Isolation of the Stereoisomers of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-HAT})]^{6+}$ (HAT = 1,4,5,8,9,12-Hexaazatriphenylene; bpy = 2,2′-Bipyridine)

Todd J. Rutherford and F. Richard Keene*

School of Biomedical and Molecular Sciences, James Cook University of North Queensland, Townsville, Queensland 4811, Australia

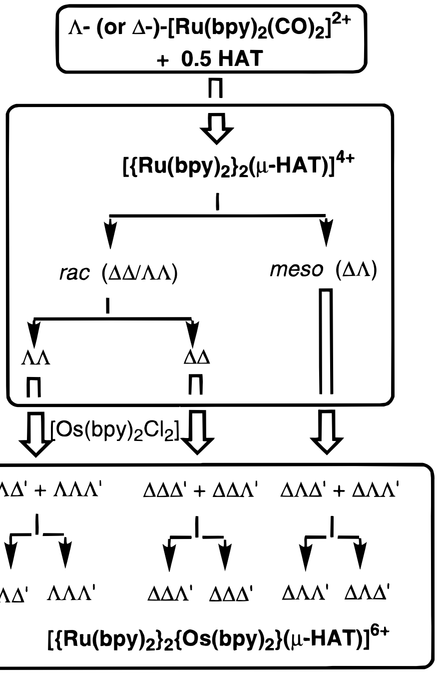
Received March 5, 1997

The synthesis and physical properties of polymetallic ligand-bridged molecular assemblies have been topics of intense interest,[1] motivated by their possible application to photochemical molecular devices.[2] An aspect receiving limited (but increasing) attention is the existence of stereoisomerism within such assemblies and its influence on intramolecular energy and electron transfer processes.[3]

The ligand bridge 1,4,5,8,9,12-hexaazatriphenylene (HAT) possesses three bidentate coordination sites, and a series of trimetallic species have been synthesized and studied,[4−7] including homonuclear (Ru_3[4,5]) and heteronuclear ($RuRe_2$[6] and Ru_2Rh[7]) systems. In earlier studies,[5] the stereochemical ambiguities were addressed but no separation of the isomeric possibilities was attempted. However, recent work in our laboratory has elucidated the stereochemistry of di- and trinuclear ruthenium complexes of this ligand, including investigations of the spatial dependence of the photophysical properties.[4]

In the present work, we report the synthesis of the heterometallic complex $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-HAT})]^{6+}$ and, most significantly, the isolation of its stereoisomeric forms by a strategy involving a combination of stereoselective synthetic procedures and chromatographic techniques[3] (Scheme 1: chromatographic procedures are indicated by single arrows; synthetic procedures, by double arrows). Previous stereochemical studies of ligand-bridged polynuclear species have generally selectively targeted one specific isomeric form. The stereoisomers of the title complex were characterized by ^{1}H NMR and CD spectroscopy, and their electrochemical and electronic spectroscopic properties were examined.

Scheme 1



The stereoisomerically pure dinuclear complexes $\Delta\Delta$-, $\Lambda\Lambda$-, and $\Delta\Lambda$-$[\{Ru(bpy)_2\}_2(\mu\text{-HAT})]^{4+}$ [4] were each reacted with *rac*-$[Os(bpy)_2Cl_2]\cdot H_2O$[8] in ethylene glycol/10% water at 120 °C for 11 h to form specifically the diastereoisomeric mixtures $\Delta\Delta\Delta'/\Delta\Delta\Lambda'$ and $\Lambda\Lambda\Lambda'/\Lambda\Lambda\Delta'$ (respectively) in the first two cases and the enantiomeric pair of one diastereoisomer $\Delta\Lambda\Lambda'/\Lambda\Delta\Delta'$ in the final case {the configuration of the osmium center is designated with a prime; the diastereoisomers are shown in Figure 1, and their ^{1}H NMR spectra are provided in the Supporting Information, Figure S1). In all cases, the yields were *ca.* 70%, and the ratio of the stereoisomers was *ca.* 1:1. Using cation exchange chromatographic techniques recently developed for the separation of diastereoisomeric oligomeric species,[3] we separated the $\Delta\Delta\Delta'/\Delta\Delta\Lambda'$ and $\Lambda\Lambda\Lambda'/\Lambda\Lambda\Delta'$ mixtures (SP-25 Sephadex C-25; aqueous 0.3 M sodium toluene-4-sulfonate eluent). As the configurations of the two ruthenium centers in the precursors were known, the CD (Figure 2) and NMR spectra allowed the assignment of the absolute configurations of the four forms. The chiral resolution of the $\Delta\Lambda\Lambda'/\Lambda\Delta\Delta'$ racemic mixture by similar chromatographic methods is more difficult than the previous separations of diastereoisomeric mixtures, but at least partial separation has been achieved (aqueous 0.2 M sodium toluoyl-D-tartrate solution eluent).

