

# Diastereoisomeric dinuclear ruthenium complexes of 2,5-di(2-pyridyl)thiazolo[5,4-*d*]thiazole

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The first metal complexes of 2,5-di(2-pyridyl)thiazolo[5,4-*d*]thiazole (**5**) are described. X-Ray crystal structures are reported for the free ligand **5**, a dinuclear copper complex **6** and the two diastereoisomers, **7<sub>meso</sub>** and **7<sub>rac</sub>**, of the dinuclear bis(2,2'-bipyridine)ruthenium complex. The two diastereoisomers of **7** and the 4,4'-dimethyl-2,2'-bipyridine analogue **8** are readily separated by cation exchange chromatography. <sup>1</sup>H NMR and visible absorption spectra and electrochemical data for the four dinuclear ruthenium complexes reveal that these have relatively small HOMO-LUMO energy gaps and exhibit relatively weak metal-metal interactions.

## Introduction

Bridging nitrogen-containing heterocyclic ligands are known to facilitate interactions between metal atoms through the  $\pi$ -system of the ligand.<sup>1-3</sup> The extent of such metal-metal communication is mediated by the metal-metal distance, the degree of conjugation between the metal centres and the electronic properties of the ligand and metals.<sup>2</sup> Ruthenium complexes of doubly-chelating bridging ligands have been particularly well studied.<sup>2</sup>

2,2'-Bipyrimidine (**1**) (Figure 1) is a highly symmetrical ligand that chelates to two metal centres separated by *ca.* 5.5 Å and allows moderately strong metal-metal interactions.<sup>4</sup> The less symmetrical ligand 2,2'-azobis(pyridine) (**2**) leads to complexes with shorter metal-metal separations and stronger interactions.<sup>5</sup> In complexes of **2** the metals are laterally displaced relative to the plane of the ligand. As part of a programme involving the study of ligands containing less commonly studied heterocyclic ring systems,<sup>6</sup> we recently described the preparations and complexes of two new bridging ligands, (**3**) and (**4**), incorporating 1,2,5-oxadiazole and 1,2,5-thiadiazole bridging subunits.<sup>7</sup> Electrochemical studies of dinuclear ruthenium complexes of these ligands

revealed unusually strong metal-metal interactions, greater than those found in the corresponding complexes of **1**, despite the greater inter-metal separation (6.0 Å). Furthermore, we observed an intriguing difference between the magnitude of the metal-metal interactions for the two diastereoisomeric (*meso* and *rac*) forms of the dinuclear complex containing the Ru(bpy)<sub>2</sub> terminal moieties (bpy = 2,2'-bipyridine).<sup>7</sup>

In search of an explanation for the origin of this amplified communication between the metals, we have embarked on a project to synthesise related bridging ligands that contain mixed heteroatoms in the bridging subunit. We now report a study of the complexes of the title ligand (**5**), which has two laterally-displaced chelating binding domains separated by a thiazolothiazole bridge.

## Results and Discussion

### Synthesis and X-ray structure of **5**

2,5-Diarylthiazolo[5,4-*d*]thiazoles are readily prepared from rubeanic acid and aromatic aldehydes.<sup>8</sup> In this way the ligand (**5**) was prepared from 2-pyridine-carboxaldehyde in 19% yield after recrystallisation, and characterised by mp, mass spectrometry and <sup>1</sup>H NMR. The only previous report<sup>9</sup> of this compound involved a screening of its potential antibacterial activity; no metal complexes have been described.

In order to establish unambiguously the structure of this potential bridging ligand, an X-ray crystal structure determination was carried out on small plates obtained by evaporation of a DMF and nitromethane solution. It crystallises in the monoclinic space group P2<sub>1</sub>/*n* with half a molecule in the asymmetric unit, the other half being related by a crystallographic centre of inversion. Figure 2 shows a perspective view of the structure with selected bonding geometry.

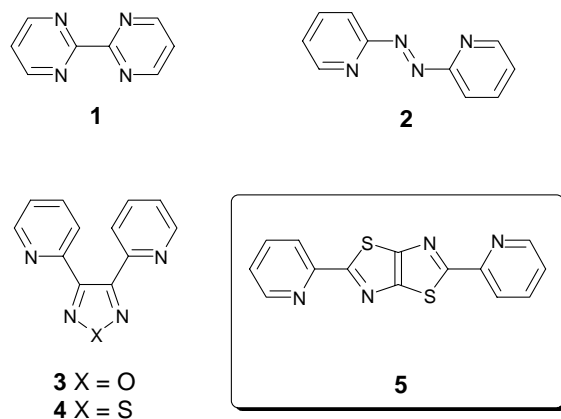
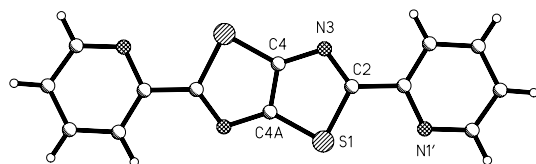


Fig. 1 Bridging doubly-chelating ligands including the title ligand **5**.

