Crystal structure of an indium–salicylhydroximate complex cation: \([\text{In}_4(\text{H}_{2\text{shi}})_8(\text{H}_2\text{O})_6] (\text{NO}_3)_4\cdot 8.57\text{H}_2\text{O}\)

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The synthesis and crystal structure for the title compound, hexaaquahexakis-\((\mu_2,\text{hydroxybenzenecarboxydamato})\text{bis}(\text{2-hydroxybenzenecarboxydamato})\text{tetraindium(III)}\) tetrinitrate 8.57-hydrate + unknown solvent, \([\text{In}_4(\text{H}_{2\text{shi}})_8(\text{H}_2\text{O})_6](\text{NO}_3)_4\cdot 8.57\text{H}_2\text{O}\)-solvent, where \(\text{H}_{2\text{shi}}\) is salicylhydroximate (\(\text{C}_7\text{H}_5\text{NO}_3\)), are reported. The complex cation of the structure, \([\text{In}_4(\text{H}_{2\text{shi}})_8(\text{H}_2\text{O})_6]^{4+}\), is a dimer with a step-like topology and possesses an inversion center that relates each \([\text{In}_2(\text{H}_{2\text{shi}})_4(\text{H}_2\text{O})_3]^{2+}\) side of the complex cation. Each \(\text{In}^{III}\) ion is seven-coordinate with a pentagonal–bipyramidal geometry, and the salicylhydroximate ligands have a \(1^{-}\) charge as only the oxime oxygen of the ligand is deprotonated. Four interstitial nitrate anions maintain the charge balance of the compound. One of the nitrate anions (and its symmetry equivalent) is disordered over two different orientations with an occupancy ratio of 0.557 (7) to 0.443 (7). The interstitial solvent water molecules show substantial disorder. Approximately 8.57 water molecules per formula unit were refined as disordered and partially occupied, while a suitable model could not be devised for the other extensively disordered solvent molecules (water and possibly methanol as this was the synthesis solvent). Thus, these latter solvent molecules were instead treated with the SQUEEZE routine [Spek (2015). Acta Cryst. C71, 9–18.] as implemented in the program PLATON, and the procedure corrected for 151 electrons within solvent-accessible voids of 367 Å³.

1. Chemical context

Salicylhydroxamic acid (\(\text{H}_{3\text{shi}}\)) has proven to be a versatile ligand for the class of inorganic macrocyclic coordination compounds known as metallacrowns (MC) (Mezei et al., 2007). Metallacrowns are the inorganic analogue of organic crown ethers (Pedersen, 1967). As crown ethers have a carbon–carbon–oxygen ring repeat unit, metallacrowns have a metal–nitrogen–oxygen repeat unit about the ring of the metallamacrocycle. In addition, as crown ethers, metallacrowns are capable of capturing a metal ion in the central cavity of the structure. Salicylhydroxamic acid in its triply deprotonated state (\(\text{shi}^{3-}\)) was used in the synthesis of the first metallacrown, a vanadium-based 9-MC-3 (Pecoraro, 1989), and since then it has been used to construct numerous MCs including other 9-MC-3 (Lah et al., 1989), 12-MC-4 (Lah & Pecoraro, 1989), and 15-MC-5 (Kessisoglou et al., 1994) compounds. Initially salicylhydroxamic acid was mainly used in conjunction with transition-metal ions in both the ring and central metal positions of the metallacrown structure. However, in 2014 our group demonstrated that 12-MC-4 compounds with a salicylhydroximate (\(\text{shi}^{3-}\)) framework...
could incorporate lanthanide ions in the central cavity while using Mn$^{III}$ ions in the ring positions of the MC (Azar et al., 2014). These molecules proved to be molecular magnets with magnetic behavior consistent with single-molecule magnetism (Boron et al., 2016). Since then the manganese(III) ions have been replaced with the main-group metals gallium(III) and aluminum(III), and both the lanthanide-gallium (Chow et al., 2016) and lanthanide-aluminum (Eliseeva et al., 2022) 12-MC-4 structures with the shi$^{3-}$ ligand are highly luminescent materials in the visible and near-infrared regions. To further explore the chemistry of H$_2$shi with other main-group metals, we decided to react the ligand with indium(III), a fellow Group 13 metal.

Indium is an appealing target for metallacrown and metalacrown-like compounds, as indium coordination complexes have applications in both the medicinal and material chemistry fields. The radioisotope indium-111 emits gamma radiation and has a half-life of 2.8 days. Numerous coordination complexes of the radiometal have been evaluated as potential imaging agents and radiolabels (Pecoraro et al., 1982; Liu et al., 2003; Nishikawa et al., 2003; Ramogida et al., 2015; Choudhary et al., 2019). In addition, indium coordination complexes have been investigated as precursors for indium oxide thin films (Xu et al., 2000; Chou et al., 2003; Lee et al., 2018; Yoo et al., 2021) and as luminophores (Lee et al., 2017). Herein we report the synthesis and single-crystal X-ray crystal structure of [In$_4$(H$_2$shi)$_8$(H$_2$O)$_6$](NO$_3$)$_4$·8.57H$_2$O-solvent, 1, where H$_2$shi$^-$ is the singly deprotonated version of salicylhydroxamic acid. Future work will focus on the potential use of the compound for radiopharmacological or thin film applications.

2. Structural commentary

Compound 1, [In$_4$(H$_2$shi)$_8$(H$_2$O)$_6$](NO$_3$)$_4$·8.57H$_2$O-solvent, consists of four indium ions with a 3+ charge (total 12+ charge) that is counterbalanced by eight singly deprotonated salicylhydroximate anions (H$_2$shi$^-$) and four interstitial nitrate ions (total 12− charge). Only the oxime oxygen atoms (O1, O4, O7, and O10) of the H$_2$shi$^-$ ligands are deprotonated. The complex cation structure of 1, [In$_4$(H$_2$shi)$_8$(H$_2$O)$_6$]$^{4+}$, is a dimer with a step-like topology (Fig. 1). The dimer features four In$^{III}$ ions in a chain [In1, In2, In2’, In1’; [symmetry code: (i) −x + 1, −y + 1, −z + 1]] and each half of the dimer is related by an inversion center located between the two central indium ions (In2) (Fig. 1). Each side of the dimer contains two indium(III) ions, four H$_2$shi$^-$ anions, and three water molecules: [In$_2$(H$_2$shi)$_4$(H$_2$O)$_3$]$^{5+}$ (Fig. 2). Each half of the complex cation is connected via the middle In2 centers where two oxime oxygens of symmetry-related H$_2$shi$^-$ ligands bind to both In2 ions. Both In$^{III}$ ions are seven-coordinate with two oxime oxygens of symmetry-related H$_2$shi$^-$ ligands. Two of the ligands bind in a bidentate fashion using both the oxime and carbonyl oxygen atoms of the ligand to form two five-membered chelate rings about the In$^{III}$ center. The third H$_2$shi$^-$ binds in a monodentate fashion via the oxime oxygen atom. The axial positions of the coordination geometry are occupied by two water molecules. In1 is connected to In2 via two bridging oxime oxygen atoms. For In2, the metal center binds to four...
H$_2$shi$^-$ anions, three from one half of the dimer and one from the symmetry-related portion of the cation. Two of the H$_2$shi$^-$ ligands bind in a bidentate fashion with oxime and carbonyl oxygen atoms and form two five-membered chelate rings, while the other two bind in a monodentate fashion via the oxime oxygen atoms. Three of the H$_2$shi$^-$ anions (two bidentate and one monodentate) provide the five oxygen atoms of the pentagonal plane. The axial direction consists of one water molecule and one oxime oxygen atom. This axial oxime oxygen atom then binds to the symmetry equivalent In$^ {2+}$ ion of the other portion of the cation and thus generates the step-like topology where each half of the dimer consists of two In$^{III}$ ions (Fig. 1b).

