Crystal structure of 2,2'-bipyridindiium (2,2'-bipyridyl-κ^2*N*,*N*')-tetrabromidorhodate(III) bromide, $(C_{10}H_{10}N_2)[RhBr_4(C_{10}H_8N_2)]Br$, $C_{20}H_{18}Br_5N_4Rh$

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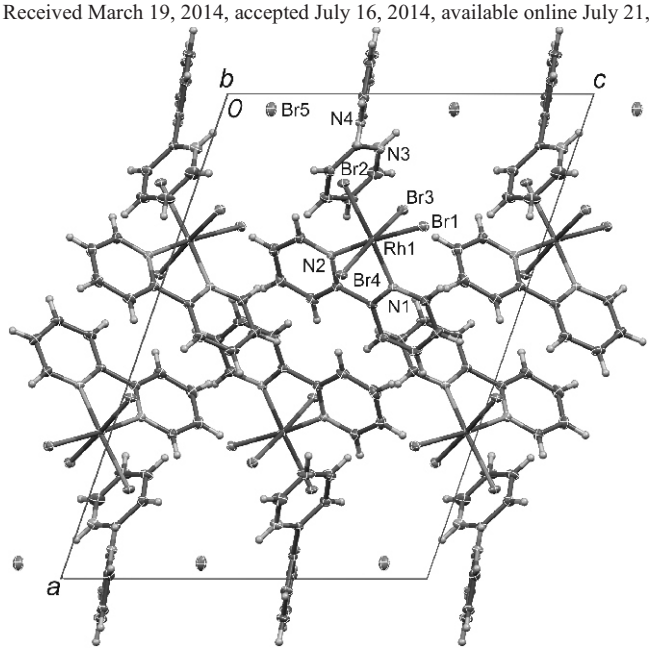

Abstract

$C_{20}H_{18}Br_5N_4Rh$, monoclinic, $P2_1/c$ (no. 14), a = 19.0663(3) Å, b = 9.9988(1) Å, c = 13.5741(2) Å, β = 108.993(2)°, V = 2446.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.0247, $wR_{ref}(F^2)$ = 0.0563, T = 295 K.

Table 1. Data collection and handling.

Crystal:	dark red tabulars, size 0.15×0.22×0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	88.78 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	57°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	54528, 6199
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5229
$N(param)_{refined}$:	271
Programs:	CrysAlis Pro [11], SHELX [12], MERCURY [13]

Source of material

$(C_{10}H_{10}N_2)[RhBr_4(C_{10}H_8N_2)]Br$ was prepared by a diffusion-controlled ligand exchange synthesis [6]. A solution of 2,2'-bipyridine (170.1 mg, 1.09 mmol) in 2 ml of concentrated hydrobromic acid was carefully added to the test tube containing a solution of $RhCl_3{\cdot}3H_2O$ (0.10 ml, 0.15 mmol $RhCl_3$), in 6 mol/l hydrochloric acid, covered by a 0.5 ml layer of concentrated hydrobromic acid. The obtained triple-layer system was allowed to stand at room temperature forming single crystals.

Experimental details

The hydrogen atoms were located in subsequent difference Fourier maps and then the riding model with idealized bond lengths and angles was applied. The isotropic displacement parameters of H-atoms were fixed to be 1.2 times larger than the equivalent displacement parameters of their carrier nitrogen and carbon atoms [12].

Discussion

Pyridine and its derivatives are important organic building blocks of many hybrid materials that are of both industrial and academic interest. Among them the particularly important role is played by 4,4'- and 2,2'-bipyridines that belong to the most frequently used oligopyridine organic components in crystal engineering of inorganic-organic hybrids [1, 2]. We have recently reported structural, spectroscopic and thermoanalytical properties of the hybrid material $[4,4'\text{-}H_2bipy][H_7O_3][RhBr_6]$ [3]. The aim of introducing the relatively large in spatial dimensions 4,4'-bipyridindiium cations was to create a pattern with appropriate cavities for inclusion of aquahydrogen guest ions, such as $[H_7O_3]^+$, a strategy that was successfully applied before using flexible α,ω-diammonio ions of medium chain lengths or semiflexible 1,4-diazoniacycloheptane ions [4-6]. To better understand the influence of different cations on the 'construction' of crystal structures of halogenidorhodates(III) we used the isomeric 2,2'-bipyridindiium as an organic counterion. In contrast to 4,4'-bipyridine the 2,2'-isomer, in most cases, adopts the flat *cis*-conformation and forms a stable chelate ring with a central metal atom [7]. The asymmetric unit of $(C_{10}H_{10}N_2)[RhBr_4(C_{10}H_8N_2)]Br$ consists of one $(C_{10}H_{10}N_2)^{2+}$ cation, one $[RhBr_4(C_{10}H_8N_2)]^-$ complex ion and one isolated Br^- ion. The ions are connected through N/C–H···Br hydrogen bonds (N/C···Br distances range from 3.141(3) to 3.829(3) Å). All the aromatic ring systems are essentially planar with no atom deviating from the least-squares planes by more than 0.030(2) Å. Their N–C and C–C distances and bond angles are as expected and similar to those previously reported [8, 9]. The bipyridine ligand in $[RhBr_4(C_{10}H_8N_2)]^-$ is not strictly planar with the angle between adjacent pyridine rings of 3.1(2)° (the dihedral N1–C5–C6–N2 angle is –1.7(3)°), whereas the same angle formed by mean planes through the $(C_{10}H_{10}N_2)^{2+}$ cation is 135.8(1)° (the dihedral N3–C15–C16–N4 angle is –137.3(3)°). The central Rh^{III} atom in the discrete $[RhBr_4(C_{10}H_8N_2)]^-$ anion is coordinated by two nitrogen donor atoms of the organic ligand and by four Br^- ligands. As a result, the octahedral environment of Rh^{III} is distorted from the

