discussion) makes elimination of all color difficult to achieve when large Li_2Te additions are made. Active metal prereduction of molten salt solvents has been found useful in controlling the oxidizing impurities.

(12) It has been shown that the solubility of Li_2Te in molten fluorides is less than 10^{-5} mole fraction (see L. E. McNeese, "Molten Salt Reactor Program Semiannual Progress Report for Period Ending Feb. 29, 1976", ORNL-5132, Oak Ridge National Laboratory, Oak Ridge, Tenn., p 24). Our addition, equivalent to 10^{-3} mole fraction, caused the appearance of a separate Li_2Te phase.

(13) D. L. Manning and G. Mamantov in "Characterization of Solutes in Nonaqueous Solvents", G. Mamantov, Ed., Plenum Press, New York, N.Y., 1978.

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Synthesis and Properties of the Chloro-Bridged Dimer $[(bpy)_2RuCl]_2^{2+}$ and Its Transient 3+ Mixed-Valence Ion

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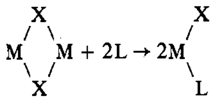
A new di-μ-chloro dimer, $[(bpy)_2RuCl]_2^{2+}$, has been synthesized. The Ru(II)–Ru(II) form of the dimer has been shown to undergo symmetrical bridge cleavage reactions in the presence of added ligands such as CH_3CN and is a convenient precursor to complexes of the type $(bpy)_2RuL(Cl)^+$. Cyclic voltammetry studies show that the dimer undergoes two reversible one-electron oxidations corresponding to stepwise oxidations at the two metal sites. Controlled-potential electrolysis just past the first oxidation wave results in the unsymmetrical cleavage of the transient mixed-valence dimer $[(bpy)_2RuCl]_2^{3+}$ to give $Ru(bpy)_2Cl_2^+$ and monomeric Ru(II) complexes. A simple molecular orbital rationale of this behavior is given in terms of weak interactions between the Ru sites in the 2+ dimer and localized Ru(II) and Ru(III) sites in the transient, mixed-valence dimer.

We describe here the preparation and properties of the dimeric ion $[(bpy)_2RuCl]_2^{2+}$ (bpy is 2,2′-bipyridine). Our interest in the ion has two origins. Halide-bridged dimers and higher oligomers have frequently been used successfully as synthetic intermediates based on, what are often, facile bridge cleavage reactions:



We and others have shown that bpy complexes of ruthenium can be of great value in the study of such diverse phenomena as excited-state redox and sensitization processes,[1] mixed-valence chemistry,[1c,2] electron-transfer processes,[3,4] and reactions of coordinated ligands.[5] In many of these studies controlled chemical syntheses are an essential feature, and $[(bpy)_2RuCl]_2^{2+}$ is a potentially useful source of the $(bpy)_2Ru^{II}Cl$ moiety.

A continuing problem in mixed-valence chemistry is to understand how details of molecular structure influence the extent and nature of electronic interactions between metal sites. One-electron oxidation of $[(bpy)_2RuCl]_2^{2+}$ would give a 3+ mixed-valence ion. From known chemical examples there are several possibilities for the orbital nature of the Ru–Ru interaction and for the effect of the Ru–Ru interaction on the properties of the ion. In the dimer $(bpy)_2ClRu^{II}(pyr)Ru^{III}Cl(bpy)_2^{3+}$ there are discrete Ru(II) and Ru(III) sites, and delocalization between them is slight.[6] Electronic orbital overlap between the Ru(II) and Ru(III) sites does occur promoted by $d\pi(Ru(II))$–π^*(pyrazine) mixing, but overlap is small and there are localized redox sites on the vibrational time scale. With enhanced overlap the sites can become vibrationally equivalent and the system delocalized. In oxo-bridged ions like $(bpy)_2ClRuORuCl(bpy)_2^{2+}$, it has been concluded that strong $d\pi(Ru)$–$p(O)$–$d\pi(Ru)$ mixing leads to delocalized molecular orbitals and that gain or loss of electrons to give the 1+ and 3+ mixed-valence ions occurs from these delocalized levels.[7,8] Extensive $d\pi(Ru)$–$p(Cl)$–$d\pi(Ru)$ mixing could lead to the same type of case in $(bpy)_2RuCl_2Ru(bpy)_2^{3+}$. Oxidation of $[(bpy)_2RuCl]_2^{2+}$ could also occur by loss of an electron from an orbital largely antibonding Ru–Ru in character to give a partial metal–metal bond. This is apparently the situation which does occur both in $(PBu^n{}_3)_2ClRuCl_3RuCl(PBu^n{}_3)_2$[9] and in the electronically analogous iron dimer $(\pi\text{-}C_5H_5)(CO)Fe(SMe)_2Fe(CO)(\pi\text{-}C_5H_5)^+$.[10] There is a further interesting example in the tri-μ-chloro-bridged "Ru blue" ions like $[(NH_3)_3RuCl_3Ru(NH_3)_3]^{2+}$ where the Ru–Ru interaction is striking in its effect upon the electronic spectra of the ions,[11] but the orbital nature of the Ru–Ru interaction in unclear in the absence of supporting structural data.