The interstitial area contains an ordered nitrate anion and a nitrate anion that is disordered over two positions with an occupancy ratio of 0.557 (7) to 0.443 (7). In addition, several solvent water molecules (ca. 8.57 per formula unit) were found to be disordered, and when possible the disorder and hydrogen bonding were refined. All of the interstitial water molecules are only partially occupied (associated with O22–O27) and due to the large amount of disorder, no attempts were made to match occupancies. In addition, some solvent molecules (water and/or methanol) were found to have excessive disorder and a suitable model could not be devised. These solvent molecules were instead augmented with the SQUEEZE routine (Spek, 2015) as implemented in the program PLATON (Spek, 2022). Complete details regarding the SQUEEZE results can be found in the Refinement section.

3. Supramolecular features

For the [In$_{11}$H$_2$shi$_4$(H$_2$O)$_{16}$]$^{2+}$ cation of I, several intramolecular hydrogen bonds exist between the protonated oxime nitrogen atoms (N1, N2, N3, and N4) of the H$_2$shi$^-$ ligands and the protonated phenol oxygen atoms (O3, O6, O9, and O12, respectively) of the same ligand with the hydrogen atom of the nitrogen atom bonding to the oxygen atom (Fig. 2; Table 2). In addition, the hydrogen atom of the oxime nitrogen

Table 1

| Shape                      | In1 | In2 |
|----------------------------|-----|-----|
| Heptagon (D$_{7h}$)        | 33.951 | 33.043 |
| Hexagonal pyramid (C$_{6v}$) | 25.413 | 23.853 |
| Pentagonal bipyramid (D$_{5h}$) | 0.290 | 1.046 |
| Capped octahedron (C$_{4v}$) | 7.067 | 5.351 |
| Capped trigonal prism (C$_{3v}$) | 5.268 | 4.128 |
| Johnson pentagonal bipyramid (J13; D$_{5h}$) | 2.708 | 4.986 |
| Johnson elongated triangular pyramid (J7, C$_{3v}$) | 22.464 | 21.243 |

Table 2

| Shape          | D–H $\cdots$ A (Å) | D–H $\cdots$ A (Å) |
|----------------|--------------------|--------------------|
| O3–H3O $\cdots$ O22$^a$ | 0.84 (1.83) | 2.664 (4) |
| O3–H3O $\cdots$ O22$^b$ | 0.84 (1.97) | 2.668 (14) |
| O6–H6O $\cdots$ O18$^a$ | 0.84 (1.98) | 2.775 (10) |
| O6–H6O $\cdots$ O17B$^a$ | 0.84 (2.06) | 2.810 (5) |
| O9–H9O $\cdots$ O20$^a$ | 0.84 (1.88) | 2.717 (3) |
| O12–H12O $\cdots$ O17 | 0.84 (1.99) | 2.778 (5) |
| O12–H12O $\cdots$ O16B | 0.84 (1.81) | 2.609 (6) |
| O13–H13B $\cdots$ O24 | 0.82 (2.09) | 2.761 (6) |
| O13–H13B $\cdots$ O25 | 0.82 (2.01) | 2.64 (3) |
| O13–H13B $\cdots$ O24B | 0.82 (2.10) | 2.485 (7) |
| O13–H13A $\cdots$ O11$^a$ | 0.84 (2.17) | 2.601 (2) |
| O14–H14A $\cdots$ O26 | 0.84 (2.18) | 2.631 (5) |
| O14–H14A $\cdots$ O26B | 0.86 (2.18) | 2.629 (8) |
| O14–H14B $\cdots$ O19$^a$ | 0.84 (2.19) | 2.782 (3) |
| O15–H15A $\cdots$ O25 | 0.84 (2.11) | 2.93 (3) |
| O15–H15A $\cdots$ O24B | 0.84 (2.10) | 2.891 (9) |
| O15–H15B $\cdots$ O20 | 0.83 (2.23) | 2.970 (4) |
| O15–H15B $\cdots$ O21 | 0.83 (2.16) | 2.924 (4) |
| O23–H23B $\cdots$ O5 | 0.89 | 2.16 | 3.006 (6) |
| O23–H23B $\cdots$ O18 | 0.82 (2.11) | 2.842 (14) |
| O24–H24A $\cdots$ O25 | 0.86 (2.03) | 2.832 (5) |
| O24–H24B $\cdots$ O21 | 0.85 (2.21) | 3.01 (5) |
| O22B–H22C $\cdots$ O21$^a$ | 0.84 | 2.00 | 2.808 (15) |
| O22B–H22C $\cdots$ O22B | 0.85 (2.02) | 2.824 (14) |
| O26–H26A $\cdots$ O27 | 0.83 (2.56) | 2.259 (16) |
| O27–H27B $\cdots$ O23 | 0.86 | 2.14 | 2.987 (19) |
| O26B–H26C $\cdots$ O27B | 0.84 | 1.73 | 2.31 (2) |
| O26B–H26D $\cdots$ O25 | 0.84 | 2.38 | 3.013 (13) |
| O27B–H27D $\cdots$ O11$^{ii}$ | 0.85 | 2.13 | 2.955 (18) |
| N1–H1N $\cdots$ O3 | 0.88 | 1.92 | 2.605 (3) |
| N2–H2N $\cdots$ O6 | 0.88 | 2.02 | 2.669 (2) |
| N2–H2N $\cdots$ O8 | 0.88 | 2.48 | 2.935 (3) |
| N3–H3N $\cdots$ O9 | 0.88 | 1.94 | 2.605 (3) |
| N3–H3N $\cdots$ O14$^{ii}$ | 0.88 | 2.24 | 2.939 (3) |
| N4–H4N $\cdots$ O2 | 0.88 | 2.33 | 2.804 (3) |
| N4–H4N $\cdots$ O12 | 0.88 | 1.97 | 2.621 (3) |

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y-1, z$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+1, z+1$; (v) $-x+1, -y, z$; (vi) $-x+2, -y+1, -z$; (vii) $-x+1, -y, z+1$. (2022). E

Figure 2

Top view of a [In$_{11}$H$_2$shi$_4$(H$_2$O)$_{16}$]$^{2+}$ unit of I with displacement ellipsoids at the 50% probability level [symmetry code: (i) $-x+1, -y+1, -z+1$]. In addition, the intramolecular hydrogen bonding in I between the hydrogen atoms (white) of the oxime nitrogen atoms and the phenol oxygen atoms and between the hydrogen atoms of the oxime nitrogen atoms and the carbonyl oxygen atoms are displayed. See Fig. 1 for additional display details.
atom (N2 and N4) also forms a hydrogen bond to the carbonyl oxygen atom (O8 and O2, respectively) of a neighboring H$_2$shi$^-$ ligand (Fig. 2), and the hydrogen atom of the oxime nitrogen atom (N3) bonds to the oxygen atom (O14) of the water molecule coordinated to In1.

There is one intermolecular hydrogen bond between neighboring complex cations of I (Table 2). The hydrogen atom of the water molecule (associated with O13) coordinated to In1 forms a hydrogen bond to an oxime oxygen atom (O1) of a neighboring complex cation. In addition, the reciprocal hydrogen bond is also formed between the two cations. Due to the inversion center of the complex cation, these hydrogen bonds occur on both sides of the [In$_4$(H$_2$shi)$_8$(H$_2$O)$_6$]$^{4+}$ ion; thus, a one-dimensional chain of the dimers is generated (Fig. 3).

Furthermore, several intermolecular hydrogen bonds exist between the partially occupied interstitial water molecules (O22–O27) themselves and between the interstitial water molecules and the protonated phenol oxygen atoms (O3 and O6) and the carbonyl oxygen atoms (O5 and O11) atoms of the H$_2$shi$^-$ ligands, the water molecules (O13–O15) coordinated to the In$_{III}$ ions, and the oxygen atoms (O18 and O21) of the interstitial nitrate anions (Table 2). Lastly, the protonated phenol oxygen atoms (O6, O9, and O12) of the H$_2$shi$^-$ ligands form hydrogen bonds to the oxygen atoms (O16, O17, O18, and O20) of interstitial nitrate ions, and the coordinated water molecules (O14 and O15) form hydrogen bonds with the oxygen atoms (O19, O20, and O21) of interstitial nitrate ions.

