

# Synthesis, Spectroscopic and X-Ray Structure Determination of a New Mononuclear Terbium (III) Complex from the Ligand *N,N'*-1,5-bis(pyridylmethylidene) Carbonohydrazone ( $H_2L$ )

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## Abstract

In the title compound,  $[Tb(H_2L)_2(H_2O)_3] \cdot 3Cl \cdot 4(H_2O) \cdot (C_2H_5OH)$ , the  $Tb^{3+}$  is nine-coordinated in a distorted monocapped square antiprism geometry by four nitrogen atoms, two oxygen atoms from the ligand molecules of the tridentate *N,N'*-1,5-bis(pyridylmethylidene) carbonohydrazone ( $H_2L$ ) and three oxygen atoms of coordinating water molecules. The structure of the complex was elucidated by X-ray diffraction analysis. Suitable crystals were grown by slow evaporation of ethanol solution. The compound crystallizes in the triclinic crystal system with a space group of  $P\bar{1}$ . The asymmetric unit of the compound contains two neutral ligand molecules, one terbium ion, three coordinated water molecules, five and half uncoordinated water molecules and one uncoordinated ethanol molecule. In the crystal, the complex cations are linked by hydrogen bonds into layers. These layers, chloride anions and non-coordinating water molecules are connected by  $O-H \cdots O$ ,  $O-H \cdots N$ ,  $O-H \cdots Cl$ ,  $N-H \cdots O$ ,  $N-H \cdots Cl$  and  $C-H \cdots Cl$  hydrogen bonds into a three-dimensional structure.

## 1. Introduction

Lanthanides and their complexes, because of the multiplicity of applications and potential uses, have not only aroused immense interest in coordination chemistry but in

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numerous other branches of science [1-4]. Due to their photoluminescence in the visible and near infrared under UV excitation, organic lanthanide complexes are of both fundamental and technological interest [5,6]. The construction of these lanthanide coordination compounds is increasingly topic due to their interesting structural topology as well as potential applications such as catalysis [7,8], magnetism [9,10], luminescence [11,12] and ion exchange [13,14]. Ln(III) ions have a variable coordination number and a flexible coordination geometry [15-20]. Thus, coordination compounds of lanthanide (III) are more difficult to design than coordination based on transition metals. When the ligand is flexible, the reaction conditions can act on its mode of coordination to give highly variable coordination geometries. Several Ln(III) coordination compounds with novel topologies have been produced using flexible ligands [21-23].

In the present work, a novel flexible ligand (*N,N'*-1,5-bis(pyridylmethylidene) carbonohydrazone) ( $H_2L$ ), which is prepared by a ready condensation reaction of carbonohydrazide with two equivalents of 2-pyridinecarbaldehyde, is used to prepare a complex of terbium(III). The Schiff base ( $H_2L$ ), which provides four soft donors *N* atoms from two pyridine rings and two imino functions and one hard donor *O* atom from carbonyl moiety, is used with chloride anions which have a weak coordinating power, to construct a mononuclear terbium(III) complex.

## 2. Materials and Methods

### 2.1. Materials and instruments

2-pyridinecarbaldehyde, carbonohydrazide, terbium chloride from Aldrich were used without purification. The melting points of the ligand and complex were determined on a Büchi capillary tube apparatus. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400  $cm^{-1}$  region. The  $^1H$  and  $^{13}C$  NMR spectra of the Schiff bases were recorded in DMSO- $d_6$  on a BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. The room temperature molar conductivity of the complex was measured using a WTWLF-330 conductivity meter on a millimolar DMF solution. Magnetic susceptibility at room temperature of the complex was measured using Gouy balance.