The diastereoisomers have been studied in detail by NMR spectroscopy (300 MHz), with the benefit of comparison with their homometallic (Ru_3) analogues.[4] However, because of the complexity of the present systems, certain assignments are difficult at this frequency and require pulse relay NMR techniques and/or a higher frequency spectrometer (500 MHz measurements are currently in progress).

The $\Delta\Delta\Delta'/\Lambda\Lambda\Lambda'$ and $\Delta\Delta\Lambda'/\Lambda\Lambda\Delta'$ forms both possess C_2 point group symmetry (Figure 1) and therefore may exhibit 27 nonequivalent proton environments (six AMJX and one AX coupled systems). Because the former diastereoisomer possesses a pseudo-C_3 symmetry axis (*cf.* the homometallic analogue $[\{Ru(bpy)_2\}_3(\mu\text{-HAT})]^{6+}$), a number of coincidental equivalences occur. The six AMJX coupled systems were identified by ^{1}H COSY and ^{1}H decoupling experiments, although connectivity between three pairs of AMJX coupled systems (allowing differentiation of the three nonequivalent bpy ligands) was not achievable at the frequency used (300 MHz).

The $\Delta\Lambda\Lambda'/\Lambda\Delta\Delta'$ diastereoisomer also possesses C_2 point group symmetry, but its NMR spectrum was more complex (as

---

(1) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759.

(2) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: Chichester, U.K., 1991.

(3) Keene, F. R. *Coord. Chem. Rev.*, in press.

(4) Rutherford, T. J.; Van Gijte, O.; Kirsch-De Mesmaeker, A.; Keene, F. R. *Inorg. Chem.*, in press.

(5) (a) Jacquet, L.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2471. (b) Kirsch-De Mesmaeker, A.; Jacquet, L.; Masschelein, A.; Vanhecke, F.; Heremans, K. *Inorg. Chem.* **1989**, *28*, 2465. (c) Masschelein, A.; Kirsch-De Mesmaeker, A.; Verhoeven, L.; Nasielski-Winkens, R. *Inorg. Chim. Acta* **1987**, *129*, 213.

(6) Sahai, R.; Rillema, D. P.; Shaver, R.; Van Wellendael, S.; Jackman, D. C.; Boldaji, M. *Inorg. Chem.* **1989**, *28*, 1022.

(7) Ortmans, I.; Didier, P.; Kirsch-De Mesmaeker, A. *Inorg. Chem.* **1995**, *34*, 3695.

(8) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587.

S0020-1669(97)00253-X CCC: $14.00

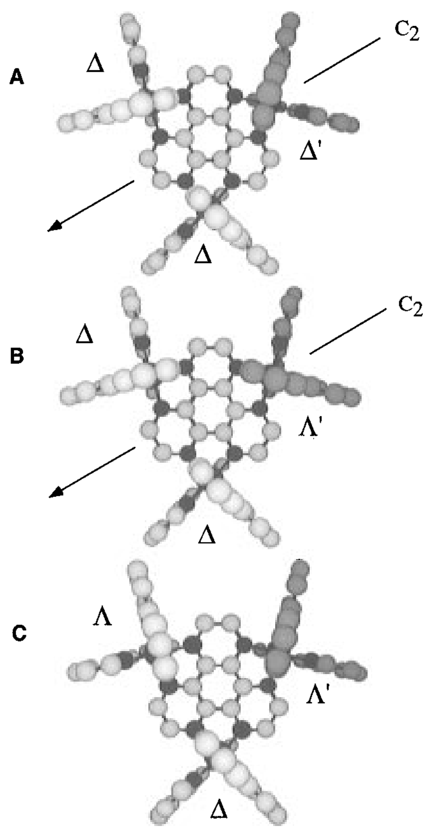


Figure 1. CHEM 3D representations of the diastereoisomeric forms of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-}HAT)]^{6+}$. Hydrogen atoms are omitted for clarity; bpy rings about the Os center are darkened to allow identification.

