Preparation and structural characterization of three adamantylcarboxylato diruthenium(II,II), diruthenium(II,III) and dimolybdenum(II,II) compounds

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Abstract

Three new compounds containing adamantylcarboxylate ligands, $[Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2]\cdot 2CH_3OH$ (**1**), $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2]\cdot 2CH_3OH$ (**2**) and $Mo_2(C_{10}H_{15}CO_2)_4(C_4H_8O)_2$ (**3**), have been prepared by reacting $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$, $K_4Mo_2Cl_8$ and $Mo_2(OAc)_4$ with $C_{10}H_{15}CO_2H$. Their crystal structures have been determined. Crystals are as follows. **1**: space group $P2_1/c$, $a=12.966(2)$, $b=16.541(4)$, $c=12.573(3)$ Å, $\beta=118.77(2)°$, $V=2364(1)$ Å^3, $Z=2$, Ru–Ru distance $=2.2809(9)$ Å. **2**: space group $P2_12_12_1$, $a=13.062(1)$, $b=26.375(4)$, $c=11.943(2)$ Å, $V=4115(1)$ Å^3, $Z=4$. The Ru–Ru distance is 2.254(8) Å. **3**: space group $P\bar{1}$, $a=12.897(2)$, $b=17.308(2)$, $c=11.927(1)$ Å, $\alpha=107.703(9)$, $\beta=92.06(1)$, $\gamma=93.01(1)°$, $V=2529.0(6)$ Å^3, $Z=2$. The average Mo–Mo distance is 2.083[2] Å. The formation of **1** from the starting tetracarbonato complex appears to involve disproportionation of $2Ru_2^{5+}$ to Ru_2^{4+} and $2Ru^{3+}$.

Introduction

The research described here was undertaken for several reasons. One very specific one was to see whether $M_2(O_2CR)_4L_2$ molecules with R = 1-adamantyl would tend to adopt the tetragonal packing arrangements that we have previously found to be characteristic of those in which R is the very large CPh_3 group [1–3]. The availability of crystals containing $M_2(O_2CR)_4L_2$ units aligned into parallel chains with rigorous four-fold rotational symmetry offers interesting opportunities for the study of spectra [1] and the influence of axial interactions on M–M bonding [2, 3]. It was hoped that the saturated adamantyl group would still be large enough to control the crystal packing while allowing us to avoid certain disadvantages of the even larger CPh_3 group. Regrettably, this does not appear to be the case.

However, there are other, more general, reasons why the compounds reported here are of interest. The new diruthenium compounds contribute to our still incomplete knowledge of the relationship between the types of ligands employed and the properties (including relative stabilities) of the various Ru_2^{n+} ($n=4$, 5, 6) cores [4–21]. The tetrakis(adamantylcarboxylato)-dimolybdenum compound is novel in having the shortest Mo–Mo distance yet reported for a $Mo_2(O_2CR)_4L_2$ compound [4].

Experimental

All manipulations were carried out under an atmosphere of oxygen-free argon, usually by employing standard Schlenk techniques. Solvents mesitylene, tetrahydrofuran (THF) and hexane were distilled over Na–K alloy/benzophenone, and methanol was distilled over magnesium. Oxygen-free water was obtained by prolonged boiling under a nitrogen atmosphere. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer, visible spectra on a Cary 17D spectrophotometer, and IR spectra in the range 4000–400 cm^{-1} on a Perkin-Elmer 783 infrared spectrophotometer.

1-Adamantylcarboxylic acid ($C_{10}H_{15}CO_2H$) was purchased from Chemical Dynamics Corp. $K_4Mo_2Cl_8$ [22] and $Mo_2(OAc)_4$ [23] were made by the literature methods. $K_3Ru_2(CO_3)_4\cdot 4H_2O$ was prepared from $Ru_2(OAc)_4Cl$ [24].

Synthesis of $[Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2]\cdot 2CH_3OH$ *(1) and* $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2]\cdot 2CH_3OH$ *(2)*

1.14 g of $C_{10}H_{15}CO_2H$ (6.33 mmol) were dissolved in 10 ml of methanol and the solution was added to

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a solution of 0.20 g of $K_3Ru_2(CO_3)_4\cdot 4H_2O$ (0.32 mmol) in 40 ml of water. After 6 h of refluxing a pale yellow solution and a brown precipitate were formed. The mixture was filtered and the filtrate was discarded. The precipitate was exhaustively extracted with methanol until nothing more dissolved and then discarded. The combined yellow washings were evaporated to dryness to yield a yellow–brown powder. This powder was first washed with 20 ml of hexane to remove what is believed to be an Ru^{III} impurity and the resulting light green solution was discarded. Then the powder was treated with 10 ml of ethanol, and the mixture was filtered. The light brown crystals obtained by slow evaporation of the yellow filtrate under argon, were shown later to be compound **1** by X-ray crystallography. Yield *c.* 0.10 g, 30%. The remaining dark brown solid was then dissolved completely in 30 ml of hexane. After addition of 30 ml of CH_3OH dark brown crystals of the composition of **2** were grown by slow evaporation of the solution under argon. Yield: *c.* 50 mg, 17%. IR (Nujol, cm^{-1}) for **1**: 3400b, m, 1660w, 1630w, 1530s, 1410s, 1340m, 1310m, 1260m, 1180w, 1110sh, 1090m, 1020w, 980m, 935w, 905w, 790s, 760s, 745s, 680s, 535s, 450s, 415m. Vis (CH_3OH, nm) for **1**: 430. IR (Nujol, cm^{-1}) for **2**: 3400b, m, 1630m, 1545s, 1480w, 1410s, 1340m, 1310s, 1290w, 1255m, 1230b, m, 1155m, 1110w, 1100w, m, 1020w, 980w, 930w, 910w, 810m, 800m, 795m, 760m, 745m, 680m, 540m, 505m, 450m, 415w. Vis (CH_3OH, nm) for **2**: 426.