### 2.2. Synthesis of *N,N'*-1,5-bis(pyridylmethylidene) carbonohydrazone ligand ( $H_2L$ )

2 g (0.0222 mol) of carbonohydrazide were suspended in 20 mL of methanol. After stirring at room temperature for half hour, 4.757g (0.0444 mol) of 2-

pyridinecarbaldehyde dissolved in 20 mL of methanol were added. After 10 minutes two drops of glacial acetic acid were added. The resulting white suspension turned in orange solution after refluxing for two hours. The resulting orange solution was stored at 4°C. After two days the white solid which appears was recovered by filtration, washed with cold methanol ( $2 \times 10$  mL) and diethyl ether ( $2 \times 10$  mL) before being dried over  $P_4O_{10}$ . M.p. = 216°C. Yield of 82%. Anal. Calc.(%) for  $C_{13}H_{12}N_6O$ : C, 58.20; H, 4.51; N, 31.33. Found(%): C, 58.18; H, 4.53; N, 31.31. IR ( $\nu$ ,  $cm^{-1}$ ): 3439, 3204, 3198, 3055; 2936, 1684, 1582, 1610, 1582, 1532, 1467, 1360, 1274, 1131;  $^1H$  NMR (dms $o$ - $d_6$ ,  $\delta$ (ppm)): 7.6 - 8.72 (m, 8H,  $H_{py}$ ), 10.82 (s, 2H, NH), 8.03 (s, 1H, HC = N)  $^{13}C$  NMR (dms $o$ - $d_6$ ,  $\delta$ (ppm)): 157.9 (C = O), 154.70 ( $C_{py}$ ), 148.07 ( $C_{py}$ ), 146.67 (C = N), 137.60 ( $C_{py}$ ), 123.00 ( $C_{py}$ ), 119.09 ( $C_{py}$ ).

### 2.3. Synthesis of complex $[Tb(H_2L)_2(H_2O)_3]_2 \cdot 6Cl \cdot 11(H_2O) \cdot 2(C_2H_5OH)$

In 10 mL of ethanol containing 100 mg (0.373 mmol) of  $H_2L$  ligand was added an ethanol solution containing 278.54 mg (0.746 mmol) of  $TbCl_3 \cdot 6H_2O$ . The mixture was stirred for one hour. The resulting yellow solution which was filtered gave suitable yellow crystals suitable for X-ray analysis after two weeks under slow evaporation. Crystal structure was determinate by X-ray diffraction. Yield: 63.26 %. Anal. Calc.(%) for  $Tb_2C_{56}H_{94}N_{24}Cl_6O_{23}$ : C, 33.60; H, 4.73; N, 16.79; Cl; 10.62. Found(%): C, 33.58; H, 4.71; N, 16.76; Cl; 10.60(%). IR ( $\nu$ ,  $cm^{-1}$ ): 3327, 3167, 3093, 3015, 1666, 1619, 1570, 1525, 1475, 1440, 1373, 1249, 1142, 1082;  $\mu_{eff}$  (MB) = 9.45;  $\Lambda$  ( $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ , DMF): fresh solution: 232.2; two weeks later: 240.3.

### 2.4. X-ray data collection, structure determination and refinement

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a XtaLAB AFC12 (RINC): Kappa single diffractometer with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [24]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on  $F^2$  by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [25]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and  $CH_3$

groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [26].

