

applied to transition-metal systems. We are presently investigating a variety of systems for which photogenerated transition-metal intermediates are hypothesized but not well characterized.

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Intervallence Transfer in Cyano-Bridged Bi- and Trinuclear Ruthenium Complexes

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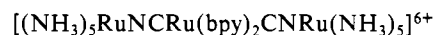
Contribution from the Istituto Chimico dell'Università, Centro di Fotochimica CNR, 44100 Ferrara, Italy, and Istituto Chimico "G. Ciamician" dell'Università, Centro di Studio di Elettrochimica Teorica e Preparativa, 40100 Bologna, Italy. Received July 2, 1984

Abstract: The binuclear and trinuclear [(NH₃)₅RuNCRu(bpy)₂CN]³⁺ [3,2] and [(NH₃)₅RuNCRu(bpy)₂CNRu(NH₃)₅]⁶⁺ [3,2,3] complexes were synthesized. The reduction at the pentaammineruthenium sites was studied chemically and electrochemically, and the visible and near-IR spectra of the [3,2] and [3,2,3] species and of their reduced forms [2,2], [3,2,2], and [2,2,2] were investigated. Several types of electronic transitions between the various low-energy redox sites of the ions were observed, including (i) Ru(II) → bpy charge transfer originating in the ruthenium atom of the Ru(bpy)₂ moiety, (ii) Ru(II) → bpy charge transfer originating in the ruthenium atoms of the pentaammine moieties, (iii) Ru(II) → Ru(III) intervalence transfer (IT) between cyano-bridged adjacent ruthenium atoms, and (iv) Ru(II) → Ru(III) IT between remote ruthenium atoms of the pentaammine units. All these transitions are present in the spectrum of the [3,2,2] ion. The various species were checked for emission or long-lived ($\tau > 50$ ns) transient absorption in laser flash photolysis. The results were negative, indicating that radiationless intramolecular electron-transfer processes are very efficient in these molecules.

In the last decade, particularly due to the work of Taube,² Meyer,³ and their associates,⁴ the chemistry and mixed-valence behavior of binuclear ruthenium complexes have been deeply and elegantly probed. When mainly Ru(NH₃)₅ⁿ⁺ ($n = 2, 3$) and Ru(bpy)₂²⁺ as building units and a variety of bridging ligands (especially diaza aromatics but also disulfides and dinitriles) were used, a large number of binuclear ruthenium complexes were synthesized and studied by these authors.⁴ Depending mainly on the type of bridging ligand, a wide range of degrees of delocalization was encountered in these complexes, going from limiting class III to class II Robin and Day⁵ behavior. In a few instances, the same authors have studied in detail^{6,7} or mentioned⁸ analogous trinuclear ruthenium species. These species are expected, and to some extent found,⁷ to exhibit a particularly rich mixed-valence behavior.

Previous work from this⁹⁻¹¹ and other^{12,13} laboratories has shown that *cis*-dicyanobis(2,2'-bipyridine)ruthenium(II), Ru(bpy)₂(CN)₂, can behave as a nitrile ligand toward a variety of aquo metal ions and metal complex moieties. We thought it worthwhile to take

advantage of this possibility to synthesize the trinuclear complex ion μ -[dicyanobis(2,2'-bipyridine)ruthenium]bis(pentaammineruthenium)(6+),



This complex may be viewed as an analogue of Taube's binuclear dinitrile complexes,¹⁴⁻¹⁶ having Ru(bpy)₂(CN)₂ as the bridging "ligand", or as an analogue of Meyer's trimeric complexes,⁶ having cyano instead of diaza aromatic bridges.

In the course of the work, we have also isolated the corresponding binuclear species



which is a cyano-bridged analogue of Meyer's unsymmetrical dimeric complexes.^{17,18}

We report here on the synthesis, the intervalence transfer behavior, and the intramolecular electron-transfer properties of these ions and of their one- and two-electron reduced forms.

Experimental Section

Materials. *cis*-Dicyanobis(2,2'-bipyridine)ruthenium(II)¹⁹ and chloropentaammineruthenium(III) chloride²⁰ were prepared by literature procedures. Ammonium hexachlororuthenate(IV) (Fluka), hexaammineruthenium(III) chloride (Johnson Matthey), europium(III) chloride (Schuchardt), chromium(III) chloride hexahydrate (Carlo Erba), ammonium hexafluorophosphate (Merck), and hydrazine hydrate (BDH) were commercial products of reagent grade. Spectrograde or-

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ganic solvents (Merck Uvasol) and triply distilled water were used. Solutions of $\text{Eu}^{2+}_{(\text{aq})}$ and $\text{Cr}^{2+}_{(\text{aq})}$ were prepared by exhaustive reduction of solutions of the corresponding trichlorides with zinc amalgam (10^{-2} M HCl) under vacuum.

Preparation of μ -[cis-Dicyanobis(2,2'-bipyridine)ruthenium(II)]bis[pentaammineruthenium(III)] Hexafluorophosphate.²¹ $\text{Ru}(\text{bpy})_2(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ (0.1245 g, 2.48×10^{-4} mol) in 20 mL of methanol was added to 0.1453 g (4.96×10^{-4} mol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in 40 mL of aqueous HCl (pH 2) and treated with zinc amalgam for 3 h under argon atmosphere, yielding a suspension of a very fine brown precipitate. After removal of the amalgam, oxygen was vigorously bubbled for 30 min through the brown suspension, which turned almost immediately dark blue-green in color. After the methanol was removed under reduced pressure, the solution was filtered, with elimination of unreacted $\text{Ru}(\text{bpy})_2(\text{CN})_2$ as a yellow solid. The solution was then passed over a 50×3 cm column of Sephadex G15 and eluted with water. Three components were eluted from the column in the following order: (1) a deep blue fraction of the trinuclear complex (typical spectrum with maxima at 392 and 653 nm, in a 1.1:1 intensity ratio), (2) a green fraction of the corresponding binuclear complex (see below; typical spectrum with maxima at 405 and 685 nm, in a 1.9:1 intensity ratio), and (3) a yellow fraction containing the residual traces of unreacted $\text{Ru}(\text{bpy})_2(\text{CN})_2$. By spectrophotometrically monitoring the elution process, a convenient volume of the head blue fraction was collected (ca. 20 mL). The solid hexafluorophosphate salt was precipitated from this solution by addition of 20 mL of a saturated aqueous solution of NH_4PF_6 . The solid was redissolved in water, reprecipitated with NH_4PF_6 , filtered, washed with small amounts of water, ethanol, and ether, and air-dried.

Anal. Calcd for $[\text{Ru}(\text{bpy})_2(\text{CN})_2][\text{Ru}(\text{NH}_3)_5]_2(\text{PF}_6)_6$: Ru, 17.76; C, 15.48; H, 2.69; N, 13.12; P, 10.88; F, 40.06. Found: Ru, 17.95; C, 15.58; H, 2.72; N, 12.94; P, 10.96; F, 39.90.

