Inorganica Chimica Acta, 213 (1993) 99–102

The structure of oxo-bridged trinuclear ruthenium and iridium hexacarboxylates

Orna Almog, Avi Bino* and Diana Garfinkel-Shweky
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem (Israel)

(Received March 10, 1993; revised May 17, 1993)

Abstract

The reactions between ruthenium trichloride or iridium trichloride and carboxylic acids produce oxygen-centered triangular trinuclear complexes which are known as 'basic' carboxylates having the general formula $[M_3O(O_2CR)_6(H_2O_3]^{n+}$. Using ion-exchange chromatography, a variety of such complexes with different carboxylates and oxidation states were isolated and crystallized. The X-ray study of five compounds is reported. Compound **1**, $[Ru_3O(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 2H_2O$ is monoclinic, space group $P2_1/c$ with $a = 11.717(1)$, $b = 15.019(2)$, $c = 15.220(2)$ Å, $\beta = 92.27(3)°$, $V = 2676(1)$ Å^3 and $Z = 4$. Compound **2**, $[Ru_3O(O_2CH)_6(H_2O)_6]BF_4 \cdot 3H_2O$ is orthorhombic, space group $Pmn2_1$ with $a = 11.362(1)$, $b = 6.676(1)$, $c = 14.447(2)$ Å, $V = 1096(1)$ Å^3 and $Z = 2$. Compound **3**, $[Ru_3O(O_2CCH_3)_6(H_2O)_3](ClO_4)_2 \cdot H_2O$ is monoclinic, space group $P2_1/n$ with $a = 17.226(2)$, $b = 15.532(2)$, $c = 11.117(1)$ Å, $\beta = 91.68(2)°$, $V = 2973(1)$ Å^3 and $Z = 4$. Compound **4**, $[Ir_3O(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 4H_2O$ is monoclinic space group $I2/a$ with $a = 22.305(6)$, $b = 14.098(3)$, $c = 20.119(5)$ Å, $\beta = 103.10(5)°$, $V = 6162(5)$ Å^3 and $Z = 8$. Compound **5**, $[Ir_3O(O_2CCH_3)_6(H_2O)_3](ClO_3)_{1.667}(ClO_4)_{0.333}$ is rhombohedral, space group $R\bar{3}$ with $a = 11.173(4)$, $c = 40.621(10)$ Å, $V = 4392(4)$ Å^3 and $Z = 6$. The structural parameters, such as M–O (central) distances, for the M(III,III,III) and M(III,III,IV) systems are almost identical. This indicates that the removal of a d-electron from a non-bonding level of the M_3O system has a very little or no effect at all on this system.

Introduction

Oxygen-centered triangular trinuclear metal carboxylates, or, so-called 'basic' metal carboxylates, are characteristic feature in the chemistry of many transition metals. Elements such as V, Cr, Mn, Fe, Co, Ru, Rh and Ir, mainly in the +3 state, have a profound tendency to form complexes, having the general formula $[M_3O(O_2CR)_6L_3]^{n+}$ where L is a ligand such as H_2O or pyridine. The chemistry, structure, physical and catalytic properties and biological relevance of many basic carboxylates of various metals have been the subject of many reports in recent years [1].

The formation of green complexes of ruthenium(III) carboxylates was reported by Mond as early as 1930 [2]. More recently it was reported that the reaction between '$RuCl_3 \cdot xH_2O$' and sodium acetate in acetic acid and ethanol produced a crude material, $[Ru_3O(O_2CCH_3)_6(H_2O)_3][O_2CCH_3]$, which can be purified by chromatography or by recrystallization. The pure substance is a green powder with μ_{eff} (298 K) of 1.77 BM per Ru_3 [3]. The above formula has not been established by X-ray crystallography. Recently, the structure of the hexabenzoato Ru(III,III,III) complex with axial pyridine ligands, $[Ru_3O(O_2CC_6H_5)_6(py)_3]PF_6$ was reported by Sasaki and co-workers [4a]. The structure of the reduced complex with a mixed oxidation state Ru(III,III,II) and axial triphenylphosphine ligands was reported by Cotton and Norman more than twenty years ago [4b]. Meyer and co-workers reported the preparation of $[Ru_3O(OAc)_6(py)_3]^{2+}$ (py = pyridine) by the oxidation of the Ru(III,III,III) complex, but this structure was never substantiated crystallographically [5].