The geometry of the central, planar thiazolothiazole subunit is similar to that observed in all other crystal structures of molecules containing this heterocyclic ring system,<sup>10,11</sup> with the S1-C2 bond significantly longer than the S1-C4A bond. The pyridine ring is almost coplanar with the central ring system {angle between meanplanes = 4.9(2)<sup>o</sup>}. In the solid state it exists in a conformation which has the two N-atoms *s-trans* with respect to the inter-ring bond, which is different from that required for N,N'-chelation to a metal centre. Unlike the corresponding 2,5-dithienyl analogue<sup>10</sup> there are no unusually short S...S interactions. Instead the molecular packing has the herringbone pattern commonly found for planar aromatic molecules in this space group.<sup>12</sup> The intermolecular interactions involve  $\pi$ - $\pi$  stacking between pyridine rings and thiazolothiazole units separated by ca. 3.47 Å and CH...S interactions between H4' and S1 of an adjacent molecule with a H...S distance of 2.86(2) Å and a C-H...S angle of 157(2)<sup>o</sup>.



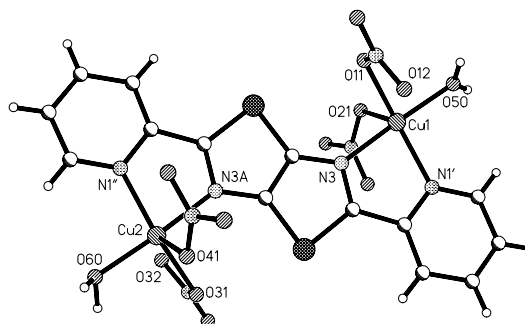
**Fig. 2** The X-ray crystal structure of **5**. Selected bond distances (Å) and angles (<sup>o</sup>): S1-C2 1.757(2), S1-C4A 1.730(2), C2-N3 1.316(2), C2-C2' 1.472(2), N3-C4 1.367(2), C4-C4A 1.384(3), C4A-S1-C2 87.90(8), S1-C2-N3 116.95(14), C2-N3-C4 107.92(15), N3-C4-C4A 117.9(2), S1-C4A-C4 109.33(18).

### Syntheses and crystal structures of metal complexes of **5**

We have prepared many complexes of **5** with various first- and second-row transition metals, including numerous dinuclear complexes.<sup>13</sup> As a representative example we herein describe the crystal structure of the complex formed by reaction of **5** with two equivalents of Cu(NO<sub>3</sub>)<sub>2</sub>. This complex (**6**) exists as dark green plates, which crystallise in the monoclinic space group P2<sub>1</sub>. Figure 3 shows a perspective view of the structure of this dinuclear complex which contains two copper atoms bridged by ligand **5** with each coordinated to two nitrate anions and a water molecule. The copper atoms are formally five coordinate with distorted square pyramidal geometries, although each has a weak semi-coordinate interaction with a sixth oxygen donor {Cu1-O12 = 2.754(4) Å; Cu2-O32 = 2.709(4) Å} in a pseudo-octahedral environment.

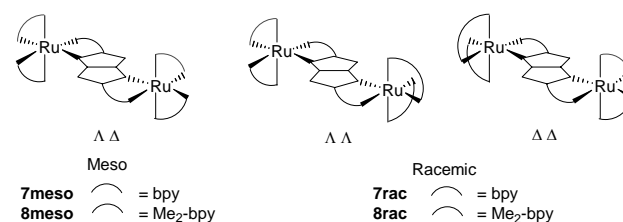
The bridging ligand displays N,N'-chelation, which requires an *s-cis* arrangement of the donors, unlike the free ligand described above. The two copper atoms are separated by 7.560(1) Å. The three ring systems are essentially coplanar, with the meanplanes of the two pyridine rings being twisted only 6.5(2) and 6.2(2)<sup>o</sup> from the plane of the central ring system. The molecular packing involves a complex network of weak intermolecular interactions dominated by hydrogen bonds between each of the water hydrogens and nitrate oxygen atoms of adjacent molecules. Intermolecular  $\pi$ - $\pi$  and CH...O interactions are also observed. Thus, ligand **5** has

been shown to act as a planar, doubly-chelating bridge between two metal centres, albeit with a relatively large metal-metal separation.