There are many examples of chloro-bridged ruthenium compounds including the cluster $Ru_5Cl_{12}^{2-}$,[12] dimers involving triply bridging chlorides as in the dimers above or in $(PPhEt_2)_3RuCl_3Ru(PPhEt_2)_3^+$,[13] and dimers involving doubly bridging chlorides as in $[(CO)_3RuCl_2]_2$,[14] $[(\pi\text{-}C_6H_6)RuCl_2]_2$,[15] $[(bpy)(PPh_3)_2RuCl]_2^{2+}$,[16] $[(CHT)RuCl_2]_2$[17] (CHT = cycloheptatriene), or $(CS_2)(PPh_3)_2RuCl_2$.[18] There are also reports of a dimer having a single chloride bridge, $[(NH_3)_3(H_2O)RuCl_2]_2^+$,[19] and of three chloride-bridged polymers, $[(norb)RuCl_2]_x$[20] (norb = norbornadiene), $[(CO)_2RuCl_2]_x$,[17] and $[(COD)RuCl_2]_x$ (COD = cycloocta-1,5-diene).[17,21]

Experimental Section

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer in potassium bromide pellets at room temperature. Ultraviolet–visible spectra were recorded on Cary Model 14, Cary Model 17, Unicam Model SP800B, or Bausch and Lomb Spectronic 210 UV spectrophotometers in 1- and 10-mm cells at room temperature. ESCA measurements were obtained on a du Pont Instruments 650 electron spectrometer equipped with a du Pont Instruments multichannel analyzer. Samples were prepared by grinding the solid complex into the surface of a gold sample probe using a clean glass rod. Electrochemical studies were conducted vs. the saturated sodium chloride calomel electrodes (SSCE) using 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. The measurements were recorded using a Princeton Applied Research Model 173 potentiostat/galvanostat with a Model 176 electrometer probe and standard three-electrode operational amplifier circuitry. A Princeton Applied Research Model 175 universal programmer was employed as a signal generator for voltammetric and chronoamperometric measurements.

Materials. Acetonitrile (MCB, Spectrograde) was used without further purification for all spectroscopic studies. Water was deionized and redistilled from alkaline $KMnO_4$ using an all-glass apparatus. All other solvents (reagent grade) were purchased commercially and used without further purification. Potassium azide was obtained commercially and recrystallized from water and ethanol–water before use. All other chemicals were used as received. The complexes *cis*-Ru(bpy)$_2$Cl$_2$[22] and [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$[23] were prepared according to previously described methods. Analyses were performed either by Galbraith Laboratories, Inc., Knoxville, Tenn., or by Integral Microanalytical Laboratories, Inc., Raleigh, N.C.

Preparations. Ru(bpy)$_2$(CO$_3$). The solid (bpy)$_2$RuCl$_2$·2H$_2$O (2.0 g, 3.85×10^{-3} mol) was suspended in 150 mL of deaerated water and heated at reflux under argon for 15 min. Sodium carbonate (6.6 g, 6.3×10^{-2} mol) was added and the solution was heated at reflux for 2 h. The burgundy red solution was filtered, yielding purple, needle-shaped crystals which were washed three times with water and air-dried; yield 1.52 g, 67%. Anal. Calcd for [(bpy)$_2$Ru(CO$_3$)]·2H$_2$O: C, 49.5; H, 3.9; N, 11.0. Found: C, 49.8; H, 4.1; N, 11.2.

[Ru(bpy)$_2$Cl]$_2$(PF$_6$)$_2$ from [Ru(bpy)$_2$(NO)Cl](PF$_6$)$_2$. The chloro-bridged dimer was first prepared by Adeyemi,[24] but subsequent refinement of the preparation has resulted in increased yields. In the preparation, 0.483 g (6.3×10^{-4} mol) of [(bpy)$_2$Ru(NO)Cl](PF$_6$)$_2$ was dissolved in 20 mL of deaerated acetone, and 0.51 g (6.32×10^{-4} mol) of KN$_3$ in 10 mL of deaerated methanol was added dropwise with stirring. The resulting solution was filtered to remove KPF$_6$ and then stirred for 4 h under nitrogen, in the dark. The red-brown solution was cooled and filtered leaving a red precipitate which was sparingly soluble in acetone, methanol, and dichloromethane. The solid was washed twice with acetone and dried under vacuum; yield 0.306 g (82%). Anal. Calcd for [(bpy)$_2$RuCl$_2$Ru(bpy)$_2$](PF$_6$)$_2$: C, 39.2; H, 2.9; N, 9.2. Found: C, 39.3; H, 2.6; N, 9.6.

