

Synthesis and Characterization of a Coordination Polymer Ce(HL)(NO₃)₂(H₂O) with H₂L = N'-[(2-hydroxyphenyl) Methylidene] pyridine-3-Carbohydrazide

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Abstract: Herein we reported the crystal structure of a new coordination polymer formulated as Ce(NO₃)₂(HL)·H₂O obtained by the reaction of N'-[(2-hydroxyphenyl)methylidene]pyridine-3-carbohydrazide (H₂L) and Cerium nitrate hexahydrate in 1:1 ratio in methanol. The ligand and the coordination polymer were firstly characterized by FTIR and physical measurement. Suitable crystals were grown by slow evaporation of methanol solution of the coordination polymer. The title compound crystallizes in the orthorhombic space group *P*2₁2₁2₁ with the following unit cell parameters: *a* = 7.8497(1) Å, *b* = 9.8380(1) Å, *c* = 22.3471(3) Å, *V* = 1725.76(4) Å³, *Z* = 5, *R*₁ = 0.019 and *wR*₂ = 0.036. For each Ce³⁺ ion the ligand acts in its monodeprotonated form, in tridentate fashion through one phenolate oxygen atom, one azomethine nitrogen atom and one oxygen atom of a carbonohydrazide moiety. One pyridine nitrogen atom of the ligand remains uncoordinated. Two nitrate anions act in η¹:η²:μ- mode, one nitrate anion acts in bidentate fashion to each Ce³⁺ while one water molecule complete the coordination around Ce³⁺. The structure, solved by single crystal X-ray diffraction, is a polymer in which the units Ce(NO₃)₂(HL)·H₂O are bridged together by two nitrate anions acting in η¹:η²:μ- mode. Thus, the cerium cations are ten coordinated and the environments are best described as a distorted bicapped square antiprism. The Ce^{III}...Ce^{III} distance is 5.2824(4) Å and the bridging angle Ce—O—Ce is 161.7(1)°. The structure is consolidated by intra and intermolecular hydrogen bond.

Keywords: Cerium, Schiff Base, Coordination Polymer, X-Rays, Bicapped Square Antiprism

1. Introduction

The use of Schiff's bases in coordination chemistry, to develop from molecular units with specific properties has undergone spectacular development in recent years thanks to very elaborate synthesis methods which make it possible to control the synthesis of complexes with original structures. Polyfunctional acyclic, symmetric, or asymmetric ligands and their complexes represent an essential component of this chemistry [1–6]. These ligands are widely used for the

synthesis of complexes with very interesting biochemical and physical properties [7–10]. The formation of acyclic ligand complexes depends on the flexibility of the arms bearing the groups having donor sites [11, 12], the nature of the donor atoms and the complexation properties of the cations and anions playing the role of charge balance. [13, 14]. These Schiff bases have made it possible to develop molecular materials with specific properties [15–19]. This article describes the synthesis of a tridentate Schiff base obtained by the reaction between nicotinohydrazide and salicylaldehyde. The flexibility and numerous coordination sites of the

resulting acyclic ligand offer several possible structures with lanthanide ions [20–25]. The use of $\text{N}'\text{-}[(2\text{-hydroxyphenyl})\text{methylidene}]\text{pyridine-3-carbohydrazide}$ (H_2L) ligand in the presence of cerium nitrate salts gives Ce^{3+} coordination polymer formulated as $\text{Ce}(\text{NO}_3)_2(\text{HL})\cdot\text{H}_2\text{O}$. The coordination polymer was characterized by IR spectra, magnetic measurements at room temperature and elemental analyses. The crystal structures of the Ce(III) based coordination polymer was determined by single crystal X-ray diffraction.

2. Materials and Methods

2.1. Starting Materials and Instrumentations

Salicylaldehyde and nicotinothyraide were purchased from Aldrich and were used without further purification.

Solvents were of reagent grade and were used without further purification. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the $4000\text{--}400\text{ cm}^{-1}$ region. The ^1H NMR spectra were recorded at 300 MHz and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at 75 MHz on a Bruker AC-300 spectrometer. In order to examine the thermal stability of the coordination polymer, thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) measurements (Figure 6) were carried out with a Setaram Sensys Evo under Argon flow, from room temperature to 800°C , with a heating rate of $5^\circ\text{C}/\text{min}$.

