

Note

Pyrazine-mediated antiferromagnetic intermolecular exchange in mixed-valent diruthenium tetracarboxylates

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Abstract

Two mixed-valent diruthenium tetracarboxylates, $[\text{Ru}_2(\text{AcO})_4(\text{H}_2\text{O})_2]\text{BPh}_4$ (**1**) and $[\text{Ru}_2(\text{AcO})_4(\text{pz})]\text{BPh}_4$ (**2**) (AcO = acetate, BPh_4 = tetraphenylborate, pz = pyrazine), were synthesized and characterized by elemental analysis, IR and UV-Vis spectroscopies, and magnetic susceptibility measurements between 6 and 320 K. The magnetic behaviour of **1** can be understood in terms of non-interacting spin 3/2 dimers undergoing a large ($c. 72 \text{ cm}^{-1}$) zero-field splitting, whereas an intermolecular antiferromagnetic interaction ($c. -2 \text{ cm}^{-1}$), in addition to a large zero-field splitting ($c. 63 \text{ cm}^{-1}$), is required to account for the data for **2**.

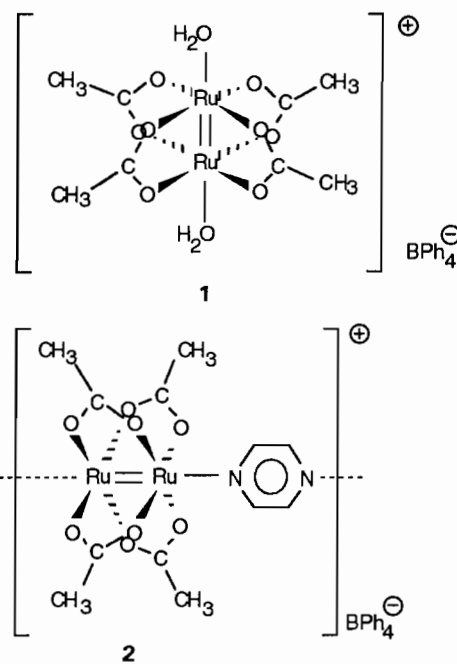
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Introduction

Diruthenium tetracarboxylates are known to exist both as homovalent Ru(II,II) and mixed-valent Ru(II,III) species. Detailed studies have been carried out on their synthesis [1], structures [1–3], electronic [4–6] and vibrational [6] spectra, magnetic properties [1–3, 5a, 7, 8a] and thermotropic behaviour [8, 9]. Particularly interesting for the inorganic chemist is the rare combination that they exhibit of a multiple metal-metal bond and of a high-spin state: bond order (b.o.) = 2 and $S = 1$ for Ru(II,II) compounds, b.o. = 2.5 and $S = 3/2$ for Ru(II,III) derivatives. Moreover, it has been shown in our laboratory that when the diruthenium tetracarboxylate core is substituted with long alkyl chains, the resulting species can exhibit liquid crystalline phases of the columnar type both in the Ru(II,II) [8a, b] and the Ru(II,III) [9] forms.

In this context, the search for extended linear chain compounds based on bridged high-spin diruthenium units and exhibiting ordered mesophases seems particularly interesting. A prerequisite to the design of such systems is a good understanding of the magnetic interactions between neighbouring units. Thus, it seemed to be judicious to investigate model systems, in which mesomorphism is absent but electronic properties are similar to those of the desired molecular materials.

Recent investigations of the crystal structures and magnetic behaviour of two diruthenium(II,III) complex cations linked axially by pyrazine [10a] or phenazine [10b] suggest that a bridging ligand can mediate antiferromagnetic interaction between adjacent Ru_2^{5+} units, but the magnitude of this interaction could not be determined owing to the modest accuracy of the magnetic measurements. This prompted us to report, in the present paper, the synthesis, characterization and detailed magnetic measurements of two mixed-valent diruthenium complexes: $[\text{Ru}_2(\text{AcO})_4(\text{H}_2\text{O})_2]\text{BPh}_4$ (**1**)* (an intermediate in the synthesis of metallo-mesogens [9]) as an example of a discrete diruthenium complex, as well as its reaction product with pyrazine, $[\text{Ru}_2(\text{AcO})_4(\text{pz})]\text{BPh}_4$ (**2**).



