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Synthesis and X-ray Structure of the First Nonpolymeric Chlorotetrakis(carboxylato)diruthenium(II,III) Compound

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Introduction

A focal point of interest in the chemistry of metal–metal bond compounds is the study of diruthenium complexes due to the variety of their electronic configurations and the unusual stability of the Ru_2^{5+} mixed-valence core.[2,3] Since the discovery[4] of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$, numerous tetrakis(carboxylato)diruthenium(II,III) compounds have been described. Some of these compounds have been structurally characterized, and in all cases, the $[Ru_2(carboxylate)_4]^+$ units are linked by bridging chlorine atoms, giving infinite zig-zag[5–7] or linear chains.[8,9] The analogous tetrakis(amidato)diruthenium(II,III) compounds are also polymers,[10,11] whereas, in contrast, the amino- or hydroxypyridinate derivatives are nonpolymers.[12–16] The nonpolymer nature of these last compounds has been attributed to the totally polar arrangement of ligands, which produces the blocking of one of the axial positions of the dimetallic unit. Herein, we describe the preparation and structural determination of the complex $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$, which constitutes the first nonpolymer chlorotetrakis(carboxylato)diruthenium(II,III) example. Furthermore, this nonpolymer nature cannot be attributed to the steric effect of the ligands.

Experimental Section

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. Ruthenium trichloride and pyrrole-2-carboxylic acid were purchased from commercial sources. Solvents were used without previous purification. $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ was prepared by the literature procedure.[17] IR spectra of samples as KBr disks were recorded on a Perkin-Elmer 1330 infrared spectrophotometer. Magnetic susceptibility measurements were made using a fully automatic DSM 8 magnetosusceptometer, on the basis of the Faraday methods. Electronic spectra in the region 280–800 nm were recorded on a GBC UV–vis 911 spectrophotometer. Elemental analyses for C, H, and N were performed by the Microanalytical Service of the Complutense University of Madrid.

Table 1. Crystallographic Data for $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$

formula: $C_{28}H_{34}N_4O_{11}ClRu_2$	$V = 1691(1)$ Å
fw: 840.2	$D_{calcd} = 1.65$ g cm^{-3}
space group: $P\bar{1}$ (No. 2)	$F(000) = 846$
$a = 10.234(7)$ Å	$T = 295$ K
$b = 12.635(2)$ Å	diffractometer: Enraf-Nonius
$c = 14.104(3)$ Å	radiation: graphited-monochromated Mo Kα ($\lambda = 0.710\,69$ Å)
$\alpha = 79.00(2)°$	μ(Mo Kα) = 10.14 cm^{-1}
$\beta = 95.71(3)°$	$R^a = 6.3$
$\gamma = 109.04(2)°$	$R_w{}^b = 7.5$
$Z = 2$	

[a] $R = \sum|\Delta^2F|/\sum|F_o|$. [b] $R_w = (\sum w\delta^2F/\sum w|F_o|^2)^{1/2}$.

Preparation of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$. To a solution of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ (0.3 g, 0.63 mmol) in methanol/water (60 mL) (1:1) was added an excess of $HOOCC_4H_4N$ (0.42 g, 3.79 mmol). The reaction mixture was heated under reflux for 4 h, giving a brown solid. The solution was filtered out, and the solid was treated again with $HOOCC_4H_4N$ (0.42 g, 3.79 mmol) to ensure the complete substitution of the acetate ligands. The precipitate was washed twice with 10 mL of water and dried in vacuo. The brown solid was dissolved in thf and layered with petroleum ether (bp 40–60 °C), giving red crystals of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$. Anal. Calcd for $C_{28}H_{34}N_4O_{11}ClRu_2$: C, 40.03; H, 4.08; N, 6.67. Found: C, 39.83; H, 3.94; N, 6.71. IR data (KBr disk, cm^{-1}): 3430 s, br, 3270 s, br, 3015 w, 2920 w, 1582 vs, 1452 vs, br, 1412 m, br, 1230 s, 1150 m, sh, 1135 m, 1102 vw, 1052 m, 971 m, 900 w, 820 m, 785 m, 715 m, 620 m, sh, 590 m, 420 w, 330 w. UV–visible (MeOH solution; λ, nm, (ε, dm^3 mol^{-1} cm^{-1})): 457 (1233). $\mu_{eff} = 3.97\ \mu_B$.

X-ray Structure Determination. A summary of the fundamental crystal data is given in Table 1. A red crystal of prismatic shape was epoxy-resin-coated and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting the θ values of 25 reflections with a 2θ range of 13–33°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru and Cl were taken from ref 18. The structure was solved by Patterson and Fourier methods. After several cycles of the overall refinement, a Fourier difference synthesis showed the thf and the H_2O molecules of crystallization. An empirical absorption correction[19] was applied at the end of the isotropic refinements.