Preparation of Pentaammineruthenium(II)-cis-dicyanobis(2,2'-bipyridine)ruthenium(III) Hexafluorophosphate.²¹ $\text{Ru}(\text{bpy})_2(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ (0.5020 g, 1.0×10^{-3} mol) in 100 mL of methanol was added to 0.1465 g (5.0×10^{-4} mol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in 40 mL of aqueous HCl (pH 2) and treated with zinc amalgam under argon for 2 h, yielding a brown suspension. After removal of the amalgam, oxygen was vigorously bubbled for 30 min through the suspension, which turned almost immediately green in color. The volume was brought to 10 mL by evaporation at 60 °C under reduced pressure, and the unreacted solid $\text{Ru}(\text{bpy})_2(\text{CN})_2$ was removed by filtration. The complex was precipitated from the solution by addition of 20 mL of a saturated solution of $(\text{NH}_4)\text{PF}_6$. The green solid was redissolved in the minimum amount of water, passed over a 50×3 cm column of Sephadex G15, and eluted with water. In this step, small head (blue) and tail (yellow) fractions of $[\text{Ru}(\text{bpy})_2(\text{CN})_2][\text{Ru}(\text{NH}_3)_5]_2^{6+}$ and $\text{Ru}(\text{bpy})_2(\text{CN})_2$, respectively, were discarded. The central green fraction was collected and evaporated to dryness under reduced pressure.

Anal. Calcd for $[\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Ru}(\text{NH}_3)_5](\text{PF}_6)_3$: Ru, 18.61; C, 24.32; H, 2.85; N, 14.18; P, 8.55; F, 31.48. Found: Ru, 19.45; C, 23.35; H, 2.76; N, 13.54; P, 8.17; F, 30.46.

Apparatus. Absorption spectra in the vis/near-IR region were taken with a Hitachi-Perkin-Elmer 323 spectrophotometer.

Polarographic, cyclic voltammetric (CV), and controlled potential coulometric (CPC) experiments were carried out with an AMEL (Milan) Mod. 552 potentiostat, driven by an AMEL Mod. 556 function generator. Current-potential curves were recorded on an AMEL Mod. 865 x-y recorder or on a Nicolet Mod. 3091 digital oscilloscope. The minimization of the effect of uncompensated resistance in CV experiments was achieved with a positive feedback network of the potentiostat. The charge exchanged in CPC experiments was determined with an AMEL Mod. 721 integrator. A conventional three-electrode cell was used in all experiments. A saturated calomel electrode (SCE), separated from the test solution by a 0.1 M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ solution sandwiched between two fritted disks, was used as the reference electrode, and all potentials are referred to it. A dropping mercury electrode and a platinum electrode with periodical renewal of the diffusion layer²² were used as working electrodes in the polarographic measurements. The hanging mercury drop electrode and stationary platinum electrode were used in CV. All measurements were performed at 25 ± 0.1 °C, using 0.1 M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ as the supporting electrolyte.

Checks for emission were performed with a Hitachi-Perkin-Elmer MPF 44E spectrofluorimeter. Attempts to detect transient absorptions

were carried out by using a 30-ns laser flash photolysis apparatus (J & K 2000 Q-switched, frequency-doubled ruby laser, Applied Photophysics detection system).

Results

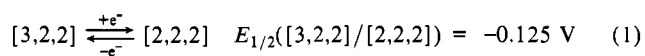
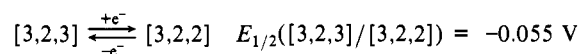
All the experiments which follow suggest a localized-valence description of the complexes. In this description, both the $[(\text{NH}_3)_5\text{RuNCRu}(\text{bpy})_2\text{CNRu}(\text{NH}_3)_5]^{6+}$ and the $[(\text{NH}_3)_5\text{RuNCRu}(\text{bpy})_2\text{CN}]^{3+}$ ions no doubt have the ruthenium atoms of the pentaammine moieties in the +3 oxidation state and that of the bis(2,2'-bipyridine) moiety in the +2 state. Thus, these two complex ions are thereafter referred to as [3,2,3] and [3,2], respectively.

Chemical Behavior. The [3,2,3] and [3,2] ions are soluble as hexafluorophosphates in water and in polar organic solvents such as DMF or CH_3CN . In solution, they appear to be stable for long periods (at least weeks) at ambient temperature under room light. In aqueous solution, the complexes remain stable even in relatively acidic conditions (at least to pH 1). The high overall stability of these complexes contrasts with the pronounced photochemical instability of the analogous pyrazine-bridged species.^{6,18}

Aqueous solutions of the [2,2,2] and [2,2], fully reduced species can be conveniently prepared by exhaustive reduction under argon of the corresponding oxidized forms by using zinc amalgam or by addition under vacuum of 2 or 1 equiv, respectively, of one-electron reductants such as $\text{Eu}^{2+}_{(\text{aq})}$ or $\text{Cr}^{2+}_{(\text{aq})}$. In organic solvents such as CH_3CN or DMF, the reduction can be conveniently carried out by using hydrazine hydrate. The fully reduced forms oxidize very rapidly in aerated aqueous solutions, whereas they are much more resistant to air oxidation in CH_3CN and DMF. The [2,2,2] complex has some tendency to release a pentaammineruthenium unit, converting to [2,2]. In fact, while rapid oxygenation of freshly prepared [2,2,2] aqueous solutions gives complete recovery of the starting [3,2,3] species, only partial recovery is obtained if the [2,2,2] solutions are allowed to age before reoxidation. The chemical oxidation-reduction behavior of the [3,2]/[2,2] couple, on the other hand, appears to be quite reversible.

Electrochemistry. Besides undergoing oxidation and reduction processes at rather positive and negative potentials (vs. SCE) characteristic of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ units,²³ both the [3,2] and the [3,2,3] ions exhibit reduction processes at potentials near zero (vs. SCE) which can be attributed to the pentaammine units.

Cyclic voltammetry of [3,2,3] in aqueous solution showed an apparently single reduction peak with a peak potential $E_{\text{pc}} = -0.140$ V (vs. SCE), paralleled by an anodic partner of the same height and with a peak potential $E_{\text{pa}} = -0.040$ V (vs. SCE). Such potentials and the peak current function $i_{\text{pc}}/v^{1/2}$ were independent of sweep rate v over the entire range explored (v , 0.1–250 V s^{-1}). The presence of shoulders on the raising (descending) part of the cathodic (anodic) peak, together with the peak-to-peak separation, suggested that both the cathodic and the anodic peaks are made up of two closely spaced components. The analysis of the peaks according to literature methods^{24,25} gave a value of 70 mV for the half-wave potential difference between the redox processes, corresponding to the two overlapping peaks. Controlled potential coulometry on the diffusion-controlled plateau of the corresponding polarographic wave indicated a two-electron process. Thus, the electrochemical processes observed correspond to the two-step redox equilibria



For [3,2] in aqueous solution, analogous experiments gave a one-electron reversible cyclic voltammetric curve with $E_{\text{pc}} =$

(21) Due to the high stability of the cis configuration of the starting $\text{Ru}(\text{bpy})_2(\text{CN})_2$ unit, there is little doubt that the same configuration is maintained in the formation of the binuclear and trinuclear pentaammine adducts.

