

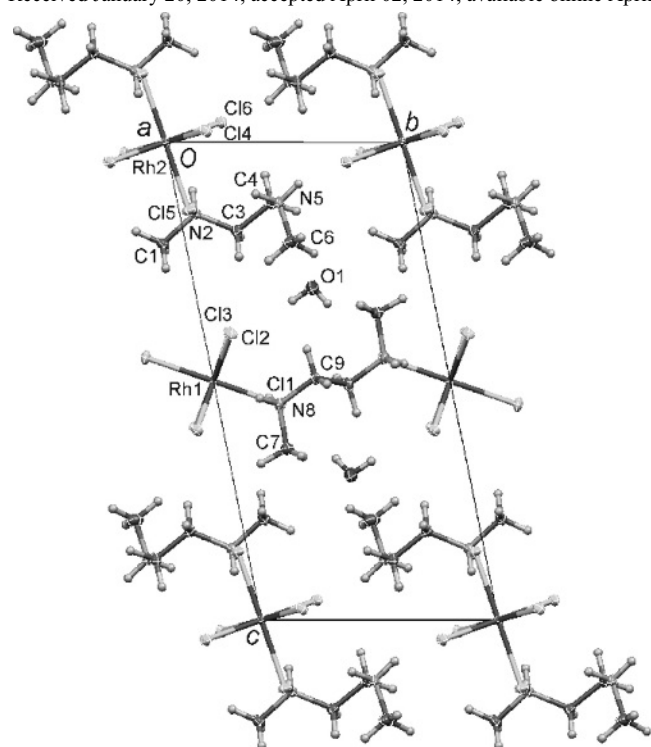
Crystal structure of the inorganic-organic hybrid material tris(*N,N*-dimethylethylenediammonium) bis(hexachloridorhodate(III)) dihydrate, $C_6H_{23}Cl_6N_3ORh$

Maciej Bujak^{*,I,II} and Walter Frank^{*,I}

^I Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Material- und Strukturforchung, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

^{II} Permanent address: Faculty of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland

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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, $\alpha = 78.590(3)^\circ$, $\beta = 89.035(2)^\circ$, $\gamma = 85.304(2)^\circ$, $V = 839.5$ Å³, $Z = 2$, $R_{gt}(F) = 0.0292$, $wR_{ref}(F^2) = 0.0585$, $T = 295$ 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}
Diffractionmeter, 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

* Correspondence author (e-mail: wfrank@uni-duesseldorf.de, maciej.bujak@uni-duesseldorf.de and mbujak@uni.opole.pl)

the environment of the [Rh₂Cl₆]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 [Rh₂Cl₆]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 N₈N₈¹ cation, respectively. The N/C–C bond lengths and N/C–C/N–C angles within (C₄H₁₄N₂)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 [RhCl₆]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 Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(11)	2i	0.5108	−0.1990	0.1874	0.063

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Rh(1)	1f	½	0	½	0.0158(1)	0.0175(1)	0.0228(1)	−0.00017(7)	−0.00079(7)	−0.00309(8)
Cl(1)	2i	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)	2i	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)	2i	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)	1a	0	0	0	0.0209(1)	0.0218(1)	0.0192(1)	−0.00030(8)	−0.00036(7)	−0.00376(8)
Cl(4)	2i	−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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	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)	2i	−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)	2i	−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)	2i	−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)	2i	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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Table 2. continued.

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