Stereoisomers of Mono-, Di-, and Triruthenium(II) Complexes Containing the Bridging Ligand 1,4,5,8,9,12-Hexaazatriphenylene and Studies of Their Photophysical Properties

Todd J. Rutherford,[†] Olivier Van Gijte,[‡] Andrée Kirsch-De Mesmaeker,[‡,§] and F. Richard Keene*[,†]

Department of Chemistry and Chemical Engineering, School of Molecular Sciences, James Cook University of North Queensland, Townsville, Queensland 4811, Australia, and Laboratoire de Chimie Organique Physique, CP 160/08, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

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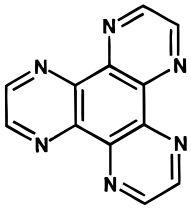
A combination of synthetic methods involving mononuclear precursors of predetermined chirality {Δ- or Λ-[Ru(pp)$_2$(CO)$_2$]$^{2+}$; pp = 2,2′-bipyridine or 1,10-phenanthroline} and chromatographic techniques has allowed the isolation of the *meso* (ΔΛ) and *rac* (ΔΔ/ΛΛ) diastereoisomers of the dinuclear complexes [{Ru(pp)$_2$}$_2$(μ-HAT)]$^{4+}$ {HAT = 1,4,5,8,9,12-hexaazatriphenylene}. The enantiomers of the *rac* forms have been separated, and characterization of all species has been achieved by NMR and CD studies. Additonally, the homochiral (Δ^3/Λ^3) and heterochiral ($\Delta^2\Lambda$/$\Lambda^2\Delta$) diastereoisomers of the trinuclear complexes [{Ru(pp)$_2$}$_3$(μ-HAT)]$^{6+}$, and the enantiomers of both forms, have been isolated and identified. Emission studies of all the dinuclear species at room temperature indicate the relative luminescence quantum yields and the emission lifetimes significantly decrease for the *meso* compared with the *rac* diastereoisomers. No significant differences were detected at room temperature in the diastereoisomeric forms of the trinuclear compounds. However, in a glass at low temperature (80 K), the luminescence lifetimes of the trinuclear heterochiral diastereoisomer were slightly shorter than those of the homochiral form.

Introduction

Complexes of the d^6 metals ruthenium(II), osmium(II), and rhenium(I) containing polypyridyl ligands have received considerable recent attention because of their potential use in photochemical molecular devices and as light-sensitive probes in biological systems.[1−3] This interest is related to their spectral properties, photophysical characteristics (particularly in terms of the longevity of the excited states), inertness in a variety of oxidation states, and the redox characteristics of both the ground and excited states.[4]



One ligand of this genre which has been investigated is 1,4,5,8,9,12-hexaazatriphenylene (HAT), where there are three sites for bidentate ligation to a metal center. It may serve as a bidentate ligand in mononuclear complexes or as a ligand bridge in di- and trinuclear species. Examples are known in each of these categories, and studies have addressed synthetic strategies for homo- and heterometallic polynuclear species,[5−9] photophysical properties,[6,9−12] and their interaction and photoreactions with various polynucleotides.[13−16]

In the studies of polynuclear complexes, the inherent problem of stereoisomerism has not been elaborated, although it has been acknowledged.[5,12] In recent studies, we have reported the separation of stereoisomers of ligand-bridged dinuclear species[17,18] and the synthesis of mononuclear and dinuclear complexes with predetermined stereochemistry.[19,20] In the present work, these techniques were applied to obtain all the stereoisomers of the mono-, di-, and triruthenium(II) complexes incorporating the ligand HAT, and studies of the photophysical characteristics are reported. Studies of the stereochemical

[†] James Cook University of North Queensland.
[‡] Université Libre de Bruxelles.
[§] Director of Research at the FNRS (Belgium).
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influence of interactions of such complexes with mononucleotides and DNA will be reported subsequently, as well as investigations of analogous polynuclear heterometallic species.

Experimental Section

Physical Measurements. ^{1}H, selective ^{1}H decoupling, NOE difference, and COSY experiments were performed on a Bruker Aspect 300 MHz NMR spectrometer using CD_3CN as the solvent. Electronic spectra were recorded in acetonitrile solution on a Hewlett Packard HP-89532K spectrophotometer using quartz cells.

All electrochemical experiments were performed under argon in an inert-atmosphere drybox using a Bioanalytical Systems BAS 100A electrochemical analyzer. Measurements were made in acetonitrile/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ solution using a platinum button working electrode and a Ag/Ag^+ (0.01 M $AgClO_4$/0.1 M $[(n\text{-}C_4H_9N]ClO_4$ in acetonitrile) reference electrode (+0.31 V vs SSCE). Cyclic voltammetry was performed with a sweep rate of 100 mV/s; differential pulse voltammetry was run with a sweep rate of 4 mV/s and a pulse amplitude, width, and period of 50 mV, 60 ms, and 1 s, respectively. Elemental analyses were performed within the Department of Chemistry and Chemical Engineering at James Cook University of North Queensland.

ORD (optical rotary dispersion) spectra were recorded on a Perkin-Elmer 141 polarimeter in a 1 dm cell. Specific rotation at λ: $[\alpha]_\lambda = 100\alpha/cl$, where α = absolute rotation (deg), c = concentration in g/100 cm^3, and l = cell path length (in dm). Molecular rotation at λ: $[M]_\lambda$ = molecular weight $\times$ $[\alpha]_\lambda/100$. CD (circular dichroism) spectra were recorded in acetonitrile solution at concentrations of $1-3 \times 10^{-5}$ M at the University of Wollongong using a Jobin Yvon Dichrograph 6 instrument. All CD spectra are presented as $\Delta\epsilon$ vs λ (nm).

Photodecomposition/Photoracemization Studies. All solutions were prepared under argon in an inert atmosphere drybox and their UV−visible spectra recorded using stoppered 1 cm quartz cells. Samples were irradiated with a low-pressure mercury lamp: the irradiation time was 7.5 h, which corresponded to the time for 50% photodecomposition of a reference complex $[Ru(phen)_3(PF_6)_2$ in acetonitrile/0.2 M $[(C_2H_5)_4N]Cl$ solution. Photodecomposition studies were carried out in acetonitrile, water, or aqueous phosphate buffer (pH 7) solutions and monitored by variations in the UV−visible spectra, with photoracemization tested by cation exchange chromatography (SP-Sephadex C25) using sodium toluene-4-sulfonate solution as the eluent.

Luminescence Spectra and Lifetimes. The noncorrected relative emission spectra of the *meso* and *rac* dinuclear compounds were recorded with a Shimadzu RF-5001 PC spectrometer equipped with a Hamamatsu R-928 red-sensitive photomultiplier (PM) tube. The corrected emission spectra were obtained using an Edinburgh Instruments FL/FS 900 spectrofluorimeter equipped with a red-sensitive Hamamatsu R-928 PM tube and an ultrasensitive liquid-nitrogen-cooled Ge detector (spectral response 0.8−1.7 μm).

The emission lifetimes were determined from decays following single-shot pulsed-laser excitation, and also by time-resolved single photon counting (SPC). The use of the two different techniques confirmed the reproducibility of the measurements and reliability of the data treatment: it was undertaken because the luminescence is far into the long-wavelength region of the spectrum where detector response is lower, so that artifacts may appear during the measurements. The data in Table 2 correspond to average values obtained from the two techniques.

Under pulsed-laser excitation, the emission lifetimes were determined with a modified Applied Photophysics laser kinetics spectrometer equipped with a Hamamatsu R-928 PM tube. The excitation source was composed of a frequency-doubled neodymium YAG laser (Continuum NY 61-10) coupled with a dye laser (Continuum ND 60; dye DCM; λ_{exc} = 640 nm) and with the mixing option (Continuum UVX), producing a 400 nm beam (10 ns pulse width, maximum of 27 mJ/pulse; measurements at ca. 8 mJ/pulse). Kinetic analyses of the luminescence decays were performed by nonlinear least-squares regressions using a modified Marquardt algorithm.[21,22]

The SPC measurements were performed with an Edinburgh Instruments FL-900 spectrofluorimeter equipped with a nitrogen-filled discharge lamp and a Peltier-cooled Hamamatsu R-928 PM tube. The emission decays were analyzed with the Edinburgh Instruments software (version 3.0), based on nonlinear least-squares regressions using a modified Marquardt algorithm.

Microwave Techniques. Reactions were performed in a modified Sharp microwave oven (Model R-2V55; 600 W, 2450 MHz) on medium-high power.[23] Reactions were carried out in a round-bottom flask filled with a condenser, using ethylene glycol as the solvent.