Synthesis of $Mo_2(C_{10}H_{15}CO_2)_4$

Method A. 0.57 g of $C_{10}H_{15}CO_2H$ (3.19 mmol) was added to a suspension of 0.1 g of $K_4Mo_2Cl_8$ (0.16 mmol) in 30 ml of mesitylene. After 20 h of refluxing a yellow solution and a colorless precipitate were formed. The solution was filtered and the solvent was removed by vacuum evaporation. The solid was washed first with 30 ml of hexane to dissolve unreacted carboxylic acid, followed by with several 10 ml portions of hexane, and finally dried *in vacuo*. Yield 0.085 g, 54%. IR (Nujol, cm^{-1}): 1485s, 1410s, 1360m, 1305m, 1260s, 1185w, 1100s, 1080s, 1020s, 980w, 975s, 760w, 750w, 680m, 445m. ^1H NMR (C_6D_6, ppm): δ 2.39 (24H), 2.01 (12H), 1.69 (24H). Vis (THF, nm): 430. On exposure to air the

TABLE 1. Crystallographic data for $[Ru(C_{10}H_{15}CO_2)_4(CH_3OH)_2]\cdot 2CH_3OH$ (**1**), $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2]\cdot 2CH_3OH$ (**2**) and $[Mo_2(C_{10}H_{15}CO_2)_4]\cdot 2C_4H_8O$ (**3**)

	1	**2**	**3**
Formula	$Ru_2O_{12}C_{48}H_{76}$	$Ru_2O_{13}C_{38}H_{61}$	$Mo_2O_{10}C_{52}H_{76}$
Formula weight	1047.27	928.04	1053.06
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a (Å)	12.966(2)	13.062(1)	12.897(2)
b (Å)	16.541(4)	26.375(4)	17.308(2)
c (Å)	12.573(3)	11.943(2)	11.927(1)
α (°)	90.0	90.0	107.703(9)
β (°)	118.77(2)	90.0	92.06(1)
γ (°)	90.0	90.0	93.01(1)
V (Å^3)	2364(1)	4115(1)	2529.0(6)
Z	2	4	2
D_{calc} (g cm^3)	1.471	1.498	1.383
Crystal size (mm)	0.20×0.20×0.05	0.32×0.20×0.20	0.20×0.30×0.35
Data collection instrument	Enraf-Nonius CAD4	Rigaku AFC5R	Rigaku AFC5R
Radiation (monochromated in incident beam)	Mo Kα ($\lambda\alpha$=0.71073 Å)	Cu Kα ($\lambda\alpha$=1.54184 Å)	Cu Kα ($\lambda\alpha$=1.54184 Å)
μ(Kα) (cm^{-1})	6.843	65.862	45.690
Orientation reflections: no.; range (2θ) (°)	25; 22–27	25; 65–75	25; 80–100
Temperature (°C)	−78	20	20
Scan method	ω–2θ	ω–2θ	ω–2θ
Data collection range (2θ) (°)	4–45	4–116	4–115
No. unique data, total with $F_o^2>3\sigma(F_o^2)$	3080, 2116	3254, 2947	6958, 5899
No. parameters refined	280	478	578
Transmission factors: max., min.	0.9983, 0.9328	1.0000, 0.9319	1.0000, 0.7822
R^a	0.056	0.047	0.048
R_w^b	0.074	0.063	0.053
Quality-of-fit indicator^c	1.604	1.685	1.979
Largest shift/e.s.d., final cycle	0.005	0.005	0.02
Largest peak (e/Å^3)	0.846	0.588	1.130

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(|F_o|)$. [c] Quality-of-fit $=[\Sigma w(|F_o|-|F_c||)^2/(N_{obs.}-N_{param})]^{1/2}$.

TABLE 2. Positional and equivalent isotropic thermal parameters for $[Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2]\cdot 2CH_3OH$

Atom	x	y	z	B_{eq} (Å^2)
Ru	−0.06187(6)	0.51486(4)	0.40061(6)	1.92(1)
O(1)	0.0541(5)	0.4633(3)	0.3577(5)	2.2(1)
O(2)	−0.1746(5)	0.5661(4)	0.4489(5)	2.3(1)
O(3)	−0.1416(5)	0.4065(4)	0.3805(5)	2.3(1)
O(4)	0.0193(5)	0.6222(4)	0.4249(5)	2.4(1)
O(5)	−0.1803(5)	0.5442(4)	0.2000(5)	2.5(1)
C(1)	0.1485(7)	0.4317(5)	0.4389(7)	2.4(2)
C(2)	0.2304(7)	0.3904(5)	0.4052(7)	2.0(2)
C(3)	0.3592(9)	0.4139(9)	0.496(1)	6.4(4)
C(4)	0.203(1)	0.411(1)	0.2767(9)	7.8(4)
C(5)	0.217(1)	0.2998(8)	0.415(1)	8.5(4)
C(6)	0.448(1)	0.3706(8)	0.459(1)	5.5(4)
C(7)	0.287(1)	0.359(1)	0.241(1)	9.4(4)
C(8)	0.315(1)	0.2538(8)	0.388(1)	6.5(4)
C(9)	0.412(1)	0.3900(9)	0.329(1)	6.9(4)
C(10)	0.435(1)	0.2860(9)	0.476(1)	5.6(4)
C(11)	0.275(1)	0.268(1)	0.264(1)	7.9(5)
C(12)	−0.1007(7)	0.3585(5)	0.4720(7)	2.1(2)
C(13)	−0.1530(7)	0.2749(5)	0.4494(7)	2.2(2)
C(14)	−0.106(1)	0.2282(6)	0.5686(8)	4.0(3)
C(15)	−0.1132(8)	0.2318(6)	0.3674(8)	3.2(2)
C(16)	−0.2888(9)	0.2787(7)	0.388(1)	4.6(3)
C(17)	−0.157(1)	0.1404(6)	0.5418(9)	4.2(3)
C(18)	−0.164(1)	0.1433(6)	0.3397(9)	3.9(3)
C(19)	−0.3383(9)	0.1916(7)	0.360(1)	5.3(4)
C(20)	−0.1171(9)	0.0983(7)	0.461(1)	4.3(3)
C(21)	−0.290(1)	0.1456(8)	0.485(1)	5.9(3)
C(22)	−0.2979(9)	0.1494(7)	0.278(1)	4.5(3)
C(23)	−0.136(1)	0.5767(7)	0.133(1)	4.9(3)
O(6)	0.5913(8)	0.513(1)	0.1083(8)	11.4(5)
C(24)	0.568(1)	0.485(1)	0.193(1)	8.0(5)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)$-$[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

solid turns quickly to black. It is poorly soluble in toluene and benzene, but has higher solubility in THF, CH_2Cl_2 and CH_3OH.

Method B. 0.42 g of $C_{10}H_{15}CO_2H$ (2.34 mmol) was added to a suspension of 0.1 g of $Mo_2(OAc)_4$ (0.23 mmol) in 30 ml of mesitylene. The mixture was refluxed for 2 days. The reaction mixture was then pumped dry, and 30 ml of hexane was used to dissolve unreacted carboxylic acid. The yellow crystalline compound was then washed with hexane and dried in vacuum. Yield 0.16 g, 75%. The IR, electronic and ^1H NMR spectra were the same as those for the product from $K_4Mo_2Cl_8$. Crystals of the THF adduct, **3**, were grown by slow evaporation of a THF/hexane solution under argon and used for X-ray crystallography.