2.2. Synthesis of $\text{N}'\text{-}[(2\text{-hydroxyphenyl})\text{methylidene}]\text{pyridine-3-carbohydrazide}$

(H_2L) and complex with cerium

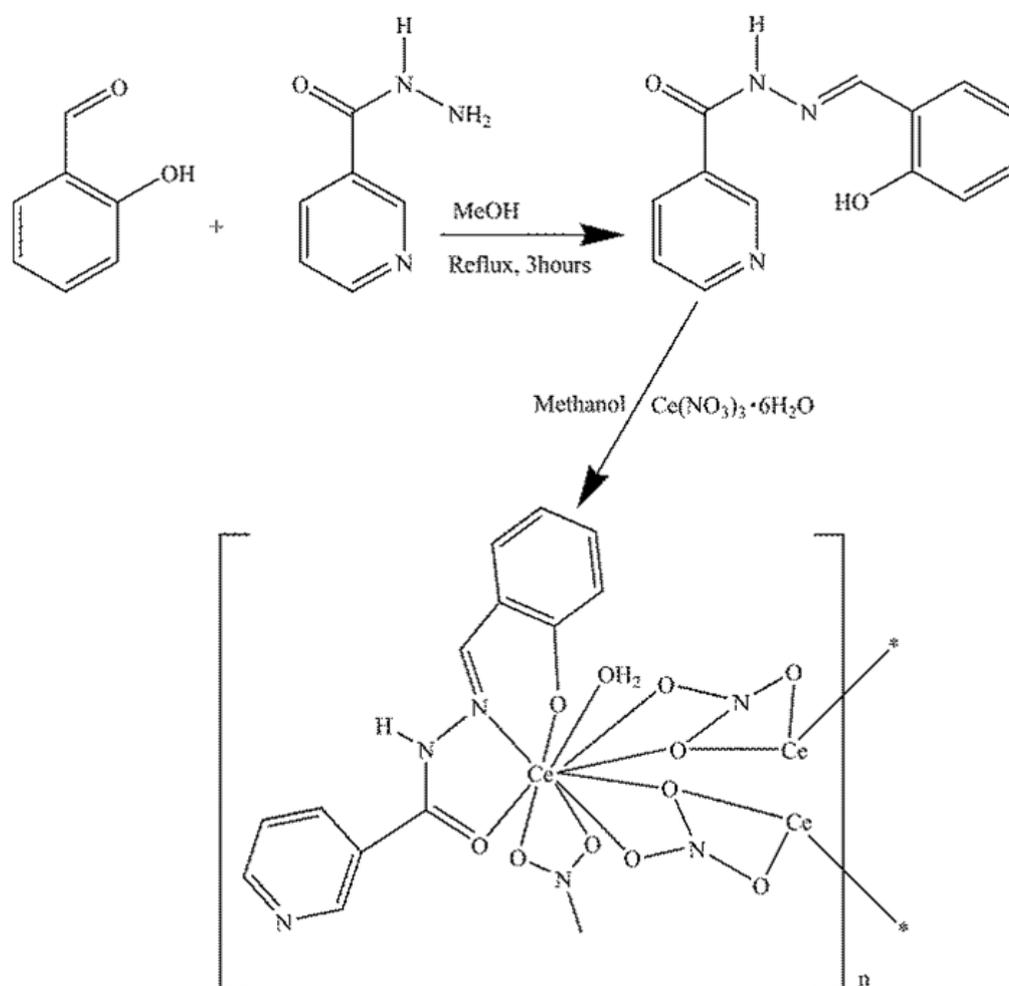


Figure 1. Synthesis pathway of the ligand H_2L and complex with cerium.

In a 250 mL flask, 1.37 g (10 mmol) of nicotinothyraide were dissolved in 10 mL of methanol and 1.22g (10 mmol) of salicylaldehyde previously dissolved in 5 mL of methanol were added. The mixture was heated under reflux for 3 hours followed by a slow evaporation. The yellow precipitate which appears was washed with ether (2 x 10 mL) and dried

in air.

Yield 66%. M.p.: $188\text{--}190^\circ\text{C}$. Anal. Calc for $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.69; H, 4.58; N, 17.70. IR: $\nu(\text{cm}^{-1})$: 3300 (O-H); 3043 (N-H); 1661 (C=O); 1605 (C=N); 1568 - 1417 (C=C) and (C=N)_{pyridine}; 1365 (C-N); 1557 (N-N); 1291 (C-O); 876-629 (C-H)_{arom}. NMR ^1H

(500 MHz, DMSO- d_6 , δ , ppm): 12.28 (s, 1H, OH), 11.18 (s, 1H, NH), 9.09 (s, 1H, =CH), 6.94-8.78 (m, 8H, Ar-H). NMR ^{13}C (125 MHz, DMSO- d_6 , δ , ppm): 161.38 (C=O), 157.39 (C_{ipso}-O), 152.41 (C_{Ar}), 148.58 (C_{Ar}), 148.43 (C=N), 135.42 (C_{Ar}), 131.58 (C_{Ar}), 129.22 (C_{Ar}), 128.63 (C_{Ar}), 123.61 (C_{Ar}), 119.38 (C_{Ar}), 118.63 (C_{Ar}), 118.38 (C_{Ar}).

