Redox Characteristics and Anion Association Behaviour of Stereoisomeric Forms of Mono- and Oligonuclear Metal Complexes Using High Pressure Electrochemistry

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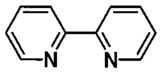
The effect of the presence of the anions PF_6^-, BF_4^-, ClO_4^-, and tosylate$^-$ on the potentials of the $Ru^{III/II}$ redox processes in a series of mono-, di-, and trinuclear complexes involving polypyridyl ligands are reported. The anions gives rise to a cathodic shift in the respective redox potentials in the sequence $PF_6^- < BF_4^- \approx ClO_4^- <$ tos$^-$, with the magnitude of the shifts being largest for the tri-nuclear and smallest for the mononuclear species. In one dinuclear complex, a variation of anion was also observed to affect the difference in potentials between the [6+/5+] and [5+/4+] couples. These effects are consistent with known specific association of the anions with metal complexes of this type. In the presence of PF_6^-, high-pressure electrochemical studies revealed the molar volume changes for successive redox couples in di- and trinuclear complexes were almost invariant ($\Delta V_{complex} = 24 \pm 2\ cm^3\ mol^{-1}$) and consistent with the value for mononuclear species. This constancy is interpreted in terms of isolated $Ru^{III/II}$ processes in all complexes and implies that the electrostrictive effects on solvent are limited to a very short range.

Introduction

We have recently established that the stereochemical relationship of the components in mono- and oligonuclear species influences intramolecular electron and energy transfer processes between them. These studies have included the variation in lifetimes of the charge-separated excited states in the four geometric isomers of the chromophore-quencher complex $[Ru(Me_2bpy)(bpy\text{-}A)(bpy\text{-}D)]^{4+}$ {Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine; bpy-A = bpy-MV^{2+} = (4′-methyl-2,2′-bipyridin-4-yl)methyl-1′-methyl-4,4′-bipyrinediium cation (MV^{2+} is an acceptor quencher); bpy-D = bpy-PTZ = 4′-methyl-2′,2-bipyridin-4-yl)methyl]phenothiazine (PTZ is a donor quencher)},[1,2] the variation in redox characteristics of the diastereoisomers of the two dimetallic systems $[\{Ru(pp)_2\}_2(\mu\text{-azo})]^{4+}$ {azo = azobis(2-pyridine), apy, or azobis(4-methyl-2-pyridine), mapy; pp = 2,2′-bipyridine (bpy) or Me_2bpy} and $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ {dpa = 2,3-bis(2-pyridyl)-1,4-diaazaanthracene},[3,4] and the variation of excited state lifetimes for the diastereoisomers of the dinuclear $[\{Ru(pp)_2\}_2(\mu\text{-HAT})]^{4+}$ and trinuclear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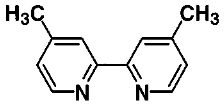
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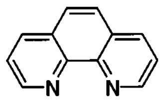
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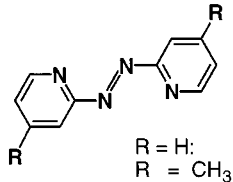
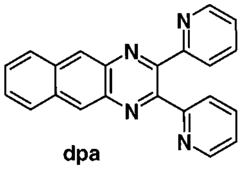

R = H: **apy**
R = CH₃: **mapy**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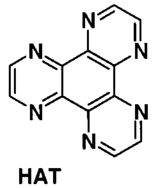
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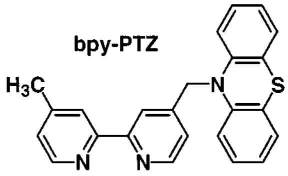
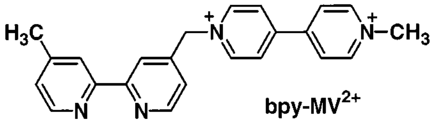

bpy-PTZ


bpy-MV²⁺

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$[\{Ru(pp)_2\}_3(\mu\text{-HAT})]^{6+}$ complexes involving the bridging ligand HAT {pp = bpy or phen (1,10-phenanthroline); HAT = 1,4,5,8,9,12-hexaazatriphenylene}.[5]

At this stage, because of the limited number of examples available, the factors which give rise to dependence of such physical characteristics on the stereochemistry are not yet clear.

As part of our stereochemical studies, we have also established a general cation-exchange chromatographic procedure which allows the separation of stereoisomers of mono- and oligonuclear complexes.[3−10] The mechanism of the separation involves differential association of the anion of the eluent with the stereoisomers of the substrate cation, and NMR titration studies reveal the association has π-stacking and hydrophobic components.[4,7,8] More detailed studies of complex−anion (and probably complex−solvent) interactions will complete our understanding of the more intimate mechanistic details of the factors which contribute to the discrimination.

Recent reports have shown that electrochemical techniques such as cyclic voltammetry and differential pulse voltammetry performed at high pressure may be used to measure redox reaction volume changes (ΔV_{cell}) for electrochemical cells involving reactions of transition metal complexes.[11] Further, the experimental ΔV_{cell} can be resolved into reference electrode and working electrode contributions and the latter in turn broken into electrostrictive and intrinsic components, so that the technique can provide otherwise inaccessible information on the solvational and structural changes which accompany metal complex reduction processes − in both aqueous and non-aqueous solutions.

