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Preparation and structural characterization of $Rh_2(O_2CCPh_3)_4(EtOH)_2$, $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH)\cdot 2EtOH$ and $Mo_2(O_2CCPh_3)_4\cdot 3CH_2Cl_2$

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Abstract

Triphenylacetic acid and its sodium salt were used in the preparation of three dimetal tetracarboxylates. The reaction of $RhCl_3$ with NaO_2CCPh_3 in ethanol gives $Rh_2(O_2CCPh_3)_4(EtOH)_2$ (**1**). The exchange reaction of $Mo_2(O_2CCH_3)_4$ with NaO_2CCPh_3 in dichloromethane yields $Mo_2(O_2CCPh_3)_4\cdot 3CH_2Cl_2$ (**2**). The reaction of $Ru_2[\mathit{l}\text{-}O_2CCH(OH)Ph]_4(H_2O)_2$ with HO_2CCPh_3 in ethanol results in $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH)$ 2EtOH (**3**). The structures of these compounds were determined by single crystal X-ray crystallography. The crystallographic data for **1** are as follows: tetragonal, space group $I\bar{4}$ with unit cell dimensions $a=b=18.340(2)$, $c=10\,646(1)$ Å, $V=3581\ 1(6)$ Å^3, $Z=2$. The structure was refined to $R=0.053$ ($R_w=0.059$) with 1431 reflections having $I>3\sigma(I)$. The Rh–Rh distance is 2.365(1) Å, Rh–O(1) = 1.967(6) Å, Rh–O(2) = 2.047(6) Å, Rh–O(axial) = 2.31(2) Å. The pertinent crystallographic data for **2** are as follows: tetragonal, space group *P4/ncc* with unit cell dimensions $a=b=20.930(4)$, $c=17.404(4)$ Å, $V=7624(5)$ Å^3, $Z=4$. The structure was refined to $R=0.048$ ($R_w=0.064$) with 1269 reflections having $I>3\sigma(I)$. The Mo–Mo distance is 2.076(1) Å, Mo–O(1) = 2.098(5) Å, Mo–O(2) = 2.095(6) Å. The crystallographic data for **3** are as follows: monoclinic, space group *C2/c* with unit cell dimensions $a=19.872(7)$, $b=16.985(6)$, $c=23.36(1)$ Å, $\beta=94.24(3)°$, $V=7864(5)$ Å^3, $Z=4$. The structure was refined to $R=0.063$ ($R_w=0\ 094$) with 2893 reflections having $I>3\sigma(I)$. The Ru–Ru distance is 2.252(2) Å; the Ru–O distances are 2.079(7), 2.061(8), 2.073(7) and 2.064(7) Å; the Ru–O(axial) distances are both 2.35(1) Å The Mo atoms of **2** do not experience any axial interactions, and there is a resulting decrease of 0.016 Å in the Mo–Mo quadruple bond distance compared to $Mo_2(O_2CR)_4$ molecules having axial coordination.

Key words. Crystal structures, Molybdenum complexes; Rhodium complexes, Carboxylate complexes, Dinuclear complexes

Introduction

The question of how axial ligation influences a metal–metal bond is important for multiply bonded species in general, and for $M_2(O_2CR)_4L_2$ species in particular [1]. The problem may be conveniently approached via comparison studies of $M_2(O_2CR)_4$ versus $M_2(O_2CR)_4L_2$ systems, where L represents a ligand coordinated in the axial position, i.e. *trans* to the M–M bond. It has been found, however, that even for $M_2(O_2CR)_4$ systems having no distinct axial ligands (M = Cr [2, 3] or Mo [4–7]) the molecular packing in the crystalline state is such that lone pairs of the oxygen atoms from one molecule are situated very nearly axially to the M–M bond in adjacent molecules. The resulting axial coordination affects the M–M bond in the same manner as attached axial ligands.

Another approach to this problem is the comparison of the gas-phase structures determined by electron diffraction, where it may be assumed that no association would occur, with the structures of crystalline solids. Several studies utilizing this method have been reported in the literature [8–10]. However, those studies are limited to rather small R groups in order to keep the problem of analysis simple and to minimize modes of decomposition.

Yet another approach to this problem is to use R groups of such size and shape as to prevent inter-

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TABLE 1 Crystal data for $Rh_2(O_2CCPh_3)_4(EtOH)_2$ (1), $Mo_2(O_2CCPh_3)_4$ $(CH_2Cl_2)_3$ (2) and $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH)$ 2EtOH (3)

