Synthesis and crystal structure of bis[trans-diaqua(1,4,8,11-tetraazacyclotetradecane-κ^4_N^1,N^4,N^8,N^11)nickel(II)] trans-(1,4,8,11-tetraazacyclotetradecane-κ^4_N^1,N^4,N^8,N^11)bis[4,4',4''-(1,3,5-trimethylbenzene-2,4,6-triyl)tris(hydrogen phenylphosphonato-κO)]nickel(II) decahydrate

Liudmyla V. Tsymbal,a Rodinel Ardeleanu,b Sergiu Shova and Yaroslaw D. Lampeka^a*

aL. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of, Sciences of Ukraine, Prospekt Nauki, 31, Kiev 03028, Ukraine, and b“Petru Poni” Institute of Macromolecular Chemistry, Department of, Inorganic, Polymers, Alea Grigore Ghica Voda 41A, RO-700487 Iasi, Romania. *Correspondence e-mail: lampeka@adamant.net

The components of the title compound, [Ni(C_{10}H_{24}N_4)(H_2O)_2][Ni(C_{10}H_{24}N_4)-(C_{27}H_{24}O_9P_3)_2]10H_2O are two centrosymmetric [Ni(C_{10}H_{24}N_4)(H_2O)_2]^2+ dications, a centrosymmetric [Ni(C_{10}H_{24}N_4)(C_{27}H_{24}O_9P_3)_2]^4- tetra-anion and five crystallographically unique water molecules of crystallization. All of the nickel ions are coordinated by the four secondary N atoms of the macrocyclic cyclam ligands, which adopt the most energetically stable trans-III conformation, and the mutually trans O atoms of either water molecules in the cations or the phosphonate groups in the anion in a tetragonally distorted NiN_4O_2 octahedral coordination geometry. Strong O—H···O hydrogen bonds between the protonated and the non-protonated phosphonate O atoms of neighboring anions result in the formation of layers oriented parallel to the bc plane, which are linked into a three-dimensional network by virtue of numerous N—H···O and O—H···O hydrogen bonds arising from the sec-NH groups of the macrocycles, phosphonate O atoms and coordinated and non-coordinated water molecules.

1. Chemical context

First-row transition-metal complexes of 14-membered cyclam-like tetraaza macrocycles (cyclam = 1,4,8,11-tetraazacyclotetradecane; C_{10}H_{24}N_4; L) are characterized by high thermodynamic stability and kinetic inertness (Yatsimirskii & Lampeka, 1985) and are popular metal-containing building units for the construction of MOFs (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh et al., 2012; Stackhouse & Ma, 2018). These crystalline coordination polymers, in which oligocarboxylates are the most common bridging ligands (Rao et al., 2004), possess permanent porosity and demonstrate many promising applications in different areas (MacGillivray & Lukehart, 2014; Kaskel, 2016).

The rigid trigonal aromatic linker 1,3,5-benzenetricarboxylate, C_{9}H_{3}O_{6}^3, is widely used for the assembly of MOFs based on azamacroyclic cations (Lampeka & Tsymbal, 2004). Its tris-monodentate coordination in the trans-axial coordination positions of the metal ions leads predominantly to the formation of two-dimensional coordination polymers with hexagonal nets of 6^3 topology (Alexandrov et al., 2017).
Usually, the modification of this bridge through the substitution of the carboxylic groups by para-carboxybenzyl fragments (the ligand H$_4$BTB, 4,4',4''-benzene-1,3,5-triyltribenzoic acid) does not affect the coordination properties of the carboxylate groups or the topological characteristics of polymeric nets but results in the enlargement of the hexagonal structural unit of the coordination polymers allowing interpenetration of the subnets (Lampek et al., 2012; Gong et al., 2016). Compared to carboxylates, linkers with other coordinating functions, in particular oligophosphonates, have been studied to a much lesser extent (Gagnon et al., 2012; Firmino et al., 2018; Yücesan et al., 2018), though one can expect that the substitution of a mono-anionic carboxylic group by a di-anionic phosphonate group with distinct acidity, number of donor atoms and spatial directivity of coordination bonds will strongly influence the composition and topology of the coordination nets. However, except for a very recent publication (Tsymbal et al., 2022), no papers dealing with structural characterization of the complexes formed by metal azamacrocyclic cations and phosphonate ligands have been published to date.

We report here the synthesis and crystal structure of the product of the reaction of [Ni(L)](ClO$_4$)$_2$ with 4,4',4''-(1,3,5-trimethylbenzene-2,4,6-triyl)triphosphonic acid, H$_6$Me$_3$BTP – the structural analogue of H$_3$BTB, namely, bis[trans-diaqua-(1,4,8,11-tetraazacyclotetradecane-κ$^4$N$_4$N$_4$,N$_8$,N$_{11}$)-nickel(II)] trans-[bis-[4,4',4''-(1,3,5-trimethylbenzene-2,4,6-triyl)tris(hydrogen phenylphosphonato-κO)-(1,4,8,11-tetraazacyclotetradecane-κ$^4$N$_4$N$_4$,N$_8$,N$_{11}$)-nickel(II)] decahydrate, [Ni(L)(H$_2$O)$_2$]$_2$[Ni(L)(H$_3$Me$_3$BTP)$_2$]·10H$_2$O, I.

2. Structural commentary

The molecular structure of I is shown in Fig. 1. It represents a non-polymeric compound in which atom Ni1 is coordinated by two monodentate H$_3$Me$_3$BTP$^{3-}$ ligands via their phosphonate O atoms, resulting in the formation of an [Ni(L)(H$_3$Me$_3$BTP)$_2$]$^{4-}$ complex anion, which is charge-balanced by two structurally non-equivalent [Ni(L)(H$_2$O)$_2$]$^{2+}$ divalent cations formed by atoms Ni2 and Ni3. The coordination geometries of all the nickel ions in I have much in common: the Ni$^{2+}$ ions (all with site symmetry 1) are coordinated by the four secondary N atoms of the macrocyclic ligands L, which adopt the most energetically stable trans-III (R,R,S,S) conformation (Bosnich et al., 1965a; Barefield et al., 1986) with the five-membered (N—Ni—N bite angles $'$85$^\circ$) and six-membered (N—Ni—N bite angles $'$85$^\circ$) coordination environments.

Table 1

| Selected geometric parameters (Å, °). |
|-------------------------------------|
| Ni$_1$—N1  | 2.067 (4) |
| Ni$_1$—N2  | 2.064 (4) |
| Ni$_1$—O1  | 2.134 (3) |
| Ni$_2$—N3  | 2.072 (4) |
| Ni$_2$—N4  | 2.076 (4) |
| N1—Ni$_1$—N2$^i$ | 85.31 (16) |
| N1—Ni$_1$—N3$^ii$ | 94.69 (16) |
| N3—Ni$_1$—N4$^iii$ | 95.34 (16) |
| N2—Ni$_2$—N3$^i$ | 84.66 (16) |
| N2—Ni$_2$—N4$^ii$ | 85.2 (2) |
| N3—Ni$_3$—N6 | 94.8 (2) |

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

Figure 1

The extended asymmetric unit in I showing the coordination environment of the Ni atoms and the atom-labeling scheme (displacement ellipsoids are drawn at the 30% probability level). C-bound H atoms and uncoordinated water molecules are omitted for clarity. Symmetry codes: (i) $-x+2,-y+1,-z+2$; (ii) $-x+2,-y+2,-z+1$; (iii) $-x+1,-y+3,-z+1$. 

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membered (N—Ni—N bite angles \( \approx 95^{\circ} \)) chelate rings in gauche and chair conformations, respectively (Table 1). The coordination polyhedra of the metal ions can be described as tetragonally elongated \( \text{trans-NiN}_2\text{O}_2 \) octahedra with the Ni—N bond lengths [average value 2.068 (3) \( \text{Å} \)] slightly shorter than the Ni—O bonds which, in turn, do not display any dependence on the nature of the donor oxygen atoms. The location of the metal ions on crystallographic inversion centers enforces strict planarity of the \( \text{Ni(N}_4 \) coordination moieties and the axial Ni—O bonds are nearly orthogonal to the \( \text{NiN}_4 \) planes (deviations of the angles N—Ni—O from 90\(^{\circ} \) do not exceed 2\(^{\circ} \)).

The pendant benzene rings of the \( \text{H}_3\text{Me}_3\text{BTP}_3^- \) tri-anion in I are substantially tilted relative to the central aromatic core [average angle between the mean planes = 76 (5)\(^{\circ} \)] and this feature is caused by repulsive interactions between the hydrogen atoms of the pendant rings and those of the methyl substituents of the central ring. The P—OH bond lengths [average value 1.57 (3) \( \text{Å} \)] are larger than the other P—O bonds [average value 1.501 (5) \( \text{Å} \)], thus indicating the partially delocalized character of the phosphonate groups.