**Table 1.** Crystallographic data and refinement parameter for the ligand and the complex.

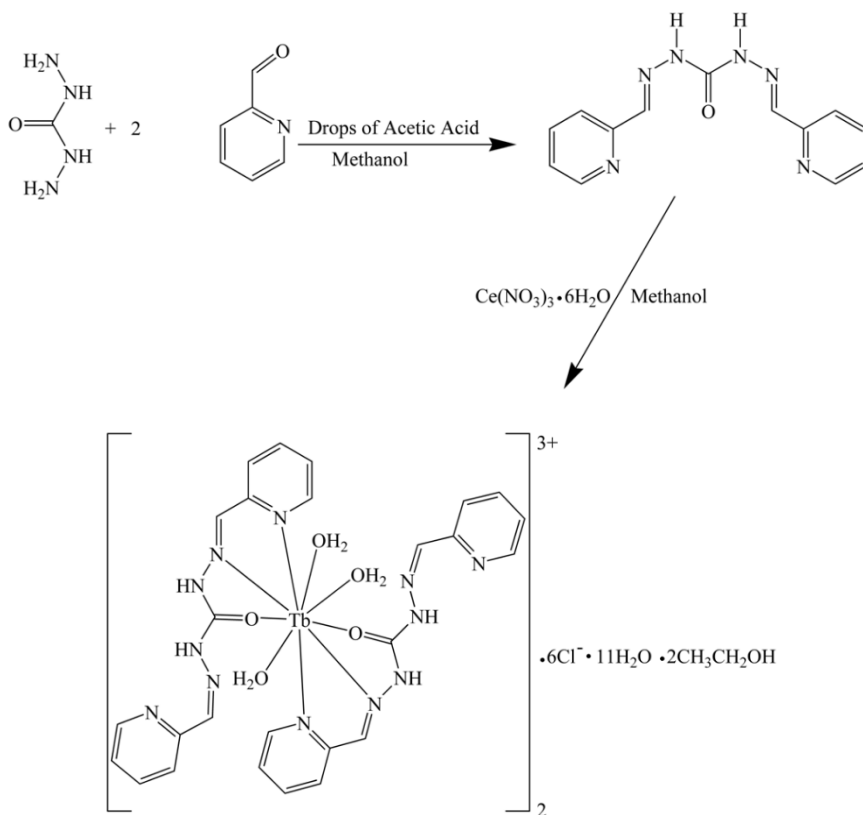
Empirical formula	$2(\text{C}_{26}\text{H}_{30}\text{N}_{12}\text{O}_5\text{Tb}) \cdot 6(\text{Cl}) \cdot 11(\text{H}_2\text{O}) \cdot 2(\text{C}_2\text{H}_6\text{O})$
Formula weight (g/mol)	2002.09
$T$ (K)	175
Crystal system	Triclinic
Space group	P-1
Crystal size (mm <sup>3</sup> )	0.03 x 0.02 x 0.02
Mo $K\alpha$ radiation, $\lambda$ (Å)	0.71073
$a$ (Å)	9.8653(1)
$b$ (Å)	12.0704(2)
$c$ (Å)	17.0759(3)
$\alpha$ (°)	104.826(1)
$\beta$ (°)	90.022(1)
$\gamma$ (°)	93.100(1)
$V$ (Å <sup>3</sup> )	1962.58(5)
$Z$	1
$D_{\text{cal}}$ (g cm <sup>-3</sup> )	1.694
$F(000)$	1014
$\mu$ (mm <sup>-1</sup> )	2.07
$\theta$ max (°)	58.256
$h, k, l$ , ranges	$-12 \leq h \leq 13, -16 \leq k \leq 15, -19 \leq l \leq 23$
Measured reflections	34267
Independent Reflections	9176
Observed Reflections [ $I > 2\sigma(I)$ ]	9374
$R_{\text{int}}$	0.054
$R[F^2 > 2\sigma(F^2)]$	0.034
$wR(F^2)$	0.090
Data/parameters/restraint	8083/576/55
Goodness-of-Fit	1.04
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.20, -0.94

### 3. Results and Discussions

#### 3.1. Spectroscopic studies of ligand H<sub>2</sub>L

The <sup>1</sup>H NMR spectrum of the ligand shows two main signals at 10.82 ppm and 8.03 ppm attributable to the protons of H—N and H—C=N groups. The signal in the range 7.60-8.72 ppm are assigned to the aromatic protons. The signal at 146.47 ppm on the <sup>13</sup>C NMR spectrum of the ligand confirms the presence of the azomethine group. The signal of the carbon atom of the carbonyl group is located at 157.9 ppm. The IR spectrum of the ligand shows main bands at 3204 cm<sup>-1</sup>, 1684 cm<sup>-1</sup> and 1610 cm<sup>-1</sup>, attributable respectively to ν(N—H), ν(C=O) and ν(C=N). Additional bands due to the aromatic ring are located in the range 1467 cm<sup>-1</sup>–1582 cm<sup>-1</sup>. Comparison of the infrared data of the ligand and that of the complex obtained upon coordination with terbium ion shows that no iminolization and no deprotonation occurs during the complexation. In fact, in the spectra of the complex band due to ν(C=O) appears *ca.* 1666 cm<sup>-1</sup>. The shift of the ν(C=N) band from 1610 cm<sup>-1</sup> in the ligand spectrum to 1619 cm<sup>-1</sup> for the complex is indicative of the involvement of the azomethine atoms in the coordination to the Tb(III). The broad band centered at 3093 cm<sup>-1</sup> is due to the stretching of H—N [27].