4. Database survey

A survey of the Cambridge Structural Database (CSD version 5.43, update March 2022; Groom et al., 2016) lists only two other structures with indium bound to hydroxamic acid ligands, though neither are salicylhydroxamic acid. One structure (JAGWUJ; Matsuba et al., 1988) contains an indium(III) ion bound to three benzohydroximate ligands in an octahedral propeller coordination geometry with Δ configuration. The other structure (VOLNIU; Seitz et al., 2008) is an indium(III) ion in a trigonal prismatic coordination geometry bound to a tripodal ligand based on 1-oxo-2-hydroxy-isoquinoline-3-carboxylic acid, an aromatic hydroxamic acid. In addition, there are five other di-metallic structures [DEYSIM (Lee et al., 2018); UWOFIY, UWOFEO, UWOGAR, UWOGEV (Yoo et al., 2021)] of indium bound to N-alkoxy carboxamide ligands. This class of ligands is closely related to hydroxamic acids as they also have a O–C–N–O connectivity, but the oxygen atom attached to the nitrogen atom is bound to an alkyl group instead of being an acidic hydrogen atom.

5. Synthesis and crystallization

**Synthetic Materials**

Salicylhydroxamic acid (H$_3$shi, >98%) was purchased from TCI America. Indium(III) nitrate hydrate (99.999%-In; Puratrem) was purchased from Strem Chemicals. Methanol (ACS grade) was purchased from VWR Chemicals BDH. All reagents were used as received and without further purification.

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Figure 3

Intermolecular hydrogen bonding in I between the hydrogen atom (white) of the water molecule associated with O13 (coordinated to In1) and the oxime oxygen atom (O1) of a neighboring complex cation of I [symmetry code: (iv) $-x+1, -y+1, -z$]. The hydrogen bonding results in a one-dimensional chain. For clarity only the oxygen atoms involved in the hydrogen bonding have been labeled. See Fig. 1 for additional display details.
Sixth Refinement
A nitrate ion (associated with N5) was refined as disordered. The two disordered moieties were restrained to have similar geometries as the ordered nitrate ion (SAME command of SHELXL, first and second esds were 0.02 and 0.04 Å). $U_{ij}$ components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar (SIMU command of SHELXL, first and second esds were 0.01 and 0.02 Å$^2$). Subject to these conditions the occupancy ratio refined to 0.443 (7) to 0.557 (7).

Solvate molecules were found to be disordered. For the better defined solvate molecules, distances to potential hydrogen-bond acceptors indicated these molecules to be water (methanol was used as the crystallization solvent and waters of hydration were present in the starting materials used) and these were refined as disordered water molecules. For molecules not directly hydrogen bonded to the main molecule, disorder was found to be excessive (greater than three- to fourfold disorder of water and/or methanol) and no suitable model could be devised. The structure factors associated with the disordered solvate molecules were instead augmented via reverse Fourier transform methods using the SQUEEZE routine (Sluis & Spek, 1990; Spek, 2015) as implemented in the program PLATON (Spek, 2020). The resultant FAB file containing the structure-factor contribution from the electron content of the void space was used together with the original hkl file in the further refinement. (The FAB file with details of the SQUEEZE results is appended to the CIF file). The SQUEEZE procedure corrected for 151 electrons within solvent-accessible voids of 367 Å$^3$.

Resolved disordered water molecules were assigned occupancy values. For ‘outlying’ water molecules occupancies did not refine to full occupancy for each site (due to excessive disorder, or part of the site overlapping with squeezed areas) and no attempts were made to match the occupancies of these water molecules with other moieties in the structure to add up to unity for each site. $U_{ij}$ components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar [SIMU command of SHELXL, first and second esds were 0.01 and 0.02 ($O_{22}$, $O_{22B}$ $O_{24B}$, $O_{25}$) or 0.001 ($O_{26}$, $O_{27}$, $O_{26B}$, $O_{27B}$) Å$^2$]. Water hydrogen-atom positions were initially refined and $O$–H and $H$–$H$ distances were restrained to 0.84 (2) and 1.36 (2) Å, respectively, while a damping factor was applied. Some water hydrogen-atom positions were further restrained based on hydrogen-bonding considerations. In the final refinement cycles, hydrogen atoms with low occupancies were constrained to ride on their carrier atoms and the damping factor was removed. Subject to these conditions, the occupancy rates refined to the values given in the tables of the CIF. Additional crystal data, data collection, and structure refinement details are summarized in Table 3.

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Table 3
Experimental details.

| Crystal data | Chemical formula |
|--------------|------------------|
| $\text{In}_4(\text{C}_7\text{H}_6\text{NO}_3)_8(\text{H}_2\text{O})_6(\text{NO}_3)_4 \cdot 8.57\text{H}_2\text{O} \cdot +\text{solute}$ | $\text{In}_4(\text{C}_7\text{H}_6\text{NO}_3)_8(\text{H}_2\text{O})_6(\text{NO}_3)_4 \cdot 8.57\text{H}_2\text{O} \cdot +\text{solute}$ |
| $M_r$ | 2186.80 |
| Crystal system, space group | Triclinic, $P\bar{T}$ |
| Temperature (K) | 150 |
| $\alpha$, $\beta$, $\gamma$ (°) | 11.8435 (5), 14.2195 (6), 14.6918 (5) |
| $\nu$ (Å$^2$) | 81.905 (2), 70.768 (2), 76.516 (2) |
| $Z$ | 1 |
| Radiation type | Mo Ka |
| $\mu$ (mm$^{-1}$) | 1.11 |
| Crystal size (mm) | 0.17 × 0.16 × 0.06 |
| Data collection | Bruker D8 Quest |
| Diffactometer | Multi-scan (SADABS, Krause et al., 2015) |
| Absorption correction | |
| $T_{\text{min}}, T_{\text{max}}$ | 0.680, 0.747 |
| No. of measured, independent and observed $|F| > 2\sigma(F)$ reflections | 118064, 17348, 12266 |
| $R_{\text{int}}$ | 0.049 |
| $wR_{\text{int}}$ | 0.771 |
| No. of reflections | 17348 |
| No. of parameters | 694 |
| No. of restraints | 215 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta R_{\text{max}}, \Delta R_{\text{min}}$ (e Å$^{-3}$) | 1.11, −1.49 |

Computer programs: APEX4 and SAINT (Bruker, 2022), SHELXTL (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), ShelXle (Hübschle et al., 2011), Mercury (Macrae et al., 2020), and pubCIF (Westrip, 2010).
Crystal structure of an indium–salicylhydroximate complex cation:

\([\text{In}_4(\text{H}_2\text{shi})_8(\text{H}_2\text{O})_6](\text{NO}_3)_4\cdot8.57\text{H}_2\text{O}\]

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Computing details

Data collection: APEX4 (Bruker, 2022); cell refinement: SAINT (Bruker, 2022); data reduction: SAINT (Bruker, 2022); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b), ShelXle (Hübschle et al., 2011); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: publCIF (Westrip, 2010).

Hexaaquahexakis(µ₂-2-hydroxybenzenecarbohydroxamato)bis(2-hydroxybenzenecarbohydroxamato)tetraindium(III) tetranitrate 8.57-hydrate

Crystal data

\([\text{In}_4(\text{C}_7\text{H}_6\text{NO}_3)_8(\text{H}_2\text{O})_6]\) (NO₃)₄·8.57H₂O·[+solvent]

\(Z = 1\)

\(F(000) = 1099\)

\(D_x = 1.603\) Mg m\(^{-3}\)

Mo Kα radiation, \(λ = 0.71073\) Å

Cell parameters from 9643 reflections

\(θ = 2.7–33.1°\)

\(μ = 1.11\) mm\(^{-1}\)

\(T = 150\) K

Plate, colourless

0.17 × 0.16 × 0.06 mm

Data collection

Bruker D8 Quest diffractometer

Radiation source: fine focus sealed tube X-ray source

Triumph curved graphite crystal monochromator

Detector resolution: 7.4074 pixels mm\(^{-1}\)

ω and phi scans

Absorption correction: multi-scan (SADABS; Krause et al., 2015)

Refinement

Refinement on \(F^2\)

\(S = 1.02\)

Least-squares matrix: full

\(R[F^2 > 2σ(F^2)] = 0.037\)

\(wR(F^2) = 0.109\)

\(R_{int} = 0.049\)

\(θ_{max} = 33.2°, θ_{min} = 2.7°\)

\(h = −18→18\)

\(k = −21→21\)

\(l = −22→22\)

Supplementary materials

Supplementary materials have been deposited| sup-1
Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement

\[ w = \frac{1}{\sigma^2(F_o^2) + (0.0494P)^2 + 2.2183P} \]

where \( P = (F_c^2 + 2F_o^2)/3 \)

\[ (\Delta/\sigma)_{\text{max}} = 0.001 \]
\[ \Delta\rho_{\text{max}} = 1.11 \text{ e Å}^{-3} \]
\[ \Delta\rho_{\text{min}} = -1.48 \text{ e Å}^{-3} \]

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. A nitrate ion was refined as disordered. The two disordered moieties were restrained to have similar geometries. Uij components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.443 (7) to 0.557 (7).

