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

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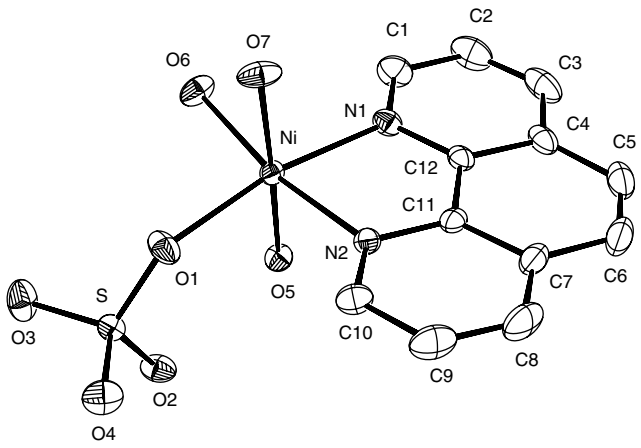
Received November 11, 2003, accepted and available on-line November 24, 2003; CCDC-No. 1267/1168



Abstract

$C_{12}H_{14}N_2NiO_7S$, monoclinic, $P12_1/c1$ (No. 14), a = 11.8362(9) Å, b = 9.9634(8) Å, c = 13.560(1) Å, β = 112.852(1)°, V = 1473.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.042, $wR_{ref}(F^2)$ = 0.106, T = 293 K.

Source of material

The title complex was synthesized by typical mixed solution method. $NiSO_4 \cdot 6H_2O$ (0.0789 g, 0.3 mmol), 4-cyanobenzoic acid (0.0882 g, 0.6 mmol) and 1,10-phenanthroline (0.0594 g, 0.3 mmol) were dissolved in 20 ml of water an methanol in a 1:1 volume ration. After three weeks at room temperature, blue crystals of the title compound were obtained by filtration.

Experimental details

All H atoms were found in the difference Fourier map and refined.

Discussion

Complexes with the formula of $[M(phen)(H_2O)_n(SO_4)] \cdot mH_2O$ (phen = 1,10-phenanthroline) have been extensively studied due to interest in both structural and biological viewpoints [1-3]. For example, at least four complexes of manganese, *fac*-$[Mn(phen)(H_2O)_3(SO_4)]$ [4], $[Mn(phen)(H_2O)_4](SO_4) \cdot 2H_2O$ [4-6], *trans*-$[Mn(phen)(H_2O)_3(SO_4)]$ [7], and $[Mn(phen)(H_2O)_2(SO_4)](H_2O)$ [8] have been reported and these complexes display interesting structural diversities. Recently, the nickel complex of $[Ni(phen)(H_2O)_3(SO_4)](H_2O)$ was synthesized [9]. Here, we present the new isomeric complex, $[Ni(phen)(H_2O)_3(SO_4)]$.

The asymmetric unit is composed of the neutral $[Ni(phen)(H_2O)_3(SO_4)]$ complex unit. The coordinated environment of the nickel(II) ions involves the six coordinate NiN_2O_4 chromophore, with tetragonaly elongated octahedral environment. The basal plane with four roughly equal short bonds involves one nitrogen atom from one phen ligand [d(Ni—N2) = 2.072(2) Å] and three oxygen atoms from three water molecules. Four atoms in the basal plane are reasonably planar (rmsd = 0.0687 Å). Two oxygen atoms from one water molecule and the sulfato ligand occupy axial positions above and below the basal plane, with Ni—O distances of 2.083 Å and 2.089 Å. The planes of N1/O1/O5/O7 and N1/O1/N2/O6 are nearly planar with the rmsd of 0.1139 Å and 0.1087 Å, respectively. The axial O1–Ni–N1 angle is 169.58(9)°. The S—O distance of the coordinated O atom is similar to those of the uncoordinated oxygen atoms, except that of the S—O2 (1.488 Å). However, the configuration of the sulfate anion is quite regular in spite of its coordination. Both the bond distances and angles for sulfato ligand are not too different and are within the range for ionic sulfate [3]. The six O–S–O angles are nearly equal. Small deviations may be due to the hydrogen-bonding network involving sulfate oxygen atoms. The structure of the title compound is comparable to the reported structural isomeric complex of $[Ni(phen)(H_2O)_3(SO_4)]$, in which involves the basal plane of two nitrogen atoms from one phen ligand and two oxygen atoms from two water molecules, and one water molecule and the sulfato ligand occupy the apical axis with significantly longer distances of Ni–O than those of the title complex.

Table 1. Data collection and handling.