	1	**2**	**3**
Formula	$Rh_2O_{10}C_{84}H_{70}$	$Mo_2Cl_6O_8C_{83}H_{66}$	$Ru_2O_{12}C_{86}H_{80}$
Formula weight	1445.30	1596.04	1507.73
Space group	$I\bar{4}$	$P4/ncc$	$C2/c$
a (Å)	18.340(2)	20.930(4)	19.872(7)
b (Å)	18.340(2)	20.930(4)	16.985(6)
c (Å)	10.646(1)	17.404(4)	23.36(1)
β (°)	90	90	94.24(3)
V (Å^3)	3581.1(6)	7624(5)	7864(5)
Z	2	4	4
D_{calc} (g/cm^3)	1.340	1.390	1.273
Crystal size (mm)	0.4×0.4×0.4	0.5×0.4×0.4	0.45×0.4×0.4
μ(Mo Kα) (cm^{-1})	5.094	5.853	4.321
Data collection instrument	CAD4	CAD4	P3/F Equiv
Radiation (monochromated in incident (beam)	Mo Kα(λ_α = 0.71073 Å)		
Orientation reflections, number, range (2θ)	25, 12.0–25.1	25, 12.1–24.9	25, 20.3–29.6
Temperature (°C)	27(2)	27(2)	20(1)
Scan method	ω–2θ	ω–2θ	ω–2θ
Data collection range, 2θ (°)	4.0–55.0	4.0–50.0	4.0–45.0
No unique data total	2132	2069	5105
with $F_o^2 > 3\sigma(F_o^2)$	1431	1269	2893
No parameters refined	216	226	442
Transmission factors. max , min	0.82, 0.70	0.79, 0.64	0.993, 0.963
R^a	0.053	0.048	0.063
$R_w{}^b$	0.059	0.064	0.094
Quality-of-fit indicator^c	1.40	1.81	1.77
Largest shift/e.s.d., final cycle	0.88	0.65	0.47
Largest peak (e/Å^3)	0.7	0.4	0.39

$^aR = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$ $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$ ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

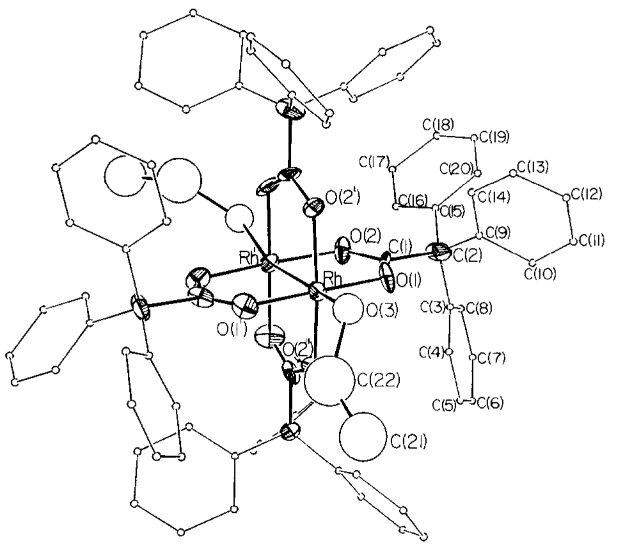

Fig 1. ORTEP drawing of $Rh_2(O_2CCPh_3)_4(EtOH)_2$ (1). The phenyl carbon atoms are drawn as small spheres for clarity, all other atoms are represented by their ellipsoids at the 35% probability level.

molecular association. In one study of the $Cr_2(O_2CR)_4$ systems the R group chosen was 2-phenylphenyl (biph) [11]. However, it turned out that all four pendant phenyl groups in each $Cr_2[O_2C(biph)]_4$ molecule oriented themselves to one end and the unencumbered ends of two dinuclear molecules then united to produce a 'dimer of dimers'.

We have recently reported [12] the synthesis and structural characterization of several dichromium compounds in which the triphenylacetate ion was used as a ligand. The arrangement of the twelve phenyl rings resulting from four bridging O_2CCPh_3 groups is of sufficient bulk to control the packing in the crystal, so that the carboxyl oxygen atoms do not use their lone pairs to reach the metal atoms of adjacent molecules. The axial positions, however, remain open to coordination. The present work is an extension of these studies to include other metallic elements. We here report the synthesis and structural characterization of dinuclear molybdenum, ruthenium and rhodium compounds having the triphenylacetate ion as a bridging ligand.

TABLE 2 Positional parameters and their e.s.d.s for $Rh_2(O_2CCPh_3)_4(EtOH)_2$ (**1**)[a]

