A second solvatomorph of poly[[μ₄-N₂,N’-(1,3,5-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)]-nickel(II)dipotassium]: crystal structure, Hirshfeld surface analysis and semi-empirical geometry optimization

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The title compound, poly[triaquabis[μ₂-N₂,N’-(1,3,5-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)]dinickel(II)tetrapotassium], [K₂Ni₂(C₇H₆N₄O₇)₂(H₂O)₃]n, is a second solvatomorph of poly[[μ₄-N₂,N’-(1,3,5-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)nickel(II)dipotassium] reported previously [Plutenko et al. (2021). Acta Cryst. E77, 298–304]. The asymmetric unit of the title compound includes two structurally independent complex anions [Ni(C₇H₆N₄O₇)]²⁻, which exhibit an L-shaped geometry and consist of two almost flat fragments perpendicular to one another: the 1,3,5-oxadiazinane fragment and the fragment including other atoms of the anion. The central Ni atom is in a square-planar N₂O₂ coordination arrangement formed by two amide N and two carboxylate O atoms. In the crystal, the title compound forms a layered structure in which layers of negatively charged complex anions and positively charged potassium cations are stacked along the a-axis direction. The polymeric framework is stabilized by a system of hydrogen-bonding interactions in which the water molecules act as donors and the carboxylic, amide and water O atoms act as acceptors.

1. Chemical context

In 1976, the products of the metal-templated reaction of hydrazide and aldehyde were separated and structurally described (Clark et al., 1976). It was further shown that such a synthetic strategy makes it possible to obtain complexes with 3d metals in high oxidation states. In particular, there are several works devoted to copper(III) complexes obtained by this method (Oliver & Waters, 1982; Fritsky et al., 1998, 2006). Moreover, the preparation of an unprecedentedly stable iron(IV) clathrochelate complex was reported (Tomyn et al., 2017). Some such compounds are promising redox catalysts, as has been shown by Pap et al. (2011) and Shylin et al. (2019). Thus, the study of the conditions and peculiarities of hydrazide-aldehyde template interactions, as well as the isolation and characterization of their products, is an important task in modern coordination chemistry.

This work is a continuation of our investigation of the interaction of oxalohydrazidehydroxamic acid with formaldehyde and nickel(II) salts. Here we report the crystal structure of the title compound poly[triaquabis[μ₄-N₂,N’-(1,3,5-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)]-nickel(II)dipotassium]: crystal structure, Hirshfeld surface analysis and semi-empirical geometry optimization.
oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)dinickel(II)tetrapotassium \[(2K_2\[Ni(L\text{-}2H)]\cdot3H_2O)\cdot2n\cdot2H_2O\text{, which is the solvatomorph of the earlier published (Plutenko et al., 2021) complex poly[pentaaquabis[\(\mu\text{-}N_2N\text{-}(1,3,5\text{-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)}\text{]}nickel(II)tetrapotassium\text{,} \[(2K_2\[Ni(L\text{-}2H)]\cdot4.8H_2O)\cdotn\cdot2\text{,}H_2L = N_2\text{-}(1,3,5\text{-oxadiazinane-3,5-diyl)bis(aminooxoacetic acid)}\]]\text{. Both compounds can be obtained in a similar fashion as the result of a one-pot template reaction (see Fig. 1).}

2. Structural commentary

The title compound, 2, \((2K_2\[Ni(L\text{-}2H)]\cdot3H_2O)\cdotn\), crystallizes in space group \(P2_1/c\), while the previously reported compound 1, \((2K_2\[Ni(L\text{-}2H)]\cdot4.8H_2O)\cdotn\), crystallizes in \(Pbca\). Similarly to 1, the asymmetric unit of 2 (Fig. 2) includes two structurally independent complex anions \([Ni(L\text{-}2H)]^{2–}\) (namely A and B, which contain NiI and NiIB, respectively). In addition, the unit cell of 2 also contains four potassium cations and three solvent water molecules.

Figure 1
A plausible mechanism for the formation of the \([Ni(L\text{-}2H)]^{2–}\) complex anion.

Figure 2
The asymmetric unit of 2 with displacement ellipsoids shown at the 50% probability level.

Similarly to 1, the complex anion \([Ni(L\text{-}2H)]^{2–}\) has an L-shaped geometry and consists of two almost flat fragments perpendicular to one another: the 1,3,5-oxadiazinane fragment and the fragment including other atoms of the anion. The dihedral angles between the mean planes formed by the non-hydrogen atoms of these fragments are 95.06 (8) and 94.06 (8)\(^\circ\) for NiI and NiIB, respectively. The ligand molecule is coordinated in a tetradentate \([O\text{carboxyl,}N\text{amide,}N\text{amide,}O\text{carboxyl})\text{-mode. The central atom of the complex anion exhibits a square-planar coordination arrangement with the N_2O_2 chromophore. The deviation of the Ni\text{II} atom from the mean plane defined by the donor atoms is 0.0073 (13) and 0.0330 (12) Å for NiI and NiIB, respectively. The Ni–N bond distances are in the range 1.836 (3)–1.849 (3) Å and Ni–O bond lengths are 1.877 (2)–1.897 (2) Å, which is typical for square-planar nickel complexes with similar ligands (Fritsky et al., 1998) and close to the Ni–N and Ni–O bond distances of 1. The O–M–O\(^\circ\), O–M–N and N–M–N\(^\circ\) bond angles have typical values for a square-planar arrangement. The bite angles O\(_1\)–NiI–N\(_4\), N\(_1\)–NiI–O\(_2\) and N\(_1\)–N\(_1\)–N\(_4\) deviate from 90\(^\circ\), which is the result of the formation of the five-membered chelate rings. The N–N\(^\circ\), N–C and C–O bond lengths of the ligand have typical values for coordinated deprotonated hydrazide and carboxyl groups.

3. Supramolecular features

In the crystal, the nickel(II) complex anions \([Ni(L\text{-}2H)]^{2–}\) form layers parallel to the \(bc\) plane (Fig. 3a). neighbouring complex anion layers are sandwiched by layers of potassium counter-cations (Fig. 4). Thus, negatively charged complex anion layers and positively charged potassium cationic layers are stacked along the \(a\)-axis direction. It is useful to note that in the previous layered structure motif was observed in the crystal of the previously published compound 1. However, in the crystal of 1 the NiN\(_2\)O\(_2\) plane is almost perpendicular to the complex anion layer plane (Fig. 3b): the angle between NiN\(_2\)O\(_2\) and the \(ab\) plane is 84.43 (4) and 85.03 (5)\(^\circ\) for NiI and NiIB,
respectively. In contrast, in the crystal of 2 the angle between NiN₂O₂ and the bc plane is 78.30 (8) and 86.29 (7)° for Ni1 and Ni1B, respectively.

The demarcation of bonded and non-bonded K—X interactions (X = N or O) is still an unclear and debatable problem (Alvarez, 2013). Therefore, the criteria of such demarcation used in this paper need to be detailed. Based on the aforementioned publication (Alvarez, 2013), we propose 3.7 Å as the maximal distance for K—N bonds. Recently, it was shown (Gagné & Hawthorne, 2016) that K—O main and maximal bond distances depend on the coordination number of K. The results of this work permits 3.4, 3.5 and 3.6 Å to be proposed as the maximal distances for K—O bonds in the case of potassium coordination numbers 7, 8 and 9, respectively. In addition, K···Namide interactions were determined as non-bonding because the existence of such bonds would lead to the presence of unstable three-membered KNamideNoxadiazinane rings with extremely small N—K—N angles.

The potassium cations are bound to the nickel(II) complex anions through the carboxylic O atoms (K4) the carboxylic and the amide O atoms (K1, K2) or through the amide O and the oxadiazinane N atoms (K3). In addition, the potassium cations have contacts with the O atoms of water molecules, with the amide and the carboxylic O atoms, and with the oxadiazinane O and N atoms of neighbouring complex anions. The K1 and K2 cations exhibit an O6N coordination, while the K3 cations have contacts with the O atoms of water molecules, with the amide and the carboxylic O atoms, and with the oxadiazinane O and N atoms of neighbouring complex anions. The K1 and K2 cations exhibit an O6N coordination, while the K3 and K4 cations exhibit O6N and O3N coordinations, respectively.

For an evaluation of the coordination geometry of each potassium cation, SHAPE 2.1 software (Llunell et al., 2013) was used. A SHAPE analysis of the potassium coordination sphere (Table 1, Fig. 5) yields the lowest continuous shape measure (CShM) value for a distorted pentagonal bipyramid (5.142 for K1 and 3.122 for K2), a distorted muffin (3.691 for K3) and a distorted triangular dodecahedron (5.187 for K4). For K4, comparable CShM values were obtained for a square antiprism (5.463).

The polyhedra around the neighbouring potassium cations are connected with each other through common vertices (K1 with K3, K1 with K4, K2 with K4), edges (K3 with K4) and faces (K1 with K2, K1 with K3, K2 with K3). The K—O bond lengths are in the range 2.628 (2)–3.271 (3) Å, K—N 2.887 (3)–3.025 (3) Å, which is close to those reported for the structures of related carboxylate and amide complexes (Fritsky et al., 1998; Mokhir et al., 2002).

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The polymeric framework of 2 is stabilized by an extensive system of hydrogen-bonding interactions in which the water molecules act as donors and the carboxylic, the amide and the water O atoms act as acceptors (Table 2). Similarly to 1, the hydrogen bonds are localized mainly at the potassium cation layers (Fig. 6). Moreover, in comparison to 1, the unit cell of 2 contains a smaller number of water molecules, which causes a smaller number of hydrogen-bond interactions in the crystal structure.

4. Hirshfeld analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon et al., 2007) were performed with Crystal-Explorer17 (Turner et al., 2017). The Hirshfeld surfaces of the complex anions are colour-mapped with the normalized contact distance ($d_{\text{norm}}$) from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii).

