in other molecules, using a vibrational force field that is obtained from the IR and Raman spectra of the anion and is consistent with the hexacarbonyl anion, cation, and neutrals of adjacent transition metals. We find the magnitude of the one-bond isotope shift of ^{93}Nb is completely consistent with the temperature dependence of the ^{93}Nb chemical shift in $[Nb(CO)_6]^-$ ion. A single parameter, $(\partial\sigma^{Nb}/\partial(\Delta r_{NbC}))_e$, which describes the sensitivity of the ^{93}Nb chemical shift to Nb–C bond extension, reproduces both the magnitude of the ^{13}C-induced isotope effect and the shape of the temperature dependence of the ^{93}Nb shift. A small correction to the latter is provided by the much smaller sensitivity of the ^{93}Nb chemical shift to the C–O bond extension, which is obtained from the ^{18}O-induced shifts. On the other hand, the very large D-induced isotope shifts of the metal M in the hydrides $[CpM(CO)_3H]$, respectively –4.7, –6.0, and –10 ppm for M = ^{51}V, ^{93}Nb, and ^{183}W, can be interpreted with analogous parameters $(\partial\sigma^{M}/\partial(\Delta r_{MH}))_e$ describing the sensitivity of the M chemical shift to M–H bond extension, which are smaller than those for M–C bond extension in the same compounds and are consistent within the series of hydrides. With these results we believe that the signs and magnitudes of the temperature dependence of transition-metal shifts and their isotope effects are generally understood. What remains to be determined are the general magnitudes of the derivatives $(\partial\sigma^{M}/\partial(\Delta r))$, $(\partial^2\sigma^{M}/\partial(\Delta r)^2)$, etc., by ab initio calculations such as those used for ^{55}Mn shielding in $Mn(CO)_5L$ complexes.[26]

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Ruthenium(II) Cluster Complexes: A Series of Homooligonuclear Complexes Based on Bidentate Bridging Ligands

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The preparation and properties of trimetallic and tetrametallic cluster complexes containing ruthenium(II) metal centers bridged by 2,2′-bipyrimidine (bpm) and 2,3-bis(2-pyridyl)quinoxaline (bpq) are reported. The tetrametallic clusters are symmetrical complexes containing a central ruthenium(II) coordinated to three $(BL)Ru(bpy)_2^{2+}$ "ligands", where BL is bpm or bpq and bpy is 2,2′-bipyridine. The trimetallic clusters are asymmetric and are of the general formula $[(bpy)Ru(BLRu(bpy)_2)_2]^{6+}$. The complexes exhibit low-energy MLCT transitions assigned as $d\pi(Ru(outer)) \rightarrow \pi^*(BL)$. The MLCT maxima of the tetrametallic complexes were at slightly higher energies than those for their trimetallic analogues. For example, λ_{max} for $[Ru(bpqRu(bpy)_2)_3]^{8+}$ was located at 618 nm; that of $[(bpy)Ru(bpqRu(bpy)_2)_2]^{3+}$ was located at 621 nm. The $E_{1/2}$ values were determined by cyclic voltammetry. The first oxidation in the case of $[(bpy)Ru(bpqRu(bpy)_2)_2]^{6+}$ was located at $E_{1/2}(1) = 1.57$ V, and the second, at $E_{1/2}(2) = 1.83$ V vs. SSCE. The wave associated with $E_{1/2}(1)$ had about twice the peak current as the wave at $E_{1/2}(2)$ and, hence, was assigned to the Ru(III/II) redox couple of the outer ruthenium(II) components. The low-energy MLCT transitions for the mononuclear precursors $(Ru(bpy)_x(BL)_{3-x}$, $x = 1$–3) and the multimetallic complexes were found to parallel $\Delta E_{1/2}$, the difference between $E_{1/2}$ values for the first oxidation and the first reduction. The excellent correlation (slope 1, correlation coefficient 0.99) indicates that either the energy of the lowest MLCT transition or $\Delta E_{1/2}$ can be used to measure the energy gap between the $d\pi$ and π^* energy levels.

Introduction

Several years ago we began a research program to develop multielectron-transfer catalysts that were photochemically and electrochemically active. We have successfully synthesized monometallic[1,2] precursor and multimetallic[3] metal complexes based on bidentate bridging ligands, which were chosen to add stability to the compounds. The bridging ligands used in our studies have been nitrogen-based heterocycles with both π-donor and π-acceptor properties, and the metal center has normally been ruthenium(II), although recently we have reported mixed-metal complexes containing both platinum(II) and ruthenium(II).[4–6]

A number of other workers have also contributed in this area. Dose and Wilson[7] reported the preparation and properties of $[Ru(bpy)_2(bpm)]^{2+}$ and $[(Ru(bpy)_2)_2bpm]^{4+}$, where bpm is 2,2′-bipyrimidine and bpy is 2,2′-bipyridine. Hunziker and Ludi reported the preparation of the tetranuclear complex $[Ru(bpmRu(bpy)_2)_3]^{8+}$, where bpm ligands served to bridge the central ruthenium(II) to the outer three ruthenium(II) centers.[8] Bimetallic and tetrametallic complexes were recently reported by Schmehl and co-workers.[9] The bridging ligand used by these investigators contained a p-$CH_2C_6H_4CH_2$ unit attached to two bipyridine molecules in the 4-position of the heterocyclic rings. Gafney and co-workers[10] have reported similar monometallic and bimetallic ruthenium(II) complexes based on the ligand 2,3-bis(2-pyridyl)pyrazine (bpp) and more recently Petersen and co-workers reported the preparation and properties of $Ru(bpp)_3^{2+}$.[11] Simlar complexes based on the ligand 2,2′-bibenzimidazole ($BiBzImH_2$) were reported by Haga.[12] The π-donor

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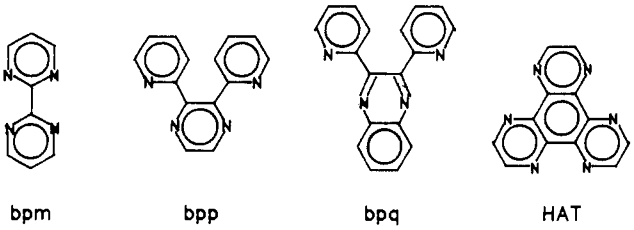


Figure 1. Bidentate bridging ligands: bpm = 2,2′-bipyrimidine; bpp = 2,3-bis(2-pyridyl)pyrazine; bpq = 2,3-bis(2-pyridyl)quinoxaline; HAT = benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]tripyrazine.

properties of the $BiBzImH_2$ ligand resulted in properties exhibited by the ruthenium(II) complexes that were quite different from those based on π-acceptor ligands such as bpm or bpp.

