КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A [(DIHYDROGEN PYROPHOSPHATO-κ²O,O′) BIS(1,10-PHENANTHROLINE-N,N′)NICKEL(II)]2.5-HYDRATE [Ni(H₂P₂O₇)(C₁₂H₈N₂)₂]·2.5H₂O

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Coordination nickel pyrophosphate $[Ni(H_2P_2O_7)(C_{12}H_8N_2)_2]\cdot2.5H_2O$ (**I**) is hydrothermally synthesized and characterized by single crystal X-ray diffraction. The title compound crystallizes in the triclinic system, space group P-1, with cell parameters $M = 640.07$, $a = 10.285(2)$ Å, $b = 10.510(3)$ Å, $c = 12.775(3)$ Å, $\alpha = 88.06(2)°$, $\beta = 77.87(2)°$, $\gamma = 89.26(2)°$, $V = 1349.2(5)$ Å³, $Z = 2$, $R_1[I > 2\sigma(I)] = 0.0438$, $wR_2[I > 2\sigma(I)] = 0.1244$. This compound displays a new structure of ladder-like 2D layers parallel to (010) consisting of $[Ni(H_2P_2O_7)(phen)_2]$ entities with the distorted octahedral NiN_4O_2 coordination geometry arising from two chelating 1,10-phenanthroline ligands and diphosphate $[H_2P_2O_7]$ ligand bridged through $\pi\cdots\pi$ stacking interactions between the neighboring 1,10-phen ligands with interplanar distances of 4.425 Å and 4.525 Å. In the compound, the phen ligands bind in a bidentate fashion to the metal atoms and the ladder-like structure of the compound extends into a three-dimensional supramolecular array via hydrogen bonds (O4—H17…O5) between diphosphate groups, which delimits b axis tunnels where water molecules are located.

The pyrophosphate anion $P_2O_7^{4-}$ or $[O_3P—O—PO_3]^{4-}$ plays a key role in biochemistry and applied materials science. Inorganic pyrophosphate materials are obtained via high-temperature solid-state precursor methods or hydrothermal techniques.

It is an interesting ligand because of its multidentate nature, and can give rise to many different coordination modes as it interacts with metal ions. In addition, it can be successively protonated to generate $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$ and $H_3P_2O_7^-$ anions, which may result in an additional large variety of structural topologies.
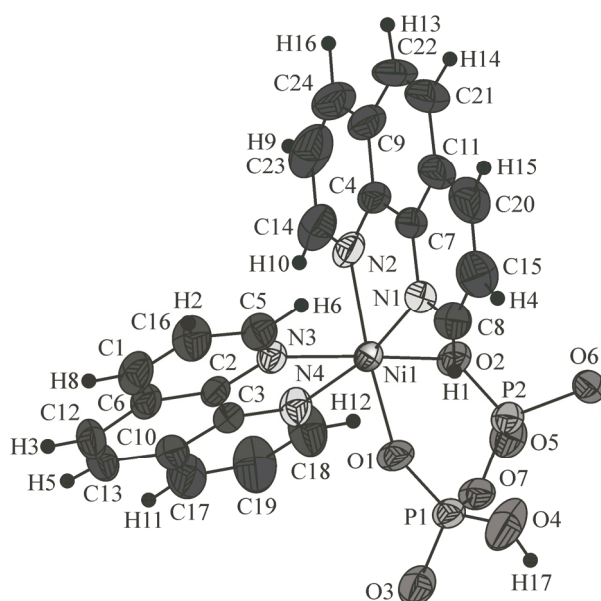
Transition metal phosphate and pyrophosphate anions are of great interest for their rich structural chemistry, magnetic properties, and potential applications (ion exchange, surface absorption chemistry, ionic conductivity, etc.) [1, 2]. The synthesis under hydrothermal conditions in the presence of organic amine, which acts as a template or a structural-directing agent, has successfully led to many organically templated transition metal phosphates or pyrophosphates. Among them nickel is of particular interest owing to its feasibility for the octahedral coordination and potential catalytic properties [3—7]. The susceptibility of tetraanion to hydrolysis, particularly in the presence of M^{II} cations, has prevented the isolation of Ni^{II} metal-organic pyrophosphate complexes for the investigation, and the number of characterized structures remains limited. However, the use of chelating ligands in the synthetic route and precise control of the factors influencing the synthetic process have recently

allowed a number of Ni^{II} pyrophosphate coordination complexes to be isolated and investigated for their biological, magnetic and catalytic properties. In such compounds the transition metal plays a key role in building interesting topologies with one-, two-, or three-dimensional networks. In these atomic arrangements, the transition element is coordinated generally to the ligand via several donor atoms such as oxygen or nitrogen. In recent years, many researchers have focused on diphosphates because they are powerful ligands that can link metal ions through their oxygen atoms, and can play an essential role in the interaction between the metallic centers [8].