3. Supramolecular features

In the crystal of I, the \([\text{Ni}_1(L)(\text{H}_3\text{Me}_3\text{BTP}_3^-)]^{\text{1}^+} \) anions, \([\text{Ni}_2/\text{Ni}_3/(L)(\text{H}_2\text{O})_2]^{\text{2}^+} \) cations and water molecules of crystallization are linked by numerous hydrogen bonds with participation of the phosphonate groups, the secondary amino groups of the macrocycles and both the coordinated and crystalline water molecules (Table 2). A distinct lamellar structure is inherent for this compound. In particular, strong hydrogen-bonding interactions between the protonated fragments of the P1 and P3 phosphate groups of one molecule as the donors with the non-protonated O4 and O5 atoms of the P2 group of another molecule as the acceptors \([\text{P1}—\text{O3—H3C—O5(x, y—1, z)}, \text{P3—O9—H9C—O49(x, y—1, z+1)} \), together with a weak N1—H1—O6 (x, y —1, z) hydrogen bond between the secondary amino group of the macrocyclic cation \([\text{Ni1}(L)] \) and protonated P2—O6 phosphonate fragment result in the formation of anionic layers oriented parallel to the \( bc \) plane. The distance between the parallel mean planes

| Table 2 Hydrogen-bond geometry (\( \text{Å}, \text{\(^{\circ} \}) \). |
| --- |
| \( D—H \cdot \cdot \cdot A \) | \( D—H \cdot \cdot \cdot A \) | \( D—A \cdot \cdot \cdot A \) | \( D—H \cdot \cdot \cdot A \) |
| N1—H1—O6 | 1.00 | 2.32 | 3.196 (5) | 146 |
| N2—H2—O6W | 1.00 | 2.18 | 3.039 (6) | 143 |
| N3—H3—O7\( ^{vii} \) | 1.00 | 2.13 | 3.102 (6) | 162 |
| N4—H4—O4W | 1.00 | 2.06 | 3.056 (6) | 173 |
| N5—H5—O9\( ^{viii} \) | 1.00 | 2.07 | 3.003 (6) | 155 |
| N6—H6—O7W\( ^{ix} \) | 1.00 | 1.98 | 2.956 (6) | 166 |
| O3—H3C—O5\( ^{vii} \) | 0.84 | 1.84 | 2.654 (5) | 164 |
| O6—H6C—O3W\( ^{ix} \) | 0.84 | 1.75 | 2.550 (5) | 159 |
| O9—H9C—O4\( ^{ix} \) | 0.84 | 1.74 | 2.517 (5) | 154 |
| O1W—H1 WB—O7 | 0.87 | 1.81 | 2.679 (5) | 173 |
| O1W—H1 WA—O4W | 0.87 | 2.45 | 3.256 (6) | 155 |
| O2W—H2 WB—O4 | 0.86 | 1.90 | 2.729 (5) | 164 |
| O2W—H2 WA—O7W\( ^{xi} \) | 0.86 | 1.81 | 2.675 (6) | 174 |
| O3W—H3 WB—O2 | 0.87 | 1.81 | 2.676 (4) | 177 |
| O3W—H3 WA—O7 | 0.85 | 1.84 | 2.689 (5) | 174 |
| O4W—H4 WB—O3 | 0.87 | 2.26 | 3.115 (6) | 167 |
| O4W—H4 WA—O8 | 0.87 | 1.93 | 2.796 (6) | 172 |
| O5W—H5 WB—O5 | 0.87 | 1.98 | 2.813 (5) | 159 |
| O5W—H5 WA—O8\( ^{xii} \) | 0.87 | 1.87 | 2.725 (5) | 168 |
| O6W—H6 WB—O2 | 0.87 | 2.02 | 2.799 (6) | 149 |
| O6W—H6 WA—O5W | 0.87 | 2.00 | 2.842 (5) | 164 |
| O7W—H7 WB—O3W | 0.85 | 2.02 | 2.731 (5) | 140 |
| O7W—H7 WA—O5W | 0.86 | 1.83 | 2.688 (5) | 173 |

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

The structure of I viewed down the \( b \) axis. C-bound H atoms have been omitted; C and N atoms of the macrocyclic cation formed by N2 and N3 are shown in green and violet, respectively. Water molecules of crystallization are not shown; hydrogen bonds are depicted as dashed lines.

Figure 2

The hydrogen-bonded (dashed lines) layers in I viewed down the \( a \) axis. C-bound H atoms and macrocyclic cations formed by Ni3 have been omitted; C and N atoms of the macrocyclic cation formed by Ni2 are shown in green.

Figure 3

The hydrogen-bonding interactions between the coordinated water molecules and the phosphonate O7 atom \([\text{O1W—H1 WB—O7(x, y, z—1)} \) (Fig. 2).

The second macrocyclic aqua cation \([\text{Ni3}(L)(\text{H}_2\text{O})_2]^{2+} \), due to hydrogen bonding of the coordinated water molecule with the phosphonate O4 atom \([O2W—H2 WB—O4] \), serves as the bridge between the layers, arranging them into a three-dimensional network (Fig. 3), which is further stabilized by ...
numerous O—H···O hydrogen bonds involving the water molecules of crystallization, O3W–O7W (Table 2).

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.43, last update March 2022; Groom et al., 2016) gave no hits related to H$_2$Me$_2$BTP or its complexes with metal ions, so the present work is the first structural characterization of a complex of this ligand. At the same time, several works dealing with the structures of the non-methylated analogue of the phosphonate under consideration, namely, 4,4',4''-benzene-1,3,5-triyl-triphosphonic acid (H$_6$BTP), have been published. They include a methanol solvate of the free acid (CSD refcode AKEPEO; Vilela et al., 2021) and its pyridinium salt (YOLGEM; Beckmann et al., 2008), molecular complexes with solvated Co$^{II}$ and Ni$^{II}$ ions (OQIZAR and OQIZEV; Pili et al., 2016) and coordination polymers formed by Sr$^{II}$ (SOTZOR; Vaidhyanathan et al., 2009), Zn$^{II}$ (ISELAV02; Hermer et al., 2016), Y$^{III}$ (AKEPOY; Vilela et al., 2021), Zr$^{IV}$ (COCLIR; Taddei et al., 2014) and Y$^{IV}$/V (COONAY; Ouellen et al., 2009). Interestingly, as in I, in all the metal complexes except COCLIR and ISELAV02, the ligand acts as a H$_3$BTP$^{-}$ tri-anion with three monodeprotonated phosphonate groups. On the other hand, because of the absence of methyl substituents, the molecules of the anions H$_n$BTP$^{(6-n)}$− as a whole are flatter than H$_3$Me$_3$BTP$^{-}$ in I with a maximal tilting angle of pendant versus central benzene rings of ca 49° observed in ISELAV02. In addition, in the majority of complexes formed by H$_4$BTP$^{(6-n)}$− ligands (except AKEPOY and ISELAV02), aromatic π–π stacking interactions of different strengths are observed with centroid-to-centroid distances between the central aromatic rings ranging from 3.4 to 3.9 Å.

The Cambridge Structural Database contains also 18 hits describing the structure of the [Ni(L)(H$_2$O)$_2$]$^{2+}$ complex cation in salts of different inorganic and organic anions as well as the charge-compensating part in anionic coordination polymers. In general, the structure of this cation in I is similar to other compounds, both from the point of view of the conformation of the macrocycle and the bond distances and angles characterizing the coordination polyhedron of the metal.

5. Synthesis and crystallization

All chemicals and solvents used in this work were purchased from Sigma–Aldrich and used without further purification. The acid H$_2$Me$_2$BTP was synthesized according to a procedure described previously for the preparation of H$_2$BTP (Vaidhyananthan et al., 2009), starting from 1,3,5-trimethyl-2,4,6-tris(4'-bromophenyl)benzene instead of 1,3,5-tris(4'-bromo-phenyl)benzene. The complex [Ni(L)](ClO$_4$)$_2$ was prepared from ethanol solutions as described in the literature (Bosnich et al., 1965b).

The title compound [Ni(L)(H$_2$O)$_2$]$_2$[Ni(L)(H$_2$Me$_2$BTP)$_2$]·10H$_2$O, I, was prepared as follows. A solution of [Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)$_2$]$_2$·[Ni(C$_{10}$H$_{24}$N$_4$)(C$_{22}$H$_{24}$O$_9$P$_3$)$_2$]·10H$_2$O 2200.09

Table 3

| Crystal data | [Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)$_2$]$_2$·[Ni(C$_{10}$H$_{24}$N$_4$)(C$_{22}$H$_{24}$O$_9$P$_3$)$_2$]·10H$_2$O |
| Crystal data | [Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)$_2$]$_2$·[Ni(C$_{10}$H$_{24}$N$_4$)(C$_{22}$H$_{24}$O$_9$P$_3$)$_2$]·10H$_2$O |
| Crystal data | [Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)$_2$]$_2$·[Ni(C$_{10}$H$_{24}$N$_4$)(C$_{22}$H$_{24}$O$_9$P$_3$)$_2$]·10H$_2$O |
| Crystal data | [Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)$_2$]$_2$·[Ni(C$_{10}$H$_{24}$N$_4$)(C$_{22}$H$_{24}$O$_9$P$_3$)$_2$]·10H$_2$O |
| Crystal data | [Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)$_2$]$_2$·[Ni(C$_{10}$H$_{24}$N$_4$)(C$_{22}$H$_{24}$O$_9$P$_3$)$_2$]·10H$_2$O |

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms in I were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.95 Å (ring H atoms), 0.98 Å (methyl H atoms), 0.99 Å (methylen H atoms), N–H distances of 1.00 Å, O–H distances of 0.84 Å (protonated phosphonate groups) and 0.87 Å (water molecules) with $U_{iso}(H)$ values of 1.2$U_{eq}$ or 1.5$U_{eq}$ times those of the corresponding parent atoms.
References