X-ray crystallography of $[Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2]\cdot 2CH_3OH$ (1)

A rhomboidal plate-like crystal was attached to the tip of a glass fiber by Apiezon T grease and kept under a cold nitrogen stream at −78 °C throughout the data collection. Unit cell parameters were determined by centering and indexing 25 reflections that were found randomly in the 2θ range 14–20° and refined with 25 reflections in the 2θ range 22–27° from a preliminary data collection. The crystal system and the axial lengths were confirmed by axial photography. Scan width parameters $0.90°+0.35°$ ($\tan\theta$) were determined from an ω–2θ profile analysis of the above 25 reflections (OTPLOT) [25], and a learned profile analysis (LEARN) [25], was also used to increase the $I/\sigma(I)$ values for those reflections with values less than 30. Three standard reflections that were checked for crystal decay after an interval of every 3 h of exposure, and checked for crystal orientation after every 200 reflections were measured, showed no decay nor change of the crystal orientation during the data collection. The intensity data were corrected for Lorentz and polarization effects and for an absorption based on the ψ scans of 7 reflections with their χ angles close to 90°.* The space group was determined to be $P2_1/c$ from the systematic absences. The position of the unique Ru atom was provided by an interpretation of a supersharp Patterson map (SHELXS-86) [26], and the remaining non-hydrogen atoms were found by alternating difference Fourier syntheses and least-squares refinements. The final refinement, in which all these atoms were refined anisotropically converged to an R value of 0.056. The final difference Fourier map was featureless with first two peaks in the vicinity of the metal atom (1.17 and 0.54 Å, respectively).

The crystallographic data are listed in Table 1. The positional and thermal parameters for all the non-hydrogen atoms are listed in Table 2. Selected bond distances and angles are shown in Table 3.

X-ray crystallography of $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2]\cdot 2CH_3OH$ (2)

Crystals for X-ray crystallography were wedged in capillaries and sealed by epoxy cement along with the mother liquor. This was necessary to avoid the development of cracks due to loss of interstitial solvent molecules. The cell parameters were obtained by indexing 25 randomly found reflections in the 2θ range of 38–42° and refined by 25 reflections in the 2θ range of 65–75°. The axial lengths and the crystal system were checked by axial photography. Three standard reflections showed a total 4.1% decay during the data collection, but no change of crystal orientation was observed. The intensity data were corrected for Lorentz and polarization effects, isotropic decay, and an empirical absorption correction based on the ψ scan data

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*Calculations were done on a local Area VAX Cluster (VMS X4.6) with the commercial package SDP/VV3.0.

TABLE 3. Selected bond distances (Å) and angles (°) for $[Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2]\cdot 2CH_3OH$

Bond distances					
Ru–Ru′	2.2809(9)	Ru–O(5)	2.287(5)	O(5)–C(23)	1.34(2)
Ru–O(1)	2.015(7)	O(1)–C(1)	1.270(9)	C(1)–C(2)	1.49(1)
Ru–O(2)	2.019(7)	O(2)–C(1)′	1.28(1)	C(12)–C(13)	1.50(1)
Ru–O(3)	2.023(6)	O(3)–C(12)	1.28(1)	O(5)–O(6)′	2.66(1)
Ru–O(4)	2.011(6)	O(4)–C(12)′	1.256(8)	O(6)–O(6)′	2.64(1)
Bond angles					
Ru′–Ru–O(5)	177.9(2)	O(3)–Ru–O(4)	178.6(2)	O(1)–C(1)–O(2)′	121.0(9)
O(1)–Ru–O(2)	178.3(2)	O(3)–Ru–O(5)	91.1(2)	O(1)–C(1)–C(2)	120.3(8)
O(1)–Ru–O(3)	89.7(3)	O(4)–Ru–O(5)	90.3(2)	O(2)′–C(1)–C(2)	118.7(7)
O(1)–Ru–O(4)	90.6(3)	Ru–O(1)–C(1)	120.9(6)	O(3)–C(12)–O(4)′	123.1(8)
O(1)–Ru–O(5)	89.2(2)	Ru–O(2)–C(1)′	119.8(5)	O(3)–C(12)–C(13)	116.4(6)
O(2)–Ru–O(3)	90.5(3)	Ru–O(3)–C(12)	118.1(5)	O(4)′–C(12)–C(13)	120.4(7)
O(2)–Ru–O(4)	89.2(3)	Ru–O(4)–C(12)′	119.9(6)		
O(2)–Ru–O(5)	92.5(2)	Ru–O(5)–C(23)	120.8(5)		

Numbers in parentheses are e.s.d.s in the the least significant digits.

of 6 reflections with their χ angles near 90°. An interpretation of a supersharp Patterson map provided the locations of the two crystallographically independent Ru atoms and fragments of their ligand molecules (SHELX-86) [26], and a combination of least-squares refinements and difference Fourier syntheses revealed all the remaining non-hydrogen atoms. All these atoms were treated anisotropically in the final least-squares refinement (SHELX-76) [27] with constrained C–C bond lengths (1.541 Å) for one of the carboxylate groups (C(5)–C(14)), which would, otherwise, give rather irregular C–C bond lengths ranging from 1.35 to 1.68 Å because of a disorder. This disorder was evidenced by the rather high thermal parameters for these carbon atoms and also by the appearance of a large number of peaks (*c.* 0.6 e/Å^3) around these atoms in a final difference Fourier map. The highest peaks were around the β-carbon atoms and there were weaker ones near th γ-carbon atoms. Their positions suggested the existence of a secondary orientation obtained by rotating the adamantyl group around a three-fold axis by 60°. No attempt was made to refine the secondary orientation, since no peaks larger than hydrogen atoms were found that could be related to the γ-carbon atoms of the secondary orientation. Refinement of its enantiometric structure was tested, and this converged to a higher R value (0.052).

Pertinent crystal data are listed in Table 1. The positional and thermal parameters of the non-hydrogen atoms are listed in Table 4. Some important bond distances and angles are listed in Table 5.

X-ray crystallography of $Mo_2(C_{10}H_{15}CO_2)_4(THF)_2$ *(3)*

Crystals were handled in an atmosphere of argon. They were examined under a layer of mineral oil that had been degassed and dried over sodium metal. A yellow plate-like crystal was wedged inside a capillary and the capillary was then sealed by flame. Indexing of 25 reflections that had been found randomly in the 2θ range 48–52° gave a triclinic cell, which was then refined by centering 25 reflections in the 2θ range 80–100°. The crystal system and the axial dimensions were confirmed by axial photography. Three standard reflections that were checked after every 250 reflections showed no obvious change of the crystal orientation, but a total 27.4% crystal decay occurred during the data collection. The intensity data were corrected for Lorentz and polarization effects, isotropic decay, and an empirical absorption correction was made by using the method of ψ scans of 7 reflections with their χ angles near 90°. The two independent Mo atoms and fragments of their ligand molecules were found by an interpretation of a supersharp Patterson map (SHELXS-86) [26], and the remaining non-hydrogen atoms were found gradually by combined difference Fourier syntheses and least-squares refinements. In the final refinement all non-hydrogen atoms were treated anisotropically. There were peaks in a final difference Fourier map around the β-carbon atoms from an adamantate group, C(24), and between the three γ-carbon atoms, similar to the disorder pattern seen in **2**. Again, we did not attempt to refine a disorder model because of the weakness of most of these peaks.

