Synthesis and crystal structure of bis[μ-N,N-bis(2-aminoethyl)ethane-1,2-diamine]bis[N,N-bis(2-aminoethyl)ethane-1,2-diamine]-μ_4-oxido-hexa-μ_3-oxido-octa-μ_2-oxido-tetraoxidotetranickel(II)hexatantalum(V) nonadecahydrate

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Reaction of K_8[Ta_6O_{19}]·16H_2O with [Ni(tren)(H_2O)Cl]Cl·H_2O in different solvents led to the formation of single crystals of the title compound, [Ni_4Ta_6O_{19}(C_6H_{18}N_4)_4]·19H_2O or [[Ni_2(k^4-tren)(μ-k^3-tren)]_2Ta_6O_{19}]·19H_2O (tren is N,N-bis(2-aminoethyl)-1,2-ethanediamine, C_6H_{18}N_4). In its crystal structure, one Lindqvist-type anion [Ta_6O_{19}]^{8-} (point group symmetry 1) is connected to two Ni^{II} cations, with both of them coordinated by one tren ligand into discrete units. Both Ni^{II} cations are sixfold coordinated by O atoms of the anion and N atoms of the organic ligand, resulting in slightly distorted [NiO_5N] octahedra for one and [NiO_3N_3] octahedra for the other cation. These clusters are linked by intermolecular O—H⋯O and N—H⋯O hydrogen bonding involving water molecules into layers parallel to the bc plane. Some of these water molecules are positionally disordered and were refined using a split model. Powder X-ray diffraction revealed that a pure crystalline phase was obtained but that on storage at room-temperature this compound decomposed because of the loss of crystal water molecules.

1. Chemical context

The investigation of synthesis conditions and crystal structures of new inorganic–organic hybrid polyoxometalates (POMs) of V, Nb, Ta, Mo or W is still an emerging research field in inorganic chemistry. The enormous variety of their structural, physical and chemical properties and the resulting potential applications are reflected in the large number of reported compounds (Tagliavini et al., 2021; Streb, 2012; Bijelic et al., 2019; Yamase, 2013; König, 2020; Ćolović et al., 2020; Monakhov et al., 2015). Within the POM family, polyoxoniobates and -tantalates have a special position because of their challenging synthesis conditions, i.e. high pH values are required as a result of the high stability of their respective oxides. This is the reason why we have been engaged in the research field of POM chemistry for several years, with the aim in developing new synthesis routes, also with an increasing focus on the PONb and POTa chemistry (Müsch-Polzin et al., 2020a,b; Dopta et al., 2018a,b, 2020). Most of the POMs are usually synthesized by solvothermal reactions using slightly soluble metal oxides. It turned out that the use of water-soluble compounds as precursor materials is more effective for
generating new compounds, which opens the possibility of developing more efficient syntheses at room temperature (Dopta et al., 2020; Mahnke et al., 2018a,b). Some transition metal (TM) decorated POTas have also been synthesized by slow crystallization at room temperature (Guo et al., 2011; Li et al., 2019), which is characterized by long reaction times and high sensibility for parameter changes during reaction. To overcome these drawbacks, we were interested in the possibility of faster crystallization times. To achieve this goal, we used preformed TM complexes and a special combination of different solvent gradients in the reaction vessel. Appropriate TM complexes are based on the tetradentate ligand N,N-bis(2-aminoethyl)-1,2-ethanediamine (tren), which offers coordination flexibility, providing two free coordination sites in an octahedral environment, with the possibilities for further ligation to O atoms of POMs or acting as charge-balancing cations. Based on that reasoning, an aqueous solution of K₈[Ta₆O₁₉]·C₁₉H₂O was reacted with the preformed complex [Ni(tren)(H₂O)Cl]·C₁H₂O at room temperature, leading to crystallization of violet needle-like crystals of the title compound, which was characterized by single-crystal X-ray diffraction. Comparison of the experimental powder X-ray diffraction pattern with that calculated from single crystal data revealed that a pure crystalline phase had formed. However, the relatively high background indicated the presence of some amount of an amorphous phase (see Fig. S1 in the supporting information). This is in line with the observation that the title compound is very unstable in air, which might be traced back to the loss of crystal water molecules, and was the reason why further investigations were not performed.

Table 1
Selected bond lengths (Å).

| Bond                  | Length (Å) |
|-----------------------|------------|
| O1—Ni1                | 2.072 (2)  |
| O5—Ni2                | 2.170 (3)  |
| O6—Ni2                | 2.149 (2)  |
| O9—Ni2                | 2.103 (2)  |
| Ni1—N1                | 2.111 (3)  |
| Ni1—N2                | 2.120 (3)  |
| Ni2—N3                | 2.105 (3)  |
| Ni1—N4                | 2.139 (3)  |
| Ni2—N11               | 2.172 (3)  |
| Ni2—N12               | 2.094 (4)  |
| Ni1—N14 i             | 2.082 (3)  |
| Ni2—N11 i             | 2.094 (3)  |

Symmetry code: (i) −x + 1, −y, −z + 2.

2. Structural commentary

The crystal structure of [Ni₂(κ⁴-tren)(μ-κ³-tren)]₂[Ta₁₀O₁₉]·19H₂O consists of one Lindqvist-type anion [Ta₁₀O₁₉]⁸⁻, located on a center of inversion, as well as two Ni⁵⁺ cations, two N,N-bis(2-aminoethyl)-1,2-ethanedi-amine ligands and nineteen water molecules that are located in general positions (Figs. 1 and 2). Some of the water O atoms are positionally disordered and were refined using a split model without locating their attached hydrogen atoms.

The [Ta₁₀O₁₉]⁸⁻ anion is composed of six TaO₆ octahedra sharing common edges. The Ta—O bond lengths range from 1.786 (2) to 2.057 (2) Å, which is consistent with common values. Bond-valence-sum calculations (Brown & Altermatt, 1985; Liu & Thorp, 1993; O’Keefe & Brese, 1991) led to values of 4.98 valence units (v.u.) for Ta1, of 1.78 v.u. for Ni1 and of 1.69 v.u. for Ni2, which is in reasonable agreement with the oxidation states of +5 and +2 for Ta and Ni, respectively. Two symmetry-related pairs of Ni⁵⁺ cations are covalently attached to the [Ta₁₀O₁₉]⁸⁻ core: Ni2 forms bonds to three μ₂-bridging O atoms with Ni—O bond lengths between 2.103 (2) and 2.120 (3) Å, while Ni1 forms bonds to two such O atoms with bond lengths of 2.111 (3) Å.

Figure 1
The molecular entities in the crystal structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. [Symmetry code: (A) −x + 1, −y, −z + 2.]

Figure 2
View of the cluster motif of the title compound. Hydrogen atoms were omitted for clarity.
2.170 (2) Å, while NiII is attached to a terminal O atom with a Ni—O bond length of 2.072 (2) Å (Fig. 3, Table 1), which is slightly larger than the sum of their ionic radii (NiII with CN6 = 0.69 Å, O2− = 1.35 Å; Shannon, 1976). The Ni1 cation is further coordinated by four N donor atoms (N1–N4) of one tren ligand and an additional N atom (N14) of another tren ligand, with Ni—N bonds ranging from 2.076 (3) to 2.172 (3) Å (Table 1), which is in agreement with reported values of similar structures (Dopta et al., 2018a; Hegtschweiler et al., 2002; Niu et al., 2011; Kim et al., 2004; Mash et al., 2019; Junk & Steed, 2007). One tren ligand connects both NiII cations via an Ni—μ-N—Ni bond of 2.082 (3) Å. Both NiII cations are in an octahedral environment, resulting in [Ni2O2N3] and [NiON12] units (Fig. 3). The bond angles within the complexes cover a wide range between 82.40 (13) and 178.92 (11)° for [Ni2O2N3] and between 74.98 (9) and 174.07 (11)° for [Ni1ON3], which shows that both NiII cations have a distorted octahedral environment. The distortion is caused by steric demands, because both NiII cations are coordinated by the anionic cluster as well as by tren ligands.

