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*Published in:*  
 Inorganic Chemistry

*DOI:*  
[10.1021/ic010473m](https://doi.org/10.1021/ic010473m)

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*Document Version*  
 Publisher's PDF, also known as Version of record

*Publication date:*  
 2001

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*Citation for published version (APA):*

Browne, WR., O'Connor, CM., Villani, C., & Vos, JG. (2001). Separation and photophysical properties of the Delta Delta, Lambda Lambda, Delta Lambda, and Lambda Delta stereoisomers of a dinuclear ruthenium(II) complex. *Inorganic Chemistry*, 40(21), 5461-5464. <https://doi.org/10.1021/ic010473m>

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# Notes

## Separation and Photophysical Properties of the $\Delta\Delta$ , $\Lambda\Lambda$ , $\Delta\Lambda$ , and $\Lambda\Delta$ Stereoisomers of a Dinuclear Ruthenium(II) Complex

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Received May 4, 2001

### Introduction

As interest in both polynuclear and asymmetric ruthenium(II) complexes increases, so too does the issue of isomerism, in terms of both connectivity<sup>1,2</sup> and stereochemistry.<sup>3–5</sup> Since through-space interactions are often as significant as through-bond interactions,<sup>6</sup> obtaining inorganic complexes with well-defined spatial and electronic structures is viewed as a prerequisite for the successful development of molecular devices. Ruthenium(II) polypyridyl complexes have been extensively investigated for their photochemical, photophysical, and molecular recognition properties, and a wide range of multinuclear complexes based on 2,2'-bipyridyl (bpy) and related ligands have been prepared.<sup>7,8</sup> It has been recognized for some time that the use of bidentate ligands results in formation of stereoisomers.<sup>3</sup> The importance of stereochemistry and, in particular, chirality is well illustrated in the studies carried out on the stereoselective intercalation of ruthenium polypyridyl complexes into DNA<sup>4,9,10</sup> and proteins.<sup>11</sup> The isolation of the stereoisomers of mono- and polynuclear ruthenium(II) and osmium(II) diimine complexes has been reviewed recently.<sup>3</sup> The more common approaches used in preparing stereochemically pure systems can be

described as: reagent induced stereochemical control,<sup>12–14</sup> the use of chiral precursors,<sup>15–18</sup> chromatographic techniques,<sup>10,19–26</sup> recrystallization,<sup>27,28</sup> or a combination of these.

There are however relatively few studies which address the relationship between stereochemistry and the photophysical properties of ruthenium(II) and osmium(II) polypyridyl complexes, and to the best of our knowledge, no studies have been carried out in chiral solvents. Several studies suggest that enantiomers exhibit no observable differences in their electrochemical or electronic properties. In addition only minor, if any, differences in the properties of diastereoisomers have been reported.<sup>20–24,28–30</sup> However, Heseck et al.<sup>13</sup> have reported a significant difference in the UV–Vis spectra of the diastereoisomers of the complex  $[\text{Ru}(\text{bpy})_2\text{Cl}(\text{L})]^+$  (where L = (R)-(+)- or (S)-(–)-methyl-*p*-tolyl sulfoxide), while Keene and co-workers<sup>23</sup> have reported significant differences in luminescence lifetimes between the meso- and homochiral isomers for the dinuclear  $[(\text{Ru}(\text{bpy})_2)_x\text{HAT}]^{2x+}$  complex<sup>23a</sup> (where  $x = 1–3$ , LL = 2,2'-bipyridine or 1,10-phenanthroline, and HAT = 1,4,5,8,9,12-hexaazatriphenylene) and for the charge separated states of a series of four geometric isomers of a ruthenium(II) mononuclear chromophore quencher system<sup>23b</sup>.