The Hirshfeld surface of the title compound is mapped over $d_{\text{norm}}$, in the colour ranges

\[
\begin{align*}
&C_{0.6388}^{0.9164} \\&C_{0.6768}^{0.7286}
\end{align*}
\]

for Ni1 and Ni1B complex anions, respectively (Fig. 7). Similarly to 1, the complex anions of 2 are connected to the other elements of the crystal packing mainly via the amide and the carboxylic O atoms. However, in contrast to 1, one of the oxadiazinane O atoms of 2 is also involved in intermolecular bond formation.

A fingerprint plot delineated into specific interatomic contacts contains information related to specific intermolecular interactions. The blue colour refers to the frequency of occurrence of the ($d_i$, $d_e$) pair with the full fingerprint plot outlined in gray. Fig. 8a and 9a show the two-dimensional fingerprint plots of the sum of the contacts contributing to the Hirshfeld surface represented in normal mode for the Ni1 and Ni1B complex anions, respectively.

The most significant contribution to the Hirshfeld surface is from O···H/H···O contacts (36.9% and 38.7% for the Ni1 and Ni1B complex anions, respectively; Fig. 8b and 9b). In addition, O···K/K···O (20.9% and 18.2% for the Ni1 and Ni1B complex anions; Fig. 8c and 9c) and H···H (10.4% and 13.1% for the Ni1 and Ni1B complex anions, respectively;

Table 2
Hydrogen-bond geometry ($\text{A, }^\circ$).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|----------|
| O8—H8O···O9i | 0.85 | 2.02 | 2.869 (4) | 173 |
| O8—H8P···O4Bii | 0.85 | 2.01 | 2.858 (3) | 166 |
| O9—H9P···O4iii | 0.86 | 1.91 | 2.722 (3) | 157 |
| O9—H9O···O6Biv | 0.86 | 2.07 | 2.864 (3) | 153 |
| O10—H10P···O4v | 0.88 | 2.02 | 2.887 (3) | 168 |
| O10—H10O···O7Bvi | 0.87 | 2.04 | 2.882 (3) | 164 |

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

Figure 5
Polyhedral views of the coordination environments for the potassium cations.

Figure 6
Crystal packing of the title compound. C—H hydrogen atoms are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

Figure 7
The Hirshfeld surfaces of the Ni1 (A) and Ni1B (B) complex anions mapped over $d_{\text{norm}}$. 

Figure 8
Fingerprint plot delineated into specific interatomic contacts contains information related to specific intermolecular interactions.
Fig. 8d and 9d make very significant contributions to the total Hirshfeld surface. This indicates that there are more K···O contacts and fewer O···H contacts compared to the crystal of 1.

5. Geometry optimization

The searching of computationally ‘cheap’ but still sufficiently accurate methods of transition-metal complex geometry optimization is an important task of modern computational chemistry. The geometry optimization calculations were carried out with three semi-empirical methods: PM7, DFTB and GFN2-xTB. The PM7 (Stewart, 2013) calculations were performed with MOPAC2016 software (Stewart, 2016). The DFTB calculations were carried out with the DFTB+ software package (Hourahine et al., 2020) using the ‘mio-1-l’ (Elstner et al., 1998) and the ‘trans3d-0-1’ (Zheng et al., 2007) Slater–Koster parameterization sets. The GFN2-xTB (Bannwarth et al., 2019) calculations were applied with xtb 6.4 package (Grimme, 2019). The geometry of the Ni1 complex anion obtained from the crystal structure was used as the starting geometry for the calculations.

In general, for all described semi-empirical methods, the calculated geometric parameters of the oxadiazinane ring are in reasonable agreement with experimental values (see Table 3). On the other hand, the accuracy of the non-oxadiazinane fragment geometry prediction varies greatly depending on the method. The worst agreement with experiments is from the PM7 method, mainly because of the pyramidalization of the amide nitrogen atom (Table 3). Such non-planarity of the amide fragment is a well-known problem of the PMx methods (Feigel & Strassner, 1993). In contrast, the DFTB method predicts the amide geometric parameters with high accuracy but demonstrates longer than experimental carboxylate C—O bonds and a slight tetragonal distortion of the nickel(II) coordination polyhedra (Table 3). The best results were obtained with the GFN2-xTB method for which the calculated geometric parameters correlate nicely with experimental values (Table 3). The maximal difference between the calculated and the experimental bond lengths concerns the C—O lengths (shorter than the experimental values within 0.024–0.033 Å). A superimposed analysis of the Ni1 complex anion with its optimized structure gives an

| Geometric parameter | X-ray | PM7  | DFTB | GFN2-xTB |
|---------------------|-------|------|------|----------|
| Oxadiazinane ring   |       |      |      |          |
| C—O                | 1.434 | 1.413| 1.467| 1.410    |
| C—N                | 1.463 | 1.489| 1.463| 1.452    |
| Carboxylate moiety  |       |      |      |          |
| C—O                | 1.287 | 1.276| 1.451| 1.260    |
| C—O                | 1.233 | 1.224| 1.196| 1.208    |
| Hydrazide moiety   |       |      |      |          |
| C—O                | 1.249 | 1.232| 1.227| 1.216    |
| C—N                | 1.321 | 1.357| 1.393| 1.332    |
| N—N                | 1.432 | 1.413| 1.413| 1.415    |
| C—Namide—Ni—N_oxadizine| 175.74| 133.89| 169.00| 162.81 |
| Ni coordination arrangement | | | |
| Ni—O               | 1.892 | 1.776| 1.788| 1.871    |
| Ni—N               | 1.840 | 1.955| 1.974| 1.871    |
| O—Ni—N chelate     | 85.24 | 93.35| 81.32| 82.94    |
| O—Ni—N non-chelate | 178.29| 173.19| 162.52| 176.77  |
| N—Ni—N            | 85.53 | 88.09| 90.73| 94.40    |

5. Geometry optimization

Table 3

Comparison of selected geometric data (Å; mean values) for the Ni1 complex anion from calculated and X-ray data.

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Figure 8
(a) Full two-dimensional fingerprint plot of the Ni1 complex anion and those delineated into (b) O···H/H···O (36.9%) (c) O···K/K···O (20.9%) and (d) H···H (10.4%) contacts.

Figure 9
(a) Full two-dimensional fingerprint plot of the Ni1B complex anion and those delineated into (b) O···H/H···O (38.7%) (c) O···K/K···O (18.2%) and (d) H···H (13.1%) contacts.
6. Database survey

A search in the Cambridge Structural Database (CSD version 5.39, update of May 2018; Groom et al., 2016) resulted in 11 hits dealing with 3d-metal complexes with macrocyclic or pseudo-macrocyclic ligands formed by template binding of several hydrazide groups by formaldehyde molecules. These complexes contain the following 3d metals: NiII (Fritsky et al., 1998), CuII (Clark et al., 1976; Fritsky et al., 2006), CuIII (Oliver & Waters, 1982; Fritsky et al., 1998, Fritsky et al., 2006) and FeIV (Tomyn et al., 2017). Thus, such macrocyclic and pseudo-macrocyclic ligand systems exhibit a tendency to stabilize the high oxidation states of 3d metals.

7. Synthesis and crystallization

A solution of Ni(ClO₄)₂·6H₂O (0.091 g, 0.25 mmol) in 5 ml of water was added to a warm solution of oxalohydrazide-hydroxamic acid (0.06 g, 0.5 mmol) in 5 ml of water. The resulting light-green mixture was stirred with heating (320–330 K) for 20 min and then 1 ml of 4M KOH solution was added. As a result, the colour of the solution changed to pink. After 5 min of stirring, 0.03 g of the paraformaldehyde (1 mmol) was added and stirring with heating (323–333 K) was continued for 30 min. The resulting orange solution was left for crystallization by slow evaporation in air. After one week, crystals were filtered off, washed with diethyl ether and dried in the air. Yield 0.044 g (42%). Elemental analysis for C₁₂H₁₀N₄O₇Ni₂ (mol. mass 844.18), calculated, %: C 19.92; H 2.15; N 13.27; Found, %: C 19.69; H 2.16; N 13.11. UV–vis (H₂O), λmax (ε, mol⁻¹ dm³ cm⁻¹): 520 nm (1380). IR (KBr, cm⁻¹): 3420 br ν(O–H) stretch, 2981, 2910, 2860 ν(C–H) stretch, 1643 (vs) ν(C=O) amide I, 1590 νas(COO⁻), 1435 νs(COO⁻).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. H atoms were positioned geometrically (O—H = 0.85–0.88, C—H = 0.99 Å) and refined as riding with Uiso(H) = 1.2 Ueq(O, C).

Table 4

| Crystal data | Chemical formula |
|--------------|------------------|
| [K₂Ni₄(C₂H₆N₄O₇)₂(H₂O)₃] | M₄ |
| Monoclinic, P2₁/c |
| Temperature (K) | 100 |
| a, b, c (Å) | 20.3825 (5), 7.7039 (3), 17.3078 (6) |
| V (Å³) | 98.240 (2) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 2.12 |
| Crystal size (mm) | 0.15 × 0.09 × 0.08 |

RMSD of 0.131 Å (Fig. 10). Thus, the GFN2-xTB method is a promising geometry prediction method for transition-metal complexes based on hydrazide and carboxylate ligands.

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References

Alvarez, S. (2013). *Dalton Trans.* 42, 8617–8636.
Bannwarth, C., Ehler, S. & Grimmie, S. (2019). *J. Chem. Theory Comput.* 15, 1652–1671.
Brandenburg, K. (2009). *DIAMOND.* Crystal Impact GbR, Bonn, Germany.
Brucker (2008). *COLLECT.* Bruker AXS Inc., Madison, Wisconsin, USA.
Clark, G. R., Skelton, B. W. & Waters, T. N. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1528–1536.
Elsner, M., Porezag, D., Jungnickel, G., Eilsner, J., Haugk, M., Frauenheim, Th., Suhai, S. & Seifert, G. (1998). *Phys. Rev. B*, 58, 7260–7268.
Feigel, M. & Strassner, T. (1993). *J. Mol. Struct. Theochem*, 283, 33–48.
Fritsky, I. O., Kozłowski, H., Kanderal, O. M., Haukka, M., Świątek-Kozłowska, J., Gumienna-Kontecka, E. & Meyer, F. (2006). *Chem. Commun.* pp. 4125–4127.