Atom	x	y	z	B (Å^2)
Rh	0.000	0.000	−0.11108(7)	2.32(1)
O(1)	0.0224(4)	−0.1049(3)	−0.1135(7)	4.1(1)
O(2)	0.0227(3)	−0.1091(3)	0.0988(6)	3.5(1)
C(1)	0.0290(4)	−0.1370(4)	−0.013(1)	3.0(1)
C(2)	0.0492(4)	−0.2210(4)	−0.013(2)	4.2(2)
C(3)	0.1344(5)	−0.2221(4)	−0.019(1)	4.2(2)
C(4)	0.1705(6)	−0.1803(6)	−0.103(1)	5.6(3)
C(5)	0.2492(6)	−0.1832(6)	−0.108(2)	6.8(3)
C(6)	0.2876(6)	−0.2281(7)	−0.030(2)	7.6(4)
C(7)	0.2519(7)	−0.2687(9)	0.055(2)	8.2(4)
C(8)	0.1732(6)	−0.2670(6)	0.067(1)	5.6(3)
C(9)	0.0158(5)	−0.2507(4)	−0.128(1)	4.7(3)
C(10)	0.0597(8)	−0.2960(7)	−0.214(2)	7.4(4)
C(11)	0.0217(9)	−0.3270(8)	−0.317(2)	8.7(4)
C(12)	−0.0492(8)	−0.3170(9)	−0.340(2)	8.6(4)
C(13)	−0.0905(8)	−0.2701(8)	−0.263(2)	7.1(4)
C(14)	−0.0572(7)	−0.2390(7)	−0.160(1)	5.7(3)
C(15)	0.0217(6)	−0.2673(6)	0.107(2)	6.4(3)
C(16)	0.0282(8)	−0.2418(7)	0.220(1)	7.0(3)
C(17)	0.0027(9)	−0.2818(8)	0.332(2)	10.3(4)
C(18)	−0.0308(8)	−0.3512(7)	0.293(2)	9.6(4)
C(19)	−0.0363(8)	−0.3733(8)	0.176(2)	10.7(5)
C(20)	−0.0125(6)	−0.3342(6)	0.074(2)	7.0(4)
O(3)	−0.0243(8)	0.0210(9)	−0.321(1)	5.7(4)*
C(21)	0.081(2)	0.094(2)	−0.525(5)	13(1)*
C(22)	0.033(3)	0.088(3)	−0.400(6)	15(2)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $1/3[a^2a^{*2}B_{11}+b^2b^{*2}B_{22}+c^2c^{*2}B_{33}+2ab(\cos\gamma)a^*b^*B_{12}+2ac(\cos\beta)a^*c^*B_{13}+2bc(\cos\alpha)b^*c^*B_{23}]$. Starred atoms were refined isotropically.

Experimental

Starting materials

All reagents were purchased from commercial sources and were used without further purification. Sodium triphenylacetate was made from sodium methoxide and triphenylacetic acid. All manipulations were carried out under an argon atmosphere. $Mo_2(O_2CCH_3)_4$ was prepared by a literature procedure [13].

Preparation of $Rh_2(O_2CCPh_3)_4(EtOH)_2$ *(1)*

$RhCl_3 \cdot 3H_2O$ (0.3 g, 1.1 mmol) and sodium triphenylacetate (1.24 g, 4.0 mmol) were dissolved in 20 ml of ethanol. After refluxing for 18 h a dark green precipitate was filtered off and redissolved in 50 ml of acetone. The solution was concentrated to 5 ml. Slow evaporation of this solution in air gave blue–green single crystals after three weeks. Yield 0.24 g (32%).

Preparation of $Mo_2(O_2CCPh_3)_4 \cdot 3CH_2Cl_2$ *(2)*

$Mo_2(O_2CCH_3)_4$ (0.10 g, 0.23 mmol) and NaO_2CCPh_3 (0.30 g, 0.97 mmol) were refluxed in 20 ml of CH_2Cl_2 for 2 h. The reaction mixture was allowed to cool and filtered into a Schlenk tube, where the solution was layered with hexanes (20 ml). Yellow crystals were produced upon standing for several days. Yield 0.16 g (51%).

Preparation of $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH) \cdot 2EtOH$ *(3)*

$Ru_2[l\text{-}O_2CCH(OH)Ph]_4(H_2O)_2$ (0.25 g, 0.30 mmol) was reacted with HO_2CCPh_3 (0.69 g, 2.4 mmol) in ethanol [14]. The resulting yellow product was dissolved in ethanol, layered with hexanes, and left to stand for one week to yield yellow–brown crystals. Yield 0.24 g (59%).

X-ray crystallography

X-ray data were collected by application of procedures fully described elsewhere [5]. Lorentz, polarization and absorption corrections were applied to the data*.

Structure of $Rh_2(O_2CCPh_3)_4(EtOH)_2$ *(1)*

A crystal of approximate dimensions 0.4×0.4×0.4 mm was mounted on a CAD4 diffractometer supplied with graphite monochromated Mo Kα radiation. The

TABLE 3 Selected bond distances (Å) and angles (°) for $Rh_2(O_2CCPh_3)_4(EtOH)_2$ (**1**)

