Refinement of the crystal structure of μ_3-chloro-μ_3-hydroxo-tris(μ-chloro)-tris[tetramethylethylenediaminenickel(II)] chloride, $\{[Ni(C_6H_{16}N_2)]_3Cl_4OH\}Cl$

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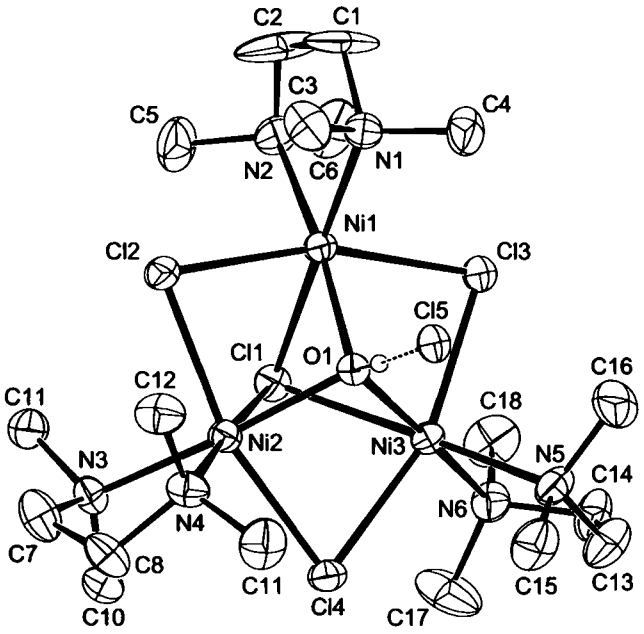

Abstract

$C_{18}H_{49}Cl_5N_6ONi_3$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 10.748(1)$ Å, $b = 16.038(1)$ Å, $c = 18.019(2)$ Å, $V = 3106.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.043$, $wR_{ref}(F) = 0.049$, $T = 273$ K.

Source of material

The title compound was prepared by adding 1.16 g of *N,N,N',N'*-tetramethylethylenediamine (tmen) to 2.38 g of $NiCl_2 \cdot 6H_2O$ dissolved in 30 ml of ethanol at 50 °C, stirred vigorously for 20 minutes, and the resulting precipitate was collected by filtration. The obtained powder was recrystallized from 1,2-dichloroethane (DCE) by slow vapor diffusion at room temperature using diethyl ether to yield single crystals.

Discussion

The interest in the title trimer and related ones is due to their potentially catalytic properties and the novel cluster formation from the respective monomeric species [1-5]. During the crystallization study of $Ni(tmen)(H_2O)_2Cl_2$, which is a continuation from our recent work [6], it was found that the nickel chloride trimer exhibits solvatochromic behavior and can be prepared much more easily than via the reported method [7]. A comparison of solid state reflectance with UV/VIS measurements of the trimer dissolved in several solvents shows the presence of the trimer (green) in EtOH, a monomer (pink) in acetone and a mixture (pink/brown) of both the monomer and the trimer in DCE. The data of the title structure (ORTEP [8] drawing with 30 % probability ellipsoids) presented here are significantly more accurate than the already published data [9,10] and than those of the respective solvated trimer which crystallizes in a different space group [7].

The Ni(II) chloride core, Ni_3Cl_4, has the three Ni atoms connected by three μ_2-chloride bridges forming a plane, and the fourth μ_3-chloride (Cl1) and μ_3-hydroxy group (O1) coordinate below and above the plane, respectively. The molecules have a pseudo non-crystallographic threefold axis of symmetry passing through Cl1, Cl5 (above the plane of the page) and O1. The fin-like tmen ligands coordinate to each nickel atom to complete their respective distorted octahedral geometry. The nickel atoms are at the non-bonding average (Ni–Ni) distance of 3.044(1) Å apart, while the average μ_2-Cl—Ni and μ_3-Cl—Ni bond lengths are 2.438(2) Å and 2.552(2) Å, respectively. The chlorine atom, Cl5, is hydrogen bonded to O1 at a Cl5—O1 distance of 3.298(4) Å.

Table 1. Data collection and handling.