2.3. Synthesis of the Coordination Polymer Ce(NO₃)₂(HL)H₂O

0.1g (0.42 mmol) of the H₂L ligand in a 100 mL flask containing 10 mL of methanol. After complete dissolution of the ligand, 0.4342 g (0.42 mmol) of cerium nitrate hexahydrate previously dissolved in 5 mL of methanol were added. The resulting mixture was refluxed for 3 hours. On cooling, the yellow precipitate which appears was collected by filtration, washed with methanol and ether and dried in air. The filtrate which was left under slow evaporation gave

crystals suitable for X-ray diffraction after a week. Anal. Calc for C₁₃H₁₂CeN₅O₉: C, 29.89; H, 2.32; N, 13.41. Found: C, 29.91; H, 2.34; N, 13.38.

2.4. X-ray Crystallography

Details of the crystal structure solution and refinement are given in table 1. Single-crystal X-ray diffraction data were measured on a Rigaku Synergy S diffractometer at the MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection reduction and multiscan ABSPACK correction were performed with CrysAlisPro (Rigaku Oxford Diffraction). The crystal structures including the anisotropic displacement parameters were refined with SHELXL-2013 [26], PLATON [27] was used to check additional symmetry elements and Crystallographic Information Files were compiled with Olex2.12. Molecular graphics were generated using Diamond and ORTEP-3.

Table 1. Crystal data and details of the structure determination.

Crystal data	
Chemical formula	C ₁₃ H ₁₂ CeN ₅ O ₉
Mr	522.38
Crystal system, Space group	Orthorhombic, P2 ₁ 2 ₁ 2 ₁
Temperature (K)	297
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.8497 (1), 9.8380 (1), 22.3471 (3)
<i>V</i> (Å ³)	1725.76 (4)
<i>Z</i>	5
Calculated density (g cm ⁻³)	2.011
F(000)	1020
Radiation type	Mo K α
μ (mm ⁻¹)	2.70
Crystal size (mm)	0.09 × 0.08 × 0.06
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix
Absorption correction	Multi-scan
<i>T</i> _{min} , <i>T</i> _{max}	0.833, 1.000
<i>h</i>	-9 → 9
<i>k</i>	-11 → 11
<i>l</i>	-26 → 27
No. of measured reflections, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	26628, 3159, 3023
<i>R</i> _{int}	0.043
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.019, 0.036, 1.06
No. of reflections	3159
No. of parameters/restraints	254/0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.31, -0.31

3. Results and Discussion

3.1. General Study

The reaction of and Ce(NO₃)₃.6H₂O in methanol afforded a coordination polymer of Ce(III) as shown in Figure 1. The infrared spectrum of the H₂L ligand shows two bands pointed at 1661 cm⁻¹ and 1605 cm⁻¹ attributed to the stretching vibrations of C=O and C=N, respectively. The stretching vibration band of N-H bond appears at 3300 cm⁻¹, while the band of the N-N moiety is pointed at 1557 cm⁻¹. Additional bands, characteristic of the aromatic ring, are pointed in the

range 1568–1417 cm⁻¹ [28].

The ¹H NMR spectrum reveals signals between 6.94 and 8.78 ppm attributed to the protons of the aromatic rings. The signal which appears at 9.09 ppm is attributed to the proton of the imine group. The signal at 11.18 ppm is assigned to the H-N of the hydrazine moiety. The signal pointed at 12.28 ppm is attributed to phenolic proton. The assignment of these signals are correlated to the signals of the ¹³C NMR spectrum which reveals a signal at 148.43 ppm attributed to imine carbon atoms. The signal at 161.38 ppm is attributed to the C=O. Additional signals in the range 118–135 ppm are attributed to the carbon atoms of the aromatic rings. Upon coordination the band attributed to C=N shifts to low

