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CRYSTAL STRUCTURE OF A NEW SUPRAMOLECULAR Ni(II) N^6-BENZYLAMINOPURINE COMPOUND

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A new mononuclear Ni(II) N^6-benzylaminopurine supramolecule $[Ni(6\text{-}BA\text{-}H_2)_2(H_2O)_4]\cdot(R)_2\cdot\cdot 4H_2O$ (**1**) (6-BA = N^6-benzylaminopurine $(C_5H_2N_3NH)(NH)CH_2(C_6H_5)$, H_3R = 5-sulfosalicylic acid $(C_6H_3)CO_2H(OH)SO_3H)$ is firstly synthesized by the volatile method. Compound **1** possesses a 3D supramolecular structure built via H-bonds and π—π stacking interactions. In the structure, a mononuclear $[Ni(6\text{-}BA\text{-}H_2)_2(H_2O)_4]^{6+}$ cation, in which the Ni(II) ion is 6-coordinated, bears six positive charges, and a fully deprotonated R^{3-} anion is located in the void surrounding the mononuclear cation to balance the charge.

Keywords: Ni(II) N^6-benzylaminopurine compound, crystal structure, supramolecule.

INTRODUCTION

Self-assembly of supramolecular architectures combining organic ligands with metal ions is currently of significant interest due to their fascinating properties, versatile intriguing structure, and topologies along with promising applications in the areas of catalysis, chirality, conductivity, luminescence, magnetism, and porosity [1]. Supramolecular interactions, including hydrogen bonds, π—π stacking, electrostatic attraction and so on, play a crucial role in the properties of the compounds as well as potential applications [2]. 6-Benzylaminopurine (6-BA) is the type of adenine derivatives with a 6-substituted group. The 6-benzyl-amino substituent has a higher activity, which made it play an important role in the tissue culture, gene expression regulation, stress resistance, anti-aging, plant growth stimulants, and anti-heavy metal pollution, etc. [3, 4]. Metal ions can lead to body lesions in life processes, so the research of the coordination of adenine derivatives with metal ions has a great significance in the life sciences and materials chemistry. However, the self-assembly technique combining 6-BA as the first ligand with a metal ion has not been well developed because of the second ligand of 5-sulfosalicylic acid (H_3R). Major efforts have been devoted to the exploration of 6-BA derivatives to get more information through the design and construction of specific supramolecular architectures [5, 6]. Up to date, there are few reports on 6-BA compounds with metal ions [7—9]. In this paper, we introduce a new Ni(II)-6-BA-R compound ($[Ni(6\text{-}BA\text{-}H_2)_2(H_2O)_4]\cdot(R)_2\cdot 4H_2O$ (**1**)), in which there are many strong hydrogen bonds and π—π stacking interactions.

EXPERIMENTAL

Materials and physical measurements. All chemicals purchased were reagent grade and used without further purification. The IR spectrum was recorded on an AVATAR360 spectrophotometer with a range 4000—400 cm^{-1} using KBr pellets. Elemental analyses were performed using an Optima-

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2000DV elemental analyzer. The absorption spectra were measured on an Australia GBC UV/Vis 916 spectrophotometer in the range 200—600 nm. Thermal gravity analysis was carried out from room temperature to 800 °C using TGA/SDTA851e under the N_2 atmosphere at a heating rate of 10 $°C \cdot min^{-1}$.

Synthesis of $[Ni(6\text{-}BA\text{-}H_2)_2(H_2O)_4]\cdot(R)_2\cdot 4H_2O$. Compound **1** was synthesized by the reaction of 0.105 g $NiSO_4\cdot 6H_2O$ (0.4 mmol), 0.045 g 6-BA (0.2 mmol) and 0.10 g 5-sulfosalicylic acid (0.4 mmol) in ethanol and deionized water (2:2, v/v). The mixture was placed in a water bath at 80 °C and stirred for 4 h, and then let set for 20 days at room temperature. The final pH value is about 6. Pink claval crystals of **1** were selected by vacuum filtration and dried in air (yield 23 %). Elemental analysis calcd. for $C_{38}H_{48}N_{10}NiO_{20}S_2$ (%): C 41.92, H 4.41, N 12.87; found: C 41.87, H 4.38, N 12.79. IR data (cm^{-1}): 3216(s), 3172(m), 3035(w), 2925(w), 1668(s), 1619(m), 1475(w), 1423(s), 1355(m), 1255(w), 1180(s), 1124(m), 1079(m), 1035(s), 989(w), 867(w), 835(w), 773(w), 721(w), 671(m), 592(m), 478(m).

