Crystal structure of hexaimidazolenickel(II) 4,4′-biphenyldisulfonate $[Ni(C_3H_4N_2)_6][C_{12}H_8S_2O_6]$

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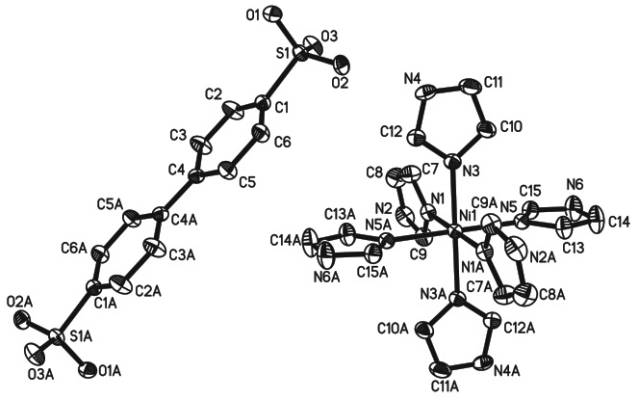
Received April 4, 2011, accepted and available on-line August 25, 2011; CCDC no. 1267/3499



Abstract

$C_{30}H_{32}N_{12}NiO_6S_2$, triclinic, $P\bar{1}$ (no. 2), a = 8.829(3) Å, b = 9.303(3) Å, c = 11.601(4) Å, α = 103.129(5)°, β = 92.989(5)°, γ = 108.096(5)°, V = 874.3 Å^3, Z = 1, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.082, T = 273 K.

Source of material

Disodium 4,4′-biphenyldisulfonate (0.34 g, 1 mmol) and imidazole (0.41 g, 6 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 75 % yield (based on Ni) after five days.

Experimental details

All H atoms were positioned geometrically and treated as riding, with d(C—H) = 0.93 Å, d(N—H) = 0.86 Å, and with U_{iso}(H) = 1.2 U_{eq}(CH or NH).

Discussion

The design and synthesis of mixed inorganic-organic hybrid materials has been attracting great interest owing to their potential application in the chemical storage, separation and catalysis [1,2]. Generally, some organic acidato anions such as carbonates and phosphonates have been used as an assembler to generate the inorganic-organic lamellar structures which possess potential functionality of host-guest interaction. The SO_3^- group, being a structural analogue of PO_3^- group, may be used to create the structural analogs of metal phosphonates. However, the weak coordination nature of SO_3^- makes its coordination mode very flexible and sensitive to the chemical environment [3]. Perusal of recent literature shows that the coordination behavior of arenesulfonates with transition metals can be tailored in the pre-sence of amino ligands [4-6]. Because the use of different amines alters the size and nature of the organic region, and the chemical environment of metal ions, the SO_3^- group can compete with water molecules and coordinate to metal ions. On the other hand, there has been great interest in the ability to assemble metal complexes through hydrogen bonds in order to create hybrid inorganic-organic materials [7]. Nevertheless, the control of hydrogen-bonding interactions to direct the formation of an ordered solid remains a challenging subject, especially in the presence of other strong hydrogen bonding candidates as sulfonate.

In the title crystal structure, the asymmetric unit consists of a Ni(II) ion, three imidazole molecules, and half of a 4,4′-biphenyldisulfonate anion. It is noted that both the 4,4′-biphenyldisulfonate anion and the complex cation possess an inversion center. The Ni(II) centre is coordinated by six imidazole nitrogen atoms with d(Ni—N) ranging from 2.110(2) Å to 2.159(2) Å and ∠N–Ni–N ranging from 88.89(7)° to 180.00(2)°, leading to a slightly distorted octahedral environment. Further analysis of the crystal structure reveals that the title compound adopts the same hybrid inorganic-organic packing pattern as that reported by Cai [4-6]. The most interesting feature is the self-complementary hydrogen bonding pattern, where H bonds play a key role in assembling three-dimensional supramolecular architectures. The title complex adopts a structure in which layers of anions alternate with layers of cations. Each anionic layer contains a single plane of co-facial naphthalene units, and is perpendicular to the (010) plane. There is a chain arrangement along [100] formed by N–H···O hydrogen bonds. The hydrogen-bonded chains are further extended into the 3D network through extensive interchain hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.15 × 0.33 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.35 cm^{-1}
Diffractometer, scan mode:	Bruker Smart 1000 CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4267, 2918
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2544
$N(param)_{refined}$:	232
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	x	y	z	U_{iso}
H(2A)	2*i*	0.0716	0.4982	0.9081	0.058
H(4A)	2*i*	0.1263	1.0347	0.8086	0.056
H(2B)	2*i*	0.1650	0.4779	0.2221	0.065
H(12A)	2*i*	0.3353	0.9454	0.7386	0.048

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(9A)	2*i*	0.4052	0.6950	0.2663	0.055
H(6A)	2*i*	0.2487	1.1455	0.1657	0.077
H(15A)	2*i*	0.2557	0.9540	0.2676	0.052
H(7A)	2*i*	0.1250	0.7661	0.5062	0.062
H(10A)	2*i*	0.2410	1.1950	0.5345	0.066
H(13A)	2*i*	0.5878	1.3486	0.4317	0.062
H(11A)	2*i*	0.0587	1.1890	0.6862	0.073
H(8A)	2*i*	–0.0138	0.5125	0.3671	0.074
H(14A)	2*i*	0.4534	1.3921	0.2596	0.085
H(5A)	2*i*	0.6063	0.7616	1.0528	0.049
H(6B)	2*i*	0.4320	0.8992	1.0413	0.048
H(3A)	2*i*	0.2439	0.3613	0.9275	0.058