 Alexandrov, E. V., Blatov, V. A. & Proserpio, D. M. (2017). *CrystEngComm*, **19**, 1993–2006.
 Barefield, E. K., Bianchi, A., Billo, E. J., Connolly, P. J., Paoletti, P., Summers, J. S. & Van Derveer, D. G. (1986). *Inorg. Chem.*, **25**, 4197–4202.
 Beckmann, J., Rüttinger, R. & Schwich, T. (2008). *Cryst. Growth Des.*, **8**, 3271–3276.
 Bosnich, B., Poon, C. K. & Tobe, M. L. (1965a). *Inorg. Chem.*, **4**, 1102–1108.
 Bosnich, B., Tobe, M. L. & Webb, G. A. (1965b). *Inorg. Chem.*, **4**, 1109–1112.
 Firmino, A. D. G., Figueira, F., Tomé, J. P. C., Paz, F. A. A. & Rocha, J. (2018). *Coord. Chem. Rev.*, **355**, 133–149.
 Gagnon, K. J., Perry, H. P. & Clearfield, A. (2012). *Chem. Rev.*, **112**, 1034–1054.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.*, **B72**, 171–179.
 Hermer, N., Reinsch, H., Mayer, P. & Stock, N. (2016). *CrystEngComm*, **18**, 8147–8150.
 Kaskel, S. (2016). Editor. *The Chemistry of Metal–Organic Frameworks: Synthesis, Characterization and Applications*. Weinheim: Wiley-VCH.
 Lampeka, Ya. D. & Tsymbal, L. V. (2004). *Theor. Exp. Chem.*, **40**, 345–371.
 Lampeka, Ya. D., Tsymbal, L. V., Barna, A. V., Shulga, Y. L., Shova, S. & Arion, V. B. (2012). *Dalton Trans.*, **41**, 4118–4125.
 MacGillivray, L. R. & Lukehart, C. M. (2014). Editors. *Metal–Organic Framework Materials*. Hoboken: John Wiley and Sons.
 Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.*, **53**, 226–235.
 Ouellette, W., Wang, G., Liu, H., Yee, G. T., O’Connor, C. J. & Zubieta, J. (2009). *Inorg. Chem.*, **48**, 953–963.
 Pili, S., Argent, S. P., Morris, C. G., Rought, P., Garcia-Sakai, V., Silverwood, I. P., Easun, T. L., Li, M., Warren, M. R., Murray, C. A., Tang, C. C., Yang, S. & Schröder, M. (2016). *J. Am. Chem. Soc.*, **138**, 6352–6355.
 Rao, C. N. R., Natarajan, S. & Vaidhyanathan, R. (2004). *Angew. Chem. Int. Ed.*, **43**, 1466–1496.
 Rigaku OD (2020). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
 Sheldrick, G. M. (2015a). *Acta Cryst.*, **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.*, **C71**, 3–8.
 Stackhouse, C. A. & Ma, S. (2018). *Polyhedron*, **145**, 154–165.
 Suh, M. P. & Moon, H. R. (2007). *Advances in Inorganic Chemistry*, Vol. 59, edited by R. van Eldik & K. Bowman-James, pp. 39–79. San Diego: Academic Press.
 Suh, M. P., Park, H. J., Prasad, T. K. & Lim, D.-W. (2012). *Chem. Rev.*, **112**, 782–835.
 Taddei, M., Costantino, F., Vivani, R., Sabatini, S., Lim, S.-H. & Cohen, S. M. (2014). *Chem. Commun.*, **50**, 5737–5740.
 Tsymbal, L. V., Andriichuk, I. L., Lozan, V., Shova, S. & Lampeka, Y. D. (2022). *Acta Cryst.*, **E78**, 625–628.
 Vaidhyanathan, R., Mahmoudkhani, A. H. & Shimizu, G. K. H. (2009). *Can. J. Chem.*, **87**, 247–253.
 Vilela, S. M. F., Navarro, J. A. R., Barbosa, P., Mendes, R. F., Pérez-Sánchez, G., Nowell, H., Ananias, D., Figueiredo, F., Gomes, J. R. B., Tomé, J. P. C. & Paz, F. A. A. (2021). *J. Am. Chem. Soc.*, **143**, 1365–1376.
 Westrip, S. P. (2010). *J. Appl. Cryst.*, **43**, 920–925.
 Yatsimirskii, K. B. & Lampeka, Ya. D. (1985). *Physicochemistry of Metal Complexes with Macrocyclic Ligands*. Kiev: Naukova Dumka (in Russian).
 Yücesan, G., Zorlu, Y., Stricker, M. & Beckmann, J. (2018). *Coord. Chem. Rev.*, **369**, 105–122.
Synthesis and crystal structure of bis[trans-diaqua(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)nickel(II)] trans-(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)bis[4,4′,4′′-(1,3,5-trimethylbenzene-2,4,6-triy)tris(hydrogen phenylphosphonato-κO)]nickel(II) decahydrate

Liudmyla V. Tsymbal, Rodinel Ardeleanu, Sergiu Shova and Yaroslaw D. Lampeka

Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2020); cell refinement: CrysAlis PRO (Rigaku OD, 2020); data reduction: CrysAlis PRO (Rigaku OD, 2020); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: publCIF (Westrip, 2010).

Bis[trans-diaqua(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)nickel(II)] trans-(1,4,8,11-tetraazacyclotetradecane-κ⁴N¹,N⁴,N⁸,N¹¹)bis[4,4′,4′′-(1,3,5-trimethylbenzene-2,4,6-triy)tris(hydrogen phenylphosphonato-κO)]nickel(II) decahydrate

Crystal data

[Ni(C₁₀H₂₄N₄)(H₂O)₂]₂[Ni(C₁₀H₂₄N₄)(C₂₇H₂₄O₉P₃)]·10H₂O

Z = 1

F(000) = 1166

Dₐ = 1.427 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 5403 reflections

θ = 2.1–26.3°

μ = 0.72 mm⁻¹

T = 160 K

Prism, clear light colourless

0.40 × 0.10 × 0.10 mm

Data collection

Rigaku Xcalibur Eos diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1593 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2020)

Tₘᵋᵣᵢₙ = 0.701, Tₚₐₓᵢₙ = 1.000

23737 measured reflections

9657 independent reflections

6598 reflections with I > 2σ(I)

Rₑₘᵋᵣᵢₙ = 0.063

θₑₓₘₐₓ = 25.7°, θₑₘᵋᵢₙ = 2.1°

h = -11→12

k = -21→20

l = -21→21

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Supporting Information

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.067$

$wR(F^2) = 0.161$

$S = 1.02$

9657 reflections

629 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 4.2781P]$

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

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

$\Delta\rho_{\text{max}} = 0.67$ e Å$^{-3}$

$\Delta\rho_{\text{min}} = -0.46$ 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 ($U^2$)