The preparation of $[Ir_3O(O_2CCH_3)_6(py)_3]^+$ by the direct reaction of iridium trichloride with acetate in acetic acid was reported by Wilkinson and co-workers twenty years ago [6]. Oxidation with ozone or by electrolysis of the Ir(III,III,III) species gives the one-electron oxidized species $[Ir_3O(O_2CCH_3)_6(py)_3]^{2+}$. There are no X-ray structures for any of the hexacarboxylate triiridium complexes.

We report here the preparation and structural characterization of a series of oxo-bridged triruthenium and triiridium hexacarboxylates. All compounds were prepared using ion-exchange chromatography and subjected to detailed X-ray structural analysis.

Compound **1**, $[Ru_3O(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 2H_2O$, and compound **2**, $[Ru_3O(O_2CH)_6(H_2O)_3]BF_4 \cdot 3H_2O$ are

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

the acetato and formato complexes of the Ru(III,III,III) core, respectively. Compound **3**, $[Ru_3O(O_2CCH_3)_6(H_2O)_3](ClO_4)_2 \cdot H_2O$, with an Ru(III,III,IV) core, is the product of a one-electron oxidation of the 1+ species in **1**.

Compound **4**, $[Ir_3O(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 4H_2O$ and **5**, $[Ir_3O(O_2CCH_3)_6(H_2O)_3](ClO_3)_{1.667}(ClO_4)_{0.333}$ contain the Ir(III,III,III) and Ir(III,III,IV) systems, respectively.

Experimental

Preparation of $[Ru_3O(O_2CR)_6(H_2O)_3]BF_4 \cdot XH_2O$ *(R=CH₃, X=2 (1); R=H, X=3 (2)) and* $[Ru_3O(O_2CCH_3)_6(H_2O)_3](ClO_4)_2 \cdot H_2O$ *(3)*

Commercial '$RuCl_3 \cdot 3H_2O$' (0.05 g, 0.19 mmol) and sodium acetate (0.032 g, 0.39 mmol) were dissolved in acetic acid (14 ml) and ethanol (6 ml). The solution was gently refluxed for 20 min and the original brown color turned deep red first, and then blue–green. 10 ml of water were added and the mixture was kept near boiling for about 10 min. After cooling to room temperature, the solution was adsorbed on a Dowex 50W-X2 cation exchange resin. The column was washed with water and the blue–green species was eluted using HBF_4 0.3 M. Upon slow evaporation, blue–green crystals of **1** were obtained. Compound **2** was prepared in an analogous procedure using $RuCl_3 \cdot 3H_2O$ (0.05 g, 0.19 mmol), sodium formate (0.032 g, 0.47 mmol) and 85% formic acid (20 ml). Compound **3** was obtained by using $HClO_4$ 0.2 M for elution of the acetato complex. Upon slow evaporation, the blue–green color of the eluate turned purple and purple crystals of **3** were deposited. Recrystallization from acetone produced X-ray quality crystals.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive.

Preparation of $[Ir_3O(O_2CCH_3)_6(H_2O)_3]BF_4 \cdot 4H_2O$ *(4) and* $[Ir_3O(O_2CCH_3)_6(H_2O)_3](ClO_3)_{1.667}(ClO_4)_{0.333}$ *(5)*

$IrCl_3$ (0.06 g, 0.2 mmol) and silver acetate (0.1 g, 0.6 mmol) in acetic acid (25 ml) were heated under reflux for 2 h. 10 ml of water were added and the silver chloride was filtered off. The blue–green solution was adsorbed on a Dowex 50W-X2 cation exchange resin. The column was washed with water and the blue species was eluted using HBF_4 0.2 M. Upon slow evaporation, blue crystals of **4** were obtained. If $HClO_4$ 0.2 M is used for the elution instead of HBF_4, dark blue crystals of **5** are obtained upon very slow (several weeks) evaporation of the eluate.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive.