In this contribution, the separation, <sup>1</sup>H NMR spectra, and photophysical properties of the four stereoisomers (**1a–d**) of the complex  $[(\text{Ru}(\text{bpy})_2)_2(\text{bpt})](\text{PF}_6)_3$  are reported. (For structure of complex see Figure 1). To assess the importance of stereochemistry on the photophysical properties of the four

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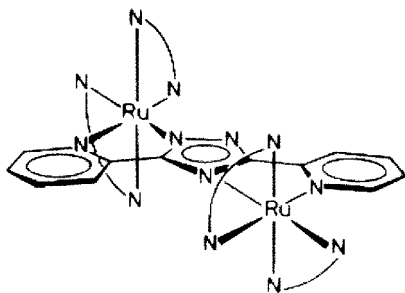
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**Figure 1.** Structure of one of the four stereoisomers of **1**.

stereoisomers, the electronic spectra and emission lifetimes were measured in both racemic and enantiomerically pure 1-phenylethanol, at 298 and 77 K.

### Experimental Section

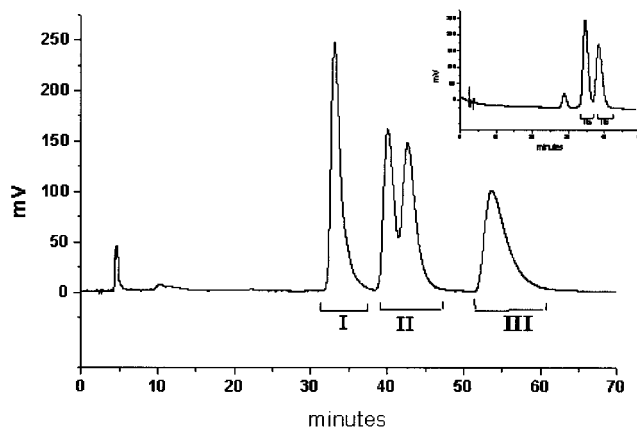
**Materials.** All solvents used for spectroscopic measurements were of Uvasol (Merck) grade. Racemic and enantiomerically pure  $\{(S)-(-)\}$  1-phenyl-ethanol (Aldrich) were used as received. The synthesis and purification of  $[(Ru(bpy)_2)_2(bpt)](PF_6)_3$  (**1** (bpy = 2,2'-bipyridine, Hbpt = 3,5-bis(pyridin-2-yl)-1*H*-1,2,4-triazole)) were carried out using previously reported methods.<sup>2</sup>

**Chromatography.** Separation of the four stereoisomers of **1** was achieved with semipreparative HPLC using a chiral stationary phase (CSP 1) containing Teicoplanin bonded to silica gel microparticles,<sup>31,32</sup> packed in a  $250 \times 10$  mm I.D. column. A Waters Delta Prep 3000 preparative HPLC apparatus, equipped with Knauer UV and RI detectors and a 7010 Rheodyne injector, was employed for the separation. Analytical control of the collected fractions was carried out on a Waters 2690 Separation Module equipped with a UV 481 detector set at 288 nm. Samples of **1** were dissolved in the eluent (40 mg/mL) and filtered through a 0.45 micron filter prior to injection. Typical column loadings were 20–30 mg per run, using  $CH_3CN/RCH_2OH/AcONH_4$  0.5 M 60/20/20 mobile phase (where R = H or  $CH_3$ ).

**Spectroscopy.**  $^1H$  NMR Spectra were obtained in  $[D_3]$ acetonitrile or  $[D_6]$ acetone and recorded on a Bruker AC400 (400 MHz) NMR spectrometer. UV–vis absorption spectra (accuracy  $\pm 2$  nm) were recorded on a Shimadzu UV–vis–NIR 3100 spectrophotometer interfaced with an Elonex PC466, using UV–vis data manager. Emission spectra (accuracy  $\pm 5$  nm) were recorded at 298 and 77 K using a Perkin-Elmer LS50B luminescence spectrophotometer, which was equipped with a red sensitive Hamamatsu R298 PMT detector and interfaced with an Elonex PC466 employing Perkin-Elmer FI WinLab custom built software. Emission and excitation slit widths were 5 nm at 77K and 10 nm at 298 K. Emission spectra are uncorrected for photomultiplier response. 10 or 2 mm path length quartz cells were used for recording spectra. Emission measurements at 77 K were carried out in a liquid nitrogen filed glass cryostat, with the sample held in a borosilicate NMR tube.

