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Host–guest properties of the trinuclear arene–ruthenium cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$

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Abstract

The trinuclear arene–ruthenium cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$, containing a μ_3-oxo cap and three arene ligands that span a hydrophobic pocket above the metal skeleton, has been crystallised as tetrafluoroborate salt in the presence of various guest molecules. The host–guest complexes have been characterised by single-crystal X-ray structure analysis. With chloroform as the guest molecule, a $CHCl_3$ molecule sits perfectly in the hydrophobic pocket, the hydrogen atom being encapsulated inside the cavity. When dioxane is added during the crystallisation process, the cluster forms infinite chains which are connected by a complex network of hydrogen bonds involving the μ_3-oxo ligand, water and dioxane molecules. Interestingly, in the presence of phenol, a water molecule is hydrogen-bonded between the μ_3-oxo ligand and the phenol molecule, forming a one-dimensional μ_3-$O\cdots H_2O\cdots HO$ hydrogen-bonded chain. Finally, with benzoic acid, a head-to-tail host–guest chain is obtained, the phenyl ring being incorporated in the hydrophobic pocket, while the acid group is hydrogen-bonded to the μ_3-oxo ligand.

Keywords: Arene ligands; Cluster compounds; Host–guest systems; Hydrophobic forces; Molecular recognition

1. Introduction

Host–guest chemistry is a flourishing research area, in particular in view of crystal engineering; self-assembly, templation, and molecular encapsulating are amongst the most studied phenomena [1]. They are governed by several factors such as hydrogen bonding [2], π–π interactions [3], and C–H $\cdots$ π interactions [4], but the prediction on the formation of a host–guest complex remains a difficult task. The inclusion of small organic molecules such as acetonitrile, nitromethane or diethylether in the organic ligand cavity of organometallic complexes has been observed in the case of $[(1,5\text{-COD})_6Ir_6W_4O_{16}]^{2-}$ [5] and $[(p\text{-}MeC_6H_4Pr^i)Ru(CTV)]^{2+}$ as well as $[(C_6Me_6)Ru(CTV)]^{2+}$ (CTV = 2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15*H*-tribenzo[*a,d,g*]-cyclononene) [6].

Recently, we synthesised in aqueous solution 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, the single-crystal X-ray structure analysis of the tetrafluoroborate salt showed the μ_3-oxo ligand to be strongly hydrogen-bonded to a water molecule [7]. Furthermore, we observed for two derivatives of the parent cluster **1**, $[H_3Ru_3\{C_6H_5(CH_2)_2OH\}(C_6Me_6)_2(O)]^+$(**2**) and $[H_3Ru_3\{C_6H_5(CH_2)_3OH\}(C_6Me_6)_2(O)]^+$(**3**), that a benzene molecule can be hosted in the hydrophobic pocket spanned by the three arene ligands [8], see Scheme 1. Therefore, we postulated that in the presence of cluster **1**, molecules which possess a phenyl ring and a functional group suitable for the formation of hydrogen-bonds will self-assemble in a predictable fashion.

Herein, we report on the crystallisation of the cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**1**) as the tetrafluoroborate salt in the presence of chloroform, dioxane, phenol or benzoic acid and on the single-crystal X-ray characterisation of the solids obtained. The results show that the hydrophobic pocket, spanned by the three arene ligands in **1**, plays a crucial role in the formation of the crystalline products.

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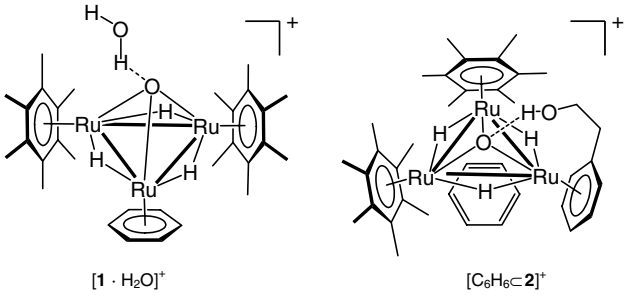

Scheme 1.

