

# Stereoisomers in heterometallic (Ru<sub>2</sub>Os) and heteroleptic homometallic (RuRu' Ru'') trinuclear complexes incorporating the bridging ligand hat (1,4,5,8,9,12-hexaazatriphenylene) ‡

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The stereoisomers ( $\Delta\Delta\Delta'$ ,  $\Delta\Delta\Delta$ ,  $\Lambda\Lambda\Lambda'$ ,  $\Lambda\Lambda\Lambda$ ,  $\Delta\Delta\Delta'$  and  $\Delta\Delta\Delta$ ; the prime indicates the chirality of the osmium centre) of the heteronuclear trimetallic Ru<sub>2</sub>Os species [ $\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})$ ]<sup>6+</sup> (hat = 1,4,5,8,9,12-hexaazatriphenylene; bpy = 2,2'-bipyridine), and the diastereoisomeric forms of the heteroleptic homometallic trinuclear species [ $\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})$ ]<sup>6+</sup> ( $\Delta^b\Delta^p\Delta^m/\Lambda^b\Lambda^p\Lambda^m$ ,  $\Delta^b\Delta^p\Lambda^m/\Lambda^b\Lambda^p\Delta^m$ ,  $\Delta^b\Lambda^p\Delta^m/\Lambda^b\Delta^p\Lambda^m$ ,  $\Delta^b\Lambda^p\Lambda^m/\Lambda^b\Delta^p\Delta^m$ ; phen = 1,10-phenanthroline, dmbpy = 4,4'-dimethyl-2,2'-bipyridine; b, p and m denote the chirality of the metal attached to the ligands bpy, phen and dmbpy, respectively) have been isolated using a combination of stereoselective syntheses and chromatographic procedures. In both cases dinuclear species with predetermined stereochemistry were used as precursors: the various stereoisomers of the target trinuclear species were characterised on the basis of the known stereochemical course of the synthetic reactions, in combination with NMR and CD spectroscopy.

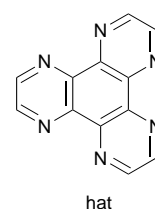
There has been significant recent interest in the stereochemistry of oligonuclear molecular assemblies containing octahedral tris(bidentate ligand) metal centres.<sup>1-17</sup> In a number of these investigations the strategy employed has been selectively to target one stereoisomer of a given system (generally of nuclearity two or three), either by use of precursors of predetermined stereochemistry,<sup>1,2,13-17</sup> or by the involvement of ligands which impose a particular stereochemistry on the ultimate product ('stereospecificity').<sup>3,4</sup>

Our own studies have utilised stereoselective syntheses involving enantiomerically pure building blocks<sup>6</sup> in combination with chromatographic techniques<sup>5,9,18</sup> to isolate the stereoisomers of a number of target di- and tri-nuclear systems, some of which would be difficult to access by synthesis alone.<sup>6-8,10-12</sup> In two of these studies we have demonstrated that the stereochemistry of the assemblies significantly influences their physical properties.<sup>7,11</sup>

Cation-exchange chromatography forms a most important part of these studies, and we have employed SP Sephadex C-25 as the support with aqueous sodium toluene-4-sulfonate,<sup>5</sup> sodium (-)-*O,O'*-dibenzoyl-L-tartrate or sodium (+)-*O,O'*-di-4-toluoyl-D-tartrate solutions as eluents.<sup>9,18,19</sup> Although this chromatographic technique is based on a cation-exchange mechanism, the mode of isomer separation arises from the differential association of the anion of the eluent with the stereoisomers of the complex. The nature of the association appears to involve specific  $\pi$ -stacking and hydrophobic interactions.<sup>9,18</sup>

One system we have studied in detail has involved 1,4,5,8,9,12-hexaazatriphenylene (hat), which possesses three sites for bidentate ligation to a metal centre. Examples are known of its co-ordination in mononuclear complexes or as a ligand bridge in di- and tri-nuclear species, and previous studies have addressed the synthesis of homo- and hetero-metallic polynuclear species,<sup>20-24</sup> their photophysical properties<sup>21,24-27</sup>

and interaction and photoreactions with various polynucleotides.<sup>28-31</sup>



We recently isolated the possible stereoisomeric forms of the homometallic dinuclear [ $\{\text{Ru}(\text{L-L})_2\}_2(\mu\text{-hat})$ ]<sup>4+</sup> and trinuclear [ $\{\text{Ru}(\text{L-L})_2\}_3(\mu\text{-hat})$ ]<sup>6+</sup> species [L-L = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen)] by a combination of stereoselective synthesis and chromatographic techniques.<sup>11</sup> In each case there are two diastereoisomers, each with enantiomeric forms. Subsequently, we communicated the extension of the methodology to isolation of the stereoisomeric forms of the heterometallic trinuclear species [ $\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})$ ]<sup>6+</sup>.<sup>8</sup> The present paper describes in detail the isolation and characterisation of the three diastereoisomers (and their enantiomeric forms). We also report herein the further extension of the techniques to the heteroleptic homometallic trinuclear species [ $\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})$ ]<sup>6+</sup> {dmbpy = 4,4'-dimethyl-2,2'-bipyridine}, for which we have isolated and characterised the four diastereoisomeric forms.

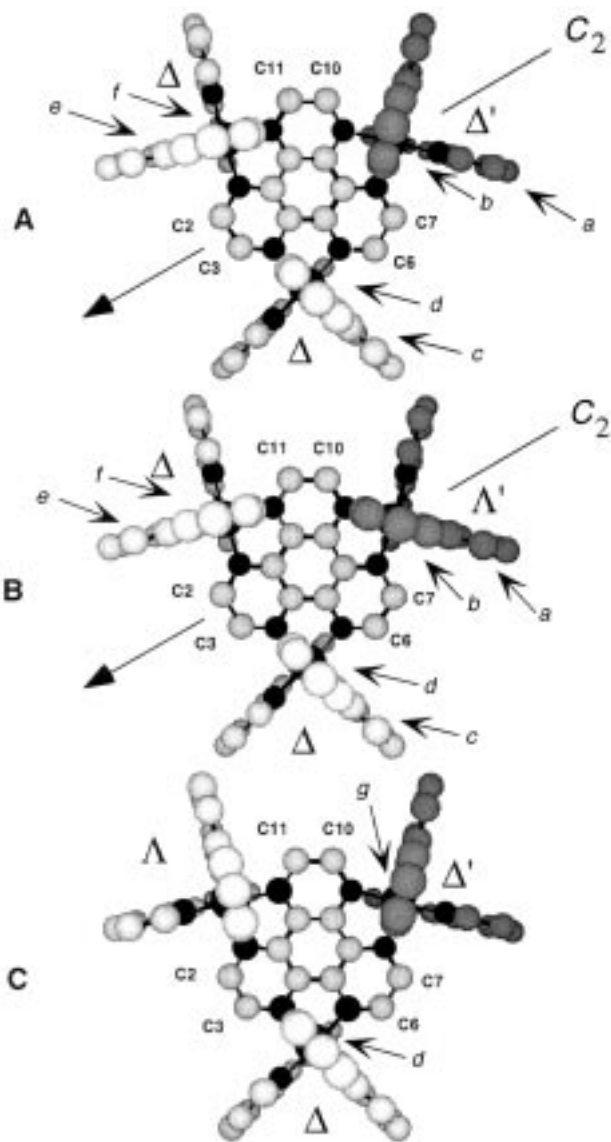
## Results and Discussion

### Syntheses

**Homoleptic heteronuclear trimetallic complex.** The synthesis of the heteronuclear complex [ $\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})$ ]<sup>6+</sup> and the isolation of its stereoisomeric forms was achieved by a combination of stereoselective synthetic procedures and chromatographic techniques, as described previously.<sup>8</sup> The stereoisomerically pure species  $\Delta\Delta$ -,  $\Lambda\Lambda$ - and  $\Delta\Lambda$ -[ $\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})$ ]<sup>4+</sup><sup>11</sup> were each treated with *rac*-[Os(bpy)<sub>2</sub>Cl<sub>2</sub>] $\cdot$ H<sub>2</sub>O to form the diastereoisomeric mixtures  $\Delta\Delta\Delta'/\Delta\Delta\Delta'$  and  $\Lambda\Lambda\Lambda'/\Lambda\Lambda\Delta'$  in the former two cases, and in the final case the enan-