Materials. 1,4,5,8,9,12-Hexaazatriphenylene (HAT) was supplied by Professor D. P. Rillema (University of North Carolina, Charlotte, NC).[10] Ethylene glycol (Ajax, 95%), $RuCl_3 \cdot xH_2O$ (Strem, 99%), 1,10-phenanthroline (phen; aldrich, 99+%), 2,2′-bipyridine (bpy; Aldrich, 99+%), potassium hexafluorophosphate (KPF_6; Aldrich 98%), ammonium hexafluorophosphate (NH_4PH_6; Aldrich, 99.99%), tris{3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato}europium(III) {[Eu(tfc)$_3$]; Fluka, 97%}, and laboratory reagent (LR) solvents were used without further purification unless specified. Trimethylamine *N*-oxide dihydrate (Fluka) was purified by sublimation at 120 °C under vacuum. $[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[24] $[Ru(phen)_2Cl_2]\cdot 2H_2O$,[25] Δ- and Λ-$[Ru(phen)_2(CO)_2](PF_6)_2$,[20] and Δ- and Λ-$[Ru(bpy)_2(CO)_2](PF_6)_2$[20] were prepared according to literature methods. Sodium toluene-4-sulfonate (Sigma, 98%), (−)-*O*,*O*′-dibenzoyl-L-tartaric acid (Fluka, >99%, $[\alpha]^{20} = -117°$), and di-4-toluoyl-D-tartaric acid (Aldrich, 97%, $[\alpha]^{19} = +138°$) were used without further purification: aqueous solutions of sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate and sodium (+)-di-4-toluoyl-D-tartrate were prepared by neutralization of the respective acids with sodium hydroxide.

Chromatography. All chromatographic procedures were carried out using SP-Sephadex C25 cation exchanger as the support and aqueous sodium toluene-4-sulfonate, sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate, or sodium (+)-di-4-toluyl-D-tartrate as the eluent. The support was contained in a column approximately 100 cm long × 2 cm in diameter. When necessary, the column was sealed, enabling the complex to be recycled several times down its length with the aid of a peristaltic pump: in these cases, an "effective column length" (ECL) for the separation represents the total length of support traveled by the sample. All chromatography was carried out in subdued light.

Syntheses. $[Ru(bpy)_2(HAT)](PF_6)_2$ was synthesized by the literature method[5] as well as by the alternative method described below.

A suspension of HAT (100 mg, 0.4 mmol) in ethylene glycol (20 cm^3) was heated in the microwave oven for 2 min to complete dissolution, and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (74 mg, 0.14 mmol) was added in three portions over 4 min. The resultant red-brown solution was heated for a further 2 min and the reaction mixture allowed to cool and then filtered to remove excess ligand. The crude product was purified by the method described by Masschelein *et al.*[5] The complex was rechromatographed (SP-Sephadex C25 cation exchanger with 0.125 M sodium toluene-4-sulfonate as eluent) and the product precipitated from the major band by the addition of KPF_6 and reprecipitated from acetone/water solution by the addition of KPF_6. Yield: 96 mg (70%).[26]

Resolution of $[Ru(bpy)_2(HAT)](PF_6)_2$ was achieved by cation exchange chromatography using 0.1 M sodium di-4-toluoyl-D-tartrate as the eluent (ECL ~ 400 cm). The two bands were collected and precipitated with KPF_6 and reprecipitated as above. By comparisons with similar complexes of known configuration,[20] band 1 (the first band eluted) was assigned as Δ-(−)-$[Ru(bpy)_2(HAT)](PF_6)_2$ and band 2 (the second band) as Λ-(+)-$[Ru(bpy)_2(HAT)](PF_6)_2$.

$[\{Ru(bpy)_2\}_2(\mu\text{-}HAT)](PF_6)_4$ was synthesized by the literature method[5] as well as by the alternative method described below.

A suspension of HAT (50 mg, 0.21 mmol) in ethylene glycol (50 cm^3) was heated for ca. 2 min in the microwave oven to complete

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dissolution, and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (218 mg, 0.42 mmol) was added in four portions over 8 min, during which time the solution changed color from red/brown to purple/black. The mixture was refluxed for a further 4 min and allowed to cool. The crude mixture was purified according to the method described by Masschelein *et al*.[5] The complex was rechromatographed (SP-Sephadex C25 cation exchanger with 0.15 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as eluent), during which procedure diastereoisomeric separation was achieved (ECL ∼ 15 cm). The two bands were collected and each was precipitated by addition of a saturated solution of KPF_6. The separated diastereoisomers were dissolved in acetone/water, reprecipitated by the addition of a saturated solution of KPF_6, filtered off, and washed with distilled water and diethyl ether. The products were separately dissolved in acetone and loaded onto a short column of silica gel, washed with acetone, water, and acetone, and then eluted with acetone containing 5% NH_4PF_6. The acetone was removed and the brown-black product collected by filtration and washed with cold distilled water and diethyl ether. Total yield: 240 mg (70%); diastereoisomeric proportions were *meso* {band 1}/*rac* {band 2} = 54/46.[26]

Resolution of *rac*-[{Ru(bpy)$_2$}$_2$(μ-HAT)](PF$_6$)$_4$. The sample from band 2 of the above synthesis was resolved chromatographically (SP-Sephadex C25 cation exchanger) using 0.15 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate was the eluent (ECL ∼ 400 cm). The resolved products were collected and isolated as described above. Bands 1 and 2 were assigned as the ΔΔ and ΛΛ enantiomers, respectively. The CD {CH_3CH; λ_{max}, nm ($\Delta\epsilon$)} data are as follows. ΔΔ: 269 (51), 288 (−162), 319 (−94), 397 (23). ΛΛ: 269 (−51), 288 (158), 319 (91), 397 (−20).

[{Ru(bpy)$_2$}$_3$(μ-HAT)](PF$_6$)$_6$ was synthesized according to the literature method[5] and by the alternative method described below.

HAT (50 mg, 0.21 mmol) and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (450 mg, 0.854 mmol) were added to a solution of ethylene glycol (30 cm^3), and the mixture was refluxed in the microwave oven (medium-high) for 8 min. On cooling, distilled water (ca. 150 cm^3) was added and then a saturated solution of KPF_6 until precipitation was complete. The mixture was stored overnight at 4 °C and the product collected by filtration and purified according to the method described by Masschelein *et al*.[5] As a further purification step, the product was rechromatographed (SP-Sephadex C25 cation exchanger using 0.3 M sodium toluene-4-sulfonate as the eluent). Diastereoisomeric separation also achieved (ECL ∼ 10 cm), the two products were collected following the addition of saturated KPF_6 to the separated bands and repreciptated as described above for the dinuclear species. Total yield: 430 mg (86%); diastereoisomeric proportions were heterochiral ($\Delta^2\Lambda/\Lambda^2\Delta$) {band 1}/homochiral ($\Delta^3/\Lambda^3$) {band 2} = 83/17.[26]

Resolution of [{Ru(bpy)$_2$}$_3$(μ-HAT)](PF$_6$)$_6$. The sample isolated from band 2 of the above synthesis, (Δ^3/Λ^3)-[{Ru(bpy)$_2$}$_3$(μ-HAT)](PF$_6$)$_6$, was resolved by cation exchange chromatography using 0.2 M sodium (+)-di-4-toluoyl-D-tartrate as the eluent. Bands 2a (eluted first) and 2b were collected and the diastereoisomers isolated as described above and assigned as Δ^3 and Λ^3, respectively (see Discussion). The CD {CH_3CN; λ_{max}, nm ($\Delta\epsilon$)} data are as follows. Δ^3: 261 (−23), 275 (87), 291 (−136), 327 (−103), 374 (14). Λ^2: 261 (25), 275 (−102), 291 (127), 327 (101), 374 (−15).

[Ru(phen)$_2$(HAT)](PF$_6$)$_2$ was synthesized and purified under conditions identical to those described for $[Ru(bpy)_2(HAT)](PF_6)_2$, but using $[Ru(phen)_2Cl_2]\cdot 2H_2O$ as the starting material. Yield: 80%.[26]

Resolution of [{Ru(phen)$_2$(HAT)](PF$_6$)$_2$ was achieved by cation exchange chromatography using 0.1 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as the eluent (ECL ∼ 300 cm). The two bands were collected and precipitated with KPF_6 and reprecipitated as above. By comparisons with similar complexes of known configuration,[20] band 1 was assigned as Δ-(−)-$[Ru(phen)_2(HAT)](PF_6)_2$ {$[\alpha]_{546} = -973°$ ($[M]_{546} = -9582°$), $[\alpha]_{578} = -1104°$ ($[M]_{578} = -10872°$); CH_3CN solution} and band 2 as Λ-(+)-$[Ru(phen)_2(HAT)](PF_6)_2$ {$[\alpha]_{546} = +987°$ ($[M]_{546} = +9719°$), $[\alpha]_{578} = +1142°$ ($[M]_{578} = +11246°$); CH_3CN solution}. The CD {CH_3CN; λ_{max}, nm ($\Delta\epsilon$)} data are as follows: Δ: 254 (150), 264 (−186), 294 (−118), 399 (16). Λ: 254 (−152), 264 (183), 295 (118), 399 (−16).

