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Hexaaquanickel(II) bis[2-carboxylato-2-(isothiouronium-*S*-ylmethyl)propane-1,3-diyl phosphate] hexahydrate

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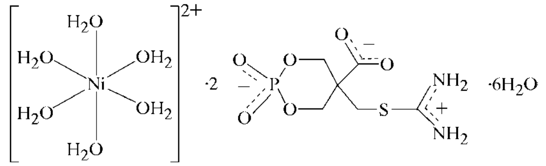
In the title complex, $[Ni(H_2O)_6](C_6H_{10}N_2O_6PS)_2{\cdot}6H_2O$, the asymmetric unit consists of one-half of an Ni atom (which lies on an inversion centre) with three coordinated water molecules, one complete 2-carboxylato-2-(isothiouronium-*S*-ylmethyl)propane-1,3-diyl phosphate anion and three noncoordinated water molecules. The hexaaquanickel(II) cations have distorted octahedral coordination and are connected *via* water chains to form two-dimensional supramolecular networks parallel to the *ab* plane. The phosphate ester anion is linked *via* N—H···O and O—H···O hydrogen bonds, thus creating various ring, dimer and chain hydrogen-bonding patterns, and building up a second two-dimensional supramolecular network parallel to the *ab* plane. The crystal structure is further stabilized by an intra- and interlayer hydrogen-bond network. This work illustrates that a carboxylate with a caged phosphate ester can open its ring in the presence of dichloridotetrakis(thiourea)nickel, and the resulting polyfunctional anion can be used for constructing a complex hydrogen-bonding scheme.

Comment

This study was initiated as an exploration of a complex containing both a proton donor and a proton acceptor, formed *via* reaction of a carboxylate with a caged phosphate ester, $OP(OCH_2)_3CCOO^-$, with $Ni(thiourea)_4Cl_2$, because there are currently two main strategies in crystal engineering, based on the use of either co-coordinative bonds or weaker intermolecular interactions (Burrows *et al.*, 2000). The reaction of the coordinated thiourea with the caged phosphate ester unexpectedly produced a polyfunctional anion, 2-carboxylato-2-(isothiouronium-*S*-ylmethyl)propane-1,3-diyl phosphate, where the structure of the bicyclic $OP(OCH_2)_3C$ cage is opened. Intermolecular interactions between the isothiouronium cation and the carboxylate anion, between the propane-1,3-diyl phosphate and water molecules, and so on, result in a wide variety of hydrogen-bond patterns. In addition, intermolecular interactions between the hexaaquanickel(II) cation and noncoordinated water molecules also create a number of interesting water chains and hydrogen-bonded ring graph sets. We describe here the interesting structure of the title compound, (I), with rich O—H···O intra- and interlayer hydrogen bonding and N—H···O dimer hydrogen-bond patterns, leading to a three-dimensional supramolecular network.



(I)

The asymmetric unit of (I) comprises one-half of an Ni atom with three coordinated water molecules, one complete 2-carboxylato-2-(isothiouronium-*S*-ylmethyl)propane-1,3-diyl phos-

