The Most Effective Packing of Layers: Synthesis and Structure of $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$

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The complex $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$, in which nickel atoms are linked by two different Ni-4,4'-bpy-Ni assemblies to form two-dimensional distorted square net structure and the most effective packing of layers, has been isolated and structurally characterized.

The formation of open framework structure based on coordination chemistry that mimic zeolite or other microporous solids was of great current interest.[1-4] The simple bis(monodentate) ligand 4,4'-bipyridine (4,4'-bpy), as a good candidates for molecular building blocks because of its rodlike rigidly and length,[5] affords a variety of two and three dimensional frameworks when coordinated to various metal ions, $\{[Cd(4,4'\text{-bpy})_2(NO_3)_2](C_6H_4Br_2)_2\}_n$,[6] $\{[Zn(4,4'\text{-bpy})_2]SiF_6\cdot xDMF\}_n$,[7] $[Cd(H_2O)_2(4,4'\text{-bpy})(PF_6)_2]\cdot(4,4'\text{-bpy})\cdot 4H_2O$,[8a] $[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})]\cdot H_2O$,[9] and $[Co(NCS)_2(4,4'\text{-bpy})_2\cdot 2(CH_3CH_2)_2O]_n$[10] have assemblies of 2-D sheets, whereas $\{[Zn(4,4'\text{-bpy})_2(H_2O)_2](SiF_6)\}_n$,[11] $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot xH_2O\}_n$ (M = Co, Ni, Zn),[8b] $[Cd(H_2O)(4,4'\text{-bpy})_2(OH)(PF_6)]_n$,[8a] $[Cu(4,4'\text{-bpy})Cl]_n$,[12a] $\{[Cu(4,4'\text{-bpy})_{1.5}]NO_3(H_2O)_{1.5}\}_n$,[12b] and $[Ag(4,4'\text{-bpy})NO_3]_n$[12c] have 3-D interpenetrating structures. Previous strategies for constructing noninterpenetrated square networks were mostly focused on clathrating anions or neutral guest molecules in their channel.[6-8,10] Here, we present one example of noninterpenetrated 2-D square network without any clathrated molecules, $[Ni(4,4'\text{-bpy})_2(NCS)_2]_n$ (**1**). It is the rigid NCS groups that prevent interpenetrating in **1**. Among those 2-D or 3-D coordination polymers in which 4,4'-bpy ligands bridge metal centers, Ni(II) complexes were very rare.[8] **1** represents the first example of Ni(II)- 4,4'-bpy complex possesses 2-D network with a very short interlayer distance (~ 4.2 Å).

Compound **1** was synthesized as blue square plates in about 90% yield by hydrothermal reaction of $Ni(NO_3)_2\cdot 6H_2O$, 4,4'-bipyridine, NaNCS and water in the molar ratio 1:2:2:1000 at 150 °C for 18 h.[13] The structure of **1** was solved by single-crystal X-ray diffraction.[14]

The crystal structure of **1** is shown in Figure 1 and 2. This structure contains two-dimensional distorted square nets of composition ${}^2_\infty[M(4,4'\text{-bpy})_{4/2}]$ that does not interpenetrate. The 4,4'-bpy ligands bridge nickel(II) centers, and the NCS groups are terminal ligands. The Ni-bpy layers are staggered relative to each other so that the Ni atoms in one layer are located above or below the squares formed by the nickel atoms of adjacent layers. Layers stack along the *c* axis, and the distance between layers is 4.20 Å. This interlayer distance is apparently shorter than that in related compounds with or without clathrated solvent molecules (6.28-7.01 Å).[6-10] As the result of this most effective packing, sulphur atoms of adjacent above layer are located slightly below the square plane formed by nickels. It is the two sulphur atoms of two adjacent layers (above and below) sitting in one square

