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An asymmetric homodinuclear complex containing the μ-oxo-bis(μ-carboxylato)diruthenium(III) core: X-ray structure of $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_3(en)(PPh_3)_2](ClO_4)\cdot 3CHCl_3$ ☆

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Abstract

Asymmetric tri-bridged diruthenium(III) complexes, $[Ru_2O(O_2CR)_3(en)(PPh_3)_2](ClO_4)$ ($R=C_6H_4$-*p*-X: X = OMe (**1a**), Me (**1b**); en = 1,2-diaminoethane), were prepared and structurally characterized. Complex **1a**·$3CHCl_3$ crystallizes in the triclinic space group $P\bar{1}$ with $a=14.029(5)$, $b=14.205(5)$, $c=20.610(6)$ Å, $\alpha=107.26(3)$, $\beta=101.84(3)$, $\gamma=97.57(3)°$, $V=3756(2)$ Å^3 and $Z=2$. The complex has an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$ core and exhibits $[O_4PRu(\mu\text{-}O)RuPO_2N_2]^+$ coordination environments for the metal centers. The novel structural feature is the asymmetric arrangement of ligands at the terminal sites of the core which shows an Ru···Ru separation of 3.226(3) Å and an Ru–O–Ru angle of 119.2(5)°. An intense visible band observed near 570 nm is assigned to a charge transfer transition involving the dπ–Ru(III) and pπ–μ-O orbitals. Cyclic voltammetry of the complexes displays a reversible $Ru_2(III,III) \rightleftharpoons Ru_2(III,IV)$ couple near 0.8 V (versus SCE) in MeCN–0.1 M TBAP.

Keywords: Crystal structures; Ruthenium complexes; Oxo complexes; Carboxylato complexes; Dinuclear complexes

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1. Introduction

The coordination environments of the metal in the tri-bridged diiron active centers in hemerythrin [1] and ribonucleotide reductase [2] are intrinsically asymmetric in nature. While the majority of the structurally characterized non-biological first-row [3–6] and heavier [7–10] transition-metal complexes with a (μ-oxo/hydroxo/alkoxo)bis(μ-carboxylato)dimetal core show a symmetric disposition of terminal ligands, the chemistry of the relatively new class of homodinuclear asymmetric tri-bridged complexes is limited to only $[Mn_2O(O_2CMe)_2(bpy)_2(H_2O)(S_2O_8)]$ [11], $Fe_2(O_2CH)_4(BIPhMe)_2$ (BIPhMe = 2,2′-bis(1-methylimidazolyl)-phenylmethoxymethane) [12], $[M_2O(O_2CMe)_2(TACN)(Me_3TACN)]^{2+}$ (M = Fe, Mn) (TACN = 1,3,7-triazacyclononane; Me_3TACN = 1,3,7-methyl-1,3,7-triazacyclononane) [13] and $[Fe_2O(O_2CMe)_2(Me_3TACN)(bipy)L]^{n+}$ (L = Cl, $n=1$; L = H_2O, $n=2$) [14]. Herein, we report an unusual reaction forming a new asymmetric diruthenium(III) complex $[Ru_2O(O_2CR)_3(en)(PPh_3)_2](ClO_4)$ ($R=C_6H_4$-*p*-X: X = OMe (**1a**), Me (**1b**); en = 1,2-diaminoethane), showing novel structural features.

2. Experimental

2.1. Preparation of $[Ru_2O(O_2CR)_3(en)(PPh_3)_2](ClO_4)$ ($R=C_6H_4$-p-X; X = OMe (1a) Me (1b))

The complexes were prepared using a general procedure in which a 5 ml MeOH solution containing $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ [10a] (0.17 mmol) was reacted with 1.5 ml of a 0.3 M MeOH solution of en (0.43 mmol) under refluxing conditions for 2 h. The solution was cooled to an ambient temperature and the crude solid was precipitated on addition of an aqueous solution of $NaClO_4$ (10 ml) to the reaction mixture. The solid was isolated, washed with water and dried over P_4O_{10}. The title complex was obtained from this mixture by chromatography on a silica-gel column in petroleum ether (b.p. 60–80 °C). The bluish purple band of the complex, eluted with a 1:9 (vol./vol.) MeOH–$CHCl_3$ mixture as eluant, gave an analytically pure solid in ~25% yield. **1a**: *Anal.* Calc. for $C_{62}H_{59}N_2O_{14}P_2ClRu_2$: C, 54.93; H, 4.39; N, 2.07. Found: C, 54.65; H, 4.50; N, 1.87%. **1b**: *Anal.*

☆ Dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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Calc. for $C_{62}H_{59}N_2O_{11}P_2ClRu_2$: C, 56.95; H, 4.52; N, 2.14. Found: C, 57.28; H, 4.73; N, 2.26%. The 1:1 electrolytic complexes were highly soluble in polar organic solvents and essentially insoluble in benzene and water (Λ_M (mho cm^2 mol^{-1}) in MeCN: **1a**, 120; **1b**, 110).