2. Experimental

2.1. General remarks

Solvents (technical grade) and other reagents were purchased (Aldrich, Fluka) and used as received. The starting compound $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)][BF_4]$ (cation **1**) was prepared according to published methods [7].

2.2. Crystallisations

2.2.1. Preparation of $[CHCl_3\subset\mathbf{1}][BF_4]\cdot CHCl_3$

In a test tube, 1 ml of chloroform is added to an acetone solution (3 ml) of $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)][BF_4]$ (1 mg). The solution is left at room temperature overnight, the test tube being slightly open, until small red plates are observed.

2.2.2. Preparation of $[\mathbf{1}][BF_4]\cdot H_2O\cdot 0.5C_4H_8O_2$

In a test tube, 1 ml of dioxane is added to an acetone solution (3 ml) of $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)][BF_4]$ (1 mg). The solution is left at room temperature for several days, the test tube being slightly open, until red blocks are observed.

2.2.3. Preparation of $[\mathbf{1}][BF_4]\cdot H_2O\cdot C_6H_5OH$

In a test tube, 1 mg of phenol is added to an acetone solution (3 ml) of $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)][BF_4]$ (1 mg). The solution is left at room temperature for two days, the test tube being slightly open, until red crystalline blocks are observed.

2.2.4. Preparation of $[C_6H_5COOH\subset\mathbf{1}][BF_4]$

To an acetone solution (3 ml) of $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)][BF_4]$ (1 mg) is added benzoic acid (1 mg). The mixture is left slightly opened overnight, and two days later small orange plates are observed.

2.3. X-ray crystallographic study

The data were measured using a Bruker SMART CCD diffractometer, using Mo Kα graphite mono-

Table 1
Crystallographic and selected experimental data of $[CHCl_3\subset\mathbf{1}][BF_4]\cdot CHCl_3$, $[\mathbf{1}][BF_4]\cdot H_2O\cdot 0.5C_4H_8O_2$, $[\mathbf{1}][BF_4]\cdot H_2O\cdot C_6H_5OH$, and $[C_6H_5COOH\subset\mathbf{1}][BF_4]$

	$[CHCl_3\subset\mathbf{1}][BF_4]\cdot CHCl_3$	$[\mathbf{1}][BF_4]\cdot H_2O\cdot 0.5C_4H_8O_2$	$[\mathbf{1}][BF_4]\cdot H_2O\cdot C_6H_5OH$	$[C_6H_5COOH\subset\mathbf{1}][BF_4]$
Chemical formula	$C_{32}H_{47}BCl_6F_4ORu_3$	$C_{32}H_{51}BF_4O_3Ru_3$	$C_{36}H_{53}BF_4O_3Ru_3$	$C_{37}H_{51}BF_4O_3Ru_3$
Formula weight	1050.42	873.75	923.80	933.80
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic
Space group	*Cmcm*	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
Crystal colour and shape	red plate	red block	red block	orange plate
Crystal size	$0.36\times0.29\times0.08$	$0.28\times0.22\times0.08$	$0.25\times0.25\times0.15$	$0.48\times0.25\times0.05$
a (Å)	20.867(3)	9.289(2)	15.986(2)	13.129(2)
b (Å)	10.891(2)	13.194 (2)	10.550(2)	13.711(2)
c (Å)	20.855(3)	13.550(2)	21.402(3)	19.901(3)
α (°)	90	85.308(3)	90	90
β (°)	90	84.475(3)	90.965(2)	90
γ (°)	90	87.940(3)	90	90
V (Å$_3$)	4739.4(12)	1646.7(5)	3608.8(9)	3582.5(8)
Z	4	2	4	4
T (K)	173(2)	173(2)	173(2)	100(2)
D_{calc} (g cm^{-3})	1.472	1.762	1.700	1.731
μ (mm^{-1})	1.319	1.412	1.294	1.305
Scan range (°)	$3.90 < 2\theta < 56.92$	$3.10 < 2\theta < 56.98$	$2.54 < 2\theta < 56.86$	$3.60 < 2\theta < 57.14$
Unique reflections	2983	7328	8599	8612
Reflections used $[I > 2\sigma(I)]$	2314	4219	6345	7187
R_{int}	0.0755	0.0607	0.0827	0.0856
Final R indices $[I > 2\sigma(I)]$	0.0458, wR_2 0.1174	0. 0651, wR_2 0.1457	0.0361, wR_2 0.0764	0.0357, wR_2 0.0668
R indices (all data)	0.0634, wR_2 0.1247	0.1190, wR_2 0.1702	0.0600, wR_2 0.0914	0.0522, wR_2 0.0723
Goodness-of-fit	1.038	0.927	1.007	1.009
Maximum, minimum $\Delta\rho$/e (Å^{-3})	1.218, −1.153	1.727, −1.138	0.821, −0.731	0.842, −0.763