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ideal octahedral geometry. As expected the Rh–N distances (2.033(2) and 2.041(2) Å) are almost equal and shorter than four the Rh–Br distances spanning in the range from 2.4736(3) to 2.4968(3) Å (difference of 0.0232(4) Å). The Rh–Br bonds (average 2.4782 Å) located *trans* to the nitrogen atoms are slightly shorter in comparison to those with mutually *trans* located Br^- ligands (average 2.4922 Å). The average Rh–Br bond length is 0.0095 Å smaller than the average bond length found in the 'non-distorted' $[RhBr_6]^{3-}$ octahedron in the structure of $[H_3N(CH_2)_4NH_3]_2[H_5O_2][RhBr_6]Br_2$ [6]. The main angular contribution to the distortion of the octahedron is the tight N–Rh–N chelate angle of 80.21(9)° that also results in the non-linearity of remaining N/Br–Rh–Br *trans* angles. The most distorted from the linearity, by 5.12(6)°, is the N1–Rh1–Br2 angle. The N–Rh–Br and Br–Rh–Br *cis* angles range from 86.68(6) to 95.84(6)° and from 88.882(11) to 92.317(11)°, respectively. A linear distortion from ideal polyhedral geometry with even larger Rh–Br deviation (0.0499(7) Å) was found in the structure of $(C_6H_{16}N_2)_2[RhBr_6]Br{\cdot}H_2O$ [10].

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.4020	–0.1225	0.7630	0.042
H(2)	4*e*	0.5115	–0.0301	0.8663	0.052
H(3)	4*e*	0.5759	0.1152	0.7944	0.053
H(4)	4*e*	0.5261	0.1719	0.6204	0.047
H(7)	4*e*	0.4665	0.2271	0.4551	0.051
H(8)	4*e*	0.4016	0.2598	0.2803	0.057
H(9)	4*e*	0.2961	0.1355	0.2022	0.052
H(10)	4*e*	0.2551	–0.0142	0.2999	0.041
H(3N)	4*e*	0.0808	0.3952	0.4952	0.046
H(4N)	4*e*	0.1059	0.0327	0.4009	0.033
H(11)	4*e*	0.1646	0.5548	0.5213	0.066
H(12)	4*e*	0.2529	0.5396	0.4393	0.066
H(13)	4*e*	0.2492	0.3600	0.3308	0.056
H(14)	4*e*	0.1586	0.1976	0.3071	0.044
H(17)	4*e*	–0.0366	0.3212	0.3715	0.044
H(18)	4*e*	–0.1299	0.1605	0.3450	0.052
H(19)	4*e*	–0.1003	–0.0637	0.3464	0.048
H(20)	4*e*	0.0210	–0.1260	0.3738	0.042

