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Nitrate salt of a hydrocarbazole oxime cation and a hydrated co-crystal of its chloride salt with cyclohexane-1,2,3-trione 1,3-dioxime

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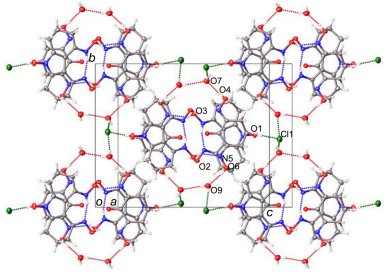
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In the presence of nickel(II) salts, cyclohexane-1,3-dione dioxime is transformed into a hydrocarbazole oxime cation, isolated as a nitrate salt, *N*,9-dihydroxy-5-(hydroxyimino)-2,3,4,5,6,7,8,9-octahydro-1*H*-carbazol-4-iminium nitrate (**1**, $C_{12}H_{16}N_3O_3^+\cdot NO_3^-$), and as a hydrated chloride co-crystal with cyclohexane-1,2,3-trione 1,3-dioxime, *N*,9-dihydroxy-5-(hydroxyimino)-2,3,4,5,6,7,8,9-octahydro-1*H*-carbazol-4-iminium chloride–cyclohexane-1,2,3-trione 1,3-dioxime–water (1/1/3) (**2**, $C_{12}H_{16}N_3O_3^+\cdot Cl^-\cdot C_6H_8N_2O_3\cdot 3H_2O$). In **1**, the cation and nitrate anion occupy mirror sites. The symmetry-related ring methylene C atoms in the cation are disordered over two positions [occupancies 0.896 (12) and 0.104 (12)]. The asymmetric unit of **2** contains one cation, one trionedioxime molecule, one chloride anion and three water molecules; one water oxygen is disordered over two sites [occupancies 0.935 (7) and 0.065 (7)]. Both cations have an intramolecular N—H···N contact, with the proton distributed over mirror-related sites in **1** but assigned to a single nitrogen site in **2**. The hydroxy group attached to the nitrogen at the 9-position of the hydrocarbazole moiety in **1** forms a hydrogen bond to the nitrate anion, whereas chloride, trionedioxime and water molecules participate in the hydrogen-bonding network of **2**.

1. Chemical context

The central carbon of 1,3-dione dioximes is reactive toward chemical transformation. Previously, we have found that, in the presence of $Cu(NO_3)_2$, acetylacetone dioxime is transformed into trioxime that coordinates to copper to form a pentanuclear complex under ambient conditions in water (Otsuki *et al.*, 2017). More recently, in the presence of $Cu(NO_3)_2$ in methanol, we found that cyclohexane-1,3-dione dioxime transformed into cyclohexane-1,2,3-trione 1,3-dioxime and its acetal or hemiacetal derivative with methanol, whereas cyclopentane-1,3-dione dioxime transformed into [1,1′-bicyclopentylidene]-2,2′,5,5′-tetrone tetraoxime (Hosoya *et al.*, 2021, 2024). These transformed compounds served as ligands to form multinuclear copper complexes. Against this background, we herein investigated the crystal structures of products from cyclohexane-1,3-dione dioxime in the presence of $Ni(NO_3)_2$ and $NiCl_2$ in methanol at room temperature.

Reactions of cyclohexane-1,3-dione dioxime in methanol in the presence of these nickel(II) salts afforded crystals containing the metal-free salts of the same unexpected hydrocarbazole-derived cation. Compound **1** is the nitrate salt, whereas compound **2** is a hydrated co-crystal of the chloride salt with neutral cyclohexane-1,2,3-trione 1,3-dioxime. This outcome prompted an examination of their hydrogen-bonding arrangements in relation to those reported for oximes, oxime salts and multicomponent crystals (Bruton *et al.*, 2003;



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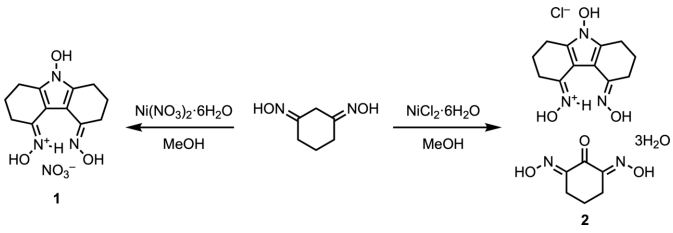
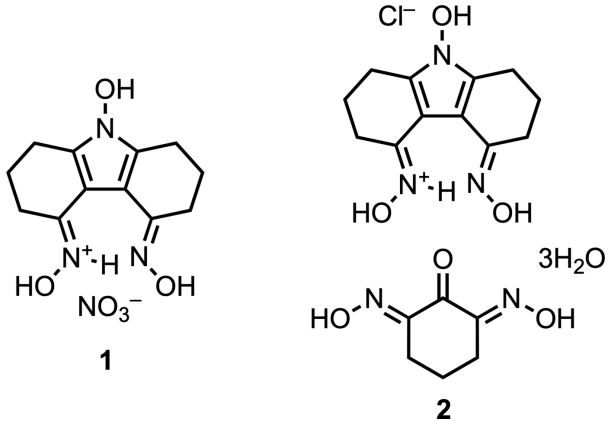


Figure 1
Formation of compounds **1** and **2** from cyclohexane-1,3-dione dioxime under the conditions shown.

Aakeröy *et al.*, 2013; Tarai & Baruah, 2016*a*,*b*). We compare the crystallographic symmetry and proton arrangement of the cation, and its association with the different counter-ions and hydrogen-bonding partners. The crystal structures establish the compositions of the isolated solids but do not establish the reaction mechanism or the composition of the complete reaction mixtures. The reactions leading to compounds **1** and **2** are shown in Fig. 1.



2. Structural commentary

Both compounds contain an *N*-hydroxy hydrocarbazole framework bearing two oxime groups. Compound **1** crystallizes in the orthorhombic space group *Cmce*, with half of the cation and half of the nitrate anion in the asymmetric unit. The complete ions are generated by mirror symmetry. A methylene carbon C5 in the saturated ring is split between two sites with occupancies 0.896 (12) and 0.104 (12). The molecular structure of **1** is shown in Fig. 2. Compound **2** crystallizes in the monoclinic space group $P2_1/n$. Its asymmetric unit comprises one hydrocarbazole cation, one neutral trionedioxime molecule, one chloride anion and three water molecules, all on general positions. One water oxygen O8 occupies alternative sites with occupancies 0.935 (7) and 0.065 (7). The molecular structure of **2** is shown in Fig. 3.

An intramolecular contact in **1** is N1—H1···N1^{i} (Table 1), with N1···N1^{i} = 2.635 (5) Å [symmetry code (i): 1 − *x*, *y*, *z*]. The N-bound proton is modelled at two half-occupied mirror-related sites. In **2**, the contact is N3—-H3*A*···N2, with N3···N2 = 2.706 (3) Å (Table 2). The model describes a symmetry-related proton distribution in **1** and inequivalent

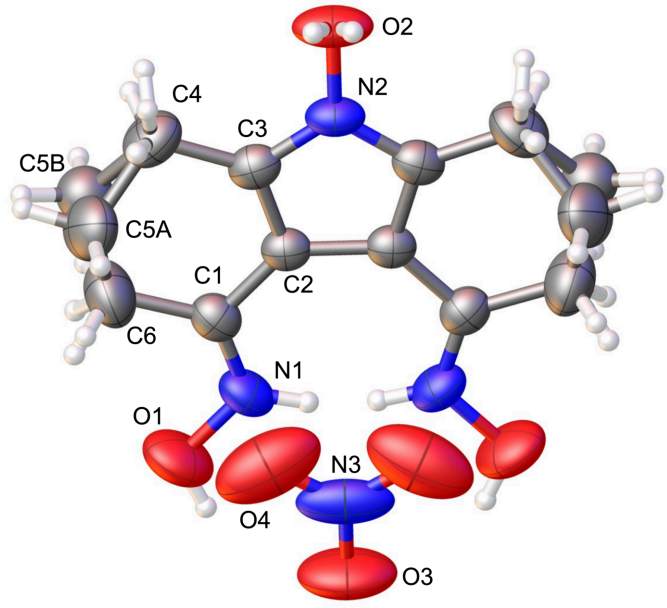


Figure 2
View of compound **1**, drawn with 50% probability displacement ellipsoids. All independent non-hydrogen atoms are labelled. Both components of the disordered C5 site are shown. The two mirror-related N-bound H-atom positions represent alternative half-occupied proton sites. The H atom attached to O2 likewise occupies two alternative half-occupied sites.