The presence of coordinated and uncoordinated water molecules is attested by the bands pointed at 3327cm<sup>-1</sup>, 3167cm<sup>-1</sup>, 920cm<sup>-1</sup> and 580 cm<sup>-1</sup> [28]. The molar conductivity values of the freshly DMF (10<sup>-3</sup> M) complex solution and fifteen days later are respectively 232.2 (S cm<sup>2</sup> mol<sup>-1</sup>) and 240.3 (S cm<sup>2</sup> mol<sup>-1</sup>). These values are in accordance with those reported for 3:1 electrolyte for the Tb(III) complex [29]. The stability of the conductivity values fifteen days later show that the complexes are stable in DMF. The value of the magnetic moment at room temperature for the diamagnetic complex is indicative of the presence of one metal atom per molecule. The magnetic moment value of 9.45μ<sub>B</sub> is in accordance with one three unpaired electrons by f<sup>8</sup> configuration. This value is comparable to that of the terbium complex prepared with *N'*-[(1E)-1-phenylethylidene]isonicotinohydrazide [30]. Micro elemental analysis of C, N, H and Cl, magnetic susceptibility measurements and molar conductance value of Tb<sup>+3</sup>/LH<sub>2</sub> complex, all point to the formation of 1:2 metal ligand stoichiometric complex. The presence of coordinated and uncoordinated water molecules in metal complex is evident from solid IR spectrum of the terbium(III) complex.



**Scheme 1.** Synthetic scheme for HL and complex preparation.

### 3.2. Crystal structure of Tb(III) complex

The title compound Tb(III) crystallizes in the triclinic space group  $P\bar{1}$ . The molecular structure of the complex is shown in Figure 1. Selected bond lengths and bond angles for the complex are compared in Table 1. The asymmetric unit of the complex is composed by one Tb(III) ion, two neutral ligand molecules, three coordinated water molecules, four uncoordinated water molecules, one lattice ethanol molecule, and three chloride ions. Each ligand molecule acts in tridentate fashion through one azomethine nitrogen atom, one pyridine nitrogen atom and one carbonyl oxygen atom. For each ligand, only one of the two arms is involved in the coordination. Therefore, there remains two soft nitrogen atoms from a pyridine ring and an imine function which are uncoordinated. The hard protonated nitrogen atoms remain non-coordinating in both arms of the ligand. The resulting nine-coordinated Tb(III) is surrounded by four nitrogen atoms and five oxygen atoms to result in a  $TbN_4O_5$  unit in which two oxygen atoms originate from the two

