Crystal structure of 1-benzoyl-2-picoloyl-hydrazine nickel(II) – methylene chloride solvate (1:0.25), $Ni[OC(C_6H_5)NHN(C_5H_4N)CO)]_2 \cdot 0.25CH_2Cl_2$

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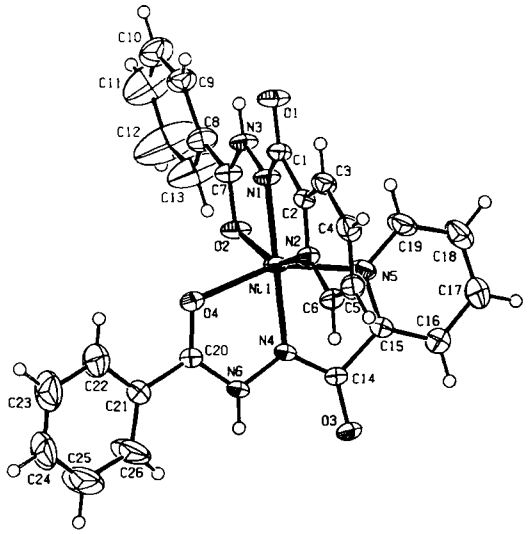

Abstract

$C_{26.5}H_{20.5}Cl_{0.5}NiN_6O_4$, monoclinic, $C12/c1$ (no. 15), a = 25.707(1) Å, b = 14.768(1) Å, c = 18.312(1) Å, β = 132.30(5)°, V = 5142.1 Å^3, Z = 8, $R_{gt(F)} = 0.060$, $wR_{ref(F^2)} = 0.176$, T = 173 K.

Source of material

Benzoyl chloride (10 mmol) was added to a solution of picolinic acid (10 mmol) in 20 ml of methylene chloride cooled with an ice-water bath. The mixture was allowed to warm to room temperature. When benzoyl hydrazide (20 mmol) was added a white product appears. The resulting suspension was filtered and the product rinsed with methylene chloride and diethylether obtain 1-benzoyl-2-picoloyl-hydrazine (H_2L). An ethanol solution of ($NiCl_2$) · $6H_2O$ (1 mmol) was then added to an ethanol solution of ligand (H_2L) (1 mmol). The resulting green solution was stirred and refluxed for two hours. After the filtrate had stood for one day in air at room temperature, a green precipitate was obtained. Crystals of $[Ni(HL)_2]$ were obtained by slow evaporation from an ethanolic solution.

Discussion

The nickel(II) atom has a distorted octahedral coordination geometry. A deviation from 90° of the bond angles involving the chelation is observed (∠O2–Ni–O4 = 93.3(1)°, ∠O4–Ni–N2 = 91.0(1)°, ∠N2–Ni–N5 = 92.6(1)°, ∠N5–Ni–O2 = 94.4(1)°) presummably due to the formation of five-membered ring [1]. Relevant bonds distances are: d(N1—Ni) = 1.964(2) Å, d(N2—Ni) = 2.1002(2) Å, d(N4—Ni) = 1.970(2) Å, d(N5—Ni) = 2.094(3) Å, d(O2—Ni) = 2.178(2) Å, d(O4—Ni) = 2.139(3) Å. The d(N1—Ni) and d(N4—Ni) lengths are indicative of a strong link between the Ni and these atoms. The d(C1—O1) = 1.245(3) Å, d(C7—O2) = 1.261(3) Å, d(C20—O4) = 1.250(3) Å and d(C14—O3) = 1.254(3) Å bonds show essentially a double bond character.

During refinement the 0.25 CH_2Cl_2 solvent per one complex molecule was restrained to idealized geometry. The methylene chloride is disordered, resulting in large U_{ij} values of the neighbored phenyl C atoms.

Table 1. Data collection and handling.

