

Doping ruthenium complexes into a molecular spin-crossover material



Laurence J. Kershaw Cook, Malcolm A. Halcrow*

School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

ARTICLE INFO

Article history:

Received 19 August 2014

Accepted 23 October 2014

Available online 30 October 2014

Keywords:

Iron

Ruthenium

N-donor ligands

Spin-crossover

Magnetic measurements

ABSTRACT

Two ruthenium compounds, $[\text{Ru}(\kappa^3\text{C},\text{N},\text{C-bip})_2][\text{BF}_4]_2$ (bip = 2,6-di{1-methylimidazol-2-ylidene-3-yl}pyridine) and $[\text{Ru}(\text{terpy})(\kappa^3\text{N},\text{N},\text{C-terpy}^*)][\text{BF}_4]_2$ (terpy = 2,2':6',2''-terpyridine and terpy* = 2,2':6',4''-terpyridine), have been investigated as dopants for the spin-crossover lattice $[\text{Fe}(\text{bpp})_2][\text{BF}_4]_2$ (bpp = 2,6-di{pyrazol-1-yl}pyridine). While $[\text{Fe}(\text{bpp})_2][\text{BF}_4]_2$ and $[\text{Ru}(\text{bip})_2][\text{BF}_4]_2$ did not co-crystallize, five different compositions of solid solutions $[\text{Fe}(\text{bpp})_2]_x[\text{Ru}(\text{terpy})(\text{terpy}^*)]_{1-x}[\text{BF}_4]_2$ were prepared, with $0.96 \geq x \geq 0.13$. The materials with intermediate compositions ($0.58 \geq x \geq 0.28$) contained a mixture of crystalline and amorphous material by powder diffraction. The spin-crossover midpoint temperature ($T_{1/2}$) in $[\text{Fe}(\text{bpp})_2]_x[\text{Ru}(\text{terpy})(\text{terpy}^*)]_{1-x}[\text{BF}_4]_2$ decreases smoothly with x , as the larger ruthenium dopant expands the host lattice and stabilizes its high-spin state. That contrasts with our previously published materials $[\text{Fe}(\text{bpp})_2]_2[\text{Ru}(\text{terpy})_2]_{1-2}[\text{BF}_4]_2$, which show a more complicated relationship between $T_{1/2}$ and their composition.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The continued world-wide interest in thermally and optically switchable spin-crossover compounds [1–3] reflects their use as switching centers in nanoscience [4], as contrast agents for magnetic resonance imaging [5], as reported groups in solid state and solution-phase sensors [6,7], and in thermochromic devices [8]. A current challenge is to prepare multifunctional materials, that use spin-crossover switching to modulate another physical property in a bulk material, or at the molecular level [9]. Thus, for example, spin-crossover complexes or hybrid materials exhibiting semiconductor [10], fluorescence [11], magnetic ordering [12] and mesophase functionalities [13] have all been obtained. In some of these cases the effect of spin-crossover on the ancillary property is small, but this remains a promising method for the production of switchable molecule-based materials.

Five years ago we introduced a new approach to this goal, of doping molecular spin-crossover materials with other functional complexes. Our initial work has produced homogeneous solid solutions of $[\text{Fe}(\text{bpp})_2][\text{BF}_4]_2$ (bpp = 2,6-di{pyrazol-1-yl}pyridine) [14] with $[\text{M}(\text{terpy})_2][\text{BF}_4]_2$ complexes (terpy = 2,2':6',2''-terpyridine; M = Ru [15,16], Co [16,17] or Cu [18]; Scheme 1). This work afforded solid materials exhibiting both spin-crossover and fluorescence, albeit at different temperatures [15], and the first observation of allosteric switching of two different spin-crossover

centers in the same material [17]. The $[\text{Fe}(\text{bpp})_2][\text{BF}_4]_2$ host and $[\text{M}(\text{terpy})_2][\text{BF}_4]_2$ dopants are particularly suited to each other because they have the same molecular symmetry and charge balance; their cations are similar (but not identical) in size and shape; and, although they are not isostructural, the two compounds adopt the same type of “terpyridine embrace” crystal packing motif [15].

