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Crystal structure of diaqua-bis(μ_2 -6-chloropyridin-2-olato- $\kappa^3N,O:O$)-tetrakis(chloropyridin-2-olato- κ^1O)-bis(phenanthroline- κ^2N,N')diterbium (III), $C_{54}H_{38}Cl_6Tb_2N_{10}O_8$

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Abstract

$C_{54}H_{38}Cl_6Tb_2N_{10}O_8$, triclinic, $P\bar{1}$, $a = 12.0062(8)$ Å, $b = 12.0072(8)$ Å, $c = 12.2324(8)$ Å, $\alpha = 115.371(3)^\circ$, $\beta = 103.452(3)^\circ$, $\gamma = 107.883(3)^\circ$, $V = 1373.64(16)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0237$, $wR_{ref}(F^2) = 0.1020$, $T = 296(2)$ K.

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Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents employed were commercially available and used as received without further purification. A mixture of $TbCl_3 \cdot 6H_2O$ (0.2 mmol, 0.075 g), 6-chloro-2-pyridinol (0.4 mmol, 0.052 g), 1,10-phenanthroline (0.2 mmol, 0.036 g) and NaOH (0.5 mL, 0.65 mol·L⁻¹) were mixed in water (5 mL) and heated at 413 K for 2 d in a sealed 15 mL Teflon-lined

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.91 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	15817, 6820, 0.018
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6354
$N(param)_{refined}$:	369
Programs:	Bruker [1, 2], SHELX [3], Diamond [4]

stainless steel vessel under autogenous pressure. After cooling to room temperature at a rate of 10 K · h⁻¹, colorless block crystals were isolated, washed with methanol and then dried in air, obtaining crystals in 25% yield.

Experimental details

H atoms were subsequently treated as riding atoms with distances O—H = 0.85 and 0.93 Å (ArH).

Comment

Syntheses of lanthanide complexes with different organic ligands have attracted considerable attention for their magnetism and fluorescence [5–9]. As widely known, the structure of complex materials significantly depends on the organic ligands. Aromatic phenol and pyridine ligands are usually used in the architectures of supramolecular compounds. In this aspect, 6-chloro-2-hydroxypyridine was selected to construct molecular polymers or clusters because of its nature, such as having more coordination sites, rigidity and suitable acidity [10–12]. However, to the best of our knowledge, there are very few examples of terbium compounds involving 6-chloro-2-pyridinol [13, 14]. Herein, we selected $TbCl_3 \cdot 6H_2O$ to react with 6-chloro-2-pyridinol under hydrothermal conditions. 1,10-Phenanthroline (phen) was introduced as auxiliary ligand.