Crystal:	green prism, size 0.08 × 0.10 × 0.13 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	8.51 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa CCD, φ
$2\theta_{max}$:	60.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	22822, 7487
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5061
$N(param)_{refined}$:	346
Programs:	SHELXS-97 [2], SHELXL-97 [3], WinGX [4], ORTEP-II [5], PLATON [6]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(3N)	8f		0.2043	0.5709	0.4444	0.043
H(6N)	8f		0.2772	0.5346	0.8971	0.040
H(3)	8f		0.3186	0.2656	0.5849	0.044
H(4)	8f		0.3458	0.1550	0.6978	0.051
H(5)	8f		0.3241	0.1856	0.7998	0.052
H(6)	8f		0.2757	0.3219	0.7865	0.046
H(16)	8f		0.0356	0.3901	0.6416	0.064
H(17)	8f		−0.0469	0.3427	0.4769	0.078
H(18)	8f		−0.0217	0.3595	0.3779	0.072
H(19)	8f		0.0852	0.4196	0.4447	0.059
H(22)	8f		0.4456	0.5964	0.9025	0.083
H(9)	8f		0.1880	0.6974	0.3779	0.058
H(13)	8f		0.1110	0.7731	0.4988	0.123
H(10)	8f		0.1457	0.8289	0.2869	0.081
H(12)	8f		0.0743	0.9085	0.4138	0.181
H(26)	8f		0.3658	0.5998	1.0254	0.203
H(23)	8f		0.5541	0.6330	1.0525	0.103
H(24)	8f		0.5694	0.6456	1.1889	0.119
H(25)	8f		0.4750	0.6380	1.1739	0.247
H(11)	8f		0.0891	0.9346	0.3041	0.134
Cl(1)	8f	0.25	0.0607(4)	0.4325(5)	0.2902(6)	0.141(3)
Cl(2)	8f	0.25	−0.0349(5)	0.5793(6)	0.219(1)	0.228(6)
C(27)	8f	0.25	−0.0213(7)	0.4646(7)	0.245(2)	0.119(9)
H(27A)	8f	0.25	−0.0574	0.4307	0.1851	0.143
H(27B)	8f	0.25	−0.0248	0.4507	0.2930	0.143

