Crystal structure of triaquatriimidazolenickel(II) naphthalene-2,6-disulfonate monohydrate, $[Co(C_3H_4N_2)_3(H_2O)_3][C_{10}H_6S_2O_6] \cdot H_2O$

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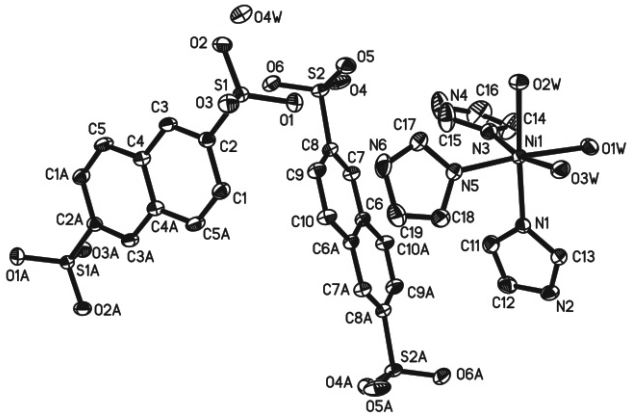

Abstract

$C_{19}H_{26}N_6NiO_{10}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 8.499(2) Å, b = 12.759(3) Å, c = 13.122(4) Å, α = 96.316(4)°, β = 98.315(4)°, γ = 109.229(4)°, V = 1310.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.078, T = 293 K.

Source of material

Disodium 2,6-naphthalenedisulfonate (0.33 g, 1 mmol) and imidazole (0.27 g, 4 mmol) were added to an aqueous solution of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol). The resulting solution was stirred at 70 °C for four hours in a water bath. After filtration, a clear solution was set aside to crystallize. Plate-like blue crystals were collected in 78 % yield (based on Ni) after three days.

Experimental details

H atoms were positioned geometrically and treated as riding, with d(C—H) = 0.93 Å and d(N—H) = 0.86 Å with U_{iso}(H) = 1.2 U_{eq}(CH or NH). Water H atoms were located on a difference Fourier map, and refined according to the riding model with d(O—H) = 0.82(2) Å.

Discussion

Sulfonate complexes have received much attention due to their potential application as functional materials [1,2]. Therefore, the efforts of many groups have produced a plethora of sulfonate structural motifs. However, in comparison with other organic acidato anions such as carbonates and phosphonates, the weak coordination nature of SO_3^- makes its coordination mode very flexible and sensitive to the chemical environment [3]. We and others have demonstrated that the coordination behavior of arene-sulfonates with transition metals can be tailored by decorating the metal centers with other amino ligands. Indeed, after introducing other organic ligands as auxiliaries to the metal centers, sulfonate anions can compete with water molecules and coordinate with transition metals [4-6]. With the infinite number of organic ligands available, a novel research area opens up that could produce numerous materials with desirable connectivity and metrics. However, compared with pyridine and its derivatives, the use of imidazole for tailoring the coordination behavior of arene-sulfonates with transition metals remains less well-explored. Due to the inherent coordination and hydrogen bonding donor/acceptor functionalities, imidazoles could be used in crystal engineering to construct extended networks sustained both by hydrogen bonds and coordination bonds.

The asymmetric unit of the title crystal structure consists of one independent Ni^{2+} cation, three coordinating imidazole molecules, three coordinating water molecules, two halves of naphthalene-2,6-disulfonate anions, and one lattice water molecule. The Ni(II) centre is coordinated by three imidazole nitrogen atoms with d(Ni—N) = 2.059(2) Å, 2.065(2) Å, and 2.066(2) Å, and three water molecules with d(Ni—O) ranging from 2.110(2) Å to 2.138(2) Å, resulting in a slightly distorted octahedral geometry.