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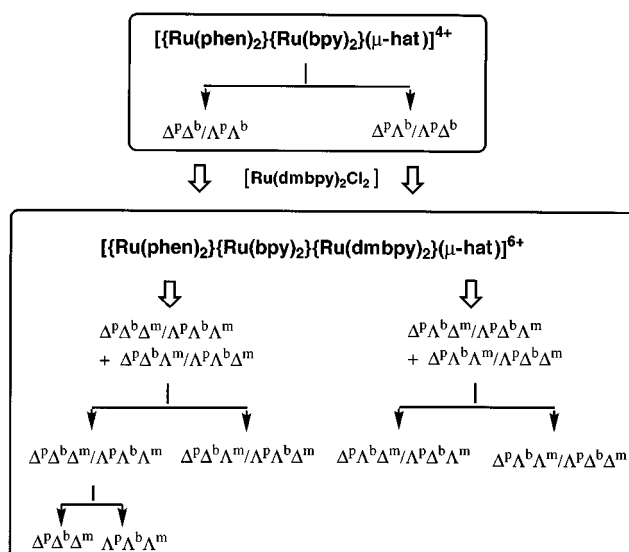
‡ Supplementary data available: NMR spectra and <sup>1</sup>H chemical shift assignments. For direct electronic access see <http://www.rsc.org/suppdata/1998/1155/>, otherwise available from BLDSC (No. SUP 57346, 7 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).



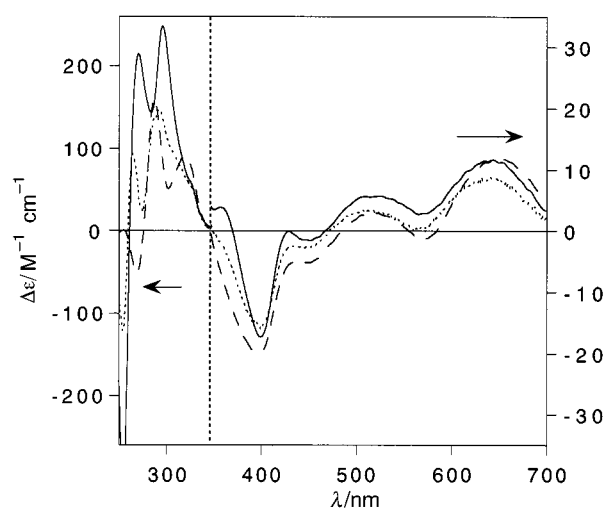
**Fig. 1** The CHEM 3D™ representations of the diastereoisomeric forms of  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$ ;  $\Delta\Delta\Delta'/\Lambda\Lambda\Lambda'$  (A),  $\Delta\Delta\Lambda'/\Lambda\Lambda\Delta'$  (B) and  $\Lambda\Delta\Lambda'/\Delta\Lambda\Delta'$  (C). Hydrogen atoms omitted for clarity; bpy rings about Os are darkened to allow identification

tiomeric pair of one diastereoisomer  $\Delta\Lambda\Lambda'/\Lambda\Delta\Delta'$  (the configuration of the osmium centre is designated with a prime; the diastereoisomers are shown in Fig. 1). In all cases, the yields were *ca.* 70%, and the ratio of the stereoisomers was *ca.* 1:1. Using cation-exchange chromatographic techniques (SP Sephadex C-25, aqueous 0.3 M sodium toluene-4-sulfonate eluent) the separation of  $\Delta\Delta\Delta'/\Delta\Delta\Lambda'$  and  $\Lambda\Lambda\Lambda'/\Lambda\Lambda\Delta'$  diastereoisomeric pairs was readily achieved. As the configurations of the two ruthenium centres in precursors were known, the CD spectra<sup>8</sup> and the NMR spectra (discussed below, Fig. 5) allowed the assignment of the absolute configurations of all four forms. The chiral resolution of the  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$  racemic mixture was attempted using a range of eluents (aqueous 0.2 M sodium *O,O'*-di-4-toluoyl-D-tartrate solution, 0.2 M sodium *O,O'*-di-4-toluoyl-L-tartrate and 0.2 M sodium *O,O'*-dibenzoyl-L-tartrate), although no separation into two bands was observed. These forms may be obtained by the alternative route of reaction of  $\Delta\Delta'$ - (or  $\Lambda\Lambda'$ -)  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{4+}$  with *rac*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$  to produce the  $\Delta\Delta\Delta'/\Delta\Delta\Lambda'$  and  $\Lambda\Lambda\Lambda'/\Lambda\Lambda\Delta'$  diastereoisomeric pairs (respectively), which may be readily separated by chromatography.

The CD spectra for the separated forms are comparable with those of the homometallic analogues having similar absolute configurations.<sup>11</sup>



**Scheme 1** Synthesis of the stereoisomers of  $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$ : p, b and m denote chirality at the ruthenium centres for the co-ordinated phen, bpy and dmbpy ligands respectively. Chromatographic procedures are indicated by bold arrows, synthetic procedures by open arrows



**Fig. 2** The CD spectra ( $\text{CH}_3\text{CN}$ ) of the chromatographically resolved (band 2)  $\Lambda\Lambda$ - $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}(\mu\text{-hat})]^{4+}$  (.....),  $\Lambda\Lambda$ - $[\{\text{Ru}(\text{phen})_2\}_2\{\text{Ru}(\text{bpy})_2\}(\mu\text{-hat})]^{4+}$  (—) and  $\Lambda\Lambda$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{phen})_2\}(\mu\text{-hat})]^{4+}$  (-----)

**Heteroleptic homonuclear trimetallic complex.** The target complex  $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$  requires sequential addition to hat of the three metal centres which possess different co-ordination environments (Scheme 1). The two diastereoisomers  $\Delta^p\Delta^b/\Lambda^p\Lambda^b$ - and  $\Delta^p\Lambda^b/\Lambda^p\Delta^b$ - $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}(\mu\text{-hat})]^{4+}$  (p and b denote chirality of the phen- and bpy-co-ordinated ruthenium centres respectively) were separated by the chromatographic technique described for the homoleptic analogues,<sup>11</sup> and characterised by <sup>1</sup>H NMR spectroscopy (see below). The  $\Delta^p\Delta^b/\Lambda^p\Lambda^b$  diastereoisomer was chromatographically resolved and each enantiomer assigned by comparison of the CD spectra with those of the analogous homoleptic dinuclear complexes of bpy and phen (Fig. 2). As expected, the CD spectra in the UV region were composed of transitions arising from both bpy and phen ligands, with transitions in the visible region nearly identical for all complexes.