frequencies and is pointed at 1599 cm⁻¹. This fact is indicative of the involvement of the azomethine nitrogen atom in the coordination to the cerium ion. The bands pointed at 1470, 1383, 1299 and 1033 cm⁻¹ are indicative of the presence of nitrate moiety. Information regarding the possible bonding modes of the nitrate group can be obtained from the positions of the bands. The band at 1470 cm⁻¹ ν (N=O) (ν_1), 1299 cm⁻¹ ν_{as} (NO₂) (ν_5) and 1033 cm⁻¹ ν_s (NO₂) (ν_2) are indicative of a coordinated nitrate. The separation $\Delta\nu = \nu_1 - \nu_5$ was used as criterion of differentiation between mono and bidentate chelating nitrates, with $\Delta\nu$ increasing as the coordination changes from mono to bidentate and/or bridging modes [28]. The magnitude of this separation of 171 cm⁻¹ is indicative of a bidentate chelating nitrate. The magnetic moment value of the cerium (III) coordination polymer is 1.43 μ_B per atom. This value is consistent with the presence of unpaired 4f electrons and are close to the value reported in the literature for the free cerium(III) ion [29]. The magnetic moment is not affected by the ligand field, suggesting that the 4f electrons do not take part in bond formation. Molar conductivities were measured for freshly prepared solutions in DMF and after standing for two weeks. The conductivities increased very slightly with time in DMF for the coordination polymer. The coordination polymer is neutral electrolyte as shown by the molar conductance values of 46 and 50 S.cm².mol⁻¹ respectively for the freshly prepared DMF solution and two weeks later [30]. The results of the elemental analysis, the IR spectra data, the magnetic moment value, and conductivities measurements allow to formulate the cerium (III) compound as a mononuclear neutral Ce(NO₃)₂(HL)·H₂O.

3.2. Crystallographic Structure Determination

The spectroscopic observations on the geometrical features are in accordance with those obtained from X-ray crystallography analyses of the Ce(III) compound. The coordination polymer crystallizes in the orthorhombic system with the space group *P*-2₁2₁2₁. For simplicity, the structure with atom numbering for one complete environment of Ce(III) in the coordination polymer is shown in Figure 2a while the packing of the coordination polymer units in the crystal structure is shown in Figure 3. Selected interatomic distances and angle are listed in Table 2. The structure of the coordination polymer is consistent with the [Ce(H₂L)(NO₃)₂(H₂O)] formulation. The asymmetric unit contains one Ce³⁺, one monodeprotonated ligand molecule, two nitrate anions and one water molecule. The crystallographic study shows that the coordination polymer is formed with Ce/HL/NO₃/H₂O ratio of 1/1/2/1. In the coordination polymer each Schiff base molecule acts in monodeprotonated form in tridentate fashion through one phenolate oxygen atom, one nitrogen atom and one carbonyl oxygen atom resulting in one six membered chelating ring CeNCCCO and one five membered chelating ring CeNNCO. The bites angles defined by the two chelating ring are 69.1(1)° and 61.6(1)°, respectively. These angles are comparable to the

values reported for six membered and five membered rings. The bond angles of the ligands, which involve the Ce(III) ion, are slightly largest than the angle subtended by the oxygen atoms of the bidentate chelating nitrate groups: O3–Ce1–O5 = 47.61(9)° and O7–Ce–O9 = 50.2(1)° [28]. The value of the bridging angle Ce1–O5–Ce1 [161.7(1)°] is in the range expected for $\eta^1:\eta^2:\mu_2$ -nitrate groups. The Ce(III) center is ten-coordinated and the geometry around the lanthanide ion can be described as distorted bicapped square antiprism (Figure 2b). The Ce1–O_{phenolate} distance value of 2.31(3) Å, is shorter than the Ce1–O_{carboxylic} distance [2.511(3) Å] and Ce–O_{water} distance [2.507(3) Å]. In fact, the negative charge phenolate oxygen atom link more strongly to the Ce³⁺ than the neutral oxygen atom. The longest distance between the Ce³⁺ and the chelating atoms from the ligand is due to the nitrogen atom of the azomethine with a value of 2.631(3) Å [31]. The Ce–ONO₂ distances are in the range 2.663(3)–2.689(3) Å and are the longest Ce–O distances. The largest Ce–O (Ce–O7 = 2.689(4) Å) distance is observed in the chelating–bridging coordination mode $\eta^1:\eta^2:\mu$ - mode, while the shortest Ce–O (Ce1–O7 = 2.563(3)Å) bond length is observed in the chelating coordination mode η^2 -NO₃. These observations are in accordance with those reported in the literature [31, 32]. The metal centers are finally bridged by a pair of chelating–bridging nitrate ligands which are acting in $\eta^1:\eta^2:\mu$ - mode. In the organic moiety –C7–N1–N2–C8–O2, C7–N1 and C8–O2 bond lengths values of 1.298(5) Å and 1.241(5) Å are consistent with double bond character while C12–N3 distance of 1.331(5)Å and N1–N2 distance of 1.399(4) Å are indicative of a simple bond character. The C–O bond in the coordinated nitrate groups has an intermediate character between single C–O bond and double C=O bond. All the bond lengths are normal and fall within similar ranges to those reported for compounds derived from the same hydrazone ligand [33]. The units pack along and perpendicular to 2₁ axes generating a non-centrosymmetric network (Figure 4). Numerous inter molecular hydrogen bonds (Table 3, Figure 5) consolidate the structure in a three-dimensional network.

