

Poly[[tetrakis(μ_2 -pyrazine N,N' -dioxide- $\kappa^2O:O'$)holmium(III)] tris(perchlorate)]

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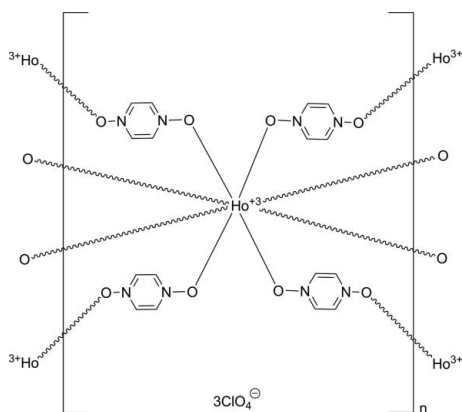
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.035; wR factor = 0.103; data-to-parameter ratio = 17.3.

The title three-dimensional coordination network, $\{[\text{Ho}(\text{C}_4\text{H}_4\text{N}_2\text{O}_2)_4](\text{ClO}_4)_3\}_n$, is isostructural to that of other lanthanides. The Ho^{+3} cation lies on a fourfold roto-inversion axis. It is coordinated in a distorted square anti-prismatic fashion by eight O atoms from bridging pyrazine N,N' -dioxide ligands. There are two unique pyrazine N,N' -dioxide ligands. One ring is located around an inversion center, and there is a twofold rotation axis at the center of the other ring. There are also two unique perchlorate anions. One is centered on a twofold rotation axis and the other on a fourfold roto-inversion axis. The perchlorate anions are located in channels that run perpendicular to (001) (110) and interact with the coordination network through $C-H \cdots O$ hydrogen bonds.

Related literature

For the isostructural La, Ce, Pr, Sm, Eu, Gd, Tb and Y coordination networks, see: Sun *et al.* (2004). For the isostructural Nd, Dy and Er coordination networks, see: Quinn-Elmore *et al.* (2010*a,b*); Buchner *et al.* (2010), respectively. Detailed background to this study is described in the first article of this series by Quinn-Elmore *et al.* (2010*a*).



Experimental

Crystal data

$[\text{Ho}(\text{C}_4\text{H}_4\text{N}_2\text{O}_2)_4](\text{ClO}_4)_3$
 $M_r = 911.65$
Tetragonal, $I4_1/acd$
 $a = 15.2302$ (4) Å
 $c = 22.6334$ (12) Å
 $V = 5250.0$ (3) Å³
 $Z = 8$
Mo $K\alpha$ radiation
 $\mu = 3.43$ mm⁻¹
 $T = 100$ K
 $0.37 \times 0.32 \times 0.17$ mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.292$, $T_{\max} = 0.558$
10709 measured reflections
1906 independent reflections
1585 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.103$
 $S = 1.04$
1906 reflections
110 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 3.23$ e Å⁻³
 $\Delta\rho_{\min} = -1.76$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots O2^i$	0.95	2.52	3.285 (4)	138
$C2-H2 \cdots O5$	0.95	2.40	3.161 (7)	137
$C3-H3 \cdots O1$	0.95	2.60	3.323 (4)	134
$C3-H3 \cdots O3$	0.95	2.46	3.230 (4)	138
$C4-H4 \cdots O3^{ii}$	0.95	2.36	3.234 (4)	153

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-y + \frac{3}{4}, x - \frac{1}{4}, -z + \frac{1}{4}$.

Data collection: SMART (Bruker, 2007); cell refinement: SAINT-Plus (Bruker, 2007); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: X-SEED.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2300).