| Atom | x     | y     | z     | $U_{eq}$/$U_{eq}$ |
|------|-------|-------|-------|-------------------|
| Ni1  | 1.000000 | 0.500000 | 1.000000 | 0.0228 (2) |
| P2   | 0.77348 (14) | 1.51832 (8) | 0.73137 (8) | 0.0273 (3) |
| P1   | 0.86291 (13) | 0.70402 (8) | 0.82874 (8) | 0.0243 (3) |
| P3   | 0.75955 (15) | 0.78200 (9) | 1.49060 (8) | 0.0332 (3) |
| O5   | 0.6838 (4) | 1.5710 (2) | 0.7750 (2) | 0.0380 (9) |
| C29  | 0.7561 (5) | 1.4015 (3) | 0.7965 (3) | 0.0241 (10) |
| O4   | 0.7456 (4) | 1.5452 (2) | 0.6413 (2) | 0.0333 (8) |
| O3W  | 1.0380 (3) | 0.6623 (2) | 0.6411 (2) | 0.0311 (8) |
| H3WA | 0.998703 | 0.703601 | 0.598132 | 0.047* |
| H3WB | 1.016063 | 0.687031 | 0.675752 | 0.047* |
| O4W  | 0.6258 (4) | 0.8895 (3) | 0.6511 (3) | 0.0607 (12) |
| H4WA | 0.622702 | 0.869018 | 0.615193 | 0.091* |
| H4WB | 0.655562 | 0.843018 | 0.696393 | 0.091* |
| C22  | 0.7292 (4) | 0.9758 (3) | 0.9717 (3) | 0.0193 (10) |
| C38  | 0.7501 (5) | 0.8505 (3) | 1.3753 (3) | 0.0274 (11) |
| C26  | 0.7310 (5) | 1.2190 (3) | 0.9041 (3) | 0.0230 (10) |
| N1   | 0.9914 (4) | 0.4354 (3) | 0.9286 (2) | 0.0275 (9) |
| H1   | 0.956271 | 0.481640 | 0.873064 | 0.033* |
| O3   | 0.7242 (4) | 0.7049 (2) | 0.7985 (2) | 0.0387 (9) |
| H3C  | 0.724711 | 0.656089 | 0.798510 | 0.058* |
| C34  | 0.7272 (4) | 0.9926 (3) | 1.1008 (3) | 0.0211 (10) |
| N2   | 1.1919 (4) | 0.5419 (3) | 0.9365 (3) | 0.0330 (10) |
| H2   | 1.173656 | 0.596679 | 0.881233 | 0.040* |
| C3   | 1.2935 (5) | 0.4794 (4) | 0.9119 (4) | 0.0421 (14) |
| H3A  | 1.320107 | 0.425875 | 0.965248 | 0.051* |
| H3B  | 1.378830 | 0.507709 | 0.878884 | 0.051* |
| O2   | 0.9773 (4) | 0.7334 (2) | 0.7517 (2) | 0.0349 (8) |
| O9   | 0.7490 (5) | 0.6880 (2) | 1.5017 (2) | 0.0490 (11) |
| H9C  | 0.757613 | 0.649777 | 1.553173 | 0.074* |
| C35  | 0.7357 (5) | 0.9486 (3) | 1.1963 (3) | 0.0245 (10) |
| Atom  | x     | y     | z     | U(eq)  |
|-------|-------|-------|-------|--------|
| C41   | 0.7258(5) | 0.9377(3) | 1.0620(3) | 0.0229(10) |
| C23   | 0.7243(5) | 1.0683(3) | 0.9212(3) | 0.0229(10) |
| C30   | 0.6330(5) | 1.3737(3) | 0.8509(3) | 0.0335(12) |
| H30   | 0.555907 | 1.416974 | 0.852158 | 0.040*   |
| C25   | 0.7243(5) | 1.1221(3) | 0.9602(3) | 0.0216(10) |
| C5    | 0.8806(6) | 0.3769(4) | 0.9791(3) | 0.0381(13) |
| H5A   | 0.916444 | 0.324112 | 1.029994 | 0.046*   |
| H5B   | 0.851180 | 0.356262 | 0.942372 | 0.046*   |
| C33   | 0.7319(5) | 1.1422(3) | 1.0923(3) | 0.0280(11) |
| H33A  | 0.769682 | 1.105369 | 1.147602 | 0.042*   |
| H33B  | 0.637231 | 1.170079 | 1.102996 | 0.042*   |
| H33C  | 0.791865 | 1.188533 | 1.053584 | 0.042*   |
| C39   | 0.6285(5) | 0.9036(3) | 1.3453(3) | 0.0321(12) |
| H39   | 0.549541 | 0.906986 | 1.385777 | 0.039*   |
| C42   | 0.7241(6) | 0.8387(3) | 1.1158(3) | 0.0333(12) |
| H42A  | 0.818887 | 0.807974 | 1.111379 | 0.050*   |
| H42B  | 0.661713 | 0.818665 | 1.094399 | 0.050*   |
| H42C  | 0.690678 | 0.825159 | 1.176739 | 0.050*   |
| O7    | 0.9019(4) | 0.7838(2) | 1.5071(2) | 0.0399(9)  |
| C36   | 0.8576(5) | 0.8993(3) | 1.2269(3) | 0.0283(11) |
| H36   | 0.938419 | 0.898840 | 1.186477 | 0.034*   |
| C19   | 0.7533(4) | 0.9154(3) | 0.9299(3) | 0.0194(10) |
| C21   | 0.6772(5) | 0.8176(3) | 0.8889(3) | 0.0282(11) |
| H21   | 0.603252 | 0.793241 | 0.844480 | 0.034*   |
| O8    | 0.6378(4) | 0.8126(3) | 1.5414(2) | 0.0476(10) |
| C20   | 0.6477(5) | 0.8787(3) | 0.9222(3) | 0.0287(11) |
| H20   | 0.553187 | 0.895677 | 0.940187 | 0.034*   |
| C2    | 1.2358(6) | 0.4512(4) | 0.8569(3) | 0.0407(14) |
| H2A   | 1.196217 | 0.505379 | 0.808660 | 0.049*   |
| H2B   | 1.314402 | 0.421415 | 0.830904 | 0.049*   |
| C37   | 0.8665(5) | 0.8500(3) | 1.3151(3) | 0.0306(12) |
| H37   | 0.952338 | 0.815768 | 1.334400 | 0.037*   |
| C32   | 0.7271(4) | 1.0848(3) | 1.0504(3) | 0.0211(10) |
| C24   | 0.7140(6) | 1.1079(3) | 0.8254(3) | 0.0314(12) |
| H24A  | 0.660985 | 1.072081 | 0.815897 | 0.047*   |
| H24B  | 0.808141 | 1.108441 | 0.793050 | 0.047*   |
| H24C  | 0.666278 | 1.168989 | 0.805139 | 0.047*   |
| Ni2   | 1.000000 | 1.000000 | 0.500000 | 0.0233(2)  |
| O1W   | 0.9604(4) | 0.8687(2) | 0.5872(2) | 0.0452(10) |
| H1WA  | 0.881040 | 0.872384 | 0.618973 | 0.068*   |
| H1WB  | 0.944450 | 0.844264 | 0.557414 | 0.068*   |
| N3    | 0.9605(4) | 0.9803(3) | 0.4004(2) | 0.0297(10) |
| H3    | 0.924717 | 0.921388 | 0.427638 | 0.036*   |
| C10   | 1.0986(5) | 0.9720(4) | 0.3496(3) | 0.0380(13) |
| H10A  | 1.128892 | 1.031639 | 0.311897 | 0.046*   |
| H10B  | 1.091906 | 0.945314 | 0.312160 | 0.046*   |
| N4    | 0.7940(5) | 1.0447(3) | 0.5321(3) | 0.0377(11) |
| H4    | 0.744740 | 0.990779 | 0.568716 | 0.045*   |
supporting information

C9  0.7973 (6)  1.0856 (4)  0.5889 (3)  0.0408 (14)
H9A  0.703665  1.090138  0.621780  0.049*
H9B  0.824723  1.146279  0.553175  0.049*
C7  0.7183 (6)  1.0577 (4)  0.4022 (3)  0.0418 (14)
H7A  0.689758  0.997677  0.440380  0.050*
H7B  0.646435  1.092349  0.362786  0.050*
C6  0.8543 (5)  1.0479 (3)  0.3477 (3)  0.0350 (12)
H6A  0.837243  1.030970  0.304733  0.042*
H6B  0.891090  1.106025  0.315290  0.042*
C8  0.7168 (6)  1.1019 (4)  0.4586 (4)  0.0434 (14)
H8A  0.758644  1.158069  0.423021  0.052*
H8B  0.618830  1.116899  0.480465  0.052*
Ni3  0.500000  1.500000  0.500000  0.0280 (2)
O2W  0.5104 (4)  1.5055 (2)  0.6168 (2)  0.0374 (9)
H2WA  0.451405  1.548647  0.620771  0.056*
H2WB  0.589347  1.520291  0.613928  0.056*
N5  0.3476 (5)  1.4161 (3)  0.5683 (3)  0.0436 (12)
H5  0.333782  1.392139  0.529340  0.052*
O7W  1.3235 (4)  0.6425 (3)  0.6174 (3)  0.0660 (14)
H7WA  1.366682  0.665639  0.637536  0.099*
H7WB  1.244232  0.671069  0.624896  0.099*
N6  0.6644 (5)  1.3992 (3)  0.5280 (3)  0.0464 (12)
H6  0.671366  1.374659  0.486100  0.056*
C14  0.7918 (6)  1.4389 (5)  0.5068 (4)  0.0558 (18)
H14A  0.873557  1.397569  0.499126  0.067*
H14B  0.802863  1.450247  0.554899  0.067*
O6W  1.2369 (4)  0.7283 (3)  0.7946 (2)  0.0541 (11)
H6WA  1.317921  0.726218  0.763661  0.081*
H6WB  1.177461  0.729258  0.764271  0.081*
O5W  1.4763 (3)  0.7022 (2)  0.6828 (2)  0.0395 (9)
H5WA  1.538341  0.732237  0.641517  0.059*
H5WB  1.524801  0.660758  0.722817  0.059*
O1  0.9002 (4)  0.6178 (2)  0.9039 (2)  0.0326 (8)
O6  0.9335 (4)  1.5164 (2)  0.7321 (2)  0.0402 (9)
H6C  0.960853  1.564111  0.692096  0.060*
C17  0.9212 (5)  0.8304 (3)  0.8664 (3)  0.0229 (10)
H17  1.015334  0.815323  0.846193  0.027*
C16  0.8155 (5)  0.7918 (3)  0.8618 (3)  0.0216 (10)
C18  0.8904 (5)  0.8913 (3)  0.9005 (3)  0.0238 (10)
H18  0.964113  0.916614  0.903815  0.029*
C40  0.6201 (5)  0.9525 (3)  1.2561 (3)  0.0302 (12)
H40  0.535465  0.988328  1.236326  0.036*
C1  1.1247 (6)  0.3895 (3)  0.9048 (3)  0.0375 (13)
H1A  1.108999  0.364727  0.867554  0.045*
H1B  1.157958  0.339182  0.958205  0.045*
C28  0.8659 (5)  1.3371 (3)  0.7957 (3)  0.0323 (12)
H28  0.950712  1.353974  0.758385  0.039*
C31  0.6206 (5)  1.2844 (3)  0.9032 (3)  0.0319 (12)
### Atomic displacement parameters (Å²)