X-ray crystallography

Data were collected at 22 °C on a PW1100 Philips diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range of $12 < \theta < 16°$. Data were measured by using an ω-2θ motion. Crystallographic data and other pertinent information are given in Table 1. For each crystal, Lorentz and polarization corrections were applied. Intensity data were corrected using the ψ-scan method. The heavy atom positions in **1–5** were obtained by using the results of SHELX86 direct method analysis.

TABLE 1. Crystallographic data for compounds **1–5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{12}H_{28}BF_4O_{18}Ru_3$	$C_6H_{18}BF_4O_{19}Ru_3$	$C_{12}H_{26}Cl_2O_{25}Ru_3$	$C_{12}H_{32}BF_4Ir_3O_{20}$	$C_{12}H_{24}Cl_2Ir_3O_{22.33}$
Formula weight	850.35	784.22	944.43	1159.84	1173.15
Space group	$P2_1/c$	$Pmn2_1$	$P2_1/n$	I2/a	$R\bar{3}$
a (Å)	11.717(1)	11.362(1)	17.226(2)	22.305(6)	11.173(4)
b (Å)	15.019(2)	6.676(1)	15.532(2)	14.098(3)	
c (Å)	15.220(2)	14.447(2)	11.117(1)	20.119(5)	40.621(10)
β (°)	92.27(3)		91.68(2)	103.10(5)	
V (Å^3)	2676(1)	1096(1)	2973(1)	6162(5)	4392(4)
Z	4	2	4	8	6
ρ_{calc} (g cm^{-3})	2.110	2.376	2.110	2.500	2.661
μ (cm^{-1})	15.98	19.49	16.09	129.78	138.2
Range of 2θ (°)	4–45	4–55	4–50	4–50	4–60
No. unique data	3437	1372	5122	4360	2861
Data with $F_o^2 > 3\sigma(F_o^2)$	2460	1173	3427	3265	2606
No. variables	278	143	379	346	131
R	0.066	0.038	0.054	0.077	0.047
R_w	0.084	0.049	0.073	0.093	0.071

Structure refinement was carried out with the full matrix least-squares program of TEXSAN*.

In structure **5** one of the ClO_3^- ions, containing Cl(2), is subjected to a two-fold disorder. Therefore, the oxygen atoms O(4) and O(4A) were refined with an occupancy factor of 0.5 for each. The other counter-ion containing Cl(1) was refined as 33% of ClO_4^- and 66% of ClO_3^-, and hence, the oxygen atom which resides on the crystallographic three-fold axis, O(3), has an occupancy factor of 0.111.

The discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table 1.

Results and discussion

Preparation

The formation of the triruthenium(III) core $\{Ru_3O(O_2CR)_6\}^+$ in the reaction between $RuCl_3 \cdot 3H_2O$ and an $RCOOH/RCOO^-$ mixture is preceded by the formation of a dinuclear species, presumably $\{Ru_2(OH)(O_2CR)_2\}^{3+}$. The red solution containing this species turns green upon prolonged refluxing of the reaction mixture [7]. A similar pathway was recently reported for the formation of basic chromium carboxylates [8]. Addition of water to the reaction mixture as well as raising of the temperature are necessary for the total replacement of the axial ligands by H_2O ligands and formation of a 1+ species. The use of ion exchange chromatography facilitates the purification and concentration of the desired species and selection of the counter-ion or eluting electrolyte. Here we chose HBF_4 for crystallization of the BF_4^- salts of the 1+ species and $HClO_4$, which acts as an oxidizing agent, for the production and crystallization of the 2+ species. The presence of chlorate ions in the crystal of compound **5** suggests that the perchloric acid has been reduced by Ir(III) to produce ClO_3^- ions in a relatively high concentration. A similar phenomenon was previously reported for Ru(II) [9].

