

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE AND MAGNETIC PROPERTY
OF A NEW TWO-DIMENSIONAL COORDINATION POLYMER CONSTRUCTED BY
1,4-BIS(1,2,4-TRIAZOL-1-YLMETHYL)-BENZENE AND 4,4'-SULFONYLDIBENZOIC ACID

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A two-dimensional Ni(II) complex $\{[\text{Ni}(\text{BTX})(\text{SDBA})(\text{H}_2\text{O})] \cdot 0.29\text{H}_2\text{O}\}_n$ (**1**) (BTX = 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene, H₂SDBA = 4,4'-sulfonyldibenzoic acid) is synthesized and characterized using single crystal X-ray diffraction, IR spectroscopy, and elemental analysis. The single crystal X-ray diffraction analysis reveals that complex **1** is a two-dimensional polymer containing 28-membered rings based on the rhomboid subunit $[\text{Ni}_2(\text{C}_{14}\text{H}_8\text{O}_6\text{S})_2]$ with a Ni—Ni separation of 12.923 Å. The thermal stability and magnetic property of the title complex are briefly investigated.

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Crystal engineering of metal—organic frameworks (MOFs) has been flourishing in recent years not only due to their intriguing structural diversity and new topologies but also owing to their potential applications in gas storage, chemical separations, microelectronics, nonlinear optics, heterogeneous catalysis, and so on [1—5]. It is well-known that the construction of MOFs is usually influenced by several factors in the self-assembly process, such as organic ligands, solvents, metal atoms, and so on [6, 7]. Among these factors, the organic ligands play a key role in directing the ultimate architectures of compounds. The main stream method to construct coordination polymers is to utilize carboxylate-containing and multidentate N-donor ligands.

4,4'-Sulfonyldibenzoic acid (H₂SDBA) as a semi-rigid V-shaped dicarboxylate ligand is a very versatile ligand for the construction of novel MOFs [8—13]. Meanwhile, 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene (BTX) as a flexible bis(triazole) ligand can adopt different conformations depending on the relative orientation of its CH₂ groups [14—19]. However, to the best of our knowledge, coordination polymers constructed from H₂SDBA and BTX ligands have not been documented so far. Here, we have selected H₂SDBA and BTX as organic ligands, generating the title new Ni(II) coordination polymer $\{[\text{Ni}(\text{C}_{12}\text{N}_6\text{H}_{12})(\text{C}_{14}\text{H}_8\text{O}_6\text{S})(\text{H}_2\text{O})] \cdot 0.29\text{H}_2\text{O}\}_n$ (**1**), the crystal structure of which we now report. In addition, the thermal and magnetic properties of the complex have been investigated.

Experimental. The 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene (BTX) ligand was synthesized according to the literature method [14]. All other reagents and solvents were commercially available and used without further purification. The IR spectrum was obtained on a VECTOR 22 spectrometer within the range 4000—400 cm⁻¹ as KBr disks. The elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. The thermal gravimetric analysis (TGA) was performed on a Perkin-

Elmer Pyris 1 TGA analyzer in the range from room temperature to 850 °C with a heating rate of 20°C·min⁻¹ under nitrogen. Magnetic measurements on a microcrystalline sample were carried out on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made for both sample holder as the background and compound estimated from Pascal's constants [20].

Synthesis of {[Ni(BTX)(SDBA)(H₂O)]·0.29H₂O}_n. A mixture of Ni(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), H₂SDBA (30.7 mg, 0.1 mmol), BTX (48.1 mg, 0.2 mmol), and KOH (11.2 mg, 0.2 mmol) in H₂O (10 ml) was sealed in a 16 ml Teflon-lined stainless steel container and heated at 160°C for 72 h. After cooling to room temperature, green block crystals of the title complex were collected by filtration and washed several times with water and ethanol (yield 11.2 %, based on H₂SDBA). Elemental analysis for C₂₆H_{22.58}N₆NiO_{7.29}S (*M_r* = 626.46) (%): C 49.85, H 3.63, N 13.41; found (%): 49.95, H 3.65, N 13.44. Selected IR peaks (cm⁻¹): 3412 (m), 1601 (s), 1478 (s), 1225 (s), 812(w), 779 (w), 721 (w).