Although the  $\Delta^p\Delta^b/\Lambda^p\Lambda^b$  diastereoisomer was resolved, for the purpose of this study only diastereoisomeric purity was required for use as a precursor in the synthesis of the target trinuclear complex. The  $\Delta^p\Delta^b/\Lambda^p\Lambda^b$  and  $\Delta^p\Lambda^b/\Lambda^p\Delta^b$  forms were each treated with *rac*- $[\text{Ru}(\text{dmbpy})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$  under conditions of microwave heating in ethylene glycol to produce the two sets

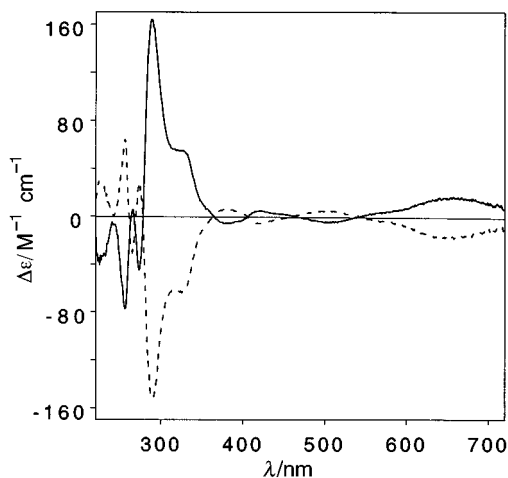


Fig. 3 The CD spectra of homochiral enantiomers of  $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$ :  $\Delta\Delta\Delta$  (----) and  $\Lambda\Lambda\Lambda$  (—)

of diastereoisomeric mixtures,  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Lambda^m + \Delta^p\Delta^b\Lambda^m/\Lambda^p\Lambda^b\Delta^m$  and  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Delta^b\Lambda^m + \Delta^p\Lambda^b\Lambda^m/\Lambda^p\Delta^b\Delta^m$  (where *m* denotes chirality of the dmbpy-co-ordinated ruthenium centre, Scheme 1).

The two diastereoisomeric mixtures were separated chromatographically (SP Sephadex C-25, aqueous 0.3 M sodium toluene-4-sulfonate eluent) to yield the four possible diastereoisomers in approximately equal proportions. Their assignments were achieved by a combination of  $^1\text{H}$  NMR studies (see below) and the known stereochemical consequences of their synthesis from the two precursors with predetermined diastereoisomeric identity. Comparisons of the chromatographic elution order with those of the homonuclear analogues confirmed the assignments.<sup>11</sup> Thus, the chromatographic separation of the target complexes derived from  $\Delta^p\Delta^b/\Lambda^p\Lambda^b$ - $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}(\mu\text{-hat})]^{4+}$  were  $\Delta^p\Delta^b\Lambda^m/\Lambda^p\Lambda^b\Delta^m$  (band 1) and  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Lambda^m$  (band 2), and from the  $\Delta^p\Lambda^b/\Lambda^p\Delta^b$  form were  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Delta^b\Lambda^m$  (band 1) and  $\Delta^p\Lambda^b\Lambda^m/\Lambda^p\Delta^b\Delta^m$  (band 2). The chromatographic separation efficiency of the  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  and  $\Delta^p\Lambda^b\Lambda^m/\Lambda^p\Delta^b\Delta^m$  diastereoisomeric pairs [effective column length (ECL) *ca.* 300 cm] was significantly reduced in comparisons with that of the  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Lambda^m$  and  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  mixture (ECL *ca.* 10 cm), presumably due to reduced structural differences between the  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  and  $\Delta^p\Lambda^b\Lambda^m/\Lambda^p\Delta^b\Delta^m$  forms as each diastereoisomer contains only two homochiral ruthenium centres.

The homochiral diastereoisomer  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Lambda^m$  was chirally resolved (SP Sephadex C-25, aqueous 0.2 M sodium *O,O'*-dibenzoyl-L-tartrate solution as eluent; ECL  $\approx$  45 cm), and the CD spectra of the two enantiomeric forms are shown in Fig. 3. The assignments of the absolute configurations of the two enantiomeric forms were achieved by comparison with those of the trinuclear homoleptic analogues.<sup>11</sup> The 'relative' ease of this chiral resolution further confirmed the assignment of  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Lambda^m$  as the chiral resolution of the heterochiral ( $\Delta\Delta\Lambda/\Lambda\Lambda\Delta$ ) diastereoisomers into their enantiomeric forms was previously observed to be extremely inefficient.<sup>11</sup>

### $^1\text{H}$ NMR studies

**Heteronuclear trimetallic complex,  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$ .** In our earlier communication<sup>8</sup> we were unable fully to characterise the three diastereoisomeric forms by  $^1\text{H}$  NMR spectroscopy at 300 MHz: the studies reported here were undertaken at higher field (500 MHz) which has enabled full characterisation. The three diastereoisomeric forms of the  $\text{Ru}_2\text{Os}$  complex exhibit  $^1\text{H}$  NMR spectra (Fig. 4) consistent with their point-group symmetry requirements (*i.e.*  $\Delta\Delta\Delta'/\Lambda\Lambda\Lambda'$  and  $\Delta\Delta\Lambda'/\Lambda\Lambda\Delta'$  forms possess  $C_2$  symmetry, and  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$

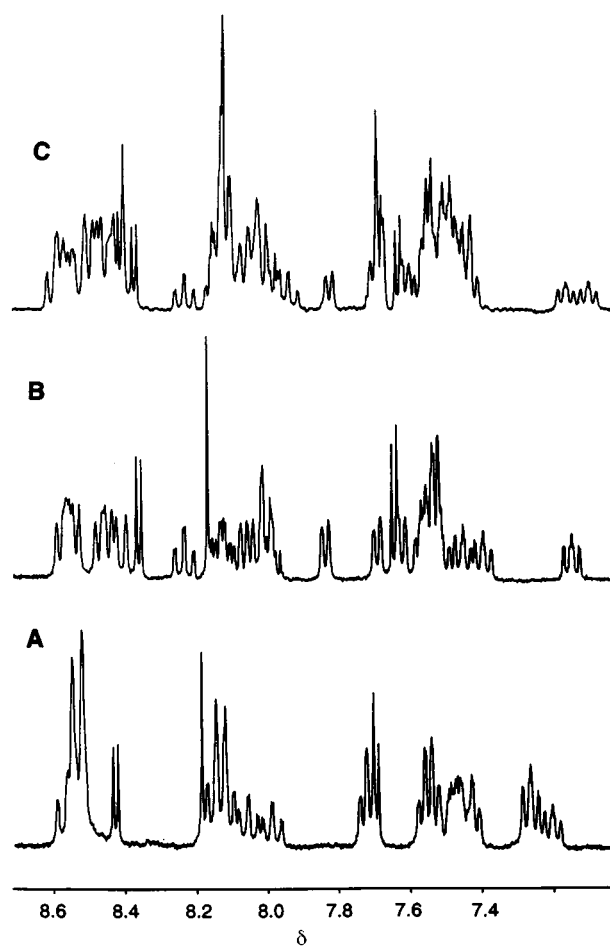
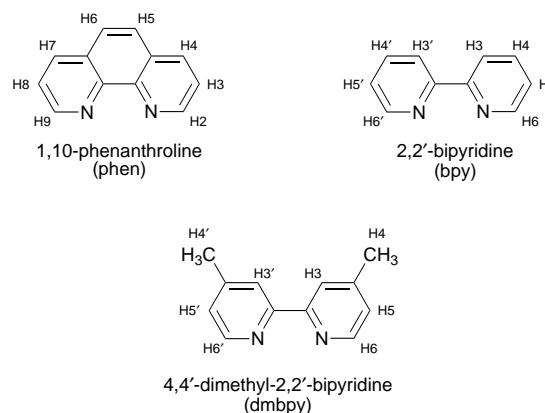


Fig. 4 Proton NMR spectra ( $\text{CD}_3\text{CN}$ , 300 MHz) of the three diastereoisomers of  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$ : (A)  $\Delta\Delta\Delta'/\Lambda\Lambda\Lambda'$ , (B)  $\Delta\Delta\Lambda'/\Lambda\Lambda\Delta'$  and (C)  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$  (the prime denotes chirality at the osmium centre)



forms possess  $C_1$  symmetry). The  $^1\text{H}$  chemical shifts are listed in SUP 57346 and were determined by  $^1\text{H}$  COSY (300 and 500 MHz),  $^1\text{H}$  NOESY (500 MHz), NOE-difference spectra and selective  $^1\text{H}$  decoupling experiments. Owing to the coincidental equivalence of certain proton resonances for these diastereoisomers, the assignment of these chemical shifts to specific proton environments was in some instances ambiguous. Nevertheless, the  $^1\text{H}$  NMR assignments do confirm the particular stereochemical features of the three diastereoisomeric forms, and are consistent with the stereochemical assignments determined by other methods.