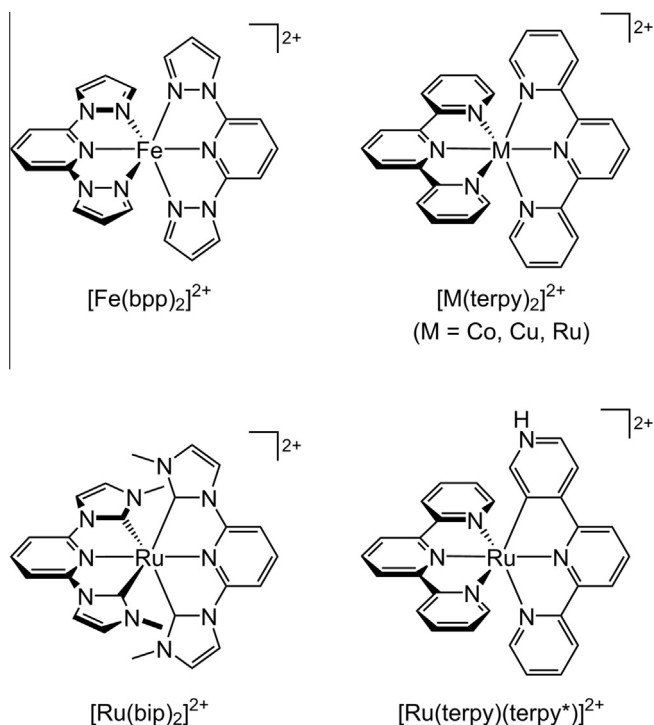
As a continuation of this work, we were interested to see what other dopant complexes we could incorporate into $[\text{Fe}(\text{bpp})_2][\text{BF}_4]_2$. We report here an investigation of two other dopant compounds, $[\text{Ru}(\text{bip})_2][\text{BF}_4]_2$ (bip = 2,6-di{1-methylimidazol-2-ylidene-3-yl}pyridine) [19] and $[\text{Ru}(\text{terpy})(\text{terpy}^*)][\text{BF}_4]_2$ (terpy* = 2':6',4''-terpyridine; Scheme 1) [20]. These dopants were selected because they are significantly more emissive than $[\text{Ru}(\text{terpy})_2]^{2+}$ at room temperature, which could lead to doped materials showing improved fluorescence properties. In addition, although they have the same symmetry and charge, the shapes of these dopant molecules differ more strongly from $[\text{Fe}(\text{bpp})_2]^{2+}$ than the $[\text{M}(\text{terpy})_2]^{2+}$ dopants we have used up to now. Hence this study also provides an important test of the flexibility of our dopant approach to multifunctional spin-crossover materials.

2. Experimental

The syntheses of 2,6-di(1'-methylimidazolium-3'-yl)pyridine dibromide ($[\text{bipH}_2]\text{Br}_2$) [19], 2,2':6',4''-terpyridine (terpy*) [20], $[\text{RuCl}_3(\text{terpy})]$ [21] and $[\text{Fe}(\text{bpp})_2][\text{BF}_4]_2$ [15] followed the literature procedures. All other manipulations were carried out in air, using reagent-grade solvents.

* Corresponding author. Tel.: +44 113 343 6506; fax: +44 113 343 6565.

E-mail address: m.a.halcrow@leeds.ac.uk (M.A. Halcrow).



Scheme 1. The compounds referred to in this work.

