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Unexpected structural and electronic effects of internal rotation in diruthenium paddlewheel complexes containing bulky carboxylate ligands

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ABSTRACT

A series of Ru,^{11,11} complexes containing the bulky carboxylate ligand 2,4,6-triisopropylbenzoate (TiPB) of type trans- $[Ru_2(TiPB)_2(O_2CCH_3)_2X]$ [X = Cl (1), PF₆ (2)] and $[Ru_2(TiPB)_4X]$ [X = Cl (3), PF₆ (4)] have been synthesised. The corresponding $\operatorname{Ru}_2^{\parallel,\parallel}$ complexes trans-[Ru₂(TiPB)₂(O₂CCH₃)₂] (**5**) and [Ru₂(TiPB)₄] (**6**) were also isolated. Magnetic susceptibility measurements indicate that the diruthenium cores have the expected three (1–4) or two (5 and 6) unpaired electrons consistent with $\sigma^2 \pi^4 \delta^2 (\delta^* \pi^*)^3$ and $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*2}$ electronic configurations. Compounds 1-4 and 6 were structurally characterised by X-ray crystallography, and show the expected paddlewheel arrangement of carboxylate ligands around the diruthenium core. The diruthenium cores of complexes 3, 4 and 6 are all distorted to minimise steric interactions between the bulky carboxylate ligands. The Ru-Ru bond length in the Ru- II,II complex 6 [2,2425(6)Å] is the shortest observed for a diruthenium tetracarboxylate and, surprisingly, is 0.014 Å shorter than in the analogous Ru₂^{II,III} complex **4**, despite an increase in the formal Ru-Ru bond order from 2.0 (**6**) to 2.5 (4). This is rationalised in terms of the extent of internal rotation, or distortion, about the diruthenium core. This was supported by density functional theory calculations on the model complexes [Ru₂(O₂CH)₄] and $[Ru_2(O_2CH)_4]^+$, that demonstrate the relationship between Ru–Ru bond length and internal rotation. Electrochemical and electronic absorption data were recorded for all complexes in solution. Comparison of the data for the 'bis-bis' (1, 2 and 5) and tetra-substituted (3, 4 and 6) complexes indicates that the shortening of the Ru–Ru bond length results in a small increase in energy of the near-degenerate δ^* and π^* orbitals.

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1. Introduction

Metal-metal multiply bonded tetracarboxylates of form $[M_2(O_2CR)_4(L)_x]^{n+}$ (L = solvent or anion, x = 0, 1, 2) typically adopt a "paddlewheel" geometry, in which each carboxylate ligand bridges the two metal atoms in equatorial positions, and solvent molecules or anions (L) occupy the axial positions [1]. Diruthenium complexes have a unique electronic structure and interesting physical properties that are responsible for the current popularity and continued expansion of this field. Potential applications for these complexes have been found in a wide variety of areas such as catalysts [2–4] and antitumour metallopharmaceuticals [5–7], as well their incorporation into supramolecular arrays [8-12] that can have interesting magnetic [13–15] and optoelectronic properties [16–18]. Recent studies have also highlighted the potential use of diruthenium compounds as molecular wires [19,20], and there is often a strong relationship between the structure of these complexes and their reactivity or electronic structure [21].

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Diruthenium tetracarboxylates of form $[Ru_2(O_2CR)_4(L)_2]^{n+}$ (L = solvent or anion) have been isolated in two forms; the mixed valence $\text{Ru}_2^{\text{II,III}}$ form and homovalent $\text{Ru}_2^{\text{II,II}}$ form. The mixed valence $\text{Ru}_2^{\text{II,III}}$ form was first synthesised in 1966, and found to have three unpaired electrons [22]. The electronic structure was elucidated with the aid of SCF-X\alpha-SW calculations [23] and resonance Raman spectra [24] that indicated a $\sigma^2 \pi^4 \delta^2 (\delta^* \pi^*)^3$ electron configuration, and a formal Ru-Ru bond order of 2.5. The Ru₂^{II,II} tetracarboxylates are more air-sensitive than their Ru₂^{II,III} counterparts, and were first isolated in 1984 by Wilkinson and co-workers [25]. These compounds have two unpaired electrons and a $\sigma^2 \pi^4 \delta^2 \delta^{*2} \pi^{*2}$ electron configuration, with a formal Ru–Ru bond order of 2.0 [26]. The Ru–Ru bond lengths in these compounds show only a small dependence on the nature of the carboxylate or axial ligands. However, in agreement with the general trend for multiply bonded compounds in which bond length is inversely proportional to bond order, the Ru-Ru bond lengths for Ru2^{11,111} tetracarboxylates are slightly shorter than observed for their analogous Ru₂^{II,II} counterparts, consistent with a reduction in the formal Ru-Ru bond order [27].

We have recent been interested in synthesising diruthenium complexes containing the bulky carboxylate ligand





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2.4.6-triisopropyl benzoic acid (HTiPB, Scheme 1). This ligand has been successfully employed by Cotton. Murillo and co-workers to synthesise quadruply bonded Cr_2^{4+} and Mo_2^{4+} species, as well as Rh_2^{4+} compounds [21,28,29], in which the steric bulk of the ligand prevent intermolecular association in the solid-state, and permitted structural characterisation without axial coordination of exogenous ligands. Diruthenium complexes with large ligands such as adamantly carboxylate [30] and metallocene carboxylates [31,32] have been previously reported. In this paper, we report the synthesis and characterisation of a series of Ru₂^{II,III} and Ru₂^{II,III} complexes containing TiPB. The use of the bulky TiPB ligand imparts unusual structural distortions that result in the shortening of the metalmetal bond. This effect was rationalised with the aid of theoretical calculations and the impact on the electronic structure and spectroscopic properties are also discussed. Some aspects of this work have been previously reported as a communication [33].