The  $\Delta\Delta\Delta'/\Lambda\Lambda\Lambda'$  and  $\Delta\Delta\Lambda'/\Lambda\Lambda\Delta'$  diastereoisomers both possess  $C_2$  point-group symmetry [Fig. 1(A) and 1(B)], and therefore may exhibit 27 non-equivalent proton environments (six AMJX, AX coupled system and singlet resonance). Since

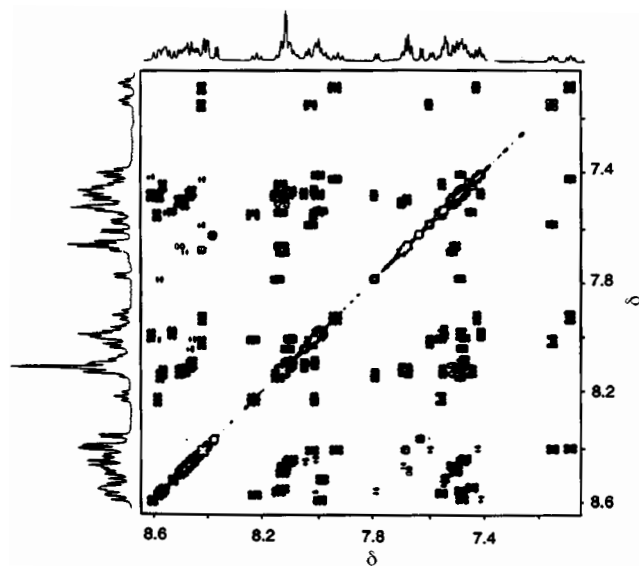


Fig. 5 The  $^1\text{H}$  COSY spectrum (500 MHz) of  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$  ( $\text{PF}_6^-$  salt,  $\text{CD}_3\text{CN}$  solvent)

the former diastereoisomer also possesses a pseudo- $C_3$  axis (*cf.* the homometallic analogue  $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})]^{6+}$ ) a number of coincidental equivalences occur in the proton chemical shifts (Fig. 4). The six AMJX coupled systems were identified by  $^1\text{H}$  COSY and  $^1\text{H}$  decoupling experiments, although connectivity between the AMJX coupled systems (which would allow full assignment of the three non-equivalent bpy ligands) was not achievable due to the equivalence of all but one of the H3/H3' proton resonances ( $d$ ,  $J = 8$  Hz) measured at either 300 or 500 MHz. Therefore, the connectivity between the H3/H3' protons indicated in SUP 57346 is based on comparisons with the other  $\text{Ru}_2\text{Os}$  diastereoisomers and the homonuclear trimetallic complexes.<sup>11</sup>

The H5 protons (bpy ligand;  $dd$ ,  $J = 5.5$ , 1.5 Hz) of pyridyl rings  $b$ ,  $d$  and  $f$  are orientated over the plane of the hat and adjacent bpy ligands and thus relatively shielded ( $\delta \approx 7.20$ – $7.30$ )<sup>11</sup> compared with the H5 protons on the pyridyl rings  $a$ ,  $c$  and  $e$  which are positioned away from the hat bridging ligand ( $\delta \approx 7.50$ ).<sup>11</sup> These chemical shift differences for the H5 protons arise from different degrees of diamagnetic anisotropic interactions between the various ligands for similar reasons to those discussed previously.<sup>11</sup> The most upfield of the three resonances associated with rings  $b$ ,  $d$  and  $f$  was assigned to ring  $b$ , due to the shielding effect of the co-ordinated osmium centre compared with that of the ruthenium centre, as a result of the increased  $\pi$ -back bonding of osmium compared to that of ruthenium.<sup>32,33</sup> Comparisons with the chemical shifts of  $\Delta^3/\Lambda^3$ - $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})]^{6+}$ <sup>11</sup> also confirmed the assignments of rings  $d$  and  $f$ . The assignment of the hat proton resonances were based on the relative shielding influences of the osmium centre and symmetry considerations. The H2/H3 protons are related by a  $C_2$  axis and thus were assigned to the  $\delta$  8.18 singlet resonance, and the resonance ( $d$ ,  $J = 3$  Hz) at  $\delta$  7.70 was assigned to H7/H10 due to shielding influences from the osmium metal centre (*cf.*  $d$ ,  $J = 3$  Hz at  $\delta$  8.42).<sup>32,33</sup>

Despite also possessing  $C_2$  point-group symmetry, the  $^1\text{H}$  NMR spectrum (Fig. 5) of the  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$  diastereoisomer [see Fig. 1(B)] was more complex (as it lacks the pseudo- $C_3$  axis), and exhibited six AJMX, one AX coupled proton systems and a singlet resonance, totalling a possible 27 magnetically non-equivalent proton environments. The assignments were obtained by  $^1\text{H}$  COSY spectra, selective  $^1\text{H}$  decoupling and coupling constant values. The connectivity between the AJMX systems was revealed by  $^1\text{H}$  NOESY and NOE-difference spectra.

Rings  $f$  and  $b$  are orientated in a near coplanar geometry

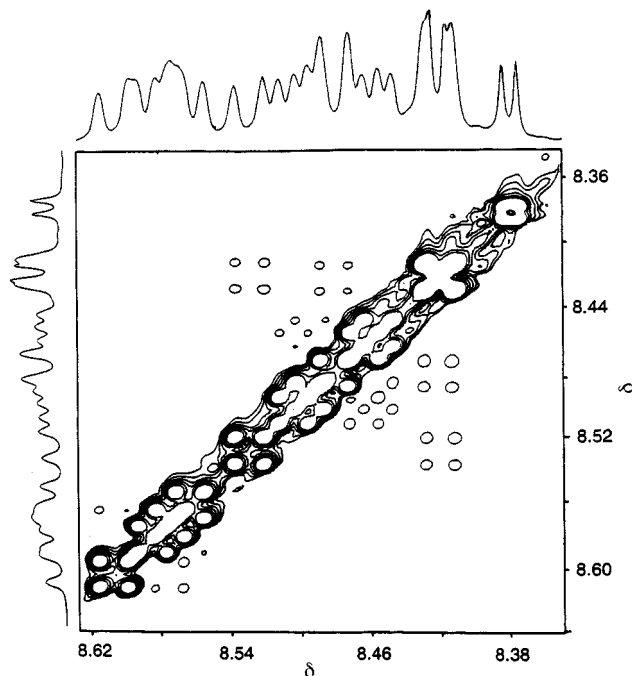


Fig. 6 The  $^1\text{H}$  NOESY (selected region) spectrum of  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$  ( $\text{PF}_6^-$  salt,  $\text{CD}_3\text{CN}$  solvent)

[Fig. 1(B)], which results in deshielding influences on their proton resonances and enables the assignment of the H6 protons ( $dd$ ,  $J = 5$ , 1.5 Hz) to  $\delta$  8.06 and 7.83.<sup>11</sup> The distinction of these resonances was based on the relative shielding influence of the osmium compared to ruthenium metal centres, and by comparison of ring  $f$  with rings  $d$  and  $f$  of the analogous  $\Delta^2\Lambda/\Lambda^2\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})]^{6+}$  complex.<sup>11</sup> The comparison allowed the assignment of the peaks at  $\delta$  8.06 and 7.83 to rings  $f$  and  $b$  respectively. The assignment of the remaining ring  $c/d$  is confirmed by the close similarity in chemical shifts with those of ring  $bla$  of  $\Delta^2\Lambda/\Lambda^2\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})]^{6+}$ , which has the same relative geometry.<sup>11</sup>