X-ray crystallography. The single crystals of compound **1** were mounted on a Bruker SMART APEX II diffractometer with graphite-monochromated MoK_α radiation (0.71073 Å). Intensity data were collected at 296±2 K and processed on a PC with the SAINT Plus software package. The structure was solved by direct methods and refined by the full-matrix leastsquares fitting on F^2 using the SHELXTL 97 [10] software. All non-hydrogen atoms of **1** were refined with anisotropic thermal parameters. The positions of hydrogen atoms were either located by difference Fourier maps or calculated geometrically and their contributions to the structural factor calculations were included. For more details see the CIF files and Supporting Information. Crystallographic data of the crystal and refinements are summarized in Table 1.

Table 1

Crystal data and structure refinements for compound **1**

Empirical formula	$C_{38}H_{48}N_{10}NiO_{20}S_2$
Formula weight	1087.69
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2/c$
a, b, c, Å; β, deg.	7.6966(1), 8.6906(2), 35.129(6); 102.483(4)
Volume, $Å^3$	2294.2(7)
Z	4
Calculated density, $Mg\cdot m^{-3}$	1.575
Absorption coefficient, mm^{-1}	0.606
$F(000)$	1132
θ range for data collection, deg.	1.19—25.00
Reflections collected / unique	15645 / 4042 [R(int) = 0.1042]
Completeness to θ = 25.00 %	100
Data / restraints / parameters	4042 / 0 / 322
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0596$, $wR_2 = 0.1391$
R indices (all data)	$R_1 = 0.1243$, $wR_2 = 0.1793$
Largest diff. peak and hole, $e/Å^{-3}$	1.195 and –0.529

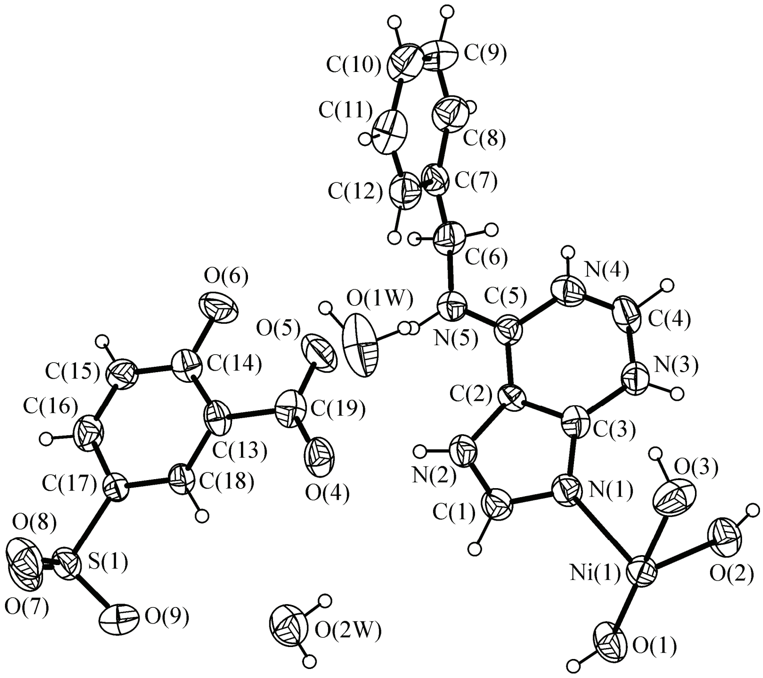

Fig. 1. ORTEP view of **1** showing the atom labeling scheme (50 % thermal ellipsoids)

