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X-ray crystallographic study of hydrogen-bonded systems formed between di- and tricarboxylic acids and the trinuclear cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$

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Abstract

The hydrogen-bonded systems formed between 5-bromo-isophthalic and trimesic acid derivatives and the trinuclear arene-ruthenium cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$(**1**) have been studied in the solid state by single-crystal X-ray structure analysis of the tetrafluoroborate salts. The structure analysis of 5-bromo-isophthalic acid with [**1**][BF_4] shows a 1:1 (acid:cluster) supramolecular system, only one hydroxyl of the acid functions interacting with the μ_3-oxo ligand of a cation of **1**, the hydroxyl group of the second acid function interacting with a tetrafluoroborate anion. With trimesic acid, a 1:2 (acid:cluster) supramolecular system is formed. Two hydroxyl groups interact with the μ_3-oxo ligand of two independent cations of **1**, while the remaining hydroxyl group of the third acid function interacts with a tetrafluoroborate anion.

Keywords: Arene ligands; Cluster complexes; Crystal packing; Hydrogen bonds; Ruthenium

1. Introduction

Recently, we have shown that the cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$(**1**), in which the three ruthenium atoms are capped by a μ_3-oxo ligand [1], interacts strongly with monocarboxylic acids [2]. In solution, the binding properties of **1** with monocarboxylic acids had been studied by CSI-MS (cold-spray ionisation mass spectroscopy), whereas in the solid state, single-crystal X-ray structure analyses of selected complexes had been performed. The study showed that in every case the hydroxyl of the acid function interacted strongly with the μ_3-oxo ligand.

Therefore, we extended this study to various di- and tricarboxylic acid derivatives, in order to check the possibility of forming supramolecular systems through μ_3-oxo···acid hydrogen bonding. The single-crystal X-ray structure analyses of two acid–cluster complexes are presented.

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2. Experimental section

2.1. General remarks

Solvents (technical grade) and other reagents were purchased (Aldrich, Fluka) and used as received. The starting compound $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)][BF_4]$ ([**1**][BF_4]) was prepared according to published methods [1].

2.2. Crystallisations

Preparation of [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·(acetone)$_2$: In a test tube, 1 mg of [**1**][BF_4] is added to an acetone solution (3 mL) of 5-Br-1,3-$C_6H_3(COOH)_2$ (1 mg). The solution is left at room temperature overnight, the test tube being slightly open, until small red blocks are observed.

Preparation of {[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·(acetone)$_{1.5}$·benzene: In a test tube, 1 mg of [**1**][BF_4] in acetone is added to a benzene solution (3 mL) of 1,3,5-$C_6H_3(COOH)_3$ (1 mg). The solution is left at room temperature for several days, the test tube being slightly open, until thin red plates are observed.

Table 1
Crystallographic and selected experimental data for [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·(acetone)$_2$ and {[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·(acetone)$_{1.5}$·benzene

	[**1**][BF_4]·5-Br-1,3-C_6H_3(-COOH)$_2$·(acetone)$_2$	{[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·(acetone)$_{1.5}$·benzene
Chemical formula	$C_{44}H_{62}BBrF_4O_7Ru_3$	$C_{79.5}H_{111}B_2F_8O_{9.5}Ru_6$
Formula weight	1172.87	1998.72
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*P2$_1$/n*
Crystal colour and shape	Red block	Red plate
Crystal size	0.20×0.17×0.12	0.25×0.21×0.09
a (Å)	10.740(2)	10.711(1)
b (Å)	13.787(3)	36.383(4)
c (Å)	16.010(3)	21.228(3)
α (°)	102.810(3)	
B (°)	95.623(3)	102.891(2)
γ (°)	92.543(3)	
V (Å^3)	2295.2(8)	8064(2)
Z	2	4
T (K)	100(2)	100(2)
D_c (g cm^{-3})	1.697	1.646
μ (mm^{-1})	1.909	1.169
Scan range (°)	$2.62<2\theta<57.38$	$2.24<2\theta<57.06$
Unique reflections	10,589	18,786
Reflections used [$I>2\sigma(I)$]	7376	11,657
R_{int}	0.0657	0.0823
Final *R* indices [$I>2\sigma(I)$]	0.0606, wR_2 0.1606	0.0482, wR_2 0.1117
R indices (all data)	0.0922, wR_2 0.1846	0.0878, wR_2 0.1296
Goodness-of-fit	1.049	0.960
Max, Min $\Delta\rho$ (e Å^{-3})	3.323, −2.213	1.907, −0.944