Solvate water molecules were found to be disordered. Where possible, disorder was refined. For molecules not directly hydrogen bound to the main molecule disorder was found to be excessive (> 3-4 fold disorder of water and/or methanol) and no suitable model that could be devised. The structure factors associated with the disordered solvate molecules were instead augmented via reverse Fourier transform methods using the SQUEEZE routine (P. van der Sluis & A.L. Spek (1990). Acta Cryst. A46, 194-201) as implemented in the program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 151 electrons within solvent accessible voids of 367 Angstrom cubed.

Resolved disordered water molecules were assigned occupancy rates. For "outlying" water molecules occupancies did not refine to full occupancy for each site (due to excessive disorder, or part of the site overlapping with squeezed areas) and no attempts were made to match occupancies. Uij components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar. Water H atom positions were refined and O-H and H···H distances were restrained to 0.84 (2) and 1.36 (2) Angstrom, respectively, while a damping factor was applied. Some water H atom positions were further restrained based on hydrogen bonding considerations. In the final refinement cycles H atoms with low occupancies were constrained to ride on their carrier atoms and the damping factor was removed. Subject to these conditions the occupancy rates refined to the values given in the tables of the cif file.

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 | Occ. (<1) |
|---|-----|-----|-----|------|------|------|------|------|------|-----------|
| In1 | 0.42730 (2) | 0.51469 (2) | 0.18905 (2) | 0.03389 (5) |
| In2 | 0.56369 (2) | 0.53389 (2) | 0.37738 (2) | 0.03459 (5) |
| O1  | 0.34520 (17) | 0.49088 (14) | 0.08522 (13) | 0.0415 (4) |
| O2  | 0.26988 (17) | 0.63287 (13) | 0.20040 (13) | 0.0397 (4) |
| O3  | 0.0717 (2) | 0.64950 (16) | 0.01075 (15) | 0.0497 (5) |
| H3O | 0.020516 | 0.657664 | −0.019345 | 0.075* |
| O4  | 0.57140 (17) | 0.45100 (14) | 0.25976 (13) | 0.0455 (5) |
| O5  | 0.52816 (17) | 0.37557 (13) | 0.12922 (13) | 0.0411 (4) |
| O6  | 0.8253 (2) | 0.21109 (16) | 0.20886 (15) | 0.0537 (6) |
| H6O | 0.896623 | 0.181703 | 0.205605 | 0.081* |
| O7  | 0.59121 (15) | 0.52804 (14) | 0.52133 (12) | 0.0364 (4) |
| O8  | 0.71809 (16) | 0.41493 (14) | 0.38087 (12) | 0.0388 (4) |
| O9  | 0.90123 (17) | 0.43199 (16) | 0.57286 (15) | 0.0472 (5) |
| H9O | 0.950869 | 0.432237 | 0.602515 | 0.071* |
| O10 | 0.44803 (17) | 0.60840 (13) | 0.28938 (13) | 0.0399 (4) |
| O11 | 0.46380 (17) | 0.67505 (13) | 0.43780 (14) | 0.0414 (4) |
| O12 | 0.2284 (2) | 0.86105 (14) | 0.30704 (15) | 0.0524 (6) |
| H12O | 0.202009 | 0.912161 | 0.277748 | 0.079* |
| Atoms | U11 (Å²) | U22 (Å²) | U33 (Å²) | U12 (Å²) | U13 (Å²) | U23 (Å²) |
|-------|----------|----------|----------|----------|----------|----------|
| O13   | 0.5494 (2) | 0.59144 (16) | 0.07719 (14) | 0.0476 (5) |
| H13B  | 0.604 (3) | 0.609 (3) | 0.088 (3) | 0.071* |
| H13A  | 0.576 (3) | 0.568 (3) | 0.0229 (18) | 0.071* |
| O14   | 0.30830 (18) | 0.43647 (15) | 0.30866 (14) | 0.0427 (4) |
| H14A  | 0.336 (3) | 0.3795 (17) | 0.330 (3) | 0.064* |
| H14B  | 0.237 (2) | 0.435 (3) | 0.309 (3) | 0.064* |
| O15   | 0.7033 (2) | 0.6145 (2) | 0.2944 (3) | 0.0810 (10) |
| H15A  | 0.680 (4) | 0.641 (4) | 0.247 (3) | 0.122* |
| H15B  | 0.7781 (19) | 0.593 (4) | 0.276 (4) | 0.122* |
| N5    | 0.1343 (10) | 1.0732 (13) | 0.1845 (15) | 0.050 (3) |
| O16   | 0.2485 (8) | 1.0514 (7) | 0.1561 (7) | 0.087 (3) |
| O17   | 0.0762 (6) | 0.1011 (4) | 0.2364 (4) | 0.0621 (18) |
| O18   | 0.0769 (9) | 1.1489 (8) | 0.1526 (7) | 0.062 (2) |
| N5B   | 0.1096 (8) | 1.0702 (11) | 0.1851 (13) | 0.051 (2) |
| O16B  | 0.2066 (5) | 1.0146 (4) | 0.1890 (4) | 0.0578 (14) |
| O17B  | 0.0105 (4) | 1.0635 (3) | 0.2483 (3) | 0.0569 (13) |
| O18B  | 0.1139 (9) | 1.1390 (6) | 0.1223 (5) | 0.0686 (19) |
| N6    | 0.9957 (2) | 0.50130 (19) | 0.2633 (2) | 0.0473 (5) |
| O19   | 1.10061 (19) | 0.45204 (17) | 0.25405 (17) | 0.0524 (5) |
| O20   | 0.9447 (2) | 0.55804 (16) | 0.32832 (18) | 0.0528 (5) |
| O21   | 0.9408 (2) | 0.4925 (2) | 0.2063 (2) | 0.0668 (7) |
| O23   | 0.3259 (5) | 0.2728 (4) | 0.1487 (5) | 0.129 (3) |
| H23A  | 0.317472 | 0.252966 | 0.095333 | 0.194* |
| H23B  | 0.396276 | 0.292362 | 0.131928 | 0.194* |
| O22   | 0.9121 (4) | 0.6555 (3) | −0.0832 (3) | 0.0795 (12) |
| H22A  | 0.901 (6) | 0.706 (2) | −0.117 (4) | 0.119* |
| H22B  | 0.942 (6) | 0.608 (3) | −0.115 (4) | 0.119* |
| O24   | 0.7903 (5) | 0.5624 (5) | 0.0717 (4) | 0.0820 (19) |
| H24A  | 0.754 (7) | 0.611 (5) | 0.107 (6) | 0.123* |
| H24B  | 0.848 (6) | 0.533 (5) | 0.094 (6) | 0.123* |
| O25   | 0.616 (2) | 0.7286 (18) | 0.1395 (18) | 0.084 (6) |
| H25A  | 0.630387 | 0.766202 | 0.171871 | 0.127* |
| H25B  | 0.591205 | 0.762305 | 0.095684 | 0.127* |
| O22B  | 0.9010 (14) | 0.5910 (19) | −0.0361 (17) | 0.077 (5) |
| H22C  | 0.938459 | 0.577782 | −0.093868 | 0.115* |
| H22D  | 0.878384 | 0.540475 | −0.005618 | 0.115* |
| O24B  | 0.6901 (10) | 0.6830 (7) | 0.1027 (6) | 0.080 (3) |
| H24C  | 0.764 (4) | 0.663 (4) | 0.069 (3) | 0.121* |
| H24D  | 0.684 (6) | 0.737 (5) | 0.123 (10) | 0.121* |
| O26   | 0.4029 (5) | 0.2921 (3) | 0.4115 (5) | 0.0826 (13) |
| H26A  | 0.426 (8) | 0.237 (3) | 0.392 (7) | 0.124* |
| H26B  | 0.446 (7) | 0.303 (6) | 0.443 (5) | 0.124* |
| O27   | 0.4387 (17) | 0.1825 (12) | 0.3027 (13) | 0.0840 (15) |
| H27A  | 0.512426 | 0.171499 | 0.267040 | 0.126* |
| H27B  | 0.398262 | 0.213590 | 0.264719 | 0.126* |
| O26B  | 0.4126 (9) | 0.2528 (6) | 0.3243 (8) | 0.0840 (13) |
| H26C  | 0.420769 | 0.212829 | 0.370989 | 0.126* |
| H26D  | 0.368061 | 0.234118 | 0.298873 | 0.126* |
| Atom | U1   | U2   | U3   | U12  | U13  | U23  |
|------|------|------|------|------|------|------|
| O27B | 0.3779 (17) | 0.2429 (11) | 0.4890 (15) | 0.0829 (14) | 0.124* | 0.179 (7) |
| H27C | 0.315208 | 0.282720 | 0.482494 | 0.124* | 0.179 (7) |
| H27D | 0.421500 | 0.276216 | 0.501045 | 0.124* | 0.179 (7) |
| N1   | 0.2471 (2) | 0.56338 (15) | 0.08175 (14) | 0.0372 (5) |
| H1N  | 0.209366 | 0.564206 | 0.039015 | 0.045* |
| N2   | 0.6447 (2) | 0.36642 (16) | 0.22369 (14) | 0.0398 (5) |
| H2N  | 0.706562 | 0.337010 | 0.244564 | 0.048* |
| N3   | 0.70532 (17) | 0.47275 (16) | 0.51926 (14) | 0.0365 (4) |
| H3N  | 0.736818 | 0.474859 | 0.565283 | 0.044* |
| N4   | 0.37305 (19) | 0.69352 (14) | 0.32306 (15) | 0.0360 (4) |
| H4N  | 0.318985 | 0.725950 | 0.295052 | 0.043* |
| C1   | 0.2100 (2) | 0.63161 (17) | 0.14285 (16) | 0.0336 (5) |
| C2   | 0.0970 (2) | 0.70401 (17) | 0.14686 (17) | 0.0334 (5) |
| C3   | 0.0299 (2) | 0.71124 (19) | 0.08285 (19) | 0.0377 (5) |
| C4   | −0.0770 (3) | 0.7813 (2) | 0.0930 (2) | 0.0451 (6) |
| H4   | −0.121786 | 0.786790 | 0.048854 | 0.054* |
| C5   | −0.1177 (3) | 0.8425 (2) | 0.1671 (2) | 0.0491 (7) |
| H5   | −0.191096 | 0.889457 | 0.174141 | 0.059* |
| C6   | −0.0528 (3) | 0.8362 (2) | 0.2313 (2) | 0.0506 (7) |
| H6   | −0.081218 | 0.878680 | 0.282113 | 0.061* |
| C7   | 0.0541 (2) | 0.7674 (2) | 0.2208 (2) | 0.0421 (6) |
| H7   | 0.098971 | 0.763232 | 0.264669 | 0.051* |
| C8   | 0.6192 (2) | 0.33083 (17) | 0.15665 (16) | 0.0344 (5) |
| C9   | 0.6919 (2) | 0.23985 (17) | 0.11285 (16) | 0.0342 (5) |
| C10  | 0.7905 (2) | 0.18173 (18) | 0.13967 (18) | 0.0390 (5) |
| C11  | 0.8506 (3) | 0.09571 (19) | 0.0951 (2) | 0.0462 (6) |
| H11  | 0.916324 | 0.055457 | 0.114215 | 0.055* |
| C12  | 0.8157 (3) | 0.0686 (2) | 0.0237 (2) | 0.0495 (7) |
| H12  | 0.857088 | 0.009470 | −0.005507 | 0.059* |
| C13  | 0.7206 (3) | 0.1266 (2) | −0.0061 (2) | 0.0479 (7) |
| C14  | 0.698139 | 0.108430 | −0.056489 | 0.058* |
| C15  | 0.6591 (3) | 0.21151 (19) | 0.03901 (19) | 0.0402 (5) |
| C16  | 0.593415 | 0.251208 | 0.019449 | 0.048* |
| C17  | 0.7656 (2) | 0.41697 (18) | 0.44685 (16) | 0.0335 (5) |
| C18  | 0.8865 (2) | 0.35688 (17) | 0.44379 (16) | 0.0324 (4) |
| H18  | 1.109663 | 0.312668 | 0.539478 | 0.050* |
| C19  | 1.1165 (3) | 0.2406 (2) | 0.4275 (2) | 0.0471 (7) |
| C19  | 1.194922 | 0.201193 | 0.421513 | 0.057* |
| C20  | 1.0535 (3) | 0.2312 (2) | 0.3664 (2) | 0.0489 (7) |
| C21  | 1.088423 | 0.184911 | 0.318902 | 0.059* |
| C22  | 0.9390 (2) | 0.28914 (19) | 0.3739 (2) | 0.0401 (5) |
| C23  | 0.896402 | 0.282595 | 0.331230 | 0.048* |
| C24  | 0.3849 (2) | 0.72507 (17) | 0.39896 (18) | 0.0333 (5) |
| C25  | 0.3071 (2) | 0.81570 (16) | 0.43989 (17) | 0.0323 (4) |
| C24  | 0.2326 (2) | 0.88216 (18) | 0.39293 (18) | 0.0376 (5) |
| C25  | 0.1637 (3) | 0.96712 (19) | 0.4359 (2) | 0.0463 (6) |
### Atomic displacement parameters (Å²)

