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Crystal structure of *fac*-triaqua(acetonitrile)(*N,N,N',N'*-tetramethylethylenediamine)]nickel(II) dibromide, $[Ni(H_2O)_3(CH_3CN)(C_6H_{16}N_2)][Br]_2$

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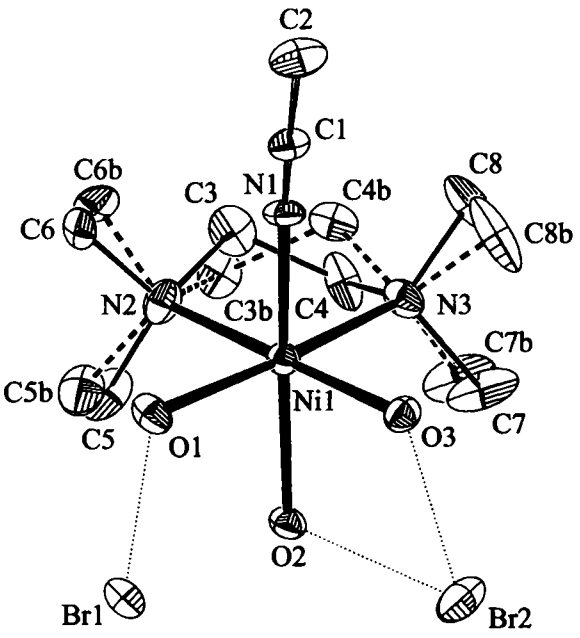

Abstract

$C_8H_{25}Br_2N_3NiO_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.0856(6) Å, b = 12.4144(8) Å, c = 16.6060(1) Å, V = 1666.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F)$ = 0.035, T = 273 K.

Source of material

2.185 g of $NiBr_2$ dissolved in 30 ml of ethanol at 50 °C was added to 1.16 g of *N,N,N',N'*-tetramethylethylenediamine (tmen), stirred vigorously for 30 minutes and the resulting precipitate filtered out. The Ni(tmen)$(H_2O)_2Br_2$ (light green powder) obtained was dehydrated in vacuum at 120 °C for 3 days to yield Ni(tmen)Br_2 as a purple microcrystalline powder, which was then dissolved in acetonitrile containing a small amount of water, and subjected to vapor diffusion crystallization with diethyl ether to provide single crystals.

Experimental details

The disorder of the tmen bridging carbon atoms were modeled as two sites per atom (the second site labeled b) with occupancies equal to 0.5. During calculations the N—C distances and C–N–C angles were restrained to 1.450(5) Å and 109(1)°, respectively. The water hydrogen atoms were located from Fourier difference maps, while the others were fixed at calculated positions [d(C—H) = 0.97 Å] and not refined.

Discussion

Nickel(II) complexes are known with a wide variety of configurations (octahedral, square pyramidal, trigonal bipyramidal, square planar and tetrahedral), and can be easily converted from one configuration to another, usually accompanied by very contrasting color changes [1]. In this regard, nickel complexes are prosperous functional materials for such applications as thermosensitive coloring materials, sensors (organic solvents and water), and Lewis-acid-base indicator [2]. Ni(tmen)X_2 (tmen = *N,N,N',N'*-tetramethylethylenediamine, X = Cl or Br) are such chromotropic compounds as they change color between monomer (pink/purple) and trimer (green) depending on the external stimuli, i.e. temperature (thermochromic behavior) and atmosphere (solvatochromic behavior) [3,4]. Although the trimer structures have been reported by several authors [5-7], no suitable crystals of a monomeric substance have been obtained to date. Here we report one of the first single crystals of a monomeric structure of this series, $[Ni(H_2O)_3(CH_3CN)(tmen)][Br]_2$.