Rh–Rh′	2.365(1)	O(1)–C(1)	1.23(1)	C(2)–C(3)	1.56(1)
Rh–O(1)	1.967(6)	O(2)–C(1)	1.30(1)	C(2)–C(9)	1.48(2)
Rh–O(2′)	2.047(6)	O(3)–C(22)	1.82(6)	C(2)–C(15)	1.62(2)
Rh–O(3)	2.31(2)	C(1)–C(2)	1.59(1)	C(21)–C(22)	1.60(7)
Rh′–Rh–O(1)	90.7(2)	O(1)–Rh–O(3′)	77.5(5)	O(1)–C(1)–O(2)	126.9(7)
Rh′–Rh–O(2′)	86.3(2)	O(2′)–Rh–O(2″)	172.7(3)	O(1)–C(1)–C(2)	119(1)
Rh′–Rh–O(3)	165.2(4)	O(2′)–Rh–O(3)	84.7(4)	O(2)–C(1)–C(2)	113.7(9)
O(1)–Rh–O(1′)	178.5(3)	O(2′)–Rh–O(3′)	102.5(4)	C(1)–C(2)–C(3)	104.2(6)
O(1)–Rh–O(2′)	90.4(3)	Rh–O(1)–C(1)	118.6(6)	C(1)–C(2)–C(9)	105.0(9)
O(1)–Rh–O(2″)	89.7(3)	Rh′–O(2)–C(1)	117.5(5)	C(1)–C(2)–C(15)	116(1)
O(1)–Rh–O(3)	101.0(5)	Rh–O(3)–C(22)	117(2)		

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

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*All calculations were performed with the Enraf-Nonius Structure Determination Package on the VAX 11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX 77843

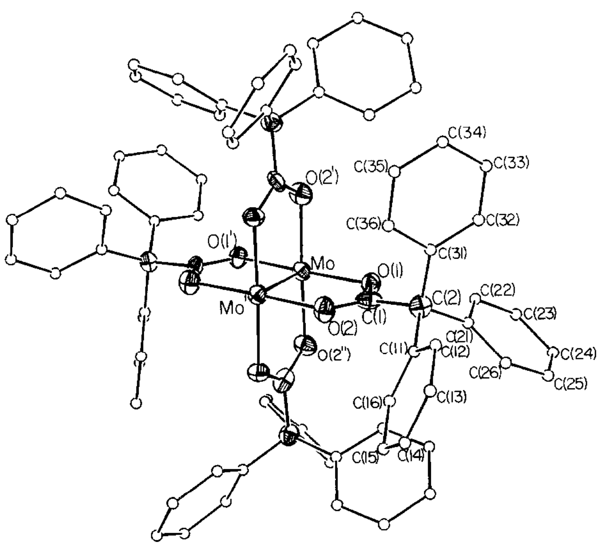

Fig 2 ORTEP drawing of the $Mo_2(O_2CCPh_3)_4$ unit in compound **2** The interstitial solvent molecules are not shown, and the carbon atoms of the phenyl rings are drawn as small spheres for clarity All other atoms are represented by their 40% probability ellipsoids

TABLE 4. Positional parameters and their estimated e.s.d s for $Mo_2(O_2CCPh_3)_4$ $3CH_2Cl_2$ (**2**)[a]

Atom	x	y	z	B (Å^2)
Mo	0.250	0.750	0.05964(5)	2.52(1)
O(1)	0.1710(2)	0.6884(2)	0.0634(3)	2.9(1)
O(2)	0.1716(3)	0.6879(3)	−0.0639(3)	3.4(1)
C(1)	0.1483(3)	0.6691(3)	−0.0007(7)	3.1(2)
C(2)	0.0944(4)	0.6196(4)	−0.0018(6)	3.0(2)
C(11)	0.0546(4)	0.6273(5)	−0.0752(5)	3.7(2)
C(12)	0.0343(5)	0.5736(5)	−0.1175(6)	4.3(3)
C(13)	−0.0036(5)	0.5833(6)	−0.1827(6)	5.4(3)
C(14)	−0.0230(5)	0.6453(6)	−0.2043(6)	5.2(3)
C(15)	−0.0038(5)	0.7013(6)	−0.1620(6)	5.9(3)
C(16)	0.0364(5)	0.6899(5)	−0.0959(6)	4.6(3)
C(21)	0.0481(5)	0.6257(4)	0.0684(5)	4.0(2)
C(22)	0.0708(5)	0.6361(5)	0.1432(6)	4.8(3)
C(23)	0.0281(6)	0.6423(6)	0.2054(6)	6.2(3)
C(24)	−0.0387(5)	0.6350(5)	0.1927(7)	5.7(3)
C(25)	−0.0601(5)	0.6230(5)	0.1195(6)	5.6(3)
C(26)	−0.0191(4)	0.6192(5)	0.0559(7)	4.8(3)
C(31)	0.1288(4)	0.5551(4)	0.0009(6)	3.8(2)
C(32)	0.1164(5)	0.5075(4)	0.0565(6)	4.9(3)
C(33)	0.1495(6)	0.4488(5)	0.0554(7)	6.3(3)
C(34)	0.1961(5)	0.4381(5)	−0.0037(8)	6.5(3)
C(35)	0.2081(5)	0.4835(5)	−0.0603(7)	5.9(3)
C(36)	0.1756(5)	0.5420(5)	−0.0576(6)	4.7(2)
C(3)	0.3437(5)	−0.344	0.250	4.5(3)*
Cl(3a)	0.3415(4)	−0.2594(3)	0.2420(4)	8.4(2)*
Cl(3b)	0.3688(3)	−0.2646(3)	0.2286(3)	6.2(1)*
Cl(4a)	0.750	0.750	0.090(4)	13 (2)*
Cl(4a)	0.693(2)	0.743(4)	0.164(2)	31(2)*
Cl(4b)	0.750	0.750	−0.073(6)	18(4)*
Cl(4b)	0.720(2)	0.692(1)	−0.148(2)	24(2)*