A final refinement was undertaken with unit weights and anisotropic thermal motions for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions, except the hydrogen atoms of the water molecule and the N1 atom that were located in a final Fourier difference synthesis and whose coordinates were subsequently refined. No trend in ΔF vs F_o or $(\sin\theta)/\lambda$ was observed. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-Ray 80 system.[20] The atomic positional parameters are given in Table 2.

Results and Discussion

The reaction of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with pyrrole-2-carboxylic acid in methanol/water leads to a brown solid, which was recrystallized from thf/petroleum ether, giving red crystals of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$. The compound is stable to air, soluble in polar organic solvents such as thf or acetone, and insoluble in toluene or petroleum ether.

The formation of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$ in the reaction of $Ru_2Cl(\mu\text{-}O_2CCH_3)_4$ with pyrrole-2-carboxylic acid contrasts with the disproportionation process observed in the

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Table 2. Atomic Parameters for $Ru_2Cl(O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$ ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathrm{a}_i\cdot a_j$)

atom	x/a	y/b	z/c	10^4U_{eq}, Å^2
Ru1	0.33038(9)	0.11260(8)	0.17086(6)	321(3)
Ru2	0.36479(9)	0.14616(8)	0.32516(6)	341(4)
Cl	0.2616(3)	0.0650(3)	0.0035(2)	512(12)
O1	0.2027(7)	−0.0457(6)	0.2208(6)	398(31)
O2	0.2439(8)	−0.0123(7)	0.3728(6)	423(33)
O3	0.4586(8)	0.2712(6)	0.1274(5)	404(31)
O4	0.4840(8)	0.3055(7)	0.2790(6)	407(32)
O5	0.1692(8)	0.1755(7)	0.1555(6)	423(32)
O6	0.2001(8)	0.2024(7)	0.3102(6)	457(34)
O7	0.4966(7)	0.0559(7)	0.1889(5)	392(31)
O8	0.5304(7)	0.0920(7)	0.3408(6)	429(32)
O9	0.4129(10)	0.1949(8)	0.4729(6)	547(39)
O10	0.6706(14)	0.3727(11)	0.9335(9)	1046(66)
O11	0.9899(10)	0.1704(8)	0.9469(8)	736(41)
N1	0.0244(11)	−0.2592(9)	0.2800(9)	610(49)
N2	0.6325(11)	0.4936(9)	0.0679(8)	543(44)
N3	−0.0455(12)	0.2652(10)	0.1285(9)	663(55)
N4	0.7335(10)	−0.0121(9)	0.2112(7)	480(43)
C1	0.1870(11)	−0.0760(10)	0.3109(8)	368(43)
C2	0.0978(12)	−0.1910(10)	0.3453(10)	476(48)
C3	0.0674(15)	−0.2471(12)	0.4347(11)	643(61)
C4	−0.0251(18)	−0.3578(14)	0.4270(16)	856(78)
C5	−0.0496(17)	−0.3579(12)	0.3296(15)	801(77)
C6	0.5049(11)	0.3359(10)	0.1903(7)	409(46)
C7	0.5864(11)	0.4541(10)	0.1581(9)	423(46)
C8	0.6263(14)	0.5443(11)	0.2078(11)	582(57)
C9	0.6994(17)	0.6378(12)	0.1483(14)	783(68)
C10	0.7014(15)	0.6081(13)	0.0598(12)	759(65)
C11	0.1395(11)	0.2093(9)	0.2277(9)	421(45)
C12	0.0284(12)	0.2606(10)	0.2124(10)	466(49)
C13	−0.0203(14)	0.3072(13)	0.2776(12)	650(66)
C14	−0.1273(15)	0.3414(14)	0.2266(14)	823(79)
C15	−0.1415(16)	0.3179(15)	0.1355(14)	821(79)
C16	0.5635(11)	0.0592(9)	0.2684(8)	374(41)
C17	0.6850(11)	0.0222(10)	0.2835(8)	382(42)
C18	0.7692(13)	0.0121(12)	0.3660(9)	489(51)
C19	0.8730(13)	−0.0256(13)	0.3398(10)	615(62)
C20	0.8493(14)	−0.0396(12)	0.2449(10)	558(59)
C21	0.3602(20)	0.2724(16)	0.5038(11)	851(89)
C22	0.4491(29)	0.3240(25)	0.5713(20)	1453(113)
C23	0.5880(31)	0.3199(28)	0.5458(25)	1785(128)
C24	0.5514(18)	0.2103(16)	0.5179(13)	914(83)
C25	0.6117(22)	0.2597(17)	0.9150(17)	1072(97)
C26	0.6489(28)	0.2615(22)	0.8246(20)	1393(115)
C27	0.7374(29)	0.3808(24)	0.7880(20)	1403(115)
C28	0.7674(25)	0.4350(21)	0.8631(16)	1215(107)

