Crystal structure of aqua(benzoylacetonato)(*R*,*R*-dibenzylstilbenediamine)(nitrato)nickel(II) ethanol disolvate, $Ni(H_2O)(C_{10}H_{10}O_2)(C_{28}H_{28}N_2)(NO_3) \cdot 1.9\,C_2H_5OH$

Keiko Miyamoto[I], Tomoko Yajima[I], Ernst Horn*[,II] and Yutaka Fukuda[I]

[I] Ochanomizu University, Faculty of Science, Department of Chemistry, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan
[II] Rikkyo University, Department of Chemistry, 3-34-1 Nishi-Ikebukuro, Toshima-ku, Tokyo 171-8501, Japan

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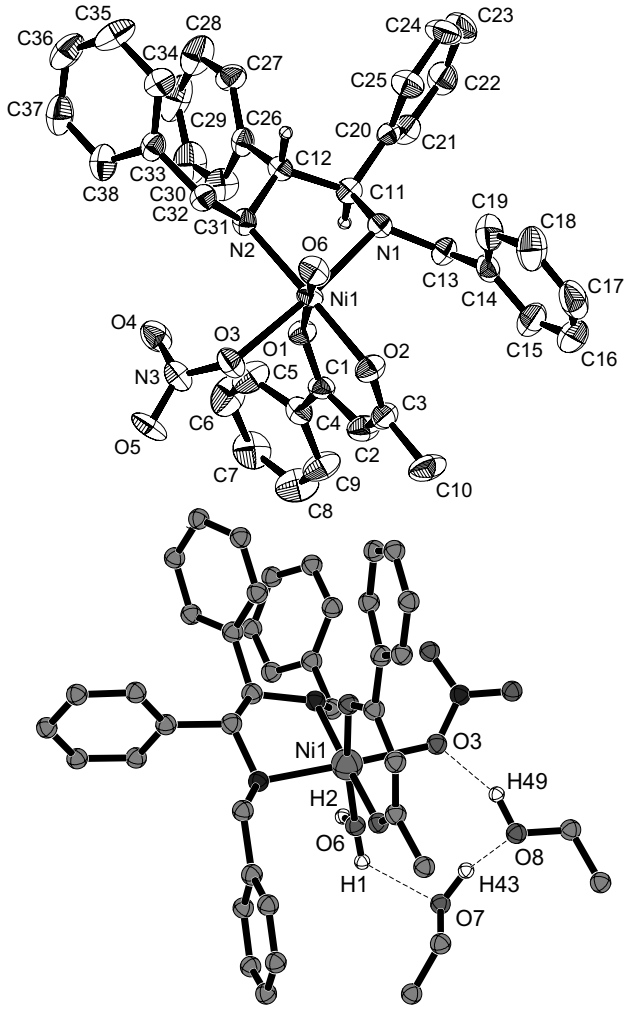

Abstract

$C_{41.82}H_{48.43}N_3NiO_{7.91}$, orthorhombic, $P2_12_12_1$ (no. 19), a = 13.491(1) Å, b = 14.260(1) Å, c = 21.430(2) Å, V = 4122.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.050, $wR_{ref}(F)$ = 0.053, T = 273 K.

Source of material

The title compound was prepared by adding 0.393 g of dibenzylstilbenediamine (dbstien) obtained according to the published method [1] to 0.291 g of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 3 ml of ethanol followed by addition of 0.162 g of benzoylacetone. The mixture was heated with stirring for 30 minutes. The resulting bluish green solution was allowed to stand overnight. The crude crystals obtained were recrystallized from an acetone/ethanol mixture via vapor diffusion using diethyl ether to yield green single crystals.

Discussion

Metal complexes of copper, nickel and zinc containing a stilbenediamine as a chiral ligand have been catching attention due to their catalytic activity in asymmetric syntheses [1-6]. Recently a chiral copper catalyst having dibenzylstilbene as its ligand has been developed to achieve enantioselective Mannich-type reactions of *N*-acylimino esters with, for example, alkyl vinyl ethers to afford the corresponding *N*-acylated amino acid derivatives [4]. To date, only a few crystal structures of these complexes have been reported, hence our interest to isolate, crystallize and to determine the molecular structure of the nickel complex presented here.

