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Relationship between metal-metal bond length and internal rotation in diruthenium tetracarboxylate paddlewheel complexes.

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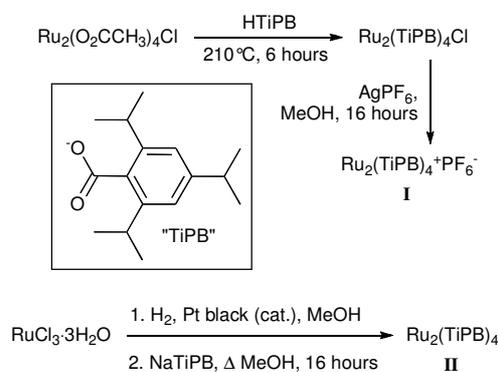
5 **The Ru-Ru bond length for Ru₂^{II,III} and Ru₂^{II,II} paddlewheel complexes containing the bulky carboxylate ligand 2,4,6-triisopropylbenzoate was found to decrease despite a reduction in Ru-Ru bond order, due to increased internal rotation.**

Metal-metal multiply bonded tetracarboxylate complexes of
10 general formula [M₂(O₂CR)₄(L)₂]ⁿ⁺ (M = transition metal; R = alkyl or aryl group; L = solvent or anion) adopt a paddlewheel-type structure, and employ a wide variety of carboxylate and axial ligands (L).¹ The metal-metal bond length for these compounds is dependant on a number of
15 factors, such as the formal bond order between the metals, or the nature of the axial ligand. For example, Cotton, Murillo and co-workers successfully employed the bulky 2,4,6-triisopropyl benzoate ligand to generate a [Cr₂(O₂CR)₄] compound without axial ligation, which has a M-M quadruple
20 bond that is considerably shorter than axially ligated [Cr₂(O₂CR)₄(L)₂] compounds.² Understanding factors that influence metal-metal bond lengths is of relevance to multiply bonded species in general, and particularly important for metal-metal multiply bonded compounds as structural information is used to aid in the interpretation of physical and spectroscopic properties, and to help determine the electronic structure.^{1, 3, 4}

Diruthenium tetracarboxylates can be isolated in a mixed
valent Ru₂^{II,III} form, having a formal Ru-Ru bond order of 2.5
30 and three unpaired electrons, or homovalent Ru₂^{II,II} form, with a formal Ru-Ru bond order of 2.0 and two unpaired electrons.⁵ These compounds have been attracting significant attention recently as they have application as catalysts^{6, 7} and antitumour metallo-pharmaceuticals,⁸ and are good candidates
35 for use in functional materials.⁹⁻¹¹ Metal-metal bond lengths in [Ru₂(O₂CR)₄(L)₂]^{0/+} species show only a small dependence on the nature of the axial ligand or R group. In common with multiply bonded compounds in general, the Ru-Ru bond length is inversely related to the formal bond order, with a
40 small increase in Ru-Ru bond length observed upon reducing Ru₂^{II,III} complexes (bond order = 2.5) to their Ru₂^{II,II} form (bond order = 2.0).⁵ In this communication we present a reversal of this trend for diruthenium species containing bulky tetracarboxylates, for which a decrease in bond length is
45 found upon reducing the Ru-Ru bond order.

The synthesis of Ru₂^{II,III}(TiPB)₄⁺PF₆⁻ (**I**), where TiPB is the deprotonated form of the bulky carboxylate 2,4,6-triisopropyl benzoic acid, proceeds via a Ru₂^{II,III}(TiPB)₄Cl intermediate. Attempts to synthesise Ru₂^{II,III}(TiPB)₄Cl in a standard fashion,
50 by refluxing Ru₂^{II,III}(O₂CCH₃)₄Cl with HTiPB in a MeOH /

H₂O mixture, resulted in incomplete substitution. Instead a melt reaction at 210°C was employed, with excess ligand recovered at the end of the reaction by vacuum sublimation. Reaction of Ru₂^{II,III}(TiPB)₄Cl with AgPF₆ in methanol resulted
55 in the formation of desired compound Ru₂^{II,III}(TiPB)₄⁺PF₆⁻, **I**. The compound Ru₂^{II,II}(TiPB)₄ (**II**) was synthesised in good yield by reducing methanolic solutions of RuCl₃·3H₂O with H₂ to give a "ruthenium blue" solution, that was refluxed with the sodium salt of the carboxylate. The synthesis of both
60 compounds is summarised in Scheme 1.



