A new Gd$^{3+}$ coordination polymer (CP), namely, poly[diaqua]$\mu_4$-1'-carboxy-3,3',5-(diazene-1,2-diyl) dibenzen-1,2,2'-tricarboxylato]gadolinium(III), [Gd-(C$_{16}$H$_{7}$N$_2$O$_8$)(H$_2$O)$_2$]$_n$ (I), has been synthesized hydrothermally from Gd(NO$_3$)$_3$.6H$_2$O and azobenzene-2,2',3,3'-tetracarboxylic acid (H$_4$abtc). The target solid has been characterized by single-crystal and powder X-ray diffraction, elemental analysis, IR spectroscopy and susceptibility measurements. CP (I) crystallizes in the monoclinic space group $C2/c$. The structure features a 4-connected topology in which Gd$^{3+}$ ions are connected by carboxylate groups into a linear chain along the monoclinic symmetry direction. Adjacent one-dimensional aggregates are bridged by Habtc$^{3-}$ ligands to form a two-dimensional CP in the (101) plane. A very short hydrogen bond [O···O = 2.4393 (4) Å] links neighbouring layers into a three-dimensional network. A magnetic study revealed antiferromagnetic Gd···Gd coupling within the chain direction. CP (I) displays a significant magnetocaloric effect (MCE), with a maximum $-\Delta S_m$ of 27.26 J kg$^{-1}$ K$^{-1}$ for $\Delta H = 7$ T at 3.0 K. As the MCE in (I) exceeds that of the commercial magnetic refrigerant GGG (Gd$_3$Ga$_5$O$_{12}$, $-\Delta S_m = 24$ J kg$^{-1}$ K$^{-1}$, $\Delta H = 30$ kG), CP (I) can be regarded as a potential cryogenic material for low-temperature magnetic refrigeration.

1. Introduction

Coordination polymers (CPs), a class of compounds based on repetition of metal cations connected by coordinated linkers, have developed rapidly in the past 20 years (Chakraborty et al., 2021) due to their interesting structures and variable applications in gas storage and separation (Roztocki et al., 2020), catalysis (Kang et al., 2019), sensing (Lustig et al., 2017) and magnetic materials (Yang et al., 2019a). In particular, due to the unique 4f electron configuration of Ln$^{3+}$ ions, lanthanide coordination polymers (Ln-CPs) usually exhibit a high coordination number, flexible coordination geometry and strong spin-orbit coupling (Sorace et al., 2011; Liu et al., 2016). These properties suggest their application in luminescence sensing (Ye et al., 2017), molecular magnetism (Liu et al., 2019), magnetic resonance imaging (Debroye & Parac-Vogt, 2014) and related fields (Kumar et al., 2019).

Magnetic refrigeration represents a focus area in the field of magnetism. This approach is based on the magnetocaloric effect (MCE) (Yang et al., 2015; Wu et al., 2021) and is considered a highly efficient and energy-saving, hence environmentally friendly, technology. Key factors for success comprise a high-spin ground state $S$, negligible magnetic
anisotropy and low-lying excited spin states (Evangelisti et al., 2006; Liu et al., 2014a). The basic principle of magnetic refrigeration is realized through repeated cycles of isothermal magnetization and adiabatic demagnetization through the MCE displayed by the magnetic materials (Han et al., 2018). Magnetic refrigeration has potential for the generation of ultra-low temperatures. The magnitude of the MCE is usually measured by magnetic entropy change (−ΔS_m) and adiabatic temperature change (ΔT_ad) under certain conditions (Franceschi et al., 2018). A large ΔS_m under a relatively low magnetic field is mandatory for an attractive cryogenic magnetorefrigerant (Liu et al., 2017). The −ΔS_m value of the well-known commercial low-temperature magnetic refrigeration material GGG (Gd_3Ga_5O_{12}) is 24 J kg^{-1} K^{-1} (ΔH = 30 kG) (Daudin et al., 1982).

The Gd^{3+} ion meets the requirements of a high-spin ground state S (S = 7/2), of low-lying excited spin states and magnetic isotropy (Niu et al., 2019). The magnetic coupling between Gd^{3+} centres is relatively weak, which allows the system to achieve a large MCE (Zhang et al., 2021). Therefore, the Gd^{3+} ion represents an ideal choice for the construction of molecular-based low-temperature magnetic refrigeration materials (Wang et al., 2019). At present, molecular materials of cryogenic magnetic refrigeration mainly include Gd-based clusters and Gd-based CPs. However, the exploration of MCE for one-dimensional (1D) linear Gd^{3+} CPs has only rarely been documented (Liu et al., 2014b).