2.3. X-ray crystallographic study

Crystals of [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·(acetone)$_2$ and {[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·(acetone)$_{1.5}$·benzene were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ=0.71073 Å) with ϕ range 0–200°, increment of 0.9 and 0.7°, respectively, 2θ range from 2.0 to 26°, $D_{max}-D_{min}$=12.45–0.81 Å. The structures were solved by direct methods using the program SHELXS-97 [3]. The refinement and all further calculations were carried out using SHELXL-97 [4]. In both structures, the hydrido ligands were located from Fourier difference maps and fixed at their positions whereas the remaining H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. In both cases the non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. In complex {[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·(acetone)$_{1.5}$·benzene, the half acetone molecule, which is located on an inversion centre, was disordered over two positions and was treated with partial occupancy factors of 0.5. In both complexes, the residual electron densities greater than 1 e Å^{-3} are observed around the ruthenium atoms at less than 1 Å. Crystallographic details are summarised in Table 1. Figs. 1

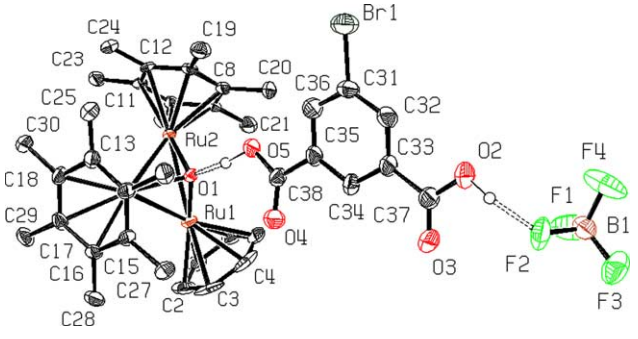


Fig. 1. ORTEP drawing of [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·(acetone)$_2$ showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, solvent molecules and hydrogen atoms are omitted for clarity.

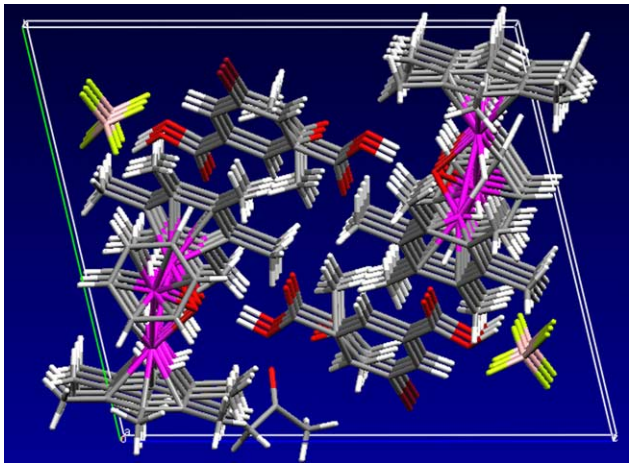
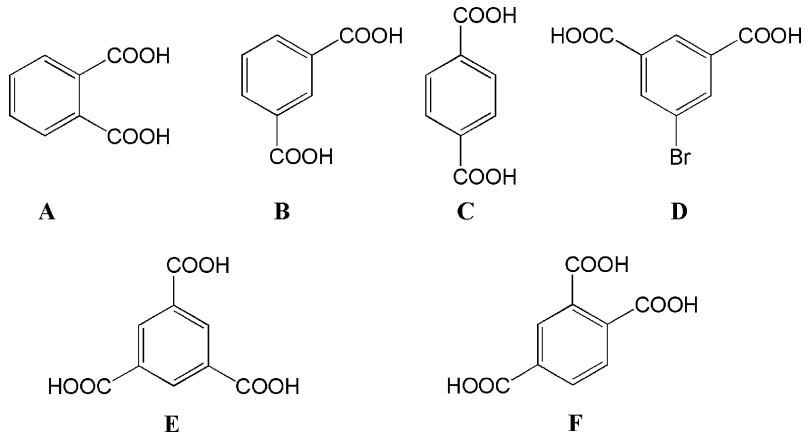


Fig. 2. Projection, along the *b*-axis, of the structure of [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·(acetone)$_2$.



Scheme 1.

and 3 were drawn with ORTEP [5] and Figs. 2 and 4 with MERCURY [6].