2.2. Measurements

Elemental analysis was carried out on an Heraeus CHN-O Rapid instrument. Electronic and ^{1}H NMR spectra were recorded with Hitachi U-3400 and Bruker AC(AF)-200 MHz spectrometers, respectively. Cyclic voltammetric measurements were performed at 25 °C using a three-electrode set-up comprising a platinum button working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode on a PAR model 174A polarographic analyzer connected with a Houston Instruments Omnigraphic X-Y recorder. Conductivity measurements were made with a Century CC603 conductivity meter.

2.3. X-ray crystallography

A purple colored rectangular shaped crystal of approximate dimensions 0.6×0.4×0.1 mm, grown by a liquid–liquid diffusion using a $CHCl_3$ solution of **1a** and petroleum ether, was sealed in a Lindemann capillary along with the mother liquor as the crystals were found to lose crystallinity outside the solution. The unit cell parameters were obtained from this crystal mounted on an Enraf-Nonius CAD4 four-circle diffractometer fitted with graphite monochromatized Mo Kα radiation. Intensity data, collected in the 2θ range 2–40° by the ω-scan method for $+h \pm k \pm l$ reflections in the triclinic crystal system, were corrected for Lorentz and polarization effects, and for absorption [15]. The crystal did not diffract beyond $\theta = 20°$.

The structure was solved in the triclinic space group $P\bar{1}$ by standard Patterson and Fourier syntheses using the SHELX system of programs [16] on a VAX-8810 computer. The atom scattering factors were taken from Ref. [17]. There were 7011 unique data of which 4474 with $F_o > 6\sigma(F_o)$ were used for structure solution and refinement. The asymmetric unit of the cell showed the presence of a dimeric cation, one perchlorate anion and three $CHCl_3$ lattice molecules. The crystal structure did not show any unusual features except thermal disorders in perchlorate oxygens, two methoxy groups, solvent molecules and positional disorder of chlorine atoms in one of the solvent molecules. The hydrogen atoms in the calculated position constrained to ride on the atoms to which they were attached with a fixed isotropic thermal parameter of 0.12 Å^2 were used only for structure factor calculations. All atoms were refined anisotropically except the disordered ones. The weakly diffracting nature of the crystal and the disorders of several atoms were the possible reasons for the high values of the R indices. Selected crystallographic data are presented in Table 1. Table 2 lists the atomic positional parameters with estimated standard deviations.

Table 1
Crystal data for $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_3(en)(PPh_3)_2]ClO_4 \cdot 3CHCl_3$ (**1a**)

Formula	$C_{65}H_{62}N_2O_{14}P_2Cl_{10}Ru_2$
Formula weight	1713.83
Crystal dimensions (mm)	0.6×0.4×0.1
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	14.029(5)
b (Å)	14.205(5)
c (Å)	20.610(6)
α (°)	107.26(3)
β (°)	101.84(3)
γ (°)	97.57(3)
V (Å^3)	3756(2)
ρ_{calc} (g cm^{-3})	1.52
Z	2
Instrument	CAD-4
Temperature (K)	293
λ(Mo Kα) (Å)	0.7107
μ(Mo Kα) (cm^{-1})	8.53
Transmission coefficient	1.00–0.91
Scan method	ω
Range of reflections	$0 \leqslant h \leqslant 13$ $-13 \leqslant k \leqslant 13$ $-19 \leqslant l \leqslant 19$
2θ range (°)	$2 \leqslant 2\theta \leqslant 40$
No. of refections	
total (unique)	7468 (7011)
observed	4474 ($F_o > 6\sigma(F_o)$)
Computer programms	SHELXS-86 SHELX-76
Parameters refined	854
$R(F_o)$ [a]	0.064
$R_w(F_o)$ [b]	0.069

[a] $R(F_o) = (\Sigma \| F_o| - |F_c \|) / \Sigma |F_o|$.

[b] $R_w(F_o) = [(\Sigma w^{1/2} \| F_o| - |F_c \|) / \Sigma (w^{1/2} |F_o|)$; $w = 1/\sigma^2(F_o)$.