For systems such as those listed above, the technique therefore had immediate appeal in probing the nature of differences in the redox characteristics of stereoisomeric forms of the same complex, and in investigating the differences in anion/solvent interactions between similar structures. The present paper reports the first such investigations.

Results and Discussion

Syntheses

Synthesis and Separation. The synthesis of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})](PF_6)_4$ was achieved by heating a 2:1 mixture of $[Ru(bpy)_2Cl_2]$ and the dpa ligand in methanol/water for 24 h. An alternative procedure involved heating an ethylene glycol solution of the reactants in a microwave oven: however, this method produced a lower yield of the dinuclear complex, with an increase in the production of mononuclear $[Ru(bpy)_2(dpa)]^{2+}$.

The dinuclear species $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ exists in two diastereoisomeric forms, one *racemic* (consisting of the ΔΔ/ΛΛ enantiomeric pairs) and the other *meso* (ΔΛ). The diastereoisomers were separated by cation-exchange chromatography: the *rac* diastereoisomer appeared to be less stable than the *meso*, and underwent slow decomposition in the solid form.

For diastereoisomer characterisation, the resolution of one of the diastereoisomers unequivocally establishes its identity as *rac*. We have developed chromatographic methods for separation of enantiomers by ion-exchange chromatography, using chiral eluents.[5,7,12] Cation-exchange chromatography of the two separated diastereoisomers of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ (isolated from Bands 1 and 2 of the their chromatographic separation) using an aqueous solution of sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as the eluent showed that the product from Band 2 separated further into two bands (designated 2A and 2B), therefore unambiguously identifying it as the *rac* form. The isolated cations from this resolution had equal and opposite CD spectra (Figure 1).

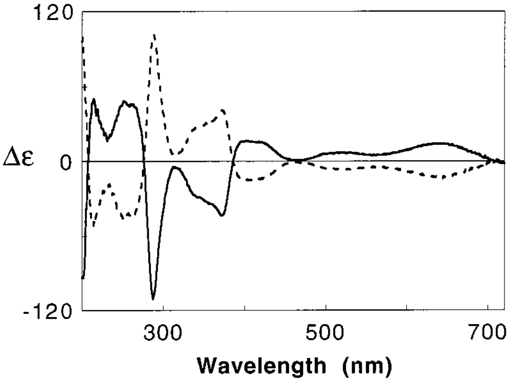

Figure 1. CD spectra (CH_3CN solution) of the ΔΔ (- - - - -) and ΛΛ (——) enantiomers of *rac*-$[\{Ru(bpy)_2\}_2(\mu\text{-dpa})](PF_6)_4$

On the basis of Exciton Theory and by comparison with previous resolutions of similar species,[5] Band 2A was assigned as ΔΔ and Band 2B as ΛΛ.

Electrochemistry

Redox potentials were determined by cyclic and differential pulse voltammetry in CH_3CN solution containing 0.1 M supporting electrolyte. The anion of the electrolyte was observed to affect the redox potentials associated with the $Ru^{III/II}$ couples in mono-, di-, and trinuclear complexes, and the separation between the formally [5+/4+] and [6+/5+] processes in dinuclear systems.

The $[FeCp_2]^{+/0}$ couple was employed as the reference in these studies, and this couple itself is known to be solvent and electrolyte dependent.[13,14] Consequently, the $[FeCp^*_2]^{+/0}$ redox couple (Cp* = pentamethylcyclopentadienyl anion), which is less susceptible to anion and solvent interactions,[14] was also used as a reference; however, we found little difference for $[FeCp_2]^{+/0}$ vs. $[FeCp^*_2]^{+/0}$ in the range of electrolytes employed {$E_{1/2}$ values of $[FeCp_2]^{+/0}$ vs. $[FeCp^*_2]^{+/0}$ in acetonitrile/0.1 M $[(n\text{-}C_4H_9)_4N]X$ solution were 520 mV (X = BF_4^-), 512 mV (PF_6^-), 510 mV (ClO_4^-), and 507 mV (tos$^-$; tosylate ion}. On this basis, the reasonable assumption is made that the data reported reflect only the changes in potential associated with working electrode half-cell of the particular complex involved.

Table 1. Electrolyte-anion dependence of redox potentials of complexes vs. $[FeCp_2]^{+/0}$ in CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]X$

	Anion X^-	$E_{1/2}$ (mV) [3+/2+]	$E_{1/2(1)}$ (mV) [5+/4+]	$E_{1/2(2)}$ (mV) [6+/5+]	$\Delta E_{1/2}$ (mV)
$[Ru(bpy)_3]^{n+}$	PF_6^-	904			
	tos$^-$	852			
$[Ru(Me_4bpy)_3]^{n+}$	PF_6^-	652			
	tos$^-$	612			
$[Ru(phen)_3]^{n+}$	PF_6^-	892			
	tos$^-$	860			
$[Ru(phen)_2(HAT)]^{n+}$	PF_6^-	1172			
	BF_4^-	1140			
	ClO_4^-	1184			
	tos$^-$	1072			
ΔΛ(*meso*)-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{n+}$	PF_6^-		1160	1384	224
	BF_4^-		1160	1356	196
	ClO_4^-		1106	1310	204
	tos$^-$		972	1054	86
ΔΛ(*meso*)-$[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{n+}$	PF_6^-		1069	1262	193
	BF_4^-		1008	1200	192
	ClO_4^-		1025	1200	175
	tos$^-$		962	1082	120
ΔΔ/ΛΛ(*rac*)-$[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{n+}$	PF_6^-		1088	1263	175
	BF_4^-		1048	1203	155
	ClO_4^-		1049	1202	153
	tos$^-$		990	1094	104