2. Experimental

2.1. Physical measurements

Matrix assisted laser desorption/ionisation time-of-flight (MAL-DI-TOF) mass spectrometry was performed on a Bruker Reflex III (Bruker, Breman, Germany) mass spectrometer operated in linear, positive ion mode with a N₂ laser. Laser power was used at the threshold level required to generate signal. DCTB [trans-2-(3-(4-tbutyl-phenyl)-2-methyl-2-propenylidene)malononitrile] was used as the matrix and prepared as a saturated solution in THF. Allotments of matrix and sample were thoroughly mixed together; 0.5 mL of this was spotted on the target plate and allowed to dry. IR spectra were recorded as solid samples with a Perkin-Elmer Spectrum RX I FT-IR spectrometer equipped with a DuraSamplIR II diamond ATR probe and universal press. Magnetic moments were determined at room temperature using a Sherwood Scientific Magway MSB Mk1 magnetic susceptibility balance. Molar diamagnetic corrections were applied to the magnetic susceptibility data on the basis of Pascal's constants [34]. Electronic absorption spectra were recorded in THF solutions at room temperature using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry at Sheffield with a Perkin-Elmer 2400 analyzer. Electrochemical studies were carried out in N2-purged methanol solutions with 0.1 M $[^{n}Bu_{4}N](PF_{6})$ as supporting electrolyte. A standard three-electrode system was used with a Pt microdisc and a large surface area Pt wire as the working and counter electrodes, respectively. Potentials were measured in reference to a Ag/AgCl reference, with all potentials quoted for a scan rate of 0.10 V s^{-1} . At the end of every experiment, ferrocene was added as an internal standard, with the Fc/Fc⁺ couple consistently observed at +0.43 V versus Ag/AgCl.

2.2. Materials

All experimental manipulations were performed under an inert atmosphere using standard Schlenk line techniques. Tetrahydrofuran was purified by distillation over sodium wire, and all other solvents obtained from a "Grubbs" solvent purification system. The sodium salt of 2,4,6-triisopropylbenzoic acid (HTiPB) was synthesised by reacting a freshly prepared NaOMe solution in MeOH with the acid. The compounds $[Ru_2(OAc)_4Cl]$ [35] and $[Ru_2(OAc)_4]$ [36] were synthesised according to literature procedures, and all other chemicals were acquired from commercial sources.

2.3. Synthesis of [Ru₂(OAc)₂(TiPB)₂Cl] (1)

A solution of Ru₂(OAc)₄Cl (0.275 g, 0.58 mmol) and TiPBH (0.360 g, 1.45 mmol) in MeOH (20 mL) was refluxed under an argon atmosphere for 16 h. The solution was allowed to cool and the solvent removed in vacuo. The solid was redissolved in THF (10 mL) and precipitated with hexane (20 mL). The light brown product was isolated by filtration and dried in vacuo. Yield = 0.34 g (71%). Crystals of [Ru₂(OAc)₂(TiPB)₂Cl]·2MeCN suitable for X-ray diffraction were grown from slow evaporation of an acetonitrile solution containing 1. MALDI-TOF-MS: calcd. monoisotopic MW for Ru₂C₃₆O₈H₅₂Cl 849.59, found *m/z* 816.27 (M⁺-Cl, 100%). IR(cm⁻¹): 2960m, 2930w, 2868w, 1604m, 1570w, 1472w, 1463w, 1440m, 1405s, 1382w, 1359m, 1348w, 1316w, 1154m, 1112m, 1088w, 1015w, 874m, 858w, 813m, 796w, 770w, 689s, 663m, 641s. Anal. Calc. for Ru₂C₃₆O₈H₅₂Cl: C, 50.9; H, 6.16. Found: C, 49.9; H, 6.47%. UV–Vis (THF) $[\lambda_{max}, nm (\epsilon, M^{-1} cm^{-1})]$: 466 (1400), 622 (110), 1130 (30).

2.4. Synthesis of [Ru₂(OAc)₂(TiPB)₂(PF₆)] (2)

A solution of $[Ru_2(OAC)_2(TiPB)_2Cl]$ (0.100 g, 0.12 mmol) and AgPF₆ (0.100 g, 0.40 mmol) in MeOH (20 mL) was stirred at room temperature for 18 h. The solvent was removed *in vacuo*, and the product was redissolved in THF (10 mL) and filtered through celite. Hexane was added to the filtrate to precipitate the product as an orange solid, which was isolated by filtration and dried *in vacuo*. Yield = 0.084 g (73%). Orange crystals of $[Ru_2(TiPB)_2(OAC)_2(-THF)_2](PF_6)$ -THF were grown by carefully layering a THF solution of **2** with hexane. MALDI-TOF-MS: calcd. monoisotopic MW for Ru₂C₃₆O₈H₅₂PF₆ 961.14, found *m/z* 816.27 (M⁺-PF₆, 100%). IR(cm⁻¹): 2961m, 2930w, 1867w, 1570w, 1441w, 1412w, 1403w, 1400w, 1366w, 1270s, 1236m, 1191m, 1149m, 1126m, 1088m, 1031s, 982w, 890w, 845s, 813m, 782m, 688m, 642m. UV-Vis (THF) [λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 458 (499).

2.5. Synthesis of $[Ru_2(TiPB)_4Cl]$ (3)

A Schlenk tube charged with a stir bar and a mixture of Ru₂(OAc)₄Cl (0.330 g, 0.70 mmol) and excess 2,4,6-triisopropylbenzoic acid (HTiPB) (1.5 g, 6.04 mmol) was heated at 220 °C for 6 h. Every 2 h, the mixture was cooled to room temperature, and the acetic acid that condensed on the upper portion of the Schlenk tube removed in vacuo. After 6 h of heating the mixture was cooled, and excess 2,4,6-triisopropylbenzoic acid (HTiPB) removed by sublimation at 130 °C, 10^{-3} Torr, to afford **3** as a pink powder. Yield = 0.839 g (98%). Excess HTiPB ligand was recovered from the sublimation finger and used in subsequent reactions. Crystals of [Ru₂(TiPB)₄Cl(MeOH)]·MeOH suitable for X-ray diffraction were grown by slow evaporation of a MeOH solution containing 3. MAL-DI-TOF-MS: calcd. monoisotopic MW for Ru₂O₈C₆₄H₉₂Cl 1227.46, found *m*/*z* 1192.22 (M–Cl⁺, 100%). IR (cm⁻¹): 2955m, 2922w, 2868w, 1605m, 1440m, 1410m, 1384s, 1361w, 1320w, 1258w, 1158w, 1109m, 940w, 876w, 811w, 778w, 734w, 642m. Anal. Calc. for Ru₂O₈C₆₄H₉₂Cl: C, 62.65; H, 7.56. Found: C, 62.45; H, 7.35%. UV-Vis (THF) $[\lambda_{max}, nm (\varepsilon, M^{-1} cm^{-1})]$: 470 (1460), 616 sh (262), 1148 (60).