X-ray crystallography. A green block-shaped crystal with dimensions of 0.21×0.19×0.18 mm was selected for the measurement. The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. A total of 9774 reflections were collected in the range of $2.02 \leq \theta \leq 25.50^\circ$, out of which 4881 ($R_{\text{int}} = 0.0347$) were independent, and 3685 with $I > 2\sigma(I)$ were used in the structure determination and refinement. Absorption correction was performed using the SADABS program [21]. The structure was solved by a direct method using the SHELXL-97 program and refined by the full-matrix least-squares technique on F^2 with SHELXL-97 [22]. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they were bonded. The final $R = 0.0446$ and $wR = 0.0999$ ($w = 1/[\sigma^2(F_0^2) + (0.0448P)^2 + 0.2974P]$, where $P = (F_0^2 + 2F_c^2)/3$). $S = 1.054$, $(\Delta\rho)_{\text{max}} = 0.282$, $(\Delta\rho)_{\text{min}} = -0.380 \text{ e/\AA}^3$ and $(\Delta/\sigma)_{\text{max}} = 0.001$. The selected bond lengths and angles are listed in Table 1.

Results and discussion. The single crystal X-ray diffraction revealed that complex **1** crystallizes in the triclinic space group $P-1$ with $a = 10.063(7) \text{ \AA}$, $b = 10.954(8) \text{ \AA}$, $c = 13.157(9) \text{ \AA}$, $\alpha = 71.219(8)^\circ$, $\beta = 88.301(9)^\circ$, $\gamma = 76.758(9)^\circ$, $V = 1335.0(16) \text{ \AA}^3$, $Z = 2$, C₂₆H_{22.58}N₆NiO_{7.29}S, *M_r* = 626.46, $D_c = 1.567 \text{ g/cm}^3$, $\mu = 0.865 \text{ mm}^{-1}$, $F(000) = 649$, GOOF = 1.054, the final $R = 0.0446$ and $wR = 0.0999$ for 3685 observed reflections with $I > 2\sigma(I)$. As shown in Fig. 1, the asymmetric unit contains a Ni^{II} atom, one fully deprotonated H₂SDBA ligand, two halves of two crystallographically different BTX ligands (BTX—A, N1—N3/C15—C20; BTX—B, N4—N6/C21—C26), one coordinated aqua molecule, and 0.29 water molecule of crystallization (the O8 water site was found to be partially occupied, with an occupancy factor of 0.289(2)). Each Ni(II) center is six-coordinated by two oxygen atoms from a chelating carboxylate group of one SDBA²⁻ ligand (Ni1—O1 = 2.087(2),

T a b l e 1

Selected bond distances (Å) and angles (deg.) for complex **1**

| | | | | | |
|--------------|----------|-------------------|------------|-------------------|-----------|
| Ni(1)—N(1) | 2.076(3) | N(1)—Ni(1)—N(4) | 90.83(11) | N(1)—Ni(1)—O(1) | 92.27(9) |
| Ni(1)—O(1) | 2.087(2) | N(1)—Ni(1)—O(2) | 88.13(11) | N(4)—Ni(1)—O(1) | 171.97(9) |
| Ni(1)—O(5)#3 | 2.047(2) | N(4)—Ni(1)—O(2) | 111.98(10) | O(1)—Ni(1)—O(2) | 60.76(8) |
| Ni(1)—N(4) | 2.077(3) | O(5)#3—Ni(1)—N(1) | 173.95(10) | O(5)#3—Ni(1)—N(4) | 87.80(10) |
| Ni(1)—O(2) | 2.225(2) | O(5)#3—Ni(1)—O(1) | 88.35(9) | O(5)#3—Ni(1)—O(2) | 86.92(10) |
| Ni(1)—O(7) | 2.044(2) | O(7)—Ni(1)—N(1) | 92.61(11) | O(7)—Ni(1)—N(4) | 90.80(10) |
| | | O(7)—Ni(1)—O(1) | 96.45(9) | O(7)—Ni(1)—O(2) | 157.20(8) |
| | | O(7)—Ni(1)—O(5)#3 | 93.30(10) | | |

#3 $-x, -y+1, -z+2$.