In this paper we report the hydrothermal synthesis and crystal structure of a [(dihydrogen pyrophosphato-K^{2}O,O′) bis(1,10-phenanthroline-N,N′)nickel(II)]·2.5-hydrate.

Experimental. The title compound was prepared from a mixture of nickel(II) nitrate hexahydrate (≥99 %), phosphoric acid (85 wt%), 1,10-phenanthroline (≥99.0 %), and ethanol. In a typical synthesis, the solution was prepared by dissolving 0.29 g of Ni(NO$_3$)$_2$·6H$_2$O in 10 ml of ethanol under constant stirring, then 0.12 ml of phosphoric acid was slowly added dropwise, followed by the addition of 0.36 g of 1,10-phenanthroline with constant stirring. The resulting mixture, with a molar ratio of 1.0 Ni(NO$_3$)$_2$·6H$_2$O: 2.0 H$_3$PO$_4$: 2.0 1,10-phenanthroline: 10 ml ethanol, was transferred into a 15 ml Teflon-lined stainless-steel autoclave and heated at 453 K for seven days. The resulting green block-like crystal product as a single phase was recovered by filtration, washed with ethanol, and dried at room temperature.

A suitable single crystal of title compound (**I**) with dimensions 0.4×0.32×0.28 mm was selected and mounted on a thin glass fiber for X-ray diffraction studies. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a sealed-tube X-ray source (graphite-monochromated radiation (MoK_α) at room temperature 293 K. Lorentz polarisation corrections were applied. The structure was solved by the heavy atom method and refined by the full-matrix least-squares technique based on F^2 using SHELXL. A ψ-scan absorption correction was applied, which resulted in transmission factors ranging from 0.5257 to 0.5825. The nickel and phosphorus atoms were first located. The carbon, nitrogen, and oxygen atoms were found in the final difference Fourier maps. All hydrogen atoms, except for H17 of O4, were identified from a difference Fourier map and refined with an isotropic temperature factor. The H17 atom was positioned geometrically. Compound **I** crystallizes in the triclinic system, space group P-1, with unit cell parameters: $M = 640.07$, $a = 10.285(2)$ Å, $b = 10.510(3)$ Å, $c = 12.775(3)$ Å, $\alpha = 88.06(2)°$, $\beta = 77.87(2)°$, $\gamma = 89.26(2)°$, $V = 1349.2(5)$ Å^3, $Z = 2$, $R_1[I > 2\sigma(I)] = 0.0438$, $wR_2[I > 2\sigma(I)] = 0.1142$, R_1[all data] = 0,0605, wR_2[all data] = 0,1244, S-factor = 1.038. CIF files containing complete information on the structure of (**I**) was deposited with the

Fig. 1. Molecular structure of the title compound with the atom numbering scheme.
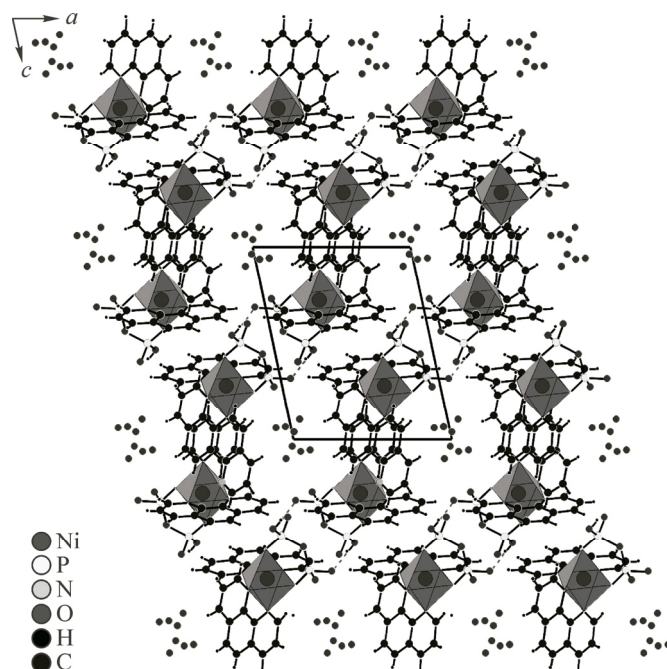The thermal ellipsoids are drawn at the 50 % probability level

