Crystal structure of the inorganic-organic hybrid material tris(*N*,*N*'-dimethylethylenediammonium) bis(hexachloridorhodate(III)) dihydrate, $C_6H_{23}Cl_6N_3ORh$

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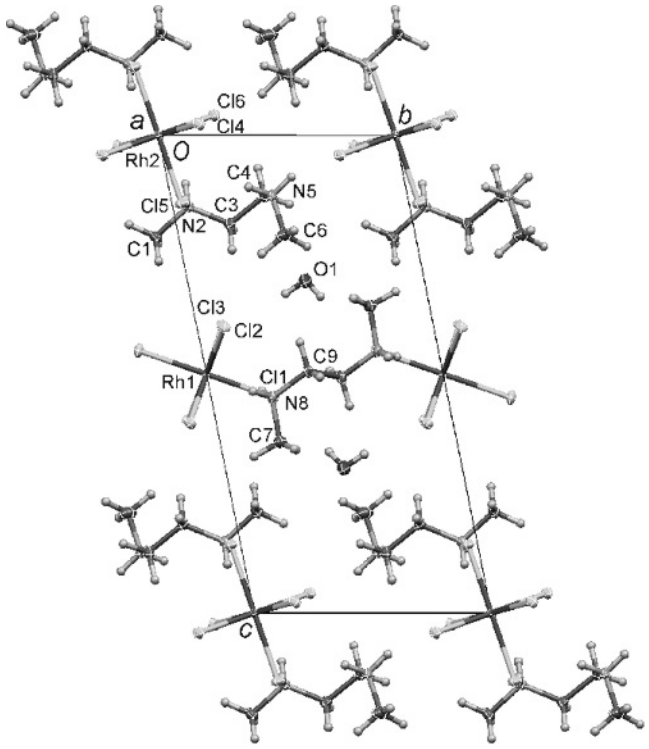

Abstract

$C_6H_{23}Cl_6N_3ORh$, triclinic, $P\bar{1}$ (no. 2), a = 6.9907(2) Å, b = 7.7437(3) Å, c = 15.8733(5) Å, α = 78.590(3)°, β = 89.035(2)°, γ = 85.304(2)°, V = 839.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.0292, $wR_{ref}(F^2)$ = 0.0585, T = 295 K.

Source of material

$(C_4H_{14}N_2)_3[RhCl_6]_2{\cdot}2H_2O$ was obtained according to the previously reported method [1, 2]. The solution of *N*,*N*'-dimethylethylenediamine (0.12 ml, 1.11 mmol) in 3 ml of concentrated hydrochloric acid was carefully added to the test tube containing 0.10 ml solution of $RhCl_3{\cdot}3H_2O$ (0.15 mmol $RhCl_3$) in 6 mol/l hydrochloric acid covered by an 1 ml layer of concentrated hydrochloric acid. The obtained triple-phase system was left at room temperature forming single crystals.

Experimental details

All H atoms were located in subsequent difference Fourier maps. The riding model was applied to the H atoms bonded to C and N atoms, whereas the positions of the water H atoms were refined restraining the O–H and H···H distances to 0.83 and 1.35 Å, respectively [10]. The isotropic displacement parameters of H atoms were constrained to 1.2 and 1.5 times that of the equivalent isotropic displacement parameters of their parent N/C-methylene and O/C-methyl atoms, respectively.

Table 1. Data collection and handling.

Crystal:	red needles, size 0.05×0.10×0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	19.61 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	68.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	24550, 6597
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5036
$N(param)_{refined}$:	167
Programs:	CrysAlis Pro [9], SHELX [10], MERCURY [11]