Fritsky, I. O., Kozłowski, H., Sadler, P. J., Yefetova, O. P., Świątek-Kozłowska, J., Kalibabchuk, V. A. & Glowiak, T. (1998). *J. Chem. Soc. Dalton Trans.* pp. 3269–3274.

Gagné, O. C. & Hawthorne, F. C. (2016). *Acta Cryst.* B72, 602–625.

Grimme, S. (2019). *xtb 6.4*. Mulliken Center for Theoretical Chemistry, University of Bonn, Bonn, Germany.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B72, 171–179.

Hourahine, B., Aradi, B., Blum, V., Bonafé, F., Buccheri, A., Camacho, C., Cevallos, C., Deshaye, M. Y., Dumitrić, T., Domínguez, A., Ehlert, S., Elstner, M., van der Heide, T., Hermann, J., Irle, S., Kranz, J. J., Köhler, C., Kowalczyk, T., Kubai, T., Lee, I. S., Lutzker, V., Maurer, R. J., Min, S. K., Mitchell, I., Negré, C., Niehaus, T. A., Niklasson, A. M. N., Page, A. J., Persson, M. P., Rezáč, J., Sánchez, C. G., Sternberg, M., Stöhr, M., Stuckenberg, F., Tkatchenko, A., Yu, V. W. & Frauenheim, T. (2020). *J. Chem. Phys.* 152, 124101.

Llunell, M., Casanova, D., Cirera, J., Alemay, P. & Alvarez, S. (2013). *SHAPE*. Barcelona, Spain.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.

Mokhir, A. A., Gumienna-Kontecka, E., Świątek-Kozłowska, J. J., Petkova, E. G., Fritsky, I. O., Jerzykiewicz, L., Kapshuk, A. A. & Silva, T. Yu. (2002). *Inorg. Chim. Acta.* 329, 113–121.

Oliver, K. J. & Waters, T. N. (1982). *J. Chem. Soc. Chem. Commun.* pp. 1111–1112.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* 276, 307–326.

Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* 40, 786–790.

Pap, J. S., Szywriel, Ł., Rówinska-Żyrek, M., Nikitin, K., Fritsky, I. O. & Kozłowski, H. J. (2011). *J. Mol. Catal. A Chem.* 334, 77–82.

Plutenko, M. O., Haukka, M., Husak, A. O., Iskenderov, T. S. & Mulloev, N. U. (2021). *Acta Cryst.* E77, 298–304.

Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C71, 3–8.

Shylin, S. I., Pavliuk, M. V., D’Amario, L., Mamedov, F., Sá, J., Berggren, G. & Fritsky, I. O. (2019). *Chem. Commun.* 55, 3335–3338.

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, 11, 19–32.

Stewart, J. J. P. (2013). *J. Mol. Model.* 19, 1–32.

Stewart, J. J. P. (2016). *MOPAC2016*. Stewart Computational Chemistry, Colorado Springs, CO, USA.

Tomy, S., Shylin, S. I., Bykov, D., Ksenofontov, V., Gumienna-Kontecka, E., Bon, V. & Fritsky, I. O. (2017). *Nat. Commun.* 8, 14099.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia.

Zheng, G., Witek, H. A., Bobadova-Parvanova, P., Irle, S., Musaev, D. G., Prabhakar, R., Morokuma, K., Lundberg, M., Elstner, M., Köhler, C. & Frauenheim, T. (2007). *J. Chem. Theory Comput.* 3, 1349–1367.
A second solvatomorph of poly\([\mu_4-N,N'-\text{(1,3,5-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)}]\text{n}
ike(II)dipotassium\]: crystal structure, Hirshfeld surface analysis and semi-empirical geometry optimization

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Computing details

Data collection: COLLECT (Bruker, 2008); cell refinement: DENZO/SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO/SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: SHELXL2018/1 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 2009); software used to prepare material for publication: SHELXL97 (Sheldrick, 2008).

Poly[triaquabis[\mu_4-N,N'-\text{(1,3,5-oxadiazinane-3,5-diyl)bis(carbamoylmethanoato)}]\text{n}
ike(II)tetrapotassium\]

Crystal data

\[\text{[K}_4\text{Ni}_2\text{(C}_7\text{H}_6\text{N}_4\text{O}_7)2\text{(H}_2\text{O})_3]\]
\[M_r = 844.18\]
Monoclinic, \(P\text{2}_1/c\)
\(a = 20.3825\) (5) Å
\(b = 7.7039\) (3) Å
\(c = 17.3078\) (6) Å
\(\beta = 98.240\) (2)°
\(V = 2689.69\) (16) Å³
\(Z = 4\)

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Horizontally mounted graphite crystal monochromator
Detector resolution: 16 pixels mm⁻¹
\(\varphi\) scans and \(\omega\) scans with \(\kappa\) offset
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.041\)
\(wR(F^2) = 0.082\)
\(S = 1.14\)

\(F(000) = 1704\)
\(D_x = 2.085\) Mg m⁻³
Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å
Cell parameters from 12179 reflections
\(\theta = 1.0–30.0^\circ\)
\(\mu = 2.12\) mm⁻¹
\(T = 100\) K
Orange, block
0.15 × 0.09 × 0.08 mm

\(T_{\text{min}} = 0.746, T_{\text{max}} = 0.842\)
25068 measured reflections
6148 independent reflections
5118 reflections with \(I > 2\sigma(I)\)
\(R_{\text{int}} = 0.043\)
\(\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 2.5^\circ\)
\(h = -26\rightarrow 26\)
\(k = -10\rightarrow 10\)
\(l = -22\rightarrow 22\)

Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 8.0539P]$ 
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta \rho_{\text{max}} = 0.63 \text{ e Å}^{-3}$

$\Delta \rho_{\text{min}} = -0.45 \text{ e Å}^{-3}$

**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      | $U_{iso}^{*}/U_{eq}$ |
|-----|--------|--------|--------|----------------------|
| Ni1 | 0.47434 (2) | 0.39867 (5) | 0.07544 (2) | 0.01087 (9) |
| K1  | 0.17619 (4)  | 0.53183 (9)  | 0.11705 (4)  | 0.01892 (16) |
| K2  | 0.19572 (3)  | 0.36084 (9)  | −0.07023 (4) | 0.01670 (15) |
| K3  | 0.27474 (3)  | 0.87045 (9)  | 0.01255 (4)  | 0.01761 (15) |
| K4  | 0.37676 (4)  | 0.05611 (9)  | −0.14504 (4) | 0.02025 (16) |
| O1  | 0.41934 (10) | 0.2347 (3)   | 0.01666 (13) | 0.0155 (5)   |
| O2  | 0.55123 (10) | 0.2576 (3)   | 0.08187 (12) | 0.0138 (4)   |
| O3  | 0.66101 (11) | 0.2786 (3)   | 0.11647 (14) | 0.0178 (5)   |
| O4  | 0.63860 (11) | 0.6017 (3)   | 0.18521 (13) | 0.0175 (5)   |
| O5  | 0.43257 (10) | 0.6088 (3)   | 0.23723 (12) | 0.0144 (4)   |
| O6  | 0.28491 (10) | 0.5095 (3)   | 0.04127 (13) | 0.0144 (5)   |
| O7  | 0.31296 (10) | 0.1927 (3)   | −0.03135 (13) | 0.0145 (4)   |
| O8  | 0.23728 (13) | 0.4224 (4)   | 0.26454 (15) | 0.0296 (6)   |
| H8O | 0.234956 | 0.311841 | 0.266821 | 0.044* |
| H8P | 0.220280 | 0.460928 | 0.303719 | 0.044* |
| O9  | 0.22781 (12) | 0.4456 (3)   | −0.21414 (15) | 0.0260 (6)   |
| H9P | 0.270092 | 0.459040 | −0.210682 | 0.039* |
| H9O | 0.209842 | 0.522979 | −0.245902 | 0.039* |
| O10 | 0.32908 (13) | 1.1134 (4)   | 0.14694 (15) | 0.0306 (6)   |
| H10O | 0.287037 | 1.137097 | 0.135669 | 0.046* |
| H10P | 0.338827 | 1.126557 | 0.197749 | 0.046* |
| N1  | 0.52942 (12) | 0.5586 (3)   | 0.13120 (14) | 0.0113 (5)   |
| N2  | 0.51068 (13) | 0.7242 (3)   | 0.15852 (15) | 0.0124 (5)   |
| N3  | 0.39268 (13) | 0.6979 (3)   | 0.10530 (15) | 0.0131 (5)   |
| N4  | 0.39871 (13) | 0.5297 (3)   | 0.07165 (15) | 0.0122 (5)   |
| C1  | 0.60452 (15) | 0.3371 (4)   | 0.11225 (18) | 0.0137 (6)   |
| C2  | 0.59253 (16) | 0.5163 (4)   | 0.14705 (18) | 0.0146 (6)   |
| C3  | 0.45459 (15) | 0.7945 (4)   | 0.10429 (19) | 0.0140 (6)   |
| H3A | 0.447429 | 0.917052 | 0.118117 | 0.017* |
| H3B | 0.466161 | 0.792495 | 0.050662 | 0.017* |
| C4  | 0.49161 (15) | 0.7092 (4)   | 0.23624 (18) | 0.0140 (6)   |
| H4A | 0.528350 | 0.654533 | 0.271547 | 0.017* |
| H4B | 0.484584 | 0.826836 | 0.256513 | 0.017* |
| C5  | 0.37883 (16) | 0.6825 (4)   | 0.18499 (18) | 0.0155 (6)   |
| H5A | 0.368739 | 0.799144 | 0.204239 | 0.019* |
| H5B | 0.338951 | 0.609318 | 0.185349 | 0.019* |
|       | U_{11}    | U_{22}    | U_{33}    | U_{12}    | U_{13}    | U_{23}    |
|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| Ni1   | 0.0117 (2) | 0.00866 (18) | 0.01215 (19) | 0.00042 (14) | 0.00137 (14) | -0.00210 (15) |
| K1    | 0.0225 (4) | 0.0128 (3) | 0.0229 (4) | 0.0021 (3) | 0.0082 (3) | 0.0018 (3) |
| K2    | 0.0181 (4) | 0.0124 (3) | 0.0182 (3) | 0.0002 (3) | -0.0022 (3) | -0.0009 (3) |
| K3    | 0.0162 (3) | 0.0130 (3) | 0.0229 (4) | -0.0001 (3) | 0.0006 (3) | 0.0043 (3) |
| K4    | 0.0253 (4) | 0.0118 (3) | 0.0265 (4) | -0.0019 (3) | 0.0134 (3) | -0.0026 (3) |
| O1    | 0.0140 (11) | 0.0129 (11) | 0.0195 (12) | -0.0001 (9) | 0.0021 (9) | -0.0028 (9) |
| O2    | 0.0149 (11) | 0.0116 (10) | 0.0149 (11) | 0.0018 (8) | 0.0020 (8) | -0.0011 (9) |
| O3    | 0.0124 (11) | 0.0158 (11) | 0.0253 (13) | 0.0022 (9) | 0.0030 (9) | -0.0007 (10) |
| O4    | 0.0151 (11) | 0.0154 (11) | 0.0207 (12) | -0.0003 (9) | -0.0016 (9) | -0.0013 (9) |
| O5    | 0.0159 (11) | 0.0146 (11) | 0.0135 (11) | -0.0009 (9) | 0.0044 (8) | 0.0014 (9) |
| O6    | 0.0135 (11) | 0.0127 (11) | 0.0168 (11) | 0.0013 (9) | 0.0016 (9) | -0.0016 (9) |
| O7    | 0.0144 (11) | 0.0138 (11) | 0.0148 (11) | -0.0021 (9) | 0.0005 (8) | -0.0015 (9) |
| O8    | 0.0368 (16) | 0.0286 (14) | 0.0253 (14) | 0.0059 (12) | 0.0103 (11) | 0.0025 (11) |
| O9    | 0.0159 (13) | 0.0345 (15) | 0.0268 (14) | -0.0018 (11) | 0.0006 (10) | 0.0045 (11) |
| O10   | 0.0259 (14) | 0.0390 (16) | 0.0269 (14) | 0.0052 (12) | 0.0038 (11) | 0.0047 (12) |
| N1    | 0.0137 (13) | 0.0095 (12) | 0.0107 (12) | 0.0008 (10) | 0.0022 (10) | -0.0013 (10) |
| N2    | 0.0151 (13) | 0.0104 (12) | 0.0118 (12) | 0.0006 (10) | 0.0018 (10) | -0.0017 (10) |
| Atom | U1  | U2  | U3  | U4  | U5  | U6  |
|------|-----|-----|-----|-----|-----|-----|
| N3   | 0.0177 (14) | 0.0090 (12) | 0.0125 (13) | 0.0001 (10) | 0.0021 (10) | −0.0040 (10) |
| N4   | 0.0176 (14) | 0.0075 (12) | 0.0116 (12) | 0.0018 (10) | 0.0024 (10) | −0.0028 (10) |
| C1   | 0.0176 (16) | 0.0137 (15) | 0.0105 (14) | −0.0010 (12) | 0.0042 (12) | 0.0031 (12) |
| C2   | 0.0179 (17) | 0.0124 (15) | 0.0141 (15) | −0.0020 (12) | 0.0039 (12) | 0.0019 (12) |
| C3   | 0.0158 (16) | 0.0091 (14) | 0.0164 (15) | 0.0002 (12) | 0.0002 (12) | −0.0002 (12) |
| C4   | 0.0174 (16) | 0.0141 (15) | 0.0106 (14) | 0.0009 (12) | 0.0022 (12) | 0.0019 (12) |
| C5   | 0.0177 (16) | 0.0152 (15) | 0.0139 (15) | −0.0005 (12) | 0.0036 (12) | −0.0020 (12) |
| C6   | 0.0149 (15) | 0.0110 (14) | 0.0092 (14) | −0.0001 (12) | 0.0023 (11) | 0.0008 (11) |
| C7   | 0.0165 (16) | 0.0098 (14) | 0.0105 (14) | −0.0003 (11) | 0.0026 (11) | 0.0020 (11) |