**Circular Dichroism (CD) Spectroscopy.** CD spectra of the four stereoisomers were recorded on a Jasco J-710 spectropolarimeter in  $CH_3CN$  at 25 °C. For these measurements, impure fractions were reprocessed by HPLC on the chiral stationary phase to obtain single stereoisomers with greater than 99% purity. After removal of the solvent at reduced pressure, complexes **1a–d** were dissolved in water and converted to their  $PF_6$  salts by addition of a concentrated solution of  $KPF_6$ . Acetonitrile solutions of the complexes **1a–d** (as  $PF_6$  salts) were used at concentrations in the  $5\text{--}8 \times 10^{-6}$  M range.

**Emission Lifetime Measurements.** Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) time-correlated single-photon counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900



**Figure 2.** Chromatogram of  $[(Ru(bpy)_2)_2(bpt)]^{3+}$  on CSP1. The insert shows the chromatogram obtained for the separation of the heterochiral isomers.

**Table 1.** Yield, Estimated Purity, and Emission Lifetimes (Samples Deaerated by 20 min Ar Purge) of the Separated Stereoisomers of Complex **1**

	yield/mg <sup>a</sup> (impurities) <sup>b</sup>	<i>rac</i> -1-phenylethanol ( $\tau$ /ns)	<i>(S)</i> -(-)-1-phenylethanol ( $\tau$ /ns)
<b>1a</b>	17(—)	146	163
<b>1b</b>	11(4% of <b>1a</b> )	145 (145 <sup>c</sup> )	156
<b>1c</b>	21(27% of <b>1b</b> )	144	155
<b>1d</b>	15(4% of <b>1c</b> )	140	156

<sup>a</sup> Total mass of isomer recovered. <sup>b</sup> Impurities as a % of peak area relative to the peak due to the main stereoisomer. <sup>c</sup> Sample degassed by four freeze–pump–thaw degassing cycles.

nanosecond flashlamp ( $N_2$  filled at 1.1 atm pressure, 40 kHz) interfaced with a personal computer via a Norland MCA card. A 500 nm cut off filter was used in emission to attenuate scatter of the excitation light (337 nm); luminescence was monitored at 640 nm. Data correlation and manipulation was carried out using EAI F900 software version 5.1.3. Samples were deaerated for 20 min using Argon prior to measurements followed by repeated purging to ensure complete oxygen exclusion. Emission lifetimes were calculated using a single-exponential fitting function, Levenberg–Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced  $\chi^2$  and residual plots were used to judge the quality of the fits. Lifetimes are  $\pm 5\%$ .

### Results and Discussion

**Chromatographic Resolution of Stereoisomers.** The analytical separation of the stereoisomers of **1** has been reported in an earlier study.<sup>32</sup> The separation of the stereoisomers was carried out on a semipreparative scale in two steps. In a first set of the separations (Figure 2), using  $CH_3CN/CH_3OH/AcONH_4$  0.5 M 60/20/20 as eluent delivered at a flow rate of 4 mL/min, three fractions were collected. The first contained one of the homochiral stereoisomers **1a** (fraction I), the second contained the two heterochiral stereoisomers **1b** and **1c** (fraction II), and the last fraction contained the second homochiral stereoisomer **1d** (fraction III) (see Figure 2). In a second set of separations (see Figure 2, inset), the two heterochiral stereoisomers, collected as fraction II, were resolved using a different eluent ( $CH_3CN/CH_3CH_2OH/AcONH_4$  0.5 M 60/20/20), yielding fractions IIa (**1b**) and IIb (**1c**). Yields from four replicate runs and a purity check are described in Table 1. Purity was estimated by integration of chromatogram peak areas, with control analytical runs being carried out. With the exception of I, the preceding peak contaminated each fraction.