[Ru(bpy)$_2$Cl]$_2$(PF$_6$)$_2$ from Ru(bpy)$_2$Cl$_2$ and Ru(bpy)$_2$(CO$_3$). To deaerated ethanol (35 mL) was added 1.030 g of Ru(bpy)$_2$(CO$_3$)·2H$_2$O followed by 1.0 mL of HPF$_6$ (48% in water). The solution was stirred magnetically for 30 min under nitrogen. After this time 1.040 g of *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O was added. The resulting mixture was heated at reflux while maintaining magnetic stirring for 24 h. The resulting deep red-violet solution was chilled overnight in a freezer (~0 °C). Filtration gave a dark red solid. The solid was washed with ethanol (three times, 20 mL) followed by CH$_2$Cl$_2$ (three times, 10 mL) and finally copiously with ether. After being dried at reduced pressure, 1.38 g (72%) of the complex was obtained.

Electrochemical Oxidation of [(bpy)$_2$RuCl]$_2$$^{2+}$. To a standard two-frit, three-compartment electrochemical cell 25 mg of the dimer was added. Either CH$_2$Cl$_2$ or propylene carbonate that was 0.2 M in TBAH was then added to give a convenient solvent level. Oxidation was performed at 1.1 V (vs. SSCE) using a Pt-gauze working electrode and a Pt-wire auxiliary electrode until the current decayed to 5% of its initial value. Addition of CH$_3$CN or of 2,2′-bipyridine to the oxidized solution produced a color change. Cyclic voltammetry and electronic spectra on the resultant solutions (after 5 min) showed the presence of approximately equal amounts of (bpy)$_2$RuCl$_2$$^+$ and either (bpy)$_2$Ru(CH$_3$CN)$_2$$^{2+}$ or Ru(bpy)$_3$$^{2+}$ (see Results and Discussion).

Results and Discussion

Chemical Properties of [(bpy)$_2$RuCl]$_2$$^{2+}$. The convenient methods used in the preparation of the dimer are shown in eq 1 and 2 and eq 3 and 4. Both of the synthetic routes involve

$$\mathrm{(bpy)_2Ru(NO)Cl^{2+} + N_3^- + S \rightarrow (bpy)_2Ru(S)Cl^+ + N_2 + N_2O} \qquad (1)$$

$$\mathrm{2(bpy)_2Ru(S)Cl^+ \rightarrow [(bpy)_2RuCl]_2^{2+} + 2S} \qquad (2)$$

(S is acetone)

$$\mathrm{(bpy)_2Ru(CO_3) + 2H^+ \rightarrow \mathit{cis}\text{-}(bpy)_2RuS_2^{2+} + CO_2 + H_2O} \qquad (3)$$

$$\mathrm{\mathit{cis}\text{-}(bpy)_2RuS_2^{2+} + \mathit{cis}\text{-}(bpy)_2RuCl_2 \xrightarrow{\Delta} [(bpy)_2RuCl]_2^{2+} + 2S} \qquad (4)$$

(S is ethanol)

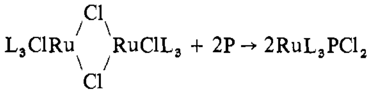
the generation of intermediates in which there are weakly bound, relatively easily displaced solvent molecules. Both of the solvento species (bpy)$_2$Ru(CH$_3$COCH$_3$)Cl$^+$[25] and (bpy)$_2$Ru(EtOH)$_2$$^{2+}$[26] can be detected spectrophotometrically in the early stages of reactions 1 and 2 or 3 and 4, respectively.

[(bpy)$_2$RuCl]$_2$$^{2+}$ can be formulated as a Ru(II) chloro-bridged dimer on the basis of the elemental analyses, the Ru 3d$_{5/2}$ binding energy of 279.8 eV observed by ESCA compared to 279.9 eV for *cis*-Ru(bpy)$_2$Cl$_2$, the appearance of two one-electron oxidations per dimer formula unit, and its reaction chemistry which is that expected for a chloro-bridged dimer. In the ESCA experiment, the C 1s peak was taken as an internal standard at 284.4 eV.

The dimer is slightly soluble in CH$_2$Cl$_2$, and there is no change in its electronic absorption spectrum with time. When the dimer is dissolved in CH$_3$CN, or when CH$_3$CN is added to a CH$_2$Cl$_2$ solution, a rapid color change from red-violet to orange-brown occurs. The color change corresponds to the disappearance of the dimer absorption at λ_{max} 495 nm accompanied by the appearance of λ_{max} 480 nm for (bpy)$_2$Ru(CH$_3$CN)Cl$^+$ (eq 5). The reaction is complete

$$\mathrm{[(bpy)_2RuCl]_2^{2+} + 2CH_3CN \rightarrow 2(bpy)_2Ru(CH_3CN)Cl^+} \qquad (5)$$

within ca. 5 min at concentrations of complex of $\sim 5 \times 10^{-3}$ M in pure CH$_3$CN. On a preparative scale, the CH$_3$CN complex was isolated quantitatively and identified by its characteristic cyclic voltammogram, $E_{1/2}$ = 0.84 for the (bpy)$_2$Ru(CH$_3$CN)Cl$^{2+/+}$ Ru(III) → Ru(II) couple, and its electronic absorption spectrum. Facile bridge cleavage reactions have been observed in other di-μ-chloro dimers of Ru(II) (eq 6), and [(bpy)$_2$RuCl]$_2$$^{2+}$ promises to be an equally valuable synthetic intermediate. We have recently exploited the symmetrical cleavage reaction to prepare ligand-bridged dimeric complexes, e.g., eq 7.