3. Supramolecular features

In the crystal, the discrete molecular moieties are linked by O—H···O and O—H···N hydrogen bonds between the crystal water molecules and the O atoms of the [Ta2O10]5− core (Table 2). The water molecules form discrete units categorized as D6 (Infantes et al., 2003; Infantes & Motherwell, 2002), of which each water molecule is attached to an Ocluster atom with Ocluster···O distances between 1.88 and 1.99 Å and condensed into chains extending parallel to [010] (Fig. 4). The [010] chains are further linked by Owater···H···N bonds with O···N separations between 2.232 and 2.537 Å, yielding another chain that propagates parallel to [001] (Table 2), finally forming a layered structure parallel to the bc plane (Fig. 5). There are

| Table 2 | Hydrogen-bond geometry (Å, °). |
|---------|--------------------------------|
| D—H···A | D—H | D—A | D—H···A |
| Cl1 — H1B···O4 | 0.99 | 2.52 | 3.293 (5) | 135 |
| N2 — H2C···O4v | 0.91 | 2.59 | 3.394 (4) | 148 |
| N2 — H2C···O8v | 0.91 | 2.42 | 3.208 (4) | 146 |
| N2 — H2D···O4 | 0.91 | 2.59 | 3.236 (4) | 129 |
| N2 — H2D···N2v | 0.91 | 2.62 | 3.338 (6) | 136 |
| C3 — H3A···O19vi | 0.99 | 2.53 | 3.253 (8) | 129 |
| C3 — H3B···O13vi | 0.99 | 2.64 | 3.301 (6) | 124 |
| C4 — H4B···O19vi | 0.99 | 2.60 | 3.135 (7) | 114 |
| N3 — H3C···O18 | 0.91 | 2.40 | 3.197 (7) | 114 |
| N3 — H3C···O19 | 0.91 | 2.45 | 3.266 (8) | 149 |
| N3 — H5D···O8v | 0.91 | 2.02 | 2.915 (4) | 169 |
| N4 — H4C···O15 | 0.91 | 2.54 | 3.244 (5) | 135 |
| C11 — H11B···O16v | 0.99 | 2.57 | 3.497 (12) | 156 |
| C12 — H12B···O20 | 0.99 | 2.47 | 2.977 (8) | 111 |
| N12 — H12C···O20 | 0.91 | 2.33 | 2.995 (7) | 130 |
| N12 — H12D···O2 | 0.91 | 2.16 | 2.951 (4) | 145 |
| N12 — H12D···O18v | 0.91 | 2.39 | 3.168 (8) | 144 |
| C13 — H13A···O13 | 0.99 | 2.59 | 3.380 (6) | 137 |
| N13 — H13C···O3 | 0.91 | 2.10 | 2.937 (5) | 153 |
| N13 — H13D···O14v | 0.99 | 2.23 | 3.103 (5) | 160 |
| C15 — H15A···O1i | 0.99 | 2.45 | 3.105 (5) | 124 |
| C16 — H16A···O6v | 0.99 | 2.63 | 3.514 (4) | 149 |
| C16 — H16B···O11v | 0.99 | 2.58 | 3.400 (5) | 140 |
| N14 — H14C···O19 | 0.91 | 2.62 | 3.447 (7) | 151 |
| N14 — H14C···O19v | 0.91 | 2.27 | 3.082 (7) | 148 |
| N14 — H14D···O2v | 0.91 | 2.04 | 2.941 (4) | 169 |
| O11 — H11C···O2 | 0.84 | 1.97 | 2.794 (4) | 165 |
| O11 — H11D···O14 | 0.84 | 2.00 | 2.826 (5) | 170 |
| O12 — H12E···O7v | 0.84 | 1.97 | 2.784 (4) | 163 |
| O12 — H12F···O16 | 0.84 | 1.86 | 2.686 (11) | 170 |
| O12 — H12F···O16v | 0.84 | 2.25 | 3.079 (11) | 169 |
| O13 — H13E···O11v | 0.84 | 1.89 | 2.696 (5) | 161 |
| O13 — H13F···O3vii | 0.84 | 1.93 | 2.698 (4) | 152 |
| O13 — H13F···O20v | 0.84 | 2.59 | 3.101 (7) | 120 |
| O14 — H14E···O20v | 0.84 | 1.94 | 2.757 (7) | 164 |
| O14 — H14F···O9 | 0.84 | 2.01 | 2.762 (4) | 149 |
| O15 — H15C···O17vii | 0.84 | 2.01 | 2.787 (9) | 153 |
| O15 — H15C···O17vii | 0.84 | 2.02 | 2.850 (10) | 170 |
| O15 — H15D···O12vii | 0.84 | 1.90 | 2.723 (6) | 168 |

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

Figure 3
View of the coordination environments of the two NiII cations with labeling of selected atoms. H atoms bonded to N atoms were omitted for clarity. [Symmetry code: (i) −x + 1, −y, −z + 2.]

Figure 4
View of the hydrogen-bonded chains running parallel to [010]. Intramolecular hydrogen bonding is indicated by dashed lines. In the left part, hydrogen atoms were omitted for clarity.

Figure 5
View of the hydrogen-bonded layer extending parallel to the bc plane by linking the [010] chains via Owater···H···N bonds (black dashed lines: Owater···Owater, green dashed lines: Owater···N). Hydrogen atoms were omitted for clarity.
additional C–H⋯N interactions (Table 2). From both the C⋯N distances and the angles, it is obvious that these represent only weak interactions.

4. Database survey

There are only a few crystal structures of POMs reported in the literature with \([\text{Ni}^{II}(\text{tren})]_6\) complexes covalently attached to the anionic core. Our group has already reported the rare \([\text{Ni}_3(\mu-\text{tren})_2(\text{tren})_2(\text{H}_2\text{O})_2]^{6+}\) complexes that act as linking units between several anionic moieties (Lüthmann et al., 2014; Wang et al., 2013). In these structures, the Ni\(^{II}\) cation is coordinated by one tetradentate ligand and one additional tren molecule connecting two Ni\(^{II}\) cations of neighboring \(\{\text{V}_{12}\text{Ge}_6\}\) clusters. A connection of two Ni\(^{II}\) cations bonded to separated clusters via two tren molecules (with \(k^3\) and \(k^6\) modes) has not been reported until now. However, the crystal structure of a similar complex, viz. \([\text{Ni}_3(\mu-\text{tren})_2(\text{tren})_2(\text{H}_2\text{O})_2]^{6+}\) was reported previously (Matelková et al., 2013).

5. Synthesis and crystallization

Synthesis

All chemicals except \(\text{K}_{16}\text{Ta}_8\text{O}_{20}\cdot16\text{H}_2\text{O}\) were purchased from commercial sources and were used without further purification \([\text{Ni}_4\text{Ta}_{16}\text{O}_{49}(\text{C}_6\text{H}_{18}\text{N}_4)_4]^{18-}\cdot19\text{H}_2\text{O}\) was prepared according to Filowitz et al. (1969), and the prefabricated complex \([\text{Ni}(\text{tren})(\text{H}_2\text{O})\text{Cl}]\text{Cl}\text{H}_2\text{O}\) using the protocol of Marzotto et al. (1993).

0.03 mmol of \(\text{Ni}[\text{tren}](\text{H}_2\text{O})\text{Cl}]\text{Cl}\text{H}_2\text{O}\) were dissolved in 1 ml of a 4:1 DMSO:water solution (v/v) and subsequently transferred into a 5 ml snap-cap glass tube. Then 1 ml of a 3:1 mixture (v/v) of DMSO and water and a solution of 0.0125 mmol of \(\text{K}_{16}\text{Ta}_8\text{O}_{20}\cdot16\text{H}_2\text{O}\) in 1 ml of water (pH = 12.3) were added slowly, one after the other, into the tube, which was then closed and left at room temperature. After a few days, pink–violet needle-shaped crystals were collected and their lengths were set to ideal values and they were refined with \(U_{iso}(\text{H}) = 1.2U_{eq}(\text{CN})\) using a riding model. Some of the hydrogen atoms belonging to water molecules were located in a difference-Fourier map. The bond lengths were set to ideal values and they were refined with \(U_{iso}(\text{H}) = 1.5U_{eq}(\text{O})\). Some of the water atoms (O16–O19) are positioned disorder and were refined using a split model with 50% occupation for each of the corresponding sites; O20 was refined with one position and an occupation of 50%. The hydrogen atoms of water molecules that could not be located were considered in the calculation of the molecular formula.