In this paper, we outline the preparation and properties of a series of oligonuclear complexes based on $[Ru(bpy)(BL)_2]^{2+}$ and $[Ru(BL)_3]^{2+}$, where BL is 2,2′-bipyrimidine and 2,3-bis(2-pyridyl)quinoxaline (bpq). These ligands are illustrated in Figure 1. The complexes described contain $Ru(bpy)_2^{2+}$ units attached to the appropriate precursor, resulting in bimetallic, asymmetric trimetallic, and symmetric tetrametallic species.

Experimental Section

Materials. The ligands 2,2′-bipyridine and 2,2′-bipyrimidine were purchased commercially and were used without further purification. Tetraethylammonium perchlorate (TEAP) was purchased as electrograde from Southwestern Analytical, Inc., Austin, TX, dried under vacuum at 70 °C, and used without further purification. Acetonitrile was of chromatographic grade and was dried over 4-Å molecular sieves for 48 h before use in electrochemistry or conductivity studies. $RuCl_3{\cdot}3H_2O$ was a gift from Johnson-Matthey, Inc. All other reagents were purchased commercially as reagent grade chemicals and were used without further purification. Elemental analyses were carried out by Atlantic Microlab, Inc., Atlanta, GA. These are given as supplementary material.

Preparations. $Ru(bpy)_2Cl_2{\cdot}2H_2O$, $[Ru(bpy)(bpm)_2](PF_6)_2$, $[Ru(bpy)(bpq)_2](PF_6)_2$, $[Ru(bpm)_3](PF_6)_2$, and $[Ru(bpq)_3](PF_6)_2$ were prepared by literature methods[2,13,14] or were available from previous work in our laboratories. The preparation of bpq followed and procedure of Goodwin and Lions.[15]

Asymmetric and Symmetric Homooligonuclear Complexes: $[(bpy)Ru(bpmRu(bpy)_2)_2](PF_6)_6$, $[(bpy)Ru(bpqRu(bpy)_2)_2](PF_6)_6$, $[Ru(bpmRu(bpy)_2)_3](PF_6)_8{\cdot}4H_2O$, $[Ru(bpqRu(bpy)_2)_3]{\cdot}2H_2O$. Method A. A 0.2-mmol quantity of $[Ru(bpy)(bpm)_2](PF_6)_2$, $[Ru(bpy)(bpq)_2](PF_6)_2$, $[Ru(bpm)_3]Cl_2$, or $[Ru(bpq)_3](PF_6)_2$ was added to a slight excess of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ needed to prepare the appropriate homooligonuclear complex. The solid were suspended in 100–150 mL of water, and the resulting suspension was heated at reflux under a nitrogen blanket for 8–12 h. The dark red suspension changed to dark green for the oligomers containing bpm and blue for bpq-based oligomers. The solution was then cooled to room temperature and filtered to remove unreacted materials. An aqueous saturated NH_4PF_6 solution was then added to precipitate the complex as the PF_6^- salt. The precipitate was filtered out, washed with ether, and then dried under vacuum.

The complexes were then purified by recrystallization. Several different solvent systems were used: acetone–CH_2Cl_2 (1:1 v/v), acetone–water (1:1 v/v), and acetone–water (2:3 v/v). $[Ru(bpqRu(bpy)_2)_3](PF_6)_8{\cdot}2H_2O$ was also purified by column chromatography.

The complex was dissolved in a minimum quantity of acetonitrile and added to a 40 mm diameter column containing neutral alumina to a depth of 4 in. The column had previously been developed with acetonitrile. A very slow flow rate was used to separate the desired material from a blue-green band at the top and a black red band at the bottom of the column. The initial band was eluted with a 1:1 methylene chloride–acetonitrile solution. The middle fraction was then eluted with acetonitrile; the solution was reduced in volume to ~10 mL and added to an excess of anhydrous ether to precipitate the desired compound. The principal impurities were the unreacted monometallic complex and a species that tenaciously held to the column which was assumed to be the μ-oxo-bridged species on the basis of color and the known chemistry of μ-oxo-bridged ruthenium(II) dimers.[16]

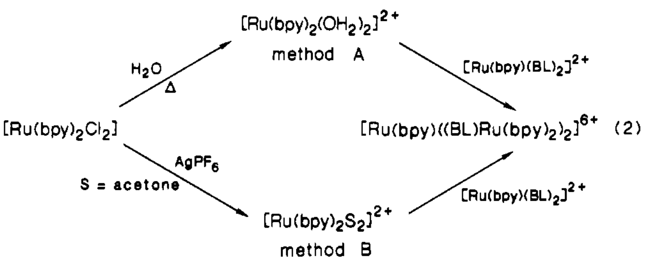
Method B. The general preparative procedure involved substitution of acetone for chloride ion in the coordination sphere of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (0.5–0.75 mmol) by reaction with $AgClO_4$ or $AgPF_6$ in 50 mL of acetone. The AgCl formed was removed by filtration, and the volume of the solvated species was reduced to ~10 mL. The solution was then added to the desired monometallic precursor complex (0.2 mmol) dissolved or suspended in 150 mL of H_2O. The resulting suspension was heated at reflux under a nitrogen blanket for 8–12 h. The isolation and purification of the product was essentially the same as described under method A.