$$\mathrm{L_3ClRu(\mu\text{-}Cl)_2RuClL_3 + 2P \rightarrow 2RuL_3PCl_2} \qquad (6)$$

(L$_3$ = π-C$_6$H$_6$,[15] cycloheptatriene;[17]
P = trialkyl- or triarylphosphine)

$$\mathrm{[(bpy)_2RuCl]_2^{2+} + Ph_2PC{\equiv}CPPh_2 \rightarrow (bpy)_2ClRu(Ph_2PC{\equiv}CPPh_2)RuCl(bpy)_2^{2+}}\,[27] \qquad (7)$$

Electronic Spectral Properties. Ru^{II}–bpy complexes characteristically have low-energy absorption bands in the visible region assignable to π*(bpy) ← dπ(Ru) CT transitions.[28] In the cis complexes B$_2$RuX$_2$ the π*(bpy) ← dπ CT band energies are sensitive to the nature of X. Changes in X result in systematic changes in CT band energies which make the bpy groups useful "spectator" ligands for the electronic interaction between Ru and X.[29,30]

The spectrum of B$_2$RuCl$_2$RuB$_2$$^{2+}$ in dichloromethane above the solvent cutoff has two broad absorption bands at λ_{max} 494 nm (ϵ 16 400) and λ_{max} 300 nm (ϵ 14 400). Spectra for the dimer and for related complexes of Ru(II) are summarized in Table I. The data show clearly the effects on the CT band energies of changes in ligands at the cis positions. Compared to ethylenediamine as the ligand in Ru(bpy)$_2$(en)$^{2+}$ where π effects are unimportant, ligands like bpy or the phosphine *cis*-Ph$_2$PCH=CHPPh$_2$ remove dπ electron density from Ru giving a greater π*(bpy)–dπ(Ru) energy separation and a higher CT λ_{max}. As a π-donor ligand, the effect of chloride ion is opposite, as shown schematically in the qualitative energy level diagram in Figure 1. An energy level diagram for the dimer is also shown in Figure 1. In the dimer, mixing can occur between Cl 3p and Ru 4d orbitals of π-type symmetry which lie along the Ru–Cl bonds (d$_{xz}$ and d$_{yz}$ in Figure 1). A direct metal–metal bond could also occur by mixing of the in-plane orbitals (d$_{xy}$) which would give rise to two molecular orbitals labeled σ_b and σ* in Figure 1. In the dimer, the lowest energy CT transition (494 nm) is only slightly red-shifted when compared to those of Ru(bpy)$_2$(en)$^{2+}$ (485 nm) which suggests that the extent of interaction between dπ levels either by Ru–Cl–Ru or by direct Ru–Ru overlap must be small.

Redox Chemistry. Figure 2A shows a cyclic voltammogram of [Ru(bpy)$_2$Cl]$_2$$^{2+}$ in CH$_2$Cl$_2$ solution with 0.1 M [N(n-C$_4$H$_9$)$_4$](PF$_6$) as supporting electrolyte at 22 ± 2 °C. Two reversible waves are observed at $E_{1/2}(1)$ = +0.91 V and $E_{1/2}(2)$

Table I. Electrochemical and Spectral Data for Selected Bis(2,2′-bipyridyl)ruthenium Complexes

	λ_{CT},[a] nm	$E_{1/2}$,[b] V vs. SSCE	Ref
$[Ru(bpy)_2\{cis\text{-}(C_6H_5)_2PCH{=}CHP\text{-}(C_6H_5)_2\}](PF_6)_2$	371	+1.75	*c*
$[Ru(bpy)_3](PF_6)_2$	450	+1.29	*d*
$[Ru(bpy)_2(NH_2CH_2CH_2NH_2)](PF_6)_2$	485	+0.96	*e*
$[Ru(bpy)_2Cl]_2(PF_6)_2$	495	+0.91, +1.46	
$Ru(bpy)_2Cl_2$	550	+0.30	*d*

[a] λ_{max} for the lowest intense CT($\pi^* \leftarrow d\pi(Ru)$) absorption band. Measured in CH_3CN solution, except for $[Ru(bpy)_2Cl]_2(PF_6)$ which was measured in CH_2Cl_2 solution. [b] Measured in 0.1 M $N(n\text{-}C_4H_9)_4(PF_6)$–$CH_3CN$ at 22 ± 2 °C vs. the saturated sodium chloride calomel electrode (SSCE). The $E_{1/2}$ values as measured by cyclic voltammetry are essentially formal reduction potentials for the appropriate Ru(III)-Ru(II) couple. The data for $Ru(bpy)_2Cl_2$ and $[Ru(bpy)_2Cl]_2(PF_6)_2$ were obtained under the same conditions but in CH_2Cl_2. [c] B. P. Sullivan, D. J. Salmon, and T. J. Meyer, submitted for publication. [d] D. J. Salmon, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, N.C., 1977. [e] G. M. Brown, T. R. Weaver, F. R. Keene, and T. J. Meyer, *Inorg. Chem.*, 15, 190 (1976).