The  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$  diastereoisomer has  $C_1$  point-group symmetry [Fig. 1(C)], resulting in a complicated  $^1\text{H}$  NMR spectrum (Fig. 4) comprising 12 AJMX, 2 AX coupling systems and two singlet resonances, totalling a possible 54 magnetically non-equivalent proton environments. Assignment of these proton environments was achieved by a combination of  $^1\text{H}$  COSY (500 MHz, Fig. 5) and  $^1\text{H}$  TOCSY (500 MHz) studies. The connectivity between the 12 AJMX systems was revealed by  $^1\text{H}$  NOESY experiments (500 MHz, Fig. 6). Although the assignment of the chemical shifts to specific ring orientations is unclear, certain generalisations may be made. There are two pairs of bpy ligands which each have an almost mutually coplanar geometry across the hat bridge: overall, three of these are co-ordinated to a ruthenium centre and one to an osmium centre. This results in three H6 resonances ( $dd$ ,  $J = 5$ , 1.5 Hz) at  $\delta \approx 8$  (*cf.* ring  $fld$  of  $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})]^{6+}$  at  $\delta$  8.0<sup>11</sup>) and the fourth H6 resonance ( $dd$ ,  $J = 5$ , 1.5 Hz) at  $\delta$  7.80 which is shielded due to the osmium centre, and is comparable to that of ring  $b$  in the  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$  diastereoisomer. The chemical shifts of the two remaining non-equivalent bpy ligands [rings  $d$  and  $g$ , Fig. 1(C)] are consistent with the chemical shifts of protons in similar geometries for the  $\Delta\Delta\Lambda'/\Lambda\Delta\Delta'$ - $\text{Ru}_2\text{Os}$  and  $\Delta^2\Lambda/\Lambda^2\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})]^{6+}$  complexes.<sup>11</sup>

**Heteroleptic homonuclear complex,  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$ .** For the  $[\{\text{Ru}(\text{bpy})_2\}(\mu\text{-hat})\{\text{Ru}(\text{phen})_2\}]^{4+}$  precursor the  $\Delta\Delta/\Lambda\Lambda$  and  $\Delta\Lambda/\Lambda\Delta$  diastereoisomers both possess  $C_1$  point-group symmetry and thus exhibit  $^1\text{H}$  NMR spectra comprising two non-equivalent bpy and phen ligands (totalling a possible 32 magnetically non-equivalent proton resonances) and six non-equivalent hat proton resonances.

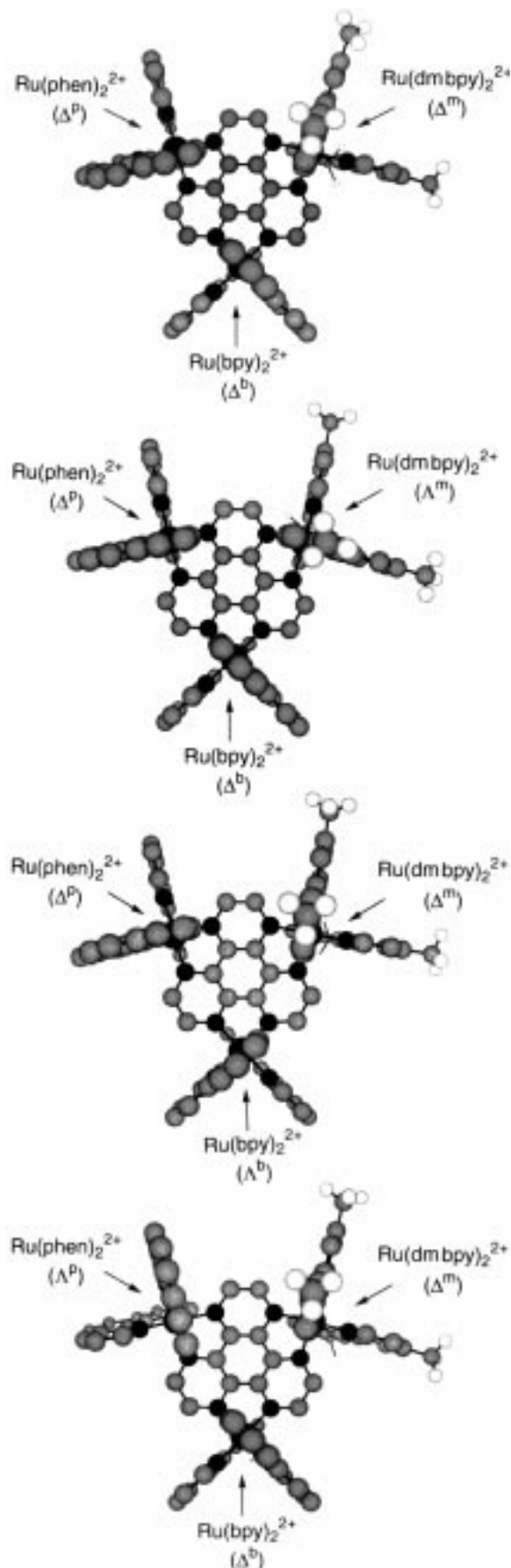


Fig. 7 The CHEM 3D™ representations of the four diastereoisomeric forms of  $[\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$ . Aromatic hydrogen atoms omitted for clarity

ances. The  $^1\text{H}$  NMR spectra of the two diastereoisomers and the resonances are in SUP 57346. The assignments of these two diastereoisomers were achieved by comparison with the  $^1\text{H}$

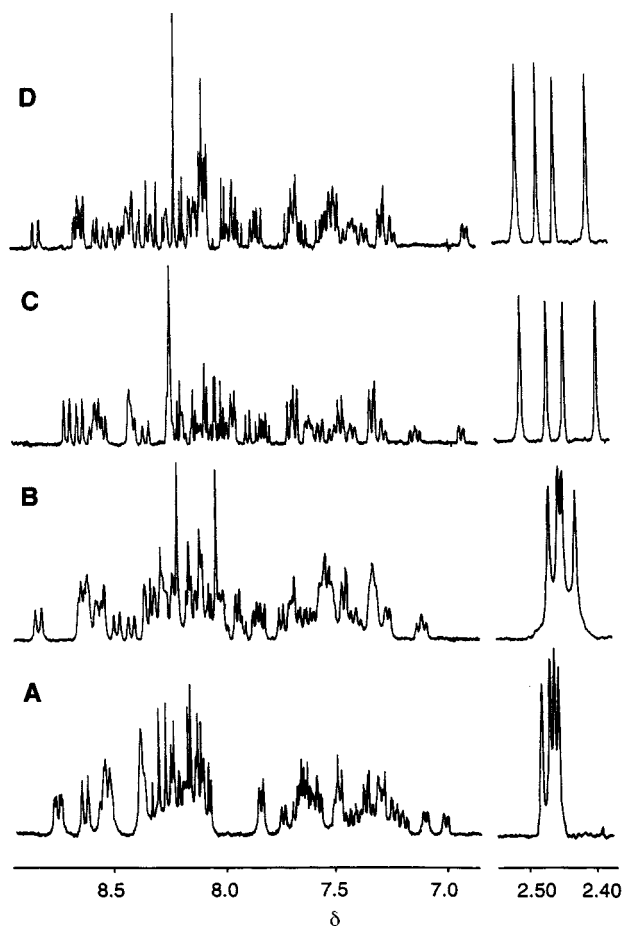


Fig. 8 Proton NMR spectra ( $\text{CD}_3\text{CN}$ , 300 MHz) of the diastereoisomers of  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$ :  $\Delta^P\Delta^B\Delta^M/\Lambda^P\Lambda^B\Lambda^M$  (A),  $\Delta^P\Delta^B\Lambda^M/\Lambda^P\Lambda^B\Delta^M$  (B),  $\Delta^P\Lambda^B\Lambda^M/\Lambda^P\Delta^B\Delta^M$  (C) and  $\Delta^P\Lambda^B\Delta^M/\Lambda^P\Delta^B\Lambda^M$  (D) where p, b and m denote chirality of the ruthenium centres with co-ordinated phen, bpy and dmbpy, respectively

