

Synthesis, Spectroscopic Characterization and X-ray Crystal Structure Determination of a New Mononuclear Gadolinium(III) Complex Derived from the Ligand N'-[(Pyridin-2-yl)methylidene]isonicotinohydrazide (HL)

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Abstract

The Schiff base ligand N'-[(pyridin-2-yl)methylidene]isonicotinohydrazide (HL) was prepared by condensation of isonicotinohydrazide with pyridine-2-carbaldehyde under reflux in methanol. The corresponding gadolinium(III) complex was obtained by reaction of HL with gadolinium(III) chloride hexahydrate. The complex was characterized by elemental analysis, IR and UV-Vis spectroscopy, molar conductivity measurements and magnetic susceptibility measurements at room temperature, and its structure was determined by single-crystal X-ray diffraction. The complex crystallizes in the triclinic system, space group *P*-1, with the following unit-cell parameters: *a* = 14.2219(4) Å, *b* = 14.5020(4) Å, *c* = 16.4273(5) Å, *V* = 2995.06(16) Å³, *Z* = 4 and *R*_{int} = 0.0471. The asymmetric unit contains two mononuclear cationic entities [Gd(HL)(L)(H₂O)₃]²⁺, four chloride anions ensuring electroneutrality, and lattice water molecules. Each cationic entity consists of one Gd(III) ion, two ligand molecules and three coordinated water molecules. One of the ligand molecules adopts the monodeprotonated iminol form, whereas the other remains in the neutral amide form; both act as tridentate N,N,O donors towards the metal centre. In each cationic entity the Gd(III) ion is nine-coordinate and its coordination polyhedron is best described as a distorted tricapped trigonal prism. In the crystal, the complex units are linked through an extensive network of hydrogen bonds, giving rise to a three-dimensional supramolecular architecture (Figure 2, Table 3).

Keywords: isonicotinohydrazide; Schiff base; gadolinium(III); complex; X-ray diffraction.

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I. Introduction

Over the past decade, lanthanide coordination chemistry has become one of the most intensively investigated research areas [1–3]. The design and synthesis of lanthanide coordination compounds continue to attract growing interest because of their diverse structural topologies and their potential applications [1–5]. The biological and pharmacological [6–11], magnetic [12–15], luminescent [16–19], catalytic [20–23] and ion-exchange [24,25] properties of lanthanide complexes have been widely documented. Ln(III) ions display variable coordination numbers and flexible coordination geometries [26–31]. When flexible ligands are used, the reaction conditions may govern their coordination modes and thus give access to a wide range of coordination geometries. Consequently, numerous Ln(III) coordination compounds exhibiting novel structural topologies have been obtained with such ligands [32–36].

Hydrazone Schiff bases and their derivatives are particularly well suited to the preparation of lanthanide complexes with original and robust structures. Some years ago, our laboratory initiated a research programme on rare-earth coordination chemistry aimed at the development of unusual molecular materials [37–43].

Recently, Ndiaye et al. [40,43], members of our research group, synthesized a series of lanthanide complexes using 1-(pyridin-2-yl)-2-(pyridin-2-ylmethylidene)hydrazine (HL) as the organic ligand and acetate as co-ligand, and characterized them by various physicochemical techniques, including single-crystal X-ray diffraction. Their antioxidant and antimicrobial properties were also investigated.

In 2019, Tamboura et al. [44] prepared lanthanide complexes of the Schiff base ligand N'-(2-hydroxy-3-methoxybenzylidene)nicotinohydrazide (H₂L) and characterized them by NMR, IR and UV-Vis spectroscopy, conductivity measurements and room-temperature magnetic moment determinations. In 2023, Seck et al. [45]

reported the original structure of a mononuclear terbium(III) complex derived from N,N'-1,5-bis(pyridylmethylidene)carbonohydrazone (H₂L).