oxime nitrogen sites in **2**. The oxime C=N bond length in **1** is 1.283 (4) Å, comparable to the two corresponding distances of 1.284 (4) and 1.291 (3) Å in **2**. In contrast, the symmetry-equivalent oxime N—O bonds in **1** [1.388 (3) Å] become inequivalent in **2**, with N2—O2 and N3—O3 distances of

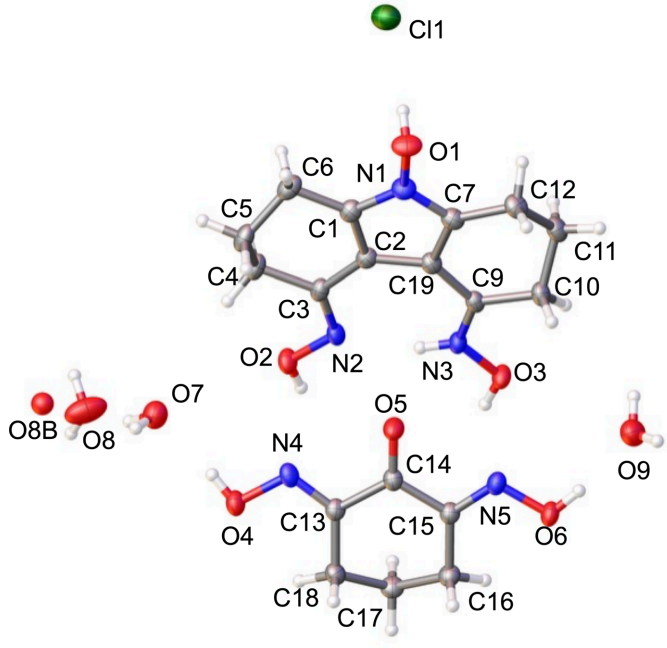


Figure 3
View of compound **2**, drawn with 50% probability displacement ellipsoids. Both alternative O8 and O8*B* water sites are displayed.

Table 1
Hydrogen-bond geometry (Å, °) for **1**.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	0.86	2.41	2.878 (4)	115
N1—H1···N1^{ii}	0.86	1.81	2.635 (5)	161
O1—H1*A*···O3^{i}	0.82	2.10	2.763 (4)	139
O2—H2···O4^{iii}	0.82	2.10	2.910 (5)	168
O2—H2···O4^{iv}	0.82	2.35	2.910 (5)	126
C5*B*—H5*BB*···O1^{v}	0.97	2.58	3.38 (5)	140

Symmetry codes: (i) $x, -y, -z+1$; (ii) $-x+1, y, z$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $x, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O9	0.84	1.78	2.614 (3)	172
O3—H3···O5	0.84	2.18	2.855 (3)	137
O3—H3···N5	0.84	2.02	2.763 (3)	146
O2—H2···O5	0.84	2.29	2.942 (3)	135
O2—H2···N4	0.84	2.25	3.005 (3)	150
O1—H1···Cl1	0.84	2.16	2.983 (2)	168
O9—H9*A*···O7^{i}	0.84 (2)	2.17 (2)	2.981 (3)	162 (4)
O9—H9*B*···Cl1^{ii}	0.82 (2)	2.40 (2)	3.205 (3)	166 (4)
C18—H18*A*···O6^{iii}	0.99	2.51	3.466 (3)	161
C16—H16*B*···O4^{iv}	0.99	2.43	3.324 (3)	150
C4—H4*B*···O6^{i}	0.99	2.56	3.466 (3)	152
C5—H5*A*···O3^{v}	0.99	2.50	3.407 (3)	152
O7—H7*A*···Cl1^{vi}	0.86 (2)	2.37 (2)	3.208 (3)	168 (4)
O7—H7*B*···O8	0.85 (2)	1.97 (2)	2.787 (4)	159 (4)
O7—H7*B*···O8*B*	0.85 (2)	2.16 (4)	2.92 (3)	150 (4)
O4—H4···O7	0.82 (2)	1.83 (2)	2.646 (3)	174 (4)
N3—H3*A*···N2	0.85 (4)	1.89 (4)	2.706 (3)	162 (4)
O8—H8*A*···Cl1^{vii}	0.83 (2)	2.48 (2)	3.271 (3)	160 (5)
O8—H8*B*···Cl1^{viii}	0.84 (2)	2.68 (5)	3.320 (3)	135 (5)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+2, -y+1, -z+1$; (vi) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (vii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (viii) $x-\frac{3}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

1.398 (3) and 1.370 (3) Å, respectively. This asymmetry accompanies the assignment of the proton to N3 in **2**.

The partially saturated six-membered rings of the hydrocarbazole cations adopt slightly distorted envelope conformations. For the major disorder component in **1**, C5*A* and its mirror-related counterpart are the flap atoms, with a C3—C4—C5*A*—C6 torsion angle of −45.2 (6)°. In **2**, the flap atoms are C5 and C11, with C3—C4—C5—C6 and C9—C10—C11—C12 torsion angles of 54.5 (3) and 52.4 (3)°, respectively. The six-membered ring of the neutral trionedioxime molecule in **2** also adopts a distorted envelope conformation, with C17 as the flap atom and a C1—C16—C17—C18 torsion angle of −52.6 (3)°.

3. Supramolecular features

In **1**, O1—H1*A*···O3($x, -y, 1-z$) and O2—H2···O4($1-x, y+\frac{1}{2}, \frac{3}{2}-z$) hydrogen bonds link the cations and nitrate anions into zigzag chains parallel to [001], as illustrated in Fig. 4. The O···O distances are 2.763 (4) and 2.910 (5) Å, with angles of 139 and 168°, respectively. H2 occupies two alternative mirror-related orientations. The minor disorder component forms a weak C5*B*—H5*BB*···O1($x, 1-y, 1-z$) contact [C···O = 3.38 (5) Å, angle 140°] with its symmetry-related counterpart forming a dimer motif. These contacts link the [001] chains into a two-dimensional network parallel to the (100) plane. Because C5*B* and H5*BB* have an occupancy of only 0.104 (12), this is a disorder-dependent extension of the chain motif.

The hydrogen-bonds in **2** are shown in Fig. 5. The cation and neutral trionedioxime molecule form hydrogen-bonded pairs through an O3—H3···N5 contact [O···N = 2.763 (3) Å, 146°]. The neutral molecule and water molecules are linked by O4—H4···O7 and O6—H6···O9 contacts [O···O = 2.646 (3) and 2.614 (3) Å], respectively. A water molecule is disordered over two alternative sites, O8 and O8*B*. O7—H7*B* forms an O–H···O contact to either site.