[a]Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $1/3[a^2a^{*2}B_{11}+b^2b^{*2}B_{22}+c^2c^{*2}B_{33}+2ab(\cos\ \gamma)a^*b^*B_{12}+2ac(\cos\ \beta)a^*c^*B_{13}+2bc(\cos\ \alpha)b^*c^*B_{23}]$ Starred atoms were refined isotropically

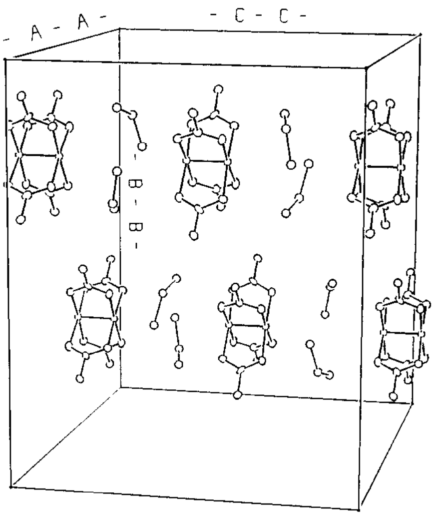

Fig 3 An indication of the unit cell packing of $Mo_2(O_2CCPh_3)_4$ $3CH_2Cl_2$ (**2**) The carbon atoms of the phenyl rings and one of the disordered solvent molecules have been removed from the drawing for clarity

unit cell was indexed on 25 strong reflections in the range $12 \leqslant 2\theta \leqslant 25°$ selected from a preliminary data collection. Systematic absences indicated $I4$ or $I\bar{4}$ as possible space groups. $I\bar{4}$ was confirmed as the correct space group by the successful solution and refinement in this group. The position of the unique metal atom was determined from a three-dimensional Patterson map, and the remaining atoms were found by the iterative application of least-squares refinement and difference Fourier maps. All of the atoms except for the carbon atoms of the ethanol molecule were refined with anisotropic displacement parameters Pertinent crystallographic data are summarized in Table 1.

Structure of $Mo_2(O_2CCPh_3)_4 \cdot 3CH_2Cl_2$ *(2)*

A well-formed crystal of approximate dimensions 0.4×0.4×0.5 mm was mounted inside a thin-walled capillary The diffraction data were collected on a CAD4 diffractometer; the unit cell was indexed on 25 strong reflections in the range $12 \leqslant 2\theta \leqslant 25°$ selected from a preliminary data collection. The position of the Mo atom was determined from a Patterson map The remaining atoms of the metal complex were located by alternating difference Fourier maps and least-squares refinement cycles. A later Fourier map indicated the positions of two disordered interstitial solvent molecules. One of the CH_2Cl_2 molecules resides on the $\bar{4}$ axis; the other is severely disordered about the four-fold axis at $\frac{3}{4}$, $\frac{3}{4}$, z. Crystallographic data for this compound are summarized in Table 1.

Structure of $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH) \cdot 2EtOH$ *(3)*

A crystal of approximate dimensions 0.4×0.4×0.45 mm was mounted on a P3/F (Equivalent) diffractometer

TABLE 5 Selected bond distances (Å) and angles (°) for $Mo_2(O_2CCPh_3)_4$ $3CH_2Cl_2$ (2)

Mo–Mo′	2.076(1)	O(1)–C(1)	1.28(1)	C(2)–C(11)	1.53(1)
Mo–O(1)	2.098(5)	O(2)–C(1)	1.26(1)	C(2)–C(21)	1.57(1)
Mo–O(2′)	2.095(6)	C(1)–C(2)	1.53(1)	C(2)–C(31)	1.53(1)
Mo′–Mo–O(1)	91.8(2)	O(2′)–Mo–O(2″)	176.0(2)	O(2)–C(1)–C(2)	119(1)
Mo′–Mo–O(2′)	92.0(2)	Mo–O(1)–C(1)	117.4(5)	C(1)–C(2)–C(11)	109.8(8)
O(1)–Mo–O(1′)	176.4(2)	Mo′–O(2)–C(1)	117.7(5)	C(1)–C(2)–C(21)	112.9(8)
O(1)–Mo–O(2′)	90.3(2)	O(1)–C(1)–O(2)	121.1(6)	C(1)–C(2)–C(31)	104.5(6)
O(1)–Mo–O(2″)	89.5(2)	O(1)–C(1)–C(2)	119.9(9)		

