Molecular and Crystal Structures of Cubane-like Ru−O Complexes and the Molecular Orbital Analysis of an Unusual π−π Interaction Stabilized by C−H···O Hydrogen Bonds

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The synthesis and structural characterization of the family of the cubane-like complexes $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[OH]_4{\cdot}12H_2O$ (**1**), $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[BF_4]_3[Cl]{\cdot}2H_2O$ (**2**), and $[(\eta^6\text{-}C_6H_6)_3\text{-}Ru_4(OH)_4(Cl)_3][BF_4]_2{\cdot}3H_2O$ (**3**) are reported. The relationship between molecular and crystal structure of the complexes has been investigated by means of theoretical calculations of the DFT type. In the solid state, compound **1** shows the presence of benzene−benzene contacts between perfectly eclipsed ligands belonging to neighboring molecules. These are surrounded by a "belt" of water molecules forming C−H···O hydrogen bonds with the coordinated benzene. These H-bonds would appear to be sufficiently strong to compensate the anticipated repulsive benzene−benzene interactions. The role of (M−)Cl···H−O and Cl^-···H−O interactions in **2** and **3** has also been investigated.

Introduction

Arene complexes and clusters have been studied extensively over the past decade.[1] The impetus for these studies came initially from the need to develop appropriate molecular models for benzene on the metal surface and also from the desire to develop a cluster-based "metallocene" chemistry. In the course of these studies we were able to observe that the benzene ligands in arene clusters of osmium and ruthenium had a pronounced tendency to form intermolecular benzene−benzene (graphitic-like) interactions in the solid state. Motifs such as "chains", "snakes", and "ribbons" could be observed depending on the number of arene ligands and on the type and number of the other ligands. The flat arenes were found to tend to aggregate in "slipped-parallel" fashion, i.e., without direct C···C overlap as in graphite.

More recently we have extended our studies to M_4O_4 metal−oxo systems, in which the arene is bonded to metal atoms with an oxidation state higher than the one (*formally* zero) observed in the carbonyl systems. Cubane-like clusters based on the M_4O_4 central unit are well established.[2] In 1966 we first reported the synthesis of the carbonyl cubane cluster $[Os_4O_4(CO)_{12}]$,[3] which was later fully characterized by single-crystal X-ray diffraction and found to contain a central Os_4O_4 cubic unit.[3e] Later, Gould and co-workers[4] reported the benzene−cubane tetracation $[(\eta^6\text{-}C_6H_6)_4Ru_4(OH)_4]^{4+}$, which was found to contain the central $Ru_4(OH)_4$ unit. Fundamentally, the osmium and ruthenium compounds are related by the progressive addition of four protons to the central M_4O_4 unit.

$$[M_4O_4] \xrightarrow{H^+} [M_4O_3(OH)]^+ \xrightarrow{H^+} [M_4O_2(OH)_2]^{2+} \xrightarrow{H^+} \xrightarrow{H^+} [M_4O(OH)_3]^{3+} \xrightarrow{H^+} [M_4(OH)_4]^{4+}$$

In this paper we report the synthesis of a range of benzene cubane clusters based on the $Ru_4(OH)_4$ central

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Scheme 1. Proposed Mechanism of the Formation of Cubane-like Ru−O Complexes via the Dimeric Form $[(\eta^6\text{-}C_6H_6)_2Ru_2(OH)_3]^+$

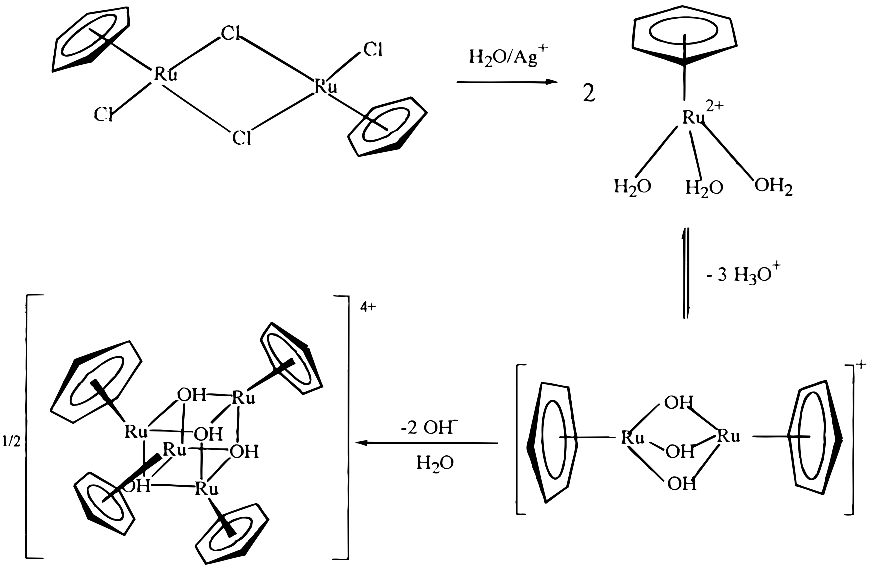

Table 1. List of Compounds

compound	formula
1	$[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[OH]_4\cdot 12H_2O$
2	$[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[BF_4]_3[Cl]\cdot 2H_2O$
3	$[(\eta^6\text{-}C_6H_6)_3Ru_4(OH)_4(Cl)_3][BF_4]_2\cdot 3H_2O$
4	$[(\eta^6\text{-}C_6H_6)\ RuH_4]_4[Cl]_2\cdot 5H_2O$ [15]

motif and an example of an eclipsed intermolecular benzene−benzene interaction. Clearly, when the −OH group is involved, it is not surprising that, at least in the solid state, the ligand can participate in noncovalent bonds, such as O−H···X hydrogen bonds with solvent molecules and/or the counterions. The compounds discussed in this paper are summarized in Table 1. With the exception of compound **4**, all other systems, including **1**, **2**, and **3**, whose synthesis and characterization are dealt with in this paper, contain four −OH bridges.

