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

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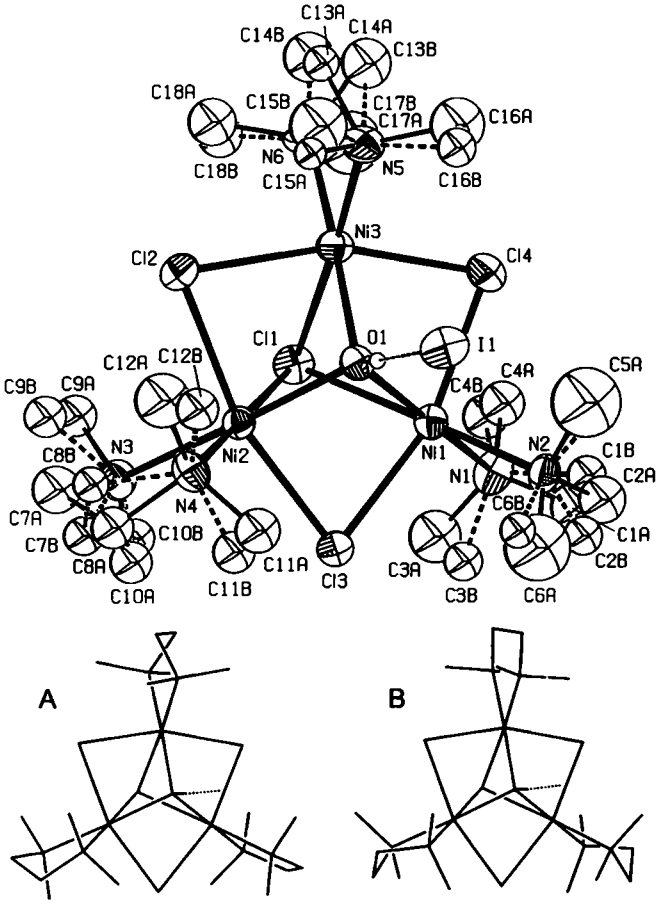

Abstract

$C_{18}H_{49}Cl_4IN_6Ni_3O$, monoclinic, $C12/c1$ (no. 15), a = 33.562(7) Å, b = 12.220(2) Å, c = 18.849(4) Å, β = 117.70(3)°, V = 6844.7 Å^3, Z = 8, $R_{gt}(F)$ = 0.059, $wR_{ref}(F)$ = 0.066, 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 and subjected to vapor diffusion crystallization with diethyl ether, suitable single crystals of the title compound were obtained.

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Experimental details

The disorder of the tmen bridging carbon atoms was modeled as two sites per atom (labeled as a and b) with occupancies set to 0.5. In the final refinement the non-hydrogen and non-carbon atoms (to retain an acceptable parameter/reflection ratio) 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 oxygen hydrogen was located in a previous difference density map, but not refined.

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]. Following the formation of a μ_3-chloro-μ_3-hydroxo-tris(μ-chloro)tris(tetramethylethylenediamine-nickel(II)) chloride [6], 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 $[NiI_2(tmen)(H_2O)_2]$ exchanges its iodo ligand (I^-) with the chloride ion (Cl^-) of the solvent (DCE, the only chloride source) to form a new complex $[Ni_3(tmen)_3Cl_4(OH)]I$.

The $Ni_3Cl_4(OH)$ core contains the nickel atoms, Cl2, Cl3 and Cl4 in a plane, while Cl1 and O1 make μ_3-coordinations to the three metal atoms. The average non-bonding Ni···Ni distance is 3.096(2) Å, while the average μ-Cl—Ni and μ_3-Cl—Ni bond lengths are 2.479(4) Å and 2.574(3) 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 (3.884(6) Å). As in the chloride trimer [6], an analogous pseudo non-crystallographic threefold axis passes through the Cl1, O1 and I1 atoms, as it can be seen from the view down the axis in that earlier structure report.

Table 1. Data collection and handling.

Crystal:	green, prismatic, size 0.100 × 0.180 × 0.640 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	28.69 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, ω/φ
$2\theta_{max}$:	51.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20466, 6636
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\,\sigma(I_{obs})$, 3203
$N(param)_{refined}$:	280
Programs:	SIR92 [7], SHELXL-97 [8], ORTEP-II [9], teXsan [10]

