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Crystal structure of μ_3-chloro-μ_3-hydroxo-tris(μ-chloro)tris(tetramethylethylenediamine)trinickel(II) triiodide, $[Ni_3(C_6H_{16}N_2)_3Cl_4(OH)][I_3]$

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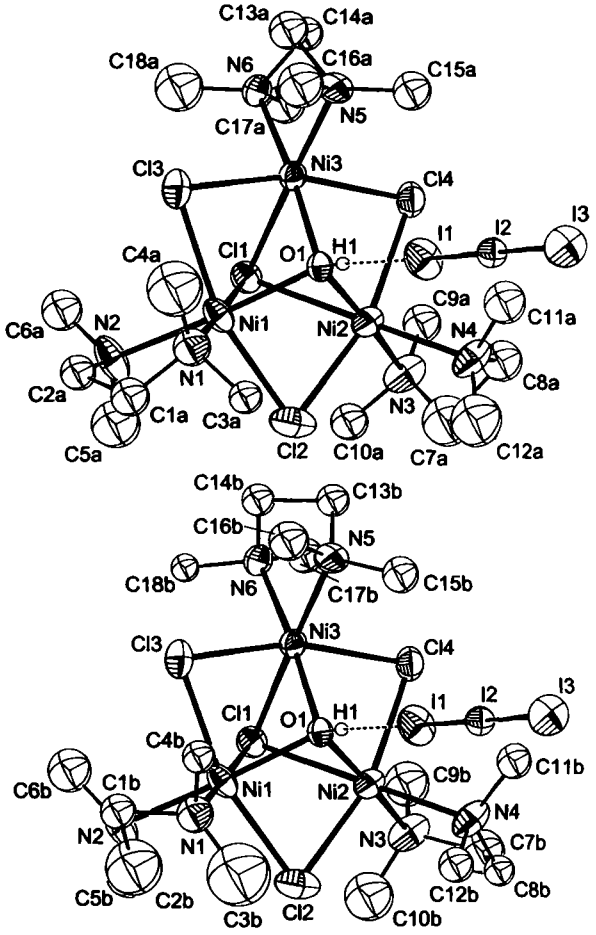

Abstract

$C_{18}H_{49}Cl_4I_3N_6Ni_3O$, triclinic, $P\bar{1}$ (no. 2), a = 15.371(3) Å, b = 11.777(2) Å, c = 11.505(2) Å, α = 96.075(7)°, β = 84.816(6)°, γ = 111.562(6)°, V = 1923.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.061, $wR_{ref}(F)$ = 0.065, T = 273 K.

Source of material

The title complex was prepared by adding 0.58 g of *N,N,N',N'*-tetramethylethylenediamine (tmen) to 1.56 g of NiI_2 dissolved in 10 ml of ethanol at 50 °C, stirred vigorously for 30 minutes, and the resulting precipitate was isolated by filtration as $[Ni(tmen)(H_2O)_2I_2]$ (light green powder, elemental analysis: found – C, 15.37 %; H, 4.49 %; N, 5.60 %; calc. for $C_6H_{20}I_2N_2NiO_2$: C, 15.51 %; H, 4.34 %; N, 6.03 %). When dissolved in 1,2-dichloroethane, heated for 30 min, and then subjected to vapor diffusion crystallization with diethyl ether, suitable single crystals were obtained.

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Experimental details

The disorder of the tmen carbon atoms was modeled as two sites per atom with occupancies set to 0.5. In the final refinement the other non-hydrogen atoms were modeled anisotropically, while the carbon hydrogen atoms were fixed at calculated positions (d(C—H) = 0.97 Å) after the least-squares cycles, and the hydroxyl hydrogen was located in a previous difference map, but not refined.

Discussion

This trimer and related ones are of interest due to their potentially catalytic properties and the novel cluster formation from the respective monomeric species [1-9]. Following the formation of a μ_3-chloro-μ_3-hydroxo-tris(μ_2-chloro)tris(tetramethylethylenediamine-nickel(II)) chloride [8], we have been working on the crystallization of $Ni(tmen)(H_2O)_2I_2$, expecting to obtain an iodide trimer, but obtained the chloride trimer reported here. This suggests there is a solvent-complex interaction that the complex $[Ni(tmen)(H_2O)_2I_2]$ exchanges its iodo ligand (I^-) with the chloride ion (Cl^-) of the solvent (DCE, the only chloride source) to form a new complex $[Ni_3(tmen)_3Cl_4(OH)]I_3$.