similar reaction with pyridine-2-carboxylic acid,[21] which also has a nitrogen atom in α position with respect to the COO group. However, the presence of an NH group in the pyrrole-2-carboxylate ligand has a strong effect on the solubility and on the polymerization trend of the compound. The magnetic measurements in the range 250–70 K show that the compound obeys the Curie–Weiss law with a magnetic moment corresponding to three unpaired electrons per dimer unit, in accordance with the ground-state configuration $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$, analogous to those found in the polymeric carboxylate complexes.[22]

The crystal structure of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$ consists of separated discrete $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)$ molecular units with tetrahydrofuran and water molecules of solvation. The molecular structure, as shown in Figure 1, has two ruthenium atoms linked by four bridging pyrrole-2-carboxylate ligands. The coordination geometry of both ruthenium atoms is octahedral, with four oxygen atoms in the equatorial positions, the Ru1 atom having one axial chlorine ligand and the Ru2 atom one thf molecule. Table 3 gives selected bond distances and angles of the compound.

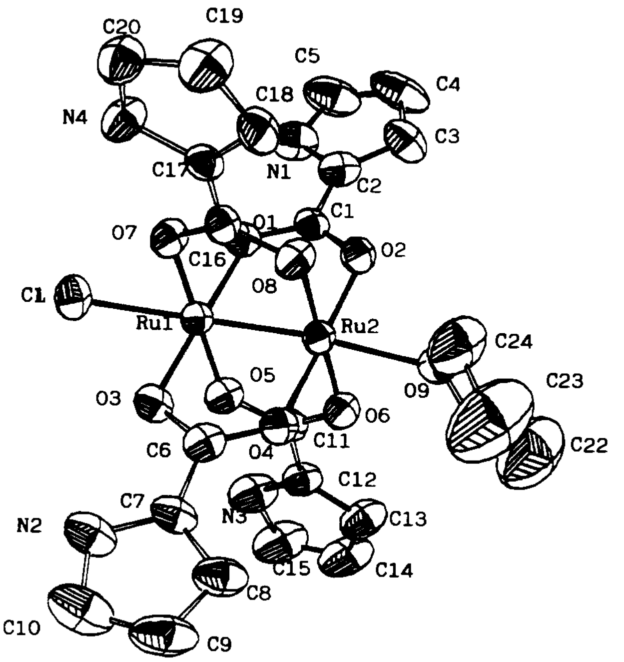

Figure 1. ORTEP view of $Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$ showing the atom-numbering scheme. Solvent molecules and hydrogen atoms are omitted for clarity.

Table 3. Principal Bond Lengths (Å) and Bond Angles (deg) for $Ru_2Cl(O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O$

Ru1–Ru2	2.268(1)	O1–C1	1.26(1)
Ru1–Cl	2.523(3)	O2–C1	1.27(1)
Ru1–O1	2.036(7)	O3–C6	1.27(1)
Ru1–O3	2.022(7)	O4–C6	1.25(1)
Ru1–O5	2.029(9)	O5–C11	1.27(2)
Ru1–O7	2.027(9)	O6–C11	1.26(1)
Ru2–O2	2.007(7)	O7–C16	1.25(1)
Ru2–O4	2.005(7)	O8–C16	1.28(2)
Ru2–O6	2.011(9)	O9–C21	1.41(3)
Ru2–O8	2.004(9)	O9–C24	1.46(2)
Ru2–O9	2.249(9)		
O5–Ru1–O7	177.4(3)	Ru1–Ru2–O9	174.8(3)
O3–Ru1–O7	88.8(3)	Ru1–Ru2–O8	89.8(2)
O3–Ru1–O5	89.3(3)	Ru1–Ru2–O6	90.6(2)
O1–Ru1–O7	91.2(3)	Ru1–Ru2–O4	90.1(2)
O1–Ru1–O5	90.7(3)	Ru1–Ru2–O2	90.6(2)
O1–Ru1–O3	177.5(3)	O8–Ru2–O9	89.6(3)
Cl–Ru1–O7	95.5(2)	O6–Ru2–O9	89.9(3)
Cl–Ru1–O5	86.4(2)	O6–Ru2–O8	179.3(3)
Cl–Ru1–O3	96.0(2)	O4–Ru2–O9	84.7(3)
Cl–Ru1–O1	86.6(2)	O4–Ru2–O8	90.6(3)
Ru2–Ru1–O7	89.5(2)	O4–Ru2–O6	88.8(3)
Ru2–Ru1–O5	88.8(2)	O2–Ru2–O9	94.7(3)
Ru2–Ru1–O3	88.9(2)	O2–Ru2–O8	90.1(4)
Ru2–Ru1–O1	88.5(2)	O2–Ru2–O6	90.5(4)
Ru2–Ru1–Cl	173.1(1)	O2–Ru2–O4	179.1(3)

