Stereocchemical Influences on Intervalance Charge Transfer in Homodinuclear Complexes of Ruthenium

Deanna M. D’Alessandro, Laurence S. Kelso, and F. Richard Keene*

School of Pharmacy & Molecular Sciences, James Cook University, Townsville, Queensland 4811, Australia

Received September 24, 2001

Introduction

The synthesis of polynuclear transition metal assemblies and their electrochemical, photochemical, and photophysical properties have attracted significant recent interest; this has been motivated largely by the potential of multicomponent systems as a basis of novel applicable materials.1 However, the existence of the stereochemical complexities inherent in such systems, and their influence on intramolecular energy- and electron-transfer processes, has not always been acknowledged.2

Work in our laboratory has established synthetic methodologies for the isolation of the stereoisomers of a variety of mono-, di-, and trinuclear complexes.2,3 Significantly, this work has given rise to the first three examples of differences in the spectral, electrochemical, and photophysical properties of stereoisomers in such assemblies.2,4

We now report the first investigation of the influence of stereocchemical factors on intervalence charge transfer (IT). Importantly, this work has revealed a dependence of the IT characteristics (including thermochromism) and redox properties on stereocchemical identity in two dinuclear complexes.

Results and Discussion.

The systems studied were of the type \[
\{\text{Ru(bpy)}_2\}[\mu-\{\mu-\text{BL}\}]^{1+},
\]
where BL represents the structurally-related ligands 2,3-bis(2-pyridyl)-1,4-benzoquinoxaline (dpb) and dipyrido(2,3-a:3,2-c)benzophenazine (dpb'). (shown in Figure 1). The dinuclear species each exist in two diastereomeric forms, meso (ΔΔ) and rac, the latter comprising an enantiomeric pair (ΔΔ and ΔΔ).3 Both bridging ligands possess unoccupied low-lying π\* orbitals and mediate electronic coupling between the metal centers via the superexchange-assisted electron-transfer mechanism.5

* To whom correspondence should be addressed.

6. Acetonitrile/0.1 mol dm\(^{-3}\) [n-C\(_5\)H\(_5\)]PF\(_6\) solution versus Ag/AgCl; Pt or glassy carbon working electrode.

Figure 1. The dpb and dpb’ bridging ligands.
Interestingly, the dihedral angle subtended by the pyridyl rings of the bridge arising from steric interaction of the H(3) protons. The difference of 230° between the diastereoisomers of the same complex. For both IT bands between not only the different complexes, but also the bridges, and a large dihedral skew of the two pyridyl rings central pyrazine rings, a twist in the benzoquinoxaline "tail" of the meso structure. In contrast, for the analogous system containing the dpb' ligand, the C–C bond connecting the C(3) atoms prevents the lateral movement of the pyridyl rings in both diastereoisomers (Figure 4).

The significant structural differences between the diastereoisomeric forms of the two complexes prompted an examination of the distribution of the ligand-based frontier orbitals which mediate electron-transfer between the metal centers. Of particular interest was whether these structural differences would translate into measurable differences in the electronic characteristics of the diastereoisomers. In the meso form of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{3+}, the LUMOs were distributed across the entire surface of the bridge with the highest densities on the pyrazine ring and the adjacent phenyl ring. In comparison, the LUMOs of the rac form were more localized, being located solely on the benzoquinoloxaline region of the bridge. For \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{3+}, no significant differences were found between the diastereoisomers; the LUMO was distributed across the entire bridge, with the highest densities on the pyrazine and the two adjacent phenyl rings.

The differing spectral and electrochemical characteristics of the diastereoisomers appear to be consistent with the variations observed in the structural features and molecular orbital distributions, which are a consequence of the different stereochimistries of the species. For example, the \(\Delta E_{\text{ox}}\) values for the diastereoisomers of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{3+} are greater than those of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{4+}, since the degree of metal–metal communication is greater for those structures where the bridging ligand assumes a less distorted conformation. Moreover, the greater \(\Delta E_{\text{ox}}\) for the meso form of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{3+}, relative to the corresponding rac form, may reflect the relatively greater degree of structural distortion evident in the molecular model of the latter.