| Atom | U1  | U2  | U3  | U4  | U5  | U6  |
|------|-----|-----|-----|-----|-----|-----|
| Ni1B | 0.0128 (2) | 0.00920 (19) | 0.0149 (2) | −0.00029 (15) | 0.00073 (15) | 0.00233 (15) |
| O1B  | 0.0159 (12) | 0.0116 (11) | 0.0224 (12) | −0.0001 (9) | 0.0028 (9) | 0.0032 (9) |
| O2B  | 0.0159 (12) | 0.0122 (11) | 0.0179 (11) | −0.0007 (9) | −0.0001 (9) | 0.0019 (9) |
| O3B  | 0.0165 (12) | 0.0134 (11) | 0.0246 (13) | 0.0028 (9) | 0.0003 (9) | 0.0034 (10) |
| O4B  | 0.0149 (12) | 0.0140 (11) | 0.0203 (12) | 0.0005 (9) | 0.0021 (9) | 0.0004 (9) |
| O5B  | 0.0202 (12) | 0.0165 (12) | 0.0138 (11) | 0.0000 (9) | 0.0007 (9) | −0.0009 (9) |
| O6B  | 0.0139 (11) | 0.0157 (11) | 0.0251 (12) | 0.0009 (9) | 0.0004 (9) | −0.0003 (10) |
| O7B  | 0.0164 (12) | 0.0168 (12) | 0.0277 (13) | −0.0025 (9) | 0.0067 (10) | 0.0025 (10) |
| N1B  | 0.0168 (14) | 0.0075 (12) | 0.0152 (13) | −0.0003 (10) | 0.0009 (10) | 0.0000 (10) |
| N2B  | 0.0158 (13) | 0.0095 (12) | 0.0149 (13) | 0.0000 (10) | 0.0021 (10) | 0.0021 (10) |
| N3B  | 0.0154 (13) | 0.0094 (12) | 0.0154 (13) | −0.0013 (10) | 0.0014 (10) | 0.0048 (10) |
| N4B  | 0.0146 (13) | 0.0101 (12) | 0.0170 (13) | −0.0006 (10) | 0.0018 (10) | 0.0021 (10) |
| C1B  | 0.0197 (17) | 0.0128 (15) | 0.0109 (14) | −0.0019 (12) | 0.0023 (12) | −0.0021 (12) |
| C2B  | 0.0188 (17) | 0.0114 (14) | 0.0104 (14) | −0.0001 (12) | 0.0004 (12) | −0.0018 (11) |
| C3B  | 0.0133 (15) | 0.0122 (15) | 0.0176 (16) | −0.0013 (12) | 0.0002 (12) | −0.0008 (12) |
| C4B  | 0.0157 (16) | 0.0129 (15) | 0.0165 (15) | −0.0008 (12) | 0.0009 (12) | 0.0037 (12) |
| C5B  | 0.0177 (17) | 0.0127 (15) | 0.0168 (16) | 0.0014 (12) | 0.0014 (12) | 0.0041 (12) |
| C6B  | 0.0170 (16) | 0.0154 (16) | 0.0137 (15) | 0.0001 (12) | 0.0017 (12) | −0.0035 (12) |
| C7B  | 0.0163 (16) | 0.0144 (15) | 0.0122 (15) | −0.0005 (12) | 0.0017 (12) | −0.0007 (12) |

Geometric parameters (Å, °)

