

Poly[*diaqua-μ-oxalato-μ-pyrazine-2-carboxylato-lanthanum(III)*]

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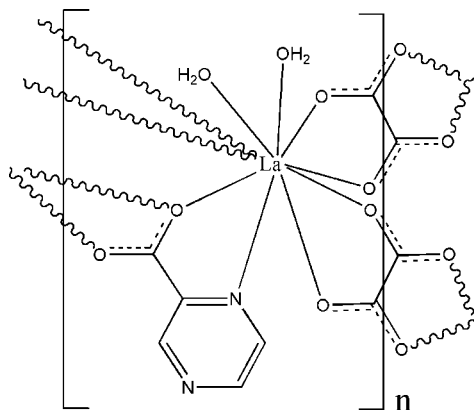
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.031; wR factor = 0.078; data-to-parameter ratio = 11.6.

In the title complex, $[\text{La}(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, the La^{III} ion is coordinated by one N and three O atoms from two pyrazine-2-carboxylate ligands, by four O atoms from two oxalate ligands and by two O atoms of two water molecules, displaying a distorted bicapped square-antiprismatic geometry. The carboxylate groups of pyrazine-2-carboxylate and oxalate ligands link the lanthanum metal centres, forming layers parallel to $(10\bar{1})$. The layers are further connected by intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions, forming a three-dimensional supramolecular network.

Related literature

For general background, see: Eddaoudi *et al.* (2001); Rizk *et al.* (2005); Zeng *et al.* (2007).



Experimental

Crystal data

$[\text{La}(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]$
 $M_r = 386.06$
 Triclinic, $P\bar{1}$
 $a = 8.040$ (3) Å
 $b = 8.7343$ (18) Å
 $c = 8.8329$ (18) Å
 $\alpha = 115.552$ (2)°
 $\beta = 101.447$ (3)°

$\gamma = 95.789$ (3)°
 $V = 536.1$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 4.02$ mm⁻¹
 $T = 296$ (2) K
 $0.17 \times 0.16 \times 0.14$ mm

Data collection

Bruker APEXII area-detector diffractometer
 Absorption correction: multi-scan (APEX2; Bruker, 2004)
 $T_{\text{min}} = 0.548$, $T_{\text{max}} = 0.603$
 (expected range = 0.518–0.569)

2761 measured reflections
 1898 independent reflections
 1787 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.078$
 $S = 1.07$
 1898 reflections
 163 parameters

6 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1W}-\text{H1W}\cdots\text{N1}^{\text{i}}$	0.84	1.97	2.796 (6)	170
$\text{O2W}-\text{H3W}\cdots\text{O2}^{\text{ii}}$	0.84	1.94	2.737 (5)	157
$\text{O1W}-\text{H2W}\cdots\text{O3}^{\text{iii}}$	0.84	2.05	2.874 (5)	167
$\text{O2W}-\text{H4W}\cdots\text{O6}^{\text{iv}}$	0.84	2.09	2.825 (5)	146

Symmetry codes: (i) $x, y - 1, z - 1$; (ii) $x, y, z - 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x + 1, -y, -z$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEPIII (Burnett & Johnson, 1996), PLATON (Spek, 2003) and SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2413).

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supplementary materials

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Poly[diaqua- μ -oxalato- μ -pyrazine-2-carboxylato-lanthanum(III)]

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Comment

The design, synthesis, characterization, and properties of supramolecular networks formed by using functionalized organic molecules as bridges between metal centers are of great interest (Eddaoudi *et al.*, 2001; Rizk *et al.*, 2005; Zeng *et al.*, 2007). As a building block, pyrazine-2-carboxylic acid and oxalic acid are excellent candidates for the construction of supramolecular complexes. Herein, we reported the new coordination polymer, (I).

In (I), each La^{III} centre is coordinated by seven oxygen atoms and one nitrogen atom from two pyrazine-2-carboxylate ligands, two oxalate ligands and two water molecules (Fig. 1), and represents a distorted bicapped square antiprismatic geometry. The La^{III} ions are linked by pyrazine-2-carboxylate ligands and oxalate ligands to form layers parallel to the (1 0 -1) plane (Fig. 2), and the adjacent La \cdots La separations are 6.570 (4) and 4.506 (5) Å, respectively. O—H \cdots O and N—H \cdots O hydrogen bonds (Table 1), involving the pyrazine-2-carboxylate ligands, coordinating water molecules and oxalate ligands assemble neighboring layers into a three-dimensional supramolecular network motif.