|   | \(U_{11}\)     | \(U_{22}\)     | \(U_{33}\)     | \(U_{12}\)     | \(U_{13}\)     | \(U_{23}\)  |
|---|----------------|----------------|----------------|----------------|----------------|-------------|
| In1| 0.03514 (8)    | 0.03784 (9)    | 0.02316 (7)    | 0.01602 (6)    | −0.01382 (6)   | −0.01154 (6) |
| In2| 0.03067 (8)    | 0.04148 (9)    | 0.02773 (8)    | 0.01479 (6)    | −0.01486 (6)   | −0.01243 (6) |
| O1 | 0.0444 (9)     | 0.0434 (9)     | 0.0328 (8)     | 0.0214 (8)     | −0.0218 (7)    | −0.0165 (7)  |
| O2 | 0.0400 (9)     | 0.0417 (9)     | 0.0350 (8)     | 0.0175 (7)     | −0.0206 (7)    | −0.0160 (7)  |
| O3 | 0.0522 (11)    | 0.0526 (11)    | 0.0476 (11)    | 0.0146 (9)     | −0.0317 (9)    | −0.0163 (9)  |
| O4 | 0.0448 (10)    | 0.0502 (10)    | 0.0360 (9)     | 0.0284 (8)     | −0.0237 (8)    | −0.0214 (8)  |
| O5 | 0.0433 (9)     | 0.0399 (9)     | 0.0370 (9)     | 0.0193 (7)     | −0.0213 (7)    | −0.0170 (7)  |
| O6 | 0.0568 (12)    | 0.0521 (11)    | 0.0475 (11)    | 0.0304 (9)     | −0.0305 (10)   | −0.0225 (9)  |
| O7 | 0.0269 (7)     | 0.0489 (10)    | 0.0306 (8)     | 0.0118 (7)     | −0.0140 (6)    | −0.0141 (7)  |
| O8 | 0.0355 (8)     | 0.0481 (10)    | 0.0282 (8)     | 0.0148 (7)     | −0.0158 (7)    | −0.0117 (7)  |
| O9 | 0.0339 (9)     | 0.0625 (12)    | 0.0457 (10)    | 0.0136 (8)     | −0.0212 (8)    | −0.0225 (9)  |
| O10| 0.0412 (9)     | 0.0390 (9)     | 0.0359 (8)     | 0.0202 (7)     | −0.0204 (7)    | −0.0172 (7)  |
| O11| 0.0380 (9)     | 0.0399 (9)     | 0.0504 (10)    | 0.0125 (7)     | −0.0267 (8)    | −0.0182 (8)  |
| O12| 0.0741 (14)    | 0.0380 (10)    | 0.0460 (11)    | 0.0218 (9)     | −0.0365 (10)   | −0.0166 (8)  |
| O13| 0.0570 (12)    | 0.0515 (11)    | 0.0289 (8)     | 0.0010 (9)     | −0.0093 (8)    | −0.0154 (8)  |
| O14| 0.0397 (9)     | 0.0436 (10)    | 0.0396 (9)     | 0.0078 (8)     | −0.0152 (8)    | −0.0061 (8)  |
| O15| 0.0360 (11)    | 0.0768 (18)    | 0.109 (2)      | −0.0005 (12)   | −0.0161 (13)   | 0.0296 (17)  |
| N5 | 0.068 (4)      | 0.042 (4)      | 0.041 (3)      | 0.019 (4)      | −0.033 (4)     | −0.021 (3)   |
| O16| 0.074 (5)      | 0.080 (5)      | 0.092 (5)      | 0.030 (4)      | −0.035 (4)     | −0.012 (4)   |
| O17| 0.078 (4)      | 0.046 (3)      | 0.061 (3)      | 0.018 (3)      | −0.039 (3)     | −0.004 (2)   |
| O18| 0.066 (5)      | 0.057 (4)      | 0.056 (4)      | 0.023 (3)      | −0.031 (3)     | −0.009 (3)   |
| N5B| 0.071 (4)      | 0.041 (3)      | 0.047 (3)      | 0.013 (3)      | −0.038 (3)     | −0.017 (2)   |
| O16B| 0.062 (3)     | 0.050 (3)      | 0.048 (3)      | 0.024 (2)      | −0.021 (2)     | −0.0088 (19) |
| O17B| 0.062 (3)     | 0.057 (3)      | 0.047 (2)      | 0.016 (2)      | −0.0244 (19)   | −0.0151 (18) |
| O18B| 0.099 (6)     | 0.044 (3)      | 0.060 (4)      | 0.008 (3)      | −0.040 (3)     | 0.006 (3)    |
| N6 | 0.0432 (12)    | 0.0472 (13)    | 0.0572 (14)    | −0.0131 (10)   | −0.0234 (11)   | 0.0038 (11)  |
| O19| 0.0382 (10)    | 0.0595 (13)    | 0.0620 (13)    | −0.0069 (9)    | −0.0186 (9)    | −0.0093 (10) |
| O20| 0.0468 (11)    | 0.0440 (11)    | 0.0691 (14)    | −0.0042 (9)    | −0.0204 (10)   | −0.0104 (10) |
| O21| 0.0627 (15)    | 0.0757 (17)    | 0.0813 (18)    | −0.0166 (13)   | −0.0461 (14)   | −0.0051 (14) |
| O23| 0.115 (5)      | 0.108 (4)      | 0.145 (5)      | −0.039 (3)     | 0.003 (4)      | −0.023 (4)   |
| O22| 0.116 (3)      | 0.067 (2)      | 0.080 (2)      | −0.005 (2)     | −0.070 (2)     | −0.0127 (17) |
| O24| 0.064 (3)      | 0.103 (4)      | 0.090 (4)      | −0.007 (3)     | −0.043 (3)     | −0.012 (3)   |
| O25| 0.084 (10)     | 0.092 (10)     | 0.071 (9)      | −0.029 (8)     | −0.012 (8)     | 0.002 (8)    |
| O22B| 0.116 (9)     | 0.055 (8)      | 0.086 (9)      | −0.007 (8)     | −0.067 (8)     | −0.025 (7)   |
| O24B| 0.099 (6)     | 0.090 (6)      | 0.068 (5)      | −0.055 (5)     | −0.029 (4)     | 0.008 (4)    |
| O26| 0.086 (3)      | 0.053 (2)      | 0.120 (4)      | −0.0028 (19)   | −0.060 (3)     | 0.010 (2)    |
| O27| 0.087 (3)      | 0.052 (2)      | 0.121 (4)      | −0.004 (2)     | −0.056 (3)     | 0.008 (2)    |
### Geometric parameters (Å, °)

| In1—O13 | 2.156 (2) | O27—H27A | 0.8477 |
|---------|-----------|-----------|--------|
| In1—O1  | 2.1594 (17) | O27—H27B | 0.8627 |
| In1—O2  | 2.1774 (16) | O26B—H26C | 0.8430 |
| In1—O5  | 2.1930 (16) | O26B—H26D | 0.8446 |
| In1—O14 | 2.205 (2) | O27B—H27C | 0.8468 |
| In1—O10 | 2.2254 (18) | O27B—H27D | 0.8479 |
| In1—O4  | 2.2348 (17) | N1—C1 | 1.314 (3) |
| In2—O15 | 2.167 (3) | N1—H1N | 0.8800 |
| In2—O10 | 2.1851 (16) | N2—C8 | 1.314 (3) |
| In2—O8  | 2.1915 (16) | N2—H2N | 0.8800 |
| In2—O4  | 2.1916 (18) | N3—C15 | 1.320 (3) |