| Bond           | Distance (Å) | Angle (°) |
|----------------|--------------|-----------|
| Ni1—N4         | 1.836 (3)    | O5—C4     | 1.433 (4) |
| Ni1—N1         | 1.844 (3)    | O5—C5     | 1.434 (4) |
| Ni1—O1         | 1.887 (2)    | O6—C6     | 1.244 (4) |
| Ni1—O2         | 1.897 (2)    | O7—C7     | 1.236 (4) |
| K1—O6B         | 2.628 (2)    | O8—H8O    | 0.8546    |
| K1—O7B         | 2.717 (2)    | O8—H8P    | 0.8575    |
| K1—O6          | 2.737 (2)    | O9—H9P    | 0.8615    |
| K1—O8          | 2.805 (3)    | O9—H9O    | 0.8567    |
| K1—O3B         | 2.834 (2)    | O10—H10O  | 0.8704    |
| K1—O1B         | 2.998 (2)    | O10—H10P  | 0.8792    |
| K1—N3B         | 3.025 (3)    | N1—C2     | 1.317 (4) |
| K1—C7B         | 3.130 (3)    | N1—N2     | 1.431 (3) |
| K1—C6B         | 3.368 (3)    | N2—C4     | 1.457 (4) |
| K1—K2          | 3.5736 (10)  | N2—C3     | 1.474 (4) |
| K1—K3          | 3.8927 (10)  | N3—N4     | 1.433 (3) |
| K2—O6          | 2.708 (2)    | N3—C5     | 1.452 (4) |
| K2—O7          | 2.717 (2)    | N3—C3     | 1.467 (4) |
K2—O3Bii 2.725 (2) N4—C6 1.324 (4)
K2—O9 2.743 (3) C1—C2 1.540 (4)
K2—O4Biii 2.760 (2) C3—H3A 0.9900
K2—O7B 2.864 (2) C3—H3B 0.9900
K2—N2Biii 2.984 (3) C4—H4A 0.9900
K2—C6 3.401 (3) C4—H4B 0.9900
K2—C7 3.443 (3) C5—H5A 0.9900
K2—C2Biii 3.458 (3) C5—H5B 0.9900
K2—K3iv 4.2728 (10) C6—C7 1.544 (4)
K3—O7i 2.742 (2) Ni1B—N4B 1.839 (3)
K3—O3Bii 2.810 (2) Ni1B—N1B 1.849 (3)
K3—O4Bii 2.826 (2) Ni1B—O2B 1.877 (2)
K3—O6 2.827 (2) Ni1B—O1B 1.895 (2)
K3—O3i 2.976 (2) O1B—C7B 1.287 (4)
K3—N3 3.003 (3) O2B—C1B 1.281 (4)
K3—O10 3.066 (3) O3B—C1B 1.235 (4)
K3—O6Bii 3.095 (2) O4B—C2B 1.249 (4)
K3—O7Bi 3.271 (2) O5B—C5B 1.430 (4)
K3—C2Bii 3.475 (3) O5B—C4B 1.434 (4)
K3—C2Bii 3.501 (3) O6B—C6B 1.255 (4)
K3—C1Bi 3.512 (3) O7B—C7B 1.235 (4)
K3—H10O 2.9446 N1B—C2B 1.323 (4)
K4—O7 2.721 (2) N1B—N2B 1.434 (3)
K4—O4i 2.733 (2) N2B—C4B 1.457 (4)
K4—O3i 2.756 (2) N2B—C3B 1.469 (4)
K4—O5iii 2.779 (2) N3B—N4B 1.431 (3)
K4—N2v 2.887 (3) N3B—C5B 1.456 (4)
K4—O2i 2.955 (2) N3B—C3B 1.480 (4)
K4—O8vi 3.047 (3) N4B—C6B 1.320 (4)
K4—C1vii 3.095 (3) C1B—C2B 1.546 (4)
K4—O1 3.127 (3) C3B—H3B1 0.9900
K4—C7 3.201 (3) C3B—H3B2 0.9900
K4—C2v 3.354 (3) C4B—H4B1 0.9900
K4—C5i 3.474 (3) C4B—H4B2 0.9900
C1—C7 1.282 (4) C5B—H5B1 0.9900
O2—C1 1.291 (4) C5B—H5B2 0.9900
O3—C1 1.229 (4) C6B—C7B 1.528 (4)
O4—C2 1.254 (4)
N4—Ni1—N1 95.53 (11) N2v—K4—O1 72.10 (7)
N4—Ni1—O1 85.30 (10) O2vi—K4—O1 88.24 (6)
N1—Ni1—O1 178.66 (11) O8vi—K4—O1 123.68 (7)
N4—Ni1—O2 177.92 (11) C1vi—K4—O1 104.79 (7)
N1—Ni1—O2 85.18 (10) O7—K4—C7 22.25 (7)
O1—Ni1—O2 94.02 (9) O4v—K4—C7 70.87 (7)
O6B—K1—O7B 165.68 (7) O3vi—K4—C7 106.35 (7)
O6B—K1—O6 95.50 (7) O5viii—K4—C7 162.77 (8)
O7B—K1—O6 70.41 (7) N2v—K4—C7 86.82 (8)
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|---------------|--------------|---------------|--------------|
| O6Bi—K1—O8   | 96.75 (8)    | O2vi—K4—C7   | 104.10 (7)   |
| O7B—K1—O8   | 83.03 (8)    | O8vi—K4—C7   | 100.36 (8)   |
| O6—K1—O8    | 97.64 (7)    | C1vi—K4—C7   | 113.38 (8)   |
| O6Bi—K1—O3Bi | 75.65 (7)    | O1—K4—C7     | 23.34 (7)    |
| O7Bi—K1—O3Bi | 100.07 (7)   | O7—K4—C2v    | 74.75 (7)    |
| O6—K1—O3Bii | 66.54 (7)    | O4v—K4—C2v   | 20.73 (7)    |
| O8—K1—O3Bii | 161.46 (8)   | O3vi—K4—C2v  | 167.98 (8)   |
| O6Bi—K1—O1B  | 147.71 (7)   | O5vi—K4—C2v  | 110.16 (7)   |
| O7B—K1—O1B  | 45.58 (6)    | N2v—K4—C2v   | 43.27 (7)    |
| O6—K1—O1B   | 110.52 (7)   | O2vi—K4—C2v  | 136.36 (7)   |
| O8—K1—O1B   | 98.30 (7)    | O8vi—K4—C2v  | 95.92 (8)    |
| O3Bi—K1—O1B | 96.98 (7)    | C1vi—K4—C2v  | 160.86 (8)   |
| O6Bi—K1—N3Bi| 58.41 (7)    | O1—K4—C2v    | 63.19 (7)    |
| O7B—K1—N3Bi | 135.57 (7)   | C7—K4—C2v    | 61.97 (8)    |
| O6—K1—N3Bi  | 147.07 (7)   | O7—K4—C5vii  | 151.88 (7)   |
| O8—K1—N3Bi  | 104.66 (8)   | O4v—K4—C5vii | 108.05 (7)   |
| O3Bi—K1—N3Bi| 86.25 (7)    | O3vi—K4—C5vii| 72.21 (7)    |
| O1B—K1—N3Bi | 90.10 (7)    | O5vi—K4—C5vii| 23.29 (7)    |
| O6Bi—K1—C7B  | 171.25 (8)   | N2v—K4—C5vii | 97.79 (7)    |
| O7B—K1—C7B  | 23.02 (7)    | O2vi—K4—C5vii| 79.33 (7)    |
| O6—K1—C7B   | 92.84 (8)    | O8vi—K4—C5vii| 73.58 (7)    |
| O8—K1—C7B   | 84.73 (8)    | C1vi—K4—C5vii| 67.75 (8)    |
| O3Bi—K1—C7B | 105.44 (8)   | O1—K4—C5vii  | 162.73 (7)   |
| O1B—K1—C7B  | 24.11 (7)    | C7—K4—C5vii  | 173.84 (8)   |
| N3Bi—K1—C7B | 112.86 (8)   | O7—K4—C5vii  | 119.08 (8)   |
| O6Bi—K1—C6Bi| 19.63 (7)    | C7—O1—Ni1    | 113.14 (19)  |
| O7B—K1—C6Bi | 166.68 (8)   | C7—O1—K4     | 81.58 (17)   |
| O6—K1—C6Bii | 106.83 (7)   | Ni1—O1—K4    | 147.60 (10)  |
| O8—K1—C6Bii | 110.29 (8)   | C1—O2—Ni1    | 113.09 (19)  |
| O3Bi—K1—C6Bii| 67.44 (7)    | C1—O2—K4vi   | 83.85 (17)   |
| O1B—K1—C6Bii| 128.70 (7)   | Ni1—O2—K4vi  | 148.49 (10)  |
| N3Bi—K1—C6Bi| 42.60 (7)    | C1—O3—K4vi   | 94.03 (19)   |
| C7Bi—K1—C6Bi| 152.81 (8)   | C1—O3—K3v    | 127.3 (2)    |
| O6Bi—K1—K2  | 120.51 (6)   | K4vi—O3—K3v  | 86.44 (6)    |
| O7B—K1—K2   | 52.02 (5)    | C2—O4—K4v    | 108.80 (19)  |
| O6—K1—K2    | 48.63 (5)    | C4—O5—C5     | 110.2 (2)    |
| O8—K1—K2    | 128.47 (6)   | C4—O5—K4viii | 133.50 (17)  |
| O3Bi—K1—K2  | 48.67 (5)    | C5—O5—K4viii | 106.70 (16)  |
| O1B—K1—K2   | 69.47 (5)    | C6—O6—K2     | 113.52 (19)  |
| N3Bi—K1—K2  | 124.43 (6)   | C6—O6—K1     | 147.0 (2)    |
| C7Bi—K1—K2  | 63.86 (6)    | K2—O6—K1     | 82.02 (6)    |
| C6Bi—K1—K2  | 116.01 (6)   | C6—O6—K3     | 112.75 (18)  |
| O6Bi—K1—K3  | 52.41 (5)    | K2—O6—K3     | 105.41 (7)   |
| O7B—K1—K3   | 114.82 (5)   | K1—O6—K3     | 88.76 (6)    |
| O6—K1—K3    | 46.56 (5)    | C7—O7—K2     | 116.01 (19)  |
| O8—K1—K3    | 115.66 (6)   | C7—O7—K4     | 101.30 (18)  |
| O3Bi—K1—K3  | 46.14 (5)    | K2—O7—K4     | 119.99 (8)   |
| O1B—K1—K3   | 139.50 (5)   | C7—O7—K3iv   | 123.27 (19)  |
N3B---K1---K3 101.21 (5) K2---O7---K3 103.04 (7)
C7B---K1---K3 134.40 (6) K4---O7---K3 91.98 (7)
C6B---K1---K3 60.40 (6) K1---O8---K4 135.32 (10)
K2---K1---K3 72.16 (2) K1---O8---H8O 108.7
O6---K2---O7 63.15 (6) K4---O8---H8O 94.8
O6---K2---O3Bii 68.50 (7) K1---O8---H8P 116.0
O7---K2---O3Bii 130.88 (7) K4---O8---H8P 91.6
O6---K2---O9 108.86 (7) H8O---O8---H8P 106.1
O7---K2---O9 91.30 (7) K2---O9---H9P 109.4
O3Bii---K2---O9 96.29 (8) K2---O9---H9O 127.8
O6---K2---O4Biii 127.95 (7) H9P---O9---H9O 107.0
O7---K2---O4Biii 71.65 (7) K3---O10---H10O 73.8
O3Bii---K2---O4Biii 153.83 (7) K3---O10---H10P 146.5
O9---K2---O4Biii 96.17 (8) H10O---O10---H10P 105.9
O6---K2---O7B 68.65 (7) C2---N1---N2 116.8 (3)
O7---K2---O7B 71.37 (7) C2---N1---Ni1 116.5 (2)
O3Bii---K2---O7B 99.16 (7) N2---N1---Ni1 126.66 (19)
O9---K2---O7B 161.85 (8) N1---N2---C4 110.7 (2)
O4Biii---K2---O7B 73.70 (7) N1---N2---C3 109.7 (2)
O6---K2---N2Bii 153.59 (7) N1---N2---K4v 104.06 (16)
O7---K2---N2Bii 129.35 (7) C4---N2---C3 116.19 (18)
O3Bii---K2---N2Bii 98.31 (7) C4---N2---K4v 106.62 (17)
O9---K2---N2Bii 94.92 (7) C3---N2---K4v 106.2 (2)
O4Biii---K2---N2Bii 57.71 (7) C2---N3---C5 110.6 (18)
O7B---K2---N2Bii 92.22 (7) C2---N3---C3 109.3 (2)
O6---K2---C6 19.59 (7) C2---N3---K3 109.7 (2)
O7---K2---C6 44.71 (7) C5---N3---K3 106.96 (16)
O3Bii---K2---C6 86.20 (7) C5---N3---K3 107.10 (18)
O9---K2---C6 99.55 (7) C3---N3---K3 113.13 (18)
O4Bii---K2---C6 114.21 (7) C6---N4---N3 115.7 (2)
O7B---K2---C6 72.17 (7) C6---N4---Ni1 116.7 (2)
N2Bii---K2---C6 164.29 (7) N3---N4---Ni1 127.1 (2)
O6---K2---C7 45.08 (7) O3---C1---O2 125.2 (3)
O7---K2---C7 18.82 (7) O3---C1---C2 120.4 (3)
O3Bii---K2---C7 112.08 (7) O2---C1---C2 114.4 (3)
O9---K2---C7 93.17 (7) O3---C1---K4vi 62.64 (17)
O4Bii---K2---C7 79.08 (7) O2---C1---K4vi 71.65 (16)
O7B---K2---C7 72.22 (7) C2---C1---K4vi 145.90 (19)
N2Bii---K2---C7 147.43 (7) O4---C2---N1 127.9 (3)
C6---K2---C7 26.07 (7) O4---C2---C1 121.8 (3)
O6---K2---C2Biii 134.22 (7) N1---C2---C1 110.2 (3)
O7---K2---C2Biii 88.06 (7) O4---C2---K4vi 50.47 (16)
O3Bii---K2---C2Biii 134.59 (7) N1---C2---K4vi 86.15 (18)
O9---K2---C2Biii 106.44 (8) C1---C2---K4vi 146.74 (19)
O4Bii---K2---C2Biii 19.29 (7) N3---C3---N2 113.3 (2)
O7B---K2---C2Biii 68.67 (7) N3---C3---H3A 108.9
N2Bii---K2---C2Biii 42.10 (7) N2---C3---H3A 108.9
C6---K2---C2Biii 126.35 (7) N3---C3---H3B 108.9

