

Bis[1-hydroxyethylidenediphosphonato(1-)](1,10-phenanthroline)nickel(II) monohydrate

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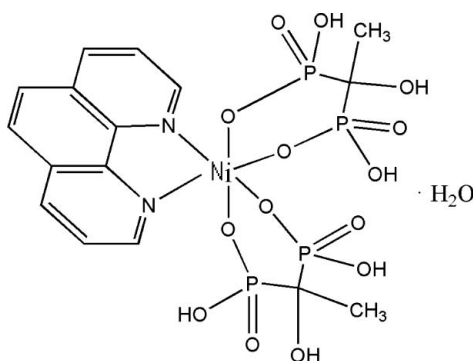
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.045; wR factor = 0.101; data-to-parameter ratio = 12.1.

In the mononuclear title compound, $[\text{Ni}(\text{C}_2\text{H}_6\text{O}_7\text{P}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$, the Ni^{II} atom (site symmetry 2) is bonded to two phosphate-based O, O' -bidentate chelate ligands and one N, N' -bidentate 1,10-phenanthroline ligand, resulting in a slightly distorted $cis\text{-NiN}_2\text{O}_4$ octahedral geometry. In the crystal structure, pairs of complexes are linked by double hydrogen bonds, forming a one-dimensional chain-like structure. Aromatic $\pi\text{-}\pi$ stacking interactions [centroid-centroid separation = $3.768(2)$ Å] and further hydrogen bonds generate a two-dimensional structure. The water O atom also lies on a crystallographic twofold axis.

Related literature

For related literature, see: Song *et al.* (1999); Xiang *et al.* (2007).



Experimental

Crystal data

$[\text{Ni}(\text{C}_2\text{H}_6\text{O}_7\text{P}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$

$M_r = 664.95$

Monoclinic, $C2/c$
 $a = 17.108(2)$ Å
 $b = 18.572(2)$ Å
 $c = 7.5142(9)$ Å
 $\beta = 90.164(2)^\circ$
 $V = 2387.5(5)$ Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.16$ mm⁻¹
 $T = 293(2)$ K
 $0.22 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\text{min}} = 0.770$, $T_{\text{max}} = 0.819$

6424 measured reflections
 2268 independent reflections
 1857 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.101$
 $S = 1.06$
 2268 reflections
 187 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|--------|-----------|--------|-----------|
| Ni1—N1 | 2.059 (3) | Ni1—O4 | 2.109 (2) |
| Ni1—O3 | 2.065 (3) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| $D\text{---}H\cdots A$ | $D\text{---}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{---}H\cdots A$ |
|----------------------------------|----------------|-------------|-------------|------------------------|
| O1W—H1WA \cdots O7 | 0.85 (6) | 1.93 (6) | 2.758 (5) | 166 (6) |
| O2—H2A \cdots O1W ⁱ | 0.84 (4) | 1.91 (4) | 2.748 (4) | 175 (6) |
| O6—H6A \cdots O4 ⁱⁱ | 0.83 (4) | 1.82 (4) | 2.644 (3) | 171 (5) |
| O7—H7 \cdots O4 | 0.82 | 2.47 | 2.894 (4) | 113 |
| O7—H7 \cdots O3 ⁱⁱⁱ | 0.82 | 2.08 | 2.889 (4) | 169 |

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2645).

References

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 Song, H.-H., Zheng, L.-M., Lin, C.-H., Wang, S.-L., Xin, X.-Q. & Gao, S. (1999). Chem. Mater. **11**, 2382–2388.
 Xiang, J., Li, M., Wu, S., Yuan, L.-J. & Sun, J. (2007). J. Mol. Struct. **826**, 143–149.

supplementary materials

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Bis[1-hydroxyethylidenediphosphonato(1-)](1,10-phenanthroline)nickel(II) monohydrate

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Comment

Metal–phosphonate compounds are of current interest due to their fascinating topologies and novel physical properties (e.g. Song et al. 1999; Xiang et al. 2007).

