inorganic compounds

Hydrogen bonding and structure of Ba₂Ru₂Cl₁₀O·10H₂O

Sihem Boufas,ᵃ* Nasr-Eddine Hadjadj,ᵃ Hocine Merazig,ᵃ Anna Grazia Moliterniᵇ and Angela Altomareᵇ

ᵃLaboratoire de Chimie Moléculaire, du Contrôle de l'Environnement et des Mesures Physico-Chimiques, Faculté des Sciences, Département de Chimie, Université Mentouri de Constantine, 25000 Constantine, Algeria, and ᵇIC, Sede di Bari, CNR, Via Amendola, 122/O, 70126 Bari, Italy
Correspondence e-mail: boufas_sihem@yahoo.fr

Dibarium μ-oxido-bis[pentachloridoruthenate(IV)] decahydrate, $Ba_2Ru_2Cl_{10}O \cdot 10H_2O$, has been prepared from ruthenium(III) chloride and barium chloride in hydrochloric acid. It crystallizes in the monoclinic system (space group $C2/c$). The structure consists of alternating layers of $[Ru_2Cl_{10}O]^{4-}$ and $[Ba(H_2O)_7]^{2+}$ complex ions along the a direction. The O atom bonded to ruthenium occupies the $4e$ site, with $\bar{1}$ symmetry, while the other atoms occupy general $8f$ sites. The overall structure is held together by $O—H\cdots O$ hydrogen bonds and $O—H\cdots Cl$ dipole–dipole interactions.

Comment

Previous investigations of MCl_2–$RuCl_3$ systems (M = K and Cs) have led to the identification of $K_4[Ru_2Cl_{10}O]$ (Deloume *et al.*, 1979) and $Cs_4Ru_2Cl_{10}O$ (Santana Da Silva *et al.*, 1999). We have investigated the hydrated systems MCl_2–$RuCl_3$–H_2O (M = Mg, Ca and Ba) and, just recently, have determined the structure of $Mg_2Ru_2Cl_{10}O \cdot 16H_2O$ (Boufas *et al.*, 2007). The structural study of the different phases of these systems has been performed in order to compare the cation coordination environments and the number of water molecules, and to study the $Ru_2Cl_{10}O$ anionic group and understand the effect of the Mg/Ba substitution.

The asymmetric unit of the title compound contains one $[Ru_2Cl_{10}O]^{4-}$ anion, one Ba^{2+} cation and five water molecules (Fig. 1). The overall structure consists of layers stacked along the c direction, with $[Ru_2Cl_{10}O]^{4-}$ dimeric units bridging adjacent sheets that are held together by $[Ba(H_2O)_7]^{2+}$ cations through atoms Cl2 and Cl3 along the (101) plane. As reported for $Mg_2Ru_2Cl_{10}O \cdot 16H_2O$ (Boufas *et al.*, 2007), the Ru atom resides in a distorted octahedron involving one bridging O atom [Ru1—O1 = 1.7657 (4) Å] and five Cl atoms with an average Ru—Cl distance of 2.3637 Å (Table 1). These distances are similar to those of the anhydrous compounds reported in the literature (1.800 and 2.362 Å for $K_4[Ru_2Cl_{10}O]$, and 1.791 and 2.357 Å for $Cs_4Ru_2Cl_{10}O$) and

agree well with those found in $Mg_2Ru_2Cl_{10}O \cdot 16H_2O$ (1.7822 and 2.3628 Å). The standard deviations from the values given by the two hydrated compounds differ by about 0.02 and 0.0008 Å. The Ru—O distance in the title compound is the shortest and the Ru—Cl distance is the longest.

The barium cation is surrounded by nine atoms, *viz.* five O atoms belonging to five water molecules *via* metal–OH₂ bonds and two Cl atoms (Cl2 and Cl3) from the $Ru_2Cl_{10}O$ octahedron *via* metal–Cl bonds. The presence of additional interactions (Ba1—O2Wⁱ and Ba1—O4Wⁱ; symmetry code as in Table 1) leads to ninefold coordination for each Ba atom. The $[Ba(H_2O)_7]^{2+}$ cations extend along the b direction in a zigzag fashion, forming layers parallel to the bc plane, and each $[Ru_2Cl_{10}O]^{4-}$ anion is surrounded by six $[Ba(H_2O)_7]^{2+}$ cations (Fig. 2). The Ba1—Cl2 and Ba1—Cl3 distances (Table 1) are similar to those found in barium dichloride dihydrate (3.0901 and 3.2836 Å; Bochkova *et al.*, 1980) and agree with the sum of the ionic radii of the Ba^{2+} (1.35 Å) and Cl^- ions (1.81 Å) (Shannon, 1976).