The growing interest in Schiff base hydrazones has prompted our group to extend the study of their coordination chemistry to lanthanide ions. In the present work, a new flexible tridentate hydrazone ligand, N'-[(pyridin-2-yl)methylidene]isonicotinohydrazide (HL), was synthesized by a straightforward condensation between isonicotinohydrazide and pyridine-2-carbaldehyde, and was subsequently used to prepare a new gadolinium(III) complex. The ligand and the complex were characterized by IR, UV-Vis, ¹H and ¹³C NMR spectroscopy, molar conductivity and magnetic susceptibility measurements, and elemental analysis. The crystal structure of the gadolinium(III) complex was determined by single-crystal X-ray diffraction.

II. Materials and Methods

2.1. Materials and instruments

Pyridine-2-carbaldehyde, isonicotinohydrazide and gadolinium(III) chloride hexahydrate were purchased from Aldrich and used without further purification. The solvents were of reagent grade and were purified by standard methods. The melting points of the ligand and of the complex were determined on a Büchi capillary melting-point apparatus. Elemental analyses (C, H, N) were carried out on a Vario EL analyser. Infrared spectra were recorded on a Perkin-Elmer Spectrum Two FT-IR spectrometer over the 4000–400 cm⁻¹ range. The ¹H and ¹³C NMR spectra were recorded in DMSO-d₆ on a Bruker 500 MHz spectrometer at room temperature, using TMS as internal reference. The UV-Vis spectra were recorded on a Perkin-Elmer Lambda spectrophotometer. The molar conductivity of a 10⁻³ M solution of the gadolinium(III) complex in DMF was measured at 25 °C with a WTW LF-330 conductivity meter fitted with a WTW conductivity cell. The magnetic susceptibility of the solid complex was measured at room temperature on a Johnson-Matthey balance, with Hg[Co(SCN)₄] as standard.