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| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| In2—O11      | 2.2179 (17)  | N3—H3N      | 0.8800       |
| In2—O7"      | 2.2228 (19)  | N4—C22      | 1.318 (3)    |
| In2—O7       | 2.2312 (16)  | N4—H4N      | 0.8800       |
| O1—N1        | 1.372 (2)    | C1—C2       | 1.476 (3)    |
| O2—C1        | 1.274 (3)    | C2—C7       | 1.395 (3)    |
| O3—C3        | 1.361 (3)    | C2—C3       | 1.397 (3)    |
| O3—H3O       | 0.8400       | C3—C4       | 1.395 (3)    |
| O4—N2        | 1.368 (2)    | C4—C5       | 1.378 (4)    |
| O5—C8        | 1.274 (3)    | C4—H4       | 0.9500       |
| O6—C10       | 1.361 (3)    | C5—C6       | 1.381 (4)    |
| O6—H6O       | 0.8400       | C5—H5       | 0.9500       |
| O7—N3        | 1.389 (2)    | C6—C7       | 1.386 (3)    |
| O8—C15       | 1.278 (3)    | C6—H6       | 0.9500       |
| O9—C17       | 1.354 (3)    | C7—H7       | 0.9500       |
| O9—H9O       | 0.8400       | C8—C9       | 1.476 (3)    |
| O10—N4       | 1.370 (2)    | C9—C10      | 1.401 (3)    |
| O11—C22      | 1.277 (3)    | C9—C14      | 1.402 (4)    |
| O12—C24      | 1.356 (3)    | C10—C11     | 1.394 (3)    |
| O12—H12O     | 0.8400       | C11—C12     | 1.376 (4)    |
| O13—H13B     | 0.817 (18)   | C11—H11     | 0.9500       |
| O13—H13A     | 0.842 (18)   | C12—C13     | 1.389 (4)    |
| O14—H14A     | 0.857 (17)   | C12—H12     | 0.9500       |
| O14—H14B     | 0.843 (17)   | C13—C14     | 1.387 (3)    |
| O15—H15A     | 0.835 (19)   | C13—H13     | 0.9500       |
| O15—H15B     | 0.829 (19)   | C14—H14     | 0.9500       |
| N5—O17       | 1.251 (12)   | C15—C16     | 1.477 (3)    |
| N5—O18       | 1.252 (11)   | C16—C21     | 1.396 (3)    |
| N5—O16       | 1.253 (11)   | C16—C17     | 1.401 (3)    |
| N5B—O18B     | 1.245 (9)    | C17—C18     | 1.398 (3)    |
| N5B—O16B     | 1.247 (9)    | C18—C19     | 1.378 (4)    |
| N5B—O17B     | 1.248 (10)   | C18—H18     | 0.9500       |
| N6—O20       | 1.240 (4)    | C19—C20     | 1.380 (4)    |
| N6—O19       | 1.250 (3)    | C19—H19     | 0.9500       |
| N6—O21       | 1.252 (3)    | C20—C21     | 1.391 (3)    |
| O23—H23A     | 0.9121       | C20—H20     | 0.9500       |
| O23—H23B     | 0.8870       | C21—H21     | 0.9500       |
| O22—H22A     | 0.824 (19)   | C22—C23     | 1.473 (3)    |
| O22—H22B     | 0.821 (19)   | C23—C28     | 1.393 (3)    |
| O24—H24A     | 0.86 (2)     | C23—C24     | 1.406 (3)    |
| O24—H24B     | 0.85 (2)     | C24—C25     | 1.393 (3)    |
| O25—H25A     | 0.8399       | C25—C26     | 1.376 (4)    |
| O25—H25B     | 0.8397       | C25—H25     | 0.9500       |
| O22B—H22C    | 0.8432       | C26—C27     | 1.377 (4)    |
| O22B—H22D    | 0.8417       | C26—H26     | 0.9500       |
| O24B—H24C    | 0.85 (2)     | C27—C28     | 1.385 (4)    |
| O24B—H24D    | 0.84 (2)     | C27—H27     | 0.9500       |
| O26—H26A     | 0.83 (2)     | C28—H28     | 0.9500       |
| O26—H26B     | 0.843 (16)   |              |              |
| Bond          | Distance (Å) | Angle (°)  |
|---------------|--------------|------------|
| O13—In1—O1   | 89.83 (8)    | C8—N2—H2N 121.3|
| O13—In1—O2   | 93.89 (8)    | O4—N2—H2N 121.3|
| O1—In1—O2    | 74.33 (6)    | C15—N3—O7 118.69 (18) |
| O13—In1—O5   | 91.12 (8)    | C15—N3—H3N 120.7 |
| O1—In1—O5    | 73.42 (6)    | O7—N3—H3N 120.7 |
| O2—In1—O5    | 147.32 (7)   | C22—N4—O10 117.54 (18) |
| O13—In1—O14  | 176.88 (8)   | C22—N4—H4N 121.2 |
| O1—In1—O14   | 93.25 (8)    | O10—N4—H4N 121.2 |
| O2—In1—O14   | 87.42 (7)    | O2—C1—N1 119.66 (19) |
| O5—In1—O14   | 89.29 (8)    | O2—C1—C2 120.4 (2) |
| O13—In1—O10  | 85.39 (8)    | N1—C1—C2 119.9 (2) |
| O1—In1—O10   | 151.22 (6)   | C7—C2—C3 118.6 (2) |
| O2—In1—O10   | 77.70 (6)    | C7—C2—C1 117.3 (2) |
| O5—In1—O10   | 134.94 (6)   | C3—C2—C1 124.1 (2) |
| O14—In1—O10  | 92.13 (8)    | O3—C3—C4 121.3 (2) |
| O13—In1—O4   | 91.89 (9)    | O3—C3—C2 118.7 (2) |
| O1—In1—O4    | 144.16 (6)   | C4—C3—C2 120.0 (2) |
| O2—In1—O4    | 141.12 (6)   | C5—C4—C3 120.1 (3) |
| O5—In1—O4    | 70.76 (6)    | C5—C4—H4 120.0 |
| O14—In1—O4   | 85.32 (8)    | C3—C4—H4 120.0 |
| O10—In1—O4   | 64.50 (6)    | C4—C5—C6 120.7 (2) |
| O15—In2—O10  | 89.73 (10)   | C4—C5—H5 119.7 |
| O15—In2—O8   | 84.54 (9)    | C6—C5—H5 119.7 |
| O10—In2—O8   | 143.67 (6)   | C5—C6—C7 119.4 (3) |
| O15—In2—O4   | 96.99 (13)   | C5—C6—H6 120.3 |
| O10—In2—O4   | 65.88 (6)    | C7—C6—H6 120.3 |
| O8—In2—O4    | 79.23 (6)    | C6—C7—C2 121.2 (3) |
| O15—In2—O11  | 84.31 (11)   | C6—C7—H7 119.4 |
| O10—In2—O11  | 71.51 (6)    | C2—C7—H7 119.4 |
| O8—In2—O11   | 142.83 (6)   | O5—C8—N2 119.10 (19) |
| O4—In2—O11   | 137.36 (6)   | O5—C8—C9 118.9 (2) |
| O15—In2—O7i  | 170.29 (11)  | N2—C8—C9 122.0 (2) |