chromated radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using the program SHELXS-97 [9]. The refinement and all further calculations were carried out using SHELXL-97 [10]. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarised in Table 1. Figs. 1, 3, 5 and 6 were drawn with ORTEP [11] and Figs. 2, 4 and 7 with MERCURY [12].

CCDC-232284 $[CHCl_3 \subset \mathbf{1}][BF_4] \cdot CHCl_3$, 232 285 $[\mathbf{1}][BF_4] \cdot H_2O \cdot 0.5C_4H_8O_2$, 232 286 $[\mathbf{1}][BF_4] \cdot H_2O \cdot C_6H_5OH$, and 232 287 $[C_6H_5COOH \subset \mathbf{1}][BF_4]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

3. Results and discussion

The trinuclear cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**1**), accessible in aqueous solution from the dinuclear precursor $[H_3Ru_2(C_6Me_6)]^+$ and the mononuclear building block $[Ru(C_6H_6)(H_2O)_3]^{2+}$, precipitates as the tetrafluoroborate salt, which is well soluble in acetone, dimethylsulfoxide, dichloromethane and ethanol, and sparingly soluble in water, methanol and chloroform [7]. The hydrophobic pocket spanned by the three arene ligands in **1** is capable of hosting small molecules, according to molecular modelling studies [13].

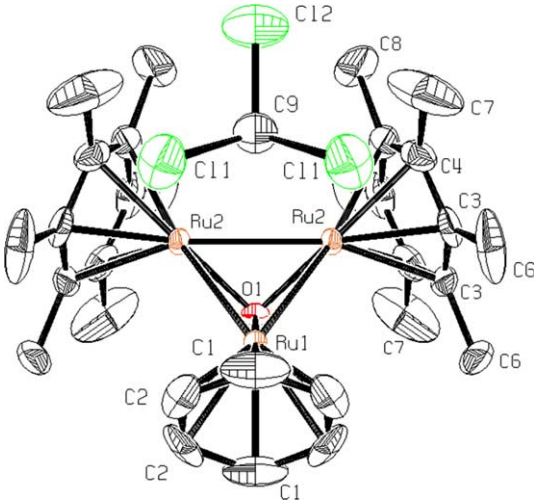

Fig. 1. ORTEP drawing of $[CHCl_3 \subset \mathbf{1}]^+$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms, hydrogen-bonded chloroform molecule and tetrafluoroborate anion are omitted for clarity.

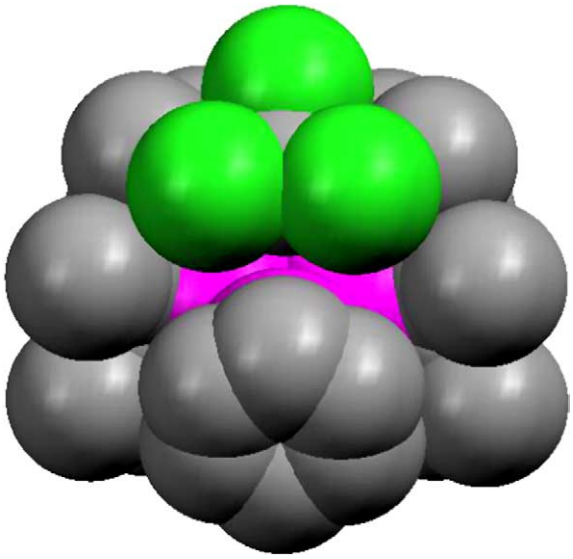

Fig. 2. Space filling representation of the host–guest complex $[CHCl_3 \subset \mathbf{1}]^+$.