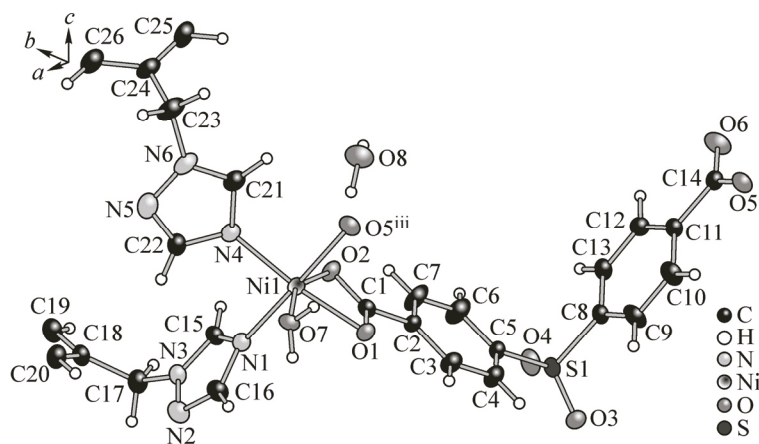


Fig. 1. View of the local coordination of the Ni^{II} cations in complex **1**, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radii (Symmetry codes: (iii) $-x, 1-y, 2-z$)

Ni1—O2 = 2.225(2) Å), one oxygen atom from the monodentate carboxylate group (Ni1—O5 = 2.047(2) Å) of another SDBA²⁻ ligand, one oxygen atom from one aqua ligand (Ni1—O7 = 2.044(2) Å), and two nitrogen atoms (Ni1—N1 = 2.076(3) Å, Ni1—N4 = 2.077(3) Å) from two different BTX ligands. The average Ni—O and Ni—N distances in complex **1** are comparable to the reported Ni-based compounds [23, 24].

The dihedral angles between the two phenyl rings is 98.1° and the C5S1C8 bond angle is 103.39(15)° in the SDBA²⁻ ligands, while the dihedral angles between the carboxylate groups and their corresponding phenyl rings are 1.3° and 5.5°, respectively. It is worth noting that H₂SDBA is completely deprotonated and links two Ni(II) atoms, while there are two coordination patterns for the SDBA²⁻ ligand with one in the $\mu_1\text{-}\eta^1\text{:}\eta^1$ chelating mode and another in the $\mu_1\text{-}\eta^1\text{:}\eta^0$ monodentate mode. Two crystallographically equivalent Ni(II) atoms are bridged by two SDBA²⁻ ligands to form a rhomboid subunit [Ni₂(C₁₄H₈O₆S)₂] with a Ni—Ni separation of 12.923 Å. On the other hand, each BTX ligand adopting the *trans* conformation acts as a bis-monodentate ligand and connects two nickel(II) atoms to form the [Ni(BTX)]_n²ⁿ⁺ zig-zig chain. The Ni···Ni contact distances through the crystallographically distinct BTX ligands are 14.198 Å and 14.734 Å. These differences are provided by conformational variances within the distinct BTX ligands. In BTX—A, the triazole group is twisted by 72.3° relative to the benzene ring plane. The related torsions in BTX—B is 65.9°. Thus, parallel [Ni(BTX)]_n²ⁿ⁺ chains are aggregated into [Ni(BTX)(SDBA)]_n 2D coordination polymer layers oriented parallel to the [1 0 1] crystal planes by SDBA²⁻ ligands (Fig. 2). In addition, the double-layered grid condenses into a 3D supramolecular architecture through O—H···O hydrogen bonds (Fig. 3). This assembly is reinforced by a S—O··· π interaction [S1—O4···Cg4ⁱ = 85.3°, O4···Cg4ⁱ = 3.855(4) Å and S1···Cg4ⁱ = 4.001(3) Å; Cg4ⁱ is the centroid of the C8—C13 ring; symmetry code: (i) $1-x, -y, 2-z$].

The thermal stability of complex **1** was investigated. As shown in Fig. 4, the weight loss of 3.96 % in the temperature range of 99—104 °C is consistent with the removal of water molecules (calcd 3.71 %). The weight loss corresponding to the release of organic ligands is observed from 160 °C to 770 °C. The remaining residue corresponds to the formation of NiO (obsd. 11.11 %, calcd. 11.92 %).

Magnetic measurements were performed on polycrystalline samples of complex **1** in the range of 1.8—300 K. The χ_{MT} product was 1.02 cm³·K·mol⁻¹, which is somewhat higher than that expected for an isolated S = 1 Ni²⁺ ion (1.00 cm³·K·mol⁻¹) at room temperature. For complex **1**, χ_{MT} products are almost a constant (1.02—1.01 emu·K·mol⁻¹) from room temperature to 1.8 K, indicating no magnetic coupling between the neighboring Ni^{II} ions.

