metal-organic compounds

(2,2-Bipyridyl N,N'-dioxide-κ^2O,O')-trichloridobis(methanol-κO)terbium(III)

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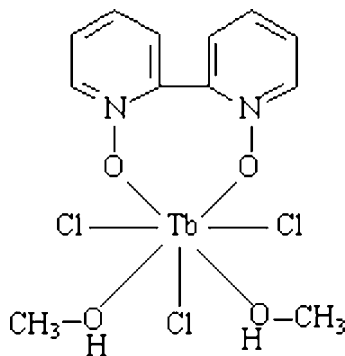Correspondence e-mail: zengxirui@jgsu.ed.cn

In the title complex, [TbCl$_3$(C$_{10}$H$_{12}$N$_2$O$_2$)(CH$_4$O)$_2$], each Tb^{III} ion is seven-coordinate in a pentagonal-bipyramidal coordination geometry. A crystallographic twofold rotation axis passes through Tb and one Cl atom.

Related literature

For related literature, see: McGehee *et al.* (1999); Ropp (2004); Tsaryuk *et al.* (2003).

Experimental

Crystal data

[TbCl$_3$(C$_{10}$H$_{12}$N$_2$O$_2$)(CH$_4$O)$_2$]
M_r = 517.54
Orthorhombic, $C222_1$
a = 13.985 (4) Å
b = 15.054 (4) Å
c = 7.976 (2) Å

V = 1679.2 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.71 mm^{-1}
T = 298 (2) K
0.20 × 0.13 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.453, T_{max} = 0.595

4917 measured reflections
1480 independent reflections
1156 reflections with $I > 2\sigma(I)$
R_{int} = 0.070

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.073
S = 0.98
1480 reflections
95 parameters
76 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −1.22 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: −0.06 (3)

Table 1
Selected geometric parameters (Å, °).

Cl1—Tb1	2.632 (3)	Tb1—O2	2.377 (7)
O1—Tb1	2.347 (6)	Tb1—Cl2	2.754 (3)
O1^i—Tb1—O2	142.8 (3)	O2—Tb1—Cl1^i	85.8 (2)
O1—Tb1—O2	73.4 (3)	Cl1—Tb1—Cl1^i	174.30 (14)
O1—Tb1—Cl1	85.13 (17)	O1—Tb1—Cl2	144.69 (16)
O2—Tb1—Cl1	96.0 (2)	O2—Tb1—Cl2	71.7 (2)
O1—Tb1—Cl1^i	90.21 (17)		

Symmetry code: (i) $x, -y, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H7$\cdots$Cl2^{ii}	0.85 (9)	2.59 (9)	3.179 (8)	128 (10)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1996); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SG2182).

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supplementary materials

(2,2-Bipyridyl *N,N'*-dioxide-κ^2O,O')trichloridobis(methanol-κO)terbium(III)

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Comment

Lanthanide complexes have been investigated intensively because of their potential application in various optical devices [Ropp *et al.*, 2004; McGehee *et al.*, 1999; Tsaryuk *et al.*, 2003]. As shown in Fig.1, in the title compound the Tb[III] ion are coordinated to three Cl atoms and four O atoms which belong to a 2,2-bipyridyl-N,*N'*-dioxide molecule and two methanol molecules, respectively in a distorted pentagonal bipyramid geometry, with atom O2 O2A O1 O1A and Cl2 locating at equatorial positions. The crystal structure of (I) contains extensive hydrogen bonding. Neighbouring molecules are connected to each other mainly *via* O(2)—H(7)···Cl(2)[(i)] hydrogen bonds [symmetry code: (i) is $-x + 2$,-*y*,*z* + 1/2], the sum of the angles and bond length of d(D···A) about O(2)—H(7)···Cl(2)[(i)] are 128 (10)/% and 3.179 (8) A/%,respectively.

Experimental

A mixture of 2,2-bipyridyl-N,*N'*-dioxide (0.182 g, 0.001 mol), TbCl$_3$6H$_2$O (0.374 g, 0.1 mol) was added to 30 ml me thanol, The mixture was heated at 350 K or so for 5 h under reflux with stirring·The resulting solution was then filtered off. Single crystals suitable for X-ray diffraction analysis formed after a week by slow evaporation of the solvent.

Refinement

The H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H distances of 0.93 Å (pyridine ring), 0.86 Å (amine group) and 0.96 Å (methyl), and with U_{iso}(H) 1.2U_{eq}(C).