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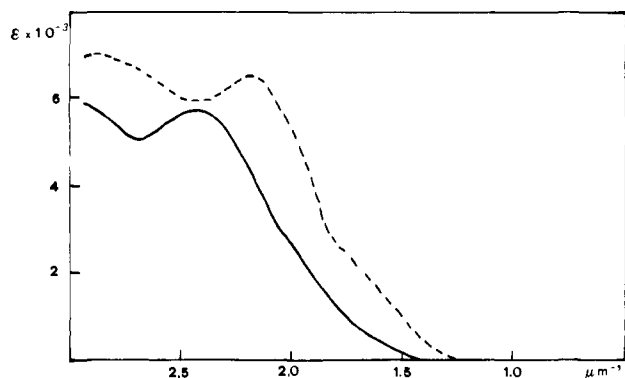


Figure 1. Absorption spectrum of the [2,2] ion in aqueous (—) and DMF (---) solutions.

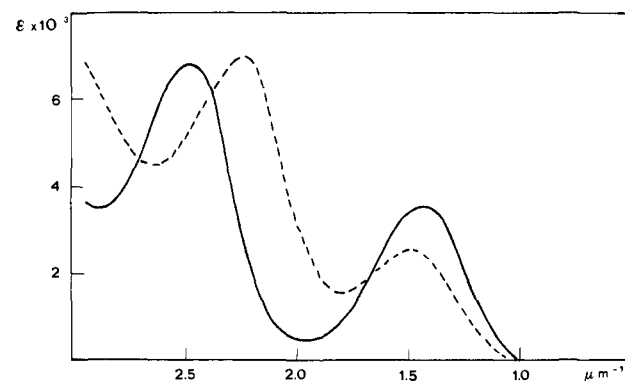


Figure 2. Absorption spectrum of the [3,2] ion in aqueous (—) and DMF (---) solutions.

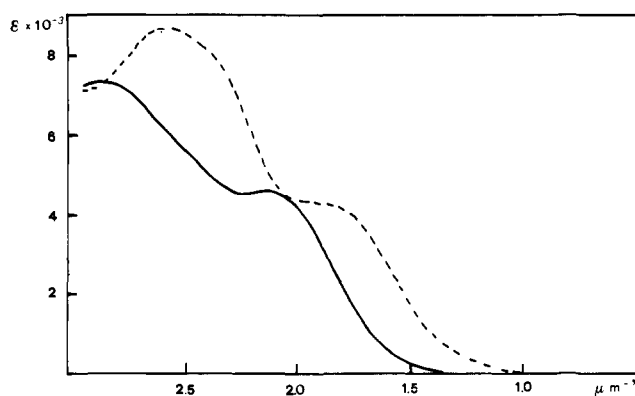
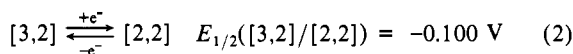


Figure 3. Absorption spectrum of the [2,2,2] ion in aqueous (—) and DMF (---) solutions.

-0.130 V (vs. SCE). Coulometric results confirmed the one-electron nature of the process. The corresponding electrode process can be written as



A complete account of the electrochemical behavior of [3,2,3] and [3,2] in water and polar organic solvents will be given elsewhere.²⁶

UV/Vis/Near-IR Absorption Spectra. The spectra of the [2,2], [3,2], [2,2,2], and [3,2,3] ions in aqueous and DMF solution are shown in Figures 1-4. When aqueous solutions of [2,2] were exposed to air, clean spectral variations with isosbestic points at 2.67, 2.35, and 1.77 μm^{-1} occurred, leading finally to the spectrum of [3,2], according to the simple redox equilibrium of eq 2. When, on the other hand, aqueous solutions of [2,2,2] were aerated, the spectrum evolved to the [3,2,3] one without isosbestic points being

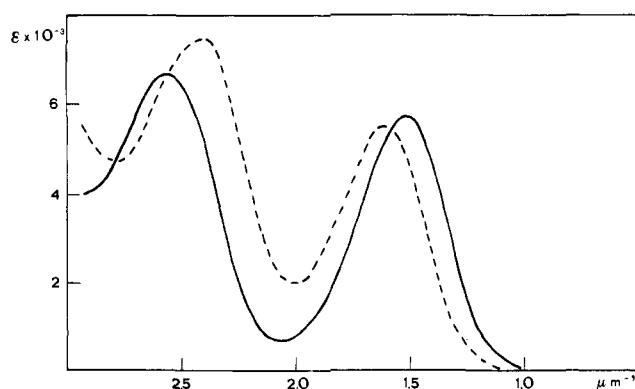


Figure 4. Absorption spectrum of the [3,2,3] ion in aqueous (—) and DMF (---) solutions.

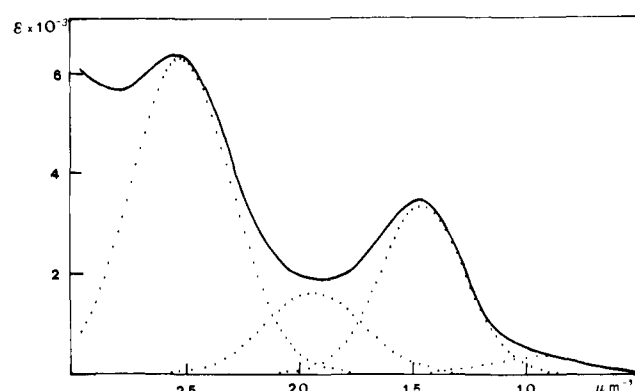
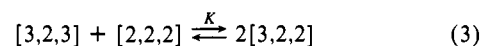


Figure 5. Absorption spectrum of the [3,2,2] ion in aqueous solution. The dotted lines represent an approximate Gaussian analysis of the spectrum.

maintained along the whole oxidation reaction. This result is in keeping with the electrochemical picture which indicates the presence of an intermediate species [3,2,2] along the redox path of eq 1.

When aqueous solutions of [3,2,3] were reduced with 1 equiv of a one-electron reductant, the spectrum obtained was definitely different from the average of the [2,2,2] and [3,2,3] spectra, again indicating the presence of substantial amounts of the [3,2,2] form. The amount of [3,2,2] present in these semireduced solutions depends on the constant of the comproportionation equilibrium



The actual difference in the sequential one-electron reduction potentials ($E([3,2,3]/[3,2,2]) - E([3,2,2]/[2,2,2]) = 0.070 \text{ V}$ and $K = 15$) indicates a 66% equilibrium concentration of [3,2,2] in these solutions. The true spectrum of the [3,2,2] species, calculated from the experimental spectrum on the basis of this figure and of the known spectra of the [2,2,2] and [3,2,3] ions, is shown in Figure 5.