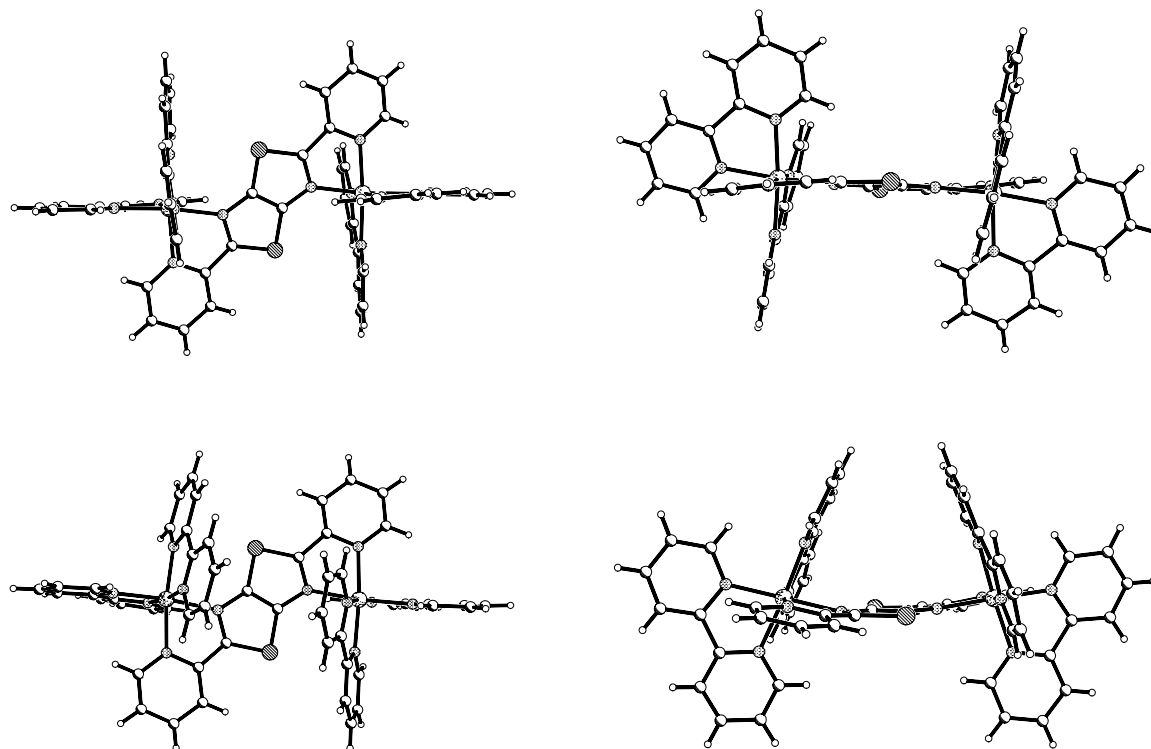
**Fig. 3** The X-ray crystal structure of **6**. Selected bond distances (Å) and angles (<sup>o</sup>): Cu1-N3 2.047(4), Cu1-N1' 2.098(4), Cu1-O11 2.101(3), Cu1-O21 2.295(4), Cu1-O50 1.989(4), N3-Cu1-O50 172.92(19), N3-Cu1-N1' 81.13(16), N1'-Cu1-O50 96.39(17), O11-Cu1-O50 89.50(16), N3-Cu1-O11 89.90(15), N1'-Cu1-O11 153.61(15), O50-Cu1-O21 95.75(18), N3-Cu1-O21 91.32(15), N1'-Cu1-O21 114.03(15), O11-Cu1-O21 90.80(14), Cu2-N3A 2.047(4), Cu2-N1'' 2.087(4), Cu2-O31 2.120(3), Cu2-O41 2.286(4), Cu2-O60 1.995(4), N3A-Cu2-O60 172.39(19), N3A-Cu2-N1'' 80.80(16), N1''-Cu2-O60 95.52(18), O31-Cu2-O60 90.62(16), N3A-Cu2-O31 90.04(15), N1''-Cu2-O31 154.82(14), O60-Cu2-O41 97.79(19), N3A-Cu2-O41 89.80(16), N1''-Cu2-O41 114.29(17), O31-Cu2-O41 88.90(15).

Reaction of ligand **5** with two equivalents of [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] in refluxing 3:1 ethanol:water for 48 hours gave a dinuclear complex (**7**) which was isolated as a hexafluorophosphate salt in 66% yield. As shown in Figure 4, this complex exists as a mixture of two diastereoisomers, a *meso* ( $\Delta/\Delta$ ) form (possessing a centre of inversion) and a *rac* ( $\Delta/\Delta$  and  $\Lambda/\Lambda$ ) form (containing a two-fold rotation axis). Normally such diastereoisomers are formed in a 1:1 ratio.<sup>14</sup> However, <sup>1</sup>H NMR analysis of the product (see below) showed that in this case the two isomers were formed in a 2:1 ratio.