In view of the above-mentioned promising properties, we report the new two-dimensional (2D) Gd^{3+} complex, [Gd-(Habtc)(H_2O)_2], for which we selected azobenzene-2,2',3,3'-tetracarboxylic acid (H_4abtc) as the ligand. The four carboxylic acid groups of this rigid H_4abtc linker may be partially or completely deprotonated and thus show flexible and diverse coordination patterns. In one of these coordination modes, the O atoms of a carboxylate group can bridge Gd^{3+} ions and thus ensure magnetic exchange and transfer between adjacent Gd^{3+} ions, at the same time maintaining an overall rigid product (Zhang et al., 2015c). In this article, we communicate the synthesis, structure and magnetic properties of (I).

2. Experimental

All reagents and solvents used were commercially available and were used without further purification. H_4abtc was purchased from Jinan Trading Company (China). FT–IR spectra were obtained with a Bruker TENSOR27 spectrometer on KBr disks in the 4000–400 cm^{-1} region. Elemental analyses (EAs) were performed using a PerkinElmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer (Cu Kα, λ = 1.5418 Å) at a rate of 10° min^{-1} in the 2θ range 2. Experimental

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5–50°. Based on the results of the single-crystal X-ray diffraction experiment, the simulated pattern was obtained with Mercury (Macrae et al., 2020) assuming Cu Kα1 radiation (λ = 1.54056 Å). The thermogravimetric analysis was performed on a Dupont thermal analyzer between room temperature and 1045 K under an N₂ flow with a heating rate of 10 K min⁻¹. Magnetic susceptibility was measured from a microcrystalline sample using a SQUID magnetometer (Quantum Design MPMS) in the range 2–300 K with a direct-current field of 1000 Oe. Isothermal field-dependent magnetization M(H) was measured in the range 0–7 T from 2 to 10 K.

2.1. Synthesis and crystallization

The reaction route to (I) is shown in Scheme 1. Gd(NO₃)₃·6H₂O (67.7 mg, 0.15 mmol) and H₂abtc (35.8 mg, 0.1 mmol) were dissolved in a mixture of N,N-dimethylformamide (DMF, 2 ml), acetonitrile (CH₃CN, 2 ml) and distilled water (H₂O, 6 ml). The solution was sealed in a stainless steel container and heated under autogenous pressure at 393 K for 72 h. After this period, heating was suspended and the container was allowed to cool to room temperature. Yellow block-shaped crystals of the product were obtained by filtration, washed with water and dried in the air (yield 67%). Analysis calculated (%) for C₁₆H₁₁GdN₂O₁₀: C 35.01, H 2.01, N 5.10; found: C 35.05, H 2.02, N 5.13.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Carbon-bound H atoms were placed in calculated positions and refined using a riding model, with aromatic C—H = 0.93 Å and Uiso(H) = 1.2Ueq(C). The water H-atom positions were fixed as found (O—H distances are approximately 0.82 Å), with Uiso(H) = 1.5Ueq(O). A difference Fourier map (Fig. 1) suggested Wyckoff position 4a for atom H4A in the short O···O contact, albeit as a very broad residual electron-density maximum. Our structure for atom H4 in this special position therefore assumes a short symmetric hydrogen bond. In the absence of high-resolution or neutron data, we can neither disprove nor support a split-atom alternative and an asymmetric hydrogen bond. Šerb et al. (2011) have compiled structures featuring very short O···O bonds. The reflection conditions for the correct space group C2/c are also compatible with the subgroup Cc; tentative refinements in this noncentrosymmetric subgroup resulted in numerous high correlations and anticorrelations for positional and displacement parameters: 26 elements of the final inverted refinement matrix showed correlation coefficients with a modulus >0.9 and more than 100 with a modulus >0.8. These high correlations resulted in an unrealistically broad range of C—C bonds, and no convergence for physically meaningful displacement parameters could be achieved.

3. Results and discussion

3.1. IR spectroscopy

The IR spectra of the ligand and (I) in the range 400–4000 cm⁻¹ are presented in Fig. 2. The broad band at 3405 cm⁻¹ indicates O—H stretching of the hydroxy groups and the coordinated water molecules in (I) (Yang et al., 2019b). The characteristic absorption peaks of the asymmetric and symmetric stretching vibrations of the carboxylate groups appear at 1383 and 1563 cm⁻¹ for (I) (Du et al., 2016; Li et al., 2012; Zhang et al., 2015a). They are clearly shifted to lower wavenumbers in comparison with free H₂abtc (1426 and 1572 cm⁻¹), suggesting that the carboxylate groups in the complex are coordinated to the Gd³⁺ ions (An et al., 2018). The absorption observed at 1468 cm⁻¹ is caused by the N≡N stretching vibration of the ligand (Goel & Kumar, 2018). The structural features of the complex deduced from IR spectra match the results of the single-crystal X-ray analysis. IR (KBr, ν, cm⁻¹, s = strong, m = medium and w = weak): 3405 (m), 1709 (w), 1563 (s), 1468 (s), 1383 (s), 1298 (w), 1147 (w), 1072 (m), 934 (w), 840 (m), 769 (s), 684 (w), 571 (s), 500 (s).

