Crystal structure of the inorganic-organic hybrid material bis(*N*,*N*-dimethyl-1,3-diammoniopropane) hexachloridorhodate(III) chloride, $[(CH_3)_2NH(CH_2)_3NH_3]_2[RhCl_6]Cl$, $C_{10}H_{32}Cl_7N_4Rh$

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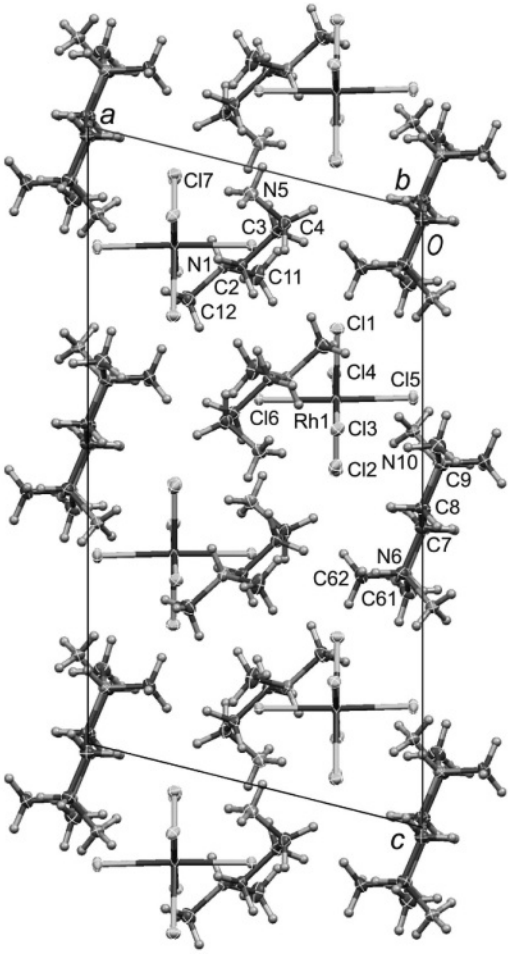

Abstract

$C_{10}H_{32}Cl_7N_4Rh$, monoclinic, $P2_1/c$ (no. 14), a = 10.6247(1) Å, b = 11.2582(1) Å, c = 19.0137(2) Å, β = 104.100(1)°, V = 2205.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.0306, $wR_{ref}(F^2)$ = 0.0889, T = 295 K.

Source of material

$[(CH_3)_2NH(CH_2)_3NH_3]_2[RhCl_6]Cl$ was synthesized on the basis of a previously described procedure [7]. *N*,*N*-Dimethyl-1,3-diaminopropane (0.14 ml, 1.12 mmol) was slowly added, with stirring, to 3 ml of concentrated hydrochloric acid. This solution was carefully transferred to a 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-layer system yielded single crystals of the title compound.

Table 1. Data collection and handling.

Crystal:	red irregular, size 0.17×0.26×0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.23 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	81690, 6414
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5506
$N(param)_{refined}$:	205
Programs:	CrysAlis Pro [8], SHELX [9], MERCURY [10]

Experimental details

All the H-atoms were located in subsequent difference Fourier maps and then the riding model based on idealized bond lengths and angles, allowing free rotation of the $-CH_3$ and $-NH_3^+$ groups, was applied. The isotropic displacement parameters of H-atoms were constrained to values 1.5 and 1.2 times larger than the equivalent displacement parameters of their carrier atoms of the $-CH_3$, $-NH_3^+$, and $=CH_2$, $\equiv NH^+$ groups, respectively [8].