Physical Measurements. Visible and UV spectra were recorded with a Perkin-Elmer Lambda Array 3840 spectrophotometer. Solution conductivities were obtained in acetonitrile at 25.0 ± 0.1 °C with a Beckman Model RC-18A conductivity bridge. The cell constant was determined by measuring the resistance of a 0.020 M KCl solution having a specific conductance at 25 °C of 0.002 768 Ω^{-1}.[17] Polarograms were obtained in acetonitrile solutions containing 0.10 M TEAP as the supporting electrolyte. The measurements were made vs the saturated sodium chloride calomel electrode (SSCE). Electrochemistry studies were carried out with a PAR 174A polarographic analyzer or a PAR 173 potentiostat in conjunction with a PAR 175 programmer. Polarograms were recorded with a YEW Model 3022 X-Y recorder. Coulometry was performed with a PAR 173 potentiostat, a PAR 179 digital coulometer, and a PAR 370 cell system.

Results

Preparations. Preparations were carried out sequentially as summarized in eq 1 and 2. The series of mononuclear precursor

$$\begin{array}{l} Ru(bpy)_2Cl_2 \\ Ru(bpy)Cl_4 \\ RuCl_3 \end{array} \xrightarrow[\Delta]{\text{BL, ethylene glycol}} \begin{array}{l} [Ru(bpy)_2BL]^{2+} \\ [Ru(BL)_2(bpy)]^{2+} \\ [Ru(BL)_3]^{2+} \end{array} \qquad (1)$$



complexes containing from one to three bidentate bridging ligands, where bridging was effected via the remote nitrogen donor atoms of the heterocyclic ligands, were synthesized by the thermal reaction of the appropriate starting reagents with excess bridging ligand in ethylene glycol. Ethylene glycol also functioned as a reducing medium, resulting in formation of ruthenium(II) trischelated complexes derived from $RuCl_3{\cdot}3H_2O$ or $(bpy)RuCl_4$. The monometallic species were isolated as PF_6^- salts and purified by chromatography as outlined in the Experimental Section.

The oligomers were then formed by either of two methods as illustrated in eq 2. Method A involved formation of the $[Ru(bpy)_2(OH_2)_2]^{2+}$ precursor (or $[Ru(bpy)_2(OH_2)Cl]^+$) immediately prior to formation of the trinuclear complex; method B involved removal of Cl^- with Ag^+ and substitution of acetone into the coordination sphere of ruthenium(II). Both procedures functioned equally well, but preference was given to method A since the possible coordination of Ag^+ at the remote nitrogen sites of the bridging ligand was avoided.

The tetranuclear complex is illustrated in Figure 2. It can be described as a symmetric metallic cluster, whereas the $[bpyRu((BL)Ru(bpy)_2)_2]^{6+}$ analogue can be described as an asymmetric metallic cluster.

Conductivity. Dilution conductivity studies were carried out by procedures previously described.[3] For strong electrolytes, the

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Table I. Electrochemical Data for Homooligonuclear and Related Complexes of Ruthenium(II)[a]

	oxidations[b]		reductions[c]					
complex	$E_{1/2}(2)$	$E_{1/2}(1)$	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(4)$	$E_{1/2}(5)$	$E_{1/2}(6)$
$[Ru(bpy)_2bpm](ClO_4)_2$[d]		1.36	−1.01					
$[(Ru(bpy)_2)_2bpm](ClO_4)_4$[d]	1.69	1.53	−0.41	−1.08				
$[Ru(bpy)(bpmRu(bpy)_2)_2](PF_6)_6$		1.70	−0.25	−0.40	−1.05	−1.22		
$[Ru(bpmRu(bpy)_2)_3](PF_6)_8$		1.75	−0.16	−0.32	−0.47	−1.09	−1.23	−1.37
$[Ru(bpm)_3](PF_6)_2$[f]		1.69	−0.91	−1.08	−1.28			
$[Ru(bpy)_2bpq](PF_6)_2$[e]		1.41	−0.78					
$[(Ru(bpy)_2)_2bpq](PF_6)_4$[e]	1.62	1.47	−0.37	−1.10				
$[Ru(bpy)(bpqRu(bpy)_2)_2](PF_6)_6$	1.83	1.57	−0.29	−0.76	−1.08	−1.28		
$[Ru(bpqRu(bpy)_2)_3](PF_6)_8$		1.60	−0.17	−0.36	−0.79	−1.21	−1.35	...
$[Pb(bpq)_3](PF_6)_2$[g]		1.70	−0.60	−0.78	−1.04			
$[Ru(bpy)_3]^{2+}$[f]		1.27	−1.31	−1.50	−1.77			

[a] Acetonitrile solutions, 0.10 M TBAH or TEAP as supporting electrolyte, Pt disk working electrode, potentials in volts vs SSCE, $E_{1/2}$ (±0.01 V). [b] Oxidations correspond to ruthenium-centered processes. [c] Reductions correspond to reduction of coordinated bpm and bpq, except those for $Ru(bpy)_3^{2+}$ which are bpy-centered reductions. [d] Reference 7. [e] Reference 1. [f] Reference 2. [g] Reference 13.

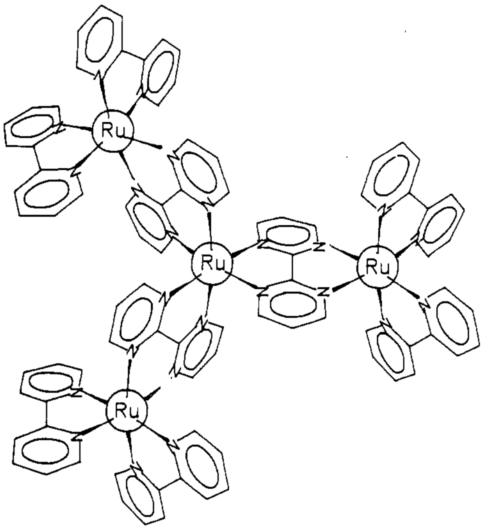

Figure 2. The tetrametallic $[Ru(bpmRu(bpy)_2)_3]^{8+}$ ion.