ligands whereas the three other oxygen atoms come from three coordinated water molecules. The coordination polyhedron is best described as a distorted monocapped square antiprism (Figure 2). The Tb—N distances vary from 2.544(2) Å to 2.570(3) Å, which fall in the range of those usually encountered for similar Schiff base nine coordinated Tb(III) complex [31-33]. The Tb—N(imine) [2.544(2)Å and 2.558(2)Å] are shorter than those of Tb—N(pyridine) [2.568(3)Å and 2.570(3)Å]. The same relations between the Tb—N(imine) and Tb—N(Py) bond lengths were observed in the structures of [TbL(NO<sub>3</sub>)<sub>3</sub>]CH<sub>3</sub>CN (L = *N,N'*-cyclohexane-1,2-diylbis[1-(pyridin-2-yl)methanimine] [34], of [Tb(H<sub>2</sub>L)(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) (H<sub>2</sub>L = (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone) [35] and of [Tb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(L)(H<sub>2</sub>O)<sub>2</sub>]·NO<sub>3</sub>·H<sub>2</sub>O (L = 1-(pyridin-2-ylmethylidene)-2-(pyridin-2-yl)-hydrazine) [31]. Tb—O(carbonyl) [2.387(2) Å and 2.378(2)Å] and Tb—OW distances involving oxygen atoms of coordinating water molecules of 2.378(2)Å, 2.411(3)Å and 2.400(2)Å are comparable with the values reported for similar complexes [36,37]. For each of the two ligands there is a C=N bond whose nitrogen atom is coordinated to Tb(III) and a C=N bond whose nitrogen atom remains uncoordinated. These two bonds have different lengths in each ligand *ie.* 1.272(4) Å and 1.276(4) Å (Table 2). Additionally, the C=O bond lengths are slightly different in the two ligand molecules with values of 1.244(4)Å and 1.235(4) Å. One of the chloride anions (Cl<sup>-</sup>) is disordered with two sites having occupancies of 0.75(1) and 0.25(1).

The coordination of each carbonohydrazone ligand to Tb(III) results in the formation of two five-membered chelating rings OCNNTb and NCCOTb which share one Tb—N bond. The bite angle values are quite equal and vary from 62.92(8)° and 62.80(7)°. In each ligand molecule, the two five-membered rings are almost coplanar with dihedral angle values of 2.012(1)° and 2.678(2)°, respectively.

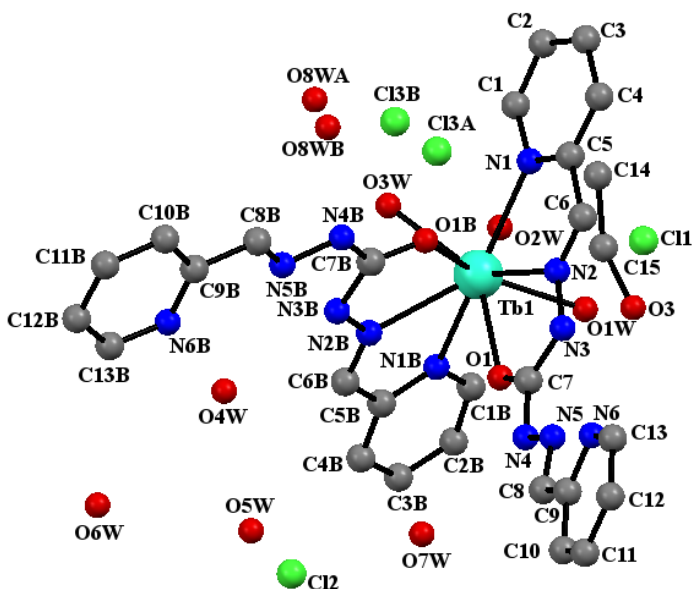
**Table 2.** Selected bond distances [Å] and angles [°] for the Tb<sup>III</sup> complex.

Bond	Bond lengths [Å]	Bond	Bond angles [°]
Tb1—O1	2.387 (2)	O1—Tb1—N1	125.65 (8)
Tb1—N1	2.568 (3)	O1—Tb1—N2	62.92 (8)
Tb1—N2	2.544 (2)	O1—Tb1—O1W	75.58 (8)

