

Tetraaquadithiocyanatonickel(II) tetrakis-(2-amino-4,6-dimethylpyrimidine) dihydrate

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Key indicators

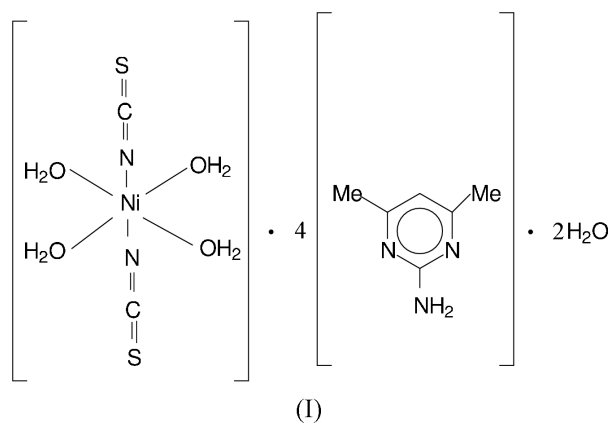
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.045
wR factor = 0.115
Data-to-parameter ratio = 20.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex, $[\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_4] \cdot 4\text{C}_6\text{H}_9\text{N}_3 \cdot 2\text{H}_2\text{O}$, the nickel(II) ion occupies an inversion centre and is octahedrally coordinated by two N-bonded thiocyanate ions and four water molecules. The two distinct 2-amino-4,6-dimethylpyrimidine molecules adopt distinct base-pairing dimerization patterns *via* different pairs of $\text{N}-\text{H} \cdots \text{N}$ bonds. They are also hydrogen bonded to the coordinated and uncoordinated water molecules and thiocyanate ions through $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{S}(\text{thiocyanate})$ and $\text{N}-\text{H} \cdots \text{N}(\text{thiocyanate})$ hydrogen bonds.

Comment

Studies of hydrogen-bonding interactions between substituted pyrimidines and coordinated ligands are of current interest (Suksangpanya *et al.*, 2004) and we have recently described the structure of 2-amino-4,6-dimethylpyrimidinium bromide 2-amino-4,6-dimethylpyrimidine monohydrate (Panneerselvam *et al.*, 2004). The present study of the title compound, (I), is aimed at gaining a better understanding of the interplay of metal-coordination and hydrogen-bonding interactions in these types of materials.



The asymmetric unit of (I) contains two 2-amino-4,6-dimethylpyrimidine molecules, one coordinated thiocyanate ion, two coordinated water molecules, an uncoordinated water molecule and a nickel ion lying on a crystallographic inversion centre (Fig. 1). The environment about the nickel ion is octahedral with two thiocyanate ions and two pairs of water molecules completing the coordination. The water molecule O atoms are positioned in the equatorial plane of the octahedron, while the N-monodentate thiocyanate ions occupy the axial positions. The nickel–ligand bond distances (Table 1) agree with those reported for similar systems (Abul-Haj *et al.*,

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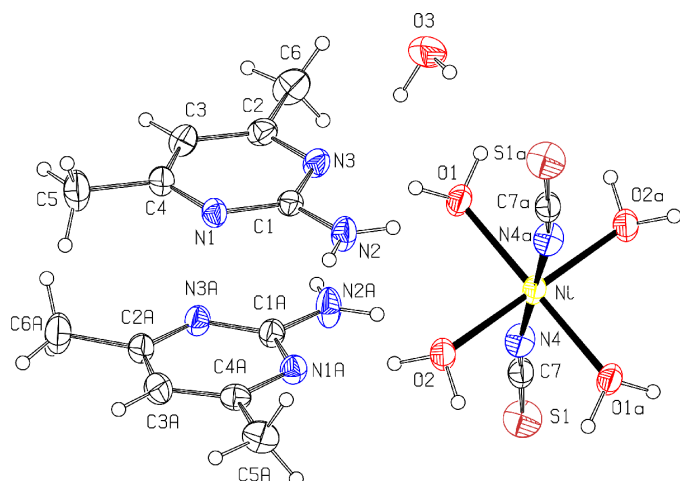


Figure 1

View of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms. [Atoms with the suffix a are generated by the symmetry code $1 - x, -y, 1 - z$.]

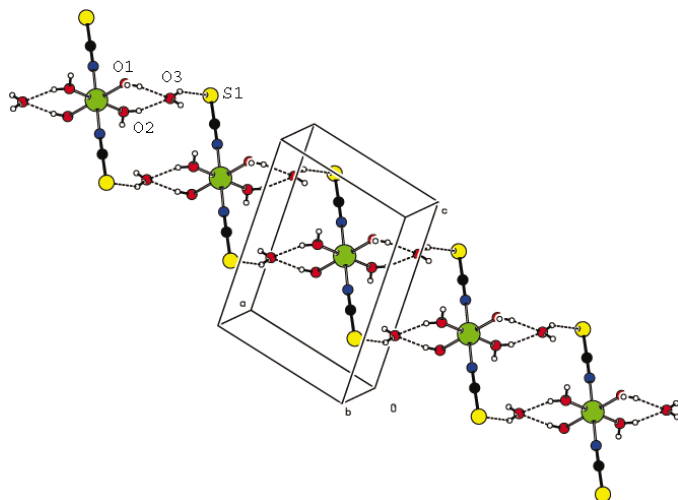


Figure 2

A chain in (I) made up of $\text{Ni}(\text{NCS})_2(\text{H}_2\text{O})_4$ molecules and uncoordinated water molecules, linked by hydrogen bonds (dashed lines).