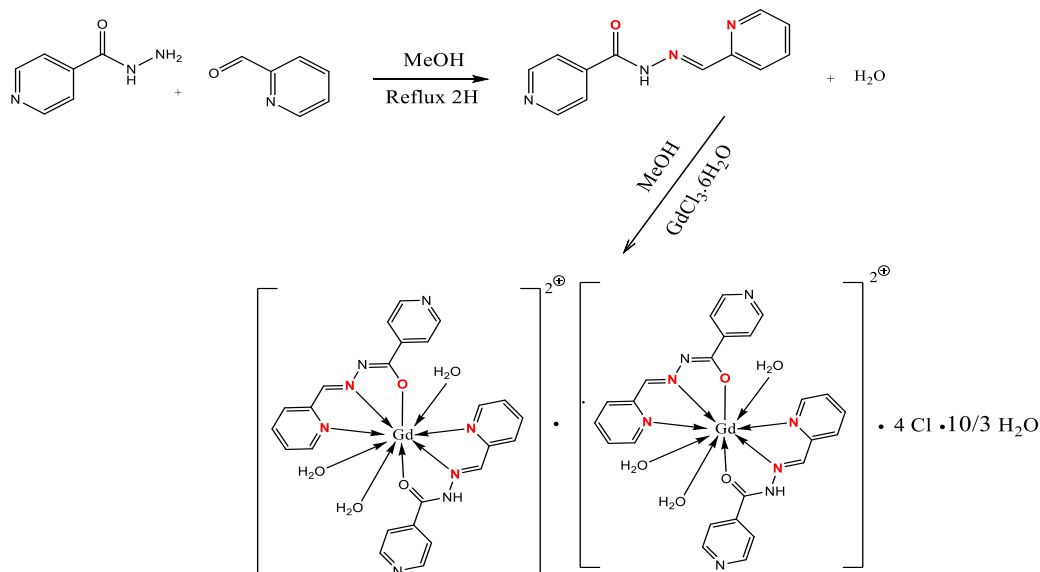
2.2. Synthesis of the ligand HL

Isonicotinic acid hydrazide (2 g, 14.58 mmol) was dissolved in methanol (20 mL) in a round-bottomed flask with stirring. Pyridine-2-carbaldehyde (1.373 mL, 14.58 mmol) and a few drops of acetic acid were then added, whereupon the solution turned orange. The mixture was refluxed for 4 h, affording a brown precipitate, which was collected by filtration and washed with methanol (2 × 10 mL). M.p. 194 °C. Yield: 68.52%. Anal. Calcd for C₁₂H₁₀N₄O: C, 63.71; H, 4.46; N, 24.76. Found: C, 63.69; H, 4.44; N, 24.74%. FT-IR (ATR, cm⁻¹): 3534, 3444, 3237, 2992, 1651, 1644, 1568, 1552, 1472, 1437, 1409, 1352, 1306, 1290, 1255, 1226, 1150, 1052, 998. ¹H NMR (500 MHz, DMSO-d₆, δ, ppm): 12.20 (s, 1H, NH-C=O), 7.40 (s, 1H, HC=N), 7.60–8.50 (m, 8H, H-Py).

¹³C NMR (125 MHz, DMSO-d₆, δ, ppm): 162.39 (C=O), 153.42 (C-ipso, Py), 150.84 (C=N), 150.06 (C-Py), 145.70 (C-Py), 140.71 (C-ipso, Py), 137.41 (C-Py), 125.12 (C-Py), 122.59 (C-Py), 120.59 (C-Py).

2.3. Synthesis of the complex [Gd(HL)(L)(H₂O)₃]₂·4Cl·10/3H₂O

A methanolic solution of GdCl₃·6H₂O (123 mg, 0.3315 mmol) was added to a solution of the ligand HL (150 mg, 0.663 mmol) in methanol (10 mL) contained in a 100 mL round-bottomed flask. The mixture was stirred at room temperature for 2 h and the resulting yellow solution was filtered. Slow evaporation of the filtrate over two weeks afforded yellow crystals suitable for single-crystal X-ray analysis. M.p. > 260 °C. Yield: 63.26%. Anal. Calcd (%) for [Gd(HL)(L)(H₂O)₃]₂·4Cl·10/3H₂O: Gd, 19.90; C, 50.17; H, 5.61; N, 14.18; O, 10.13. Found (%): Gd, 19.87; C, 50.20; H, 5.56; N, 14.21; O, 10.09. IR (ATR, cm⁻¹): 3558, 3300, 3230, 2987, 1633, 1591, 1570, 1504, 1467, 1440, 1373, 1358, 1319, 1049 and 847. μ_{eff} = 7.93 μB. ΛM (S cm² mol⁻¹, DMF, 10⁻³ M): freshly prepared solution, 146.33; after two weeks, 146.54.



Scheme 1. Synthetic route to the Schiff base ligand N' -[(pyridin-2-yl)methylidene]isonicotinohydrazide (HL) and to its gadolinium(III) complex $[Gd(HL)(L)(H_2O)_3]^{2+} \cdot 4Cl \cdot 10/3H_2O$.

2.4. X-ray data collection, structure solution and refinement

Crystals of the title compound suitable for X-ray diffraction were grown by slow evaporation of a methanolic solution of the complex. Details of the structure solution and refinement are given in Table 1. Diffraction data were collected on a Rigaku XtaLAB AFC12 (RINC) Kappa single-crystal diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects; no absorption correction was applied. Complex scattering factors were taken from the SHELXTL program package [46]. The structure was solved by direct methods, which revealed the positions of all non-hydrogen atoms, and was refined on F^2 by full-matrix least-squares procedures using anisotropic displacement parameters for all non-hydrogen atoms [47]. The hydrogen atoms of the water molecules and of the NH groups were located in difference Fourier maps and refined. The remaining hydrogen atoms (CH) were placed in geometrically idealized positions and refined as riding, using AFIX instructions. Molecular graphics were generated with ORTEP-3 [48].