In the title compound, (I), the Ni^{II} ion with site symmetry 2, is chelated by four oxygen atoms from two phosphate-containing O,O-chelate ligands and two nitrogen atoms from an N,N-chelating 1,10-phenanthroline (phen) ligand to generate a cis-NiN₂O₄ distorted octahedral coordination geometry (Fig. 1, Table 1).

Intermolecular hydrogen bond interactions (Table 2) occur between the phosphate ligands. Each complex is connected with its neighbours by hydrogen bonds to form one-dimensional chain (Fig. 2). Aromatic π - π stacking interactions with distance between ring centroids of 3.768 (2) Å extend the width of the chain. Water molecules between those chains act as bridges to generate two dimensional structure through further O—H \cdots O hydrogen bonds.

Experimental

1,10-Phenanthroline (1 mmol), Ni(NO₃)₂·6H₂O (2 mmol), 1-hydroxyethylidenediphosphonic acid (0.2 ml) and ethanol/H₂O (v:v = 1:3, 40 ml) were mixed. The resulting mixture was heated and stirred for 4 h and the solution was filtered. By slow evaporation of the solvent, blue blocks of (I) were obtained after several months.

Refinement

The water H atoms were located from difference maps and their positions freely refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The other H atoms were geometrically placed (C—H = 0.93–0.97 Å, O—H = 0.82 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

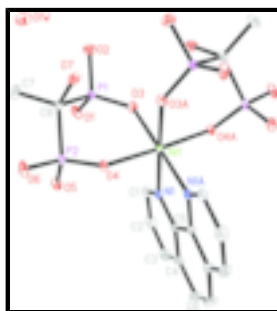


Fig. 1. View of the molecular structure of (I), showing displacement ellipsoids drawn at the 30% probability level. H atoms are omitted for clarity. Atoms with the suffix A are generated by the symmetry operation $(-x, y, 1/2 - z)$.

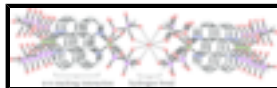


Fig. 2. Two-dimensional structure of (I) formed by π - π stacking interactions between hydrogen bonded chains.

Bis[1-hydroxyethylidenediphosphonato(1-)](1,10-phenanthroline)nickel(II) monohydrate

Crystal data

| | |
|---|---|
| $[\text{Ni}(\text{C}_2\text{H}_6\text{O}_7\text{P}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$ | $F_{000} = 1360$ |
| $M_r = 664.95$ | $D_x = 1.850 \text{ Mg m}^{-3}$ |
| Monoclinic, $C2/c$ | Mo $K\alpha$ radiation |
| Hall symbol: $-C2yc$ | $\lambda = 0.71073 \text{ \AA}$ |
| $a = 17.108 (2) \text{ \AA}$ | Cell parameters from 542 reflections |
| $b = 18.572 (2) \text{ \AA}$ | $\theta = 2.8\text{--}24.7^\circ$ |
| $c = 7.5142 (9) \text{ \AA}$ | $\mu = 1.16 \text{ mm}^{-1}$ |
| $\beta = 90.164 (2)^\circ$ | $T = 293 (2) \text{ K}$ |
| $V = 2387.5 (5) \text{ \AA}^3$ | Block, blue |
| $Z = 4$ | $0.22 \times 0.20 \times 0.18 \text{ mm}$ |