Cubane-like clusters are all cationic, while most ruthenium arene clusters are neutral. They are precipitated from water solution; thus it is not surprising that they incorporate a large number of water molecules upon crystallization. These molecules form O−H···O hydrogen bonds with the cluster.

The formation of cubane-like clusters is also quite intriguing. There is no evidence of their existence in solution, which means that their formation occurs upon crystallization. The factors that actually control their formation are both the pH and the anion concentration, as already concluded in previous works,[4,5] and the stable species in acidic aqueous solution is the mononuclear aqua complex $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$. When the aqueous solution is not sufficiently acidic, the triaqua(benzene)ruthenium(II) cation $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ shows a strong tendency to dimerize and tetramerize. A mechanism for the formation of the cubane-like aggregate has been put forward by Stephenson and co-workers;[4] they suggested that deprotonation of the triaqua cation $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ occurs to give $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_2(OH)]^+$, which then tetramerizes to give the cubane cluster cation $[(\eta^6\text{-}C_6H_6)_4Ru_4(OH)_4]^{4+}$ with concomitant elimination of water. This process has been shown to be enhanced by the presence of sulfate ions, which shift the equilibrium toward the formation of the more insoluble cubane-like Ru−O cluster.

Our contribution to understanding the mechanism of the formation of these metal−oxo clusters comes from the isolation of the dinuclear intermediate $[(\eta^6\text{-}C_6H_6)_2Ru_2(OH)_3]^+$, which had been synthesized via a *different* route and characterized by means of single-crystal X-ray diffraction by Kim and co-workers.[6] This compound was used to produce the tetramer from a further dissolution in water, as illustrated in Scheme 1.

The formation of these compounds may be envisaged as a sort of *nucleation process* in which the cubane-like supramolecular aggregate is the result of a self-recognition and self-assembly process leading to the crystallization of an aqua complex. In other words, the crystallization of **1** (as well as of the other cubane-like clusters) can be seen to proceed in two stages, namely, (i) aggregation of the mononuclear benzene−Ru complex to form the dimeric structure and (ii) aggregation of the dimer to form the insoluble cubane moiety, which precipitates with an adequate number of counterions and solvent molecules.

Experimental Section

General Considerations. All reactions were carried out without any particular precautions. $RuCl_3\cdot 3H_2O$, 1,3-cyclohexadiene, and $AgBF_4$ were purchased from Aldrich and used as provided.

Synthesis of $[(\eta^6\text{-}C_6H_6)_2RuCl_2]_2$.[7] Excess 1,3-cyclohexadiene (10 mL) was added to a solution of $RuCl_3\cdot 3H_2O$ (1 g) in EtOH (95%) and stirred under reflux for 2 h. This mixture was then cooled in ice for about 1 h, and the resulting precipitate was isolated by filtration to yield the dimeric $[(\eta^6\text{-}C_6H_6)_2RuCl_2]_2$ as a brown solid.

Synthesis of $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[OH]_4\cdot 12H_2O$ (1). $[(\eta^6\text{-}C_6H_6)_2RuCl_2]_2$ (100 mg, 0.2 mmol) was dissolved in an acidic solution of H_2SO_4 (0.01M, 50 mL), $AgBF_4$ (77.8 mg, 0.4 mmol) was then added, and the mixture was stirred for 2 h. The

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Table 2. Crystal Data and Details of Measurements for Crystals of 1, 2, and 3

	1	**2**	**3**
formula	$C_{24}H_{44}O_{14}Ru_4$	$C_{24}H_{40}B_3ClF_{12}O_6Ru_4$	$C_{18}H_{28}B_2Cl_3F_8O_7Ru_4$
M	960.87	1124.72	1040.65
T/K	180(2)	180(2)	180(2)
system	trigonal	orthorhombic	monoclinic
space group	$R\bar{3}$	$Cmma$	$P2_1/c$
Z	2	4	4
a/Å	12.5206(14)	15.351(4)	10.994(2)
b/Å	12.5206(14)	19.300(10)	17.646(2)
c/Å	12.5206(14)	12.618(7)	16.042(2)
α/deg	87.40(2)	90	90
β/deg	87.40(2)	90	97.91(2)
γ/deg	87.40(2)	90	90
U/Å^3	1956.9(4)	3738(3)	3082.5(8)
cryst size/mm^3	0.08 × 0.08 × 0.08	0.30 × 0.10 × 0.10	0.10 × 0.10 × 0.08
F(000)	952	2192	2004
λ(Mo Kα)/Å	0.71073	0.71073	0.71073
μ(Mo Kα)/mm^{-1}	1.566	1.752	2.267
θ range/deg	2.5−25.0	3.5−25.0	3.5−25.0
ψ scan corr min, max transm	0.75, 1.00	0.62, 1.00	none (see Experimental Section)
octants explored	$-11 < h < 14$ $-5 < k < 14$ $-11 < l < 10$	$-18 < h < 18$ $-22 < k < 22$ $-14 < l < 2$	$0 < h < 13$ $0 < k < 21$ $-19 < l < 19$
no. of measured reflns	3665	2119	8516
no. of unique reflns	2305	1765	5230
no. ref params	126	74	356
goodness of fit on F^2	1.130	1.069	0.980
R1 [on F, $I > 2\sigma(I)$]	0.0766	0.0726	0.0542
wR2 (F^2, all data)	0.2590	0.2072	0.1149

resulting mixture was filtered to give a clear yellow solution. Slow evaporation from the latter gave rise to the formation of small orange cubic crystals suitable for X-ray analysis.