To gain further insight in the host–guest properties of **1**, we attempted to crystallise $[\mathbf{1}][BF_4]$ in a first series with simple molecules such as methanol, ethanol, tetrahydrofuran, dioxane, dichloromethane and chloroform. In the presence of methanol, ethanol, tetrahydrofuran, and dichloromethane, no crystals containing a guest molecule could be obtained; only the already known complex containing a water molecule hydrogen-bonded to the μ_3-oxo ligand was obtained [7]. Interestingly, in one instance $[\mathbf{1}][BF_4] \cdot H_2O$ was found to crystallise in a higher symmetry group, but it shows the same geometric parameters. [1] However, in the presence of chloroform and dioxane host–guest systems have been observed.

The crystallisation of $[\mathbf{1}][BF_4]$ in a mixed acetone–chloroform solution gave the host–guest complex $[CHCl_3 \subset \mathbf{1}][BF_4] \cdot CHCl_3$, see Fig. 1. In the crystal, two chloroform molecules per asymmetric unit are present, one being hosted in the hydrophobic pocket of **1** and the second being involved in a weak hydrogen bond with the tetrafluoroborate anion. The guest chloroform molecule sits perfectly in the hydrophobic pocket of **1** with its hydrogen atom being encapsulated inside the cavity. The distance between the carbon atom of the incorporated chloroform molecule and the Ru_3 plane is 4.144(7) Å.

[1] X-ray data for $[\mathbf{1}][BF_4] \cdot H_2O$; $C_{30}H_{47}BF_4O_2Ru_3$, $M = 829.70$ g mol^{-1}, monoclinic, $P2_1/n$, $a = 10.0820(15)$, $b = 16.329(2)$, $c = 18.767(3)$ Å, $\beta = 90.964(2)°$, $U = 3089.2(8)$ Å^3, $T = 173$ K, $Z = 4$, μ(Mo Kα) = 1.498 mm^{-1}, 7293 reflections measured, 6129 unique ($R_{int} = 0.0608$) which were used in all calculations. The final $wR(F^2)$ was 0.0775 (all data). CCDC-232203 contains the supplementary crystallographic data for this structure.

In the $[CHCl_3 \subset \mathbf{1}]^+$ host–guest system; Ru1, O1, C1, C9, and the Cl2 atoms lie on a mirror plane. Therefore, the Cl_3 and Ru_3 moieties are by symmetry in a perfect staggered conformation, minimising steric repulsions, see Fig. 2.

In the crystals obtained in the presence of dioxane, no solvent molecule was observed in the hydrophobic pocket of the cluster cation **1**. Instead, a dioxane molecule, situated on the centre of symmetry, forms a hydrogen-bonded network with two water molecules, which are as well hydrogen-bonded to the μ_3-oxo ligand of a cluster cation, see Fig. 3. Thus, a μ_3-oxo-H_2O-dioxane-H_2O-μ_3-oxo hydrogen-bonded chain is obtained. The O–O distances of the hydrogen bonds are, respectively, 2.753(6) Å for the μ_3-oxo ligand and H_2O, and 2.807(6) Å between the dioxane and the water molecule. The total distance between the two bridged μ_3-oxo ligands is 11.27(1) Å.

However, in the solid state, the hydrophobic cavity is not totally unoccupied. A benzene ligand of a symmetry related neighbouring cluster cation is slightly incorporated in the hydrophobic pocket of **1**. This benzene ligand is as well involved in a slipped-parallel π–π stacking interactions with a second cluster cation, thus forming a multimer of cations, see Fig. 4.

The benzene ligand inside the cavity of a neighbouring cluster interacts weakly through hydrophobic and van der Waals contacts. The shortest distances between the metal-bound hydrogen atoms and the closest carbon atoms of the benzene ligand are 3.41 and 3.90 Å. The distance observed between the π-stacking interacting systems (centroid $\cdots$ centroid 3.65 Å) is in good agreement with the theoretical value calculated for these stacking modes [14].