Crystal:	blue plate, size 0.218 × 0.403 × 0.537 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.97 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8608, 3327
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2868
$N(param)_{refined}$:	265
Programs:	SHELXL-97 [10], ORTEP-3 [11], WinGX [12]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.190(3)	0.614(3)	1.135(3)	0.056(9)
H(2)	4*e*	–0.017(3)	0.598(4)	1.107(3)	0.07(1)
H(3)	4*e*	–0.150(2)	0.740(3)	0.987(3)	0.06(1)
H(4)	4*e*	–0.194(3)	0.907(3)	0.857(3)	0.07(1)
H(5)	4*e*	–0.110(3)	1.079(3)	0.761(3)	0.07(1)
H(6)	4*e*	0.071(3)	1.167(3)	0.734(2)	0.07(1)
H(7)	4*e*	0.267(3)	1.157(4)	0.769(3)	0.07(1)
	4*e*	0.391(2)	0.990(3)	0.883(2)	0.037(7)
H(9)	4*e*	0.302(3)	0.523(2)	0.944(3)	0.06(1)
H(10)	4*e*	0.348(3)	0.600(4)	0.888(3)	0.08(1)
H(11)	4*e*	0.456(3)	0.558(4)	1.142(3)	0.06(1)
H(12)	4*e*	0.480(3)	0.654(4)	1.214(2)	0.07(1)
H(13)	4*e*	0.420(3)	0.893(3)	1.203(2)	0.051(9)
H(14)	4*e*	0.417(3)	0.991(2)	1.132(3)	0.07(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	4*e*	0.35201(2)	0.76169(3)	1.02567(2)	0.0258(2)	0.0210(2)	0.0231(2)	0.0026(1)	0.0082(1)	0.0002(1)
S	4*e*	0.56735(5)	0.71861(6)	0.92750(5)	0.0298(3)	0.0202(3)	0.0289(3)	0.0009(2)	0.0143(2)	0.0010(2)
O(1)	4*e*	0.5095(2)	0.7819(2)	0.9935(2)	0.0332(9)	0.046(1)	0.048(1)	–0.0090(8)	0.0206(9)	–0.0243(9)
O(2)	4*e*	0.4797(2)	0.6220(2)	0.8528(1)	0.048(1)	0.036(1)	0.036(1)	–0.0113(8)	0.0213(9)	–0.0127(8)
O(3)	4*e*	0.6765(2)	0.6462(2)	0.9948(2)	0.039(1)	0.038(1)	0.069(1)	0.0115(8)	0.022(1)	0.022(1)
O(4)	4*e*	0.5995(2)	0.8203(2)	0.8647(2)	0.059(1)	0.027(1)	0.044(1)	–0.0020(9)	0.0225(9)	0.0093(9)
O(5)	4*e*	0.2965(2)	0.6033(2)	0.9185(1)	0.0327(9)	0.0278(9)	0.0312(9)	–0.0028(7)	0.0097(8)	–0.0034(8)
O(6)	4*e*	0.4264(2)	0.6306(2)	1.1519(2)	0.056(1)	0.024(1)	0.030(1)	0.0098(9)	0.0029(9)	0.0002(8)
O(7)	4*e*	0.4116(2)	0.9091(2)	1.1389(2)	0.075(1)	0.0220(9)	0.025(1)	–0.0015(9)	0.0184(9)	–0.0016(8)
N(1)	4*e*	0.1771(2)	0.7489(2)	1.0284(2)	0.036(1)	0.028(1)	0.035(1)	–0.0005(8)	0.020(1)	0.0013(8)
N(2)	4*e*	0.2618(2)	0.9084(2)	0.9146(2)	0.0279(9)	0.026(1)	0.0245(9)	0.0015(8)	0.0104(8)	0.0005(8)
C(1)	4*e*	0.1362(3)	0.6658(3)	1.0830(2)	0.054(2)	0.045(2)	0.049(2)	–0.005(1)	0.030(2)	0.008(1)
C(2)	4*e*	0.0117(3)	0.6600(4)	1.0676(3)	0.066(2)	0.059(2)	0.070(2)	–0.018(2)	0.048(2)	–0.004(2)
C(3)	4*e*	–0.0692(3)	0.7423(3)	0.9967(3)	0.043(2)	0.069(2)	0.073(2)	–0.018(2)	0.038(2)	–0.028(2)
C(4)	4*e*	–0.0295(2)	0.8327(3)	0.9381(2)	0.029(1)	0.049(2)	0.041(1)	–0.005(1)	0.015(1)	–0.022(1)
C(5)	4*e*	–0.1074(2)	0.9257(4)	0.8614(3)	0.028(1)	0.067(2)	0.052(2)	0.009(1)	0.006(1)	–0.023(2)
C(6)	4*e*	–0.0640(3)	1.0106(4)	0.8095(3)	0.046(2)	0.062(2)	0.041(2)	0.025(2)	–0.003(1)	–0.006(2)
C(7)	4*e*	0.0632(2)	1.0127(3)	0.8268(2)	0.043(1)	0.039(2)	0.027(1)	0.013(1)	0.003(1)	–0.002(1)
C(8)	4*e*	0.1176(3)	1.1025(3)	0.7782(2)	0.076(2)	0.040(2)	0.038(2)	0.019(2)	0.011(2)	0.015(1)
C(9)	4*e*	0.2375(3)	1.0948(3)	0.7980(2)	0.077(2)	0.039(2)	0.040(2)	–0.002(2)	0.025(2)	0.013(1)
C(10)	4*e*	0.3086(3)	0.9952(3)	0.8668(2)	0.045(2)	0.033(1)	0.033(1)	–0.005(1)	0.016(1)	0.002(1)
C(11)	4*e*	0.1418(2)	0.9190(2)	0.8976(2)	0.033(1)	0.027(1)	0.021(1)	0.0043(9)	0.0069(9)	–0.0043(9)
C(12)	4*e*	0.0958(2)	0.8302(3)	0.9566(2)	0.029(1)	0.031(1)	0.029(1)	–0.0005(9)	0.0125(9)	–0.009(1)

Acknowledgment. The project was supported by the National Natural Science Foundation of China (grant No. 50073019).

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