Synthesis of $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[Cl][BF_4]_3\cdot 2H_2O$ (2) and $[(\eta^6\text{-}C_6H_6)_3Ru_4(OH)_4Cl_3][BF_4]_2\cdot 3H_2O$ (3). $[(\eta^6\text{-}C_6H_6)_2RuCl_2]_2$ (100 mg, 0.2 mmol) was dissolved in water (50 mL); $AgBF_4$ (77.8 mg, 0.4 mmol) was added to the solution. The resulting mixture was stirred for 2 h and then filtered to give a clear yellow solution. Slow evaporation from the latter gave rise to the formation of small crystalline orange prisms of the compound **2**. Compound **3** was present in the same batch as an impurity, with a different shape and deeper color.

Crystal Structure Determination. Crystal data and details of measurements for crystalline **1**, **2**, and **3** are reported in Table 2. Diffraction intensities for compounds **1** and **2** were collected on a STOE diffractometer; for compound **3** the data were collected on a Rigaku R-Axis II-c imaging plate system. Both diffractometers were equipped with a graphite monochromator (Mo Kα radiation, $\lambda = 0.71073$ Å) and with an Oxford Cryosystem device for low-temperature collection. No attempt was made for absorption correction in **3**, since this is not necessary when the data are collected on an imaging plate system. All refinements have been carried out on F^2 using all reflections. The computer program SHELX97[8] was used for structure solution and refinement of **1** and **2**. In **2** only the Ru and Cl atoms were refined anisotropically. The computer programs SIR92 and SHELX97[8] were used for structure solution and refinement of **3**. In **3**, anisotropic thermal parameters were refined for all non-H atoms except the disordered F atoms and one of the two B atoms. For all compounds, hydrogen atoms were added in calculated positions: C−H = 0.95 Å; $B = 1.2B_{eq}$ of the corresponding carbon atoms; O−H = 1.00 Å; $B = 1.5B_{eq}$ of the corresponding oxygen atoms. The $H_{(water)}$ atoms were not observed, as is usually the case with heavy metal clusters, and no attempt was made to model them. For all molecular representations the graphic program SCHAKAL97[9] was used. The program PLATON[10] was used to calculate the hydrogen-bonding interactions of the C−H···F, C−H···O, O−H···O, O−H···Cl, and C−H···Cl type reported in Table 4. For these calculations all C−H distances were normalized to the neutron-derived value (1.08 Å). Crystal data and details of measurement, tables of atomic coordinates, tables of anisotropic thermal parameters and tables of bond lengths and angles are all available as Supporting Information and have been deposited with the Cambridge Crystallographic Data Centre.

Table 3. Ru−O and Ru−C Distances (Å) in Crystalline 1, 2, and 3

atoms	**1**	**2**	**3**
Ru(1)−O(1)	2.110(9)	2.113(6)	2.130(7)
Ru(1)−O(1)*	2.105(9)		
Ru(1)−O(2)	2.110(7)	2.133(9)	2.137(6)
Ru(1)−O(4)			2.146(6)
Ru(2)−O(1)	2.107(9)	2.134(9)	2.130(6)
Ru(2)−O(2)		2.106(6)	2.141(6)
Ru(2)−O(3)			2.121(6)
Ru(3)−O(2)			2.116(6)
Ru(3)−O(3)			2.116(6)
Ru(4)−O(4)			2.129(6)
Ru(4)−O(1)			2.071(6)
Ru(4)−O(3)			2.072(6)
Ru(4)−O(4)			2.095(7)
mean Ru−$C_{(bz)}$	2.15(2)	2.15(3)	2.17(3)

Dft Calculations. Density functional calculations[11] were carried out with the Amsterdam Density Functional (ADF) program[12] developed by Baerends and co-workers[13] using nonlocal exchange and correlation corrections.[14] The structures of the complex $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ and of the cubane cluster

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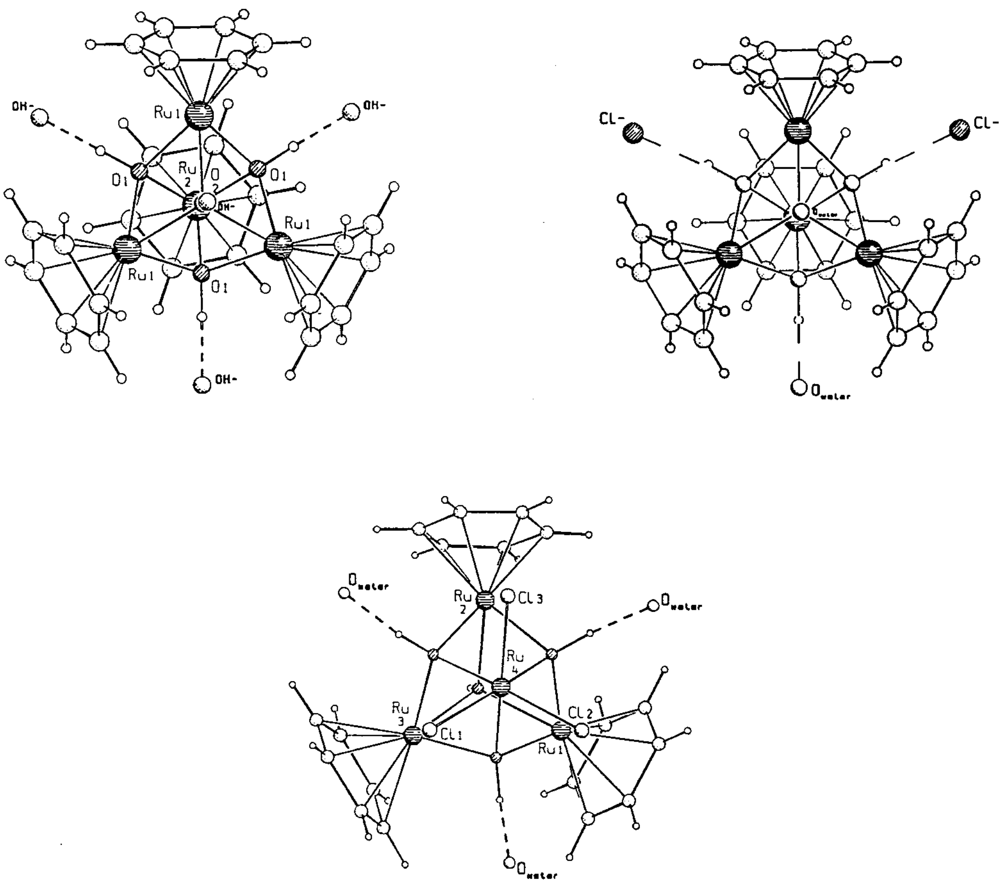