**Circular Dichroism.** On the basis of single wavelength CD detection of the HPLC traces, the two homo- and heterochiral

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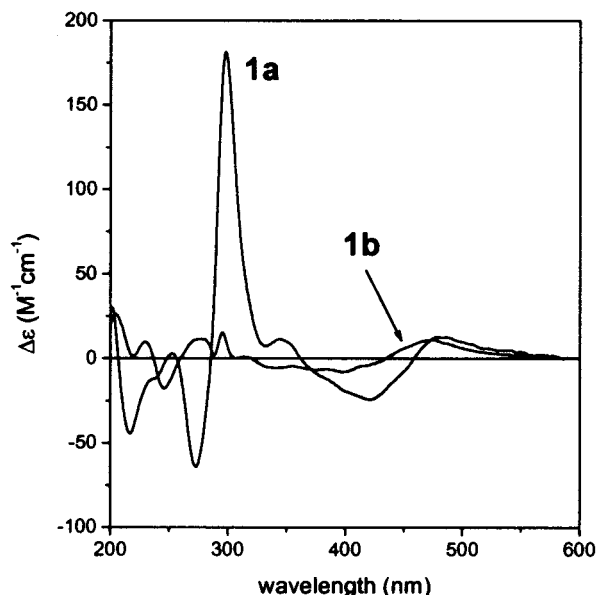


Figure 3. CD spectra of **1a** and **1b** measured in CH<sub>3</sub>CN.

isomers are identifiable.<sup>32</sup> The CD spectra of the **1a** and **1b** (Figure 3) further suggest that the  $\Lambda\Lambda$  isomer (**1a**) is obtained as the first fraction, followed by the two heterochiral isomers, and finally the  $\Delta\Delta$  (**1d**) isomer, on the basis of comparison with the CD spectra of [Ru(LL)<sub>3</sub>]<sup>2+</sup> (where LL = 2,2'-bipyridine or 1,10-phenanthroline) and the known selectivity of the Teicoplanin packing material for the  $\Delta$  isomer over the  $\Lambda$  isomer of these tris-homoleptic complexes.<sup>32</sup> Since for the present semi-preparative separation the same stationary phase, packed into a 10 mm I.D. column, that was employed for analytical separation was used, the same elution order is obtained. The stereoisomers of **1** are named in accordance with previously assigned labels as homochiral ( $\Lambda\Lambda$  (**1a**) and  $\Delta\Delta$  (**1d**)) and heterochiral ( $\Lambda\Delta/\Delta\Lambda$ , **1b/1c**).<sup>32</sup> The origin of the differences, which allow for resolution of the heterochiral stereoisomers, is the inherent asymmetry of the complex. The N2 and N4 coordination sites of the triazole ring are nonequivalent, and hence, the  $\Delta\Lambda$  and  $\Lambda\Delta$  stereoisomers form an enantiomeric pair. Fractions IIa and IIb cannot be assigned to either of the two heterochiral isomers (**1b/1c**).

CD spectra of **1a** and **1d** (and those of **1b** and **1c**) show a mirror image relationship as expected for enantiomeric pairs. The spectrum of **1a** is very similar to that of the parent mononuclear [Ru(bpy)<sub>3</sub>]<sup>2+</sup> having  $\Lambda$  configuration,<sup>5</sup> thus confirming the original assignment of  $\Lambda\Lambda$  configuration to the first eluted homochiral complex. The two diagnostic couplets for the  $\Lambda$  configuration were found in the LCT (ligand centered transition) (272 nm negative and 298 nm positive) and MLCT (421 nm negative and 480 nm positive) regions. There is no significant mutual influence of the two chromophoric units of **1a**, and the spectrum of **1a** is simply the sum of that of two mononuclear units. The original heterochiral assignment to **1b** and **1c** is confirmed by their CD spectra. The spectrum of **1b** shows very weak bands, especially in the LCT region, presumably as a result of the near complete compensation of the two metal centers of opposite chirality.