**Fig. 4** Stereoisomeric forms of **7** and **8**.

These diastereoisomers were readily separated by column chromatography on SP Sephadex C-25 cation exchanger with 0.125M sodium toluene-4-sulfonate as the eluent, using techniques pioneered in one of our laboratories.<sup>15</sup> Separation relies on differential interaction of the toluene-4-sulfonate anion leading to different effective charges for the complexes.<sup>16</sup> In this case the major isomer, which was subsequently shown by X-ray crystallography to be the *rac* isomer (**7rac**), eluted first. For analogous complexes it is generally found that the *meso* isomer elutes first, but we have recently found that with bridging ligands such as **5**, that laterally displace



**Fig. 5** Two perspective views of the X-ray structures of **7meso** (top) and **7rac** (bottom), emphasizing the very different shapes of these two diastereoisomeric cations. Hexafluorophosphate counterions and acetonitrile solvate molecules are omitted for clarity. The Ru-N bond lengths lie in the relatively narrow range of 2.031(7)-2.086(7) Å, with the longest bond in each case being to the pyridine nitrogen of the bridging ligand. The *cis*-disposed bond angles lie in the range 77.6(3)-100.8(3)°, with the smallest angles being within the chelate rings. The *trans*-disposed bond angles are in the range 170.7(1)-175.2(1)°.

(“stepped parallel”<sup>14b</sup>) the metal centres relative to the bridging plane, the reverse is sometimes the case.<sup>5b,14b,17</sup> In the present example complete separation was achieved over a very short elution distance.

In order to establish unambiguously the structures of these two isomers, a single crystal X-ray structure determination of each isomer as its hexafluorophosphate salt was carried out. The minor isomer crystallised as small red blocks in the monoclinic space group *C2/c* with half the dinuclear cation, two PF<sub>6</sub><sup>-</sup> anions and an acetonitrile solvate molecule in the asymmetric unit (Figure 5). The other half of the complex is related by a crystallographic centre of inversion at the centre of the bridging ligand. This is the  $\Delta/\Lambda$  isomer (**7meso**), within which the thiazolothiazole ligand acts as a planar bridge between two ruthenium atoms separated by 7.490(1) Å. The bonding geometry about the octahedral ruthenium atoms and within the coordinated ligands is unexceptional. The molecular packing involves numerous weak interactions between the various components, including C-H $\cdots$ F (2.42-2.53 Å) and S $\cdots$ F (3.21-3.32 Å) contacts with the hexafluorophosphate anions.

The major diastereoisomer (**7rac**) crystallises as very small, weakly diffracting plates in the space group *P2<sub>1</sub>/c* with a full dinuclear complex in the asymmetric unit. As shown in Figure 5, the bridging ligand within this complex is significantly non-planar and adopts a bowed shape in order to facilitate  $\pi$ - $\pi$  interactions between two

cofacial bpy-pyridine rings within the complex. This distortion results in a reduction of the inter-metal separation to 7.359(1) Å and leads to a very different overall shape for the two diastereoisomers. This accounts for the ease with which they are separated by chromatography as one can envisage quite different associations of the stereoisomers with the toluene-4-sulfonate anion. The molecular packing involves similar interactions to those described above for the *meso* isomer.

In order to assist with the interpretation of the <sup>1</sup>H NMR spectra of **7**, a second complex (**8**) was prepared by reaction of **5** with [Ru(Me<sub>2</sub>-bpy)<sub>2</sub>Cl<sub>2</sub>] {Me<sub>2</sub>-bpy = 4,4'-dimethyl-2,2'-bipyridine}. Once again the resulting reaction product was readily separated into **8rac** and **8meso** diastereoisomers.

#### Spectroscopic and electrochemical studies of **7** and **8**

The <sup>1</sup>H NMR spectrum of the mixture of diastereoisomers of **7** (Figure 6) shows that they are isolated in a 2:1 ratio of **7rac**:**7meso**. The spectra of the separated isomers each shows a total of 20 aromatic signals corresponding to the five non-equivalent pyridine rings. Despite this complexity these signals were readily grouped into sets corresponding to the individual pyridine rings by means of 1D-TOCSY experiments, as previously described for related complexes.<sup>18</sup> However, distinction between the rings was not possible. In fact, we were unable to

definitively identify the pyridine ring corresponding to the bridging ligand.