III. Results and Discussion

3.1. Spectroscopic studies

The 1H NMR spectrum of the ligand displays two characteristic singlets at 12.20 and 7.40 ppm, assigned to the N–H and HC=N protons, respectively [49–54]. The signals observed between 7.60 and 8.50 ppm are attributed to the aromatic protons [55]. In the ^{13}C NMR spectrum, the signal at 150.84 ppm is assigned to the azomethine carbon (C=N), whereas that at 162.39 ppm corresponds to the carbonyl carbon (C=O) [49–54]. The IR spectrum of the ligand exhibits characteristic bands at 3237, 1651, 1644 and 1568 cm^{-1} , assigned to the $\nu(N-H)$, $\nu(C=O)$ carbonyl, $\nu(C=N)$ imine and $\nu(CAr=N)$ stretching vibrations, respectively [55, 56, 57]. These data indicate that the free ligand exists in the amide form. Comparison of the IR spectra of the free ligand and of the gadolinium(III) complex shows that the ligand coordinates in both the amide and the iminol forms, the latter being deprotonated upon complex formation. Upon coordination, the $\nu(C=O)$ (carbonyl), $\nu(C=N)$ (imine) and $\nu(CAr=N)$ stretching bands are shifted to lower wavenumbers, which confirms the involvement of the carbonyl oxygen, the imine nitrogen and the pyridine nitrogen atoms in coordination to the Gd(III) ion [44, 53, 55]; in the spectrum of the complex these bands are observed at 1633, 1591 and 1570 cm^{-1} , respectively. The $\nu(C-O)$ stretching band of the iminol form of the ligand is observed at 1319 cm^{-1} . The absence of the $\nu(O-H)$ stretching band of the iminol hydroxyl group in the spectrum of the complex indicates that deprotonation has occurred and that the iminol oxygen atom is coordinated to the Gd(III) ion. The presence of coordinated water molecules is confirmed by the bands at 3300 and 847 cm^{-1} , assigned to the $\nu(H_2O)$ and $\delta(H_2O)$ vibrations, respectively [58]. The molar conductivity of a freshly prepared 10^{-3} M solution of the complex in DMF and that of the same solution measured fifteen days later are 146.33 and 146.54 $S \text{ cm}^2 \text{ mol}^{-1}$, respectively. These values are consistent with those reported for a 1:2 electrolyte, i.e. two chloride counter-ions per cationic entity [59]. The fact that the conductivity remains unchanged after fifteen days indicates that the complex is stable in DMF. The magnetic moment of 7.93 μ_B is consistent with the $4f^7$ electronic configuration of the Gd(III) ion and is comparable with the value reported for a gadolinium(III) complex of 1,5-bis(phenyl(pyridin-2-yl)methylidene)carbonohydrazide [60]. The UV–Vis spectrum of the Gd(III) complex in DMF shows three main absorption bands at 226, 305 and 377 nm, assigned to

$\pi \rightarrow \pi^*$ transitions of the aromatic rings, $n \rightarrow \pi^*$ transitions of the C=N and C=O groups, and a ligand-to-metal charge-transfer (LMCT) transition, respectively [60].

3.2. Description of the crystal structure of the complex $[\text{Gd}(\text{HL})(\text{L})(\text{H}_2\text{O})_3]_2 \cdot 4\text{Cl} \cdot 10/3\text{H}_2\text{O}$

The complex, formulated as $[\text{Gd}(\text{HL})(\text{L})(\text{H}_2\text{O})_3]_2 \cdot 4\text{Cl} \cdot 10/3\text{H}_2\text{O}$, crystallizes in the triclinic system, space group P-1. Crystal data, data collection and refinement details are given in Table 1. An ORTEP view of the mononuclear complex is shown in Figure 1, and selected bond lengths and angles are listed in Table 2.

Table 1. Crystal data and structure refinement.