Acknowledgements

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References

Bijelic, A., Aureliano, M. & Rompel, A. (2019). Angew. Chem. Int. Ed. 58, 2980–2999.
Brandenburg, K. & Putz, H. (1999). DIAMOND. Crystal Impact GbR, Bonn, Germany.
Brown, I. D. & Altermatt, D. (1985). Acta Cryst. B41, 244–247.
Colović, M. B., Lacković, A., Lalatović, J., Mougharbel, A. S., Kortz, U. & Krštić, D. Z. (2020). Curr. Med. Chem. 27, 362–379.
Dopta, J., Grzanna, S., Näther, C. & Bensch, W. (2018a). Dalton Trans. 47, 15103–15113.
Dopta, J., Krause, D.-C., Näther, C. & Bensch, W. (2018b). Cryst. Growth Des. 18, 4130–4139.
Dopta, J., Mahnke, L. K. & Bensch, W. (2020). CrystEngComm, 22, 3254–3268.
Filowitz, M., Ho, R. K. C., Klemperer, W. G. & Shum, W. (1979). Inorg. Chem. 18, 93–103.
Guo, G.-L., Xu, Y.-Q., Chen, B.-K., Lin, Z.-G. & Hu, C.-W. (2011). Inorg. Chem. Commun. 14, 1448–1451.

Table 3

| Crystal data | \[\text{Ni}_4\text{Ta}_{16}\text{O}_{49}(\text{C}_6\text{H}_{18}\text{N}_4)_4\]·19\text{H}_2\text{O} |
|-------------|-------------------------------------------------------------|
| Chemical formula | \[\text{Ni}_4\text{Ta}_{16}\text{O}_{49}(\text{C}_6\text{H}_{18}\text{N}_4)_4\]·19\text{H}_2\text{O} |
| \(M_r\) | 2551.81 |
| Crystal system, space group | Triclinic, \(\text{P}\overline{1}\) |
| Temperature (K) | 100 |
| \(a\), \(b\), \(c\) (Å) | 10.5033 (1), 12.0980 (2), 13.8640 (2) |
| \(\alpha\), \(\beta\), \(\gamma\) (°) | 73.748 (1), 80.918 (1), 80.842 (1) |
| \(V\) (Å\(^3\)) | 1657.76 (4) |
| \(Z\) | 1 |
| Radiation type | Mo Ka |
| Crystal size (mm) | 11.06 |
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 44996, 7897, 7404 |
| \(R_{int}\) | 0.030 |
| \(\sin \theta\lambda_{max}\) (Å\(^{-1}\)) | 0.658 |
| Refinement | |
| \(R[F^2 > 2\sigma(F^2)]\), \(w(R^2)\), \(S\) | 0.021, 0.059, 1.05 |
| No. of reflections | 7897 |
| No. of parameters | 439 |
| H-atom treatment | H-atom parameters constrained |
| \(\Delta \rho_{max}\), \(\Delta \rho_{min}\) (e Å\(^{-3}\)) | 2.83, –1.13 |

Computer programs: CrysAlis PRO (Rigaku OD, 2021), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), DIAMOND (Brandenburg & Putz, 1999) and pubCIF (Westrip, 2010).
Hegetsweiler, K., Finn, R. C., Rarig, R. S., Sander, J., Steinhauser, S., Wörle, M. & Zubiaeta, J. (2002). Inorg. Chim. Acta. 337, 39–47.
Infantes, L., Chisholm, J. & Motherwell, S. (2003). CrystEngComm, 5, 480–486.
Infantes, L. & Motherwell, S. (2002). CrystEngComm, 4, 454–461.
Junk, P. C. & Steed, J. W. (2007). Inorg. Chim. Acta, 360, 1661–1668.
Kim, J. C., Cho, J., Kim, H. & Lough, A. J. (2004). Chem. Commun., pp. 1796–1797.
König, B. (2020). Editor. Chemical Photocatalysis. Berlin: De Gruyter.
Li, Z., Zhang, J., Lin, L.-D., Liu, J.-H., Li, X.-X. & Zheng, S.-T. (2019). Chem. Commun. 55, 11735–11738.
Liu, W. & Thorp, H. H. (1993). Inorg. Chem. 32, 4102–4105.
Lühmann, H., Näther, C., Kögerler, P. & Bensch, W. (2014). Inorg. Chim. Acta, 421, 549–552.
Mahnke, L. K., Warzok, U., Lin, M., Näther, C., Schalley, C. A. & Bensch, W. (2018a). Chem. Eur. J. 24, 5522–5528.
Mahnke, L. K., Wendt, M., Näther, C. & Bensch, W. (2018b). Cryst. Growth Des. 18, 6100–6106.
Marzotto, A., Clemente, D. A. & Valle, G. (1993). Acta Cryst. C49, 1252–1255.
Mash, B. L., Raghavan, A. & Ren, T. (2019). Eur. J. Inorg. Chem. 2019, 2065–2070.
Matelková, K., Moncol, J., Herchel, R., Dlháň, Ž., Ivaniková, R., Svoboda, I., Padělková, Z. & Maslejová, A. (2013). Polyhedron, 56, 1–8.
Monakhov, K. Y., Bensch, W. & Kögerler, P. (2015). Chem. Soc. Rev. 44, 8443–8483.
Müsscher-Polzin, P., Näther, C. & Bensch, W. (2020a). Z. Naturforsch. Teil B, 75, 583–588.
Müsscher-Polzin, P., Näther, C. & Bensch, W. (2020b). Z. Anorg. Allg. Chem. 646, 193–198.
Niu, J., Wang, G., Zhao, J., Sui, Y., Ma, P. & Wang, J. (2011). Cryst. Growth Des. 11, 1253–1261.
O’Keefe, M. & Brese, N. E. (1991). J. Am. Chem. Soc. 113, 3226–3229.
Rigaku OD (2021). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, England.
Shannon, R. D. (1976). Acta Cryst. A32, 751–767.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Streb, C. (2012). Dalton Trans. 41, 1651–1659.
Tagliavini, V., Honisch, C., Serrati, S., Azzariti, A., Bonchio, M., Ruzza, P. & Carraro, M. (2021). RSC Adv. 11, 4952–4957.
Yamase, T. (2013). Prog. Mol. Subcell. Biol. 54, 65–116.
Synthesis and crystal structure of \( \text{bis[µ-N,N-bis(2-aminoethyl)ethane-1,2-diamine]bis[N,N-bis(2-aminoethyl)ethane-1,2-diamine]-µ}_4\text{-oxido-hexa-µ}_3\text{-oxido-octa-µ}_2\text{-oxido-tetraoxidotetranickel(II)hexatantalum(V) nonadecahydrate} \)

Dana-Céline Krause, Christian Näther and Wolfgang Bensch

**Computing details**

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

**Bis[µ-N,N-bis(2-aminoethyl)ethane-1,2-diamine]bis[N,N-bis(2-aminoethyl)ethane-1,2-diamine]-µ_4\text{-oxido-hexa-µ}_3\text{-oxido-octa-µ}_2\text{-oxido-tetraoxidotetranickel(II)hexatantalum(V) nonadecahydrate}**

**Crystal data**

\[\text{[Ni}_4\text{Ta}_6\text{O}_{19}(\text{C}_6\text{H}_{18}\text{N}_4)_4]\cdot19\text{H}_2\text{O}\]

\[M_r = 2551.81\]

Triclinic, \(P\bar{1}\)

\(a = 10.5033\) (1) Å

\(b = 12.0980\) (2) Å

\(c = 13.8640\) (2) Å

\(\alpha = 73.748\) (1)°

\(\beta = 80.918\) (1)°

\(\gamma = 80.842\) (1)°

\(V = 1657.76\) (4) Å\(^3\)

\(Z = 1\)

\(F(000) = 1210\)

\(D_\text{x} = 2.556\) Mg m\(^{-3}\)

Mo Ka radiation, \(\lambda = 0.71073\) Å

Cell parameters from 37095 reflections

\(\theta = 2.4–34.0°\)

\(\mu = 11.06\) mm\(^{-1}\)

\(T = 100\) K

Needle, light violet

\(0.11 \times 0.06 \times 0.01 \times 0.02\) (radius) mm

**Data collection**

XtaLAB Synergy, Dualflex, HyPix diffractometer

Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2021)

44996 measured reflections

7897 independent reflections

7404 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.030\)

\(\theta_{\text{max}} = 27.9°, \theta_{\text{min}} = 2.4°\)

\(h = -13\rightarrow 13\)

\(k = -15\rightarrow 15\)

\(l = -18\rightarrow 18\)

**Refinement**

Refinement on \(F^2\)

Least-squares matrix: full

\(R(F^2 > 2\sigma(F^2)) = 0.021\)

\(wR(F^2) = 0.059\)

\(S = 1.05\)

7897 reflections

439 parameters

0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained

\[ w = \frac{1}{\sigma^2(F_o^2) + (0.0386P)^2 + 3.1986P} \]
where \( P = (F_o^2 + 2F_c^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} = 0.003 \)
\( \Delta \rho_{\text{max}} = 2.83 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -1.13 \text{ e Å}^{-3} \)

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.