*Abbreviations used in this work: AcO = acetate, prop = propionate, chp = 6-chloro-2-hydroxypyridinate, Ph = phenyl, pz = pyrazine, phz = phenazine, eq = equatorial

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Experimental

Synthesis of $[Ru_2(AcO)_4(H_2O)_2]BPh_4$ (**1**)

500 mg (1.06 mmol) of $Ru_2(AcO)_4Cl$ (synthesized by the Mitchell method [11]) were dissolved in 250 ml of water by vigorous stirring at room temperature for 4 h. The solution was filtered and then concentrated to c. 40 ml by evaporation under reduced pressure. 364 mg (1.06 mmol) of $NaBPh_4$ (dissolved in c. 5 ml of water) were added dropwise to the concentrated solution, and the resulting mixture was stirred for 30 min after the end of the addition. The precipitate formed was filtered off, washed with water, then with petroleum ether, and dried under vacuum at 40 °C for 5 h. 630 mg of an orange powder were obtained (yield 76%). *Anal.* Found: C, 48.01; H, 4.50; Ru, 25.48; B, 1.17. Calc.: C, 48.43; H, 4.58; Ru, 25.47; B, 1.36%.

Synthesis of $[Ru_2(AcO)_4(pz)]BPh_4$ (**2**)

300 mg (0.38 mmol) of **1** were dissolved in 3 ml of EtOH, and 300 mg (3.74 mmol) of pyrazine (dissolved in 3 ml of EtOH) were added to this solution. After stirring for 1 h, the precipitate was filtered off, washed with EtOH and dried *in vacuo*. Yield 310 mg (94%). *Anal.* Found: C, 51.73; H, 4.31; Ru, 22.80; B, 1.30; N, 3.14. Calc.: C, 51.62; H, 4.33; Ru, 24.13; B, 1.29; N, 3.34%.

Physicochemical measurements

UV–Vis–near-IR spectra were recorded with a Lambda 9 Perkin-Elmer spectrometer on $1-9 \times 10^{-4}$ M solutions. IR spectra were obtained from KBr pellets with a Beckman IR 4250 spectrophotometer. Magnetic measurements between 6 and 320 K were carried out on powdered samples (20–30 mg) placed in plastic containers, using an SHE 905 SQUID susceptometer. Raw data were corrected from the container contribution, and then from the diamagnetic susceptibilities of the complexes, calculated with Pascal's constants [12]: -393×10^{-6} cm³/mol for **1** and -439×10^{-6} cm³/mol for **2**.

Results and discussion

Synthesis and characterization

1 was obtained as an orange precipitate by a simple exchange of the chloride anion in $Ru_2(AcO)_4Cl$ by the tetraphenylborate ion, in an aqueous solution. The resulting tetraphenylborate salt **1** exhibits a solution UV–Vis spectrum with four distinct bands (see Table 1), consistent with results previously published for other mixed-valent diruthenium tetracarboxylates [6]; the orange colour of this species – both in solution and in the solid state – is due to the electronic transition

TABLE 1 Electronic absorptions of **1** in the UV–Vis–near-IR region (λ in nm, ϵ in M⁻¹ cm⁻¹)

Band	λ_{max} (ϵ) in CH ₃ CH ₂ OH
I	1005 (21)
II	530 (shoulder)
III	428 (820) ^a
IV	295 (shoulder) 280 (2400)

^aIn other solvents: H₂O, 423 (680), CH₃OH, 426 (806), n-C₃H₇OH, 429 (880), acetone, 431 (935)

$6e_u \rightarrow 6e_g$ [6b] appearing near 430 nm. Its IR spectrum exhibits several clear features, the most significant of them being two bands at 350 and 405 cm⁻¹ (assigned to the in-plane stretchings of Ru–O(eq) [6c]), a strong and sharp band at 700 cm⁻¹ (assigned to a $\delta(CO_2)$ characteristic of these dinuclear acetates [6b]), and a strong and broad absorption at c. 3400–3500 cm⁻¹, revealing the presence of water molecules. The latter most likely occupy two axial coordination sites, as in the closely related analogue $[Ru_2(AcO)_4(H_2O)_2]BF_4$ [2a]. Stretching carbonyl modes (in the 1500–1400 cm⁻¹ region) are masked by the phenyl ring vibrations

