

ring, while X might be among the 6 possible T-sites. Only T₁ is connected with one of the four-membered-ring silicons. The assignment can thus be started at this point, i.e. W = 1 and the assignments X = 10, E = 17, C = 3 and L, B = 2, 4 can now be made. The complete assignment shown in Figure 9 is made by combining the NMR results with diffraction data²⁸ as described previously. Again, the diffraction experiment was carried out on a single crystal and the positional parameters of the silicon atoms are very accurately defined.

Conclusions

We have thus demonstrated that 2D ²⁹Si NMR connectivity experiments may be successfully applied to investigate the three-dimensional bonding in zeolite ZSM-5 in both monoclinic and two orthorhombic forms, the INADEQUATE experiment

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being particularly useful. Since ZSM-5 has the most complex unit cell of any known zeolite, with either 12 or 24 inequivalent silicons in the asymmetric unit depending on the form, it should be possible in the future to apply these techniques together with diffraction studies to the determination of unknown zeolite structures. Work of this nature is currently in progress.

Note Added in Proof. A single crystal study of the high-temperature structure has recently been completed (van Koningsveld, H.; et al. *Acta Crystallogr. B*, in press). The data are in agreement with the assignment of the resonances of this phase reported in the present work.

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Photoinduced Energy Transfer in Multinuclear Transition-Metal Complexes. Reversible and Irreversible Energy Flow between Charge-Transfer and Ligand Field Excited States of Cyanide-Bridged Ruthenium(II)-Chromium(III) and Ruthenium(II)-Rhodium(III) Complexes¹

Yabin Lei, Tione Buranda, and John F. Endicott*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received July 20, 1989

Abstract: Excited-state relaxation pathways have been examined for some bi- and trinuclear transition-metal complexes containing the Ru(bpy)₂²⁺ chromophore linked (or metalated) through cyanide to an ammine chromium(III) or rhodium(III) complex. The (³CT)Ru(bpy)₂²⁺ absorption and emission maxima and the Ru(III)-(II) reduction potentials all increase in energy with metalation. In most instances energy migration from the initially excited ruthenium center to the acceptor metal centers occurred in discrete steps analogous to elementary chemical reactions between independent molecular species. The migration of energy was manifested by quenching of the (³CT)Ru donor emission. This was sometimes accompanied either by (²E)Cr(III) phosphorescence emission in the chromium metalates or by the growth of a metal-to-metal charge-transfer absorption in a rhodium metalate. Picosecond flash photolysis has been used to observe the equilibration (in about 1 ns) between the (³CT)Ru(bpy)₂²⁺ and the triplet ligand field excited states of Rh(NH₃)₅³⁺. The strongly temperature dependent (³CT)Ru(bpy)₂²⁺ emission lifetimes of the Rh(NH₃)₅³⁺ metalates are simply described by two competing relaxation channels, one involving unmetalated cyanide (*k*_{RuCN}) and the other involving energy transfer to Rh(III) (*k*_{Rh}); in principle, one should also allow for a Ru(II)-centered relaxation pathway of the fully metalated complex (*k*_{Ru} ≪ *k*_{RuCN}), so that τ⁻¹ = *k*_{Ru} + (2-*n*)*k*_{RuCN} + *n**k*_{Rh} where *n* is the number of metalated cyanides. On the basis of the photophysical behavior (77-298 K) of the parent rhodium hexammine complex, the Ru(bpy)₂²⁺ donor is inferred to be strongly coupled to the Rh(NH₃)₅³⁺ and Rh(NH₃)₄X²⁺ (X = CN, Br, I) acceptor centers but electronically independent unless the donor and acceptor energies become comparable, a situation which may be the case when X = I.

Introduction

The study of photoinduced electron and energy transfer in simple molecular systems has been a source of conceptual and synthetic chemical challenge to many research groups during the past few years.² Much recent work has focused on unresolved

problems in evaluating the factors contributing to the strength of the electronic coupling between donors and acceptors and the relationship between the strength of this coupling and the energy or electron transfer efficiency.²⁻²³ Covalently linked donor and acceptor systems have been especially useful in some of the more definitive studies.^{2,7-10} The strength of the coupling, often ex-

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pressed by the electronic matrix element, H_{RP} , necessarily varies with the distance between the donor and acceptor and with the extent to which the linking molecules mediate the donor-acceptor coupling.²⁻¹⁵

The extreme limits of donor-acceptor coupling strengths are readily visualized: (a) in one extreme the donor-acceptor coupling could be so strong that it contributes significantly to the molecular bond energy and electrons are shared in the donor and acceptor orbitals; and (b) at the other extreme the donor and acceptor could be separated and electronically isolated so that H_{RP} is inconsequential and no transfer of charge or energy occurs between them. Most systems of interest seem to lie between these extremes²⁻²³ with the magnitude of H_{RP} being small enough that the donor-acceptor interaction can be treated as a perturbation of the isolated donor and acceptor electronic structures but large enough that energy- or electron-transfer processes do occur. The requirements on H_{RP} are especially severe in designing systems in which it is possible to clearly define energy or electron transfer between an electronically excited donor covalently linked to a potential acceptor, since H_{RP} must be (a) large enough that the transfer process is faster than the normal donor excited-state decay processes but (b) small enough that it is meaningful to discuss as discrete steps of the electronic excitation of the donor, vibrational and electronic relaxation among the donor electronic excited states and the transfer of energy or charge to the acceptor. In such systems there is a strong coupling limit in which electronic relaxation of the covalently linked donor-acceptor system must be treated as a normal cascade through molecular excited states and in which it is not meaningful to discuss energy or electron transfer between discrete donor and acceptor centers.