Fig. 2. View of the 2D framework of complex 1

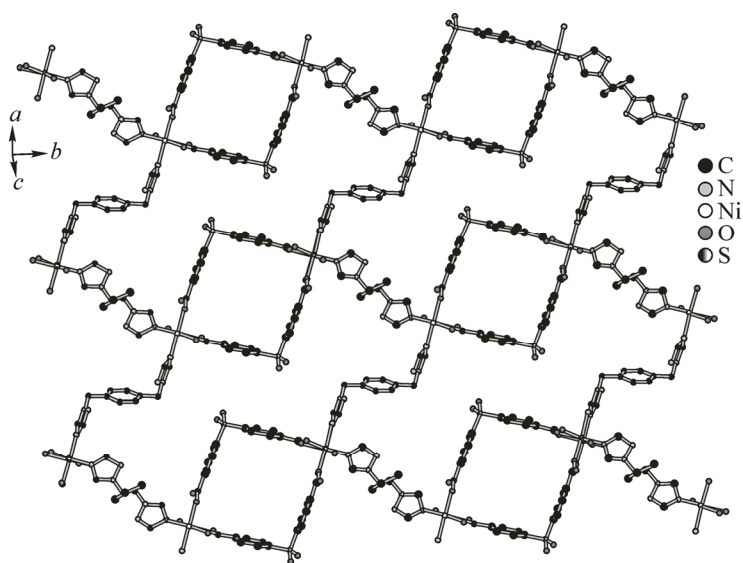


Fig. 3. Perspective view of the 3D supramolecular structure of complex 1, incorporating O—H...O hydrogen bonds (dashed lines)

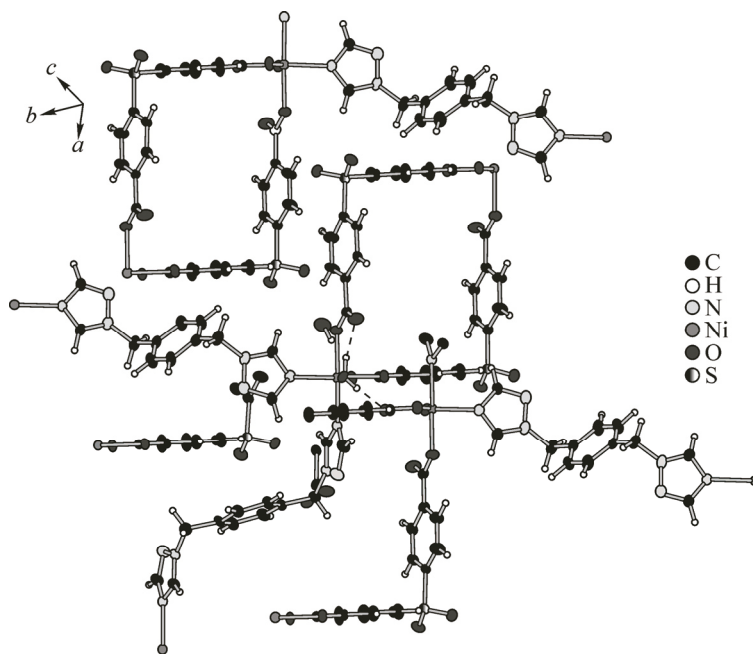
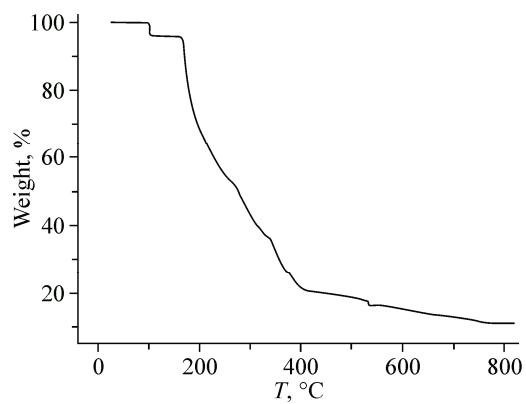


Fig. 4. TG curve of complex 1



In summary, we have synthesized a 2D polymer containing 28-membered rings based on the rhomboid subunit $[\text{Ni}_2(\text{C}_{14}\text{H}_8\text{O}_6\text{S})_2]$ with a Ni—Ni separation of 12.923 Å. Moreover, the thermal stability and magnetic properties of the title complex have been briefly investigated.

Crystallographic data for the structural analysis of complex **1** has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 985946. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EQ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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