3.2. Structure description

Coordination polymer (I) crystallizes in the monoclinic space group C2/c, adopting a 2D framework based on coordination and covalent bonds; we originally expected a three-dimensional (3D) solid from the reaction between Gd(NO₃)₃·6H₂O and H₂abtc. The asymmetric unit of (I) contains a Gd³⁺ ion situated on a twofold axis (Wyckoff position 4e), one half of the Habtc³⁻ ligand and a coordinated H₂O molecule. As shown in Fig. 3, each Gd³⁺ ion is eight-coordinated by O atoms in a [GdO₆] environment, in which six O atoms [O1, O2, O3, O1′, O2′ and O3′; symmetry code: (i) −x, −y + 1, −z + 1] are derived from the carboxylate groups of four Habtc³⁻ moieties and two O atoms (O5 and O5′) represent aqua ligands. The Gd—O distances are in the range 2.3449 (15)–2.4503 (16) Å and the O—Gd—O angles vary from 68.66 (5) to 149.37 (5)° (Table 2), consistent with values observed in related compounds (Nakamura et al., 2021). The coordination polyhedron about the Gd³⁺ ion displays a
Table 2
Selected geometric parameters (Å, °).

|        | Gd1–O1 | Gd1–O2 | Gd1–O3 | Gd1–O5 | O1–Gd1–O3 | O1–Gd1–O2 | O1–Gd1–O5 | O2–Gd1–O3 | O2–Gd1–O2 |
|--------|--------|--------|--------|--------|-----------|-----------|-----------|-----------|-----------|
| Distance (Å) | 2.3449 (15) | 2.3722 (15) | 2.4446 (15) | 2.4502 (16) | 138.46 (5) | 140.25 (5) | 72.12 (5) | 78.93 (6) |

Symmetry code: (i) x, y, −z + 1/2; (ii) x, y + 1, z; (iii) −x + 1, −y + 1, z − 1.

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

|        | D−H−A | D−H−A | D−H−A | D−H−A |
|--------|--------|--------|--------|--------|
| Distance (Å) | 2.12 | 2.42 | 2.756 (2) | 2.821 (3) |

Symmetry codes: (ii) −x, −y + 1, −z + 1; (iii) x, y − 1, z; (iv) x, −y + 1, z − 1.

3.3. Powder X-ray diffraction (PXRD) and thermal stability

To verify the phase purity of the compound, the as-synthesized samples were characterized by PXRD at room temperature. As shown in Fig. 5(a), the experimental PXRD pattern of (I) is in excellent agreement with the simulated one, demonstrating the phase purity of the bulk sample. Minor differences in line intensities can probably be attributed to preferred orientation of the powder sample. Thermal stability was investigated by a thermogravimetric analysis (TGA) under an N2 atmosphere. Fig. 5(b) summarizes the weight loss for (I) between room temperature and 1045 K. In the temperature range 325–471 K, the TGA curve shows a weight loss of 6.88% which may be attributed to the elimination of two coordinated water molecules (calculated 6.56%). At higher temperatures, the framework of (I) gradually collapses.

3.4. Magnetic properties

Magnetic properties of (I) were studied in order to understand potential magnetic interactions. Variable-temperature magnetic susceptibility measurements of (I) were conducted in the range 2–300 K with an applied magnetic field of 1000 Oe. As shown in Fig. 6, the experimental \( \chi_m T \) value for (I) amounts to 8.00 cm\(^3\) mol\(^{-1}\) K at 300 K, close to the expected value of 7.88 cm\(^3\) mol\(^{-1}\) K calculated for an isolated Gd\(^{3+}\) ion \((S = 7/2, g = 2)\) (Xi et al., 2020). As the temperature is decreased, the \( \chi_m T \) value of (I) decreases slowly to 7.93 cm\(^3\) mol\(^{-1}\) K around 10 K, and then increases gradually to 8.14 cm\(^3\) mol\(^{-1}\) K at 2 K. The data in the whole temperature range 2–300 K fit well the Curie–Weiss law with \( C = 8.06 \text{ cm}^3 \text{ mol}^{-1} \text{ K} \) and \( \theta = -0.08 \text{ K} \). The negative \( \theta \) value indicates the existence of weak antiferromagnetic interactions between the metal centres in the 1D chain of (I). To further quantitatively analyze the magnetic interactions, the molar susceptibility of (I) can be described by a Fisher expression for a classical spin chain which allows an evaluation of the magnetic coupling \( J \) between adjacent Gd\(^{3+}\) ions (Farger et al., 2018). The best least-squares fit parameters are \( g = 2.01 \) and \( J = -0.02 \text{ cm}^{-1} \), with an agreement factor \( R = 6.27 \times 10^{-5} \) in the range 35–300 K. The value for \( J \) further proves the existence of weak antiferromagnetic interactions between adjacent Gd\(^{3+}\) ions in (I).

