Crystal structure of methanol[4-bromo-*N*-(2-pyridylmethyl)salicylal-diminato-*N,N',O*]nickel(II) perchlorate, $[\text{Ni}(\text{CH}_3\text{OH})(\text{C}_{14}\text{H}_{14}\text{BrN}_2\text{O}_2)]\text{ClO}_4$

S.-J. Peng*, D.-W. Yang, Z.-L. Xiao, D.-X. Wu and Z. Cao

Changsha University of Science and Technology, Department of Chemistry and Environmental Engineering, Changsha, 410076 P. R. China

Received November 25, 2005, accepted and available on-line December 14, 2005; CCDC no. 1267/1687

Abstract

$\text{C}_{14}\text{H}_{14}\text{BrClN}_2\text{NiO}_6$, monoclinic, $P12_1/n1$ (no. 14), $a = 7.204(1) \text{ \AA}$, $b = 19.110(2) \text{ \AA}$, $c = 12.704(2) \text{ \AA}$, $\beta = 95.897(2)^\circ$, $V = 1739.7 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.043$, $wR_{\text{ref}}(F^2) = 0.109$, $T = 298 \text{ K}$.

Source of material

All the chemicals used were of AR grade. 5-Bromosalicylaldehyde (40.2 mg, 0.2 mmol) and 2-aminomethylpyridine (21.6 mg, 0.2 mmol) were refluxed in 10 ml methanol for 30 min. To the above solution was added $\text{Ni}(\text{ClO}_4)_2 \cdot 7\text{H}_2\text{O}$ (76.8 mg, 0.2 mmol) in 10 ml methanol. The mixture was refluxed for 1 h. The mixture was filtered after cooling to room temperature. After keeping the filtrate in air for 21 d, green needle crystals were formed.

Experimental details

Atom H6 was located in a difference Fourier map and refined isotropically, with the O–H distance restrained to $0.84(1) \text{ \AA}$. All other H atoms were positioned geometrically and constrained as riding atoms, with C–H distances of $0.93 \text{ \AA}$ – $0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H})$ set to $1.2 U_{\text{eq}}(\text{C})$ of the parent atom. The O atoms of the perchlorate anion are disordered over two distinct sites, with occupancies of $0.44(2)$ and 0.56 , respectively.

Discussion

Nickel compounds with Schiff bases have received much attention in recent years [1]. Some of the compounds have been found

to have pharmacological and catalytic properties [2,3]. In order to develop further the coordination chemistry of such nickel compounds, we have synthesized a nickel compound based on the Schiff base ligand 4-bromo-2-(pyridinylmethylaminomethyl)-phenol. The analysis of the molecular structure revealed the cation as a mononuclear nickel complex, which is structurally similar to the zinc(II) complex reported earlier [4]. The environment around the central nickel atom is approximately square planar (r.m.s. deviation of $0.037(2) \text{ \AA}$). Three of the coordination sites are occupied by the three donor atoms of the Schiff base ligand and the fourth donor is an oxygen atom of methanol. The Schiff base ligand is nearly coplanar with an average deviation of $0.162(2) \text{ \AA}$. The Ni–N_{pyridine} distance ($1.989(2) \text{ \AA}$) is appreciably longer than that for Ni–N_{imine} ($1.937(3) \text{ \AA}$), because of the steric requirement of the rigid Schiff base ligand.

Table 1. Data collection and handling.