2.1. Synthesis of [Ru(bip)₂][BF₄]₂

A solution of RuCl₃·3H₂O (0.10 g, 0.39 mmol) and [bipH₂]Br₂ (0.31 g, 0.78 mmol) in ethylene glycol (7 cm³) was held at 190 °C for 4 h. After cooling water was added (10 cm³), and the solution was then saturated with NaBF₄. Stirring for 30 min yielded a yellow precipitate which was collected, washed in succession with H₂O, MeOH and Et₂O and dried *in vacuo*. Yield 0.12 g, 41%. *Anal.* Calc. for C₂₆H₂₆B₂F₈N₁₀Ru·H₂O: C, 40.5; H, 3.66; N, 18.2. Found: C, 40.8; H, 3.40; N, 18.3%. ES MS *m/z* 290.1 [Ru(bip)₂]²⁺. ¹H NMR (CD₃NO₂) δ 2.74 (s, 12H, CH₃), 7.02 (d, 2.3 Hz, 4H, Im H⁵), 7.91 (d, 8.3 Hz, 4H, Py H^{3/5}), 8.04 (d, 2.3 Hz, 4H, Im H⁴), 8.28 (t, 8.1 Hz, 2H, Py H⁴). ¹³C NMR (CD₃NO₂) δ 36.4 (4C, CH₃), 107.0 (4C, Im C⁵),

117.5 (4C, Py H^{3/5}), 125.4 (4C, Im C⁴), 138.9 (4C, Py C²), 153.0 (2C, Py H⁴), 192.0 (4C, Im C²). UV/Vis (MeCN) λ_{max}, nm (ε_{max}, 10³ dm³ mol⁻¹ cm⁻¹) 236 (45.3), 273 (34.9), 280 (sh), 345 (14.1), 383 (19.0), 415 (sh). Fluorescence (MeCN, excitation wavelength 383 nm) λ_{max}^{em} 531 nm.

2.2. Synthesis of [Ru(terpy)(terpy*)]₂[BF₄]₂

Solid terpy* (0.18 g, 0.78 mmol) was added to a suspension of [RuCl₃(terpy)] (0.34 g, 0.78 mmol) in ethylene glycol (15 cm³) and the mixture was then heated to reflux for 30 min. After cooling to room temperature the solution was filtered, and saturated aqueous NaBF₄ (150 cm³) was added to the filtrate which resulted in precipitation of the complex which was collected by filtration. The dark purple complex was recrystallized from MeNO₂/Et₂O. Yield 0.45 g, 77%. *Anal.* Calc. for C₃₀H₂₂B₂F₈N₆Ru·MeNO₂·H₂O: C, 45.4; H, 3.32; N, 10.8. Found: C, 45.2; H, 3.00; N, 11.2%. ES MS *m/z* 284.0 [Ru(terpy)(terpy*)]²⁺, 567.1 [Ru(terpy)(terpy* - H)]⁺. ¹H NMR (CD₃CN) δ 7.05 (s, 1H, H^{2*}), 7.06 (ddd, 1.3, 5.6 and 7.3 Hz, 2H, H⁵), 7.17 (ddd, 1.3, 5.2 and 7.3 Hz, 1H, H^{5*}), 7.29 (ddd, 0.9, 1.7 and 5.6 Hz, 2H, H⁶), 7.52 (ddd, 0.9, 1.7 and 5.2 Hz, 1H, H^{6*}), 7.82 (pseudo-td, 1.7 and 7.3 Hz, 2H, H⁴), 7.93 (pseudo-td, 1.7 and 7.7 Hz, 1H, H^{4*}), 7.95 (dd, 1.3 and 6.0 Hz, 1H, H^{6*}), 8.17 (d, 6.0 Hz, 1H, H^{5*}), 8.22 (t, 8.1 Hz, 1H, H⁴), 8.25 (t, 8.1 Hz, 1H, H^{4*}), 8.43 (ddd, *J* = 0.8, 1.6 and 8.2 Hz, 2H, H³), 8.51 (ddd, 0.9, 1.2 and 8.3 Hz, 1H, H^{3*}), 8.61 (dd, 0.9 and 8.1 Hz, 1H, H^{5*}), 8.65 (d,