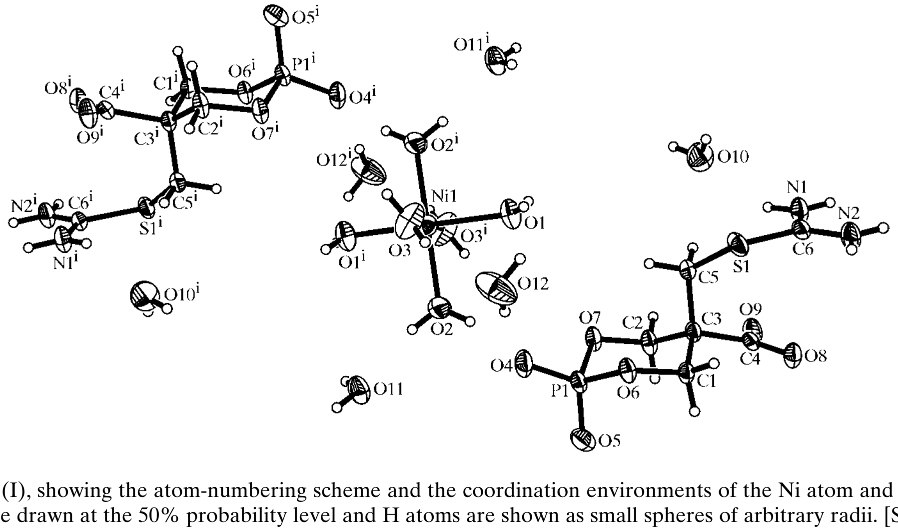


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination environments of the Ni atom and the phosphate ester anion. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

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phate anion and three noncoordinated water molecules, and is shown in Fig. 1 in a symmetry-expanded view, which displays the full coordination of the hexaaquanickel(II) cation and the phosphate ester anion. Selected geometric parameters are given in Table 1.

The hexaaquanickel(II) cation has a distorted octahedral environment. The interactions of the coordinated water molecules and atoms O11 and O12 form network architectures of interesting topology. In the crystallographic *b* direction, atoms H3*B* and H2*B* coordinate to atoms O11$^{\text{iv}}$ and O11, respectively [symmetry code: (iv) *x*, *y* + 1, *z*]. Similarly, atoms H3*A* and H1*A* connect to atoms O12 and O12$^{\text{iii}}$, respectively, in the crystallographic *a* direction [symmetry code: (iii) *x* − 1, *y*, *z*]. Each of the sets of interactions results in the formation of a 12-membered hydrogen-bonded $R_4^2(12)$ ring graph set (Bernstein *et al.*, 1995) which links two hexaaquanickel(II) cations together. These distinct hydrogen-bonding interactions (Fig. 2) are together responsible for the formation of a 20-membered hydrogen-bonded $R_8^4(20)$ ring graph set with two chains of five water molecules. In this way, the hexaaquanickel(II) cations are interconnected and a two-dimensional supramolecular network of the structure parallel to the *ab* plane is formed (Fig. 2).

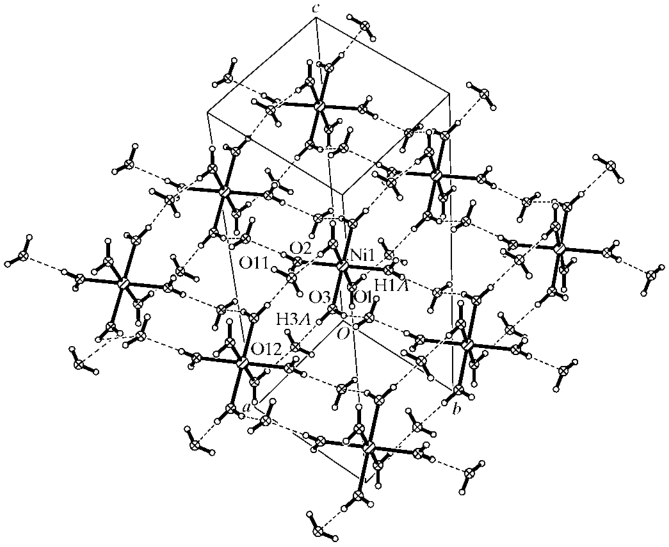

Figure 2
A packing plot for (I), showing the two-dimensional layer connectivity and the hydrogen-bonding interactions (dashed lines) of the hexaaquanickel(II) cations and water molecules O11 and O12 parallel to the *ab* plane, viewed down the *c* axis.