**<sup>1</sup>H NMR Spectroscopy.** The <sup>1</sup>H NMR spectra obtained for the stereoisomers **1a** and **1b** are shown in Figure 4. The spectra obtained are in agreement with those reported by Hage et al.<sup>2</sup> for materials obtained from fractional crystallization. The nature of the two species obtained was at that stage, however, uncertain.<sup>2</sup> As expected, the <sup>1</sup>H NMR spectra of the homochiral

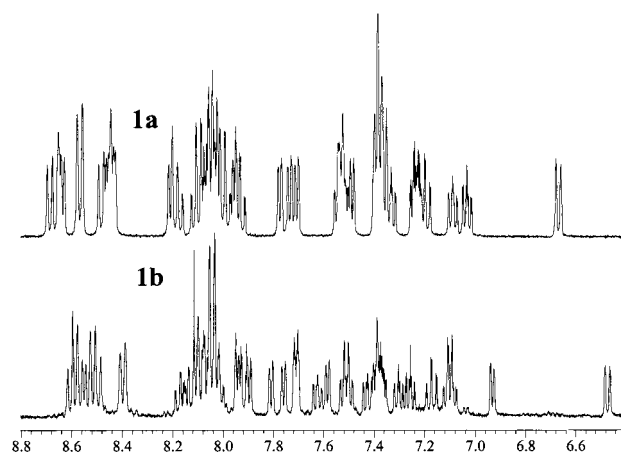


Figure 4. <sup>1</sup>H NMR Spectra of **1a** (homochiral isomer  $\Lambda\Lambda$ ) and **1b** (heterochiral isomer  $\Lambda\Delta$ ) in [D<sub>3</sub>]acetonitrile.

stereoisomers **1a** and **1d** ( $\Lambda\Lambda$  and  $\Delta\Delta$ ) are identical, as are the spectra of the heterochiral stereoisomers **1b** and **1c** ( $\Lambda\Delta$  and  $\Delta\Lambda$ ). The spectra obtained are assignable using <sup>1</sup>H COSY techniques and are in full agreement with previously reported assignments.<sup>2</sup> Since there is substantial through space interaction between the bridging ligand and the bpy rings and between the bpy ligands themselves, the complexity of this spectrum does not allow for a detailed discussion of the differences observed. It is, however, clear that the fractions obtained by Hage et al. can be assigned as the homochiral and heterochiral enantiomeric pairs.<sup>2</sup>

**Electronic Properties.** It is surprising that despite the considerable interest in stereochemical control of ruthenium(II) and osmium(II) complex, few studies of the differences in photophysical properties between stereoisomers have been reported, and to the authors knowledge, no comparative study of the emissive properties of enantiomeric pairs and diastereoisomers in racemic and enantiomerically pure environments has been carried out. The photophysical properties of the four stereoisomers of **1** have been examined in racemic 1-phenylethanol, (*S*)-(-)-1-phenylethanol, and acetonitrile (butyronitrile at 77 K). The 1-phenylethanol was chosen as a solvent for two reasons. First, the solvent is inherently chiral and can be obtained in enantiomerically pure form. Second, the presence of a phenyl group and a hydroxy moiety allows for the possibility of a  $\pi$ -stacking interaction and hydrogen bonding interaction between the pyridyl rings of the complex and the solvent phenyl group and hydroxy group, respectively. That such interactions may occur has been observed both intermolecularly by Patterson et al.<sup>25</sup> and intramolecularly by Heseck et al.<sup>13</sup> In both *rac*- and (*S*)-(-)-1-phenylethanol, no significant changes in the electronic spectra were obtained; the absorption and emission maxima for all four isomers was within experimental error ( $\pm 2$  nm) at 452 and 640 nm, respectively, with no differences in band shape. At 77 K in butyronitrile, a value of 610 and 604 nm in both *rac*- and (*S*)-(-)-1-phenylethanol ( $\pm 5$  nm) was observed for all stereoisomers. The emission lifetime data at 298 K for **1a-d** in 1-phenylethanol are presented in Table 1. No significant differences were observed between the lifetimes of the four stereoisomers. The values given in Table 1 are average values for a set of four measurements each, and no differences greater than the experimental error were observed between measurements. The slight increase in lifetime observed in (*S*)-(-)-1-phenylethanol compared with the racemic solvent is probably due to different H<sub>2</sub>O contents in the solvents employed. In each case, measurements were recorded under identical conditions