3. Results and discussion

The reaction of en with $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ gave a mixture of products. Three successive fractions containing purple $Ru_2O(O_2CR)_4(PPh_3)_2$ [10a] (~5%), the bluish purple title complex (~25%) and symmetric purple $[Ru_2O(O_2CR)_2(en)_2(PPh_3)_2](ClO_4)_2$ [10e] (~25%) were eluted using 1:49, 1:9 and 1:4 (vol./vol.) MeOH–$CHCl_3$ mixtures, respectively, as eluant. The fourth component of the mixture was a yellow species that was adsorbed strongly to the column and could not be separated by chromatographic procedure. This complex was, however, isolated by dissolving the crude mixture in water and precipitating

Table 2

Fractional atomic coordinates and equivalent isotropic thermal parameters ($\times 10^3$) for the non-hydrogen atoms of $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_3(en)(PPh_3)_2]ClO_4\cdot 3CHCl_3$ (**1a**) with their e.s.d.s.

Atom	x/a	y/b	z/c	U_{eq} [a]
Ru1	0.7992(1)	0.7853(1)	0.7398(1)	50(1)
Ru2	0.8086(1)	0.5767(1)	0.7709(1)	53(1)
O1	0.7455(6)	0.6863(5)	0.7713(4)	50(4)
P1	0.7482(2)	0.8956(2)	0.8245(2)	49(2)
P2	0.6584(3)	0.4726(2)	0.7475(2)	59(2)
N1	0.8305(8)	0.6227(7)	0.8801(5)	61(5)
N2	0.8979(8)	0.4711(8)	0.7945(7)	76(6)
C1	0.9100(12)	0.5783(11)	0.9109(8)	85(8)
C2	0.8990(11)	0.4713(11)	0.8669(9)	87(9)
O11	0.9379(6)	0.8212(6)	0.8031(4)	52(4)
O12	0.9567(6)	0.6629(7)	0.7943(4)	61(4)
C10	0.9901(10)	0.7560(12)	0.8125(6)	57(7)
C11	1.0979(9)	0.7976(10)	0.8491(6)	50(6)
C12	1.1566(10)	0.7311(10)	0.8648(7)	58(6)
C13	1.2579(10)	0.7726(11)	0.9023(7)	66(7)
C14	1.2961(10)	0.8740(10)	0.9226(8)	70(7)
C15	1.2374(11)	0.9378(10)	0.9073(8)	73(8)
C16	1.1379(10)	0.9011(10)	0.8711(7)	59(7)
O13	1.3914(7)	0.9168(8)	0.9598(6)	92(5)
C17	1.4537(13)	0.8544(13)	0.9767(12)	125(13)
O21	0.8436(7)	0.6816(7)	0.6556(4)	66(4)
O22	0.8074(7)	0.5263(7)	0.6675(5)	70(5)
C20	0.8285(10)	0.5888(14)	0.6339(7)	65(8)
C21	0.8283(12)	0.5348(12)	0.5583(8)	89(9)
C22	0.8588(13)	0.5871(16)	0.5213(8)	106(10)
C23	0.8512(18)	0.5377(22)	0.4465(14)	173(18)
C24	0.8150(27)	0.4494(26)	0.4168(16)	174(21)
C25	0.7947(27)	0.3998(20)	0.4516(17)	182(21)
C26	0.7940(21)	0.4325(14)	0.5284(10)	156(15)
O23	0.8037(15)	0.3935(15)	0.3474(8)	229(12)
C27	0.8211(24)	0.4584(25)	0.3086(16)	293(23)
O31	0.8170(8)	0.8765(7)	0.6727(5)	70(5)
O32	0.6769(7)	0.7786(7)	0.6572(4)	66(50
C30	0.7264(13)	0.8395(12)	0.6352(8)	69(8)
C31	0.6850(11)	0.8674(10)	0.5786(7)	73(7)
C32	0.7436(18)	0.9201(15)	0.5528(9)	109(12)
C33	0.7107(21)	0.9519(19)	0.4942(14)	130(15)
C34	0.6115(31)	0.9286(21)	0.4649(15)	150(21)