In order to resolve this problem the corresponding methyl substituted complex **8** was prepared. Once again the isomers were readily separated. As shown in Figure 7 for the isomer **8meso**, the various pyridine rings in the  $^1\text{H}$  NMR spectrum were assigned into groups which are colour coded. Because of the different spin-spin coupling patterns of the 4-methyl-2-pyridyl rings it was then a

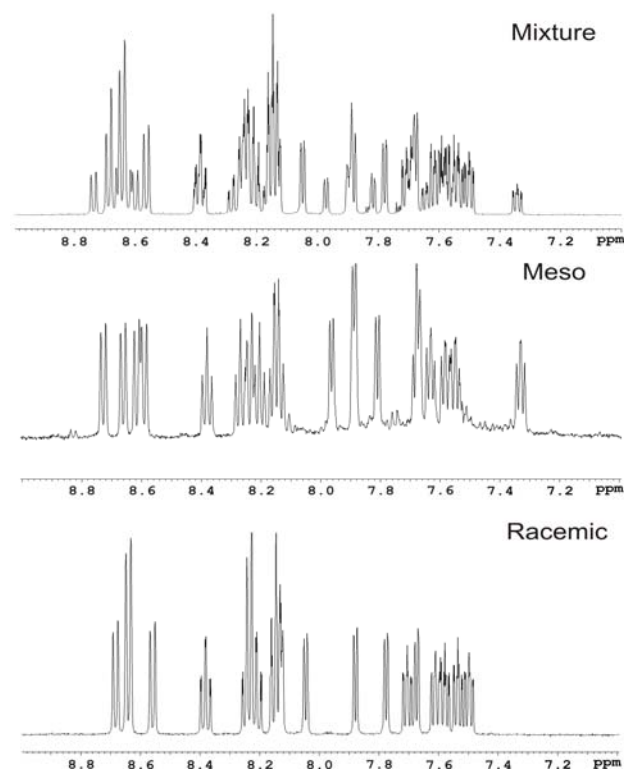


Fig. 6  $^1\text{H}$  NMR spectra of **7**.

Table 1  $^1\text{H}$  NMR chemical shift values for **7** and **8** in  $\text{CD}_3\text{CN}$ .

	H6 (d)	H5 (t)	H4 (t)	H3 (d)
<b>7meso</b> 5-py	7.89	7.58	8.14	8.21
bpy-py	7.96	7.68	8.38	8.73
bpy-py	7.89	7.63	8.27	8.66
bpy-py	7.67	7.55	8.21	8.62
bpy-py	7.81	7.33	8.16	8.59
<b>7rac</b> 5-py	7.87	7.57	8.14	8.24
bpy-py	8.05	7.70	8.38	8.68
bpy-py	8.16	7.61	8.23	8.63
bpy-py	7.66	7.52	8.20	8.63
bpy-py	7.77	7.48	8.12	8.55
	H6 (d)	H5 (d)	H4	H3 (s)
<b>8meso</b> 5-py	7.89	7.57(t)	8.13(t)	8.22(d)
Me <sub>2</sub> -bpy-py	7.77	7.51	-	8.58
Me <sub>2</sub> -bpy-py	7.67	7.45	-	8.51
Me <sub>2</sub> -bpy-py	7.47	7.38	-	8.47
Me <sub>2</sub> -bpy-py	7.62	7.16	-	8.44
<b>8rac</b> 5-py	7.88	7.57(t)	8.13(t)	8.22(d)
Me <sub>2</sub> -bpy-py	7.85	7.54	-	8.53
Me <sub>2</sub> -bpy-py	7.93	7.41	-	8.49
Me <sub>2</sub> -bpy-py	7.45	7.36	-	8.49
Me <sub>2</sub> -bpy-py	7.55	7.31	-	8.42

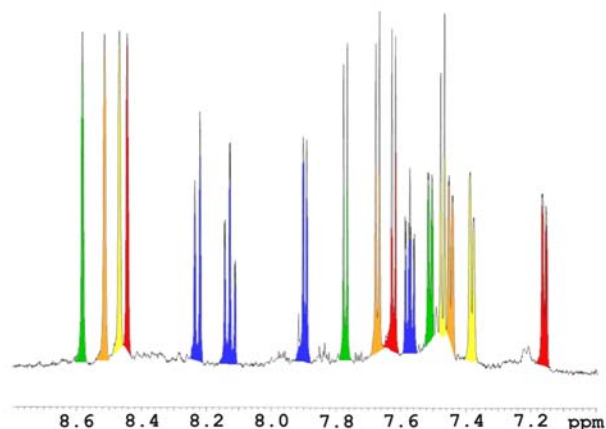


Fig. 7  $^1\text{H}$  NMR spectrum of **8meso**.

simple matter to identify the pyridine ring corresponding to the bridging ligand (coloured blue in Figure 7). The assignments of the various pyridine rings are given in Table 1. Unfortunately, the free ligand **5** was not soluble in a common solvent to the complex and the coordination-induced-shift values could not be calculated.