The $Ni_3Cl_4(OH)$ core shows the nickel atoms, Cl2, Cl3 and Cl4 in a plane, while Cl1 and O1 make μ_3-coordinations to the three metals. The average non-bonding Ni···Ni distance is 3.083(3) Å, while the average μ-Cl—Ni and μ_3-Cl—Ni bond lengths are 2.475(4) Å and 2.566(4) Å, respectively. The coordination of a tmen to each of the nickel atoms completes the distorted octahedral environment. The average Ni—N bond length is 2.16(1) Å. The I1 atom is within hydrogen bonding distance from O1 (4.185(8) Å). As in the chloride trimer [8], an analogous pseudo non-crystallographic threefold axis passes through the atoms, Cl1, O1, I1, I2 and I3, as is also seen from the view down the axis in that earlier structure report. In particularly, the thermal ellipsoids of the tmen bridging carbon atoms, C1, C2, C7 and C8, are large due to the common disorder in such ligands.

Table 1. Data collection and handling.

Crystal:	brown plate, size 0.080 × 0.100 × 0.480 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	41.61 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	56.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11317, 8115
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4057
$N(param)_{refined}$:	316
Programs:	SIR92 [10], SHELXL-97 [11], ORTEP-II [12], teXsan [13]

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

Atom	Site	Occ.	x	y	z	U_{iso}
N(1)	2*i*		0.692(3)	−0.692(4)	0.464(3)	0.084(2)
C(1a)	2*i*	0.5	0.695(6)	−0.647(6)	0.589(5)	0.0860(8)
C(1b)	2*i*	0.5	0.645(4)	−0.737(8)	0.577(5)	0.0772(8)
C(2a)	2*i*	0.5	0.684(5)	−0.753(7)	0.665(6)	0.0732(9)
C(2b)	2*i*	0.5	0.746(5)	−0.701(5)	0.62(1)	0.1950(3)
C(3a)	2*i*	0.5	0.749(7)	−0.576(6)	0.42(1)	0.0631(5)
C(3b)	2*i*	0.5	0.76(2)	−0.57(1)	0.44(3)	0.2495(3)
C(4a)	2*i*	0.5	0.597(7)	−0.74(2)	0.43(2)	0.1826(3)
C(4b)	2*i*	0.5	0.610(5)	−0.73(1)	0.395(8)	0.0669(6)
C(5a)	2*i*	0.5	0.84(1)	−0.77(2)	0.69(3)	0.1384(4)
C(5b)	2*i*	0.5	0.84(1)	−0.80(2)	0.68(3)	0.1302(3)
C(6a)	2*i*	0.5	0.70(1)	−0.942(9)	0.68(2)	0.0984(4)
C(6b)	2*i*	0.5	0.68(1)	−0.94(1)	0.67(2)	0.1180(5)
C(7a)	2*i*	0.5	1.103(8)	−0.705(5)	0.239(6)	0.1521(4)
C(7b)	2*i*	0.5	1.129(5)	−0.762(8)	0.184(7)	0.1216(6)
C(8a)	2*i*	0.5	1.076(5)	−0.750(8)	0.110(7)	0.0979(6)
C(8b)	2*i*	0.5	1.100(3)	−0.660(6)	0.144(6)	0.0579(6)
C(9a)	2*i*	0.5	1.08(1)	−0.943(8)	0.24(1)	0.0849(6)