|      | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| Ni1  | 0.0278 (5) | 0.0183 (4) | 0.0225 (4) | 0.0031 (4) | −0.0059 (3) | −0.0108 (4) |
| P2   | 0.0380 (8) | 0.0178 (6) | 0.0273 (7) | −0.0020 (6) | −0.0117 (6) | −0.0089 (5) |
| P1   | 0.0314 (7) | 0.0195 (6) | 0.0258 (6) | 0.0026 (6) | −0.0079 (5) | −0.0139 (5) |
| P3   | 0.0495 (9) | 0.0290 (7) | 0.0222 (7) | −0.0109 (7) | −0.0112 (6) | −0.0074 (6) |
| O5   | 0.056 (2)  | 0.0220 (18) | 0.042 (2)  | 0.0005 (18) | −0.0129 (18) | −0.0184 (17) |
| C29  | 0.031 (3)  | 0.023 (2)  | 0.019 (2)  | 0.000 (2)   | −0.0063 (19) | −0.010 (2)  |
| O4   | 0.051 (2)  | 0.0229 (18) | 0.0265 (18) | −0.0077 (17) | −0.0132 (16) | −0.0072 (15) |
| O3W  | 0.0317 (19) | 0.0298 (19) | 0.0354 (19) | 0.0021 (16) | −0.0082 (15) | −0.0185 (16) |
| O4W  | 0.064 (3)  | 0.059 (3)  | 0.060 (3)  | −0.013 (2)  | −0.008 (2)  | −0.026 (2)  |
| C22  | 0.017 (2)  | 0.022 (2)  | 0.020 (2)  | −0.002 (2)  | 0.0003 (18) | −0.012 (2)  |
| C38  | 0.040 (3)  | 0.022 (2)  | 0.025 (3)  | −0.007 (2)  | −0.011 (2)  | −0.010 (2)  |
| C26  | 0.030 (3)  | 0.019 (2)  | 0.022 (2)  | −0.002 (2)  | −0.005 (2)  | −0.011 (2)  |
| N1   | 0.036 (2)  | 0.021 (2)  | 0.026 (2)  | 0.0064 (19) | −0.0090 (18) | −0.0131 (18) |
| O3   | 0.049 (2)  | 0.027 (2)  | 0.054 (2)  | 0.0082 (18) | −0.0240 (18) | −0.0272 (19) |
| C34  | 0.019 (2)  | 0.025 (2)  | 0.021 (2)  | 0.006 (2)   | −0.0042 (18) | −0.014 (2)  |
| N2   | 0.039 (3)  | 0.031 (2)  | 0.030 (2)  | −0.003 (2)  | −0.0034 (19) | −0.016 (2)  |
| C3   | 0.033 (3)  | 0.052 (4)  | 0.046 (3)  | −0.004 (3)  | 0.006 (2)   | −0.032 (3)  |
| O2   | 0.047 (2)  | 0.031 (2)  | 0.0312 (19) | −0.0057 (17) | 0.0045 (16) | −0.0216 (17) |
| O9   | 0.090 (3)  | 0.034 (2)  | 0.028 (2)  | −0.021 (2)  | −0.022 (2)  | −0.0065 (17) |
| C35  | 0.028 (3)  | 0.023 (2)  | 0.024 (2)  | −0.004 (2)  | −0.004 (2)  | −0.012 (2)  |
| C41  | 0.023 (2)  | 0.019 (2)  | 0.027 (2)  | 0.000 (2)   | −0.0026 (19) | −0.012 (2)  |
| C23  | 0.026 (3)  | 0.022 (2)  | 0.019 (2)  | 0.004 (2)   | −0.0033 (19) | −0.010 (2)  |
| C30  | 0.028 (3)  | 0.022 (3)  | 0.046 (3)  | 0.003 (2)   | −0.006 (2)  | −0.014 (2)  |
| C25  | 0.021 (2)  | 0.018 (2)  | 0.025 (2)  | 0.001 (2)   | −0.0017 (19) | −0.010 (2)  |
| C5   | 0.053 (4)  | 0.030 (3)  | 0.034 (3)  | −0.007 (3)  | −0.010 (3)  | −0.014 (2)  |
| C33  | 0.035 (3)  | 0.022 (2)  | 0.031 (3)  | 0.000 (2)   | −0.008 (2)  | −0.016 (2)  |
C39  0.033 (3)  0.040 (3)  0.023 (3)  −0.007 (3)  −0.003 (2)  −0.013 (2)
C42  0.052 (3)  0.021 (3)  0.027 (3)  −0.004 (2)  −0.009 (2)  −0.010 (2)
O7   0.053 (2)  0.038 (2)  0.0282 (19)  −0.0107 (19)  −0.0119 (17)  −0.0096 (17)
C36  0.038 (3)  0.025 (3)  0.024 (3)  0.001 (2)  −0.006 (2)  −0.014 (2)
C19  0.023 (2)  0.018 (2)  0.015 (2)  0.001 (2)  −0.0015 (18)  −0.0077 (19)
C21  0.026 (3)  0.032 (3)  0.036 (3)  −0.002 (2)  −0.006 (2)  −0.023 (2)
O8   0.054 (2)  0.053 (3)  0.0258 (19)  −0.001 (2)  −0.0044 (17)  −0.0116 (19)
C20  0.023 (3)  0.033 (3)  0.036 (3)  0.004 (2)  −0.001 (2)  −0.024 (2)
C2   0.036 (3)  0.048 (4)  0.041 (3)  0.010 (3)  −0.005 (2)  −0.029 (3)
C37  0.038 (3)  0.025 (3)  0.003 (3)  −0.002 (2)  −0.009 (2)  −0.019 (2)
C19  0.023 (2)  0.018 (2)  0.015 (2)  0.001 (2)  −0.0015 (18)  −0.0077 (19)
C21  0.026 (3)  0.032 (3)  0.036 (3)  −0.002 (2)  −0.006 (2)  −0.023 (2)
O8   0.054 (2)  0.053 (3)  0.0258 (19)  −0.001 (2)  −0.0044 (17)  −0.0116 (19)
C20  0.023 (3)  0.033 (3)  0.036 (3)  0.004 (2)  −0.001 (2)  −0.024 (2)
C2   0.036 (3)  0.048 (4)  0.041 (3)  0.010 (3)  −0.005 (2)  −0.029 (3)
C37  0.038 (3)  0.025 (3)  0.003 (3)  −0.002 (2)  −0.009 (2)  −0.019 (2)
C19  0.023 (2)  0.018 (2)  0.015 (2)  0.001 (2)  −0.0015 (18)  −0.0077 (19)
C21  0.026 (3)  0.032 (3)  0.036 (3)  −0.002 (2)  −0.006 (2)  −0.023 (2)
O8   0.054 (2)  0.053 (3)  0.0258 (19)  −0.001 (2)  −0.0044 (17)  −0.0116 (19)
C20  0.023 (3)  0.033 (3)  0.036 (3)  0.004 (2)  −0.001 (2)  −0.024 (2)
C2   0.036 (3)  0.048 (4)  0.041 (3)  0.010 (3)  −0.005 (2)  −0.029 (3)
C37  0.038 (3)  0.025 (3)  0.003 (3)  −0.002 (2)  −0.009 (2)  −0.019 (2)
C19  0.023 (2)  0.018 (2)  0.015 (2)  0.001 (2)  −0.0015 (18)  −0.0077 (19)
C21  0.026 (3)  0.032 (3)  0.036 (3)  −0.002 (2)  −0.006 (2)  −0.023 (2)
O8   0.054 (2)  0.053 (3)  0.0258 (19)  −0.001 (2)  −0.0044 (17)  −0.0116 (19)
C20  0.023 (3)  0.033 (3)  0.036 (3)  0.004 (2)  −0.001 (2)  −0.024 (2)
C2   0.036 (3)  0.048 (4)  0.041 (3)  0.010 (3)  −0.005 (2)  −0.029 (3)
### Geometric parameters (Å, °)