equivalent conductance, Λ_e is expected to vary linearly with the square root of the equivalent concentration, $C_{eq}^{1/2}$.[18] According to eq 3, a plot of $\Lambda_0 - \Lambda_e$, where Λ_0 is the equivalent conductance

$$\Lambda_0 - \Lambda_e = AC_{eq}^{1/2} \quad (3)$$

at infinite dilution, vs $C_{eq}^{1/2}$ will result in a straight line of slope A indicative of the electrolyte type.[18-20] Figure 3 is such a plot and supports the formulation of the oligonuclear compounds described in this paper. The experimental slopes for the monometallic, bimetallic, trimetallic, and tetrametallic complexes were in the ranges 600–700 (±90), 1300–1600 (±60), 2400–2500 (±350), and 3700–4000 (±400) mhos $L^{1/2}$ $equiv^{-1/2}$, respectively; the theoretical values determined by the Onsager equation were 700–800, 1500–1600, 2500–2600, and 3700–4000 mhos $L^{1/2}$ $equiv^{-1/2}$, in the same order. The theoretical slopes vary due to different ionic mobilities of the cations, λ_+, determined from the intercept, Λ_0. (The equivalent conductance at infinite dilution, Λ_0, equals $\lambda_+ + \lambda_-$, where λ_- is the ionic conductivity of the anion.[3,16]) Standards were run for direct comparison purposes; the experimental slope for $Ru(bpy)_3Cl_2$, a 2:1 electrolyte, was 734 ± 30 mhos $L^{1/2}$ $equiv^{-1/2}$.

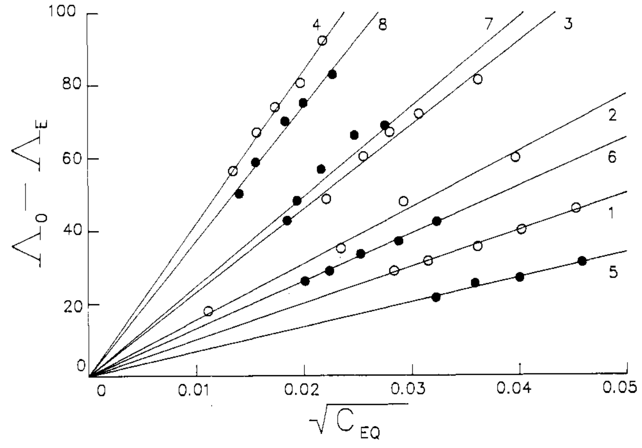

Figure 3. Dilution conductivity results. Open circles correspond to bpm complexes; closed circles correspond to bpq complexes: (1) $[Ru(bpy)_2bpm](ClO_4)_2$; (2) $[(Ru(bpy)_2)_2bpm](ClO_4)_4$; (3) $[(bpy)Ru(bpmRu(bpy)_2)_2](PF_6)_6$; (4) $[Ru(bpmRu(bpy)_2)_3](PF_6)_8$; (5) $[Ru(bpy)_2(bpq)](PF_6)_2$; (6) $[(Ru(bpy)_2)_2bpq](PF_6)_4$; (7) $[(bpy)Ru(bpqRu(bpy)_2)_2](PF_6)_6$; (8) $[Ru(bpqRu(bpy)_2)_3](PF_6)_8$.

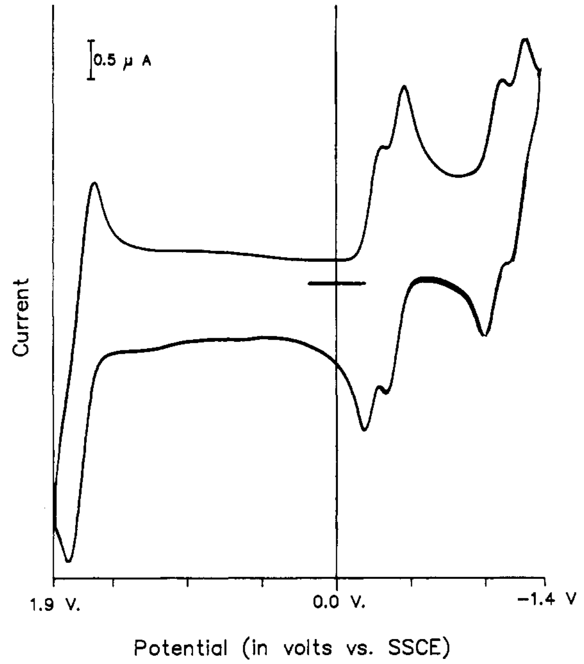

Figure 4. Cyclic voltammogram of $[(bpy)Ru(bpmRu(bpy)_2)_2]^{6+}$ in acetonitrile. The electrolyte was 0.10 M TEAP and the scan rate was 100 mV/s. The working electrode was a Pt disk, the counter electrode was a Pt wire, and the reference was a SSCE.

Electrochemistry. Redox properties were determined by cyclic voltammetry. Oxidation of ruthenium(II) centers were observed in the positive potential region, whereas reduction of the coordinated ligands occurred in the negative region. The complexity of the redox processes increased as the number of metal centers increased. This is illustrated in Figure 4 for the reduction of $[(bpy)Ru(bpmRu(bpy)_2)_2]^{6+}$. A sequence of two reductions is observed, which correspond to the first and second reductions of