Data collection

| | |
|--|--|
| Bruker SMART CCD diffractometer | 2268 independent reflections |
| Radiation source: fine-focus sealed tube | 1857 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.043$ |
| $T = 293(2) \text{ K}$ | $\theta_{\text{max}} = 25.7^\circ$ |
| ω scans | $\theta_{\text{min}} = 1.6^\circ$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | $h = -20 \rightarrow 20$ |
| $T_{\text{min}} = 0.770$, $T_{\text{max}} = 0.819$ | $k = -14 \rightarrow 22$ |
| 6424 measured reflections | $l = -8 \rightarrow 9$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: difmap and geom |
| $R[F^2 > 2\sigma(F^2)] = 0.045$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.101$ | $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 5.7735P]$ |
| $S = 1.06$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2268 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 187 parameters | $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$ |
| 3 restraints | $\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| H2A | 0.093 (2) | 0.050 (3) | 0.236 (8) | 0.07 (2)* |
| H6A | 0.0606 (18) | 0.256 (3) | 0.852 (6) | 0.044 (15)* |
| O1W | 0.0000 | 0.0069 (3) | 0.7500 | 0.0356 (11) |
| O7 | 0.03755 (15) | 0.11993 (14) | 0.5280 (4) | 0.0245 (6) |
| H7 | 0.0046 | 0.1455 | 0.4800 | 0.037* |
| O5 | 0.17574 (14) | 0.28983 (14) | 0.5476 (3) | 0.0220 (6) |
| Ni1 | 0.0000 | 0.27786 (4) | 0.2500 | 0.01343 (19) |
| P1 | 0.13862 (5) | 0.15397 (5) | 0.27824 (13) | 0.0161 (2) |
| P2 | 0.10427 (5) | 0.24696 (6) | 0.59910 (12) | 0.0157 (2) |
| O3 | 0.07673 (14) | 0.19644 (14) | 0.1833 (3) | 0.0192 (6) |
| O4 | 0.02826 (14) | 0.27551 (13) | 0.5233 (3) | 0.0159 (6) |
| N1 | 0.07336 (17) | 0.36185 (17) | 0.1867 (4) | 0.0175 (7) |
| O2 | 0.13487 (17) | 0.07260 (16) | 0.2226 (4) | 0.0295 (7) |
| O1 | 0.22184 (14) | 0.17731 (16) | 0.2446 (4) | 0.0265 (7) |
| O6 | 0.10100 (15) | 0.24085 (17) | 0.8048 (3) | 0.0257 (7) |
| C5 | 0.0390 (2) | 0.4269 (2) | 0.2147 (5) | 0.0177 (8) |
| C1 | 0.1439 (2) | 0.3607 (2) | 0.1143 (5) | 0.0219 (9) |
| H1 | 0.1674 | 0.3164 | 0.0931 | 0.026* |
| C2 | 0.1846 (2) | 0.4237 (2) | 0.0684 (5) | 0.0293 (10) |
| H2 | 0.2338 | 0.4210 | 0.0164 | 0.035* |
| C8 | 0.1142 (2) | 0.1545 (2) | 0.5157 (5) | 0.0177 (8) |
| C6 | 0.0362 (3) | 0.5580 (2) | 0.2142 (6) | 0.0347 (11) |
| H6 | 0.0605 | 0.6016 | 0.1889 | 0.042* |
| C4 | 0.0760 (3) | 0.4923 (2) | 0.1766 (5) | 0.0258 (9) |
| C7 | 0.1711 (2) | 0.1109 (2) | 0.6265 (6) | 0.0293 (10) |
| H7A | 0.1533 | 0.1091 | 0.7475 | 0.044* |
| H7B | 0.2218 | 0.1330 | 0.6225 | 0.044* |
| H7C | 0.1743 | 0.0628 | 0.5798 | 0.044* |
| C3 | 0.1510 (3) | 0.4888 (2) | 0.1011 (6) | 0.0317 (11) |
| H3 | 0.1776 | 0.5310 | 0.0734 | 0.038* |