Table 2. Selected interatomic distances (Å).

Bond	Bond lengths [Å]	Bond	Bond lengths [Å]
Ce1–O5 ⁱ	2.687 (3)	Ce1–O7	2.563 (3)
Ce1–O5	2.663 (3)	Ce1–O9	2.539 (3)
Ce1–O1	2.310 (3)	Ce1–O6	2.507 (3)
Ce1–O4 ⁱ	2.774 (3)	Ce1–N1	2.631 (3)
Ce1–O2	2.511 (3)	Ce1–O3	2.689 (3)

Symmetry code: (i) x-1/2, -y+1/2, -z+1.

Table 3. Hydrogen-bond geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
O6–H6A...O1 ⁱⁱ	0.93	2.11	3.026(4)	166.6
O6–H6B...N3 ⁱⁱⁱ	0.93	1.89	2.785(4)	160.9
C7–H7...O3 ^{iv}	0.93	2.57	3.298(5)	135.8
N2–H2...O3 ^{iv}	0.86	2.26	3.036(5)	150.4

Symmetry codes: (ii) x+1/2, -y+1/2, -z+1; (iii) -x+1, y-1/2, -z+1/2; (iv) x-1/2, -y+3/2, -z+1.

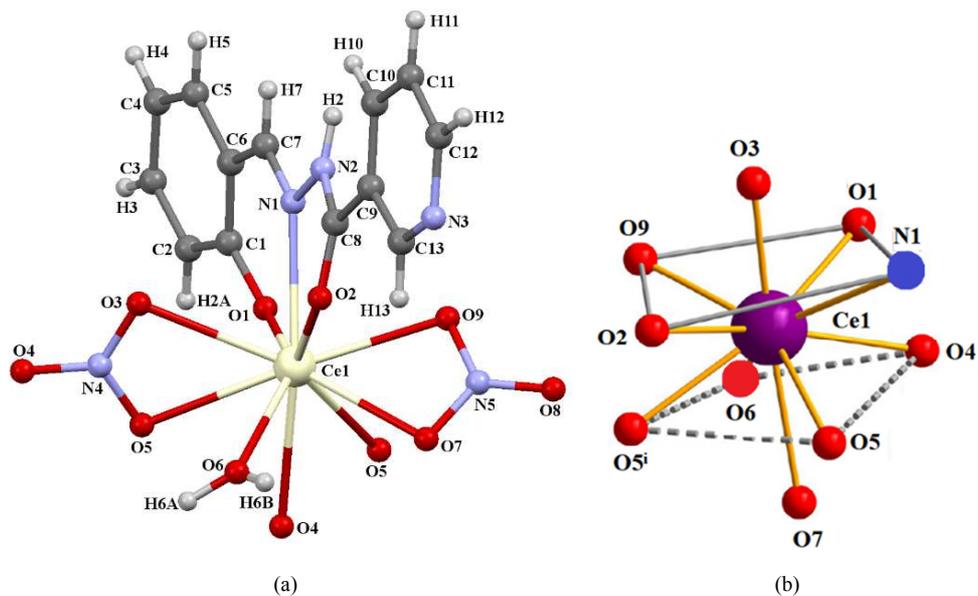


Figure 2. (a): Coordination polymer $Ce(NO_3)_2(HL) \cdot H_2O$ (Only one complete environment of the Ce is presented for clarity). (b): Perspective showing the distorted bicapped square antiprism coordination geometry of central Ce(III) ion.