The 2-carboxylato-2-(isothiouronium-*S*-ylmethyl)propane-1,3-diyl phosphate anion contains a phosphate ester anion, a carboxylate anion and an isothiouronium cation. The carboxylate group (O8/C4/O9) lies on the equatorial site of atom C2 of the chair six-membered ring and the two C—O bonds are equivalent. The isothiouronium cation (N1/C6/N2) is connected to the methyl group on the axial site of atom C2 *via* atom S1 and the N—C—N bond is also in a conjugated system (Table 1). In the present structure, there is an intermolecular dimeric hydrogen-bonded $D_2^2(8)$ graph-set interaction between the O atoms of the carboxylate group and the N—H bonds of the isothiouronium cation (Fig. 3). Interactions between N2—H2*D* and atom O8$^{\text{iii}}$ result in the connectivity of these $D_2^2(8)$ graph sets to form two *C*(6) graph sets along the crystallographic *a* direction. N1—H1*D* and water molecules O10 and O9$^{\text{iv}}$ are also engaged in connectivity with the phosphate ester anion and are responsible for the formation of a hydrogen-bonded $C_2^2(10)$ graph set in the crystallographic *b* direction. Thus, another two-dimensional layer network of the phosphate ester anion parallel to the *ab* plane is formed.

The structure of (I) as a whole consists of these two distinct types of layers, which are stacked alternately in the [001] direction. The connectivity between neighbouring layers is mainly completed *via* hydrogen-bond interactions between the O atoms of the P—O bond and the water molecules. The P atom has a distorted tetrahedral environment. The P1—O bonds are longer than the corresponding bonds in $C_{12}H_9N_2^{+}$·-

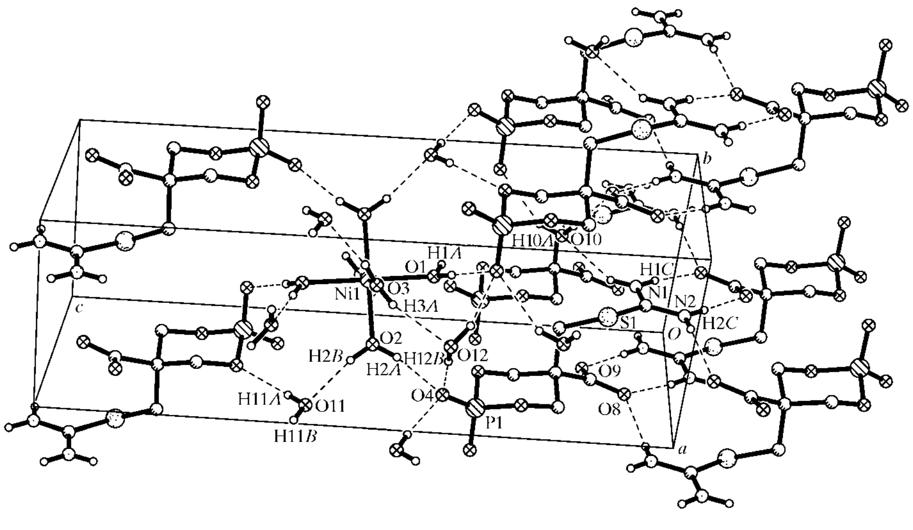

Figure 3
A packing diagram for (I), showing the hydrogen-bonding interactions as dashed lines in the *ab* plane.

$OP(OCH_2)_3CCOO^-\cdot OP(OCH_2)_3CCOOH\cdot H_2O$ (Wang *et al.*, 2007) and in $O{=}P(OCH_2)_3CCH_2OH$ (Guo & Zang, 2007), where the P=O distances are in the range 1.446 (3)–1.4573 (15) Å, while the P—O single-bond distances cover the range 1.535 (4)–1.5667 (15) Å. This indicates that the ring stretch of the present phosphate ester anion is smaller than that of the caged phosphate ester. The O4—P1—O5 bond shares a negative charge, so atoms O4 and O5 can act as efficient H-atom acceptors. Thus, for atom O4 there are three hydrogen-bond interactions (Table 2). Interestingly, atom H11*A* is involved in an unexpected intermolecular O11—H11*A*···O7^{vi} hydrogen bond [symmetry code: (vi) $-x+1, -y, -z+1$], where the O atom of the C2—O7—P1 group acts as acceptor. The water molecules (atoms O10, O11 and O12) act as both proton donors and acceptors, linking the phosphate ester anion to the Ni atoms *via* coordinated water molecules. The whole three-dimensional structure is maintained and stabilized by the presence of these intra- and interlayer hydrogen bonds (Table 2).