Scheme 1

Satisfactory elemental analyses were obtained for both **I**
65 and **II**, and fragments consistent with their formulation are observed in their MALDI-MS-TOF spectra. The magnetic susceptibility value for **I** of 4.0 B.M. is within the range observed for Ru₂^{II,III} tetracarboxylates, and consistent with 3 unpaired electrons in a $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$ electronic configuration.
70 In contrast, compound **II** has a magnetic susceptibility of 2.2 B.M. that indicates 2 unpaired electrons and a $\sigma^2\pi^4\delta^2\delta^*\pi^{*2}$ electron configuration.¹² In addition, the infrared $\nu\text{CO}_2(\text{symm})$ and $\nu\text{CO}_2(\text{asymm})$ stretching frequencies observed at 1389 and 1458 cm⁻¹ for **I**, and 1403 and 1517 cm⁻¹
75 for **II**, are consistent with the respective Ru₂^{II,III} and Ru₂^{II,II} oxidation state assignments.⁵

Crystals of **I** and **II** suitable for a single crystal X-ray diffraction study were grown from THF solutions. Both Ru₂ cores have an identical coordination environment, having four
80 bridging TiPB ligands and two axially coordinated THF molecules, which, importantly, allows direct comparison of the structural parameters.

The crystal structure of [Ru₂^{II,III}(TiPB)₄(THF)₂][PF₆], **I**(THF)₂, with selected bond-lengths and angles, is presented
85 in Figure 1. The Ru-Ru bond length of 2.2567(3) Å observed for **I**(THF)₂ falls at the lower end of the range observed for

Ru₂^{II,III} tetracarboxylates (2.248-2.310 Å).¹ In common with other [M₂(O₂CR)₄(L)₂] compounds, the {Ru₂(O₂C)₄} cores of cationic and neutral diruthenium tetracarboxylate paddlewheel complexes adopt a paddlewheel structure with essentially D_{4h} symmetry. The solid state structure of **I** shows an unusual distortion, or internal rotation, of the {Ru₂(O₂C)₄} core. This results in the Ru₂^{II,III} core having *pseudo*-D₄ symmetry, with O_{carboxy}-Ru-Ru-O_{carboxy} torsion angles ranging from 6.68(8)° to 8.82(8)°. The internal rotation is a result of steric effects from the bulky 2,4,6-triisopropylbenzoate ligand.

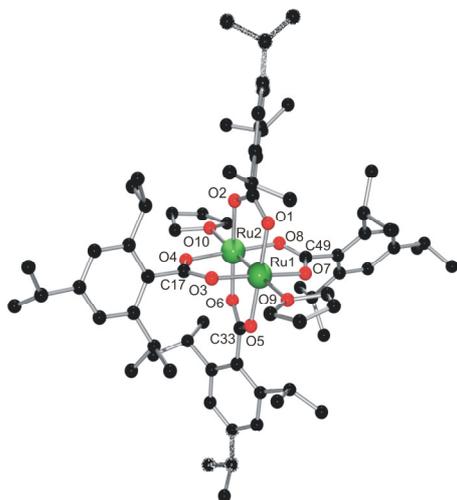


Fig. 1 Molecular structure of the cationic core of [Ru₂^{II,III}(TiPB)₄(THF)₂][PF₆], **I**(THF)₂. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and torsion angles (°) for **I**(THF)₂: Ru1-Ru2 2.2567(3), Ru1-O1 2.0161(19), Ru1-O3 2.0216(19), Ru1-O5 2.0139(19), Ru1-O7 2.020(2), Ru2-O2 2.0201(19), Ru2-O4 2.025(2), Ru2-O6 2.0147(19), Ru2-O8 2.0139(19), Ru1-O9 2.255(2), Ru2-O10 2.263(2), O1-Ru1-Ru2-O2 8.71(8), O3-Ru1-Ru2-O4 6.68(8), O5-Ru1-Ru2-O6 8.82(8), O7-Ru1-Ru2-O8 7.91(8).