C35	0.5512(23)	0.8743(18)	0.4877(13)	146(15)
C36	0.5902(18)	0.8440(13)	0.5475(9)	106(11)
O33	0.5610(10)	0.9460(10)	0.4030(7)	170(7)
C37	0.6258(16)	1.0085(16)	0.3771(11)	188(12)
C41	0.7759(10)	0.8677(8)	0.9061(6)	43(6)
C42	0.7039(11)	0.8149(10)	0.9279(7)	59(7)
C43	0.7295(13)	0.7896(11)	0.9875(9)	78(8)
C44	0.8272(13)	0.8154(10)	1.0276(8)	72(8)
C45	0.9003(12)	0.8663(10)	1.0068(7)	71(7)
C46	0.8739(10)	0.8929(8)	0.9443(7)	54(7)
C51	0.8100(10)	1.0291(9)	0.8555(7)	55(6)
C52	0.7974(11)	1.0931(9)	0.9160(7)	70(6)
C53	0.8497(14)	1.1973(12)	0.9364(10)	88(10)
C54	0.9060(14)	1.2325(13)	0.9007(10)	86(9)
C55	0.9164(12)	1.1674(13)	0.8421(10)	83(10)
C56	0.8718(10)	1.0665(10)	0.8174(7)	70(7)
C61	0.6130(9)	0.8882(10)	0.8043(6)	50(7)
C62	0.5713(10)	0.9703(11)	0.8259(8)	81(8)
C63	0.4710(14)	0.9624(19)	0.8137(12)	97(14)
C64	0.4073(16)	0.8655(15)	0.7731(10)	92(9)
C65	0.4516(12)	0.7834(12)	0.7491(9)	95(9)
C66	0.5513(11)	0.7967(12)	0.7652(8)	81(8)
C71	0.5690(9)	0.4669(10)	0.6692(7)	61(6)
C72	0.5711(11)	0.5426(11)	0.6420(8)	69(8)
C73	0.4964(13)	0.5418(13)	0.5885(9)	93(9)
C74	0.4100(13)	0.4563(14)	0.5589(8)	108(11)
C75	0.4071(15)	0.3814(13)	0.5864(9)	97(10)
C76	0.4848(14)	0.3840(13)	0.6403(10)	94(10)
C81	0.5935(10)	0.5064(9)	0.8154(7)	61(6)
C82	0.6266(12)	0.4978(11)	0.8810(9)	83(9)
C83	0.5724(13)	0.5311(12)	0.9329(9)	102(9)
C84	0.4896(13)	0.5737(13)	0.9177(12)	100(11)
C85	0.4591(15)	0.5818(13)	0.8555(10)	95(10)
C86	0.5098(12)	0.5492(10)	0.8035(8)	83(9)
C91	0.6687(10)	0.3410(9)	0.7309(8)	69(7)
C92	0.7087(11)	0.2974(10)	0.6782(9)	85(8)
C93	0.7192(20)	0.1991(16)	0.6604(16)	122(15)
C94	0.6866(21)	0.1453(24)	0.6929(17)	149(20)
C95	0.6421(24)	0.1812(20)	0.7474(17)	166(21)
C96	0.6332(14)	0.2841(13)	0.7674(11)	106(10)
Cl1	0.1826(4)	0.4793(6)	0.9152(5)	160(5)
O2	0.1271(16)	0.4857(15)	0.8516(12)	206(14)
O3	0.1388(17)	0.5395(16)	0.9629(12)	211(17)
O4	0.1784(15)	0.3947(11)	0.9277(9)	276(12)
O5	0.2685(13)	0.5022(17)	0.9108(10)	334(15)
C3	0.3401(27)	0.2690(24)	0.8260(17)	161(21)
Cl11	0.4437(10)	0.2638(9)	0.8827(6)	227(8)
Cl12	0.2584(10)	0.1497(10)	0.8063(7)	258(10)
Cl13	0.3569(9)	0.2877(9)	0.7561(6)	299(10)
C4	0.9759(27)	1.1253(28)	0.3490(22)	163(26)
Cl21	0.8936(8)	1.2132(9)	0.3347(6)	283(8)
Cl22	0.9775(9)	1.1351(9)	0.4337(6)	299(9)
Cl23	0.9293(9)	1.0200(10)	0.2905(7)	309(9)
C5	0.0429(29)	0.2579(28)	0.6654(19)	303(27)
Cl31	0.1283(8)	0.2137(8)	0.6124(6)	337(7)
Cl32	−0.0301(15)	0.3414(16)	0.6396(16)	207(6) [b]
Cl33	0.0656(17)	0.2978(17)	0.7306(13)	246(8) [b]
Cl34	−0.0264(20)	0.1496(21)	0.6640(14)	299(10) [b]
Cl35	−0.0597(23)	0.2638(24)	0.5873(16)	326(11) [b]