Fig. 2. View of the crystal structure of (**I**) along the *b* axis
(hydrogen bonds are shown by dashed lines)

Cambridge Crystallographic Data Center (No. 1403526); the file is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The crystal structure of (**I**) is constructed from neutral ladder-like 2D layers parallel to (010) consisting of $[\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)(\text{phen})_2]$ entities. In this layer there are significant π—π stacking interactions between the neighboring 1,10-phen ligands with interplanar distances of 4.425 Å and 4.525 Å. These generate two-dimensional layers parallel to (010) (Fig. 2) interconnected to the framework through hydrogen bonds (O4—H17…O5) (2.664 Å (1.877 Å)) between diphosphate groups, strong enough to form a three-dimensional framework, which delimits *b* axis tunnels under the elliptic shape of diameters $r_{min} = 5.15(6)$ Å, $r_{max} = 7.27(3)$ Å, where water molecules are located. The two independent complex molecules interact with each other by two strong O—H…O hydrogen bonds between the adjacent dihydrogen pyrophosphate ligands. This defines a classical 8-membered ring graph-set motif $R_2^2(8)$ [12]. Each Ni^{2+} ion adopts a distorted octahedral coordination geometry of $\{\text{NiO}_2\text{N}_4\}$, defined by four nitrogen donors from two phen molecules, two oxygen donors from the $\text{H}_2\text{P}_2\text{O}_7$ group. The O2, N1, N3, N4 atoms constitute the equatorial plane of the octahedron, the mean deviation being 0.222(1) Å and the Ni atom being 0.350(2) Å. In $[\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)(\text{phen})_2]$ entities the two 1,10-phen molecules are almost planar (the largest deviation of atoms from the mean plane is 0.061(2) for the N2 atom and –0.033(4) for the C19 atom).

In each octahedral $\{\text{NiO}_2\text{N}_4\}$ unit, the Ni—O bonds of 2.054(2) Å and 2.075(2) Å are in the range of values observed in other Ni diphosphate complexes such as $(\text{NH}_4)_2\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ [9], $(\text{C}_2\text{N}_2\text{H}_{10})[\text{Ni}(\text{HP}_2\text{O}_7)_2(\text{H}_2\text{O})_2]$ [10], and $(\text{C}_3\text{N}_2\text{H}_{12})_2(\text{Ni}(\text{H}_2\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ [11]. The Ni—N bonds are in the range of 2.082(3)—2.128(2) Å. Taking into account the irregular bond angles the N—Ni—N angles are in the range of 79.40(9)—167.67(9)°, the N—Ni—O angles are in the range of 86.35(9)—172,77(9)°, and the O1—Ni—O2 angle is 93.68(8)°. The two phosphorous atoms are tetrahedrally coordinated and covalently linked through O7 to form a P_2O_7 group with a quasi-eclipsed conformation as confirmed by the torsion angle values 1.34(2)°, 0.19(4)°, and –1.17(3)° of respectively O2—P2—P1—O1, O5—P2—P1—O3, and O6—P2—P1—O4 and it bridges the Ni(II) ion through O1—P1 and O2—P2 linkages. The P_2O_7 group is bent, with a P1—O7—P2 bond angle of 129.4(2)° as ob-

T a b l e 1

Selected bonds lengths (Å) *and angles* (deg.) *for* **I**

Ni1—O1, Ni1—O2, Å	2.054(2), 2.075(2)
Ni1—N1, Ni1—N2, Ni1—N3, Ni1—N4, Å	2.082(3), 2.108(2), 2.128(2), 2.094(3)
P1—O1, P1—O2, Å	1.496(2), 1.500(2)
P1—O7, P2—O7, Å	1.648(3), 1.608(3)
P1—P2, Å	2.944(1)
∠N—Ni1—N range, deg.	79.40(9)—95.12(11)
∠N—Ni1—O range, deg.	86.35(9)—97.04(9)
∠O1—Ni1—O2, deg.	93.68(8)
∠O1—Ni1—N2, deg.	172,74(10)
∠O2—Ni1—N3, deg.	172.77(9)
∠N1—Ni1—N4, deg.	167.67(9)

served in other M(II)-organic diphosphate frameworks [13—18]. In the P_2O_7 group, the P—O distances are in the range of 1.406—1.615(9) Å while the shared oxygen atom is at P1—O7—P2 between 1.608(3)—1.674(5) Å.

We may thus conclude that the hydrogen bonding and π—π stacking interactions of phen groups play an important role in the stability of the whole structure of compound (**I**).

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