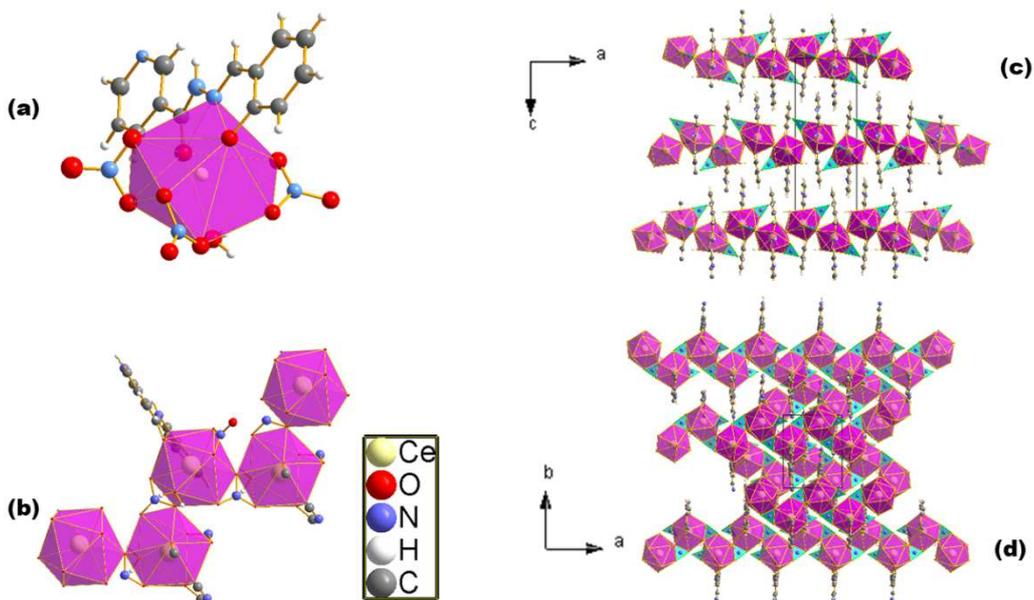
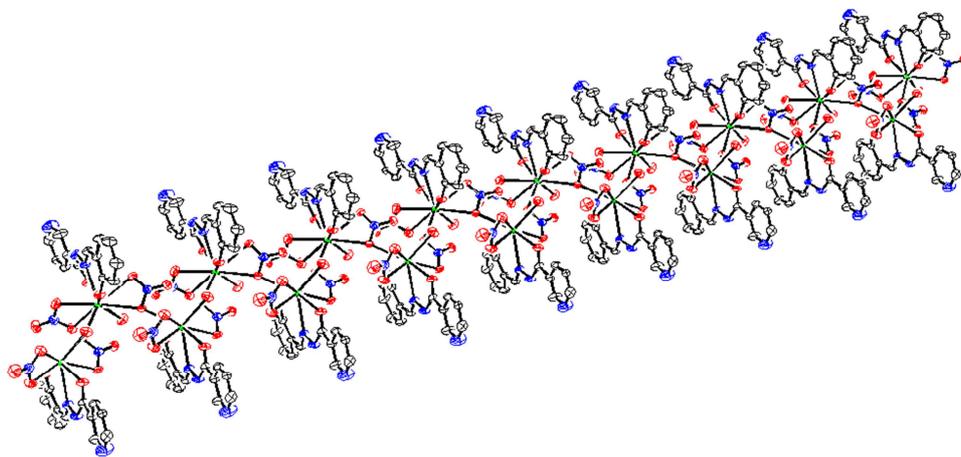


Figure 3. View of the coordination polymer; (a) isolated metal center; (b) isolated polymeric chain; (c) network along the b face; (d) network along the c axis.