Figure 3
Expanded asymmetric unit and coordination environment of the Gd\(^{3+}\) ion in (I). Displacement ellipsoids are drawn at 30% probability and H atoms are represented as spheres of arbitrary radius. [Symmetry codes: (i) −x, y, −z + 1/2; (ii) x, y + 1, z; (iii) −x + 1, −y + 1, z − 1.]
The magnetization of (I) was measured in the interval between 0 and 7 T at temperatures between 2 and 10 K (Fig. 7a). The $M$ values for (I) show a steady increase with increasing $H$ and a saturation value of 7.14 N/$\beta$ at 7 T and 2 K, which is close to the expected value of $S \times g = 7/2 \times 2 = 7$ N/$\beta$ for an isolated Gd$^{3+}$ ion ($S = 7/2$, $g = 2$). To evaluate the magne-

Figure 4
(a) Distances between adjacent Gd$^{3+}$ ions in the 1D metal chain constructed by Gd$^{3+}$ ions and the carboxylate groups of the Habt$^{3-}$ ligands (H atoms have been omitted for clarity). (b) The 2D layer of (I). The inset is the local coordination geometry of the Gd$^{3+}$ ion of (I). [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$] (c) The 3D framework formed by hydrogen bonds in (I) (different colours represent different layers and H4A atoms are shown in red). (d) The 2D topology of (I) with point symbol (446).

Figure 5
(a) Experimental and simulated PXRD patterns of (I) in the range 5–50$^\circ$. (b) Thermogravimetric analysis for (I).

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**Table 4**
Comparison of $-\Delta S_m$ for (I) and several previously reported 1D Gd$^{3+}$ complexes.

| Complex | Dimensionality | $-\Delta S_m$ max (J kg$^{-1}$ K$^{-1}$) | Gd $\cdot$ Gd (Å) | $M_w/N_{Gd}$ | Reference |
|---------|----------------|--------------------------------------|----------------|---------------|-----------|
| [Gd(OAc)$_3$(H$_2$O)$_2$]$_n$ | One-dimensional | 50.4 | 4.0 | 343 | Guo et al. (2012) |
| [Gd(pda)(ox)$_3$]$_n$ | Three-dimensional | 46.8 | 4.1–6.1 | 303 | Liu et al. (2017) |
| [Gd(HCOO)(OAc)$_2$(H$_2$O)$_2$]$_n$ | One-dimensional | 46.1 | 4.3–6.3 | 321 | Liu et al. (2017) |
| [Gd(piv)$_3$(MeOH)$_2$]$_n$ | Three-dimensional | 45.9 | 5.9 | 572 | Lorusso et al. (2012) |
| [Gd(piv)$_3$(MeOH)$_2$]$_n$ | One-dimensional | 45.0 | 4.1 | 366 | Guo et al. (2012) |
| [Gd(piv)$_3$(MeOH)$_2$]$_n$ | Two-dimensional | 45.0 | 4.2–6.2 | 339 | Liu et al. (2017) |
| [Gd(HPA)(NO$_3$)(H$_2$O)$_2$]$_n$ | Three-dimensional | 43.6 | 4.5 | 363 | Liu et al. (2014b) |
| [Gd(pda)(ox)$_3$]$_n$ | One-dimensional | 37.5 | 3.7 | 427 | Liu et al. (2014b) |
| [Gd(MMA)(INA)(H$_2$O)$_2$]$_n$ | Two-dimensional | 36.0 | 4.7 | 431 | Li et al. (2017a) |
| [Gd(glu)$_3$(H$_2$O)$_2$,4H$_2$O]$_n$ | One-dimensional | 36.0 | 4.2 | 406 | Zheng et al. (2017) |
| [Gd(HPA)$_3$(H$_2$O)$_2$]$_n$ | Three-dimensional | 35.6 | 3.9 | 415 | Li et al. (2017b) |
| [Gd(HPA)$_3$(H$_2$O)$_2$]$_n$ | Two-dimensional | 35.4 | 3.9 | 415 | Li et al. (2017b) |
| [Gd(hfac)$_3$]$_n$ | Three-dimensional | 34.9 | 3.9 | 470 | Zhang et al. (2015b) |
| [Gd$_2$(DMA)$_3$]$_n$ | One-dimensional | 34.3 | 4.8 | 844 | Li et al. (2017a) |
| [Gd$_2$(SO$_4$)$_3$(phen)$_2$(H$_2$O)$_2$]$_n$ | Three-dimensional | 31.7 | 4.3 | 499 | Zheng et al. (2017) |
| [Gd$_2$(2,5-TDA)$_3$(DMA)$_2$]$_n$ | Two-dimensional | 31.0 | 4.1 | 499 | Kumar et al. (2020) |
| [Gd$_2$(OH)$_2$]$_2$:DMF·4H$_2$O]$_n$ | Three-dimensional | 30.3 | 3.8–3.9 | 417 | Peng et al. (2018) |
| [Gd$_2$(BDC)$_3$(DMA)]$_n$ | Three-dimensional | 29.0 | 10.5–12.1 | 366 | Lorusso et al. (2012) |
| [Gd$_2$(DOB)$_3$(DMA)]$_n$ | Two-dimensional | 27.3 | 5.0 | 548 | This work |
| [Gd$_2$(tmnb)$_3$(μ-OH)(H$_2$O)]$_n$ | One-dimensional | 27.1 | 3.8 | 515 | Liu et al. (2014b) |
| [Gd($\beta$-$\eta$)$_3$(H$_2$O)$_2$]$_n$ | One-dimensional | 26.7 | 4.0 | 580 | Li et al. (2017c) |
| [Gd[IN][HIN][CH$_2$OCH$_2$O]$_2$]$_n$ | One-dimensional | 26.2 | 3.7 | 462 | Li et al. (2020) |
| [Gd(azd)$_3$(DMA)$_2$·2DMA]$_n$ | Three-dimensional | 22.3 | 4.6 | 734 | Zhang et al. (2014) |