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

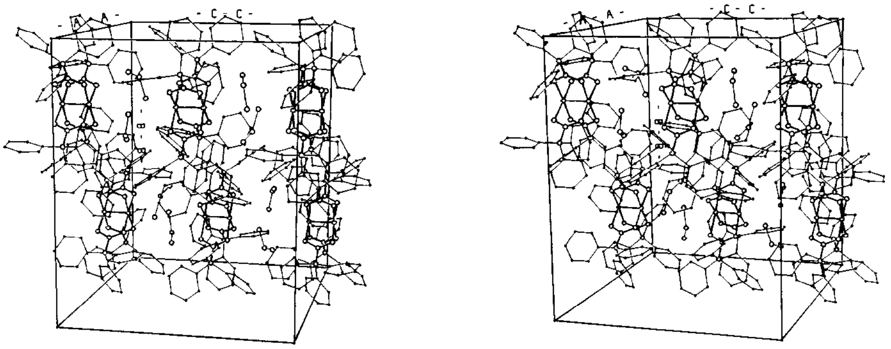

Fig. 4. A stereopair depicting the unit cell packing for $Mo_2(O_2CCPh_3)_4 \cdot 3CH_2Cl_2$ (2). One of the disordered solvent molecules is not included.

TABLE 6. Comparison of Mo–Mo distances in crystal structures of $Mo_2(O_2CR)_4$ compounds having intermolecular Mo–O axial interactions

R	Axial Mo–O distance (Å)	Mo–Mo distance (Å)	Ref.
H	2.65(1)	2.091(2)	4
CH_3	2.645(4)	2.093(1)	5
CF_3	2.71(1)	2.090(4)	6
$C(CH_3)_3$	2.90(3)	2.088(1)	7
C_6H_5	2.876(2)	2.096(1)	7
$C(C_6H_5)_3$	[a]	2.076(1)	this work

[a] No intermolecular axial interactions.

supplied with graphite monochromated Mo Kα radiation. The unit cell was indexed on 25 strong reflections in the range $20.3 \leqslant 2\theta \leqslant 29.6°$ selected from a preliminary data collection. The space groups *Cc* or *C*2/*c* were possible choices based on the systematic absences; the centrosymmetric space group was suggested by intensity statistics and was confirmed as correct by successful solution and refinement. The position of the Ru and O atoms were located by direct methods. The remaining atoms were found during iterations of least-squares refinement cycles and difference Fourier maps. The Ru and axial O atoms are located on a crystallographic two-fold axis, which causes the C atoms of the axially-coordinated ethanol moiety do be disordered over two orientations (as in **1**). Another non-coordinated ethanol molecule is located on a general position in the cell. All of the atoms except for those of the ethanol molecules were refined with anisotropic displacement parameters. Crystallographic data for this compound are also summarized in Table 1.

Results and discussion

The structure of **1** is represented in Fig. 1, and atomic positional parameters are presented in Table 2. Selected bond distances and angles are given in Table 3. The metal–metal vector is coincident with the crystallographic $\bar{4}$ axis and the molecule has strict $\bar{4}$ symmetry. The Rh–Rh bond length of 2.365(1) Å is similar to that for other $Rh_2(O_2CR)_4L_2$ compounds [1c]. This result supports our assumption that the axial molecules of the solvent are protonated and that we indeed have a Rh_2^{4+} system with a formal single bond. The perfect alignment of all molecules parallel to the *c* axis was, of course, not unexpected, and offers the potential of a relatively straightforward study of the polarizations of electronic transitions in this otherwise typical $Rh_2(O_2CR)_4L_2$ compound. In view of the considerable difficulty and controversy that has attended the previous efforts to establish the electronic spectral assignments [1b], this could be of value.

The structure of **2** is shown in Fig. 2. Positional parameters appear in Table 4 and selected bond distances and angles in Table 5. Unlike other $Mo_2(O_2CR)_4$