Figures

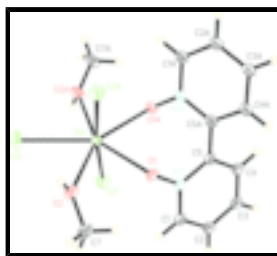Fig. 1. The molecular structure of (I), showing 30% probability displacement ellipsoids.
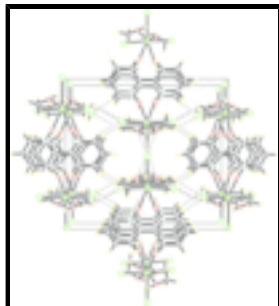
supplementary materials

Fig. 2. The packing diagram of (I), viewed along the *z* axis; hydrogen bonds are shown as dashed lines.

(2,2-Bipyridyl N,*N'*-dioxide-$\kappa^2 O,O'$)trichloridobis(methanol-κO)terbium(III)

Crystal data

$[\text{TbCl}_3(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2)(\text{C}_1\text{H}_4\text{O}_1)_2]$	$Z = 4$
$M_r = 517.54$	$F_{000} = 1000$
Orthorhombic, $C222_1$	$D_x = 2.047$ Mg m^{-3}
Hall symbol: C 2c 2	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 13.985$ (4) Å	$\mu = 4.71$ mm^{-1}
$b = 15.054$ (4) Å	$T = 298$ (2) K
$c = 7.976$ (2) Å	Block, yellow
$V = 1679.2$ (8) Å^3	$0.20 \times 0.13 \times 0.12$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	1480 independent reflections
Radiation source: fine-focus sealed tube	1156 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.070$
$T = 298(2)$ K	$\theta_{max} = 25.3°$
φ and ω scans	$\theta_{min} = 2.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -16 \rightarrow 16$
$T_{min} = 0.453$, $T_{max} = 0.595$	$k = -18 \rightarrow 18$
4917 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.018P)^2 + 0.004P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{max} = 0.002$
$S = 0.98$	$\Delta\rho_{max} = 0.94$ e Å^{-3}

1480 reflections	$\Delta\rho_{min} = -1.22$ e Å^{-3}
95 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
76 restraints	Extinction coefficient: 0.00061 (16)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with how many Friedel pairs?
Secondary atom site location: difference Fourier map	Flack parameter: −0.06 (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_{iso}*/U_{eq}
Cl1	0.7799 (2)	0.15435 (17)	−0.1542 (4)	0.0439 (7)
N3	0.5828 (3)	0.0943 (3)	0.0755 (7)	0.0290 (10)
C5	0.5081 (4)	0.0484 (3)	−0.0001 (9)	0.0292 (11)
C4	0.4313 (3)	0.0947 (4)	−0.0678 (8)	0.0308 (12)
H4	0.3814	0.0640	−0.1184	0.037*
C3	0.4292 (3)	0.1869 (4)	−0.0600 (8)	0.0320 (12)
H3	0.3778	0.2179	−0.1053	0.038*
C2	0.5039 (4)	0.2328 (3)	0.0156 (9)	0.0315 (12)
H2	0.5025	0.2945	0.0208	0.038*
C1	0.5807 (3)	0.1865 (3)	0.0834 (8)	0.0302 (11)
H1	0.6307	0.2172	0.1339	0.036*
O1	0.6523 (4)	0.0482 (4)	0.1438 (8)	0.0287 (11)
Tb1	0.78927 (4)	0.0000	0.0000	0.0237 (2)
O2	0.8425 (6)	0.0574 (6)	0.2615 (10)	0.0487 (19)
C7	0.8075 (8)	0.1191 (8)	0.3768 (13)	0.052 (2)
H7A	0.8356	0.1082	0.4847	0.077*
H7B	0.7393	0.1136	0.3847	0.077*
H7C	0.8236	0.1781	0.3404	0.077*
Cl2	0.9862 (2)	0.0000	0.0000	0.0493 (9)
H7	0.860 (8)	0.013 (11)	0.320 (13)	0.08 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0432 (16)	0.0358 (14)	0.0528 (18)	−0.0030 (15)	0.0040 (16)	0.0116 (12)