Crystal:	green, prismatic, size 0.30 × 0.38 × 0.62 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	22.52 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX CCD, ω/π
$2\theta_{max}$:	54.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19869, 3884
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3000
$N(param)_{refined}$:	299
Programs:	SIR92 [11], teXsan [12], ORTEP-II [8]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	0.9570	–0.0369	0.4191	0.076
H(2)	4*a*	1.0807	0.1374	0.1832	0.123
H(3)	4*a*	0.9519	0.0947	0.1635	0.123
H(4)	4*a*	0.9131	0.2150	0.1694	0.156
H(5)	4*a*	1.0019	0.2302	0.2382	0.156
H(6)	4*a*	1.1572	0.0278	0.3324	0.086
H(7)	4*a*	1.2050	0.0625	0.2552	0.086
H(8)	4*a*	1.1512	0.1247	0.3155	0.086
H(9)	4*a*	0.9284	–0.0328	0.2110	0.083
H(10)	4*a*	1.0726	–0.0310	0.1928	0.083
H(11)	4*a*	1.0257	–0.0656	0.2702	0.083

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12)	4a	0.9056	0.2815	0.3282	0.095
H(13)	4a	0.8186	0.3143	0.2635	0.095
H(14)	4a	0.7592	0.2732	0.3351	0.095
H(15)	4a	0.6487	0.1861	0.2626	0.110
H(16)	4a	0.7084	0.2273	0.1910	0.110
H(17)	4a	0.7129	0.1293	0.2018	0.110
H(18)	4a	1.0341	0.2087	0.6078	0.080
H(19)	4a	0.9511	0.2063	0.6804	0.080
H(20)	4a	0.9449	0.0649	0.6760	0.074
H(21)	4a	1.0852	0.0951	0.6765	0.074
H(22)	4a	0.9153	0.2791	0.5257	0.082
H(23)	4a	0.7686	0.2695	0.5242	0.082
H(24)	4a	0.8353	0.3070	0.5952	0.082
H(25)	4a	0.7357	0.2108	0.6704	0.069
H(26)	4a	0.6673	0.1737	0.5999	0.069
H(27)	4a	0.7419	0.1139	0.6538	0.069
H(28)	4a	0.9536	−0.0579	0.6174	0.085
H(29)	4a	1.0506	−0.0738	0.5528	0.085
H(30)	4a	1.0982	−0.0524	0.6338	0.085

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(31)	4a	1.2166	0.0515	0.5866	0.078
H(32)	4a	1.1680	0.0303	0.5058	0.078
H(33)	4a	1.1589	0.1227	0.5363	0.078
H(34)	4a	0.5881	−0.2477	0.4067	0.090
H(35)	4a	0.5789	−0.2007	0.4838	0.090
H(36)	4a	0.4201	−0.1592	0.4173	0.083
H(37)	4a	0.5053	−0.1422	0.3472	0.083
H(38)	4a	0.7989	−0.2596	0.4811	0.087
H(39)	4a	0.8864	−0.1803	0.4759	0.087
H(40)	4a	0.7707	−0.1799	0.5303	0.087
H(41)	4a	0.7728	−0.2575	0.3540	0.096
H(42)	4a	0.7262	−0.1768	0.3117	0.096
H(43)	4a	0.8601	−0.1782	0.3484	0.096
H(44)	4a	0.4563	0.0219	0.5047	0.122
H(45)	4a	0.3688	−0.0561	0.4910	0.122
H(46)	4a	0.4978	−0.0677	0.5323	0.122
H(47)	4a	0.4462	0.0543	0.3818	0.094
H(48)	4a	0.4805	−0.0122	0.3201	0.094
H(49)	4a	0.3584	−0.0236	0.3683	0.094