TABLE 7 Positional parameters and their estimated e s d s for $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH)$ 2EtOH (**3**)[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Ru(1)	0.000	0.31066(7)	0.250	3.24(3)
Ru(2)	0.000	0.17808(7)	0.250	3.32(3)
O(1)	0.0835(4)	0.3083(4)	0.2014(3)	3.9(2)
O(2)	0.0771(4)	0.1771(4)	0.1957(3)	4.5(2)
O(3)	0.0596(4)	0.3114(4)	0.3267(3)	3.9(2)
O(4)	0.0683(4)	0.1813(4)	0.3209(3)	4.2(2)
O(5)	0.000	0.4489(7)	0.250	8.5(4)
O(6)	0.000	0.0400(8)	0.250	10.9(6)
O(7)	−0.100(1)	−0.016(1)	0.2771(9)	19.9(8)
C(1)	0.1022(5)	0.2437(7)	0.1833(4)	4.3(2)
C(2)	0.1601(5)	0.2388(7)	0.1419(5)	4.6(3)
C(3)	0.2037(7)	0.3148(8)	0.1449(5)	6.1(3)
C(4)	0.1728(8)	0.3874(9)	0.1361(6)	7.3(4)
C(5)	0.2133(9)	0.4549(9)	0.1371(7)	8.9(5)
C(6)	0.2835(8)	0.452(1)	0.1513(7)	10.0(4)
C(7)	0.3141(9)	0.379(1)	0.1611(8)	9.6(5)
C(8)	0.2739(7)	0.3089(9)	0.1579(6)	7.3(4)
C(9)	0.1266(6)	0.2287(9)	0.0805(5)	6.0(3)
C(10)	0.0728(6)	0.1788(7)	0.0689(6)	5.2(3)
C(11)	0.0458(7)	0.1665(9)	0.0125(6)	6.5(4)
C(12)	0.073(1)	0.204(1)	−0.0340(7)	9.9(6)
C(13)	0.130(1)	0.253(1)	−0.0224(7)	11.5(6)
C(14)	0.1567(9)	0.271(1)	0.0364(6)	9.4(5)
C(15)	0.2023(6)	0.1672(7)	0.1582(5)	4.8(3)
C(16)	0.2217(7)	0.1519(8)	0.2156(7)	6.6(4)
C(17)	0.2648(8)	0.086(1)	0.2329(8)	8.7(5)
C(18)	0.2884(9)	0.035(1)	0.1928(9)	10.6(5)
C(19)	0.2716(8)	0.051(1)	0.1337(9)	10.8(5)
C(20)	0.2270(8)	0.116(1)	0.1153(7)	8.3(5)
C(21)	0.0814(5)	0.2449(6)	0.3457(4)	3.8(2)
C(22)	0.1336(5)	0.2471(7)	0.3990(4)	3.8(2)
C(23)	0.1280(5)	0.1746(6)	0.4384(5)	4.0(3)
C(24)	0.1406(6)	0.1846(7)	0.4987(5)	4.7(3)
C(25)	0.1398(6)	0.1186(7)	0.5345(6)	5.3(3)
C(26)	0.1265(6)	0.0420(8)	0.5130(6)	5.6(3)
C(27)	0.1131(8)	0.0331(8)	0.4546(6)	7.1(4)
C(28)	0.1146(7)	0.0977(7)	0.4172(6)	5.6(3)
C(29)	0.1210(6)	0.3218(6)	0.4341(5)	4.0(3)
C(30)	0.1747(6)	0.3688(7)	0.4536(5)	4.5(3)
C(31)	0.1627(7)	0.4340(8)	0.4910(6)	6.2(4)
C(32)	0.0972(7)	0.4475(8)	0.5073(6)	6.3(3)
C(33)	0.0450(7)	0.4006(9)	0.4866(6)	6.6(4)
C(34)	0.0561(6)	0.3367(7)	0.4500(5)	5.2(3)
C(35)	0.2030(5)	0.2488(7)	0.3736(4)	4.1(2)
C(36)	0.2540(6)	0.1957(8)	0.3918(6)	5.4(3)
C(37)	0.3174(7)	0.203(1)	0.3681(6)	7.1(4)
C(38)	0.3294(7)	0.2618(9)	0.3281(6)	7.2(4)
C(39)	0.2784(7)	0.3149(9)	0.3087(6)	6.9(4)
C(40)	0.2144(6)	0.3082(7)	0.3336(5)	5.0(3)
C(41)	0.004(3)	0.501(3)	0.180(2)	15(2)*
C(42)	−0.035(2)	0.507(3)	0.148(2)	12(1)*
C(43)	−0.082(2)	−0.028(2)	0.336(1)	19(1)*
C(44)	−0.023(2)	−0.058(2)	0.344(2)	22(1)*

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $1/3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred atoms were refined isotropically.

compounds [4–7] the $Mo_2(O_2CCPh_3)_4$ molecules do not form intermolecular chains in which the oxygen atoms of one molecule are located approximately in the axial coordination position of adjacent molecules. This lack of strong axial interactions, along with the fact that the Mo–Mo bond is rigorously aligned with the crystal *c* axis, allowed us to provide strong evidence for assigning the weak feature that occurs in the spectra of all $Mo_2(O_2CR)_4$ compounds to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition [16]. The general packing of the molecule can be seen in Fig. 3, which shows the lack of intermolecular axial interactions. Figure 4 indicates how the array of phenyl groups dominates the packing in the unit cell and therefore prevents such interactions. As in the Rh structure, the metal–metal vector is coincident with the crystallographic $\bar{4}$ axis and the molecule has strict $\bar{4}$ symmetry. The Mo–Mo bond length of 2.076(1) Å is essentially equal to the Mo–Mo bond length determined in the gas-phase scattering experiment (2.079(3) Å) for the acetate [8a], and very close to that (2.082(1) Å) found in the 2-phenylbenzoate where axial ligation is also absent [8b]. All these results support earlier assumptions that the Mo–Mo quadruple bond lengths depend very little on the inductive properties of R in $Mo_2(O_2CR)_4$ compounds [7] Table 6 compares the Mo–Mo bond lengths in a series of $Mo_2(O_2CR)_4$ compounds in which there are intermolecular axial interactions to the present structure. The lack of an effect on the metal–metal bond distance due to the changes in R (for O_2CR) is evident in the constant (within 3 standard deviations) Mo–Mo distance for these compounds. The weighted average Mo–Mo distance for the five compounds in Table 6 that have intermolecular axial interactions is 2.092 Å with a standard deviation of 0.001; the Mo–Mo distance in **2** without axial coordination is 0.016(2) Å shorter.