Pertinent crystallography data are listed in Table 1. The positional and thermal parameters of the non-hydrogen atoms are listed in Table 6. Some important bond distances and angles are listed in Table 7.

Results and discussion

Synthesis of $Mo_2(C_{10}H_{15}CO_2)_4$

Two synthetic routes based on ligand substitution reactions on $K_4Mo_2Cl_8$ and $Mo_2(OAc)_4$ have been developed

TABLE 4. Positional and equivalent isotropic thermal parameters for $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2]\cdot 2CH_3OH$

Atom	x	y	z	B_{eq} (Å^2)
Ru(1)	0.93979(5)	0.16257(3)	1.00034(7)	3.43(2)
Ru(2)	1.09254(5)	0.14384(3)	0.92285(6)	3.46(2)
O(1)	0.7812(6)	0.1838(3)	1.0634(6)	4.5(2)
O(2)	1.2491(6)	0.1259(3)	0.8489(6)	4.5(2)
O(3)	0.9983(6)	0.2278(3)	1.0573(7)	4.7(2)
O(4)	1.1487(6)	0.2084(3)	0.9794(7)	4.6(2)
O(5)	0.8837(5)	0.0955(2)	0.9427(6)	4.0(2)
O(6)	1.0347(6)	0.0777(3)	0.8660(6)	4.2(2)
O(7)	0.9836(5)	0.1269(3)	1.1437(6)	3.9(2)
O(8)	1.1342(5)	0.1090(3)	1.0669(6)	4.1(2)
O(9)	0.8965(6)	0.1963(3)	0.8571(6)	4.1(2)
O(10)	1.0460(6)	0.1774(3)	0.7785(6)	4.5(2)
C(1)	0.770(1)	0.2064(5)	1.172(1)	6.0(3)
C(2)	1.275(1)	0.1399(7)	0.739(1)	7.7(4)
C(3)	1.091(1)	0.2393(4)	1.0341(8)	4.5(3)
O(11)	1.1278(8)	0.2822(3)	1.0613(9)	6.7(2)
C(4)	0.9422(8)	0.0661(4)	0.8855(8)	4.0(2)
C(5)	0.9011(8)	0.0173(4)	0.8477(9)	4.0(2)
C(6)	0.7839(9)	0.013(1)	0.846(4)	21(2)
C(7)	0.953(2)	−0.0011(7)	0.739(2)	20(1)
C(8)	0.941(3)	−0.0223(6)	0.932(2)	19(1)
C(9)	0.745(1)	−0.0365(7)	0.789(2)	15(1)
C(10)	0.922(2)	−0.0552(6)	0.703(1)	10.6(7)
C(11)	0.889(2)	−0.0748(7)	0.924(2)	25(2)
C(12)	0.807(2)	−0.0475(9)	0.682(2)	14(1)
C(13)	0.777(2)	−0.070(1)	0.888(2)	17(1)
C(14)	0.939(1)	−0.0868(7)	0.810(2)	9.5(6)
C(15)	1.0708(8)	0.1070(4)	1.1470(9)	3.8(2)
C(16)	1.1018(9)	0.0774(4)	1.2484(9)	3.8(2)
C(17)	1.084(1)	0.0213(4)	1.224(1)	5.5(3)
C(18)	1.219(1)	0.0878(5)	1.277(1)	6.2(3)
C(19)	1.031(1)	0.0917(5)	1.347(1)	6.2(3)
C(20)	1.114(1)	−0.0092(5)	1.330(1)	6.3(4)
C(21)	1.243(1)	0.0552(6)	1.388(1)	6.2(4)
C(22)	1.064(1)	0.0601(5)	1.456(1)	6.4(4)
C(23)	1.229(1)	0.0006(5)	1.355(1)	5.9(3)
C(24)	1.046(1)	0.0058(6)	1.424(1)	6.6(3)
C(25)	1.179(1)	0.0704(6)	1.481(1)	7.3(4)
C(26)	0.9585(8)	0.1982(4)	0.7754(9)	4.1(2)
C(27)	0.9269(8)	0.2221(4)	0.6670(9)	3.7(2)
C(28)	0.915(1)	0.1810(5)	0.579(1)	6.2(3)
C(29)	1.007(1)	0.2605(5)	0.634(1)	5.1(3)
C(30)	0.8201(9)	0.2488(5)	0.682(1)	5.2(3)
C(31)	0.885(1)	0.2048(5)	0.463(1)	5.8(3)
C(32)	0.977(1)	0.2849(5)	0.519(1)	5.7(3)
C(33)	0.7923(9)	0.2710(5)	0.564(1)	4.9(3)
C(34)	0.967(1)	0.2416(6)	0.424(1)	6.7(4)
C(35)	0.784(1)	0.2309(5)	0.478(1)	5.6(3)
C(36)	0.875(1)	0.3116(5)	0.534(1)	6.4(4)
O(12)	0.910(1)	0.3663(8)	1.022(1)	13.1(6)
C(37)	0.894(1)	0.3335(6)	0.931(1)	7.4(4)
O(13)	1.046(1)	0.3472(8)	1.196(3)	21(1)
C(38)	1.111(2)	0.380(1)	1.253(3)	14(1)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: (4/3)-$[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

$$K_4Mo_2Cl_8+4C_{10}H_{15}CO_2H \xrightarrow{\text{mesitylene, reflux}} Mo_2(C_{10}H_{15}CO_2)_4+4KCl+4HCl \quad (1)$$

$$Mo_2(OAc)_4+4C_{10}H_{15}CO_2H \xrightarrow{\text{mesitylene, reflux}} Mo_2(C_{10}H_{15}CO_2)_4+4HOAc \quad (2)$$

Although ligand substitution reactions on $K_4Mo_2Cl_8$ and $Mo_2(OAc)_4$ for the preparation of other carboxylates, $Mo_2(O_2CR)_4$, have been well documented, care is generally necessary to drive such reactions to completion [28]. It is easy to follow reaction (1) since $K_4Mo_2Cl_8$ is purple and has a low solubility in mesitylene, and a yellow solution and a colorless KCl precipitate are formed once the reaction is complete. The reaction did not proceed in toluene, since both the starting material, $K_4Mo_2Cl_8$, and the products have very low solubilities. In this report, the solvent mesitylene, with a high boiling point (162–164 °C) plays a key role by increasing the solubility of the starting material and expelling HCl more effectively at the elevated temperature. In reaction (2) exchange of carboxylate groups makes no observable color change. However, the reaction is promoted by effective removal of HOAc (b.p. 116 °C) at the boiling point of mesitylene. Both methods have afforded the adamantylcarboxylato Mo dimer in good yields.