In a second series of crystallisation experiments, molecules with phenyl substituents such as aniline, ani-

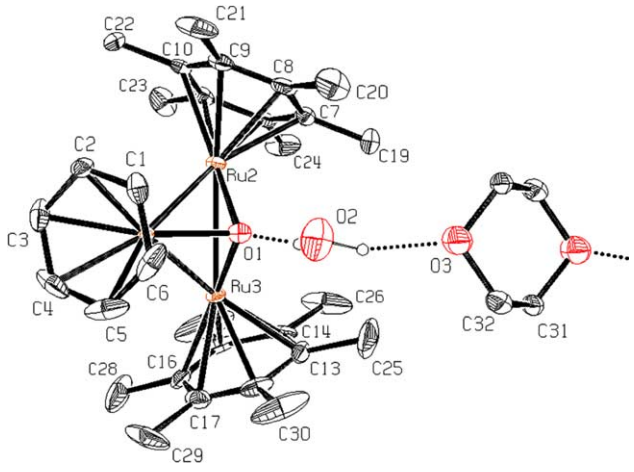

Fig. 3. ORTEP drawing of $[\mathbf{1}][BF_4] \cdot H_2O \cdot 0.5C_4H_8O_2$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and tetrafluoroborate anion are omitted for clarity.

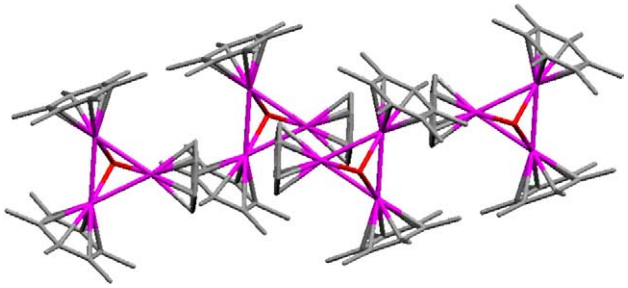

Fig. 4. Infinite chain of $[\mathbf{1}]^+$ in $[\mathbf{1}][BF_4] \cdot H_2O \cdot 0.5C_4H_8O_2$.

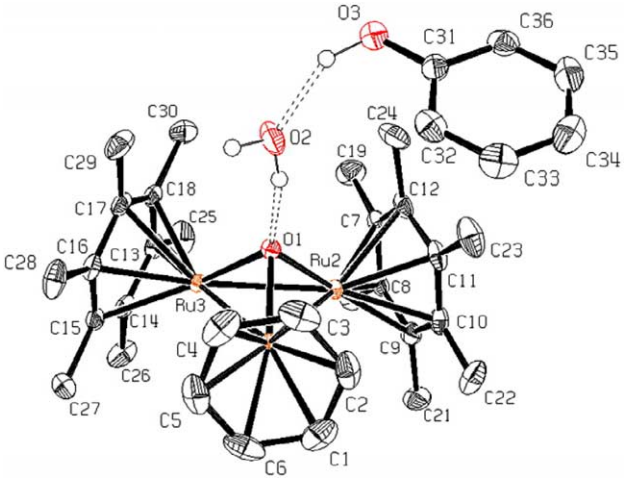

Fig. 5. ORTEP drawing of $[\mathbf{1}][BF_4] \cdot H_2O \cdot C_6H_5OH$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and tetrafluoroborate molecule are omitted for clarity.