| O10—In2—O7i  | 90.28 (7)    | C10—C9—C14 118.8 (2) |
| O8—In2—O7i   | 101.08 (7)   | C10—C9—C8 124.5 (2) |
| O4—In2—O7i   | 91.88 (8)    | C14—C9—C8 116.7 (2) |
| O11—In2—O7i  | 86.49 (7)    | O6—C10—C11 121.6 (2) |
| O15—In2—O7   | 98.35 (11)   | O6—C10—C9 118.8 (2) |
| O10—In2—O7   | 143.60 (6)   | C11—C10—C9 119.5 (2) |
| O8—In2—O7    | 72.67 (6)    | C12—C11—C10 120.6 (2) |
| O4—In2—O7    | 146.36 (7)   | C12—C11—H11 119.7 |
| O11—In2—O7   | 74.06 (6)    | C10—C11—H11 119.7 |
| O7i—In2—O7   | 76.08 (7)    | C11—C12—C13 120.8 (2) |
| N1—O1—In1    | 111.75 (13)  | C11—C12—H12 119.6 |
| C1—O2—In1    | 114.73 (14)  | C13—C12—H12 119.6 |
| C3—O3—H3O    | 109.5        | C14—C13—C12 118.9 (3) |
| N2—O4—In2    | 132.33 (13)  | C14—C13—H13 120.5 |
| N2—O4—In1    | 114.14 (13)  | C12—C13—H13 120.5 |
| Bond                      | Distance  | | Bond                      | Distance  | |
|--------------------------|-----------|---|--------------------------|-----------|
| In2—O4—In1               | 113.49 (7)|   | C13—C14—C9              | 121.3 (2)  |
| C8—O5—In1                | 118.44 (15)|  | C13—C14—H14             | 119.4     |
| C10—O6—H6O               | 109.5     |   | C9—C14—H14              | 119.4     |
| N3—O7—In2                | 113.96 (15)|  | O8—C15—N3               | 119.61 (19)|
| N3—O7—In2                | 110.00 (12)|  | O8—C15—C16              | 120.8 (2)  |
| In2—O7—In2               | 103.92 (7) |   | N3—C15—C16              | 119.5 (2)  |
| C15—O8—In2               | 114.99 (14)|  | C21—C16—C17             | 118.9 (2)  |
| C17—O9—H9O               | 109.5     |   | C21—C16—C15             | 117.4 (2)  |
| N4—O10—In2               | 114.93 (13)|  | C17—C16—C15             | 123.7 (2)  |
| N4—O10—In1               | 127.85 (14)|  | O9—C17—C18              | 120.7 (2)  |
| In2—O10—In1              | 114.12 (7) |   | O9—C17—C16              | 119.1 (2)  |
| C22—O11—In2              | 116.63 (15)|  | C18—C17—C16             | 120.2 (2)  |
| C24—O12—H12O             | 109.5     |   | C19—C18—C17             | 120.0     |
| In1—O13—H13B             | 120 (3)   |   | C19—C18—H18             | 120.0     |
| In1—O13—H13A             | 115 (3)   |   | C17—C18—H18             | 120.0     |
| H13B—O13—H13A            | 110 (3)   |   | C18—C19—C20             | 120.4 (2)  |
| In1—O14—H14A             | 120 (2)   |   | C18—C19—H19             | 119.8     |
| In1—O14—H14B             | 120 (3)   |   | C20—C19—H19             | 119.8     |
| H14A—O14—H14B            | 105 (2)   |   | C19—C20—C21             | 120.3 (3)  |
| In2—O15—H15A             | 105 (4)   |   | C19—C20—H20             | 119.8     |
| In2—O15—H15B             | 127 (4)   |   | C21—C20—H20             | 119.8     |
| H15A—O15—H15B            | 110 (3)   |   | C20—C21—C16             | 120.3 (2)  |
| O17—N5—O18               | 118.9 (11)|  | C20—C21—H21             | 119.9     |
| O17—N5—O16               | 118.6 (11)|  | C16—C21—H21             | 119.9     |
| O18—N5—O16               | 121.8 (11)|  | O11—C22—N4              | 119.0 (2)  |
| O18B—N5B—O16B            | 119.0 (9) |   | O11—C22—C23             | 120.2 (2)  |
| O18B—N5B—O17B            | 119.5 (9) |   | N4—C22—C23              | 120.8 (2)  |
| O16B—N5B—O17B            | 121.1 (9) |   | C28—C23—C24             | 118.8 (2)  |
| O20—N6—O19               | 121.3 (3) |   | C28—C23—C22             | 117.8 (2)  |
| O20—N6—O21               | 119.4 (3) |   | C24—C23—C22             | 123.3 (2)  |
| O19—N6—O21               | 119.3 (3) |   | O12—C24—C25             | 121.6 (2)  |
| H23A—O23—H23B            | 108.5     |   | O12—C24—C23             | 118.9 (2)  |
| H22A—O22—H22B            | 112 (3)   |   | C25—C24—C23             | 119.5 (2)  |
| H24A—O24—H24B            | 105 (3)   |   | C26—C25—C24             | 120.3 (2)  |
| H25A—O25—H25B            | 107.9     |   | C26—C25—H25             | 119.8     |
| H22C—O22B—H22D           | 107.4     |   | C24—C25—H25             | 119.8     |
| H24C—O24B—H24D           | 109 (3)   |   | C25—C26—C27             | 120.8 (2)  |
| H26A—O26—H26B            | 112 (3)   |   | C25—C26—H26             | 119.6     |
| H27A—O27—H27B            | 104.7     |   | C27—C26—H26             | 119.6     |
| H26C—O26B—H26D           | 107.9     |   | C26—C27—C28             | 119.5 (3)  |
| H27C—O27B—H27D           | 106.0     |   | C26—C27—H27             | 120.2     |
| C1—N1—O1                | 119.36 (19)|  | C28—C27—H27             | 120.2     |
| C1—N1—H1N               | 120.3     |   | C27—C28—C23             | 120.9 (2)  |
| O1—N1—H1N               | 120.3     |   | C27—C28—H28             | 119.5     |
| C8—N2—O4                | 117.36 (18)|  | C23—C28—H28             | 119.5     |

