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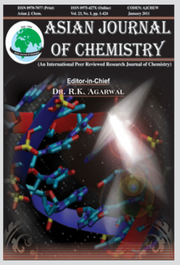

NOTE

Synthesis and Crystal Structure of Nickel(II) Complex Derived from Benzotriazole-4-Sulfonate

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A novel complex $[Ni(C_{10}H_8N_2)_2(C_7H_6N_3SO_3)][OH]\cdot 2.5H_2O$ was synthesized and characterized by IR spectra, elemental analysis and single-crystal X-ray. The crystal structure analysis shows that the Ni(II) is a six-coordinated in a distorted octahedron environment, then complex packs in 3D-superamolecular network through intermolecular hydrogen bonds and π-π staking. The crystal is orthorhombic, space group Pccn with unit cell parameters: a = 30.142(4) Å, b = 10.4659(16) Å, c = 18.497(3) Å, V = 5835.1(15) Å3, Z = 4, Mr = 1289.66, Dc = 1.468 Mg/cm^3, μ = 0.792 mm^{-1}, F(000) = 2676, T = 293(2) K, R = 0.0466, wR = 0.1582 for 5726 reflections with $I > 2\sigma(I)$.

Key Words: 7-Methylbenzotriazole-4-sulfonate, Nickel(II) complex, Crystal structure, Hydrogen bonds.

Nickel is vital for organism as a trace element and it often acts as component or secondary factor of enzyme. In the latest two decades, biological inorganic chemistry of nickel has become one of the pioneer fields and the coordination chemistry of nickel has made a great progress[1]. However because of the weak coordination strength of the sulfonate compared with that of the phosphonate and carboxylate, little attention has been paid to complexes derived from sulfonate[2-13]. Herein reported is a new 3D hydrogenbonding supramolecular nickel complex derived from benzotriazole-4-sulfonate $[Ni(C_{10}H_8N_2)_2(C_7H_6N_3SO_3)][OH]\cdot 2.5H_2O$.

All reagents were of AR grade and used without further purification. 7-Methyl-benzotriazole-4-sulfonic acid was prepared by a modified literature method[14]. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm^{-1}) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

Synthesis: To a solution of 7-methylbenzotriazole-4-sulfonic acid (0.1 mmol) and $NiCl_2\cdot 2H_2O$ (0.1 mmol) in water (15 mL) was dropped with 1M NaOH until the pH of solution is *ca.* 8.0. The solution was stirred for 10 min, then 0.2 mmol of 2,2'-bipy dissolved in 4 mL ethanol was added dropwise, resulting in a change from light blue to dark blue. After additional stirring of 10 min, the filtrate was evaporated for a week and brown block crystals were collected (Yield: 43 %). Anal. calcd. for $C_{54}H_{56}N_{14}Ni_2O_{13}S_2$: C, 50.25; H, 4.37; N, 15.19 %. Found: C, 5.66; H, 4.16; N, 15.82%. IR (KBr, ν_{max}, cm^{-1}): 3446(s), 3056(w), 1626(m), 1589(m), 1518(s), 1427(s), 1236(s), 1175(s), 1195(s), 1141(w), 1106(w), 1043(s), 849(s), 800(w), 727(s), 664(s), 633(m), 576(m).

Crystal structure determination: A single crystal of compound with dimensions of 0.18 mm × 0.16 mm × 0.12 mm was selected for crystallographic data collection at 293(2)K and structure determination on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoK_α radiation (λ = 0.71073 Å). A total of 33041 reflections were collected in the range of 1.35° ≤ θ ≤ 26.00°, of which 5726 reflections were unique with $R_{int} = 0.0343$. The data were integrate using the Siemens SAINT program[15]. With the intensities corrected for Lorentz factor, polarization, air absorption and absorption due to variation in the path length through the detector face plate. Empirical absorption and extinction corrections were applied. The structure was solved by direct methods and expanded using Fourier techniques and SHELXTL program[16] system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 389 variable parameters for 5726 reflections with $I>2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R1 = S(||F_0|-|F_c||)/S|F_0| = 0.0457 \qquad (1)$$

and

$$wR_2 = \{S[w(F_0^2-F_C^2)^2]/Sw(F_0^2)^2\}^{1/2} = 0.0941 \qquad (2)$$

where w = $1/[\sigma^2(F_0^2) + (0.0734P)^2 + 4.665P]$ and P = $(F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.603 and -0.536 e/Å^3, respectively.

The selected bond lengths and bond angles are given in Table-1. Fig. 1 shows the molecular structure of the present nickel(II) complex. Fig. 2 shows the packing diagram of the this compound. This compound crystallizes in the orthorhombic lattice with Pccn space group. The asymmetric unit consists of one Ni atom, two 2,2'-bipy molecules, one 7-methylbenzotriazole-4-sulfonate, one hydroxyl anion and two and a haf lattice water molecules. The Ni(II) atom has a distorted octahedron coordination geometry, formed by two 2,2'-bipy molecules and one 7-methylbenzotriazole-4-sulfonate. The Ni-N bond distances range from 2.040(3) Å to 2.093(3) Å and the Ni-O bond distance is 2.129(2) Å (Table-1).

