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# Bis(picolinato-$\kappa^2N,O$)bis(urea-$\kappa O$)nickel(II) urea disolvate monohydrate

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.004 Å
Disorder in solvent or counterion
$R$ factor = 0.042
$wR$ factor = 0.109
Data-to-parameter ratio = 11.6

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

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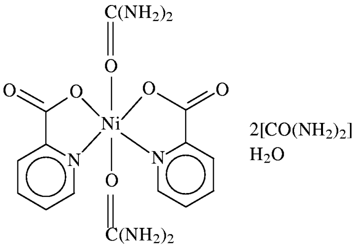
A new compound, $[Ni(pic)_2\{CO(NH_2)_2\}_2]\cdot 2[CO(NH_2)_2]\cdot H_2O$ (Hpic is picolinic acid) or $[Ni(C_6H_4NO_2)_2(CH_4N_2O)_2]\cdot 2CH_4N_2O\cdot H_2O$, has been synthesized and structurally characterized by single-crystal X-ray diffraction analysis. The structure shows that the Ni atom has an octahedral environment in which it is coordinated by two N and two O atoms of two picolinate ligands and two O atoms of two urea molecules. The Ni atom lies at an inversion center, with Ni—N = 2.0531 (18) Å, Ni—O(pic) = 2.0349 (15) Å and Ni—O(urea) = 2.1255 (15) Å. Both urea solvent molecules lie on mirror planes and have approximate $C_{2v}$ symmetry, and the water molecule has exact mirror symmetry. $\pi$–$\pi$ stacking and hydrogen-bonding interactions result in a three-dimensional network.

## Comment

In the past few years, the molecular-based magnetic properties of heteronuclear compounds containing, in the same molecule, rare earth and transition metal ions have attracted increasing interest (Bencini *et al.*, 1985; Andruh *et al.*, 1993). In our laboratory, we have successfully synthesized such types of complexes having different carboxylic bridging ligands (Cui *et al.*, 2000). As an extension of this research area, our present work is aimed at synthesizing novel rare earth-transition metal complexes, using picolinic acid as a chelating ligand. In the course of our investigation, we unexpectedly obtained a new compound, $[Ni(pic)_2\{CO(NH_2)_2\}_2]\cdot 2[CO(NH_2)_2]\cdot H_2O$, (I). Since it contains non-coordinated O atoms of the picolinic carboxylate ligands, it can be used as a 'metallo ligand' to bind rare earth metal ions for further preparation of heteronuclear complexes.



(I)

It should be noted that the coordination chemistry of picolinic acid has been studied widely since its derivatives have a broad spectrum of physiological effects on activity functions of both animal and plant organisms; these are attributed to their ability to form compounds with transition metals (Bovikin *et al.*, 1985). Complexes formulated as $M(pic)_2(H_2O)_n$ ($M$ = Mn, Fe, Co, Ni, Cu, Zn; $n$ = 0, 2) have been reported (Segl'a *et al.*, 1998; Takenaka *et al.*, 1970; Barandika *et al.*, 1999; Kiani *et al.*, 2000; Chang *et al.*, 1972;

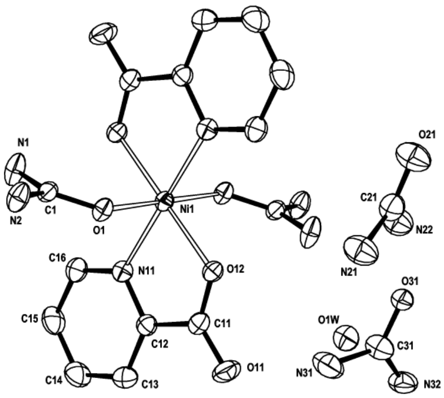


**Figure 1**
The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted.

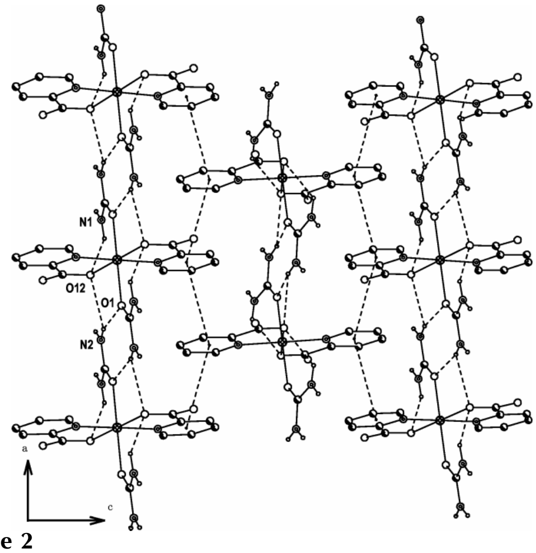


**Figure 2**
The layer-like structure constructed from hydrogen bonds and $\pi$–$\pi$ stacking interactions extending along the *a* and *c* directions, resepctively.