of solvent and temperature. To confirm that deaeration using argon gas was sufficient in precluding any excited-state quenching by oxygen, the heterochiral **1b** was subjected to four freeze–pump–thaw degassing cycles prior to the lifetime measurements being made. No difference was observed using either method of deoxygenation.

The excited  $^3\text{MLCT}$  state of  $[\text{Ru}(\text{bpy})_3]^{2+}$  is known to possess a considerable amount of charge transfer to solvent character (CTTS),<sup>33</sup> and this is expected to be the case for other ruthenium(II) polypyridyl complexes. Hence, for the system under examination, excited-state interaction with the solvent would be expected to be substantial. The use of chiral solvents amenable to intermolecular interactions such as  $\pi$ -stacking and hydrogen bonding could, in principle, effect the electronic structure of stereoisomers of transition metal complexes. However, for such interactions to produce measurable differences in the photophysical properties of such complexes, the interactions must be sufficiently strong/nonrandom to affect the complex over the time scale of the lifetime of the excited states of such molecules. Since in fluid solutions and glassy matrixes the randomness of the solvent orientation around the complex would be almost complete, and solvent interactions significantly affect the excited state lifetime, then multiexponential behavior would be expected. Changes in symmetry may result in the loss or diminishment of deactivating vibrationally linked pathways. This is not observed in any of the measurements carried out in this study. In achiral environments the differences between the homo- (**1a/1d**) and heterochiral (**1b/1c**) stereoisomers of **1** are almost entirely due to differences in intramolecular interactions. Only if such intramolecular interactions are significant will differences in the photophysical properties of the homo- and heterochiral stereoisomers be observed. For each enantiomeric pair, both intramolecular and intermolecular interactions (in achiral solvents) are identical, and hence, no differences in their photophysical properties are expected. However, the use of enantiomerically pure hosts could in principle result in differential stabilization of the enantiomers. No differences are

observed in the photophysical properties of the stereoisomers of **1** in both achiral and chiral solvents.

The results obtained indicate that the presence of stereoisomers does not affect the general photophysical properties of the dinuclear complex **1**. That no differences in the photophysical properties of the stereoisomers of **1** are observable either at 77 K or at room temperature in both achiral, racemic, and enantiomerically pure solvents, suggests strongly that the differences in either ground or excited-state structures are not significant. In strained systems,<sup>21,23</sup> differences in intramolecular interactions have been shown to effect differences in electrochemical and photophysical properties between stereoisomers; however, no such differences should occur between enantiomeric pairs. Hence, differences in intermolecular rather than intramolecular interactions are of most concern. In the present system differences in intermolecular interactions do not result in measurable differences in photophysical properties. Meskers et al.<sup>34</sup> have found significant enantioselectivity in the quenching of chiral lanthanide complexes by vitamin B<sub>12</sub>. In this case the lanthanide complex forms a close association with the B<sub>12</sub> molecule. This strongly suggests that only where the environments of the stereoisomers of an inorganic complex are significantly different, i.e., in the case of DNA intercalation or photosystem II, differences in photophysical properties may become observable.

### Conclusions

These results suggest that the presence of stereoisomers in multinuclear supramolecular assemblies is unlikely to affect the photophysical properties of these assemblies, and the importance of stereochemistry in solution is relatively low in comparison to electronic factors.

**Acknowledgment.** The authors thank Enterprise Ireland for financial assistance.

IC010473M

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