| Bond/Distance | Value | Description |
|---------------|-------|-------------|
| Ni1—N1i       | 2.067 (4) | C24—H24A 0.9800 |
| Ni1—N1        | 2.067 (4) | C24—H24B 0.9800 |
| Ni1—N2        | 2.064 (4) | C24—H24C 0.9800 |
| Ni1—N2i       | 2.064 (4) | Ni2—N3u 2.072 (4) |
| Ni1—O1i       | 2.134 (3) | Ni2—N3 2.072 (4) |
| Ni1—O1        | 2.134 (3) | Ni2—N4 2.076 (4) |
| P2—O5         | 1.495 (4) | Ni2—N4u 2.076 (4) |
| P2—C29        | 1.804 (5) | Ni2—O1Wu 2.105 (4) |
| P2—O4         | 1.502 (3) | Ni2—O1W 2.105 (4) |
| P2—O6         | 1.576 (4) | O1W—H1WA 0.8701 |
| P1—O3         | 1.570 (4) | O1W—H1WB 0.8691 |
| P1—O2         | 1.518 (3) | N3—H3 1.0000 |
| P1—O1         | 1.483 (3) | N3—C10 1.481 (6) |
| P1—C16        | 1.811 (5) | N3—C6 1.479 (6) |
| P3—C38        | 1.813 (5) | C10—H10A 0.9900 |
| P3—O9         | 1.562 (4) | C10—H10B 0.9900 |
| P3—O7         | 1.506 (4) | C10—C9u 1.496 (7) |
| P3—O8         | 1.499 (4) | N4—H4 1.0000 |
| C29—C30       | 1.391 (7) | N4—C9 1.486 (6) |
| C29—C28       | 1.381 (7) | N4—C8 1.457 (7) |
| O3W—H3WA      | 0.8523  | C9—H9A 0.9900 |
| O3W—H3WB      | 0.8700  | C9—H9B 0.9900 |
| O4W—H4WA      | 0.8687  | C7—H7A 0.9900 |
| O4W—H4WB      | 0.8702  | C7—H7B 0.9900 |
| C22—C41       | 1.400 (6) | C7—C6 1.504 (7) |
| C22—C23       | 1.402 (6) | C7—C8 1.513 (7) |
| C22—C19       | 1.497 (6) | C6—H6A 0.9900 |
| C38—C39       | 1.380 (7) | C6—H6B 0.9900 |
| C38—C37       | 1.390 (7) | C8—H8A 0.9900 |
| C26—C25       | 1.488 (6) | C8—H8B 0.9900 |
| C26—C31       | 1.388 (6) | Ni3—N5 2.070 (4) |
| C26—C27       | 1.392 (6) | Ni3—N5ii 2.070 (5) |
| N1—H1         | 1.0000  | Ni3—N6 2.056 (5) |
| N1—C5         | 1.482 (6) | Ni3—N6ii 2.056 (5) |
| N1—C1         | 1.474 (6) | Ni3—O2Wii 2.137 (3) |
| O3—H3C        | 0.8400  | Ni3—O2W 2.136 (3) |
| C34—C35       | 1.497 (6) | O2W—H2WA 0.8638 |
| C34—C41       | 1.414 (6) | O2W—H2WB 0.8553 |
| C34—C32       | 1.401 (6) | N5—H5 1.0000 |
| N2—H2         | 1.0000  | N5—C15 1.497 (7) |
| N2—C3         | 1.469 (6) | N5—C11 1.431 (8) |
| N2—C4         | 1.477 (6) | O7W—H7WA 0.8613 |
| C3—H3A        | 0.9900  | O7W—H7WB 0.8521 |
| C3—H3B        | 0.9900  | N6—H6 1.0000 |
| C3—C2         | 1.521 (7) | N6—C14 1.452 (7) |
| O9—H9C        | 0.8400  | N6—C13 1.487 (8) |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| C35—C36      | 1.368 (7)    | C14—H14A     | 0.9900       |
| C35—C40      | 1.392 (6)    | C14—H14B     | 0.9900       |
| C41—C42      | 1.507 (6)    | C14—C15iii   | 1.507 (9)    |
| C23—C25      | 1.396 (6)    | O6W—H6WA     | 0.8706       |
| C23—C24      | 1.510 (6)    | O6W—H6WB     | 0.8688       |
| C30—H30      | 0.9500       | O5W—H5WA     | 0.8696       |
| C30—C31      | 1.382 (7)    | O5W—H5WB     | 0.8704       |
| C25—C32      | 1.409 (6)    | O6—H6C       | 0.8400       |
| C5—H5A       | 0.9900       | C17—H17      | 0.9500       |
| C5—H5B       | 0.9900       | C17—C16      | 1.387 (6)    |
| C5—C4′       | 1.513 (7)    | C17—C18      | 1.396 (6)    |
| C33—H33A     | 0.9800       | C18—H18      | 0.9500       |
| C33—H33B     | 0.9800       | C40—H40      | 0.9500       |
| C33—H33C     | 0.9800       | C1—H1A       | 0.9900       |
| C33—C32      | 1.506 (6)    | C1—H1B       | 0.9900       |
| C39—H39      | 0.9500       | C28—H28      | 0.9500       |
| C39—C40      | 1.399 (6)    | C28—C27      | 1.375 (7)    |
| C42—H42A     | 0.9800       | C31—H31      | 0.9500       |
| C42—H42B     | 0.9800       | C13—H13A     | 0.9900       |
| C42—H42C     | 0.9800       | C13—H13B     | 0.9900       |
| C36—H36      | 0.9500       | C13—C12      | 1.506 (9)    |
| C36—C37      | 1.385 (6)    | C15—H15A     | 0.9900       |
| C19—C20      | 1.391 (6)    | C15—H15B     | 0.9900       |
| C19—C18      | 1.393 (6)    | C11—H11A     | 0.9900       |
| C21—H21      | 0.9500       | C11—H11B     | 0.9900       |
| C21—C20      | 1.389 (6)    | C11—C12      | 1.514 (10)   |
| C21—C16      | 1.398 (6)    | C27—H27      | 0.9500       |
| C20—H20      | 0.9500       | C12—H12A     | 0.9900       |
| C2—H2A       | 0.9900       | C12—H12B     | 0.9900       |
| C2—H2B       | 0.9900       | C4—H4A       | 0.9900       |
| C2—C1        | 1.513 (7)    | C4—H4B       | 0.9900       |
| C37—H37      | 0.9500       |               |              |

| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| N1—Ni1—N1i  | 180.0        | N4—Ni2—O1W   | 89.10 (17)   |
| N1—Ni1—O1i  | 91.79 (14)   | N4′—Ni2—O1W  | 90.90 (17)   |
| N1′—Ni1—O1i | 88.21 (14)   | N4′—Ni2—O1W ″| 89.10 (17)   |
| N1′—Ni1—O1  | 91.79 (14)   | N4—Ni2—N4′   | 180.00 (13)  |
| N1—Ni1—O1   | 88.21 (14)   | Ni2—O1W—H1WA | 106.8        |
| N1—Ni1—N2i  | 85.31 (16)   | Ni2—O1W—H1WB | 108.1        |
| N1′—Ni1—N2  | 85.31 (16)   | H1WA—O1W—H1WB| 104.5        |
| N1′—Ni1—N2i | 94.69 (16)   | Ni2—N3—H3    | 107.3        |
| N1—Ni1—N2   | 94.69 (16)   | C10—N3—Ni2   | 105.7 (3)    |
| N2′—Ni1—N2  | 180.0        | C10—N3—H3    | 107.3        |
| N2—Ni1—O1   | 90.47 (15)   | C6—N3—Ni2    | 114.6 (3)    |
| N2—Ni1—O1   | 89.53 (15)   | C6—N3—H3     | 107.3        |
| N2′—Ni1—O1i | 89.53 (15)   | C6—N3—C10    | 114.3 (4)    |
| N2′—Ni1—O1i | 90.47 (15)   | N3—C10—H10A  | 109.9        |
| O1′—Ni1—O1  | 180.0        | N3—C10—H10B  | 109.9        |
O5—P2—C29 110.3 (2)  N3—C10—C9\textsuperscript{ii} 109.1 (4) 
O5—P2—O4 115.4 (2)  H10A—C10—H10B 108.3 
O5—P2—O6 111.3 (2)  C9\textsuperscript{ii}—C10—H10A 109.9 
O4—P2—C29 108.0 (2)  C9\textsuperscript{ii}—C10—H10B 109.9 
O4—P2—O6 110.5 (2)  Ni2—N4—H4 106.9 
O6—P2—C29 100.2 (2)  C9—N4—Ni2 106.4 (3) 
O3—P1—C16 102.1 (2)  C9—N4—H4 106.9 
O2—P1—O3 110.2 (2)  C8—N4—Ni2 115.2 (3) 
O2—P1—C16 107.1 (2)  C8—N4—H4 106.9 
O1—P1—O3 111.4 (2)  C8—N4—C9 114.0 (4) 
O1—P1—O2 115.2 (2)  C10\textsuperscript{ii}—C9—H9A 110.1 
O1—P1—C16 110.06 (19)  C10\textsuperscript{ii}—C9—H9B 110.1 
O9—P3—C38 101.5 (2)  N4—C9—C10\textsuperscript{ii} 108.1 (4) 
O7—P3—C38 107.6 (2)  N4—C9—H9A 110.1 
O7—P3—O9 109.8 (2)  N4—C9—H9B 110.1 
O8—P3—C38 109.4 (2)  H9A—C9—H9B 110.1 
O8—P3—O9 111.8 (2)  H7A—C7—H7B 110.1 
O8—P3—O7 115.7 (2)  C6—C7—H7A 108.1 
C30—C29—P2 120.9 (4)  C6—C7—H7B 108.1 
C28—C29—P2 121.0 (4)  C6—C7—C8 116.9 (5) 
C28—C29—C30 118.0 (4)  C8—C7—H7A 116.9 (5) 
H3WA—O3W—H3WB 98.3  C8—C7—H7B 116.9 (5) 
H4WA—O4W—H4WB 104.4  N3—C6—C7 112.6 (4) 
C41—C22—C23 120.1 (4)  N3—C6—H6A 109.1 
C41—C22—C19 118.6 (4)  N3—C6—H6B 109.1 
C23—C22—C19 120.9 (4)  C7—C6—H6A 109.1 
C39—C38—P3 121.3 (4)  C7—C6—H6B 109.1 
C39—C38—C37 118.6 (4)  C6A—C6—H6B 108.1 
C37—C38—P3 120.1 (4)  N4—C8—C7 111.9 (5) 
C31—C26—C25 123.6 (4)  N4—C8—H8A 109.2 
C31—C26—C27 116.3 (4)  N4—C8—H8B 109.2 
C27—C26—C25 120.1 (4)  C7—C8—H8A 109.2 
Ni1—N1—H1 106.9  C7—C8—H8B 109.2 
C5—N1—Ni1 104.8 (3)  H8A—C8—H8B 107.9 
C5—N1—H1 106.9  O2W—Ni3—O2W\textsuperscript{ii} 180.0 
C1—N1—Ni1 116.4 (3)  N5\textsuperscript{iii}—Ni3—O2W 91.54 (15) 
C1—N1—H1 106.9  N5—Ni3—O2W 88.46 (15) 
C1—N1—C5 114.2 (4)  N5\textsuperscript{iii}—Ni3—O2W\textsuperscript{iii} 88.46 (15) 
P1—O3—H3C 109.5  N5—Ni3—O2W\textsuperscript{iii} 91.54 (15) 
C41—C34—C35 117.8 (4)  N5—Ni3—N5\textsuperscript{iii} 180.0 
C32—C34—C35 121.4 (4)  N6—Ni3—O2W 89.19 (16) 
C32—C34—C41 120.8 (4)  N6\textsuperscript{iii}—Ni3—O2W 90.81 (16) 
Ni1—N2—H2 106.6  N6\textsuperscript{iii}—Ni3—O2W\textsuperscript{iii} 89.19 (16) 
C3—N2—Ni1 116.1 (3)  N6—Ni3—O2W\textsuperscript{iii} 90.81 (16) 
C3—N2—H2 106.6  N5—Ni3—N5\textsuperscript{iii} 180.0 
C3—N2—C4 114.4 (4)  N5—Ni3—N6 94.8 (2) 
C4—N2—Ni1 106.0 (3)  N5\textsuperscript{iii}—Ni3—N6 85.2 (2) 
C4—N2—H2 106.6  N5\textsuperscript{iii}—Ni3—N6\textsuperscript{iii} 94.8 (2)
| Bond/Angle | Value |
|-----------|-------|
| N2—C3—H3A | 109.1 |
| N2—C3—H3B | 109.1 |
| N2—C3—C2  | 112.3 (4) |
| H3A—C3—H3B | 107.9 |
| H3A—C3—H3A | 109.1 |
| C2—C3—H3A | 109.1 |
| C2—C3—H3B | 109.1 |
| P3—O9—H9C | 109.5 |
| C36—C35—C34 | 119.7 (4) |
| C36—C35—C40 | 118.5 (4) |
| C40—C35—C34 | 121.7 (4) |
| C22—C41—C34 | 119.4 (4) |
| C22—C41—C42 | 119.5 (4) |
| C34—C41—C42 | 121.1 (4) |
| C22—C23—C24 | 118.7 (4) |
| C25—C23—C22 | 120.0 (4) |
| C25—C23—C24 | 121.2 (4) |
| C29—C30—H30 | 119.4 |
| C31—C30—C29 | 121.2 (5) |
| C31—C30—H30 | 119.4 |
| C23—C25—C26 | 118.9 (4) |
| C23—C25—C32 | 120.8 (4) |
| C32—C25—C26 | 120.2 (4) |
| N1—C5—H5A | 110.0 |
| N1—C5—H5B | 110.0 |
| C32—C33—H33A | 109.5 |
| C32—C33—H33B | 109.5 |
| C32—C33—H33C | 109.5 |
| C38—C39—H39 | 119.6 |
| C38—C39—C40 | 120.8 (5) |
| C40—C39—H39 | 119.6 |
| C41—C42—H42A | 109.5 |
| C41—C42—H42B | 109.5 |
| C41—C42—H42C | 109.5 |
| H42A—C42—H42B | 109.5 |
| H42A—C42—H42C | 109.5 |
| C35—C36—H36 | 119.1 |
| C35—C36—C37 | 121.8 (5) |
| C37—C36—H36 | 119.1 |
| C20—C19—C22 | 124.0 (4) |
| C20—C19—C18 | 117.9 (4) |