C(9b)	2*i*	0.5	1.07(2)	−0.952(9)	0.27(2)	0.1255(4)
C(10a)	2*i*	0.5	1.091(9)	−0.804(9)	0.404(6)	0.0796(6)
C(10b)	2*i*	0.5	1.10(1)	−0.76(1)	0.392(9)	0.1445(4)
C(11a)	2*i*	0.5	0.94(1)	−0.73(2)	0.024(8)	0.1087(5)
C(11b)	2*i*	0.5	0.966(8)	−0.75(1)	0.010(6)	0.0781(7)
C(12a)	2*i*	0.5	1.02(1)	−0.573(7)	0.15(2)	0.1575(4)
C(12b)	2*i*	0.5	0.982(7)	−0.588(6)	0.16(1)	0.0772(6)
C(13a)	2*i*	0.5	0.582(3)	−1.213(4)	0.140(6)	0.0847(5)
C(13b)	2*i*	0.5	0.632(5)	−1.219(4)	0.081(4)	0.0642(6)
C(14a)	2*i*	0.5	0.658(4)	−1.275(5)	0.147(4)	0.0653(6)
C(14b)	2*i*	0.5	0.604(3)	−1.279(5)	0.200(5)	0.0644(6)
C(15a)	2*i*	0.5	0.68(1)	−1.04(1)	−0.006(9)	0.0884(8)
C(15b)	2*i*	0.5	0.68(1)	−1.01(1)	0.008(9)	0.0833(7)
C(16a)	2*i*	0.5	0.564(6)	−1.045(8)	0.13(2)	0.1196(5)
C(16b)	2*i*	0.5	0.550(5)	−1.077(8)	0.13(2)	0.0959(7)
C(17a)	2*i*	0.5	0.775(5)	−1.27(1)	0.26(1)	0.0892(7)
C(17b)	2*i*	0.5	0.768(5)	−1.28(1)	0.22(1)	0.0762(8)
C(18a)	2*i*	0.5	0.638(4)	−1.27(2)	0.374(7)	0.1375(5)
C(18b)	2*i*	0.5	0.660(4)	−1.27(1)	0.384(5)	0.049(1)
H(1)	2*i*		0.7671	−0.8079	0.2115	0.054
H(2a)	2*i*	0.5	0.7551	−0.5829	0.6045	0.101
H(2b)	2*i*	0.5	0.6080	−0.6915	0.6170	0.092
H(3a)	2*i*	0.5	0.6453	−0.6154	0.6120	0.101
H(3b)	2*i*	0.5	0.6085	−0.8236	0.5740	0.092
H(4a)	2*i*	0.5	0.6182	−0.8144	0.6571	0.087
H(4b)	2*i*	0.5	0.7505	−0.6545	0.7005	0.208
H(5a)	2*i*	0.5	0.6902	−0.7244	0.7460	0.087
H(5b)	2*i*	0.5	0.7940	−0.6537	0.5702	0.208
H(6a)	2*i*	0.5	0.8156	−0.5417	0.4121	0.126
H(6b)	2*i*	0.5	0.8134	−0.5483	0.4744	0.171
H(7a)	2*i*	0.5	0.7581	−0.6192	0.3432	0.126
H(7b)	2*i*	0.5	0.7776	−0.5833	0.3459	0.171
H(8a)	2*i*	0.5	0.7243	−0.5111	0.4048	0.126
H(8b)	2*i*	0.5	0.7299	−0.5126	0.4396	0.171
H(9a)	2*i*	0.5	0.5584	−0.6958	0.4084	0.163
H(9b)	2*i*	0.5	0.5671	−0.6886	0.4282	0.098
H(10a)	2*i*	0.5	0.6198	−0.7511	0.3369	0.163
H(10b)	2*i*	0.5	0.6297	−0.7042	0.3149	0.098
H(11a)	2*i*	0.5	0.5601	−0.8255	0.4302	0.163
H(11b)	2*i*	0.5	0.5783	−0.8163	0.3920	0.098
H(12a)	2*i*	0.5	0.8462	−0.8410	0.6325	0.141
H(12b)	2*i*	0.5	0.8416	−0.8783	0.6914	0.158
H(13a)	2*i*	0.5	0.8873	−0.6976	0.6640	0.141
H(13b)	2*i*	0.5	0.8865	−0.7518	0.6337	0.158
H(14a)	2*i*	0.5	0.8408	−0.7875	0.7640	0.141
H(14b)	2*i*	0.5	0.8360	−0.7572	0.7603	0.158
H(15a)	2*i*	0.5	0.7241	−0.9161	0.7505	0.128
H(15b)	2*i*	0.5	0.6744	−0.9334	0.7566	0.115
H(16a)	2*i*	0.5	0.6438	−1.0108	0.6501	0.128

Table 2. Continued.