Syntheses of the Ru_2 compounds 1 and 2

In the synthesis of the dinuclear Ru complexes, $RuCl_3\cdot 3H_2O$, $Ru_2(OAc)_4$ and $Ru_2(OAc)_4Cl$ have been the most commonly used starting materials [4, 28]. However, in our preparative work $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ has proven to be another valuable starting material. Its reaction with adamantylcarboxylic acid has yielded a tetracarboxylato Ru_2 complex **1**, and a tricarboxylato Ru_2 complex, **2**. The isolation of **2** is consistent with the idea that the substitution proceeds by stages, with the tricarboxylato complex as possibly the last of the intermediates leading to the fully substituted tetracarboxylate complex

$$[Ru_2(CO_3)_4]^{3-}+3C_{10}H_{15}CO_2H \longrightarrow Ru_2(C_{10}H_{15}CO_2)_3(CO_3)+3HCO_3^- \quad (3)$$

However, if this is so, the final stage from the tricarboxylato to the tetracarboxylato complex, at least as we have observed it, is not a simple substitution. The oxidation state of the Ru atoms in the tetracarboxylato complex has changed from +2.5 to +2. Since carboxylic acid, methanol and water are generally oxidizing agents for such low-valence transition metals rather than reducing agents, the driving force for the reduction must be found somewhere else. It is interesting to note that our present observations are reminiscent of the reaction

TABLE 5. Selected bond distances (Å) and angles (°) for $[Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2]\cdot 2CH_3OH$

Bond distances					
Ru(1)–Ru(2)	2.254(1)	Ru(2)–O(8)	2.025(7)	O(8)–C(15)	1.27(1)
Ru(1)–O(1)	2.274(8)	Ru(2)–O(10)	2.031(7)	O(9)–C(26)	1.27(1)
Ru(1)–O(3)	2.002(7)	O(1)–C(1)	1.44(1)	O(10)–C(26)	1.27(1)
Ru(1)–O(5)	2.035(7)	O(2)–C(2)	1.40(2)	C(3)–O(11)	1.27(1)
Ru(1)–O(7)	2.035(7)	O(3)–C(3)	1.28(2)	C(4)–C(5)	1.46(1)
Ru(1)–O(9)	2.009(7)	O(4)–C(3)	1.29(1)	C(15)–C(16)	1.50(1)
Ru(2)–O(2)	2.277(8)	O(5)–C(4)	1.29(1)	C(26)–C(27)	1.50(1)
Ru(2)–O(4)	1.973(7)	O(6)–C(4)	1.27(1)		
Ru(2)–O(6)	2.018(7)	O(7)–C(15)	1.25(1)		
Bond angles					
Ru(2)–Ru(1)–O(1)	175.0(2)	O(2)–Ru(2)–O(10)	91.7(3)	Ru(1)–O(9)–C(26)	119.5(7)
O(1)–Ru(1)–O(3)	91.4(3)	O(4)–Ru(2)–O(6)	179.6(3)	Ru(2)–O(10)–C(26)	118.9(7)
O(1)–Ru(1)–O(5)	89.9(3)	O(4)–Ru(2)–O(8)	90.0(3)	O(3)–C(3)–O(4)	121(1)
O(1)–Ru(1)–O(7)	95.2(3)	O(4)–Ru(2)–O(10)	91.5(3)	O(3)–C(3)–O(11)	121(1)
O(1)–Ru(1)–O(9)	85.2(3)	O(6)–Ru(2)–O(8)	89.7(3)	O(4)–C(3)–O(11)	118(1)
O(3)–Ru(1)–O(5)	178.6(3)	O(6)–Ru(2)–O(10)	88.8(3)	O(5)–C(4)–O(6)	121.2(9)
O(3)–Ru(1)–O(7)	90.2(3)	O(8)–Ru(2)–O(10)	177.9(3)	O(5)–C(4)–C(5)	118.4(9)
O(3)–Ru(1)–O(9)	90.9(3)	Ru(1)–O(1)–C(1)	119.7(7)	O(6)–C(4)–C(5)	120.4(9)
O(5)–Ru(1)–O(7)	89.1(3)	Ru(2)–O(2)–C(2)	121.7(8)	O(7)–C(15)–O(8)	123.5(9)
O(5)–Ru(1)–O(9)	89.7(3)	Ru(1)–O(3)–C(3)	119.4(7)	O(7)–C(15)–C(16)	119.3(9)
O(7)–Ru(1)–O(9)	178.7(3)	Ru(2)–O(4)–C(3)	120.0(7)	O(8)–C(15)–C(16)	117.1(9)
Ru(1)–Ru(2)–O(2)	178.4(2)	Ru(1)–O(5)–C(4)	119.4(6)	O(9)–C(26)–O(10)	122(1)
O(2)–Ru(2)–O(4)	88.7(3)	Ru(2)–O(6)–C(4)	120.3(7)	O(9)–C(26)–C(27)	120.4(9)
O(2)–Ru(2)–O(6)	91.5(3)	Ru(1)–O(7)–C(15)	118.4(7)	O(10)–C(26)–C(27)	117.1(9)
O(2)–Ru(2)–O(8)	89.7(3)	Ru(2)–O(8)–C(15)	119.0(6)		

Numbers in parentheses are e.s.d.s in the least significant digits.

of $Ru_2(OAc)_4Cl$ and L-mandelic acid in water [8], in which $Ru_2(mand)_4\cdot 2H_2O$ and a characteristic green solution of $[Ru_3O(mand)_6(H_2O)_3]^+$ were formed as products of a disproportionation reaction

$$6Ru(mand)_4Cl + 8H_2O \longrightarrow 3Ru_2(mand)_4 + 2[Ru_3O(mand)_6(H_2O)_3]Cl + HCl$$

Since the reaction conditions in both reactions are similar and the characteristic green substance has also been found in our reaction, we conclude that a disproportionation reaction has occurred in the present case although we are not certain as to when it happens in the sequence of substitutions of the carbonato groups. For this kind of disproportionation reaction one of the driving forces is obviously the preference of the carboxylate group for a Ru_2 metal center with lower oxidation state.

It is also worth mentioning that the starting material $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ can be prepared from $Ru_2(OAc)_4$ and K_2CO_3 in water [6]

$$5Ru_2(OAc)_4 + 16K_2CO_3 \longrightarrow 2Ru + 4K_3[Ru_2(CO_3)_4] + 20KOAc$$

Here a disproportionation reaction has changed the Ru_2(II,II) center back to the Ru_2(II,III) center in the favor of the 'harder' carbonato groups. That a harder bridging ligand prefers a Ru_2 center with a higher oxidation state and a softer ligand prefers a Ru_2 center with a lower oxidation state is well documented [7]. In compound **2** both harder and softer ligands coexist, and so do the opposite driving forces. One question arises naturally: whether a compromise between these two forces allows a Ru_2(II,II) center to exist. It is now well established from electrochemical measurements and synthetic practice that carboxylato dimers can have Ru_2(II,II) and Ru_2(II,III) cores, while hard ligands, e.g. SO_4^{2-}, can have Ru_2(II,III) and Ru_2(III,III) cores [20, 21]. We think that by a careful choice of a mixture of such ligands not only an affirmative answer can be addressed to the above question, but also it is possible to make a molecule which can span a wider range of core electrons and to make the electron flow tunable.