Empirical formula	$\text{C}_{24}\text{H}_{28.33}\text{Cl}_2\text{GdN}_8\text{O}_{6.67}$
Formula weight	763.71
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	14.2219(4)
b/Å	14.5020(4)
c/Å	16.4273(5)
$\alpha/^\circ$	76.365(2)
$\beta/^\circ$	83.728(2)
$\gamma/^\circ$	65.466(3)
Volume/Å ³	2995.06(16)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.694
μ/mm^{-1}	2.447
F(000)	1519.0
Crystal size/mm ³	0.1 × 0.04 × 0.03
Radiation	Mo K α ($\lambda = 0.71075$)
2 θ range for data collection/ $^\circ$	3.444 to 72.64
Index ranges	$-23 \leq h \leq 23$, $-24 \leq k \leq 24$, $-27 \leq l \leq 27$
Reflections collected	123666
Independent reflections	28822 [$R_{\text{int}} = 0.0471$, $R_{\text{sigma}} = 0.0467$]
Data/restraints/parameters	28822/4/815
Goodness-of-fit on F^2	1.054
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0306$, $wR_2 = 0.0583$
Final R indexes [all data]	$R_1 = 0.0478$, $wR_2 = 0.0617$
Largest diff. peak/hole / e Å ⁻³	1.16/-0.82

The asymmetric unit consists of two mononuclear cationic moieties $[\text{Gd}(\text{HL})(\text{L})(\text{H}_2\text{O})_3]^{2+}$, four chloride anions ensuring charge neutrality, and lattice water molecules. The two cationic moieties are linked by intermolecular N7–H7 $\cdots$ N16 and N11–H11A $\cdots$ N4 hydrogen bonds. These interactions are formed between the hydrazinic N–H group of a ligand in one cationic entity, which acts as hydrogen-bond donor, and the pyridine nitrogen atom of a ligand in the other entity, which acts as hydrogen-bond acceptor. Each mononuclear entity comprises one Gd(III) ion, two ligand molecules — one in the amide form and the other in the deprotonated iminol form — and three coordinated water molecules. Each ligand binds the Gd(III) ion in a tridentate fashion through the imine nitrogen, the pyridine nitrogen and the carbonyl or iminol oxygen atom. The resulting nine-coordinate environment around the Gd(III) ion is best described as a distorted tricapped trigonal prism (Figure 1).