The nickel coordination polyhedron is a slightly distorted octahedron with the largest angular deviation occurring in the tmen bite angle, ∠N2–Ni1–N3 = 84.8(2)°. The three water molecules are in a mutually *fac* relationship with average Ni—O distances of 2.095(4) Å. The CH_3CN group in the axial position with d(Ni1—N1) = 2.059(5) Å) is tilted by 11.3(5)° with respect to the octahedral axis (Ni1–N1 direction). The ligand maintains its carbon-nitrogen triple bond, d(C1≡N1) = 1.132(8) Å. The two bromide atoms, Br1 and Br2, are involved in intramolecular hydrogen bonding to the water oxygens, O2 and O3, at the respective distances, d(Br1···O2) = 3.281(4) Å, d(Br2···O2) = 3.202(4) Å and d(Br2···O3) = 3.216(4) Å. In addition, Br1 is H-bonded to two other molecules via O1′ and O3″ in a continuous 3D network, with d(Br1···O1′) = 3.270(4) Å and d(Br1···O3″) = 3.306(4) Å, where O1′ and O3″ are related to the original asymmetric unit at x–1,y,z by the respective symmetry operations –½+x,½–y,2–z and –1+x,y,z.

Table 1. Data collection and handling.

Crystal:	blue block, size 0.150 × 0.160 × 0.290 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	59.74 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	57.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10780, 2332
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1795
$N(param)_{refined}$:	210
Programs:	SIR92 [8], SHELXL-97 [9], ORTEP-II [10]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4a		−0.1994	0.1746	0.9223	0.062
H(2)	4a		−0.0069	0.2253	0.9219	0.047
H(3)	4a		−0.1911	−0.0355	1.0055	0.062
H(4)	4a		−0.0661	−0.0904	1.0399	0.062
H(5)	4a		0.1769	0.1262	1.0418	0.040
H(6)	4a		0.1598	0.0185	1.0663	0.040
H(7)	4a		0.5609	0.2659	0.8806	0.057
H(8)	4a		0.5121	0.2649	0.7882	0.057
H(9)	4a		0.4199	0.3434	0.8485	0.057
H(10)	4a	0.5	0.0150	−0.1280	0.7311	0.053
H(10b)	4a	0.5	−0.0625	−0.1726	0.8097	0.048
H(11)	4a	0.5	0.1681	−0.0544	0.7537	0.053
H(11b)	4a	0.5	−0.0030	−0.1265	0.7256	0.048
H(12)	4a	0.5	0.1992	−0.2263	0.8091	0.055
H(12b)	4a	0.5	0.2536	−0.0761	0.7829	0.044
H(13)	4a	0.5	0.0329	−0.2104	0.8581	0.055
H(13b)	4a	0.5	0.2275	−0.2015	0.7950	0.044
H(14)	4a	0.5	−0.2744	0.0080	0.8473	0.059
H(14b)	4a	0.5	−0.2581	0.0589	0.8359	0.067
H(15)	4a	0.5	−0.2598	−0.0661	0.7699	0.059
H(15b)	4a	0.5	−0.2731	−0.0314	0.7689	0.067

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(16)	4a	0.5	−0.2089	−0.1118	0.8555	0.059
H(16b)	4a	0.5	−0.2499	−0.0642	0.8604	0.067
H(17)	4a	0.5	0.0754	0.1128	0.7552	0.041
H(17b)	4a	0.5	0.1156	0.0675	0.7356	0.054
H(18)	4a	0.5	−0.0724	0.0657	0.7034	0.041
H(18b)	4a	0.5	−0.0572	0.0421	0.6949	0.054
H(19)	4a	0.5	−0.1097	0.1395	0.7791	0.041
H(19b)	4a	0.5	−0.0422	0.1364	0.7588	0.054
H(20)	4a	0.5	0.0932	−0.1993	0.9822	0.106
H(20b)	4a	0.5	0.0534	−0.2302	0.9302	0.093
H(21)	4a	0.5	0.2590	−0.2570	0.9554	0.106
H(21b)	4a	0.5	0.2315	−0.2777	0.9125	0.093
H(22)	4a	0.5	0.2660	−0.1548	1.0124	0.106
H(22b)	4a	0.5	0.1978	−0.2140	0.9935	0.093
H(23)	4a	0.5	0.4497	−0.1638	0.8707	0.064
H(23b)	4a	0.5	0.4537	−0.1659	0.8854	0.098
H(24)	4a	0.5	0.4019	−0.0501	0.8341	0.064
H(24b)	4a	0.5	0.4324	−0.0390	0.8837	0.098
H(25)	4a	0.5	0.4418	−0.0610	0.9271	0.064
H(25b)	4a	0.5	0.4199	−0.1022	0.9664	0.098