Crystal structure of 1

There are two ruthenium dimer molecules of $Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2$ and four interstitial CH_3OH molecules in the unit cell. The configuration of the dimer molecule is shown in Fig. 1 along with the atomic numbering scheme. The molecule is situated on an inversion center so that only a half of the molecule is unique. The metal atom is coordinated by four oxygen atoms from four carboxylate groups in four equatorial positions and bonded in the axial positions by an oxygen atom from a methanol ligand and an equivalent ruthenium atom related by the inversion center. The Ru–Ru distance 2.2809(9) Å is in the normal range for a Ru_2(II,II) compound, 2.235(1) [11]–2.474(1)[13] Å. The distances from the metal to the oxygen atoms of the carboxylate groups and of the axial ligand, 2.017[4]* and 2.287(5) Å respectively, are also normal. This is a typical paddle wheel structure that is adopted by almost all the known dinuclear tetracarboxylato ruthenium. Although we were unable to locate hydrogen atoms from the final difference Fourier map, we have found a zigzag –O(5)–O(6)′–O(6)–O(5)′– chain with distances between these methanol oxygen atoms distances of around 2.65[1] Å, consistent with the occurrence of hydrogen bonding. It is evident that this hydrogen bonding scheme ties the dinuclear molecules into an infinite structure.

TABLE 6. Positional and equivalent isotropic thermal parameters for $Mo_2(C_{10}H_{15}CO_2)_4(C_4H_8O)_2$

Atom	x	y	z	B_{eq} (Å^2)
Mo(1)	0.46004(4)	0.00383(3)	0.07582(4)	3.48(1)
O(1)	0.4576(3)	−0.1237(2)	0.0414(3)	4.11(9)
O(2)	0.4574(3)	0.1308(2)	0.1197(3)	4.06(9)
O(3)	0.3149(3)	−0.0107(2)	−0.0163(3)	4.10(9)
O(4)	0.6004(3)	0.0188(2)	0.1781(3)	4.02(9)
C(1)	0.5005(5)	−0.1641(3)	−0.0500(5)	4.0(1)
C(2)	0.4957(5)	−0.2563(3)	−0.0814(5)	4.1(1)
C(3)	0.4951(7)	−0.2820(4)	0.0323(6)	6.0(2)
C(4)	0.3952(6)	−0.2901(4)	−0.1570(7)	6.1(2)
C(5)	0.5919(6)	−0.2888(4)	−0.1502(7)	6.1(2)
C(6)	0.4891(7)	−0.3765(4)	−0.0025(6)	6.3(2)
C(7)	0.3888(7)	−0.3855(4)	−0.1908(8)	7.0(2)
C(8)	0.5842(7)	−0.3835(4)	−0.1846(7)	6.9(2)
C(9)	0.3893(7)	−0.4086(4)	−0.0768(8)	7.0(2)
C(10)	0.5852(7)	−0.4078(4)	−0.0719(8)	7.2(2)
C(11)	0.4833(8)	−0.4157(5)	−0.2596(7)	7.6(2)
C(12)	0.3161(5)	−0.0189(3)	−0.1257(5)	4.0(1)
C(13)	0.2126(5)	−0.0319(3)	−0.1971(5)	3.9(1)
C(14)	0.1807(6)	−0.1240(4)	−0.2389(6)	5.6(2)
C(15)	0.1283(6)	0.0142(4)	−0.1205(6)	5.6(2)
C(16)	0.2243(6)	−0.0015(4)	−0.3049(6)	5.7(2)
C(17)	0.1176(6)	−0.0172(4)	−0.3786(6)	6.3(2)
C(18)	0.0739(6)	−0.1388(4)	−0.3124(7)	6.0(2)
C(19)	0.0216(6)	−0.0018(4)	−0.1944(6)	5.9(2)
C(20)	0.0889(7)	−0.1091(5)	−0.4194(7)	6.7(2)
C(21)	0.0343(6)	0.0286(5)	−0.3015(7)	6.7(2)
C(22)	−0.0086(6)	−0.0927(5)	−0.2346(7)	6.5(2)
Mo(2)	0.93799(4)	0.46086(3)	0.50704(4)	4.54(1)
O(5)	1.0390(4)	0.3762(2)	0.5347(4)	5.0(1)
O(6)	0.8285(3)	0.5410(3)	0.4806(4)	5.1(1)
O(7)	0.9342(3)	0.3981(2)	0.3269(4)	4.9(1)
O(8)	0.9335(3)	0.5190(2)	0.6896(3)	4.8(1)
C(23)	1.1357(6)	0.3929(4)	0.5335(5)	4.9(2)
C(24)	1.2120(6)	0.3322(4)	0.5461(5)	4.9(2)
C(25)	1.158(1)	0.2715(6)	0.601(1)	14.4(4)
C(26)	1.230(1)	0.2784(7)	0.428(1)	16.4(3)
C(27)	1.301(1)	0.3720(7)	0.617(2)	22.6(5)
C(28)	1.2466(9)	0.2072(5)	0.6199(9)	10.0(3)
C(29)	1.324(1)	0.2124(6)	0.4358(9)	10.7(3)
C(30)	1.3970(9)	0.3071(7)	0.630(1)	11.1(4)
C(31)	1.2609(9)	0.1673(7)	0.496(1)	10.2(3)
C(32)	1.328(1)	0.2607(9)	0.6891(9)	13.1(4)
C(33)	1.4063(8)	0.2708(7)	0.5061(9)	11.0(3)
C(34)	1.0022(5)	0.4197(4)	0.2662(5)	4.5(1)
C(35)	1.0058(5)	0.3711(4)	0.1386(5)	4.4(1)
C(36)	1.0251(9)	0.2839(5)	0.1337(7)	8.4(3)
C(37)	0.9022(7)	0.3757(7)	0.0743(7)	9.4(3)
C(38)	1.0965(7)	0.4022(5)	0.0792(6)	7.4(2)
C(39)	1.0262(9)	0.2303(5)	0.0015(8)	9.2(3)
C(40)	0.9011(8)	0.3169(8)	−0.0600(8)	10.5(3)
C(41)	1.0951(7)	0.3484(5)	−0.0532(6)	7.3(2)
C(42)	0.9240(8)	0.2331(7)	−0.0563(9)	10.2(3)
C(43)	1.1139(8)	0.2640(6)	−0.0577(8)	8.4(3)
C(44)	0.9918(9)	0.3531(6)	−0.1155(8)	9.8(3)
O(9)	0.3730(4)	−0.0075(3)	0.2665(4)	6.5(1)
C(45)	0.2717(7)	−0.0518(6)	0.2446(7)	8.4(2)
C(46)	0.279(1)	−0.1162(7)	0.297(1)	13.2(4)
C(47)	0.379(1)	−0.1053(7)	0.362(1)	12.6(4)
C(48)	0.4340(8)	−0.0342(6)	0.3478(7)	9.9(3)
O(10)	0.7463(8)	0.3745(5)	0.5093(7)	15.5(3)
C(49)	0.6763(8)	0.4205(7)	0.594(1)	11.3(3)
C(50)	0.706(1)	0.3955(8)	0.697(1)	12.5(4)
C(51)	0.769(2)	0.3264(8)	0.648(1)	18.0(6)
C(52)	0.780(1)	0.3170(7)	0.526(1)	15.2(5)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: (4/3)-$[a^2\beta_{11}+b^2\beta_{22}+c^2\beta_{33}+ab(\cos\ \gamma)\beta_{12}+ac(\cos\ \beta)\beta_{13}+bc(\cos\ \alpha)\beta_{23}]$.