2.6. Synthesis of $[Ru_2(TiPB)_4(PF_6)]$ (4)

A suspension of Ru₂(TiPB)₄Cl (0.200 g, 0.16 mmol) and AgPF₆ (0.100 g, 0.40 mmol) in MeOH (20 mL) was stirred for 18 h. The solvent was removed *in vacuo* from the resulting orange solution with grey precipitate. The mixture was redissolved in THF (10 mL) and filtered through celite. Red-orange crystals of [Ru₂(-TiPB)₄(THF)₂](PF₆) were grown by layering this solution with hexane. The axially coordinated THF molecules were removed by heating the crystals at 70 °C for 5 h *in vacuo* to give Ru₂(TiPB)₄(PF₆) as an orange powder. Yield = 0.203 g (93%). MALDI-TOF-MS: calcd. monoisotopic MW for Ru₂O₈C₆₄H₉₂PF₆ 1336.51, found *m/z* 1192.39 (M–PF₆⁺, 100%). IR (cm⁻¹): 2962m, 2928w, 2872w, 1605m, 1458m, 1389s, 1362w, 1320w, 1157w, 1109w, 1028w, 835vs, 738w, 645m. *Anal.* Calc. for Ru₂O₈C₆₄H₉₂PF₆: C, 57.51; H, 6.94. Found: C, 56.88; H, 7.25%. UV–Vis (THF) [λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 439 (367), 1080 (10).

2.7. Synthesis of [Ru₂(OAc)₂(TiPB)₂] (5)

A solution of $\text{Ru}_2(\text{OAc})_4$ (0.250 g, 0.57 mmol) and TiPBH (0.360 g, 1.45 mmol) in MeOH (20 mL) was refluxed under an argon atmosphere for 14 h. The solvent was removed under vacuum, and the solid redissolved in THF (10 mL) and filtered. Solvent was removed from the filtrate, and the light brown solid was washed with hexanes before drying *in vacuo*. Yield = 0.32 g (69%). Numerous attempts to grow crystals of **5** from a variety of solvents were unsuccessful. MALDI-TOF-MS: calcd. monoisotopic MW for Ru₂-C₃₆O₈H₅₂ 816.17, found *m*/*z* 816.19 (M, 100%). IR(cm⁻¹): 2961m, 2930w, 2866w, 1605w, 1528m, 1481w, 1437m, 1408s, 1363m, 1343vw, 1320w, 1260m, 1155w, 1089w, 1021m, 942w, 872w, 814w, 690s, 663w, 643s. UV–Vis (THF) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)]: 448 (1176).

2.8. Synthesis of $[Ru_2(TiPB)_4]$ (6)

Hydrogen gas was bubbled through a MeOH solution (50 mL) containing RuCl₃·3H₂O (0.300 g, 1.15 mmol) and a catalytic amount of platinum black (10 mg) for 4 h. The resulting ruthenium "blue" solution was filtered through celite into a Schlenk flask charged with NaTiPB (0.650 g, 2.41 mmol). A reflux condensor was attached to the Schlenk flask, and the solution refluxed for 16 h to give a brown-yellow solution. The solution was cooled to room temperature and filtered through celite. The filtrate was dried in vacuo, and the product redissolved in hexane and filtered again before removing the solvent in vacuo to afford 6 as a brown-red powder. Yield = 0.683 g (50%). Crystals of [Ru₂(-TiPB)₄(THF)₂] suitable for X-ray diffraction were grown by slow evaporation of a THF solution. MALDI-TOF-MS: calcd. monoisotopic MW for Ru₂O₈C₆₄H₉₂PF₆ 1192.49, found *m/z* 1192.43 (M⁺, 100%). IR (cm⁻¹): 2958m, 2927w, 2871w, 1604m, 1517m, 1460m, 1403s, 1361w, 1317w, 1257w, 1156w, 1108m, 1005w, 938w, 875m, 801w, 775w, 640w. Anal. Calc. for Ru₂O₈C₆₄H₉₂: C, 64.51; H, 7.78. Found: C, 64.16; H, 8.06%.

2.9. DFT calculations

Molecular structure calculations on the model complexes $[Ru_2(O_2CH)_4]^+$ and $[Ru_2(O_2CH)_4]$ were performed using density functional theory as implemented in the GAUSSIANO3 suite of programs [37]. The B3LYP functional [38–40] and the 6-31G^{*}(5d) basis set [41] were used for H, C, and O, along with the SDD energy consistent pseudopotentials for ruthenium [42]. This functional and basis set combination was chosen as it has been found to be the most effective in benchmark studies on related $[M_2(O_2CR)_4]$ complexes [43]. Unrestricted open-shell calculations were performed

in every case. The internal rotation angle (χ) was constrained from 0° to 20° in 2° increments with the rest of the geometry allowed to fully optimise in D_4 symmetry.

2.10. X-ray crystallography

Data were collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. After integration of the raw data and merging of equivalent reflections, an empirical absorption correction was applied (sADABS) based on comparison of multiple symmetry-equivalent measurements [44]. The structures were solved by direct methods (sHELXS-97) and refined by full-matrix least squares on weighted F^2 values for all reflections using the SHELX suite of programs [45]. All hydrogens were included in the models at calculated positions using a riding model with $U(H) = 1.5 \times U_{eq}$ (bonded carbon atom) for methyl and hydrogens and $U(H) = 1.2 \times U_{eq}$ (bonded carbon atom) for methine, methylene and aromatic hydrogens.

The isopropyl groups and solvent molecules present in the structures caused disorder problems in all of the structures. Two of the TiPB isopropyl groups in **1** were disordered over two sites with occupancies of 0.80/0.20 and 0.75/0.25. This disorder is responsible for the short intermolecular contact between the calculated hydrogens H17C and H19D. A THF solvent molecule in **2**(THF)₂ was disordered over two positions about a centre of inversion with equal occupancy. One of the TiPB groups in **3**(MeOH) was disordered over two positions (0.47/0.53 site occupancy), along with the methyl group of the axially coordinated MeOH molecule (0.58/0.32 site occupancy), and atoms associated with the both disordered components refined isotropically. The full experimental details and CIF files for complexes **4**(THF)₂ and **6**(THF)₂ have been communicated previously [33].

Experimental data relating to the structure determinations of all complexes are displayed in Table 5.

3. Results and discussion

3.1. Synthesis and characterisation

We first attempted to synthesise the diruthenium(II,III) complex [Ru₂(TiPB)₄Cl] (TiPB = 2,4,6-triisopropylbenzoate) by traditional metathesis reactions. The reaction of [Ru₂(O₂CCH₃)₄Cl] with 4 equiv. of HTiPB in refluxing methanol solutions did not produce the desired tetra-substituted complex. Instead, the 'bis-bis' complex trans- $[Ru_2(TiPB)_2(O_2CCH_3)_2Cl]$ (1) was formed. The trans arrangement of the bulky ligands was determined by X-ray crystallography, vide infra, and is observed in related 'bis-bis' TiPB complexes of dimolybdenum [46] and dirhodium [47] carboxylates as it minimises steric interactions between the ligands. Synthesis of diruthenium 'bis-bis' complexes have been previously reported; refluxing 2 equiv. of HO_2CCMe_3 with $[Ru_2(O_2CCH_3)_4Cl]$ in a MeOH/H₂O mixture generates [Ru₂(O₂CCH₃)₂(O₂CCMe₃)₂Cl] [48]. Despite the presence of excess HTiPB in the synthesis of 1, it does not undergo further substitution to tri- and tetra-substituted species under these conditions. The mechanism for substitution in $[M_2(O_2CR)_4]$ complexes involves initial coordination of the incoming carboxylate ligand to the axial position [49], and it is likely that blocking this position with two bulky carboxylate ligands provides a kinetic barrier to further substitution.

