

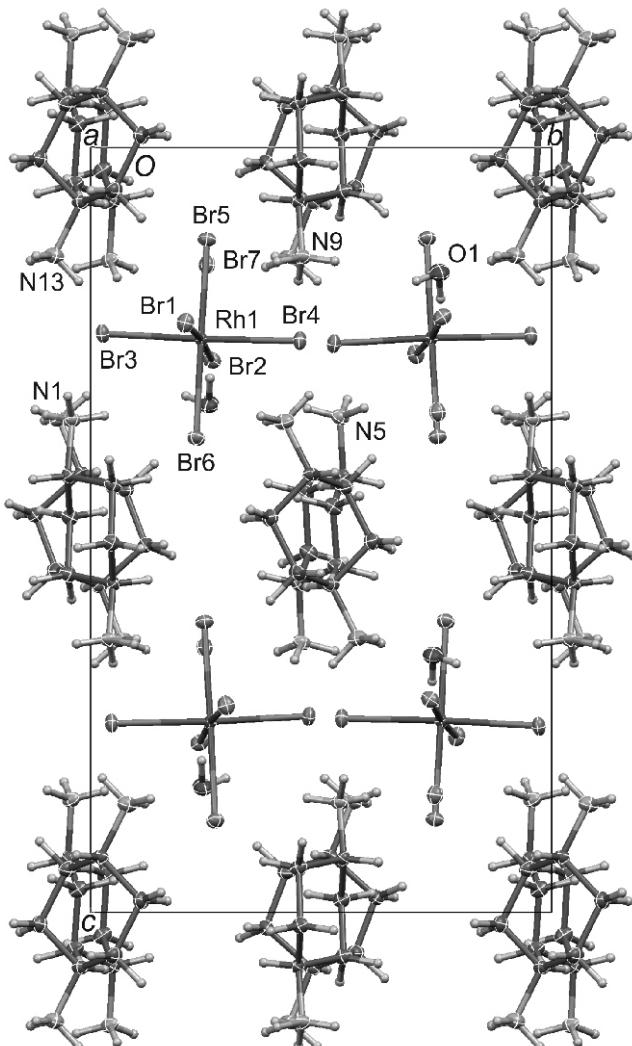
Crystal structure of the layered inorganic-organic hybrid material bis(*trans*-cyclohexane-1,4-diammonium) hexabromidorhodate(III) bromide monohydrate, $C_{12}H_{34}Br_7N_4ORh$

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Abstract

$C_{12}H_{34}Br_7N_4ORh$, monoclinic, $P2_1/c$ (no. 14), $a = 11.3677(5)$ Å, $b = 11.4644(5)$ Å, $c = 19.0407(9)$ Å, $\beta = 92.443(4)^\circ$, $V = 2479.2$ Å³, $Z = 4$, $R_{gt}(F) = 0.0290$, $wR_{ref}(F^2) = 0.0578$, $T = 295$ K.

Source of material

($C_6H_{16}N_2$)₂[RhBr₆]Br·H₂O was prepared according to a general, previously reported procedure [1, 2]. *Trans*-1,4-

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diaminocyclohexane (80.0 mg, 0.70 mmol) was dissolved in 3.5 ml of concentrated hydrobromic acid. This solution was transferred to a glass tube (the internal diameter of 5 mm and the wall 3.5 mm thick) containing 0.10 ml solution of RhCl₃·3H₂O (0.15 mmol RhCl₃) in 6 mol/l hydrochloric acid. The tube was sealed by melting the top, transferred into an oven and heated up to *ca.* 400 K. The single crystals were grown by cooling (0.5 K·min⁻¹) the reaction mixture down to *ca.* 295 K slowly.

Table 1. Data collection and handling.

Crystal:	dark red plates, size 0.10×0.20×0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	119.81 cm ⁻¹
Diffractometer, scan mode:	STADI4 CCD, ω
$2\theta_{\max}$:	53°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	16858, 5082
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3122
$N(\text{param})_{\text{refined}}$:	236
Programs:	CrysAlis CCD [11], CrysAlis Pro [12], SHELX [13], MERCURY [14]

Experimental details

A suitable single crystal was sealed in a thin-walled glass capillary. All the intensity data were recorded for Lorentz, polarisation and absorption corrections [12]. The structure was solved by the Patterson method and refined by the full-matrix least-squares method against F^2 using SHELX-97 [13]. Anisotropic displacement parameters were refined for all the non-H atoms. All the H atom positions were located in the subsequent difference Fourier maps. The riding model was applied for 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 1.31 Å with the standard uncertainties of 0.02 and 0.03, respectively [13]. 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 C and N/O atoms, respectively.