Crystal structure of 2

The unit cell contains four equivalent diruthenium molecules, $Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2$, and eight interstitial CH_3OH solvent molecules. The configuration of the dimer is shown in Fig. 2. Each Ru atom is coordinated in the equatorial positions by three oxygen atoms from three carboxylate groups and one from a carbonato group, and bonded in the axial positions by an oxygen atom from a methanol ligand and the other Ru atom to fulfill an octahedral environment. The Ru–Ru distance 2.254(8) Å lies toward the lower end of a narrow range of Ru–Ru bond distances for the known Ru_2(II,III) compounds, 2.2506[3] [24]—2.303(1) [21] Å, with the shortest ones found in the carbonato dimers [6, 24], intermediate ones in the carboxylato and hydroxypyridinato dimers [4, 14–19], and the longest one in a sulfato dimer [21]. The distances between the metal atoms and the oxygen atoms from the carboxylato groups (2.026[9] Å) are only a little longer, if at all, than those from the carbonato group (1.988[15] Å). However, they are much shorter than those to the axial ligands (2.276[2] Å). All metal–ligand bond lengths are comparable to those already known. It is obvious that exchange between carbonato and carboxylato bridges does not cause a substantial change of the coordination environment for the Ru metal atoms. Therefore, other observations seem to be needed to probe the transform between Ru_2(II,II) and Ru_2(II,III).

It must be pointed out that, although we are unable to locate hydrogen atoms from the final difference Fourier map, we are able to distinguish the carbonato group from a possible bicarbonato group by considering the entire hydrogen bonding scheme and the bond strengths in this group. One oxygen atom, O(2), initiates

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*Square brackets denote mean deviation from the unweighted arithmetic mean.

TABLE 7. Selected interatomic distances (Å) and angles (°) for $Mo_2(C_{10}H_{15}CO_2)_4(C_4H_8O)_2$

Bond distances					
Mo(1)–Mo(1)′	2.0865(7)	O(3)–C(12)	1.269(7)	O(5)–C(23)	1.266(8)
Mo(1)–O(1)	2.117(4)	O(4)–C(12)′	1.264(8)	O(6)–C(23)′	1.272(8)
Mo(1)–O(2)	2.101(4)	Mo(2)–Mo(2)′	2.0861(8)	O(7)–C(34)	1.268(8)
Mo(1)–O(3)	2.100(4)	Mo(2)–O(5)	2.101(5)	O(8)–C(34)′	1.276(7)
Mo(1)–O(4)	2.105(4)	Mo(2)–O(6)	2.111(5)	Mo(1)–O(9)	2.627(5)
O(1)–C(1)	1.266(7)	Mo(2)–O(7)	2.090(4)	Mo(2)–O(10)	2.83(1)
O(2)–C(1)′	1.268(8)	Mo(2)–O(8)	2.107(4)		
Bond angles					
O(1)–Mo(1)–O(2)	176.4(2)	Mo(1)–O(3)–C(12)	116.5(4)	O(6)–Mo(2)–O(8)	88.0(2)
O(1)–Mo(1)–O(3)	89.4(2)	Mo(1)–O(4)–C(12)′	117.1(4)	O(7)–Mo(2)–O(8)	176.2(2)
O(1)–Mo(1)–O(4)	90.5(2)	O(1)–C(1)–O(2)′	122.3(5)	Mo(2)–O(5)–C(23)	117.4(4)
O(2)–Mo(1)–O(3)	90.5(2)	O(3)–C(12)–O(4)′	122.7(5)	Mo(2)–O(6)–C(23)′	117.0(4)
O(2)–Mo(1)–O(4)	89.4(2)	O(5)–Mo(2)–O(6)	176.4(2)	Mo(2)–O(7)–C(34)	117.6(3)
O(3)–Mo(1)–O(4)	176.3(2)	O(5)–Mo(2)–O(7)	88.1(2)	Mo(2)–O(8)–C(34)′	116.5(4)
Mo(1)–O(1)–C(1)	117.2(4)	O(5)–Mo(2)–O(8)	91.8(2)	O(5)–C(23)–O(6)′	122.0(6)
Mo(1)–O(2)–C(1)′	116.9(3)	O(6)–Mo(2)–O(7)	91.9(2)	O(7)–C(34)–O(8)′	121.9(5)

Numbers in parentheses are e.s.d.s in the least significant digits.

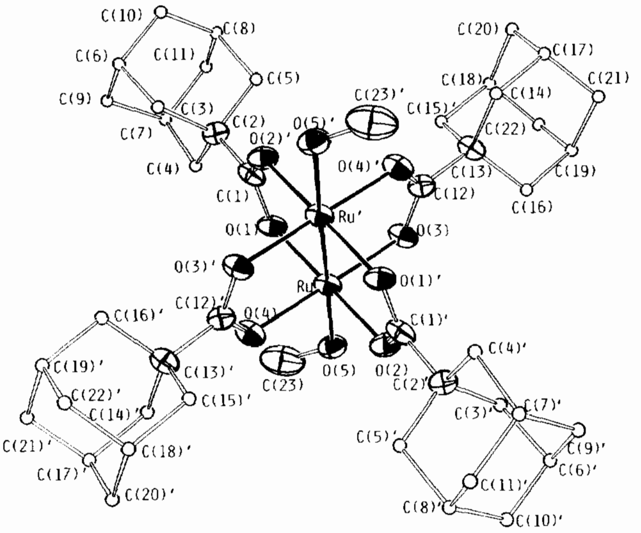

Fig. 1. Configuration of $[Ru_2(C_{10}H_{15}CO_2)_4(CH_3OH)_2$ showing the atom-labeling scheme. Thermal ellipsoids are presented at the 50% probability level, and the remaining carbon atoms of the adamantyl groups are drawn with arbitrary radii for clarity.

