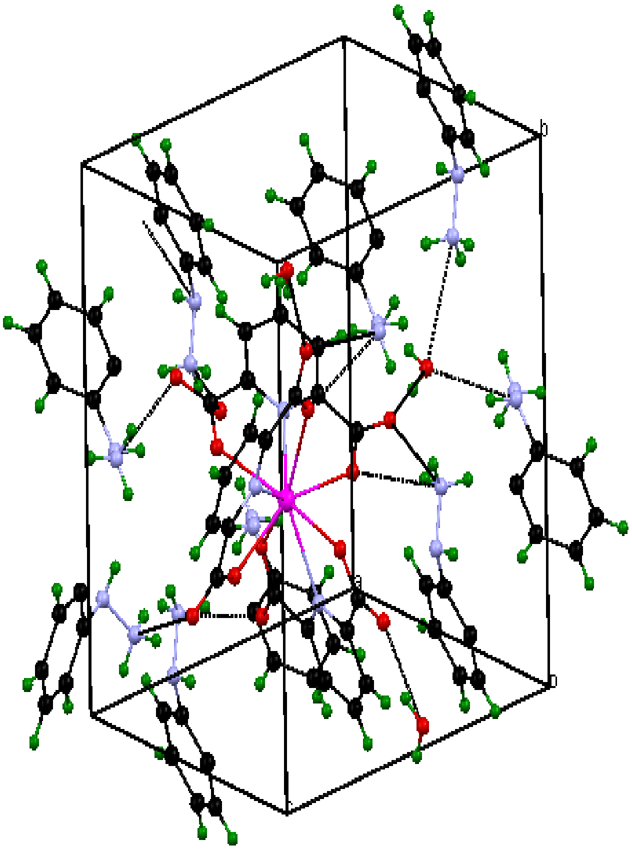

**Fig. 2 Packing diagram of lanthanum complex**

**Table 2. Crystal data and structure refinement of lanthanum complex**

| | |
|---|---|
| Identification code | shelxl |
| Empirical formula | $C_{39} H_{39} La N_9 O_{16}$ |
| Formula weight | 1069.77 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Trigonal, P-3 |
| Unit cell dimensions | a = 16.4870(3) A alpha = 90 deg.<br>b = 16.4870(3) A beta = 90 deg.<br>c = 9.2900(2) A gamma = 120 deg. |
| Volume | 2186.90(7) A^3 |
| Z, Calculated density | 2, 1.562 Mg/m^3 |
| Absorption coefficient | 1.058 mm^-1 |
| F(000) | 1042 |
| Crystal size | 0.15 x 0.15 x 0.10 mm |
| Theta range for data collection | 2.19 to 24.99 deg. |
| Limiting indices | -19<=h<=17, -18<=k<=19, -11<=l<=11 |

| | |
|---|---|
| Reflections collected / unique | 12117 / 2581 [R(int) = 0.0441] |
| Completeness to theta | = 24.99 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9359 and 0.8486 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2581 / 6 / 230 |
| Goodness-of-fit on F^2 | 1.111 |
| Final R indices [I>2sigma(I)] | R1 = 0.0273, wR2 = 0.0733 |
| R indices (all data) | R1 = 0.0338, wR2 = 0.0799 |
| Largest diff. peak and hole | 1.080 and -0.563 e.A^-3 |

**Table 3. Selected bond lengths [A] and bond angles [deg] of lanthanum complex**

| **Bond Length [Å]** | | **Bond Angle [deg]** | |
|---|---|---|---|
| | | C(6)-N(1)-La(1) | 120.74(16) |
| | | C(2)-N(1)-La(1) | 120.36(17) |
| | | C(1)-O(2)-La(1) | 126.66(16) |
| N(1)-La(1) | 2.640(2) | C(7)-O(3)-La(1) | 126.97(16) |
| O(2)-La(1) | 2.5264(18) | O(2)#1-La(1)-O(2)#2 | 78.03(7) |
| O(3)-La(1) | 2.5275(19) | O(2)#1-La(1)-O(2) | 78.04(7) |
| La(1)-O(2)#1 | 2.5264(18) | O(2)#2-La(1)-O(2) | 78.04(7) |
| La(1)-O(2)#2 | 2.5264(18) | O(2)#1-La(1)-O(3)#1 | 122.54(6) |
| La(1)-O(3)#1 | 2.5275(19) | O(2)#2-La(1)-O(3)#1 | 151.25(7) |
| La(1)-O(3)#2 | 2.5275(19) | O(2)-La(1)-O(3)#1 | 86.55(7) |
| La(1)-N(1)#1 | 2.640(2) | O(2)#1-La(1)-O(3)#2 | 86.55(7) |
| La(1)-N(1)#2 | 2.640(2) | O(2)#2-La(1)-O(3)#2 | 122.53(6) |
| | | O(2)-La(1)-O(3)#2 | 151.25(7) |
| | | O(3)#1-La(1)-O(3)#2 | 81.47(8) |
| | | O(2)#1-La(1)-O(3) | 151.25(7) |
| | | O(2)#2-La(1)-O(3) | 86.55(7) |
| | | O(2)-La(1)-O(3) | 122.53(6) |
| | | O(3)#1-La(1)-O(3) | 81.47(8) |
| | | O(3)#2-La(1)-O(3) | 81.47(8) |
| | | O(2)#1-La(1)-N(1)#1 | 61.37(6) |
| | | O(2)#2-La(1)-N(1)#1 | 134.96(6) |
| | | O(2)-La(1)-N(1)#1 | 75.37(6) |
| | | O(3)#1-La(1)-N(1)#1 | 61.19(6) |
| | | O(3)#2-La(1)-N(1)#1 | 75.95(6) |
| | | O(3)-La(1)-N(1)#1 | 138.48(7) |
| | | O(2)#1-La(1)-N(1) | 134.96(6) |
| | | O(2)#2-La(1)-N(1) | 75.37(6) |
| | | O(2)-La(1)-N(1) | 61.36(6) |
| | | O(3)#1-La(1)-N(1) | 75.95(6) |
| | | O(3)#2-La(1)-N(1) | 138.48(7) |
| | | O(3)-La(1)-N(1) | 61.19(6) |
| | | N(1)#1-La(1)-N(1) | 119.985(2) |
| | | O(2)#1-La(1)-N(1)#2 | 75.37(6) |
| | | O(2)#2-La(1)-N(1)#2 | 61.36(6) |
| | | O(2)-La(1)-N(1)#2 | 134.96(6) |
| | | O(3)#1-La(1)-N(1)#2 | 138.48(7) |
| | | O(3)#2-La(1)-N(1)#2 | 61.19(6) |
| | | O(3)-La(1)-N(1)#2 | 75.95(6) |
| | | N(1)#1-La(1)-N(1)#2 | 119.984(2) |
| | | N(1)-La(1)-N(1)#2 | 119.986(2) |

**Symmetry transformations used to generate equivalent atoms:**
**#1 -x+y+1,-x+1,z #2 -y+1,x-y,z**