Discussion

The interest in crystal engineering of inorganic-organic materials derives from both fundamental and practical aspects and is concentrated on techniques and methods to design, synthesize as well as control the final properties of a desired hybrid material. One of the main strategies in crystal engineering of those mixed materials is based on systematic construction of crystalline solids using simple inorganic and organic building blocks in relation to knowledge of their self-organization behaviour influenced by formation of specific interactions *e.g.* hydrogen bonds [3, 4]. The solid-state structure of ($C_6H_{16}N_2$)₂[RhBr₆]Br·H₂O consists of iso-

lated [RhBr₆]³⁻ octahedra, isolated Br⁻ ions, organic (C₆H₁₆N₂)²⁺ cations and water molecules. It could be described as an alternating inorganic-organic layered packing in which organic layers are built from the organic cations, whereas the inorganic ones are formed by inorganic [RhBr₆]³⁻ and Br⁻ ions, and water molecules. Both layers are held together by the N/C/O-H...Br/O hydrogen bonds. The arrangement of hydrogen bonded ions forming anionic inorganic layers is similar to those found in the related chloridorhodates(III) [5-7]. The diprotonated (C₆H₁₆N₂)²⁺ cations, that all lie on inversion centres, adopt a *trans* conformation with the expected dimensions [8]. The [RhBr₆]³⁻ ions are distorted from an ideal octahedral geometry with the Rh-Br distances ranging from 2.4658(5) to 2.5157(5) Å (difference of 0.0499(7) Å). Both the Br-Rh-Br angles involving Br atoms mutually *cis* and *trans* to each other are also distorted from the ideal values of 90 and 180° - they range from 88.08(2) to 93.08(2)° and from 176.06(2) to 178.62(2)°, respectively. It is noteworthy that the average Br-Rh-Br *cis* angle is 90.0°. The octahedral distortion, both in terms of differences between Rh-Br bond lengths as well as Br-Rh-Br angles, found in (C₆H₁₆N₂)₂[RhBr₆]Br·H₂O is the largest among all hexabromidorhodate(III) compounds and is associated with the presence of N-H...Br hydrogen bonds between the anionic substructure and the organic cations. The linear distortion from ideal octahedral geometry in (C₆H₁₆N₂)₂[RhBr₆]Br·H₂O is less pronounced than that in the [Rh₂Cl₉]³⁻ dinuclear anion in the structure of trimethylphenylammonium nonachloridodirhodate(III), where the differences in Rh-Cl bond lengths are 0.215(16) Å [9], but on the other hand is clearly more pronounced than in the most distorted isolated [RhCl₆]³⁻ octahedron found in the structure of bis(1,2-diammoniopropane) hexachloridorhodate(III) chloride (0.035(3) Å [10]).

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)	4e	0.4382	-0.1199	0.3433	0.060
H(12)	4e	0.5632	-0.0994	0.3571	0.060
H(13)	4e	0.4897	-0.0085	0.3252	0.060
H(21)	4e	0.3882	0.0127	0.4248	0.036
H(31)	4e	0.6331	0.0447	0.4464	0.047
H(32)	4e	0.5455	0.1379	0.4139	0.047
H(41)	4e	0.4554	0.1583	0.5196	0.047
H(42)	4e	0.5913	0.1760	0.5337	0.047
H(51)	4e	0.5303	0.5573	0.3299	0.055
H(52)	4e	0.4099	0.5933	0.3408	0.055
H(53)	4e	0.4403	0.4702	0.3416	0.055
H(61)	4e	0.5195	0.6275	0.4405	0.035
H(71)	4e	0.3515	0.4496	0.4584	0.042
H(72)	4e	0.3228	0.5836	0.4559	0.042
H(81)	4e	0.5679	0.3857	0.4396	0.042
H(82)	4e	0.6610	0.4839	0.4267	0.042
H(91)	4e	0.0048	0.4510	0.1743	0.050
H(92)	4e	-0.1087	0.4046	0.1499	0.050
H(93)	4e	-0.0879	0.5297	0.1491	0.050
H(101)	4e	0.0282	0.3757	0.0656	0.033
H(111)	4e	-0.1684	0.3906	0.0247	0.040
H(112)	4e	-0.1599	0.5271	0.0237	0.040
H(121)	4e	0.0386	0.6234	0.0667	0.040
H(122)	4e	0.1429	0.5408	0.0909	0.040
H(131)	4e	0.0361	-0.0260	0.1753	0.063
H(132)	4e	0.0920	-0.1298	0.1483	0.063
H(133)	4e	-0.0353	-0.1175	0.1422	0.063
H(141)	4e	0.1115	0.0303	0.0746	0.037
H(151)	4e	-0.0038	-0.1659	0.0148	0.046
H(152)	4e	0.1333	-0.1524	0.0257	0.046
H(161)	4e	0.1347	-0.0015	-0.0570	0.047
H(162)	4e	0.0723	-0.1099	-0.0925	0.047
H(1)	4e	0.272(4)	0.759(5)	0.198(2)	0.075
H(2)	4e	0.177(2)	0.707(2)	0.175(3)	0.075