An investigation of the thermochromic behavior of the IT transitions in butyronitrile/0.1 mol dm\(^{-3}\) \([\text{m-CaH}_3]\)NPF\(_6\) solution made use of the well-resolved absorption and emission spectra of the diastereoisomers of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{4+} cation. The nature of the structural distortions obtained in the geometry optimizations are closely reflected in X-ray crystal structures of the meso-\([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{3+} cation. (D'Alessandro, D. M.; Junk P. C.; Keene, F. R., unpublished results).

**Table 1.** Properties of the Intervalance Transition of the Mixed-Valence Complexes \([\text{Ru}(bpy)_2]_{2}(\mu-\text{Bi})^{3+}\) \((\text{Bi} = \text{dpb, dpb}')\) at \(-35\, ^\circ\text{C}\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(E_{\text{op}}(\pm 10)) (cm(^{-1}))</th>
<th>(\epsilon_{\text{max}}(\pm 10)) (mol(^{-1})dm(^{3})cm(^{-1}))</th>
<th>(\Delta\nu/2(\pm 20)) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso-([\text{Ru}(bpy)<em>2]</em>{2}(\mu-\text{dpb}))^{3+}</td>
<td>5340</td>
<td>1790</td>
<td>2250</td>
</tr>
<tr>
<td>rac-([\text{Ru}(bpy)<em>2]</em>{2}(\mu-\text{dpb}))^{3+}</td>
<td>5110</td>
<td>1750</td>
<td>2020</td>
</tr>
<tr>
<td>meso-([\text{Ru}(bpy)<em>2]</em>{2}(\mu-\text{dpb}))^{4+}</td>
<td>5300</td>
<td>4610</td>
<td>1130</td>
</tr>
<tr>
<td>rac-([\text{Ru}(bpy)<em>2]</em>{2}(\mu-\text{dpb}))^{4+}</td>
<td>5320</td>
<td>3580</td>
<td>1230</td>
</tr>
</tbody>
</table>

There are measurable differences in the characteristics of the IT bands between not only the different complexes, but also between the diastereoisomers of the same complex. For both complexes, the intensities of the IT bands \((\epsilon_{\text{max}})\) for the meso diastereoisomers were higher than those for the corresponding rac forms, suggesting a greater degree of metal–metal interaction in the former. The difference of 230 ± 20 cm\(^{-1}\) observed between the energies of the IT band maxima \((E_{\text{op}})\) for the diastereoisomers of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{5+} lies well outside the limits of experimental error.

The equilibrium geometries of the diastereoisomers were examined using semiempirical PM3(tm) techniques\(^7\) to provide an insight into differential structural features induced by the stereochemistry. These gas-phase calculations predicted significant distortions in the conformations of the bridging ligands; in particular, the PM3(tm) minimized forms of \([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{4+} (Figure 3) revealed considerable distortion of the central pyrazine rings, a twist in the benzoquinoloxaline "tail" of the bridges, and a large dihedral skew of the two pyridyl rings of the bridge arising from steric interaction of the H(3) protons. Interestingly, the dihedral angle subtended by the pyridyl rings was greater in the rac form (38.4 versus 36.8°), as was the degree of twist in the benzoquinoloxaline "tail" compared with that of the meso structure.\(^8\) In contrast, for the analogous system containing the dpb' ligand, the C–C bond connecting the C(3) atoms prevents the lateral movement of the pyridyl rings in both diastereoisomers (Figure 4).


\(^{(8)}\) The nature of the structural distortions obtained in the geometry optimizations are closely reflected in X-ray crystal structures of the meso-\([\text{Ru}(bpy)_2]_{2}(\mu-\text{dpb})\)^{3+} cation. (D'Alessandro, D. M.; Junk P. C.; Keene, F. R., unpublished results).
tion revealed different temperature responses for the two complexes and variations between the diastereoisomeric forms of the same species. Over the temperature range examined, the energies of the IT band maxima were independent of temperature, as observed in the present study.