Description of the structures

Figure 1 presents the structure of the triruthenium hexacarboxylato complex $[Ru_3O(O_2CR)_6(H_2O)_3]^{n+}$ as found in compound **2** (R = H; $n = 1$). Figure 2 shows the triiridium complex as found in **5** (for **1**, **3** and **4**, see 'Supplementary material'). Table 2 presents some important average bond distances for structures **1–5** along with those found in $[Ru_3O(O_2CCH_3)_6(PPh_3)_3]$ and $[Ru_3O(O_2CC_6H_5)_6(py)_3]PF_6$ [4].

All trinuclear complexes in **1–5** consist of a planar M_3O system, six bridging carboxylates and three axial H_2O ligands in a virtual D_{3h} symmetry. In compounds **1**, **3** and **4** the asymmetric unit contains an entire $[M_3O(O_2CR)_6L_3]^{n+}$ ion, hence there is no crystallographic symmetry imposed upon the complex. With $Z = 2$ in space group $Pmn2_1$ there is only half a $[Ru_3O(O_2CH)_6(H_2O)_3]^+$ ion in the asymmetric unit of **2**, with the other half related to it by a crystallographic mirror plane. In **5** the trinuclear unit $[Ir_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ and the two counter-ions reside on a crystallographic three-fold axis which passes through the central oxygen atom O(1), Cl(1) and Cl(2).

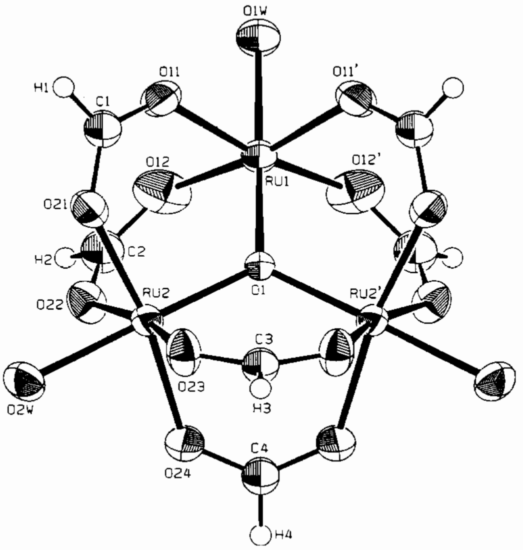

Fig. 1. The structure of $[Ru_3O(O_2CH)_6(H_2O)_3]^+$ as found in **2**.

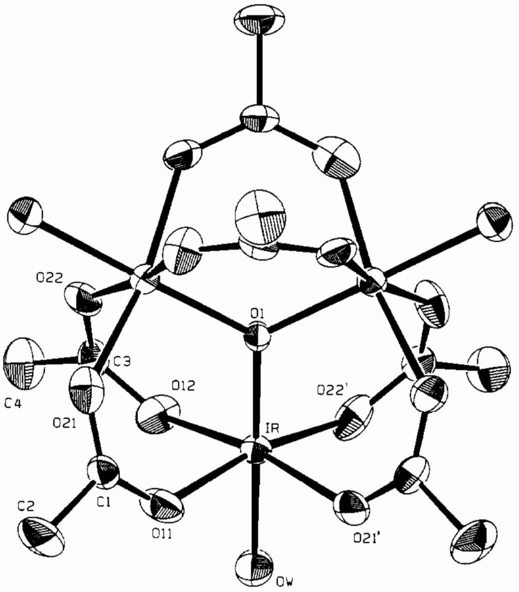

Fig. 2. The structure of $[Ir_3O(O_2CCH_3)_6(H_2O)_3]^{2+}$ as found in **5**.

Comparison and correlation of structures

The structures and dimensions of the $[M_3O(O_2CR)_6L_3]^{n+}$ units in compounds **1–5** are similar

---

*All crystallographic computing was done on a VAX 9000 computer at the Hebrew University of Jerusalem.