NMR chemical shifts of the homoleptic analogues.<sup>11</sup> These assignments are in agreement with the chromatographic elution order (band 1,  $\Delta\Lambda/\Lambda\Delta$ ; 2,  $\Delta\Delta/\Lambda\Lambda$ ) and CD spectra of the stereoisomeric forms of the homoleptic analogues.<sup>11</sup>

The diastereoisomers of the  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$  target complex,  $\Delta^P\Delta^B\Lambda^M/\Lambda^P\Lambda^B\Delta^M$ ,  $\Delta^P\Lambda^B\Delta^M/\Lambda^P\Delta^B\Lambda^M$ ,  $\Delta^P\Lambda^B\Lambda^M/\Lambda^P\Delta^B\Delta^M$  and  $\Delta^P\Delta^B\Lambda^M/\Lambda^P\Lambda^B\Delta^M$  (Fig. 7) possess  $C_1$  point-group symmetry and therefore exhibit  $^1\text{H}$  NMR spectra (Fig. 8) comprising a possible 54 magnetically non-equivalent proton resonances (4 AJMX coupling systems from bpy; 4 AMX and 2AB from phen, 4 AX, 4 singlet aromatic and 4 singlet methyl resonances from dmbpy, a possible 3 AB coupling patterns from hat). The chemical shift assignments (SUP) were obtained using  $^1\text{H}$  COSY (SUP), with the connectivity between two 'pyridyl rings' of each ligand and between the methyl resonances ( $\delta \approx 2.4\text{--}2.5$ ) and the H3 proton in dmbpy determined by  $^1\text{H}$  NOESY studies (SUP).

The assignment of the above complexes was achieved knowing the stereochemical consequences of the reactions involving the diastereoisomerically pure  $[\{\text{Ru}(\text{bpy})_2\}(\mu\text{-hat})\{\text{Ru}(\text{phen})_2\}]^{4+}$  precursor complexes, the comparisons of the  $^1\text{H}$  NMR assignments previously determined for the di- and trimetallic homonuclear complexes,<sup>11</sup> and the known chromatographic elution order for the separation of the diastereoisomers of the trimetallic homo- and hetero-nuclear species.

For the  $\Delta^P\Delta^B\Delta^M/\Lambda^P\Lambda^B\Lambda^M$  diastereoisomer all the bpy, phen and dmbpy ligands are orientated over the plane of hat and over the plane of the adjacent terminal ligands, thus the  $^1\text{H}$  spectrum contains two bpy H5 resonances at  $\delta \approx 7.20$  (cf. two at  $\delta 7.45$ ), two H9 phen resonances at  $\delta \approx 8.20$  (cf. two at  $\delta \approx 7.84$ ) and two H5 dmbpy resonances at  $\delta \approx 7.05$  (cf. two at  $\delta \approx 7.25$ )

(a full listing of resonances is available in SUP 57346). These observations indicate no terminal ligands were orientated in the plane of an adjacent ligand across the hat bridge. This assignment was further confirmed by the simplified  $^1\text{H}$  NMR spectrum observed for the  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Lambda^m$  species due to the presence of a pseudo- $C_3$  axis of symmetry; this symmetry resulted in the coincidental equivalence of a number of proton resonances and thus the connectivity between selected pyridyl rings could not be revealed by  $^1\text{H}$  NOESY at 500 MHz.

The  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  diastereoisomer contains one bpy and one phen ligand over the plane of the adjacent phen and bpy terminal ligands respectively, and the second bpy and phen ligand orientated in the plane of the two adjacent dmbpy terminal ligands respectively. This geometry results in one H5 bpy resonance at  $\delta \approx 7.40$  (in the plane), the other at  $\delta \approx 7.10$  (over the plane), one phen H9 resonance at  $\delta \approx 8.10$  (over the plane) and one at  $\delta \approx 8.54$  (in the plane). Both dmbpy ligands are orientated in the plane of the adjacent terminal ligands across the bridge and thus the observed downfield shift of two H6 resonances to  $\delta 7.74$  and  $7.82$  (*cf.*  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  diastereoisomer where H6 at  $\delta \approx 7.30$ – $7.45$ ).

There is no comparative basis for the chromatographic behaviour of the  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Delta^b\Delta^m$  and  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Delta^b\Delta^m$  diastereoisomers as they are the first examples of the separation of heterochiral heteronuclear trinuclear species. Accordingly, their assignments were solely based on NMR comparisons. The particular relative orientation of the grouping of terminal ligands provides a characteristic pattern of proton resonances with specific chemical shifts. The  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Delta^b\Delta^m$  (band 1) diastereoisomer exhibits one bpy ligand orientated over the plane of dmbpy and one in the plane of phen, whereas both phen ligands are orientated in the plane of the dmbpy and bpy terminal ligands. Thus, one H5 bpy resonance is observed upfield at  $\delta 7.14$  (over the plane), the other bpy H6 resonance at  $\delta 8.08$  (in the plane), and the two H9 phen resonances downfield at  $\delta 8.54$  and  $8.52$  (in the plane). One dmbpy ligand is orientated in the plane of the adjacent phen ligand and the second over the plane of the bpy ligand, thus the resonances for H6 were observed at  $\delta 7.87$  (in the plane) and H5 at  $\delta 6.90$  (over the plane) respectively.

The  $\Delta^p\Delta^b\Delta^m/\Lambda^p\Delta^b\Delta^m$  (band 2) diastereoisomer (Fig. 7) contains both bpy ligands orientated in the plane of a dmbpy and a phen terminal ligand, and thus the two downfield H6 resonances were observed at  $\delta 8.06$  and  $7.96$ . One phen ligand is orientated in the plane of the bpy terminal ligand and the second phen ligand orientated over the plane of a dmbpy ligand, which results in the two H9 resonances at  $\delta 8.55$  (in the plane) and  $8.12$  (over the plane). This diastereoisomer also contains one dmbpy ligand orientated in the plane of the bpy ligand and the second over the plane of the phen, thus the H5 resonance was observed at  $\delta 6.89$  (over the plane) and the H6 resonance at  $\delta 7.81$  (in the plane).

### Electrochemistry and electronic spectroscopy

The redox potentials and spectral characteristics of the  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$  complex have been reported previously,<sup>9</sup> and show no detectable differences between the diastereoisomers.

The redox potentials of the  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}(\mu\text{-hat})]^{4+}$  complex and  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$  were consistent with the homoleptic analogues.<sup>8</sup> For the homometallic trinuclear species, cyclic voltammetry showed three reversible couples in the anodic region [ $+2.06$ ,  $+1.87$  and  $+1.58$  V; *vs.* sodium chloride saturated calomel electrode (SSCE),  $\text{CH}_3\text{CN}$  solvent], two reductions of the hat ligand ( $-0.23$  and  $-0.59$  V) and a terminal ligand reduction at  $-1.05$  V. No differences were observable between the diastereoisomeric forms.

The  $\lambda_{\text{max}}$  values in the electronic spectra of the heteroleptic complexes  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}(\mu\text{-hat})]^{4+}$  and  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$  were virtually identical with those of their homoleptic analogues,<sup>11,20</sup> except for small variations in the UV region due to differences in the  $\pi \rightarrow \pi^*$  transitions of the different ligands. No significant differences were observed between the diastereoisomers of the respective heteroleptic complexes.

