

Poly[[aqua(μ_2 -oxalato)(μ_2 -2-oxido-pyridinium-3-carboxylato)holmium(III)] monohydrate]

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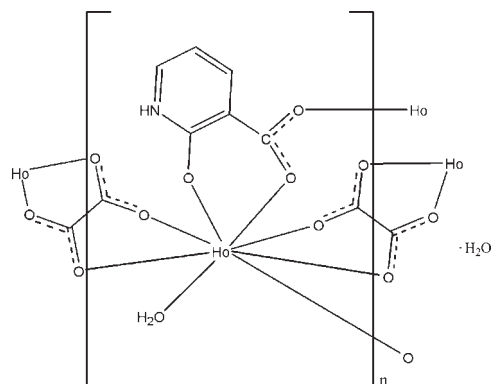
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.011$ Å; R factor = 0.034; wR factor = 0.090; data-to-parameter ratio = 10.8.

In the title complex, $\{[\text{Ho}(\text{C}_2\text{O}_4)(\text{C}_6\text{H}_4\text{NO}_3)(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})\}_n$, the Ho^{III} ion is coordinated by three O atoms from two 2-oxidopyridinium-3-carboxylate ligands, four O atoms from two oxalate ligands and one water molecule in a distorted bicapped trigonal-prismatic geometry. The 2-oxidopyridinium-3-carboxylate and oxalate ligands link the Ho^{III} ions into a layer in (100). These layers are further connected by intermolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds involving the coordinated water molecules to assemble a three-dimensional supramolecular network. The uncoordinated water molecule is involved in $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds within the layer.

Related literature

For general background to molecular self-assembly of supramolecular architectures, see: Deng *et al.* (2008); Zeng *et al.* (2007). For 2-oxidopyridinium-3-carboxylic acid and oxalic acid as building blocks, see: Huang *et al.* (2009).



Experimental

Crystal data

$[\text{Ho}(\text{C}_2\text{O}_4)(\text{C}_6\text{H}_4\text{NO}_3)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$
 $M_r = 427.08$
 Triclinic, $P\bar{1}$
 $a = 6.5391$ (11) Å
 $b = 9.5305$ (16) Å
 $c = 9.7391$ (16) Å
 $\alpha = 71.810$ (2)°
 $\beta = 78.862$ (2)°
 $\gamma = 80.359$ (2)°
 $V = 562.01$ (16) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 7.09$ mm⁻¹
 $T = 296$ K
 $0.20 \times 0.18 \times 0.17$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.332$, $T_{\text{max}} = 0.379$
 2884 measured reflections
 1983 independent reflections
 1862 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.090$
 $S = 1.06$
 1983 reflections
 184 parameters
 6 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 2.75$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.19$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ho1—O1	2.354 (5)	Ho1—O5 ⁱⁱ	2.364 (5)
Ho1—O2 ⁱ	2.348 (5)	Ho1—O6	2.394 (5)
Ho1—O3	2.279 (5)	Ho1—O7 ⁱⁱⁱ	2.392 (5)
Ho1—O4	2.406 (4)	Ho1—O1W	2.348 (5)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O1W—H1W \cdots O2 ^{iv}	0.84 (6)	2.02 (6)	2.737 (7)	142 (8)
O1W—H2W \cdots O4 ^v	0.85 (7)	1.96 (4)	2.749 (7)	154 (8)
O2W—H3W \cdots O6	0.84 (7)	2.36 (11)	2.882 (10)	121 (8)
O2W—H4W \cdots O1	0.86 (7)	2.27 (3)	3.082 (8)	157 (9)
N1—H1 \cdots O2W ^{vi}	0.86	1.99	2.781 (10)	154

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); 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: HY2226).

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supplementary materials

Acta Cryst. (2009). E65, m1217-m1218 [doi:10.1107/S1600536809036344]

Poly[[aqua(μ_2 -oxalato)(μ_2 -2-oxidopyridinium-3-carboxylato)holmium(III)] monohydrate]

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Comment

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Deng *et al.*, 2008; Zeng *et al.*, 2007). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metal ions and the bridging building blocks, as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π - π stacking interactions. As a building block, 2-oxynicotinic acid and oxalic acid are good ligands with multifunctional coordination sites providing a high likelihood for the generation of structures with high dimensions (Huang *et al.*, 2009). Recently, we obtained the title coordination polymer, which was synthesized under hydrothermal conditions.