Discussion

The inorganic-organic title hybrid material might be considered as an addition compound $[(CH_3)_2NH(CH_2)_3NH_3]_3[RhCl_6]_2 \cdot [(CH_3)_2NH(CH_2)_3NH_3]Cl_2$ consisting of diammonium hexachloridorhodate(III) and diammonium dihydrochloride. The formula clearly shows a close relationship to *Gutbier's* 'rhodium heptachloride' $[H_3N(CH_2)_2NH_3]_2[RhCl_7]$ [1] that played an important role in the rhodium refining process for a long time. The structure of that and other rhodium containing compounds were later discussed by *Werner* [2] with respect to the apparent heptacoordinated rhodium center and the substances were shown, like the title hybrid and some other diammonioalkane chloridorhodates(III) [3, 4], to be hexachloridorhodate(III) chlorides. The asymmetric unit of $[(CH_3)_2NH(CH_2)_3NH_3]_2[RhCl_6]Cl$ consists of one $[RhCl_6]^{3-}$ octahedron, one non-coordinated Cl^- ion and two $[(CH_3)_2NH(CH_2)_3NH_3]^{2+}$ cations that adopt an extended conformation with expected dimensions [5]. The crystal packing is established by N/C–H···Cl hydrogen bonds, that are formed between the oppositely charged components of the solid, with the shortest N···Cl and C···Cl distances of 3.227(2) and 3.394(3) Å, respectively. The octahedral complex $[RhCl_6]^{3-}$ is somewhat distorted from the ideal geometry with Rh–Cl distances that range from 2.3465(6) to 2.3767(5) Å, giving the maxi-

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mum difference of 0.0302(8) Å. The Cl–Rh–Cl angles involving Cl atoms mutually *cis* and *trans* to each other are also slightly distorted and range from 87.98(2) to 91.29(2)°, and from 177.50(2) to 179.16(2)°, respectively. Although the octahedral distortion found in the title compound is quite significant, it is not the first example of such large differences in Rh–Cl bond lengths. A similar situation with even larger Rh–Cl deviation (0.035(3) Å) within the same octahedron was found in the structure of bis(1,2-diammoniopropane) hexachloridorhodate(III) chloride [3], whereas the largest linear distortion (difference in Rh–Cl bond lengths of 0.215(16) Å) was reported for the $[Rh_2Cl_9]^{3-}$ dinuclear anion in the structure of trimethylphenylammonium nonachloridodirhodate(III) [6].

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.6295	0.5181	0.1345	0.039
H(111)	4*e*	0.4333	0.5947	0.1260	0.084
H(112)	4*e*	0.5333	0.6694	0.1833	0.084
H(113)	4*e*	0.4479	0.5730	0.2091	0.084
H(121)	4*e*	0.7685	0.4551	0.2363	0.077
H(122)	4*e*	0.6677	0.4898	0.2808	0.077
H(123)	4*e*	0.7350	0.5890	0.2451	0.077
H(21)	4*e*	0.5063	0.3593	0.2045	0.038
H(22)	4*e*	0.6108	0.3239	0.1627	0.038
H(31)	4*e*	0.4605	0.4027	0.0547	0.043
H(32)	4*e*	0.3558	0.3995	0.1004	0.043
H(41)	4*e*	0.4122	0.1891	0.1210	0.052
H(42)	4*e*	0.3271	0.2226	0.0439	0.052
H(51)	4*e*	0.5406	0.1127	0.0642	0.068
H(52)	4*e*	0.5789	0.2319	0.0486	0.068
H(53)	4*e*	0.4786	0.1695	–0.0041	0.068
H(6)	4*e*	–0.0015	0.7542	0.6174	0.040
H(611)	4*e*	0.0703	0.9235	0.6766	0.079
H(612)	4*e*	–0.0439	0.9531	0.6094	0.079
H(613)	4*e*	0.1001	0.9746	0.6057	0.079
H(621)	4*e*	0.2205	0.7684	0.6684	0.071
H(622)	4*e*	0.2356	0.7885	0.5893	0.071
H(623)	4*e*	0.1808	0.6677	0.6102	0.071
H(71)	4*e*	0.0424	0.8523	0.4932	0.040
H(72)	4*e*	–0.0953	0.8252	0.5057	0.040
H(81)	4*e*	–0.0496	0.6203	0.5083	0.049
H(82)	4*e*	0.0875	0.6479	0.4950	0.049
H(91)	4*e*	–0.0793	0.5914	0.3884	0.056
H(92)	4*e*	–0.1405	0.7169	0.3931	0.056
H(101)	4*e*	–0.0182	0.7660	0.3239	0.067
H(102)	4*e*	0.0705	0.6668	0.3449	0.067
H(103)	4*e*	0.0855	0.7730	0.3896	0.067

