Crystal structure of 4-bromo-2-[(2-propylaminoethylimino)methyl]-phenolatonickel(II) thiocyanate, [Ni($C_{12}H_{16}BrN_2O$)][NCS]

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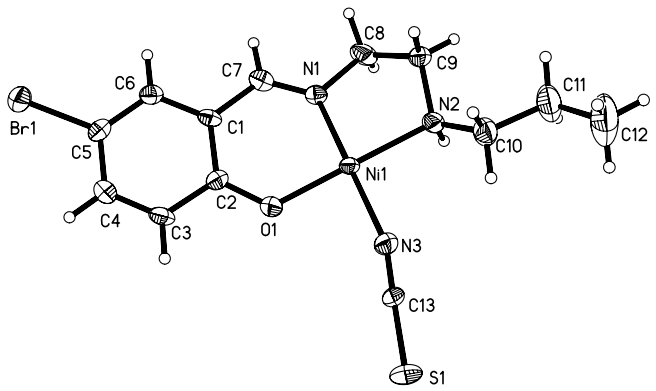

Abstract

$C_{13}H_{16}BrN_3NiOS$, monoclinic, $P12_1/n1$ (no. 14), a = 6.005(2) Å, b = 21.154(3) Å, c = 12.346(2) Å, β = 94.661(4)°, V = 1563.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.066, $wR_{ref}(F^2)$ = 0.152, T = 298 K.

Source of material

5-Bromo-2-hydroxybenzaldehyde (20.1 mg, 0.1 mmol), *N*-propyl-1,2-diaminoethane (12.2 mg, 0.1 mmol), ammonium thiocyanate (7.6 mg, 0.1 mmol), and $Ni(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol) were dissolved in a methanol solution (20 ml). The mixture was stirred for 30 min at room temperature to give a clear red solution. Red block-shaped crystals, suitable for X-ray structure determination were formed by slow evaporation of the solvent on air for three days. Elemental analysis — found: C, 38.7 %; H, 4.1 %; N, 10.7 %; calculated for $C_{13}H_{16}BrN_3NiOS$: C, 38.9 %; H, 4.0 %; N, 10.5 %. IR data are available in CIF.

Experimental details

H2 was located from a difference Fourier map and refined isotropically, with d(N—H) restrained to 0.90 Å. Other H atoms were placed in calculated positions and constrained to ride on their parent atoms, with d(C—H) = 0.93 - 0.97 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) and 1.5 U_{eq}(C12).

Discussion

Nickel complexes with Schiff base ligands have received much attention in many fields. Some of the complexes have been found to have pharmacological and catalytic properties [1,2], as well as the magnetic properties [3-5]. Thiocyanate anion is a versatile ligand, which readily coordinates the metal atoms either in the bridging or in the terminal mode [6-8].

The title compound is a Schiff base being thiocyanato-coordinated mononuclear nickel(II) complex. The Ni atom is in a square planar geometry, and is four-coordinated by one O and two N atoms of one Schiff base ligand and by one N atom of a thiocyanate ligand. The significant distortion of the octahedron is revealed by the bond angles subtended at the nickel atom, ranging from 85.0(2) to 94.7(2)°. The bond angle of N1–Ni1–N2 deviates from the value by 5.0(2)°, which is due to the strain created by the five-membered chelate ring Ni1–N1–C8–C9–N2. The Ni—O and Ni—N bond lengths are comparable with the corresponding values observed in other Schiff base nickel(II) complexes [6-8]. The Ni atom is located at 0.092(2) Å from the plane defined by the four donor atoms. The conformation of the chain containing azomethine N atom, two C atoms of the connecting 1,2-diaminoethane, amine N atom and the three propyl C atoms in the complex is toothed. The thiocyanate ligand is nearly linear and shows bent coordination mode with the nickel atom (the N3–C13–S1 and Ni1–N3–C13 angles are 178.5(7)° and 162.9(6)°, respectively).

Table 1. Data collection and handling.