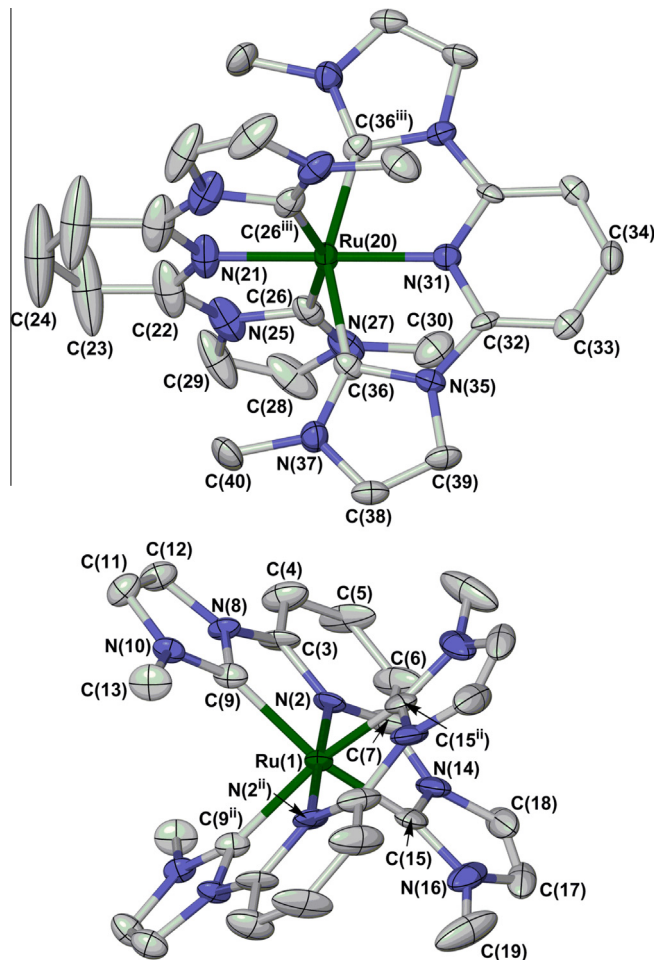


Fig. 1. The two unique complex molecules in the crystal structure of [Ru(bip)₂][BF₄]₂·0.75CH₃NO₂. Displacement ellipsoids are at the 50% probability level, and H atoms are omitted for clarity. The large displacement ellipsoids on C(23) and C(24) reflect librational disorder, caused by a close intermolecular C...C contact to the disordered solvent. Symmetry codes: (ii) -x, y, ½ - z; (iii) 1 - x, y, ½ - z.

Table 1

Experimental details for the single crystal structure determination of [Ru(bip)₂][BF₄]₂·0.75CH₃NO₂.

Formula	C _{26.75} H _{28.25} B ₂ F ₈ N _{10.75} O _{1.50} Ru
<i>M_r</i>	799.04
Crystal system	monoclinic
Space group	C2/c
<i>a</i> (Å)	17.1318(14)
<i>b</i> (Å)	21.361(2)
<i>c</i> (Å)	18.508(2)
β (°)	99.124(9)
<i>V</i> (Å ³)	6687.6(11)
<i>Z</i>	8
<i>D_{calc}</i> (g cm ⁻³)	1.587
μ (Mo Kα, mm ⁻¹)	0.556
<i>T</i> (K)	100(2)
Measured reflections	15014
Independent reflections	7491
<i>R_{int}</i>	0.104
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	4088
Data, restraints, parameters	7491, 12, 483
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a , <i>wR</i> ₂ (all data) ^b	0.091, 0.180
Goodness-of-fit (GOF)	1.041
Δρ _{min} , Δρ _{max} (e Å ⁻³)	-0.95, 0.85

^a *R* = Σ[|*F_o*| - |*F_c*|]/Σ|*F_o*|.

^b *wR* = [Σ*w*(*F_o*² - *F_c*²)/Σ*wF_c*⁴]^{1/2}.

Download English Version:

<https://daneshyari.com/en/article/1337343>

Download Persian Version:

<https://daneshyari.com/article/1337343>

[Daneshyari.com](https://daneshyari.com)