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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)	8*f*	0.22086(2)	0.50086(2)	0.65257(2)	0.0386(2)	0.0415(2)	0.0235(2)	0.0003(1)	0.0236(2)	0.0011(1)
N(4)	8*f*	0.2150(1)	0.5035(2)	0.7544(2)	0.036(1)	0.041(1)	0.0210(9)	–0.0071(9)	0.0200(9)	–0.0043(9)
N(1)	8*f*	0.2284(1)	0.4959(2)	0.5529(2)	0.046(1)	0.037(1)	0.026(1)	0.007(1)	0.028(1)	0.0071(9)
O(2)	8*f*	0.1796(1)	0.6310(1)	0.5775(1)	0.058(1)	0.047(1)	0.035(1)	0.0081(9)	0.038(1)	0.0044(9)
O(4)	8*f*	0.3197(1)	0.5573(1)	0.7783(1)	0.042(1)	0.048(1)	0.0317(9)	–0.0077(9)	0.0279(9)	–0.0019(8)
O(3)	8*f*	0.1538(1)	0.4605(2)	0.7999(1)	0.053(1)	0.077(2)	0.032(1)	–0.022(1)	0.033(1)	–0.007(1)
N(2)	8*f*	0.2674(1)	0.3734(2)	0.6800(2)	0.035(1)	0.040(1)	0.023(1)	–0.0034(9)	0.0199(9)	0.0022(9)
N(5)	8*f*	0.1215(1)	0.4443(2)	0.5774(2)	0.036(1)	0.049(2)	0.023(1)	–0.001(1)	0.018(1)	–0.0029(9)
N(3)	8*f*	0.2038(1)	0.5691(2)	0.4909(2)	0.049(1)	0.041(1)	0.028(1)	0.010(1)	0.030(1)	0.010(1)
N(6)	8*f*	0.2742(1)	0.5335(2)	0.8474(1)	0.037(1)	0.042(1)	0.022(1)	–0.007(1)	0.021(1)	–0.0055(9)
C(1)	8*f*	0.2585(1)	0.4286(2)	0.5470(2)	0.038(1)	0.039(2)	0.023(1)	–0.000(1)	0.021(1)	0.000(1)
C(2)	8*f*	0.2803(1)	0.3556(2)	0.6213(2)	0.033(1)	0.035(1)	0.022(1)	–0.004(1)	0.017(1)	–0.001(1)
C(3)	8*f*	0.3099(1)	0.2756(2)	0.6260(2)	0.040(1)	0.039(2)	0.027(1)	–0.000(1)	0.020(1)	0.000(1)
C(4)	8*f*	0.3263(2)	0.2101(2)	0.6934(2)	0.041(2)	0.039(2)	0.031(1)	–0.001(1)	0.018(1)	0.003(1)
C(5)	8*f*	0.3133(2)	0.2282(2)	0.7539(2)	0.046(2)	0.042(2)	0.030(1)	–0.008(1)	0.020(1)	0.006(1)
C(6)	8*f*	0.2841(1)	0.3100(2)	0.7454(2)	0.043(2)	0.045(2)	0.028(1)	–0.006(1)	0.024(1)	0.002(1)
C(7)	8*f*	0.1790(2)	0.6374(2)	0.5083(2)	0.043(1)	0.044(2)	0.030(1)	0.005(1)	0.027(1)	0.004(1)
C(15)	8*f*	0.1067(1)	0.4348(2)	0.6352(2)	0.038(1)	0.043(2)	0.027(1)	–0.006(1)	0.021(1)	–0.003(1)
C(14)	8*f*	0.1618(1)	0.4683(2)	0.7398(2)	0.039(1)	0.039(1)	0.026(1)	–0.005(1)	0.024(1)	0.000(1)
C(16)	8*f*	0.0446(2)	0.3966(3)	0.6005(2)	0.052(2)	0.066(2)	0.044(2)	–0.018(2)	0.033(2)	–0.008(2)
C(17)	8*f*	–0.0044(2)	0.3681(3)	0.5023(3)	0.048(2)	0.079(3)	0.048(2)	–0.026(2)	0.025(2)	–0.016(2)
C(18)	8*f*	0.0105(2)	0.3776(3)	0.4437(2)	0.047(2)	0.077(3)	0.034(2)	–0.014(2)	0.018(2)	–0.016(2)
C(19)	8*f*	0.0745(2)	0.4149(3)	0.4840(2)	0.047(2)	0.067(2)	0.026(1)	–0.002(2)	0.021(1)	–0.005(1)
C(20)	8*f*	0.3264(1)	0.5607(2)	0.8525(2)	0.040(1)	0.037(1)	0.029(1)	–0.004(1)	0.025(1)	–0.002(1)
C(21)	8*f*	0.3939(2)	0.5905(2)	0.9494(2)	0.044(2)	0.053(2)	0.035(1)	–0.013(1)	0.025(1)	–0.007(1)
C(22)	8*f*	0.4510(2)	0.6028(3)	0.9578(3)	0.047(2)	0.090(3)	0.057(2)	–0.020(2)	0.030(2)	–0.009(2)
C(9)	8*f*	0.1637(2)	0.7387(2)	0.3839(2)	0.060(2)	0.047(2)	0.041(2)	0.002(2)	0.036(2)	0.008(1)
C(8)	8*f*	0.1527(2)	0.7197(2)	0.4466(2)	0.051(2)	0.047(2)	0.042(2)	0.012(1)	0.033(1)	0.014(1)
C(13)	8*f*	0.1187(3)	0.7843(4)	0.4567(4)	0.147(4)	0.095(4)	0.140(4)	0.079(3)	0.127(4)	0.075(3)
C(10)	8*f*	0.1392(2)	0.8181(3)	0.3303(3)	0.070(2)	0.075(3)	0.052(2)	0.004(2)	0.039(2)	0.024(2)
C(12)	8*f*	0.0959(4)	0.8651(5)	0.4050(6)	0.220(7)	0.125(5)	0.216(8)	0.126(5)	0.191(7)	0.122(5)
C(26)	8*f*	0.4037(3)	0.6049(7)	1.0293(4)	0.099(4)	0.37(1)	0.066(3)	–0.137(6)	0.066(3)	–0.110(5)
C(23)	8*f*	0.5161(2)	0.6248(4)	1.0478(4)	0.045(2)	0.102(4)	0.073(3)	–0.024(2)	0.024(2)	–0.007(3)
O(1)	8*f*	0.2689(1)	0.4188(2)	0.4901(2)	0.070(1)	0.047(1)	0.039(1)	0.012(1)	0.045(1)	0.0080(9)
C(24)	8*f*	0.5250(2)	0.6343(4)	1.1277(3)	0.071(3)	0.123(5)	0.052(2)	–0.052(3)	0.020(2)	–0.017(3)
C(25)	8*f*	0.4697(4)	0.6275(8)	1.1190(4)	0.127(5)	0.44(2)	0.059(3)	–0.174(8)	0.065(3)	–0.108(6)
C(11)	8*f*	0.1055(3)	0.8813(4)	0.3405(5)	0.134(5)	0.089(4)	0.142(5)	0.064(3)	0.105(4)	0.080(4)

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