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}
Br(1)	4a		−0.4009(2)	0.1032(2)	1.0394(1)	0.0260(8)	0.0358(9)	0.049(1)	0.0006(9)	0.003(1)	−0.006(1)
Br(2)	4a		0.0472(3)	−0.0948(2)	1.1664(1)	0.066(2)	0.064(1)	0.036(1)	−0.020(1)	−0.009(1)	0.016(1)
Ni(1)	4a		0.0784(3)	0.0240(2)	0.9200(1)	0.026(1)	0.0235(9)	0.029(1)	0.001(1)	0.002(1)	0.000(1)
O(1)	4a		−0.072(2)	0.161(1)	0.9325(9)	0.030(6)	0.022(5)	0.059(9)	0.002(4)	0.006(7)	0.001(6)
O(2)	4a		−0.097(2)	−0.059(1)	0.9889(8)	0.024(6)	0.029(6)	0.038(7)	−0.002(5)	0.006(5)	0.003(5)
O(3)	4a		0.196(2)	0.059(1)	1.0288(8)	0.034(7)	0.037(7)	0.028(5)	−0.005(6)	−0.003(5)	0.003(6)
N(1)	4a		0.253(2)	0.127(1)	0.872(1)	0.032(8)	0.036(8)	0.032(8)	−0.005(6)	0.014(7)	0.005(7)
N(2)	4a		−0.040(2)	−0.011(1)	0.8093(9)	0.051(9)	0.036(8)	0.028(6)	0.002(8)	−0.009(6)	−0.004(6)
N(3)	4a		0.217(2)	−0.118(1)	0.897(1)	0.033(7)	0.025(6)	0.049(9)	0.006(5)	0.008(8)	−0.004(7)
C(1)	4a		0.348(3)	0.191(2)	0.858(1)	0.04(1)	0.034(9)	0.028(9)	−0.008(6)	0.005(9)	0.001(9)
C(2)	4a		0.472(3)	0.273(2)	0.842(1)	0.06(1)	0.04(1)	0.05(1)	−0.033(8)	0.01(1)	0.00(1)
C(3)	4a	0.5	0.072(5)	−0.093(3)	0.775(3)	0.05(3)	0.05(2)	0.04(2)	0.00(2)	−0.01(2)	−0.03(1)
C(3b)	4a	0.5	0.005(6)	−0.120(3)	0.784(3)	0.05(2)	0.03(2)	0.04(2)	−0.01(2)	−0.01(2)	−0.01(2)
C(4)	4a	0.5	0.130(5)	−0.174(3)	0.834(3)	0.03(2)	0.02(2)	0.08(2)	0.00(2)	−0.02(2)	−0.02(1)
C(4b)	4a	0.5	0.190(6)	−0.130(3)	0.810(2)	0.04(2)	0.02(2)	0.05(1)	−0.01(2)	0.01(2)	−0.01(2)
C(5)	4a	0.5	−0.208(4)	−0.049(4)	0.820(4)	0.07(2)	0.04(3)	0.05(3)	−0.04(2)	−0.02(3)	0.01(2)
C(5b)	4a	0.5	−0.219(4)	−0.012(5)	0.818(4)	0.05(1)	0.05(3)	0.07(4)	−0.02(3)	−0.01(3)	0.02(3)
C(6)	4a	0.5	−0.037(6)	0.084(3)	0.757(2)	0.04(2)	0.03(2)	0.03(2)	0.02(2)	0.00(2)	−0.01(1)
C(6b)	4a	0.5	−0.004(7)	0.064(3)	0.744(2)	0.06(3)	0.04(2)	0.02(2)	0.01(2)	0.01(2)	−0.01(1)
C(7)	4a	0.5	0.21(1)	−0.188(3)	0.967(2)	0.18(6)	0.03(2)	0.09(3)	0.07(3)	0.09(4)	0.04(2)
C(7b)	4a	0.5	0.172(9)	−0.218(3)	0.937(3)	0.16(6)	0.02(2)	0.07(2)	0.03(3)	0.06(3)	0.00(2)
C(8)	4a	0.5	0.392(4)	−0.098(4)	0.883(3)	0.03(1)	0.04(2)	0.08(3)	0.01(2)	0.00(2)	−0.05(2)
C(8b)	4a	0.5	0.393(4)	−0.107(6)	0.912(4)	0.03(1)	0.07(4)	0.16(7)	0.02(3)	−0.02(4)	−0.04(5)

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