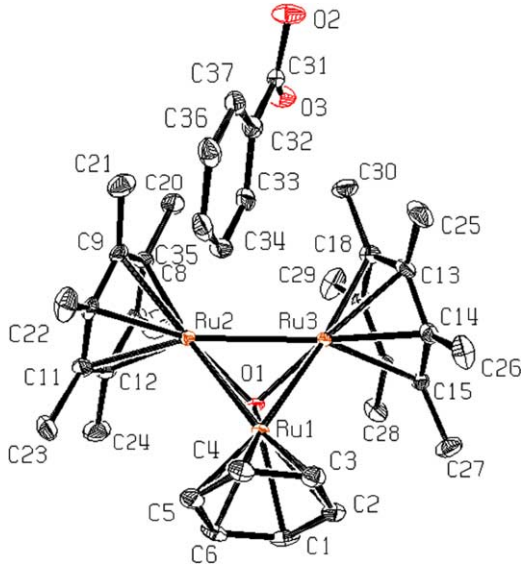

Fig. 6. ORTEP drawing of $[C_6H_5COOH \subset \mathbf{1}]^+$. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and tetrafluoroborate molecule are omitted for clarity.

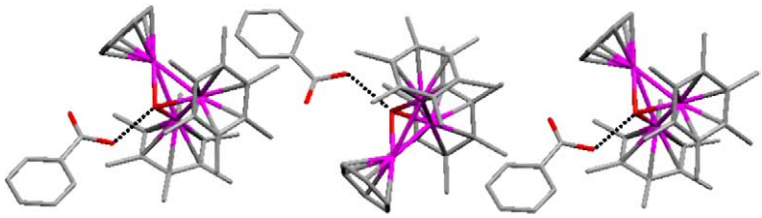

Fig. 7. Infinite host–guest chain of $[C_6H_5COOH\subset\mathbf{1}]^+$, along the *c*-axis.

sole, benzaldehyde, benzoic acid, methyl benzoate, phenol, and styrene have been added to an acetone solution containing [**1**][BF_4]. Crystals suitable for X-ray diffraction studies were obtained only with phenol and benzoic acid.

Surprisingly, addition of phenol to an acetone solution of [**1**][BF_4] gives rise to the formation of [**1**][BF_4]·H_2O·C_6H_5OH, in which the phenyl ring is not incorporated in the hydrophobic pocket of **1**. As observed with dioxane, a water molecule is inserted between the μ_3-oxo ligand of cation **1**, and the hydroxy function of a phenol molecule, forming a μ_3-O···H_2O···HO–C_6H_5 hydrogen-bonded monomer, see Fig. 5.

The μ_3-O···OH_2 distance is 2.771(4) Å with an angle of 166.6° and the H_2O···O-phenol distance is 2.668(4) Å with an angle of 149.7°. The tetrafluoroborate anion participates as well to a hydrogen bond with the water molecule, F–OH_2 distance is 2.771(5) Å with an angle of 161.4°.

Finally, with benzoic acid, the phenyl ring acts as predicted as a guest molecule inside the hydrophobic pocket of a cluster cation ($[C_6H_5COOH\subset\mathbf{1}]^+$), while the carboxylic acid function interacts with a μ_3-oxo ligand of a second cluster cation. Thus, giving rise to a head to tail host–guest chain. The atoms numbering scheme of $[C_6H_5COOH\subset\mathbf{1}]^+$ is presented in Fig. 6.

The benzoic acid molecule is incorporated inside the hydrophobic pocket. The phenyl ring interacts weakly with the host molecule only by hydrophobic and van der Waals contacts. The angle formed by the C_6 plane and the Ru_3 plane is 86.81(9)°, the guest molecule being held almost upright in the hydrophobic pocket. On the other hand, the acid function allows the guest molecule to form hydrogen bonds. Indeed, in the solid state, a strong hydrogen bond with the μ_3-oxo ligand is observed. The O···O distance is 2.558(4) Å with an O–H···O angle of 162°. Thus, forming along the *c*-axis, a host–guest–host infinite one dimensional chain, see Fig. 7.

4. Conclusion

The cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ has shown interesting host–guest behaviour. The hydrophobic pocket spanned by the three arene ligands can be seen as a bowl to guest molecules, whereas the μ_3-oxo ligand is a strong acceptor to form hydrogen bonds. We have shown that these two different sites could be occupied by benzoic acid molecules, the phenyl group being incorporated in the hydrophobic pocket and the acid group hydrogen-bonded to the μ_3-oxo ligand of a neighbouring molecule, thus giving rise to an infinite host–guest chain.

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