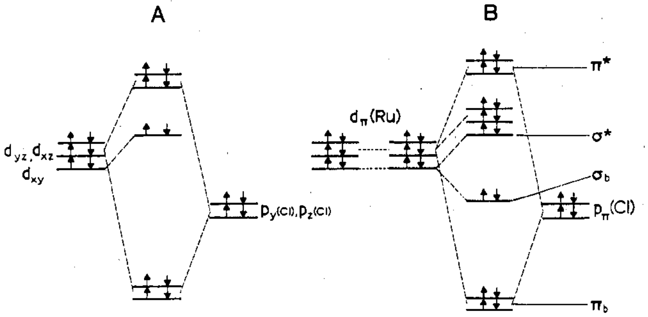


Figure 1. Schematic molecular orbital diagram for the metal–Cl π system in (A) $(bpy)_2RuCl_2$ and (B) $[(bpy)_2RuCl_2(bpy)_2](PF_6)_2$.

= +1.46 V. The $E_{1/2}$ values were calculated from the average of the anodic and cathodic peak potentials ($(E_{p,a} + E_{p,c})/2$). The redox processes appear to be electrochemically reversible.[31]

The appearance of two oxidation waves shows that the dimer can be oxidized in two successive stages, first to a mixed-valence 3+ ion $[(bpy)_2RuCl]_2^{3+}$ and then to a 4+ ion. Both oxidation products are stable in the medium on the cyclic-voltammetry time scale. The measured redox potentials refer to the reversible processes in reactions 8 and 9. Attempted two-electron oxidations of $[(bpy)_2RuCl]_2^{2+}$ in CH_2Cl_2 at potentials more positive than $E_{1/2}(2)$ were unsuccessful because of severe electrode fouling. Oxidation past $E_{1/2}(1)$ in either CH_2Cl_2 or propylene carbonate occurred with $n = 1.0$ as shown by coulometry. However, in neither case was it possible to observe the one-electron oxidized dimer. In both solvents, oxidation is followed by decomposition to give $Ru^{III}(bpy)_2Cl_2^+$ (as shown by cyclic voltammetry, $E_{1/2} = 0.29$ V in CH_2Cl_2 and 0.27 V in propylene carbonate, and by its characteristic electronic absorption spectrum). The second product is presumably a disolvento complex, $(bpy)_2RuS_2^{2+}$ (eq 10 and 11).

$$[(bpy)_2RuCl]_2^{4+} + e^- \rightarrow [(bpy)_2RuCl]_2^{3+} \qquad E_{1/2}(2) \tag{8}$$

$$[(bpy)_2RuCl]_2^{3+} + e^- \rightarrow [(bpy)_2RuCl]_2^{2+} \qquad E_{1/2}(1) \tag{9}$$

$$[(bpy)_2RuCl]_2^{2+} \xrightarrow{-e^-} [(bpy)_2RuCl]_2^{3+} \tag{10}$$

$$[(bpy)_2RuCl]_2^{3+} + 2S \rightarrow (bpy)_2Ru^{III}Cl_2^+ + (bpy)_2Ru^{II}S_2^{2+} \tag{11}$$

(S is CH_2Cl_2 or propylene carbonate)

Figure 2B shows the cyclic voltammogram of the dimer after exhaustive electrolysis at 1.1 V in CH_2Cl_2 followed by addition of CH_3CN to the cell. Three waves having approximately equal peak currents are found to occur at 0.32, 1.44, and 1.97 V. The $E_{1/2}$ values are exactly those for the $Ru(bpy)_2Cl_2^{+/0}$, $Ru(bpy)_2(CH_3CN)_2^{3+/2+}$, and $Ru(bpy)_2Cl_2^{2+/+}$ couples, respectively. ESCA analysis of the solid from the reaction mixture gave two Ru peaks (Ru($3d_{5/2}$) binding energies) of equal intensity at 281.5 and 279.9 eV (vs. C 1s at 285.0 eV). The peaks coincide exactly with those of samples of $[Ru(bpy)_2Cl_2](PF_6)$ and $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$ obtained independently. The elemental analysis of the reaction product was correct for a 1:1 mixture of $[Ru(bpy)_2Cl_2](PF_6)$ and $[Ru(bpy)_2(CH_3CN)_2](PF_6)_2$. In a similar experiment, one-electron oxidation in propylene carbonate solution followed by addition of excess bpy resulted in the formation of $Ru(bpy)_2Cl_2^+$ and $Ru(bpy)_3^{2+}$ (as shown by the electronic absorption spectrum and by cyclic voltammetry). The two complexes were formed in approximately equal amounts as shown by the similarity in peak currents for the voltammetric waves for the two couples.