The dependencies of redox potentials of complexes studied in this work on the anion of the electrolyte are listed in Table 1. There is a cathodic shift of potentials in solutions containing certain electrolyte anions, with tos$^-$ having the greatest effect. The induced shifts are less for $Ru^{III/II}$ couples in monouclear complexes (50 mV for complexes containing only bpy and phen ligands and their derivatives; 100 mV for mononuclear complexes containing the ligand HAT) than those) in dinuclear systems for the formally [5+/4+] (100−200 mV) and [6+/5+] processes (150−300 mV.

For the mononuclear complex couples $[Ru(bpy)_3]^{3+/2+}$, $[Ru(Me_4bpy)_3]^{3+/2+}$, and $[Ru(phen)_3]^{3+/2+}$, a cathodic shift in the redox potential was observed in the order $PF_6^- < BF_4^- < ClO_4^- <$ tos$^-$, with the same trend being observed for $[Ru(phen)_2(HAT)]^{3+/2+}$ but of larger magnitude. Ion-pairing between the cationic complex and electrolyte anion would be expected to result in a cathodic shift in the redox potential due to the lesser net charge of the ion-pair,[13,14] so the shift of potentials to less positive values in solutions with different electrolyte anions can be correlated with differential ion-pairing;[4,8] i.e. the tos$^-$ anion interacts with the complex to a greater extent than does PF_6^-. The effect observed for $[Ru(phen)_2(HAT)]^{3+/2+}$ suggests an even greater interaction.

For dinuclear complexes, the electrochemistry of $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-mapy})]^{4+}$,[3] $[Ru(phen)_2(HAT)]^{2+}$, $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$, and $[\{Ru(phen)_2\}_3(HAT)]^{6+}$ [5] have been reported elsewhere. In the present study, in CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ solution the diastereoisomers of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ each exhibited two reversible one-electron oxidations corresponding to successive oxidation of the metal centres, and multiple reversible ligand-based reductions. However, the *meso* and *rac* forms differed (Figure 2); in the *meso* complex the first oxidation ($E_{1/2(1)}$) occurred at a less positive potential than the *rac* form, resulting in a greater separation of the two oxidations ($\Delta E_{1/2}$). The separation between such oxidations in a dinuclear species is used as an indication of the degree of M−M interaction.[15]

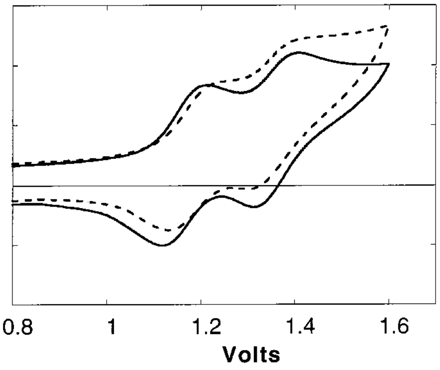

Figure 2. Cyclic voltammograms (CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ solution) of the *meso*- (——) and *rac*- (- - - - -) diastereoisomers of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{n+}$ {[5+/4+] and [6+/5+] couples only}

In dinuclear systems, the anions also affect this separation between [5+/4+] {$E_{1/2(1)}$} and [6+/5+] {$E_{1/2(2)}$} redox couples. For example, $\Delta E_{1/2}$ for ΔΛ-$[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ ranged from 193 mV {$[(n\text{-}C_4H_9)_4N]PF_6$} to 120 mV {$[(n\text{-}C_4H_9)_4N]$tos}, with $\Delta E_{1/2}$ decreasing in the order $PF_6^- > BF_4^- > ClO_4^- >$ tos$^-$. Even more dramatic effects were observed for $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ (Table 1). The effects were always in the order that the separation for $PF_6^- > BF_4^- >$ tos$^-$: the effect of ClO_4^- was more variable, but generally comparable with that of BF_4^-. In all cases, the absolute potentials of both couples shifted, and the greater negative shift of the [6+/5+] couple leads to the decrease in separation. Changing the electrolyte cation {e.g.

$[(C_2H_5)_4N]ClO_4$ cf. $[(n\text{-}C_4H_9)_4N]ClO_4\}$ made no difference to the voltammetry.

For dinuclear species, ion-pairing offers one possible explanation for the remarkable observations of the dependence of $\Delta E_{1/2}$ on the identity of the anion in the electrolytes. For these dinuclear complexes, on purely electrostatic grounds ion-pairing would be stronger for the [6+]/[5+] couple (cf. [5+]/[4+]) because of the larger charges involved, resulting in $E_{1/2(2)}$ ([6+]/[5+]) shifting more cathodically than $E_{1/2(1)}$.

An alternative rationalization of the effect is more speculative. Recent work has shown specific interactions between a variety of aliphatic and aromatic anions with ruthenium(II) complexes containing polypyridyl ligands,[8] and in the case of dinuclear species, specific interactions have been identified in the region between the metal centres. The presence of the anion(s) in that region might result in an increased metal−metal separation, with the resultant decrease in metal−metal interaction manifested in a smaller separation between the two metal-based oxidations ($\Delta E_{1/2}$), as observed for tos^- (for which the association would be strongest) with $[\{Ru(bpy)_2\}(\mu\text{-dpa})]^{4+}$ and $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$.