Bond/Angle | Value |
|-----------|-------|
| N6—Ni3—N6 | 180.0 |
| Ni3—O2W—H2WA | 110.2 |
| Ni3—O2W—H2WB | 109.7 |
| H2WA—O2W—H2WB | 103.1 |
| Ni3—N5—H5 | 106.1 |
| C15—N5—Ni3 | 105.8 (4) |
| C15—N5—H5 | 106.1 |
| C15—N5—C15 | 114.5 (5) |
| H2WA—O7W—H7WB | 94.0 |
| Ni3—N6—H6 | 106.1 |
| C14—N6—Ni3 | 107.9 (4) |
| C14—N6—H6 | 106.1 |
| C14—N6—C15 | 114.0 (5) |
| Ni3—N6—H6 | 106.1 |
| N6—C14—H14A | 109.8 |
| N6—C14—H14B | 109.8 |
| N6—C14—C15iii | 109.4 (5) |
| H14A—C14—H14B | 108.2 |
| C15iii—C14—H14A | 109.8 |
| C15iii—C14—H14B | 109.8 |
| H6WA—O6W—H6WB | 104.5 |
| H5WA—O5W—H5WB | 104.5 |
| P1—O1—Ni1 | 167.3 (2) |
| P2—O6—H6C | 109.5 |
| C16—C17—H17 | 119.7 |
| C16—C17—C18 | 120.5 (4) |
| C18—C17—H17 | 119.7 |
| C21—C16—P1 | 122.4 (4) |
| C17—C16—P1 | 118.7 (3) |
| C17—C16—C21 | 118.7 (4) |
| C19—C18—C17 | 121.1 (4) |
| C19—C18—H18 | 119.5 |
| C17—C18—H18 | 119.5 |
| C35—C40—C39 | 120.0 (5) |
| C35—C40—H40 | 120.0 |
| C39—C40—H40 | 120.0 |
| N1—C1—C2 | 112.0 (4) |
| N1—C1—H1A | 109.2 |
| C2—C1—H1B | 109.2 |
| C2—C1—H1A | 109.2 |
| C29—C28—H28 | 120.0 |
| C27—C28—C29 | 120.1 (5) |
| C27—C28—H28 | 120.0 |
| Bond/Distance | Angle | Bond/Distance | Angle |
|--------------|-------|--------------|-------|
| C18—C19—C22 | 118.0 (4) | C26—C31—H31 | 119.3 |
| C20—C21—H21 | 119.9 | C30—C31—C26 | 121.4 (4) |
| C20—C21—C16 | 120.2 (4) | C30—C31—H31 | 119.3 |
| C16—C21—H21 | 119.9 | N6—C13—H13A | 109.2 |
| C19—C20—H20 | 119.3 | N6—C13—H13B | 109.2 |
| C21—C20—C19 | 121.5 (4) | N6—C13—C12 | 112.1 (5) |
| C21—C20—H20 | 119.3 | H13A—C13—H13B | 107.9 |
| C3—C2—H2A | 108.4 | C12—C13—H13A | 109.2 |
| C3—C2—H2B | 108.4 | C12—C13—H13B | 109.2 |
| H2A—C2—H2B | 107.5 | N5—C15—C14 | 110.1 (5) |
| C1—C2—C3 | 115.4 (4) | N5—C15—H15A | 109.6 |
| C1—C2—H2A | 108.4 | N5—C15—H15B | 109.6 |
| C1—C2—H2B | 108.4 | C14—C15—H15A | 109.6 |
| C38—C37—H37 | 120.0 | C14—C15—H15B | 109.6 |
| C36—C37—C38 | 120.1 (5) | H15A—C15—H15B | 108.2 |
| C36—C37—H37 | 120.0 | N5—C11—H11A | 109.3 |
| C34—C32—C25 | 118.8 (4) | N5—C11—H11B | 109.3 |
| C34—C32—C33 | 120.2 (4) | N5—C11—C12 | 111.5 (5) |
| C25—C32—C33 | 121.0 (4) | H11A—C11—H11B | 108.0 |
| C23—C24—H24A | 109.5 | C12—C11—H11A | 109.3 |
| C23—C24—H24B | 109.5 | C12—C11—H11B | 109.3 |
| C23—C24—H24C | 109.5 | C26—C27—H27 | 118.5 |
| H24A—C24—H24B | 109.5 | C28—C27—C26 | 123.0 (5) |
| H24B—C24—H24C | 109.5 | C28—C27—H27 | 118.5 |
| O1W—Ni2—O1W | 180.0 | C13—C12—C11 | 118.5 (6) |
| N3—Ni2—O1W | 88.65 (15) | C13—C12—H12A | 107.7 |
| N3—Ni2—O1W | 88.65 (15) | C13—C12—H12B | 107.7 |
| N3—Ni2—O1W | 91.35 (15) | C11—C12—H12A | 107.7 |
| N3—Ni2—O1W | 91.35 (15) | C11—C12—H12B | 107.7 |
| N3—Ni2—N3 | 180.0 | N2—C4—H4A | 110.2 |
| N3—Ni2—N3 | 84.66 (16) | N2—C4—H4B | 110.2 |
| N3—Ni2—N3 | 95.34 (16) | C5—C4—H4A | 110.2 |
| N3—Ni2—N4 | 95.34 (16) | C5—C4—H4B | 110.2 |
| Ni1—Ni2—O1W | 44.0 (4) | H4A—C4—H4B | 108.5 |
| Ni1—Ni2—O1W | 44.0 (4) | O7—P3—C38—C37 | 38.0 (5) |
| Ni1—Ni2—C5—C4 | 55.0 (5) | C36—C35—C40—C39 | −2.7 (7) |
| Ni1—Ni2—C5—C4 | 55.3 (5) | C19—C22—C41—C34 | 169.3 (4) |
| Ni1—Ni2—C5—C4 | −42.6 (4) | C19—C22—C41—C42 | −9.3 (6) |
| P2—C29—C30—C31 | −177.8 (4) | C19—C22—C23—C25 | −169.7 (4) |
| P2—C29—C28—C27 | 177.0 (4) | C19—C22—C23—C24 | 12.3 (6) |
| P3—C28—C39—C40 | −176.5 (4) | O8—P3—C38—C39 | −15.9 (5) |
| P3—C28—C37—C36 | 177.2 (4) | O8—P3—C38—C37 | 164.4 (4) |
| O5—P2—C29—C30 | 29.0 (5) | C20—C19—C18—C17 | −1.5 (7) |
| O5—P2—C29—C28 | −149.2 (4) | C20—C19—C16—C17 | 173.3 (4) |
| C29—C30—C31—C26 | 0.7 (8) | C20—C21—C16—C17 | −2.0 (7) |
| Bond  | Distance (Å) | Bond Angle (°) |
|-------|--------------|----------------|
| C29—C28—C27—C26 | 1.1 (8) | C37—C38—C39—C40 | 3.2 (7) |
| O4—P2—C29—C30 | -98.0 (4) | C32—C34—C35—C36 | -105.9 (5) |
| O4—P2—C29—C28 | 83.8 (4) | C32—C34—C35—C40 | 77.4 (6) |
| C22—C23—C25—C26 | 175.0 (4) | C32—C34—C41—C22 | 2.2 (7) |
| C22—C23—C25—C32 | -1.0 (7) | C32—C34—C41—C42 | -179.2 (4) |
| C22—C19—C20—C21 | -174.9 (4) | C24—C23—C25—C26 | -7.1 (7) |
| C22—C19—C18—C17 | 175.5 (4) | C24—C23—C25—C32 | 176.9 (4) |
| C38—C39—C40—C35 | -0.6 (8) | Ni2—N3—C10—C9i | 43.0 (5) |
| C26—C25—C32—C34 | -177.1 (4) | Ni2—N3—C6—C7 | -54.7 (5) |