1 reacts readily with pyrazine in ethanol, giving a greenish grey powder of **2**. The IR spectrum of **2** exhibits the main features of the diruthenium(II,III) tetraacetate core, but the absence of the O–H stretching strongly suggests that pyrazine has replaced water as the axial ligand. The lack of the characteristic centrosymmetric ring stretching band of pyrazine at c. 1600 cm⁻¹ can be taken as evidence of bidentate coordination of pyrazine [13], giving rise to infinite chains (only a very weak absorption is seen at 1580 cm⁻¹ and it may correspond to terminal pyrazine molecules). The complete insolubility of **2** in most solvents is also consistent with a polymeric nature. The high temperature value of the magnetic moment of **2** (3.9 BM, see below), is only consistent with a Ru_2^{5+} formulation. This result, as well as the spectroscopic characterization and the good elemental analysis data, clearly show that we deal here with pure homogeneous compounds.

Both complexes undergo a solid-phase reaction above 80 °C, giving a brown powder in the case of **1** and a violet one in the case of **2**. Preliminary characterization by UV–Vis and IR spectroscopies and magnetic susceptibility measurements indicates that the main product in both cases is a mixture of an Ru(II,II) dimer with some biphenyl, suggesting a thermally induced tetraphenylborate oxidation by the Ru_2^{5+} core. The same reaction – which is presumably related to the low reduction potential of the Ru_2^{5+} cation – proceeds quickly in solutions of **1** at room temperature, precluding the obtention of single crystals suitable for structural characterization. Nevertheless, we have enough exper-

imental evidences of the structure of both compounds, even in the absence of crystallographic structures, to perform a detailed study of their magnetic behaviour.

Magnetic properties

The temperature dependence of the effective magnetic moment of complex **1** is shown in Fig. 1. The value of μ_{eff} at room temperature (*c.* 4.2 BM) is consistent with an $S=3/2$ system possessing a large g value; its fall at low temperature is assigned to a large magnetic anisotropy. The molar magnetic susceptibility describing the resulting zero-field splitting (*ZFS*) is made up of two terms: χ_{\parallel} and χ_{\perp} , expressed by eqns. (1) and (2).

$$\chi_{\parallel} = C \frac{1 + 9 \exp(-2x)}{4(1 + \exp(-2x))} \quad (1)$$

$$\chi_{\perp} = C \frac{4 + (3/x)(1 - \exp(-2x))}{4(1 + \exp(-2x))} \quad (2)$$

where $x = D/kT$ and $C = Ng^2\beta^2/kT$ (expressions were taken from ref. 14 and corrected after ref. 7b).

For a powdered sample, the total molar magnetic susceptibility is given by $\chi = 1/3 (\chi_{\parallel} + 2\chi_{\perp})$. The magnetic susceptibility corresponding to the bulk sample was measured and the experimental data were refined with an expression of χ_{mol} versus temperature which takes into account the *ZFS* term, the temperature independent paramagnetism (*TIP*) and the contribution of an impurity present in a proportion p and following the Curie law for $S=1/2$ with a g factor noted as g_{mo} . The complete expression of the magnetic susceptibility used for the refinements was therefore:

$$\chi_{\text{mol}} = (1-p)[(\chi_{\parallel} + 2\chi_{\perp})/3 + \text{TIP}] + pN\beta^2g_{\text{mo}}^2/4kT \quad (3)$$

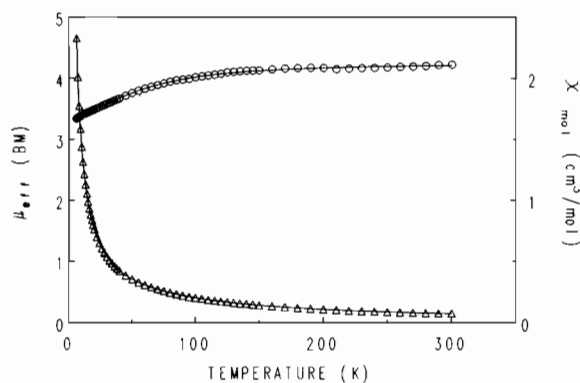


Fig 1 Temperature dependence of the experimental effective magnetic moment (\circ) and magnetic susceptibility (Δ) of **1** and calculated curves (full lines) using eqn. (3) with parameters of Table 2.