[a] $U_{eq} = 1/3[\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j]$.

[b] Refined isotropically with a 0.5 site occupancy.

a yellow solid in ~30% yield by $NaBPh_4$. Preliminary studies [18] show that the yellow product is a mixture of two monomeric cationic ruthenium complexes, viz. $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$ and $[Ru(O_2CR)(en)_2(PPh_3)](ClO_4)_2$.

The formation of $[Ru_2O(O_2CR)_3(en)(PPh_3)_2](ClO_4)$ (**1**) containing three carboxylato ligands from a dicarboxylato bridged precursor $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$ [10a] involves substitution of four terminal nitrile ligands by chelating en and RCO_2^-. A cleavage of the dimeric core of the precursor by en with a concomitant release of the carboxylato ligands for ligation at the terminal site of the uncleaved dimeric core is envisaged from the isolation of this unusual product which has been characterized from analytical and physico-chemical data (Table 3). The asymmetric nature of the complex is evidenced from the ^1H NMR

Table 3
Physico-chemical data for $[Ru_2O(O_2CR)_3(en)(PPh_3)_2](ClO_4)$ ($R=C_6H_4$-*p*-X; X=OMe (**1a**) Me (**1b**))

	1a	**1b**
¹H NMR data [a]		
$Me(O_2CR)$	3.66, 3.76, 3.85, (s, 3×3H)	2.17, 2.30, 2.40 (s, 3×3H)
CH_2, NH_2(en)	2.40, 3.20, 3.55, 5.40, 5.90 (m, 6H)	2.40, 3.20, 3.65, 5.40, 5.85 (m, 6H)
NH_2, R, PPh_3	6.49, 6.72, 6.89, 8.02 (d, 4×2H, 9)	6.82, 7.02, 7.94 (d, 3×2H, 8)
	6.48–8.40 (m, 36H)	6.79–7.96 (m, 38H)
Electronic spectra [b]		
λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))	567 (5300); 371 (sh)	565 (5100); 375 (sh)
Cyclic voltammetry [c]		
$E_{1/2}$ (V) (ΔE_p (mV))	+0.75 (60)	+0.78 (70)

[a] δ (ppm) (multiplicity, *n*H, *J* (Hz)) in $CDCl_3$. s. singlet; d, doublet; m, multiplet.

[b] In MeCN.

[c] In MeCN–0.1 M TBAP; $E_{1/2}=(E_{pa}+E_{pc})/2$; $\Delta E_p=E_{pa}-E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively, at scan rate 20 mV s^{-1}.