Enantiomeric purity was confirmed by ^{1}H NMR using the chiral lanthanide-induced shift reagent tris{3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato}europium(III), [Eu(tfc)$_3$]. $[Ru(phen)_2(HAT)](PF_6)_2$ was converted to the Cl^- salt by anion exchange chromatography and ^{1}H NMR experiments performed in CD_3CN.

[{Ru(phen)$_2$}$_3$(μ-HAT)](PF$_6$)$_4$ was synthesized and purified under conditions identical to those described for $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})](PF_6)_4$, but using $[Ru(phen)_2Cl_2]\cdot 2H_2O$ as the starting material. Total yield: 71%; diastereoisomeric proportions were *meso* {band 1}/*rac* {band 2} = 51/49.[26]

Resolution of [{Ru(phen)$_2$}$_2$(μ-HAT)](PF$_6$)$_4$ was carried out in a manner identical to that described for $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})](PF_6)_4$. The CD {$CH_3CN$ λ_{max}, nm ($\Delta\epsilon$)} data are as follows. ΔΔ: 255 (304), 270 (−210), 296 (−257), 399 (19). ΛΛ: 255 (−298), 270 (214), 296 (247), 399 (−17).

[{Ru(phen)$_2$}$_3$(μ-HAT)](PF$_6$)$_6$ was synthesized and purified under conditions identical to those described for $[\{Ru(bpy)_2\}_3(\mu\text{-HAT})](PF_6)_6$, but using $[Ru(phen)_2Cl_2]\cdot 2H_2O$ as the starting material. Total yield: 90% diastereoisomeric proportions were heterochiral {band 1}/homochiral {band 2} = 80/20.[26]

Resolution of homochiral [{Ru(phen)$_2$}$_3$(μ-HAT)](PF$_6$)$_6$ was achieved by cation exchange chromatography using 0.2 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as the eluent (ECL ∼ 330 cm). The two bands were collected and precipitated with KPF_6 and reprecipitated as described above. Bands 1 and 2 were assigned to Δ^3 and Λ^3, respectively (see Discussion). The CD {CH_3CN; λ_{max}, nm ($\Delta\epsilon$)} data are as follows. Δ^3: 217 (91), 259 (336), 278 (−220), 295 (−236). Λ^3: 217 (−94), 260 (−326), 277 (220), 295 (226).

Stereoselective Syntheses of ΔΔ-[{Ru(bpy)$_2$}$_2$(μ-HAT)](PF$_6$)$_4$ and Δ^3-[{Ru(bpy)$_2$}$_3$(μ-HAT)}](PF$_6$)$_6$. A suspension of HAT (5 mg, 0.0213 mmol) in 2-methoxyethanol (5 cm^3) was degassed with dry N_2 for 15 min. Δ-(−)-$[Ru(bpy)_2(CO)_2](PF_6)_2$[19] (64 mg, 0.0852 mmol) and trimethylamine *N*-oxide (40 mg, 0.51 mmol) were added, and the reaction mixture was stirred at room temperature in subdued light for 11 days. A further addition of trimethylamine *N*-oxide (15 mg, 0.2 mmol) was made after approximately 6 days. The reaction produced both dinuclear and trinuclear products, which were separated by SP-Sephadex C25 cation exchange chromatography; ΔΔ-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ was eluted with a solution 0.3 NaCl in water/acetone (5:3) and Δ^3-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$ with a solution 0.5 M NaCl in water/acetone (5:3). ΔΔ-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ and Δ^3-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$ were further purified separately by cation exchange chromatography with elution by 0.2 and 0.3 M sodium toluene-4-sulfonate solution, respectively. The products were collected as described above. Yield: ΔΔ-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})](PF_6)_4$, 23% (8 mg); Δ^3-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})](PF_6)_6$, 24% (12 mg).[26] The CD data are as follows. ΔΔ {CH_3CN; λ_{max}, nm ($\Delta\epsilon$)}: 269 (69), 288 (−156), 319 (−96), 397 (20). Δ^3 {λ_{max}, nm ($\Delta\epsilon$)}: 261 (−23), 275 (89), 291 (−126), 327 (−96), 374 (13).

Stereoselective Syntheses of ΛΛ-[{Ru(phen)$_2$}$_2$(μ-HAT)](PF$_6$)$_4$ and Λ^3-[{Ru(phen)$_2$}$_3$(μ-HAT)](PF$_6$)$_6$. The syntheses and purification were performed under conditions similar to those described for ΔΔ-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})](PF_6)_4$ and Δ^3-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})](PF_6)_6$, but using Λ-(+)-$[Ru(phen)_2(CO)_2](PF_6)_2$ rather than Δ-(−)-$[Ru(bpy)_2(CO)_2](PF_6)_2$; the reaction mixture was stirred for a further 3 days. Yield: ΛΛ-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})](PF_6)_4$, 19% (7 mg); Λ^3-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})](PF_6)_6$, 28% (15 mg).[25] The CD data are as follows. ΛΛ {CH_3CN; λ_{max}, nm ($\Delta\epsilon$)}: 255 (−267), 270 (195), 296 (260), 399 (−21). Λ^3 {λ_{max}, nm ($\Delta\epsilon$)}: 218 (−93), 260 (−309), 277 (210), 295 (224).

Results and Discussion

Synthesis. The various $[\{Ru(pp)_2\}_n(HAT)]^{(2n)+}$ species {pp = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)} have been synthesized previously by the reaction of *n* equiv (*n* = 1−3) of $[Ru(pp)_2Cl_2]$ with HAT in methanol/water (1/1) under reflux.[5] In the first of two alternative synthetic methods developed in the present work, the reaction of the same starting materials in ethylene glycol solution under microwave conditions[23] produced reaction yields equivalent to or increased over those produced by the conventional method, but with a ca. 50-fold decrease in reaction time. The second method involved decarbonylation of chiral Δ- or Λ-$[Ru(pp)_2(CO)_2]^{2+}$ in 2-methoxyethanol solution in the presence of the ligand HAT. Such

decarbonylation reactions are known to proceed with retention of stereochemical integrity of the metal center when undertaken at room temperature and subdued light.[19,20] In the present case, due to the low solubility of HAT in the 2-methoxyethanol solvent at low temperatures, the mixture was stirred for 8−10 days, after which time both the di- and trinuclear complexes were isolated in ca. 20% yield.

Stereochemistry. The development of synthetic methodologies involving enantiomerically pure building blocks[19] and chromatographic techniques[17] has enabled us to isolate individual stereoisomers (diastereoisomers, enantiomers, and/or geometric isomers) in these and related systems.[27] This has allowed assessment of the effect of stereoisomerism on physical properties such as electrochemical and photophysical characteristics, and on the interaction with chiral assemblies such as mononucleotides and DNA. Such studies have previously been limited because stereoisomerically pure polynuclear complexes were not available. In addition, in earlier investigations of polynuclear polypyridyl complexes of ruthenium,[5,28,29] the existence of stereoisomerism complicated structural determinations and characterization: for example, NMR spectroscopy has been of limited value because the diastereoisomeric complexes have nonequivalent NMR spectra.[17,30]

The chromatographic separation of stereoisomers forms a most important part of this study. Cation exchange chromatography was employed, using SP-Sephadex C25 as the support, with aqueous sodium toluene-4-sulfonate, sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate, or sodium (+)-di-4-toluoyl-D-tartrate solutions as the eluents. While the technique is based on a cation exchange mechanism, the mode of isomer separation is influenced by a differential association between the stereoisomers of the complex with both the anion of the eluent and the chiral support. The precise nature of the associations is currently under investigation and appears to have components involving specific π-stacking and hydrophobic interactions.[31]