The solid-state structure of Ru₂^{II,II}(TiPB)₄(THF)₂, **II**(THF)₂, is presented in Figure 2, along with selected bond lengths and angles. The Ru-O_{carboxylate} bond lengths [2.058 Å (average)] and Ru-O_{THF} bond length [2.308(3) Å] are in the range expected for [Ru₂^{II,II}(O₂CR)₄(L)₂] species.⁵ These bond lengths are slightly longer than those observed in the cationic Ru₂ core of compound **I** [Ru-O_{carboxylate} = 2.018 Å (average), Ru-O_{THF} = 2.259 Å (average)], due to a reduction in the electrostatic interaction between the diruthenium core and carboxylate ligands.⁵

Ru₂^{II,II} tetracarboxylates exhibit slightly longer Ru-Ru bond lengths than their Ru₂^{II,III} analogues. For example, the Ru-Ru bond length increases from 2.248(1) Å in [Ru₂^{II,III}(O₂CMe)₄(H₂O)₂]⁺ to 2.262(3) Å for [Ru₂^{II,II}(O₂CMe)₄(H₂O)₂].^{13, 14} The relatively small increase observed in Ru-Ru bond lengths for these species supports the addition of an extra electron into the weakest δ* orbital, and a decrease in the formal bond order from 2.5 (Ru₂^{II,III}) to 2.0 (Ru₂^{II,II}). Surprisingly, the Ru-Ru bond length observed for the Ru₂^{II,II} complex **II** is *shorter* than observed for the analogous Ru₂^{II,III} complex **I**. In fact, the Ru-Ru bond length for **I** [2.2425(6) Å] is outside the range previously observed for Ru₂^{II,III} tetracarboxylates (2.252-2.311 Å), and is even less

than the shortest diruthenium tetracarboxylate Ru-Ru bond length, found for [Ru₂^{II,III}(O₂CMe)₄(H₂O)₂]⁺, 2.248(1) Å.¹³ Another unusual feature in the structure of compound **II** is the extent of distortion about the {Ru₂(O₂C)₄} core, with O_{carboxy}-Ru-Ru-O_{carboxy} internal rotation angles ranging from 11.9(1)° to 15.2(1)°, which is highlighted in Figure 2. Only the δ-orbital strength in [M₂(O₂CR)₄(L)₂] species is dependant on the internal rotation angle,¹ with the greatest overlap observed for eclipsed structures that have no internal rotation. Hence, the increased internal rotation angles for **II** are consistent with a reduction in the overall δ-bond order by comparison to compound **I**, and a σ²π⁴δ²δ*²π*² electron configuration. The rotation angles observed for **II** are comparable to the dirhodium complexes [Rh₂(TiPB)₄] (13.2°) and [Rh₂(TiPB)₄(OCMe₂)₂] (15.7°) that also have no net δ bond and short Rh-Rh bond lengths.¹⁵ For **I**, the overall δ-bond order of 0.5 is sufficient in strength to restrict the internal rotation to relieve any steric interactions. The internal rotation angles in **I** are intermediate between those of **II**, which has no net δ-bond, and those of [Cr(TiPB)₄] and [Mo₂(TiPB)₄] which have a δ-bond order of 1 and essentially no internal rotation of the {M₂(O₂CR)₄} core.^{2, 16}

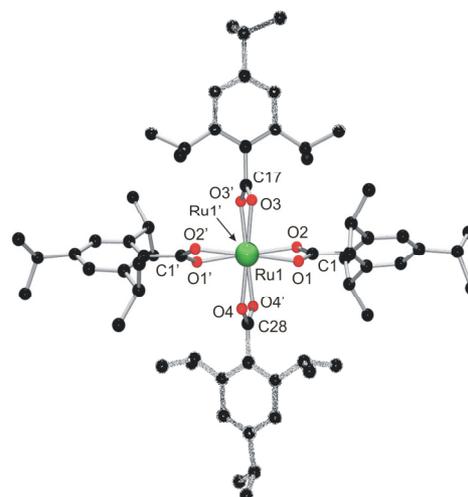
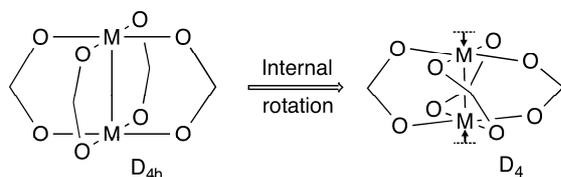


Fig. 2 Molecular structure of Ru₂^{II,II}(TiPB)₄(THF)₂, **II**(THF)₂, viewed along the Ru-Ru bond to highlight internal rotation about the Ru₂ core. Axially coordinated THF molecules and hydrogen atoms have been omitted for clarity. Symmetry equivalent atoms generated using the symmetry operation -x, y, 1/2-z. Selected bond lengths (Å) and torsion angles (°) for **II**(THF)₂: Ru1-Ru1' 2.2425(6), Ru1-O1 2.051(3), Ru1-O2' 2.059(3), Ru1-O3 2.065(3), Ru1-O4 2.055(3), Ru1-O5(THF) 2.308(3), O1-Ru1-Ru1'-O2 15.2(1), O3-Ru1-Ru1'-O3' 11.9(1), O4-Ru1-Ru1'-O4' 12.9(1).