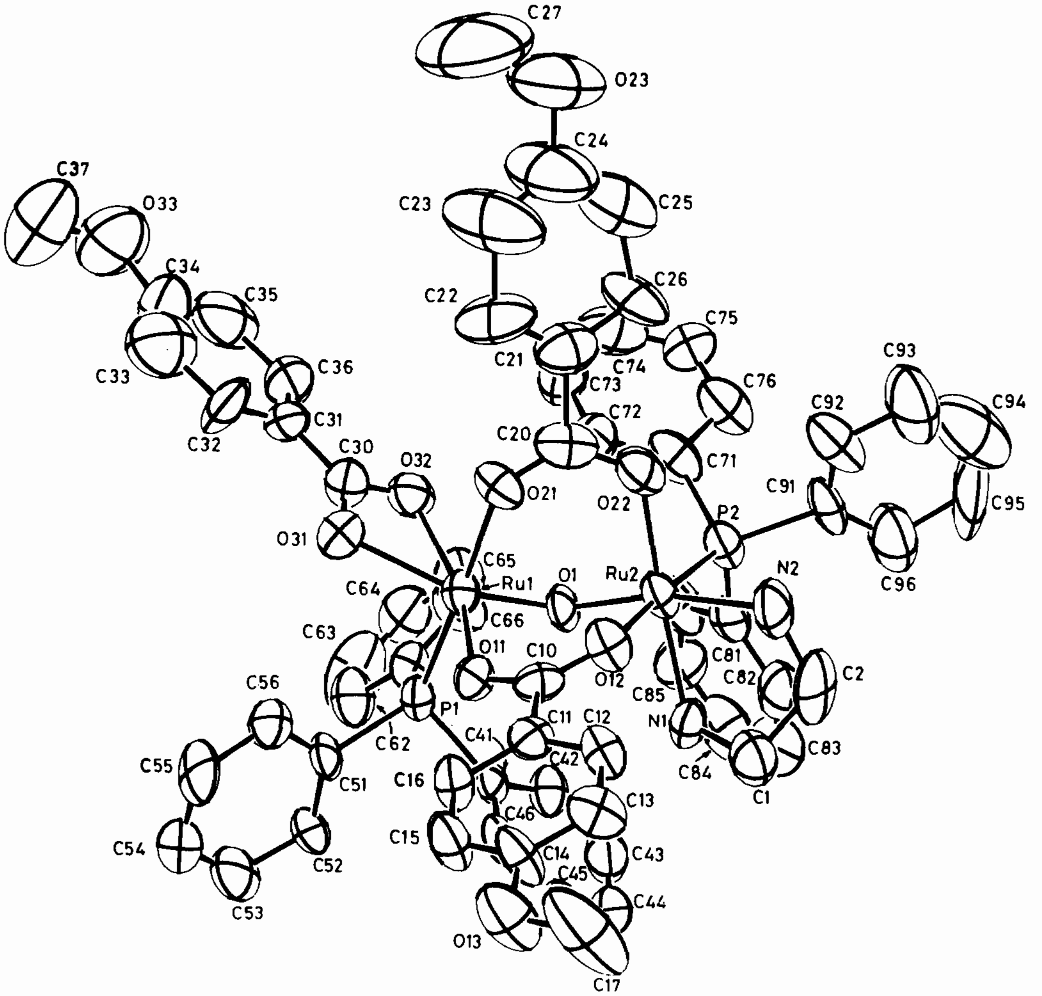

Fig. 1. An ORTEP plot of the complex cation in $[Ru_2O(O_2CC_6H_4\text{-}p\text{-}OMe)_3(en)(PPh_3)_2](ClO_4)\cdot 3CHCl_3$ (**1a**) showing 50% probability thermal ellipsoids and the atom numbering scheme.

spectra, showing three sharp singlets in a 1:1:1 ratio for the methyl protons of the carboxylato ligands. The complex exhibits an intense visible band near 570 nm. The band is diagnostic [8–10] of a μ-oxo-bis(μ-carboxylato)diruthenium(III) core and is assignable to a charge transfer (CT) transition involving the dπ–Ru(III) and pπ–μ-O orbitals. The complex undergoes a one-electron oxidation near 0.8 V (versus SCE) in MeCN–

Table 4
Selected bond lengths and bond angles for [$Ru_2O(O_2CC_6H_4$-*p*-$OMe)_3(en)(PPh_3)_2]ClO_4 \cdot 3CHCl_3$ (**1a**)

(a) Bond distances (Å)			
Ru1–Ru2	3.226(3)	Ru2–O1	1.888(8)
Ru1–O1	1.852(9)	Ru2–P2	2.280(4)
Ru1–P1	2.280(4)	Ru2–N1	2.092(10)
Ru1–O11	2.013(8)	Ru2–N2	2.176(13)
Ru1–O21	2.177(9)	Ru2–O12	2.149(8)
Ru1–O31	2.185(12)	Ru2–O22	2.033(10)
Ru1–O32	2.124(9)	P2–C71	1.803(14)
P1–C41	1.818(14)	P2–C81	1.805(16)
P1–C51	1.838(12)	P2–C91	1.829(13)
P1–C61	1.838(13)	O11–C10	1.288(19)
N1–C2	1.476(21)	O12–C10	1.257(18)
C1–C2	1.490(20)	O21–C20	1.233(21)
N2–C2	1.488(25)	O22–C20	1.317(23)
O31–C30	1.292(18)	O32–C30	1.281(22)
(b) Bond angles (°)			
Ru1–O1–Ru2	119.2(5)	O12–Ru2–O22	89.4(4)
O31–Ru1–O32	60.1(4)	N2–Ru2–O22	92.1(5)
O21–Ru1–O32	83.6(3)	N2–Ru2–O12	78.7(4)
O21–Ru1–O31	78.9(4)	N1–Ru2–O22	171.5(5)
O11–Ru1–O32	160.7(4)	N1–Ru2–O12	85.0(4)
O11–Ru1–O31	100.7(4)	N1–Ru2–N2	80.5(5)
O11–Ru1–O21	91.4(4)	P2–Ru2–O22	90.5(3)
P1–Ru1–O32	94.1(3)	P2–Ru2–O12	174.4(3)
P1–Ru1–O31	99.4(3)	P2–Ru2–N2	95.7(4)
P1–Ru1–O21	177.6(3)	P2–Ru2–N1	94.5(3)
P1–Ru1–O11	90.6(3)	O1–Ru2–O22	99.0(4)
O1–Ru1–O32	100.7(4)	O1–Ru2–O12	95.0(4)
O1–Ru1–O31	160.2(4)	O1–Ru2–N2	167.2(4)
O1–Ru1–O21	94.9(4)	O1–Ru2–N1	87.9(4)
O1–Ru1–O11	98.3(4)	O1–Ru2–P2	90.5(3)
O1–Ru1–P1	86.2(3)	Ru2–P2–C91	112.3(5)
Ru1–P1–C61	114.1(4)	Ru2–P2–C81	114.2(5)
Ru1–P1–C51	118.1(5)	Ru2–P2–C71	114.9(5)
Ru1–P1–C41	110.5(5)	C81–P2–C91	108.0(7)
C51–P1–C61	108.1(7)	C71–P2–C91	102.8(7)
C41–P1–C61	103.8(6)	C71–P2–C81	103.6(7)
C41–P1–C51	100.6(6)	Ru1–O11–C10	124.0(9)
Ru2–N1–C1	109.5(8)	Ru2–O12–C10	131.9(9)
Ru2–N2–C2	108.4(9)	O11–C10–O12	125.0(13)
N1–C1–C2	110.4(13)	O21–C20–O22	128.1(13)
N2–C2–C1	106.6(13)	Ru1–O31–C30	91.3(10)
Ru1–O21–C20	131.0(9)	Ru1–O32–C30	94.4(9)
Ru2–O22–C20	121.7(10)	O31–C30–O32	114.1(14)

0.1 M TBAP. The i_{pc}/i_{pa} ratio of 1.0 for the $Ru_2(III,IV) \rightleftharpoons Ru_2(III,III)$ couple at scan rates 20–200 mV s^{-1} and a ΔE_p value of 60 mV for **1a** at 20 mV s^{-1} suggest a reversible nature of the electron-transfer process.