The refinement was achieved by adjustment of the following parameters*: g , D , *TIP*, p , g_{mo} by a least-squares fitting procedure. A good agreement between experimental and calculated data (see Fig. 1) was obtained with the values listed in Table 2. Moreover, its limiting value at very low temperatures is consistent with that predicted from the zero-temperature limit of eqn. (3) ($\mu_{\text{eff}} \rightarrow 3.1$ BM as $T \rightarrow 0$ for values of Table 2).

In contrast, the magnetic behaviour of complex **2** cannot be interpreted in the same fashion. Indeed, at low temperature the magnetic moment decreases markedly, reaching values considerably lower than that calculated from the zero-temperature limit of the *ZFS* law of a quadruplet state system. Figure 2 shows the experimental data and theoretical curves corresponding to different values of zero field splitting. It appears clearly that eqn (3) cannot describe satisfactorily the behaviour of **2**, because it cannot take into account the fall in the curve at low temperature. The latter indicates the existence in complex **2** of a strong anti-

TABLE 2 Magnetic parameters* obtained by refinement of experimental data as described in the text

Complex	g	D	<i>TIP</i>	zJ	p	σ^2
1	2.190	71.8	$< 10^{-6}$		0.11	7.1×10^{-6}
2	2.098	62.9	$< 10^{-6}$	-2.3	0.61	3.7×10^{-5}

* D and zJ in cm^{-1} , *TIP* in cm^3/mol , p in %, $\sigma^2 = \sum(\chi_{\text{calc}} - \chi_{\text{exp}})^2 / \sum\chi_{\text{exp}}^2$.

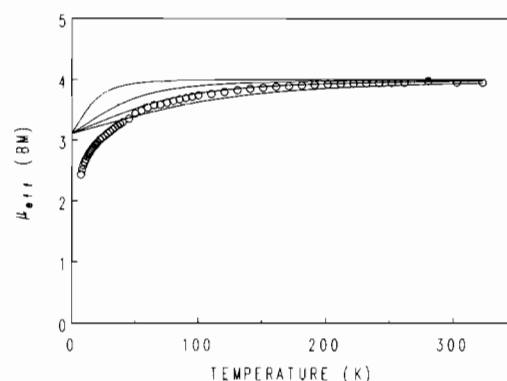


Fig 2 Temperature dependence of the effective magnetic moment of **2** experimental data (\circ) and calculated curves (full lines) using eqn (3) and different values of the zero-field splitting parameter* from the upper to the lower curves $D=20, 50, 80, 120 \text{ cm}^{-1}$

*Attempts were made to use a more rigorous expression of the magnetic susceptibility curve containing two different g factors: g_{\parallel} in eqn (1) and g_{\perp} in eqn. (2). No significant improvement of the refinements could be obtained, and the values of g_{\parallel} and g_{\perp} were found to be very close (2.17 and 2.20, respectively)

ferromagnetic interaction, either intra- (in other words the *ZFS*) or intermolecular.

If a strong intermolecular coupling was present, it should lead to a maximum in the χ versus T curve. As can be seen on Fig. 3, this is not observed. Therefore, it means that the intramolecular antiferromagnetism (i.e. the *ZFS*) is strong, and also supplemented by a weak intermolecular interaction. Accordingly, a reasonable model was developed, in which quadruplet units undergoing a strong *ZFS* are antiferromagnetically coupled through a one-dimensional chain mechanism. Such a magnetic system has never been mathematically treated, owing to its complexity, but the intermolecular interaction is most likely weak, as no maximum in the $\chi(T)$ curve is observed above 6 K. A simple method to describe such systems is to apply the molecular field approximation [14], using eqn. (4).

$$\chi' = \frac{\chi}{1 - (2zJ/Ng^2\beta^2)\chi} \quad (4)$$

where zJ is the exchange energy J multiplied by the number z of interacting neighbours and χ the magnetic susceptibility of an isolated molecule. As in the refinement procedure followed for complex **1**, χ contains a *TIP* term and we have added the contribution of a paramagnetic impurity. The adjustable parameters were therefore g , D , *TIP*, zJ , g_{mo} and p .