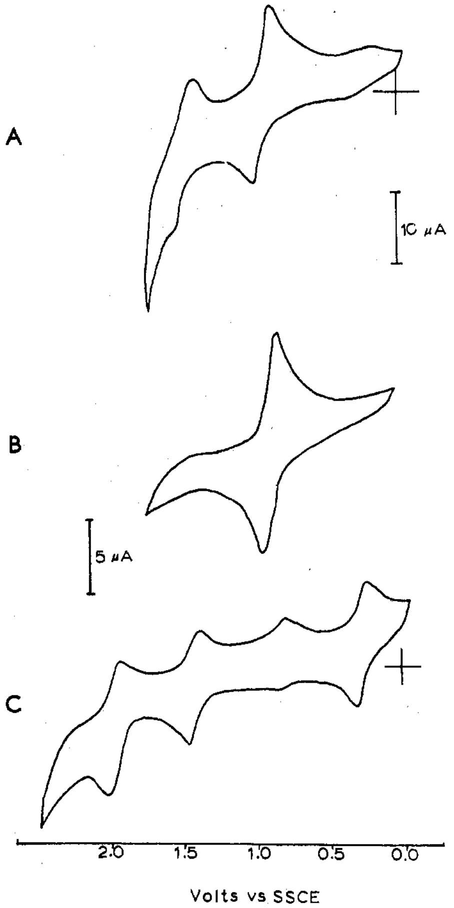


Figure 2. Cyclic voltammetry of $[(bpy)_2RuCl_2Ru(bpy)_2](PF_6)_2$ at a scan rate of 500 mV/s with 0.1 M $N(n\text{-}C_4H_9)_4(PF_6)$ as supporting electrolyte: (A) cyclic voltammogram in CH_2Cl_2 solution; (B) cyclic voltammogram after addition of CH_3CN; (C) cyclic voltammogram after controlled-potential electrolysis at +1.15 V followed by addition of CH_3CN.

All of the above results are consistent with eq 10 and 11 followed by reaction of "$Ru(bpy)_2S_2^{2+}$" with added ligand (CH_3CN or bpy). There is no clear-cut evidence for the nature of the assumed disolvento product, but it is important to note that similar, highly reactive intermediates can be prepared from *cis*-$Ru(bpy)_2Cl_2$ and Ag^+ or by the reaction of $(bpy)_2Ru(CO_3)$ with H^+ in the appropriate solvent.[26]

Properties of the Intermediate Mixed-Valence Ion. Because of its decomposition on a time scale slightly longer than the cyclic-voltammetry time scale, we have been unable to obtain direct spectral information concerning the transient mixed-valence ion $[(bpy)_2RuCl]_2^{3+}$. However, given the electrochemical data, the chemistry involved in the decomposition, and the properties of the 2+ ion, it is possible to draw some reasonable conclusions regarding the electronic structure of the ion.

According to the qualitative molecular orbital diagram in Figure 1B, oxidation of $[(bpy)_2RuCl]_2^{2+}$ to the 3+ ion will occur by loss of an electron from a slightly destabilized π^* orbital which is largely Ru in character. The extent of Ru–Cl–Ru (or Ru–Ru) interaction leading to the destabilization is relatively small as shown by λ_{max} and $E_{1/2}(1)$ values for the 2+ ion when compared to $Ru(bpy)_2(en)^{2+}$ (Table I). For purposes of comparison, in the oxo-bridged dimer $(bpy)_2ClRuORuCl(bpy)_2^{2+}$ there is a strong Ru–O–Ru interaction. The highest levels are appreciably antibonding and largely d in character which is also the case for the chloro-bridged ion in Figure 2. Since the μ-oxo dimer is formally a Ru(III)–Ru(III) case, its orbital scheme is somewhat like that in Figure 1B except that two electrons are removed from the π^* levels. The importance of the strong Ru–O–Ru interaction shows up clearly in comparative redox potential measurements. Potentials for the couples $(bpy)_2ClRuORuCl(bpy)_2^{2+/+}$ and $(bpy)_2ClRuORuCl(bpy)_2^{+/0}$ are at −0.32 V and $E_{p,c} = -1.0$ V in CH_3CN vs. the SSCE. The much more negative potentials for reduction of the oxo-bridged ion are consistent with electrons entering orbitals which are significantly antibonding when compared with the chloro-bridged case. This is also suggested by the instabilities of the reduced 1+ and neutral oxo-bridged dimers and by the fact that the oxo-bridged dimer can be oxidized to the stable 3+ ion $(bpy)_2ClRuORuL(bpy)_2^{3+}$ which is formally a Ru(III)–Ru(IV) mixed-valence case. The differences in redox behavior between the two systems are striking and suggest that they represent entirely different cases.