Electronic absorption spectroscopy and electrochemical studies were used to probe the nature of the metal-ligand and metal-metal interactions in the ruthenium complexes **7** and **8**. The results are summarised in Table 2, along with the corresponding values for  $[\text{Ru}(\text{bpy})_3]^{2+}$ . All four complexes show strong ligand-centred absorptions at around 370 and 390 nm and two metal-to-ligand charge transfer (MLCT) bands at  $> 400$  nm. The stronger of these is near 430 nm, which we attribute to electron transfer into the auxiliary bpy (or Me<sub>2</sub>-bpy) ligands. The lowest energy visible absorption bands are centred at 526 nm for the isomers of **7** and 542 nm for **8**. These represent relatively low energy transitions corresponding to a small HOMO-LUMO energy difference and are assigned to electron transfer into the bridging ligand. The lower energy of the MLCT for **8** compared to **7** reflects the electron donating nature of the methyl groups in the ancillary ligands.

Further insights into the electronic nature of these complexes come from the electrochemical data. Cyclic voltammetry of each of the isomers shows two closely spaced reversible one-electron oxidations. The small difference in oxidation potentials ( $\Delta E_{\text{ox}} = 70\text{-}90\text{mV}$ ) for each isomer indicates relatively weak metal-metal interactions, as measured by the comproportionation constants ( $K_c = 15\text{-}30$ ). The corresponding complexes of ligands **3** and **4** showed<sup>7</sup> much larger  $\Delta E_{\text{ox}}$  values (260-360mV) corresponding to  $K_c$  values in the range  $2.3 \times 10^4 - 1.2 \times 10^6$ . Thus, ligand **5**, with its N,S-mixed heteroatom five-membered ring system, does not facilitate the strong inter-metal interactions observed for ligands **3** and **4**. Furthermore, the significant differences observed in the  $K_c$  values for the two stereoisomers of complexes of **3** and **4** are not observed with the stereoisomers of complexes **7** or **8**. The oxidation potentials of **8** are shifted by about 100mV relative to those of **7**, consistent with the electron-donating effect of about 25mV per methyl group.<sup>19</sup>

**Table 2** Visible absorption maxima<sup>a</sup> and redox potentials<sup>b</sup> for **7** and **8**.

	$\lambda_{\max}$ ( $\epsilon$ ) M $\rightarrow$ S	$\lambda_{\max}$ ( $\epsilon$ ) M $\rightarrow$ bpy	$E_{\text{ox1}}$ [5+/4+]	$E_{\text{ox2}}$ [6+/5+]	$E_{\text{red1}}$ [4+/3+]	$E_{\text{red2}}$ [3+/2+]	$E_{\text{red3}}$ [2+/1+]	$\Delta E_{\text{ox1-red1}}$
<b>7meso</b>	526 (8240)	429 (13,490)	+1.37	+1.45	-0.67 <sup>c</sup>			2.04
<b>7rac</b>	527 (11,290)	428 (17,820)	+1.37	+1.46	-0.69	-1.11	-1.60 (2e)	2.06
<b>8meso</b>	542 (6180)	427 (11,410)	+1.26	+1.33	-0.77 <sup>c</sup>			2.03
<b>8rac</b>	543 (7640)	428 (12,940)	+1.26	+1.35	-0.74	-1.07		2.00
Ru(bpy) <sub>3</sub> <sup>2+</sup>		452 (13,600)	+1.26		-1.33	-1.51	-1.77	2.59

a In nm ( $\text{M}^{-1} \text{cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$  ( $\pm 2\text{nm}$ ). b In V vs SCE in  $\text{CH}_3\text{CN}$  /0.1M  $\text{Bu}_4\text{NPF}_6$ . c Irreversible (quoted as  $E_{\text{p,c}}$ ).

Complexes **7** and **8** show a first reduction potential at *ca.* -0.7V, which for the *meso* isomers are irreversible processes. These are interpreted as electron transfer into the bridging ligand and indicate relatively low energy LUMOs for these complexes. For the *rac* isomers a second reversible reduction is observed at *ca.* -1.1V, which is also believed to involve the bridging ligand. A subsequent two-electron reduction of **7rac** involves electron transfer into the outer bpy ligands.

Thus compared to  $[\text{Ru}(\text{bpy})_3]^{2+}$  these dinuclear complexes have a lower HOMO-LUMO energy gap, as reflected in the  $\lambda_{\max}$  and  $\Delta E_{\text{ox-red}}$  values, but do not display the amplified metal-metal interactions or differences in redox properties of the diastereoisomers that were observed with complexes of **3** and **4**. Finally, the readily synthesised ligand **5** represents a useful new addition to the library of bridging heterocyclic ligands available for use in coordination and metallocsupramolecular chemistry.