Discussion

Crystal engineering of inorganic-organic hybrid materials is relevant to several important applications including *e.g.* gas storage, chemical separation and catalysis [3, 4]. Halogenidorhodates(III) with organic cations constitute a subgroup of the large family of inorganic-organic hybrids. The properties of those mixed materials relate to both the inorganic rigid structural skeleton that is usually given by the arrangement of isolated $[RhX_6]^{3-}$ octahedra, and to the more flexible organic substructure. Also, in most cases, along with the mononuclear inorganic anions water molecules and/or aquahydrogen cations are present in the inorganic segments of those solids [5, 6]. The asymmetric unit of the title hexachloridorhodate(III) consists of two half isolated inorganic $[RhCl_6]^{3-}$ octahedra, one and a half of the flexible organic $(C_4H_{14}N_2)^{2+}$ cations, and one water molecule. The components of the solid are joined by N/C/O–H···Cl hydrogen bonds. The shortest is an O–H···Cl bond with the O···Cl distance of 3.217(2) Å.The most characteristic structural feature of the solid is the presence of two independent octahedra with significantly different environments. The arrangement of chlorido ligands around the central Rh^{III} atoms slightly deviates from the ideal octahedral geometry. The lengths of crystallographically independent Rh–Cl bonds vary from 2.3379(5) to 2.3480(5) Å and from 2.3422(5) to 2.3525(5) Å for the $[Rh1Cl_6]^{3-}$ and $[Rh2Cl_6]^{3-}$ octahedron, respectively. The Cl–Rh–Cl angles involving Cl atoms mutually *cis* to each other are close to the ideal value of 90°- they range from 89.335(17) to 90.665(17)° and from 89.351(19) to 90.649(19)° for $[Rh1Cl_6]^{3-}$ and $[Rh2Cl_6]^{3-}$, respectively. The $[Rh1Cl_6]^{3-}$ octahedron is surrounded by six N8N8^{I} cations (^{I} –*x*, 1–*y*, 1–*z*; all located at inversion centres) and four water molecules, whereas

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the environment of the $[Rh2Cl_6]^{3-}$ octahedron is composed of only six N2N5 organic cations, all in general positions. Furthermore, only in the case of the N2N5 cations both nitrogen atoms, belonging to the same ion, are involved in hydrogen-bonding interactions with the same $[Rh2Cl_6]^{3-}$ octahedron. As a result the cations adopt different conformations that are clearly reflected in the different torsion angles as well as N···N and the terminal methyl C···C distances of 3.224(3) and 4.971(4) Å, and 3.793(3) and 5.344(5) Å for the N2N5 and $N8N8^{I}$ cation, respectively. The N/C–C bond lengths and N/C–C/N–C angles within $(C_4H_{14}N_2)^{2+}$ cations are similar in both ions and consistent with the values found in the structures of related compounds [7]. A closely related structure of a hexachloridorhodate(III), containing two halves of $[RhCl_6]^{3-}$ octahedra, organic cations and a water molecule in the asymmetric unit, but with somewhat different preferences of the N/O–H···Cl hydrogen-bonds formation to the inorganic octahedra was found for tris(guanidinium) hexachloridorhodate(III) monohydrate [8].

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

Atom	Site	x	y	z	U_{iso}
H(11)	2*i*	0.5108	–0.1990	0.1874	0.063
H(12)	2*i*	0.4473	–0.1054	0.2635	0.063
H(13)	2*i*	0.6568	–0.0944	0.2272	0.063
H(21)	2*i*	0.5340	0.0732	0.1020	0.037
H(22)	2*i*	0.3386	0.0610	0.1346	0.037
H(31)	2*i*	0.6099	0.2360	0.1981	0.042
H(32)	2*i*	0.4063	0.2139	0.2397	0.042
H(41)	2*i*	0.4540	0.4939	0.1445	0.046
H(42)	2*i*	0.4428	0.3922	0.0691	0.046
H(51)	2*i*	0.1548	0.5267	0.0869	0.045
H(52)	2*i*	0.1366	0.3378	0.1087	0.045
H(61)	2*i*	–0.0358	0.4911	0.1997	0.095
H(62)	2*i*	0.1622	0.5318	0.2331	0.095
H(63)	2*i*	0.1048	0.3365	0.2481	0.095
H(71)	2*i*	–0.0135	0.1319	0.6724	0.060
H(72)	2*i*	–0.1490	0.3068	0.6566	0.060
H(73)	2*i*	0.0741	0.3154	0.6584	0.060
H(81)	2*i*	–0.0995	0.1816	0.5363	0.035
H(82)	2*i*	0.1005	0.2196	0.5355	0.035
H(91)	2*i*	–0.1981	0.4766	0.5063	0.039
H(92)	2*i*	–0.0652	0.4229	0.4335	0.039
H(1)	2*i*	0.497(4)	0.548(5)	0.337(2)	0.140
H(2)	2*i*	0.602(6)	0.402(3)	0.332(2)	0.140