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

Atom	Site	Occ.	x	y	z	U_{iso}
C(1a)	8f	0.5	0.161(3)	−0.114(8)	0.460(5)	0.12(3)
C(1b)	8f	0.5	0.175(2)	−0.084(4)	0.474(3)	0.06(2)
C(2a)	8f	0.5	0.183(2)	−0.101(7)	0.543(4)	0.09(2)
C(2b)	8f	0.5	0.166(2)	−0.122(5)	0.544(3)	0.06(2)
C(3a)	8f	0.5	0.085(2)	−0.060(7)	0.358(5)	0.11(3)
C(3b)	8f	0.5	0.092(2)	−0.101(5)	0.380(4)	0.06(2)
C(4a)	8f	0.5	0.147(2)	0.021(7)	0.356(4)	0.08(2)
C(4b)	8f	0.5	0.135(2)	0.017(7)	0.342(4)	0.08(2)
C(5a)	8f	0.5	0.216(3)	0.04(1)	0.646(7)	0.20(6)
C(5b)	8f	0.5	0.220(2)	0.020(5)	0.638(3)	0.05(1)
C(6a)	8f	0.5	0.157(4)	−0.07(1)	0.640(7)	0.18(5)
C(6b)	8f	0.5	0.155(2)	−0.035(5)	0.648(3)	0.05(1)
C(7a)	8f	0.5	−0.035(2)	0.311(6)	0.458(4)	0.09(2)
C(7b)	8f	0.5	−0.036(2)	0.246(5)	0.467(2)	0.06(1)
C(8a)	8f	0.5	−0.014(1)	0.252(6)	0.537(3)	0.07(2)
C(8b)	8f	0.5	−0.010(1)	0.314(4)	0.542(3)	0.05(1)
C(9a)	8f	0.5	−0.022(2)	0.337(5)	0.342(3)	0.07(2)
C(9b)	8f	0.5	−0.030(2)	0.368(4)	0.372(4)	0.07(2)
C(10a)	8f	0.5	−0.037(2)	0.155(4)	0.372(4)	0.07(2)
C(10b)	8f	0.5	−0.032(2)	0.169(5)	0.347(4)	0.06(2)
C(11a)	8f	0.5	0.054(2)	0.168(6)	0.645(4)	0.08(2)
C(11b)	8f	0.5	0.037(2)	0.160(4)	0.628(4)	0.07(2)
C(12a)	8f	0.5	0.051(3)	0.369(5)	0.629(5)	0.12(3)
C(12b)	8f	0.5	0.065(2)	0.340(5)	0.653(3)	0.07(2)
C(13a)	8f	0.5	0.190(2)	0.557(4)	0.530(3)	0.05(1)
C(13b)	8f	0.5	0.208(2)	0.523(7)	0.535(4)	0.10(3)
C(14a)	8f	0.5	0.196(2)	0.509(5)	0.461(3)	0.05(1)
C(14b)	8f	0.5	0.177(3)	0.550(7)	0.451(4)	0.10(3)
C(15a)	8f	0.5	0.175(1)	0.506(4)	0.638(2)	0.04(1)
C(15b)	8f	0.5	0.184(3)	0.524(9)	0.626(6)	0.13(4)
C(16a)	8f	0.5	0.238(2)	0.415(8)	0.624(5)	0.12(4)
C(16b)	8f	0.5	0.233(2)	0.396(5)	0.635(3)	0.06(2)
C(17a)	8f	0.5	0.156(4)	0.40(1)	0.341(5)	0.16(5)
C(17b)	8f	0.5	0.162(2)	0.391(6)	0.353(3)	0.06(2)
C(18a)	8f	0.5	0.113(2)	0.537(6)	0.373(5)	0.09(3)
C(18b)	8f	0.5	0.109(2)	0.510(6)	0.346(4)	0.08(2)
H(1)	8f		0.1433	0.2402	0.6227	0.057
H(2a)	8f	0.5	0.1914	−0.1055	0.4483	0.134
H(2b)	8f	0.5	0.1802	−0.1479	0.4496	0.087
H(3a)	8f	0.5	0.1525	−0.1834	0.4432	0.134
H(3b)	8f	0.5	0.1997	−0.0358	0.4946	0.087
H(4a)	8f	0.5	0.2159	−0.1018	0.5681	0.111
H(4b)	8f	0.5	0.1882	−0.1788	0.5769	0.072
H(5a)	8f	0.5	0.1743	−0.1703	0.5619	0.111
H(5b)	8f	0.5	0.1363	−0.1525	0.5263	0.072
H(6a)	8f	0.5	0.0664	−0.0010	0.3287	0.106
H(6b)	8f	0.5	0.0646	−0.0637	0.3432	0.074
H(7a)	8f	0.5	0.0849	−0.1175	0.3213	0.106
H(7b)	8f	0.5	0.0968	−0.1621	0.3495	0.074
H(8a)	8f	0.5	0.0713	−0.0952	0.3900	0.106
H(8b)	8f	0.5	0.0872	−0.1350	0.4223	0.074
H(9a)	8f	0.5	0.1773	0.0480	0.3840	0.091
H(9b)	8f	0.5	0.1596	0.0684	0.3539	0.097
H(10a)	8f	0.5	0.1453	−0.0357	0.3178	0.091
H(10b)	8f	0.5	0.1386	−0.0427	0.3086	0.097
H(11a)	8f	0.5	0.1268	0.0807	0.3253	0.091
H(11b)	8f	0.5	0.1067	0.0560	0.3031	0.097
H(12a)	8f	0.5	0.2371	−0.0156	0.6836	0.128
H(12b)	8f	0.5	0.2379	−0.0397	0.6768	0.075
H(13a)	8f	0.5	0.2311	0.0686	0.6155	0.128
H(13b)	8f	0.5	0.2352	0.0257	0.6021	0.075
H(14a)	8f	0.5	0.2112	0.0961	0.6749	0.128
H(14b)	8f	0.5	0.2235	0.0851	0.6649	0.075
H(15a)	8f	0.5	0.1485	−0.0040	0.6731	0.119
H(15b)	8f	0.5	0.1586	0.0400	0.6773	0.072
H(16a)	8f	0.5	0.1253	−0.1002	0.6110	0.119
H(16b)	8f	0.5	0.1240	−0.0498	0.6220	0.072