| H1WA | 0.014 (5) | 0.036 (3) | 0.669 (8) | 0.14 (3)* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1W | 0.042 (3) | 0.025 (3) | 0.040 (3) | 0.000 | -0.001 (2) | 0.000 |
| O7 | 0.0212 (14) | 0.0220 (15) | 0.0303 (17) | -0.0014 (12) | 0.0010 (12) | 0.0085 (13) |
| O5 | 0.0159 (13) | 0.0305 (17) | 0.0198 (14) | -0.0035 (12) | 0.0005 (11) | -0.0011 (12) |
| Ni1 | 0.0139 (3) | 0.0141 (4) | 0.0122 (3) | 0.000 | -0.0011 (3) | 0.000 |
| P1 | 0.0134 (5) | 0.0183 (5) | 0.0165 (5) | 0.0021 (4) | -0.0013 (4) | -0.0034 (4) |
| P2 | 0.0128 (5) | 0.0219 (6) | 0.0124 (5) | 0.0008 (4) | -0.0010 (4) | -0.0011 (4) |
| O3 | 0.0180 (13) | 0.0239 (15) | 0.0156 (14) | 0.0043 (11) | 0.0016 (11) | -0.0013 (11) |
| O4 | 0.0153 (13) | 0.0201 (14) | 0.0122 (13) | 0.0008 (11) | -0.0010 (10) | -0.0008 (11) |
| N1 | 0.0176 (16) | 0.0212 (18) | 0.0136 (16) | -0.0013 (14) | -0.0031 (13) | 0.0015 (13) |
| O2 | 0.0306 (17) | 0.0215 (16) | 0.0365 (18) | 0.0042 (14) | 0.0010 (14) | -0.0063 (14) |
| O1 | 0.0150 (13) | 0.0427 (18) | 0.0218 (15) | -0.0044 (13) | 0.0006 (11) | -0.0085 (13) |
| O6 | 0.0179 (14) | 0.0456 (19) | 0.0134 (14) | 0.0072 (13) | -0.0002 (12) | -0.0013 (13) |
| C5 | 0.028 (2) | 0.013 (2) | 0.0125 (19) | -0.0014 (16) | -0.0047 (16) | -0.0007 (15) |
| C1 | 0.0205 (19) | 0.026 (2) | 0.019 (2) | -0.0005 (17) | -0.0023 (16) | -0.0004 (17) |
| C2 | 0.023 (2) | 0.043 (3) | 0.022 (2) | -0.009 (2) | 0.0021 (17) | 0.005 (2) |
| C8 | 0.0162 (18) | 0.017 (2) | 0.020 (2) | 0.0003 (15) | -0.0008 (15) | 0.0045 (16) |
| C6 | 0.051 (3) | 0.015 (2) | 0.038 (3) | -0.009 (2) | -0.007 (2) | 0.0020 (19) |
| C4 | 0.037 (2) | 0.021 (2) | 0.019 (2) | -0.0084 (19) | -0.0071 (18) | 0.0027 (17) |
| C7 | 0.026 (2) | 0.034 (3) | 0.028 (2) | 0.0110 (19) | -0.0049 (18) | 0.006 (2) |
| C3 | 0.037 (3) | 0.028 (3) | 0.030 (2) | -0.014 (2) | -0.003 (2) | 0.005 (2) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------------------|------------|--------------------|-----------|
| O1W—H1WA | 0.85 (6) | N1—C5 | 1.360 (5) |
| O7—C8 | 1.464 (4) | O2—H2A | 0.84 (2) |
| O7—H7 | 0.8200 | O6—H6A | 0.83 (4) |
| O5—P2 | 1.511 (3) | C5—C4 | 1.400 (5) |
| Ni1—N1 | 2.059 (3) | C5—C5 ⁱ | 1.438 (7) |
| Ni1—N1 ⁱ | 2.059 (3) | C1—C2 | 1.406 (6) |
| Ni1—O3 ⁱ | 2.065 (3) | C1—H1 | 0.9300 |
| Ni1—O3 | 2.065 (3) | C2—C3 | 1.362 (6) |
| Ni1—O4 | 2.109 (2) | C2—H2 | 0.9300 |
| Ni1—O4 ⁱ | 2.109 (2) | C8—C7 | 1.514 (5) |
| P1—O3 | 1.499 (3) | C6—C6 ⁱ | 1.352 (9) |
| P1—O1 | 1.510 (3) | C6—C4 | 1.426 (6) |
| P1—O2 | 1.569 (3) | C6—H6 | 0.9300 |
| P1—C8 | 1.834 (4) | C4—C3 | 1.405 (6) |
| P2—O4 | 1.514 (3) | C7—H7A | 0.9600 |
| P2—O6 | 1.551 (3) | C7—H7B | 0.9600 |
| P2—C8 | 1.836 (4) | C7—H7C | 0.9600 |
| N1—C1 | 1.326 (5) | C3—H3 | 0.9300 |
| C8—O7—H7 | 109.5 | P1—O2—H2A | 119 (4) |
| N1—Ni1—N1 ⁱ | 81.47 (17) | P2—O6—H6A | 116 (3) |