Spectroelectrochemistry

Detailed spectroelectrochemical studies of the dinuclear complexes bridged by apy and mapy have previously been reported.[3] Similar studies were undertaken in the present work for the complexes $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$, $[\{Ru(phen)_2\}_3(\mu\text{-HAT})]^{6+}$, and $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$, and the absorption data for the resulting electrogenerated species are collated and presented as Supporting Information (Table S1). All three compounds showed clear isosbestic points for the first oxidation process, and reversibility was demonstrated by coincidence of the various isosbestic points during the reverse reduction step, which led to ultimate recovery of the starting compound.

For the dinuclear complexes the first oxidation was a one-electron process, producing the mixed-valence species $[(pp)_2Ru^{III}(\mu\text{-L})Ru^{II}(pp)_2]^{5+}$ (pp = bpy or phen) which possess intense intervalence charge transfer or metal-to-metal charge transfer (MMCT) bands in the near infrared (NIR) region of the spectrum. The formation of such a band in a spectroelectrochemical experiment is shown for the oxidation of *meso*-$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ in Figure 3. Additionally, the overlayed spectra of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ and its electrogenerated [5+] and [6+] analogues are shown in Figure 4. The first oxidation of both these dinuclear complexes was accompanied by a 50% decrease in the intensity of their respective MLCT absorptions (at 15600 cm^{-1} and 18200 cm^{-1}, respectively). This is consistent with the notional conversion of one of the d^6 metal centres in each dimer to a d^5 entity. The band attributed to the $d\pi(Ru^{II})\rightarrow\pi^*$(bridge) MLCT absorption collapsed completely following removal of a second electron.

An analysis of the NIR absorbances using Hush theory[16,17] reveals a large discrepancy between calculated and experimentally derived values of $\Delta v_{1/2}$ (Table 2). While a strong solvent dependency may account for this (our measurements were primarily carried out in CH_3CN solution), the non-applicability of the theory suggests a large degree of delocalisation and thus strongly interacting (Robin and Day "Class III") behaviour.[18−20] This is further supported by the unsymmetrical (non-gaussian) appearence of the bands and the apparent fine structure within the NIR region absorbances. No differences in band energy, intensity or shape were observed between the diastereoisomeric pairs of the dinuclear species investigated.

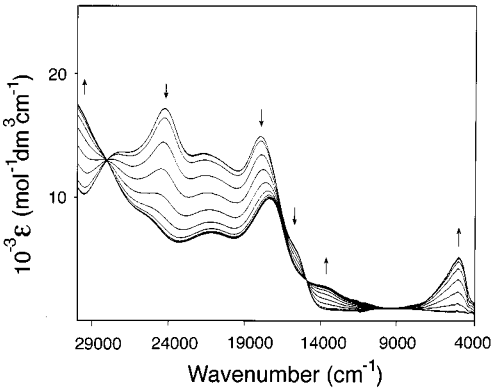

Figure 3. Spectroelectrochemical study of one-electron oxidation of *meso*- $[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{4+}$ (CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$ solution)

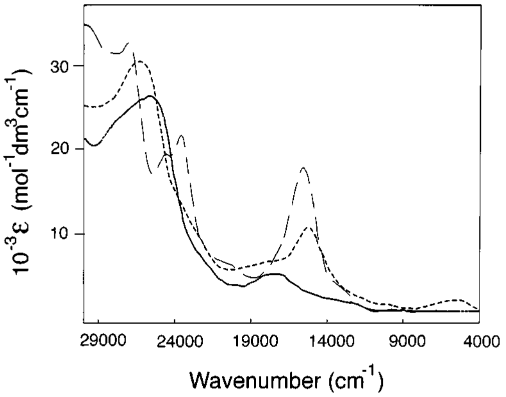

Figure 4. UV/Visible spectra of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{4+}$ (− − − −) and the electrogenerated 5+ (- - - - -) and 6+ (——) analogues (CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$ solution)

Table 2. MMCT band analysis of mixed-valence dinuclear species in CH_3CN solution at −32 °C

Dinuclear Complex	$\tilde{\nu}_{max}$ [cm^{-1}]	$\Delta\tilde{\nu}_{1/2}$ (calcd.) [cm^{-1}]	$\Delta\tilde{\nu}_{1/2}$ (exp.) [cm^{-1}]
$[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{5+}$	5600	3600	2800
$[\{Ru(bpy)_2\}_2(\mu\text{-mapy})]^{5+}$ [3]	6900	3990	1600
$[\{Ru(phen)_2\}_2(\mu\text{-HAT})]^{5+}$	5200	3470	1700
$[\{Ru(^*phen^*)_2\}_2(\mu\text{-HAT})]^{5+}$	8200	4350	1900

For the dinuclear complexes, some problems were encountered when attempts were made to fully oxidize both metal centres to the trivalent state. A spectrum of $[\{Ru(bpy)_2\}_2(\mu\text{-dpa})]^{6+}$ was obtained at −32 °C, however the compound was only metastable when held at a high anodic potential for extended periods of time. A gradual reduction in the absorption intensity was observed across the entire spectral region and following regeneration the original [4+] cation also exhibited a reduced intensity.