Experimental

A mixture of La₂O₃ (0.245 g; 0.75 mmol), pyrazine-2-carboxylic acid (0.186 g; 1.5 mmol), oxalic acid (0.135 g; 1.5 mmol), water (10 mL) in the presence of HNO₃ (0.024 g; 0.385 mmol) was stirred vigorously for 20 min and then sealed in a Teflon-lined stainless-steel autoclave (20 mL, capacity). The autoclave was heated and maintained at 433 K for 3 days, and then cooled to room temperature at 5 K h⁻¹ and obtained the colorless block crystals.

Refinement

Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of O—H = 0.84 Å and H \cdots H = 1.35 Å, and with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$. In the last cycles of refinement they were treated as riding on the O atoms. Carbon-bound H atoms were placed at calculated positions and were treated as riding on their parent C atoms with C—H = 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

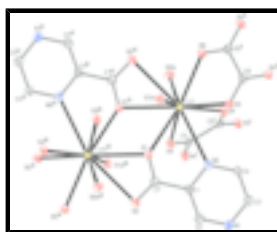


Fig. 1. ORTEP view showing the atomic-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) 1-x, -y, -z; (iii) 1-x, -y, 1-z]

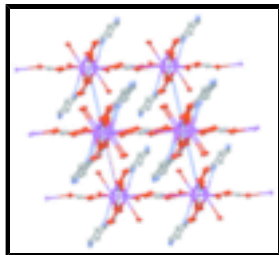


Fig. 2. View of the layered network of the title structure.

Poly[*diaqua-μ-oxalato-μ-pyrazine-2-carboxylato-lanthanum(III)*]

Crystal data

[La(C₅H₃N₂O₂)(C₂O₄)(H₂O)₂]

M_r = 386.06

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 8.040 (3) Å

b = 8.7343 (18) Å

c = 8.8329 (18) Å

α = 115.552 (2)°

β = 101.447 (3)°

γ = 95.789 (3)°

V = 536.1 (3) Å³

Z = 2

*F*₀₀₀ = 368

D_x = 2.391 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6377 reflections

θ = 1.7–28.0°

μ = 4.02 mm⁻¹

T = 296 (2) K

Block, colourless

0.17 × 0.16 × 0.14 mm

Data collection

Bruker APEXII area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 296(2) K

φ and ω scans

Absorption correction: multi-scan
(APEX2; Bruker, 2004)

*T*_{min} = 0.548, *T*_{max} = 0.603

2761 measured reflections

1898 independent reflections

1787 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.020

θ_{max} = 25.2°

θ_{min} = 2.6°

h = -5→9

k = -10→10

l = -10→10

Refinement

Refinement on *F*²

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

wR(*F*²) = 0.078

S = 1.07

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001

1898 reflections $\Delta\rho_{\max} = 1.61 \text{ e } \text{\AA}^{-3}$
 163 parameters $\Delta\rho_{\min} = -1.22 \text{ e } \text{\AA}^{-3}$
 6 restraints Extinction correction: none
 Primary atom site location: structure-invariant direct methods