RESULTS AND DISCUSSION

Crystal structural studies. The asymmetric unit of **1** (Fig. 1) contains a crystallographically independent Ni(II) atom, a 6-BAH$_2^{2+}$ cation, three aqua ligands as well a free R^{3-} anion and two lattice water molecules. The Ni(1) atom is 6-coordinated with two nitrogen atoms (N(1), N(1A)) from two 6-BAH$_2^{2+}$ ligands and four water oxygen atoms (O(1), O(2A), O(2), O(3)) to form its octahedral coordination geometry. Ni—O/N bond distances ranging from 2.019(5) to 2.166(4) Å, *cis*-angles from 87.67(1)° to 92.39(1)°, and *trans*-angles from 176.1(2)—180.0(2) are close to those in the reported metal 6-BA compounds. Selected bond lengths and angles listed in Table 2.

The coordinating pattern of the 6-BA ligand in **1** is simply the form of unidentate bridging allowing one nitrogen atom N(1) to bridge a Ni(II) atom. The remaining nitrogen atoms (N(2), N(3), N(5))

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for compound* **1**

Ni(1)—O(3)	2.019(5)	O(3)—Ni(1)—O(1)	180.00(2)	O(3)—Ni(1)—N(1)	89.11(1)
Ni(1)—O(1)	2.027(5)	O(3)—Ni(1)—O(2)	91.93(1)	O(1)—Ni(1)—N(1)	90.89(1)
Ni(1)—O(2)	2.064(4)	O(1)—Ni(1)—O(2)	88.07(1)	O(2)—Ni(1)—N(1)	92.39(1)
Ni(1)—O(2)#1	2.065(4)	O(3)—Ni(1)—O(2)#1	91.93(1)	O(2)#1—Ni(1)—N(1)	87.67(1)
Ni(1)—N(1)#1	2.116(4)	O(1)—Ni(1)—O(2)#1	88.07(1)	N(1)#1—Ni(1)—N(1)	178.2(2)
Ni(1)—N(1)	2.116(4)	O(2)—Ni(1)—O(2)#1	176.1(2)		
S(1)—O(8)	1.448(4)	O(3)—Ni(1)—N(1)#1	89.11(1)		
S(1)—O(7)	1.457(4)	O(1)—Ni(1)—N(1)#1	90.89(1)		
S(1)—O(9)	1.457(4)	O(2)—Ni(1)—N(1)#1	87.67(1)		
S(1)—C(17)	1.763(5)	O(2)#1—Ni(1)—N(1)#1	92.39(1)		

Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z+1/2$.

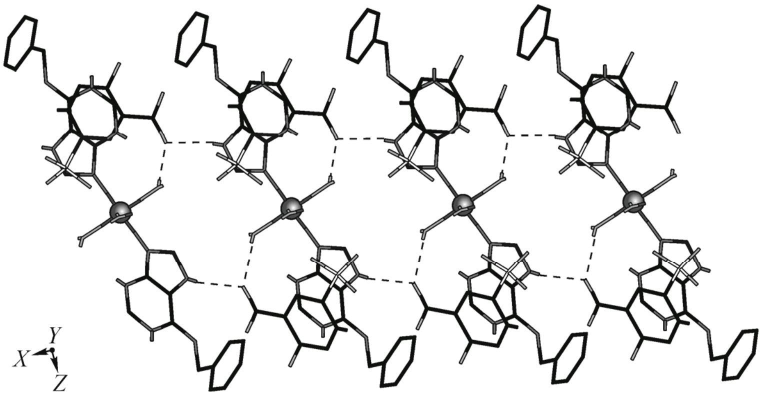

Fig. 2. 1D supramolecular double chain of **1** via H-bonds along the *a* axis. Hydrogen bonds are drawn as dashed lines