Figure 1. Molecular structure of crystalline **1** (top left) and **2** (top right) and the cation in **3** (bottom). The water molecules of cocrystallization in **1** and **2** and the BF_4^- anions in **3** are omitted for clarity.

Table 4. Hydrogen Bonds (Å) in Crystalline 1, 2, and 3[a]

type of interaction	1	2	3
D···A in (Ru)–O–H···O(H^-)	2.57 2.56		
D···A in (Ru)–O–H···O_{water}		2.59 2.64 2.60	2.63
D···A in (Ru)–O–H···Cl			2.99
D···A in (Ru)–O–H···Cl^-		3.05	
H···A in C–H···O	2.55 2.48 2.47	2.43	
H···A in C–H···Cl^-		2.69 2.72 2.60 2.69	
H···F in C–H···$F(BF_3)^-$		2.14 2.48 2.46 2.43 2.42 2.36 2.22 2.16 2.31	2.38 2.14 2.52 2.37 2.33 2.45 2.16 2.33

[a] The O–H···X angles are > 170°, whereas for C–H···X are > 115°.

cation $[(\eta^6\text{-}C_6H_6)_4Ru_4(OH)_4]^{4+}$ were used in the starting geometries for the calculations. Optimizations were performed under C_{3v} symmetry. In all the calculations, a triple-ζ Slater-type orbital STO basis set was used for Ru 5s and 5p; triple-ζ STO augmented with a 3d single-ζ polarization function was used for C 2s and 2p, O 2s and 2p, and H 1s. A frozen-core approximation was used to treat the core electrons of C, O, and Ru.

Results and Discussion

The first two tetracations listed in Table 1 will be discussed together. In all cases the metal framework consists of four ruthenium atoms and four hydroxo groups situated at alternate corners of a cube (d_{Ru-O} = 2.11–2.13 Å, see Table 3). As shown in Figure 1, each ruthenium carries a benzene ligand bound in η^6-fashion with average Ru–C distances of 2.15(2) and 2.15(3) Å in **1** and **2**, respectively, very similar to the average Ru–C distance of 2.151(8) Å observed in $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[SO_4]_2\cdot 12H_2O$.[4] In compound **3**, one of the ruthenium atoms carries three chlorine atoms instead of a benzene ring. The oxidation state of this ruthenium must be III, whereas the oxidation state of all the other ruthenium atoms is II. The resulting metal framework is a slightly different distorted cube with respect to the ones observed in **1** and **2**, with shorter Ru–O distances between the ruthenium atom carrying the chlorines (Ru4) and the adjacent hydroxo groups (see Scheme 2 and Table 3). The average Ru–C distance is 2.17(3) Å, slightly longer than in **1** and **2**.

The metal framework of compound **4** [15] is different from those discussed previously since the cation consists

