Crystal structure of triaqua(1,10-phenanthroline-*N*,*N*′)sulfatonickel(II) hydrate, $Ni(H_2O)_3(C_{12}H_8N_2)(SO_4) \cdot H_2O$

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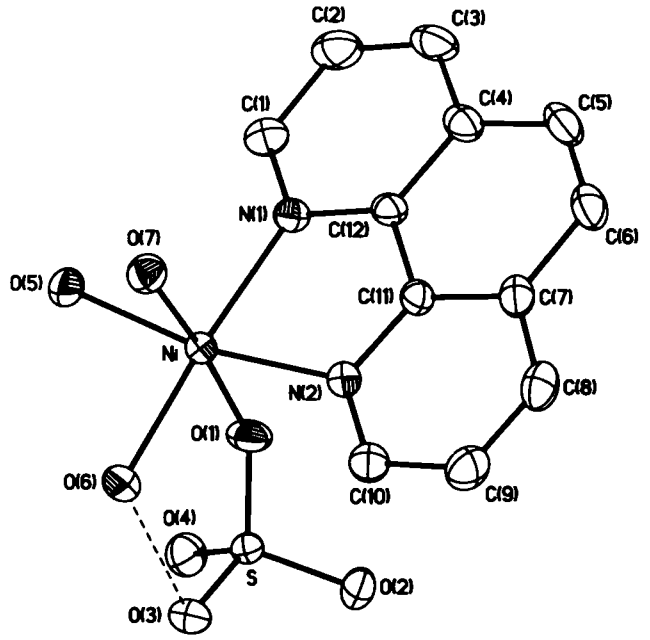

Abstract

$C_{12}H_{16}N_2NiO_8S$, triclinic, $P\bar{1}$ (No. 2), $a = 7.968(1)$ Å, $b = 8.571(1)$ Å, $c = 11.555(1)$ Å, $\alpha = 91.95(1)°$, $\beta = 92.08(1)°$, $\gamma = 104.31(1)°$, $V = 763.4$ Å^3, $Z = 2$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.118$, $T = 293$ K.

Source of material

After 0.66 g (2.03 mmol) $NiSO_4 \cdot 6H_2O$ was completely dissolved in 50.0 ml CH_3OH/H_2O (1:1 v/v) containing 0.50 g (2.50 mmol) 1,10-phenanthroline monohydrate and 0.29 g (2.50 mmol) maleic acid, 1.0 ml (1.0 M) NaOH was dropwise added. The resulting redish solution (pH = 2.50) was allowed to stand at room temperture. Well-shaped blue crystals were grown by slow evaporation for several weeks.

Discussion

The crystal structure of the title compound is built up by the $[Ni(H_2O)_3(phen)(SO_4)]$ complex molecules and the lattice H_2O molecules. The Ni atoms are each surrounded by two N atoms from one phen ligand, four O atoms from three H_2O molecules and one sulfato group to form distorted octahedra with d(Ni—N) = 2.065 Å, 2.075 Å, and d(Ni—O) = 2.053 Å – 2.127 Å. The complex molecule displays a strong intramolecular hydrogen bond between water O(6) and sulfato O(3) atoms with d(O6···O3) = 2.627 Å and ∠O6–H···O3 = 171°. Along the [100] direction, the complex molecules are assembled by the intermolecular π-π stacking interactions between the adjacent phen planes (interplanar distances: 3.25 Å, 3.41 Å) and the intermolecular hydrogen bonds with d(O5···O2^I) = 2.732 Å and ∠O5–H···O2^I = 174° (I: 1+x, y, z) into 1D double chains with the hydrophilic coordinating groups orientated outwards to favor formation of interchain hydrogen bonds (d(O···O) = 2.750 Å, 2.762 Å, and the corresponding ∠O–H···O = 167°, 176°). The interchain hydrogen bonding interactions force the double chains to be further assembled to 2D supramolecular layers parallel to $(01\bar{1})$. The lattice H_2O molecules sandwiched between the 2D layers accept hydrogen atoms from the coordinating water molecules and donate hydrogen atoms to the non-coordinating O atoms of the sulfato groups to form hydrogen bonds (d(O···O) = 2.730 Å – 2.803 Å; ∠O–H···O = 158° – 172°). Such hydrogen bonding interactions are found to be responsible for the suparmolecular assembly of the 2D layers. Owing to the side and coordination effect, the sulfato group with d(S—O) = 1.458 Å – 1.500 Å exhibits signicant deviation from an ideal T_d symmetry.

Table 1. Data collection and handling.

Crystal:	blue plate, size 0.222 × 0.444 × 0.511 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.54 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4247, 3499
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3358
$N(param)_{refined}$:	283
Programs:	SHELXS-97 [1], SHELXL-97 [2]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.348(4)	0.062(4)	0.886(3)	0.032(7)
H(2)	2*i*	0.416(5)	0.077(5)	1.082(4)	0.06(1)
H(3)	2*i*	0.393(5)	0.319(4)	1.185(3)	0.040(8)
H(5)	2*i*	0.315(5)	0.583(4)	1.186(3)	0.044(9)
H(6)	2*i*	0.191(4)	0.763(4)	1.086(3)	0.033(8)
H(8)	2*i*	0.057(4)	0.837(4)	0.894(3)	0.029(7)
H(9)	2*i*	-0.011(5)	0.772(5)	0.710(4)	0.06(1)
H(10)	2*i*	0.025(4)	0.538(4)	0.620(3)	0.030(7)
HA(O5)	2*i*	0.423(5)	0.085(4)	0.674(3)	0.039(8)
HB(O5)	2*i*	0.270(4)	0.015(4)	0.605(3)	0.033(8)
HA(O6)	2*i*	0.021(6)	0.229(5)	0.523(4)	0.06(1)
HB(O6)	2*i*	0.179(6)	0.241(5)	0.487(4)	0.06(1)
HA(O7)	2*i*	0.488(5)	0.373(5)	0.615(3)	0.05(1)
HB(O7)	2*i*	0.426(4)	0.503(4)	0.626(3)	0.040(8)
HA(O8)	2*i*	0.513(6)	0.764(5)	0.562(3)	0.05(1)
HB(O8)	2*i*	0.365(6)	0.741(5)	0.528(4)	0.06(1)