Experimental

$Ni(thiourea)_4Cl_2$ (0.69 g, 1.6 mmol) was added to a mixture of an aqueous solution (20 ml) of anhydrous sodium carbonate (0.16 g, 1.5 mmol) and 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylic acid (0.61 g, 3.2 mmol) with stirring at room temperature for 20 min. After filtration, slow evaporation of the filtrate for three weeks at room temperature provided crystals of the title compound.

Crystal data

$[Ni(H_2O)_6](C_6H_{10}N_2O_6PS)_2\cdot 6H_2O$
$M_r = 813.28$
Triclinic, $P\overline{1}$
$a = 6.2701$ (12) Å
$b = 6.4816$ (12) Å
$c = 19.616$ (4) Å
$\alpha = 95.807$ (3)°
$\beta = 93.091$ (3)°
$\gamma = 93.760$ (3)°
$V = 789.9$ (3) $Å^3$
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.95$ mm^{-1}
$T = 294$ (2) K
0.28 × 0.24 × 0.22 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.765$, $T_{max} = 0.818$
4055 measured reflections
2789 independent reflections
2482 reflections with $I > 2\sigma$
$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.084$
$S = 1.05$
2789 reflections
205 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.49$ e $Å^{-3}$
$\Delta\rho_{min} = -0.49$ e $Å^{-3}$

All water H atoms were found in a difference Fourier map and were fixed during refinement at O—H distances of 0.85 Å, with $U_{iso}(H) = 1.2U_{eq}(O)$. The H atoms of the C—H and N—H groups were treated as riding, with C—H = 0.97 Å, N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Table 1
Selected geometric parameters (Å, °).

P1—O5	1.4893 (19)	C4—O8	1.251 (3)
P1—O4	1.4896 (18)	C4—O9	1.256 (3)
P1—O6	1.5862 (16)	C6—N2	1.301 (3)
P1—O7	1.6042 (17)	C6—N1	1.312 (3)
O5—P1—O4	118.18 (11)	O4—P1—O7	107.75 (10)
O5—P1—O6	111.08 (10)	O6—P1—O7	102.45 (9)
O4—P1—O6	106.96 (10)	O8—C4—O9	125.5 (2)
O5—P1—O7	109.23 (10)	N2—C6—N1	121.9 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···O8^{i}	0.86	2.05	2.911 (3)	174
N1—H1*D*···O10	0.86	2.14	2.904 (3)	149
N2—H2*C*···O9^{i}	0.86	1.90	2.758 (3)	179
N2—H2*D*···O8^{ii}	0.86	2.10	2.910 (3)	156
O1—H1*A*···O12^{iii}	0.85	1.91	2.764 (3)	180
O1—H1*B*···O5^{iv}	0.85	1.96	2.816 (3)	176
O2—H2*A*···O4	0.85	1.87	2.696 (3)	163
O2—H2*B*···O11	0.85	1.96	2.798 (3)	170
O3—H3*A*···O12	0.84	2.15	2.944 (4)	156
O3—H3*B*···O11^{iv}	0.85	1.94	2.767 (3)	164
O10—H10*A*···O5^{v}	0.85	2.23	3.007 (3)	152
O10—H10*B*···O9^{iv}	0.86	1.95	2.770 (3)	159
O11—H11*A*···O7^{vi}	0.85	2.08	2.902 (2)	162
O11—H11*B*···O4^{vii}	0.85	1.91	2.735 (2)	162
O12—H12*A*···O5^{iv}	0.86	2.01	2.795 (3)	152
O12—H12*B*···O4	0.85	2.03	2.877 (3)	180

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

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3143). Services for accessing these data are described at the back of the journal.

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