Cotton *et al.*, 1992). In this paper, we report the synthesis and crystal structure of (I).

The molecular structure of (I) is similar to that of $[Ni(pic)_2(H_2O)_2]\cdot 2H_2O$ (Takenaka *et al.*, 1970; Loiseleur, 1972), in which coordinated water molecules replace the coordinated urea molecules. The coordination environment of the Ni atom is octahedral. The Ni atom, located at a crystallographic inversion center, is coordinated by two carboxylic O atoms (O12) and two pyridine N atoms (N11) from two symmetry-related picolinate ligands and two O atoms of two symmetry-related urea molecules; the equatorial plane consists of N and O atoms from the two pic ligands and the axial positions are occupied by two urea O atoms. The Ni atom is not displaced from the equatorial plane of the octahedron. The bond lengths around the Ni atom are Ni—O12 = 2.0349 (15) Å, Ni—N11 = 2.0531 (18) Å and Ni—O1 = 2.1255 (15) Å, which are in reasonable agreement with the values found in $[Ni(pic)_2(H_2O)_2]\cdot 2H_2O$ (Takenaka *et al.*, 1970; Loiseleur, 1972). Both urea solvent molecules lie on mirror planes and have approximate $C_{2v}$ symmetry, and the water molecule has exact mirror symmetry. The other bond lengths and angles in the title compound are unexceptional.

There are $\pi$–$\pi$ stacking and hydrogen-bonding interactions in the title complex, as shown in Figs. 2 and 3. The molecules are linked into a one-dimensional chain extending along the *a* direction through N—H$\cdots$O hydrogen bonds, *viz*. N2—H2*A*$\cdots$O1$^{ii}$, N2—H2*A*$\cdots$O12$^{ii}$ and N1—H1*A*$\cdots$O12$^{i}$ (symmetry codes as in Table 2). A $\pi$–$\pi$ stacking interaction exists between a pair of rings [at $(x, y, z)$ and $(\frac{1}{2}+x, y, -\frac{1}{2}-z)$], which are almost parallel to each other [dihedral angle between them is 1.63 (9)°]; the 'perpendicular' separation of the rings is 3.880 Å, and the ring centroid-to-centroid distance is 3.887 Å. These $\pi$–$\pi$ stacking interactions link the chains into a two-dimensional layer structure extending along the *c* direction (Fig. 2). Interestingly, one of the urea solvent molecules is linked by a single hydrogen bond to a symmetry-related urea molecule, forming a one-dimensional chain in the *a* direction (Fig. 3*a*). The other urea molecule is linked to a symmetry-related urea molecule by cyclic N—H$\cdots$O hydrogen bonds, forming a chain-like structure extending along the *a* direction (Fig. 3*c*), and the water molecules are anchored to these chains through the N22—H22*B*$\cdots$O1*W* hydrogen bond, approximately in the *c* direction. These two urea chains are located between the layers and link the layers into a three-dimensional network along the *b* axis, through the hydrogen-bonding interactions O1*W*—H1*C*$\cdots$O11, N32—H32*A*$\cdots$O11$^{vi}$ and N1—H1*B*$\cdots$O31$^{i}$ (symmetry codes as in Table 2), as shown in Fig. 3*b*. The hydrogen-bonding and $\pi$–$\pi$ stacking interactions lead to the stabilization of the crystal structure.

## Experimental

The title compound was prepared by mixing 2 ml of an aqueous solution of $Ni(CH_3COO)_2\cdot 4H_2O$ (125 mg, 0.50 mmol), $Nd(NO_3)_3\cdot 6H_2O$ (100 mg, 0.23 mmol) and picolinic acid (125 mg, 1.02 mmol) in 10 ml $C_2H_5OH/CH_3CN$ solution; urea was added to adjust the pH to 5, and the solution was stirred thoroughly at room temperature. After a few minutes, pale-blue precipitates appeared and stirring was continued for 4 h. The precipitates were filtered off and the filtrate allowed to stand at room temperature. Transparent gray–blue crystals of the title compound were obtained after a few days, were filtered off, washed with a small amount of ethanol, air-dried and kept in a sealed ampoule (yield: 80.3%; calculation based on Ni).