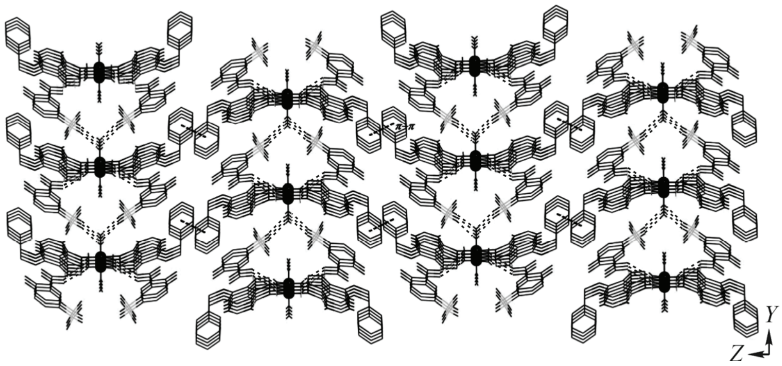

Fig. 3. 3D supramolecular framework via H-bonds and π—π stacking interactions along the *a* axis. Hydrogen bonds and π—π stacking are drawn as dashed lines

are involved in the formation of hydrogen bonds, along with the free R^{3-} anion and water molecules. Based on the charge balance, both N(3) and N(4) atoms are protonated (these hydrogen atoms being located from the difference Fourier map and refined isotropically).

Compound **1** displays a mononuclear molecular unit $[Ni(6\text{-}BAH_2)_2(H_2O)_4]^{6+}$ with six positive charges. Two R^{3-} anions are placed under the boat built from a $[Ni(6\text{-}BAH_2)_2(H_2O)_4]^{6+}$ cation, and they are joined together via the O(2)—H(21)···O(4) hydrogen bond (2.716(5) Å, 167.2°) to form a neutral second building unit (SBU) $[Ni(6\text{-}BAH_2)_2(R)_2]$. SBUs are interconnected with each other via the N(2)—H(21A)···O(4) hydrogen bond (2.770(5) Å, 170.9°) to extend its structure into a 1D ladder-like supramolecular chain along the *a* axis (Fig. 2). The adjacent 1D chains are further linked with each other through the O(3)—H(31)···O(9) hydrogen bond (2.642(5) Å, 172.3°) and offset π—π stacking interactions arise from between the C(7)—C(8)—C(9)—C(10)—C(11)—C(12) rings (code: 1–*X*, –*Y*, –*Z*, centroid distance 3.6982 Å, perpendicular distance 3.565 Å, dihedral angle 0.00°, slippage 0.983 Å) to lead to a 3D supramolecular framework (Fig. 3). Also the hydrogen bonds formed among the other molecules and other π—π stacking interactions further consolidate the structure stability of **1**. Hydrogen bonds lengths and angles are shown in Table 3.

Thermal Analysis. The TG-DTA analysis was conducted to examine the stability of compound **1**, and the TGA curve exhibits mainly three weight loss steps (Fig. 4). The process of weight loss in the first step, covering a temperature range 80—150 °C, is attributed to the release of four lattice water molecules and four coordinated water molecules. The weight loss of 13.5 % is in good agreement with the calculated value (13.2 %). The second step of 41.4 % is from 225 °C and 350 °C, corresponding to the pyrolysis of the organic 6-BAH_2 ligand (calc. 41.7 %). The last step of 38.9 % starts at 350 °C, owing chiefly to the collapse of the organic H_3R molecule, and completes at 620 °C (calc. 39.5 %). Based on XRD powder studies, the main residue is Ni and the total weight loss of 5.9 % is close to the calculated value (5.6 %).