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| Bond                  | Angle (deg) | Deviation (deg) |
|-----------------------|-------------|-----------------|
| C7—K2—C2Bⅲ           | 105.43 (7)  | N2—C3—H3B      | 108.9 |
| O6—K2—K1             | 49.34 (5)   | H3A—C3—H3B     | 107.7 |
| O7—K2—K1             | 99.18 (5)   | O5—C4—N2       | 112.9 (2) |
| O3Bⅲ—K2—K1           | 51.36 (5)   | O5—C4—H4A      | 109.0 |
| O9—K2—K1             | 143.89 (6)  | N2—C4—H4A      | 109.0 |
| O4Bⅲ—K2—K1           | 119.94 (5)  | O5—C4—H4B      | 109.0 |
| O7B—K2—K1            | 48.41 (5)   | N2—C4—H4B      | 109.0 |
| N2Bⅲ—K2—K2—K1       | 104.38 (6)  | H4A—C4—H4B     | 107.8 |
| C6—K2—K1             | 66.77 (5)   | O5—C5—N3       | 113.3 (2) |
| C7—K2—K1             | 86.75 (5)   | O5—C5—K4ⅷ     | 50.01 (13) |
| C2Bⅲ—K2—K1           | 108.36 (5)  | N3—C5—K4ⅷ     | 151.1 (2) |
| O6—K2—K3ⅵ            | 87.29 (5)   | O5—C5—H5A      | 108.9 |
| O7—K2—K3ⅵ            | 38.69 (5)   | N3—C5—H5A      | 108.9 |
| O3Bⅲ—K2—K3ⅵ          | 147.21 (6)  | K4ⅷ—C5—H5A    | 99.6 |
| O9—K2—K3ⅵ            | 112.80 (6)  | O5—C5—H5B      | 108.9 |
| O4Bⅲ—K2—K3ⅵ          | 40.67 (5)   | N3—C5—H5B      | 108.9 |
| O7B—K2—K3ⅵ           | 49.92 (5)   | K4ⅷ—C5—H5B    | 65.4 |
| N2Bⅲ—K2—K2—K3ⅵ      | 94.10 (5)   | H5A—C5—H5B    | 107.7 |
| C6—K2—K3ⅵ            | 74.71 (5)   | O6—C6—N4       | 128.1 (3) |
| C7—K2—K3ⅵ            | 53.87 (5)   | O6—C6—C7       | 123.0 (3) |
| C2Bⅲ—K2—K3ⅵ          | 52.13 (5)   | O6—C6—K2       | 46.89 (15) |
| K1—K2—K3ⅵ            | 96.17 (2)   | O6—C6—K2       | 162.9 (2) |
| O7ⅷ—K3—O3Bⅷ         | 130.32 (7)  | C7—C6—K2      | 78.47 (16) |
| O7ⅷ—K3—O4Bⅷ         | 70.29 (6)   | O6—C6—K3       | 48.13 (15) |
| O3Bⅲ—K3—O4Bⅷ        | 60.07 (7)   | N4—C6—K3       | 87.33 (18) |
| O7ⅷ—K3—O6            | 157.32 (7)  | C7—C6—K3      | 147.92 (19) |
| O3Bⅲ—K3—O6           | 65.69 (6)   | K2—C6—K3      | 79.28 (7) |
| O4Bⅲ—K3—O6           | 121.88 (7)  | O7—C7—O1       | 124.8 (3) |
| O7ⅷ—K3—O3ⅷ           | 88.18 (7)   | O7—C7—C6       | 119.9 (3) |
| O3Bⅲ—K3—O3ⅷ          | 92.43 (7)   | O7—C7—K4       | 56.45 (16) |
| O4Bⅲ—K3—O3ⅷ          | 88.69 (7)   | O1—C7—K4       | 75.08 (16) |
| O6—K3—O3ⅷ            | 73.94 (6)   | C6—C7—K4      | 148.43 (19) |
| O7ⅷ—K3—N3            | 108.15 (7)  | C6—C7—K2      | 45.16 (15) |
| O3Bⅲ—K3—N3           | 120.86 (7)  | O1—C7—K2       | 164.7 (2) |
| O4Bⅲ—K3—N3           | 168.61 (7)  | C6—C7—K2      | 75.46 (16) |
| O6—K3—N3             | 55.78 (7)   | K4—C7—K2      | 90.18 (8) |
| O3ⅷ—K3—N3            | 79.96 (7)   | N4B—Ni1B—N1B   | 95.93 (11) |
| O3Bⅲ—K3—O10          | 136.54 (7)  | N4B—Ni1B—O2B   | 178.25 (11) |
| O4Bⅲ—K3—O10          | 115.82 (7)  | N1B—Ni1B—O2B   | 85.75 (10) |
| O6—K3—O10            | 117.23 (7)  | N4B—Ni1B—O1B   | 85.46 (10) |
| O3ⅷ—K3—O10           | 130.90 (7)  | N1B—Ni1B—O1B   | 178.61 (11) |
| N3—K3—O10            | 71.96 (7)   | O2B—Ni1B—O1B   | 92.86 (9) |
| O7ⅷ—K3—O6Bⅳ         | 115.43 (7)  | C7B—O1B—Ni1B   | 112.2 (2) |
| O3Bⅲ—K3—O6Bⅳ        | 69.03 (7)   | C7B—O1B—K1     | 83.73 (17) |
| O4Bⅲ—K3—O6Bⅳ        | 94.66 (6)   | Ni1B—O1B—K1    | 152.27 (11) |
| O6—K3—O6Bⅳ           | 84.13 (6)   | C1B—O2B—Ni1B   | 113.4 (2) |
| O3ⅷ—K3—O6Bⅳ         | 155.90 (7)  |
| Bond                                      | Distance (Å) | Angle (°) |
|-------------------------------------------|--------------|-----------|
| N3—K3—O6B                                | 96.08 (7)    | 132.9 (2) |
| O10—K3—O6B                               | 68.32 (7)    | 114.8 (2) |
| O7i—K3—O7Bi                              | 64.91 (6)    | 105.44 (8) |
| O3Bii—K3—O7Bi                            | 92.46 (6)    | 124.0 (2) |
| O4Bii—K3—O7Bi                            | 66.72 (6)    | 79.97 (6) |
| O6—K3—O7Bi                               | 136.08 (6)   | 87.20 (7) |
| O3v—K3—O7Bi                              | 147.96 (7)   | 113.82 (19) |
| N3—K3—O7Bi                               | 123.44 (7)   | 110.98 (19) |
| O10—K3—O7Bi                              | 53.97 (6)    | 99.81 (7) |
| O6B—K3—O7Bi                              | 52.04 (6)    | 109.9 (2) |
| O7i—K3—C2Bi                              | 87.34 (7)    | 115.7 (2) |
| O3Bii—K3—C2Bii                           | 43.53 (7)    | 107.9 (2) |
| O4Bii—K3—C2Bii                           | 19.60 (7)    | 85.30 (7) |
| O6—K3—C2Bii                              | 108.83 (7)   | 97.60 (19) |
| O3v—K3—C2Bii                             | 99.07 (7)    | 115.0 (2) |
| N3—K3—C2Bii                              | 164.39 (7)   | 79.58 (6) |
| O10—K3—C2Bii                             | 118.22 (7)   | 106.4 (2) |
| O6B—K3—C2Bii                             | 78.38 (7)    | 155.85 (9) |
| O7B—K3—C2Bii                             | 64.41 (7)    | 88.02 (6) |
| O7i—K3—C6                                | 138.54 (7)   | 117.3 (3) |
| O3Bii—K3—C6                              | 83.02 (7)    | 115.9 (2) |
| O4Bii—K3—C6                              | 133.08 (7)   | 126.6 (2) |
| O6—K3—C6                                 | 19.12 (6)    | 110.4 (2) |
| O3v—K3—C6                                | 63.31 (7)    | 109.6 (2) |
| N3—K3—C6                                 | 41.19 (7)    | 109.0 (2) |
| O10—K3—C6                                | 110.86 (7)   | 106.33 (17) |
| O6B—K3—C6                                | 98.09 (7)    | 106.21 (18) |
| O7B—K3—C6                                | 148.73 (7)   | 115.23 (18) |
| C2Bii—K3—C6                              | 124.54 (7)   | 110.0 (2) |
| O7i—K3—C1Bii                             | 112.89 (7)   | 109.1 (2) |
| O3Bii—K3—C1Bii                           | 18.63 (7)    | 109.6 (2) |
| O4Bii—K3—C1Bii                           | 43.75 (7)    | 103.54 (16) |
| O6—K3—C1Bii                              | 84.28 (7)    | 109.54 (18) |
| O3v—K3—C1Bii                             | 99.41 (7)    | 114.86 (18) |
| N3—K3—C1Bii                              | 138.92 (7)   | 116.8 (3) |
| O10—K3—C1Bii                             | 128.16 (7)   | 116.5 (2) |
| O6B—K3—C1Bii                             | 67.97 (7)    | 126.6 (2) |
| O7B—K3—C1Bii                             | 77.36 (7)    | 125.3 (3) |
| C2Bii—K3—C1Bii                           | 25.56 (7)    | 119.7 (3) |
| C6—K3—C1Bii                              | 101.59 (7)   | 115.0 (3) |
| O7i—K3—H100                              | 64.6         | 46.60 (16) |
| O3Bii—K3—H100                            | 122.7        | 160.3 (2) |
| O4Bii—K3—H100                            | 102.2        | 75.88 (17) |
| O6—K3—H100                               | 124.2        | 128.7 (3) |
| O3v—K3—H100                              | 144.2        | 121.8 (3) |
| N3—K3—H100                               | 86.8         | 109.5 (3) |
| O10—K3—H100                              | 16.5         | 46.89 (15) |
| O6B—K3—H100                              | 58.1         | 87.87 (18) |
| Bond/Angle | Distance/Value | Bond/Distance/Value |
|------------|---------------|-------------------|
| O7B—K3—H10O | 37.8 | C1B—C2B—K2\textsuperscript{iii} | 150.1 (2) |
| C2B\textsuperscript{ii}—K3—H10O | 102.2 | O4B—C2B—K3\textsuperscript{iv} | 49.41 (15) |
| C6—K3—H10O | 122.8 | N1B—C2B—K3\textsuperscript{iv} | 154.7 (2) |
| C1B\textsuperscript{ii}—K3—H10O | 112.1 | C1B—C2B—K3\textsuperscript{v} | 78.56 (17) |
| O7—K4—O4\textsuperscript{v} | 76.22 (7) | K2\textsuperscript{ii}—C2B—K3\textsuperscript{v} | 76.10 (7) |
| O7—K4—O3\textsuperscript{vi} | 93.28 (7) | N2B—C3B—N3B | 113.8 (3) |
| O4—K4—O3\textsuperscript{vi} | 157.43 (7) | N2B—C3B—H3B1 | 108.8 |
| O7—K4—O5\textsuperscript{vii} | 174.39 (7) | N3B—C3B—H3B1 | 108.8 |
| O4—K4—O5\textsuperscript{vii} | 107.36 (7) | N2B—C3B—H3B2 | 108.8 |
| O3\textsuperscript{vi}—K4—O5\textsuperscript{vii} | 81.84 (7) | N3B—C3B—H3B2 | 108.8 |
| O7—K4—N2\textsuperscript{v} | 107.43 (7) | H3B1—C3B—H3B2 | 107.7 |
| O4—K4—N2\textsuperscript{v} | 58.50 (7) | O5B—C4B—N2B | 112.4 (3) |
| O3\textsuperscript{vi}—K4—N2\textsuperscript{v} | 143.96 (7) | O5B—C4B—H4B1 | 109.1 |
| O5\textsuperscript{v}—K4—N2\textsuperscript{v} | 78.18 (7) | O5B—C4B—H4B1 | 109.1 |
| O7—K4—O2\textsuperscript{vi} | 108.20 (7) | O5B—C4B—H4B2 | 109.1 |
| O4—K4—O2\textsuperscript{vi} | 156.33 (7) | N2B—C4B—H4B2 | 109.1 |
| O3\textsuperscript{vi}—K4—O2\textsuperscript{vi} | 45.97 (6) | H4B1—C4B—H4B2 | 107.9 |
| O5\textsuperscript{iv}—K4—O2\textsuperscript{vi} | 70.34 (6) | O5B—C5B—N3B | 113.5 (2) |
| N2—K4—O2\textsuperscript{vi} | 98.69 (7) | O5B—C5B—H5B1 | 108.9 |
| O7—K4—O8\textsuperscript{vii} | 80.97 (7) | N3B—C5B—H5B1 | 108.9 |
| O4—K4—O8\textsuperscript{vii} | 75.67 (7) | O5B—C5B—H5B2 | 108.9 |
| O3\textsuperscript{vi}—K4—O8\textsuperscript{vii} | 83.04 (7) | N3B—C5B—H5B2 | 108.9 |
| O5\textsuperscript{v}—K4—O8\textsuperscript{vii} | 95.62 (7) | H5B1—C5B—H5B2 | 107.7 |
| N2—K4—O8\textsuperscript{vii} | 128.35 (8) | O6B—C6B—N4B | 129.5 (3) |
| O2\textsuperscript{ii}—K4—O8\textsuperscript{vii} | 127.72 (7) | O6B—C6B—C7B | 121.0 (3) |
| O7—K4—C1\textsuperscript{iv} | 107.76 (8) | N4B—C6B—C7B | 109.5 (3) |
| O4—K4—C1\textsuperscript{iv} | 175.75 (8) | O6B—C6B—K1\textsuperscript{v} | 44.70 (15) |
| O3\textsuperscript{vi}—K4—C1\textsuperscript{iv} | 23.33 (7) | N4B—C6B—K1\textsuperscript{v} | 90.89 (19) |
| O5\textsuperscript{v}—K4—C1\textsuperscript{iv} | 68.56 (7) | C7B—C6B—K1\textsuperscript{v} | 149.0 (2) |
| N2—K4—C1\textsuperscript{iv} | 120.66 (8) | O7B—C7B—O1B | 124.2 (3) |
| O2—K4—C1\textsuperscript{iv} | 24.50 (7) | O7B—C7B—C6B | 120.1 (3) |
| O8\textsuperscript{iv}—K4—C1\textsuperscript{iv} | 103.22 (8) | O1B—C7B—C6B | 115.7 (3) |
| O7—K4—O1 | 44.19 (6) | O7B—C7B—K1 | 59.38 (17) |
| O4—K4—O1 | 79.06 (6) | O1B—C7B—K1 | 72.16 (17) |
| O3\textsuperscript{vi}—K4—O1 | 107.45 (7) | C6B—C7B—K1 | 150.1 (2) |
| O5\textsuperscript{v}—K4—O1 | 140.07 (6) | \multicolumn{3}{l}{} |