The calculated magnetic entropy change (-ΔS$_m$) of (I) was calculated for a field between 0 and 7 T in the temperature range 2–10 K, and it can be obtained (Fig. 7b) by the Maxwell relation in the equation $\Delta S_m(T) = [M(T,H)/T]dH$. The resulting maximum value of $-\Delta S_m$ amounts to 27.26 J kg$^{-1}$ K$^{-1}$ for ΔH = 7 T at 3.0 K, which is smaller than the theoretical value of 31.52 J kg$^{-1}$ K$^{-1}$, as calculated from the equation $-\Delta S_m = N_{Gd} R \ln(2s+1)/M_w$ with $S = 7/2$. In this equation, $M_w$ is the formula mass of 548.52 g mol$^{-1}$ and $N_{Gd}$ is the number of Gd$^{3+}$ ions present per mole of (I). The difference in $-\Delta S_m$ between the theoretical and experimental values may be attributed to the existence of antiferromagnetic interactions between Gd$^{3+}$ ions. The experimental $-\Delta S_m$ value is also smaller than several previously prepared 1D linear-chain Gd$^{3+}$ complexes (Table 4), which can be ascribed to the large $M_w/N_{Gd}$ ratio arising from the large H$_2$abtc ligand and the antiferromagnetic interactions between the neighbouring Gd$^{3+}$ ions in (I).

3.5. Conclusion

In summary, the novel coordination polymer (I) has been successfully constructed under hydrothermal conditions via the combination of Gd$^{3+}$ ions and the H$_2$abtc linker. The underlying structural principles in (I) comprise a 1D chain antiferromagnetic Gd coupling and a cryogenic MCE with the maximum $-\Delta S_m$ of 27.26 J kg$^{-1}$ K$^{-1}$ for ΔH = 7 T at 3.0 K. This small $-\Delta S_m$ value can be ascribed to the high $M_w/N_{Gd}$ ratio arising from the large H$_2$abtc ligand and the antiferromagnetic interactions between neighbouring Gd$^{3+}$ ions in (I). The selection of low molecular-weight ligands that transfer weak coupling may be a promising approach for obtaining Gd$^{3+}$ complexes as molecule-based magnetic refrigerants. Further studies on Gd$^{3+}$ complexes for magnetic refrigeration are underway in our laboratory.

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Figure 7
(a) $M$ versus $H$ plots from 2 to 10 K. (b) Calculated $-\Delta S_m$ from the magnetization data of (I) at various fields and temperatures.

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Supporting information

**Acta Cryst.** (2021). C77, 591-598  [https://doi.org/10.1107/S2053229621008871]

**Synthesis, structure and magnetocaloric properties of a new two-dimensional gadolinium(III) coordination polymer based on azobenzene-2,2',3,3'-tetracarboxylic acid**

**Wen-Wen Wei, Li-Ping Lu, Si-Si Feng, Miao-Li Zhu and Ulli Englert**

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Bruker, 2009); software used to prepare material for publication: *SHELXTL* (Bruker, 2009).