N3	0.0264 (18)	0.027 (2)	0.033 (2)	0.0045 (17)	0.0051 (18)	−0.0006 (19)
C5	0.027 (2)	0.028 (2)	0.033 (3)	0.0028 (18)	0.005 (2)	0.000 (2)
C4	0.029 (2)	0.030 (2)	0.034 (3)	0.004 (2)	0.004 (2)	0.001 (2)
C3	0.030 (2)	0.030 (2)	0.035 (3)	0.005 (2)	0.005 (2)	0.001 (2)
C2	0.031 (2)	0.028 (2)	0.036 (3)	0.0040 (19)	0.006 (2)	0.001 (2)
C1	0.028 (2)	0.027 (2)	0.035 (3)	0.0028 (19)	0.006 (2)	−0.001 (2)
O1	0.0264 (19)	0.027 (2)	0.033 (3)	0.0063 (18)	0.0041 (17)	−0.002 (2)
Tb1	0.0189 (3)	0.0285 (3)	0.0238 (3)	0.000	0.000	−0.0023 (7)
O2	0.041 (3)	0.069 (5)	0.036 (3)	0.024 (4)	−0.013 (3)	−0.025 (3)
C7	0.043 (4)	0.070 (6)	0.041 (4)	0.024 (4)	−0.013 (4)	−0.027 (3)
Cl2	0.0222 (12)	0.083 (3)	0.042 (2)	0.000	0.000	0.000 (5)

Geometric parameters (Å, °)

Cl1—Tb1	2.632 (3)	C1—H1	0.9300
N3—O1	1.312 (7)	O1—Tb1	2.347 (6)
N3—C5	1.3900	Tb1—O1^i	2.347 (6)
N3—C1	1.3900	Tb1—O2	2.377 (7)
C5—C4	1.3900	Tb1—O2^i	2.377 (7)
C5—C5^i	1.45723	Tb1—Cl1^i	2.632 (3)
C4—C3	1.3900	Tb1—Cl2	2.754 (3)
C4—H4	0.9300	O2—C7	1.396 (12)
C3—C2	1.3900	O2—H7	0.85 (14)
C3—H3	0.9300	C7—H7A	0.9600
C2—C1	1.3900	C7—H7B	0.9600
C2—H2	0.9300	C7—H7C	0.9600
O1—N3—C5	118.3 (5)	O1^i—Tb1—Cl1	90.21 (17)
O1—N3—C1	121.7 (5)	O1—Tb1—Cl1	85.13 (17)
C5—N3—C1	120.0	O2—Tb1—Cl1	96.0 (2)
N3—C5—C4	120.0	O2^i—Tb1—Cl1	85.8 (2)
N3—C5—C5^i	119.8 (5)	O1^i—Tb1—Cl1^i	85.13 (17)
C4—C5—C5^i	120.1 (5)	O1—Tb1—Cl1^i	90.21 (17)
C3—C4—C5	120.0	O2—Tb1—Cl1^i	85.8 (2)
C3—C4—H4	120.0	O2^i—Tb1—Cl1^i	96.0 (2)
C5—C4—H4	120.0	Cl1—Tb1—Cl1^i	174.30 (14)
C4—C3—C2	120.0	O1^i—Tb1—Cl2	144.69 (16)
C4—C3—H3	120.0	O1—Tb1—Cl2	144.69 (16)
C2—C3—H3	120.0	O2—Tb1—Cl2	71.7 (2)
C1—C2—C3	120.0	O2^i—Tb1—Cl2	71.7 (2)
C1—C2—H2	120.0	Cl1—Tb1—Cl2	92.85 (7)
C3—C2—H2	120.0	Cl1^i—Tb1—Cl2	92.85 (7)
C2—C1—N3	120.0	C7—O2—Tb1	135.3 (7)
C2—C1—H1	120.0	C7—O2—H7	105 (9)
N3—C1—H1	120.0	Tb1—O2—H7	107 (10)
N3—O1—Tb1	124.4 (5)	O2—C7—H7A	109.5
O1^i—Tb1—O1	70.6 (3)	O2—C7—H7B	109.5

O1^i—Tb1—O2	142.8 (3)	H7A—C7—H7B	109.5
O1—Tb1—O2	73.4 (3)	O2—C7—H7C	109.5
O1^i—Tb1—O2^i	73.4 (3)	H7A—C7—H7C	109.5
O1—Tb1—O2^i	142.8 (3)	H7B—C7—H7C	109.5
O2—Tb1—O2^i	143.5 (4)		

Symmetry codes: (i) x, −y, −z.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H7···Cl2^{ii}	0.85 (9)	2.59 (9)	3.179 (8)	128 (10)

Symmetry codes: (ii) −x+2, −y, z+1/2.

Fig. 1

Fig. 2