### Conclusion

The isomeric complexity of the previously reported homotri-metallic complexes ( $\Delta^3/\Lambda^3$  and  $\Delta^2/\Lambda^2/\Delta$ ) was increased by the incorporation of an osmium metal centre to yield the heteronuclear complex  $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Os}(\text{bpy})_2\}(\mu\text{-hat})]^{6+}$ ; (three diastereoisomers  $\Delta\Delta\Delta'/\Lambda\Lambda\Lambda'$ ,  $\Delta\Delta\Delta'/\Delta\Lambda\Lambda'$  and  $\Delta\Delta\Delta'/\Lambda\Lambda\Delta'$ ). The stereoisomers were obtained by combination of stereoselective syntheses and a chromatographic technique. The three diastereoisomeric forms were characterised by  $^1\text{H}$  NMR studies and selected enantiomeric forms characterised by CD spectroscopy.

The generality of the strategy for stereoisomeric control of polynuclear species was demonstrated in the separation and characterisation of the four diastereoisomers of the heteroleptic complex  $[\{\text{Ru}(\text{bpy})_2\}\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})]^{6+}$ . Each diastereoisomer was characterised by  $^1\text{H}$  NMR spectroscopy and known stereochemical consequences of reactions involving diastereoisomerically pure precursor complexes. It is clear from this study that in cases where there is diastereoisomeric purity we have demonstrated the ability of  $^1\text{H}$  NMR spectroscopic techniques to characterise and probe the stereochemical features of oligonuclear assemblies.

### Experimental

#### Materials

1,4,5,8,9,12-Hexazatriphenylene (hat) was supplied by Professor D. P. Rillema (University of North Carolina, Charlotte).<sup>25</sup> Ethylene glycol (Ajax, 95%),  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (Strem, 99%), 1,10-phenanthroline (Aldrich, 99+%), 2,2'-bipyridine (Aldrich, 99+%), 4,4'-dimethyl-2,2'-bipyridine (Aldrich, 99%), potassium hexafluorophosphate (Aldrich, 98%), ammonium hexafluorophosphate (Aldrich, 99.99%), and laboratory reagent (LR) solvents were used without further purification unless specified. The complexes  $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,<sup>34</sup>  $[\text{Ru}(\text{dmbpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,<sup>34</sup>  $[\text{Ru}(\text{phen})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,<sup>35</sup>  $[\text{Os}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,<sup>36</sup> and  $\Delta$ - and  $\Lambda$ - $[\text{Ru}(\text{bpy})_2(\text{CO})_2][\text{PF}_6]_2$ <sup>6</sup> were prepared according to literature methods. Sodium toluene-4-sulfonate (Sigma, 98%), (-)-*O,O'*-dibenzoyl-L-tartaric acid (Fluka, >99%,  $[\alpha]^{20} = -117^\circ$ ) and *O,O*-di-4-toluoyl-D-tartaric acid (Aldrich, 97%,  $[\alpha]^{19} = +138^\circ$ ) were used without further purification: aqueous solutions of sodium (-)-*O,O'*-dibenzoyl-L-tartrate and sodium (+)-*O,O*-di-4-toluoyl-D-tartrate were prepared by neutralisation of the respective acids with sodium hydroxide.

#### Instrumentation

Proton NMR, as well as selective  $^1\text{H}$  decoupling, NOE-difference and  $^1\text{H}$  COSY experiments were performed on a Bruker Aspect 300 MHz spectrometer using  $\text{CD}_3\text{CN}$  (99.8% atom D%, 0.03%  $\text{SiMe}_4$ , Aldrich) as the solvent. For selected complexes  $^1\text{H}$ ,  $^1\text{H}$  NOESY,  $^1\text{H}$  COSY and  $^1\text{H}$  TOCSY experiments were also performed on a Varian Unity Inova-500 spectrometer using  $\text{CD}_3\text{CN}$ ; mixing times used for NOESY and TOCSY were 0.6 and 0.03 s respectively. Electronic spectra were recorded in acetonitrile solution on a Hewlett-Packard HP-89532K spectrophotometer using quartz cells. All electrochemical, spectral and ORD/CD measurements were performed as described previously.<sup>11</sup> All chromatographic procedures were carried out as described previously.<sup>11</sup>

## Syntheses

Syntheses conducted under microwave conditions were performed in a modified Sharp microwave oven (model R-2V55; 600 W, 2450 MHz) on medium-high power,<sup>37</sup> and carried out in a round-bottom flask fitted with a condenser, using ethylene glycol as the solvent.

Mononuclear  $[\text{Ru}(\text{bpy})_2(\text{hat})][\text{PF}_6]_2$  and  $[\text{Ru}(\text{phen})_2(\text{hat})][\text{PF}_6]_2 \cdot \text{H}_2\text{O}$  were synthesized and chromatographically resolved using literature procedures.<sup>11</sup> The dinuclear species  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$  was synthesized and chromatographically separated into its two diastereoisomeric form (*meso* and *rac*), and *rac*- $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$  was chromatographically resolved, as reported previously.<sup>11</sup> The complex  $\Delta\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$  was obtained by stereoselective synthesis involving the reaction of  $\Delta(-)-[\text{Ru}(\text{bpy})_2(\text{CO})_2][\text{PF}_6]_2$  with hat in appropriate molar ratio.<sup>11</sup>

**Stereoselective synthesis of  $\Delta\Delta\Delta'/\Lambda\Delta\Delta'$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Os}(\text{bpy})_2\}][\text{PF}_6]_6$ .** A solution of *rac*- $[\text{Os}(\text{bpy})_2\text{Cl}_2]$  (18 mg, 0.0304 mmol) in ethylene glycol–10% water (12 cm<sup>3</sup>) was de-aerated with N<sub>2</sub> for 20 min. The complex  $\Delta\Lambda$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$  (25 mg, 0.0152 mmol) was added and the solution heated at 120 °C for 11 h. The violet solution was cooled to room temperature and water (50 cm<sup>3</sup>) added followed by a saturated solution of KPF<sub>6</sub>, and the mixture stored overnight at 4 °C to precipitate the crude product. The solid was collected and reprecipitated from acetone–water solution by the addition of KPF<sub>6</sub>, filtered off and washed with ice-cold water and diethyl ether. Yield: 67% (25 mg) (Found: C, 35.8; H, 2.34; N, 10.3. Calc. for C<sub>72</sub>H<sub>54</sub>F<sub>36</sub>N<sub>18</sub>OsP<sub>6</sub>Ru<sub>2</sub>: C, 35.5; H, 2.24; N, 10.4%). UV/VIS:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 288 (104 000), 416 (15 750), 520 (21 000) and 588 (27 000).

**Stereoselective synthesis of  $\Delta^2\Delta'/\Lambda^2\Lambda'$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Os}(\text{bpy})_2\}][\text{PF}_6]_6$ .** The synthesis and purification were performed under similar conditions to those described above for  $\Delta\Delta\Delta'/\Lambda\Delta\Delta'$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Os}(\text{bpy})_2\}][\text{PF}_6]_6$  but using  $\Delta\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$  in place of  $\Delta\Lambda$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$ . Diastereoisomeric separation was achieved (ECL  $\approx$  10 cm) by cation-exchange chromatography (SP Sephadex C25) using 0.3 M sodium toluene-4-sulfonate solution as the eluent. The two bands were collected and each precipitated by addition of a saturated solution of KPF<sub>6</sub>. The separated diastereoisomers were dissolved in acetone–water, reprecipitated by the addition of a saturated solution of KPF<sub>6</sub>, filtered off and washed with distilled water and diethyl ether. Total yield: 24 mg (65%). The diastereoisomeric ratio of the heterochiral ( $\Delta\Delta\Delta'$ ) (band 1) to the homochiral ( $\Lambda\Lambda\Lambda'$ ) (band 2) was 52:48, where the prime denotes chirality at osmium. The UV/VIS spectrum was identical to that observed for  $\Delta\Delta\Delta'/\Lambda\Delta\Delta'$ . CD [CH<sub>3</sub>CN;  $\lambda_{\text{max}}/\text{nm}$  ( $\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )]:<sup>8</sup>  $\Delta\Delta\Delta'$ , 281 (97), 299 (–123) and 485 (–14);  $\Lambda\Lambda\Lambda'$ , 273 (37), 291 (–54), 327 (–36) and 517 (5).