| Bond/Angle | Distance/Value | Bond/Distance/Value |
|------------|---------------|-------------------|
| N4—Ni1—O1—C7 | −5.2 (2) | K3—C6—C7—O1 | 121.4 (3) |
| O2—Ni1—O1—C7 | 172.8 (2) | O6—C6—C7—K4 | 80.9 (5) |
| N4—Ni1—O1—K4 | 106.9 (2) | N4—C6—C7—K4 | −98.5 (4) |
| O2—Ni1—O1—K4 | −75.08 (19) | K2—C6—C7—K4 | 65.4 (3) |
| N1—Ni1—O2—C1 | −6.6 (2) | K3—C6—C7—K4 | 18.5 (7) |
| O1—Ni1—O2—C1 | 172.3 (2) | O6—C6—C7—K2 | 15.5 (3) |
| N1—Ni1—O2—K4\textsuperscript{iv} | 111.6 (2) | N4—C6—C7—K2 | −163.9 (2) |
| O1—Ni1—O2—K4\textsuperscript{iv} | −69.5 (2) | K3—C6—C7—K2 | −46.9 (3) |
| N4—Ni1—N1—C2 | −179.1 (2) | N4B—Ni1B—O1B—C7B | 4.4 (2) |
| O2—Ni1—N1—C2 | 2.9 (2) | O2B—Ni1B—O1B—C7B | −175.1 (2) |
| N4—Ni1—N1—N2 | 0.5 (2) | N4B—Ni1B—O1B—K1 | −117.2 (2) |
| Bond                                      | Value (°)   |
|-------------------------------------------|-------------|
| O2—Ni1—N1—N2                             | -177.6 (2)  |
| C2—N1—N2—C4                              | -90.7 (3)   |
| Ni1—N1—N2—C4                             | 89.7 (3)    |
| C2—N1—N2—C3                              | 148.5 (3)   |
| Ni1—N1—N2—C3                             | -31.1 (3)   |
| C2—N1—N2—K4v                             | 34.8 (3)    |
| Ni1—N1—N2—K4v                            | -144.78 (16) |
| C5—N3—N4—C6                              | 83.1 (3)    |
| C3—N3—N4—C6                              | -156.0 (3)  |
| K3—N3—N4—C6                              | -33.3 (3)   |
| C5—N3—N4—Ni1                            | -88.9 (3)   |
| C3—N3—N4—Ni1                            | 32.0 (3)    |
| K3—N3—N4—Ni1                            | 154.80 (16) |
| Ni1—Ni1—N4—C6                            | -172.8 (2)  |
| O1—Ni1—N4—C6                            | 8.2 (2)     |
| N1—Ni1—N4—N3                            | -1.0 (2)    |
| O1—Ni1—N4—N3                            | -179.9 (2)  |
| K4vi—O3—C1—O2                           | -36.9 (3)   |
| K3—O3—C1—O2                             | 51.7 (4)    |
| K4vi—O3—C1—C2                           | 141.0 (2)   |
| K3—O3—C1—C2                             | -130.4 (2)  |
| K3—O3—C1—K4vi                          | 88.59 (18)  |
| Ni1—O2—C1—O3                            | -173.4 (2)  |
| K4vi—O2—C1—O3                           | 34.2 (3)    |
| Ni1—O2—C1—C2                            | 8.5 (3)     |
| K4vi—O2—C1—C2                           | -143.9 (2)  |
| Ni1—O2—C1—K4vi                         | 152.39 (15) |
| K4vi—O4—C2—N1                           | -41.1 (4)   |
| K4vi—O4—C2—C1                           | 139.8 (2)   |
| N2—N1—C2—C4                             | 2.0 (5)     |
| Ni1—N1—C2—O4                            | -178.4 (3)  |
| N2—N1—C2—C1                             | -178.8 (2)  |
| Ni1—N1—C2—C1                            | 0.8 (3)     |
| N2—N1—C2—K4v                            | -28.5 (2)   |
| Ni1—N1—C2—K4v                           | 151.09 (15) |
| O3—C1—C2—O4                             | -5.2 (5)    |
| O2—C1—C2—O4                             | 173.0 (3)   |
| K4vi—C1—C2—O4                           | 79.9 (4)    |
| O3—C1—C2—N1                             | 175.5 (3)   |
| O2—C1—C2—N1                             | -6.3 (4)    |
| K4vi—C1—C2—N1                           | -99.3 (4)   |
| O3—C1—C2—K4v                            | 60.0 (5)    |
| K4vi—C1—C2—K4v                          | -121.8 (3)  |
| N4—N3—C3—N2                             | 145.1 (2)   |
| N4—N3—C3—N2                             | -69.2 (3)   |
| C5—N3—N4—C6                             | 52.2 (3)    |
| K3—N3—N4—Ni1                            | 171.75 (18) |
| N1—N2—C3—N3                             | 69.0 (3)    |

