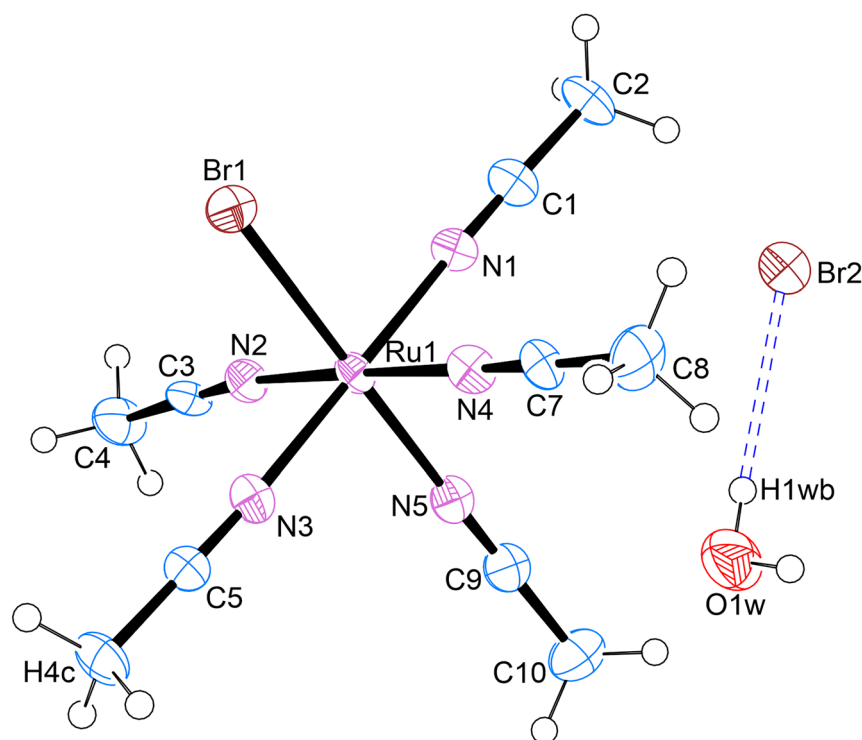


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The crystal structure of (OC-6-22)-pentakis(acetonitrile)bromidoruthenium(II) bromide monohydrate, $C_{10}H_{15}Br_2N_5Ru$



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Abstract

$C_{10}H_{15}Br_2N_5Ru$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.9081(4)$ Å, $b = 8.4334(4)$ Å, $c = 25.9374(13)$ Å, $V = 1729.82(15)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0637$, $wR_{ref}(F^2) = 0.1579$, $T = 173(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	$0.14 \times 0.13 \times 0.11$ mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.50 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Microfocus with Photon III, ω
θ_{max} , completeness:	25.5° , 93 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8350, 8350
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 7978
$N(\text{param})_{\text{refined}}$:	178
Programs:	Bruker (1), WinGX/ORTEP (2), Shelx (3), PLATON (4)

1 Source of materials

$[Ru(\eta^6\text{-}p\text{-cymene})Br_2CO]$ (0.030 g, 0.059 mmol) was dissolved in acetonitrile (15 mL). Diethyl ether was added slowly to this solution by solvent diffusion at ambient temperature. Crystals were obtained after several days. Yield 60 % (0.017 g, 0.035 mmol).

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	−0.1031 (19)	0.4340 (16)	0.6694 (7)	0.029 (4)
C2	−0.263 (2)	0.5141 (18)	0.6743 (8)	0.038 (4)
H2A	−0.253549	0.5991	0.699911	0.057*
H2B	−0.349799	0.438201	0.685461	0.057*
H2C	−0.295611	0.559407	0.640955	0.057*
C3	0.1576 (19)	−0.0647 (17)	0.6938 (6)	0.026 (3)
C4	0.119 (2)	−0.2285 (18)	0.7075 (8)	0.039 (4)
H4A	0.091226	−0.288333	0.676262	0.058*
H4B	0.022734	−0.230717	0.731215	0.058*
H4C	0.2178	−0.276457	0.724248	0.058*
C5	0.6154 (17)	0.1223 (16)	0.6395 (6)	0.025 (3)
C6	0.7806 (18)	0.0494 (19)	0.6355 (8)	0.034 (4)
H6A	0.851032	0.110702	0.61168	0.052*
H6B	0.768521	−0.059258	0.622642	0.052*
H6C	0.834157	0.047312	0.669607	0.052*
C7	0.3579 (18)	0.6030 (17)	0.6058 (7)	0.028 (3)
C8	0.404 (3)	0.7588 (19)	0.5840 (8)	0.043 (4)
H8A	0.524839	0.778494	0.589756	0.064*
H8B	0.337606	0.842013	0.60078	0.064*
H8C	0.380865	0.759208	0.546853	0.064*
C9	0.152 (2)	0.1647 (17)	0.5417 (7)	0.031 (3)
C10	0.107 (3)	0.118 (2)	0.4893 (8)	0.045 (4)
H10A	0.003196	0.054348	0.490105	0.068*
H10B	0.198794	0.055366	0.474285	0.068*
H10C	0.088003	0.213106	0.468339	0.068*
Br1	0.34149 (19)	0.37254 (17)	0.74202 (6)	0.0297 (4)
Ru1	0.25485 (14)	0.27526 (11)	0.65352 (5)	0.0216 (3)
N1	0.0225 (14)	0.3713 (14)	0.6645 (5)	0.026 (3)
N2	0.1858 (15)	0.0619 (14)	0.6824 (6)	0.026 (3)
N3	0.4872 (15)	0.1816 (13)	0.6430 (6)	0.026 (3)
N4	0.3273 (15)	0.4865 (13)	0.6229 (5)	0.025 (3)
N5	0.1869 (15)	0.2007 (14)	0.5819 (6)	0.026 (3)
Br2	−0.0740 (2)	0.7021 (2)	0.56338 (8)	0.0435 (5)
O1W	0.1939 (19)	0.5021 (15)	0.4854 (6)	0.054 (4)
H1WA	0.22319	0.587047	0.468557	0.081*
H1WB	0.11218	0.533776	0.503608	0.081*