CCDC-264361 [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·$(acetone)_2$ and 264362 {[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·$(acetone)_{1.5}$·benzene contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033. E-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

The trinuclear cluster $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$(**1**) is accessible in aqueous solution from the dinuclear precursor $[H_3Ru_2(C_6Me_6)]^+$ and the mononuclear building block $[Ru(C_6H_6)(H_2O)_3]^{2+}$ [1]. The μ_3-oxo ligand is capable of forming hydrogen bonds with monocarboxylic acids, as observed in the crystal structures of [**1**][BF_4]·4-BrC_6H_4-COOH [2], [**1**][BF_4]·3,5-$Cl_2C_6H_3COOH$·acetone·$CHCl_3$ [1], [**1**][BF_4]·(4-$MeOC_6H_4COOH)_2$·acetone [1], [**1**][BF_4]·2-$C_{10}H_7COOH$ [1] and [**1**][BF_4]·C_6H_5COOH [7]. The persistence of these interactions between the μ_3-oxo ligand of the complex and the hydroxyl group of monocarboxylic acid molecules even in solution was demonstrated by CSI-MS [2].

In order to investigate the potential of forming supramolecular systems, we studied solution of [**1**][BF_4] with di- and tricarboxylic acids. We carried out a series of CSI-MS measurements in acetone of di- and tricarboxylic acids with an excess of [**1**][BF_4]. The di- and tricarboxylic acid derivatives used for the present study are presented in Scheme 1; phthalic acid (**A**), isophthalic acid (**B**), terephthalic acid (**C**), 5-bromo-isophthalic acid (**D**), trimesic acid (**E**), trimellitic acid (**F**).

In all cases a major peak at *m/z* 725 corresponding to $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ was observed. However, no adducts (1:1, 1:2, 1:3) acid:cluster have been identified in the CSI-MS spectrum [8]. Similarly by NMR spectroscopy, at low temperature, no interaction was observed, the chemical shift of the acid signal was unchanged in the presence of [**1**][BF_4] [9]. To gain further insight in the binding mode of **1** with di- and tricarboxylic acids, we attempted to crystallise [**1**][BF_4] with the same series of carboxylic acids. In most cases no crystalline compounds were obtained. However, with 5-bromo-isophthalic acid (**D**) and trimesic acid (**E**) crystals containing a supramolecular system were isolated. Crystallographic details are summarised in Table 1, significant hydrogen bonds and contacts are summarised in Table 2. The crystal structure of [**1**][BF_4] with 5-bromo-isophthalic acid is presented in Fig. 1.

The crystallisation of [**1**][BF_4] with 5-bromo-isophthalic acid (5-Br-1,3-$C_6H_3(COOH)_2$) in an acetone solution gives

Table 2
Selected hydrogen bonds and contacts in the crystal structure of [**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$·$(acetone)_2$ and {[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·$(acetone)_{1.5}$·benzene

D–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A*(°)
*[**1**][BF_4]·5-Br-1,3-$C_6H_3(COOH)_2$···$(acetone)_2$*				
O5–H···O1	1.04	1.47	2.502(6)	167.7
O2–H···F2	1.10	1.69	2.586(7)	134.4
*{[**1**][BF_4]}$_2$·1,3,5-$C_6H_3(COOH)_3$·$(acetone)_{1.5}$·benzene*				
O2–H···O1	0.84	1.69	2.497(5)	159.4
O6–H···O11	0.84	1.67	2.503(5)	174.4
O4–H···F1	0.84	1.86	2.690(5)	169.4
C52–H···O8	0.95	2.35	3.29(1)	167.5

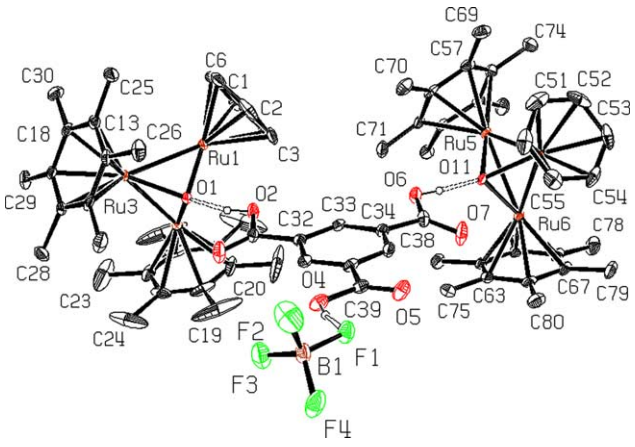


Fig. 3. ORTEP drawing of $\{[\mathbf{1}][BF_4]\}_2 \cdot 1,3,5\text{-}C_6H_3(COOH)_3 \cdot (acetone)_{1.5} \cdot benzene$ showing the numbering scheme. Displacement ellipsoids are drawn at the 25% probability level, one anion, solvent molecules and hydrogen atoms are omitted for clarity.