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

| x      | y      | z      | Uiso*/Ueq | Occ. (<1) |
|--------|--------|--------|-----------|-----------|
| Ta1    | 0.64607 (2) | -0.03553 (2) | 1.12174 (2) | 0.01205 (4) |
| Ta2    | 0.63326 (2) | 0.13631 (2) | 0.89100 (2) | 0.01300 (4) |
| Ta3    | 0.37445 (2) | 0.14420 (2) | 1.07511 (2) | 0.01322 (4) |
| O1     | 0.7572 (2)  | -0.0558 (2) | 1.21206 (18) | 0.0165 (5)  |
| O2     | 0.7303 (2)  | 0.2421 (2)  | 0.8064 (2)  | 0.0217 (5)  |
| O3     | 0.2829 (3)  | 0.2550 (2)  | 1.1292 (2)  | 0.0234 (6)  |
| O4     | 0.7273 (2)  | 0.0788 (2)  | 1.00901 (19) | 0.0147 (5)  |
| O5     | 0.4815 (2)  | 0.1550 (2)  | 0.81001 (18) | 0.0158 (5)  |
| O6     | 0.7149 (2)  | -0.1593 (2) | 1.04715 (19) | 0.0149 (5)  |
| O7     | 0.5176 (2)  | 0.0863 (2)  | 1.15884 (19) | 0.0164 (5)  |
| O8     | 0.7070 (2)  | -0.0048 (2) | 0.85123 (18) | 0.0159 (5)  |
| O9     | 0.5036 (2)  | 0.2344 (2)  | 0.96735 (19) | 0.0156 (5)  |
| O10    | 0.500000    | 0.000000    | 1.000000    | 0.0136 (7)  |
| Ni1    | 0.92251 (4) | -0.03103 (4) | 1.26360 (3) | 0.01532 (9) |
| N1     | 0.8699 (3)  | 0.1472 (3)  | 1.2539 (2)  | 0.0201 (6)  |
| C1     | 0.8585 (4)  | 0.2037 (3)  | 1.1455 (3)  | 0.0230 (8)  |
| H1A    | 0.853129    | 0.288863    | 1.133133    | 0.028*      |
| H1B    | 0.777943    | 0.185909    | 1.127343    | 0.028*      |
| C2     | 0.9754 (4)  | 0.1607 (4)  | 1.0799 (3)  | 0.0270 (8)  |
| H2A    | 0.960794    | 0.188815    | 1.007761    | 0.032*      |
| H2B    | 1.053812    | 0.191245    | 1.088285    | 0.032*      |
| N2     | 0.9951 (3)  | 0.0334 (3)  | 1.1095 (2)  | 0.0211 (6)  |
| H2C    | 1.081340    | 0.008218    | 1.099923    | 0.025*      |
| H2D    | 0.953545    | 0.005768    | 1.069973    | 0.025*      |
| C3     | 0.9730 (4)  | 0.1919 (4)  | 1.2894 (3)  | 0.0292 (9)  |
| H3A    | 0.931892    | 0.250220    | 1.326166    | 0.035*      |
| H3B    | 1.029801    | 0.231278    | 1.229806    | 0.035*      |
| C4     | 1.0561 (4)  | 0.0973 (4)  | 1.3584 (3)  | 0.0253 (8)  |
| H4A    | 1.137072    | 0.126636    | 1.363251    | 0.030*      |
| H4B    | 1.008365    | 0.075941    | 1.427187    | 0.030*      |
| N3     | 1.0883 (3)  | -0.0053 (3) | 1.3184 (2)  | 0.0197 (6)  |
| H3C    | 1.113045    | -0.068663   | 1.368206    | 0.024*      |
| H3D    | 1.155159    | 0.005610    | 1.267602    | 0.024*      |
| C5     | 0.7429 (4)  | 0.1552 (4)  | 1.3166 (3)  | 0.0257 (8)  |
|   |   |   |   |   |
|---|---|---|---|---|
| H5A | 0.674670 | 0.141584 | 1.280900 | 0.031* |
| H5B | 0.721195 | 0.234233 | 1.326618 | 0.031* |
| C6  | 0.7451 (4) | 0.0670 (4) | 1.4187 (3) | 0.0268 (8) |
| H6A | 0.798205 | 0.090586 | 1.460793 | 0.032* |
| H6B | 0.655662 | 0.063614 | 1.454163 | 0.032* |
| N4  | 0.8004 (3) | —0.0488 (3) | 1.4047 (2) | 0.0234 (7) |
| H4C | 0.734953 | —0.090387 | 1.405737 | 0.028* |
| H4D | 0.847421 | —0.087973 | 1.456312 | 0.028* |
| Ni2 | 0.37645 (4) | 0.30477 (4) | 0.85661 (4) | 0.01769 (9) |
| N11 | 0.2586 (3) | 0.3909 (3) | 0.7352 (3) | 0.0228 (6) |
| C11 | 0.3553 (4) | 0.4394 (4) | 0.6485 (4) | 0.0384 (11) |
| H11A| 0.308709 | 0.496041 | 0.595074 | 0.046* |
| H11B| 0.401692 | 0.375854 | 0.619627 | 0.046* |
| C12 | 0.4526 (5) | 0.4980 (4) | 0.6785 (4) | 0.0476 (14) |
| H12A| 0.524285 | 0.514673 | 0.622820 | 0.057* |
| H12B| 0.410697 | 0.572483 | 0.691769 | 0.057* |
| N12 | 0.5045 (4) | 0.4215 (3) | 0.7703 (3) | 0.0384 (10) |
| H12C| 0.521448 | 0.465760 | 0.809050 | 0.046* |
| H12D| 0.580819 | 0.380862 | 0.752063 | 0.046* |
| C13 | 0.1726 (4) | 0.4869 (3) | 0.7696 (3) | 0.0282 (8) |
| H13A| 0.092034 | 0.504736 | 0.736649 | 0.034* |
| H13B| 0.217298 | 0.557486 | 0.748922 | 0.034* |
| C14 | 0.1381 (4) | 0.4544 (3) | 0.8830 (3) | 0.0260 (8) |
| H14A| 0.087344 | 0.521228 | 0.905006 | 0.031* |
| H14B| 0.084937 | 0.389170 | 0.903890 | 0.031* |
| N13 | 0.2613 (3) | 0.4200 (3) | 0.9300 (3) | 0.0247 (7) |
| H13C| 0.244850 | 0.385428 | 0.997304 | 0.030* |
| H13D| 0.302153 | 0.483347 | 0.922462 | 0.030* |
| C15 | 0.1831 (4) | 0.3213 (3) | 0.6974 (3) | 0.0222 (7) |
| H15A| 0.241988 | 0.254676 | 0.681442 | 0.027* |
| H15B| 0.150923 | 0.369778 | 0.633641 | 0.027* |
| C16 | 0.0684 (3) | 0.2759 (3) | 0.7707 (3) | 0.0197 (7) |
| H16A| 0.098349 | 0.228688 | 0.835662 | 0.024* |
| H16B| 0.005448 | 0.341548 | 0.784192 | 0.024* |
| N14 | 0.0054 (3) | 0.2040 (3) | 0.7259 (2) | 0.0202 (6) |
| H14C| 0.004942 | 0.240942 | 0.658896 | 0.024* |
| H14D| —0.079034 | 0.205534 | 0.754004 | 0.024* |
| O11 | 0.8066 (3) | 0.3844 (3) | 0.9091 (3) | 0.0378 (7) |
| H11C| 0.779756 | 0.353130 | 0.870404 | 0.057* |
| H11D| 0.733546 | 0.387800 | 0.943614 | 0.057* |
| O12 | 1.4219 (4) | 0.0650 (4) | 1.3614 (3) | 0.0536 (10) |
| H12E| 1.450539 | 0.085993 | 1.299839 | 0.080* |
| H12F| 1.428029 | —0.007777 | 1.376809 | 0.080* |
| O13 | —0.1468 (4) | 0.5884 (3) | 0.7766 (3) | 0.0537 (11) |
| H13E| —0.177526 | 0.528101 | 0.812709 | 0.081* |
| H13F| —0.198956 | 0.645501 | 0.786419 | 0.081* |
| O14 | 0.5770 (3) | 0.3988 (3) | 1.0444 (3) | 0.0459 (9) |
| H14E| 0.550254 | 0.380175 | 1.106447 | 0.069* |
H14F 0.528754 0.354705 1.034817 0.069*
O15 0.6112 (4) −0.2362 (3) 1.5414 (3) 0.0511 (9)
H15C 0.683268 −0.271482 1.557895 0.077*
H15D 0.595218 −0.177272 1.563995 0.077*
O16 1.4662 (9) −0.1666 (9) 1.3937 (7) 0.0297 (19) 0.5
O16’ 1.4319 (10) −0.1976 (9) 1.3891 (8) 0.0316 (19) 0.5
O17 −0.1862 (9) 0.5860 (7) 0.5871 (6) 0.0354 (18) 0.5
O17’ −0.1465 (9) 0.6271 (8) 0.5822 (8) 0.042 (2) 0.5
O18 1.2376 (6) −0.2566 (6) 1.4074 (4) 0.0351 (14) 0.5
O18’ 1.2585 (6) −0.3647 (6) 1.3875 (5) 0.0398 (16) 0.5
O19 −0.0677 (7) 0.4198 (6) 0.5130 (5) 0.0403 (17) 0.5
O19’ 1.0608 (8) −0.2496 (6) 1.4918 (5) 0.0445 (17) 0.5
O20 0.5580 (6) 0.6592 (5) 0.7647 (4) 0.0285 (12) 0.5