If the ordering of orbitals for $[(bpy)_2RuCl]_2^{2+}$ is as shown in Figure 1B, oxidation to the 3+ ion leads to a degeneracy in the π^* orbitals. For a weak Ru–Cl–Ru interaction, the degeneracy can be lifted by an unsymmetrical distortion involving shortening and lengthening of the Ru–Cl–Ru bonds to give essentially a localized valence case, $(bpy)_2Ru^{II}Cl_2Ru^{III}(bpy)_2^{3+}$ in which the coordination spheres around the Ru^{II} and Ru^{III} sites are inequivalent on the infrared time scale. In the absence of significant Ru–Cl–Ru overlap, the distorted structure must be favored energetically. The situation is the same as for any mixed-valence case and is conceptually related to the problem of Jahn–Teller distortions.[34] In the absence of an appreciable electronic resonance energy, a localized Ru–Ru vibrational structure will always be favored just as it would be for isolated Ru(II) and Ru(III) complexes.

The localized valence model suggested here is also appealing in that it explains the decomposition chemistry. $Ru(bpy)_2Cl_2$ is known to be somewhat labile in solution. Over a period of hours it undergoes a thermal reaction with acetonitrile to give $Ru(bpy)_2(CH_3CN)Cl^+$. In acetonitrile, $Ru(bpy)_2Cl_2^+$ is inert and stable indefinitely.[33] If the mixed-valence ion $B_2Ru^{III}Cl_2Ru^{II}B_2^{3+}$ is unsymmetrical, the greater affinity of Ru(III) for the bridging Cl^- groups would ensure an unsymmetrical bridge splitting reaction and explain the appearance of the decomposition products $Ru(bpy)_2Cl_2^+$ and $Ru(bpy)_2S_2^{2+}$.

In the pyrazine-bridged dimers $(bpy)_2ClRu(pyr)ClRu(bpy)_2^{2+}$ and $(NH_3)_5Ru(pyr)Ru(NH_3)_5^{4+}$, the splittings between voltammetric waves analogous to $E_{1/2}(1)$ and $E_{1/2}(2)$ (eq 8 and 9) can be attributed in part to statistical and electrostatic effects.[6] It has been argued that the large splitting observed for the pentaammine dimer may also reflect an enhanced delocalization from Ru(II) to Ru(III).[6] The peak splitting $E_{1/2}(2) - E_{1/2}(1)$, for the chloro-bridged dimer is quite large, 0.55 V, but can be explained as a combination of the electrostatic effect and an electronic substituent effect rather than by extensive Ru(II) → Ru(III) delocalization.

Potentials for the $Ru(bpy)_2Cl_2^{+/0}$ couple (0.30 V) and for the dimer couples $[B_2RuCl]_2^{3+/2+}$ (0.91 V) and $[B_2RuCl]_2^{4+/3+}$ (1.46 V) increase steadily as the cis ligands on Ru(II) are varied from $RuCl_2$ to $RuCl_2Ru^{II}B_2$ to $RuCl_2Ru^{III}B_2$. The potentials increase as the p electron density on the chloride groups decreases. The trend indicates, for example, that the "chelate ligand" $Cl_2Ru^{III}B_2$ is a net electron acceptor relative to two Cl groups. This is expected given the π-acceptor properties of Ru(III). Given the higher one-electron reduction potential for $(bpy)_2Ru^{III}Cl_2Ru^{III}(bpy)_2^{4+}$ when compared to that of $(bpy)_2Ru(bpy)^{3+}$ (1.29 V), it is apparent that the $Cl_2Ru^{III}B_2$ group is more effective at withdrawing electron density from ruthenium(II) than is bpy.

The lack of a strong Ru–Cl–Ru or Ru–Ru interaction in either $[(bpy)_2RuCl]_2^{2+}$ or its mixed-valence ion is apparently a consequence of $d\pi(Ru) \rightarrow \pi^*(bpy)$ back-bonding. Mixing of the π^* orbitals on the bpy ligands with $d\pi(Ru)$ orbitals withdraws electron density from the metal. The loss of electron density causes a contraction in the radial extension of the $d\pi(Ru)$ orbitals resulting in poor overlap with the p(Cl) orbitals. The same argument explains the apparent absence of a significant, direct metal–metal bond via d_{xy}–d_{xy} overlap.

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Registry No. $[Ru(bpy)_2Cl]_2(PF_6)_2$, 66416-92-0; $[(bpy)_2RuCl]_2^{3+}$, 66454-94-2; $[(bpy)_2RuCl]_2^{4+}$, 66416-90-8; $Ru(bpy)_2(CO_3)$, 59460-48-9; *cis*-$Ru(bpy)_2Cl_2$, 19542-80-4; $[(bpy)_2Ru(NO)Cl](PF_6)_2$, 29102-12-3.