The X-ray structure of the cationic complex in **1a**·$3CHCl_3$ shows three novel bonding features: (i) the asymmetric coordination environments of the metal ions as observed in the ORTEP diagram (Fig. 1), (ii) significantly different Ru–O(oxo) distances; (iii) considerably long Ru–O distances of the bridging carboxylato ligands (Table 4).

The complex has a diruthenium(III) unit bridged by an oxo ligand and two *p*-methoxybenzoato ligands. The presence of a chelating RCO_2^- on Ru(1) and a chelating en on Ru(2) makes the complex asymmetric showing $[O_4PRu(1)(\mu\text{-}O)Ru(2)PO_2N_2]^+$ coordination environments for the metal centers. The asymmetric arrangement of ligands has made the Ru–O(oxo) bonds inequivalent. A difference of 0.04 Å between the Ru(1)–O(1) and Ru(2)–O(1) bond lengths is statistically significant. The Ru(1)–Ru(2) distance of 3.226(3) Å and the Ru(1)–O(1)–Ru(2) angle of 119.2(5)° compare well with those reported [8–10] for complexes having an $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$ core.

The *trans* effect of the μ-oxo ligand is apparent from the Ru(1)–O(31) and Ru(2)–N(2) distances which are longer than the *cis*-oxo bond lengths Ru(1)–O(32) and Ru(2)–N(1) (Table 4). The O(1)–Ru(1)–O(31) and O(1)–Ru(2)–N(2) angles deviate considerably from linearity. A deviation of similar magnitude is known [10] in analogous diruthenium(III) complexes containing terminal PPh_3 ligands *cis* to the oxobridge.

In the tribridged core of **1a**, the difference between the Ru(1)–O(11) and Ru(1)–O(21) distances is 0.16 Å. A similar effect but to a lesser extent has also been observed at the other metal center. The Ru–O(μ-O_2CR) values reported [8–10] in $Ru_2O(O_2CC_6H_4$-*p*-$OMe)_4(PPh_3)_2$, $[Ru_2O(O_2CPh)_2(MeCN)_4(PPh_3)_2]^{2+}$, $[Ru_2O(O_2CMe)_2(py)_6]^{2+}$ and $[Ru_2O(O_2CMe)_2(Me_3\text{-}TACN)_2]^{2+}$ are 0.11, 0.10, 0.0 and 0.02 Å, respectively. The strength of the Ru–O bond *trans* to the PPh_3 ligand is less than the *cis* one. This is a general feature observed [10] in all tri-bridged diruthenium(III) complexes containing PPh_3 terminal ligands *cis* to the μ-oxo ligand. The extent of bond lengthening is, however, maximum in the present complex.

In summary, new asymmetric tri-bridged diruthenium(III) complexes, isolated from a novel reaction, are structurally characterized. The metal centers have PO_5 and PO_2N_2 coordination environments. The susceptibility of the $\{Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2{}^{2+}\}$ core to undergo cleavage at the μ-carboxylato binding sites is evidenced from the crystal structure of **1** and related species. The incorporation of the facial carboxylato ligand takes place with the concomitant formation of $[Ru(MeCN)(en)_2(PPh_3)](ClO_4)_2$. Finally, the discovery of the first tri-bridged asymmetric diruthenium(III) complex augments the development of the emerging chemistry [11–14,20] of asymmetric homo- and heterodinuclear complexes with a (μ-oxo/hydroxo/alkoxo)-bis(μ-carboxylato)dimetal core.

4. Supplementary material

Observed and calculated structure factors, anisotropic thermal parameters and hydrogen atom coordinates are available from Professor A.R. Chakravarty on request.

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References

[1] (a) R.E. Stenkamp, L.C. Sieker and L.H. Jensen, *J. Am. Chem. Soc., 106* (1984) 618; (b) P.C. Wilkins and R.G. Wilkins, *Coord. Chem. Rev., 79* (1987) 195.

[2] (a) P. Nordlund, B.-M. Sjöberg and H. Eklund, *Nature (London), 345* (1990) 593; (b) J. Stubbe, *J. Biol. Chem., 265* (1990) 5329.