*Crystal data*

$[Ni(C_6H_4NO_2)_2(CH_4N_2O)_2]\cdot 2CH_4N_2O\cdot H_2O$
$M_r = 561.18$
Orthorhombic, *Pnma*
$a = 7.4562$ (5) Å
$b = 20.3619$ (14) Å
$c = 15.8017$ (10) Å
$V = 2399.1$ (3) Å$^3$
$Z = 4$
$D_x = 1.554$ Mg m$^{-3}$
Mo *K*$\alpha$ radiation
Cell parameters from 3906 reflections
$\theta = 3.0$–25.1°
$\mu = 0.88$ mm$^{-1}$
$T = 293$ (2) K
Prism, pale blue
0.42 × 0.38 × 0.25 mm

*Data collection*

Siemens SMART CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.583$, $T_{max} = 0.803$
7104 measured reflections
2167 independent reflections
1564 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.1°$
$h = -7 \rightarrow 8$
$k = -18 \rightarrow 24$
$l = -8 \rightarrow 18$

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*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.109$
$S = 1.01$
2167 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 4.0512P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.27$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ni1—O12 | 2.0349 (15) | Ni1—O1 | 2.1255 (15) |
| Ni1—N11 | 2.0531 (18) | | |
| O12$^{i}$—Ni1—O12 | 180 | O12—Ni1—O1 | 87.12 (6) |
| O12$^{i}$—Ni1—N11 | 99.24 (7) | N11—Ni1—O1 | 90.22 (7) |
| O12—Ni1—N11 | 80.76 (7) | N11$^{i}$—Ni1—O1 | 89.78 (7) |
| N11—Ni1—N11$^{i}$ | 180 | O1—Ni1—O1$^{i}$ | 180 |
| O12$^{i}$—Ni1—O1 | 92.88 (6) | | |

Symmetry code: (i) $1 - x, 1 - y, -1 - z$.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O12$^{i}$ | 0.86 | 2.19 | 2.866 (3) | 135 |
| N1—H1$B$···O31$^{i}$ | 0.86 | 2.17 | 2.932 (3) | 147 |
| N2—H2$A$···O1$^{ii}$ | 0.86 | 2.18 | 3.019 (3) | 166 |
| N2—H2$A$···O12$^{ii}$ | 0.86 | 2.53 | 2.980 (3) | 114 |
| N21—H21$A$···O21$^{iii}$ | 0.86 | 2.19 | 3.045 (5) | 175 |
| N22—H22$B$···O1$W$ | 0.86 | 2.03 | 2.889 (5) | 176 |
| N22—H22$A$···O21$^{iv}$ | 0.86 | 2.08 | 2.944 (5) | 179 |
| N31—H31$B$···N32$^{v}$ | 0.86 | 2.32 | 3.036 (7) | 141 |
| N32—H32$A$···O11$^{vi}$ | 0.86 | 2.05 | 2.874 (5) | 161 |
| O1$W$—H1$C$···O11 | 0.950 (9) | 1.909 (12) | 2.823 (3) | 161 (2) |

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

One of the two uncoordinated urea molecules is disordered and was refined with the site-occupancy factors of atoms N31 and N32 and their attached H atoms fixed at 0.5. The water H atom was located in a difference Fourier synthesis and refined isotropically, with O—H = 0.950 (9) Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(O). The remaining H atoms were positioned geometrically, assigned isotropic displacement parameters and allowed to ride on their respective parent atoms; N—H = 0.86 Å, C—H = 0.93 Å and $U_{\rm iso}$(H) values were set equal to $1.2U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SAINT* and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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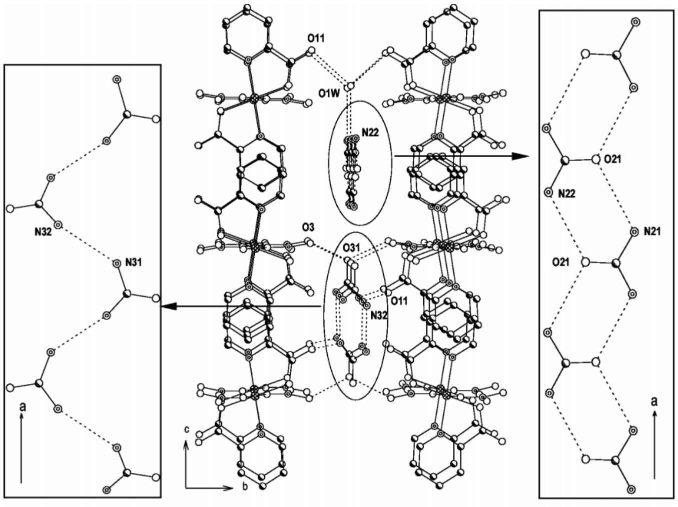

(a) (b) (c)

**Figure 3**
The three-dimensional hydrogen-bonded framework of the title compound, showing (*b*) the two urea chains and the water molecules located between the layers. The two chains extending along the *a* direction are shown in (*a*) and (*c*). Hydrogen bonds are represented by dashed lines. Hydrogen bonds and π–π stacking interactions in the layers have been omitted for clarity.

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