Photophysical Behavior. Aqueous solutions of [3,2], [2,2], [3,2,3], and [2,2,2] did not exhibit any new luminescent emission in the 500-900-nm spectral range. All solutions, however, gave a very weak emission in the same wavelength range as $\text{Ru}(\text{bpy})_2(\text{CN})_2$ (λ_{max} , 620 nm). The intensity of this emission was always at least 100 times lower than that of a corresponding solution of free $\text{Ru}(\text{bpy})_2(\text{CN})_2$. That this emission was actually caused by trace impurities (less than 1%) of unreacted $\text{Ru}(\text{bpy})_2(\text{CN})_2$ in the samples was shown by pulsed laser measurements, which indicated that the emission, while being much weaker, had always the same lifetime (250 ns) as that of free $\text{Ru}(\text{bpy})_2(\text{CN})_2$. Thus, the long-lived emission of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ chromophore appears to be completely quenched by the presence of one or two attached pentaammineruthenium units, regardless of their +2 or +3 oxidation state.

Absorption laser flash photolysis measurements failed to give evidence for any transient phenomenon on the same solutions in

a time range longer than 50 ns.

Discussion

[3,2,3] Ion. The visible spectrum of the [3,2,3] ion in aqueous solution (Figure 4) exhibits two cleanly resolved intense bands at 2.55 and 1.52 μm^{-1} . The band at 2.55 μm^{-1} can be confidently assigned to the typical $d-\pi^*$ ($\text{Ru(II)} \rightarrow \text{bpy}$) charge-transfer transition of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore. This band has comparable intensity and is blue-shifted with respect to that (2.35 μm^{-1}) of free $\text{Ru}(\text{bpy})_2(\text{CN})_2$. Shifts of this type and magnitude are expected for metal binding to $\text{Ru}(\text{bpy})_2(\text{CN})_2$ through cyanide bridges.⁹⁻¹³ Also, the red shift observed when the solvent is changed from water to DMF is quite typical for this type of transition in both free $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and its metallic adducts.¹¹

The band at 1.52 μm^{-1} , which gives the deep blue color to the aqueous solutions of this complex, is not exhibited by any of the constituent units and can be assigned with confidence to an intervalence-transfer (IT)^{5,27} transition from the Ru(II) atom of the central bipyridine unit to one of the Ru(III) atoms of the terminal pentaammine units, i.e.,



The energy and the half-width (0.44 μm^{-1}) of this band are consistent with this assignment. For asymmetric class II systems, the energy and the half-width of the IT band and the thermodynamic barrier to electron transfer are mutually related.^{4,27} Allowing for a typical 30% excess of the experimental half-width over the theoretical one,⁴ a thermodynamic barrier of about 1.04 μm^{-1} (1.3 eV) can be calculated from the IT band characteristics. This is quite close to the difference in redox potentials between the [3,2,3]/[3,2,2] and [3,3,3]/[3,2,3]²⁶ couples (a figure which seems to indicate relatively small synergistic effects)⁴ and similar to the difference in redox potentials between the [3,2,3]/[3,2,2] couple and the $\text{Ru(II)}/\text{Ru(III)}$ couple of the [(dien)Pt(NC)Ru(bpy)₂(CN)]²⁺ model compound.¹¹ While solvent shifts of IT bands for asymmetric systems of this type depend on the combined effects of solvent on outer-shell barrier and redox potentials, the blue shift observed in changing the solvent from water to DMF (Figure 1) is in keeping with analogous results obtained by Powers et al.²⁸ on similar pyrazine-bridged systems.

The intensity of the IT band (ϵ_{max} , 5700) appears to be normal for cyanide-bridged mixed-valence systems^{8,29-31} but is remarkably higher than that of the corresponding pyrazine-bridged complex (ϵ_{max} , 1000).⁶ When standard equations^{4,5,27} and a typical metal-metal distance of 5 Å are used and the twofold degeneracy of the IT excited state is allowed for, the experimental intensity leads to values of 1.4×10^{-1} and 0.18 μm^{-1} for the valence delocalization parameter α^2 and for the electronic matrix element H_{AB} , respectively. Values of H_{AB} of $\sim 0.2 \mu\text{m}^{-1}$ can be typically obtained from the IT spectra of cyanide-bridged complexes,^{6,29-31} while values of 0.05 μm^{-1} seem to be typical of class II pyrazine-bridged ruthenium complexes.^{6,18,32} Thus, while still remaining within class II behavior, cyanide seems to bring about a definitely stronger metal-metal electronic coupling than pyrazine. Both types of bridges are considered to be amenable to the same second-order perturbational approach,³⁰ in which "local" charge-transfer states involving the bridging ligand provide the major pathway for mixing the metal-localized initial and final states of the IT transition. From this viewpoint, the reasons for the high electronic coupling provided by cyanide are not obvious, since $\text{Ru(II)} \rightarrow \text{CN}$ and $\text{CN} \rightarrow \text{Ru(III)}$ charge-transfer states are likely to lie at quite high energies in the [3,2,3] ion. It seems that specific features of

Table I. Assignments for the Visible and Near-IR Spectra of the Bi- and Trinuclear Complexes

assignment ^a	ν_{max} , μm^{-1}				
	[2,2]	[3,2]	[2,2,2]	[3,2,3]	[3,2,2]
$d-\pi^*$ Ru(II) \rightarrow bpy	2.42	2.48	2.82 ^b	2.55	2.51 ^c
$d-\pi^*$ Ru _i (II) \rightarrow bpy	2.1 ^d		2.10		1.92 ^c
IT Ru(II) \rightarrow Ru _i (III)		1.44		1.52	1.46 ^c
IT Ru _i (II) \rightarrow Ru _i (III)					0.95 ^c

^a Ru indicates the ruthenium atom of the $\text{Ru}(\text{bpy})_2^{2+}$ unit; Ru_i indicates the ruthenium atom of a terminal $\text{Ru}(\text{NH}_3)_5^{2+,3+}$ unit. ^b Maximum of a complex band system containing the assigned transition. ^c Band maxima from Gaussian analysis. ^d Shoulder.

cyanide, such as its very short bridge length or its cylindrical nature (no steric requirements for π overlap), must be responsible for its good metal-metal coupling characteristics.

The spectral assignments for the [3,2,3] ion are summarized in Table I.