Crystal:	red block, size 0.17 × 0.18 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	39.28 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11221, 3391
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1906
$N(param)_{refined}$:	185
Programs:	SHELXS-97 [9], SHELXL-97 [10], SHELXTL [11]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4*e*	0.8717	0.0244	0.7449	0.052
H(4)	4*e*	0.6503	–0.0577	0.7813	0.058
H(6)	4*e*	0.1527	0.0123	0.5826	0.049
H(7)	4*e*	0.2046	0.1022	0.4734	0.047
H(8A)	4*e*	0.1849	0.1923	0.3807	0.064
H(8B)	4*e*	0.4028	0.1848	0.3193	0.064
H(9A)	4*e*	0.3728	0.2907	0.3457	0.051
H(9B)	4*e*	0.3144	0.2816	0.4666	0.051
H(10A)	4*e*	0.8672	0.3315	0.5158	0.074
H(10B)	4*e*	0.6273	0.3412	0.5538	0.074
H(11A)	4*e*	0.7380	0.3764	0.3441	0.104
H(11B)	4*e*	0.5113	0.3919	0.3929	0.104
H(12A)	4*e*	0.6967	0.4556	0.5189	0.208
H(12B)	4*e*	0.7311	0.4783	0.4005	0.208
H(12C)	4*e*	0.9212	0.4409	0.4675	0.208
H(2)	4*e*	0.73(1)	0.261(4)	0.392(4)	0.080

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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(1)	4*e*	0.7179(1)	0.19360(4)	0.54625(7)	0.0227(5)	0.0381(5)	0.0316(5)	0.0002(4)	–0.0022(4)	0.0046(4)
Br(1)	4*e*	0.1963(1)	–0.09918(4)	0.72470(7)	0.0504(5)	0.0488(5)	0.0750(7)	–0.0075(4)	0.0077(5)	0.0091(4)
S(1)	4*e*	1.4285(3)	0.2410(1)	0.7125(2)	0.030(1)	0.072(1)	0.041(1)	0.0006(9)	–0.0039(9)	–0.015(1)
O(1)	4*e*	0.7913(8)	0.1173(2)	0.6197(4)	0.036(3)	0.045(3)	0.066(4)	–0.002(2)	–0.009(3)	0.014(3)
N(1)	4*e*	0.4463(9)	0.1577(3)	0.4771(4)	0.032(3)	0.040(3)	0.025(3)	0.000(3)	–0.002(3)	–0.003(3)
N(2)	4*e*	0.644(1)	0.2698(3)	0.4479(5)	0.035(4)	0.050(4)	0.039(4)	0.002(3)	0.000(3)	0.013(3)
N(3)	4*e*	1.003(1)	0.2279(3)	0.6083(5)	0.037(4)	0.051(4)	0.048(4)	–0.007(3)	–0.004(3)	0.007(3)
C(1)	4*e*	0.432(1)	0.0658(3)	0.5889(5)	0.030(4)	0.036(4)	0.034(4)	0.008(3)	–0.008(3)	–0.007(3)
C(2)	4*e*	0.653(1)	0.0712(3)	0.6382(6)	0.030(4)	0.039(4)	0.041(4)	–0.003(3)	0.003(3)	–0.002(3)
C(3)	4*e*	0.727(1)	0.0225(3)	0.7116(6)	0.032(4)	0.045(4)	0.051(5)	0.009(3)	–0.011(4)	0.000(4)
C(4)	4*e*	0.595(1)	–0.0261(3)	0.7341(6)	0.048(5)	0.046(5)	0.051(5)	0.005(4)	–0.001(4)	0.011(4)
C(5)	4*e*	0.377(1)	–0.0297(3)	0.6880(6)	0.035(4)	0.042(4)	0.047(5)	–0.007(3)	0.011(4)	–0.006(3)
C(6)	4*e*	0.298(1)	0.0154(3)	0.6150(6)	0.032(4)	0.043(4)	0.047(5)	0.004(3)	0.002(4)	–0.002(4)
C(7)	4*e*	0.346(1)	0.1100(3)	0.5069(6)	0.043(4)	0.037(4)	0.036(4)	0.006(3)	–0.007(4)	–0.012(3)
C(8)	4*e*	0.346(1)	0.1976(3)	0.3873(6)	0.049(5)	0.059(5)	0.047(5)	0.009(4)	–0.018(4)	0.003(4)
C(9)	4*e*	0.404(1)	0.2655(3)	0.4108(6)	0.033(4)	0.049(4)	0.045(5)	0.000(3)	0.000(4)	0.007(4)
C(10)	4*e*	0.710(2)	0.3326(3)	0.4911(7)	0.064(6)	0.054(5)	0.065(6)	–0.009(4)	–0.013(5)	0.019(4)
C(11)	4*e*	0.671(2)	0.3868(4)	0.4106(8)	0.114(9)	0.053(6)	0.089(7)	–0.012(6)	–0.016(7)	0.020(5)
C(12)	4*e*	0.762(2)	0.4452(5)	0.453(1)	0.21(2)	0.081(8)	0.12(1)	–0.052(9)	–0.05(1)	0.038(7)
C(13)	4*e*	1.178(1)	0.2325(3)	0.6518(5)	0.025(4)	0.038(4)	0.036(4)	–0.001(3)	0.006(3)	–0.001(3)

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