| Bond                      | Distance  |   | Bond                      | Distance  |   |
|--------------------------|-----------|---|--------------------------|-----------|
| In1—O1—N1—C1            | −4.7 (3)  |   | C12—C13—C14—C9          | 0.6 (5)   |
| In2—O4—N2—C8            | 174.4 (2) |   | C10—C9—C14—C13          | 1.3 (4)   |
### Hydrogen-bond geometry (Å, °)

| D—H⋯A            | D—H | H⋯A | D⋯A   | D—H⋯A |
|------------------|-----|-----|-------|-------|
| O3—H3⋯O22\textsuperscript{ii} | 0.84 | 1.83 | 2.664 (4) | 171   |
| O3—H3⋯O22\textsuperscript{Bii} | 0.84 | 1.97 | 2.668 (17) | 140   |

Symmetry code: (i) \(-x+1, -y+1, -z+1\).
| Bond                | D1   | D2   | D3   | D4   |
|---------------------|------|------|------|------|
| O6—H6O···O18\textsuperscript{ii} | 0.84 | 1.98 | 2.775 (10) | 157 |
| O6—H6O···O17B\textsuperscript{ii} | 0.84 | 2.06 | 2.810 (5) | 149 |
| O9—H9O···O20\textsuperscript{xv} | 0.84 | 1.88 | 2.717 (3) | 176 |
| O12—H12O···O17B | 0.84 | 1.99 | 2.778 (5) | 156 |
| O12—H12O···O16B | 0.84 | 1.81 | 2.609 (6) | 158 |
| O13—H13B···O24 | 0.82 (2) | 2.09 (3) | 2.761 (6) | 140 (4) |
| O13—H13B···O25 | 0.82 (2) | 2.01 (4) | 2.64 (3) | 134 (4) |
| O13—H13B···O24B | 0.82 (2) | 1.70 (2) | 2.485 (7) | 160 (5) |
| O13—H13A···O1\textsuperscript{v} | 0.84 (2) | 1.77 (2) | 2.601 (2) | 170 (4) |
| O14—H14A···O26 | 0.86 (2) | 1.83 (2) | 2.631 (5) | 154 (4) |
| O14—H14B···O26B | 0.86 (2) | 1.82 (2) | 2.629 (8) | 158 (4) |
| O14—H14B···O19\textsuperscript{ii} | 0.84 (2) | 1.99 (2) | 2.782 (3) | 157 (4) |
| O15—H15A···O25 | 0.84 (2) | 2.11 (3) | 2.93 (3) | 171 (6) |
| O15—H15A···O24B | 0.84 (2) | 2.10 (3) | 2.891 (9) | 158 (5) |
| O15—H15B···O20 | 0.83 (2) | 2.27 (3) | 2.970 (4) | 142 (5) |
| O15—H15B···O21 | 0.83 (2) | 2.16 (3) | 2.924 (4) | 154 (6) |
| O23—H23B···O5 | 0.89 | 2.16 | 3.003 (6) | 160 |
| O22—H22A···O18\textsuperscript{vi} | 0.82 (2) | 2.11 (4) | 2.842 (12) | 148 (6) |
| O22—H22B···O21\textsuperscript{ii} | 0.82 (2) | 2.03 (3) | 2.832 (5) | 164 (7) |
| O24—H24A···O25 | 0.86 (2) | 2.03 (2) | 2.80 (3) | 149 (6) |
| O24—H24B···O21 | 0.85 (2) | 2.21 (4) | 3.003 (5) | 155 (6) |
| O22B—H22C···O21\textsuperscript{vii} | 0.84 | 2.00 | 2.808 (16) | 159 |
| O24B—H24C···O22B | 0.85 (2) | 2.02 (2) | 2.824 (19) | 156 (7) |
| O26—H26A···O27 | 0.83 (2) | 1.56 (6) | 2.259 (16) | 140 (9) |
| O27—H27B···O23 | 0.86 | 2.14 | 2.987 (19) | 168 |
| O26B—H26C···O27B | 0.84 | 1.73 | 2.31 (2) | 124 |
| O26B—H26D···O23 | 0.84 | 2.38 | 3.033 (13) | 134 |
| O27B—H27D···O11\textsuperscript{i} | 0.85 | 2.13 | 2.955 (18) | 163 |
| N1—H1N···O3 | 0.88 | 1.92 | 2.605 (3) | 134 |
| N2—H2N···O6 | 0.88 | 2.02 | 2.669 (2) | 130 |
| N2—H2N···O8 | 0.88 | 2.48 | 2.935 (3) | 113 |
| N3—H3N···O9 | 0.88 | 1.94 | 2.605 (3) | 132 |
| N3—H3N···O14\textsuperscript{i} | 0.88 | 2.24 | 2.939 (3) | 137 |
| N4—H4N···O2 | 0.88 | 2.33 | 2.804 (3) | 114 |
| N4—H4N···O12 | 0.88 | 1.97 | 2.621 (3) | 130 |

Symmetry codes: (i) \(-x+1, -y+1, -z+1\); (ii) \(x, y, z\); (iii) \(x+1, y-1, z\); (iv) \(-x+2, -y+1, -z\); (v) \(-x+1, -y+1, -z\); (vi) \(-x+1, -y+2, -z\); (vii) \(-x+2, -y+1, -z\).