This procedure led to good refinements, and allowed us to assess the magnitude of the intermolecular exchange. Final values of the parameters used in the best fit of the experimental data of **2** are also shown in Table 2. The good agreement between the calculated and experimental curves of χ_{mol} and μ_{eff} versus T is illustrated in Fig. 3.

Most of the magnetic studies carried out up to now on mixed-valent diruthenium tetracarboxylates have dealt essentially with determinations of the magnetic moment at room temperature [1–3]. The values found

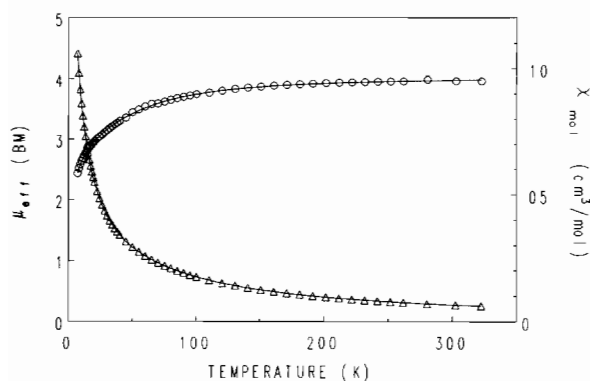


Fig. 3. Temperature dependence of the experimental effective magnetic moment (○) and magnetic susceptibility (△) of **2** and calculated curves (full lines) using eqn (4) with parameters of Table 2.

for more than 20 complexes range between 3.7 and 4.6 BM, consistent with a $3/2$ spin per dimer. These results were satisfactorily explained by the theoretical work of Norman *et al* [4], who predicted for $\text{Ru}_2(\text{HCO}_2)_4^+$ the existence of a three-fold accidentally degenerate HOMO, with 3 unpaired electrons. A detailed experimental study carried out by Drago and co-workers [7a, b] on the magnetic behaviour of $\text{Ru}_2(\text{C}_4\text{H}_7\text{O}_2)_4\text{Cl}$ in a wide temperature range confirmed this prediction, and it clearly showed that the $S=3/2$ ground state of such $\text{Ru}_2(\text{C}_n\text{H}_{2n-1}\text{O}_2)_4^+$ moieties exhibits a zero-field splitting, with a D value of 70.6 cm^{-1} . A similar case was found here for $[\text{Ru}_2(\text{AcO})_4(\text{H}_2\text{O})_2]\text{-BPh}_4$, and as can be seen in Table 2 we obtained a close value of D .

On the other hand, it is clear that complex **2** exhibits a weak (but non-negligible) antiferromagnetic intermolecular exchange of $c. 2 \text{ cm}^{-1}$. This coupling appears in the presence of pyrazine, as it is not detected in complex **1**, and it seems reasonable to conclude that pyrazine mediates an antiferromagnetic exchange between $S=3/2$ units (supporting also the hypothesis that it bridges adjacent dimers). The experimental magnetic susceptibility curves recently published for $[\{\text{Ru}_2(\text{chp})_4\}_2(\text{pz})](\text{BF}_4)_2$ [10a] and $[\text{Ru}_2(\text{prop})_4(\text{phz})]\text{-BF}_4$ [10b] show the same type of behaviour, indicating clearly the occurrence of the same kind of interactions in both complexes. However no quantitative assessment of the zero-field splitting and antiferromagnetic interaction was performed in those investigations.

Conclusions

The present study confirms that diruthenium tetracarboxylates possessing an $S=3/2$ spin state can magnetically interact if they are linked by an appropriate bridging ligand like pyrazine. In contrast to previous studies on bridged mixed-valent diruthenium species [10], which afforded only a qualitative estimate of the magnetic exchange, the rigorous curve-fitting methodology used in the present work allows a quantitative estimate of the relevant magnetic parameters (D , zJ) to be made. Further studies are under way on the influence of other bridging ligands on the magnetic exchange and on the design of interacting diruthenium complexes exhibiting ordered mesophases.

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