Mononuclear Complexes. $[Ru(bpy)_2(HAT)]^2$ and $[Ru(phen)_2(HAT)]^{2+}$ were each chromatographically resolved into enantiomeric forms using the chiral eluents 0.1 M sodium (+)-di-4-toluoyl-D-tartrate and 0.1 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate, respectively. The enantiomers of each compound showed equal and opposite ORD and CD spectra (shown for $[Ru(phen)_2(HAT)]^{2+}$ in Figure S1, Supporting Information), and ^{1}H NMR studies of Δ- and Λ-$[Ru(phen)_2(HAT)]^{2+}$ in the presence of the chiral lanthanide-shift reagent $[Eu(tfc)_3]$ confirmed optical purity. The absolute configurations were determined by comparisons of the CD spectra with related complexes with known absolute configurations (Figure 1).[20]

Dinuclear Complexes. $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ was chromatographically separated into the *rac* (ΔΔ/ΛΛ) and *meso* (ΔΛ) diastereoisomeric forms (Figure 2) using 0.15 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as eluent, the separation being observed within 15 cm of travel. Bands 1 (eluted first) and 2 (eluted second) were determined to be the *meso* and *rac* diastereoisomers, respectively, as established by NMR characterization and comparison with an authentic sample of the ΔΔ isomer deliberately synthesized using Δ-$[Ru(bpy)_2(CO)_2]^{2+}$ as the precursor. In addition, band 2 could be chromatographically resolved (ECL ∼ 400 cm) using 0.15 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as eluent, thereby confirming it as the *rac* form: bands 2a and 2b were assigned as the ΔΔ and ΛΛ enantiomers, respectively. The absolute configurations of the two bands were established by comparison of the CD spectra with that of the stereoselectively synthesized ΔΔ-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$.

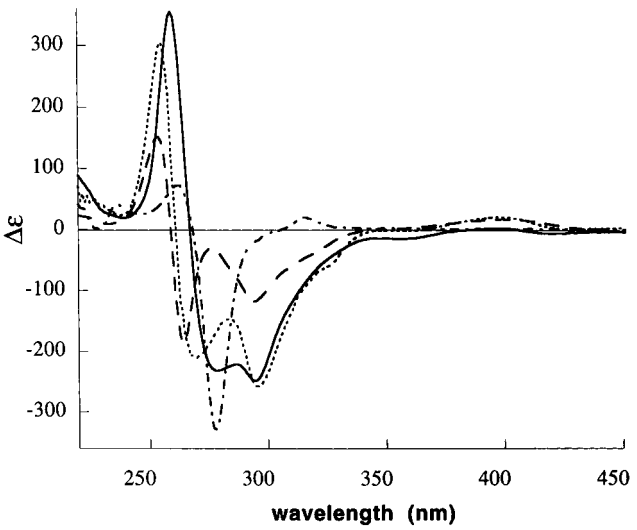

Figure 1. CD spectra of Δ-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ (—), Δ-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ (- - -), Δ-$[Ru(phen)_2(HAT)]^{2+}$ (— — —), and Δ-$[Ru(phen)_2(CO)_2]^{2+}$ (—•—•).

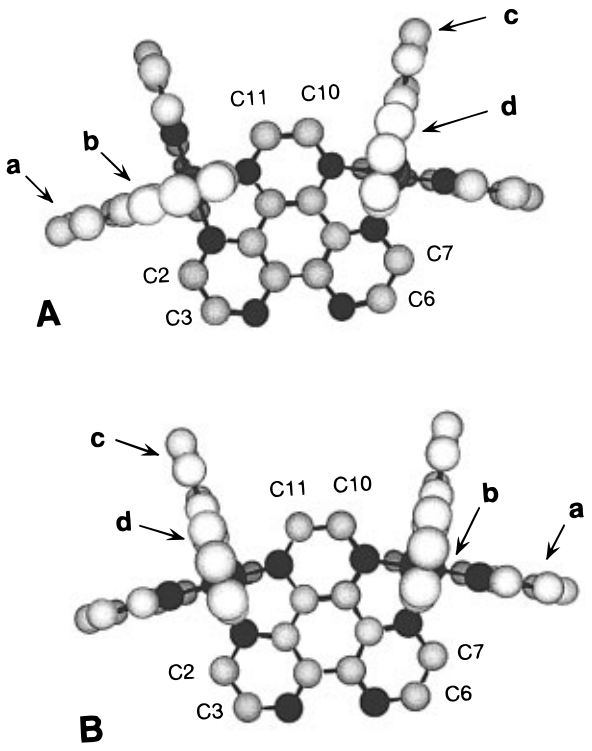

Figure 2. Chem 3D representation of diastereoisomeric forms of $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$: (A) *rac* {ΔΔ (≡ΛΛ)}; (B) *meso* {ΛΔ}. Hydrogen atoms are omitted for clarity; the notation shown is the same for the phen analogues and is used in the discussion of the ^{1}H NMR spectra.

Diastereoisomeric separation, resolution, and the assignment of absolute configurations of $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ were achieved as described above for $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$. The diastereoisomeric separation (ECL ∼ 8 cm) and the subsequent resolution of the *rac* form into its enantiomers (ECL ∼ 300 cm) were achieved, with the elution order (ΔΛ, ΔΔ, and ΛΛ) being identical to that of the bpy analogue above. The CD

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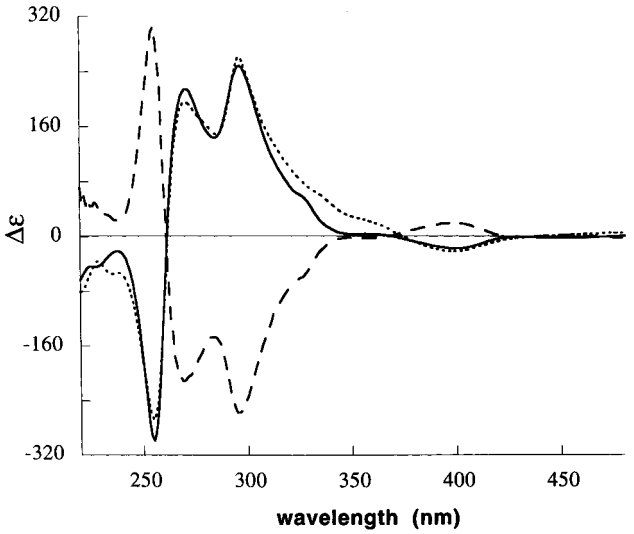

Figure 3. CD spectra for stereoisomeric forms of $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$: ΛΛ synthesized from Λ-$[\{Ru(phen)_2\}_2(CO)_2]^{2+}$ (- - -); ΛΛ (—) and ΔΔ (— — —) from chromatographic separation.

spectra of the chromatographically separated ΔΔ- and ΛΛ-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ forms, and the ΔΔ enantiomer stereoselectively synthesized from Δ-$[Ru(phen)_2(CO)_2]^{2+}$, are shown in Figure 3, and for the bpy analogues in Figure S2 (Supporting Information).

Trinuclear Complexes. $[\{Ru(bpy)_2\}_3(\mu\text{-HAT})\}^{6+}$ was chromatographically separated into the homochiral (Δ^3/Λ^3) and heterochiral ($\Delta^2\Lambda/\Lambda^2\Delta$) diastereoisomeric forms (Figure 4) using 0.3 M sodium toluene-4-sulfonate as eluent. Bands 1 and 2 were determined to be the $\Delta^2\Lambda/\Lambda^2\Delta$ and Δ^3/Λ^3 diastereoisomers, respectively, by NMR spectroscopy (the D_3 symmetry of Δ^3/Λ^3, compared to the C_2 symmetry of $\Delta^2\Lambda/\Lambda^2\Delta$, resulting in a simplified spectrum for Δ^3/Λ^3 (see below), and comparisons with the spectrum of the stereoselectively synthesized Δ^3 form). The Δ^3/Λ^3 diastereoisomer (band 2) was chromatographically resolved using 0.2 M sodium (+)-di-4-toluoyl-D-tartrate as the eluent. Bands 2a and 2b were assigned as the Δ^3 and Λ^3 enantiomers, respectively, by comparisons of the CD spectra ($\Delta\epsilon$ values) with the CD spectrum of the stereoselectively synthesized Δ^3 form.