We were unable to observe the $[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{6+}$ cation. Subjecting the [5+] species to high anodic potentials over a 3 h period led to a new unidentified [6+] compound in which one or more of the phenanthroline ligands appeared to have undergone oxidation. The product species is characterised by an intense absorption at 11300 cm^{-1} which can tentatively be assigned as a $\sigma(ligand)\rightarrow d^5(Ru^{III})$ (LMCT) transition. The oxidation of phenanthroline to 1,10-phenanthroline-5,6-dione while coordinated to a ruthenium or cobalt(III) centre is a well-documented phenomenon: the reaction is known to proceed readily (and at much lower potentials) relative to the oxidation of an uncoordinated ligand.[21,22] This oxidative conversion was completely irreversible, however the new species was itself very stable and displayed its own completely reversible spectroelectrochemistry. Upon reduction to the 5+ state, this new complex exhibited a unique MMCT band which predictably collapsed upon further reduction to a [4+] species (Figure 5). Repeated oxidations and reductions via bulk electrolysis gave reproducible isosbestic points and uniform absorption intensities.

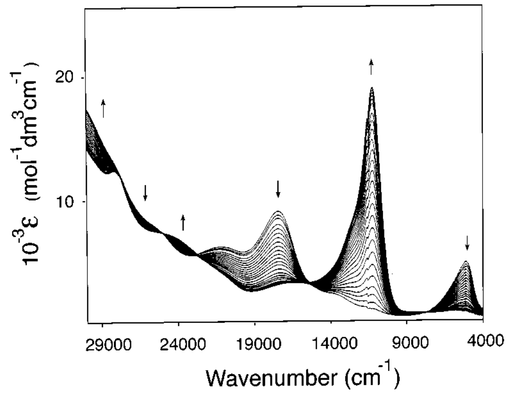

Figure 5. Spectroelectrochemical trace of the reduction of $[\{Ru(*phen*)_2\}_2(\mu\text{-}HAT)]^{5+}$ (CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]ClO_4$ solution)

Reduction of the dinuclear complexes bridged by dpa or HAT led to rapid decomposition of the original [4+] species. Re-oxidation of the dpa species produced a compound whose visible spectrum was very similar to that of $[Ru(bpy)_2(dpa)]^{2+}$. This is consistent with a previous spectroelectrochemical investigation of $[\{Ru(bpy)_2\}_2(\mu\text{-}dpp)]^{4+}$ where it was determined that mononuclear $[Ru(bpy)_2(dpp)]^{2+}$ was produced via de-chelation of dinuclear starting material subjected to large cathodic potentials.[18]

The spectroelectrochemistry of the $[\{Ru(phen)_2\}_3(\mu\text{-}HAT)]^{6+}$ trinuclear complex presented none of the problems associated with the dinuclear species. Two successive oxidations {[6+]→[7+] and [7+]→[8+]} and two reversible reductions {[6+]→[5+] and [5+]→[4+]} were easily achieved. The starting compound was also regenerated without any appreciable degradation. No NIR absorption bands were observed for the potentially mixed-valent [5+] or [6+] species. The absence of a MMCT transition implies that electron density is totally delocalised across the entire molecule and hence removal of an electron from the system only results in a small change in the effective charge on all three metal centres. This is borne out by the relatively small differences between the visible absorption spectra following each successive redox event.

High-Pressure Electrochemistry

High-pressure voltammetry techniques enable the measurement of molar volume changes of electron-transfer reactions.[11] The standard molar volume change (ΔV°_{cell}) for a redox reaction is given by $\Delta V^{\circ}_{cell} = (d\Delta G^{\circ}/dP)$, or $\Delta V^{\circ}_{cell} = -n\mathrm{F}(dE^{\circ}/dP)$, where n is the number of electrons transferred and F is the Faraday constant. The cell reaction volume (ΔV_{cell}) of a redox couple can therefore be determined by measuring the pressure dependence of $E_{1/2}$ for the redox couple. ΔV_{cell} is the sum of the two half-cell components, $\Delta V_{complex}$ and ΔV_{ref}, arising from the molar volume changes of the reference and working electrodes, respectively. The same reference {Ag/Ag^+ (0.01 M in CH_3CN)} was employed for all experiments; ΔV_{ref} for this system has been determined to be -20.7 cm^3 mol^{-1}.[11] Using this value for ΔV_{ref}, molar volumes changes for the reduction processes of the complexes, $\Delta V_{complex}$, were then calculated and are listed with the measured ΔV_{cell} values in Table 3.

The $\Delta V_{complex}$ will be made up of two components, ΔV_{elec} and ΔV_{intr}: the former is an electrostrictive contribution arising from interaction of solvent molecules and counterions with the ionic charge of the complex, and the latter is an intrinsic contribution arising from bond length and structural changes within the molecule. For the ruthenium complexes containing polypyridyl ligand studied here, minimal structural changes occur within the $Ru^{III/II}$ redox process,[23] so that the major component of $\Delta V_{complex}$ will be ΔV_{elec}, reflecting the interaction of solvent and electrolyte with the complex cation.

