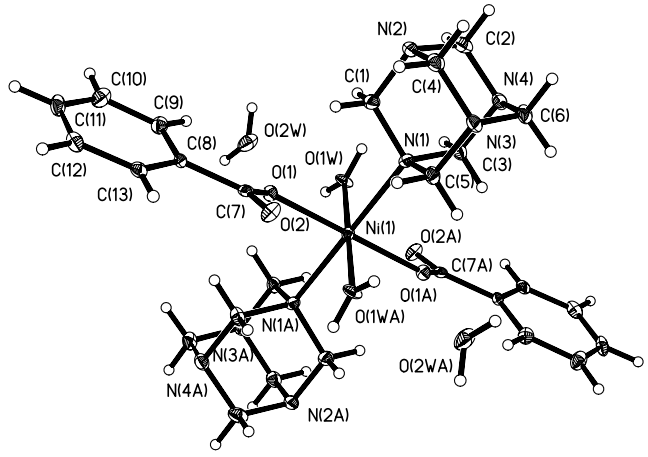
Crystal structure of diaqua-dibenzoato-dihexamethylenetetramine-nickel(II) dihydrate, $Ni(C_6H_{12}N_4)_2(C_7H_5O_2)_2(H_2O)_2 \cdot 2H_2O$

H.-L. Zhu*[I,II], L. Sun[I], S. Yang[I], X.-Y. Qiu[I], S.-C. Shao[I] and J.-L. Ma[I]

[I] Fuyang Normal College, Department of Chemistry, Fuyang, Anhui, 236041 P. R. China
[II] Wuhan University of Science and Engineering, Department of Chemistry, Wuhan, 430073 P. R. China

Received August 22, 2003, accepted and available on-line November 9, 2003; CCDC-No. 1267/1142



Abstract

$C_{26}H_{42}N_8NiO_8$, monoclinic, *C*12/*c*1 (No. 15), $a = 22.784(5)$ Å, $b = 10.886(2)$ Å, $c = 12.208(2)$ Å, $\beta = 95.50(3)°$, $V = 3014.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.074$, $wR_{ref}(F^2) = 0.156$, $T = 293$ K.

Source of material

Nickel benzoate dihydrate (1 mmol, 321 mg) and hexamethylenetetramine (1 mmol, 140 mg) were dissolved in ammonium solution (20 ml). The solution was stirred for ca. 10 min to obtain a clear blue solution. After keeping the solution in air for a week with the ammonium gas escaping, large blue crystals were formed. The product was collected, washed three times with water, and dried in a vacuum desiccator using $CaCl_2$ (yield 74%). All reagents and solvents were used as obtained without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer elemental analyzer. Elemental analysis: found - C, 48.00; H, 6.55; N, 17.31%; calculated for $C_{26}H_{42}N_8NiO_8$ - C, 47.80; H, 6.48; N, 17.15%.

Experimental details

All the other H atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with O—H and C—H distances of 0.85 Å and 0.96 Å, respectively, and the values of U_{iso}(H) were fixed to 0.80 Å^2. The quality of the crystals used for the X-ray investigation was poor, resulting in quite large *R* values. However, any relevant features could not be detected in the final residual electron density map.

Discussion

The title compound is a discrete mononuclear nickel(II) complex. The central nickel(II) atom is six-coordinated by two nitrogen atoms from two hexamethylenetetramine molecules and four oxygen atoms, two of which from two water molecules and the other two from different benzoate anions. The three diagonal angles of the NiO_4N_2 polyhedron are all of 180°, and the other angles around Ni(1) atom are close to 90° (from 85.33(12)° to 94.67(12)°), indicating a slightly distorted octahedral geometry of Ni(1) atom. The Ni—O distance (from the water) is 2.061(3) Å, the Ni—O distance (from the benzoate anion) is 2.038(3) Å, and *d*(Ni—N) = 2.213(4) Å, which are all in the normal ranges compared to the relative chemical bonds in relative nickel(II) complexes. The dihedral angle between the benzene ring and the carboxyl group is 16.8(2)°. In the crystal structure, the molecules are connected by intermolecular hydrogen bonds O(1W)–H(1WB)···O(2W), O(2W)–H(2WA)···O(2), and O(2)–H(2WB)···N(2) to form layers parallel to the *bc* plane.

Table 1. Data collection and handling.

Crystal:	blue prism, size 0.44 × 0.46 × 0.55 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.05 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6642, 2953
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2279
$N(param)_{refined}$:	197
Programs:	SADABS [1], SHELXTL [2]

* Correspondence author (e-mail: hlzhu@wist.edu.cn)

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	8*f*	0.2340	–0.0341	–0.0327	0.08
H(1B)	8*f*	0.1989	0.0239	–0.1353	0.08
H(2A)	8*f*	0.0647	–0.1091	–0.1031	0.08
H(2B)	8*f*	0.0966	–0.0197	–0.1771	0.08
H(3A)	8*f*	0.1248	0.1796	–0.1117	0.08
H(3B)	8*f*	0.1128	0.2202	0.0060	0.08
H(4A)	8*f*	0.1850	–0.1696	0.0850	0.08
H(4B)	8*f*	0.1186	–0.1999	0.0571	0.08
H(5A)	8*f*	0.1661	0.1309	0.1650	0.08
H(5B)	8*f*	0.2137	0.0312	0.1518	0.08
H(6A)	8*f*	0.0633	0.0820	0.1206	0.08
H(6B)	8*f*	0.0462	–0.0481	0.0763	0.08
H(9A)	8*f*	0.3647	0.0059	–0.1677	0.08
H(10A)	8*f*	0.4383	–0.1146	–0.2342	0.08
H(11A)	8*f*	0.5095	–0.2088	–0.1103	0.08
H(12A)	8*f*	0.5039	–0.1913	0.0788	0.08
H(13A)	8*f*	0.4265	–0.0796	0.1459	0.08
H(1WA)	8*f*	0.1978	0.2066	–0.1941	0.08
H(1WB)	8*f*	0.2418	0.3031	–0.2081	0.08
H(2WA)	8*f*	0.2835	0.1559	–0.3626	0.08
H(2WB)	8*f*	0.3262	0.2569	–0.3425	0.08