The cations, neutral trionedioxime molecules, chloride ions and water molecules O7 and O9 form hydrogen-bonded sheets parallel to ($\bar{1}01$), as shown in Fig. 5(*a*). These hydrogen-bonded sheets are distinct from the apparent molecular packing layers parallel to ($\bar{1}02$); the ($\bar{1}01$) assignment reflects the connectivity of the hydrogen-bond network. The chloride ion accepts an O1—H1···Cl1 hydrogen bond [O···Cl = 2.983 (2) Å, 168°]. Water molecules O7, O8 and O9 also donate O—H···Cl contacts: O7—H7*A*···Cl1 [O···Cl =

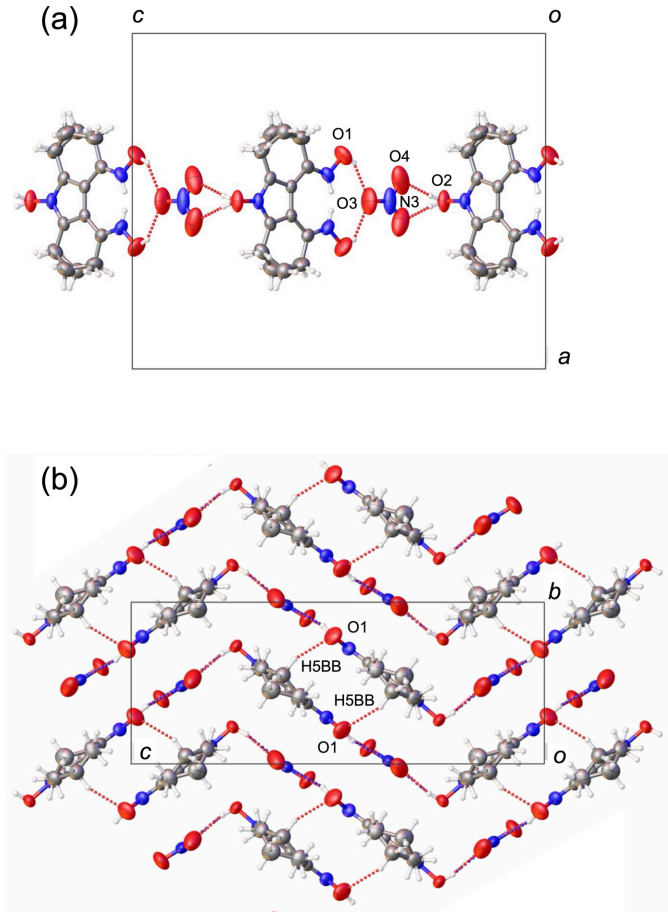


Figure 4
Crystal packing of compound **1**. Dotted lines indicate hydrogen-bond contacts. Intramolecular N—H···N hydrogen bonds across the mirror plane involving disordered H atoms are omitted. (*a*) View from the *b* axis. (*b*) View from the *a* axis. The C5*B*—H5*BB*···O1 contacts depict minor-disorder component contacts.

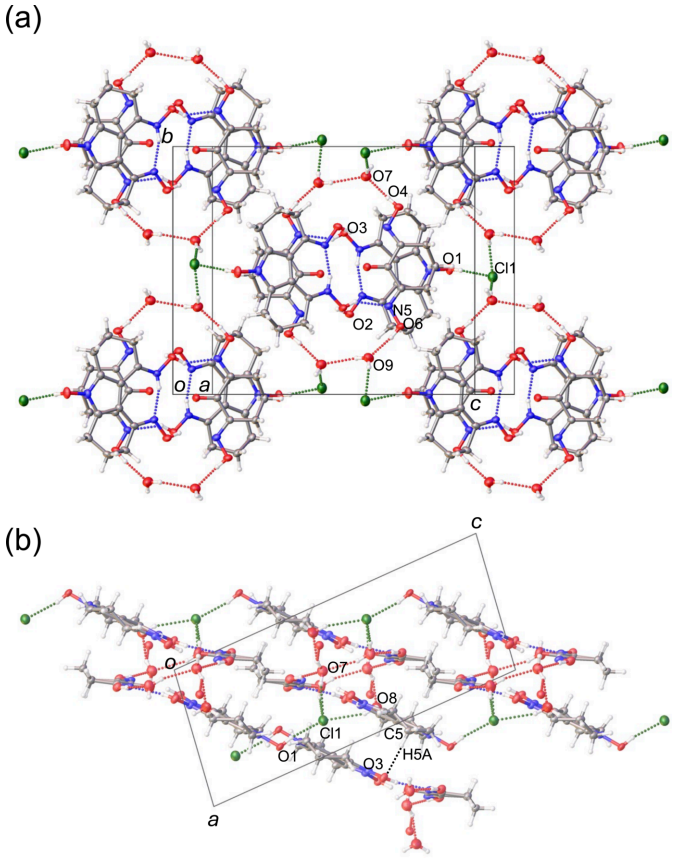


Figure 5
Crystal packing of compound **2**. Dotted lines indicate hydrogen-bond contacts. (*a*) A hydrogen-bonded sheet parallel to ($\bar{1}$01), viewed perpendicular to this plane. O8/O8*B* and their attached H atoms are omitted. (*b*) View along the *b* axis showing O7—H7*B*···O8 and O8—H8*A*···Cl1 and O8—H8*B*···Cl1 hydrogen bonds and the intersheet C5—H5*A*···O3 contact (black dotted line; acceptor symmetry code: 2 − *x*, 1 − *y*, 1 − *z*). Only part of the neighbouring sheet is shown to illustrate the latter contact.

3.208 (3) Å, 168 (4)°], O8—H8*A*···Cl1 [3.271 (3) Å, 160 (5)°], O8—H8*B*···Cl1 [3.320 (3) Å, 135 (5)°], and O9—H9*B*···Cl1 [3.205 (3) Å, 166 (4)°]. The weak C4—H4*B*···O6(1 − *x*, 1 − *y*, 1 − *z*) contact [C···O = 3.466 (3) Å, angle 152°] lies within these sheets. Water molecules at the major O8 site connect neighbouring sheets through O7—H7*B*···O8, O8—H8*A*···Cl1 and O8—H8*B*···Cl1 hydrogen bonds, producing a three-dimensional network. The C5—H5*A*···O3(2 − *x*, 1 − *y*, 1 − *z*) contact [C···O = 3.407 (3) Å, angle 152°] provides an additional intersheet link, illustrated in Fig. 5(*b*).

The present structures illustrate how additional hydrogen-bonding partners modify the assembly of oxime-containing molecules. Whereas intermolecular oxime–oxime O—H···N dimers are common in neutral dioximes (Bruton *et al.*, 2003), the hydrocarbazole cations in **1** and **2** contain an intramolecular N—H···N contact and participate in extended networks involving counter-ions and, in **2**, neutral trione-dioxime and water. Tarai & Baruah (2016*a*) reported the nitrate and hydrated chloride salts of quinoline-4-carbaldoxime. Their nitrate structure contains anion-bridged cyclic motifs, whereas the chloride structure contains hydrogen-bonded chloride–water chains. Similarly, nitrate links the cations in **1**, while chloride and water participate in the assembly of **2**. Tarai & Baruah (2016*b*) reported anion-assisted assemblies of 1,3-benzenedialdoxime with tetrabutylammonium fluoride and chloride, with water participating in the chloride-containing structure. Compound **2** likewise incorporates chloride, water and a neutral dioxime into its hydrogen-bonding network, but additionally contains a hydrocarbazole oxime cation.

4. Synthesis and crystallization

Compound **1**. A solution of cyclohexane-1,3-dione dioxime (285 mg, 2.00 mmol) in methanol (11.5 mL) was added to a solution of $Ni(NO_3)_2·6H_2O$ (394 mg, 1.35 mmol) in methanol (1 mL). Slow solvent evaporation at room temperature afforded precipitates after 31 days. After the precipitates were removed by filtration, methanol (approximately 10 mL) was added to the concentrated filtrate and diethyl ether vapour was allowed to diffuse into the solution. After 3 days, black precipitate formed, which was again removed and methanol (approximately 3 mL) was added to concentrated filtrate and the solvent was allowed to evaporate slowly at room temperature. After another 16 days, brown crystals were obtained.

Compound **2**. A solution of cyclohexane-1,3-dione dioxime (285 mg, 2.00 mmol) in methanol (11.5 mL) was added to a solution of $NiCl_2·6H_2O$ (239 mg, 1.00 mmol) in methanol (1.0 mL). Slow solvent evaporation at room temperature afforded yellow column-shaped crystals together with a black powder after 23 days. Selected crystals were used for single-crystal X-ray diffraction.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Refinement of compound **1**. The structure was refined by full-matrix least squares on F^2 using *SHELXL2018/3*. Non-H atoms were refined anisotropically, except for the minor disorder component C5*B*, which was refined isotropically. Atom C5 was modelled over two sites with occupancies of 0.896 (12) and 0.104 (12), constrained to sum to unity. Corresponding C4—C5*A*/C4—C5*B* and C6—C5*A*/C6—C5*B* distances were restrained to be similar using two SADI restraints with standard uncertainties of 0.02 Å. Hydrogen atoms on C4, C5 and C6 were assigned to the corresponding disorder components.