The asymmetric unit of the crystal structure consists of one Ni complex and two ethanol molecules (figure, top, 30 % probability ellipsoids). The central nickel atom has a slightly distorted octahedral coordination, with the angles on nickel ranging from 85.6(2)° to 98.9(3)°, and 173.0(2)° to 178.2(2)°, respectively. The average Ni—N distance (Ni—N1, Ni—N2) is 2.108(7) Å, which is in the normal range for octahedral Ni complexes. The Ni—O(bzac) distances Ni—O1 and Ni—O2 of 2.030(5) Å and 1.986(5) Å, respectively, reflect the relative *trans* effect exhibited by N2 as opposed to O6, making the latter distance shorter. The nitrate ion coordinates at the expected distance, Ni—O3, of 2.202(5) Å. The dibenzylstilbene and bzac bidentate chelate planes are virtually perpendicular to each other. The dihedral angle between the least square planes (C26→C31) and (C33→C38), is 24.12°, while the angle between the planes (C14→C31) and (C20→C25) is 78.0(7)°, which is much larger than expected from a more symmetrical placement of the four phenyl groups of dibenzylstilbene. In fact, the phenyl (C14→C19), lines up with bzac phenyl (C4→C9) with a respective dihedral angle of 4.5(8)°, but out of range for intra π-stacking. The atomic arrangement about C11 and C12 reflects the *R*,*R* configuration of dibenzylstilbene of the overall absolute molecular structure. Finally, the oxygen of water molecule locates at the distance of 2.057(5) Å from the nickel. The two ethanol molecules are involved in an intermolecular hydrogen bonding network with the nickel complex and themselves (figure, bottom). More specifically, O7 from the first ethanol hydrogen bonds to H1 of O6(water), while O8 of the second ethanol hydrogen bonds to H43 of O7, and O3(nitro) in turn hydrogen bonds to H49 of O8, at the respective O···O distances of 2.72(1) Å, 2.78(1) Å, and 2.85(1) Å. The occupancy factor of the second ethanol molecule was refined to 0.905 presumably because of evaporation of the molecule from the crystal.

* Correspondence author (e-mail: ehorn_chem@grp.rikkyo.ne.jp)

Table 1. Data collection and handling.