| C26—C25—C32—C33 | 2.1 (7) | Ni2—N4—C9—C10i | -41.1 (5) |
| O3—P1—O1—Ni1 | 149.1 (9) | Ni2—N4—C8—C7 | 55.8 (5) |
| O3—P1—O1—Ni1 | 25.1 (4) | C10—N3—C6—C7 | -176.9 (4) |
| O3—P1—C16—C21 | -159.6 (3) | C9—N4—C8—C7 | 179.2 (5) |
| O3—P1—C16—C21 | 71.1 (6) | C6—N3—C10—C9i | 170.0 (4) |
| O2—P1—O1—Ni1 | 22.6 (10) | C34—C35—C6—C3 | -71.3 (6) |
| O2—P1—O1—Ni1 | 141.0 (4) | Ni3—N5—C15—C14iii | 37.7 (5) |
| O2—P1—C16—C21 | -43.8 (4) | Ni3—N5—C11—C12 | -53.9 (6) |
| O2—P1—C16—C21 | 102.4 (4) | Ni3—N6—C14—C15iii | -39.2 (5) |
| O9—P3—C38—C39 | -77.3 (4) | Ni3—N6—C13—C12 | 52.9 (6) |
| O9—P3—C38—C39 | 175.0 (4) | C35—C34—C11—C12 | 69.6 (7) |
| C35—C34—C32—C33 | -173.4 (4) | C14—N6—C13—C11 | -69.2 (7) |
| C35—C34—C32—C33 | 174.0 (4) | C6—C7—C8—N4 | -71.7 (6) |
| N2—C3—C2—C1 | -71.6 (6) | C8—N4—C9—C10i | -169.2 (4) |
| C3—N2—C4—C5i | -171.9 (4) | C8—C7—C6—N3 | 71.3 (6) |
| C3—C2—C1—N1 | 71.1 (6) | Ni3—N5—C15—C14iii | 37.7 (5) |
| C2—C1—C2—C3 | -22.6 (10) | Ni3—N5—C11—C12 | -53.9 (6) |
| C2—C1—C2—C3 | 141.0 (4) | Ni3—N6—C14—C15iii | -39.2 (5) |
| O2—P1—C16—C21 | -43.8 (4) | Ni3—N6—C13—C12 | 52.9 (6) |
| O2—P1—C16—C21 | 102.4 (4) | N5—C11—C12—C13 | 69.6 (7) |
| O2—P1—C16—C21 | -77.3 (4) | N6—C13—C12—C11 | -69.2 (7) |
| C35—C34—C41—C22 | -175.0 (4) | C14—N6—C13—C12 | 178.9 (5) |
| C35—C34—C41—C22 | 3.6 (7) | O1—P1—C16—C21 | -93.2 (4) |
| C35—C34—C32—C25 | 177.6 (4) | O1—P1—C16—C17 | 82.0 (4) |
| C35—C34—C32—C33 | -1.6 (7) | O6—P2—C29—C30 | 146.4 (4) |
| C35—C36—C37—C38 | -0.8 (8) | O6—P2—C29—C28 | -31.8 (4) |
| C41—C22—C23—C25 | 3.8 (7) | C16—P1—O1—Ni1 | -98.5 (10) |
| C41—C22—C23—C24 | -174.2 (4) | C16—C21—C20—C19 | -0.2 (7) |
| C41—C22—C19—C20 | 85.7 (6) | C16—C17—C18—C19 | -0.7 (7) |
| C41—C22—C19—C18 | -91.1 (5) | C18—C19—C20—C21 | 1.9 (7) |
| C41—C34—C35—C36 | 71.2 (6) | C18—C17—C16—P1 | -173.0 (3) |
| C41—C34—C35—C40 | -105.5 (5) | C18—C17—C16—C21 | 2.4 (7) |
| C41—C34—C32—C25 | 0.6 (7) | C40—C35—C36—C37 | 3.4 (7) |
| C41—C34—C32—C33 | -178.6 (4) | C1—N1—C5—C4i | 172.6 (4) |
| C23—C22—C41—C42 | -4.4 (7) | C28—C29—C30—C31 | 0.4 (8) |
| C23—C22—C41—C42 | 177.0 (4) | C31—C26—C25—C23 | 110.8 (5) |
| C23—C22—C19—C20 | -100.7 (5) | C31—C26—C25—C32 | -73.2 (6) |
| C23—C22—C19—C18 | 82.5 (5) | C31—C26—C27—C28 | 0.1 (7) |
| C23—C25—C32—C34 | -1.2 (7) | C13—N6—C14—C15iii | -169.4 (5) |
| C23—C25—C32—C33 | 178.0 (4) | C15—N5—C11—C12 | -179.0 (5) |
| C30—C29—C28—C27 | -1.3 (7) | C11—N5—C15—C14iii | 168.7 (5) |
| C25—C26—C31—C30 | 178.9 (5) | C27—C26—C25—C23 | -69.4 (6) |
| C25—C26—C27—C28 | -179.7 (5) | C27—C26—C25—C32 | 106.6 (5) |
| C5—N1—C1—C2 | -177.5 (4) | C27—C26—C31—C30 | -0.9 (7) |
Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|------|-------|-------|---------|
| N1—H1···O6vi | 1.00 | 2.32  | 3.196 (5) | 146 |
| N2—H2···O6W  | 1.00 | 2.18  | 3.039 (6) | 143 |
| N3—H3···O7v  | 1.00 | 2.13  | 3.102 (6) | 162 |
| N4—H4···O4W  | 1.00 | 2.06  | 3.056 (6) | 173 |
| N5—H5···O9v  | 1.00 | 2.07  | 3.003 (6) | 155 |
| N6—H6···O7Wvi | 1.00 | 1.98  | 2.956 (6) | 166 |
| O3—H3C···O5v | 0.84 | 1.84  | 2.654 (5) | 162 |
| O6—H6C···O3Wvii | 0.84 | 1.75  | 2.550 (5) | 159 |
| O9—H9C···O4viii | 0.84 | 1.74  | 2.517 (5) | 154 |
| O1W—H1WB···O7v | 0.87 | 1.81  | 2.679 (5) | 173 |
| O1W—H1WA···O4W | 0.87 | 2.45  | 3.256 (6) | 155 |
| O2W—H2WB···O4   | 0.86 | 1.90  | 2.729 (5) | 164 |
| O2W—H2WA···O7Wvii | 0.86 | 1.81  | 2.675 (6) | 174 |
| O3W—H3WB···O2   | 0.87 | 1.81  | 2.676 (4) | 177 |
| O3W—H3WA···O7v  | 0.85 | 1.84  | 2.689 (5) | 174 |
| O4W—H4WB···O3   | 0.87 | 2.26  | 3.115 (6) | 167 |
| O4W—H4WA···O8v  | 0.87 | 1.93  | 2.796 (6) | 172 |
| O5W—H5WB···O5v  | 0.87 | 1.98  | 2.813 (5) | 159 |
| O5W—H5WA···O8vi | 0.87 | 1.87  | 2.725 (5) | 168 |
| O6W—H6WB···O2   | 0.87 | 2.02  | 2.799 (6) | 149 |
| O6W—H6WA···O5W  | 0.87 | 2.00  | 2.842 (5) | 164 |
| O7W—H7WB···O3W  | 0.85 | 2.02  | 2.731 (5) | 140 |
| O7W—H7WA···O5W  | 0.86 | 1.83  | 2.688 (5) | 173 |

Symmetry codes: (ii) −x+2, −y+2, −z+1; (iv) x, y−1, z; (v) x, y, z−1; (vi) −x+1, −y+2, −z+2; (vii) x, y+1, z; (viii) x, y−1, z+1; (ix) x−1, y+1, z; (x) x+1, y−1, z; (xi) x+1, y, z−1.