## Experimental

### General

<sup>1</sup>H NMR experiments were performed on a Varian INOVA 500 MHz NMR spectrometer at room temperature. <sup>1</sup>H NMR assignments were made with the assistance of 1D-TOCSY experiments to identify each pyridine ring spin system, while individual protons within a ring were assigned on the basis of their chemical shifts and the following typical <sup>3</sup>J coupling patterns for pyridine protons: H3 (d, J = 8 Hz), H4 (t, J = 8 Hz), H5 (dd, J = 8, 5 Hz), H6 (d, J = 5 Hz). Mass spectra were recorded using a Kratos MS80RFA mass spectrometer with a Mach 3 data system. Electron Impact (EI) spectra were obtained at 70 eV with a source temperature of 250°C.

Cyclic voltametric measurements were made on a PAR Model 175 Universal Programmer coupled to a PAR Model 173 potentiostat. Measurements were made of acetonitrile solutions containing *ca.* 1 mmol of complex and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte, using a scan rate of 100 mVs<sup>-1</sup> and a glassy carbon electrode (area 0.07 cm<sup>2</sup>), with a platinum wire as the auxiliary electrode. Ferrocene was used as an internal standard and potentials are given *vs* the saturated calomel electrode [ $E^{\circ}(\text{Fc}/\text{Fc}^+) = 0.31 \text{ V vs SCE}$ ].

Elemental analyses were performed by the Campbell Microanalytical laboratory at the University of Otago.

### Syntheses

#### Preparation of ligand **5**

Dithiooxamide (2.07g, 0.017 mol) was refluxed with excess 2-pyridine carboxaldehyde (8.0ml, 0.084 mol) for 45 min. Hot pyridine was added to dissolve the black solid present in the mixture, and upon cooling the resulting rich brown powder was filtered off. Rectangular orange crystals of the ligand were obtained from slow evaporation of a solution of the ligand in DMF and nitromethane. Yield 0.98 g (19%). Mp 322 °C (lit.<sup>9</sup> mp 325-6). EI mass spectrum: calc. *m/z* for C<sub>14</sub>H<sub>8</sub>N<sub>4</sub>S<sub>2</sub> 296; found 296. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : H6, 8.65; H3, 8.24; H4, 7.84; H5, 7.37.  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>): 362nm,  $\epsilon$  18,570 M<sup>-1</sup> cm<sup>-1</sup>.

#### Preparation of copper complex **6**

A methanolic solution of Cu(NO<sub>3</sub>)<sub>2</sub> (33.1 mg, 0.137 mmol) was layered upon ligand **5** (15.1 mg, 0.051 mmol) in dichloromethane, and the resulting green precipitate was filtered off two days later. Dark green plate-like crystals were obtained by slow evaporation of the mother liquor. Yield 20.1 mg (59%). Mp > 335 °C. Found: C, 25.07; H, 1.13; N, 16.11. Calc for C<sub>14</sub>H<sub>8</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>12</sub>S<sub>2</sub>: C, 25.04; H, 1.20; N, 16.69 %.

#### Preparation and separation of ruthenium complexes **7meso** and **7rac**

Ligand **5** (18.6 mg, 0.063 mmol) and  $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  (52.5 mg, 0.101 mmol) were refluxed in 3:1 EtOH/H<sub>2</sub>O (5ml) for 48 h. After cooling, the solvent was removed *in vacuo*. The sample was redissolved in the minimum of water and filtered to remove unreacted ligand. Addition of aqueous NH<sub>4</sub>PF<sub>6</sub> precipitated the red complex which was then filtered off. Yield 63.2 mg (66%). Found: C, 35.53; H, 2.11; N, 8.41. Calc. For C<sub>54</sub>H<sub>40</sub>N<sub>12</sub>S<sub>2</sub>Ru<sub>2</sub>P<sub>4</sub>F<sub>24</sub>·2H<sub>2</sub>O·2CH<sub>2</sub>Cl<sub>2</sub>: C, 35.23; H, 2.53; N, 8.80%. The sample was dissolved in a large amount of water and loaded onto a cation-exchange column (SP Sephadex C-25). Elution with 0.125 M sodium toluene-4-sulfonate separated the diastereoisomers within 20cm of column length. The collected bands were converted to the PF<sub>6</sub><sup>-</sup> salts by adding NH<sub>4</sub>PF<sub>6</sub> then extracted from the aqueous layer with dichloromethane. This organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and the remaining solvent removed by rotary evaporation. Crystals of **7rac** were grown by slow evaporation of a dichloromethane/acetone solution, while crystals of **7meso** were obtained by evaporation of an acetonitrile solution. <sup>1</sup>H NMR and UV/Vis spectra and electrochemical data are given in Tables 1 and 2.