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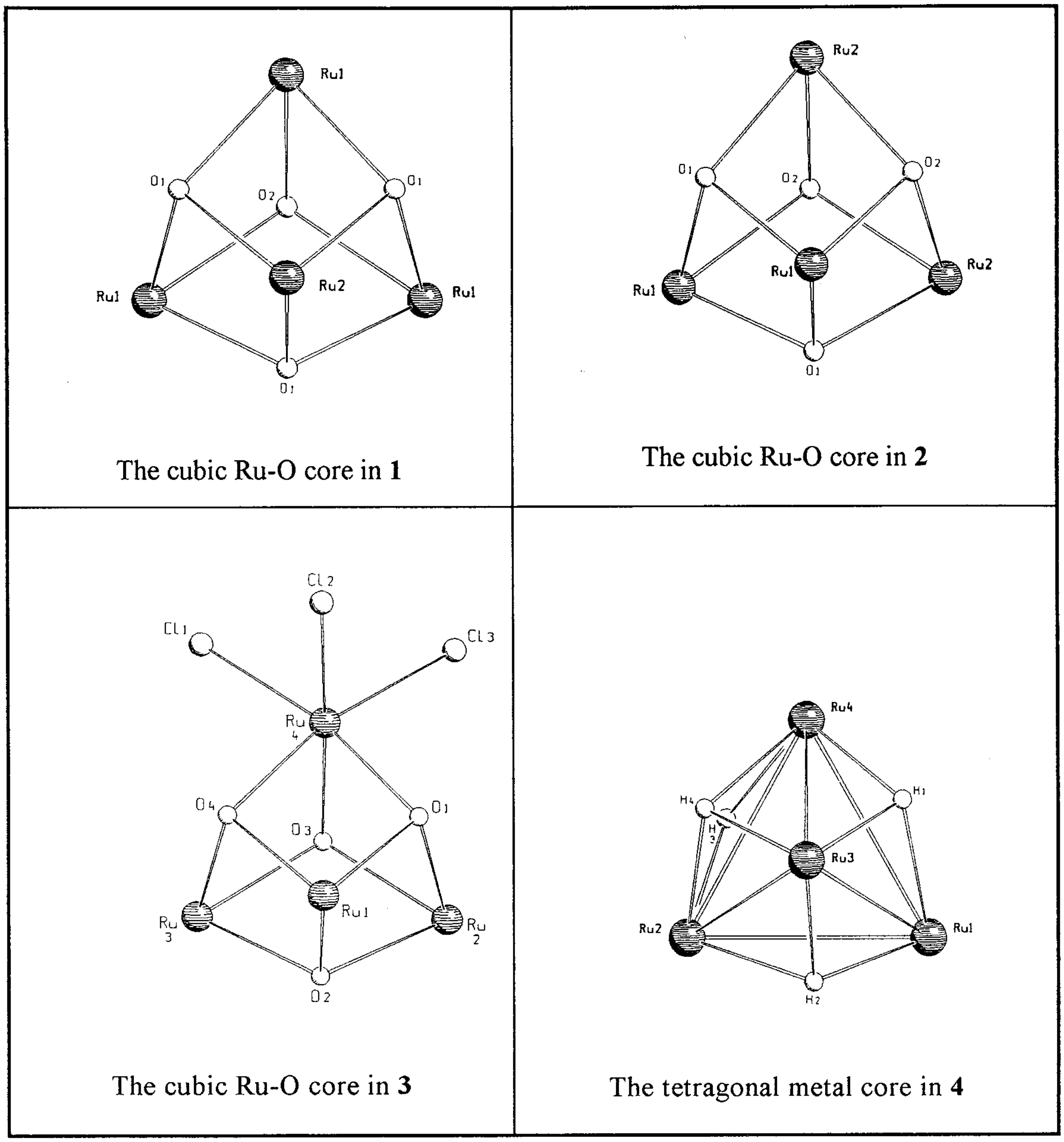
Scheme 2



The cubic Ru-O core in **1**

The cubic Ru-O core in **2**

The cubic Ru-O core in **3**

The tetragonal metal core in **4**

of a tetranuclear ruthenium cluster which coordinates four benzene and four hydrido ligands. The four Ru atoms of the metal skeleton define a slightly distorted tetrahedron, with Ru−Ru distances in the range 2.75−2.80 Å, the distortion due to the arrangement of the hydride ligands being asymmetric. The four benzene rings are coordinated to the ruthenium atoms in η^6-fashion (average Ru−C distance 2.19 Å); the resulting cluster cation $[(\eta^6\text{-}C_6H_6)RuH_4]^{2+}$ is very similar to the cubane-like ruthenium cluster cation $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4^{4+}$ in crystalline **1** and **2**.

The *Eclipsed* Benzene Rings in 1. Crystalline **1** shows the presence of an unusual packing motif. The benzene ligands belonging to neighboring cations $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4^{4+}$ face one another in the crystal at a distance that is shorter than in graphite ($d_{\pi-\pi} = 3.41$ Å). This is an intriguing observation not because of the presence of π-stack, a rather common phenomenon in the crystal structure of arene clusters, but because the two benzene rings are *eclipsed*. In general π-stack is attained via shifted (rather than staggered) benzene or arene ligands. This is usually understood as a way to optimize attraction between the C atom nuclei and the electrons in the p-orbitals of the neighboring fragment. An eclipsed configuration would lead to direct juxtaposition of the electronic clouds, screening the C atoms from the attractive contributions.

This would per se call for an explanation. The problem is made even more intriguing by the presence of a "belt" of disordered water molecules (see Figure 3) surrounding the juxtaposed benzene ligands.

The water oxygens accept hydrogen bond donation from the C−H groups of the benzenes, forming a web of weak C−H···O hydrogen bonds around the two ligands. An analysis of the anisotropic displacement parameters ("thermal ellipsoids") shows how the two eclipsed rings are less free to vibrate around their molecular axes (passing through the Ru atom and the midpoint of the ring) with respect to the remaining benzene ligands in the cluster. This means that the

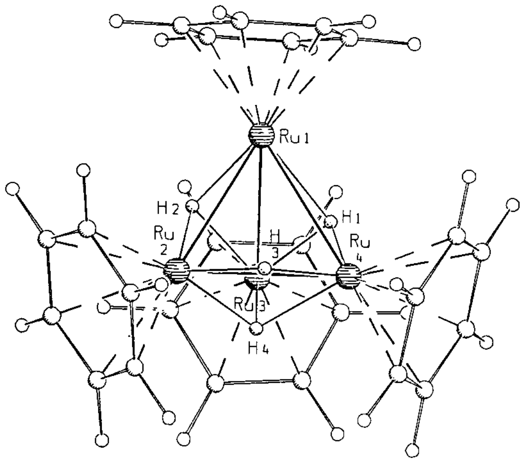


Figure 2. Molecular structure of the cation $[(\eta^6\text{-}C_6H_6)\text{-}RuH_4]^{2+}$ in **4**.[15]