In the title compound (Fig. 1), the Ho^{III} centre is eight-coordinated by seven O atoms from two 2-oxynicotinate ligands and two oxalate ligands, and by one water molecule in a distorted bicapped trigonal prismatic geometry, with Ho—O distances and O—Ho—O angles ranging from 2.279 (5) to 2.406 (4) Å and 67.30 (17) to 148.26 (17)°, respectively (Table 1). The carboxylate groups of the 2-oxynicotinates and oxalates act as bridging ligands, linking the Ho centres into a layer parallel to the (100) plane (Fig. 2). The layers are further connected by intermolecular O—H \cdots O hydrogen bonds involving the coordinated water molecules into a three-dimensional supramolecular network (Table 2). The uncoordinated water molecule is involved in N—H \cdots O and O—H \cdots O hydrogen bonds within the layer (Table 2).

Experimental

A mixture of Ho₂O₃ (0.375 g, 1 mmol), 2-oxynicotinic acid (0.127 g, 1 mmol), oxalic acid (0.09 g, 1 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 446 K for 2 d, and then cooled to room temperature at 5 K h⁻¹, giving colourless block crystals.

Refinement

Water H atoms were tentatively located in difference Fourier maps and refined with distance restraints of O—H = 0.84 (1) and H \cdots H = 1.35 (1) Å, and with a fixed $U_{\text{iso}}(\text{H}) = 0.064 \text{ \AA}^2$. H atoms attached to C and N atoms were placed at calculated positions and treated as riding on their parent atoms, with C—H = 0.93 and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The highest residual electron density was found 0.94 Å from Ho1 and the deepest hole 0.91 Å from Ho1.

Figures

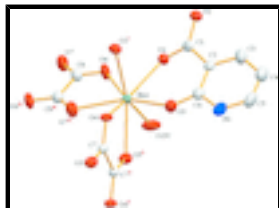


Fig. 1. The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-x, 1 - y, -z$; (iii) $-x, 1 - y, 1 - z$.]

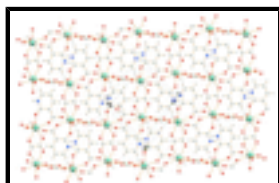


Fig. 2. View of a layered network of the title compound.

Poly[[aqua(μ_2 -oxalato)(μ_2 -2-oxidopyridinium-3-carboxylato)holmium(III)] monohydrate]

Crystal data

[Ho(C₂O₄)(C₆H₄NO₃)(H₂O)]·H₂O

$M_r = 427.08$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 6.5391$ (11) Å

$b = 9.5305$ (16) Å

$c = 9.7391$ (16) Å

$\alpha = 71.810$ (2)°

$\beta = 78.862$ (2)°

$\gamma = 80.359$ (2)°

$V = 562.01$ (16) Å³

$Z = 2$

$F_{000} = 404$

$D_x = 2.524$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2285 reflections

$\theta = 2.2$ – 28.1 °

$\mu = 7.09$ mm⁻¹

$T = 296$ K

Block, colourless

$0.20 \times 0.18 \times 0.17$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.332$, $T_{\max} = 0.379$

2884 measured reflections

1983 independent reflections

1862 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$

$\theta_{\text{max}} = 25.2$ °

$\theta_{\text{min}} = 2.2$ °

$h = -7 \rightarrow 6$

$k = -11 \rightarrow 11$

$l = -11 \rightarrow 10$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.034$$