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Table II. Visible–UV Spectral Data for Homooligonuclear and Related Complexes of Ruthenium(II)[a–c]

complex	$d\pi \rightarrow \pi^*$(BL)	$d\pi \rightarrow \pi^*$(bpy)	$\pi \rightarrow \pi^*$ [d]	ref
$[Ru(bpy)_2bpm](ClO_4)_2$	478 (sh)	422 (9.1 × 10^3)	284 (5.6 × 10^4) 236 (4.0 × 10^4)	*e*
$[(Ru(bpy)_2)_2bpm](ClO_4)_4$	594 (8.2 × 10^3) 545 (sh)	411 (2.4 × 10^4)	280 (7.5 × 10^4) 243 (sh)	*e*
$[Ru(bpy)(bpmRu(bpy)_2)_2](PF_6)_6$	597 (1.5 × 10^4)	411 (3.6 × 10^4)	280 (9.5 × 10^4) 253 (5.5 × 10^4)	*f*
$[Ru(bpmRu(bpy)_2)_3)](PF_6)_8$	590 (2.1 × 10^4) 553 (sh)	417 (4.8 × 10^4)	283 (1.1 × 10^5) 243 (7.2 × 10^4) 253 (1.2 × 10^5)	*f*
$[Ru(bpy)_2bpq](PF_6)_2$	515 (8.1 × 10^3)	427 (sh)	348 (sh) 284 (6.6 × 10^4) 253 (sh)	*e*
$[(Ru(bpy)_2)_2bpq](PF_6)_4$	605 (9.8 × 10^3)	423 (sh) 399 (1.2 × 10^4)	382 (sh) 287 (1.8 × 10^5) 248 (1.0 × 10^5)	*e*
$[Ru(bpy)(bpqRu(bpy)_2)_2](PF_6)_6$	621 (2.4 × 10^4)	403 (2.8 × 10^4)	286 (1.5 × 10^5) 247 (5.8 × 10^4)	*f*
$[Ru(bpqRu(bpy)_2)_3](PF_6)_8$	618 (4.2 × 10^4) 513 (sh)	399 (4.2 × 10^4)	286 (1.5 × 10^5) 253 (sh) 247 (9.2 × 10^4)	*f*
$[Ru(bpy)_3]^{2+}$		451 (1.4 × 10^4)	285 (8.7 × 10^4) 250 (2.5 × 10^4) 238 (3.0 × 10^4)	*g*

[a] λ max in nm; error ±1 nm. [b] ϵ values follow in parentheses; units are M^{-1} cm^{-1}. [c] Spectra were reported in acetonitrile solutions; $T = 20 \pm 1$ °C. ϵ values were calculated from slopes of plots of A vs C, where A was the absorbance and C the concentration of complex in solution. [d] Transitions of $\pi \rightarrow \pi^*$ for both bridging and bpy ligands. [e] Refernce 2. [f] This work. [g] Reference 13.

each bipyrimidine ligand. This assignment is reasonable given that reduction of coordinated bipyrimidine commences at −0.91 V[2,21] for $[Ru(bpm)_3]^{2+}$, while reduction of coordinated bipyridine commences at −1.31 V[22] vs SSCE for $[Ru(bpy)_3]^{2+}$. In like manner, reduction of coordinated bpq starts at −0.60 V[13] for $[Ru(bpq)_3]^{2+}$. The accumulated data are summarized in Table I and indicate that the primary reductions found for the trimetallic and tetrametallic complexes are reductions of the π^* energy levels of the bridging ligands. The number of reductions in a sequence is equal to the number of bridging ligands, and there are two sequences corresonding to the first and second reductions of the bridging ligands, respectively. These results are in agreement with the report by DeArmond and co-workers[23] for $[Ru(bpy)_3]^{2+}$, where each ligand is singly reduced followed by a second reduction approximately 1 V more negtive than the first.

According to the data in Table I, the final reductions of the bridging ligands of the tetrametallic complexes fall in a region where coordinated bpy ligands commence reduction in $[Ru(bpy)_3]^{2+}$. However, the bpy reductions would be expected to shift to more negative potential due to electrostatic effects imposed on the complex after bridging-ligand reductions. Thus, in most cases for trimetallic and tetrametallic complexes, the bpy reductions occur at potentials more negative than −1.4 V and do not interfere with the bridging-ligand reductions (see Figure 4). There is one exception to this: the final bridging-ligand reduction for $[Ru(bpqRu(bpy)_2)_3]^{8+}$ occurs in a region where bpy reductions commence as noted by a large increase in current and the inability to determine the $E_{1/2}(6)$ value. This difficulty occurs for reductions for the other complexes at potentials more negative than the −1.4 V found for $[Ru(bpqRu(bpy)_2)_3]^{8+}$. Either the current increases rapidly and returns irreversibly or waves having the appearance of stripping waves are observed.

Oxidations associated with the ruthenium(II) centers are also tabulated in Table I. It is interesting to note that the potentials for the bpm-bridged complexes are shifted more positive than those for the bpq-bridged complexes. This may be due to the fact that the net electron-donor strength of bpq (pK_a(py) = 5.2,[24] pK_a(quinoxaline) = 0.7)[25] is greater than that of bpm (pK_a = 1.3).[25] As previously shown, the more electron density placed on a metal center, the more negative is its reduction potential.[26] For $[(bpy)Ru(bpqRu(bpy)_2)_2]^{6+}$, two oxidations were observed with peak current ratios of 2:1 for $E_{1/2}(1)$ compared to $E_{1/2}(2)$. These data suggest that the outer ruthenium centers are oxidized first, then the inner ruthenium center. For the other trimetallic and tetrametallic complexes, the second oxidation is presumably shifted too far positive to be observed. ΔE_p values, where ΔE_p was the difference in potential between the peak current of the oxidation wave and the potential of the peak current of the reduction wave for a given redox couple, were determined from the intercepts of plots of ΔE_p vs the square root of the sweep rate. For the first oxidation, ΔE_p was 87 mV for $[(bpy)Ru(bpmRu(bpy)_2)_2]^{6+}$ and 128 mV for $[Ru(bpmRu(bpy)_2)_3]^{8+}$. The theoretical value should be $59/n$ mV, where n is the number of electrons transferred for a reversible electron-transfer process.[27] Clearly, $E_{1/2}(1)$ with the 87-mV spacing corresponds to two closely spaced one-electron-transfer waves for the trimetallic complexes and with the 128-mV

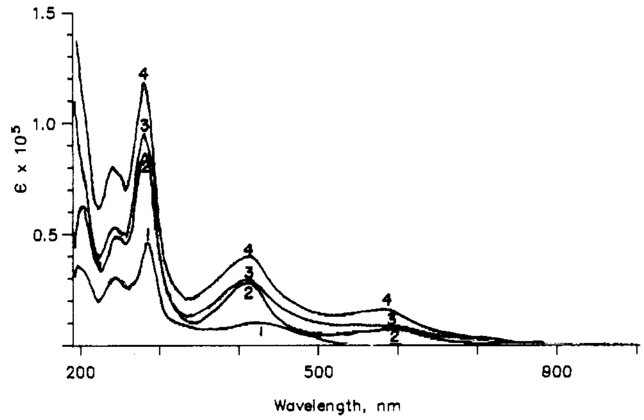

Figure 5. Visible–UV spectral comparison of the bpm complexes in acetonitrile at room temperature: (1) $[Ru(bpy)_2bpm]^{2+}$; (2) $[(Ru(bpy)_2)_2bpm]^{4+}$; (3) $[(bpy)Ru(bpmRu(bpy)_2)_2]^{6+}$; (4) $[Ru(bpmRu(bpy)_3]^{8+}$.