UV/Vis absorption analysis. The UV/Vis absorption spectra of **1** in ethanol are shown in Fig. 5; the bands are centered at 210.6 nm and 270.3 nm. The result reveals that the absorption bands

Table 3

Hydrogen bond lengths (Å) *and angles* (deg.) *for compound* **1**

D—H...A	*d*(D—H)	*d*(H...A)	*d*(D...A)	∠(DHA)
O(2W)—H(22W)...S(1)#2	0.86	2.84	3.585(5)	146.0
O(2W)—H(22W)...O(9)#2	0.86	2.64	3.106(6)	115.9
O(2W)—H(22W)...O(7)#2	0.86	2.08	2.923(6)	166.6
O(2W)—H(21W)...O(7)#3	0.85	2.06	2.810(6)	147.9
O(1W)—H(12W)...S(1)#4	0.84	2.96	3.716(4)	149.5
O(1W)—H(12W)...O(8)#4	0.84	1.90	2.735(6)	170.8
O(1W)—H(11W)...N(3)#5	0.88	2.34	2.819(6)	114.6
O(3)—H(31)...O(9)#4	0.82	1.83	2.642(5)	172.3
O(2)—H(22)...O(1W)#3	0.80	2.15	2.866(6)	148.4
O(2)—H(21)...O(4)#3	0.83	1.90	2.716(5)	167.2
O(1)—H(11)...O(2W)#6	0.82	1.94	2.752(5)	177.5
N(5)—H(5)...O(5)	0.85	1.90	2.724(6)	163.6
N(3)—H(3)...O(1W)#3	0.86	1.98	2.819(6)	163.3
N(2)—H(21A)...O(4)	0.84	1.94	2.770(5)	170.9

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$; #2 $-x+2, y, -z+1/2$; #3 $x-1, y, z$; #4 $x-1, y-1, z$; #5 $x+1, y, z$; #6 $-x+1, y, -z+1/2$.

are mainly in accordance with those of parent 6-BAP (207.8 nm, 267.5 nm) [11] and are slightly red-shifted, which may be caused by the protonation and coordination of 6-BAP.

CONCLUSIONS

The first example of a mononuclear Ni(II)-6-BA systemic compound $[Ni(6\text{-}BA\text{-}H_2)_2(H_2O)_4](R)_2\cdot 4H_2O$ (**1**) is obtained based on the second ligand H_3R under volatile conditions. Compound **1** possesses a 3D supramolecular structure with a mononuclear $[Ni(6\text{-}BA\text{-}H_2)_2(H_2O)_4]^{6+}$ cation in which the Ni(II) ion is 6-coordinated and two nitrogen atoms (N(3), N(4)) are protonated.

Supplementary material. CCDC No. 836354 **1** contains the supplementary crystallographic data. These data can be obtained via the Cambridge Crystallographic Data Centre (deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit).

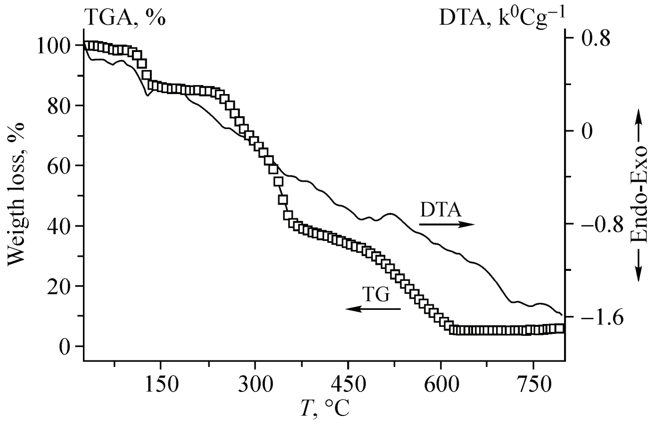

Fig. 4. TG-DTA curves of **1**

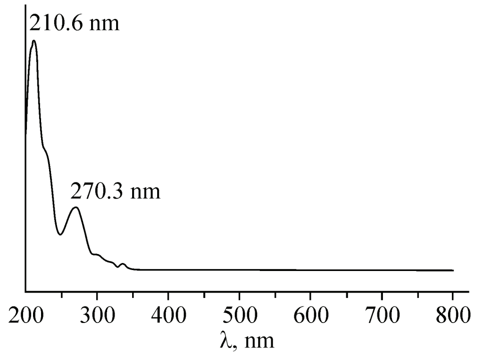

Fig. 5. UV/Vis absorption spectrum of **1**

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