| | | | |
|--------------------------------------|-------------|------------------------|-------------|
| N1—Ni1—O3 ⁱ | 177.81 (11) | N1—C5—C4 | 122.9 (4) |
| N1 ⁱ —Ni1—O3 ⁱ | 96.34 (11) | N1—C5—C5 ⁱ | 117.3 (2) |
| N1—Ni1—O3 | 96.34 (11) | C4—C5—C5 ⁱ | 119.8 (2) |
| N1 ⁱ —Ni1—O3 | 177.81 (11) | N1—C1—C2 | 122.6 (4) |
| O3 ⁱ —Ni1—O3 | 85.85 (14) | N1—C1—H1 | 118.7 |
| N1—Ni1—O4 | 95.88 (11) | C2—C1—H1 | 118.7 |
| N1 ⁱ —Ni1—O4 | 85.92 (11) | C3—C2—C1 | 119.0 (4) |
| O3 ⁱ —Ni1—O4 | 83.84 (10) | C3—C2—H2 | 120.5 |
| O3—Ni1—O4 | 94.41 (9) | C1—C2—H2 | 120.5 |
| N1—Ni1—O4 ⁱ | 85.92 (11) | O7—C8—C7 | 107.8 (3) |
| N1 ⁱ —Ni1—O4 ⁱ | 95.88 (11) | O7—C8—P1 | 105.4 (2) |
| O3 ⁱ —Ni1—O4 ⁱ | 94.41 (9) | C7—C8—P1 | 112.6 (3) |
| O3—Ni1—O4 ⁱ | 83.84 (10) | O7—C8—P2 | 107.7 (2) |
| O4—Ni1—O4 ⁱ | 177.63 (14) | C7—C8—P2 | 111.9 (3) |
| O3—P1—O1 | 115.74 (16) | P1—C8—P2 | 111.03 (19) |
| O3—P1—O2 | 110.59 (16) | C6 ⁱ —C6—C4 | 121.2 (2) |
| O1—P1—O2 | 105.64 (16) | C6 ⁱ —C6—H6 | 119.4 |
| O3—P1—C8 | 107.32 (15) | C4—C6—H6 | 119.4 |
| O1—P1—C8 | 112.24 (16) | C5—C4—C3 | 117.2 (4) |
| O2—P1—C8 | 104.79 (17) | C5—C4—C6 | 119.0 (4) |
| O5—P2—O4 | 114.45 (15) | C3—C4—C6 | 123.8 (4) |
| O5—P2—O6 | 109.01 (15) | C8—C7—H7A | 109.5 |
| O4—P2—O6 | 111.53 (14) | C8—C7—H7B | 109.5 |
| O5—P2—C8 | 109.23 (16) | H7A—C7—H7B | 109.5 |
| O4—P2—C8 | 106.25 (16) | C8—C7—H7C | 109.5 |
| O6—P2—C8 | 105.99 (17) | H7A—C7—H7C | 109.5 |
| P1—O3—Ni1 | 135.93 (15) | H7B—C7—H7C | 109.5 |
| P2—O4—Ni1 | 124.60 (14) | C2—C3—C4 | 120.0 (4) |
| C1—N1—C5 | 118.2 (3) | C2—C3—H3 | 120.0 |
| C1—N1—Ni1 | 129.7 (3) | C4—C3—H3 | 120.0 |
| C5—N1—Ni1 | 111.9 (2) | | |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1W—H1WA \cdots O7 | 0.85 (6) | 1.93 (6) | 2.758 (5) | 166 (6) |
| O2—H2A \cdots O1W ⁱⁱ | 0.84 (4) | 1.91 (4) | 2.748 (4) | 175 (6) |
| O6—H6A \cdots O4 ⁱⁱⁱ | 0.83 (4) | 1.82 (4) | 2.644 (3) | 171 (5) |
| O7—H7 \cdots O4 | 0.82 | 2.47 | 2.894 (4) | 113 |
| O7—H7 \cdots O3 ^{iv} | 0.82 | 2.08 | 2.889 (4) | 169 |