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*c*	1/4	1/4	0	0.0151(5)	0.0132(4)	0.0166(4)	0.0013(4)	0.0034(3)	0.0007(4)
O(1)	8*f*	0.3127(1)	0.1237(3)	–0.0289(2)	0.017(2)	0.015(2)	0.020(2)	0.004(1)	–0.001(1)	0.004(1)
O(2)	8*f*	0.3293(1)	0.0332(3)	0.1360(2)	0.033(2)	0.021(2)	0.020(2)	0.007(2)	0.008(2)	0.002(1)
N(1)	8*f*	0.1819(2)	0.1057(3)	0.0058(3)	0.020(2)	0.017(2)	0.016(2)	0.001(2)	0.002(2)	–0.003(2)
N(2)	8*f*	0.1517(2)	–0.0985(4)	–0.0590(3)	0.020(2)	0.024(2)	0.024(2)	–0.006(2)	0.005(2)	–0.005(2)
N(3)	8*f*	0.1317(2)	–0.0327(4)	0.1246(3)	0.017(2)	0.023(2)	0.024(2)	–0.006(2)	0.004(2)	0.002(2)
N(4)	8*f*	0.0771(2)	0.0585(4)	–0.0366(3)	0.016(2)	0.022(2)	0.031(2)	–0.002(2)	0.002(2)	0.001(2)
C(1)	8*f*	0.1963(2)	–0.0017(4)	–0.0607(4)	0.025(3)	0.021(3)	0.026(3)	–0.005(2)	0.008(2)	–0.005(2)
C(2)	8*f*	0.0943(2)	–0.0463(5)	–0.1026(4)	0.030(3)	0.029(3)	0.023(3)	–0.013(2)	0.003(2)	–0.001(2)
C(3)	8*f*	0.1231(2)	0.1514(4)	–0.0376(4)	0.016(3)	0.024(3)	0.032(3)	0.000(2)	0.000(2)	0.005(2)
C(4)	8*f*	0.1477(2)	–0.1365(4)	0.0555(4)	0.022(3)	0.020(3)	0.031(3)	–0.001(2)	0.002(2)	0.002(2)
C(5)	8*f*	0.1763(2)	0.0626(4)	0.1209(4)	0.019(3)	0.024(3)	0.020(2)	–0.003(2)	0.006(2)	0.002(2)
C(6)	8*f*	0.0753(2)	0.0156(4)	0.0761(4)	0.022(3)	0.020(3)	0.034(3)	–0.004(2)	0.012(2)	0.005(2)
C(7)	8*f*	0.3394(2)	0.0493(4)	0.0373(4)	0.018(2)	0.014(2)	0.019(2)	–0.005(2)	0.002(2)	–0.004(2)
C(8)	8*f*	0.3881(2)	–0.0262(4)	–0.0048(3)	0.012(2)	0.015(2)	0.020(2)	–0.002(2)	0.004(2)	–0.002(2)
C(9)	8*f*	0.3927(2)	–0.0363(4)	–0.1173(4)	0.024(3)	0.020(3)	0.027(3)	0.001(2)	0.005(2)	0.001(2)
C(10)	8*f*	0.4367(2)	–0.1054(4)	–0.1564(4)	0.036(3)	0.022(3)	0.033(3)	0.000(2)	0.016(2)	0.001(2)
C(11)	8*f*	0.4781(2)	–0.1625(5)	–0.0833(4)	0.018(3)	0.022(3)	0.048(3)	–0.001(2)	0.013(2)	0.005(3)
C(12)	8*f*	0.4750(2)	–0.1520(4)	0.0282(4)	0.018(3)	0.017(3)	0.040(3)	0.000(2)	–0.002(2)	0.009(2)
C(13)	8*f*	0.4294(2)	–0.0854(4)	0.0682(4)	0.018(3)	0.015(3)	0.029(3)	–0.005(2)	0.003(2)	0.001(2)
O(1W)	8*f*	0.2250(1)	0.2541(3)	–0.1667(2)	0.024(2)	0.024(2)	0.018(2)	–0.016(2)	0.002(1)	0.000(2)
O(2W)	8*f*	0.2998(2)	0.2105(3)	–0.3201(3)	0.053(3)	0.023(2)	0.046(2)	–0.008(2)	0.032(2)	–0.006(2)

Acknowledgments. The authors thank the Education Office of Hubei Province, P. R. China, for the research grant No. 2002B29002 and the Natural Science Foundation of Hubei Province, P. R. China, for the research grant No. 2003ABB010.

References

1. Sheldrick, G. M.: SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany 1996.
2. Sheldrick, G. M.: SHELXTL V5.1 Software Reference Manual, Bruker AXS Inc., Madison, Wisconsin, USA 1997.