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)	4a	0.8736(3)	0.0906(2)	0.3396(1)	0.038(1)	0.037(1)	0.034(1)	−0.003(1)	0.001(1)	0.003(1)
Ni(2)	4a	0.8825(3)	0.0852(2)	0.5078(1)	0.037(1)	0.040(1)	0.034(1)	−0.002(1)	0.000(1)	0.000(1)
Ni(3)	4a	0.7096(2)	−0.0324(1)	0.4241(2)	0.033(1)	0.037(1)	0.038(1)	−0.0018(9)	0.002(1)	0.002(1)
Cl(1)	4a	0.6975(4)	0.1275(3)	0.4282(3)	0.042(2)	0.042(2)	0.046(3)	0.004(2)	0.000(3)	0.000(3)
Cl(2)	4a	1.0023(5)	0.1724(3)	0.4241(3)	0.051(3)	0.053(3)	0.040(2)	−0.019(2)	0.000(2)	0.002(2)
Cl(3)	4a	0.7223(5)	−0.0082(4)	0.2903(3)	0.052(3)	0.050(3)	0.040(3)	−0.013(2)	−0.004(2)	−0.002(2)
Cl(4)	4a	0.7345(5)	−0.0155(4)	0.5578(3)	0.051(3)	0.056(3)	0.038(2)	−0.014(2)	0.004(2)	0.006(2)
Cl(5)	4a	1.1264(4)	−0.1281(3)	0.4128(3)	0.035(2)	0.036(2)	0.044(3)	0.007(2)	−0.002(2)	−0.005(2)
O(1)	4a	0.891(1)	0.0034(7)	0.4217(8)	0.033(3)	0.036(5)	0.035(5)	0.001(5)	−0.001(7)	0.001(2)
N(1)	4a	1.020(2)	0.059(1)	0.263(1)	0.039(8)	0.052(9)	0.05(1)	−0.002(8)	0.015(6)	−0.006(7)
N(2)	4a	0.835(2)	0.190(1)	0.266(1)	0.09(1)	0.039(8)	0.05(1)	0.00(1)	−0.008(8)	0.018(6)
N(3)	4a	0.854(2)	0.182(1)	0.587(1)	0.052(9)	0.044(7)	0.04(1)	0.000(8)	0.002(7)	−0.010(5)
N(4)	4a	1.032(1)	0.046(1)	0.579(1)	0.040(7)	0.062(9)	0.040(8)	0.005(8)	−0.006(6)	0.008(9)
N(5)	4a	0.722(2)	−0.165(1)	0.423(1)	0.055(9)	0.037(2)	0.065(9)	−0.006(7)	0.01(1)	0.01(1)
N(6)	4a	0.515(1)	−0.052(1)	0.424(1)	0.033(3)	0.055(8)	0.061(9)	−0.004(7)	0.009(9)	−0.01(1)
C(1)	4a	0.999(4)	0.123(2)	0.202(2)	0.13(3)	0.12(2)	0.06(2)	0.05(2)	0.06(2)	0.06(2)
C(2)	4a	0.941(4)	0.193(3)	0.216(2)	0.13(3)	0.12(3)	0.14(3)	0.07(3)	0.11(3)	0.09(3)
C(3)	4a	1.144(2)	0.069(2)	0.294(1)	0.04(1)	0.10(2)	0.07(2)	0.00(1)	0.00(1)	−0.02(2)
C(4)	4a	1.011(3)	−0.025(2)	0.232(2)	0.06(2)	0.06(1)	0.09(2)	−0.01(1)	0.03(2)	−0.03(1)
C(5)	4a	0.829(3)	0.272(2)	0.301(2)	0.11(3)	0.04(1)	0.09(2)	0.00(2)	−0.02(2)	0.00(1)
C(6)	4a	0.716(3)	0.183(2)	0.227(2)	0.10(2)	0.07(2)	0.10(2)	−0.01(2)	−0.06(2)	0.03(2)
C(7)	4a	0.968(3)	0.179(2)	0.633(2)	0.06(1)	0.08(1)	0.06(2)	0.01(1)	−0.02(1)	−0.02(1)
C(8)	4a	1.009(2)	0.093(2)	0.648(1)	0.07(2)	0.08(1)	0.04(1)	0.01(1)	−0.01(1)	−0.01(1)
C(9)	4a	0.842(3)	0.267(2)	0.555(1)	0.10(2)	0.04(1)	0.06(2)	0.00(1)	0.02(1)	−0.00(1)
C(10)	4a	0.740(2)	0.169(2)	0.632(1)	0.06(1)	0.06(2)	0.05(1)	0.00(1)	0.02(1)	−0.01(1)
C(11)	4a	1.034(3)	−0.042(2)	0.597(2)	0.08(2)	0.06(1)	0.08(2)	0.01(1)	−0.02(1)	0.01(1)
C(12)	4a	1.154(2)	0.064(2)	0.550(1)	0.04(1)	0.09(2)	0.06(2)	0.00(1)	0.00(1)	0.01(1)
C(13)	4a	0.595(2)	−0.194(2)	0.431(2)	0.05(1)	0.06(1)	0.11(2)	−0.01(1)	0.01(2)	0.01(2)
C(14)	4a	0.501(3)	−0.140(2)	0.401(2)	0.05(1)	0.06(1)	0.10(2)	−0.02(1)	0.00(1)	−0.01(1)
C(15)	4a	0.801(3)	−0.199(2)	0.483(2)	0.08(2)	0.05(2)	0.09(2)	0.01(1)	−0.02(2)	0.02(1)
C(16)	4a	0.775(3)	−0.197(2)	0.353(2)	0.13(3)	0.05(2)	0.07(2)	0.02(2)	0.02(2)	−0.01(1)
C(17)	4a	0.454(3)	−0.037(3)	0.494(2)	0.05(2)	0.20(4)	0.06(2)	0.00(2)	0.02(1)	−0.02(2)
C(18)	4a	0.444(3)	−0.004(2)	0.369(2)	0.05(2)	0.09(2)	0.09(2)	0.01(1)	−0.03(1)	0.03(2)

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