While broadly similar formalisms are used to treat the different classes of nonradiative relaxations, including electron and energy transfer with various degrees of electronic coupling,²⁴⁻²⁷ the detailed differences in the way in which the electronic and vibronic contributions to the transition probability are handled can lead to qualitatively different interpretations of the observations. Consequently, it is important to find systems in which the coupling strength can be varied and in which the effects of variations in electronic coupling are manifested in spectroscopic and/or relaxation rate patterns.

We have undertaken a systematic study of photoinduced energy and electron transfer among some cyano-bridged transition-metal complexes in order to better define the behavior of donor-acceptor systems near to the strongly coupled regime. We have selected bis(bipyridine)ruthenium(II) donors and metal-ammine acceptors since the component metal complex electronic structures have been thoroughly characterized and are reasonably well understood. This enables us to make detailed comparisons of the multinuclear complexes to their mononuclear components, thus facilitating the assessment of donor-acceptor coupling. This report describes our observations on some simple energy-transfer systems, those employing a (³CT)Ru(bpy)₂²⁺ donor covalently linked through cyanide to acceptors which are ammine complexes of chromium(III) or rhodium(III). These acceptors were selected because they are thermodynamically difficult to oxidize or reduce,²⁸ because the spectroscopy²⁹ and photophysics^{30,31} of a variety of their ammine complexes has been thoroughly investigated, and because certain of the acceptor energy states can be varied in a relatively straightforward and systematic way.²⁹ Related complexes with other classes of acceptors, including some electron-transfer systems, have been examined^{1,28b} and will be developed elsewhere. Overall, these cyanide-bridged complexes span a wide range of donor-acceptor couplings. Some of the complexes have vibronically isolated donor and acceptor excited states and can be treated as the sum of their constituent parts, while the donor and acceptor may be so strongly coupled in other complexes that the cyanide-bridged excited state must be regarded as a delocalized electronic species which is different in its properties from the sum of its constituents.

Experimental Section

A. Preparation of Complexes. The mononuclear complexes Ru(bpy)₂(CN)₂,³² [Rh(NH₃)₅Br]Br₂,³³ [Rh(NH₃)₅I](ClO₄)₂,³³ [trans-Rh(NH₃)₄Cl]Cl,³⁴ [trans-Rh(NH₃)₄Br]Br,³⁴ [trans-Rh(NH₃)₄I]I,³⁴ [Rh(NH₃)₅O₃SCF₃](CF₃SO₃)₂,³⁵ trans-Rh(NH₃)₄(CN)SO₃,^{36b} and [Cr(NH₃)₅O₃SCF₃](CF₃SO₃)₂³⁷ were all synthesized from commercial starting materials by using literature procedures or minor modifications

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of literature procedures. $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was obtained from Johnson-Matthey Corp. and recrystallized before use. Commercial $\text{Ru}(\text{bpy})_2\text{Cl}_2$ was obtained from Strem Chemicals, Inc.

$[(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_5)](\text{PF}_6)_3$.³⁸ Equal molar amounts of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ (about 100 mg) and $[\text{Rh}(\text{NH}_3)_5\text{O}_3\text{SCF}_3](\text{CF}_3\text{SO}_3)_2$ were mixed in either methanol or acetone. The mixture was then refluxed for 24 h. The reaction progress was monitored by means of the changes in visible-UV absorption spectrum of samples withdrawn from the reaction mixture. When no further spectral changes occurred, the solvent was removed by rotary evaporation. The yellow solid residue was dissolved in the minimum amount of water and loaded into a cation exchange column (Sephadex SP-C25-120 from Sigma Chemical). NaCl solutions of increasing concentration (0.3, 0.6, 0.9 and 1.0 M) were used to elute the complex. The band with an absorption maximum at 415 nm was collected, and this solution was rotary evaporated. Ethanol (or a 1:1 mixture of acetone and ethanol) was used to dissolve the yellow solid, and insoluble residues were removed by filtration. The solvent was removed from the filtrate by rotary evaporation. This process was repeated at least three times. Finally, the solid was dissolved in a small amount of water, and this solution was mixed with a saturated NH_4PF_6 solution. The precipitate which formed was separated, dissolved in methanol, and reprecipitated by the addition of ether.