While there is little influence of the anion on the value of $\Delta V_{complex}$ for the mononuclear species $[Ru(phen)_2(HAT)]^{3+/2+}$ {$\Delta V_{complex}$ = 22.2 cm^3 mol^{-1} in $[(n\text{-}C_4H_9)_4N]PF_6$ and 20.0 cm^3 mol^{-1} in $[(C_2H_5)_4N]ClO_4$}, in all other complexes studied there appears to be a significant effect, which is noticably more positive (by 7−12 cm^3 mol^{-1}) in PF_6^- than in ClO_4^- media. This effect is presumably related to the specific interactions/association of some anions: it is consistent with a greater release of solvent in the presence of the less strongly associated anion PF_6^- because the effective complex charge is higher, and $\Delta V_{complex}$ is proportional to Δz^2 (see below). The discrimination of the anions in dinuclear complexes indicates that the region between the metal centres is additionally important.[8]

For all species except the monomer, shifts in $E_{1/2}$ at 1 bar indicate that ClO_4^- associates more strongly than PF_6^-, and the differences in ΔV values seem to parallel the differences (or lack thereof) in $E_{1/2}$ measured in the respective media. However, leaving aside the data for the $[Ru(phen)_2(HAT)]^{3+/2+}$ couple in perchlorate media, the values of $\Delta V_{complex}$ are remarkably constant across charge

Table 3. ΔV_{cell} and corresponding molar volume changes ($\Delta V_{complex}$) for reduction of mono-, di-, and trinuclear complexes in CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]X$ ($X = PF_6^-$, ClO_4^-) solution

Redox Couple	Δz^2	0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ ΔV_{cell} cm^3mol^{-1}	$\Delta V_{complex}$[a] cm^3mol^{-1}	0.1 M $[(C_2H_5)_4N]ClO_4$ ΔV_{cell} cm^3mol^{-1}	$\Delta V_{complex}$ [a] cm^3mol^{-1}
$[Ru(phen)_2(HAT)]^{3+/2+}$	5	+1.5	+22.2	−0.7	+20.0
$\Delta\Delta/\Lambda\Lambda$-$[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{6+/5+}$	11	+0.7	+21.4	−8.6	+12.1
$\Delta\Delta/\Lambda\Lambda$-$[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{5+/4+}$	9	+4.7	+25.4	−7.6	+13.1
$\Delta\Lambda$-$[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{6+/5+}$	11	+1.1	+21.8	−6.1	+14.6
$\Delta\Lambda$-$[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{5+/4+}$	9	+1.7	+22.4	−5.5	+15.2
$\Delta\Delta\Delta/\Lambda\Lambda\Lambda$-$[\{Ru(phen)_2\}_3(\mu\text{-}HAT)]^{8+/7+}$	15	+2.4	+23.1		
$\Delta\Delta\Delta/\Lambda\Lambda\Lambda$-$[\{Ru(phen)_2\}_3(\mu\text{-}HAT)]^{7+/6+}$	13	+4.2	+24.9		
$\Delta\Delta/\Lambda\Lambda$-$[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)]^{6+/5+}$	11	+2.9	+23.6	−4.5	+16.2
$\Delta\Delta/\Lambda\Lambda$-$[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)]^{5+/4+}$	9	+4.4	+25.1	−2.4	+18.3
$\Delta\Lambda$-$[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)]^{6+/5+}$	11	+4.6	+25.3	−4.6	+16.1
$\Delta\Lambda$-$[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)]^{5+/4+}$	9	+5.2	+25.9	−2.2	+18.5
$\Delta\Delta/\Lambda\Lambda$-$[\{Ru(Me_2bpy)_2\}_2(\mu\text{-}mapy)]^{5+/4+}$	9	+2.9	+23.6		
$\Delta\Lambda$-$[\{Ru(Me_2bpy)_2\}_2(\mu\text{-}mapy)]^{5+/4+}$	9	+3.4	+24.1		

[a] $\Delta V_{complex} = \Delta V_{cell} - \Delta V_{ref}$ ($\Delta V_{ref} = -20.7\ cm^3\ mol^{-1}$); ref.[11]

changes and across complexes within each charge change group ($\Delta V_{complex} = 24 \pm 2\ cm^3\ mol^{-1}$). Furthermore, there does not appear to be any significant difference in $\Delta V_{complex}$ between the diastereoisomers within the $[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)]^{n+}$ and $[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{n+}$ species: the values of $\Delta V_{complex}$ for the *meso* isomers of both dinuclear complexes are generally within $2\ cm^3\ mol^{-1}$ of the *rac* form, which is not significantly greater than experimental error.

This is a surprising result. Previous studies have discussed the correlation between electrostrictive changes ΔV_{elec} and $\Delta z^2/r$ $\{\Delta z^2 = (z_{ox})^2 - (z_{red})^2$; r = radius of species$\}$.[24] Calculated van der Waal's volumes for the mono-, di-, and trinuclear complexes $\{[Ru(phen)_2(HAT)]^{n+}$, $[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{n+}$, and $[\{Ru(phen)_2\}_2(\mu\text{-}HAT)]^{n+}\}$ were 518, 847, and 1177 Å^3, respectively: even allowing for the approximation incurred because of the non-spherical nature of the di- and trinuclear species, the constancy of $\Delta V_{complex}$ cannot be accounted for by this simple $\Delta z^2/r$ relationship.