In the crystal structure, the naphthalene-2,6-disulfonate anions have two different orientions, with one coplanar to the crystallographic (100) plane, and the other one to the (010) plane. This arrangement may result in an overall closer-packing structure pattern. Further analysis of the crystal structure reveals that the title complex adopts a structure in which layers of anions alternate with layers of cations. It is noted that the most dominant intermolecular hydrogen bonding interactions are formed between the sulfonate oxygens and both coordinated and lattice water molecules, between the imidazole nitrogens and both coordinated and lattice water molecules, as well as between the imidazole nitrogens and the sulfonate oxygens, which extended the overall strcuture into three-dimensional network. Therefore, the hydrogen-bonds play a key role in consolidating the crystal packing.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.18 × 0.29 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.63 cm^{-1}
Diffractometer, scan mode:	Bruker Smart 1000 CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6406, 4356
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3940
$N(param)_{refined}$:	375
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	2*i*	0.6193	0.3375	1.0309	0.041
H(2A)	2*i*	0.0220	0.2764	0.0336	0.051
H(9A)	2*i*	0.5255	0.3449	0.6958	0.043
H(7A)	2*i*	0.8175	0.5115	0.5090	0.038
H(10A)	2*i*	0.3046	0.3955	0.6238	0.043
H(5A)	2*i*	0.7653	0.5247	1.1458	0.046
H(13A)	2*i*	0.0255	0.1002	0.0715	0.046
H(1A)	2*i*	0.2136	0.2926	0.8086	0.043
H(18A)	2*i*	0.0350	0.1663	0.3616	0.053
H(11A)	2*i*	0.3584	0.3381	0.2856	0.053
H(17A)	2*i*	0.3770	0.0670	0.5104	0.055
H(4A)	2*i*	0.8713	0.3340	0.4259	0.101
H(19A)	2*i*	0.0024	0.1762	0.5435	0.061
H(15A)	2*i*	0.6014	0.2161	0.4453	0.090
H(14A)	2*i*	0.6195	0.1869	0.1504	0.085
H(12A)	2*i*	0.2256	0.4287	0.1630	0.056
H(6A)	2*i*	0.2178	0.1139	0.6294	0.061
H(16A)	2*i*	0.8870	0.3296	0.2435	0.094
H(1WB)	2*i*	0.365(4)	–0.028(3)	0.094(2)	0.055(9)
H(1WA)	2*i*	0.301(4)	0.043(3)	0.060(2)	0.052(9)
H(2WA)	2*i*	0.465(4)	–0.063(3)	0.287(3)	0.06(1)
H(2WB)	2*i*	0.329(4)	–0.106(3)	0.325(2)	0.048(9)
H(3WB)	2*i*	–0.021(4)	–0.066(3)	0.189(3)	0.06(1)
H(3WA)	2*i*	0.075(4)	–0.118(3)	0.184(3)	0.07(1)
H(4WB)	2*i*	0.783(5)	0.228(3)	0.902(3)	0.07(1)
H(4WA)	2*i*	0.885(4)	0.309(3)	0.860(3)	0.08(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	2*i*	0.29398(3)	0.07039(2)	0.26003(2)	0.0317(2)	0.0288(2)	0.0250(2)	0.0128(1)	0.0029(1)	0.0060(1)
S(1)	2*i*	0.39285(7)	0.15559(4)	0.88327(4)	0.0318(3)	0.0310(3)	0.0276(3)	0.0148(2)	0.0055(2)	0.0065(2)
S(2)	2*i*	0.85734(7)	0.37614(5)	0.65899(4)	0.0294(3)	0.0362(3)	0.0376(3)	0.0145(2)	0.0063(2)	0.0162(2)
C(4)	2*i*	0.5585(3)	0.4790(2)	1.0271(2)	0.031(1)	0.032(1)	0.035(1)	0.0127(9)	0.0044(9)	0.0090(9)
C(8)	2*i*	0.6922(3)	0.4230(2)	0.6070(2)	0.027(1)	0.031(1)	0.031(1)	0.0105(9)	0.0025(8)	0.0094(8)
C(3)	2*i*	0.5428(3)	0.3660(2)	0.9967(2)	0.033(1)	0.035(1)	0.037(1)	0.018(1)	0.0020(9)	0.0097(9)
C(2)	2*i*	0.4157(3)	0.2984(2)	0.9172(2)	0.031(1)	0.031(1)	0.032(1)	0.0134(9)	0.0088(9)	0.0091(9)