Atomic displacement parameters (Å²)

| Atoms | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Ta1   | 0.00591 (6) | 0.01739 (7) | 0.01444 (7) | −0.00135 (5) | −0.00280 (5) | −0.00589 (5) |
| Ta2   | 0.00604 (6) | 0.01679 (7) | 0.01625 (7) | −0.00248 (5) | −0.00202 (5) | −0.00348 (5) |
| Ta3   | 0.00737 (7) | 0.01741 (7) | 0.01720 (7) | −0.00015 (5) | −0.00273 (5) | −0.00837 (5) |
| O1    | 0.0090 (10) | 0.0255 (13) | 0.0164 (11) | −0.0017 (9)  | −0.0042 (9)  | −0.0066 (10) |
| O2    | 0.0119 (11) | 0.0221 (13) | 0.0267 (14) | −0.0055 (10) | −0.0021 (10) | 0.0025 (10)  |
| O3    | 0.0181 (13) | 0.0254 (14) | 0.0306 (15) | 0.0042 (10)  | −0.0039 (11) | −0.0168 (12) |
| O4    | 0.0074 (10) | 0.0169 (11) | 0.0214 (12) | −0.0026 (8)  | −0.0033 (9)  | −0.0061 (9)  |
| O5    | 0.0092 (11) | 0.0213 (12) | 0.0160 (11) | −0.0015 (9)  | −0.0029 (9)  | −0.0027 (9)  |
| O6    | 0.0068 (10) | 0.0188 (12) | 0.0204 (12) | −0.0006 (9)  | −0.0035 (9)  | −0.0065 (9)  |
| O7    | 0.0117 (11) | 0.0225 (12) | 0.0186 (12) | −0.0007 (9)  | −0.0040 (9)  | −0.0108 (10) |
| O8    | 0.0079 (10) | 0.0237 (12) | 0.0169 (12) | −0.0019 (9)  | −0.0003 (9)  | −0.0071 (10) |
| O9    | 0.0109 (11) | 0.0147 (11) | 0.0230 (12) | −0.0017 (9)  | −0.0054 (9)  | −0.0060 (10) |
| O10   | 0.0076 (15) | 0.0186 (17) | 0.0148 (16) | 0.0005 (12)  | −0.0037 (12) | −0.0045 (13) |
| N1    | 0.00831 (18)| 0.0236 (2)  | 0.0161 (2)  | −0.00135 (16)| −0.00322 (15)| −0.00786 (17)|
| C1    | 0.0167 (14) | 0.0240 (15) | 0.0215 (15) | −0.0018 (11) | −0.0066 (12) | −0.0070 (12) |
| C2    | 0.0216 (17) | 0.0240 (18) | 0.0272 (19) | −0.0046 (14) | −0.0089 (15) | −0.0035 (15) |
| C3    | 0.0162 (17) | 0.037 (2)   | 0.0244 (19) | −0.0087 (15) | −0.0005 (14) | −0.0015 (16) |
| C4    | 0.0090 (13) | 0.0366 (17) | 0.0192 (14) | −0.0031 (12) | −0.0028 (11) | −0.0089 (13) |
| C5    | 0.0099 (13) | 0.0309 (17) | 0.0186 (14) | −0.0041 (12) | −0.0021 (11) | −0.0068 (12) |
| C6    | 0.00177 (17)| 0.032 (2)   | 0.030 (2)   | 0.0053 (15)  | −0.0036 (15) | −0.0151 (17) |
| C7    | 0.0197 (18) | 0.041 (2)   | 0.0228 (18) | −0.0021 (16) | 0.0011 (14)  | −0.0165 (17) |
| C8    | 0.0099 (15) | 0.0321 (18) | 0.0201 (15) | −0.0046 (13) | −0.0021 (12) | −0.0093 (13) |
| C9    | 0.0109 (2)  | 0.0159 (2)  | 0.0260 (2)  | −0.00212 (16)| −0.00576 (17)| −0.00300 (18)|
| C10   | 0.0168 (14)| 0.0200 (15) | 0.0290 (17) | −0.0044 (12) | −0.0038 (12) | −0.0004 (13) |
| C11   | 0.023 (2)   | 0.037 (2)   | 0.040 (3)   | −0.0050 (17) | −0.0006 (18) | 0.013 (2)    |
| C12   | 0.027 (2)   | 0.034 (2)   | 0.065 (3)   | −0.0093 (19) | −0.013 (2)   | 0.020 (2)    |
| C13   | 0.0217 (17) | 0.0235 (18) | 0.060 (3)   | −0.0055 (14) | −0.0129 (17) | 0.0115 (17)  |
| C14   | 0.0221 (18) | 0.0206 (18) | 0.041 (2)   | −0.0010 (14) | −0.0138 (17) | −0.0023 (16) |
| C15   | 0.0184 (17) | 0.0202 (18) | 0.041 (2)   | 0.0011 (14)  | −0.0110 (16) | −0.0091 (16) |
|     |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| N13 | 0.0204 (15) | 0.0174 (15) | 0.0394 (19) | 0.0006 (12) | −0.0121 (14) | −0.0093 (13) |
| C15 | 0.0183 (17) | 0.0265 (19) | 0.0201 (17) | −0.0004 (14) | −0.0057 (14) | −0.0030 (14) |
| C16 | 0.0144 (16) | 0.0237 (18) | 0.0233 (18) | 0.0009 (13) | −0.0061 (13) | −0.0094 (14) |
| N14 | 0.0122 (13) | 0.0271 (16) | 0.0231 (15) | 0.0001 (11) | −0.0059 (11) | −0.0089 (13) |
| O11 | 0.0335 (17) | 0.0356 (17) | 0.0454 (19) | −0.0087 (13) | 0.0052 (14) | −0.0152 (14) |
| O12 | 0.061 (2) | 0.077 (3) | 0.0222 (16) | −0.006 (2) | 0.0038 (16) | −0.0188 (17) |
| O13 | 0.085 (3) | 0.0301 (17) | 0.042 (2) | −0.0068 (18) | 0.0191 (19) | −0.0177 (15) |
| O14 | 0.0352 (18) | 0.058 (2) | 0.058 (2) | −0.0262 (16) | 0.0025 (16) | −0.0311 (18) |
| O15 | 0.0348 (19) | 0.0385 (19) | 0.075 (3) | −0.0001 (15) | −0.0046 (18) | −0.0100 (18) |
| O16 | 0.026 (5) | 0.048 (6) | 0.018 (3) | −0.007 (3) | −0.002 (3) | −0.013 (3) |
| O16' | 0.035 (5) | 0.037 (5) | 0.025 (4) | −0.002 (3) | −0.006 (4) | −0.012 (3) |
| O17 | 0.043 (5) | 0.035 (5) | 0.027 (3) | 0.006 (3) | −0.001 (3) | −0.014 (3) |
| O17' | 0.035 (5) | 0.047 (6) | 0.051 (5) | −0.001 (4) | −0.005 (4) | −0.029 (4) |
| O18 | 0.035 (3) | 0.047 (4) | 0.023 (3) | −0.009 (3) | −0.009 (2) | −0.004 (3) |
| O18' | 0.037 (4) | 0.050 (4) | 0.024 (3) | 0.010 (3) | −0.003 (3) | −0.004 (3) |
| O19 | 0.039 (4) | 0.039 (4) | 0.038 (4) | −0.003 (3) | 0.005 (3) | −0.008 (3) |
| O19' | 0.061 (5) | 0.040 (4) | 0.034 (3) | 0.008 (3) | −0.005 (3) | −0.019 (3) |
| O20 | 0.026 (3) | 0.037 (3) | 0.029 (3) | −0.008 (2) | −0.005 (2) | −0.016 (2) |