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supporting information

Acta Cryst. (2010). E66, m1108–m1109 [https://doi.org/10.1107/S1600536810031831]

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S1. Comment

The description of the structure of the title compound is part of a series of consecutive papers on three-dimensional coordination networks of the type $\{[\text{Ln}(\text{C}_4\text{H}_4\text{N}_2\text{O}_2)_4](\text{ClO}_4)_3\}_n$, with Ln = Nd (Quinn-Elmore *et al.* 2010*a*), Dy (Quinn-Elmore *et al.* 2010*b*), Ho (this publication), and Er (Buchner *et al.* 2010), respectively. All four compounds are also isostructural to the previously reported La, Ce, Pr, Sm, Eu, Gd, Tb and Y coordination networks (Sun *et al.* 2004). The background to this study is given in the first article of this series by Quinn-Elmore *et al.* (2010*a*).

S2. Experimental

Pyrazine *N,N'*-dioxide (0.025 g, 0.223 mmol) was dissolved in deionized water (1.5 ml) and methanol (1.5 ml). An aqueous solution of $\text{Ho}(\text{ClO}_4)_3$ (0.160 ml of a 0.0860 *M* solution, 0.0139 mmol) was diluted with methanol (0.840 ml) and CH_2Cl_2 (2.5 ml). The pyrazine *N,N'*-dioxide solution was layered over the $\text{Ho}(\text{ClO}_4)_3$ solution, and the two solutions were allowed to slowly mix. Orange plate-like crystals formed upon the slow evaporation of the resultant solution.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$.

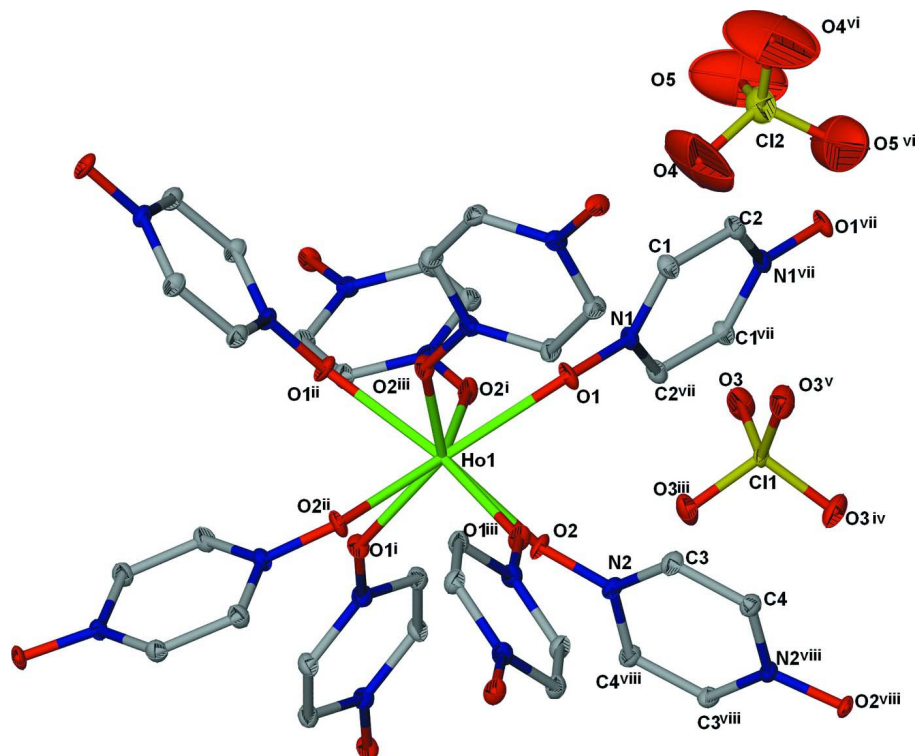


Figure 1

The coordination environment of the Ho⁺³ cation in title compound with atom labels and 50% probability displacement ellipsoids. Hydrogen atoms have been omitted for clarity. Symmetry codes: (i) $y + 1/4, x - 1/4, -z + 3/4$; (ii) $-y + 3/4, -x + 3/4, -z + 3/4$; (iii) $-x + 1, -y + 1/2, z$; (iv) $-y + 3/4, x - 1/4, -z + 1/4$; (v) $y + 1/4, -x + 3/4, -z + 1/4$; (vi) $y + 3/4, x - 3/4, -z + 1/4$; (vii) $-x + 3/2, -y + 1/2, -z + 1/2$; (viii) $x, -y + 1, -z + 1/2$.