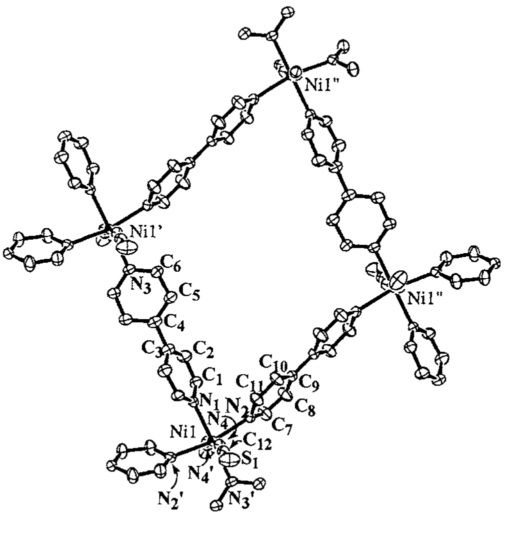

Figure 1. ORTEP diagram of **1** with labeling scheme. Selected bond length(Å) and angles(°): Ni_1-N_1 2.132(5), Ni_1-N_2 2.164(4), Ni_1-N_4 2.056(4), Ni_1-N_3' 2.148(5), N_1-Ni_1-N_2 84.01(9), N_1-Ni_1-N_3' 180.0, N_1-Ni_1-N_4 93.00(10), N_2-Ni_1-N_2' 168.0(2), N_2-Ni_1-N_3' 95.99(9), N_2-Ni_1-N_4 89.7(1), N_2-Ni_1-N_4' 90.9(1), N_3'-Ni_1-N_4 87.0(1), N_4-Ni_1-N_4' 174.0(2), Ni_1-N_4-C_{12} 169.4(4), S_1-C_{12}-N_4 178.3(5).

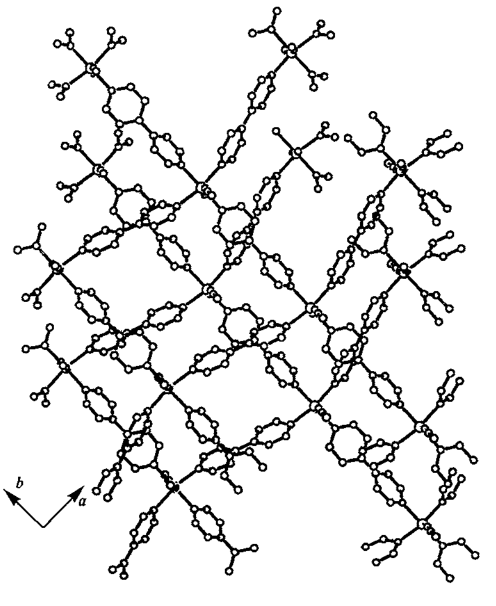

Figure 2. Packing diagram for **1** along the *c* axis.

that distort the square (S1-S1*, 4.485(3) Å). Locally, Ni is in a compressed octahedron with four long Ni-N (bpy) bonds (2.164-2.132 Å) and two short Ni-N (NCS) bonds (2.056 Å). The NCS group is almost linear with a N-C-S angle of 178.3°. The connection between Ni atoms and NCS groups are slightly bent with C12-N4-Ni angle of 169.4°. Different to previously reported relative structures,[5a,7,8,10-12] two dimensional chains along *a* and *b* axis in **1** possess different structural features, see Figure 2. The Ni-bpy-Ni chain along *b* is straight and the two pyridine rings of the bpy molecule are not coplanar. The bipyridine dihedral angle is 54.6(3)°.[6] The chain along *a* axis has a wavy structure and the two pyridine rings of the bpy molecule adopt a sterically unfavorable coplanar arrangement.

The planar squares are distorted to the largest extent among related structures.[6-10] The square planar angles are 84.01(9) and 95.99(9)° and dimensions of the square is 11.38 × 11.48 Å. No solvent molecules are clathrated in the square cavities. **1** stacks the closest interlayer structure with two sulphur atoms sit in one square that without interpenetrating may due to two linear and rigid NCS arms extending perpendicular to the 2D net.

The staggered stacking between the 2D sheets makes this structure less intriguing. But, it is interesting that the 2-D network of **1** can be considered as isostructure of $[Co(NCS)_2(4,4'\text{-bpy})_2 \cdot 2(CH_3CH_2)_2O]_n$[10] when its clathrated ether molecules were removed. It shows us a possible application that this 4,4'-bipyridine sustained 2-D square network with two coordinated NCS arms may work as free shelve layers for storing different guest molecules. Further work is in progress.

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13 Analysis found: C, 54.10; H, 3.18; N, 17.11%. Calc. for 1: C, 54.18; H, 3.28; N, 17.24%.

14 Crystal data for 1: M = 487.23, monoclinic, space group $C2/c$ (no. 15), a = 12.156(3), b = 11.381(2), c = 16.646(8) Å, β = 100.43(3)°, V = 2265(1) Å^3, $F(000)$ = 1000, Z = 4, Dc = 1.429 g/cm^3, T = 296 K, μ(Mo-Kα) = 10.62 cm^{-1}, λ(Mo-Ka) = 0.71070 Å. A crystal of approximate dimensions 0.30 × 0.30 × 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-II imaging plate area detector with graphite monochromated Mo-Kα radiation. Scattering factors were taken from Cromer and Waber.[15] The ω-2θ scan mode with a maximum 2θ value being 49.9° were used to collect intensity data. A total of 1912 reflections were collected, of which 1829 had $I > 3\sigma(I)$ with 151 parameters. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods using SIR92[16] and expanded using Fourier techniques, and refined by full-matrix least-squares calculation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined. ,All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Final R = 0.067, Rw = 0.097, goodness of fit = 4.48, max. shift/e.s.d. =0.09.

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