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F, with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2750 (6)	0.2794 (6)	0.7523 (6)	0.0218 (10)
C2	0.2577 (7)	0.4053 (7)	0.9066 (7)	0.0285 (11)
H2	0.3191	0.4122	1.0111	0.034*
C3	0.0676 (7)	0.4974 (7)	0.7564 (7)	0.0304 (12)
H3	-0.0079	0.5706	0.7529	0.036*
C4	0.0849 (7)	0.3716 (7)	0.6014 (7)	0.0289 (11)
H4	0.0202	0.3621	0.4968	0.035*
C5	0.5718 (6)	0.4928 (6)	0.5701 (6)	0.0204 (10)
C6	0.0553 (6)	-0.0282 (6)	-0.0653 (6)	0.0218 (10)
C7	0.3936 (6)	0.1564 (7)	0.7458 (6)	0.0238 (10)
La1	0.33941 (3)	0.08521 (3)	0.32247 (3)	0.01745 (13)
N1	0.1560 (6)	0.5173 (6)	0.9109 (6)	0.0284 (10)
N8	0.1914 (5)	0.2634 (5)	0.5974 (5)	0.0235 (9)
O1	0.3920 (5)	0.0398 (4)	0.5980 (4)	0.0248 (8)
O2	0.4933 (5)	0.1760 (5)	0.8841 (5)	0.0314 (8)
O3	0.5571 (5)	0.3495 (4)	0.5715 (4)	0.0246 (7)
O4	0.6879 (4)	0.6241 (4)	0.6678 (4)	0.0264 (8)
O5	-0.0155 (4)	-0.0721 (5)	-0.2201 (4)	0.0299 (8)
O6	0.2119 (4)	-0.0240 (5)	-0.0025 (4)	0.0292 (8)
O1W	0.2022 (5)	-0.2208 (4)	0.2499 (4)	0.0271 (8)
O2W	0.5746 (5)	0.1980 (5)	0.2097 (4)	0.0300 (8)
H1W	0.1827	-0.2913	0.1441	0.045*
H3W	0.5293	0.2079	0.1210	0.045*
H2W	0.2583	-0.2630	0.3071	0.045*
H4W	0.6611	0.1534	0.1900	0.045*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.018 (2)	0.027 (2)	0.021 (2)	0.007 (2)	0.005 (2)	0.012 (2)
C2	0.024 (3)	0.033 (3)	0.026 (3)	0.008 (2)	0.004 (2)	0.012 (2)
C3	0.030 (3)	0.030 (3)	0.033 (3)	0.012 (2)	0.010 (2)	0.014 (2)
C4	0.031 (3)	0.033 (3)	0.029 (3)	0.017 (2)	0.007 (2)	0.018 (2)
C5	0.015 (2)	0.025 (2)	0.021 (2)	0.0083 (19)	0.005 (2)	0.009 (2)
C6	0.017 (2)	0.023 (2)	0.024 (2)	0.0043 (19)	0.004 (2)	0.010 (2)
C7	0.018 (2)	0.033 (3)	0.025 (3)	0.005 (2)	0.007 (2)	0.016 (2)
La1	0.01352 (18)	0.01999 (18)	0.01806 (18)	0.00464 (11)	0.00163 (12)	0.00898 (13)
N1	0.022 (2)	0.027 (2)	0.031 (2)	0.0072 (18)	0.0067 (19)	0.0093 (19)
N8	0.022 (2)	0.027 (2)	0.023 (2)	0.0084 (17)	0.0035 (17)	0.0132 (18)
O1	0.0267 (19)	0.0270 (18)	0.0238 (18)	0.0104 (15)	0.0089 (15)	0.0126 (15)
O2	0.028 (2)	0.046 (2)	0.0244 (18)	0.0153 (17)	0.0049 (16)	0.0195 (17)
O3	0.0261 (19)	0.0225 (17)	0.0260 (18)	0.0047 (14)	0.0020 (15)	0.0143 (15)
O4	0.0196 (18)	0.0241 (18)	0.0316 (19)	0.0037 (15)	-0.0015 (15)	0.0131 (16)
O5	0.0172 (18)	0.049 (2)	0.0197 (18)	0.0097 (16)	0.0016 (15)	0.0132 (16)
O6	0.0147 (18)	0.046 (2)	0.0220 (17)	0.0100 (16)	0.0020 (14)	0.0123 (16)
O1W	0.0262 (19)	0.0239 (18)	0.0263 (18)	0.0031 (15)	0.0015 (15)	0.0100 (15)
O2W	0.027 (2)	0.039 (2)	0.0272 (19)	0.0109 (17)	0.0114 (16)	0.0166 (17)

Geometric parameters (\AA , $^\circ$)

C1—N8	1.340 (6)	C7—O1	1.259 (6)
C1—C2	1.378 (7)	La1—O1W	2.533 (3)
C1—C7	1.497 (7)	La1—O4 ⁱ	2.536 (3)
C2—N1	1.330 (7)	La1—O6	2.544 (3)
C2—H2	0.9300	La1—O3	2.551 (3)
C3—N1	1.336 (7)	La1—O5 ⁱⁱ	2.555 (4)
C3—C4	1.382 (7)	La1—O1	2.592 (3)
C3—H3	0.9300	La1—O2W	2.600 (4)
C4—N8	1.332 (7)	La1—O1 ⁱⁱⁱ	2.623 (3)
C4—H4	0.9300	La1—N8	2.828 (4)
C5—O4	1.242 (6)	La1—O2 ⁱⁱⁱ	2.889 (4)
C5—O3	1.250 (6)	La1—C7 ⁱⁱⁱ	3.124 (5)
C5—C5 ⁱ	1.574 (9)	O1W—H1W	0.8385
C6—O5	1.239 (6)	O1W—H2W	0.8353
C6—O6	1.261 (6)	O2W—H3W	0.8400
C6—C6 ⁱⁱ	1.539 (9)	O2W—H4W	0.8421
C7—O2	1.252 (6)		
N8—C1—C2	122.0 (5)	O5 ⁱⁱ —La1—O1 ⁱⁱⁱ	154.21 (12)
N8—C1—C7	115.3 (4)	O1—La1—O1 ⁱⁱⁱ	60.45 (13)
C2—C1—C7	122.7 (5)	O2W—La1—O1 ⁱⁱⁱ	75.58 (11)
N1—C2—C1	122.1 (5)	O1W—La1—N8	97.55 (12)