The relationship between bond order and bond length for MM multiple bonds is often complicated by other factors. Increases in bond order that are accompanied by increases in the metal oxidation state often display irregular and small decreases in bond length.¹⁷ This is due, in part, to contraction of the d-orbitals upon increasing the effective positive charge, weakening the σ, π and δ components and counteracting the increase in bond order.¹⁸ In a rare example, this effect was shown to outweigh the bond-strengthening effect of increasing the bond order for the [Tc₂Cl₈]³⁻ ion. Oxidation of [Tc₂Cl₈]³⁻, having a σ²π⁴δ²δ* configuration, to [Tc₂Cl₈]²⁻, having a σ²π⁴δ²

configuration, results in a 0.5 increase in bond order with a concomitant ~ 0.05 Å increase in the Tc-Tc bond length.¹⁹ Likewise, oxidation of the Ru₂^{II,III} core of **II** to give **I** also results in a 0.5 increase in the overall δ bond order, and a small (0.014 Å), although unusual, increase in the Ru-Ru bond length. However, the change in oxidation state cannot fully account for the unusually short Ru-Ru bond length in **II**, as it is shorter than observed for any other Ru₂^{II,II} tetracarboxylates, and the trend is not observed for other Ru₂^{II,II}/Ru₂^{II,III} pairs, that are essentially isostructural. In this case, the lack of a net δ bond and use of a bulky carboxylate ligand for **II** causes a distortion of the Ru₂^{II,II} core, reducing the effective bridging distance of the carboxylate and reducing the Ru-Ru bond length as highlighted in Scheme 2. The oxidised core of **I** has a net δ bond of 0.5, which is of sufficient strength to reduce this distortion and minimise this effect.



Scheme 2

In summary, we report the synthesis and characterisation of Ru₂^{II,III} (**I**) and Ru₂^{II,II} (**II**) complexes containing bulky 2,4,6-triisopropyl benzoate ligands. The solid-state structures of the THF adducts of these compounds have diruthenium cores with identical composition that display shorter Ru-Ru bond lengths for **II** than for **I**, despite a decrease in the formal bond order from 2.5 to 2.0. This is due to the relationship between electronic structure and internal rotation of the {Ru₂(O₂C)₄} cores, which relieves steric interactions. The greater internal rotation for the Ru₂^{II,II} complex (**II**), which reduces the effective bridging distance of the carboxylate ligand, is proposed to be responsible for it having the shortest diruthenium tetracarboxylate Ru-Ru bond length [2.2425(6) Å] found to date.

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Notes and references

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Crystal data for [**I**(THF)₂(PF₆)]: C₇₂H₁₀₈F₆O₁₀P₁Ru₂, *M* = 1480.69, monoclinic, space group P2₁/n, *a* = 17.8308(9), *b* = 25.3963(13), *c* = 18.4580(9) Å, β = 117.629(2)°, *V* = 7405.3(7) Å³, *Z* = 4, *T* = 120(2) K, λ = 0.71073 Å, *R*_{int} = 0.0372; a total of 102554 reflections collected in the range 1.31 < θ < 27.59, of which 17065 were unique. GOF = 1.116, *R*₁ = 0.0435 [for 12943 reflections with *I* > 2 σ (*I*)] and *wR*₂ = 0.1215 (for all data). CCDC No. 706412.

Crystal data for [**II**(THF)₂]: C₇₂H₁₀₈O₁₀Ru₂, *M* = 1335.72, monoclinic, space group C2/c, *a* = 17.4405(19), *b* = 25.876(3), *c* = 17.9577(19) Å, β = 116.524(2)°, *V* = 7251.1(14) Å³, *Z* = 4, *T* = 100(2) K, λ = 0.71073 Å, *R*_{int} = 0.0376; a total of 36056 reflections collected in the range 1.52 < θ < 27.56, of which 8372 were unique. GOF = 1.035, *R*₁ = 0.0533 [for 6175

reflections with *I* > 2 σ (*I*)] and *wR*₂ = 0.1557 (for all data). CCDC No. 706413.

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