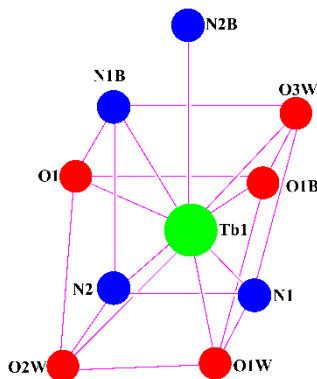
Tb1—O1W	2.400 (2)	O1—Tb1—O2W	136.53 (8)
Tb1—O2W	2.411 (2)	O1—Tb1—N1B	73.57 (8)
Tb1—O3W	2.378 (2)	O1—Tb1—N2B	69.18 (8)
Tb1—N1B	2.570 (3)	N1—Tb1—N1B	156.18 (9)
Tb1—O1B	2.378 (2)	N2—Tb1—N1	62.75 (8)
Tb1—N2B	2.558 (2)	N2—Tb1—N1B	134.40 (8)
O1—C7	1.244 (4)	N2—Tb1—N2B	110.42 (8)
N2—C6	1.272 (4)	O1W—Tb1—N1	89.12 (8)
N4—C7	1.353 (4)	O1W—Tb1—N2	74.71 (8)
N5—C8	1.276 (4)	O1W—Tb1—O2W	68.56 (8)
O1B—C7B	1.235 (4)	O1W—Tb1—N1B	82.21 (8)
N2B—C6B	1.275 (4)	O1W—Tb1—N2B	135.41 (8)
N4B—N5B	1.369 (4)	O2W—Tb1—N1	78.27 (9)
N4B—C7B	1.343 (4)	O2W—Tb1—N2	126.02 (8)
N5B—C8B	1.272 (4)	O2W—Tb1—N1B	77.92 (9)

The carbonohydrazide moiety C6=N3—N2—C7=O1 and its related coordinated pyridine ring N1C1/C5 are almost coplanar with dihedral angle of 8.008(2)°. The same observation is done with the second ligand molecule with dihedral angle of 7.599(3)° between C6B=N3B—N2B—C7B=O1B and N1BC1B/C5B. The mean planes defined by the atoms of the two ligand molecules coordinated to Tb(III) form a dihedral angle of 76.75 (5)°. The O/N—Tb—O/N bond angles fall in the range 62.47(8)° to 156.18(9)°. These values are comparable to other reported values for oxygen/nitrogen-coordinated Tb(III) complexes [31,38].





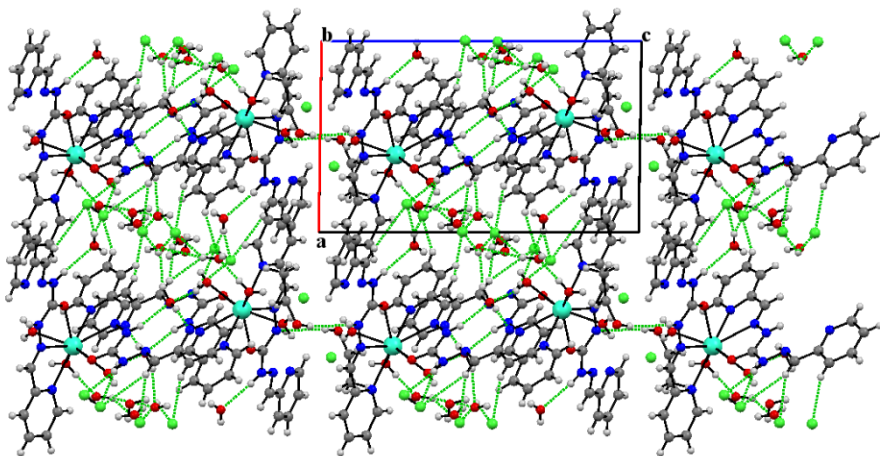
**Figure 1.** ORTEP plot showing the molecule structure of the  $[\text{Tb}(\text{H}_2\text{L})_2(\text{H}_2\text{O})_3]_2 \cdot 6\text{Cl} \cdot 11(\text{H}_2\text{O}) \cdot 2(\text{C}_2\text{H}_5\text{OH})$  complex.



