Crystal structure of *trans*-diacetonitritrile(diaqua)(*N,N,N′,N′*-tetramethylethylenediamine)nickel(II)dibromide tetrahydrate, $[Ni(tmen)(CH_3CN)_2(H_2O)_2]^{2+}\cdot 2Br^-\cdot 4H_2O$, $C_{10}H_{34}Br_2N_4NiO_6$

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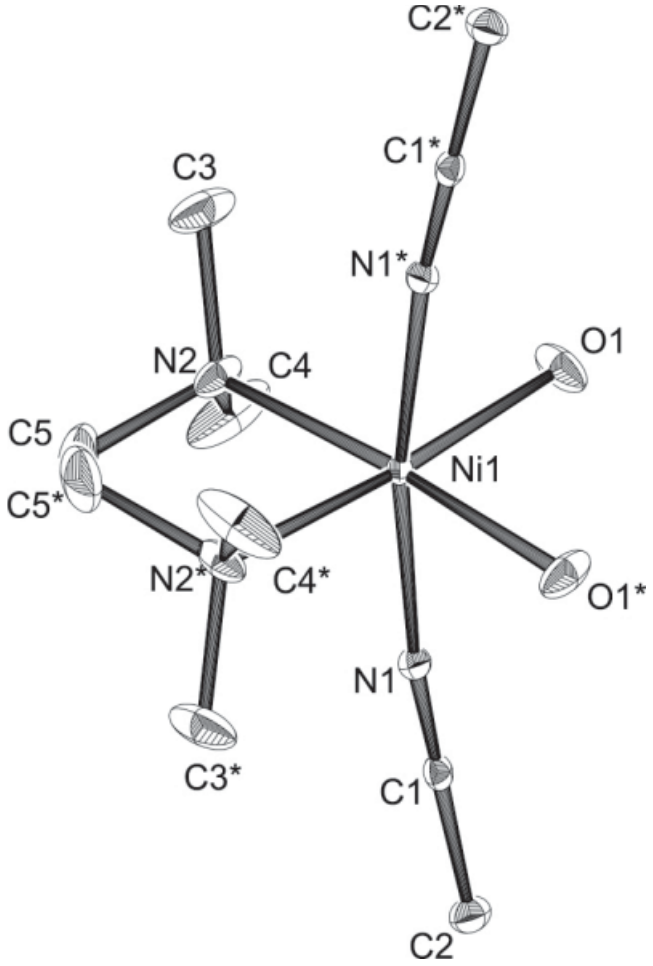

Abstract

$C_{10}H_{34}Br_2N_4NiO_6$, monoclinic, *C*2/*c* (no. 15), a = 19.062(4) Å, b = 8.106(2) Å, c = 15.484(3) Å, β = 112.96(3)°, V = 2203.0(9) Å^3, Z = 4, $R_{gt}(F)$ = 0.0348, $wR_{ref}(F^2)$ = 0.0405, T = 273.2 K.

Source of material

The title monomer complex was prepared from $NiBr_2$ in ethanol after the dropwise addition of *N,N,N′,N′*-tetramethylethylenediamine (*tmen*) and left at room temperature for one day. Subsequently, the filtered product dissolved in acetnitrile was crystallized by vapor diffusion at -10 °C temperature.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.80×0.42×0.12 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	45.47 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ and ω
$2\theta_{max}$:	55.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24402, 2496
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 2312
$N(param)_{refined}$:	114
Programs:	SHELXTL [1], SADABS [2], TEXSAN [3], ORTEP-II [9]

Experimental details

All non-hydrogen atoms have been modeled anisotropically using SHELXTL [1] using absorption corrected data [2]. While, the carbon hydrogen atoms were fixed at calculated positions [d(C–H) = 0.97 Å] after the least squares cycles (teXsan [3]). The water hydrogen atoms were not found, therefore, not included in the calculations.