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)	4e	0.24537(3)	0.23996(3)	0.25076(2)	0.0192(2)	0.0217(2)	0.0274(2)	0.0003(1)	0.0021(1)	0.0014(2)
Br(1)	4e	0.03266(4)	0.20576(4)	0.22956(3)	0.0208(2)	0.0375(3)	0.0497(4)	-0.0014(2)	0.0012(2)	-0.0035(3)
Br(2)	4e	0.46257(4)	0.26313(4)	0.27811(3)	0.0224(2)	0.0428(3)	0.0374(3)	-0.0021(2)	-0.0003(2)	0.0057(2)
Br(3)	4e	0.27754(4)	0.02704(4)	0.24355(3)	0.0367(3)	0.0242(3)	0.0478(4)	0.0032(2)	0.0050(2)	0.0021(2)
Br(4)	4e	0.21293(4)	0.45461(4)	0.25312(3)	0.0373(3)	0.0232(3)	0.0487(4)	0.0017(2)	-0.0026(2)	-0.0007(2)
Br(5)	4e	0.26869(4)	0.25289(4)	0.12102(3)	0.0339(3)	0.0438(3)	0.0285(3)	-0.0009(2)	0.0037(2)	0.0020(2)
Br(6)	4e	0.21726(4)	0.22936(4)	0.38035(3)	0.0402(3)	0.0411(3)	0.0300(3)	0.0002(2)	0.0072(2)	0.0024(2)
Br(7)	4e	0.73572(4)	0.25254(4)	0.15357(3)	0.0313(3)	0.0329(3)	0.0475(4)	-0.0025(2)	0.0011(2)	-0.0020(3)
N(1)	4e	0.4921(3)	-0.0668(4)	0.3561(2)	0.041(2)	0.053(3)	0.026(3)	0.006(2)	0.000(2)	-0.010(2)
C(2)	4e	0.4674(4)	-0.0211(4)	0.4270(3)	0.028(2)	0.036(3)	0.025(3)	0.008(2)	-0.002(2)	-0.007(2)
C(3)	4e	0.5534(4)	0.0745(4)	0.4475(3)	0.047(3)	0.043(3)	0.027(4)	-0.006(2)	-0.001(3)	0.000(2)
C(4)	4e	0.5312(5)	0.1194(4)	0.5200(3)	0.051(3)	0.033(3)	0.033(4)	-0.003(2)	-0.005(3)	-0.003(2)
N(5)	4e	0.4655(3)	0.5416(3)	0.3528(2)	0.036(2)	0.042(2)	0.031(3)	0.009(2)	0.003(2)	0.005(2)
C(6)	4e	0.4924(4)	0.5481(4)	0.4297(3)	0.027(2)	0.030(3)	0.031(4)	0.000(2)	0.003(2)	0.002(2)
C(7)	4e	0.3824(4)	0.5265(4)	0.4698(3)	0.022(2)	0.045(3)	0.039(4)	0.000(2)	0.001(2)	0.007(3)
C(8)	4e	0.5909(4)	0.4650(4)	0.4517(3)	0.025(2)	0.046(3)	0.035(4)	0.005(2)	0.009(2)	0.007(2)
N(9)	4e	-0.0554(3)	0.4599(3)	0.1433(2)	0.037(2)	0.039(2)	0.026(3)	-0.004(2)	0.005(2)	0.001(2)
C(10)	4e	-0.0121(4)	0.4506(4)	0.0704(3)	0.030(2)	0.027(2)	0.027(3)	0.004(2)	0.004(2)	-0.002(2)
C(11)	4e	-0.1161(4)	0.4557(4)	0.0169(3)	0.027(2)	0.038(3)	0.035(4)	-0.005(2)	0.005(2)	-0.001(2)
C(12)	4e	0.0755(4)	0.5487(4)	0.0582(3)	0.031(3)	0.039(3)	0.030(4)	-0.003(2)	0.003(2)	-0.004(2)
N(13)	4e	0.0329(3)	-0.0795(4)	0.1414(2)	0.039(2)	0.053(3)	0.034(3)	0.006(2)	0.002(2)	0.005(2)
C(14)	4e	0.0430(4)	-0.0216(4)	0.0721(3)	0.030(3)	0.037(3)	0.025(3)	-0.005(2)	0.003(2)	0.000(2)
C(15)	4e	0.0605(4)	-0.1102(4)	0.0156(3)	0.043(3)	0.033(3)	0.040(4)	0.013(2)	0.004(3)	0.001(3)
C(16)	4e	0.0655(4)	-0.0509(4)	-0.0564(3)	0.041(3)	0.042(3)	0.034(4)	0.015(2)	0.005(3)	-0.003(3)
O(1)	4e	0.2237(3)	0.7567(3)	0.1638(2)	0.055(2)	0.055(2)	0.038(3)	-0.004(2)	-0.014(2)	0.001(2)

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