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*	0.30223(1)	–0.10507(2)	0.53151(2)	0.0188(1)	0.0215(1)	0.0253(1)	–0.00211(7)	0.00613(7)	0.00140(7)
Br(1)	4*e*	0.27360(2)	–0.25473(3)	0.65845(2)	0.0315(2)	0.0377(2)	0.0386(2)	–0.0026(1)	0.0136(1)	0.0115(1)
Br(2)	4*e*	0.18404(2)	–0.17495(3)	0.39897(2)	0.0228(1)	0.0310(2)	0.0404(2)	–0.0017(1)	0.0021(1)	–0.0043(1)
Br(3)	4*e*	0.23971(2)	0.08591(3)	0.58600(2)	0.0335(2)	0.0322(2)	0.0382(2)	0.0038(1)	0.0115(1)	–0.0039(1)
Br(4)	4*e*	0.37330(2)	–0.28690(3)	0.48043(2)	0.0254(1)	0.0290(1)	0.0422(2)	–0.0004(1)	0.0131(1)	–0.0012(1)
Br(5)	4*e*	0.03261(2)	0.10987(3)	0.13191(2)	0.0658(2)	0.0350(2)	0.0365(2)	–0.0072(2)	0.0189(2)	–0.0051(1)
N(1)	4*e*	0.3986(1)	–0.0328(2)	0.6324(2)	0.022(1)	0.027(1)	0.031(1)	–0.0028(9)	0.0064(9)	–0.0016(9)
N(2)	4*e*	0.3335(1)	0.0190(2)	0.4340(2)	0.028(1)	0.021(1)	0.031(1)	–0.0017(9)	0.0111(9)	0.0001(9)
C(1)	4*e*	0.4272(2)	–0.0630(3)	0.7339(2)	0.033(2)	0.034(2)	0.033(1)	–0.001(1)	0.004(1)	–0.000(1)
C(2)	4*e*	0.4929(2)	–0.0082(3)	0.7960(2)	0.038(2)	0.045(2)	0.035(2)	0.000(1)	–0.003(1)	–0.004(1)
C(3)	4*e*	0.5308(2)	0.0791(3)	0.7536(3)	0.027(2)	0.044(2)	0.055(2)	–0.006(1)	0.004(1)	–0.016(2)
C(4)	4*e*	0.5013(2)	0.1124(3)	0.6502(3)	0.029(2)	0.036(2)	0.053(2)	–0.011(1)	0.014(1)	–0.009(1)
C(5)	4*e*	0.4343(2)	0.0567(3)	0.5903(2)	0.024(1)	0.026(1)	0.039(1)	–0.002(1)	0.011(1)	–0.006(1)
C(6)	4*e*	0.3975(2)	0.0874(3)	0.4798(2)	0.029(1)	0.027(1)	0.038(2)	–0.003(1)	0.014(1)	–0.001(1)
C(7)	4*e*	0.4234(2)	0.1788(3)	0.4230(3)	0.039(2)	0.034(2)	0.059(2)	–0.010(1)	0.024(2)	0.002(1)
C(8)	4*e*	0.3850(2)	0.1979(3)	0.3189(3)	0.060(2)	0.038(2)	0.057(2)	–0.003(2)	0.035(2)	0.014(2)
C(9)	4*e*	0.3221(2)	0.1249(3)	0.2728(2)	0.057(2)	0.040(2)	0.036(2)	0.003(2)	0.018(2)	0.010(1)
C(10)	4*e*	0.2976(2)	0.0357(3)	0.3317(2)	0.040(2)	0.031(2)	0.032(1)	–0.001(1)	0.012(1)	0.001(1)
N(3)	4*e*	0.1127(1)	0.3882(2)	0.4630(2)	0.037(1)	0.028(1)	0.053(2)	–0.004(1)	0.018(1)	–0.009(1)
N(4)	4*e*	0.0608(1)	0.0577(2)	0.3892(2)	0.024(1)	0.025(1)	0.033(1)	0.0002(9)	0.0102(9)	0.0003(9)
C(11)	4*e*	0.1642(2)	0.4827(3)	0.4777(3)	0.050(2)	0.033(2)	0.080(3)	–0.012(2)	0.018(2)	–0.018(2)
C(12)	4*e*	0.2165(2)	0.4743(3)	0.4290(3)	0.035(2)	0.033(2)	0.093(3)	–0.012(1)	0.015(2)	0.002(2)
C(13)	4*e*	0.2142(2)	0.3674(3)	0.3648(3)	0.033(2)	0.048(2)	0.061(2)	–0.004(1)	0.019(2)	0.011(2)
C(14)	4*e*	0.1600(2)	0.2704(3)	0.3503(2)	0.034(2)	0.035(2)	0.041(2)	–0.003(1)	0.013(1)	–0.003(1)
C(15)	4*e*	0.1082(1)	0.2827(3)	0.4005(2)	0.025(1)	0.024(1)	0.032(1)	0.000(1)	0.006(1)	0.002(1)
C(16)	4*e*	0.0462(2)	0.1892(3)	0.3878(2)	0.027(1)	0.026(1)	0.028(1)	–0.003(1)	0.010(1)	–0.001(1)
C(17)	4*e*	–0.0255(2)	0.2306(3)	0.3718(2)	0.031(2)	0.034(2)	0.046(2)	0.005(1)	0.012(1)	–0.002(1)
C(18)	4*e*	–0.0811(2)	0.1344(3)	0.3560(2)	0.024(2)	0.053(2)	0.053(2)	0.001(1)	0.015(1)	–0.004(2)
C(19)	4*e*	–0.0636(2)	0.0010(3)	0.3569(2)	0.032(2)	0.043(2)	0.043(2)	–0.011(1)	0.012(1)	–0.007(1)
C(20)	4*e*	0.0086(2)	–0.0360(3)	0.3735(2)	0.042(2)	0.027(1)	0.040(2)	–0.007(1)	0.018(1)	–0.005(1)

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