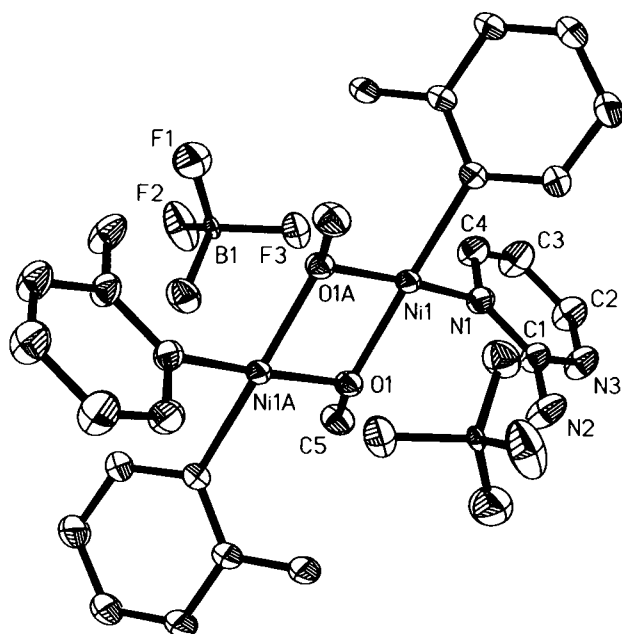


Crystal structure of tetra(2-aminopyrimidine)dimethanolato-dinickel(II) di(tetrafluoroborate), $[\text{Ni}_2(\text{CH}_3\text{O})_2(\text{C}_4\text{H}_5\text{N}_3)_4][\text{BF}_4]_2$

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Abstract

$\text{C}_{18}\text{H}_{26}\text{B}_2\text{F}_8\text{N}_{12}\text{Ni}_2\text{O}_2$, monoclinic, $C12/m1$ (no. 12), $a = 16.341(6)$ Å, $b = 14.796(2)$ Å, $c = 12.051(4)$ Å, $\beta = 132.36(1)^\circ$, $V = 2153.1$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.063$, $wR_{\text{ref}}(F^2) = 0.201$, $T = 293$ K.

Source of material

$\text{Ni}(\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ and 2-aminopyrimidine in a molar ratio of 1:2 were dissolved in methanol, and the resulting solution was kept standing in air for two days. The precipitated crystals were filtered, washed three times with methanol and dried in air (yield 63 %). Interestingly, during the crystallization, the presence of 5-bromosalicylaldehyde increases the yield of the product.

Discussion

Urease, the first enzyme crystallized with nickel ions, is an important enzyme in both agriculture and medicine, which rapidly catalyzes the hydrolysis of urea to form ammonia and carbamic acid. In recent years, some simple mono- and dinuclear nickel(II) complexes with organic ligands-containing nitrogen donors were prepared and structurally determined to mimic the structure and property in the activity center of urease [1–4]. We hoped to obtain a nickel(II) complex with the new ligand 5-bromosalicylaldehyde; but isolated the title complex unexpectedly.

The title complex is a dinuclear nickel(II) complex. In each of the dimer unit, there were one coordination dication and two uncoordinated tetrafluoroborate anions. In the cation, each of the Ni(II) atom is four-coordinated by two nitrogen atoms from two 2-aminopyrimidine ligands and two oxygen atoms from two deprotonated methanolate anions, forming a slightly distorted square environment. The central nickel(II) atom is precisely located inside the square plane with no deviation. The Ni_2O_2 plane has an angle of $66.9(1)^\circ$ with the neighboring pyrimidine ring, and the diagonal angle between the two adjacent aromatic rings is $78.1(1)^\circ$, which is closely perpendicular to each other. All 2-aminopyrimidine molecules are monodentate ligands, and all of the deprotonated methanol molecules act as a bidentate ligand, two of which bridged two nickel(II) atoms at the distance of $2.964(6)$ Å. The amine groups and the imine nitrogen atoms in pyrimidine rings and two of the fluorine atoms in each tetrafluoroborate anion contribute to the formation of hydrogen bonds. A large network of hydrogen contacts connects the dimers into a 3D structure.

Table 1. Data collection and handling.

Crystal:	yellow, rectangular, size $0.30 \times 0.34 \times 0.45$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	9.37 cm^{-1}
Diffraction, scan mode:	Siemens SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	54.98°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	2643, 2556
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2018
$N(\text{param})_{\text{refined}}$:	108
Program:	SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(5A)	8j	0.2443	−0.0568	0.2526	0.08
H(5B)	4i	0.2222	0	0.1312	0.08
H(2A)	8j	0.1825	0.1805	0.4338	0.08
H(2B)	8j	0.1015	0.1201	0.2910	0.08
H(2)	8j	0.3163	0.3826	0.3314	0.08
H(3)	8j	0.2371	0.3515	0.0865	0.08
H(4)	8j	0.1038	0.2363	−0.0447	0.08

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni(1)	4g	0	0.10015(4)	0	0.0447(4)	0.0325(4)	0.0341(4)	0	0.0206(3)	0
O(1)	4i	0.0972(3)	0	0.1197(4)	0.041(2)	0.044(2)	0.041(2)	0	0.021(2)	0
C(5)	4i	0.2122(5)	0	0.2007(8)	0.049(3)	0.064(4)	0.068(4)	0	0.029(3)	0
N(1)	8j	0.1164(3)	0.1969(2)	0.1246(4)	0.065(2)	0.042(2)	0.048(2)	−0.010(2)	0.034(2)	−0.005(1)
N(2)	8j	0.1491(4)	0.1671(3)	0.3384(5)	0.107(3)	0.083(3)	0.058(2)	−0.058(3)	0.053(2)	−0.026(2)
N(3)	8j	0.2423(4)	0.2853(3)	0.3459(5)	0.091(3)	0.068(3)	0.063(2)	−0.040(2)	0.049(2)	−0.023(2)
C(1)	8j	0.1687(4)	0.2154(3)	0.2685(5)	0.066(2)	0.051(2)	0.052(2)	−0.018(2)	0.037(2)	−0.012(2)
C(2)	8j	0.2640(5)	0.3337(4)	0.2769(6)	0.097(4)	0.069(3)	0.079(3)	−0.039(3)	0.058(3)	−0.017(3)
C(3)	8j	0.2177(6)	0.3168(4)	0.1334(7)	0.126(5)	0.076(3)	0.089(4)	−0.043(4)	0.081(4)	−0.016(3)
C(4)	8j	0.1409(5)	0.2485(3)	0.0581(6)	0.093(3)	0.055(3)	0.062(3)	−0.019(2)	0.051(3)	−0.004(2)
B(1)	4i	0.0628(4)	0	−0.2230(5)	0.040(2)	0.014(2)	0.042(2)	0	0.035(2)	0
F(1)	4i	−0.0454(5)	0	−0.3598(6)	0.111(4)	0.092(3)	0.089(3)	0	0.056(3)	0
F(2)	4i	0.1393(6)	0	−0.2365(9)	0.168(5)	0.068(3)	0.222(7)	0	0.175(6)	0
F(3)	8j	0.0765(3)	0.0785(2)	−0.1434(4)	0.095(2)	0.057(2)	0.097(2)	0.002(1)	0.070(2)	−0.008(2)

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