A rationalization for the effect may be found in ion association, which is known to occur between the cationic mono-, di-, and trinuclear complexes used in this study and a variety of anions.[8] Indeed, NMR titration studies of the interaction of a number of mononuclear (2+) and dinuclear (4+) complexes with strongly associating anions were interpreted to indicate a 2:1 and 4:1 ratio of anions/cation, respectively.[8] Accordingly, the "effective charge" would be expected to be less than the formal charge in these species. Furthermore, if in di- and trinuclear species there were differences in the extent of association between the oxidized and reduced forms, then their effective charges would also be less than the formal charges, and actually closer to the charges applying to the mononuclear situation. Thus for each redox couple in the systems studied, the measured values of $\Delta V_{complex}$ could be similar. This situation is represented by the Equation (1).

$$[M^{n+} \ldots pX^-]^{(n-p)+} + e^- \rightarrow [M^{(n-1)+} \ldots (p-q)X^-]^{(n-p-1+q)+} + qX^- \qquad (1)$$

However, consideration of the Nernst equation would a require a linear relationship between $E_{1/2}$ and $\ln[X^-]$ with a slope of $-0.059q$ (q is the number of anions released from association on a one-electron reduction of the substrate).[25] Our studies of the dependence of $E_{1/2}$ on the concentration of the anion indicated that there was no significant release of associated anions on reduction within any nuclearity regime.

Another rationale has its basis within the nature of the redox changes. Regardless of the nuclearity, each redox process involves a change at one ruthenium centre from oxidation state III to II. The observed consistency of $\Delta V_{complex}$ values may indicate that the effects on solvent are localised around individual ruthenium centres. In other words, the system behaves as a sequence of localised 3+/2+ charge changes and that in all cases Δz^2 is effectively 5, regardless of the overall charge. The consistent value of ca. 20−26 $cm^3\ mol^{-1}$ is in agreement with the [3+/2+] couples measured both in this work, and in other independent observations of [3+/2+] reductions: e.g. $\Delta V_{complex} = 22.2\ cm^3\ mol^{-1}$ (acetonitrile/0.1 M $[(C_2H_5)_4]ClO_4$) for $[Fe(phen)_3]^{3+/2+}$.[11] The interpretation that all centres are acting as independent $Ru^{III/II}$ couples appears to be in conflict with the communication between the metal centres in the di- and trinuclear species, as evidenced by our observation of MMCT bands in such complexes (discussed above). However, in 1,4-pyrazine-bridged dinuclear ruthenium complexes, in which there is also strong communication between the metal centres, reaction entropies ($\Delta S°$) for successive redox changes are independent of the oxidation state of the second Ru centre, and correspond to the $\Delta S°$ values for the corresponding mononuclear moieties. This was interpreted to demonstrate that the entropy change upon reduction of the Ru was caused by short-range effects not reaching further than two solvent molecules.[26] It is not unreasonable to conclude that the constancy of the values of $\Delta V_{complex}$ across successive redox changes and across complexes within each charge group observed in the present work reflects isolated events where the solvent effect is limited to a short range.

Experimental Section

Physical Measurements: Electronic spectra were recorded using a Cary 5E UV/Vis/NIR spectrophotometer. NMR spectra were recorded on Bruker AM300 or Varian Mercury 300 MHz spectrometers. Electrochemical measurements at atmospheric pressure were performed in an argon-filled drybox using a Bioanalytical Systems (BAS) 100A electrochemical analyzer. Cyclic voltammetry in acetonitrile employed a platinum disk (1 mm diameter) working electrode, platinum wire counter electrode and Ag/Ag^+ (0.01 M) reference electrode. Solutions contained 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ or $[(C_2H_5)_4N]ClO_4$ as electrolyte. Typically, scan rates were 100−200 mV s^{-1}. Ferrocene ($[FeCp_2]$ was added as an internal standard after each experiment (oxidation at +0.095 V vs. Ag/Ag^+). For differential pulse voltammetry (DPV) measurements the conditions used were scan rate 4 mV/s, pulse amplitude 50 mV, pulse width 60 msec and pulse period 1 s. Spectra of oxidized and reduced species were obtained at 240 K by electrogeneration within a cryostatted optical semi-thin-layer electrochemical (OSTLE) cell, utilizing a Perkin−Elmer Lambda 9 UV/Vis/NIR spectrophotometer, as described previously.[27] High resolution mass spectra were obtained at the Australian Institute of Marine Science (Townsville) on a Bruker BioApex 47e ICR Mass Spectrometer with an electrospray source, using solutions ca. 2 μg/mL in acetonitrile.

The high pressure electrochemical cell is a development of our earlier design[24,28] and has a sample volume of ca. 1 mL, uses a 1 mm Pt disk working electrode, 2 mm Pt disk counter electrode and a Ag/Ag^+ (0.01 M in 0.1 M supporting electrolyte) reference electrode separated from the working solution by a Vycor™ frit mounted in a flexible Teflon™ sleeve.[11] The high-pressure electrochemical experiments were performed in acetonitrile solution containing 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$ or $[(C_2H_5)_4N]ClO_4$ as supporting electrolyte: samples were prepared in air, then purged with N_2 before closing the cell and mounting it in the high pressure bomb, thermostatted at 298 K. Cyclic voltammetry and differential pulse experiments were carried out using a MacLab potentiostat and data acquisition system with E-Chem software (AD Instruments). Data were recorded at intervals of about 500 psi (34 bar) up to the maximum pressure, allowing the cell to thermally equilibrate for about 20 mins between measurements, and then at intermediate pressures as the pressure was lowered, to check the integrity of measurements over the period of the measurements, typically 4 h.