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spacing to three closely spaced one-electron-transfer waves for the tetrametallic species.

Electronic Spectra. The visible–UV spectra of the 2,2′-bipyrimidine series shown in Figure 5 are illustrative of the observations for both bpq and bpm complexes. Starting with the monometallic complex, the low-energy transition shifts to the red after addition of the first and second $[Ru(bpy)_2]^{2+}$ components but then blue-shifts upon incorporation of the third $[Ru(bpy)_2]^{2+}$ fragment. The data are summarized in Table II and separated into MLCT transitions associated with each ligand and π–π^* transitions generally found in the 240–290-nm region. The π^* levels of 2,3-bis(2-pyridyl)quinoxaline, bipyrimidine, and bipyridine are at different energies (reductions of free ligands occur at −1.56,[13] −1.80,[21] and −2.21 V[28] vs SSCE, respectively). Thus, different $d\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions are expected for these complexes due to the fact that (1) they contain different heterocyclic ligands, (2) the ruthenium(II) centers are nonequivalent, and (3) even for the simplest case, more than one $d\pi \rightarrow \pi^*$ transition is theoretically possible. For example, for $[Ru(bpy)_3]^{2+}$ there are two $d\pi \rightarrow \pi^*$ transitions expected, one approximately 6000 cm^{-1} higher in energy than the other.[29]

The assignment of the lowest energy MLCT transition can be made on the basis of the ligand with the lowest π^* energy levels; thus, $d\pi \rightarrow \pi^*$(bpq) and $d\pi \rightarrow \pi^*$(bpm) are expected at lower energy than $d\pi \rightarrow \pi^*$(bpy). The metal center most likely associated with the low-energy transition is the outer ruthenium. This is based on both electrochemical information and molar extinction coefficients. The electrochemical data indicate that the energy gap between the $d\pi$ and π^* levels is less for the outer ruthenium centers than for the inner one. It is also noted that the extinction coefficients generally increase as the number of $[(BL)Ru(bpy)_2]^{2+}$ units increase. This increase for the $d\pi \rightarrow \pi^*$(BL) transition is nearly additive as the number of $[(BL)Ru(bpy)_2]^{2+}$ units increases. The variations to this are probably the result of overlapping absorption components that vary in position as substitution takes place from one complex to the next within a given series. One likely contributor to the variation is the $d\pi \rightarrow \pi^*$(BL) transition associated with the inner ruthenium.

The remaining assignments were made on the basis of the dominance of bpy to bridging ligands. The transition in the 400–420-nm region is assigned to $d\pi \rightarrow \pi^*$(bpy), and the ultraviolet absorptions are primarily due to $\pi \rightarrow \pi^*$(bpy) by analogy to $[Ru(bpy)_3]^{2+}$. The other ultraviolet absorptions can be assigned to $\pi \rightarrow \pi^*$(BL), where BL is bpm or bpq.

Discussion

The oligonuclear complexes reported here represent a class of compounds formed by the addition of $Ru(bpy)_2{}^{2+}$ fragments to a $[Ru(bpy)_x(BL)_{3-x}]^{2+}$ core, x = 0–2. As shown in Figure 2, the tetrametallic complex is metal centered with appended $[(bpm)Ru(bpy)_2]^{2+}$ units, which could be regarded as "ligands". This complex can be contrasted with the ligand-centered system recently published by Masschelein et al.[30] The complex reported by these workers is the trimetallic $[(Ru(bpy)_2)_3HAT]^{6+}$, where HAT is as shown in Figure 1. On the basis of geometry, the trimetallic complexes of bpm and bpq could be classified as metal centered but asymmetric, whereas the binuclear complexes could best be described as ligand-centered systems. These various types of multimetal systems give rise to properties that are similar in some situations but different in others.

Similarities are noted in trends related to MLCT transitions and coordinated ligand reductions. The MLCT absorption maxima red-shift in the energy sequence monometallic > bimetallic > trimetallic. The absorption maxima occur at 484 nm for $[Ru(bpy)_2HAT]^{2+}$, at 572 nm for $[(Ru(bpy)_2)_2HAT]^{4+}$, and at 580 nm for $[(Ru(bpy)_2)_3HAT]^{6+}$ compared to 478 nm for $[Ru(bpy)_2bpm]^{2+}$, 594 nm for $[(Ru(bpy)_2)_2bpm]^{4+}$, and 597 nm for $[(bpy)Ru(bpmRu(bpy)_2)_2]^{6+}$. For another similarity, the coordinated ligand reduction potentials shift positively as the number of $[Ru(bpy)_2]^{2+}$ fragments increases. The bpq, bpm, and HAT ligands contain lower energy π^* orbitals than bpy and, hence, represent the initial reduction sites in the molecules as illustrated in eq 4. Expressed in volts vs SSCE for the bpm series and in

$$[(bpy)_2Ru^{II}(bpm)Ru^{II}(bpy)_2]^{4+} + e^- \rightarrow [(bpy)_2Ru^{II}(bpm^-)Ru^{II}(bpy)_2]^{3+} \quad (4)$$

volts vs SCE for the HAT series, the first reduction occurs at $E_{1/2} = -1.0$ V for $[Ru(bpy)_2bpm]^{2+}$, at $E_{1/2} = -0.41$ V for $[(Ru(bpy)_2)_2bpm]^{4+}$, and at −0.25 V for $[(bpy)Ru(bpmRu(bpy)_2)_2]^{6+}$ compared to $E_{1/2} = -0.84$ V for $[Ru(bpy)_2HAT]^{2+}$, $E_{1/2} = -0.49$ V for $[(Ru(bpy)_2)_2HAT]^{4+}$, and $E_{1/2} = -0.25$ V for $[(Ru(bpy)_2)_3HAT]^{6+}$.[26]