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}
Rh(1)	1*f*	½	0	½	0.0158(1)	0.0175(1)	0.0228(1)	–0.00017(7)	–0.00079(7)	–0.00309(8)
Cl(1)	2*i*	0.47989(7)	0.26603(7)	0.54938(4)	0.0313(3)	0.0241(3)	0.0464(3)	–0.0009(2)	0.0007(2)	–0.0145(2)
Cl(2)	2*i*	0.25194(7)	0.11466(7)	0.40197(3)	0.0226(2)	0.0371(3)	0.0289(2)	0.0022(2)	–0.0051(2)	–0.0007(2)
Cl(3)	2*i*	0.73011(7)	0.10927(7)	0.39811(3)	0.0235(2)	0.0316(3)	0.0314(2)	–0.0034(2)	0.0040(2)	–0.0010(2)
Rh(2)	1*a*	0	0	0	0.0209(1)	0.0218(1)	0.0192(1)	–0.00030(8)	–0.00036(7)	–0.00376(8)
Cl(4)	2*i*	–0.28719(7)	0.18056(7)	–0.02389(3)	0.0261(2)	0.0316(3)	0.0363(3)	0.0058(2)	–0.0002(2)	–0.0021(2)
Cl(5)	2*i*	0.00179(8)	0.04128(8)	0.14280(3)	0.0369(3)	0.0451(3)	0.0220(2)	–0.0081(2)	0.0018(2)	–0.0097(2)
Cl(6)	2*i*	0.17220(7)	0.25172(7)	–0.04172(3)	0.0355(3)	0.0309(3)	0.0317(3)	–0.0090(2)	0.0012(2)	–0.0046(2)
C(1)	2*i*	0.5247(3)	–0.0978(3)	0.2126(2)	0.046(1)	0.034(1)	0.040(1)	0.001(1)	–0.002(1)	0.003(1)
N(2)	2*i*	0.4612(3)	0.0664(2)	0.1497(1)	0.0341(9)	0.030(1)	0.0285(9)	–0.0030(8)	–0.0012(7)	–0.0044(7)
C(3)	2*i*	0.4761(3)	0.2266(3)	0.1857(1)	0.041(1)	0.034(1)	0.032(1)	–0.000(1)	–0.0058(9)	–0.0097(9)
C(4)	2*i*	0.3993(3)	0.3953(3)	0.1272(2)	0.045(1)	0.031(1)	0.039(1)	–0.006(1)	–0.003(1)	–0.006(1)
N(5)	2*i*	0.1868(3)	0.4281(3)	0.1262(1)	0.053(1)	0.028(1)	0.031(1)	0.0036(9)	–0.0081(8)	–0.0070(8)
C(6)	2*i*	0.0966(4)	0.4487(5)	0.2091(2)	0.076(2)	0.075(2)	0.037(2)	0.023(2)	–0.002(1)	–0.015(2)
C(7)	2*i*	–0.0276(3)	0.2526(3)	0.6422(1)	0.046(1)	0.041(1)	0.033(1)	–0.005(1)	0.003(1)	–0.009(1)
N(8)	2*i*	–0.0191(2)	0.2579(2)	0.5489(1)	0.0310(9)	0.0232(9)	0.0342(9)	–0.0026(7)	0.0003(7)	–0.0079(7)
C(9)	2*i*	–0.0687(3)	0.4342(3)	0.4933(2)	0.031(1)	0.025(1)	0.041(1)	–0.0042(9)	–0.0099(9)	–0.0022(9)
O(1)	2*i*	0.5667(5)	0.4989(3)	0.3040(2)	0.185(2)	0.040(1)	0.053(1)	0.011(2)	–0.032(2)	–0.009(1)

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