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(17a)	8f	0.5	0.1747	−0.1152	0.6819	0.119
H(17b)	8f	0.5	0.1726	−0.0851	0.6884	0.072
H(18a)	8f	0.5	−0.0278	0.3910	0.4653	0.114
H(18b)	8f	0.5	−0.0670	0.2722	0.4401	0.069
H(19a)	8f	0.5	−0.0681	0.3063	0.4302	0.114
H(19b)	8f	0.5	−0.0352	0.1705	0.4808	0.069
H(20a)	8f	0.5	−0.0215	0.1744	0.5259	0.089
H(20b)	8f	0.5	−0.0247	0.3113	0.5756	0.063
H(21a)	8f	0.5	−0.0279	0.2785	0.5697	0.089
H(21b)	8f	0.5	−0.0074	0.3891	0.5285	0.063
H(22a)	8f	0.5	−0.0144	0.4143	0.3643	0.074
H(22b)	8f	0.5	−0.0189	0.4249	0.4148	0.083
H(23a)	8f	0.5	−0.0041	0.3200	0.3175	0.074
H(23b)	8f	0.5	−0.0182	0.3832	0.3358	0.083
H(24a)	8f	0.5	−0.0541	0.3404	0.3021	0.074
H(24b)	8f	0.5	−0.0627	0.3724	0.3448	0.083
H(25a)	8f	0.5	−0.0623	0.1842	0.3071	0.070
H(25b)	8f	0.5	−0.0704	0.1572	0.3473	0.077
H(26a)	8f	0.5	−0.0123	0.1645	0.3223	0.070
H(26b)	8f	0.5	−0.0307	0.1346	0.3259	0.077
H(27a)	8f	0.5	−0.0310	0.0997	0.3734	0.070
H(27b)	8f	0.5	−0.0271	0.0922	0.4081	0.077
H(28a)	8f	0.5	0.0191	0.1650	0.6569	0.078
H(28b)	8f	0.5	0.0425	0.1737	0.6832	0.078
H(29a)	8f	0.5	0.0249	0.0971	0.5907	0.078
H(29b)	8f	0.5	0.0438	0.0991	0.6156	0.078
H(30a)	8f	0.5	0.0679	0.1380	0.6683	0.078
H(30b)	8f	0.5	0.0866	0.1685	0.6728	0.078
H(31a)	8f	0.5	0.0956	0.3134	0.6833	0.079
H(31b)	8f	0.5	0.0840	0.3658	0.6685	0.130
H(32a)	8f	0.5	0.0665	0.4124	0.6303	0.079
H(32b)	8f	0.5	0.0473	0.4286	0.5928	0.130
H(33a)	8f	0.5	0.0521	0.3513	0.6889	0.079
H(33b)	8f	0.5	0.0352	0.3848	0.6595	0.130
H(34a)	8f	0.5	0.2160	0.5968	0.5593	0.118
H(34b)	8f	0.5	0.1624	0.5975	0.5109	0.058
H(35a)	8f	0.5	0.2328	0.4898	0.5339	0.118
H(35b)	8f	0.5	0.2153	0.6074	0.5625	0.058
H(36a)	8f	0.5	0.1987	0.5718	0.4317	0.128
H(36b)	8f	0.5	0.2208	0.4567	0.4819	0.065
H(37a)	8f	0.5	0.1605	0.6091	0.4535	0.128
H(37b)	8f	0.5	0.2029	0.5669	0.4330	0.065
H(38a)	8f	0.5	0.1941	0.5625	0.6697	0.063
H(38b)	8f	0.5	0.2064	0.5776	0.6613	0.120
H(39a)	8f	0.5	0.1441	0.5298	0.6086	0.063
H(39b)	8f	0.5	0.1539	0.5628	0.6066	0.120
H(40a)	8f	0.5	0.1753	0.4455	0.6751	0.063
H(40b)	8f	0.5	0.1809	0.4787	0.6767	0.120
H(41a)	8f	0.5	0.2412	0.3617	0.6646	0.102
H(41b)	8f	0.5	0.2268	0.3507	0.6742	0.070
H(42a)	8f	0.5	0.2460	0.3790	0.5857	0.102
H(42b)	8f	0.5	0.2413	0.3446	0.6055	0.070
H(43a)	8f	0.5	0.2592	0.4745	0.6494	0.102
H(43b)	8f	0.5	0.2574	0.4438	0.6665	0.070
H(44a)	8f	0.5	0.1265	0.3693	0.3045	0.124
H(44b)	8f	0.5	0.1386	0.3471	0.3153	0.085
H(45a)	8f	0.5	0.1622	0.4598	0.3131	0.124
H(45b)	8f	0.5	0.1747	0.4380	0.3265	0.085
H(46a)	8f	0.5	0.1783	0.3490	0.3619	0.124
H(46b)	8f	0.5	0.1881	0.3383	0.3870	0.085
H(47a)	8f	0.5	0.1082	0.5697	0.4138	0.097
H(47b)	8f	0.5	0.0938	0.5556	0.3701	0.091
H(48a)	8f	0.5	0.1215	0.5944	0.3449	0.097
H(48b)	8f	0.5	0.1137	0.5572	0.3086	0.091
H(49a)	8f	0.5	0.0853	0.5030	0.3324	0.097
H(49b)	8f	0.5	0.0844	0.4565	0.3102	0.091