Table 7 contains atomic positional parameters for **3**, and selected bond lengths and angles appear in Table 8. The structure of **3** is generally the same as for other $M_2(O_2CCPh_3)_4$ compounds, with the axial ligands EtOH and H_2O in this case. The Ru and axial O atoms lie on a two-fold axis. The Ru–Ru bond length of 2.252(2) Å is similar to those of other $Ru_2(O_2CR)_4L_2$ compounds [14, 17]. All solvent molecules, including the ones in axial positions, can be removed by heating **3** for 2 h at 170 °C under vacuum. The resulting compound crystallized from CH_2Cl_2/hexanes is $Ru_2(O_2CCPh_3)_4 \cdot xCH_2Cl_2$, (**4**). **4** and **2** are essentially isomorphous. The cell dimensions of **4** are $a = b = 20.827(5)$, $c = 17.308(1)$ Å. The structure was solved and refined to $R = 0.11$ in space group *P4/ncc*, but proved intractable due to severely disordered CH_2Cl_2 molecules. In this incomplete structure, the Ru–Ru distance is 2.255(2) Å, almost identical to that in **3**. The Ru–O distances are 2.047(9) and 2.049(9) Å.

TABLE 8 Selected bond distances (Å) and angles (°) for $Ru_2(O_2CCPh_3)_4(H_2O)(EtOH) \cdot 2EtOH$ (**3**)

Ru(1)–Ru(2)	2.252(2)	Ru(2)–O(4)	2.064(7)	O(4)–C(21)	1.24(1)
Ru(1)–O(1)	2.079(7)	Ru(2)–O(6)	2.35(1)	C(1)–C(2)	1.56(2)
Ru(1)–O(3)	2.073(7)	O(1)–C(1)	1.24(1)	C(21)–C(22)	1.56(1)
Ru(1)–O(5)	2.35(1)	O(2)–C(1)	1.28(1)		
Ru(2)–O(2)	2.061(8)	O(3)–C(21)	1.28(1)		
Ru(2)–Ru(1)–O(1)	88.9(2)	Ru(1)–Ru(2)–O(2)	90.5(2)	Ru(1)–O(1)–C(1)	118.3(7)
Ru(2)–Ru(1)–O(3)	90.3(2)	Ru(1)–Ru(2)–O(4)	88.5(2)	Ru(2)–O(2)–C(1)	117.0(7)
Ru(2)–Ru(1)–O(5)	180	Ru(1)–Ru(2)–O(6)	180	Ru(1)–O(3)–C(21)	116.9(6)
O(1)–Ru(1)–O(1′)	177.8(3)	O(2)–Ru(2)–O(2′)	179.1(3)	Ru(2)–O(4)–C(21)	119.9(6)
O(1)–Ru(1)–O(3)	92.5(3)	O(2)–Ru(2)–O(4)	91.1(3)	O(1)–C(1)–O(2)	125(1)
O(1)–Ru(1)–O(3′)	87.5(3)	O(2)–Ru(2)–O(4′)	88.9(3)	O(1)–C(1)–C(2)	121(1)
O(1)–Ru(1)–O(5)	91.1(2)	O(2)–Ru(2)–O(6)	89.5(2)	O(3)–C(21)–O(4)	123.6(9)
O(3)–Ru(1)–O(3′)	179.3(3)	O(4)–Ru(2)–O(4′)	177.0(3)	O(3)–C(21)–C(22)	116.4(9)
O(3)–Ru(1)–O(5)	89.7(2)	O(4)–Ru(2)–O(6)	91.5(2)	O(4)–C(21)–C(22)	119.6(9)

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

We have shown that the triphenylacetate ion can be used to prepare dinuclear metal carboxylates using several different metal atoms, but that the resulting coordination environment does not necessarily exclude axial ligands. However, when the reaction is carried out in a non-coordinating medium the axial site may remain unoccupied.

Supplementary material

Complete tables of bond distances, bond angles, anisotropic displacement parameters, and an ORTEP drawing of **3** (15 pages), and observed and calculated structure factors (31 pages) for **1**, **2** and **3** are available from the author.

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