Poly[diaqua[μ-1'-carboxy-3,3'-(diazene-1,2-diyl)dibenzene-1,2,2'-tricarboxylato]gadolinium(III)]

Crystal data

\[\text{[Gd(C}_{16}\text{H}_{7}\text{N}_{2}\text{O}_{8})(\text{H}_{2}\text{O})_{2}]}\]

\[M_r = 548.52\]

Monoclinic, \(C2/c\)

\(a = 25.725\) (4) \(\text{Å}\)

\(b = 5.0236\) (9) \(\text{Å}\)

\(c = 17.274\) (3) \(\text{Å}\)

\(β = 127.393\) (4)°

\(V = 1773.6\) (5) \(\text{Å}^3\)

\(Z = 4\)

\(F(000) = 1060\)

\(\rho = 2.054\) Mg m\(^{-3}\)

Mo Ka radiation, \(λ = 0.71073\) Å

Cell parameters from 5374 reflections

\(θ = 3.0–25.2°\)

\(μ = 3.80\) mm\(^{-1}\)

\(T = 298\) K

Block, yellow

0.20 × 0.15 × 0.15 mm

Data collection

Bruker APEXII CCD
diffractometer

\(φ\) and \(ω\) scans

Absorption correction: multi-scan

\(\text{(SADABS; Krause et al., 2015)}\)

\(T_{\text{min}} = 0.600, T_{\text{max}} = 0.747\)

6278 measured reflections

1568 independent reflections

1508 reflections with \(I > 2σ(I)\)

\(R_{\text{int}} = 0.024\)

\(θ_{\text{max}} = 25.2°, θ_{\text{min}} = 3.0°\)

\(h = −30→29\)

\(k = −5→5\)

\(l = −20→20\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

\(R[F^2 > 2σ(F^2)] = 0.013\)

\(wR(F^2) = 0.034\)

\(S = 1.11\)

1568 reflections

133 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

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**Supporting Information**

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1568 reflections

133 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
\[ w = \frac{1}{[\sigma^2(F^2_o) + (0.0155P)^2 + 1.5784P]} \]

where \( P = \frac{F^2_o + 2F^2_c}{3} \)

\( (\Delta/\sigma)_{\text{max}} = 0.001 \)

\( \Delta \rho_{\text{max}} = 0.29 \text{ e Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.33 \text{ e Å}^{-3} \)

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Single-crystal X-ray diffraction data for (I) were collected on a Bruker APEXII diffractometer equipped with 1 K CCD instrument, using a graphite monochromator with Mo Ka radiation (\( \lambda = 0.71073 \) Å) at room temperature. Absorption corrections were performed via the SADABS program (Bruker, 2001). All the structures were solved by means of direct methods with SHELXS-97 program (Sheldrick, 2008) and refined on \( F^2 \) with full-matrix least-squares techniques using the program SHELXL-2014 program (Sheldrick, 2015). All non-H atoms were refined anisotropically. H positions and isotropic displacement parameters constrained; H4a with refined Uiso on center of symmetry, hence coordinates fixed.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|      | x          | y          | z          | U_{11}   | U_{22}   | U_{33}   | U_{12}   | U_{13}   | U_{23}   |
|------|------------|------------|------------|----------|----------|----------|----------|----------|----------|
| Gd1  | 0.000000   | 0.56130(3) | 0.250000   | 0.01598  |          |          |          |          |          |
| O1   | 0.07997(8) | 0.8943(3)  | 0.31251(11)| 0.0227(3)|          |          |          |          |          |
| O2   | 0.07378(8) | 0.2637(3)  | 0.37795(11)| 0.0262(4)|          |          |          |          |          |
| O3   | 0.02231(7) | 0.7317(3)  | 0.40008(10)| 0.0235(3)|          |          |          |          |          |
| O4   | 0.05656(10)| 0.5732(4)  | 0.54375(14)| 0.0499(6)|          |          |          |          |          |
| O5   | 0.07156(8) | 0.3538(4)  | 0.21824(12)| 0.0327(4)|          |          |          |          |          |
| H4A  | 0.078437   | 0.195005   | 0.232767   | 0.049*   |          |          |          |          |          |
| H5A  | 0.064136   | 0.369310   | 0.165148   | 0.049*   |          |          |          |          |          |
| N1   | 0.22255(9) | 1.1967(4)  | 0.47574(13)| 0.0253(4)|          |          |          |          |          |
| C1   | 0.21412(11)| 1.0106(5)  | 0.53013(17)| 0.0224(5)|          |          |          |          |          |
| C2   | 0.14953(11)| 0.9340(4)  | 0.48480(16)| 0.0187(4)|          |          |          |          |          |
| C3   | 0.13547(11)| 0.7600(5)  | 0.53305(15)| 0.0233(5)|          |          |          |          |          |
| C4   | 0.18693(13)| 0.6585(5)  | 0.62331(17)| 0.0339(6)|          |          |          |          |          |
| H4   | 0.177983   | 0.544331   | 0.656255   | 0.041*   |          |          |          |          |          |
| C5   | 0.25089(12)| 0.7240(5)  | 0.66474(18)| 0.0360(6)|          |          |          |          |          |
| H5   | 0.284663   | 0.647226   | 0.723624   | 0.043*   |          |          |          |          |          |
| C6   | 0.26517(12)| 0.9030(5)  | 0.61938(18)| 0.0316(6)|          |          |          |          |          |
| H6   | 0.308258   | 0.950938   | 0.648062   | 0.038*   |          |          |          |          |          |
| C7   | 0.09661(10)| 1.0408(4)  | 0.38454(16)| 0.0186(5)|          |          |          |          |          |
| C8   | 0.06676(11)| 0.6860(5)  | 0.48759(16)| 0.0259(5)|          |          |          |          |          |