A different synthetic route was used for the synthesis of the mixed-valence compound [$Ru_2(TiPB)_4CI$]. Excess of the carboxylic acid (HTiPB) and [$Ru_2(OAC)_4CI$] were heated at 210 °C in a melt reaction. Every 2 h, the reaction was allowed to cool and acetic acid removed *in vacuo*, to drive the reaction to completion. Excess ligand was recovered by sublimation, and [$Ru_2(TiPB)_4CI$] (**3**) isolated

in essentially quantitative yield. In order to more accurately compare structural parameters between related species, complexes of form $[Ru_2(O_2CR)_4(THF)_2]^{0/+}$ were targeted, that would have isostructural diruthenium cores. The complexes $[Ru_2(TiP-B)_2(OAc)_2(PF_6)]$ (2) and $[Ru_2(TiPB)_4(PF_6)]$ (4), which could be crystallised as THF diadducts from THF solutions, were prepared by reaction of the corresponding chloride complexes 1 and 3 with AgPF₆.

Incomplete substitution was also observed from the reaction of the diruthenium(II,II) complex [Ru₂(O₂CCH₃)₄] and HTiPB in refluxing methanol solutions, and the complex *trans*-[Ru₂(TiP-B)₂(O₂CCH₃)₂] (**5**) was isolated. The homoleptic complex [Ru₂(TiPB)₄] (**6**) was synthesised in good yield using a slight modification of the original preparation described by Wilkinson and coworkers; a "ruthenium blue" solution, generated from reduction of [RuCl₃·3H₂O] with H₂ in methanol, was refluxed with NaTiPB. The synthesis of compounds **1–6** is summarised in Scheme 2.

All complexes are significantly more soluble than the parent $[Ru_2(OAc)_4]^{0/+}$ complexes, and can be dissolved in non-donor solvents such as dichloromethane. Complex **6** is also soluble in hexane solutions. Signals corresponding to the $[Ru_2(O_2CR)_4]^+$ parent ion were observed in the MALDI-TOF mass spectra of complexes **1–6**. The same molecular ions are observed for analogous $Ru_2^{11,11}$ and $Ru_2^{11,111}$ complexes as the chloride ion was removed upon ionisation, as observed in previous studies [50]. The magnetic susceptibilities of 3.3 and 2.9 BM for the $Ru_2^{11,11}$ complexes **5** and **6**

indicate the presence of two unpaired electrons and a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ electron configuration. The higher magnetic susceptibility values for Ru_{2^{II,III}} complexes **1–4**, ranging from 4.0 to 4.5 BM, are consistent with three unpaired electrons and a $\sigma^2 \pi^4 \delta^2 (\delta^* \pi^*)^3$ electron configuration. Further confirmation of the oxidation state of the complexes comes from examination of the separation between the symmetric and asymmetric carboxylate stretching frequencies (Δv_{CO_2}) in their IR spectra. In agreement with previous studies [27], the Ru₂^{II,III} complexes show a much smaller separation between the symmetric and asymmetric CO₂ stretching frequencies (38- 69 cm^{-1}) than the Ru₂^{II,II} complexes (91–120 cm⁻¹). The magnetic susceptibilities, and asymmetric and symmetric carboxylate stretching frequencies in the IR spectra of complexes 1-6 are shown in Table 1. The stretching frequencies for the TiPB and OAc carboxylate groups in the 'bis,bis' complexes are sufficiently different to allow them both to be resolved, and both sets are reported in Table 1.

3.2. Solid-state structures

Crystals suitable for X-ray crystallography were obtained from THF solutions in the case of **2**, **4** and **6**, an acetonitrile solution in the case of **1**, and a methanol solution in the case of **3**.

The structures of the '*bis–bis*' complexes **1** (Fig. 1) and **2** (Fig. 2) show the expected 'paddlewheel' arrangement of ligands about the diruthenium core, with bulky carboxylate ligands orientated *trans*

$$\begin{aligned} & \operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{4}\operatorname{Cl} + 2\operatorname{HTiPB} \xrightarrow{\operatorname{MeOH/H_{2}O}}_{\Delta, \ 16h} \operatorname{trans-\operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{2}(\operatorname{TiPB})_{2}\operatorname{Cl}}_{1} \\ & \operatorname{trans-\operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{2}(\operatorname{TiPB})_{2}\operatorname{Cl} + \operatorname{AgPF_{6}} \xrightarrow{\operatorname{MeOH}}_{16h} \operatorname{trans-\operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{2}(\operatorname{TiPB})_{2}(\operatorname{PF_{6}})}_{2} \\ & \operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{4}\operatorname{Cl} + 4\operatorname{HTiPB} \xrightarrow{\operatorname{HTiPB}}_{210^{\circ}\operatorname{C}, \ 6h} \operatorname{Ru}_{2}(\operatorname{TiPB})_{4}\operatorname{Cl} \\ & \operatorname{Ru}_{2}(\operatorname{TiPB})_{4}\operatorname{Cl} + \operatorname{AgPF_{6}} \xrightarrow{\operatorname{MeOH}}_{16h} \operatorname{Ru}_{2}(\operatorname{TiPB})_{4}(\operatorname{PF_{6}}) \\ & \operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{4} + 2\operatorname{HTiPB} \xrightarrow{\operatorname{MeOH/H_{2}O}}_{\Delta, \ 16h} \operatorname{trans-\operatorname{Ru}_{2}(\operatorname{O}_{2}\operatorname{CCH}_{3})_{2}(\operatorname{TiPB})_{2}}_{5} \\ & \operatorname{RuCl}_{3}\cdot\operatorname{3H_{2}O} \xrightarrow{1. \ Pt \ black \ (cat.), \ H_{2}, \ MeOH}_{2. \ \operatorname{NaTiPB}, \ \Delta \ MeOH, \ 16h} \operatorname{Ru}_{2}(\operatorname{TiPB})_{4} \\ & \operatorname{Ru}_{2}(\operatorname{TiPB})_{4} \end{aligned}$$

Scheme 2

I UDIC I

Infrared carboxylate stretching frequencies and magnetic susceptibility data for complexes 1-6. All data were obtained from solid samples at 298 K.