Crystal:	green needle, size $0.08 \times 0.10 \times 0.23 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	35.99 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	14792, 3971
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2750
$N(\text{param})_{\text{refined}}$:	267
Program:	SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(6)	4e	0.549(4)	0.023(2)	0.602(4)	0.080
H(2)	4e	0.6537	−0.0472	0.2591	0.075
H(3)	4e	0.7207	−0.0427	0.0863	0.079
H(5)	4e	0.7403	0.1648	0.0978	0.068
H(7)	4e	0.6973	0.2275	0.2499	0.064
H(8A)	4e	0.5540	0.2931	0.4029	0.079
H(8B)	4e	0.7729	0.2914	0.4102	0.079
H(10)	4e	0.7043	0.3682	0.5796	0.086
H(11)	4e	0.7079	0.3577	0.7613	0.098
H(12)	4e	0.6785	0.2484	0.8347	0.086
H(13)	4e	0.6512	0.1523	0.7275	0.072
H(14A)	4e	0.8652	−0.0103	0.5881	0.132
H(14B)	4e	0.7867	−0.0193	0.6979	0.132
H(14C)	4e	0.9032	0.0473	0.6755	0.132

* Correspondence author (e-mail: sanjunpeng@163.com)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ni(1)	4e		0.63886(6)	0.12252(2)	0.49012(3)	0.0463(3)	0.0328(2)	0.0371(2)	−0.0047(2)	0.0083(2)	−0.0012(2)
Br(1)	4e		0.79545(8)	0.06399(3)	−0.06609(4)	0.1116(5)	0.1211(5)	0.0438(3)	−0.0131(3)	0.0247(3)	0.0008(3)
Cl(1)	4e		0.1528(1)	0.15850(5)	0.54371(8)	0.0561(6)	0.0550(6)	0.0616(6)	0.0002(5)	0.0110(5)	−0.0034(5)
O(1)	4e		0.6139(3)	0.0511(1)	0.3859(2)	0.069(2)	0.041(1)	0.042(1)	−0.013(1)	0.016(1)	−0.002(1)
O(2)	4e	0.44(2)	0.308(1)	0.1107(5)	0.535(1)	0.044(4)	0.067(6)	0.118(9)	0.008(3)	0.006(5)	0.000(5)
O(3)	4e	0.44	0.223(2)	0.2260(4)	0.5195(7)	0.117(9)	0.054(4)	0.090(5)	−0.002(5)	0.001(5)	0.008(4)
O(4)	4e	0.44	−0.005(2)	0.1348(9)	0.482(1)	0.057(6)	0.14(1)	0.064(7)	0.026(6)	−0.020(5)	−0.014(7)
O(5)	4e	0.44	0.124(2)	0.1596(8)	0.6533(6)	0.10(1)	0.079(7)	0.052(5)	0.008(7)	−0.002(4)	−0.011(4)
O(2')	4e	0.56	0.2943(9)	0.1389(6)	0.4800(7)	0.042(3)	0.118(7)	0.085(6)	0.000(4)	0.022(3)	−0.014(5)
O(4')	4e	0.56	−0.003(1)	0.1130(6)	0.513(1)	0.047(5)	0.072(5)	0.12(1)	−0.009(4)	0.014(5)	−0.006(5)
O(3')	4e	0.56	0.088(1)	0.2280(3)	0.5126(5)	0.079(6)	0.053(3)	0.086(4)	0.001(3)	0.008(4)	0.008(3)
O(5')	4e	0.56	0.206(2)	0.1536(8)	0.6515(6)	0.12(1)	0.120(7)	0.059(5)	0.040(7)	−0.009(4)	0.011(4)
O(6)	4e		0.6399(4)	0.0505(1)	0.6032(2)	0.062(2)	0.044(2)	0.049(2)	−0.009(1)	0.010(1)	0.005(1)
N(1)	4e		0.6570(4)	0.1966(1)	0.3876(2)	0.053(2)	0.039(2)	0.054(2)	0.003(1)	0.007(2)	0.003(1)
N(2)	4e		0.6601(4)	0.2016(2)	0.5918(2)	0.042(2)	0.045(2)	0.054(2)	−0.001(1)	0.007(1)	−0.007(1)
C(1)	4e		0.6561(5)	0.0570(2)	0.2869(3)	0.045(2)	0.046(2)	0.042(2)	−0.006(2)	0.008(2)	−0.002(2)
C(2)	4e		0.6710(6)	−0.0040(2)	0.2278(3)	0.090(3)	0.050(2)	0.052(2)	−0.010(2)	0.024(2)	−0.003(2)
C(3)	4e		0.7109(6)	−0.0014(2)	0.1241(3)	0.085(3)	0.062(3)	0.053(2)	−0.008(2)	0.024(2)	−0.012(2)
C(4)	4e		0.7361(6)	0.0613(2)	0.0767(3)	0.066(3)	0.082(3)	0.039(2)	−0.005(2)	0.013(2)	0.001(2)
C(5)	4e		0.7234(5)	0.1223(2)	0.1310(3)	0.061(2)	0.061(2)	0.050(2)	−0.004(2)	0.010(2)	0.010(2)
C(6)	4e		0.6847(5)	0.1211(2)	0.2373(3)	0.049(2)	0.049(2)	0.044(2)	−0.002(2)	0.010(2)	0.008(2)
C(7)	4e		0.6809(5)	0.1876(2)	0.2900(3)	0.061(2)	0.043(2)	0.057(2)	−0.002(2)	0.009(2)	0.011(2)
C(8)	4e		0.6641(7)	0.2673(2)	0.4310(3)	0.089(3)	0.036(2)	0.072(3)	0.003(2)	0.004(2)	0.002(2)
C(9)	4e		0.6731(5)	0.2648(2)	0.5488(3)	0.044(2)	0.043(2)	0.071(3)	0.002(2)	0.005(2)	−0.007(2)
C(10)	4e		0.6928(6)	0.3245(2)	0.6106(4)	0.080(3)	0.046(2)	0.088(3)	−0.001(2)	0.002(3)	−0.013(2)
C(11)	4e		0.6951(7)	0.3182(2)	0.7183(4)	0.088(4)	0.063(3)	0.090(4)	0.004(3)	−0.004(3)	−0.032(3)
C(12)	4e		0.6785(6)	0.2534(2)	0.7619(3)	0.085(3)	0.071(3)	0.058(3)	0.002(2)	0.003(2)	−0.024(2)
C(13)	4e		0.6618(6)	0.1963(2)	0.6975(3)	0.066(3)	0.063(3)	0.051(2)	−0.001(2)	0.006(2)	−0.013(2)
C(14)	4e		0.8142(7)	0.0138(3)	0.6449(4)	0.111(4)	0.073(3)	0.080(3)	−0.018(3)	0.013(3)	−0.002(3)