The structure of this complex is centrosymmetric and contains two Tb³⁺ atoms, six 6-chloro-2-pyridinolato and two phen ligands (*cf.* the figure). Each Tb³⁺ ion is eight-coordinated. Two $[Tb(C_5H_3ClNO)_3(Phen)(H_2O)]$ units are bridged by two μ_2 -O atoms of 6-chloro-2-pyridinolato ligands to give a terbium to terbium separation of 3.921 Å.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
Tb1	0.09568(2)	0.64189(2)	0.19172(2)	0.02562(7)
Cl3	0.35375(10)	1.05587(10)	0.28026(11)	0.0506(2)
N2	0.2154(3)	0.8795(3)	0.4109(3)	0.0324(6)
N5	0.1500(3)	0.8150(3)	0.1085(3)	0.0308(6)
N1	−0.0229(3)	0.7934(3)	0.2328(3)	0.0320(6)
N4	−0.2603(3)	0.3550(3)	0.1109(3)	0.0373(6)
C12	0.0432(3)	0.9276(3)	0.3358(3)	0.0311(6)
N3	0.3557(3)	0.5330(4)	0.2435(4)	0.0397(7)
C1	−0.1419(4)	0.7485(5)	0.1493(4)	0.0424(9)
H1	−0.1876	0.6560	0.0783	0.051*
C18	0.4201(4)	0.4595(4)	0.2315(5)	0.0453(10)
C7	0.2422(4)	1.1134(4)	0.5361(4)	0.0400(8)
C13	0.0475(4)	0.7183(4)	−0.0095(4)	0.0336(7)
C10	0.3322(4)	0.9230(4)	0.4994(4)	0.0419(8)
H10	0.3633	0.8588	0.4886	0.050*
C11	0.1705(3)	0.9740(3)	0.4290(3)	0.0317(7)
C26	−0.1536(4)	0.4483(4)	0.2263(4)	0.0363(7)
C17	0.2165(4)	0.9377(4)	0.1287(4)	0.0389(8)
C22	0.2898(4)	0.5362(4)	0.3192(4)	0.0391(8)
C2	−0.2019(4)	0.8331(5)	0.1628(5)	0.0503(10)
H2	−0.2860	0.7974	0.1025	0.060*
C23	−0.3479(4)	0.2549(4)	0.1092(4)	0.0427(9)
C5	0.0673(5)	1.1621(4)	0.4659(5)	0.0502(10)
H5	0.0335	1.2244	0.4786	0.060*
C4	−0.0091(4)	1.0211(4)	0.3559(4)	0.0390(8)
C9	0.4097(4)	1.0586(4)	0.6064(4)	0.0499(10)
H9	0.4912	1.0847	0.6651	0.060*
C6	0.1868(5)	1.2059(4)	0.5508(5)	0.0503(10)
H6	0.2349	1.2986	0.6210	0.060*
C27	−0.1398(5)	0.4380(5)	0.3385(5)	0.0525(10)
H27	−0.0672	0.5044	0.4189	0.063*
C24	−0.3418(5)	0.2347(5)	0.2123(5)	0.0566(12)
H24	−0.4074	0.1608	0.2031	0.068*
C8	0.3652(4)	1.1529(4)	0.6244(4)	0.0497(10)
H8	0.4166	1.2446	0.6960	0.060*
C3	−0.1353(4)	0.9692(5)	0.2659(5)	0.0480(10)
H3	−0.1738	1.0273	0.2761	0.058*
C25	−0.2338(6)	0.3296(5)	0.3289(5)	0.0592(12)
H25	−0.2237	0.3211	0.4021	0.071*
C21	0.2932(5)	0.4642(5)	0.3852(5)	0.0531(10)
H21	0.2508	0.4685	0.4405	0.064*
C14	0.0100(5)	0.7483(5)	−0.1050(5)	0.0591(13)
H14	−0.0609	0.6810	−0.1866	0.071*
C19	0.4260(5)	0.3838(5)	0.2881(6)	0.0595(12)
H19	0.4717	0.3328	0.2743	0.071*
C20	0.3600(6)	0.3876(6)	0.3669(6)	0.0652(14)
H20	0.3605	0.3380	0.4080	0.078*
C16	0.1869(6)	0.9776(5)	0.0415(6)	0.0683(16)
H16	0.2364	1.0658	0.0608	0.082*
C15	0.0785(7)	0.8781(6)	−0.0777(7)	0.087(2)
H15	0.0520	0.9003	−0.1400	0.104*
Cl1	0.50333(12)	0.46459(13)	0.13293(14)	0.0630(3)
Cl2	−0.48563(12)	0.13917(13)	−0.04380(15)	0.0700(4)
O1	−0.0129(3)	0.5980(2)	−0.0235(2)	0.0335(5)
O3	0.2225(3)	0.6035(3)	0.3279(3)	0.0424(6)
O4	0.2692(3)	0.6538(3)	0.1274(3)	0.0434(6)
O2	−0.0664(3)	0.5473(3)	0.2313(3)	0.0457(6)
H4A	0.262(8)	0.648(8)	0.055(5)	0.13(3)*
H4B	0.308(4)	0.613(5)	0.148(4)	0.054(14)*

The Tb1–O1–Tb1A and O1–Tb1–O1A angle in the bridge are 110.17° and 69.83°, respectively. The distances of O(1)–Tb(1) and O(1)–Tb(1A) are 2.388 Å and 2.393 Å respectively. The ligand 6-chloro-2-pyridinol shows two coordination modes: κ^3N,O,O and κ^1O . In the crystal structure, the molecular conformation is stabilized by O–H···N hydrogen bonds of complexes.

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