Compound	"TiPB"			"OAc"			μ_{eff} (BM)
	$v_{\rm sym}({\rm CO_2})({\rm cm^{-1}})$	$v_{asym}(CO_2) (cm^{-1})$	$\Delta v(\text{CO}_2) (\text{cm}^{-1})$	$v_{\rm sym}({\rm CO_2})~({\rm cm^{-1}})$	$v_{asym}(CO_2) (cm^{-1})$	$\Delta v(\text{CO}_2) \text{ cm}^{-1}$	
$Ru_2(II,III)$				1204	1452	50	4.1
[RU ₂ (OAC) ₄ CI] ⁻	1000		-	1394	1453	59	4.1
$Ru_2(OAc)_2(TiPB)_2CI(1)$	1382	1440	58	1405	1463	58	4.5
$Ru_2(OAc)_2(TiPB)_2(PF_6)$ (2)	1403	1441	38	1412	1450	38	4.5
$Ru_2(TiPB)_4Cl(3)$	1384	1440	56				4.2
$Ru_2(TiPB)_4(PF_6)$ (4)	1389	1458	69				4.0
$Ru_2(II,II)$							
$Ru_2(OAc)_4^b$				1440	1560	120	2.8
$[Ru_2(OAc)_2(TiPB)_2]$ (5)	1408	1528 ^c	120	1437	1528 ^c	91	3.3
[Ru ₂ (TiPB) ₄] (6)	1403	1517	114				2.9

^a Data obtained from Refs. [51,22].

^b Data obtained from Ref. [25].

^c Coincident peaks.



Fig. 1. Extended packing structure of **1**, highlighting the 'zig-zag' one-dimensional chain that is propagated along the crystallographic *c*-axis. Solvent molecules, hydrogen atoms and some minor disorder components have been omitted for clarity.



Fig. 2. Molecular structure of the diruthenium core of $trans-[Ru_2(OAc)_2(-TiPB)_2(THF)_2](PF_6)$, [**2**(THF₂)] with anisotropic displacement parameters drawn at the 50% level. Hydrogen atoms have been omitted for clarity, and symmetry-equivalent atoms generated using the symmetry operation -x, -y, -z.

to one another. This trans arrangement of the ligands is a reflection of the steric factors involved, analogous to the behaviour observed in both the solid-state and solution for other $[M_2(TiPB)_2(O_2CR)_2]$ (M = Mo [46], W [46], Rh [47]) complexes. Complex 1 contains two crystallographically independent {Ru₂(O₂CR)₄} units that are linked by chloride ions [Ru1–Cl1–Ru2 = 125.96(3)°] propagating a zig-zag polymeric chain structure in the solid-state, as observed in other $Ru_2^{II,III}$ tetracarboxylate chlorides [27]. Complex 2 crystallises as the axially coordinated THF adduct, [Ru2(TiP- $B_{2}(OAc)_{2}(THF)_{2}](PF_{6})$ [2(THF)₂], with a typical Ru–O_{THF} bond distance of 2.269(2) Å. Other bond lengths and angles associated with the diruthenium core in these complexes are presented in Table 2. The Ru-Ru bond lengths of 2.2827(6) Å and 2.2858(5) Å in 1 and 2.2688(6) Å in 2 are within the narrow range of 2.248-2.310 Å found for Ru₂^{II,III} tetracarboxylates [1]. The slightly shorter Ru–Ru bond length of the diadduct 2 by comparison to the polymeric 1 is also consistent with previous studies [27]. The $\{Ru_2(O_2C)_4\}$ core

in both of these species shows little distortion and essentially has the expected *pseudo-D*_{4h} symmetry.

The crystal structure of **3**(MeOH), is shown in Fig. 3. The bond lengths associated with this complex (Table 2) are unremarkable, although it can be seen that the diruthenium core of this molecule is distorted to minimise steric interactions. This distortion, or internal rotation (χ), can be measured by examining the O_{CO2}-Ru-Ru-O_{CO2} torsion angle. The internal rotation for **3**(MeOH) is similar to that observed in the other diruthenium(II,III) homoleptic complex **4**(THF)₂, $\chi_{ave} \sim 8.0^{\circ}$.

The identical coordination environment about the diruthenium cores in complexes **4**(THF)₂ and **6**(THF)₂ allows direct comparison of their structural parameters, summarised in Table 2. The average Ru–O_{CO₂} bond lengths in **4**(THF)₂ (2.018 Å) and **6**(THF)₂ (2.058 Å) are in the range expected for Ru₂^{II,III} and Ru₂^{II,II} tetracarboxylates, with the small increase in the bond lengths a reflection of the reduction in electrostatic attraction from the respective Ru₂⁵⁺ and Ru₂⁴⁺ cores [27].

The Ru-Ru bond lengths for diruthenium tetracarboxylates show a small decrease upon going from related Ru₂^{II,II} to Ru₂^{II,II} complexes. For example, the Ru-Ru bond length of 2.262(3) Å in $[Ru_2(O_2CCH_3)_4(OH_2)_2]$ decreases to 2.248(1) Å in $[Ru_2(O_2C-$ CH₃)₄(OH₂)₂][BF₄] [36,52]. This reduction reflects the increase in the formal bond order from 2.0 ($\text{Ru}_2^{II,II}$) to 2.5 ($\text{Ru}_2^{II,III}$). It is a relatively small change because the bond being formed is the most weakly-bonding δ -bond, and there is an increase in oxidation state which leads to d-orbital contraction that weakens the strength of the σ - and π -bonds. The Ru–Ru bond length of 2.2567(3) Å for $4(THF)_2$ is at the shorter end of the range expected for $Ru_2^{11,111}$ tetracarboxylates but, remarkably, the bond length for the Ru₂^{II,II} complex $6(THF)_2$ is even shorter, 2.2425(6) Å. This is the shortest reported Ru-Ru bond length for a diruthenium tetracarboxylate; the previous shortest being 2.248(1) Å found in [Ru₂(O₂C-CH₃)₄(OH₂)₂][BF₄] [53]. The observed decrease in metal-metal bond length concomitant with a decrease in formal bond order is a rare phenomenon in metal-metal multiply bonded compounds. It has been observed for $[Tc_2Cl_8]^{2-/3-}$ ions, for which a ~ 0.05 Å increase in bond length was observed despite a 0.5 increase in the formal Tc–Tc bond order, ascribed to changes in the σ , π and δ bond-strengths upon changing the oxidation states [54]. However, the oxidation state of the metals does not fully explain why 6(THF)₂ should have the shortest Ru–Ru bond length found to date given that this trend is not observed in other isostructural $[Ru_2(O_2CR)_4]^{0/+}$ pairs. Inspection of the structures of **4**(THF)₂ and 6(THF)₂ reveals unusually large internal rotation about the diruthenium core to minimise steric interactions between the bulky ligands, as highlighted in Fig. 4. This distortion can be measured by examining the O_{CO_2} -Ru-Ru- O_{CO_2} torsion angle (χ), which is greater for **6**(THF)₂ ($\chi_{ave} = 13.8^{\circ}$) than **4**(THF)₂ ($\chi_{ave} = 8.0^{\circ}$). Only the δ bond overlap and strength is dependent on internal rotation, and χ is greater for **6**(THF)₂ as Ru₂^{II,II} complexes have no net δ -bond to restrict the rotation. We previously proposed [33] that this internal rotation is responsible for the unusually short Ru-Ru