Geometric parameters (Å, °)

| Ta1—Ta2 | 3.3013 (2) | N3—H3D | 0.9100 |
| Ta1—Ta3 | 3.3325 (2) | C5—H5A | 0.9900 |
| Ta1—O1 | 1.786 (2) | C5—H5B | 0.9900 |
| Ta1—O4 | 1.957 (2) | C5—C6 | 1.517 (6) |
| Ta1—O5i | 2.057 (2) | C6—H6A | 0.9900 |
| Ta1—O6 | 2.030 (2) | C6—H6B | 0.9900 |
| Ta1—O7 | 1.957 (2) | C6—N4 | 1.482 (5) |
| Ta1—O10 | 3.641 (1) | N4—H4C | 0.9100 |
| Ta2—Ta3 | 3.3056 (2) | N4—H4D | 0.9100 |
| Ta2—O2 | 1.803 (3) | Ni2—N11 | 2.172 (3) |
| Ta2—O4 | 1.947 (2) | Ni2—N12 | 2.094 (4) |
| Ta2—O5 | 2.040 (2) | Ni2—N13 | 2.076 (3) |
| Ta2—O8 | 1.947 (2) | N11—C11 | 1.493 (5) |
| Ta2—O9 | 2.029 (2) | N11—C13 | 1.494 (5) |
| Ta2—O10 | 2.3737 (1) | N11—C15 | 1.484 (5) |
| Ta2—Ni2 | 3.1254 (4) | C11—H11A | 0.9900 |
| Ta3—O3 | 1.791 (3) | C11—H11B | 0.9900 |
| Ta3—O6 | 2.015 (2) | C11—C12 | 1.501 (7) |
| Ta3—O7 | 1.964 (2) | C12—H12A | 0.9900 |
| Ta3—O8 | 1.959 (3) | C12—H12B | 0.9900 |
| Ta3—O9 | 2.045 (3) | C12—N12 | 1.475 (6) |
| Ta3—O10 | 2.3912 (1) | N12—H12C | 0.9100 |
| Ta3—Ni2 | 3.1064 (5) | N12—H12D | 0.9100 |
| O1—Ni1 | 2.072 (2) | C13—H13A | 0.9900 |
| O5—Ni2 | 2.170 (3) | C13—H13B | 0.9900 |
| O6—Ni2 | 2.149 (2) | C13—C14 | 1.509 (6) |
| O9—Ni2 | 2.103 (2) | C14—H14A | 0.9900 |
Ni1—N1  2.111 (3)  C14—H14B  0.9900
Ni1—N2  2.120 (3)  C14—N13  1.489 (5)
Ni1—N3  2.105 (3)  N13—H13C  0.9100
Ni1—N4  2.139 (3)  N13—H13D  0.9100
Ni1—N14i 2.082 (3)  C15—H15A  0.9900
N1—C1  1.482 (5)  C15—H15B  0.9900
N1—C3  1.486 (5)  C15—C16  1.516 (5)
N1—C5  1.478 (5)  C16—H16A  0.9900
C1—H1A  0.9900  C16—H16B  0.9900
C1—H1B  0.9900  C16—N14  1.482 (5)
C1—C2  1.522 (6)  N14—H14C  0.9100
N2—H2A  0.9900  N14—H14D  0.9100
N2—H2B  0.9900  O11—H11C  0.8399
C2—N2  1.467 (5)  O11—H11D  0.8396
C3—H3A  0.9900  O12—H12E  0.8400
C3—H3B  0.9900  O12—H12F  0.8401
C3—C4  1.523 (5)  O13—H13E  0.8402
C4—H4A  0.9900  O13—H13F  0.8399
C4—H4B  0.9900  O14—H14E  0.8400
C4—N3  1.468 (5)  O14—H14F  0.8400
N3—H3C  0.9100

Ta2—Ta1—Ta3  62.304 (4)  C5—N1—C3  113.4 (3)
O1—Ta1—Ta2  132.06 (8)  N1—C1—H1A  109.6
O1—Ta1—Ta3  132.68 (8)  N1—C1—H1B  109.6
O1—Ta1—O4  99.95 (11)  N1—C1—C2  110.2 (3)
O1—Ta1—O5i  104.23 (11)  H1A—C1—H1B  108.1
O1—Ta1—O6  104.25 (10)  C2—C1—H1A  109.6
O1—Ta1—O7  100.84 (11)  C2—C1—H1B  109.6
O1—Ta1—O10 177.50 (8)  C1—C2—H2A  109.8
O4—Ta1—Ta2  32.17 (7)  C1—C2—H2B  109.8
O4—Ta1—Ta3  84.14 (7)  H2A—C2—H2B  108.2
O4—Ta1—O5i  155.30 (10)  N2—C2—C1  109.5 (3)
O4—Ta1—O6  89.21 (10)  N2—C2—H2A  109.8
O4—Ta1—O7  90.86 (10)  N2—C2—H2B  109.8
O4—Ta1—O10 78.10 (7)  Ni1—N2—H2C  109.5
O5i—Ta1—Ta2  123.66 (7)  Ni1—N2—H2D  109.5
O5i—Ta1—Ta3  83.23 (7)  C2—N2—Ni1  110.6 (2)
O5i—Ta1—O10 77.86 (7)  C2—N2—H2C  109.5
O6—Ta1—Ta2  83.44 (7)  C2—N2—H2D  109.5
O6—Ta1—Ta3  123.02 (7)  H2C—N2—H2D  108.1
O6—Ta1—O5i  80.09 (10)  N1—C3—H3A  108.9
O6—Ta1—O10 77.37 (7)  N1—C3—H3B  108.9
O7—Ta1—Ta2  83.14 (7)  N1—C3—C4  113.3 (3)
O7—Ta1—Ta3  31.87 (7)  H3A—C3—H3B  107.7
O7—Ta1—O5i  89.53 (10)  C4—C3—H3A  108.9