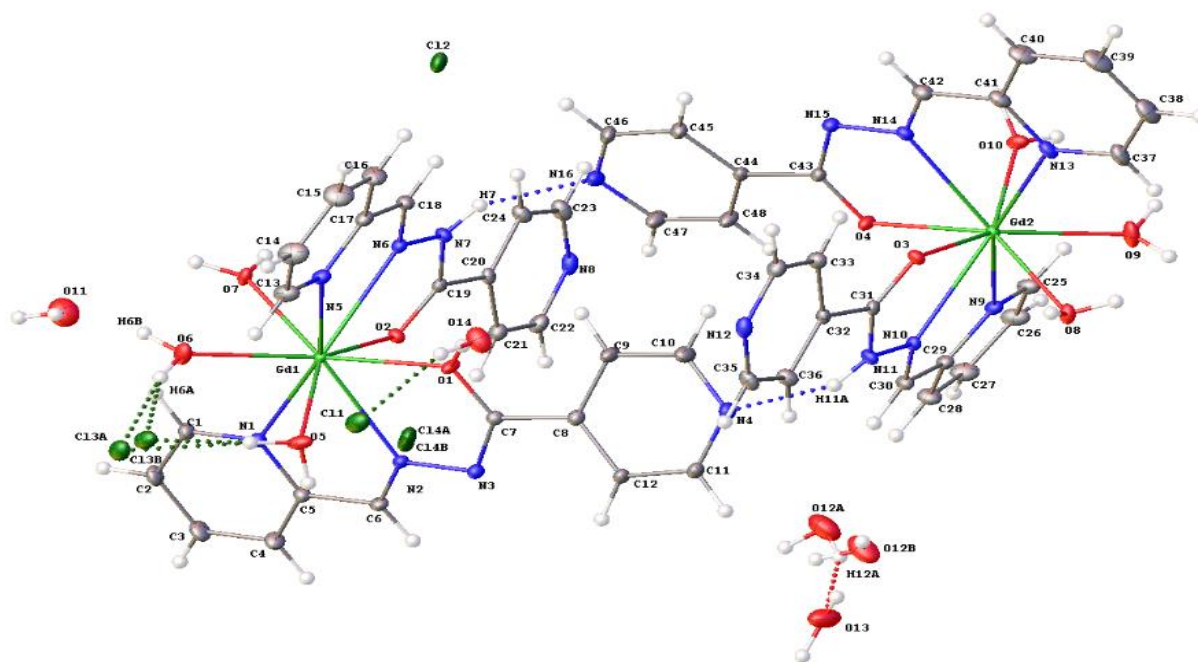


Figure 1. ORTEP view of the two crystallographically independent mononuclear cations in the asymmetric unit of $[\text{Gd}(\text{HL})(\text{L})(\text{H}_2\text{O})_3]_2 \cdot 4\text{Cl} \cdot 10/3\text{H}_2\text{O}$, showing the atom-numbering scheme (thermal ellipsoids drawn at the 50% probability level). The dashed lines indicate the intermolecular $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds linking the two cationic entities; most hydrogen atoms have been omitted for clarity.

The $\text{Gd}-\text{N}$ bond lengths range from 2.5327(13) to 2.6149(12) Å and fall within the range usually observed for related nine-coordinate $\text{Gd}(\text{III})$ complexes of isonicotinohydrazone Schiff bases [44]. The $\text{Gd}-\text{N}(\text{imine})$ distances [2.544(2) and 2.558(2) Å] are shorter than the $\text{Gd}-\text{N}(\text{pyridine})$ distances [2.568(3) and 2.570(3) Å]. The $\text{Gd}-\text{O}(\text{carbonyl})$ distances [2.3784(12)–2.4480(10) Å] are comparable with the values reported for similar complexes [65]. The $\text{Gd}-\text{OW}$ distances involving the coordinated water molecules [2.4037(11)–2.4313(12) Å] are also in agreement with literature values [61].

Table 2. Selected bond lengths [Å] and bond angles [°] for the $\text{Gd}(\text{III})$ complex

Gd1 N1	2.5997(13)	Gd2 N9	2.5854(12)
Gd1 N2	2.5327(13)	Gd2 N10	2.5639(13)
Gd1 N5	2.6149(12)	Gd2 N13	2.5819(13)
Gd1 N6	2.5562(13)	Gd2 N14	2.5237(14)
Gd1 O1	2.3784(12)	Gd2 O3	2.4367(10)
Gd1 O2	2.4480(10)	Gd2 O4	2.3827(12)
Gd1 O5	2.4037(11)	Gd2 O8	2.4313(12)
Gd1 O6	2.4264(13)	Gd2 O9	2.4299(13)
Gd1 O7	2.4304(12)	Gd2 O10	2.3831(11)
O5 Gd1 N1	88.76(4)	O3 Gd2 N14	68.09(4)
O5 Gd1 N2	71.80(4)	O4 Gd2 N9	71.79(4)
O5 Gd1 N5	81.60(4)	O4 Gd2 N10	66.71(4)
O5 Gd1 N6	134.91(4)	O4 Gd2 N13	125.78(4)
O5 Gd1 O2	141.31(4)	O4 Gd2 N14	62.29(4)
O5 Gd1 O6	71.19(4)	O4 Gd2 O3	84.49(4)
O5 Gd1 O7	139.84(4)	O4 Gd2 O8	138.57(4)
O6 Gd1 N1	79.90(4)	O4 Gd2 O9	138.00(4)
O6 Gd1 N2	127.23(4)	O4 Gd2 O10	79.38(4)
O6 Gd1 N5	75.96(5)	O8 Gd2 N9	93.41(4)
O6 Gd1 N6	119.39(4)	O8 Gd2 N10	72.14(4)
O6 Gd1 O2	137.58(4)	O8 Gd2 N13	81.31(4)
O6 Gd1 O7	68.93(4)	O8 Gd2 N14	131.83(4)
O7 Gd1 N1	79.97(4)	O8 Gd2 O3	72.08(4)
O7 Gd1 N2	132.06(4)	O9 Gd2 N9	76.12(5)
O7 Gd1 N5	93.16(4)	O9 Gd2 N10	119.43(5)
O7 Gd1 N6	71.90(4)	O9 Gd2 N13	81.43(5)
O7 Gd1 O2	72.82(4)	O9 Gd2 N14	130.72(5)
N10 Gd2 N9	62.06(4)	O9 Gd2 O3	136.77(4)
N10 Gd2 N13	134.85(4)	O9 Gd2 O8	68.66(4)
N13 Gd2 N9	157.32(5)	O10 Gd2 N9	83.57(4)