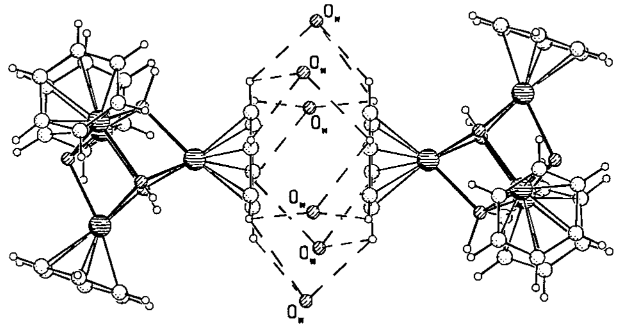


Figure 3. "Belt" of disordered water molecules surrounding the two eclipsed benzene rings in **1**. Note that only three molecules of water can be present simultaneously.

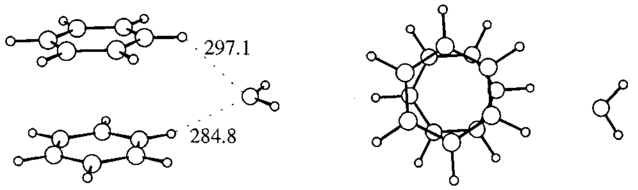
eclipsing is real and not a consequence of an average of different images of disordered benzene rings, as is the case with $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4[SO_4]_2{\cdot}12H_2O$,[4] where a similar arrangement of the benzene rings is observed, but the disorder of the ligands does not allow one to distinguish between eclipsed or staggered rings in the solid state.

If these two observations are considered together, a spontaneous question arises: (i) are the C−H···O bonds able to compensate or overcompensate for the unfavorable arrangement of the benzene ligands or—which is the same—(ii) is the eclipsing of the benzenes a consequence of the need to optimize C−H···O bonding with the water molecules?

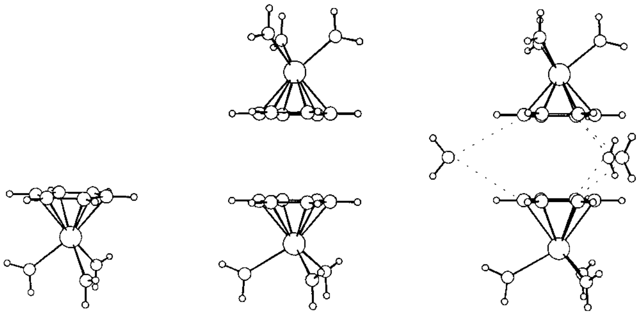
To address this question, we have carried out DFT calculations (ADF program), starting by studying a simple model, namely, two benzene molecules interacting with one water molecule. The interaction between one benzene and one water molecule was studied in detail a few years ago,[16] and the water molecule was shown to approach preferentially the benzene molecule with both hydrogen atoms pointing toward the π cloud of benzene. This is a very different arrangement from the one found in cluster **1**; therefore, we optimized the geometry of an aggregate containing one water molecule placed between the planes of the two benzenes, without symmetry constraints.

The geometry after optimization is shown in Scheme 3, from a side view (left) and a top view (right).

Scheme 3



Scheme 4



The oxygen atom remains at a relatively large distance from the benzene hydrogens, as seen in Scheme 3, but there is a bonding energy of 1.14 kcal mol^{-1}, with a strong contribution of the electrostatic term. The benzene rings and the water molecule have not departed significantly from their initial geometries. On the other hand, the energy of two benzene molecules in the same positions as before, but without any added water, is higher than that of two isolated benzene molecules by 4.7 kcal mol^{-1}. Therefore the water molecule plays an evident role in keeping the benzene rings together.

What happens when the benzene rings belong to the $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4^{4+}$ clusters? We studied the monomer $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4^{4+}$ optimizing totally the geometry under C_{3v} symmetry. In the final cluster, the Ru−O distances were found to be 2.203 and 2.198 Å (two different types of Ru atoms under C_{3v} symmetry), while the Ru−C distances ranged from 2.214 to 2.227 Å, all slightly longer than the experimental distances. The size of this monomer was treatable, but the dimer became too large for the calculations. Therefore, we considered a smaller model consisting of two $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ units to which three water molecules were added, maintaining C_{3v} symmetry. The monomer was optimized under C_{3v} symmetry, keeping the C−C and C−H distances within the benzene ring fixed (Scheme 4, left). A dimer was built, putting the two benzene rings eclipsed at the experimental distance, and the same parameters as before were optimized (Scheme 4, center). There are no relevant changes in the calculated bond lengths and angles; for instance, the Ru−O distances are 2.23 Å in the monomer and in the dimer, while Ru−C is 2.20 Å in the monomer and 2.17 Å in the dimer. The energies indicate repulsion between the two units, as the energy of the dimer is higher by 8.3 kcal mol^{-1} than twice the energy of the monomer.

Three water molecules were added to the dimer, and the resulting geometry was optimized under C_{3v} symmetry. This constraint makes it difficult for the benzene rings to become staggered and for the water molecules to move away from their initial positions (Scheme 4, right). The optimization concerns the same bonds and angles as before, the bonds and angles in the water

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[16] Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942.