TABLE-1
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Ni(1)-N(3)	2.040(3)	Ni(1)-N(4)	2.076(2)
Ni(1)-N(5)	2.091(2)	Ni(1)-N(6)	2.092(2)
Ni(1)-N(7)	2.093(3)	Ni(1)-O(1)	2.129(2)
S(1)-O(2)	1.444(3)	S(1)-O(3)	1.447(3)
S(1)-O(1)	1.468(2)	S(1)-C(1)	1.761(3)
N(3)-Ni(1)-N(4)	96.33(11)	N(3)-Ni(1)-N(5)	174.20(10)
N(4)-Ni(1)-N(5)	78.40(10)	N(3)-Ni(1)-N(6)	90.79(10)
N(4)-Ni(1)-N(6)	172.19(10)	N(5)-Ni(1)-N(6)	94.62(10)
N(3)-Ni(1)-N(7)	96.61(10)	N(4)-Ni(1)-N(7)	96.99(10)
N(5)-Ni(1)-N(7)	86.53(10)	N(6)-Ni(1)-N(7)	78.93(10)
N(3)-Ni(1)-O(1)	86.82(9)	N(4)-Ni(1)-O(1)	91.37(9)
N(5)-Ni(1)-O(1)	90.84(9)	N(6)-Ni(1)-O(1)	92.24(9)
N(7)-Ni(1)-O(1)	170.53(10)	–	–

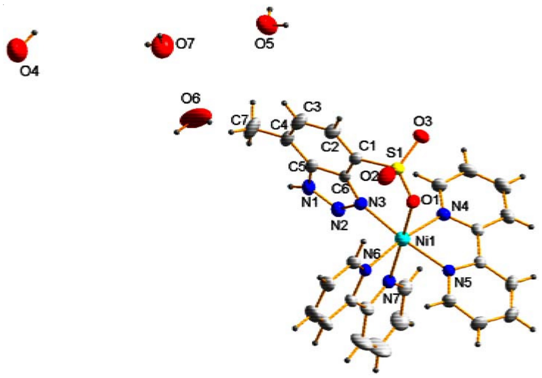

Fig. 1. Molecular structure of the nickel(II) complex

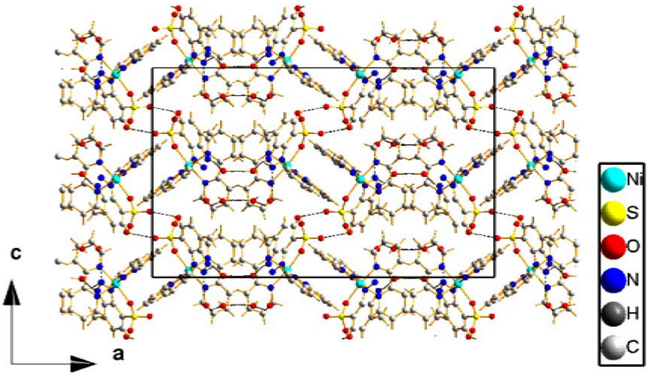

Fig. 2. View of a 3D supramolecular framework of Ni(II) complex showing the intermolecular hydrogen bonding.

In crystal packing, it is interesting to observe that the O–H···O, O–H···S, N–H···O, N–H···S intermolecular hydrogen bonds (Table-2) are formed between adjacent molecules and aromatic π-π staking interaction is existent between the neighbouring 2,2'-bipy and benzotriazole resulting in a 3D-supramolecular framework.

TABLE-2
HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

D–H···A	D–H	H···A	D···A	∠DHA
N(1)–H(1A)···O(4)#1	0.86	2.01	2.854(6)	165.0
O(4) –H(4B)···O(4)#2	0.90	1.79	2.694(11)	175.0
O(6)–H(6C)···O(6)#2	0.85	1.87	2.70(3)	167.0
O(5)–H(5A)···O(2)#3	0.85	2.08	2.809(4)	143.0
O(5)–H(5B)···O(3)#4	0.85	2.11	2.907(4)	155.0
O(7)–H(7E)···N(2)#5	0.85	2.24	3.054(4)	161.0
O(7)–H(7D)···O(6)#6	0.90	2.05	2.820(10)	142.0

Symmetry codes: #1 -X+1/2,-Y+1/2,Z-1 #2 -X+1/2,-Y+1/2,Z #3 X,Y-1,Z #4 -X,Y-1/2,-Z+1/2 #5 X,Y,Z+1 #6 X,-Y+1/2,Z+1/2

Conclusion

A novel nickel(II) complex with 3D-superamolecular structure has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 784500.

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