Discussion

Our research focuses include the self-assembling clusters [4-7] and chromotropic behavior of mixed ligand complexes of transition metals [8]. Addition of *tmen* to ethanolic solutions of Ni(II)X_2 (X = F, Cl, Br) results in formation of monomeric complexes [Ni(*tmen*)X_2] which in turn self-assemble into corresponding trimeric complexes, $[Ni_3(tmen)_3F_5]F\cdot 3H_20$, $[Ni_3(tmen)_3X_4(OH)]X$ (X = Cl, Br). However, the cluster may decompose to form a monomeric complex depending on the solvent or temperature. The unit cell of the title structure is filled with four monomeric, cationic nickel complexes, eight bromide anions and sixteen lattice water molecules. The bromide anions and water molecules are connected *via* hydrogen bonds, and are located on a layer between the packing arrangements of the Ni complexes. The corresponding hydrogen bonding distances are: (Br1···O2) = 3.413(3)Å, (Br1···O3) = 3.386(3)Å, (O1···O2) = 2.748(3)Å, and (O1*···O3) = 2.727(4)Å. The ORTEP plot [9] (30% probability ellipsoids) excludes the hydrogen atoms for simplicity. The nickel complex is located on a crystallographic 2-fold axis of symmetry, which passes through Ni1, and half way between the atom pairs, (O1, O1*), and (C5, C5*). The coordination geometry is a slightly distorted octahedron, with the acetonitrile ligands tilted away from the *tmen* ligand with a (N1–Ni1–N1*) angle of 170.8(2)°. The respective average bond lengths, (N1–Ni1), (N2–Ni1), and (O1–Ni1), are equal to 2.068(3) Å, 2.125(3) Å and 2.069(3) Å.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	8*f*	0.2791	–0.0968	–0.0397	0.0258
H(2)	8*f*	0.2895	–0.0816	–0.1360	0.0258
H(3)	8*f*	0.2677	0.0759	–0.0913	0.0258
H(4)	8*f*	–0.1079	–0.3486	–0.4043	0.0533
H(5)	8*f*	–0.0726	–0.2434	–0.4636	0.0533
H(6)	8*f*	–0.0620	–0.4374	–0.4570	0.0533
H(7)	8*f*	0.1161	–0.2938	–0.3158	0.0734
H(8)	8*f*	0.0710	–0.4004	–0.4063	0.0734
H(9)	8*f*	0.0617	–0.2060	–0.4094	0.0734
H(10)	8*f*	0.0057	–0.5654	–0.3214	0.0704
H(11)	8*f*	0.0747	–0.4739	–0.2430	0.0704

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}
Br(1)	8*f*	0.25762(2)	0.06612(4)	0.14153(2)	0.0191(1)	0.0245(2)	0.0214(1)	0.0013(1)	0.0085(1)	0.0020(1)
Ni(1)	4*e*	0	–0.12674(7)	–¼	0.0105(2)	0.0101(2)	0.0140(2)	0	0.0034(2)	0
O(1)	8*f*	0.0009(1)	0.0488(4)	–0.3466(2)	0.020(1)	0.035(1)	0.044(1)	0.000(1)	0.009(1)	0.025(1)
O(2)	8*f*	0.3737(1)	0.2668(3)	0.0550(2)	0.022(1)	0.022(1)	0.025(1)	–0.004(1)	0.0066(9)	–0.005(1)
O(3)	8*f*	0.1342(1)	0.1996(3)	0.6733(2)	0.023(1)	0.022(1)	0.030(1)	–0.0019(9)	0.0126(9)	0.004(1)
N(1)	8*f*	0.1174(1)	–0.1063(3)	–0.1889(2)	0.015(1)	0.014(1)	0.016(1)	0.001(1)	0.0046(9)	–0.001(1)
N(2)	8*f*	0.0049(2)	–0.3197(4)	–0.3405(2)	0.018(1)	0.031(2)	0.029(1)	–0.002(1)	0.009(1)	–0.017(1)
C(1)	8*f*	0.1802(2)	–0.0788(4)	–0.1509(2)	0.019(1)	0.012(1)	0.016(1)	0.003(1)	0.008(1)	0.000(1)
C(2)	8*f*	0.2609(2)	–0.0419(4)	–0.1003(2)	0.017(1)	0.023(2)	0.023(1)	0.001(1)	0.005(1)	–0.006(1)
C(3)	8*f*	–0.0655(2)	–0.3382(6)	–0.4237(3)	0.030(2)	0.060(3)	0.037(2)	0.001(2)	0.004(2)	–0.031(2)
C(4)	8*f*	0.0691(2)	–0.3046(7)	–0.3703(3)	0.033(2)	0.092(4)	0.070(2)	–0.022(2)	0.033(2)	–0.059(2)
C(5)	8*f*	0.0204(3)	–0.4698(6)	–0.2809(4)	0.056(3)	0.022(2)	0.083(4)	0.005(2)	0.010(2)	–0.019(2)

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