Poly[[tetrakis(μ_2 -pyrazine N,N' -dioxide- $\kappa^2O:O'$)holmium(III)] tris(perchlorate)]

Crystal data

[Ho(C₄H₄N₂O₂)₄](ClO₄)₃

$M_r = 911.65$

Tetragonal, $I4_1acd$

Hall symbol: $-I\ 4bd\ 2c$

$a = 15.2302(4)\ \text{\AA}$

$c = 22.6334(12)\ \text{\AA}$

$V = 5250.0(3)\ \text{\AA}^3$

$Z = 8$

$F(000) = 3568$

$D_x = 2.307\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4928 reflections

$\theta = 2.6\text{--}30.5^\circ$

$\mu = 3.43\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Plate, orange

$0.37 \times 0.32 \times 0.17\ \text{mm}$

Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.292, T_{\max} = 0.558$

10709 measured reflections

1906 independent reflections

1585 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 30.5^\circ, \theta_{\min} = 2.6^\circ$

$h = -7 \rightarrow 21$

$k = -20 \rightarrow 21$

$l = -27 \rightarrow 28$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.103$
 $S = 1.04$
 1906 reflections
 110 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 37.1849P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 3.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.76 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ho1	0.5000	0.2500	0.3750	0.00486 (12)
Cl1	0.5000	0.2500	0.1250	0.0107 (4)
Cl2	0.72659 (6)	-0.02341 (6)	0.1250	0.0279 (3)
O1	0.59106 (13)	0.21881 (15)	0.29529 (10)	0.0149 (4)
O2	0.53202 (15)	0.39424 (13)	0.34396 (10)	0.0145 (4)
O3	0.57646 (17)	0.24391 (17)	0.16195 (12)	0.0249 (6)
O4	0.6466 (4)	-0.0166 (5)	0.1510 (4)	0.137 (3)
O5	0.7914 (4)	-0.0059 (4)	0.1660 (4)	0.126 (3)
N1	0.66932 (17)	0.23422 (18)	0.27425 (13)	0.0135 (5)
N2	0.52691 (17)	0.44463 (16)	0.29771 (12)	0.0125 (5)
C1	0.70854 (19)	0.17233 (19)	0.24034 (14)	0.0149 (6)
H1	0.6800	0.1178	0.2336	0.018*
C2	0.78932 (19)	0.18805 (19)	0.21558 (14)	0.0145 (6)
H2	0.8163	0.1448	0.1914	0.017*
C3	0.5262 (2)	0.41170 (19)	0.24238 (14)	0.0149 (6)
H3	0.5259	0.3499	0.2366	0.018*
C4	0.5259 (2)	0.46676 (19)	0.19448 (15)	0.0150 (6)
H4	0.5249	0.4430	0.1557	0.018*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ho1	0.00537 (13)	0.00537 (13)	0.0038 (2)	-0.00033 (6)	0.000	0.000
Cl1	0.0132 (5)	0.0132 (5)	0.0058 (10)	0.000	0.000	0.000
Cl2	0.0261 (4)	0.0261 (4)	0.0315 (8)	-0.0103 (5)	0.0037 (3)	-0.0037 (3)