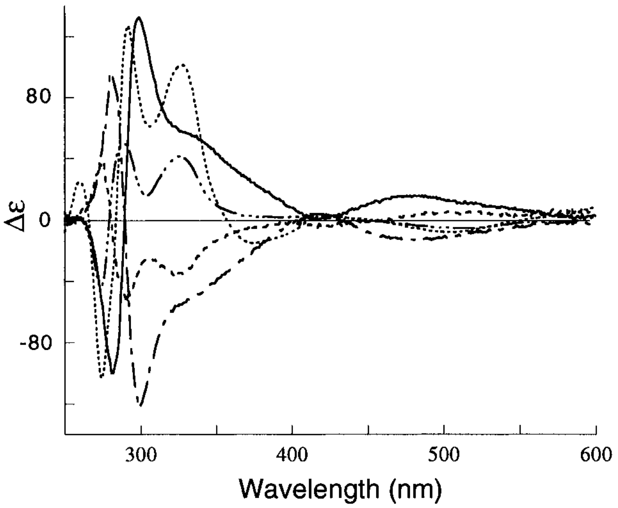


Figure 2. CD spectra (acetonitrile solution) for ΛΛΛ-$[\{Ru(bpy)_2\}_3)\mu\text{-}HAT)]^{6+}$ (···) and stereoisomers of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-}HAT)]^{6+}$: ΔΔΛ′ (- - -), ΛΛΔ′ (— - - - - —), ΛΛΛ′ (—), and ΔΔΔ′ (— - —).

the pseudo-C_3 symmetry axis is lacking), exhibiting six AMJX and one AX coupled proton systems, which together with a singlet resonance (two equivalent HAT protons) gave a possible total of 27 magnetically nonequivalent proton environments. A complete assignment of this diastereoisomer was possible because of the well-dispersed proton resonances and the reduced point group symmetry. The assignments were obtained using ^{1}H COSY spectra (provided in the Supporting Information, Figure S2), coupling constant values, and NOE effects.

The ΔΛΛ′/ΛΔΔ′ diastereoisomer has C_1 symmetry, resulting in a complicated ^{1}H NMR spectrum comprising 12 AMJX and 2 AX coupling systems and a singlet resonance (two protons from an AB system on the HAT ligand which are accidentally equivalent), totaling 53 magnetically nonequivalent proton environments. A full assignment of these proton environments by ^{1}H COSY spectra, decoupling effects, or NOE effects was not achievable at 300 MHz, although integration confirmed 54 proton resonances.

The CD spectra for the separated forms are comparable with those of the homometallic analogues.[4] The "heterochiral" enantiomers ΔΔΛ′- and ΛΛΔ′-$[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-}HAT)]^{6+}$ exhibit $\Delta\epsilon$ values about one-third those of the homochiral ΔΔΔ′- and ΛΛΛ′-enantiomers, presumably due to attentuation between Δ and Λ centers.

Electrochemical studies were undertaken on the diastereoisomers of the Ru_2Os trinuclear species. As suggested by Kirsch-de Mesmaeker *et al.*,[5a] and confirmed in this study, the one-electron reversible oxidation waves are directly correlated with the number of coordinated metal centers, suggesting significant metal−metal electonic communication which is a characteristic of conjugated bridging ligands.[9] As expected (and characteristic of osmium complexes), the first oxidation wave of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-}HAT)]^{6+}$ occurred at +1.27 V (*vs* the saturated calomel electrode, SCE; CH_3CN solvent) compared with +1.63 V for $[\{Ru(bpy)_2\}_3(\mu\text{-}HAT)]^{6+}$ as a result of the raised $d\pi$ level of Os compared to Ru.[10] The oxidations of the two ruthenium centers (at 1.81 and 2.06 V *vs* SCE) in the Ru_2-Os species are slightly cathodic of those for subsequent oxidations in the Ru_3 analogue (1.86 and 2.09 V *vs* SCE). The electronic spectrum of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-}HAT)]^{6+}$ $\{\lambda_{max}/nm\ (\epsilon/M^{-1}\ cm^{-1})$: 288 (104 000), 416 (15 750), 520 (21 000), 588 (27 000)} shows a slight bathochromic shift in the MLCT transitions in comparison with that of $[\{Ru(bpy)_2\}_3(\mu\text{-}HAT)]^{6+}$ for the same reason.[11] The electronic spectra of the Ru_3 and Ru_2Os trinuclear species are provided in the Supporting Information, Figure 3.

While the redox and electronic absorption spectral characteristics of the diastereoisomeric forms of $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mu\text{-}HAT)]^{6+}$ were indistinguishable, we seek to study photophysical characteristics in view of the differences observed in the homometallic analogues.[4] It is our contention that the variation of physical properties between stereoisomers of such complexes will be magnified in larger polymetallic systems with increased stereochemical differences.

Acknowledgment. This work was supported by the Australian Research Council.

Supporting Information Available: ^{1}H NMR, COSY, and electronic spectra (Figures S1−S3) (3 pages). Ordering information is given on any current masthead page.

IC9702532

---

(9) Giuffrida, G.; Campagna, S. *Coord. Chem. Rev.* **1994**, *135*, 517.
(10) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614.
(11) Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 5762.