Acta Cryst. (2021). E77, 1253-1257 sup-6
| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| O7—Ta1—O6 | 154.51 (10) | C4—C3—H3B | 108.9 |
| O7—Ta1—O10 | 77.71 (7) | C3—C4—H4A | 109.6 |
| O10—Ta1—Ta2 | 45.949 (3) | C3—C4—H4B | 109.6 |
| O10—Ta1—Ta3 | 45.842 (3) | H4A—C4—H4B | 108.1 |
| Ta1—Ta2—Ta3i | 61.789 (4) | N3—C4—C3 | 110.1 (3) |
| O2—Ta2—Ta1 | 135.83 (8) | N3—C4—H4A | 109.6 |
| O2—Ta2—Ta3i | 134.41 (9) | N3—C4—H4B | 109.6 |
| O2—Ta2—O4 | 103.52 (11) | Ni1—N3—H3C | 110.0 |
| O2—Ta2—O5 | 100.46 (11) | Ni1—N3—H3D | 110.0 |
| C4—C3—H3B | 108.9 | O8—Ta2—O10 | 78.04 (7) |
| C4—C3—H3B | 108.9 | O8—Ta2—O5 | 155.76 (10) |
| C4—C3—H3B | 108.9 | O8—Ta2—O8 | 87.94 (10) |
| C4—C3—H3B | 108.9 | O8—Ta2—O5 | 82.10 (10) |
| Ta2—Ta1 | 32.35 (7) | Ta2—Ta3 | 81.68 (7) |
| Ta2—Ta3i | 123.50 (7) | Ta2—Ta3i | 130.95 (7) |
| Ta2—Ta1 | 32.35 (7) | Ta2—Ta3i | 123.50 (7) |
| Ta2—Ta3 | 84.17 (7) | Ta2—Ta3i | 130.95 (7) |
| Ta2—Ta3i | 84.17 (7) | Ta2—Ta3i | 123.50 (7) |
| Ta2—Ta1 | 32.35 (7) | Ta2—Ta3i | 130.95 (7) |
| Ta2—Ta3i | 84.17 (7) | Ta2—Ta3i | 123.50 (7) |
| Ta2—Ta1 | 32.35 (7) | Ta2—Ta3i | 130.95 (7) |
| Ta2—Ta3i | 84.17 (7) | Ta2—Ta3i | 123.50 (7) |

**Notes:**
- Sup-7
- Acta Cryst. (2021). E77, 1253-1257
| Bond                  | Distance (Å) | Error  | Bond                  | Distance (Å) | Error  |
|----------------------|--------------|--------|----------------------|--------------|--------|
| O3—Ta3—Ni2           | 92.55 (9)    |        | N12—Ni2—O5           | 95.51 (14)   |        |
| O6—Ta3—Ta1           | 121.97 (7)   |        | N12—Ni2—O6           | 166.92 (12)  |        |
| O6—Ta3—Ta2           | 83.52 (7)    |        | N12—Ni2—O9           | 92.05 (13)   |        |
| O6—Ta3—O9            | 81.65 (10)   |        | N12—Ni2—N11          | 82.07 (13)   |        |
| O6—Ta3—O10           | 76.99 (7)    |        | N13—Ni2—Ta2          | 136.14 (9)   |        |
| O6—Ta3—Ni2           | 43.43 (7)    |        | N13—Ni2—Ta3          | 82.71 (10)   |        |
| O7—Ta3—Ta1           | 31.73 (7)    |        | N13—Ni2—O5           | 167.02 (12)  |        |
| O7—Ta3—Ta2           | 82.02 (7)    |        | N13—Ni2—O6           | 92.56 (12)   |        |
| O7—Ta3—O6            | 153.41 (10)  |        | N13—Ni2—O9           | 96.59 (12)   |        |
| O7—Ta3—O9            | 87.26 (10)   |        | N13—Ni2—N12          | 96.20 (16)   |        |
| O7—Ta3—Ni2           | 129.41 (7)   |        | C11—N11—Ni2          | 103.7 (2)    |        |
| O8—Ta3—Ta1           | 82.41 (7)    |        | C11—N11—C13          | 110.2 (3)    |        |
| O8—Ta3—Ta2           | 32.08 (7)    |        | C13—N11—Ni2          | 105.8 (2)    |        |
| O8—Ta3—O6            | 91.15 (10)   |        | C15—N11—Ni2          | 119.3 (2)    |        |
| O8—Ta3—O7            | 88.35 (11)   |        | C15—N11—C11          | 106.1 (3)    |        |
| O8—Ta3—O9            | 154.04 (10)  |        | C15—N11—C13          | 111.3 (3)    |        |
| O8—Ta3—O10           | 77.93 (7)    |        | N11—C11—H11A         | 109.0        |        |
| O8—Ta3—Ni2           | 134.43 (7)   |        | N11—C11—H11B         | 109.0        |        |
| O9—Ta3—Ta1           | 80.45 (7)    |        | N11—C11—C12          | 112.7 (4)    |        |
| O9—Ta3—Ta2           | 121.97 (7)   |        | H11A—C11—H11B        | 107.8        |        |
| O9—Ta3—O10           | 76.15 (7)    |        | C12—C11—H11A         | 109.0        |        |
| O9—Ta3—Ni2           | 42.21 (7)    |        | C12—C11—H11B         | 109.0        |        |
| O10—Ta3—Ta1          | 45.177 (3)   |        | C11—C12—H12A         | 109.8        |        |
| O10—Ta3—Ta2          | 45.855 (3)   |        | C11—C12—H12B         | 109.8        |        |
| O10—Ta3—Ni2          | 86.339 (9)   |        | H12A—C12—H12B        | 108.3        |        |
| Ni2—Ta3—Ta1          | 115.241 (9)  |        | N12—C12—C11          | 109.2 (4)    |        |
| Ni2—Ta3—Ta2          | 118.381 (9)  |        | N12—C12—H12A         | 109.8        |        |
| Ta1—O1—Ni1           | 155.51 (15)  |        | N12—C12—H12B         | 109.8        |        |
| Ta2—O4—Ta1           | 115.48 (11)  |        | Ni2—N12—H12C         | 109.0        |        |
| Ta1—O5—Ni2           | 99.62 (10)   |        | Ni2—N12—H12D         | 109.0        |        |
| Ta2—O5—Ta1           | 112.10 (11)  |        | C12—Ni2—Ni2          | 112.7 (3)    |        |
| Ta2—O5—Ni2           | 95.80 (10)   |        | C12—Ni2—H12C         | 109.0        |        |
| Ta1—O6—Ni2           | 101.20 (10)  |        | C12—N12—H12D         | 109.0        |        |
| Ta3—O6—Ta1           | 114.00 (11)  |        | H12C—N12—H12D        | 107.8        |        |
| Ta3—O6—Ni2           | 96.43 (10)   |        | N11—C13—H13A         | 109.4        |        |
| Ta1—O7—Ta3           | 116.40 (12)  |        | N11—C13—H13B         | 109.4        |        |
| Ta2—O8—Ta3           | 115.63 (12)  |        | N11—C13—C14          | 111.3 (3)    |        |
| Ta2—O9—Ta3           | 114.78 (11)  |        | H13A—C13—H13B        | 108.0        |        |
| Ta2—O9—Ni2           | 98.30 (11)   |        | C14—C13—H13A         | 109.4        |        |
| Ta3—O9—Ni2           | 96.99 (10)   |        | C14—C13—H13B         | 109.4        |        |
| Ta1—O10—Ta1          | 180.0        |        | C13—C14—H14A         | 110.1        |        |
| Ta1—O10—Ta2          | 88.341 (5)   |        | C13—C14—H14B         | 110.1        |        |
| Ta1—O10—Ta3          | 188.341 (5)  |        | H14A—C14—H14B        | 108.4        |        |
| Ta1—O10—Ta2           | 91.659 (4)   |        | N13—C14—C13          | 107.9 (3)    |        |
| Ta1—O10—Ta3           | 91.659 (4)   |        | N13—C14—H14A         | 110.1        |        |
| Ta1—O10—Ta1           | 91.980 (4)   |        | N13—C14—H14B         | 110.1        |        |
| Ta1—O10—Ta3           | 91.020 (5)   |        | Ni2—N13—H13C         | 110.4        |        |
| Bond          | Distance   | Bond          | Distance   |
|--------------|------------|--------------|------------|
| Ta1—O10—Ta3  | 91.020 (4) | Ni2—N13—H13D| 110.4      |
| Ta1—O10—Ta3' | 88.980 (4) | C14—N13—Ni2 | 106.8 (2)  |
| Ta2—O10—Ta2  | 180.0      | C14—N13—H13C| 110.4      |
| Ta2—O10—Ta3  | 87.852 (5) | C14—N13—H13D| 110.4      |
| Ta2—O10—Ta3' | 92.147 (5) | H13C—N13—H13D| 108.6    |
| Ta2—O10—Ta3' | 87.854 (5) | N11—C15—H15A| 108.7      |
| Ta3—O10—Ta3  | 92.147 (5) | N11—C15—H15B| 108.7      |
| Ta3—O10—Ta3' | 180.0      | N11—C15—C16 | 114.4 (3)  |
| O1—Ni1—N1   | 96.31 (11) | H15A—C15—H15B| 107.6    |
| O1—Ni1—N2   | 86.87 (11) | C16—C15—H15A| 108.7      |
| O1—Ni1—N3   | 178.92 (11)| C16—C15—H15B| 108.7      |
| O1—Ni1—N4   | 83.49 (11) | C15—C16—H16A| 109.9      |
| O1—Ni1—N14i | 89.60 (11) | C15—C16—H16B| 109.9      |
| N1—Ni1—N2   | 82.40 (13) | H16A—C16—H16B| 108.3    |
| N1—Ni1—N4   | 82.30 (13) | N14—C16—C15 | 108.9 (3)  |
| N2—Ni1—N4   | 160.88 (12)| N14—C16—H16A| 109.9      |
| N3—Ni1—N1   | 83.27 (12) | N14—C16—H16B| 109.9      |
| N3—Ni1—N2   | 94.05 (12) | Ni1—N14—H14C| 107.1      |
| N3—Ni1—N4   | 95.46 (12) | Ni1—N14—H14D| 107.1      |
| N14—Ni1—N1  | 173.85 (12)| C16—N14—Ni1 | 120.8 (2)  |
| N14—Ni1—N2  | 96.26 (13) | C16—N14—H14C| 107.1      |
| N14—Ni1—N3  | 90.85 (12) | C16—N14—H14D| 107.1      |
| N14—Ni1—N4  | 100.14 (13)| H14C—N14—H14D| 106.8    |
| C1—N1—Ni1   | 105.6 (2)  | H11C—O11—H11D| 92.0    |
| C1—N1—C3    | 111.1 (3)  | H12E—O12—H12F| 106.4   |
| C3—N1—Ni1   | 109.3 (2)  | H13E—O13—H13F| 107.5   |
| C5—N1—Ni1   | 105.5 (2)  | H14E—O14—H14F| 89.4    |
| C5—N1—C1    | 111.5 (3)  | H15C—O15—H15D| 108.4   |
| Ta2—Ta1—O1—Ni1 | −5.5 (4) | C5—N1—C1—C2 | −161.0 (3) |
| Ta3—Ta1—O1—Ni1 | −94.3 (3)| C5—N1—C3—C4 | 95.1 (4)  |
| O4—Ta1—O1—Ni1 | −3.1 (4) | C5—C6—N4—Ni1 | 24.0 (4)  |
| O5—Ta1—O1—Ni1 | 171.7 (3)| Ni2—N11—C11—C12| −45.1 (4) |
| O6—Ta1—O1—Ni1 | 88.6 (4) | Ni2—N11—C13—C14| −32.3 (3) |
| O7—Ta1—O1—Ni1 | −96.0 (3)| Ni2—N11—C15—C16| 70.5 (4)  |
| Ni1—N1—C1—C2 | −46.8 (3) | N11—C11—C12—N12| 48.2 (6)  |
| Ni1—N1—C3—C4 | −22.4 (4) | N11—C13—C14—N13| 55.0 (4)  |
| Ni1—N1—C5—C6 | 47.6 (3)  | N11—C15—C16—N14| −177.5 (3) |
| N1—C1—C2—N2  | 50.5 (4)  | C11—N11—C13—C14| −143.9 (3) |
| N1—C3—C4—N3  | 42.7 (5)  | C11—N11—C15—C16| −173.1 (3) |
| N1—C5—C6—N4  | −48.8 (4) | C11—C12—N12—Ni2| −24.9 (6)  |
| C1—N1—C1—C2  | −138.5 (4) | C13—N11—C11—C12| 67.8 (4)  |
| C1—N1—C5—C6  | 161.7 (3)  | C13—N11—C15—C16| −53.2 (4)  |
| C1—C2—N2—Ni1 | −27.3 (4)  | C13—C14—N13—Ni2| −48.0 (3)  |
| C3—N1—C1—C2  | 71.5 (4)  | C15—N11—C11—C12| −171.6 (4) |
C3—N1—C5—C6 $-72.0 \ (4)$
C3—C4—N3—Ni1 $-40.5 \ (4)$
C15—N11—C13—C14 98.6 (4)
C15—C16—N14—Ni1 $i$ 82.7 (3)