N1—C2—H2	118.9	O4 ⁱ —La1—N8	72.37 (12)
C1—C2—H2	118.9	O6—La1—N8	128.17 (11)
N1—C3—C4	122.0 (5)	O3—La1—N8	68.57 (12)
N1—C3—H3	119.0	O5 ⁱⁱ —La1—N8	66.44 (11)
C4—C3—H3	119.0	O1—La1—N8	58.52 (11)
N8—C4—C3	121.9 (5)	O2W—La1—N8	131.02 (12)
N8—C4—H4	119.0	O1 ⁱⁱⁱ —La1—N8	115.86 (11)
C3—C4—H4	119.0	O1W—La1—O2 ⁱⁱⁱ	66.41 (11)
O4—C5—O3	126.6 (4)	O4 ⁱ —La1—O2 ⁱⁱⁱ	129.49 (11)
O4—C5—C5 ⁱ	117.0 (5)	O6—La1—O2 ⁱⁱⁱ	68.05 (11)
O3—C5—C5 ⁱ	116.4 (5)	O3—La1—O2 ⁱⁱⁱ	112.40 (11)
O5—C6—O6	126.1 (4)	O5 ⁱⁱ —La1—O2 ⁱⁱⁱ	121.50 (11)
O5—C6—C6 ⁱⁱ	118.0 (5)	O1—La1—O2 ⁱⁱⁱ	99.45 (10)
O6—C6—C6 ⁱⁱ	115.9 (5)	O2W—La1—O2 ⁱⁱⁱ	65.10 (11)
O2—C7—O1	122.7 (5)	O1 ⁱⁱⁱ —La1—O2 ⁱⁱⁱ	46.83 (10)
O2—C7—C1	119.7 (5)	N8—La1—O2 ⁱⁱⁱ	157.23 (11)
O1—C7—C1	117.5 (4)	O1W—La1—C7 ⁱⁱⁱ	68.77 (12)
O2—C7—La1 ⁱⁱⁱ	67.6 (3)	O4 ⁱ —La1—C7 ⁱⁱⁱ	137.10 (12)
O1—C7—La1 ⁱⁱⁱ	55.5 (3)	O6—La1—C7 ⁱⁱⁱ	91.66 (12)
C1—C7—La1 ⁱⁱⁱ	169.0 (3)	O3—La1—C7 ⁱⁱⁱ	95.00 (12)
O1W—La1—O4 ⁱ	150.33 (12)	O5 ⁱⁱ —La1—C7 ⁱⁱⁱ	139.98 (12)
O1W—La1—O6	82.82 (11)	O1—La1—C7 ⁱⁱⁱ	78.74 (11)
O4 ⁱ —La1—O6	82.26 (12)	O2W—La1—C7 ⁱⁱⁱ	70.04 (12)
O1W—La1—O3	139.37 (10)	O1 ⁱⁱⁱ —La1—C7 ⁱⁱⁱ	23.29 (11)
O4 ⁱ —La1—O3	63.95 (11)	N8—La1—C7 ⁱⁱⁱ	136.97 (12)
O6—La1—O3	136.33 (11)	O2 ⁱⁱⁱ —La1—C7 ⁱⁱⁱ	23.62 (11)
O1W—La1—O5 ⁱⁱ	77.14 (12)	C2—N1—C3	116.0 (5)
O4 ⁱ —La1—O5 ⁱⁱ	73.25 (12)	C4—N8—C1	115.9 (4)
O6—La1—O5 ⁱⁱ	63.19 (11)	C4—N8—La1	126.3 (3)
O3—La1—O5 ⁱⁱ	124.85 (11)	C1—N8—La1	114.8 (3)
O1W—La1—O1	68.69 (11)	C7—O1—La1	122.9 (3)
O4 ⁱ —La1—O1	122.78 (11)	C7—O1—La1 ⁱⁱⁱ	101.2 (3)
O6—La1—O1	151.51 (12)	La1—O1—La1 ⁱⁱⁱ	119.55 (13)
O3—La1—O1	71.74 (11)	C7—O2—La1 ⁱⁱⁱ	88.8 (3)
O5 ⁱⁱ —La1—O1	108.11 (11)	C5—O3—La1	120.1 (3)
O1W—La1—O2W	130.93 (11)	C5—O4—La1 ⁱ	120.6 (3)
O4 ⁱ —La1—O2W	67.57 (12)	C6—O5—La1 ⁱⁱ	121.0 (3)
O6—La1—O2W	72.86 (11)	C6—O6—La1	121.8 (3)
O3—La1—O2W	69.18 (11)	La1—O1W—H1W	113.1
O5 ⁱⁱ —La1—O2W	123.82 (12)	La1—O1W—H2W	115.0
O1—La1—O2W	126.58 (11)	H1W—O1W—H2W	107.3
O1W—La1—O1 ⁱⁱⁱ	77.11 (11)	La1—O2W—H3W	111.1