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)	8*f*	0.19343(7)	0.2476(2)	0.7865(1)	0.094(1)	0.070(1)	0.060(1)	–0.010(1)	0.0352(8)	–0.005(1)
Ni(1)	8*f*	0.1317(1)	0.0982(3)	0.4945(2)	0.047(2)	0.048(2)	0.045(2)	0.002(2)	0.020(1)	–0.002(2)
Ni(2)	8*f*	0.0570(1)	0.2472(3)	0.4917(2)	0.042(1)	0.042(2)	0.047(1)	0.001(2)	0.016(1)	–0.001(2)
Ni(3)	8*f*	0.1413(1)	0.3503(3)	0.4912(2)	0.049(2)	0.051(2)	0.044(2)	–0.006(2)	0.017(1)	0.003(2)
Cl(1)	8*f*	0.0800(2)	0.2313(6)	0.3814(3)	0.061(3)	0.062(4)	0.039(3)	–0.003(3)	0.018(2)	–0.002(3)
Cl(2)	8*f*	0.0747(2)	0.4450(6)	0.4891(5)	0.063(4)	0.045(4)	0.086(5)	0.002(3)	0.029(3)	0.003(4)
Cl(3)	8*f*	0.0598(2)	0.0452(6)	0.4924(4)	0.054(3)	0.048(4)	0.074(4)	–0.002(3)	0.028(3)	–0.002(3)
Cl(4)	8*f*	0.1933(2)	0.2054(7)	0.4935(5)	0.058(4)	0.070(5)	0.102(5)	–0.003(3)	0.046(3)	0.000(4)
O(1)	8*f*	0.1264(5)	0.234(1)	0.5544(8)	0.042(3)	0.051(7)	0.037(7)	–0.002(7)	0.013(5)	–0.003(5)
N(1)	8*f*	0.1321(7)	–0.025(2)	0.414(1)	0.08(1)	0.06(1)	0.04(1)	0.01(1)	0.029(9)	–0.011(8)
N(2)	8*f*	0.1731(7)	–0.016(2)	0.588(1)	0.05(1)	0.05(1)	0.06(1)	0.012(9)	0.018(9)	0.007(8)
N(3)	8*f*	–0.0149(7)	0.260(2)	0.411(1)	0.046(5)	0.06(1)	0.06(1)	0.00(1)	–0.002(9)	0.00(1)
N(4)	8*f*	0.0370(6)	0.262(2)	0.585(1)	0.05(1)	0.07(1)	0.051(9)	0.00(1)	0.027(7)	–0.01(1)
N(5)	8*f*	0.1906(7)	0.457(2)	0.580(1)	0.06(1)	0.06(1)	0.06(1)	–0.02(1)	0.02(1)	–0.01(1)
N(6)	8*f*	0.1501(8)	0.453(2)	0.407(1)	0.09(2)	0.08(2)	0.04(1)	–0.03(1)	0.03(1)	0.02(1)

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