Table 2

Selected bond lengths (Å), angles (°) and torsion angles (°) for complexes 1, 2, 3, 4 and 6. Average values are given for Ru-O_{CO2} bond lengths and O_{CO2}-Ru-Ru-O_{CO2} torsion angles.

Complex	[Ru ₂ (TiPB) ₂ (OAc) ₂ Cl]	$[Ru_2(TiPB)_2(OAc)_2(THF)_2](PF_6)$	[Ru ₂ (TiPB) ₄ Cl(MeOH)]	$[Ru_2(TiPB)_4(THF)_2](PF_6)$	[Ru ₂ (TiPB) ₄ (THF) ₂]
Abbreviation	1	2 (THF) ₂	3 (MeOH)	4 (THF) ₂	6 (THF) ₂
Ru–Ru	2.284 ^a	2.2688(6)	2.2797(5)	2.2567(3)	2.2425(6)
Ru–O _{CO2}	2.020 ^a	2.021 ^a	2.026 ^a	2.018 ^a	2.058 ^a
Ru–L _{Ax}		2.269(2)	2.261(3)	2.259 ^a	2.308(3)
Ru–Cl	2.539 ^a		2.4880(12)		
Ru-Ru-L _{Ax}		174.91(7)	176.22(10)	178.3 ^a	177.19(9)
Ru–Ru–Cl	174.9 ^a		178.18(3)		
O_{CO_2} -Ru-Ru- O_{CO_2} (χ_{ave})	1.3ª	0.3 ^a	7.7 ^a	8.0 ^a	13.8 ^a

^a Average values.



Fig. 3. Crystal structure of 3(MeOH) with anisotropic displacement parameters drawn at the 50% level. Hydrogen atoms and disordered components have been omitted for clarity.



Fig. 4. Comparison of the distorted { $Ru_2(O_2CR)_4$ } cores in the crystal structures of **4**(THF)₂, (a), and **6**(THF)₂, (b). The structures are viewed down the Ru–Ru bond, with axial THF ligands and the phenyl and ⁱPr groups of the TiPB ligands removed for clarity.

distance in $\mathbf{6}$ (THF)₂ because it reduces the effective bridging distance of the carboxylate, as demonstrated in Scheme 3.

3.3. Computational studies

In order to support the proposed relationship between Ru–Ru bond length and internal rotation, calculations on the model compounds $[Ru_2(O_2CH)_4]^*$ and $[Ru_2(O_2CH)_4]$ were performed using density functional theory (DFT) as implemented in the GAUSSIAN 03 program. Geometry optimisation was performed on the model complexes in D_4 symmetry, whilst varying the internal rotation angle from 0° to 20° in 2° increments.

The variation in the calculated Ru–Ru bond length by comparison to the internal rotation is shown in Fig. 5. With no internal rotation ($\chi = 0$), the calculated Ru–Ru bond lengths of 2.271 Å and 2.266 Å, for the [Ru₂(O₂CH)₄] and [Ru₂(O₂CH)₄]⁺ complexes, respectively, are comparable to those obtained from recent detailed computational studies on [Ru₂(O₂CR)₄]^{0/+} complexes employing the similar functionals and basis sets [55,56]. As expected, the Ru–Ru bond length is slightly longer for the Ru₂^{II,II}



Fig. 5. Calculated Ru–Ru bond lengths with increasing internal rotation for $[Ru_2(O_2CH)_4]^*$ (blue) and $[Ru_2(O_2CH)_4]$ (red). (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

complex by comparison to its Ru₂^{II,III} analogue, reflecting the increase in formal Ru–Ru bond order from 2.0 to 2.5. As the internal rotation increases, the metal–metal bond length decreases for both [Ru₂(O₂CH)₄] and [Ru₂(O₂CH)₄]⁺. The calculations for these model complexes suggest that when $\chi > 10^{\circ}$ for a Ru₂^{II,III} tetracarboxylate it will have a shorter bond length than an analogous Ru₂^{II,III} tetracarboxylate with D_{4h} symmetry ($\chi = 0^{\circ}$), highlighting that relatively small distortions can have a significant influence. The calculations also support that the proposed relationship between internal rotation and metal–metal bond length. The unusual experimental results, in which **6**(THF)₂ ($\chi_{ave} = 13.8^{\circ}$) has a shorter Ru–Ru bond length than **4**(THF)₂ ($\chi_{ave} = 8.0^{\circ}$) is reflected in the calculations; the calculated Ru–Ru bond length for [Ru₂(O₂CH)₄] at $\chi = 13.8^{\circ}$ (~2.260 Å) is shorter than for [Ru₂(O₂CH)₄]⁺ at $\chi = 8.0^{\circ}$ (~2.264 Å).

Fig. 5 also show that internal rotation does not affect the Ru–Ru bond length in $[Ru_2(O_2CH)_4]^+$ to as greater extent as $[Ru_2(O_2CH)_4]$, which is likely to be due to increased electrostatic repulsion between the Ru atoms in the higher oxidation state. The δ -bond overlap will also be reduced by twisting the molecule, which will in turn reduce Ru–Ru bond strength for $[Ru_2(O_2CH)_4]^+$. However, δ bond overlap is related to internal rotation by the value of $\cos^2 \chi$ [57], so at $\chi = 8^\circ$ there is only a 4% reduction in overlap meaning this is likely to only have a small effect, especially given that this molecule only has a net δ -bond order of 0.5.