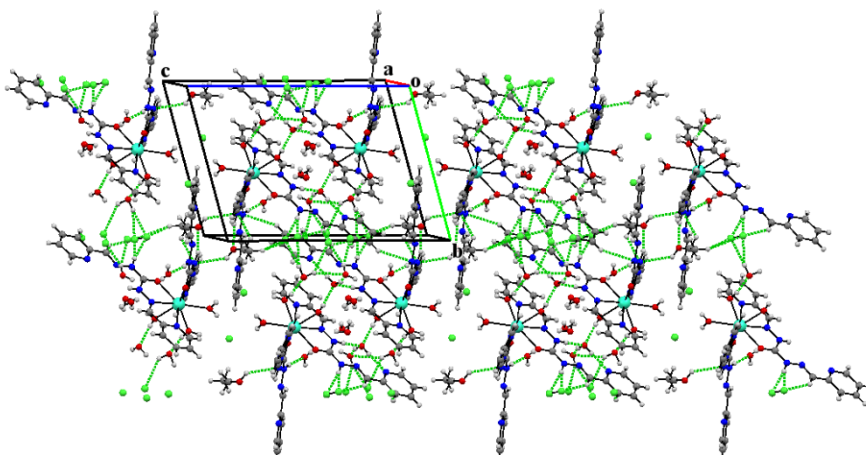
**Figure 2.** Plot showing the coordination sphere of Tb(III).

In the crystals, the Tb(III) complexes are connected by O—H $\cdots$ O, O—H $\cdots$ N, O—H $\cdots$ Cl, N—H $\cdots$ O, N—H $\cdots$ Cl and C—H $\cdots$ Cl hydrogen bonds (Table 3). The crystal structure of the Tb(III) complex is discussed, and the crystal packing is shown in Figures 3 and 4. The complexes are linked by numerous hydrogen bonds. Uncoordinated water molecules (O5W, O6W, O8W) act as hydrogen-atom donor with non-coordinating chloride anions. Uncoordinated ethanol molecule acts as hydrogen-atom donor with nitrogen atom of the ligand. Coordinated water molecule (O1W, O2W, O3W) acts as

hydrogen-atom donor with non-coordinating chloride ( $O1W-H\cdots Cl1^v$ , (v)  $-x+1$ ,  $-y+1$ ,  $-z$ ) or uncoordinated water molecules ( $O2W-H\cdots O6W^{vi}$  and  $O3W-H\cdots O4W^{vi}$ , (vi)  $-x+1$ ,  $-y+1$ ,  $-z+1$ ). The O atoms of the uncoordinated ethanol molecule act as acceptor in the hydrogen bonds with the *HN* groups of the ligand of adjacent complex ( $N3-H\cdots O3^i$ , (i)  $x$ ,  $y-1$ ,  $z$ ). The various components are linked by  $O-H\cdots Cl$  and  $N-H\cdots Cl$  hydrogen bonds, forming layers parallel to *b* axis, as illustrated in Figure 3. The layers are linked by  $O-H\cdots O$ ,  $O-H\cdots Cl$  and  $N-H\cdots Cl$  hydrogen bonds, forming a three-dimensional supramolecular framework, which is reinforced by a series of  $C-H\cdots Cl$  hydrogen bonds (Figure 4 and Table 3).



**Figure 3.** A view along the *b* axis of the hydrogen-bonded (dashed lines) layer structure of the  $Tb^{III}$  complex. The  $Cl^-$  ions are shown as green balls.