$$wR(F^2) = 0.090$$

$$S = 1.06$$

1983 reflections

184 parameters

6 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 2.75 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -2.19 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ho1	0.09083 (4)	0.29059 (3)	0.30045 (3)	0.01784 (15)
O4	-0.1655 (7)	0.3863 (5)	0.1370 (5)	0.0219 (10)
O3	0.1549 (8)	0.1295 (6)	0.1626 (5)	0.0311 (11)
O6	0.1351 (9)	0.3228 (5)	0.5267 (6)	0.0338 (12)
O1	0.2127 (8)	0.0581 (5)	0.4520 (5)	0.0251 (10)
O5	-0.2292 (7)	0.5458 (5)	-0.0767 (5)	0.0258 (10)
N1	0.2729 (11)	-0.0557 (8)	0.0581 (7)	0.0366 (15)
H1	0.2407	0.0054	-0.0227	0.044*
C6	0.2307 (12)	-0.0067 (8)	0.1802 (8)	0.0266 (15)
C8	0.0606 (11)	0.4422 (8)	0.5578 (8)	0.0261 (15)
C5	0.3624 (14)	-0.1948 (10)	0.0574 (10)	0.044 (2)
H5	0.3862	-0.2213	-0.0290	0.052*
C4	0.4170 (14)	-0.2947 (9)	0.1807 (10)	0.048 (3)
H4	0.4851	-0.3882	0.1795	0.057*
C3	0.3695 (13)	-0.2550 (9)	0.3094 (10)	0.0396 (19)
H3	0.3999	-0.3250	0.3960	0.048*
C2	0.2776 (10)	-0.1133 (7)	0.3126 (7)	0.0251 (15)
C1	0.2306 (10)	-0.0747 (7)	0.4529 (7)	0.0236 (14)
C7	-0.1147 (10)	0.4807 (7)	0.0161 (7)	0.0190 (13)
O2W	0.2278 (13)	0.0635 (9)	0.7646 (8)	0.0621 (19)
O2	0.2125 (7)	-0.1813 (5)	0.5703 (5)	0.0262 (10)
O7	0.0730 (9)	0.4748 (6)	0.6691 (5)	0.0358 (13)
O1W	0.4526 (8)	0.2970 (7)	0.2822 (6)	0.0427 (15)
H3W	0.164 (16)	0.149 (7)	0.758 (10)	0.064*
H4W	0.203 (16)	0.041 (10)	0.691 (6)	0.064*
H1W	0.508 (12)	0.263 (11)	0.359 (5)	0.064*
H2W	0.549 (10)	0.332 (11)	0.215 (6)	0.064*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ho1	0.0166 (2)	0.0197 (2)	0.0158 (2)	-0.00221 (12)	-0.00168 (12)	-0.00363 (13)

supplementary materials

O4	0.018 (2)	0.027 (2)	0.017 (2)	-0.0088 (18)	-0.0019 (18)	0.0028 (19)
O3	0.039 (3)	0.031 (3)	0.020 (2)	0.002 (2)	-0.005 (2)	-0.007 (2)
O6	0.046 (3)	0.023 (3)	0.034 (3)	0.010 (2)	-0.013 (2)	-0.013 (2)
O1	0.027 (3)	0.024 (2)	0.022 (2)	-0.0029 (19)	-0.0024 (19)	-0.0050 (19)
O5	0.016 (2)	0.035 (3)	0.023 (2)	-0.0035 (19)	-0.0071 (19)	-0.001 (2)
N1	0.040 (4)	0.043 (4)	0.028 (3)	-0.009 (3)	0.003 (3)	-0.016 (3)
C6	0.025 (4)	0.027 (4)	0.029 (4)	-0.007 (3)	-0.001 (3)	-0.010 (3)
C8	0.024 (4)	0.026 (4)	0.028 (4)	-0.005 (3)	-0.003 (3)	-0.007 (3)
C5	0.048 (5)	0.046 (5)	0.042 (5)	-0.011 (4)	0.014 (4)	-0.028 (4)
C4	0.055 (6)	0.036 (5)	0.050 (6)	-0.008 (4)	0.013 (5)	-0.021 (5)
C3	0.038 (5)	0.032 (4)	0.047 (5)	0.000 (3)	0.001 (4)	-0.015 (4)
C2	0.018 (3)	0.025 (3)	0.029 (4)	-0.008 (3)	0.007 (3)	-0.006 (3)
C1	0.012 (3)	0.026 (3)	0.028 (4)	0.000 (3)	-0.003 (3)	-0.003 (3)
C7	0.018 (3)	0.020 (3)	0.020 (3)	-0.006 (2)	0.001 (3)	-0.007 (3)
O2W	0.069 (5)	0.078 (5)	0.041 (4)	-0.022 (4)	-0.020 (4)	-0.005 (4)
O2	0.019 (2)	0.027 (3)	0.027 (3)	-0.0043 (19)	-0.0037 (19)	0.002 (2)
O7	0.056 (4)	0.031 (3)	0.024 (3)	0.008 (2)	-0.018 (2)	-0.013 (2)
O1W	0.021 (3)	0.062 (4)	0.029 (3)	-0.012 (3)	-0.008 (2)	0.015 (3)