[3] (a) J.B. Vincent, G.A. Olivier-Lilley and B.A. Averill, *Chem. Rev., 90* (1990) 1447; (b) D.M. Kurtz, Jr., *Chem. Rev., 90* (1990) 585; (c) S.J. Lippard, *Angew. Chem., Int. Ed. Engl., 27* (1988) 344.

[4] (a) M.S. Mashuta, R.J. Webb, J.K. McCusker, E.A. Schmitt, K.J. Oberhausen, J.F. Richardson, R. M. Buchanan and D.N. Hendrickson, *J. Am. Chem. Soc., 114* (1992) 3815, and refs. therein; (b) S.H. Cho, D. Whang, K.N. Han and K. Kim, *Inorg. Chem., 31* (1992) 519; (c) R.H. Beer, W.B. Tolman, S.G. Bott and S.J. Lippard, *Inorg. Chem., 30* (1991) 2082; (d) S.M. Gorun and S.J. Lippard, *Inorg. Chem., 30* (1991) 1625.

[5] (a) U. Bossek, K. Wieghardt, B. Nuber and J. Weiss, *Inorg. Chim. Acta, 165* (1989) 123, and refs. therein; (b) J.B. Vincent, K. Folting, J.C. Huffman and G. Christou, *Biochem. Soc. Trans., 16* (1988) 822; (c) H. Diril, H. Chang, M.J. Nilges, X. Zhang, J.A. Potenza, H.J. Schugar, S.S. Isied and D.N. Hendrickson, *J. Am. Chem. Soc., 111* (1989) 5102.

[6] (a) P. Knopp and K. Wieghardt, *Inorg. Chem., 30* (1991) 4061, and refs. therein; (b) R.M. Buchanan, M.S. Mashuta, K.J. Oberhausen, J.F. Richardson, Q. Li and D.N. Hendrickson, *J. Am. Chem. Soc., 111* (1989) 4497.

[7] (a) K. Weighardt, U. Bossek, A. Neves, B. Nuber and J. Weiss, *Inorg. Chem., 28* (1989) 432; (b) J.E. Armstrong, W.R. Robinson and R.A. Walton, *Inorg. Chem., 22* (1983) 1301.

[8] Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara, T. Yamaguchi, C. Kabuto, T. Ochi and T. Ito, *Inorg. Chem., 30* (1991) 4903.

[9] P. Neubold, K. Weighardt, B. Nuber and J. Weiss, *Inorg. Chem., 28* (1989) 459.

[10] (a) B.K. Das and A.R. Chakravarty, *Inorg. Chem., 29* (1990) 2078; (b) A. Syamala, B.K. Das and A.R. Chakravarty, *Polyhedron, 11* (1991) 335; (c) A. Syamala and A.R. Chakravarty, *Inorg. Chem., 30* (1991) 4699; (d) M.C. Barral, R. Jiménez-Aparicio, E.C. Royer, F.A. Urbanos, A. Monge and C. Ruiz-Valero, *Polyhedron, 10* (1991) 113; (e) A. Syamala and A.R. Chakravarty, *Polyhedron, 12* (1993) 1545.

[11] A.G. Blackman, J.C. Huffman, E.B. Lobkovsky and G. Christou, *J. Chem. Soc., Chem. Commun.*, (1991) 989.

[12] W.B. Tolman, S. Liu, J.B. Bentsen and S.J. Lippard, *J. Am. Chem. Soc., 113* (1991) 152.

[13] R. Hotzelmann, K. Wieghardt, U. Flörke, H.-J. Haupt, D.C. Weatherburn, J. Bonvoisin, G. Blondin and J.-J. Girerd, *J. Am. Chem. Soc., 114* (1992) 1681.

[14] B. Mauerer, J. Crane, J. Schuler, K. Wieghardt and B. Nuber, *Angew. Chem., Int. Ed. Engl., 32* (1993) 289.

[15] (a) F. Vgozzoli, *Comput. Chem., 11* (1987) 109; (b) N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

[16] (a) G.M. Sheldrick, *SHELXS-86*, a computer program for automatic solution of crystal structures, Universität Göttingen, Germany, 1986; (b) G.M. Sheldrick, *SHELX-76*, a program for crystal structure determination, Cambridge University Press, Cambridge, UK, 1976.

[17] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974.

[18] A. Syamala and A.R. Chakravarty, unpublished results.

[19] C.K. Johnson, ORTEP, *Rep. ORNL-3794*, Oak Ridge National Laboratory, TN, 1971.

[20] R. Hotzelmann, K. Wieghardt, J. Ensling, H. Romstedt, P. Gutlich, E. Bill, U. Flörke and H.-J. Haupt, *J. Am. Chem. Soc., 114* (1992) 9470, and refs. therein.