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)	1*f*	½	1	½	0.0322(2)	0.0303(2)	0.0235(2)	0.0113(2)	0.0012(2)	0.0024(1)
S(1)	2*i*	0.09736(6)	0.82064(5)	0.97901(4)	0.0334(3)	0.0259(3)	0.0324(3)	0.0114(2)	–0.0021(2)	0.0021(2)
N(1)	2*i*	0.3126(2)	0.7855(2)	0.4074(2)	0.041(1)	0.0339(9)	0.0297(9)	0.0114(8)	–0.0031(8)	0.0033(7)
N(3)	2*i*	0.3349(2)	1.0578(2)	0.6114(2)	0.038(1)	0.0387(9)	0.0299(9)	0.0149(8)	0.0045(8)	0.0040(7)
N(5)	2*i*	0.4360(2)	1.1206(2)	0.3798(1)	0.0368(9)	0.0373(9)	0.0278(9)	0.0147(8)	0.0022(8)	0.0059(7)
C(1)	2*i*	0.2335(2)	0.7134(2)	0.9753(2)	0.034(1)	0.029(1)	0.030(1)	0.0117(9)	0.0032(9)	0.0043(8)
C(2)	2*i*	0.1787(3)	0.5519(2)	0.9395(2)	0.032(1)	0.031(1)	0.070(2)	0.0094(9)	–0.008(1)	–0.005(1)
O(1)	2*i*	0.0410(2)	0.8258(2)	1.0940(1)	0.0383(8)	0.0435(8)	0.0397(8)	0.0170(7)	0.0063(7)	0.0062(7)
O(2)	2*i*	0.1919(2)	0.9744(2)	0.9681(1)	0.0477(9)	0.0300(7)	0.0500(9)	0.0131(7)	0.0031(7)	0.0118(7)
O(3)	2*i*	–0.0293(2)	0.7356(2)	0.8794(1)	0.051(1)	0.0394(8)	0.0452(9)	0.0197(8)	–0.0160(8)	–0.0045(7)
N(4)	2*i*	0.1720(2)	1.0550(2)	0.7477(2)	0.042(1)	0.061(1)	0.035(1)	0.016(1)	0.0141(9)	0.0079(9)
N(2)	2*i*	0.1850(3)	0.5581(2)	0.2820(2)	0.062(1)	0.037(1)	0.048(1)	0.013(1)	–0.015(1)	–0.0085(9)
C(12)	2*i*	0.2899(3)	1.0072(3)	0.7056(2)	0.042(1)	0.043(1)	0.031(1)	0.014(1)	0.004(1)	0.0035(9)
C(9)	2*i*	0.3187(3)	0.6824(3)	0.3099(2)	0.054(1)	0.038(1)	0.038(1)	0.012(1)	–0.002(1)	–0.002(1)
N(6)	2*i*	0.3151(3)	1.1624(3)	0.2281(2)	0.074(2)	0.062(1)	0.050(1)	0.014(1)	–0.025(1)	0.021(1)
C(15)	2*i*	0.3224(3)	1.0579(3)	0.2881(2)	0.046(1)	0.047(1)	0.035(1)	0.013(1)	–0.004(1)	0.010(1)
C(7)	2*i*	0.1654(3)	0.7204(3)	0.4404(2)	0.041(1)	0.052(1)	0.049(2)	0.007(1)	0.003(1)	0.000(1)
C(10)	2*i*	0.2379(3)	1.1432(3)	0.5946(2)	0.064(2)	0.073(2)	0.047(1)	0.043(2)	0.020(1)	0.024(1)
C(13)	2*i*	0.5039(3)	1.2739(3)	0.3771(2)	0.060(2)	0.040(1)	0.050(1)	0.011(1)	–0.011(1)	0.011(1)
C(11)	2*i*	0.1368(3)	1.1408(4)	0.6783(2)	0.060(2)	0.089(2)	0.052(2)	0.047(2)	0.019(1)	0.020(1)
C(8)	2*i*	0.0876(3)	0.5803(3)	0.3638(3)	0.045(2)	0.052(2)	0.069(2)	–0.000(1)	–0.006(1)	0.002(1)
C(14)	2*i*	0.4298(4)	1.2988(3)	0.2825(3)	0.088(2)	0.050(2)	0.069(2)	0.013(2)	–0.021(2)	0.026(1)
C(4)	2*i*	0.4445(2)	0.5446(2)	0.9938(2)	0.030(1)	0.0270(9)	0.032(1)	0.0088(8)	0.0057(9)	0.0034(8)
C(5)	2*i*	0.4980(3)	0.7073(2)	1.0256(2)	0.028(1)	0.028(1)	0.059(2)	0.0045(9)	–0.002(1)	0.008(1)
C(6)	2*i*	0.3935(3)	0.7904(2)	1.0177(2)	0.037(1)	0.023(1)	0.056(1)	0.0066(9)	0.001(1)	0.0072(9)
C(3)	2*i*	0.2833(3)	0.4700(2)	0.9503(2)	0.035(1)	0.023(1)	0.076(2)	0.0084(9)	–0.004(1)	–0.004(1)

Acknowledgment. The authors gratefully acknowledge the financial support of Henan Institute of Science and Technology (grant no. 20070029).

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