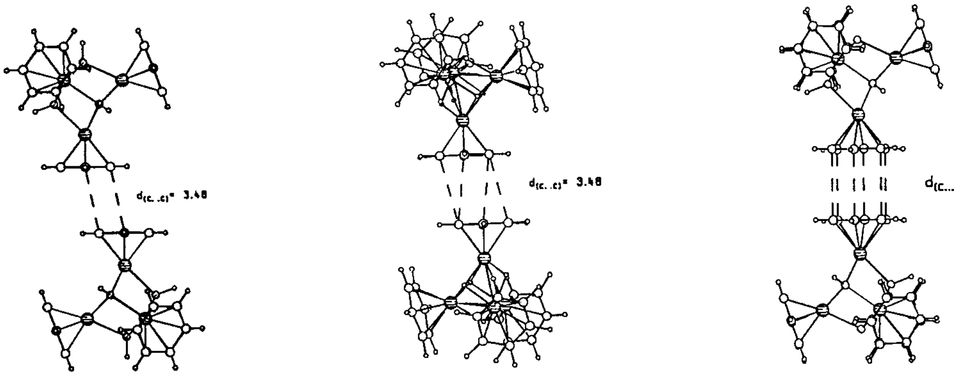

Figure 4. Benzene−benzene interaction between cations in **2** (left), **4** (center), and **1** (right).

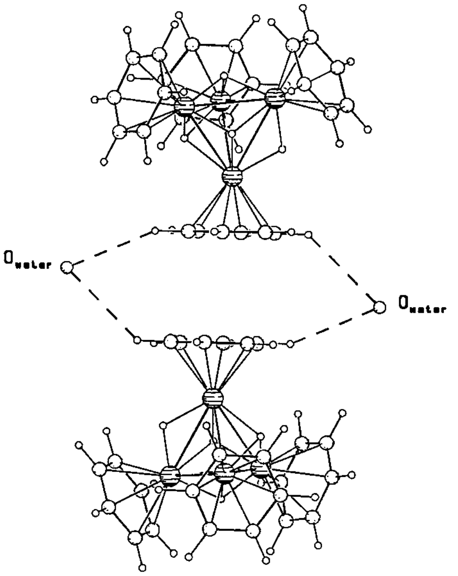

Figure 5. Almost "eclipsed" benzene rings in crystalline **4**.

molecules and their positions. The bonding energy between the three water molecules and the dimer is -31.9 kcal mol^{-1}, which corresponds to -10.6 kcal mol^{-1} per water molecule. The electrostatic component is essentially the same as this, while other contributions cancel out. This value is probably an overestimate, because in the structure the charge of the cationic dimer is compensated, at least in part, by the anions.

Examination of the crystal structure of **1**, **2**, and **4** (see Figure 4) reveals that the overlap between benzene rings facing each other can vary, whereas the distance between the π systems is the same, or nearly so, in all systems. The intermediate situation is given by the interaction between two neighboring cations $[(\eta^6\text{-}C_6H_6)RuH]_4^{2+}$, where the two benzene rings are almost eclipsed.

The reason for this can be found in the presence of two molecules of water surrounding the two benzene rings, as shown in Figure 5. The C−H···O hydrogen bonds formed by the water molecules and the carbon rings are slightly weaker (3.00 and 3.52 Å) than those observed in **1**. Furthermore, only two water molecules are involved in this interaction.

Charge-Assisted (Ru−)O$^{(+)}$−H···O(H)$^{-}$ Hydrogen Bonds and (Ru−)O$^{(+)}$−H···O$_{water}$. A recurrent packing feature in these compounds is the presence of a plethora of interionic O−H···X interactions between the cubane-like cations and the surrounding anions and water molecules (see Table 4). The distances between cluster-bound −OH groups and anions or water molecules −OH are appreciably shorter than those usually observed in ice or in water hydrates composed of neutral objects. We can then define them as charge-assisted (Ru−)O$^{(+)}$−H···O(H)$^{-}$ hydrogen bonds in **1** (2.56−2.57 Å) and charge-assisted (Ru−)O$^{(+)}$−H···O$_{water}$ in **2** (2.59−2.65 Å) and **3** (2.61 Å).

The reason is similar to that applied in rationalization of electrostatically compressed negative O−H$^{(-)}$···O$^{(-)}$ and C−H$^{(-)}$···O$^{(-)}$ interactions.[17] The presence of a strong ionic field generated by the ions in the crystal structure allows the atoms to get closer than when neutral groups are involved. (In support of this consideration we can observe that there is no difference when the donor is a cation and the acceptor an anion or vice versa.) Of course, since the hydrogen atoms could not be observed, there is an ambiguity: the presence of hydrogen bonds does not per se permit identifying with certainty whether the groups are present as H_2O or OH^{-}. Support for the cationic nature of these cubane compounds is provided by the analogous formation of such compounds with −OH^{-} replaced as counterion by either BF_4^- or Cl^{-}.

M−Cl···H−O and Cl^{-}···H−O Hydrogen Bonds. It has recently been shown that although C−Cl and C−F moieties have rather similar hydrogen-bonding characteristics, M−Cl moieties (M = transition metal) and Cl^{-} anions are much better hydrogen-bond acceptors.[18] In **2** and **3**, Cl^{-}···H−O and M−Cl···H−O types of interactions are observed, respectively, as reported in Table 4. In contrast to the results obtained by a detailed examination of this kind of contact from Cambridge Structural Database,[18] we find that the M−Cl···(H−)O hydrogen bond is shorter than the Cl^{-}···(H−)O interaction (2.99 and 3.05 Å in **2** and **3**, respectively). M−Cl···H−O interactions are usually considered "short" if $d_{(H\cdots Cl)} <$ 2.52 Å: in this respect the M−Cl···H−O contact in crystalline **3** appears to be very short ($d_{(H\cdots Cl)} \cong 2$ Å) and close to the minimum values observed in the Cambridge Structural Database.[18] Moreover, this Ru−Cl···H−O interaction present in **3** links together the $[(\eta^6\text{-}C_6H_6)_3Ru_4(OH)_4Cl_3]$ cations, forming ribbons along the crystal as shown in Figure 6. In crystalline **2**, the anion

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[17] Braga, D.; Grepioni, F.; Novoa, J. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1959. (b) Braga, D.; Grepioni, F.; Tagliavini, E.; Novoa, J. J.; Mota, F. *New J. Chem.* **1998**, 755.