| Bond                                      | Value (°)   |
|-------------------------------------------|-------------|
| O2B—Ni1B—O1B—C1B                         | 63.2 (2)    |
| N1B—Ni1B—O2B—C1B                        | -1.5 (2)    |
| O1B—Ni1B—O2B—C1B                         | 178.5 (2)   |
| N4B—Ni1B—N1B—C2B                        | 177.3 (2)   |
| O2B—Ni1B—N1B—C2B                        | -3.2 (2)    |
| N4B—Ni1B—N1B—N2B                        | 2.3 (3)     |
| O2B—Ni1B—N1B—N2B                        | -178.2 (2)  |
| C2B—N1B—N2B—C4B                         | -86.4 (3)   |
| Ni1B—N1B—N2B—C4B                        | 88.5 (3)    |
| C2B—N1B—N2B—C3B                        | 153.5 (3)   |
| Ni1B—N1B—N2B—C3B                        | -31.3 (3)   |
| C2B—N1B—N2B—K2iii                      | 28.4 (3)    |
| Ni1B—N1B—N2B—K2ii                      | -156.67 (16) |
| C5B—N3B—N4B—C6B                         | 89.9 (3)    |
| C3B—N3B—N4B—C6B                         | -149.9 (3)  |
| K1iv—N3B—N4B—C6B                        | -27.1 (3)   |
| C5B—N3B—N4B—Ni1B                       | -85.9 (3)   |
| C3B—N3B—Ni1B—Ni1B                      | 34.3 (3)    |
| K1iv—N3B—Ni1B—Ni1B                    | 157.07 (16) |
| C1B—O3—C1B—O2B                         | -179.7 (2)  |
| K3ii—O3B—C1B—C2B                     | 0.3 (2)     |
| K3ii—O3B—C1B—C2B                     | 176.1 (2)   |
| K2ii—O3B—C1B—O2B                    | -57.3 (4)   |
| K3ii—O3B—C1B—O2B                     | 156.7 (2)   |
| K2ii—O3B—C1B—C2B                  | 52.5 (4)    |
| K2ii—O3B—C1B—C2B                  | 124.0 (3)   |
| K2ii—O3B—C1B—C2B                  | -22.0 (3)   |
| K1iv—O3B—C1B—C2B                   | -126.2 (2)  |
| K2ii—O3B—C1B—K3i                  | 146.0 (3)   |
| K2ii—O3B—C1B—K3i                  | -104.2 (2)  |
| K2ii—O3B—C1B—K3i                  | -173.6 (3)  |
| Ni1B—O2B—C1B—O3B                | 5.2 (3)     |
| Ni1B—O2B—C1B—C2B                | -115.0 (6)  |
| Ni1B—O2B—C1B—K3i              | -35.3 (4)   |
| Ni1B—O2B—C1B—C2B              | -147.0 (3)  |
| Ni1B—O2B—C1B—K3i              | 144.7 (2)   |
| K3ii—O4B—C2B—C1B            | 33.1 (3)    |
| K3ii—O4B—C2B—C2B            | -111.64 (18) |
| K2ii—O4B—C2B—K3ii           | 111.64 (18) |
| Ni1B—N1B—C2B—O4B         | 1.8 (5)     |
| Ni1B—N1B—C2B—C1B         | -173.7 (3)  |
| Ni1B—N1B—C2B—K2ii        | 6.2 (3)     |
| N2B—N1B—C2B—C1B        | -178.3 (2)  |
| N2B—N1B—C2B—C1B        | 6.2 (3)     |
| N2B—N1B—C2B—K2ii       | 161.31 (15) |
| N2B—N1B—C2B—K3ii     | -73.4 (6)   |
| Ni1B—N1B—C2B—K3ii     | 111.1 (5)   |

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| Bond                        | Value (deg)  |
|----------------------------|--------------|
| C4—N2—C3—N3               | -52.6 (3)    |
| K4v—N2—C3—N3              | -178.98 (19) |
| C5—O5—C4—N2               | -57.2 (3)    |
| K4viii—O5—C4—N2           | 162.24 (18)  |
| N1—N2—C4—O5               | -66.0 (3)    |
| C3—N2—C4—O5               | 54.9 (3)     |
| K4v—N2—C4—O5              | 175.62 (17)  |
| C4—O5—C5—N3               | 56.9 (3)     |
| K4viii—O5—C5—N3           | -151.9 (2)   |
| C4—O5—C5—K4v              | -151.2 (2)   |
| N4—N3—C5—K4v              | 66.4 (3)     |
| C3—N3—C5—O5               | -54.2 (3)    |
| K3—N3—C5—O5               | -177.35 (19) |
| N4—N3—C5—K4v              | 18.2 (5)     |
| C3—N3—C5—K4v              | -102.4 (4)   |
| K3—N3—C5—K4v              | 134.4 (3)    |
| K2—O6—C6—N4               | 158.3 (3)    |
| K1—O6—C6—N4               | -88.6 (5)    |
| K3—O6—C6—N4               | 38.5 (4)     |
| K2—O6—C6—C7               | -21.0 (3)    |
| K1—O6—C6—C7               | 92.1 (4)     |
| K3—O6—C6—C7               | -140.8 (2)   |
| K1—O6—C6—K2               | 113.1 (4)    |
| K3—O6—C6—K2               | -119.79 (19) |
| K2—O6—C6—K3               | 119.79 (19)  |
| K1—O6—C6—K3               | -127.1 (4)   |
| N3—N4—C6—O6               | -0.9 (5)     |
| Ni1—N4—C6—O6              | 171.9 (2)    |
| N3—N4—C6—C7               | 178.5 (2)    |
| Ni1—N4—C6—C7              | -8.7 (3)     |
| N3—N4—C6—K2               | 65.3 (8)     |
| Ni1—N4—C6—K2              | -121.9 (6)   |
| N3—N4—C6—K3               | 26.8 (2)     |
| Ni1—N4—C6—K3              | -160.42 (15) |
| K2—O7—C7—O1               | -164.9 (2)   |
| K4—O7—C7—O1               | -33.2 (3)    |
| K3v—O7—C7—O1              | 66.7 (4)     |
| K2—O7—C7—C6               | 113.3 (3)    |
| K4—O7—C7—C6               | 142.9 (2)    |
| K3v—O7—C7—C6              | -117.1 (2)   |
| K2—O7—C7—K4               | -131.67 (18) |
| K3v—O7—C7—K4              | 99.98 (18)   |
| K4—O7—C7—K2               | 131.67 (18)  |
| K3v—O7—C7—K2              | -128.3 (2)   |
| Ni1—O1—C7—O7              | 178.1 (2)    |
| K4—O1—C7—O7               | 28.2 (3)     |
| Ni1—O1—C7—C6              | 1.8 (3)      |
| K4—O1—C7—C6               | -148.1 (2)   |
supporting information

Ni1—O1—C7—K4 149.87 (15) Ni1B—O1B—C7B—K1 −156.51 (16)
Ni1—O1—C7—K2 133.7 (7) O6B—C6B—C7B—O7B 7.6 (5)
K4—O1—C7—K2 −16.1 (8) N4B—C6B—C7B—O7B −173.3 (3)
O6—C6—C7—O7 7.3 (4) K1iv—C6B—C7B—O7B −44.8 (5)
N4—C6—C7—O7 −172.2 (3) O6B—C6B—C7B—O1B −171.3 (3)
K2—C6—C7—O7 −8.2 (2) N4B—C6B—C7B—O1B 7.8 (4)
K3—C6—C7—O7 −55.2 (5) K1iv—C6B—C7B—O1B 136.3 (3)
O6—C6—C7—O1 168.3 (2) K1iv—C6B—C7B—K1 −124.7 (4)
N4—C6—C7—O1 4.4 (4) N4B—C6B—C7B—K1 106.7 (4)
K2—C6—C7—O1 168.3 (2) K1iv—C6B—C7B—K1 −124.7 (4)

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

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| O8—H8O···O9viii | 0.85 | 2.02 | 2.869 (4) | 173 |
| O8—H8P···O4Bv | 0.85 | 2.01 | 2.858 (3) | 166 |
| O9—H9P···O4v | 0.86 | 1.91 | 2.722 (3) | 157 |
| O9—H9O···O6Bvi | 0.86 | 2.07 | 2.864 (3) | 153 |
| O10—H10P···O4v | 0.88 | 2.02 | 2.887 (3) | 168 |
| O10—H10O···O7Bv | 0.87 | 2.04 | 2.882 (3) | 164 |

Symmetry codes: (i) x, y+1, z; (v) −x+1, −y+1, −z; (vii) x, −y+1/2, z−1/2; (viii) x, −y+1/2, z+1/2; (ix) −x+1, y+1/2, z−1/2; (x) −x+1, y+1/2, −z+1/2.