Atom	Site	Occ	x	y	z	U_{iso}
H(16b)	2*i*	0.5	0.6206	−0.9581	0.6400	0.115
H(17a)	2*i*	0.5	0.7545	−0.9587	0.6334	0.128
H(17b)	2*i*	0.5	0.7050	−1.0038	0.6450	0.115
H(18a)	2*i*	0.5	1.0701	−0.6532	0.2767	0.179
H(18b)	2*i*	0.5	1.1928	−0.7261	0.2080	0.144
H(19a)	2*i*	0.5	1.1699	−0.6625	0.2459	0.179
H(19b)	2*i*	0.5	1.1259	−0.8217	0.1173	0.144
H(20a)	2*i*	0.5	1.0550	−0.8376	0.0936	0.116
H(20b)	2*i*	0.5	1.1354	−0.6325	0.0711	0.068
H(21a)	2*i*	0.5	1.1246	−0.7102	0.0517	0.116
H(21b)	2*i*	0.5	1.1166	−0.5916	0.2037	0.068
H(22a)	2*i*	0.5	1.0288	−0.9819	0.2985	0.097
H(22b)	2*i*	0.5	1.0265	−0.9987	0.3306	0.131
H(23a)	2*i*	0.5	1.0577	−0.9859	0.1629	0.097
H(23b)	2*i*	0.5	1.0400	−0.9919	0.1930	0.131
H(24a)	2*i*	0.5	1.1351	−0.9529	0.2557	0.097
H(24b)	2*i*	0.5	1.1286	−0.9536	0.2694	0.131
H(25a)	2*i*	0.5	1.0693	−0.8836	0.4401	0.107
H(25b)	2*i*	0.5	1.1663	−0.7656	0.4006	0.145
H(26a)	2*i*	0.5	1.1519	−0.7885	0.4321	0.107
H(26b)	2*i*	0.5	1.1039	−0.6842	0.4018	0.145
H(27a)	2*i*	0.5	1.0527	−0.7782	0.4660	0.107
H(27b)	2*i*	0.5	1.0626	−0.8123	0.4571	0.145
H(28a)	2*i*	0.5	0.8894	−0.7151	0.0595	0.117
H(28b)	2*i*	0.5	0.8979	−0.7661	0.0111	0.092
H(29a)	2*i*	0.5	0.9734	−0.6779	−0.0366	0.117
H(29b)	2*i*	0.5	0.9968	−0.6891	−0.0468	0.092
H(30a)	2*i*	0.5	0.9205	−0.8174	−0.0126	0.117
H(30b)	2*i*	0.5	0.9764	−0.8241	−0.0138	0.092
H(31a)	2*i*	0.5	1.0491	−0.5411	0.2212	0.150
H(31b)	2*i*	0.5	0.9954	−0.5598	0.2378	0.099
H(32a)	2*i*	0.5	1.0260	−0.5685	0.0699	0.150
H(32b)	2*i*	0.5	1.0192	−0.5256	0.1062	0.099
H(33a)	2*i*	0.5	0.9508	−0.5657	0.1705	0.150
H(33b)	2*i*	0.5	0.9151	−0.6034	0.1480	0.099
H(34a)	2*i*	0.5	0.5488	−1.2102	0.2152	0.102
H(34b)	2*i*	0.5	0.5850	−1.2604	0.0251	0.079
H(35a)	2*i*	0.5	0.5376	−1.2575	0.0813	0.102
H(35b)	2*i*	0.5	0.6921	−1.2222	0.0498	0.079
H(36a)	2*i*	0.5	0.7095	−1.2462	0.0880	0.080
H(36b)	2*i*	0.5	0.5804	−1.3675	0.1867	0.079
H(37a)	2*i*	0.5	0.6304	−1.3638	0.1363	0.080
H(37b)	2*i*	0.5	0.5564	−1.2532	0.2433	0.079
H(38a)	2*i*	0.5	0.7437	−1.0506	−0.0288	0.094
H(38b)	2*i*	0.5	0.7401	−1.0173	−0.0184	0.102
H(39a)	2*i*	0.5	0.6506	−1.0459	−0.0730	0.094
H(39b)	2*i*	0.5	0.6377	−1.0442	−0.0571	0.102
H(40a)	2*i*	0.5	0.6981	−0.9589	0.0363	0.094
H(40b)	2*i*	0.5	0.6859	−0.9296	0.0310	0.102
H(41a)	2*i*	0.5	0.5860	−0.9570	0.1132	0.138
H(41b)	2*i*	0.5	0.5597	−0.9897	0.1562	0.106
H(42a)	2*i*	0.5	0.5151	−1.0538	0.0769	0.138
H(42b)	2*i*	0.5	0.5114	−1.1036	0.0675	0.106
H(43a)	2*i*	0.5	0.5451	−1.0138	0.2076	0.138
H(43b)	2*i*	0.5	0.5175	−1.1232	0.2002	0.106
H(44a)	2*i*	0.5	0.7688	−1.3497	0.2479	0.105
H(44b)	2*i*	0.5	0.7424	−1.3709	0.2294	0.085
H(45a)	2*i*	0.5	0.8370	−1.2200	0.2097	0.105
H(45b)	2*i*	0.5	0.7899	−1.2610	0.1486	0.085
H(46a)	2*i*	0.5	0.7857	−1.2318	0.3360	0.105
H(46b)	2*i*	0.5	0.8176	−1.2469	0.2801	0.085
H(47a)	2*i*	0.5	0.6783	−1.2297	0.4408	0.126
H(47b)	2*i*	0.5	0.6117	−1.2423	0.4145	0.072
H(48a)	2*i*	0.5	0.5829	−1.2552	0.3820	0.126
H(48b)	2*i*	0.5	0.6395	−1.3594	0.3848	0.072
H(49a)	2*i*	0.5	0.6504	−1.3502	0.3642	0.126
H(49b)	2*i*	0.5	0.7143	−1.2348	0.4349	0.072