[2,2,2] Ion. The visible spectrum of the [2,2,2] ion aqueous solution (Figure 3) exhibits a broad band system peaking at 2.82 μm^{-1} and a distinct shoulder at 2.1 μm^{-1} . The 2.8- μm^{-1} band system is clearly composite in nature and must contain the $d-\pi^*$ transition of the $\text{Ru}(\text{bpy})_2^{2+}$ unit. The lack of resolution makes it difficult to obtain the energy of this transition, which is expected to be slightly red-shifted with respect to the corresponding band of the [3,2,3] ion. In DMF, the band system shifts to the red, as expected for the $d-\pi^*$ transition of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore.¹¹ The assignment of the 2.1- μm^{-1} shoulder is not obvious. Aside from the already discussed $d-\pi^*$ transition within the $\text{Ru}(\text{bpy})_2$ chromophore, a number of other allowed transitions are conceivable in the [2,2,2] ion, namely, (i) $\pi-\pi^*$ transitions localized on the bipyridine ligands, (ii) $d-\pi^*$ transitions from the Ru(II) atom of the $\text{Ru}(\text{bpy})_2^{2+}$ unit to cyanide, (iii) $d-\pi^*$ transitions from the Ru(II) atom of the $\text{Ru}(\text{NH}_3)_5^{2+}$ unit to cyanide, and (iv) $d-\pi^*$ transitions from the Ru(II) atom of the $\text{Ru}(\text{NH}_3)_5^{2+}$ unit to bipyridine. Possibilities (i) and (ii) can be easily discarded, as $\pi-\pi^*$ transitions are known to occur at much higher energies in bipyridine complexes³³⁻³⁵ and no $d-\pi^*$ transitions other than those of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore are present in the visible spectrum of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and of its metallic adducts.¹¹ Bands of type (iii) are believed to lie at quite high energies in nitrile complexes such as $\text{Ru}(\text{NH}_3)_5(\text{CH}_3\text{CN})^{2+}$.³⁶ Furthermore, they are absent in the visible spectrum of $[(\text{NH}_3)_5\text{RuNCRu}(\text{CN})_5]^{2+}$,³⁷ which seems to be a reasonably good model molecule for this purpose. Thus, one is left with hypothesis (iv). In such a hypothesis, the energy of the transition relative to that of the $\text{Ru}(\text{bpy})_2^{2+}$ $d-\pi^*$ one seems to be reasonable, since the ruthenium of the pentaammine moiety is more oxidizable by some 1.3 V than that of the $\text{Ru}(\text{bpy})_2^{2+}$ unit.²⁶ It may be remarked that this type of assignment would imply a considerable intensity for a transition between relatively remote centers. However, space-filling models show that the minimum distance between the bipyridine ligands of the central unit and the ruthenium atoms of the pentaammine groups is of the same order as that between two cyano-bridged ruthenium atoms. In view of this short distance and of the relatively strong through-ligand interaction provided by cyanide, the intensity of the band (i.e., allowing for the twofold degeneracy, one-fourth of the $d-\pi^*$ transition of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore, and one-half of the $\text{Ru(II)}-\text{Ru(III)}$ IT transition of the mixed-valence species) seems to be compatible with the proposed assignment. The solvent shift observed (Figure 3) is as expected for a $d-\pi^*$ transition.

The spectral assignments proposed for the [2,2,2] ion are summarized in Table I.

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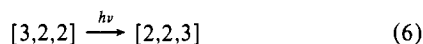
(37) Prepared by reduction with hydrazine hydrate of the corresponding mixed-valence³¹ species.

[3,2,2] Ion. An approximate Gaussian analysis³⁸ of the spectrum of this ion is shown in Figure 5. The spectrum is seen to consist of four main bands with maxima at approximately 2.51, 1.92, 1.46, and 0.95 μm^{-1} . By comparison with the spectra of the [3,2,3] and [2,2,2] ions, the first three bands can be assigned as follows. The band at 2.51 μm^{-1} is the usual $d-\pi^*$ transition within the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore. That at 1.92 μm^{-1} can be attributed to the $d-\pi^*$ transition from the Ru(II) atom of one pentaammine unit to the bpy ligands of the central metal. The band at 1.46 μm^{-1} is the IT transition to the Ru(III) atom of the other pentaammine unit from the Ru(II) atom of the $\text{Ru}(\text{bpy})_2^{2+}$ unit, i.e.,



It should be noted that the intensities of the 1.92- and 1.46- μm^{-1} bands are here, as expected, about one-half of the corresponding bands in the [2,2,2] and [3,2,3] ions, respectively. Also, the IT band at 1.46 is slightly red-shifted with respect to the corresponding band of the [3,2,3] ion, in keeping with the lower electron-withdrawing effect of the reduced pentaammine moiety on the central metal.

The near-IR band at 0.92 μm^{-1} is absent in the spectra of both limiting [2,2,2] and [3,2,3] redox forms and can be assigned as the symmetrical end-to-end IT transition between the two pentaammine units, i.e.,



The spectral parameters estimated for this band give, according to standard equations,^{4,5,27} a value for the electronic interaction H_{AB} between the remote pentaammineruthenium units of about $3.4 \times 10^{-2} \mu\text{m}^{-1}$. It is noteworthy that no end-to-end IT transition was observed in the analogous pyrazine-bridged complex $[(\text{NH}_3)_5\text{RupzRu}(\text{bpy})_2\text{pzRu}(\text{NH}_3)_5]^{7+}$ studied by Meyer.⁶ On the other hand, this type of transition was present with high intensity in the spectrum of the *trans*- $[(\text{NH}_3)_5\text{RupzRu}(\text{NH}_3)_4\text{pzRu}(\text{NH}_3)_5]^{7+}$ ion studied by von Kameke and Taube.⁷ These authors indicated in the difference in energy gap between the [2,3,2] and [2,2,3] states (and thus different configuration interaction mixing) the main reason for the difference between their results and Meyer's ones. It should be noted that in the present case, the energy of the [2,3,2] IT transfer state is quite similar to that of the analogous pyrazine-bridged complex, so that other factors, such as the shorter end-to-end distance (estimated 7 vs. 10 Å) and especially the stronger electronic interaction provided by the cyanide bridge (see above), should be invoked to make the difference between this ion and the analogous pyrazine-bridged one.

The spectral assignments for the [3,2,2] ion are summarized in Table I.

[3,2] and [2,2] Ions. The spectrum of the [3,2] ion (Figure 2) is very similar to that of the [3,2,3] ion (Figure 4), and the band assignments are the same as for the trinuclear ion. The main differences are the red shift of both bands and the reduced (about one-half) intensity of the IT band. These features can be understood in terms of the electron-withdrawing effect of the additional pentaammineruthenium(III) unit and of the doubly degenerate nature of the IT transition in the trimer, respectively.

The spectrum of the [2,2] ion (Figure 1) is very similar to that of the [2,2,2] ion (Figure 3) except for the fact that the $d-\pi^*$ band of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore is now well resolved. The same assignments can be made as for the trimer. Again, the intensity of the low-energy shoulder is considerably lower than in the trimer, which is consistent with the singly vs. doubly degenerate nature of the transition.

The spectral assignments for the [3,2] and [2,2] ions are summarized in Table I.

Photophysical Behavior. The free $\text{Ru}(\text{bpy})_2(\text{CN})_2$ molecule has a relatively long-lived (τ , 250 ns in water) $d-\pi^*$ ($\text{Ru} \rightarrow \text{bpy}$) excited state of triplet³⁹ multiplicity at about 1.8 μm^{-1} .^{12,40-42} The

results show that this state is completely quenched when one or two ruthenium pentaammine units are bound to the chromophore, irrespective of their +2 or +3 oxidation state. This result contrasts with the lack of quenching (actually lifetime enhancement) observed when Ag(I) ions,¹³ Cu(I) ions,⁴³ or Pt(II) complex moieties¹¹ are bound via cyanide bridges to the chromophore.