Resolution of the $\Delta^2\Lambda/\Lambda^2\Delta$ diastereoisomer was attempted using a range of eluents at varying concentrations, but without success. However, the $\Delta^2\Lambda$ and $\Lambda^2\Delta$ enantiomers may be obtained by a combination of chromatographic separations and stereoselective syntheses: the resolved ΔΔ and ΛΛ forms of $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ were separately reacted with *rac*-$[Ru(bpy)_2Cl_2]$, resulting in the two diastereoisomeric mixtures $\Delta^3/\Delta^2\Lambda$ and $\Lambda^3/\Lambda^2\Delta$, respectively, which were separated chromatographically, thus realizing the $\Delta^2\Lambda$ and $\Lambda^2\Delta$ forms. Since the absolute configuration of the precursor complex $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ is known, the absolute configuration assignments of $\Delta^2\Lambda$- and $\Lambda^2\Delta$-$[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$ may be made. The same technique has been used to isolate the stereoisomers of mixed Ru/Os trinuclear systems.[32]

$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ was chromatographically separated into the Δ^3/Λ^3 and $\Delta^2\Lambda/\Lambda^2\Delta$ diastereoisomeric forms using 0.3 M sodium toluene-4-sulfonate as eluent (ECL ~ 8 cm). Band 1 (eluted first) and band 2 (eluted second) were determined to be $\Delta^2\Lambda/\Lambda^2\Delta$ and Δ^3/Λ^3 in a manner similar to that described for $[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$. The Δ^3/Λ^3 diastereoisomer (band 2) was resolved using 0.2 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as eluent (ECL ~ 250 cm). Bands 2a and 2b were assigned as the Δ^3 and Λ^3 enantiomers, respectively. Enantiomer assignment and purity were achieved by comparisons of the CD spectra ($\Delta\epsilon$ values) with the CD spectrum of the stereoselectively synthesized Λ^3 form. The CD spectra of the Λ^3- and Δ^3-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ enantiomers are shown in Figure 5, and the bpy analogues in Figure S3 (Supporting Information).

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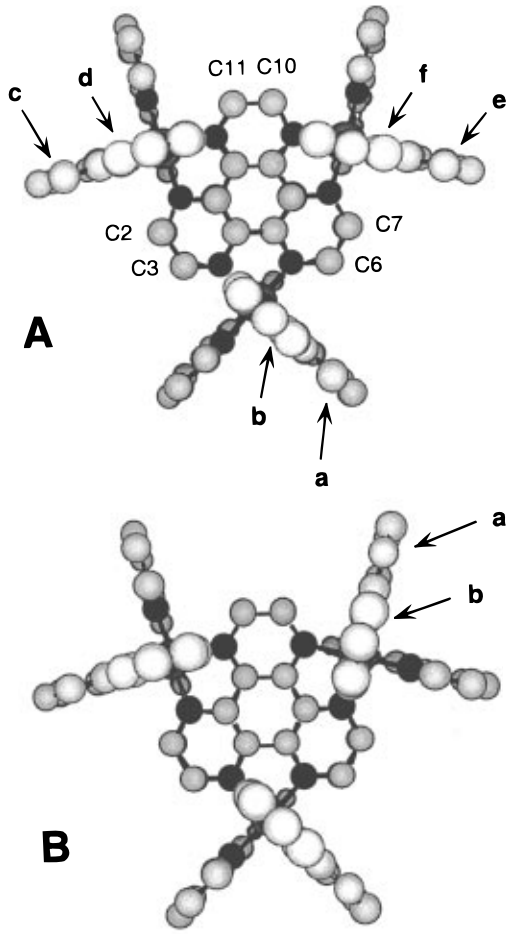

Figure 4. Chem 3D representation of diastereoisomeric forms of $[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$: (A) heterochiral $\{\Delta^2\Lambda\}$; (B) homochiral $\{\Delta^3 (\equiv\Lambda^3)\}$. Hydrogen atoms are omitted for clarity; the notation shown is the same for the phen analogues and is used in the discussion of the ^{1}H NMR spectra.

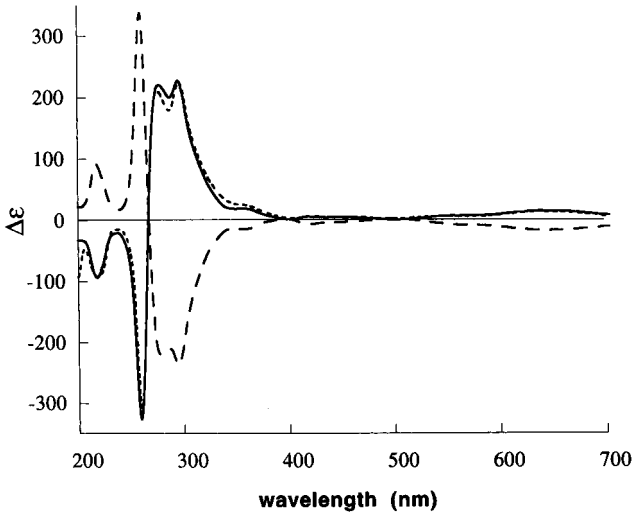

Figure 5. CD spectra for stereoisomeric forms of $[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$: Λ^3 synthesized from Λ-$[\{Ru(phen)_2\}_2(CO)_2]^{2+}$ (- - -); Λ^3 (—) and Δ^3 (— — —) from chromatographic separation.

With the characterization of the separated diastereoisomers achieved, the stereochemical features of the synthetic procedures may be revisited. No difference was observed in the diastereoisomeric ratios (*rac*/*meso* in $[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ and homochiral/heterochiral in $[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$) between the conventional heating and microwave heating methods. The diastereoisomeric ratios were approximately 50/50 (*rac*/*meso*) for $[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ and 17/83 (homochiral/heterochiral) for $[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$, which compare with the respective statistical ratios of 50/50 and 25/75 and suggest that electronic or steric influences play little part in the determination of diastereoisomer proportions.

^{1}H NMR Studies. The ^{1}H NMR data for the mononuclear complex and the diastereoisomeric forms of the di- and trinuclear complexes containing 1,10-phenanthroline (phen) terminal ligands and the HAT bridging ligand are shown in Table 1. The ^{1}H NMR data for the analogous series of complexes containing 2,2′-bipyridine as the terminal ligands are given in Table S1 (Supporting Information). The notation for the phen and HAT ligands for the above complexes is indicated in Figures 2 and 4.

In all cases, the phen ligands exhibited the expected coupling constant values[28] $\{J_{2,3} = J_{8,9} = 5$ Hz, $J_{2,4} = J_{7,9} = 1.5$ Hz, $J_{3,4} = J_{7,8} = 8$ Hz, and $J_{5,6} = 9$ Hz ($J_{5,6}$ variable due to second-order effects)$\}$ and coupling patterns based on the symmetry requirements of the above complexes (i.e., $[\{Ru(phen)_2(HAT)]^{2+}$ (C_2 point group symmetry), $\Lambda\Lambda/\Delta\Delta$-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ (C_2) and $\Delta\Lambda$-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ (C_s), Δ^3/Λ^3-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ (D_3) and $\Delta^2\Lambda/\Lambda^2\Delta$-$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$ (C_2).

The ^{1}H NMR chemical shifts listed in Tables 1 and S1 were determined by ^{1}H COSY spectra, selective ^{1}H decoupling, and NOE experiments and were assigned as described below. Connectivity between the H4 and H5, H5 and H6, and H6 and H7 protons in the individual ligands of complexes containing two or more nonequivalent phen ligands was confirmed by NOE experiments. The complete assignment of chemical shifts to the ligands in the structure (given in Table 1) was based on the relative degree of diamagnetic anisotropic interactions between adjacent ligands (these anisotropic interactions may occur between the phen and HAT ligands, the two phen ligands on the same metal center, the phen ligands on the adjacent metal centers, or combinations of these interactions).

$[Ru(phen)_2(HAT)]^{2+}$. The C_2 symmetry of $[\{Ru(phen)_2(HAT)]^{2+}$ results in an AMX, A′M′X′, and AX spectrum with three additional singlet resonances. The two AMX coupled systems were assigned to the chemical shifts seen in Table 1, by the reduced diamagnetic anisotropic interaction (less shielding influence) between H9 (8.18 ppm) and the electron deficient ligand HAT relative to H2 (8.00 ppm) and phen. The electron density (and therefore the degree of anisotropic interactions) in these polypyridyl ligands has been shown to be influenced significantly more by the incorporation of nitrogen donor atoms than by the number of aromatic rings (aromaticity).[19] Selective ^{1}H decoupling of the H9 and H2 resonances and NOE effects between H4 and H5 confirmed the subsequent assignments in Table 1. The expected coupling pattern was observed from the HAT ligand with H2/H11 assigned to 8.26 ppm (d, $J = 3$ Hz) on the basis of increased diamagnetic anisotropic interactions with the phen ligands.