All H atoms were treated using constrained models. Methylene C—H distances were set to 0.97 Å, N—H to 0.86 Å and O—H to 0.82 Å. Hydrogen displacement parameters were tied to those of the parent atoms, with U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(O). The N-bound H1 was modelled with occupancy 0.5 at each of two mirror-related sites, giving one proton per cation. The hydroxy H atom H2 was modelled over two mirror-related orientations with equal occupancies.

Table 3
Experimental details.

	1	**2**
Crystal data		
Chemical formula	$C_{12}H_{16}N_3O_3^+\cdot NO_3^-$	$C_{12}H_{16}N_3O_3^+\cdot Cl^-\cdot C_6H_8N_2O_3\cdot 3H_2O$
M_r	312.29	495.92
Crystal system, space group	Orthorhombic, *Cmce*	Monoclinic, $P2_1/n$
Temperature (K)	298	100
a, b, c (Å)	16.7097 (10), 8.0402 (6), 20.5509 (11)	8.3193 (1), 14.4635 (2), 19.3327 (2)
α, β, γ (°)	90, 90, 90	90, 98.301 (1), 90
V (Å^3)	2761.0 (3)	2301.86 (5)
Z	8	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.12	2.00
Crystal size (mm)	0.25 × 0.2 × 0.1	0.25 × 0.05 × 0.03
Data collection		
Diffractometer	XtaLAB Mini II	XtaLAB AFC10 (RCD3): quarter-chi single
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD)	Multi-scan (*CrysAlis PRO*; Rigaku OD)
T_{min}, T_{max}	0.658, 1.000	0.737, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13480, 2153, 1253	14657, 4420, 4106
R_{int}	0.089	0.022
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.718	0.619
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.097, 0.238, 1.11	0.060, 0.177, 1.08
No. of reflections	2153	4420
No. of parameters	113	333
No. of restraints	2	10
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.26, −0.24	0.51, −0.76

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022, 2024), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Reflection 002 was omitted from the refinement. Inspection of its predicted positions showed proximity to the beam-stop support shadow, and no clear peak was observed on the inspected frames.

Refinement of compound **2**. The structure was refined by full-matrix least squares on F^2 using *SHELXL2018/3*. Non-H atoms were refined anisotropically, except for the minor water site O8*B*, which was refined isotropically. O8 and O8*B* were assigned complementary occupancies, which refined to 0.935 (7) and 0.065 (7). The H atoms attached to O8 shared its occupancy. The minor water site O8*B* has occupancy 0.065 (7); its hydrogen atoms were not included because their positions could not be established reliably. The reported formula, formula mass and F(000) assume two hydrogens for this minor water component, so the atom-site sum is lower by 0.13 H.

Methylene H atoms were treated using riding models, and H atoms on O1, O2, O3 and O6 were treated as rotating hydroxyl groups. The O4–H4 distance was restrained to 0.84 (2) Å. Water O—H distances were restrained to 0.85 (2) Å, and intramolecular H···H distances to 1.35 (4) Å for O7 and O8 and 1.35 (2) Å for O9. Water-H atom displacement parameters were fixed at $1.5U_{eq}$(O). The N-bound H3*A* atom was refined with independent coordinates and an isotropic displacement parameter.

The measurements were made at room temperature for **1** and 100.15 K for **2**, due to instrumental availability. Consequently, differences in displacement parameters or disorder should not be attributed solely to the counter-ion or co-crystal composition.

Acknowledgements

Single-crystal X-ray diffraction data for compound **2** were collected using the X-ray facilities of the Microstructural Characterization Division, Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM), The University of Tokyo (26UT0286).

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References

Aakeröy, C. B., Sinha, A. S., Epa, K. N., Chopade, P. D., Smith, M. M. & Desper, J. (2013). *Cryst. Growth Des.* **13**, 2687–2695.
Bruton, E. A., Brammer, L., Pigge, F. C., Aakeröy, C. B. & Leinen, D. S. (2003). *New J. Chem.* **27**, 1084–1094.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Hosoya, Y., Kobori, S., Kojima, Y., Sugawa, K. & Otsuki, J. (2021). *J. Indian Chem. Soc.* **98**, 100110.
Hosoya, Y., Yoshikawa, H., Tsukamoto, A., Sugawa, K. & Otsuki, J. (2024). *Chem. Lett.* **53**, upad033.
Otsuki, J., Sekine, T., Kida, Y., Shinozaki, Y., Kobayashi, S., Tamura, T., Sugawa, K., Yoshikawa, I., Houjou, H., Yoshikawa, H. & Tsukamoto, A. (2017). *Dalton Trans.* **46**, 2760–2764.
Rigaku OD (2022). *CrysAlis PRO*. Version 1.171.42.72a. Rigaku Oxford Diffraction.
Rigaku OD (2024). *CrysAlis PRO*. Version 1.171.43.121a. Rigaku Oxford Diffraction.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Tarai, A. & Baruah, J. B. (2016*a*). *CrystEngComm* **18**, 298–308.
Tarai, A. & Baruah, J. B. (2016*b*). *CrystEngComm* **18**, 5482–5491.

supporting information

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Nitrate salt of a hydrocarbazole oxime cation and a hydrated co-crystal of its chloride salt with cyclohexane-1,2,3-trione 1,3-dioxime

Joe Otsuki, Yosuke Hosoya and Kosuke Sugawa

Computing details

N,9-Dihydroxy-5-(hydroxyimino)-2,3,4,5,6,7,8,9-octahydro-1*H*-carbazol-4-iminium nitrate (1)

Crystal data

$C_{12}H_{16}N_3O_3^+ \cdot NO_3^-$
M_r = 312.29
Orthorhombic, *Cmce*
a = 16.7097 (10) Å
b = 8.0402 (6) Å
c = 20.5509 (11) Å
V = 2761.0 (3) Å^3
Z = 8
F(000) = 1312
D_x = 1.503 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3029 reflections
θ = 2.4–23.3°
μ = 0.12 mm^{-1}
T = 298 K
Block, clear dark brown
0.25 × 0.2 × 0.1 mm

Data collection

XtaLAB Mini II diffractometer
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD)
T_{min} = 0.658, T_{max} = 1.000
13480 measured reflections
2153 independent reflections
1253 reflections with $I > 2\sigma(I)$
R_{int} = 0.089
θ_{max} = 30.7°, θ_{min} = 2.4°
h = −23→23
k = −11→11
l = −29→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.097
$wR(F^2)$ = 0.238
S = 1.11
2153 reflections
113 parameters
2 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 3.6082P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 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. The structure was refined by full-matrix least squares on F^2 using SHELXL-2018/3. Non-H atoms were refined anisotropically, except for the minor disorder component C5B, which was refined isotropically. Atom C5 was modelled over two sites with occupancies of 0.896 (12) and 0.104 (12), constrained to sum to unity. Corresponding C4-C5A/C4-C5B and C6-C5A/C6-C5B distances were restrained to be similar using two SADI restraints with standard uncertainties of 0.02 Å. Hydrogen atoms on C4, C5 and C6 were assigned to the corresponding disorder components. All H atoms were treated using constrained models. Methylene C-H distances were set to 0.97 Å, N-H to 0.86 Å and O-H to 0.82 Å. Hydrogen displacement parameters were tied to those of the parent atoms, with Uiso(H) = 1.2Ueq(C,N) or 1.5Ueq(O). The N-bound proton H1 was modelled with occupancy 0.5 at each of two mirror-related sites, giving one proton per cation. The hydroxyl H atom H2 was modelled over two mirror-related orientations with equal occupancies. Its orientation should be regarded as less certain than the non-H-atom framework. Reflection 002 was omitted from the refinement. Inspection of its predicted positions showed proximity to the beam-stop support shadow, and no clear peak was observed on the inspected frames. Shadowing is a suspected, rather than demonstrated, explanation for its anomalously low intensity. Including this reflection in a comparison refinement gave R1 = 0.0995 and wR2 = 0.2503, compared with 0.0965 and 0.2382 when it was omitted. The lower residuals alone do not establish a reason for omission.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O2	0.500000	0.7287 (4)	0.74574 (14)	0.0719 (10)	
H2	0.516070	0.683086	0.778953	0.108*	0.5
N2	0.500000	0.6157 (4)	0.69510 (14)	0.0469 (8)	
N1	0.42116 (15)	0.2871 (3)	0.52719 (11)	0.0535 (7)	
H1	0.471258	0.275552	0.518747	0.064*	0.5
O1	0.36352 (16)	0.2091 (4)	0.48930 (14)	0.0892 (9)	
H1A	0.385338	0.144662	0.463961	0.134*	
C2	0.45684 (16)	0.4571 (3)	0.61516 (12)	0.0406 (6)	
C3	0.43279 (17)	0.5574 (3)	0.66599 (13)	0.0446 (7)	
N3	0.500000	−0.0186 (5)	0.6233 (2)	0.0924 (18)	
C1	0.39770 (18)	0.3770 (4)	0.57514 (13)	0.0474 (7)	
O3	0.500000	−0.0990 (6)	0.5732 (2)	0.1174 (18)	
C4	0.3495 (2)	0.5922 (5)	0.68612 (18)	0.0687 (10)	
H4BC	0.344125	0.708897	0.697235	0.082*	0.104 (12)
H4BD	0.336471	0.526991	0.724412	0.082*	0.104 (12)
H4AA	0.332367	0.698619	0.668801	0.082*	0.896 (12)
H4AB	0.346067	0.596830	0.733208	0.082*	0.896 (12)
C6	0.3113 (2)	0.4084 (6)	0.59144 (19)	0.0805 (12)	
H6AA	0.291290	0.496006	0.563365	0.097*	0.896 (12)
H6AB	0.280859	0.308522	0.582143	0.097*	0.896 (12)
H6BC	0.282310	0.421757	0.550897	0.097*	0.104 (12)
H6BD	0.290476	0.309620	0.612566	0.097*	0.104 (12)
C5B	0.2929 (18)	0.550 (4)	0.6325 (16)	0.066 (12)*	0.104 (12)
H5BA	0.240707	0.531228	0.651695	0.079*	0.104 (12)
H5BB	0.288326	0.646999	0.604623	0.079*	0.104 (12)
O4	0.4376 (3)	0.0245 (4)	0.64895 (16)	0.1381 (16)	
C5A	0.2970 (3)	0.4573 (7)	0.6609 (3)	0.0811 (18)	0.896 (12)