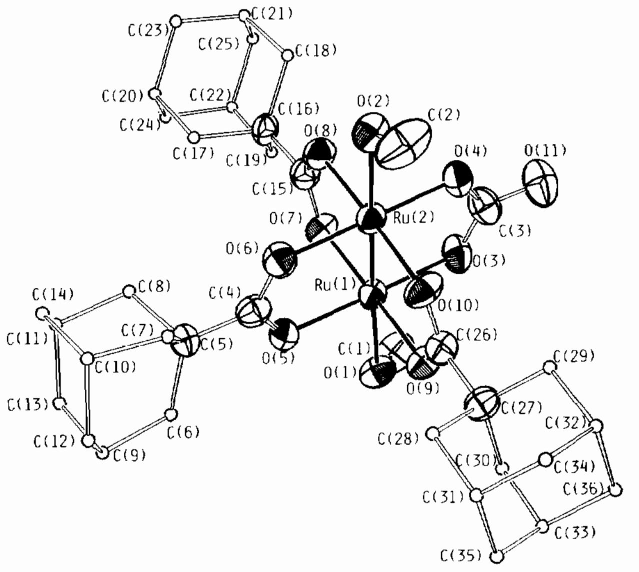

Fig. 2. Configuration of $Ru_2(C_{10}H_{15}CO_2)_3(CO_3)(CH_3OH)_2$ showing the atom-labeling scheme. Thermal ellipsoids are presented at the 50% probability level, and the remaining carbon atoms of the adamantyl groups are drawn with arbitrary radii for clarity.

a hydrogen bond, i.e. provides its hydrogen, to a methanol solvent, O(12), which in turn initiates another hydrogen bond to the other solvent, O(13). Then the external or terminal oxygen atom of the carbonato group O(11) is the proton acceptor in hydrogen bonding from both the above solvent O(13) and the other axial methanol ligand O(1) from a neighboring dinuclear unit to complete the entire hydrogen bonding scheme. No clue has been found that could imply the existence of a hydrogen atom bonded to the carbonato group. Moreover, the terminal C–O bond is the shortest in this carbonato group, which clearly shows that the terminal oxygen atom does not form a normal O–H bond at the expense of π bonding with the central carbon atom C(3). A similar rationalization has been elaborated in a phosphate case [29]. See also 'Supplementary material'.

Crystal structure of 3

There are two molecules of $Mo_2(C_{10}H_{15}CO_2)_4(C_4H_8O)_2$ in the unit cell, each situated on an inversion center. The configurations of the two dinuclear molecules are drawn with the atomic numbering scheme in Figs. 3 and 4, where it can be seen that the two molecules are essentially the same. Each Mo atom is

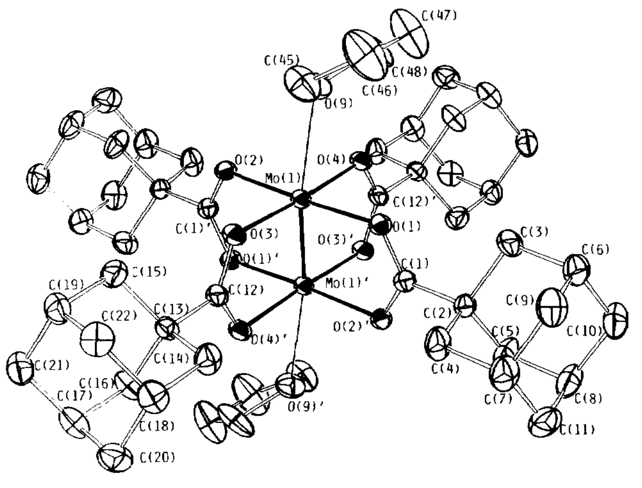

Fig. 3. Configuration of the first independent dinuclear cluster of $Mo_2(C_{10}H_{15}CO_2)_4(C_4H_8O)_2$ showing the atom-labeling scheme. Thermal ellipsoids are presented at the 40% probability level.

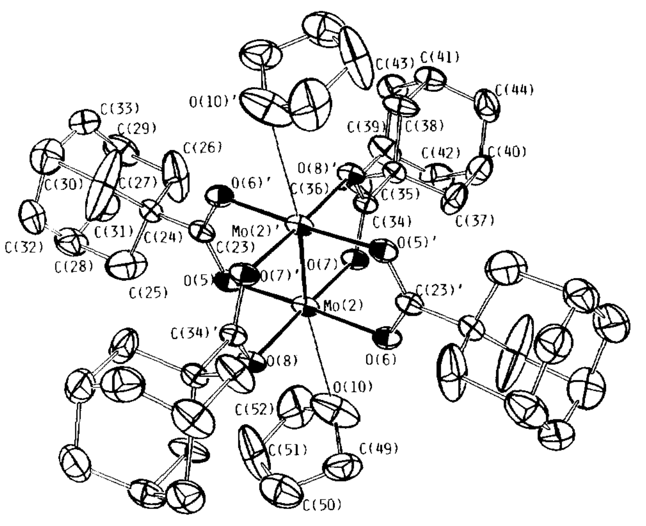

Fig. 4. Configuration of the second independent dinuclear cluster of $Mo_2(C_{10}H_{15}CO_2)_4(C_4H_8O)_2$ showing the atom-labeling scheme. Thermal ellipsoids are presented at the 40% probability level.

coordinated by four oxygen atoms from four adamantylcarboxylate groups in the equatorial positions, and its inversion-center-related Mo atom and an oxygen atom from a THF molecule occupy the axial positions to complete an octahedral coordination environment for the Mo atom. Such a configuration is very common in the quadruply bonded Mo dimer realm [4]. The average distances of metal to metal, metal to carboxylate oxygen and metal to weakly coordinated oxygen atoms are 2.083[2], 2.104[8] and 2.73[10] Å, all of which are normal. The crystals are extremely air sensitive, as mentioned in th synthetic part, and thus must be related to their structural feature. From available stability data of carboxylato and sulfato dimers, we can categorize them in two groups according to the type of their axial ligands: (1) those with separate axial ligands, such as THF, pyridine, piperidine and phosphine [30], which are very air sensitive; (2) those with polymeric structures in which axial oxygen ligands are provided by neighboring dinuclear units [31], which are more stable. Most likely the loosely bound ligands in the first group can be readily displaced by dioxygen, whereas in the second group, the molecules, being bound to their neighbors, are locked into the entire polymeric structure, so that the possibility for dioxygen to reach the axial positions is considerably reduced. Of course once such shielding is destroyed, e.g. in solution, compounds in the second category also become air sensitive [30].

Finally, we note that no $Mo_2(O_2CR)_2L_2$ compound, that is, one with separate axial ligands in place, has previously been found [4, 32–36] to have a Mo–Mo distance as short as the one found here.

Supplementary material

For the crystal structures of **1**–**3** full tables of bond distances and angles, anisotropic thermal parameters (17 pages); tables of observed and calculated structure factors (56 pages); ORTEP drawings of unit cell contents (6 pages); and corresponding hydrogen bonding distances and angles (1 page) are available on request from author F.A.C.

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