In bimetallic adducts of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ chromophore with 3d metal ions (e.g., Cu^{2+} , Ni^{2+} , Co^{2+}), quenching of the $d-\pi^*$ state was observed.¹² In these systems, intramolecular energy transfer to the low-lying ligand-field states of the metal ion no doubt constitutes a major quenching pathway. With the $\text{Ru}(\text{NH}_3)_5^{2+,3+}$ units used in this work, the ligand-field states are certainly much higher than in the previously mentioned systems, although the exact energies of the lowest, spin-forbidden ligand-field states are unknown. An estimate of the zero-zero energy of the $^3T_{1g}$ state of the $\text{Ru}(\text{NH}_3)_6^{2+}$ model compound can be made by using standard theory,⁴⁴ the ligand-field and Racah parameters given by Ford,⁴⁵ and assuming an excited-state distortion of the same size as that deducible from the absorption⁴⁶ and emission⁴⁷ spectra of the isoelectronic $\text{Rh}(\text{NH}_3)_6^{3+}$. For the $\text{Ru}(\text{NH}_3)_6^{3+}$ model compound, an estimate of the zero-zero energy of the $^4T_{1g}$ state can be made by using the vertical energy from the absorption spectrum⁴⁸ and assuming similar excited-state distortion as in the previous case. These estimates give values of $\sim 1.5 \mu\text{m}^{-1}$ for $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\sim 1.7 \mu\text{m}^{-1}$ for $\text{Ru}(\text{NH}_3)_6^{3+}$. Energy-transfer experiments⁴⁹ also tend to sandwich the lowest excited-state energy of $\text{Ru}(\text{NH}_3)_6^{3+}$ between 1.4 and 2.0 μm^{-1} . Altogether, the above arguments suggest that intramolecular energy transfer from the $d-\pi^*$ triplet state of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore to ligand-field states of the pentaammine units could be slightly exergonic and cannot be ruled out as the quenching mechanism in the systems studied on thermodynamic grounds. The kinetic factors⁵⁰ for such a process, however, are not expected to be very favorable. In fact, besides the orbital overlap problems which seem to characterize energy transfer to metal-centered states,⁵¹⁻⁵⁹ the relatively high distortional barriers (Stokes shifts^{46,47}) associated with these states

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(43) Addition of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)_2$ to acetonitrile solutions of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ yields results which are qualitatively similar to those reported by Kinnaird and Whitten¹³ for Ag(I). Bignozzi, C. A., unpublished results.

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(49) $\text{Ru}(\text{NH}_3)_6^{3+}$ quenches at different rates the excited states of $\text{Rh}(\text{phen})_3^{3+}$ (2.22 μm^{-1}), $\text{Ir}(5,6\text{-Me}_2\text{phen})_2\text{Cl}_2^{2+}$ (2.03 μm^{-1}), and $\text{Cr}(\text{bpy})_3^{3+}$ (1.37 μm^{-1}). The bimolecular rate constants are 3×10^7 , 2×10^7 , and $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The only plausible quenching mechanism is energy transfer, since the excited states used do not show any appreciable reducing power. Indelli, M. T., unpublished results.

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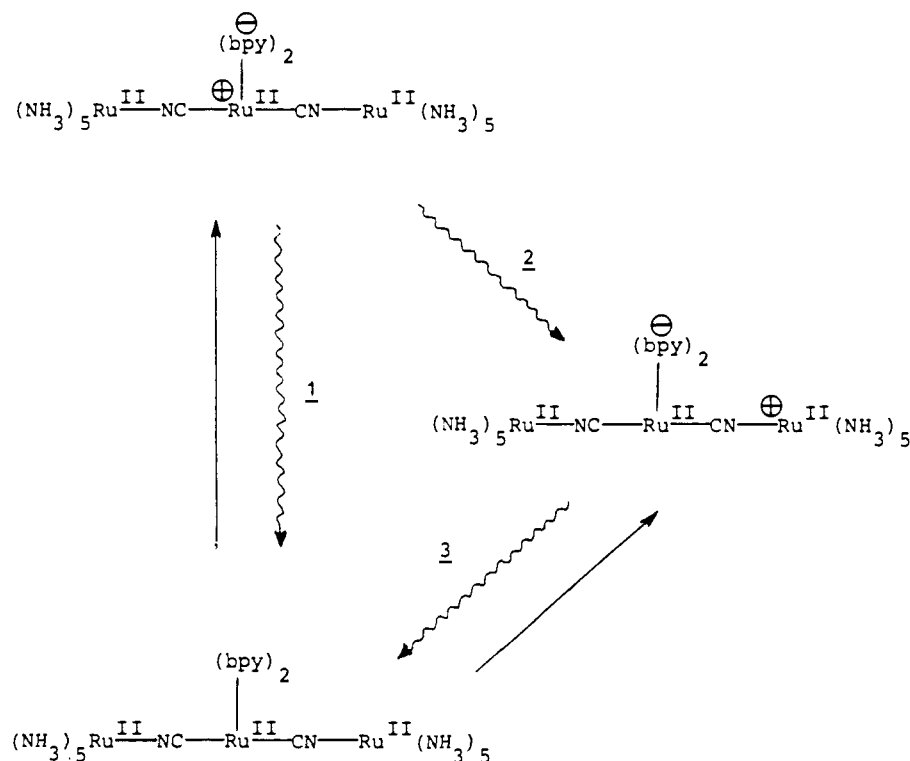
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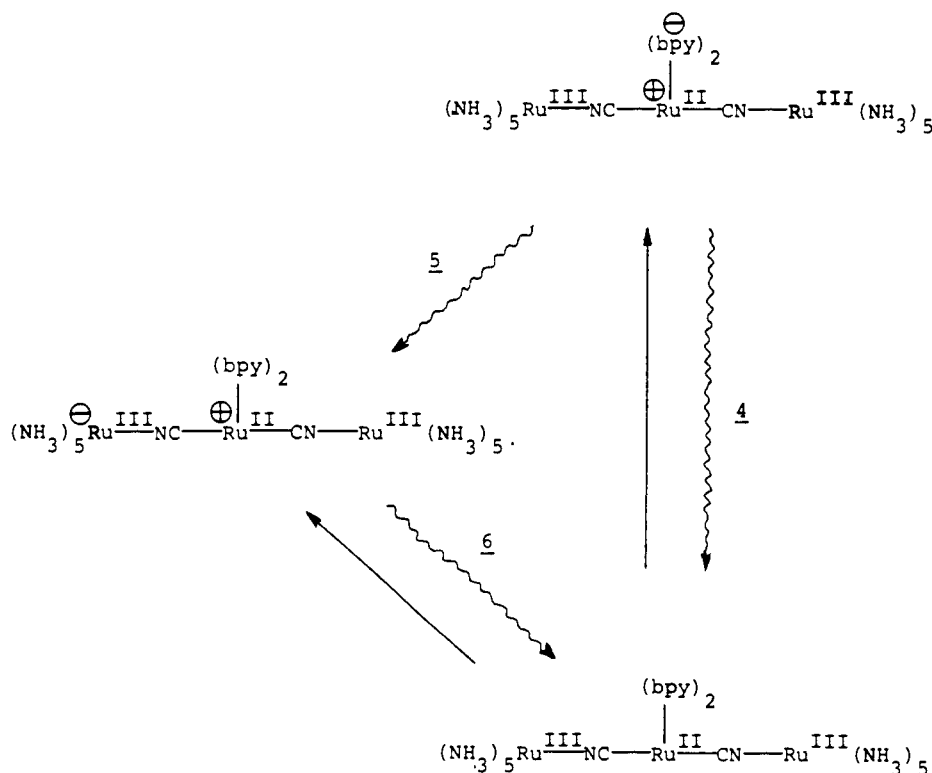
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(38) Analysis based on a computer fit in which the half-widths of the bands at 2.51 and 1.46 μm^{-1} were held constant at values taken from the corresponding bands of the [3,2,3] complex.