The observed properties of bpq, bpm, and HAT complexes differ in a number of ways. The Ru(III/II) potentials of the $[Ru(bpy)_2]^{2+}$ fragments of the bpq and bpm complexes shift positively as the number of $[Ru(bpy)_2]^{2+}$ components increases, but the potentials of the analogous HAT complexes remain relatively constant. ($Ru^{III/II}$ potentials are as follows: $E_{1/2} = 1.56$ V for $[Ru(bpy)_2HAT]^{2+}$, $E_{1/2} = 1.53$ V for $[(Ru(bpy)_2)_2HAT]^{4+}$, and $E_{1/2} = 1.61$ V for $[(Ru(bpy)_2)_3HAT]^{6+}$).[26] Exchange of $[(BL)Ru(bpy)_2]^{2+}$ for BL ligands, where BL = bpm or bpq (or addition of $[Ru(bpy)_2]^{2+}$ fragments to $[Ru(BL)_x(bpy)_{3-x}]^{2+}$, where x = 1–3), gives rise to a similar trend, as noted for the monometallic analogues. Both π^* and $d\pi$ levels are lowered in energy, as noted by the more positive redox potentials, whereas, in the ligand-centered HAT homooligomers, the $d\pi$ level remains relatively constant even though the π^* levels of the HAT ligand are lowered in energy. The energies of the π^* levels are lowered due to an increase in electrostatic charge of incoming $[Ru(bpy)_2]^{2+}$ fragments,[31] although the effect becomes less significant as more $[Ru(bpy)_2]^{2+}$ fragments are added.

The change in energy of the $d\pi$ levels is more complex. For neutral bridging ligands that share a heterocyclic ring, the effect varies from very little change to one where the $d\pi$ levels are lowered in energy due to electron withdrawal by the $[(BL)Ru(bpy)_2]^{2+}$ ligands. In cases where the bridging ligand stereochemistry requires that it remain planar (e.g. HAT), the monometallic and bimetallic complexe exhibit nearly the same Ru(III/II) potentials. In cases where twisting is permitted, some electron withdrawal occurs, but not always. The monometallic $[Ru(bpy)_2bpp]^{2+}$ and bimetallic $[(Ru(bpy)_2)_2bpp]^{4+}$ exhibit nearly the same Ru(III/II) redox potentials (±0.01 V);[10] the analogous bpq complexes discussed here differ by 0.06 V, and the bpm analogues differ by 0.17 V. These conclusions are opposed to those of Gafney and co-workers.[10] Gafney argues that planar bridging ligands result in greater metal–metal interaction across the bridge, which gives rise to larger potential differences between $E_{1/2}(1)$ of the monometallic complex and $E_{1/2}(1)$ of the multimetallic complex. It is possible the HAT results are anomalous. However, crystal structures of bimetallic bpq- and bpm-bridged species will be needed to resolve this issue.

In the past a number of correlations between spectroscopic properties and $\Delta E_{1/2}$, where $\Delta E_{1/2}$ is the difference in potential between the first oxidation and first reduction, have been observed. The parameter, $\Delta E_{1/2}$, is the thermodynamic energy gap between the $d\pi$ and π^* energy levels. Lever and co-workers[32] have suggested that this difference can be taken as a measure of the optical transition energy, which, in this case, is the energy of the MLCT transition. It is interesting to note that this same idea can be carried over to account for absorption properties of both monometallic and multimetallic complexes, as shown in Figure 6. The

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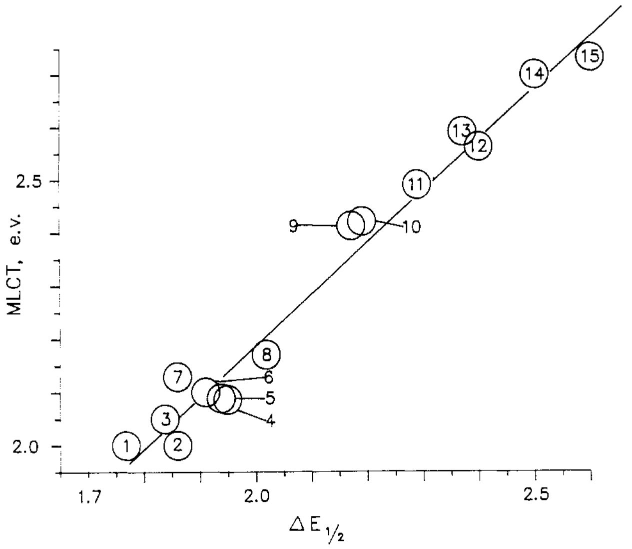

Figure 6. Free energy correlation equating the optical energy gap (MLCT, in eV) to the thermodynamic energy gap ($\Delta E_{1/2}$). The numbered entries are as follows: (1) $[bpyRu(bpqRu(bpy)_2)_2]^{6+}$; (2) $[Ru(bpqRu(bpy)_2)_3]^{6+}$; (3) $[(Ru(bpy)_2)_2bpq]^{4+}$; (4) $[(bpy)(bpm)(Ru(bpy)_2)_2]^{6+}$; (5) $[(Ru(bpy)_2)_2bpm]^{4+}$; (6) $[Ru(bpmRu(bpy)_2)_3]^{8+}$; (7) $[(Ru(bpy)_2)_3HAT]^{6+}$; (8) $[(Ru(bpy)_2)_2HAT]^{4+}$; (9) $[Ru(bpy)_2(bpq)]^{2+}$; (10) $[Ru(bpy)(bpq)_2]^{2+}$; (11) $[Ru(bpq)_3]^{2+}$; (12) $[Ru(bpy)_2HAT]^{2+}$; (13) $[Ru(bpy)_2bpm]^{2+}$; (14) $[Ru(bpy)(bpm)_2]^{2+}$; (15) $[Ru(bpm)_3]^{2+}$. The correlation includes related bpm complexes from ref 2, related bpq complexes from ref 13, and related HAT complexes from ref 26.

correlation between the MLCT energy in electronvolts and $\Delta E_{1/2}$ in volts is linear, the slope is 1.0, and the correlation coefficient is 0.99.