$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$. The C_2 symmetry of the *rac* diastereoisomer requires two nonequivalent phen ligands with each phen exhibiting a spectrum consisting of AMX, A′M′X′, and AB coupling patterns, and an AX coupled system and a singlet resonance from the HAT (see Figure 6). The two nonequivalent phen ligands are orientated in a pseudoorthogonal geometry on the same face of the HAT bridging ligand (see Figure 2). The assignment of the HAT proton resonances for both diastereoisomers was based on coupling constants and the relative degree of diamagnetic anisotropic interactions with the phen ligands. The singlet resonance (H10 and H11; see Table 1) in both isomers was the most shielded due to the anisotropic interaction with the four phen ligands.

Ring b (see Figure 2) is orientated over the plane of two ligands, the phen across the bridge and the HAT bridging ligand, resulting in increased diamagnetic anisotropic effects (shielding effect) in the H8 and H9 protons. As H8 is affected significantly more by the phen across the bridge relative to that with HAT (see influence of HAT on H8 and H3 in $[Ru(phen)_2(HAT)]^{2+}$ complex, Table 1), H8 ring b can be assigned to the most shielded H8/H3 resonance (dd, $J = 5$, 8 Hz) at 7.48 ppm. The subsequent assignments for rings a and b were achieved as described above. The upfield shift of H9 ring b (7.92 ppm) relative to H9 (8.18 ppm) of $[Ru(phen)_2(HAT)]^{2+}$ is attributed to the diamagnetic anisotropic interactions with the phenanthroline across the bridge as H9 ring b experiences a less shielding influence from the HAT with two coordinated metal centers. The assignment of H9 ring d to 8.28 ppm (most downfield dd, $J = 5$, 1.5 Hz) is in agreement with the above argument as H9 ring d is orientated over the plane of the electon deficient HAT ligand (two metal centers coordinated) and not in the shielding cone of the phen across the bridge and thus is deshielded relative to H9 (8.18 ppm) of $[Ru(phen)_2(HAT)]^{2+}$. The assignments based on this discussion are shown in Table 1.

The C_s symmetry of the *meso* diastereoisomer also requires the nonequivalence of two phen ligands (similar coupling patterns to *rac* isomer above and the ^{1}H NMR spectrum observed in Figure 6), which are orientated on the opposite faces of the HAT bridging ligand and the same ruthenium center (see Figure 2). The ^{1}H chemical shifts of the nonequivalent phen ligands and the HAT bridging ligand were assigned in a similar manner to those of the *rac* isomer (shown above) and are listed in Table 1.

H9 (ring b) was assigned to the most deshielded H2/H9 proton resonance at 8.45 ppm (dd, $J = 5$, 1.5 Hz) due to the diamagnetic anisotropic interactions with the HAT ligand and the equivalent phen ligand across the bridge (see Figure 2). As suggested above, H9 and H8 (ring b) are orientated in the deshielding cone of the equivalent phen, which is illustrated by their downfield shift relative to H9 and H8 (ring b) of the *rac* isomer (compare Figure 2 and Table 1). The subsequent assignments of rings b and a were achieved as described above.

As expected, the ^{1}H chemical shifts of ring a between the two diastereoisomers are near identical due their similar environments. H9 (ring d) was assigned to 8.19 ppm (dd, $J = 5$, 1.5 Hz) due the reduced diamagnetic anisotropic interactions with the HAT bridging ligand. The upfield shift H9 and H8 (ring d) relative to the *rac* isomer (ring d) is a result of anisotropic interactions between the equivalent phen ligands across the bridge. This shielding influence is also observed in the minor differences between H9 and H8 (ring d) of the *rac* isomer and H9 and H8 (ring b) of $[\{Ru(phen)_2(HAT)]^{2+}$, as H9 and H8 (ring d) should experience an increased deshielding influence from the more electron deficient HAT bridge (coordinated to two metal centers).

$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$. The D_3 symmetry of the homochiral (Δ^3/Λ^3) diastereoisomer requires the equivalence of the six phen ligands (see Figure 4). As the two halves of the phen ligands are nonequivalent, the ^{1}H spectrum consists of AMX,

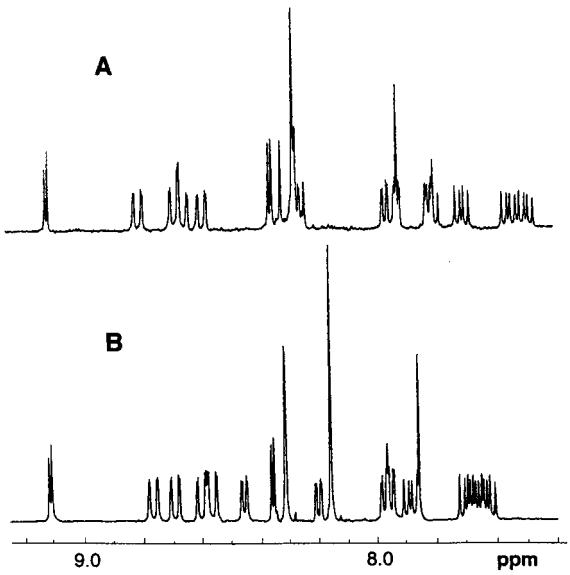

Figure 6. ^{1}H NMR spectra (300 MHz; CD_3CN solution) of the *rac* (A) and *meso* (B) diastereoisomers of $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$.

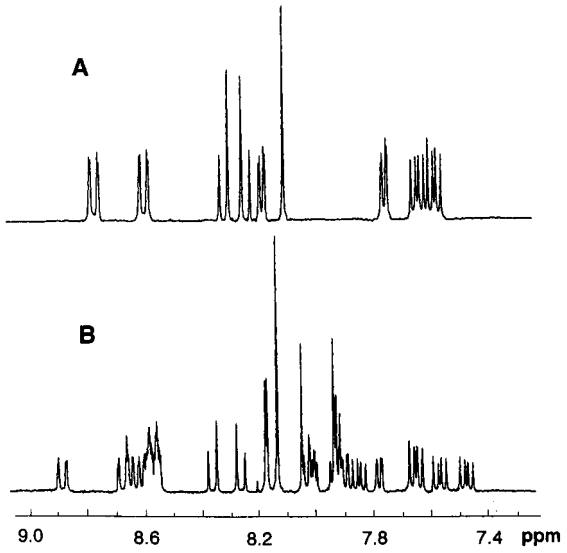

Figure 7. ^{1}H NMR spectra (300 MHz; CD_3CN solution) of the homochiral (A) and heterochiral (B) diastereoisomers of $[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$.

A′M′X′, and AB coupling patterns with an additional singlet resonance from the HAT bridging ligand (see Figure 7). The ^{1}H chemical shift assignments were achieved as described above and are shown in Table 1.

The assignment of H9 (ring b) and H2 (ring a) to 8.18 and 7.75 ppm (dd, $J = 5$, 1.5 Hz) was based on the following argument: H9 (ring b) is orientated over the HAT ligand with three coordinated metal centers (reduced shielding environment compared with two coordinated metal centers) and over the plane of the phen ligand across the bridge (shielding environment, similar to the *rac* dinuclear species). These comparisons suggest that the chemical shift of H9 (ring b) is downfield relative to H9 (ring b) of the *rac* dinuclear complex and is thus assigned to 8.18 ppm. Comparison between the chemical shift of H2 (ring a) (7.75 ppm) and the *rac* dinuclear H2 (ring c) (7.80 ppm) (similar relative environment with respect to other terminal ligands) is also in agreement with the above assignment.

The C_2 symmetry of the heterochiral ($\Delta^2\Lambda/\Lambda^2\Delta$) diastereoisomer requires three nonequivalent phen ligands (see Figure

Table 1. Chemical Shifts (ppm) from 300 MHz ^{1}H NMR Spectra of the Diastereoisomeric Forms of $[\{Ru(phen)_2\}_n(HAT)]^{2+}$ Complexes (PF_6^- Salts; CD_3CN Solvent)