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

Ho1—O1	2.354 (5)	C6—C2	1.421 (10)
Ho1—O2 ⁱ	2.348 (5)	C8—O7	1.237 (9)
Ho1—O3	2.279 (5)	C8—C8 ⁱⁱⁱ	1.546 (15)
Ho1—O4	2.406 (4)	C5—C4	1.347 (13)
Ho1—O5 ⁱⁱ	2.364 (5)	C5—H5	0.9300
Ho1—O6	2.394 (5)	C4—C3	1.384 (11)
Ho1—O7 ⁱⁱⁱ	2.392 (5)	C4—H4	0.9300
Ho1—O1W	2.348 (5)	C3—C2	1.390 (10)
O4—C7	1.262 (8)	C3—H3	0.9300
O3—C6	1.279 (9)	C2—C1	1.487 (10)
O6—C8	1.263 (9)	C1—O2	1.271 (8)
O1—C1	1.249 (8)	C7—C7 ⁱⁱ	1.554 (12)
O5—C7	1.232 (8)	O2W—H3W	0.84 (7)
O5—Ho1 ⁱⁱ	2.364 (4)	O2W—H4W	0.86 (7)
N1—C5	1.358 (11)	O1W—H1W	0.84 (6)
N1—C6	1.373 (10)	O1W—H2W	0.85 (7)
N1—H1	0.8600		
O3—Ho1—O1W	90.4 (2)	C5—N1—C6	123.9 (7)
O3—Ho1—O2 ⁱ	90.37 (18)	C5—N1—H1	118.0
O1W—Ho1—O2 ⁱ	148.26 (17)	C6—N1—H1	118.0
O3—Ho1—O1	73.45 (17)	O3—C6—N1	116.8 (7)
O1W—Ho1—O1	75.15 (18)	O3—C6—C2	127.2 (7)
O2 ⁱ —Ho1—O1	74.69 (16)	N1—C6—C2	116.1 (7)
O3—Ho1—O5 ⁱⁱ	81.80 (17)	O7—C8—O6	127.4 (7)
O1W—Ho1—O5 ⁱⁱ	67.83 (16)	O7—C8—C8 ⁱⁱⁱ	117.7 (8)