H5AA	0.241732	0.492533	0.665221	0.097*	0.896 (12)
H5AB	0.304134	0.359761	0.688041	0.097*	0.896 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.133 (3)	0.0431 (17)	0.0393 (14)	0.000	0.000	−0.0088 (13)
N2	0.073 (2)	0.0356 (17)	0.0322 (14)	0.000	0.000	−0.0033 (13)
N1	0.0613 (15)	0.0497 (15)	0.0496 (13)	−0.0099 (12)	−0.0146 (12)	−0.0025 (11)
O1	0.099 (2)	0.085 (2)	0.0837 (19)	−0.0169 (16)	−0.0330 (16)	−0.0227 (14)
C2	0.0508 (14)	0.0357 (13)	0.0352 (12)	−0.0004 (12)	0.0017 (11)	0.0037 (10)
C3	0.0564 (17)	0.0389 (14)	0.0385 (13)	0.0015 (13)	0.0059 (12)	0.0046 (11)
N3	0.196 (6)	0.037 (2)	0.044 (2)	0.000	0.000	0.0046 (19)
C1	0.0527 (17)	0.0447 (15)	0.0449 (14)	−0.0051 (13)	−0.0038 (13)	0.0056 (12)
O3	0.200 (5)	0.083 (3)	0.069 (2)	0.000	0.000	−0.035 (2)
C4	0.071 (2)	0.069 (2)	0.066 (2)	0.0113 (18)	0.0181 (17)	−0.0035 (17)
C6	0.055 (2)	0.103 (3)	0.083 (2)	−0.014 (2)	−0.0051 (18)	−0.007 (2)
O4	0.224 (4)	0.104 (3)	0.086 (2)	0.062 (3)	0.030 (2)	0.020 (2)
C5A	0.061 (3)	0.087 (4)	0.095 (3)	−0.006 (2)	0.022 (2)	−0.002 (3)

Geometric parameters (Å, º)

O2—H2	0.8200	C4—H4BC	0.9700
O2—H2^{i}	0.82 (5)	C4—H4BD	0.9700
O2—N2	1.381 (4)	C4—H4AA	0.9700
N2—C3	1.356 (3)	C4—H4AB	0.9700
N2—C3^{i}	1.356 (3)	C4—C5B	1.491 (18)
N1—H1	0.8600	C4—C5A	1.488 (5)
N1—O1	1.388 (3)	C6—H6AA	0.9700
N1—C1	1.283 (4)	C6—H6AB	0.9700
O1—H1A	0.8200	C6—H6BC	0.9700
C2—C2^{i}	1.442 (5)	C6—H6BD	0.9700
C2—C3	1.379 (4)	C6—C5B	1.450 (18)
C2—C1	1.438 (4)	C6—C5A	1.499 (6)
C3—C4	1.479 (4)	C5B—H5BA	0.9700
N3—O3	1.214 (6)	C5B—H5BB	0.9700
N3—O4	1.219 (4)	C5A—H5AA	0.9700
N3—O4^{i}	1.220 (4)	C5A—H5AB	0.9700
C1—C6	1.503 (5)		
H2—O2—H2^{i}	38.2	H4AA—C4—H4AB	108.3
N2—O2—H2^{i}	109.5 (14)	C5B—C4—H4BC	109.6
N2—O2—H2	109.5	C5B—C4—H4BD	109.6
C3^{i}—N2—O2	124.05 (15)	C5A—C4—H4AA	110.0
C3—N2—O2	124.04 (15)	C5A—C4—H4AB	110.0
C3^{i}—N2—C3	111.8 (3)	C1—C6—H6AA	108.7
O1—N1—H1	120.9	C1—C6—H6AB	108.7
C1—N1—H1	120.9	C1—C6—H6BC	107.9

C1—N1—O1	118.2 (3)	C1—C6—H6BD	107.9
N1—O1—H1A	109.5	H6AA—C6—H6AB	107.6
C3—C2—C2^{i}	106.94 (17)	H6BC—C6—H6BD	107.2
C3—C2—C1	119.7 (3)	C5B—C6—C1	117.7 (13)
C1—C2—C2^{i}	133.41 (16)	C5B—C6—H6BC	107.9
N2—C3—C2	107.2 (2)	C5B—C6—H6BD	107.9
N2—C3—C4	126.2 (3)	C5A—C6—C1	114.2 (3)
C2—C3—C4	126.6 (3)	C5A—C6—H6AA	108.7
O3—N3—O4^{i}	121.2 (3)	C5A—C6—H6AB	108.7
O3—N3—O4	121.2 (3)	C4—C5B—H5BA	107.7
O4—N3—O4^{i}	117.6 (6)	C4—C5B—H5BB	107.7
N1—C1—C2	118.8 (3)	C6—C5B—C4	118.3 (15)
N1—C1—C6	124.0 (3)	C6—C5B—H5BA	107.7
C2—C1—C6	117.2 (3)	C6—C5B—H5BB	107.7
C3—C4—H4BC	109.6	H5BA—C5B—H5BB	107.1
C3—C4—H4BD	109.6	C4—C5A—C6	115.4 (4)
C3—C4—H4AA	110.0	C4—C5A—H5AA	108.4
C3—C4—H4AB	110.0	C4—C5A—H5AB	108.4
C3—C4—C5B	110.3 (12)	C6—C5A—H5AA	108.4
C3—C4—C5A	108.6 (3)	C6—C5A—H5AB	108.4
H4BC—C4—H4BD	108.1	H5AA—C5A—H5AB	107.5