				$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$		$[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$	
		$[Ru(phen)_3]^{2+}$	$[Ru(phen)_2(HAT)]^{2+}$	$\Lambda\Lambda/\Delta\Delta$	$\Delta\Lambda$	Δ^3/Λ^3	$\Delta^2\Lambda/\Lambda^2\Delta$
phen ring a (over phen)[a]	H2	8.05	8.00	7.96	7.98	7.75	7.89
	H3	7.65	7.65	7.70	7.70	7.61	7.65
	H4	8.61	8.66	8.68	8.68	8.58	8.56
	H5	8.28	8.27	8.26	8.30	8.22	8.13
phen ring b (over HAT)[a]	H6		8.27	8.26	8.31	8.30	8.13
	H7		8.66	8.64	8.76	8.77	8.56
	H8		7.68	7.48	7.87	7.61	7.48
	H9		8.18	7.92	8.45	8.18	8.01
phen ring c (over phen)[a]	H2			7.80	7.94		7.78
	H3			7.53	7.65		7.57
	H4			8.59	8.55		8.61
	H5			8.24	8.15		8.25
phen ring d (over HAT)[a]	H6			8.31	8.15		8.35
	H7			8.80	8.59		8.87
	H8			7.80	7.65		8.01
	H9			8.28	8.19		8.66
phen ring e (over phen)[a]	H2						7.93
	H3						7.65
	H4						8.57
	H5						8.17
phen ring f (over HAT)[a]	H6						8.17
	H7						8.68
	H8						7.85
	H9						8.59
HAT							
H			8.26 (H2/H11; d, $J = 3$ Hz)	7.91	7.85 (H11/H10; s)	8.10 H2/H3/H6/H7/H10/H11; s)	8.05 (H2/H3; s)
H			9.01 (H3/H10; d, $J = 3$ Hz)	8.34	8.34 (H2/H7; d, $J = 3$ Hz)		7.94 (H6/H11; s)
H			9.39 (H6/H7; s)	9.10	9.10 (H3/H6; d, $J = 3$ Hz)		7.92 (H7/H10; s)

[a] H2, H9 (dd, $J = 5$, 1.5 Hz); H3, H8 (dd, $J = 5$, 8 Hz); H4, H7 (dd, $J = 8$, 1.5 Hz).

4), thus producing a complicated ^{1}H NMR spectrum comprising six AMX, possibly three AB coupling systems from the phen ligands, and three singlet resonances from the HAT ligand (see Figure 7). The three singlet HAT resonances were assigned by comparison with the *meso* and *rac* dinuclear complex and the homochiral trinuclear complex (Table 1).

H9 (ring d) and H9 (ring f) are assigned to the two most downfield H2/H9 resonances (dd, $J = 5$, 1.5 Hz) at 8.66 and 8.59 ppm, respectively, on the basis of reduced diamagnetic anisotropic interactions described for the *meso* dinuclear complex (ring b) discussed above, and further information gained by comparisons between the *rac* and *meso* isomers (i.e., the H9 (ring d) of the *rac* isomer is downfield (8.28 ppm) relative to H9 (ring d) of the *meso* isomer (8.19 ppm)). For ring d of the *rac* isomer the phen ligand is in a similar perpendicular orientation to ring d of the heterochiral form. This results in a downfield shift relative to H9 (ring f), which contains the phen ligands in a parallel orientation (similar to ring d in the *meso* isomer). The subsequent assignments for rings d and f were achieved as describe above. The third phen ligand was assigned by comparisons with the homochiral isomer (see above) which indicate that the H9 proton orientated over the HAT bridge is downfield relative to the H2 orientated over a phen; thus H9 (ring b) and H2 (ring a) were assigned to 8.01 and 7.89 ppm, respectively. The relative shifts of H2 and H9 (rings a and b) in comparison with H2 and H9 (rings a and b) of the homochiral isomer can also be rationalized in a manner similar to the above on the basis of the relative chemical shifts of the *rac* and *meso* isomers.

Electrochemistry and Electronic Absorption Spectroscopy. Cyclic voltammetry and differential pulse voltammetry were performed on the separated diastereoisomers, *rac*- and *meso*-$[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$, and homochiral and heterochiral $\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$ (where pp = bpy or phen), with the data reported in Table S2 (Supporting Information) and are in agreement with those reported previously.[5] The absorption spectra of $[\{Ru(pp)_2\}_n(HAT)]^{(2n)+}$ ($n = 1-3$ and pp = bpy or phen) were also measured and are in agreement with those described previously.[5,11]

No significant differences were observed in the electrochemical and spectral properties of the diastereoisomers in the dinuclear and in the trinuclear series.

Photoinduced Stereoisomerism. The photoracemization of mononuclear tris(bidentate) complexes of the type $[Ru(bpy)_3]^{2+}$ is known.[33] The related phenomenon may occur in polynuclear species, but is more appropriately designated as "photoinduced stereoisomerism" since the complexes may exist in diastereoisomeric and enantiomeric forms.

In a semiquantitative investigation, the complexes $\Delta\Lambda$-, $\Delta\Delta$-, and $\Lambda\Lambda$-$[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ and Δ^3-, Λ^3-, and $\Delta^2\Lambda/\Lambda^2\Delta$-$[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$ (pp = bpy and phen) were irradiated in acetonitrile, aqueous or buffered aqueous solution, with decomposition being monitored by spectroscopy and photoinduced stereoisomerism by chromatography. In each system, the diastereoisomers are readily separated and even very minor interconversion would be detected because of the high absorption coefficients of the complexes involved. There was no detectable photoinduced stereoisomerism, although the chromatography suggested photodecomposition of approximately 1−2% in trimetallic complexes.

Luminescence Spectra and Lifetimes. Figure 8 shows the uncorrected emission spectra of the three stereoisomers ($\Delta\Lambda$, $\Delta\Delta$, and $\Lambda\Lambda$) of $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ in buffered aqueous (A) and in CH_3CN (B) solutions, recorded for comparable excitation intensities (at 500 nm) and for comparable percentages of absorbed light at the same excitation wavelength. There were no significant differences in intensities for the enantiomers of the *rac* form, whereas the *meso* diastereoisomer behaved as a slightly weaker emitter both in water and in CH_3CN. Moreover, as is generally observed, the intensity of emission was higher in the organic solvent than in aqueous solution.

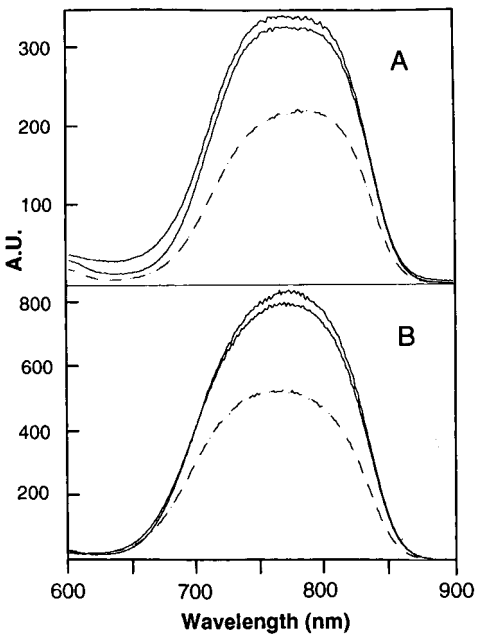

Figure 8. Noncorrected emission spectra of the three stereoisomers of $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ for the same % of absorbed light, in (A) TRIS buffer at pH 7 and (B) CH_3CN solutions: the enantiomers of the *rac* form (—), and the *meso* form (- - -). Excitation at 500 nm. Shimadzu spectrofluorimeter, Hamamatsu R-928 PMT.

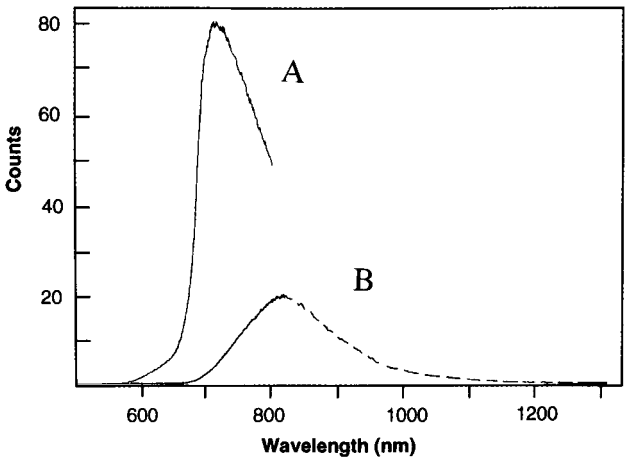

Figure 9. Corrected emission spectra in H_2O solution of (A) $[Ru(phen)_2(HAT)]^{2+}$ and (B) $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$, measured with the Hamamatsu R-928 PMT (—) and with the Ge detector (- - -). For comparable absorbance at the excitation wavelength (432 nm) and comparable intensities of excitation at that wavelength, an intensity ratio of 15/1 can be estimated for the mono-/dinuclear compound.

Comparison of the uncorrected spectra of Figure 8 (measured with a red-sensitive PM detector) with the corrected emission spectrum of the dinuclear complex in Figure 9 (where the emission at $\lambda > 800$ nm was measured with an IR-sensitive Ge detector) illustrates the experimental problems encountered in determining reliable quantum yields of emission for the bimetallic species. Indeed, an adjustment had to be made between the two portions of the emission spectrum measured with the two different detectors under different optical conditions. Therefore,

(33) Porter, G. B.; Sparks, R. H. *J. Photochem.* **1980**, *123*, 13.