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

Fig. 1

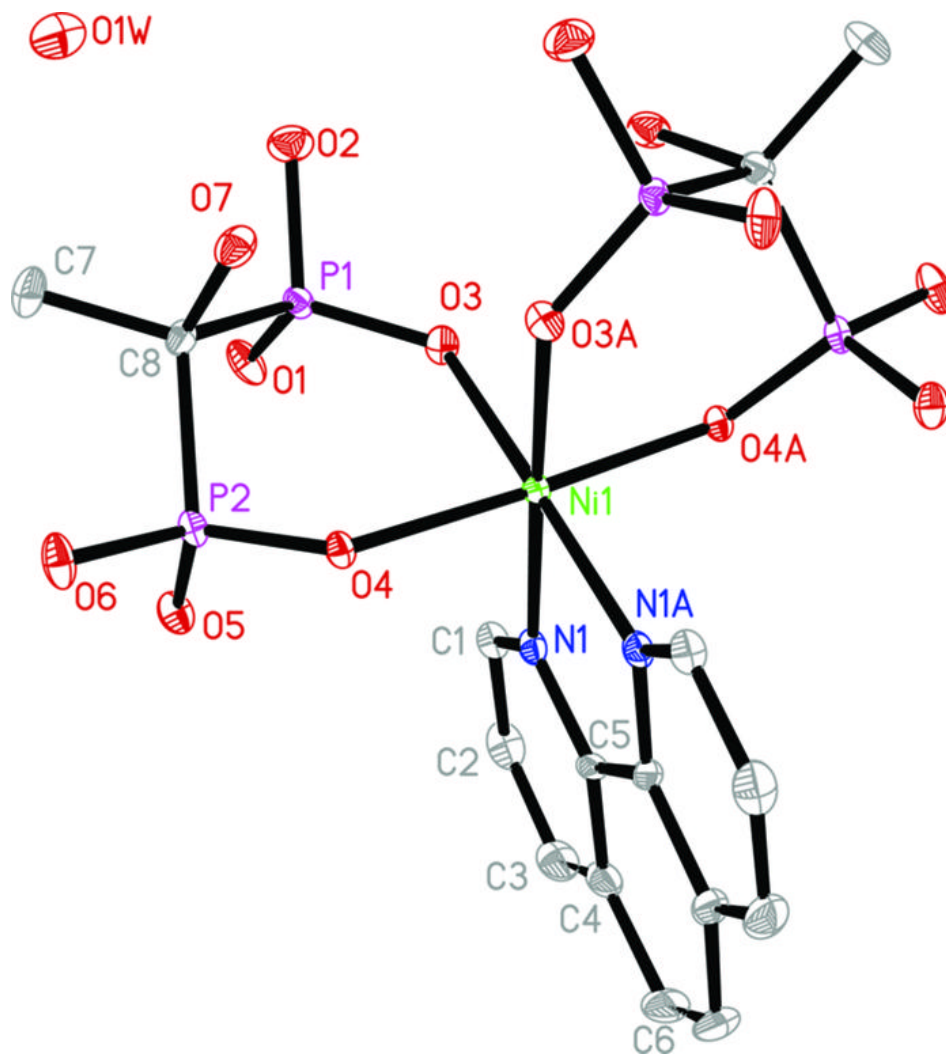


Fig. 2