**Stereoselective synthesis of  $\Lambda^2\Lambda'/\Lambda^2\Lambda'$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Os}(\text{bpy})_2\}][\text{PF}_6]_6$ .** The synthesis and purification were performed under similar conditions to those described above for  $\Delta\Delta\Delta'/\Lambda\Delta\Delta'$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Os}(\text{bpy})_2\}][\text{PF}_6]_6$  but using  $\Lambda\Lambda$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$  in place of  $\Delta\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$ . Separation of the diastereoisomers was similar to that described for  $\Delta\Delta\Delta'/\Lambda\Delta\Delta'$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Os}(\text{bpy})_2\}][\text{PF}_6]_6$ . Total yield: 26 mg (70%). The diastereoisomeric proportions of the heterochiral ( $\Lambda\Lambda\Lambda'$ ) (band 1) to homochiral ( $\Lambda\Lambda\Lambda'$ ) (band 2) was 53:47, where the prime denotes the chirality at osmium. The UV/VIS spectrum was identical to that observed for  $\Delta\Delta\Delta'/\Lambda\Delta\Delta'$ . CD [CH<sub>3</sub>CN;  $\lambda_{\text{max}}/\text{nm}$  ( $\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )]:<sup>8</sup>  $\Lambda\Lambda\Lambda'$ , 281 (–103), 299 (131) and 485 (15);  $\Lambda\Lambda\Lambda'$ , 273 (–43), 291 (50), 327 (40) and 517 (–5).

**$[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Ru}(\text{phen})_2\}][\text{PF}_6]_4$ .** The synthesis was performed in a similar manner to that described previously.<sup>23</sup>

The complex  $[\text{Ru}(\text{phen})_2(\text{hat})][\text{PF}_6]_2$  (100 mg, 0.10 mmol) was added to nitrogen-purged methanol–water (1:1, 60 cm<sup>3</sup>) and the solution brought to reflux, and a solution of  $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$  (52 mg, 0.10 mmol) in methanol–water (1:1; 30 cm<sup>3</sup>) added dropwise over several hours. The reaction mixture refluxed for 12 h. The methanol was removed under reduced pressure and the crude product purified according as described by Masschelein *et al.*<sup>20</sup> The diastereoisomers were separated as described for  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$ .<sup>11</sup> Total yield: 65%. The proportion of  $\Delta\Lambda/\Lambda\Delta$  (band 1) to  $\Delta\Delta/\Lambda\Lambda$  (band 2) was 50:50 (Found: C, 39.8; H, 2.34; N, 11.4. Calc. for C<sub>56</sub>H<sub>38</sub>F<sub>24</sub>N<sub>14</sub>P<sub>4</sub>Ru<sub>2</sub>: C, 39.8; H, 2.27; N, 11.6%). UV/VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 208 (82 530), 266 (88 356), 412 (17 360), 450 (15 890) and 554 (15 270). Electrochemistry (platinum-disc electrode, CH<sub>3</sub>CN solvent):  $E_3 = +1.82, +1.56, -0.43$  and  $-1.00$  V (vs. SSCE).

**Resolution of  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Ru}(\text{phen})_2\}][\text{PF}_6]_4$ .** Resolution was carried out in an identical manner to that described for  $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})][\text{PF}_6]_4$ .<sup>11</sup> CD [CH<sub>3</sub>CN;  $\lambda_{\text{max}}/\text{nm}$  ( $\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )]:  $\Delta\Delta$  (band 1), 254 (122), 264 (–90), 290 (–147), 399 (17), 516 (–3) and 644 (–10);  $\Lambda\Lambda$  (band 2), 254 (–121), 264 (+96), 290 (146), 399 (–16), 516 (3) and 644 (8).

**Stereoselective synthesis of  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$ - and  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})][\text{PF}_6]_6$ .** A suspension of  $[\text{Ru}(\text{dmbpy})_2\text{Cl}_2]$  (27 mg, 0.044 mol) and  $\Delta\Delta/\Lambda\Lambda$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Ru}(\text{phen})_2\}][\text{PF}_6]_4$  (25 mg, 0.0148 mmol) in ethylene glycol–10% water (5 cm<sup>3</sup>) was heated for *ca.* 4 min in a microwave oven (medium-high power). The purple reaction mixture was diluted with water and purified by the method described previously.<sup>20</sup> Total yield: 28 mg, 80% (Found: C, 39.5; H, 2.39; N, 10.3. Calc. for C<sub>80</sub>H<sub>62</sub>F<sub>36</sub>N<sub>18</sub>P<sub>6</sub>Ru<sub>3</sub>: C, 39.2; H, 2.55; N, 10.3%). UV/VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ) = 208 (130 500), 280 (124 130), 406 (20 570), 516 (26 830) and 576 (20 570). Diastereoisomer separation was achieved by the same method as described for  $[\{\text{Ru}(\text{bpy})_2\}_3(\mu\text{-hat})][\text{PF}_6]_6$ .<sup>11</sup> The diastereoisomeric ratio of  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  (band 1) to  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  (band 2) = 55:45.

**Resolution of  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})][\text{PF}_6]_6$ .** This was performed by cation-exchange chromatography on SP Sephadex C-25 using 0.2 M sodium (–)-*O,O'*-dibenzoyl L-tartrate solution as the eluent (ECL  $\approx$  40 cm). The two bands were collected and the complexes precipitated with KPF<sub>6</sub>, and reprecipitated as described above. Bands 1 and 2 were assigned to  $\Delta\Delta\Delta$  and  $\Lambda\Lambda\Lambda$  respectively (see Results and Discussion). CD [CH<sub>3</sub>CN;  $\lambda_{\text{max}}/\text{nm}$  ( $\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )]:  $\Delta\Delta\Delta$  (band 1), 256 (63), 273 (35), 289 (–155), 324 (–63), 386 (5), 423 (–6), 506 (4) and 650 (–18);  $\Lambda\Lambda\Lambda$  (band 2), 256 (–78), 273 (–45), 289 (+163), 324 (+54), 386 (–6), 423 (4), 506 (–5) and 650 (15).

**Stereoselective synthesis of  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$ - and  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})][\text{PF}_6]_6$ .** The synthesis and purification were performed under identical conditions to those described for  $\Delta\Delta\Delta/\Lambda\Lambda\Lambda$ - and  $\Delta\Delta\Lambda/\Lambda\Lambda\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_2\{\text{Ru}(\text{phen})_2\}\{\text{Ru}(\text{dmbpy})_2\}(\mu\text{-hat})][\text{PF}_6]_6$ , but using  $\Delta\Lambda/\Lambda\Delta$ - $[\{\text{Ru}(\text{bpy})_2\}_2(\mu\text{-hat})\{\text{Ru}(\text{phen})_2\}][\text{PF}_6]_4$  as the precursor. The crude mixture exhibited identical UV/VIS properties to those of the analogous diastereoisomer mixture above. Total yield: 76%. The two diastereoisomers were separated by cation-exchange chromatography using 0.2 M sodium toluene-4-sulfonate solution as eluent (ECL > 300 cm) and the two bands collected as described above. The ratio of  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  (band 1) to  $\Delta^p\Lambda^b\Delta^m/\Lambda^p\Lambda^b\Delta^m$  (band 2) was *ca.* 50:50.

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