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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	2*i*	0.19817(3)	0.26252(3)	0.69618(2)	0.0197(2)	0.0235(2)	0.0176(2)	0.0075(1)	–0.0009(1)	–0.0024(1)
N(1)	2*i*	0.2680(2)	0.2598(2)	0.8698(2)	0.0208(8)	0.0271(9)	0.0211(8)	0.0060(7)	–0.0005(6)	0.0002(7)
N(2)	2*i*	0.1316(2)	0.4689(2)	0.7567(2)	0.0242(8)	0.0260(8)	0.0211(8)	0.0093(7)	0.0002(6)	–0.0018(6)
C(1)	2*i*	0.3276(3)	0.1501(3)	0.9257(2)	0.029(1)	0.031(1)	0.031(1)	0.0100(9)	–0.0017(9)	0.0045(9)
C(2)	2*i*	0.3717(3)	0.1662(3)	1.0452(2)	0.035(1)	0.047(1)	0.033(1)	0.014(1)	–0.001(1)	0.013(1)
C(3)	2*i*	0.3593(3)	0.3018(4)	1.1064(2)	0.030(1)	0.056(2)	0.020(1)	0.008(1)	–0.0019(8)	0.0069(9)
C(4)	2*i*	0.3001(3)	0.4218(3)	1.0497(2)	0.0209(9)	0.038(1)	0.021(1)	0.0012(8)	0.0011(7)	–0.0010(8)
C(5)	2*i*	0.2795(3)	0.5670(3)	1.1068(2)	0.032(1)	0.046(1)	0.020(1)	0.002(1)	0.0004(9)	–0.0101(9)
C(6)	2*i*	0.2114(3)	0.6727(3)	1.0491(2)	0.030(1)	0.035(1)	0.029(1)	0.0018(9)	0.0035(9)	–0.0117(9)
C(7)	2*i*	0.1595(3)	0.6453(3)	0.9288(2)	0.023(1)	0.027(1)	0.029(1)	0.0024(8)	0.0044(8)	–0.0055(8)
C(8)	2*i*	0.0841(3)	0.7494(3)	0.8644(2)	0.034(1)	0.025(1)	0.041(1)	0.0086(9)	0.008(1)	–0.0049(9)
C(9)	2*i*	0.0359(4)	0.7121(3)	0.7511(2)	0.040(1)	0.034(1)	0.039(1)	0.019(1)	0.002(1)	0.005(1)
C(10)	2*i*	0.0612(3)	0.5701(3)	0.6990(2)	0.034(1)	0.035(1)	0.026(1)	0.0150(9)	–0.0001(9)	0.0019(9)
C(11)	2*i*	0.1800(3)	0.5058(2)	0.8697(2)	0.0193(9)	0.0261(9)	0.0209(9)	0.0044(7)	0.0018(7)	–0.0023(7)
C(12)	2*i*	0.2520(3)	0.3924(3)	0.9311(2)	0.0172(9)	0.028(1)	0.0200(9)	0.0036(7)	–0.0002(7)	–0.0001(7)
S	2*i*	–0.21968(6)	0.05742(6)	0.65424(4)	0.0179(3)	0.0279(3)	0.0223(3)	0.0080(2)	–0.0021(2)	–0.0057(2)
O(1)	2*i*	–0.0511(2)	0.1087(2)	0.7194(1)	0.0200(7)	0.0412(9)	0.0253(8)	0.0030(6)	–0.0048(6)	0.0023(6)
O(2)	2*i*	–0.3541(2)	0.1093(2)	0.7161(2)	0.0260(8)	0.055(1)	0.0368(9)	0.0176(8)	–0.0001(7)	–0.0167(8)
O(3)	2*i*	–0.2030(2)	0.1291(2)	0.5373(1)	0.0296(8)	0.0357(8)	0.0258(8)	0.0102(7)	–0.0058(6)	–0.0004(6)
O(4)	2*i*	–0.2675(2)	–0.1194(2)	0.6363(2)	0.0339(9)	0.0281(8)	0.0358(9)	0.0076(7)	0.0000(7)	–0.0047(6)
O(5)	2*i*	0.3017(2)	0.0701(2)	0.6591(2)	0.0270(8)	0.0299(8)	0.0321(9)	0.0122(6)	–0.0023(7)	–0.0087(7)
O(6)	2*i*	0.1245(2)	0.2830(2)	0.5264(1)	0.0275(9)	0.0370(9)	0.0200(7)	0.0096(7)	–0.0009(6)	–0.0013(6)
O(7)	2*i*	0.4378(2)	0.4168(2)	0.6582(2)	0.0255(8)	0.0289(8)	0.0290(8)	0.0064(6)	0.0021(6)	0.0011(6)
O(8)	2*i*	0.4276(3)	0.6929(2)	0.5409(2)	0.0300(9)	0.0286(9)	0.053(1)	0.0096(8)	–0.0005(8)	0.0030(8)

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