The average Ba1—OW distance is 2.8724 Å, similar to that in $Ba(OH)I(H_2O)_4$ (2.8425 Å), where Ba is coordinated by
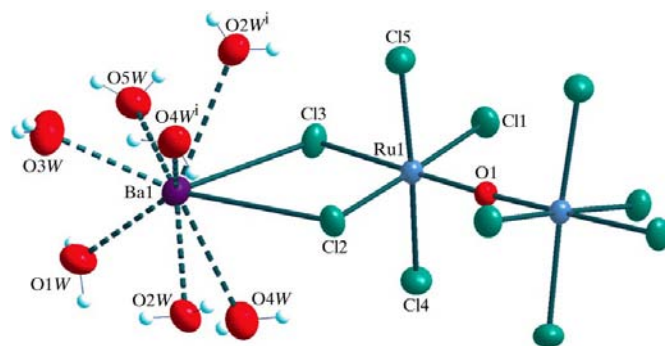

Figure 1
The structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids for non-H atoms are drawn at the 90% probability level. (The symmetry code is as in Table 1.)
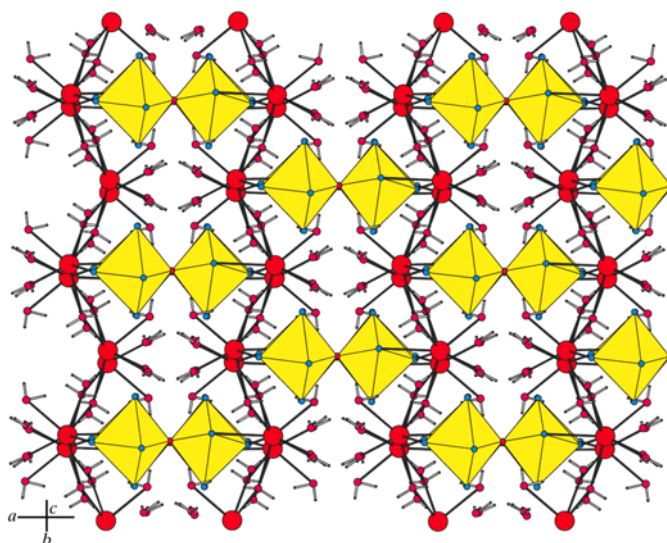

Figure 2
The packing of the title compound, viewed down the c axis.

only four water molecules (Fromm & Goesmann, 2000), and somewhat longer than that in $Ba(C_{10}H_4O_8)(H_2O)_5$ (2.8094 Å), where Ba is surrounded by five O atoms (Dale *et al.*, 2003). This difference is due to the presence of Ba–carboxylate bonds that reduce the Ba—OH$_2$ distances.

The cations and anions of the title compound are linked into a three-dimensional network by means of O—H$\cdots$Cl and O—H$\cdots$O interactions (Table 2 and Fig. 2). The first type links the $Ru_2Cl_{10}O$ octahedra to water molecules through all the Cl atoms, with distances of between 2.36 (6) and 2.81 (6) Å. Atoms Cl4 and Cl5 are involved in two hydrogen bonds each, Cl2 and Cl3 establish one hydrogen bond each, and Cl1 is engaged in three interactions. The O2W—H12$W\cdots$Cl1^{iii} interaction is the strongest, with an O—H$\cdots$Cl distance of 2.36 (6) Å. Only three O—H$\cdots$O hydrogen bonds are formed, *via* O3W [2.58 (4) Å], O1W [2.25 (9) Å] and O5W [2.20 (7) Å]. The environment of the $[Ru_2Cl_{10}O]^{4-}$ anion contains nine O—H$\cdots$Cl dipole–dipole interactions between the anion and the water molecules, *i.e.* this structure displays a lower degree of cohesion than that reported for $Mg_2Ru_2Cl_{10}O\cdot16H_2O$, characterized by 12 O—H$\cdots$Cl dipole–dipole interactions and five O—H$\cdots$O hydrogen bonds.

Overall, the various interactions bridge the ruthenate anions within and between layers and form cavities occupied by the $[BaCl_2(H_2O)_7]$ sheets.

Experimental

The title compound was crystallized from a supersaturated hydrochloric acid solution (50%, 5 ml) prepared using doubly distilled water and a mixture of ruthenium(III) chloride trihydrate (2.61 g) and dehydrated barium chloride (2.263 g). Brown plates of $Ba_2Ru_2Cl_{10}O\cdot10H_2O$ were obtained at ambient temperature by slow evaporation of the solution.

Crystal data

$Ba_2Ru_2Cl_{10}O\cdot10H_2O$	$V = 2454.5$ (4) Å^3
$M_r = 1027.48$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 20.9386$ (18) Å	$\mu = 5.49$ mm^{-1}
$b = 8.8654$ (7) Å	$T = 293$ (2) K
$c = 16.0560$ (15) Å	$0.25 \times 0.13 \times 0.03$ mm
$\beta = 124.559$ (5)°	

Data collection

Nonius KappaCCD diffractometer	10480 measured reflections
Absorption correction: part of the refinement model (ΔF) (*SADABS*; Sheldrick, 1996)	2488 independent reflections
	2103 reflections with $I > 2\sigma(I)$
$T_{min} = 0.441$, $T_{max} = 0.862$	$R_{int} = 0.05$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	15 restraints
$wR(F^2) = 0.070$	Only H-atom coordinates refined
$S = 1.06$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
2488 reflections	$\Delta\rho_{min} = -1.28$ e Å^{-3}
144 parameters	

H atoms were positioned geometrically and then O—H distances were restrained to 0.85 Å to ensure a chemically reasonable geometry, with U_{iso}(H) values fixed at $1.5U_{eq}$(O).