TABLE 2. Important bond distances in **1–5** and related compounds

Complex/Compound	M···O (central)	M···M	M–OH$_2$	M–O(O$_2$CR)
[Ru$_3$O(OAc)$_6$(PPh$_3$)$_3$]^a	1.92[4]^c	3.33[1]		2.06[2]
[Ru$_3$O(O$_2$CC$_6$H$_5$)$_6$(py)$_3$]$^{+,b}$	1.935(2)	3.350(2)		2.02[1]
[Ru$_3$O(OAc)$_6$(H$_2$O)$_3$]$^+$ (**1**)	1.91[1]	3.30[2]	2.13[1]	2.03[1]
[Ru$_3$O(O$_2$CH)$_6$(H$_2$O)$_3$]$^+$ (**2**)	1.93[2]	3.33[1]	2.09[2]	2.035[2]
[Ru$_3$O(OAc)$_6$(H$_2$O)$_3$]$^{2+}$ (**3**)	1.907[4]	3.303[7]	2.10[2]	1.999[6]
[Ir$_3$O(OAc)$_6$(H$_2$O)$_3$]$^+$ (**4**)	1.93[2]	3.343[4]	2.07[1]	2.01[1]
[Ir$_3$O(OAc)$_6$(H$_2$O)$_3$]$^{2+}$ (**5**)	1.9256(8)	3.335(1)	2.057(7)	2.017[6]

[a] Ref. 4b. [b] Ref. 4a. [c] Numbers in brackets are grand average values obtained by the expression $[(\Sigma\Delta_i^2)/n(n-1)]^{1/2}$.

to those found in other trinuclear basic acetates. For ruthenium, compound **1–3**, together with the already known [Ru$_3$O(O$_2$CCH$_3$)$_6$(PPh$_3$)$_3$], complete a unique series of Ru$_3$O cores having three different oxidation states, i.e. Ru(III,III,II), Ru(III,III,III) and Ru(III,III,IV). A simplified MO treatment for the Ru$_3$O system in D_{3h} symmetry was proposed by Cotton and Norman [4]. The MO scheme for the Ru$_3$O π system has one strongly bonding, one strongly antibonding, and eight essentially non-bonding MOs. In the case of [Ru$_3$O(O$_2$CCH$_3$)$_6$(PPh$_3$)$_3$] a total of 16 electrons from the three metal atoms and two oxygen electrons fill all of the bonding and non-bonding orbitals. In the oxidized species [Ru$_3$O(O$_2$CR)$_6$(H$_2$O)$_3$]$^{n+}$, $n=1$ (**1** and **2**) and $n=2$ (**3**), the number of d-electrons is 17 and 16, respectively. In principle, the removal of one or even two electrons from the non-bonding A$_2'$ orbital should not have a substantial effect on the Ru$_3$O system. From Table 2 it can be seen that the Ru–O (central) distances for all the compounds are essentially equal. In fact, all the other structural parameters listed in Table 2, such as Ru···Ru, Ru---OH$_2$ and Ru---O(O$_2$CR) distances, are very similar, within the e.s.d.s.

Similarly the 1+ and 2+ triiridium complexes in **4** and **5** possess almost the same structural parameters, indicating that the removal of an electron from a non-bonding level has very little or no effect at all on the Ir$_3$O π system.

Supplementary material

Tables of positional and thermal parameters, bond distances and angles, structural factors for **1–5**, and ORTEP drawings of the trinuclear structures in **1, 3** and **4** are available from the authors.

References

1 R.D. Cannon and R.P. White, *Prog. Inorg. Chem., 36* (1988) 195.
2 A.W. Mond, *J. Chem. Soc.,* (1930) 1247.
3 A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* (1972) 1570.
4 (a) M. Abe, Y. Sasaki, T. Yamaguchi and T. Ito, *Bull. Chem. Soc. Jpn., 65* (1992) 1585; (b) F.A. Cotton and J.G. Norman, *Inorg. Chim. Acta, 6* (1972) 411.
5 J.A. Baumann, D.J. Salmon, S.T. Wilson, T.J. Meyer and W.E. Hatfield, *Inorg. Chem., 17* (1978) 3342.
6 S. Uemura, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* (1973) 2565.
7 Y. Sasaki, M. Suzuki, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto and T. Ito, *J. Am. Chem. Soc., 110* (1988) 6251.
8 P.N. Turowski, A. Bino and S.J. Lippard, *Angew. Chem., Int. Ed. Engl., 29* (1990) 811.
9 K.W. Kallen and J.E. Early, *Inorg. Chem., 10* (1971) 1152.