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Further Studies on the Role of Adduct Formation in the Extraction of Nickel with 8-Quinolinols in the Presence of Pyridine and Its Analogues

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Pyridine and its methyl analogues (2-methyl, 2,4-dimethyl, 2,4,6-trimethyl) were found to enhance the extraction of nickel into chloroform with 8-quinolinol and its 2-methyl, 4-methyl, 5-chloro, and 5-nitro analogues. From a quantitative evaluation of extraction equilibrium data, the adduct formation constants of what proved to be 1:2 chelate–nitrogen base adducts are determined. The results are consistent with Lewis acid–base concepts. The special role of steric factors is discussed.

Introduction

Much work has been done in the formation equilibria of simple metal chelates, and the role of such factors as ligand basicity, metal ion (Lewis) acidity, and steric factors have been reasonably well described. Relatively little is known, however, about the factors affecting the reaction of neutral, coordinatively unsaturated chelates with adducting ligands, which may be either the chelating agent itself or another base such as pyridine, TBP, etc., viz.

$$M^{n+} + (n + a)HL \rightleftarrows ML_n \cdot aHL + nH^+$$

$$M^{n+} + nHL + aB \rightleftarrows ML_n \cdot aB + nH^+$$

Adduct formation is of great importance in the solvent extraction of many metal ions.

In earlier studies with 8-quinolinolatonickel (NiQ_2), an adduct $NiQ_2 \cdot HQ$ was found in which the neutral 8-quinolinol acted as a monodentate ligand involving its nitrogen atom.[1,2] Although the 4-methyl-8-quinolinol behaved similarly, the 2-methyl analogue did not form an adduct but only a simple 1:2 chelate with nickel. This behavior, analogous to that observed with zinc and 8-quinolinols,[3,4] is indicative of the adverse effect of the steric influence of the 2-methyl substituent on adduct, as well as simple chelate, formation.

This communication represents an extension of our work to the examination of electronic as well as steric influences on adduct formation with nickel chelates of 8-quinolinols and various pyridines.

Experimental Section

Apparatus. A Kahn-type shaking machine in which 10-mL centrifuge tubes with stoppers could be accommodated was used to equilibrate the solutions at ambient temperature.

Radioactivity was counted on a NaI (Tl) detector connected to a scintillation spectrometer, supplied by ECIL (India).

AR grade 8-quinolinol (Merck), 2-methyl-8-quinolinol (Fluka), 5-chloro-8-quinolinol (Aldrich), and 5-nitro-8-quinolinol (K & K) were recrystallized from absolute alcohol. 4-Methyl-8-quinolinol was synthesized from *o*-aminophenol and methyl vinyl ketone as described earlier. The crude product was purified by vacuum distillation followed by two recrystallizations from absolute alcohol. The melting point of the purified product was 140–142 °C (lit. mp 141 °C). Pyridine, 2,4,6-collidine (trimethylpyridine) (BDH AnalaR), and 2-picoline (2-methylpyridine) and 2,4-lutidine (2,4-dimethylpyridine) (Fluka AG) were purified by distillation after drying over potassium hydroxide.

Nickel-65 ($t_{1/2}$ = 2.56 h) was obtained by irradiating ~0.1 mg of enriched nickel-64 in a pneumatic rabbit facility at CIRUS, Trombay. The irradiated target was dissolved in hydrochloric acid. The final strength of the nickel tracer solution used was $\leq 10^{-6}$ M.

A potassium hydrogen phthalate–sodium hydroxide buffer solution at pH 5 was prepared and the ionic strength was maintained constant at 0.25 by sodium perchlorate.

Five milliliters of a buffered ^{65}Ni solution at 0.25 ionic strength and 5 mL of the reagent solutions in chloroform (8-quinolinol + varying amounts of heterocyclic base) were equilibrated by shaking for 30 min. The mixtures were then centrifuged, and equal volumes of both phases were pipetted out and counted at constant geometry.

Results and Discussion

As has been previously shown,[4] the stoichiometry (a) and equilibrium constant (K_{AD}) of adduct formation in the organic phase

$$ML_n(o) + aB(o) \xrightleftharpoons{K_{AD}} ML_n \cdot aB(o)$$

can be obtained from a log–log plot of the distribution ratio of the metal ion, D, vs. the concentration of the adducting ligand, B, under extraction conditions of constant pH and organic-phase chelating agent concentration. Such a plot will consist primarily of two linear portions: the first at zero slope, reflecting the extraction of the simple chelate at very low $[B]_0$

$$\log D = \log K_{ex} + n \log [HQ]_0 + n\text{pH} \qquad \text{(a)}$$

and the second at high $[B]_0$, where the adduct extraction predominates

$$\log D = \log K_{ex} + n \log [HQ]_0 + n \log K_{AD} + a \log [B]_0 \qquad \text{(b)}$$

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