To assess the influence of ion-pairing effects, the thermochromism of the IT transitions for \{([Ru(bpy)2]2(µ-dpb))\}+ was investigated in butyronitrile/0.02 mol dm\(^{-3}\) \{[n-C\(_4\)H\(_9\)]PF\(_6\)\} solution, since the \{B(C\(_6\)F\(_5\))\}\(^+\) anion is known to associate weakly in comparison with PF\(_6\)\(^-\). As with the PF\(_6\)\(^-\) electrolyte, the IT bands were red-shifted with an increase in temperature, however, the effect was significantly less pronounced in the presence of the \{B(C\(_6\)F\(_5\))\}\(^+\) anion: from the linear variation (Figure 5), \(dE_{op}/dT = -4.0 \pm 0.3\) cm\(^{-1}\) K\(^{-1}\) (meso) and -0.6 ± 0.1 cm\(^{-1}\) K\(^{-1}\) (rac). This suggests that ion pairing has a significant effect on the redox asymmetry and, hence, the thermochromic behavior of the IT transitions in the species investigated. Importantly, the greater temperature dependence of meso-\{([Ru(bpy)2]2(µ-dpb))\}\(^3+\) relative to the corresponding rac form appears to reflect the greater extent of ion pairing in the former. Indeed, the preferential interaction of the meso isomer with anions accounts for the increased rate of elution of this isomer in the cation exchange separation process.

The present study has detailed the first observation of the influence of stereochemistry on intervalence charge transfer. The elucidation of the factors involved will be significant in completing our understanding of intramolecular energy- and electron-transfer processes.

### Experimental Section

**Materials.** [Ru(bpy)\(_2\)]\(^{2+}\)Cl\(_2\)\(\cdot\)2H\(_2\)O,\(^{13}\) 4,7-phenanthroline-5,6-dione,\(^{16}\) \([n-C\(_4\)H\(_9\)]\)\(_4\)NPF\(_6\) solution; meso (C) and rac (A) in butyronitrile/0.02 mol dm\(^{-3}\) \{[n-C\(_4\)H\(_9\)]PF\(_6\)\} solution.

**Figure 5.** \(E_{op}\) as a function of temperature for the diastereomeric forms of \{([Ru(bpy)2]2(µ-dpb))\}\(^3+\): meso (■) and rac (▲) in butyronitrile/0.1 mol dm\(^{-3}\) \{[n-C\(_4\)H\(_9\)]PF\(_6\)\} solution; meso (■) and rac (▲) in butyronitrile/0.02 mol dm\(^{-3}\) \{[n-C\(_4\)H\(_9\)]PF\(_6\)\} solution.

$$
\Delta E = \Delta E' + \Delta E_{inner} + \Delta E_{outer}
$$


(10) \(\Delta E\) is the thermodynamic energy difference between the equilibrium vibrational states of the two different redox isomers; \(\Delta E_{inner}\) and \(\Delta E_{outer}\) are the reorganization energies for the inner and outer nuclear modes, respectively; \(\Delta E'\) is an additional term reflecting possible energy contributions due to spin–orbit coupling effects and/or ligand field asymmetry.


phenanthroline-5,6-dione (0.5 g, 2.4 mmol) was refluxed for 0.5 h. Water was added, and the volume was reduced via rotary evaporation. The yellow crystalline solid was collected by filtration and recrystallized from methanol. Yield: 0.662 g (83%).

1H NMR (CDCl₃): δ (ppm)