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}
I(1)	2*i*	0.7032(3)	−0.6481(4)	0.0410(3)	0.116(3)	0.097(3)	0.070(2)	0.050(2)	−0.017(2)	0.016(2)
I(2)	2*i*	0.6391(2)	−0.5046(3)	−0.1109(2)	0.053(2)	0.060(2)	0.054(2)	0.017(1)	−0.005(1)	0.002(1)
I(3)	2*i*	0.5857(3)	−0.3675(4)	−0.2685(4)	0.090(3)	0.106(3)	0.099(3)	0.040(2)	−0.026(2)	0.026(2)
Ni(1)	2*i*	0.7640(4)	−0.8239(5)	0.4406(4)	0.083(4)	0.067(4)	0.038(3)	0.041(3)	−0.010(3)	0.002(2)
Ni(2)	2*i*	0.9263(4)	−0.8288(5)	0.2631(5)	0.048(3)	0.053(3)	0.061(3)	0.013(2)	−0.010(2)	0.017(2)
Ni(3)	2*i*	0.7332(4)	−1.0378(5)	0.2521(4)	0.050(3)	0.049(3)	0.044(3)	0.014(2)	−0.002(2)	0.010(2)
Cl(1)	2*i*	0.8462(8)	−0.981(1)	0.4179(9)	0.063(7)	0.069(7)	0.047(5)	0.020(5)	−0.012(3)	0.011(4)
Cl(2)	2*i*	0.927(1)	−0.673(1)	0.425(1)	0.11(1)	0.064(8)	0.09(1)	0.023(8)	−0.044(8)	−0.009(7)
Cl(3)	2*i*	0.6197(8)	−1.006(1)	0.404(1)	0.067(8)	0.091(9)	0.064(7)	0.034(7)	0.015(6)	0.016(6)
Cl(4)	2*i*	0.8770(8)	−1.014(1)	0.124(1)	0.074(8)	0.066(7)	0.059(7)	0.026(6)	0.014(6)	0.008(5)
O(1)	2*i*	0.785(2)	−0.848(2)	0.260(2)	0.050(7)	0.050(4)	0.039(4)	0.02(1)	0.00(1)	0.01(1)
N(2)	2*i*	0.747(3)	−0.822(4)	0.631(3)	0.15(4)	0.11(3)	0.039(4)	0.08(3)	−0.01(2)	0.01(2)
N(3)	2*i*	1.067(3)	−0.827(4)	0.281(4)	0.06(2)	0.08(3)	0.11(3)	0.02(2)	−0.03(2)	0.04(3)
N(4)	2*i*	0.999(2)	−0.702(4)	0.127(4)	0.05(2)	0.08(3)	0.11(3)	0.01(2)	−0.01(2)	0.04(3)
N(5)	2*i*	0.641(2)	−1.090(3)	0.107(3)	0.07(3)	0.08(3)	0.05(2)	0.01(2)	−0.03(1)	0.01(2)
N(6)	2*i*	0.691(2)	−1.234(3)	0.265(3)	0.08(3)	0.050(7)	0.05(2)	0.01(2)	0.00(2)	0.02(2)

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