Scheme I



Scheme II



should slow down considerably the process.

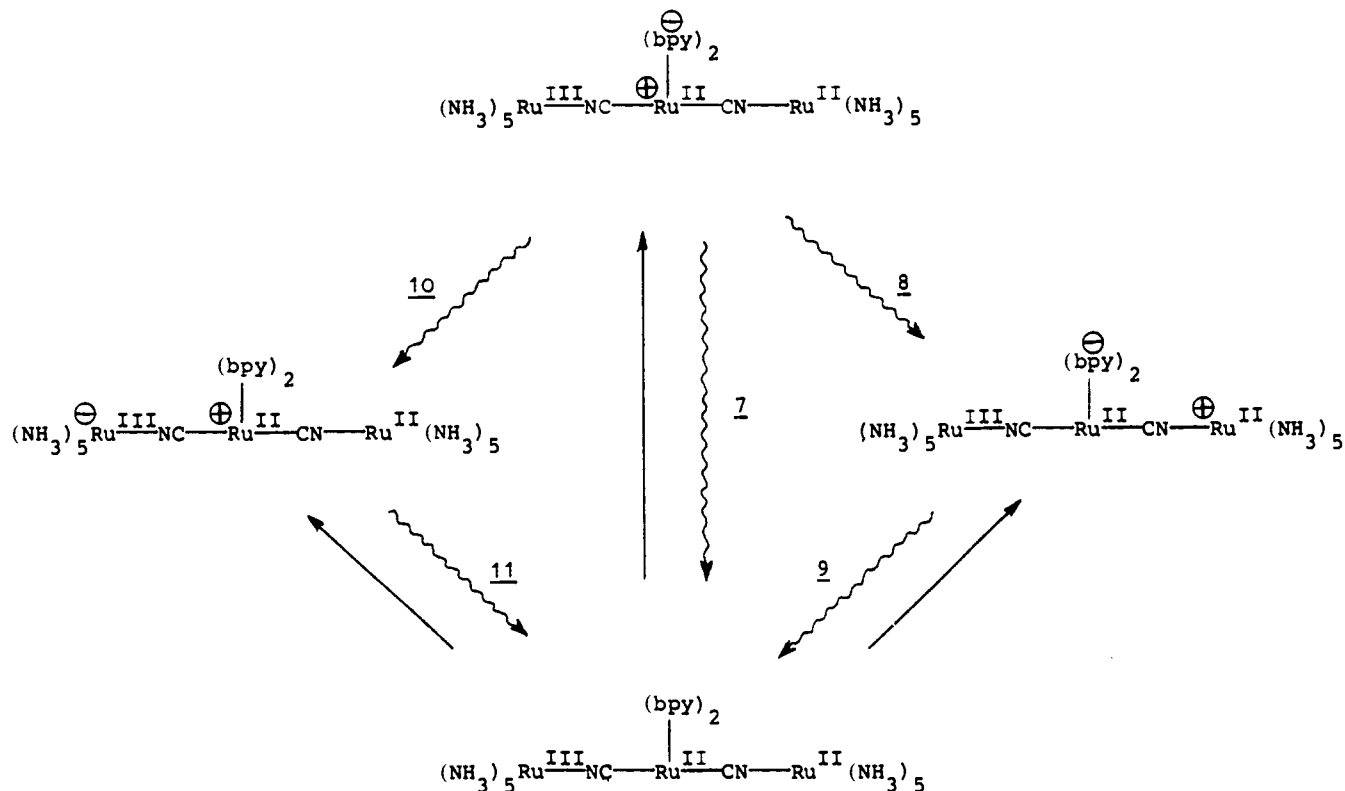
A number of intramolecular electron-transfer processes⁶⁰ can be envisioned along the quenching pathway of the $d-\pi^*$ excited state of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore. The various types of excited

states of charge or electron-transfer character present in the [2,2,2], [3,2,3], and [3,2,2] ions are represented in Schemes I-III. In this representation, a localized electron-hole picture is used for all the excited states, including the $d-\pi^*$ state of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore.⁶¹ For the sake of simplicity, spin labels have been

(60) Admittedly, the distinction between intramolecular electron-transfer and energy-transfer processes is somewhat artificial, since both processes are radiationless transitions within the excited-state manifold of the whole molecular system. A discussion in terms of electron-transfer processes has the advantage of emphasizing charge migration aspects and of allowing reference to properties (oxidation states) of the isolated subunits.

(61) Evidence in favor of the description of $d-\pi^*$ states of $\text{Ru}(\text{II})$ polypyridine complexes as containing $\text{Ru}(\text{III})$ and a reduced polypyridine ligand has been accumulating in recent years. Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834 and references therein.

Scheme III



omitted in Schemes I–III.⁶² Nevertheless, it should be recognized that each one-electron configuration shown in the schemes actually corresponds to a set of states of different spin multiplicity and energy,⁶² and this is likely to be quite important in determining the detailed fate of the electronic excitation energy. It should also be noticed that the final state of the end-to-end electron-transfer process of the [3.2.2] ion is not shown in Scheme III, since it coincides, as a thermally equilibrated species, with the ground state. Arrows corresponding to optical (continuous) and radiationless (wavy) transitions between the various one-electron configurations are included in Schemes I–III.

The transitions labeled 1, 4, and 7 in Schemes I–III are known to have rate constants of the order of $1\text{--}5 \times 10^6 \text{ s}^{-1}$.⁶³ The negative laser photolysis results indicate⁶⁴ that processes 3, 6, 9, and 11 have rate constants higher than $2 \times 10^7 \text{ s}^{-1}$. Furthermore, if energy transfer can be considered as a minor quenching path (see above), processes 2, 5, 8, and 10 should have rate constants higher than $5 \times 10^8 \text{ s}^{-1}$.⁶⁵ The high rate of the other processes relative to processes 1, 4, and 7 can be rationalized following standard electron-transfer theoretical models^{66–69} in terms of the differences in ergonicity and distortional barriers involved in the various types

of processes. The decay of the $d\text{--}\pi^*$ state of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore can be viewed as a highly exergonic electron-transfer process with small reorganizational energy, thus lying in the so-called Marcus “inverted region”.^{66–72} The other electron-transfer processes are certainly less exergonic and are likely to have larger reorganizational energies (outersphere) due to the larger electron-transfer distances involved. Thus, these processes should fall in the “normal” free energy region and are expected to be fast.