**Figure 4.** Crystal structure of the title compound showing layers of molecules along the *bc* plane.

**Table 3.** Hydrogen-bond geometric parameters (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 $\cdots$ O3i	0.878(18)	1.929(18)	2.772(5)	161(2)
O4W—H4WA $\cdots$ O5W	0.886(18)	2.07(3)	2.909(4)	157(4)
O4W—H4WB $\cdots$ N6B	0.837(19)	2.08(2)	2.911(4)	172(5)
N4—H4 $\cdots$ O7W	0.82(4)	2.08(4)	2.887(5)	172(4)
O5W—H5WA $\cdots$ Cl2	0.777(19)	2.26(6)	2.84(3)	132(6)
O5W—H5WA $\cdots$ Cl2 <sup>ii</sup>	0.777(19)	2.37(5)	2.92(3)	129(5)
O5W—H5WB $\cdots$ O8WA <sup>iii</sup>	0.805(19)	2.53(4)	3.106(4)	130(4)
O6W—H6WA $\cdots$ O5W	0.852(19)	2.37(3)	3.155(5)	153(5)
O6W—H6WA $\cdots$ Cl2 <sup>ii</sup>	0.852(19)	2.72(6)	3.35(2)	131(5)
O6W—H6WB $\cdots$ Cl3A <sup>iv</sup>	0.903(16)	2.270(16)	3.154(4)	166(5)
O6W—H6WB $\cdots$ Cl3B <sup>iv</sup>	0.903(16)	2.25(3)	3.112(9)	159(6)
O7W—H7WA $\cdots$ Cl3A <sup>iii</sup>	0.863(18)	2.37(2)	3.220(4)	170(7)
O7W—H7WA $\cdots$ Cl3B <sup>iii</sup>	0.863(18)	2.07(4)	2.891(8)	157(7)
C8—H8 $\cdots$ Cl3A <sup>iii</sup>	0.95	2.86	3.721(4)	150.6
O1W—H1WA $\cdots$ Cl1	0.820(18)	2.333(19)	3.133(2)	165(4)
O1W—H1WB $\cdots$ Cl1 <sup>v</sup>	0.839(18)	2.34(3)	3.096(2)	150(3)
O2W—H2WA $\cdots$ Cl1	0.843(18)	2.303(18)	3.133(2)	168(4)

O2W—H2WB···O6W <sup>vi</sup>	0.831(18)	1.85(2)	2.666(4)	169(4)
O3W—H3WA···O4W <sup>vi</sup>	0.817(18)	1.96(2)	2.749(3)	163(5)
O3W—H3WB···O8WA	0.804(14)	2.413(14)	3.215(4)	175(4)
O3W—H3WB···O8WB	0.804(14)	1.747(18)	2.550(9)	176(3)
C10—H10···Cl3A <sup>iii</sup>	0.95	2.98	3.805(4)	145.7
N3B—H3BA···O4W	0.855(18)	2.05(2)	2.890(4)	168(4)
N4B—H4BA···Cl3A	0.874(19)	2.35(2)	3.212(3)	171(4)
N4B—H4BA···Cl3B	0.874(19)	2.36(2)	3.204(9)	162(4)
C8B—H8B···Cl2 <sup>vii</sup>	0.95	2.65	3.529(17)	154.4
C8B—H8B···Cl3B	0.95	2.87	3.682(8)	143.7
C10B—H10B···Cl2 <sup>iv</sup>	0.95	2.53	3.285(18)	136.6
O3—H3C···N3 <sup>v</sup>	0.84	2.52	3.188(6)	136.8
C15—H15A···Cl1	0.99	2.67	3.246(11)	117.2
C15—H15B···N3 <sup>viii</sup>	0.99	2.51	3.167(11)	123.6
C14—H14A···Cl1	0.98	2.80	3.397(10)	119.8
C14—H14B···Cl3A <sup>viii</sup>	0.98	1.91	2.836(16)	155.7
C14—H14B···Cl3B <sup>viii</sup>	0.98	2.87	3.80(2)	159.3

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

#### 4. Conclusion

The results presented in this study indicate that terbium(III) forms stable complex with Schiff basis derivate from 2-pyridinecarbaldehyde and carbohydrazide. According to the data of elemental analysis, molar conductivity, FT-IR, and X-ray crystallographic structure determination, the complex has a metal to carbonohydrazide stoichiometry of 1:2. This coordination mode is in full accordance with the corresponding species suggested in the solution studies. The counter-ions, with a weak binding ability, are not coordinated to metal center. In the terbium complex, the metal ion is nine-coordinated. In the crystal the geometry around the Tb(III) ion is best described as a distorted monocapped square antiprism.

#### 5. Supporting information

CCDC-2206332 contains the supplementary crystallographic data for the compound. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

#### Conflicts of Interest

The authors declare that they have no conflict of interest.

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