3.4. Electrochemical studies

 $\operatorname{Ru_2}^{II,III}$ tetracarboxylates typically show a one electron quasireversible reduction, the potential of which can vary by up to 0.5 V depending on the nature of the solvent, electrolyte or axially coordinated ligand [58]. The redox potentials of **1–6** in MeOH solutions are given in Table 3. All complexes show a single electron quasi-reversible reduction ($\operatorname{Ru_2}^{II,II}$) or oxidation ($\operatorname{Ru_2}^{II,II}$) process between 0.02 and 0.08 V (*versus* Ag/AgCl), corresponding to the $\operatorname{Ru_2}^{5+}/\operatorname{Ru_2}^{4+}$ couple. These values are comparable to that observed for the $\operatorname{Ru_2}^{4+}/\operatorname{Ru_2}^{5+}$ couple in [$\operatorname{Ru_2}(O_2CCH_3)_4$] (0.04 V in THF

Table 3

Electrochemical data for complexes I-VI.

Compound	$E_{\rm pc}\left(V\right)$	$E_{\rm pa}\left(V\right)$	$E_{1/2} (V)^{a}$
$\begin{array}{l} Ru_2(II,III) \\ [Ru_2(OAc)_2(TiPB)_2CI] (1) \\ [Ru_2(OAc)_2(TiPB)_2(PF_6)] (2) \\ [Ru_2(TiPB)_4CI] (3) \\ [Ru_2(TiPB)_4(PF_6)] (4) \end{array}$	-0.50 -0.50 -0.46 -0.46	-0.25 -0.26 -0.37 -0.37	-0.38 -0.38 -0.41 -0.41
$Ru_{2}(II,II) [Ru_{2}(OAc)_{2}(TiPB)_{2}] (5) [Ru_{2}(TiPB)_{4}] (6) [Ru_{2}(O_{2}CCH_{3})_{4}] [36]^{b}$	$-0.47 \\ -0.45$	-0.32 -0.36	$-0.39 \\ -0.41 \\ -0.39$

^a Cyclic voltammograms recorded in 0.1 M [NnBu₄](PF_6) MeOH solutions. Values are referenced with respect to the Fc/Fc⁺ couple.

^b Electrolyte solution 0.2 M $[N^n Bu_4](PF_6)$ in THF.

solution) [36]. In methanol solutions, any axially coordinated PF_6^- or Cl^- ions will dissociate to give the solvent coordinated complex of form $[Ru_2(O_2CR)_4(MeOH)_2]^+$, hence complexes with the same

carboxylate ligand set will have the same redox potentials. The Ru₂^{II,III} complexes **3** and **4** ($E_{1/2} = 0.02$) are slightly more difficult to reduce than their '*bis-bis*' counterparts **1** and **2** ($E_{1/2} = 0.08$ V). This trend is consistent with a shorter Ru–Ru bond length for the tetra-substituted complexes, which would increase the energy of the antibonding ($\delta^* \pi^*$) orbitals making the complexes more difficult to reduce. A similar trend is observed for the Ru₂^{II,II} complexes, with the increase in energy of these orbitals reflected in the fact that the homoleptic complex **6** is easier to oxidise than the '*bis-bis*' analogue **5**. This suggests that the internal rotation, and short Ru–Ru bond lengths, observed in the solid-state structures of the homoleptic complexes persist in solution.

3.5. UV–Vis spectroscopy

The electronic absorption spectra of diruthenium tetracarboxylates were first interpreted with the aid of SCF-X α -SW calculations by Norman and co-workers [23], and a number of subsequent

Table 4

Electronic absorption data for complexes 1–5 recorded in THF solutions. No $\pi(Ru-O, Ru_2) \rightarrow \pi^*(Ru_2)$ absorption for complex 6 was observed in the visible region.

Complex	$\pi(\text{Ru-O, Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$			$\delta(Ru_2) \rightarrow \delta^*(Ru_2)$	$\delta(Ru_2) \to \delta^*(Ru_2)$		
	λ (nm)	λ (cm ⁻¹)	3	λ (nm)	λ (cm ⁻¹)	3	
Ru ₂ (II,III)							
$[Ru_2(OAc)_2(TiPB)_2Cl]$ (1)	466	21459	1400	1130	8850	30	
$[Ru_2(OAc)_2(TiPB)_2(PF_6)]$ (2)	458	21834	499	a	a	а	
$[Ru_2(TiPB)_4Cl]$ (3)	470	21277	1460	1148	8710	60	
$[Ru_2(TiPB)_4(PF_6)]$ (4)	439	22779	367	1080	9259	10	
$[Ru_2(OAc)_2(TiPB)_2] (5)$	448	22321	1176				

^a Absorption too weak to be observed.

Table 5

Crystallographic details for complexes [$Ru_2(TiPB)_2(OAc)_2CI$] (1), [$Ru_2(TiPB)_2(OAc)_2(THF)_2$](PF_6) [**2**(THF)_2], [$Ru_2(TiPB)_4CI(MeOH)$] [**3**(MeOH)], [$Ru_2(TiPB)_4(THF)_2$](PF_6) [**4**(THF)_2], [$Ru_2(TiPB)_4(THF)_2$] [**6**(THF)_2].