O2—N2—C3—C2	175.9 (3)	C2—C3—C4—C5A	21.2 (5)
O2—N2—C3—C4	−5.3 (5)	C2—C1—C6—C5B	17 (2)
N2—C3—C4—C5B	163.2 (18)	C2—C1—C6—C5A	−24.4 (5)
N2—C3—C4—C5A	−157.3 (4)	C3^{i}—N2—C3—C2	−0.4 (4)
N1—C1—C6—C5B	−161 (2)	C3^{i}—N2—C3—C4	178.3 (2)
N1—C1—C6—C5A	157.4 (4)	C3—C2—C1—N1	178.5 (2)
O1—N1—C1—C2	179.4 (2)	C3—C2—C1—C6	0.1 (4)
O1—N1—C1—C6	−2.4 (4)	C3—C4—C5B—C6	35 (4)
C2^{i}—C2—C3—N2	0.3 (2)	C3—C4—C5A—C6	−45.2 (6)
C2^{i}—C2—C3—C4	−178.5 (3)	C1—C2—C3—N2	179.9 (2)
C2^{i}—C2—C1—N1	−2.0 (3)	C1—C2—C3—C4	1.2 (4)
C2^{i}—C2—C1—C6	179.7 (2)	C1—C6—C5B—C4	−37 (4)
C2—C3—C4—C5B	−18.2 (19)	C1—C6—C5A—C4	49.0 (6)

Symmetry code: (i) −*x*+1, *y*, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3^{ii}	0.86	2.41	2.878 (4)	115
N1—H1···N1^{i}	0.86	1.81	2.635 (5)	161
O1—H1*A*···O3^{ii}	0.82	2.10	2.763 (4)	139
O2—H2···O4^{iii}	0.82	2.10	2.910 (5)	168
O2—H2···O4^{iv}	0.82	2.35	2.910 (5)	126
C5*B*—H5*BB*···O1^{v}	0.97	2.58	3.38 (5)	140

Symmetry codes: (i) −*x*+1, *y*, *z*; (ii) *x*, −*y*, −*z*+1; (iii) −*x*+1, *y*+1/2, −*z*+3/2; (iv) *x*, *y*+1/2, −*z*+3/2; (v) *x*, −*y*+1, −*z*+1.

N,9-Dihydroxy-5-(hydroxyimino)-2,3,4,5,6,7,8,9-octahydro-1*H*-carbazol-4-iminium chloride; cyclohexane-1,2,3-trione 1,3-dioxime; trihydrate (2)

Crystal data

$C_{12}H_{16}N_3O_3^+\cdot Cl^-\cdot C_6H_8N_2O_3\cdot 3H_2O$
M_r = 495.92
Monoclinic, $P2_1/n$
a = 8.3193 (1) Å
b = 14.4635 (2) Å
c = 19.3327 (2) Å
β = 98.301 (1)°
V = 2301.86 (5) Å^3
Z = 4
$F(000)$ = 1048
D_x = 1.431 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 8445 reflections
θ = 4.6–72.4°
μ = 2.00 mm^{-1}
T = 100 K
Block, light yellow
0.25 × 0.05 × 0.03 mm

Data collection

XtaLAB AFC10 (RCD3): quarter-chi single diffractometer
Detector resolution: 5.8140 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD)
T_{min} = 0.737, T_{max} = 1.000
14657 measured reflections
4420 independent reflections
4106 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 72.7°, θ_{min} = 3.8°
h = −10→8
k = −17→17
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.177
S = 1.08
4420 reflections
333 parameters
10 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 3.991P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O6	0.4445 (2)	0.72565 (13)	0.31859 (10)	0.0266 (4)	
H6	0.474250	0.770057	0.345412	0.040*	
O4	0.3968 (2)	0.24394 (14)	0.33120 (11)	0.0278 (4)	
O5	0.5412 (3)	0.48624 (13)	0.41726 (10)	0.0290 (5)	
O3	0.6888 (2)	0.65128 (13)	0.47759 (10)	0.0269 (4)	
H3	0.623674	0.626219	0.445849	0.040*	
O2	0.6814 (2)	0.32387 (13)	0.49552 (11)	0.0270 (4)	
H2	0.607123	0.344148	0.465256	0.041*	
O1	1.3080 (2)	0.50619 (16)	0.74488 (11)	0.0315 (5)	

H1	1.281009	0.500305	0.784865	0.047*
N2	0.7728 (3)	0.39780 (15)	0.52672 (12)	0.0221 (5)
N3	0.7759 (3)	0.58442 (16)	0.51679 (12)	0.0212 (5)
N1	1.1711 (3)	0.50173 (17)	0.69507 (13)	0.0253 (5)
N4	0.4410 (3)	0.32626 (16)	0.36361 (12)	0.0234 (5)
N5	0.4762 (3)	0.64389 (16)	0.35393 (12)	0.0228 (5)
O9	0.5338 (3)	0.85258 (17)	0.41255 (13)	0.0449 (6)
H9A	0.521 (5)	0.854 (3)	0.4547 (12)	0.067*
H9B	0.601 (5)	0.890 (3)	0.403 (2)	0.067*
C14	0.4623 (3)	0.48511 (18)	0.35847 (14)	0.0220 (5)
C15	0.4189 (3)	0.57234 (18)	0.31953 (14)	0.0214 (5)
C9	0.8920 (3)	0.61089 (18)	0.56425 (13)	0.0206 (5)
C3	0.8802 (3)	0.37307 (18)	0.57786 (14)	0.0222 (5)
C13	0.4076 (3)	0.39697 (18)	0.32365 (14)	0.0212 (5)
C1	1.0999 (3)	0.42056 (19)	0.66911 (14)	0.0237 (6)
C18	0.3244 (3)	0.39694 (19)	0.24921 (14)	0.0241 (6)
H18A	0.254301	0.341567	0.240942	0.029*
H18B	0.406960	0.394019	0.217178	0.029*
C2	0.9813 (3)	0.44475 (19)	0.61475 (14)	0.0218 (5)
C7	1.1064 (3)	0.5767 (2)	0.65991 (14)	0.0240 (6)
C19	0.9847 (3)	0.54413 (19)	0.60853 (14)	0.0218 (5)
C16	0.3223 (3)	0.5715 (2)	0.24732 (14)	0.0257 (6)
H16A	0.397447	0.576421	0.212195	0.031*
H16B	0.249328	0.625905	0.241843	0.031*
C10	0.9346 (3)	0.71158 (19)	0.57331 (15)	0.0247 (6)
H10A	0.835044	0.748919	0.560559	0.030*
H10B	1.011699	0.728179	0.540800	0.030*
C6	1.1407 (3)	0.3264 (2)	0.69631 (15)	0.0285 (6)
H6A	1.086419	0.314146	0.737696	0.034*
H6B	1.259510	0.320673	0.710427	0.034*
C11	1.0106 (3)	0.7362 (2)	0.64784 (15)	0.0276 (6)
H11A	0.927180	0.730391	0.679312	0.033*
H11B	1.047295	0.801360	0.649084	0.033*
C17	0.2214 (3)	0.48385 (19)	0.23378 (15)	0.0255 (6)
H17A	0.169779	0.482856	0.184318	0.031*
H17B	0.133865	0.484182	0.263475	0.031*
C4	0.9069 (3)	0.27526 (19)	0.60450 (16)	0.0265 (6)
H4A	0.878096	0.231766	0.565122	0.032*
H4B	0.833389	0.262983	0.639404	0.032*
C12	1.1548 (3)	0.6739 (2)	0.67445 (16)	0.0281 (6)
H12A	1.248776	0.689608	0.650597	0.034*
H12B	1.186826	0.682925	0.725334	0.034*
C5	1.0826 (3)	0.2569 (2)	0.63807 (16)	0.0287 (6)
H5A	1.154768	0.260424	0.601667	0.034*
H5B	1.090498	0.193550	0.657704	0.034*
Cl1	1.26422 (10)	0.47444 (6)	0.89347 (4)	0.0409 (2)
O7	0.4417 (3)	0.12075 (16)	0.43339 (13)	0.0396 (5)
H7A	0.518 (4)	0.091 (3)	0.418 (2)	0.059*