Acknowledgment. This work was supported by the Natural Science Foundation of Changsha University of Science and Technology, P. R. China (project no. 1004084).

References

- Marganian, C. A.; Vazir, H.; Baidya, N.; Olmstead, M. M.; Mascharak, P. K.: Toward Functional Models of the Nickel Sites in [FeNi] and [FeNiSe] Hydrogenases: Syntheses, Structures, and Reactivities of Nickel(II) Complexes Containing [NiN₃S₂] and [NiN₃Se₂] Chromophores. *J. Am. Chem. Soc.* **117** (1995) 1584–1594.
- Harrop, T. C.; Olmstead, M. M.; Mascharak, P. K.: Dioxygen activation by a dinuclear nickel thiolate complex: structural characterization of the ligand oxidized product. *Chem. Commun.* (2003) 410–411.
- Brückner, C.; Rettig, S. J.; Dolphin, D.: 2-Pyrrolylthiones as Monoanionic Bidentate N,S-Chelators: Synthesis and Molecular Structure of 2-Pyrrolylthionato Complexes of Nickel(II), Cobalt(III), and Mercury(II). *Inorg. Chem.* **39** (2000) 6100–6106.
- Li, Z.-X.; Zhang, X.-L.: Aqua[2-(pyridin-2-ylmethyliminomethyl)phenolato]zinc(II) nitrate monohydrate. *Acta Crystallogr. E* **60** (2004) m1017–m1019.
- Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 5.0. Siemens Industrial Automation, Analytical Instrumentation, Madison, Wisconsin, USA 1995.