2000). The thiocyanate ligand is almost linear [$\text{N}-\text{C}-\text{S}$] = $179.2(2)^\circ$].

The 2-amino-4,6-dimethylpyrimidine molecules are not coordinated to nickel, but are hydrogen bonded to the coordinated water molecule, uncoordinated water molecules and thiocyanate ions (Table 2). The non-coordinated water molecule (O3) accepts H bonds from the coordinated water molecules (O1 and O2) and acts as a donor to nearby S atoms, forming $\text{O}-\text{H}\cdots\text{S}$ hydrogen bonds, leading to a chain along the *a* axis, as shown in Fig. 2. The pyrimidine N atom N3 acts as a hydrogen-bond acceptor from both the coordinated water molecule (O1) and uncoordinated water molecule (O3). The pyrimidine N atom N1A also accepts a hydrogen bond from the coordinated water molecule, O2 (Fig. 3).

Two kinds of base-pairing interactions are observed for the 2-amino-4,6-dimethylpyrimidine species. Molecule *A* is paired about an inversion centre through a pair of $\text{N2A}-\text{H21A}\cdots\text{N3A}$ hydrogen bonds, whereas the other 2-amino-4,6-

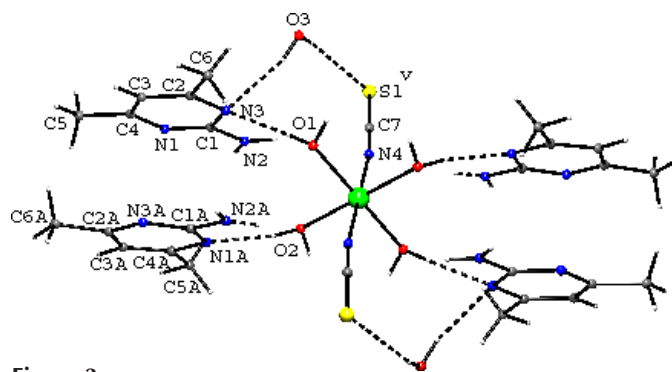


Figure 3

Fragment of (I), illustrating the hydrogen bonding (dashed lines) of the pyrimidine molecules with the coordinated ligands and the uncoordinated water molecules. Symmetry code as in Table 2.

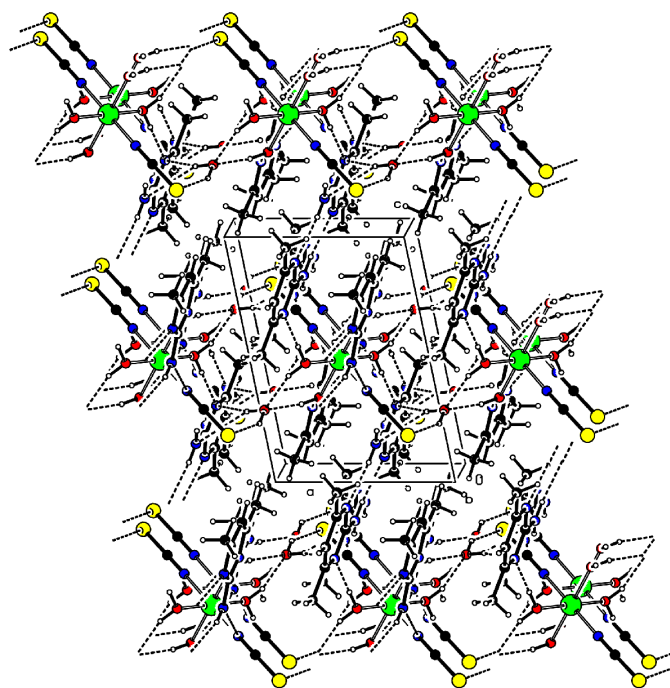


Figure 4

A view of the molecular packing in (I). Dashed lines indicate hydrogen bonds.

dimethylpyrimidine is paired about an inversion centre through a pair of $\text{N2}-\text{H2B}\cdots\text{N1}$ hydrogen bonds. The former mode of pairing has been already observed in trimethoprim sulfate trihydrate (Muthiah *et al.*, 2001) and the latter mode has been noted in the structure of pyrimethamine (Sethuraman & Muthiah, 2001). Molecule *A* interacts with the metal atom *via* the coordinated water molecule (O2) by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds and through $\text{N}-\text{H}\cdots\text{N}(\text{NCS})$ hydrogen bonds involving the 2-amino H atom (H22B) and the N atom of the thiocyanate ligand. A view of the crystal packing is shown in Fig. 4.