O2 ⁱ —Ho1—O5 ⁱⁱ	143.49 (16)	O6—C8—C8 ⁱⁱⁱ	114.9 (8)
O1—Ho1—O5 ⁱⁱ	134.91 (16)	C4—C5—N1	120.6 (8)
O3—Ho1—O7 ⁱⁱⁱ	148.06 (18)	C4—C5—H5	119.7
O1W—Ho1—O7 ⁱⁱⁱ	105.7 (2)	N1—C5—H5	119.7
O2 ⁱ —Ho1—O7 ⁱⁱⁱ	89.77 (18)	C5—C4—C3	118.5 (8)
O1—Ho1—O7 ⁱⁱⁱ	136.83 (16)	C5—C4—H4	120.7
O5 ⁱⁱ —Ho1—O7 ⁱⁱⁱ	79.25 (18)	C3—C4—H4	120.7
O3—Ho1—O6	144.55 (17)	C4—C3—C2	121.7 (8)
O1W—Ho1—O6	75.0 (2)	C4—C3—H3	119.1
O2 ⁱ —Ho1—O6	86.35 (18)	C2—C3—H3	119.1
O1—Ho1—O6	71.64 (16)	C3—C2—C6	119.1 (7)
O5 ⁱⁱ —Ho1—O6	119.81 (18)	C3—C2—C1	120.1 (7)
O7 ⁱⁱⁱ —Ho1—O6	67.30 (17)	C6—C2—C1	120.8 (6)
O3—Ho1—O4	77.17 (17)	O1—C1—O2	122.8 (6)
O1W—Ho1—O4	135.57 (16)	O1—C1—C2	119.9 (6)
O2 ⁱ —Ho1—O4	75.25 (15)	O2—C1—C2	117.3 (6)
O1—Ho1—O4	137.32 (16)	O5—C7—O4	126.5 (6)
O5 ⁱⁱ —Ho1—O4	68.24 (14)	O5—C7—C7 ⁱⁱ	117.4 (7)
O7 ⁱⁱⁱ —Ho1—O4	72.00 (17)	O4—C7—C7 ⁱⁱ	116.0 (7)
O6—Ho1—O4	135.14 (16)	H3W—O2W—H4W	105 (9)
C7—O4—Ho1	118.2 (4)	C1—O2—Ho1 ⁱ	128.4 (4)
C6—O3—Ho1	136.0 (5)	C8—O7—Ho1 ⁱⁱⁱ	119.8 (5)
C8—O6—Ho1	120.3 (5)	Ho1—O1W—H1W	119 (6)
C1—O1—Ho1	136.8 (4)	Ho1—O1W—H2W	136 (6)
C7—O5—Ho1 ⁱⁱ	119.9 (4)	H1W—O1W—H2W	106 (3)

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

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 O2 ^{iv}	0.84 (6)	2.02 (6)	2.737 (7)	142 (8)
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Symmetry codes: (iv) $-x+1, -y, -z+1$; (v) $x+1, y, z$; (vi) $x, y, z-1$.

Fig. 1

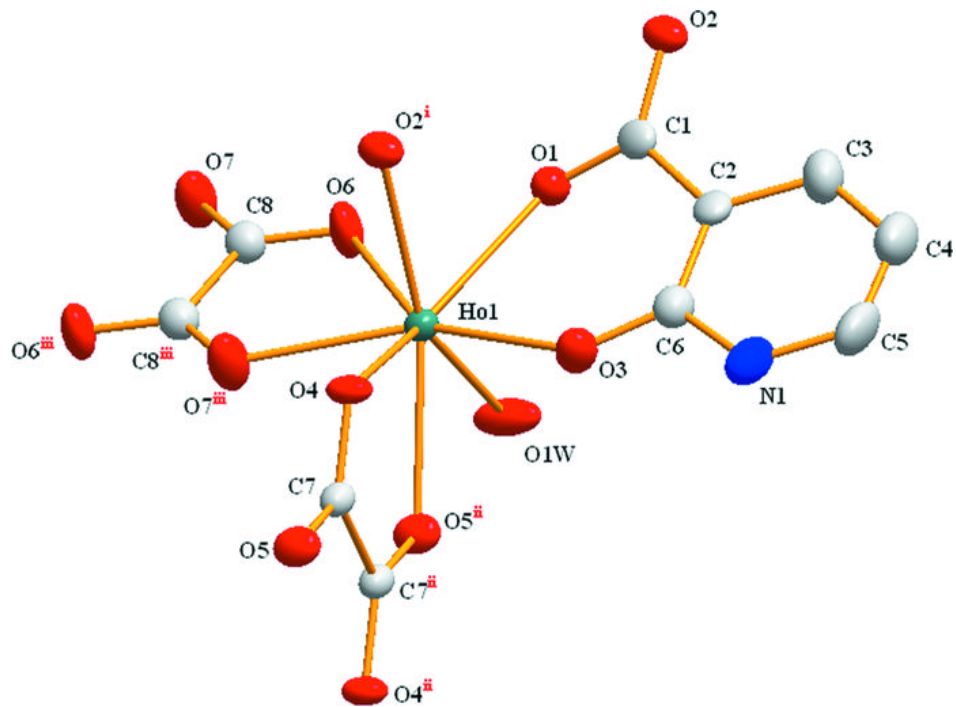


Fig. 2