Crystal:	green, prismatic, size 0.10 × 0.16 × 0.25 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	5.24 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	51.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	25025, 7238
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5757
$N(param)_{refined}$:	488
Programs:	SIR92 [7], teXsan [8], ORTEP-II [9]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(1)	4*a*		0.7950	0.8749	0.4835	0.048
H(2)	4*a*		0.7942	0.7788	0.4894	0.048
H(3)	4*a*		0.3906	1.0203	0.6061	0.074
H(4)	4*a*		0.3612	0.7042	0.6279	0.088
H(5)	4*a*		0.2012	0.6534	0.6687	0.108
H(6)	4*a*		0.0758	0.7684	0.6962	0.102
H(7)	4*a*		0.1092	0.9323	0.6819	0.108
H(8)	4*a*		0.2715	0.9866	0.6457	0.088
H(9)	4*a*		0.5937	1.1396	0.5735	0.105
H(10)	4*a*		0.5435	1.1184	0.5082	0.105
H(11)	4*a*		0.4767	1.1403	0.5672	0.105
H(12)	4*a*		0.6050	0.7426	0.6854	0.049
H(13)	4*a*		0.7464	0.6326	0.6238	0.051
H(14)	4*a*		0.6338	0.9195	0.6828	0.065
H(15)	4*a*		0.7226	0.8816	0.7240	0.065
H(16)	4*a*		0.6623	1.0842	0.6933	0.104
H(17)	4*a*		0.7572	1.2187	0.6647	0.131
H(18)	4*a*		0.9228	1.1978	0.6213	0.119
H(19)	4*a*		0.9853	1.0409	0.6003	0.116
H(20)	4*a*		0.8869	0.9032	0.6278	0.092
H(21)	4*a*		0.5999	0.7027	0.7914	0.068
H(22)	4*a*		0.6913	0.6719	0.8876	0.086
H(23)	4*a*		0.8742	0.6491	0.8846	0.095
H(24)	4*a*		0.9610	0.6682	0.7858	0.093
H(25)	4*a*		0.8712	0.7067	0.6899	0.074
H(26)	4*a*		0.7584	0.4871	0.6735	0.074
H(27)	4*a*		0.6713	0.3517	0.7182	0.106
H(28)	4*a*		0.4893	0.3522	0.7286	0.118
H(29)	4*a*		0.3975	0.4919	0.6942	0.104
H(30)	4*a*		0.4825	0.6222	0.6474	0.084
H(31)	4*a*		0.6593	0.6498	0.4749	0.058
H(32)	4*a*		0.7592	0.6554	0.5136	0.058
H(33)	4*a*		0.8510	0.5206	0.5328	0.072
H(34)	4*a*		0.8559	0.3460	0.5415	0.108
H(35)	4*a*		0.7044	0.2572	0.5345	0.101
H(36)	4*a*		0.5469	0.3349	0.5133	0.102
H(37)	4*a*		0.5400	0.5070	0.5033	0.084
H(38)	4*a*		0.7233	1.1053	0.4021	0.371
H(39)	4*a*		0.7108	1.0753	0.4729	0.371
H(40)	4*a*		0.8709	1.0820	0.4848	0.295
H(41)	4*a*		0.8821	1.1140	0.4143	0.295
H(42)	4*a*		0.8248	1.1785	0.4625	0.295
H(43)	4*a*		0.6761	0.9653	0.4106	0.148
H(44)	4*a*	0.91	0.5357	0.9371	0.3198	0.157
H(45)	4*a*	0.91	0.4373	0.9827	0.3464	0.157
H(46)	4*a*	0.91	0.6030	1.0812	0.3093	0.235
H(47)	4*a*	0.91	0.5029	1.0732	0.2710	0.235
H(48)	4*a*	0.91	0.5045	1.1267	0.3358	0.235
H(49)	4*a*	0.91	0.5261	0.9226	0.4206	0.151