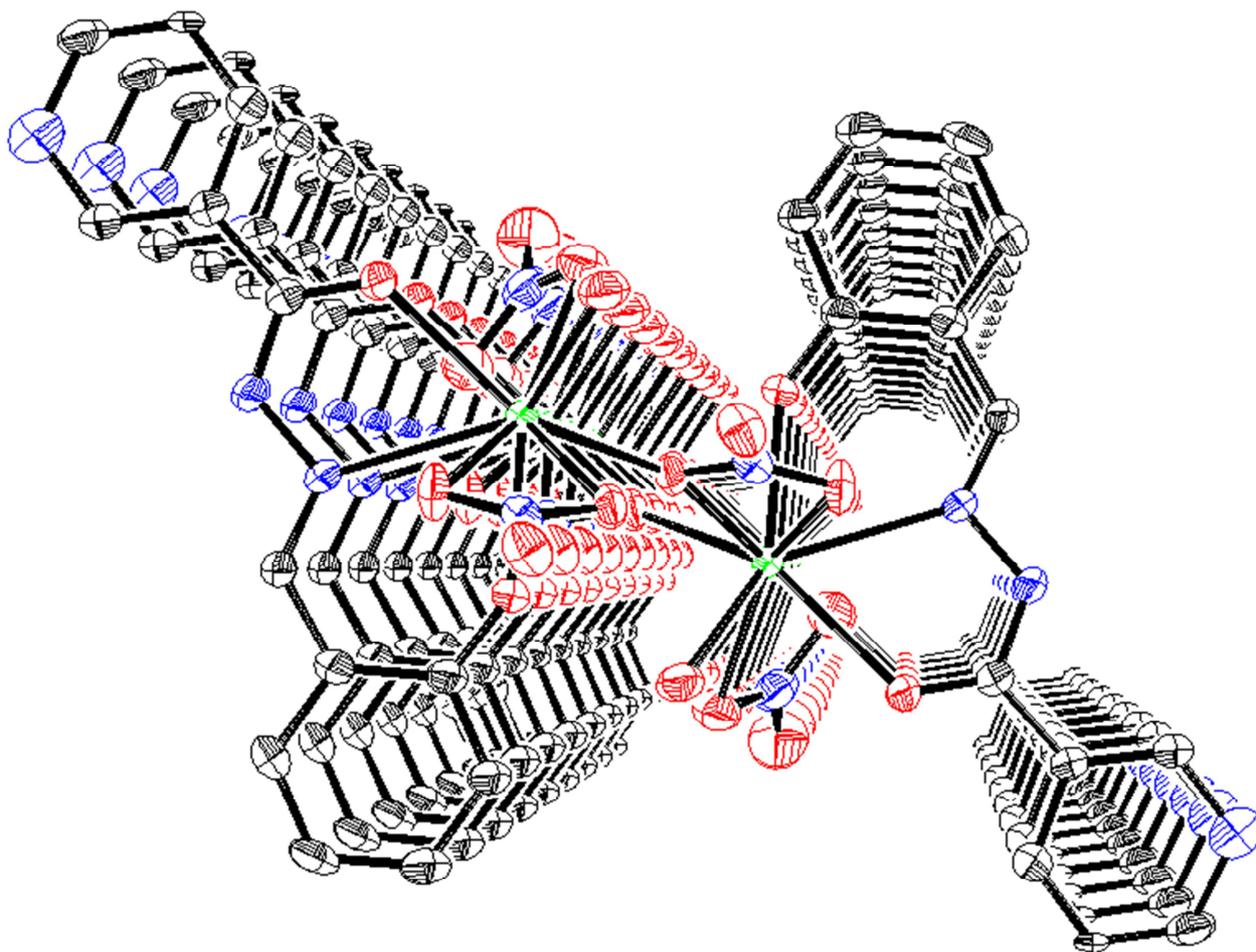


Figure 4. View of non-linear chains resulting in the chiral crystal structure.