N14 Gd2 N9	131.29(4)	O10 Gd2 N10	137.24(4)
N14 Gd2 N10	109.85(4)	O10 Gd2 N13	85.99(4)
N14 Gd2 N13	63.49(5)	O10 Gd2 N14	73.28(4)
O3 Gd2 N9	124.10(4)	O10 Gd2 O3	141.32(4)
O3 Gd2 N10	62.10(4)	O10 Gd2 O8	138.70(4)
O3 Gd2 N13	75.40(4)	O10 Gd2 O9	70.67(5)

The hydrogen-bond geometry of the compound is summarized in Table 3. Several intramolecular hydrogen bonds are observed within the asymmetric unit: N(hydrazine)–H···N(pyridine) (N7–H7···N16 and N11–H11A···N4), O(water)–H···Cl (O6–H6A···Cl3A, O6–H6A···Cl3B, O5–H5B···Cl3A, O5–H5B···Cl3B and O14–H14B···Cl1) and O(water)–H···O (O12–H12A···O13). Together with the intermolecular hydrogen bonds, these interactions ensure the cohesion and stability of the crystal and generate a three-dimensional supramolecular network (Figure 2, Table 3).

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

D—H···A	D—H	H···A	D···A	D—H···A
C38—H38···O13 ¹	0.95	2.66	3.271(4)	122.6
N7—H7···N16	0.84(2)	2.09(2)	2.842(2)	149(2)
N11—H11A···N4	0.82(2)	2.05(2)	2.781(2)	148(2)
O5—H5A···N3 ²	0.88	2.00	2.7718(18)	146.2
O5—H5B···Cl3A	0.88	2.15	2.9923(15)	160.3
O5—H5B···Cl3B	0.88	2.34	3.217(2)	174.2
O6—H6A···Cl3A	0.87	2.21	3.0456(14)	160.1
O6—H6A···Cl3B	0.87	2.11	2.9682(19)	168.8
O6—H6B···Cl2 ³	0.87	2.23	3.0868(14)	168.9
O7—H7A···N12 ⁴	0.87	1.92	2.7488(16)	156.8
O7—H7B···Cl2 ³	0.88	2.29	3.1032(13)	153.4
O8—H8A···N8 ⁵	0.85	1.93	2.7307(17)	155.6
O8—H8B···Cl4A ⁶	0.85	2.29	3.055(2)	148.8
O8—H8B···Cl4B ⁶	0.85	2.26	3.055(4)	155.5
O9—H9A···Cl4A ⁶	0.85	2.17	3.009(2)	168.8
O9—H9A···Cl4B ⁶	0.85	2.36	3.189(3)	163.4
O9—H9B···Cl1 ⁷	0.88	2.14	3.0134(14)	170.6
O10—H10A···N15 ⁸	0.98	1.77	2.7460(18)	179.1
O10—H10B···Cl1 ⁷	0.80	2.39	3.1541(13)	160.9
O11—H11B···Cl2 ³	0.87	2.51	3.3288(16)	157.2
O11—H11C···Cl1 ⁴	0.88	2.44	3.3134(19)	175.3
O12—AH12A···O13	0.87	2.02	2.831(4)	154.9
O12—AH12B···Cl3A ²	0.87	2.37	3.230(3)	169.0
O12—BH12C···Cl3B ²	0.88	2.47	3.321(6)	165.7
O13—H13A···Cl4A ⁵	0.87	2.26	3.123(3)	168.5
O13—H13B···Cl2 ⁹	0.87	2.48	3.346(3)	171.4
O14—H14A···O1	0.92	2.09	2.993(2)	167.0
O14—H14B···Cl1	0.87	2.39	3.235(2)	163.2