2 Experimental details

Intensity data was determined on a Bruker D8 Venture Microfocus with Photon III CCD area detector diffractometer at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program SAINT+, version 6.02 (1) and empirical absorption corrections were made using SADABS (1). Space group assignment was made using XPREP (1). The structure was solved in the WinGX (2) Suite of programs, using intrinsic phasing through SHELXT-2018/2 (3) and refined using SHELXL-2019/3 (3). All C and O-bound hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.5 times those of their parent atoms.

The structure was refined as a two-component twin with batch scale factors of 0.8619(16) and 0.1381(16). Diagrams and publication material were generated using ORTEP-3 (2) and PLATON (4).

3 Comment

Nitrile ligands (N≡CR, where R = CH₃, C(CH₃)₃, C₆H₅) are well-known in coordination chemistry. Metal-nitrile complexes are useful precursors for the synthesis of complexes with application in catalysis and medicine due to of the labile nature of the metal-nitrile bond (5–7).

The CH₃CN ligand can exhibit three coordinating modes; as a κ¹–N donor, as an η²-nitrile with both the C and N atoms bound to the metal and as a CH-metalated ligand. The most common mode of bonding of CH₃CN is as a κ¹–N mode, while the M(H)–CH₂CN metalated and η²-nitrile modes are less common (8). The N-donor nitrile ligand coordinates to both neutral and positively charged metals, while η²-nitrile and CH-metalated ligands prevalently coordinate to low-valence metal complexes (8).

While there are 1482 complexes with a Ru–NCCH₃ moiety in the Cambridge Structural Database (CSD version 5.44, September 2023 update), there are only seven crystal structures of the type [Ru(NCCH₃)₅L]⁺. The low number of reported structures for this class of complex may be attributed to the poor σ-donor ability of CH₃CN ligands (9).

The title complex crystallizes in an orthorhombic crystal system with the space group *P*2₁2₁2₁ (no. 19). The cationic [Ru(NCCH₃)₅Br]⁺ complex ion adopts an MA₅B octahedral geometry, with a bromide anion and water molecule in the outer sphere.

The Ru1–N bond lengths were measured between 2.018(12) and 2.033(14) Å which falls within the comparable range of similar, previously reported Ru–NCCH₃ complexes (10). The Ru1–Br1 bond length was measured as 2.532(2) Å which is comparable with Ru–Br bond lengths of the reported similar complex (11). The N≡C bond length of the CH₃CN *trans* to Br1 was measured as 1.12(2) Å which is similar to the N≡C bond lengths for the four CH₃CN ligands in the equatorial positions.

The N–Ru1–N angles in the equatorial plane were measured in the range 87.0(5)° to 93.3(5)° showing slight deviation from the ideal angle of 90° for this geometry. The N5–Ru1–Br1 angle for the mutually *trans* bromido and acetonitrile ligands was measured as 179.0(3)° which is negligibly distorted, deviating only slightly from linearity (180°). The four N_{eq}–Ru1–Br1 bond angles for the acetonitrile ligands at the equatorial positions were measured in the range 89.3(4)° to 91.4(4)° also showing negligible distortion from ideal. The Ru1–N≡C bond angles were measured in the range 171.8(13)° to 177.4(12)° showing deviation

from linearity due to Ru–N backbonding which effects a change in the hybridization of the metal-bound N atom.

The crystal growth of the title complex is supported by weak intermolecular hydrogen bonds. The cationic ruthenium complex is linked to the bromide counterion via the hydrogen of C2 with a distance of 2.927 Å. Additionally, there is a strong hydrogen bond [O–H...Br (2.556 Å)] where Br2 in the outer coordination sphere acts as the hydrogen bond acceptor. The oxygen atom of the water molecule act as a hydrogen acceptor in the [C10–H...O (2.615 Å)] interaction. There is also a tetrel bond between the oxygen atom of the water molecule and C9 of the acetonitrile ligand [C...O (3.215 Å)].

In the packing diagram, the oxygen atom of the water molecule acts as a nexus that connects the cationic ruthenium complex ion and the bromide counterion. A chalcogen bond [O...Br (3.346 Å)] was also observed in the packing diagram.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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