O1	0.0093 (9)	0.0224 (11)	0.0129 (11)	-0.0028 (8)	0.0047 (8)	-0.0037 (8)
O2	0.0242 (11)	0.0106 (9)	0.0088 (12)	-0.0021 (8)	-0.0029 (8)	0.0043 (7)
O3	0.0177 (12)	0.0432 (16)	0.0138 (14)	0.0043 (9)	-0.0044 (10)	-0.0029 (10)
O4	0.066 (4)	0.116 (5)	0.228 (8)	-0.013 (3)	0.098 (5)	-0.016 (5)
O5	0.078 (4)	0.094 (4)	0.205 (9)	0.002 (3)	-0.059 (5)	-0.072 (5)
N1	0.0112 (11)	0.0188 (11)	0.0106 (15)	-0.0002 (9)	0.0020 (9)	0.0003 (10)
N2	0.0147 (11)	0.0114 (10)	0.0114 (14)	-0.0003 (9)	-0.0016 (9)	0.0027 (9)
C1	0.0151 (13)	0.0162 (13)	0.0132 (16)	-0.0013 (10)	0.0014 (10)	-0.0032 (11)
C2	0.0139 (13)	0.0183 (13)	0.0113 (16)	-0.0003 (10)	0.0014 (10)	-0.0023 (11)
C3	0.0195 (14)	0.0112 (12)	0.0140 (17)	-0.0018 (10)	-0.0018 (12)	0.0000 (10)
C4	0.0192 (13)	0.0123 (12)	0.0137 (16)	-0.0003 (11)	0.0005 (11)	0.0007 (10)

Geometric parameters (Å, °)

Ho1—O1 ⁱ	2.325 (2)	Cl2—O5 ^{vi}	1.381 (6)
Ho1—O1 ⁱⁱ	2.325 (2)	O1—N1	1.305 (3)
Ho1—O1	2.325 (2)	O2—N2	1.300 (3)
Ho1—O1 ⁱⁱⁱ	2.325 (2)	N1—C1	1.354 (4)
Ho1—O2 ⁱ	2.357 (2)	N1—C2 ^{vii}	1.361 (4)
Ho1—O2 ⁱⁱ	2.357 (2)	N2—C3	1.349 (4)
Ho1—O2	2.357 (2)	N2—C4 ^{viii}	1.361 (4)
Ho1—O2 ⁱⁱⁱ	2.357 (2)	C1—C2	1.373 (4)
Cl1—O3	1.437 (3)	C1—H1	0.9500
Cl1—O3 ^{iv}	1.437 (3)	C2—N1 ^{vii}	1.361 (4)
Cl1—O3 ⁱⁱⁱ	1.437 (3)	C2—H2	0.9500
Cl1—O3 ^v	1.437 (3)	C3—C4	1.371 (4)
Cl2—O4 ^{vi}	1.357 (4)	C3—H3	0.9500
Cl2—O4	1.357 (4)	C4—N2 ^{viii}	1.361 (4)
Cl2—O5	1.381 (6)	C4—H4	0.9500
O1 ⁱ —Ho1—O1 ⁱⁱ	78.19 (11)	O3 ^{iv} —Cl1—O3 ⁱⁱⁱ	109.81 (11)
O1 ⁱ —Ho1—O1	147.80 (10)	O3—Cl1—O3 ^v	109.81 (11)
O1 ⁱⁱ —Ho1—O1	111.01 (12)	O3 ^{iv} —Cl1—O3 ^v	108.8 (2)
O1 ⁱ —Ho1—O1 ⁱⁱⁱ	111.01 (12)	O3 ⁱⁱⁱ —Cl1—O3 ^v	109.80 (11)
O1 ⁱⁱ —Ho1—O1 ⁱⁱⁱ	147.80 (10)	O4 ^{vi} —Cl2—O4	109.0 (6)
O1—Ho1—O1 ⁱⁱⁱ	78.19 (11)	O4 ^{vi} —Cl2—O5	114.2 (4)
O1 ⁱ —Ho1—O2 ⁱ	80.55 (8)	O4—Cl2—O5	109.6 (5)
O1 ⁱⁱ —Ho1—O2 ⁱ	72.64 (7)	O4 ^{vi} —Cl2—O5 ^{vi}	109.6 (5)
O1—Ho1—O2 ⁱ	73.60 (7)	O4—Cl2—O5 ^{vi}	114.2 (4)
O1 ⁱⁱⁱ —Ho1—O2 ⁱ	138.15 (7)	O5—Cl2—O5 ^{vi}	100.2 (8)
O1 ⁱ —Ho1—O2 ⁱⁱ	72.64 (7)	N1—O1—Ho1	142.32 (19)
O1 ⁱⁱ —Ho1—O2 ⁱⁱ	80.55 (8)	N2—O2—Ho1	141.03 (18)
O1—Ho1—O2 ⁱⁱ	138.15 (7)	O1—N1—C1	119.0 (3)
O1 ⁱⁱⁱ —Ho1—O2 ⁱⁱ	73.60 (7)	O1—N1—C2 ^{vii}	121.2 (3)
O2 ⁱ —Ho1—O2 ⁱⁱ	145.32 (11)	C1—N1—C2 ^{vii}	119.8 (3)
O1 ⁱ —Ho1—O2	73.60 (7)	O2—N2—C3	121.9 (2)
O1 ⁱⁱ —Ho1—O2	138.15 (7)	O2—N2—C4 ^{viii}	118.8 (3)
O1—Ho1—O2	80.55 (8)	C3—N2—C4 ^{viii}	119.3 (3)

