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Diaquatris(nitrato-κ^2O,O')bis(4-pyridone-κO)-lanthanum(III)

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.016
wR factor = 0.040
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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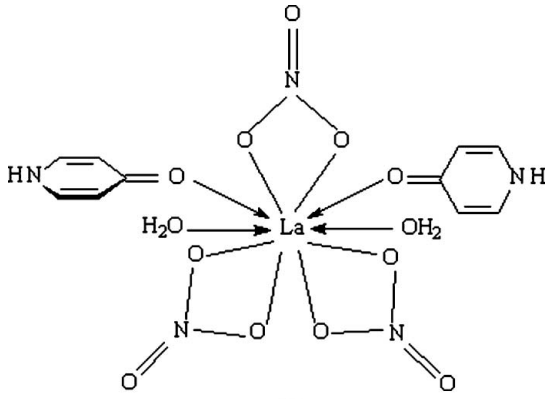
In the mononuclear title compound, $[La(NO_3)_3(C_5H_5NO)_2(H_2O)_2]$, the La^{III} atom is ten-coordinate, with a coordination polyhedron made up of the O atoms of two 4-pyridone ligands, six O atoms of three O,O'-chelating nitrate groups and two water molecules, the polyhedron approximating a dodecahedron. The molecule lies on a twofold rotation axis. A three-dimensional network structure is formed by hydrogen-bonding and π–π stacking interactions.

Comment

4-Hydroxypyridine (4-PyOH) is a bifunctional ligand that is capable of binding to metal centers and also forming classical hydrogen bonds (as both donor and acceptor) (Kawata *et al.*, 1997). It exists in the tautomeric 4-pyridone form. In contrast to the many metal complexes of the related 2-hydroxypyridine, there are few reports of structures of complexes of 4-hydroxypyridine or 4-pyridone (Masse & Le Fur, 1998). We have recently reported the structures of two mononuclear Co complexes, one dimeric Cu complex and one catenated Ag complex, *viz.* $[CoCl_2(4\text{-pyridone})_2]$ (Gao, Lu, Huo, Zhao & Zhao, 2004), $[Co(NO_3)(4\text{-pyridone})_2(H_2O)_2](NO_3)$ (Lu, Gao, Huo, Zhang *et al.*, 2004), $[Cu_2(acetate)_4(4\text{-pyridone})_2]$ (Lu, Gao, Huo, Zhao & Zhao, 2004) and $[Ag(4\text{-PyO})(4\text{-PyOH})]_n$ (Gao, Lu, Huo & Zhao, 2004). When La^{III} interacts with the ligand, the resulting title mononuclear complex, $[La(4\text{-pyridone})_2(NO_3)_3(H_2O)_2]$, (I), has the metal center in a ten-coordinate environment (Fig. 1).



(I)

The La^{III} ion is ten-coordinated by the O atoms of two 4-pyridone ligands, six O atoms of three chelating nitrate ions and two water molecules in a docecahedral geometry (Fig. 2). The molecule lies on a twofold rotation axis. The C1—C2, C4—C5 and C3—O1 bond lengths are 1.362 (3), 1.351 (3) and

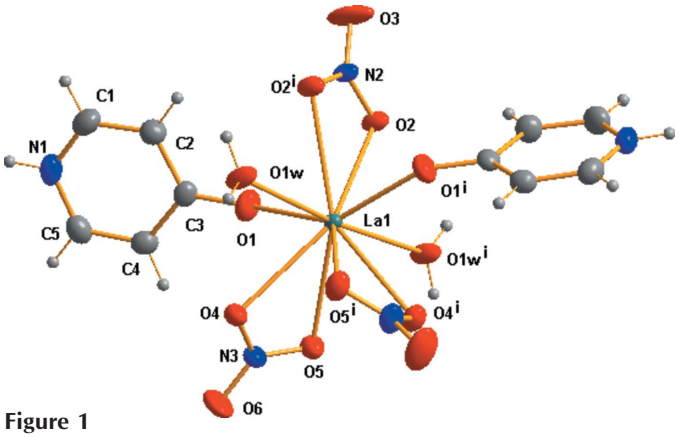


Figure 1
ORTEPII plot (Johnson, 1976) of (I), with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.]

1.278 (2) Å; the distances are in agreement with those of a 4-pyridone form. The water molecules and the O atoms of nitrate ligands form extensive intermolecular hydrogen bonds (Table 2), connecting the molecules into a layer structure. There are π–π stacking interactions between adjacent 4-pyridone rings, with a centroid–centroid separation of 3.789 (3) Å; the π–π stackings lead to a three-dimensional supramolecular network.

Experimental

Lanthanum trinitrate tetrahydrate (3.97 g, 10 mmol) was added to an aqueous solution of 4-PyOH (1.05 g, 10 mmol). The solution was allowed to evaporate at room temperature, and colorless prismatic single crystals were isolated after five days. Analysis calculated for $C_{10}H_{14}LaN_5O_{13}$: C 21.79, H 2.56, N 12.71%; found: C 21.76, H 2.54, N 12.75%.