Finally, we would note some properties concerning the stability of oxidized and reduced oligonuclear complexes. Attempts were made to obtain global n values for oxidation and reduction of the bimetallic, trimetallic, and tetrametallic complexes. The processes were effected electrochemically in acetonitrile at a Pt working electrode. Oxidations were difficult, at best. Apparently, either the oxidized complexes oxidized the solvent, which then formed a film on the electrode, or the oxidized oligomer itself formed a decomposition product that formed a film on the electrode surface. In the case of $[Ru(bpmRu(bpy)_2)_3]^{8+}$, the cyclic voltammogram after electrolysis suggested that the oligomer had dissociated into monometallic species. An additional wave located at about $E_{1/2}$ = 1.41 V vs SSCE was present, which can be associated with $[Ru(bpy)_2(bpm)]^{2+}$. Reductions, on the other hand, were reversible for studies effected at potentials more positive than -1.0 V vs SSCE. $[Ru(bpmRu(bpy)_2)_3]^{8+}$ was reduced by 3 electrons (n = 3.0) at -0.7 V, $[(bpy)Ru(bpmRu(bpy)_2]^{6+}$ was reduced by 2 electrons (n = 1.9) at -0.6 V, and $[(Ru(bpy)_2)_2bpm]^{4+}$ was reduced by 2 electrons (n = 1.9) at -1.1 V. Each of these reductions was reversible; that is, upon reoxidation of the complexes in solution at zero volts, the required number of coulombs was obtained. The fact that the processes were reversible was verified by cyclic voltammetry. The voltammograms before and after electrolysis were the same.

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Registry No. $Ru(bpy)_2Cl_2$, 15746-57-3; $[Ru(bpy)(bpm)_2](PF_6)_2$, 85335-57-5; $[Ru(bpy)(bpq)_2](PF_6)_2$, 106471-69-6; $[Ru(bpq)_3](PF_6)_2$, 106222-81-5; $[Ru(bpm)_3]Cl_2$, 65034-88-0; $[Ru(bpy)(bpmRu(bpy)_2)_2](PF_6)_6$, 116026-59-6; $[Ru(bpmRu(bpy)_2)_3](PF_6)_8$, 116209-67-7; $[Ru(bpy)(bpqRu(bpy)_2)_2](PF_6)_6$, 116052-56-3; $[Ru(bpqRu(bpy)_2)_3](PF_6)_8$, 116052-54-1.

Supplementary Material Available: A listing of elemental analyses (1 page). Ordering information is given on any current masthead page.

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(Hexamethylbenzene)ruthenium(II) Complexes: Synthesis and Coordination Chemistry of a Novel Tridentate Ligand with an O,O,Cl Donor Set

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Trimethyl phosphite reacts with $[\{(C_6Me_6)RuCl_2\}_2]$ in methanol to yield the cation $[(C_6Me_6)RuCl\{P(OCH_3)_3\}_2]^+$, which has been isolated as a chloride or hexafluorophosphate salt. $[(C_6Me_6)RuCl\{P(OCH_3)_3\}_2]^+$ undergoes a sequence of two Michaelis–Arbuzov type reactions to give the neutral complex $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}\{P(OCH_3)_3\}]$ and the L^- anion $[(C_6Me_6)RuCl\{P(O)(OCH_3)_2\}_2]^-$. Attempts to isolate the anion in the form of its sodium salt NaL have led to products that always contain additional sodium iodide or sodium hexafluorophosphate. The free acid HL can be prepared by protonation from NaL or directly from the reaction of $[\{(C_6Me_6)RuCl_2\}_2]$ with dimethyl phosphonate, $HP(O)(OCH_3)_2$. L^- is a uninegative, potentially bidentate or tridentate ligand with an O,O,Cl donor set. It reacts with many transition-metal and main-group-metal ions, e.g. $M^{n+} = Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}$, or Fe^{3+}, to give 2:1 complexes of the composition $[ML_2]^{(n-2)+}$. The reactions of the complexes $[\{(ring)MCl_2\}_2]$, (ring)M = $(C_5Me_5)Rh$, $(C_6Me_6)Ru$, and (p-cymene)Ru, with L^- lead to the cationic complexes $[(C_5Me_5)RhL]^+$, $[(C_6Me_6)RuL]^+$, and $[(p\text{-cymene})RuL]^+$, which have been isolated as hexafluorophosphate salts. L^- also functions as a tridentate O,O,Cl ligand in $LRe(CO)_3$, which has been prepared from HL and $ReBr(CO)_5$. HL oxidatively adds to the metal(0) complexes $[Mo(CH_3CN)_3(CO)_3]$ and $[W(DMF)_3(CO)_3]$ to yield metal hydride complexes of the composition $[LM(CO)_3H]$. The molybdenum hydride is labile and rapidly gives HL and $Mo(CO)_6$ under an atmosphere of CO gas. The tungsten hydride is unreactive under the same conditions. The copper carbonyl complex LCu(CO) has been prepared in a comproportionation reaction of CuL_2 with copper metal under an atmosphere of carbon monoxide. LCu(CO) is the first neutral complex with a Cu(CO)Cl unit that could be isolated.

Introduction

Polydentate organic ligands with practically all combinations of the donor centers N, O, P, S, As, and Se are well-known, but chelating ligands with a halogen atom as one of the donor centers are very rare. The coordination chemistry of such ligands is only just emerging.[1] As a rule organic halides seem to be extremely

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