### Atomic displacement parameters (Å²)

|      | U^1^1 | U^2^2 | U^3^3 | U^1^2 | U^1^3 | U^2^3 |
|------|-------|-------|-------|-------|-------|-------|
| Gd1  | 0.01432(9) | 0.01587(9) | 0.01428(8) | 0.000 | 0.00689(7) | 0.000 |
| O1   | 0.0215(8) | 0.0262(9) | 0.0185(8) | -0.0045(6) | 0.0112(7) | -0.0014(6) |
| O2   | 0.0275(9) | 0.0244(9) | 0.0251(8) | 0.0078(7) | 0.0151(7) | 0.0057(7) |
| O3   | 0.0197(8) | 0.0306(9) | 0.0207(8) | -0.0040(6) | 0.0125(7) | -0.0025(7) |
| O4   | 0.0400(12) | 0.0872(17) | 0.0256(10) | -0.0310(11) | 0.0216(9) | -0.0025(10) |

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|      |   0.0396 (10) |   0.0347 (9) |   0.0334 (9) |   0.0130 (8) |   0.0272 (9) |   0.0112 (8) |
|------|---------------|---------------|---------------|---------------|---------------|---------------|
| O5   | N1            | C1            | C2            | C3            | C4            | C5            |
| N1   | 0.0181 (9)    | 0.0278 (11)   | 0.0261 (10)   | −0.0058 (8)   | 0.0114 (8)    | 0.0019 (9)    |
| C1   | 0.0185 (11)   | 0.0233 (11)   | 0.0210 (11)   | −0.0035 (9)   | 0.0097 (10)   | 0.0010 (9)    |
| C2   | 0.0176 (11)   | 0.0180 (11)   | 0.0174 (10)   | −0.0015 (8)   | 0.0091 (9)    | −0.0010 (9)   |
| C3   | 0.0233 (12)   | 0.0259 (12)   | 0.0192 (11)   | −0.0049 (9)   | 0.0122 (10)   | 0.0000 (9)    |
| C4   | 0.0373 (14)   | 0.0352 (14)   | 0.0237 (12)   | −0.0080 (12)  | 0.0157 (11)   | 0.0071 (11)   |
| C5   | 0.0265 (13)   | 0.0404 (16)   | 0.0221 (12)   | −0.0015 (11)  | 0.0048 (11)   | 0.0099 (11)   |
| C6   | 0.0178 (12)   | 0.0374 (15)   | 0.0273 (13)   | −0.0039 (10)  | 0.0074 (11)   | 0.0036 (11)   |
| C7   | 0.0143 (10)   | 0.0218 (12)   | 0.0204 (11)   | −0.0040 (9)   | 0.0108 (10)   | 0.0019 (9)    |
| C8   | 0.0300 (13)   | 0.0303 (13)   | 0.0218 (12)   | −0.0102 (11)  | 0.0180 (11)   | −0.0041 (10)  |