Crystal data

$[La(NO_3)_3(C_5H_5NO)_2(H_2O)_2]$
$M_r = 551.17$
Monoclinic, $C2/c$
$a = 11.051$ (2) Å
$b = 8.9055$ (18) Å
$c = 19.203$ (4) Å
$\beta = 96.31$ (3)°
$V = 1878.4$ (7) Å^3
$Z = 4$
$D_x = 1.949$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8926 reflections
$\theta = 3.1$–27.5°
$\mu = 2.35$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
0.36 × 0.25 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scan
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.494$, $T_{max} = 0.645$
8972 measured reflections
2150 independent reflections
2106 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -11 \rightarrow 11$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.040$
$S = 1.24$
2150 reflections
139 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 0.6564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

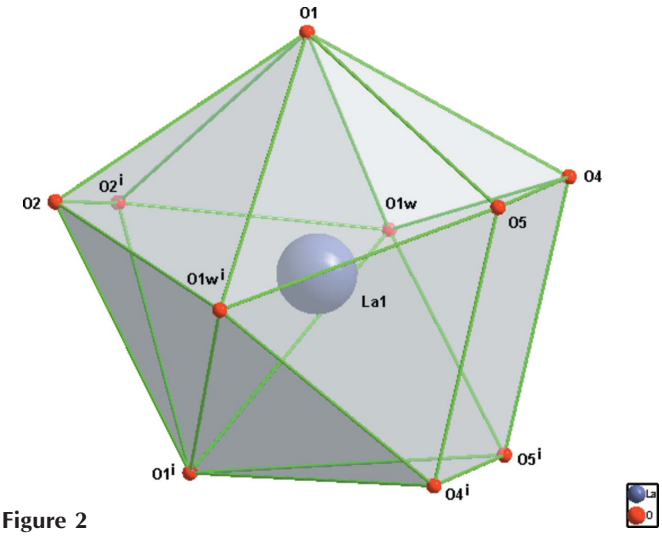


Figure 2
The coordination dodecahedron of the La atom in (I). [Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.]

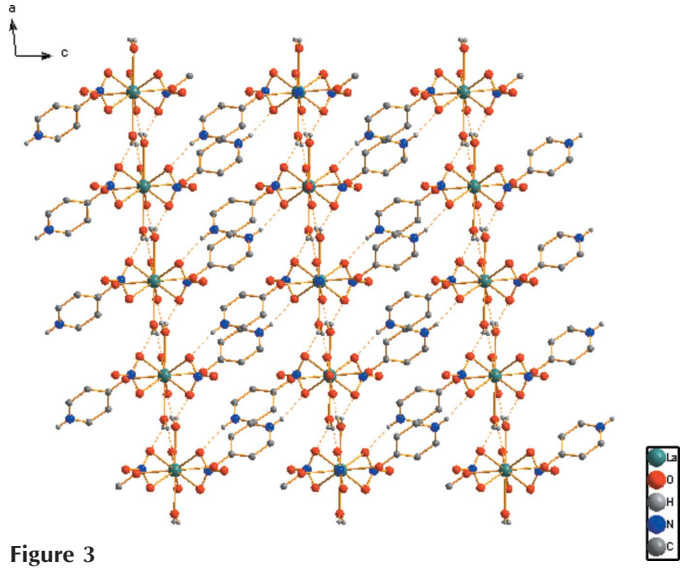


Figure 3
Packing diagram of the title complex, viewed along the *b* axis. The hydrogen bonds are shown as dashed lines.

Table 1
Selected geometric parameters (Å, °).

La1—O1*w*	2.5452 (15)	La1—O5	2.6978 (15)
La1—O1	2.3830 (14)	O1—C3	1.278 (2)
La1—O2	2.6946 (14)	C1—C2	1.362 (3)
La1—O4	2.6612 (14)	C4—C5	1.351 (3)
O1*w*^{i}—La1—O1*w*	174.03 (7)	O1—La1—O4	71.41 (6)
O1*w*—La1—O2	110.25 (4)	O1—La1—O5^{i}	134.74 (6)
O1*w*—La1—O2^{i}	63.80 (4)	O1—La1—O5	75.34 (6)
O1*w*—La1—O4^{i}	115.57 (5)	O2—La1—O2^{i}	47.15 (5)
O1*w*—La1—O4	69.26 (5)	O2—La1—O5	118.39 (5)
O1*w*—La1—O5	116.39 (5)	O2—La1—O5^{i}	150.30 (5)
O1*w*—La1—O5^{i}	68.40 (5)	O4—La1—O2^{i}	124.24 (5)
O1^{i}—La1—O1	144.20 (9)	O4—La1—O2	143.27 (5)
O1—La1—O1*w*	83.79 (7)	O4—La1—O4^{i}	83.82 (7)
O1—La1—O1*w*^{i}	94.37 (7)	O4—La1—O5	47.18 (5)
O1—La1—O2	72.05 (6)	O4—La1—O5^{i}	65.69 (5)
O1—La1—O2^{i}	75.21 (6)	O5—La1—O5^{i}	85.69 (8)
O1—La1—O4^{i}	140.92 (6)		

Symmetry code: (i) $-x+1, y, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1w—H1w1···O5^{ii}	0.85 (1)	2.27 (1)	3.087 (2)	161 (3)
O1w—H1w2···O2^{iii}	0.85 (1)	2.03 (1)	2.873 (2)	171 (3)
O1w—H1w2···O3^{iii}	0.85 (1)	2.51 (3)	3.0296 (16)	121 (2)
N1—H6···O4^{iv}	0.86	2.05	2.849 (2)	153

Symmetry codes: (ii) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

The H atoms attached to C atoms and 4-pyridone N atoms were placed in calculated positions, with C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(C,N), and were refined in the riding-model approximation. The water H atoms were located in a difference map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, and with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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