The existence of $\pi\cdots\pi$ interactions can also be inferred in (I). The (N1,N3/C1-C4) and (N1A,N3A/C1A-C4A) pyrimidine rings have a perpendicular separation of 3.515 \AA , a centroid-to-centroid distance of $3.554(14) \text{ \AA}$ and a slip angle (the angle between the centroid vector and the normal to the

plane) of 8.4°. These values are typical for aromatic $\pi \cdots \pi$ stacking interactions (Hunter, 1994).

Compounds related to (I) include a nickel(II) thiocyanate complex of bis(3-aminopropyl)methylamine (Mukherjee *et al.*, 1999), diaquabis(4,5-dihydro-1,2,4-triazolo-1,5-pyrimidin-5-one)bis(thiocyanato)nickel(II) (Abul-Haj *et al.*, 2000), and *trans*-bis(diethanolamine)bis(isothiocyanato)nickel(II) (Yilmaz *et al.*, 2000).

Experimental

An aqueous solution of [Ni(NO₃)₂].6H₂O (72.71 mg in 5 ml of water) was added to a solution of NH₄CNS (76.1 mg in 5 ml of water). The mixture was stirred for 20 min. The 2-amino-4,6-dimethyl pyrimidine ligand (63.25 mg dissolved in 10 ml of methanol) was added slowly to this mixture. The resultant solution was stirred for 20 min and then filtered. After a few days, pale green crystals of (I) were obtained from the filtrate (on slow evaporation at room temperature).

Crystal data

[Ni(NCS) ₂ (H ₂ O) ₄].4C ₆ H ₉ N ₃ .2H ₂ O	Z = 1
<i>M_r</i> = 775.61	<i>D_x</i> = 1.339 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 7.8006 (5) Å	Cell parameters from 7595 reflections
<i>b</i> = 11.6289 (8) Å	θ = 1.9–28.3°
<i>c</i> = 11.9121 (8) Å	μ = 0.67 mm ⁻¹
α = 67.701 (1)°	<i>T</i> = 293 (2) K
β = 75.488 (1)°	Plate, pale green
γ = 78.896 (1)°	0.66 × 0.60 × 0.15 mm
<i>V</i> = 962.12 (11) Å ³	

Data collection

Bruker SMART CCD diffractometer	4605 independent reflections
ω scans	3465 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: refined from ΔF (SHELXA; Bruker, 2001)	<i>R</i> _{int} = 0.024
<i>T</i> _{min} = 0.667, <i>T</i> _{max} = 0.906	θ _{max} = 28.3°
7595 measured reflections	<i>h</i> = -10 → 10
	<i>k</i> = -14 → 15
	<i>l</i> = -15 → 14

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.1851P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.115$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.05	$\Delta\rho$ _{max} = 0.23 e Å ⁻³
4605 reflections	$\Delta\rho$ _{min} = -0.25 e Å ⁻³
227 parameters	
H-atom parameters constrained	

Table 1

Selected bond lengths (Å).

Ni–O1	2.0731 (17)	Ni–N4	2.058 (2)
Ni–O2	2.0728 (16)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2B...N1 ⁱ	0.86	2.18	3.040 (3)	175
O1–H11...N3	0.90	1.92	2.816 (3)	174
O1–H12...O3 ⁱⁱ	0.92	1.94	2.818 (3)	159
O2–H21...O3 ⁱⁱⁱ	0.91	1.94	2.836 (3)	168
N2A–H21A...N3A ^{iv}	0.86	2.16	2.997 (3)	164
O2–H22...N1A	0.93	1.82	2.736 (3)	170
N2A–H22B...N4	0.86	2.48	3.322 (3)	167
O3–H31...N3	0.92	2.26	3.137 (3)	158
O3–H32...S1 ^v	0.95	2.52	3.377 (3)	150

Symmetry codes: (i) 1 – *x*, –*y*, 2 – *z*; (ii) 2 – *x*, –*y*, 1 – *z*; (iii) *x* – 1, *y*, *z*; (iv) 1 – *x*, 1 – *y*, 1 – *z*; (v) 1 – *x*, –*y*, 1 – *z*.

The H atoms of the water molecules were located in a difference Fourier map and refined as riding in their as-found relative positions. Other H atoms were placed in idealized locations [*d*(C–H) = 0.93 Å–0.96 Å and *d*(N–H) = 0.86 Å] and refined as riding on their carrier atoms. The constraint *U*_{iso}(H) = 1.2*U*_{eq}(carrier) or 1.5*U*_{eq}(methyl carrier) was applied as appropriate.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT and SHELXTL (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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