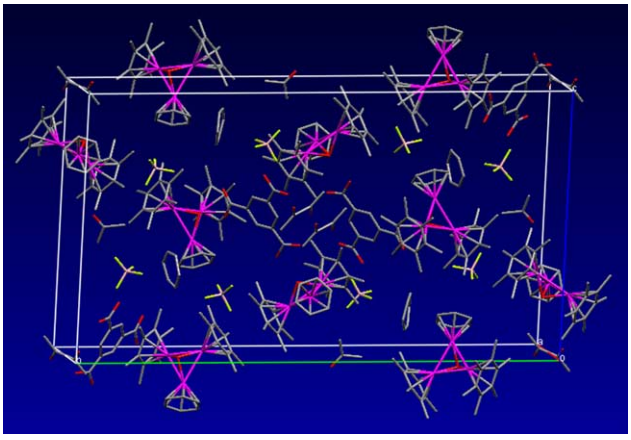


Fig. 4. Crystal packing of $\{[\mathbf{1}][BF_4]\}_2 \cdot 1,3,5\text{-}C_6H_3(COOH)_3 \cdot (acetone)_{1.5} \cdot benzene$, H-atoms are omitted for clarity.

the 1:1 (acid:cluster) supramolecular complex $[\mathbf{1}][BF_4] \cdot 5\text{-}Br\text{-}1,3\text{-}C_6H_3(COOH)_2 \cdot (acetone)_2$. One of the carboxylic acid functions interacts with a μ_3-oxo ligand of the cluster cation whereas the second acid function interacts with the tetrafluoroborate anion. The O···O distance of the μ_3-oxo···acid hydrogen bond is 2.502(6) Å with an O–H···O angle of 167.7°. The O···F distance of the acid···BF_4 interaction is 2.586(7) with an angle of 134.4°.

In the crystal packing of $[\mathbf{1}][BF_4] \cdot 5\text{-}Br\text{-}1,3\text{-}C_6H_3(COOH)_2 \cdot (acetone)_2$, the different components are arranged in columns parallel to the *b*-axis, see Fig. 2. The solvent molecules make no meaningful interaction, other than normal coulombic attractions, with their neighbouring molecules. Their role is mostly to fill the void left between columns of acids and cations.

In the crystals obtained with trimesic acid ($1,3,5\text{-}C_6H_3(COOH)_3$), two cluster cations **1** interact with hydroxyl group of two different acid functions. The remaining acid function of the trimesic acid interacts with a tetrafluoroborate anion. The atoms numbering scheme of $[\mathbf{1}][BF_4] \cdot 1,3,5\text{-}C_6H_3(COOH)_3 \cdot (acetone)_{1.5} \cdot benzene$ is presented in Fig. 3. The O···O distances of the μ_3-oxo···acid hydrogen bonds are 2.497(5) and 2.503(5) Å with an O–H···O angle of 159.4 and 174.4°, respectively. The O···F distance of the acid···BF_4 interaction is 2.690(5) with an angle of 169.4°.

In the crystal packing of $\{[\mathbf{1}][BF_4]\}_2 \cdot 1,3,5\text{-}C_6H_3(COOH)_3 \cdot (acetone)_{1.5} \cdot benzene$, acetone and benzene molecules are observed, see Fig. 4. The acetone molecules form weak hydrogen contacts with neighbouring cations of **1**. In the case of the benzene, the solvate molecule is slightly incorporated in the hydrophobic pocket of cation **1**. The angle formed by the C_6 plane and the Ru_3 plane of **1** is 69.6(3)°, the benzene being held almost upright in the hydrophobic pocket. The shortest distances between the metal-bound hydrogen and the closest carbon atoms of the benzene molecule are 3.44 and 3.68 Å. These values are comparable to those reported for the related complexes $[H_3Ru_3(C_6H_5CH_2CH_2OH)(C_6Me_6)_2(O)][PF_6] \cdot benzene$ and $[H_3Ru_3(C_6H_5CH_2CH_2CH_2OH)(C_6Me_6)_2(O)][BF_4] \cdot benzene$ [10].

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[8] CSI-MS experiment conditions; 10 µmol of $[\mathbf{1}][BF_4]$ in acetone (3 mL) with 1 µmol of the acid, injection at −20 °C by syringe pump in the cold-spray ion source. The mass spectrum measurements were performed with a sector (BE) mass spectrometer (JMS-700, JEOL) equipped with a CSI source.
[9] NMR experiment conditions; 1 mg of acids, 20 mg of $[\mathbf{1}][BF_4]$ in 0.7 mL of acetone-D_6, Bruker 400 MHz spectrometer, −20 °C.
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