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)	4*e*	0.25816(2)	0.41581(2)	0.342372(9)	0.02317(9)	0.02656(9)	0.02521(9)	–0.00092(6)	0.00617(6)	0.00237(6)
Cl(1)	4*e*	0.25507(6)	0.33994(6)	0.22702(3)	0.0422(3)	0.0404(3)	0.0299(3)	–0.0033(2)	0.0104(2)	–0.0049(2)
Cl(2)	4*e*	0.25837(6)	0.49328(6)	0.45727(3)	0.0376(3)	0.0391(3)	0.0295(3)	0.0022(2)	0.0113(2)	0.0000(2)
Cl(3)	4*e*	0.25471(6)	0.22272(5)	0.38954(4)	0.0418(3)	0.0275(3)	0.0445(3)	0.0013(2)	0.0196(3)	0.0070(2)
Cl(4)	4*e*	0.26396(6)	0.61215(5)	0.30041(3)	0.0398(3)	0.0290(3)	0.0330(3)	–0.0018(2)	0.0080(2)	0.0056(2)
Cl(5)	4*e*	0.02813(5)	0.41720(6)	0.30783(4)	0.0214(2)	0.0433(3)	0.0437(3)	–0.0014(2)	0.0052(2)	0.0074(2)
Cl(6)	4*e*	0.48879(5)	0.41338(5)	0.37362(3)	0.0211(2)	0.0346(3)	0.0307(3)	–0.0006(2)	0.0046(2)	0.0008(2)
Cl(7)	4*e*	0.73902(6)	0.39613(6)	0.04908(4)	0.0348(3)	0.0449(3)	0.0472(3)	0.0020(2)	0.0185(3)	–0.0051(3)
N(1)	4*e*	0.5947(2)	0.5023(2)	0.1727(1)	0.0292(9)	0.031(1)	0.039(1)	0.0014(8)	0.0109(8)	0.0015(8)
C(11)	4*e*	0.4934(3)	0.5929(3)	0.1728(2)	0.047(2)	0.032(1)	0.094(3)	0.007(1)	0.025(2)	–0.004(2)
C(12)	4*e*	0.7008(3)	0.5097(3)	0.2396(2)	0.050(2)	0.051(2)	0.047(2)	–0.012(1)	0.001(1)	–0.002(1)
C(2)	4*e*	0.5409(2)	0.3790(2)	0.1632(1)	0.034(1)	0.028(1)	0.035(1)	0.0016(9)	0.0092(9)	–0.0013(9)
C(3)	4*e*	0.4354(2)	0.3632(2)	0.0945(1)	0.032(1)	0.039(1)	0.038(1)	0.005(1)	0.0084(9)	–0.002(1)
C(4)	4*e*	0.4119(3)	0.2323(3)	0.0768(2)	0.035(1)	0.047(2)	0.048(2)	–0.004(1)	0.011(1)	–0.012(1)
N(5)	4*e*	0.5127(2)	0.1815(2)	0.0430(1)	0.046(1)	0.047(1)	0.042(1)	0.006(1)	0.007(1)	–0.013(1)
N(6)	4*e*	0.0495(2)	0.8008(2)	0.5967(1)	0.032(1)	0.037(1)	0.032(1)	–0.0035(8)	0.0092(8)	0.0015(8)
C(61)	4*e*	0.0435(4)	0.9240(3)	0.6246(2)	0.062(2)	0.042(2)	0.050(2)	–0.001(1)	0.007(2)	–0.011(1)
C(62)	4*e*	0.1835(3)	0.7520(3)	0.6180(2)	0.034(1)	0.062(2)	0.041(1)	0.003(1)	0.000(1)	0.002(1)
C(7)	4*e*	–0.0060(2)	0.7981(2)	0.5164(1)	0.033(1)	0.040(1)	0.030(1)	0.0000(9)	0.0102(9)	0.0031(9)
C(8)	4*e*	–0.0018(3)	0.6748(3)	0.4850(1)	0.046(1)	0.040(1)	0.037(1)	–0.001(1)	0.011(1)	0.001(1)
C(9)	4*e*	–0.0596(3)	0.6728(3)	0.4038(2)	0.042(1)	0.062(2)	0.035(1)	–0.011(1)	0.009(1)	–0.006(1)
N(10)	4*e*	0.0285(2)	0.7249(2)	0.3613(1)	0.041(1)	0.060(2)	0.035(1)	0.003(1)	0.0126(9)	–0.004(1)

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