[(Ru(bpy)₂]₂(μ-dpb)](PF₆)₄ was prepared according to the literature procedure.¹⁷ The identity of the meso diastereomer was confirmed from X-ray crystal structures of the [(Ru(bpy)₂]₂(μ-dpb)]⁺ cation.⁵ Anal. Calcd for C₆₂H₄₄N₁₂F₂₄P₄Ru₂: C, 42.8; H, 2.66; N, 9.6. Found: (meso) C, 42.5; H, 2.58; N, 9.7; (rac) C, 42.8; H, 2.66; N, 9.6. ¹H NMR (CD₃CN): δ (ppm) (meso)
6.58 (2H, J = 5, 1.5 Hz, dd), 6.97 (2H, J = 5, 1.5 Hz, dd), 7.18 (2H, J = 8, 5 Hz, dd), 7.26 (2H, J = 8, 5 Hz, dd), 7.38–7.68 (10H, m), 7.72–8.40 (12H, m), 8.49 (2H, J = 8, 1.5 Hz, dd), 8.58 (2H, J = 8, 1.5 Hz, dd), 8.60 (2H, J = 8, 1.5 Hz, dd), 8.75 (4H, J = 8, 1.5 Hz, dd), 8.80 (2H, J = 8, 1.5 Hz, dd); (rac) 7.09 (2H, J = 8, 5 Hz, dd), 7.34 (2H, dd), 7.45 (4H, J = 8, 5 Hz, dd), 7.53 (2H, dd), 7.62 (2H, J = 8, 5 Hz, dd), 7.64 (2H, J = 5, 1.5 Hz, dd), 7.70 (2H, J = 5, 1.5 Hz, dd), 7.79 (2H, J = 5, 1.5 Hz, dd), 8.00 (2H, J = 8, 8 Hz, dd), 8.06 (2H, J = 8, 8 Hz, dd), 8.06 (2H, s), 8.07–8.10 (6H, m), 8.11 (2H, J = 8, 8 Hz, dd), 8.20 (2H, J = 8, 8 Hz, dd), 8.23 (2H, J = 5, 1.5 Hz, dd), 8.31 (2H, J = 8, 1.5 Hz, dd), 8.33 (2H, J = 8, 1.5 Hz, dd), 8.67 (2H, dd), 8.68 (2H, J = 8, 1.5 Hz, dd), 8.71 (2H, J = 8, 1.5 Hz, dd).

[(Ru(bpy)₂]₂(μ-dpb)](PF₆)₄.¹⁸ Yield: 93 mg (71%). The diastereoisomeric proportions were meso/rac = 63/37. Anal. Calcd for C₆₂H₄₄N₁₂F₂₄P₄Ru₂: C, 42.8; H, 2.55; N, 9.7. Found: (meso) C, 42.5; H, 2.58; N, 9.6; (rac) C, 42.8; H, 2.55; N, 9.7. ¹H NMR (CD₃CN): δ (ppm) (meso)
6.97 (2H, J = 5, 1.5 Hz, dd), 7.15 (2H, J = 8, 5 Hz, dd), 7.25 (1H, J = 8, 5 Hz, dd), 7.33 (2H, dd), 7.48 (2H, J = 8, 5 Hz, dd), 7.58 (2H, dd), 7.70 (2H, J = 8, 5 Hz, dd), 7.72 (2H, J = 5, 1.5 Hz, dd), 7.75 (2H, J = 5, 1.5 Hz, dd), 7.76 (2H, J = 8, 8 Hz, dd), 7.97 (2H, J = 5, 1.5 Hz, dd), 7.98 (2H, dd), 8.06 (2H, J = 8, 1.5 Hz, dd), 8.13 (2H, J = 8, 8 Hz, dd), 8.16 (2H, d), 8.19 (2H, J = 8, 8 Hz, dd), 8.24 (2H, J = 8, 8 Hz, dd), 8.24 (2H, s), 8.27 (2H, J = 8, 1.5 Hz, dd), 8.45 (2H, J = 8, 1.5 Hz, dd), 8.72 (2H, J = 8, 1.5 Hz, dd), 9.33 (2H, d); (rac) 7.01 (2H, J = 8, 5 Hz, dd), 7.15 (2H, dd), 7.25 (2H, J = 8, 5 Hz, dd), 7.34 (2H, J = 5, 1.5 Hz, dd), 7.54 (2H, J = 5, 1.5 Hz, dd), 7.57 (2H, dd), 7.62 (2H, J = 8, 5 Hz, dd), 7.68 (2H, J = 5, 1.5 Hz, dd), 7.99 (2H, dd), 8.00 (2H, J = 5, 1.5 Hz, dd), 8.02 (2H, J = 8, 8 Hz, dd), 8.05 (2H, J = 8, 8 Hz, dd), 8.07 (2H, s), 8.18 (2H, d), 8.21 (2H, J = 8, 8 Hz, dd), 8.25 (2H, J = 8, 8 Hz, dd), 8.45 (2H, J = 8, 1.5 Hz, dd), 8.57 (2H, J = 8, 1.5 Hz, dd), 8.57 (2H, J = 8, 1.5 Hz, dd), 8.63 (2H, J = 8, 1.5 Hz, dd), 9.26 (2H, d).

Acknowledgment. We thank Professor J. T. Hupp for helpful discussions on the manuscript, and we gratefully acknowledge the financial support of the Australian Research Council.

IC010857C