[18] Aullon, G.; Bellamy, D.; Brammer, L.; Bruton, E. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1998**, 653.

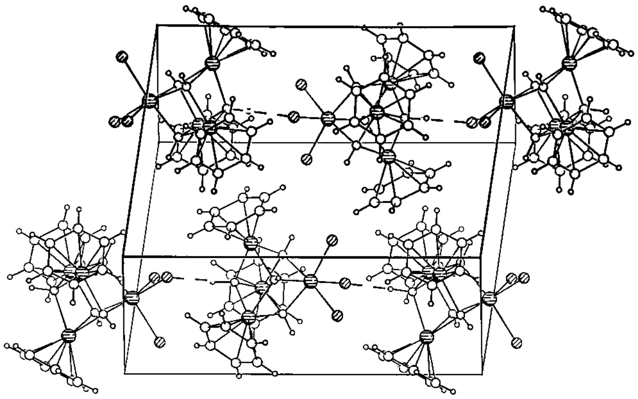

Figure 6. Cl contacts of the type M−Cl···H−O giving rise to the formation of "ribbons" in crystalline **3**.

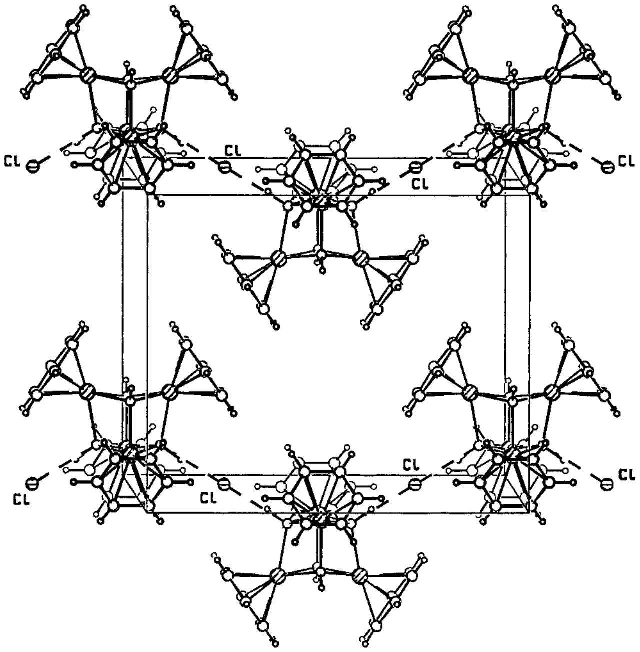

Figure 7. Cl contacts of the type Cl^-···H−O in crystalline **2**. The chloride lies on an inversion center, and its charge is shared between two neighboring cationic clusters.

Cl^-, which lies on an inversion center, is halfway between two cations, $[(\eta^6\text{-}C_6H_6)Ru(OH)]_4{}^{4+}$, as shown in Figure 7, giving rise to a polymeric arrangement of the cations linked via Cl^-···H−O interactions. This feature is probably the reason we observe the M−Cl···H−O distance to be shorter than the Cl^-···H−O interaction. Crystalline **4** also contains Cl^- as a counterion and interacts via short C−H···Cl^- hydrogen bonds with $[(\eta^6\text{-}C_6H_6)RuH_4)]_4{}^{2+}$ ($d_{(H\cdots Cl)}$ = 2.63−2.83 Å).

Conclusions

Cubane-like arene clusters were considered oddities in the vast family of transition metal clusters. The chemistry of clusters in aqueous solution has never been given much attention. With this paper we have shown that there exists a rich chemistry of these complexes. In a sense, it could even be said that this is mainly a piece of solid-state chemistry and crystal engineering, as the species are subjected to complex equilibria in solution and appear to self-assemble in the cubane-like superstructures only upon crystallization. A deliberate choice of the building blocks for the construction of solid materials based on their supramolecular functionalities is the paradigm of crystal engineering.[19] Furthermore, we have discussed an intriguing structural feature of the ion organization in the crystals, namely, the existence of exactly eclipsed benzene ligands in the packing. This anomalous relative arrangement of the arenes has been accounted for in terms of the web of weak intermolecular C−H···O hydrogen bonds between the hydrogen atoms on the rim of the benzenes and cocrystallization water molecules. This structural observation has been substantiated by DFT of theoretical calculations showing that the gain in energy associated with the formation of C−H···O bonds overcompensates for the energetically less favorable juxtaposition of the benzene ligands. The unusual π−π interaction stabilized by C−H···O hydrogen bonds is, therefore, another case of intermolecular competition in which less stable arrangements are permitted because of the optimization of several additional noncovalent bonds.

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Supporting Information Available: X-ray crystallographic files, in CIF and PDF format, for compounds **1**−**3** are available free of charge via the Internet at http://pubs.acs.org.

OM990619D

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[19] See for a general entry: *Crystal Engineering: from Molecules and Crystals to Materials*; Braga, D., Grepioni, F., Orpen, A. G., Eds.; Kluwer Academic Publishers: Dordrecht, 1999. See for entries in the organometallic area: (b) Braga, D.; Grepioni, F. *Coord. Chem. Rev.* **1999**, *183*, 19. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375.