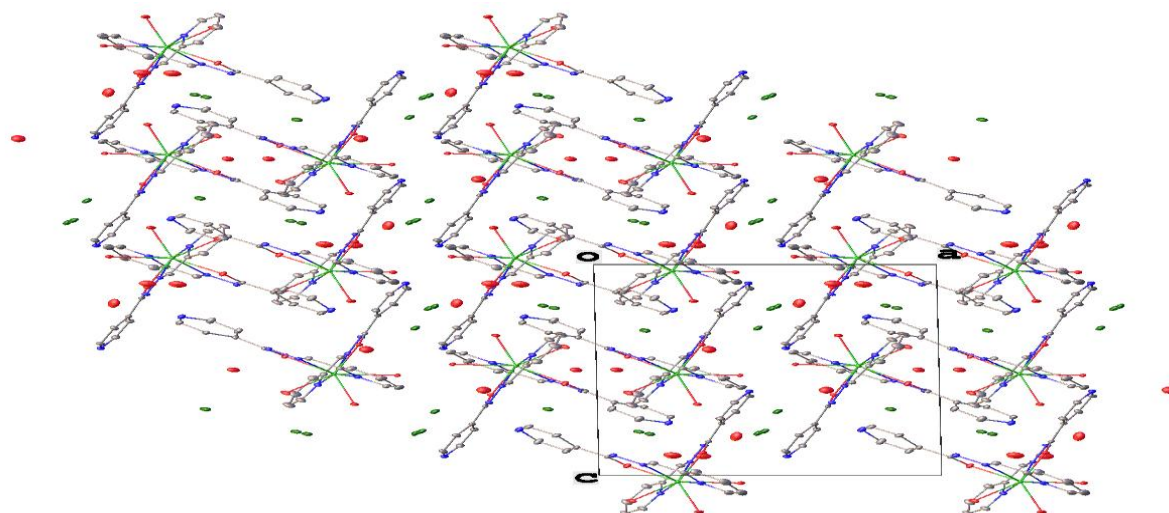


Figure 2. Packing diagram showing the three-dimensional supramolecular network built up through intermolecular hydrogen bonds, viewed down the b axis.

IV. Conclusion

A gadolinium(III) complex of the Schiff base ligand *N'*-[(pyridin-2-yl)methylidene]isonicotinohydrazide (HL) was synthesized and characterized by NMR, IR and UV–Vis spectroscopy, conductivity measurements and room-temperature magnetic moment determination, and its structure was established by single-crystal X-ray diffraction. The IR data of the complex reveal the presence of the ligand in both the amide and the iminol forms. In the Gd(III) complex, each ligand molecule is coordinated to the metal centre through the imine nitrogen atom, the pyridine nitrogen atom and the oxygen atom of either the amide or the deprotonated iminol group. The electronic spectrum displays ligand-centred bands together with an LMCT band. Room-temperature magnetic susceptibility measurements indicate that the complex is paramagnetic and mononuclear, while the molar conductivity data show that it behaves as a 2:1 electrolyte in DMF. The X-ray crystallographic analysis reveals that the asymmetric unit consists of two cationic entities of formula $[\text{Gd}(\text{HL})(\text{L})(\text{H}_2\text{O})_3]^{2+}$, four chloride anions ensuring electroneutrality, and lattice water molecules. The coordination polyhedron around the Gd(III) ion in each cationic entity is best described as a distorted tricapped trigonal prism.

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