H7B	0.365 (4)	0.081 (2)	0.426 (2)	0.059*	
H4	0.416 (4)	0.208 (2)	0.3641 (15)	0.038 (10)*	
H3A	0.762 (5)	0.527 (3)	0.511 (2)	0.046 (11)*	
O8	0.1642 (4)	0.0144 (3)	0.43836 (16)	0.0584 (11)	0.935 (7)
H8A	0.159 (7)	−0.003 (4)	0.4789 (13)	0.088*	0.935 (7)
H8B	0.084 (5)	−0.008 (4)	0.412 (2)	0.088*	0.935 (7)
O8B	0.266 (4)	−0.052 (2)	0.4463 (15)	0.027 (9)*	0.065 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O6	0.0263 (10)	0.0183 (9)	0.0340 (10)	0.0006 (7)	0.0001 (8)	0.0033 (8)
O4	0.0274 (10)	0.0197 (10)	0.0353 (11)	−0.0030 (8)	0.0016 (8)	−0.0013 (8)
O5	0.0316 (11)	0.0238 (10)	0.0284 (10)	−0.0028 (8)	−0.0064 (8)	0.0011 (8)
O3	0.0257 (10)	0.0195 (9)	0.0326 (10)	0.0004 (8)	−0.0058 (8)	0.0029 (8)
O2	0.0242 (10)	0.0198 (9)	0.0353 (11)	−0.0040 (7)	−0.0018 (8)	−0.0011 (8)
O1	0.0161 (10)	0.0503 (13)	0.0263 (10)	−0.0007 (8)	−0.0029 (8)	0.0012 (9)
N2	0.0201 (11)	0.0184 (11)	0.0276 (11)	−0.0028 (8)	0.0032 (9)	−0.0024 (9)
N3	0.0192 (11)	0.0174 (11)	0.0267 (11)	0.0011 (8)	0.0023 (9)	0.0008 (9)
N1	0.0146 (11)	0.0328 (13)	0.0272 (12)	0.0011 (9)	−0.0008 (9)	−0.0003 (9)
N4	0.0172 (11)	0.0208 (11)	0.0320 (12)	−0.0026 (8)	0.0033 (9)	−0.0042 (9)
N5	0.0187 (11)	0.0204 (11)	0.0293 (12)	0.0010 (8)	0.0035 (9)	0.0026 (9)
O9	0.0602 (16)	0.0344 (13)	0.0390 (13)	−0.0091 (11)	0.0040 (11)	−0.0026 (10)
C14	0.0167 (12)	0.0214 (13)	0.0277 (14)	0.0009 (10)	0.0028 (10)	−0.0010 (10)
C15	0.0157 (12)	0.0221 (13)	0.0262 (13)	0.0007 (10)	0.0022 (10)	0.0005 (10)
C9	0.0171 (12)	0.0201 (13)	0.0254 (13)	−0.0011 (10)	0.0057 (10)	−0.0028 (10)
C3	0.0189 (12)	0.0198 (13)	0.0288 (13)	0.0025 (10)	0.0071 (10)	0.0026 (10)
C13	0.0143 (12)	0.0220 (13)	0.0270 (13)	−0.0012 (9)	0.0023 (10)	0.0003 (10)
C1	0.0166 (13)	0.0271 (14)	0.0281 (13)	0.0025 (10)	0.0054 (10)	0.0016 (11)
C18	0.0227 (13)	0.0233 (13)	0.0259 (13)	−0.0022 (10)	0.0025 (10)	−0.0029 (10)
C2	0.0164 (12)	0.0246 (13)	0.0248 (13)	0.0015 (10)	0.0041 (10)	0.0011 (10)
C7	0.0162 (12)	0.0298 (15)	0.0261 (13)	−0.0001 (10)	0.0035 (10)	−0.0027 (11)
C19	0.0163 (12)	0.0236 (13)	0.0259 (13)	−0.0007 (10)	0.0046 (10)	−0.0019 (10)
C16	0.0228 (13)	0.0259 (14)	0.0269 (14)	0.0011 (11)	−0.0009 (10)	0.0016 (11)
C10	0.0226 (13)	0.0194 (13)	0.0322 (14)	−0.0017 (10)	0.0037 (11)	−0.0022 (11)
C6	0.0184 (13)	0.0327 (15)	0.0341 (15)	0.0035 (11)	0.0034 (11)	0.0101 (12)
C11	0.0234 (14)	0.0248 (14)	0.0347 (15)	−0.0040 (11)	0.0051 (11)	−0.0065 (11)
C17	0.0176 (13)	0.0306 (15)	0.0271 (14)	−0.0003 (11)	−0.0007 (10)	−0.0001 (11)
C4	0.0218 (14)	0.0210 (14)	0.0369 (15)	0.0018 (10)	0.0048 (11)	0.0066 (11)
C12	0.0207 (13)	0.0297 (15)	0.0331 (15)	−0.0046 (11)	0.0013 (11)	−0.0054 (12)
C5	0.0229 (14)	0.0234 (14)	0.0408 (16)	0.0052 (11)	0.0083 (12)	0.0105 (12)
Cl1	0.0413 (5)	0.0462 (5)	0.0350 (4)	0.0041 (3)	0.0050 (3)	−0.0013 (3)
O7	0.0437 (14)	0.0330 (12)	0.0421 (13)	−0.0013 (10)	0.0061 (10)	0.0020 (10)
O8	0.0414 (17)	0.095 (3)	0.0398 (16)	−0.0085 (16)	0.0071 (12)	0.0218 (16)

Geometric parameters (Å, º)

O6—H6	0.8400	C18—H18B	0.9900
O6—N5	1.372 (3)	C18—C17	1.526 (4)
O4—N4	1.371 (3)	C2—C19	1.443 (4)
O4—H4	0.821 (18)	C7—C19	1.394 (4)
O5—C14	1.228 (3)	C7—C12	1.478 (4)
O3—H3	0.8400	C16—H16A	0.9900
O3—N3	1.370 (3)	C16—H16B	0.9900
O2—H2	0.8400	C16—C17	1.522 (4)
O2—N2	1.398 (3)	C10—H10A	0.9900
O1—H1	0.8400	C10—H10B	0.9900
O1—N1	1.383 (3)	C10—C11	1.529 (4)
N2—C3	1.284 (4)	C6—H6A	0.9900
N3—C9	1.291 (3)	C6—H6B	0.9900
N3—H3A	0.85 (4)	C6—C5	1.535 (4)
N1—C1	1.377 (4)	C11—H11A	0.9900
N1—C7	1.349 (4)	C11—H11B	0.9900
N4—C13	1.288 (4)	C11—C12	1.529 (4)
N5—C15	1.284 (4)	C17—H17A	0.9900
O9—H9A	0.837 (18)	C17—H17B	0.9900
O9—H9B	0.822 (19)	C4—H4A	0.9900
C14—C15	1.487 (4)	C4—H4B	0.9900
C14—C13	1.482 (4)	C4—C5	1.535 (4)
C15—C16	1.507 (4)	C12—H12A	0.9900
C9—C19	1.439 (4)	C12—H12B	0.9900
C9—C10	1.503 (4)	C5—H5A	0.9900
C3—C2	1.455 (4)	C5—H5B	0.9900
C3—C4	1.511 (4)	O7—H7A	0.855 (19)
C13—C18	1.504 (4)	O7—H7B	0.851 (19)
C1—C2	1.378 (4)	O8—H8A	0.831 (19)
C1—C6	1.482 (4)	O8—H8B	0.839 (19)
C18—H18A	0.9900		

N5—O6—H6	109.5	C15—C16—H16B	109.2
N4—O4—H4	101 (3)	C15—C16—C17	111.9 (2)
N3—O3—H3	109.5	H16A—C16—H16B	107.9
N2—O2—H2	109.5	C17—C16—H16A	109.2
N1—O1—H1	109.5	C17—C16—H16B	109.2
C3—N2—O2	113.2 (2)	C9—C10—H10A	108.9
O3—N3—H3A	125 (3)	C9—C10—H10B	108.9
C9—N3—O3	117.8 (2)	C9—C10—C11	113.2 (2)
C9—N3—H3A	117 (3)	H10A—C10—H10B	107.8
C1—N1—O1	124.2 (2)	C11—C10—H10A	108.9
C7—N1—O1	122.8 (2)	C11—C10—H10B	108.9
C7—N1—C1	112.4 (2)	C1—C6—H6A	110.1
C13—N4—O4	113.3 (2)	C1—C6—H6B	110.1
C15—N5—O6	114.0 (2)	C1—C6—C5	108.1 (2)