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVAL* (Nonius, 2002);

Table 1
Selected geometric parameters (Å, °).

Ba1—O3W	2.713 (4)	Ba1—Cl3	3.2882 (13)
Ba1—O1W	2.780 (4)	Ru1—O1	1.7657 (4)
Ba1—O5W	2.809 (4)	Ru1—Cl3	2.3394 (12)
Ba1—O2W	2.882 (4)	Ru1—Cl4	2.3627 (14)
Ba1—O2W^i	2.931 (4)	Ru1—Cl1	2.3665 (12)
Ba1—O4W	2.988 (4)	Ru1—Cl2	2.3744 (12)
Ba1—O4W^i	3.004 (4)	Ru1—Cl5	2.3755 (15)
Ba1—Cl2	3.1986 (12)		
O3W—Ba1—O1W	72.33 (13)	O2W—Ba1—Cl2	66.31 (8)
O3W—Ba1—O5W	68.55 (14)	O5W—Ba1—Cl3	69.25 (9)
O1W—Ba1—O5W	68.89 (12)	O1—Ru1—Cl3	179.48 (13)
O3W—Ba1—O2W	106.46 (14)	O1—Ru1—Cl4	92.49 (13)
O1W—Ba1—O2W	90.31 (12)	O1—Ru1—Cl1	91.93 (4)
O3W—Ba1—O2W^i	85.88 (14)	O1—Ru1—Cl2	91.45 (4)
O2W—Ba1—O2W^i	127.12 (6)	O1—Ru1—Cl5	91.19 (13)

Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1W—H11$W\cdots$O3W^{ii}	0.845 (14)	2.58 (4)	3.347 (7)	151 (6)
O2W—H12$W\cdots$Cl1^{iii}	0.82 (6)	2.36 (6)	3.176 (4)	177 (7)
O3W—H13$W\cdots$Cl4^i	0.73 (7)	2.66 (6)	3.354 (6)	161 (7)
O4W—H14$W\cdots$Cl4	0.78 (6)	2.62 (8)	3.395 (5)	171 (7)
O5W—H15$W\cdots$O1W^{ii}	0.81 (9)	2.25 (9)	3.040 (9)	166 (7)
O1W—H21$W\cdots$Cl2^{iv}	0.79 (5)	2.65 (5)	3.357 (5)	151 (6)
O1W—H21$W\cdots$Cl1^v	0.79 (5)	2.80 (6)	3.354 (5)	130 (5)
O2W—H22$W\cdots$Cl5^{iv}	0.76 (8)	2.42 (8)	3.144 (5)	161 (7)
O3W—H23$W\cdots$O5W^{ii}	0.79 (6)	2.20 (7)	2.932 (8)	155 (8)
O4W—H24$W\cdots$Cl1^v	0.85 (6)	2.71 (6)	3.519 (5)	160 (5)
O4W—H24$W\cdots$Cl3^v	0.85 (6)	2.81 (6)	3.324 (5)	121 (6)
O5W—H25$W\cdots$Cl5^{vi}	0.87 (8)	2.38 (8)	3.251 (6)	173 (4)

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x, -y + 1, -z + 1$; (iii) $x, -y + 1, z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vi) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998) and *ATOMS* (Dowty, 1995); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Bochkova, R. I., Grishin, I. A., Kuz'min, E. A. & Belov, N. V. (1980). *Kristallografiya*, **25**, 1064–1065.

Boufas, S., Merazig, H., Bendjeddou, L., Dénés, G., Beghidja, A. & Moliterni, A. G. (2007). *Acta Cryst.* C**63**, i7–i9.

Brandenburg, K. (1998). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.

Castellari, C., Comelli, F. & Ottani, S. (1999). *Acta Cryst.* C**55**, 1054–1056.

Dale, S. H., Elsegood, M. R. J. & Kainth, S. (2003). *Acta Cryst.* C**59**, m505–m508.

inorganic compounds

Deloume, J.-P., Faure, R. & Thomas-David, G. (1979). *Acta Cryst.* B**35**, 558–561.

Dowty, E. (1995). *ATOMS*. Version 6.0. Shape Software, Kingsport, Tennessee, USA.

Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Fromm, K. M. & Goesmann, H. (2000). *Acta Cryst.* C**56**, 1179–1180.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Nonius (2002). *COLLECT* and *EVAL*. Nonius BV, Delft, The Netherlands.

Santana Da Silva, R., Zukerman-Schpector, J., Tfouni, E. & Lever, A. B. P. (1999). *Z. Kristallogr. New Cryst. Struct.* **214**, 303–304.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.