Symmetry code: (i) $-x+1, -y, -z+2$.

Hydrogen-bond geometry ($\AA$, °) 

| D—H···A     | D—H | H···A | D···A | D—H···A |
|-------------|-----|-------|-------|---------|
| C1—H1B···O4 | 0.99| 2.52  | 3.293 (5) | 135     |
| N2—H2C···O4ii | 0.91| 2.59  | 3.394 (4) | 148     |
| N2—H2C···O8ii | 0.91| 2.42  | 3.208 (4) | 146     |
| N2—H2D···O4 | 0.91| 2.59  | 3.236 (4) | 129     |
| N2—H2D···N2ii | 0.91| 2.62  | 3.338 (4) | 136     |
| C3—H3A···O19ii | 0.99| 2.53  | 3.253 (8) | 129     |
| C3—H3B···O13vi | 0.99| 2.64  | 3.301 (6) | 124     |
| C4—H4B···O19vi | 0.99| 2.60  | 3.135 (7) | 114     |
| N3—H3C···O18 | 0.91| 2.40  | 3.197 (7) | 146     |
| N3—H3C···O19i | 0.91| 2.45  | 3.266 (8) | 149     |
| N3—H3D···O8ii | 0.91| 2.02  | 2.915 (4) | 169     |
| N4—H4C···O15 | 0.91| 2.54  | 3.244 (5) | 135     |
| C11—H11B···O16ii | 0.99| 2.57  | 3.497 (12) | 156    |
| C12—H12B···O20 | 0.99| 2.47  | 2.977 (8) | 111     |
| N12—H12C···O20 | 0.91| 2.33  | 2.995 (7) | 130     |
| N12—H12D···O2 | 0.91| 2.16  | 2.951 (4) | 145     |
| N12—H12D···O18vi | 0.91| 2.39  | 3.168 (8) | 144     |
| C13—H13A···O13 | 0.99| 2.59  | 3.380 (6) | 137     |
| N13—H13C···O3 | 0.91| 2.10  | 2.937 (5) | 153     |
| N13—H13D···O14vi | 0.91| 2.23  | 3.103 (5) | 160     |
| C15—H15A···O1i | 0.99| 2.45  | 3.105 (5) | 124     |
| C16—H16A···O6i | 0.99| 2.63  | 3.514 (4) | 149     |
| C16—H16B···O11i | 0.99| 2.58  | 3.400 (5) | 140     |
| N14—H14C···O19 | 0.91| 2.62  | 3.447 (7) | 151     |
| N14—H14C···O19h | 0.91| 2.27  | 3.082 (7) | 148     |
| N14—H14D···O2v | 0.91| 2.04  | 2.941 (4) | 169     |
| O11—H11C···O2 | 0.84| 1.97  | 2.794 (4) | 165     |
| O11—H11D···O14 | 0.84| 2.00  | 2.826 (5) | 170     |
| O12—H12E···O7vi | 0.84| 1.97  | 2.784 (4) | 163     |
| O12—H12F···O16 | 0.84| 1.86  | 2.686 (11) | 170     |
| O12—H12F···O16i | 0.84| 2.25  | 3.079 (11) | 169     |
| O13—H13E···O11v | 0.84| 1.89  | 2.696 (5) | 161     |
| O13—H13F···O3vii | 0.84| 1.93  | 2.698 (4) | 152     |
| O13—H13F···O20v | 0.84| 2.59  | 3.101 (7) | 120     |
| O14—H14E···O20v | 0.84| 1.94  | 2.757 (7) | 164     |
| O14—H14F···O9  | 0.84| 2.01  | 2.762 (4) | 149     |
| O15—H15C···O17viii | 0.84| 2.01  | 2.787 (9) | 153    |
| Bond          | d (Å) | R (Å) | D (Å)      | E (°) |
|--------------|-------|-------|------------|-------|
| O15—H15C⋯O17<sup>viii</sup> | 0.84  | 2.02  | 2.850 (10) | 170   |
| O15—H15D⋯O12<sup>iii</sup> | 0.84  | 1.90  | 2.723 (6)  | 168   |

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