The thf molecule of solvation is linked by one hydrogen bond to the N2 atom, whereas the water molecule is bonded by five hydrogen bonds with two different Ru_2^{5+} units. Thus, the oxygen atom O11 of the water molecule is linked with the O5 and the N3 of a $[Ru_2(\mu\text{-}O_2CC_4H_4N)_4]^+$ unit through an intermolecular hydrogen bond. It is also linked with the chlorine atom and with the O1 atom of another $[Ru_2(\mu\text{-}O_2CC_4H_4N)_4]^+$ unit through an asymmetrically bifurcated hydrogen bond; O11 is also hydrogen-bonded to the N1 atom of this last unit. Finally, the N4 atom of each $[Ru_2(\mu\text{-}O_2CC_4H_4N)_4]^+$ unit is hydrogen-bonded with the Cl atom of another unit. Thus, all nitrogen atoms and the chlorine atom of the compound are involved in hydrogen bonds. The geometrical features of the hydrogen-bond network were calculated with PARST5[23] (Table 4). The presence of these hydrogen bonds could be the cause of the nonpolymer nature of the compound.

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Table 4. Hydrogen-Bond Distances (Å) and Angles (deg)

D–H···A[a]	D–H	D···A	H···A	D–H···A
O11–H111···O5[1]	1.06(16)	3.31(1)	2.32(16)	153(12)
O11–H112···Cl[2]	0.83(15)	3.245(9)	2.48(14)	155(16)
O11–H112···O1[2]	0.83(15)	3.23(1)	2.71(17)	123(14)
N1–H1···O11[2]	1.02	3.19	2.18	172
N2–H2···O10[3]	1.00	2.78	1.83	156
N3–H3···O11[4]	1.00	3.12	2.12	179
N4–H4···Cl[5]	1.00	3.23	2.42	137

[a] Symmetry transformations: (1) $1 + x, y, 1 + z$; (2) $1 - x, -y, 1 - z$; (3) $x, y, z - 1$; (4) $x - 1, y, z - 1$; (5) $1 - x, -y, -z$.

The Ru–Ru distance of 2.268(1) Å is very close to that found[8a] in $\mathrm{Ru_2Cl(\mu\text{-}O_2CCH_3)_4\cdot 2H_2O}$ and slightly shorter those found in the other diruthenium(II,III) carboxylate compounds [Ru–Ru = 2.283–2.290 Å).[5–9]

The axial Ru–Cl bond length, 2.523(3) Å, expected to be longer than those in the polymeric $\mathrm{Ru_2Cl(\mu\text{-}O_2CR)_4}$ compounds [2.5016(6)–2.587(5) Å][5–9] is nonetheless similar.

The torsion angles about the metal–metal bond lie in the range 0.79–2.59° and are consistent with the fact that there are not strong steric forces that would operate to induce a twist in the molecule.

The most important characteristic of the $\mathrm{Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O}$ compound is its molecular nature in contrast with the polymeric nature of all known chlorotetrakis(carboxylato)-diruthenium(II,III) compounds. In the case of the $\mathrm{Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)\cdot thf\cdot H_2O}$ compound, the axial site on the Ru2 atom is not blocked by pendant groups of the ligands, so the nonpolymer nature cannot be attributed to steric hindrance. The synthesis[24] of $\mathrm{Ru_2(\mu\text{-}pfap)_4(CCC_6H_5)_2}$ (pfap = 2,3,4,5,6-pentafluoro-2-anilinopyridinate), with two axial phenylacetylide ligands, suggests that also in the amino- and hydroxypyridinate complexes the nonpolymer nature could not be determined solely by steric hindrance.

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Supplementary Material Available: Tables giving details of the crystal structure determination, bond distances and angles, and refined and calculated atomic coordinates and anisotropic thermal parameters and a table listing magnetic measurement data in the range 250–70 K (17 pages). Ordering information is given on any current masthead page.

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