**Geometric parameters (Å, °)**

|      |   2.3449 (15) |           |           | O5—H5B 0.8191 |
|------|---------------|-----------|-----------|---------------|
| Gd1—O1i | 2.3449 (15) |           |           |               |
| Gd1—O1  | 2.3722 (15) |           |           |               |
| Gd1—O2  | 2.4446 (15) |           |           |               |
| Gd1—O3  | 2.4502 (16) |           |           |               |
| Gd1—O5  | 2.4502 (16) |           |           |               |
| O1—C7  | 1.275 (3)    |           |           |               |
| O2—C7   | 1.243 (3)    |           |           |               |
| O3—C8   | 1.281 (3)    |           |           |               |
| O4—C8   | 1.2196       |           |           |               |
| O5—H5A  | 0.8224       |           |           |               |
| O1—Gd1—O1i | 88.98 (8) |           |           | 132.45 (15)  |
| O1i—Gd1—O2 | 149.37 (5) |           |           | 112.33       |
| O1—Gd1—O2 | 92.22 (6)    |           |           | 113.3        |
| O1i—Gd1—O2i | 92.22 (6) |           |           | 120.9        |
| O1—Gd1—O2i | 149.36 (5)  |           |           | 107.1        |
| O2—Gd1—O2i | 101.87 (8)  |           |           |               |
| O1—Gd1—O3 | 79.27 (5)    |           |           | 121.1        |
| O1i—Gd1—O3 | 71.73 (5)    |           |           | 124.3        |
| O1—Gd1—O3i | 71.73 (5)    |           |           | 114.6        |
| O1—Gd1—O3i | 79.27 (5)    |           |           | 119.3        |
| O2—Gd1—O3  | 72.12 (5)    |           |           | 118.92 (19)  |
| O2i—Gd1—O3  | 138.46 (5)   |           |           | 121.8 (2)    |
| O2—Gd1—O3i | 138.46 (5)   |           |           | 118.8 (2)    |
| O2i—Gd1—O3i | 72.11 (5)    |           |           | 121.3 (2)    |
| O3—Gd1—O3i | 139.00 (8)   |           |           | 119.9 (2)    |
| O1—Gd1—O5i | 80.69 (6)    |           |           | 121.2 (2)    |
| O1—Gd1—O5i | 140.25 (5)   |           |           | 119.4        |
| O1i—Gd1—O5i | 140.25 (5)   |           |           | 119.4        |
| O1—Gd1—O5  | 80.69 (6)    |           |           | 120.4 (2)    |
| O2—Gd1—O5i | 78.93 (6)    |           |           | 119.8        |
O2—Gd1—O5i  69.86 (6)  C6—C5—H5  119.8
O2—Gd1—O5   69.85 (6)  C5—C6—C1  119.0 (2)
O2—Gd1—O5   78.93 (6)  C5—C6—H6  120.5
O3—Gd1—O5i  68.66 (5)  C1—C6—H6  120.5
O3i—Gd1—O5i 131.45 (5)  O2iv—C7—O1  125.0 (2)
O3—Gd1—O5   131.45 (5)  O2iv—C7—C2  118.32 (19)
O5—Gd1—O5i  129.63 (9)  O1—C7—C2  116.69 (18)
C7—O1—Gd1   122.79 (13)  O3—C8—O4  122.9 (2)
C7—O1—Gd1   136.28 (14)  O3—C8—C3  121.22 (19)
C7—O1—Gd1   166.3 (3)   O4—C8—C3  115.9 (2)
C7—O1—Gd1   4.4 (3)    N1—C1—C2—C3  166.3 (3)
N1ii—N1—C1—C6  −16.0 (4)  N1—C1—C2—C3  −179.7 (2)
N1ii—N1—C1—C2  166.3 (3)  C6—C1—C2—C3  4.4 (3)
N1—C1—C2—C3  −177.8 (2)  Gd1—O1—C7—O2iv  −94.9 (2)
C6—C1—C2—C7  −175.3 (2)  Gd1—O1—C7—C2  86.9 (2)
N1—C1—C2—C7  2.4 (3)    C1—C2—C3—C4  −2.9 (3)
C1—C2—C3—C4  −2.9 (3)   C1—C2—C3—C4  95.1 (2)
C7—C2—C3—C4  176.8 (2)  C3—C2—C3—C4  −84.7 (3)
C1—C2—C3—C8  177.4 (2)  Gd1—O3—C8—O4  −114.6 (2)
C7—C2—C3—C8  −2.9 (3)   Gd1—O3—C8—C3  65.3 (3)
C2—C3—C4—C5  −0.8 (4)   C4—C3—C2—C7  97.0 (3)
C8—C3—C4—C5  178.9 (3)  C2—C3—C4—C5  −165.9 (2)
C3—C4—C5—C6  3.1 (4)    C4—C3—C2—C7  14.2 (4)
C4—C5—C6—C1  −1.6 (4)   O4—H4···O3v  1.22  2.42  3.130 (2)  114
C7—O1—Gd1   122.79 (13)  O5—H5···O1ii  0.82  2.03  2.756 (2)  147
C7—O1—Gd1   136.28 (14)  O5—H5B···O4vi  0.82  2.01  2.821 (3)  173

Symmetry codes: (i) −x, y, −z+1/2; (ii) x, y−1, z; (iii) −x+1/2, −y+5/2, −z+1; (iv) x, y+1, z; (v) −x, −y+1, −z+1; (vi) x, −y+1, z−1/2.

Hydrogen-bond geometry (Å, °)

| D—H···A        | D—H | H···A | D···A  | D—H···A  |
|----------------|------|-------|--------|-----------|
| O4—H4· · · O3v | 1.22 | 2.42  | 3.130 (2) | 114       |
| O4—H4· · · O4v | 1.22 | 1.22  | 2.439 (4) | 180       |
| O5—H5· · · O1ii| 0.82 | 2.03  | 2.756 (2) | 147       |
| O5—H5B· · · O4vi| 0.82| 2.01 | 2.821 (3) | 173       |

Symmetry codes: (ii) x, y−1, z; (v) −x, −y+1, −z+1; (vi) x, −y+1, z−1/2.