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O4 ⁱ —La1—O1 ⁱⁱⁱ	132.53 (11)	La1—O2W—H4W	123.8
O6—La1—O1 ⁱⁱⁱ	114.65 (11)	H3W—O2W—H4W	106.5
O3—La1—O1 ⁱⁱⁱ	75.79 (11)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y, -z$; (iii) $-x+1, -y, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W \cdots N1 ^{iv}	0.84	1.97	2.796 (6)	170
O2W—H3W \cdots O2 ^v	0.84	1.94	2.737 (5)	157
O1W—H2W \cdots O3 ⁱⁱⁱ	0.84	2.05	2.874 (5)	167
O2W—H4W \cdots O6 ^{vi}	0.84	2.09	2.825 (5)	146

Symmetry codes: (iv) $x, y-1, z-1$; (v) $x, y, z-1$; (iii) $-x+1, -y, -z+1$; (vi) $-x+1, -y, -z$.

Fig. 1

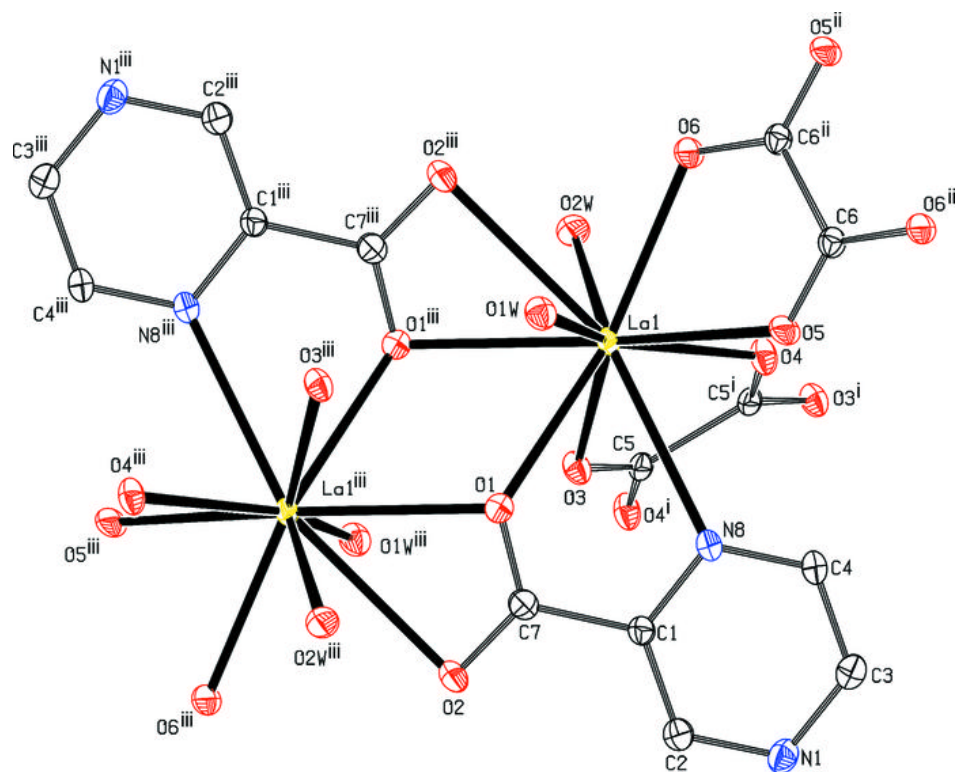


Fig. 2