Materials: Ammonium hexafluorophosphate (Aldrich), potassium hexafluorophosphate (Aldrich), 2,3-diaminonaphthalene (Fluka), sodium toluene-4-sulfonate (sodium tosylate; Aldrich), tetra-*n*-butylammonium hexafluorophosphate $\{[(n\text{-}C_4H_9)_4N]PF_6$; Aldrich$\}$, tetra-*n*-butylammonium perchlorate $\{[(n\text{-}C_4H_9)_4N]ClO_4$; Fluka$\}$, tetra-*n*-butylammonium tosylate $\{[(n\text{-}C_4H_9)_4N]$tos; Fluka$\}$, tetraethylammonium perchlorate $\{[(C_2H_5)_4N]PF_6$; Kodak Eastman$\}$, and decamethylferrocene (Aldrich) were used as supplied. SP Sephadex C-25 (Pharmacia) was used for chromatographic separation of ruthenium complexes.[4] HPLC grade acetonitrile (BDH) was used for electrochemical measurements; all other solvents were of reagent grade and used without purification. The ruthenium complexes $[Ru(bpy)_2Cl_2]\cdot 2\,H_2O$,[29] $[Ru(pp)_3](PF_6)_2$ {pp = bpy, phen, or Me_4bpy (4,4′,5,5′-tetramethyl-2,2′-bipyridine)},[12] $[Ru(phen)_2(HAT)](PF_6)_2$,[5] $[\{Ru(phen)_2\}_2(\mu\text{-}HAT)](PF_6)_4$,[5] $[\{Ru(phen)_2\}_3(\mu\text{-}HAT)](PF_6)_6$,[5] and $[\{Ru(bpy)_2\}_2(\mu\text{-}mapy)](PF_6)_4$ and $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-}mapy)](PF_6)_4$[3] were prepared and purified by literature methods.

2,3-Bis(2-pyridyl)-1,4-diazaanthracene (dpa): Preparation by a modified procedure of Goodwin and Lions[30] for 2,3-bis(2-pyridyl)quinoxaline. 2,3-Diaminonaphthalene (1.0 g, 6.3 mmol) and 2,2′-pyridil (= di-2-pyridylglyoxal; 1.34 g, 6.3 mmol) were refluxed in ethanol (20 cm^3) for 0.5 h. The volume of the reaction mixture was reduced to half via rotary evaporation. The yellow crystalline solid was collected by filtration and recrystallised from ethanol. Yield: 1.53 g (77%); m.p. 184−185 °C. ^{13}C NMR ($CDCl_3$): δ = 123.0, 124.0, 126.9, 127.8, 128.6, 134.2, 136.6, 137.6, 148.3, 153.0, 157.5.

$[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)](PF_6)_4$. − Method A: 2,3-Bis(2-pyridyl)-1,4-diazaanthracene (dpa; 31.7 mg, 0.095 mmol) was dissolved in nitrogen-purged 50% aqueous methanol (20 cm^3). $[Ru(bpy)_2Cl_2]\cdot 2\,H_2O$ (105 mg; 0.202 mmol) was added and the mixture heated at reflux for 24 h. Methanol was removed via rotary evaporation and the crude product precipitated from the aqueous solution by addition of a saturated solution of KPF_6. A dark green solid was isolated by vacuum filtration and washed sparingly with water. Purification was achieved by cation-exchange chromatography (SP-Sephadex C-25; eluent 0.5 M NaCl). A claret band of mononuclear material eluted first, followed by the desired dark green product, which was isolated as the PF_6^- salt. Yield: 117 mg (71%). ESMS (accurate mass): observed *m/z* 1597.1009 (most abundant isotope peak within cluster); $[C_{62}H_{46}N_{12}Ru_2](PF_6)_3^+$ requires 1597.1005.

Method B: A mixture of $[Ru(bpy)_2Cl_2]\cdot 2\,H_2O$ (170 mg, 0.33 mmol) and dpa (50 mg; 0.15 mmol) in ethylene glycol (3 cm^3) was heated in a modified microwave oven[31] (Sharp model R-2V55; 600 W, 2450 MHz) on medium-high power for 5 min. The green solution was poured into distilled water (50 cm^3) and a saturated solution of KPF_6 added dropwise yielding a dark green solid, which was collected and washed with distilled water. Purification of the crude product was achieved as above. Yield: 85 mg (33%).

Column Conditions for Separation/Resolution of $[\{Ru(bpy)_2\}_2(\mu\text{-}dpa)](PF_6)_4$: Separation of the diastereoisomers and resolution of the enantiomers of the *rac* form were achieved by cation exhange chromatography on SP Sephadex C-25 support using 0.25 M sodium toluene-4-sulfonate and 0.075 M sodium (−)-*O*,*O*′-dibenzoyl-L-tartrate as eluents, respectively.[7] The diastereoisomers separated after passing through an effective column length (ECL) of 150 cm (the *meso* band eluting first). Resolution to give the two enantiomers (ΔΔ and ΛΛ) of the *rac* form was achieved over an ECL of 80 cm. All products were precipitated as the PF_6^- salts by addition of a saturated solution of KPF_6 to each green band after elution. Diastereoisomeric ratio (*rac*/*meso*): 44:56. Enantiomeric ratio (ΔΔ/ΛΛ): 49:51.

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