The arguments outlined above emphasize the fact that for electron transfer within a complex molecule, the shortest way may not always be the fastest one. The actual pathway is chosen on the basis of a balance between electronic interaction, reorganizational energies, and ergonicities. For example, the deactivation of the $d\text{--}\pi^*$ state of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore in the [3,2,3] ion is likely to occur by a two-step transfer via a terminal pentaammineruthenium rather than by direct return of the electron to the central ruthenium. The indirect path should have poorer electronic factors but is highly favored over the direct one by nuclear factors.

Finally, it can be hoped that in suitably engineered polynuclear systems of this type, some of the intramolecular electron-transfer processes shown in Schemes I–III are slow enough as to be observed in laser photolysis. In spite of its intrinsic importance, the direct measurement of fast intramolecular electron-transfer events has been quite rare.^{73,74} If sufficiently long-lived, the transients

(62) For a given complex, the number and energy of the states arising from each configuration depends on the number of singly occupied orbitals and on the magnitude of the exchange interactions between these orbitals. Thus, inclusion of spin would complicate to a different extent Schemes I–III. As an extreme example of such complication, it may be shown that the single $d\text{--}\pi^*$ excited configuration of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore in the [3,2,3] ion (upper configuration in Scheme II) should be replaced by six excited states of different energy, namely two singlet, three triplet, and one quintet states.

(63) The upper limit is obtained from the excited-state lifetime of free $\text{Ru}(\text{bpy})_2(\text{CN})_2$. Binding of redox inactive metal moieties to this unit is known to enhance the lifetime.¹¹

(64) If sufficiently long-lived ($\tau \geq 50 \text{ ns}$), all the intermediate species shown in Schemes I–III should have been detected in laser photolysis, since their spectra must differ sharply from those of the ground-state molecules in the visible IT region.

(65) This figure is based on the spectrofluorimetric evidence for at least 99% quenching of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ emission.

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(71) In terms of radiationless transition theory, this situation is described as weak coupling, and the effect of ergonicity takes the form of an energy-gap law.⁷⁰

(72) For $\text{Ru}(\text{bpy})_3^{2+}$, the small reorganizational energy is demonstrated by the small Stokes shift (Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275). For $\text{Ru}(\text{bpy})_2(\text{CN})_2$, in spite of the difficulties encountered in the definition of the Stokes shift,¹¹ it seems unlikely that the reorganizational energy is so much higher as to change substantially the situation.

(73) Extensive studies have been carried out chemically on slow systems containing $\text{Co}(\text{NH}_3)_3^{3+}$ as the oxidizing moiety. Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273 and references therein.

(74) An outstanding exception is the measurement of the back electron transfer rate in $(\text{NH}_3)_3\text{RupzRu}(\text{EDTA})^+$ following picosecond laser excitation. Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T. L.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442.

involved in these processes could serve as models for charge separation in artificial photosynthetic systems.

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nalizzato Chimica Fine e Secondaria, Tematica Ah1).

Registry No. [2,2], 94499-30-6; [2,2,2], 94499-29-3; [3,2]·(PF₆)₃, 94499-27-1; [3,2,2], 94499-28-2; [3,2,3]·(PF₆)₆, 94499-25-9; Ru(bpy)₂·(CN)₂, 58356-63-1; [Ru(NH₃)₃Cl]₂, 18532-87-1.

The Iron(III) Complex of *N*-[2-((*o*-Hydroxyphenyl)glycino)ethyl]salicylideneimine. A Model Complex for the Iron(III) Environment in the Transferrins

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Abstract: The structure of an iron(III) complex of the *N*-[2-((*o*-hydroxyphenyl)glycino)ethyl]salicylideneimine (EHGS) has been determined by single-crystal X-ray diffraction. The complex crystallizes in the rhombohedral space group *R* $\bar{3}$ with *a* = 14.112 (2) Å, α = 107.49 (1)°. The metal ion is bound by the two nitrogen atoms, the two phenolate oxygen atoms, the carboxylate oxygen atom, and the oxygen atom of a coordinated methanol so as to describe a pseudooctahedral geometry about the metal. The nitrogens and the two phenolate oxygens form the equatorial plane with the metal lying on it. In aqueous solution the methanol is replaced by water. Optical titration shows that this coordinated water undergoes hydrolysis with a *pK*_a of 6.7. The hydrolysis has been followed by Mössbauer spectroscopy, and the aquo and hydroxo forms show distinct spectral signatures. These complexes serve as model compounds for the iron binding site in the transferrins as indicated by the similarity of their optical and magnetic parameters to those of the proteins. A novel interpretation of the iron binding site of the proteins is suggested.

The transferrins, also known as siderophilins, are vertebrate glycoproteins of about 80 000 daltons which tightly but reversibly bind 2 mol of ferric ion.⁵⁻⁷ In mammals, serum transferrin is responsible for iron transport from sites of absorption to sites of storage and utilization and may have several other significant roles including "buffering" metal concentrations in the blood and acting as an antibacterial agent. The other members of the group, conalbumin, or ovotransferrin (egg white), and lactoferrin (milk and other mammalian secretions), do not have well-defined roles but may serve as antibacterials for their respective fluids. Despite their differing biological functions, all the siderophilins are known to contain very similar iron binding sites. Although the area of transferrin chemistry has been studied extensively, important questions remain on the nature and number of ligating groups that comprise the metal binding sites. Recent studies have focused on these questions by examining suitable small molecule model compounds whose stability constants and physical properties are similar to those of transferrin.⁸⁻¹⁰ Our initial model was based

on *N,N'*-ethylenebis[*o*-hydroxyphenyl]glycine], EHPG. This ligand forms very stable complexes with Fe(III) and other transition elements by octahedrally encapsulating the metal ion, using two secondary amine nitrogen atoms, two carboxylate oxygen atoms, and two phenolate oxygen atoms. This assignment has been confirmed by X-ray structure determinations.^{11,12} It is believed that the binding sites of transferrin contain two histidines,¹³ two tyrosines,^{8,14} a (bi)carbonate^{15,16} anion, and water¹⁷ or hydroxide⁸ as a sixth ligand. EHPG has similar donor groups, but in one coordination position a carboxylate oxygen replaces a water molecule. For this reason we attempted to improve our model by synthesizing the pentadentate ligand *N*-[2-((*o*-hydroxyphenyl)glycino)ethyl]salicylideneimine, EHGS, which would allow a solvent molecule to occupy the sixth coordination site. Thus, the present complex more closely resembles the en-

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