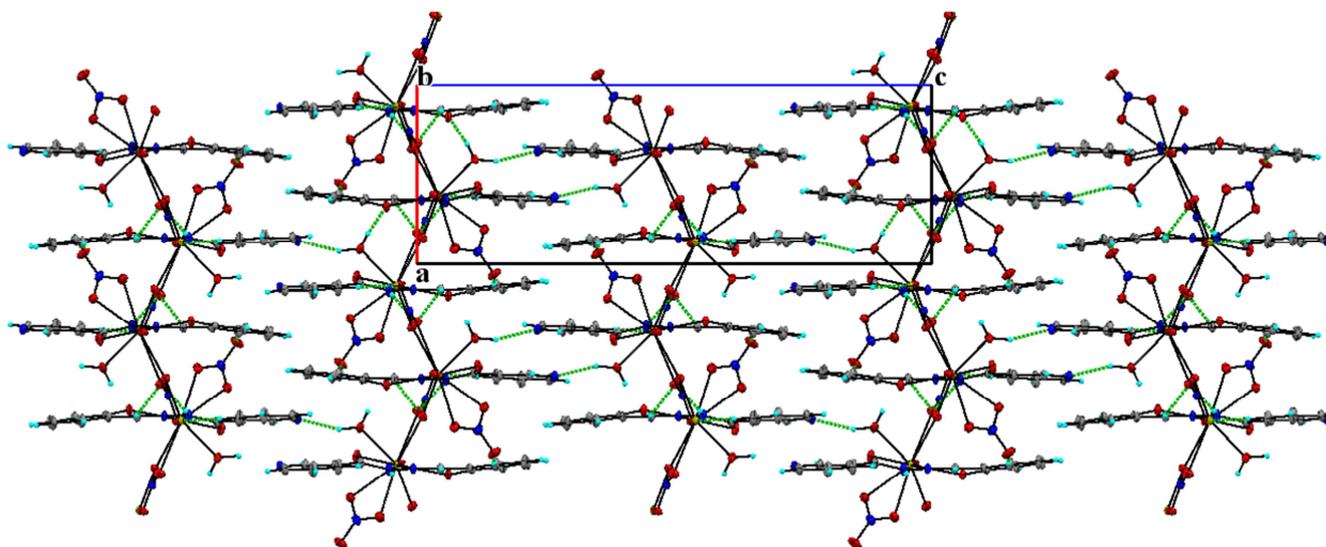


Figure 5. Plot showing the intermolecular hydrogens bonds along the b axis.

3.3. TG/DSC Analysis

The TG data shows three mass losses (Figure 6). The first loss of 5% between room temperature and 200°C corresponds to the loss of the water molecule (calculated loss: 5%). The second weight loss of 30% between 200°C

and 300°C can be attributed to the decomposition of two NO_3 into NO and O_2 (calculated loss: 29%). The last loss starting from 300°C corresponds to the degradation of coordination polymer. The analysis shows that the coordination polymer is stable up to 200°C. The experimental weight loss matches with the calculated one.

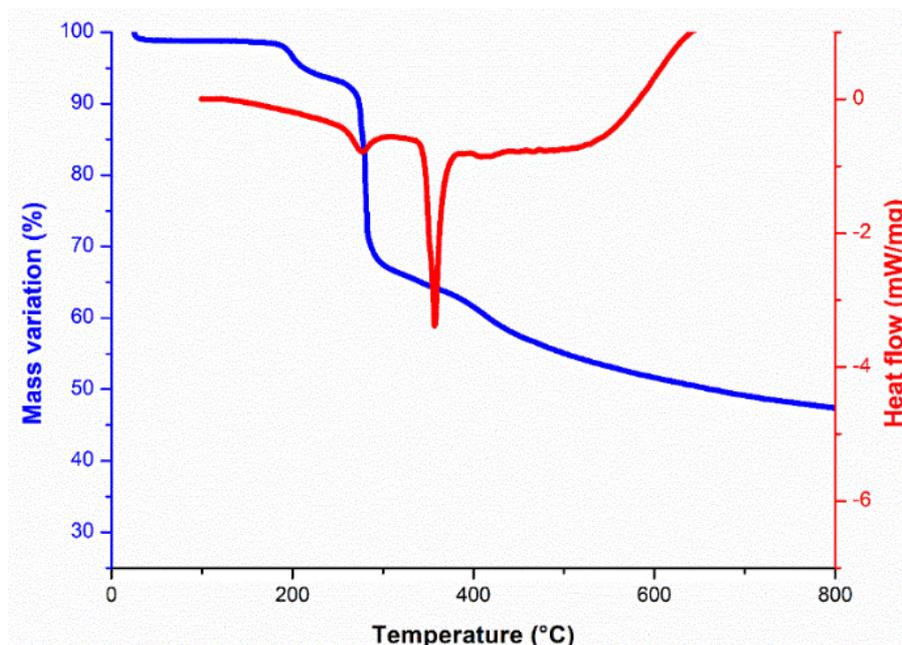


Figure 6. Thermogravimetric and differential scanning calorimetry of the coordination polymer.

4. Conclusion

The reported work concerned the synthesis of a Schiff base and its use to prepare a new Ce(III) based coordination polymer. The reaction of the Schiff base and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salts leads to the formation of the coordination polymer $\text{Ce}(\text{HL})(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})$. In the crystal structure, each Ce(III) ion is ten coordinated. The Ce(III) ions are bridged by two nitrate groups acting in $\eta^1: \eta^2: \mu\text{-NO}_3$ mode. The geometries around each Ce(III) ion can be best described as a distorted bicapped square antiprism. The coordination polymer crystallized in $P\text{-}2_12_12_1$ space group, offering chiral properties the resulting material. Thermogravimetric and differential scanning calorimetry show that the coordination polymer is stable up to 200°C.

Supporting Information

CCDC-2205602 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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