Table 2. Luminescence Lifetimes of the Diastereoisomers of the Dinuclear and Trinuclear HAT-Bridged Species in Water and CH_3CN Solutions under Air at Room Temperature, Determined by SPC and under Pulsed Laser Excitation[a]

complexes	τ (ns)	
	H_2O	CH_3CN
$\Delta\Delta$-[{Ru(bpy)$_2$}$_2$(μ-HAT)]$^{4+}$	200	458
$\Lambda\Lambda$-[{Ru(bpy)$_2$}$_2$(μ-HAT)]$^{4+}$	200	455
$\Lambda\Delta$-[{Ru(bpy)$_2$}$_2$(μ-HAT)]$^{4+}$	135	405
Δ^3-[{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$	40	120
Λ^3-Δ[{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$	40	110
Λ^3/Δ^3-[{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$	40	105
$\Lambda^2\Delta/\Delta^2\Lambda$-[{Ru(bpy)$_2$}$_3$($\mu$-HAT)]$^{6+}$	34	110
$\Delta\Delta$-[{Ru(phen)$_2$}$_2$(μ-HAT)]$^{4+}$	310	690
$\Lambda\Lambda$-[{Ru(phen)$_2$}$_2$(μ-HAT)]$^{4+}$	306	680
$\Lambda\Delta$-[{Ru(phen)$_2$}$_2$(μ-HAT)]$^{4+}$	225	635

[a] See Experimental Section. In water, the decays are single exponentals. For the complexes in CH_3CN, the lifetimes given correspond to the highest % of contribution in the decays varying from 80 to 100% (see text). Error: ~3%, estimated from the reproducibility of the lifetime values determined by SPC and pulsed laser methods.

Φ_{em} values are not given, nor the λ_{max} of emission,[5] which cannot be easily differentiated for the three stereoisomers.

When the emissions of the trinuclear compounds [{Ru(pp)$_2$}$_3$(μ-HAT)]$^{6+}$ (pp = bpy or phen) were measured under the same conditions as those for the dinuclear species which gave the data presented in Figure 8, no significant differences in luminescence intensity were detected between the different diastereoisomers.

The emission lifetimes at room temperature in water and CH_3CN solutions for the stereoisomers of [{Ru(pp)$_2$}$_2$(μ-HAT)]$^{4+}$ and [{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$ are given in Table 2. For the dinuclear compounds, the emission lifetimes were significantly shorter for the *meso* complexes than for the enantiomers of the *rac* form. However, no differences were observed for the trinuclear compounds, in accordance with the measurements of the relative emission intensities given above. For these measurements, the lifetimes were longer in CH_3CN than in water, as is generally the case.

The decay analyses for the data in Table 2 require additional comment. Problems were encountered for the measurements in CH_3CN solutions, where for the same compound single-exponential decays were not consistently observed, but were contaminated by other emitting species which contributed up to 20% to the total decays when analyzed according to biexponential functions. This effect appeared under laser excitation or in the SPC measurements (see Experimental Section) and probably originated from some (photo/dark) decomposition in CH_3CN which produced monometallic species with a much higher Φ_{em} (e.g., see the comparison between the mono- and dinuclear compounds in Figure 9). This problem of decomposition in organic solvents was mentioned previously,[11] but does not occur in water.

In order to detect possible differences of luminescence lifetimes between the diastereoisomers of the trinuclear complexes, the measurements were performed in a MeOH/EtOH (1/4) glass at low temperature (80 K). Under those experimental conditions, all the decays were observed as single exponentials and, as shown in Table 3, the emission lifetimes of the heterochiral [{Ru(pp)$_2$}$_3$(μ-HAT)]$^{6+}$ were slightly shorter than those of the homochiral forms.

Photophysics of the Diastereoisomers. Conclusions. It was shown previously[11] that thermal activation from the emitting ^{3}MLCT states to the ^{3}MC states of the bi- and trimetallic HAT complexes does not take place at room temperature because the ^{3}MLCT$-^3$MC energy gap is too large. The expected photostability is confirmed by the experimental observation that photoinduced stereoisomerism does not occur for the diastereoisomers of either nuclearity. The problems of contamination of the luminescence decays by other luminescent species under pulsed excitation in CH_3CN should thus be attributed to some dark thermal decomposition, which is inhibited in a glass at low temperature, as single-exponential decays were observed under such conditions. The absence of detectable photoisomerization establishes the accuracy of the emission quantum yields and lifetimes for the individual diastereoisomers. Although the photophysical differences between the stereoisomers are not large, this paper demonstrates their existence. They are therefore considered significant. For the first time there is evidence for inherent differences in such properties between diastereoisomers, and not differences arising from interactions with a chiral partner such as DNA or a luminescent quencher.

Table 3. Luminescence Lifetimes of the Diastereoisomeric Forms of [{Ru(pp)$_2$}$_3$(μ-HAT)]$^{6+}$ in a MeOH/EtOH 1/4 Glass at 80 K, Determined under Pulsed Laser Excitation[a]

complexes	τ (ns), MeOH/EtOH (1/4) at 80 K
Λ^3-[{Ru(phen)$_2$}$_3$(μ-HAT)]$^{6+}$	1676
Δ^3/Λ^3-[{Ru(phen)$_2$}$_3$(μ-HAT)]$^{6+}$	1655
$\Delta^2\Lambda/\Lambda^2\Delta$-[{Ru(phen)$_2$}$_3$($\mu$-HAT)]$^{6+}$	1517
Λ^3-[{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$	1855
Δ^3/Λ^3-[{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$	1800
$\Delta^2\Lambda/\Lambda^2\Delta$-[{Ru(bpy)$_2$}$_3$($\mu$-HAT)]$^{6+}$	1428

[a] All of the decays correspond to single exponentials. Error: ~3%, estimated from the reproducibility of the lifetime values determined by SPC and pulsed laser methods.

On the other hand, it was also concluded previously[11] that the nonradiative deactivation rate constants, k_{nr}, of the ^{3}MLCT states of the polynuclear HAT complexes are dramatically smaller than those for the corresponding mononuclear HAT compound.[11] This indicates that the vibration modes are very different in the mono- and polynuclear HAT complexes,[12] an origin of which may be the symmetry differences between each species. As the symmetries of the *rac* and *meso* forms of [{Ru(pp)$_2$}$_2$(μ-HAT)]$^{4+}$ differ (as they do also for the homo- and heterochiral forms of [{Ru(pp)$_2$}$_3$(μ-HAT)]$^{6+}$), different vibration modes would participate in the deactivation. This would explain the difference observed in the excited state lifetimes between the diastereoisomers.

It is noted also that the absence of significant shifts of λ_{max} for absorption and emission in the *meso* and *rac* diastereoisomers of the dinuclear species is in accordance with the electrochemical data, where the potentials of the first oxidation (related to the dπ level) and reduction waves (related to the π^* level) are not significantly shifted for the different diastereoisomers.

Summary

By the use of a combination of chromatographic techniques and stereoselective synthetic methods, all stereoisomers of the mononuclear [{Ru(pp)$_2$(HAT)]$^{2+}$, dinuclear [{Ru(pp)$_2$}$_2$(μ-HAT)]$^{4+}$, and trinuclear [{Ru(pp)$_2$}$_3$(μ-HAT)]$^{6+}$ species {pp = 2,2′-bipyridine or 1,10-phenanthroline} have been isolated and characterized. While the existence of such isomers had been recognized in earlier studies on the latter two systems,[5,12] their isolation in the present work has allowed investigation of the dependence of physical characteristics on the stereochemistry. Photophysical studies revealed small but significant differences between luminescence behavior of diastereoisomeric pairs in both the di- and trinuclear cases. While the differences between stereoisomers of such complexes are relatively subtle for these

small oligomers, it is clear that they will be magnified in larger polymetallic systems with increased stereochemical complexity.

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Supporting Information Available: Tables listing ^{1}H NMR chemical shifts (300 MHz) for the stereoisomeric forms of $[\{Ru(bpy)_2\}_n(HAT)]^{2n+}$ $\{n = 1-3\}$ complexes (CD_3CN solvent) and redox potentials for diastereoisomers of $[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ and $[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$ {pp = 2,2′-bipyridine or 1,10-phenanthroline} and plots of CD spectra for the enantiomers of $[\{Ru(phen)_2(HAT)]^{2+}$, the enantiomers of *rac*-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$, and the enantiomers of homochiral $[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ (5 pages). Ordering information is given on any current masthead page.

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