O1 ⁱⁱⁱ —Ho1—O2	72.64 (7)	N1—C1—C2	120.3 (3)
O2 ⁱ —Ho1—O2	72.73 (11)	N1—C1—H1	119.8
O2 ⁱⁱ —Ho1—O2	118.32 (11)	C2—C1—H1	119.8
O1 ⁱ —Ho1—O2 ⁱⁱⁱ	138.15 (7)	N1 ^{vii} —C2—C1	119.8 (3)
O1 ⁱⁱ —Ho1—O2 ⁱⁱⁱ	73.60 (7)	N1 ^{vii} —C2—H2	120.1
O1—Ho1—O2 ⁱⁱⁱ	72.64 (7)	C1—C2—H2	120.1
O1 ⁱⁱⁱ —Ho1—O2 ⁱⁱⁱ	80.55 (8)	N2—C3—C4	120.4 (3)
O2 ⁱ —Ho1—O2 ⁱⁱⁱ	118.32 (11)	N2—C3—H3	119.8
O2 ⁱⁱ —Ho1—O2 ⁱⁱⁱ	72.73 (11)	C4—C3—H3	119.8
O2—Ho1—O2 ⁱⁱⁱ	145.33 (11)	N2 ^{viii} —C4—C3	120.3 (3)
O3—C11—O3 ^{iv}	109.80 (11)	N2 ^{viii} —C4—H4	119.9
O3—C11—O3 ⁱⁱⁱ	108.8 (2)	C3—C4—H4	119.9

Symmetry codes: (i) $y+1/4, x-1/4, -z+3/4$; (ii) $-y+3/4, -x+3/4, -z+3/4$; (iii) $-x+1, -y+1/2, z$; (iv) $-y+3/4, x-1/4, -z+1/4$; (v) $y+1/4, -x+3/4, -z+1/4$; (vi) $y+3/4, x-3/4, -z+1/4$; (vii) $-x+3/2, -y+1/2, -z+1/2$; (viii) $x, -y+1, -z+1/2$.

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C2—H2 \cdots O2 ^{vii}	0.95	2.52	3.285 (4)	138
C2—H2 \cdots O5	0.95	2.40	3.161 (7)	137
C3—H3 \cdots O1	0.95	2.60	3.323 (4)	134
C3—H3 \cdots O3	0.95	2.46	3.230 (4)	138
C4—H4 \cdots O3 ^{iv}	0.95	2.36	3.234 (4)	153

Symmetry codes: (iv) $-y+3/4, x-1/4, -z+1/4$; (vii) $-x+3/2, -y+1/2, -z+1/2$.