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4*a*		0.6251(1)	0.8223(1)	0.55952(9)	0.0394(8)	0.0469(9)	0.0416(8)	0.000(1)	−0.001(1)	0.008(1)
O(1)	4*a*		0.4945(7)	0.8123(8)	0.6061(5)	0.040(4)	0.046(6)	0.057(6)	0.002(5)	0.008(4)	0.004(6)
O(2)	4*a*		0.6087(8)	0.9603(7)	0.5529(5)	0.051(6)	0.046(2)	0.075(7)	0.000(5)	0.011(7)	0.004(6)
O(3)	4*a*		0.5432(8)	0.8158(9)	0.4708(5)	0.056(6)	0.070(7)	0.057(6)	−0.017(6)	−0.015(5)	0.009(7)
O(4)	4*a*		0.4581(8)	0.687(1)	0.4864(5)	0.059(7)	0.076(8)	0.076(7)	−0.022(8)	−0.015(6)	0.019(7)
O(5)	4*a*		0.4149(9)	0.785(1)	0.4144(5)	0.062(7)	0.11(1)	0.066(7)	0.003(7)	−0.037(5)	0.017(7)
O(6)	4*a*		0.7477(7)	0.8402(8)	0.5037(5)	0.039(5)	0.067(8)	0.060(6)	−0.011(6)	0.010(4)	0.009(6)
O(7)	4*a*		0.749(1)	0.983(1)	0.4198(7)	0.14(1)	0.12(1)	0.12(1)	0.00(1)	0.01(1)	0.03(1)
O(8)	4*a*	0.91	0.545(1)	0.985(1)	0.4002(8)	0.14(2)	0.11(1)	0.13(1)	−0.03(1)	−0.04(1)	0.06(1)
N(1)	4*a*		0.7103(8)	0.8172(9)	0.6421(5)	0.042(6)	0.043(6)	0.039(5)	−0.004(7)	0.000(4)	0.006(5)
N(2)	4*a*		0.6375(9)	0.6756(9)	0.5663(5)	0.055(7)	0.045(2)	0.034(5)	−0.005(8)	0.002(6)	0.001(7)
N(3)	4*a*		0.470(1)	0.762(1)	0.4569(6)	0.047(7)	0.077(8)	0.044(7)	−0.010(6)	−0.004(5)	0.002(6)
C(1)	4*a*		0.432(1)	0.876(1)	0.6106(7)	0.040(7)	0.056(7)	0.045(9)	0.012(5)	−0.001(7)	−0.003(8)
C(2)	4*a*		0.449(1)	0.971(1)	0.5959(9)	0.049(9)	0.058(8)	0.08(1)	0.007(9)	0.004(9)	0.01(1)
C(3)	4*a*		0.535(1)	1.006(1)	0.5690(8)	0.053(8)	0.044(7)	0.07(1)	0.003(6)	0.002(8)	−0.002(9)
C(4)	4*a*		0.332(1)	0.850(1)	0.6352(7)	0.047(7)	0.067(9)	0.032(8)	0.001(6)	0.006(7)	−0.003(8)
C(5)	4*a*		0.307(1)	0.756(1)	0.6411(9)	0.06(1)	0.065(9)	0.09(1)	0.01(1)	0.04(1)	0.01(1)
C(6)	4*a*		0.216(2)	0.727(1)	0.663(1)	0.07(1)	0.07(1)	0.13(2)	−0.028(9)	0.03(1)	−0.01(1)
C(7)	4*a*		0.147(1)	0.791(2)	0.678(1)	0.04(1)	0.11(1)	0.10(1)	−0.014(9)	0.03(1)	0.00(1)
C(8)	4*a*		0.166(1)	0.882(2)	0.671(1)	0.06(1)	0.11(1)	0.10(2)	0.02(1)	0.04(1)	0.01(1)
C(9)	4*a*		0.258(1)	0.913(1)	0.6504(9)	0.07(1)	0.06(1)	0.09(1)	0.019(8)	0.03(1)	0.01(1)
C(10)	4*a*		0.537(1)	1.111(1)	0.553(1)	0.08(1)	0.048(8)	0.14(2)	0.00(1)	0.00(2)	0.03(1)
C(11)	4*a*		0.674(1)	0.732(1)	0.6746(7)	0.038(8)	0.046(7)	0.040(7)	−0.005(7)	0.012(6)	0.005(5)
C(12)	4*a*		0.677(1)	0.649(1)	0.6295(7)	0.039(8)	0.050(8)	0.038(6)	0.000(7)	0.001(7)	0.001(5)
C(13)	4*a*		0.703(1)	0.900(1)	0.6822(8)	0.06(1)	0.047(8)	0.05(1)	0.004(8)	0.003(9)	−0.009(7)
C(14)	4*a*		0.764(1)	0.982(1)	0.6630(7)	0.07(1)	0.051(8)	0.040(8)	−0.008(7)	−0.017(8)	0.003(8)
C(15)	4*a*		0.734(2)	1.073(1)	0.672(1)	0.09(2)	0.057(9)	0.11(2)	0.01(1)	−0.01(1)	−0.02(1)
C(16)	4*a*		0.787(2)	1.149(1)	0.657(1)	0.12(2)	0.04(1)	0.16(2)	−0.01(1)	−0.05(2)	0.00(1)
C(17)	4*a*		0.878(2)	1.138(1)	0.632(1)	0.13(1)	0.08(1)	0.09(1)	−0.05(1)	−0.05(1)	0.02(1)
C(18)	4*a*		0.913(2)	1.050(2)	0.621(1)	0.10(2)	0.09(1)	0.10(2)	−0.05(1)	0.01(1)	−0.01(1)
C(19)	4*a*		0.858(1)	0.972(1)	0.6367(9)	0.07(1)	0.08(1)	0.08(1)	−0.02(1)	0.00(1)	−0.02(1)

Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(20)	4*a*		0.729(1)	0.709(1)	0.7347(7)	0.049(6)	0.036(8)	0.045(6)	0.005(8)	–0.002(5)	0.000(7)
C(21)	4*a*		0.680(1)	0.697(1)	0.7902(7)	0.07(1)	0.05(1)	0.047(7)	–0.00(1)	0.011(6)	0.009(9)
C(22)	4*a*		0.731(2)	0.678(2)	0.8439(7)	0.10(1)	0.07(1)	0.040(8)	0.00(1)	–0.001(8)	0.00(1)
C(23)	4*a*		0.834(2)	0.666(2)	0.8424(8)	0.10(1)	0.08(1)	0.049(8)	0.00(1)	–0.029(8)	0.01(1)
C(24)	4*a*		0.882(1)	0.677(2)	0.7874(8)	0.07(1)	0.10(1)	0.061(8)	0.03(1)	–0.018(7)	0.01(1)
C(25)	4*a*		0.831(1)	0.698(1)	0.7332(8)	0.049(6)	0.08(1)	0.052(8)	0.01(1)	0.006(7)	0.00(1)
C(26)	4*a*		0.627(1)	0.563(1)	0.6568(6)	0.063(7)	0.047(7)	0.028(7)	–0.005(7)	0.005(9)	–0.004(6)
C(27)	4*a*		0.679(1)	0.488(1)	0.6772(8)	0.09(1)	0.06(1)	0.04(1)	0.014(8)	–0.002(9)	0.008(8)
C(28)	4*a*		0.629(2)	0.412(1)	0.7027(8)	0.15(1)	0.06(1)	0.06(1)	–0.02(1)	0.02(2)	0.016(9)
C(29)	4*a*		0.528(2)	0.412(1)	0.709(1)	0.15(1)	0.05(1)	0.09(1)	–0.04(1)	0.04(1)	0.00(1)
C(30)	4*a*		0.477(2)	0.489(2)	0.6892(9)	0.10(2)	0.08(1)	0.08(1)	–0.04(1)	0.02(1)	0.01(1)
C(31)	4*a*		0.525(1)	0.563(1)	0.6634(9)	0.063(7)	0.07(1)	0.07(1)	–0.01(1)	0.01(1)	0.01(1)
C(32)	4*a*		0.692(1)	0.632(1)	0.5136(7)	0.06(1)	0.050(7)	0.039(8)	0.003(9)	0.005(7)	–0.001(7)
C(33)	4*a*		0.694(1)	0.525(1)	0.5178(7)	0.070(8)	0.049(7)	0.035(8)	0.000(7)	0.006(9)	–0.005(8)
C(34)	4*a*		0.784(1)	0.480(1)	0.5284(8)	0.07(1)	0.058(8)	0.05(1)	0.006(9)	0.01(1)	0.003(9)
C(35)	4*a*		0.786(2)	0.382(1)	0.534(1)	0.10(1)	0.058(8)	0.11(2)	0.03(1)	0.03(1)	0.01(1)
C(36)	4*a*		0.702(2)	0.333(1)	0.5292(9)	0.13(1)	0.04(1)	0.08(1)	0.00(1)	0.03(1)	0.01(1)
C(37)	4*a*		0.614(2)	0.376(1)	0.5179(9)	0.11(1)	0.068(8)	0.08(1)	–0.03(1)	0.00(1)	–0.01(1)
C(38)	4*a*		0.610(1)	0.473(1)	0.5121(8)	0.07(1)	0.069(8)	0.07(1)	–0.02(1)	0.01(1)	–0.01(1)
C(39)	4*a*		0.753(3)	1.071(2)	0.437(3)	0.27(4)	0.16(2)	0.51(6)	–0.07(3)	0.08(5)	–0.21(3)
C(40)	4*a*		0.840(3)	1.115(3)	0.450(2)	0.24(4)	0.29(5)	0.20(3)	–0.05(4)	0.01(4)	–0.12(3)
C(41)	4*a*	0.91	0.508(2)	0.989(2)	0.343(1)	0.12(2)	0.14(2)	0.13(2)	–0.04(2)	–0.03(2)	0.01(2)
C(42)	4*a*	0.91	0.532(3)	1.075(2)	0.312(2)	0.24(4)	0.18(3)	0.16(3)	–0.10(3)	–0.10(3)	0.09(2)

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