N(2)	2*i*	0.0870(3)	0.2680(2)	0.0862(2)	0.051(1)	0.050(1)	0.036(1)	0.030(1)	0.0056(9)	0.0160(9)
C(9)	2*i*	0.5377(3)	0.3880(2)	0.6428(2)	0.035(1)	0.040(1)	0.037(1)	0.013(1)	0.0110(9)	0.021(1)
C(6)	2*i*	0.5781(3)	0.5179(2)	0.4828(2)	0.028(1)	0.031(1)	0.030(1)	0.0089(9)	0.0059(8)	0.0102(8)
C(7)	2*i*	0.7135(3)	0.4874(2)	0.5303(2)	0.026(1)	0.035(1)	0.037(1)	0.0100(9)	0.0087(9)	0.0146(9)
C(10)	2*i*	0.4060(3)	0.4177(2)	0.5993(2)	0.028(1)	0.044(1)	0.042(1)	0.013(1)	0.0122(9)	0.022(1)
C(5)	2*i*	0.6883(3)	0.5518(2)	1.1099(2)	0.034(1)	0.039(1)	0.042(1)	0.018(1)	–0.006(1)	0.008(1)
C(13)	2*i*	0.0929(3)	0.1704(2)	0.1101(2)	0.046(1)	0.039(1)	0.032(1)	0.020(1)	0.003(1)	0.0046(9)
C(1)	2*i*	0.2990(3)	0.3397(2)	0.8629(2)	0.034(1)	0.034(1)	0.037(1)	0.011(1)	–0.0024(9)	0.0045(9)
C(18)	2*i*	0.1008(3)	0.1474(2)	0.4145(2)	0.045(1)	0.056(2)	0.038(1)	0.025(1)	0.009(1)	0.009(1)
C(11)	2*i*	0.2746(3)	0.3010(2)	0.2268(2)	0.055(2)	0.033(1)	0.042(1)	0.016(1)	–0.002(1)	0.002(1)
C(17)	2*i*	0.2878(4)	0.0932(2)	0.4949(2)	0.056(2)	0.053(2)	0.031(1)	0.025(1)	0.003(1)	0.010(1)
N(4)	2*i*	0.7908(3)	0.2942(3)	0.3748(2)	0.041(1)	0.094(2)	0.083(2)	–0.006(1)	0.014(1)	–0.039(2)
C(19)	2*i*	0.0817(4)	0.1531(2)	0.5145(2)	0.054(2)	0.055(2)	0.046(1)	0.019(1)	0.021(1)	0.002(1)
C(15)	2*i*	0.6374(4)	0.2269(3)	0.3824(3)	0.044(2)	0.096(3)	0.058(2)	–0.004(2)	0.013(1)	–0.022(2)
C(14)	2*i*	0.6479(4)	0.2125(3)	0.2221(2)	0.053(2)	0.094(3)	0.049(2)	–0.000(2)	0.008(1)	0.024(2)
N(5)	2*i*	0.2316(2)	0.1098(2)	0.4016(1)	0.040(1)	0.038(1)	0.0283(9)	0.0163(9)	0.0050(8)	0.0067(8)
N(1)	2*i*	0.2066(2)	0.1861(2)	0.1954(1)	0.042(1)	0.031(1)	0.0278(9)	0.0179(8)	0.0045(8)	0.0050(7)
N(3)	2*i*	0.5440(2)	0.1779(2)	0.2912(2)	0.034(1)	0.036(1)	0.039(1)	0.0116(8)	0.0045(8)	0.0072(8)
C(12)	2*i*	0.2019(3)	0.3517(2)	0.1597(2)	0.059(2)	0.034(1)	0.053(1)	0.021(1)	0.011(1)	0.012(1)
N(6)	2*i*	0.2008(3)	0.1186(2)	0.5641(2)	0.071(2)	0.054(1)	0.026(1)	0.018(1)	0.010(1)	0.0064(9)
C(16)	2*i*	0.7975(4)	0.2889(3)	0.2729(3)	0.045(2)	0.083(2)	0.090(3)	–0.003(2)	0.018(2)	0.023(2)
O(2)	2*i*	0.5446(2)	0.1436(1)	0.9406(1)	0.0390(9)	0.0385(9)	0.0440(9)	0.0218(7)	0.0005(7)	0.0043(7)
O(1W)	2*i*	0.3151(3)	0.0131(2)	0.1073(1)	0.072(1)	0.046(1)	0.0309(9)	0.037(1)	0.0157(8)	0.0136(8)
O(2W)	2*i*	0.3883(3)	–0.0506(2)	0.3176(1)	0.040(1)	0.037(1)	0.0432(9)	0.0189(9)	0.0101(8)	0.0144(8)
O(5)	2*i*	0.7872(2)	0.2543(1)	0.6337(1)	0.057(1)	0.0369(9)	0.054(1)	0.0224(8)	0.0072(8)	0.0119(8)
O(3W)	2*i*	0.0581(2)	–0.0681(2)	0.2234(1)	0.036(1)	0.041(1)	0.046(1)	0.0133(8)	–0.0012(8)	0.0047(8)
O(1)	2*i*	0.3791(2)	0.1336(1)	0.7709(1)	0.059(1)	0.051(1)	0.0294(8)	0.0285(9)	0.0099(7)	0.0060(7)
O(3)	2*i*	0.2402(2)	0.0895(1)	0.9165(1)	0.0372(9)	0.0371(9)	0.0430(9)	0.0126(7)	0.0095(7)	0.0121(7)
O(6)	2*i*	0.8974(2)	0.4159(2)	0.7708(1)	0.059(1)	0.053(1)	0.0409(9)	0.0295(9)	–0.0078(8)	0.0065(8)
O(4)	2*i*	0.9954(2)	0.4225(2)	0.6057(2)	0.036(1)	0.081(1)	0.080(1)	0.030(1)	0.0240(9)	0.049(1)
O(4W)	2*i*	0.8778(3)	0.2522(2)	0.8937(2)	0.042(1)	0.052(1)	0.050(1)	0.0141(9)	0.0022(8)	0.0210(9)

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