**Table 3** X-ray crystal data for compounds **5** - **7**.

Compound	<b>5</b>	<b>6</b>	<b>7meso</b>	<b>7rac</b>
Formula	C <sub>14</sub> H <sub>8</sub> N <sub>4</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>12</sub> N <sub>8</sub> O <sub>14</sub> S <sub>2</sub> Cu <sub>2</sub>	C <sub>58</sub> H <sub>46</sub> N <sub>14</sub> F <sub>24</sub> P <sub>4</sub> S <sub>2</sub> R	C <sub>54</sub> H <sub>40</sub> N <sub>12</sub> F <sub>24</sub> P <sub>4</sub> S <sub>2</sub> R
Formula Weight	296.36	707.52	1785.23	1751.12
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
<i>a</i> (Å)	5.7522(7)	7.478(2)	16.237(4)	16.046(3)
<i>b</i> (Å)	6.2611(7)	16.096(5)	20.003(5)	25.921(4)
<i>c</i> (Å)	17.442(2)	10.468(3)	21.200(5)	16.712(3)
β (°)	94.017(2)	98.084(4)	101.414(3)	94.061(2)
<i>V</i> (Å <sup>3</sup> )	626.62(13)	1247.5(6)	6749.45(3)	6933.5(19)
Space Group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Z</i>	2	2	4	4
D <sub>c</sub> (Mg m <sup>-3</sup> )	1.571	1.884	1.757	1.678
<i>F</i> (000)	304	708.0	3552.0	3408.0
Temperature (K)	168(2)	168(2)	168(2)	168(2)
Crystal Form	orange block	green plate	red block	red plate
Crystal Size (mm)	0.38 x 0.10 x 0.03	0.33 x 0.31 x 0.08	0.43 x 0.11 x 0.05	0.28 x 0.28 x 0.01
μ (mm <sup>-1</sup> )	0.418	1.957	0.722	0.704
2θ <sub>max</sub> (°)	52.73	52.69	52.85	45.00
Reflections collected	7550	13814	41113	64134
Unique reflections	1279	4642	6870	9024
Parameters	91	373	507	915
GooF	1.019	1.001	1.024	1.004
R <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0316	0.0363	0.0299	0.0589
wR <sup>b</sup> (all data)	0.0788	0.0913	0.0703	0.1751

$$^a R = \sum |F_o| - |F_c| / \sum |F_o| \quad ^b wR = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)])^{1/2}$$

#### Preparation and separation of ruthenium complexes **8meso** and **8rac**

Ligand **5** (16.4 mg, 0.055 mmol) and [Ru(Me<sub>2</sub>-bpy)<sub>2</sub>Cl<sub>2</sub>] (57.6 mg, 0.112 mmol) were refluxed in 3:1 EtOH/H<sub>2</sub>O (5ml) for 46 h, and isolated as described above. Yield 69.1 mg (69%). To increase solubility in water, the crude product was converted to the chloride salt before separation of the diastereoisomers as described above. Red block crystals were obtained of both diastereoisomers from acetone/acetonitrile solutions.

#### X-Ray Crystallography

The crystal data, data collection and refinement parameters for compounds **5-7** are given in Table 3. Measurements were made with a Siemens CCD area detector using graphite monochromatised Mo Kα (λ = 0.71073 Å) radiation. The intensities were corrected for Lorentz and polarisation effects and for absorption.<sup>20</sup> The structures were solved by direct methods using SHELXS,<sup>21</sup> and refined on *F*<sup>2</sup> using all data by full-matrix

least-squares procedures using SHELXL-97.<sup>22</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters, except for three water solvate molecules disordered over eight positions in the structure of **7rac**. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbon atoms. The functions minimised were Σ*w* (*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>), with *w* = [σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + *aP*<sup>2</sup> + *bP*]<sup>-1</sup>, where *P* = [max(*F*<sub>o</sub><sup>2</sup>) + 2*F*<sub>c</sub><sup>2</sup>]/3.

Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre (CCDC No 247013 - 247016). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### Acknowledgements

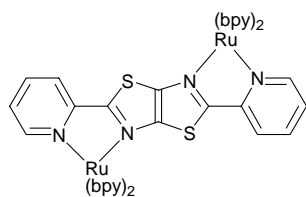
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## Graphical Content



### **Diastereoisomeric dinuclear ruthenium complexes of 2,5-di(2-pyridyl)thiazolo[5,4-*d*]thiazole**

Jennifer A. Zampese, F. Richard Keene and Peter J. Steel

The *meso* and *racemic* diastereoisomers of the dinuclear ruthenium complexes of the title ligand have been separated and shown to have very similar spectroscopic and redox properties with only weak metal-metal interactions.