Compound	1	2 (THF) ₂	3 (MeOH)	4 (THF) ₂	6 (THF) ₂
Empirical formula Formula weight T (K) λ (Å) Crystal system	C ₄₀ H ₅₈ Cl ₁ N ₂ O ₈ Ru ₂ 932.47 100(2) 0.71073 monoclinic	C ₄₈ H ₇₆ F ₆ O ₁₁ P ₁ Ru ₂ 1176.20 150(2) 0.71073 triclinic	C ₆₆ H ₉₉ Cl ₁ O ₁₀ Ru ₂ 1290.04 100(2) 0.71073 monoclinic	C ₇₂ H ₁₀₈ F ₆ O ₁₀ P ₁ Ru ₂ 1480.69 120(2) 0.71073 monoclinic	C ₇₂ H ₁₀₈ O ₁₀ Ru ₂ 1335.72 100(2) 0.71073 monoclinic
Space group	C2/c	PĪ	Сс	P21/n	C2/c
a (Å) b (Å)	26.875(4) 13.725(2)	8.1076(14) 12.585(2)	25.7872(17) 16.5393(12)	17.8308(9) 25.3963(13)	17.4405(19) 25.876(3)
<i>c</i> (A)	23.720(4)	14.136(2)	20.4714(14)	18.4580(9)	17.9577(19)
α (°)	90	73.449(3)	90	90	90
β (°)	94.706(9)	76.284(3)	127.926(2)	117.629(2)	116.524(2)
γ(°)	90	83.977(3)	90	90	90
$V(A^3)$	8720(2)	1342.1(4)	6887.1(8)	7405.3(7)	7251.1(14)
Z	8	1	4	4	4
$d_{\text{calc}} (\text{Mg m}^{-3})$	1.421	1.455	1.244	1.328	1.224
$\mu (\mathrm{mm}^{-1})$	0.803	0.667	0.529	0.498	0.469
F(0 0 0)	3848	609	2720	3108	2832
θ range (°)	1.52-27.67	1.54-26.46	1.59-28.18	1.31-27.59	1.52-27.56
Index ranges	$-30 \leqslant h \leqslant 35$	$-10 \leqslant h \leqslant 9$	$-34 \leq h \leq 33$	$-23 \leqslant h \leqslant 22$	$-22 \leqslant h \leqslant 22$
	$-17 \leqslant k \leqslant 17$	$-15 \leqslant k \leqslant 15$	$-21 \leqslant k \leqslant 21$	$-33 \leqslant k \leqslant 29$	$-15 \leqslant k \leqslant 33$
	$-30 \leqslant l \leqslant 30$	$-17 \leqslant l \leqslant 17$	$-27 \leqslant l \leqslant 26$	$-24 \leqslant l \leqslant 23$	$-23 \leqslant l \leqslant 21$
Reflections collected	64 730	11 100	50 120	102 554	36 056
Independent reflections $[R_{(int)}]$	10 083 [0.0476]	5502 [0.0356]	15 315 [0.0347]	17 065 [0.0372]	8372 [0.0376]
Observed reflections $[I > 2\sigma(I)]$	7930	4397	13277	12943	6175
Data completeness to θ_{max}	0.989	0.992	0.986	0.994	0.998
Data/restraints/parameters	10 083/96/520	5502/0/313	15 315/12/709	17 065/115/811	8372/447/440
Goodness-of-fit (GOF) on F^2	1.025	1.015	1.072	1.116	1.050
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0350,$	$R_1 = 0.0440,$	$R_1 = 0.0415$,	$R_1 = 0.0435$,	$R_1 = 0.0538,$
	$wR_2 = 0.0837$	$wR_2 = 0.1015$	$wR_2 = 0.0954$	$wR_2 = 0.1064$	$wR_2 = 0.1391$
R indices (all data)	$R_1 = 0.0538$,	$R_1 = 0.0598$,	$R_1 = 0.0576$,	$R_1 = 0.0642$,	$R_1 = 0.0783,$
	$wR_2 = 0.0953$	$wR_2 = 0.1175$	$wR_2 = 0.1072$	$wR_2 = 0.1175$	$wR_2 = 0.1567$
Largest difference peak and hole $(e \text{ Å}^{-3})$	1.127/-0.723	0.859/-0.574	0.984/-0.877	2.850/-0.761	1.033/-1.462

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Fig. 6. UV–Vis spectrum of **1** in THF at room temperature. The marked absorptions are assigned to the following transitions: $\pi(Ru-O, Ru_2) \rightarrow \pi^*(Ru_2)$, **I**; $\sigma(Ru$ -axial ligand) $\rightarrow \pi^*(Ru_2)$, **II**; $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$, **III**.

experimental studies were used to correctly assign the transitions observed in the electronic spectra [59-61]. The electronic absorption spectra for complexes 1-6 were recorded in THF, and the data is summarised in Table 4. The most intense band in the visible region of Ru₂^{II,III} tetracarboxylates in solution is typically observed at ~450 nm and has been assigned to a $\pi(Ru-O, Ru_2) \rightarrow \pi^*(Ru_2)$ transition. This transition is observed at a similar energy for the Ru₂ complexes 1, 2 and 3, but is shifted to higher energy for complex **4**, as shown in Table 4. The shift of the $\pi(\text{Ru}-0, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transition to higher energy for 4 is consistent with a shorter Ru-Ru bond length, resulting in higher energy $Ru_2 \pi^*$ orbitals by comparison to the other complexes. In addition for Ru₂^{II,III} tetracarboxylates, a weak low energy band at \sim 1100 nm is observed in solution corresponding to the $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transition. A similar trend is observed in the energy of this transition, with the highest energy absorption observed for complex 4. A weak absorption near 620 nm also appears in the spectra of the chloride containing complexes 1 and 3, which can be seen in the absorption spectrum of 1 presented in Fig. 6. Based on earlier studies [59,62], this absorption is assigned to a $\sigma(\text{Ru-axial ligand}) \rightarrow \pi^*(\text{Ru}_2)$ transition.

The electronic absorption spectra of Ru₂^{II,II} tetracarboxylates have not been studied as extensively as their Ru₂^{II,III} counterparts. However, the peak observed at 448 nm in the electronic absorption spectrum of **5** can be assigned to the $\pi(\text{Ru}-0, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transition observed in related Ru₂^{II,III} complexes [63]. Surprisingly, the $\pi(\text{Ru}-0, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transition for complex **6** is not observed. Given that this complex has the shortest Ru–Ru bond length, the Ru₂ π^* orbitals are likely to be destabilised the most, and the $\pi(\text{Ru}-0, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transition shifted to even higher energy than observed for **4**. Therefore, it is possible that this absorption in **6** is now obscured by intense absorptions in the UV region.

4. Conclusions

Diruthenium tetracarboxylate '*bis*-*bis*' complexes of form *trans*- $[Ru_2(OAc)_2(TiPB)_2]^{0/+}$ have been synthesised *via* carboxylate exchange reactions between HTiPB and the corresponding diruthenium tetracetate complex in refluxing methanol solutions, with the bulky carboxylate ligands orientated *trans* to one another to minimise steric interactions. Structural studies on the tetra-substituted complexes **4** and **6** show an unusual reduction in the Ru-Ru bond length despite a decrease in the formal Ru-Ru bond order from 2.5 to 2.0, respectively. These studies also revealed unusual structural distortion, or internal rotation, about the diruthenium cores that serves to minimise steric interactions between the bulky

ligands, and is greater for **6** as is has no net δ -bond. The increased internal rotation was proposed to account for the unusually short Ru–Ru bond length in **6**, which was supported by DFT calculations that show a decrease in the Ru–Ru bond length as the internal rotation increases. Spectroscopic and electrochemical studies on all the complexes showed that the shortening of the Ru–Ru bond also influences the relative energies of the Ru₂ δ^* and π^* orbitals. This relationship between metal–metal bond length and internal rotation is important in relation to metal–metal multiply bonded paddlewheel complexes in general, as metal–metal bond lengths are also likely to be related to the physical properties or reactivity of such species.

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Appendix A. Supplementary material

CCDC 743819, 743820, 743821, 706412 and 706413 contain the supplementary crystallographic data for **1**, $[2(THF)_2]$, [3(MeOH)], $[4(THF)_2]$ and $[6(THF)_2]$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.024.

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