H9A—O9—H9B	113 (3)	H6A—C6—H6B	108.4
O5—C14—C15	121.0 (2)	C5—C6—H6A	110.1
O5—C14—C13	121.3 (2)	C5—C6—H6B	110.1
C13—C14—C15	117.6 (2)	C10—C11—H11A	109.2
N5—C15—C14	112.1 (2)	C10—C11—H11B	109.2
N5—C15—C16	126.5 (2)	C10—C11—C12	112.1 (2)
C14—C15—C16	121.3 (2)	H11A—C11—H11B	107.9
N3—C9—C19	120.4 (2)	C12—C11—H11A	109.2
N3—C9—C10	120.7 (2)	C12—C11—H11B	109.2
C19—C9—C10	118.9 (2)	C18—C17—H17A	109.2
N2—C3—C2	117.9 (2)	C18—C17—H17B	109.2
N2—C3—C4	125.1 (2)	C16—C17—C18	111.8 (2)
C2—C3—C4	117.0 (2)	C16—C17—H17A	109.2
N4—C13—C14	112.6 (2)	C16—C17—H17B	109.2
N4—C13—C18	127.1 (2)	H17A—C17—H17B	107.9
C14—C13—C18	120.2 (2)	C3—C4—H4A	109.0
N1—C1—C2	106.5 (2)	C3—C4—H4B	109.0
N1—C1—C6	126.1 (2)	C3—C4—C5	113.0 (2)
C2—C1—C6	127.3 (3)	H4A—C4—H4B	107.8
C13—C18—H18A	109.5	C5—C4—H4A	109.0
C13—C18—H18B	109.5	C5—C4—H4B	109.0
C13—C18—C17	110.8 (2)	C7—C12—C11	108.5 (2)
H18A—C18—H18B	108.1	C7—C12—H12A	110.0
C17—C18—H18A	109.5	C7—C12—H12B	110.0
C17—C18—H18B	109.5	C11—C12—H12A	110.0
C1—C2—C3	119.5 (2)	C11—C12—H12B	110.0
C1—C2—C19	107.2 (2)	H12A—C12—H12B	108.4
C19—C2—C3	133.3 (2)	C6—C5—H5A	109.2
N1—C7—C19	106.5 (2)	C6—C5—H5B	109.2
N1—C7—C12	126.2 (2)	C4—C5—C6	112.1 (2)
C19—C7—C12	127.3 (3)	C4—C5—H5A	109.2
C9—C19—C2	134.7 (2)	C4—C5—H5B	109.2
C7—C19—C9	118.0 (2)	H5A—C5—H5B	107.9
C7—C19—C2	107.3 (2)	H7A—O7—H7B	101 (3)
C15—C16—H16A	109.2	H8A—O8—H8B	108 (4)

O6—N5—C15—C14	177.5 (2)	C14—C13—C18—C17	−33.8 (3)
O6—N5—C15—C16	−0.9 (4)	C15—C14—C13—N4	−175.3 (2)
O4—N4—C13—C14	−177.6 (2)	C15—C14—C13—C18	5.3 (4)
O4—N4—C13—C18	1.8 (4)	C15—C16—C17—C18	−52.6 (3)
O5—C14—C15—N5	1.4 (4)	C9—C10—C11—C12	52.4 (3)
O5—C14—C15—C16	179.9 (3)	C3—C2—C19—C9	−0.2 (5)
O5—C14—C13—N4	5.1 (4)	C3—C2—C19—C7	178.2 (3)
O5—C14—C13—C18	−174.4 (3)	C3—C4—C5—C6	54.5 (3)
O3—N3—C9—C19	178.1 (2)	C13—C14—C15—N5	−178.3 (2)
O3—N3—C9—C10	−3.0 (4)	C13—C14—C15—C16	0.2 (4)
O2—N2—C3—C2	−179.3 (2)	C13—C18—C17—C16	57.8 (3)
O2—N2—C3—C4	−1.3 (4)	C1—N1—C7—C19	0.7 (3)

O1—N1—C1—C2	−172.3 (2)	C1—N1—C7—C12	179.9 (3)
O1—N1—C1—C6	9.4 (4)	C1—C2—C19—C9	−178.4 (3)
O1—N1—C7—C19	172.4 (2)	C1—C2—C19—C7	0.0 (3)
O1—N1—C7—C12	−8.5 (4)	C1—C6—C5—C4	−48.7 (3)
N2—C3—C2—C1	−178.8 (2)	C2—C3—C4—C5	−30.2 (3)
N2—C3—C2—C19	3.1 (4)	C2—C1—C6—C5	23.1 (4)
N2—C3—C4—C5	151.8 (3)	C7—N1—C1—C2	−0.8 (3)
N3—C9—C19—C2	−0.4 (4)	C7—N1—C1—C6	−179.1 (3)
N3—C9—C19—C7	−178.6 (2)	C19—C9—C10—C11	−28.4 (3)
N3—C9—C10—C11	152.8 (2)	C19—C7—C12—C11	24.3 (4)
N1—C1—C2—C3	−178.1 (2)	C10—C9—C19—C2	−179.2 (3)
N1—C1—C2—C19	0.5 (3)	C10—C9—C19—C7	2.5 (4)
N1—C1—C6—C5	−159.0 (3)	C10—C11—C12—C7	−48.3 (3)
N1—C7—C19—C9	178.3 (2)	C6—C1—C2—C3	0.2 (4)
N1—C7—C19—C2	−0.4 (3)	C6—C1—C2—C19	178.7 (3)
N1—C7—C12—C11	−154.7 (3)	C4—C3—C2—C1	3.0 (4)
N4—C13—C18—C17	146.8 (3)	C4—C3—C2—C19	−175.0 (3)
N5—C15—C16—C17	−158.2 (3)	C12—C7—C19—C9	−0.8 (4)
C14—C15—C16—C17	23.5 (4)	C12—C7—C19—C2	−179.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O9	0.84	1.78	2.614 (3)	172
O3—H3···O5	0.84	2.18	2.855 (3)	137
O3—H3···N5	0.84	2.02	2.763 (3)	146
O2—H2···O5	0.84	2.29	2.942 (3)	135
O2—H2···N4	0.84	2.25	3.005 (3)	150
O1—H1···Cl1	0.84	2.16	2.983 (2)	168
O9—H9*A*···O7^{i}	0.84 (2)	2.17 (2)	2.981 (3)	162 (4)
O9—H9*B*···Cl1^{ii}	0.82 (2)	2.40 (2)	3.205 (3)	166 (4)
C18—H18*A*···O6^{iii}	0.99	2.51	3.466 (3)	161
C16—H16*B*···O4^{iv}	0.99	2.43	3.324 (3)	150
C6—H6*B*···N5^{v}	0.99	2.73	3.490 (4)	134
C11—H11*A*···O6^{vi}	0.99	2.75	3.468 (3)	130
C11—H11*A*···O4^{i}	0.99	2.70	3.483 (3)	136
C4—H4*B*···O6^{i}	0.99	2.56	3.466 (3)	152
C5—H5*A*···O3^{v}	0.99	2.50	3.407 (3)	152
O7—H7*A*···Cl1^{vii}	0.86 (2)	2.37 (2)	3.208 (3)	168 (4)
O7—H7*B*···O8	0.85 (2)	1.97 (2)	2.787 (4)	159 (4)
O7—H7*B*···O8*B*	0.85 (2)	2.16 (4)	2.92 (3)	150 (4)
O4—H4···O7	0.82 (2)	1.83 (2)	2.646 (3)	174 (4)
N3—H3*A*···N2	0.85 (4)	1.89 (4)	2.706 (3)	162 (4)
O8—H8*A*···Cl1^{viii}	0.83 (2)	2.48 (2)	3.271 (3)	160 (5)
O8—H8*B*···Cl1^{ix}	0.84 (2)	2.68 (5)	3.320 (3)	135 (5)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1/2, −*y*+3/2, *z*−1/2; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*+1/2, *y*+1/2, −*z*+1/2; (v) −*x*+2, −*y*+1, −*z*+1; (vi) *x*+1/2, −*y*+3/2, *z*+1/2; (vii) *x*−1/2, −*y*+1/2, *z*−1/2; (viii) −*x*+3/2, *y*−1/2, −*z*+3/2; (ix) *x*−3/2, −*y*+1/2, *z*−1/2.