$[(\text{bpy})_2\text{Rh}(\text{CNRh}(\text{NH}_3)_5)](\text{PF}_6)_6$. The above procedure was repeated with a 1:2 mole ratio of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and $[\text{Rh}(\text{NH}_3)_5\text{O}_3\text{SCF}_3](\text{CF}_3\text{SO}_3)_2$.

$[(\text{bpy})_2(\text{CN})\text{Ru}(\text{trans-CNRh}(\text{NH}_3)_4\text{I})](\text{PF}_6)_2$. This complex was obtained from the reaction of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ with $\text{trans-Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ carried out in the dark. The latter was typically generated by combining 0.10 g of $[\text{trans-Rh}(\text{NH}_3)_4\text{I}_2]$ with the stoichiometric amount of AgNO_3 in water. The mixture was boiled gently for 2 h. The formation of $\text{trans-Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ was determined from the visible-UV absorption spectrum.³⁹ The AgI was removed by filtration, and the filtrate was combined with an equal molar amount of $\text{Ru}(\text{bpy})_2(\text{CN})_2$, dissolved in hot water. The reaction mixture was kept at 80 °C for 3–5 h, then the volume of solutions was reduced about 50% by rotary evaporation, and solid NH_4PF_6 was added. The yellow solid which formed on cooling was dissolved in acetone and reprecipitated by the addition of ether. This procedure was repeated twice more, and the final product was dried in air.

$[(\text{bpy})_2(\text{CN})\text{Ru}(\text{trans-CNRh}(\text{NH}_3)_4\text{Br})](\text{PF}_6)_2$. This complex was synthesized in the dark by substituting $[\text{trans-Rh}(\text{NH}_3)_4\text{Br}_2]\text{Br}$ for the trans -diiodo complex in the preceding procedure.

$[(\text{bpy})_2(\text{CN})\text{Ru}(\text{trans-CNRh}(\text{NH}_3)_4\text{CN})](\text{PF}_6)_2$. Two-tenths g of $\text{trans-Rh}(\text{NH}_3)_4(\text{CN})\text{SO}_3$ in neat HCF_3SO_3 was heated to 90 °C for 10 min. This solution was carefully added to ether cooled in an ice bath, and a white precipitate formed. The precipitate of $[\text{trans-Rh}(\text{NH}_3)_4(\text{O}_3\text{SCF}_3)\text{CN}]\text{CF}_3\text{SO}_3$ was filtered and washed several times with ether. About 0.1 g of $[\text{trans-Rh}(\text{NH}_3)_4(\text{O}_3\text{SCF}_3)\text{CN}]\text{CF}_3\text{SO}_3$ was added to water, and the solution was warmed until it became clear. An equal molar amount of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ was then added, and the reaction mixture was maintained at 80–90 °C for 5 h. The resulting solution was rotary evaporated until a yellow solid formed. This solid was collected, recrystallized from aqueous NH_4PF_6 three times, and finally dissolved in acetone and precipitated with ether.

$[(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)](\text{PF}_6)_6$. A solution of $[\text{Cr}(\text{NH}_3)_5\text{O}_3\text{SCF}_3](\text{CF}_3\text{SO}_3)_2$ in acetone was combined with an equal molar amount of $\text{Ru}(\text{bpy})_2(\text{CN})_2$. The resulting mixture was allowed to stand in the dark for a week, or, alternatively, the mixture was refluxed in the dark for 2 days. The solvent was then removed by rotary evaporation, the yellow solid which remained was dissolved in a minimum amount of water, and the solution was loaded onto a SP-C25-120 cation exchange column. A sequence of solutions increasing in $[\text{NaCl}]$ (0.3, 0.6, 1.0, 1.5, and 2.0 M) and containing a $\text{NaCH}_3\text{CO}_2\text{-CH}_3\text{CO}_2\text{H}$ buffer (0.1 M) was used to elute the compound from the resin. The eluate with an absorption band at 379 nm was collected, and the solvent removed by rotary evaporation. The solid, yellow residue was dissolved in a small amount of water. The $[(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)](\text{PF}_6)_6$ was precipitated by the addition of a saturated solution of aqueous NH_4PF_6 . This solid was separated by filtration. The product was dissolved in acetone and reprecipitated by

the addition of ether. All steps were carried out in the dark.

$[(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNCr}(\text{NH}_3)_5)](\text{CF}_3\text{SO}_3)_3$. This complex was isolated from early fractions of the cation-exchange separations in the preceding procedure. We were unable to prepare solids which gave reproducible analytical results. Solutions of the complex were characterized by visible-UV absorption spectroscopy and cyclic voltammetry.

Reagent or spectroscopic grade materials and redistilled water were used.

B. Characterization of Complexes. Spectroscopic and electrochemical methods were used for complex characterization, in addition to elemental analysis, since successive metalations were found to result in systematic, nearly predictable variations in band maxima and halfwave potentials.

1. Infrared Spectra. Spectra were determined for samples in KBr pellets by using either a Nicolet 20DX-FT IR or a Perkin-Elmer IR spectrometer. The cyanide stretching frequencies were most useful because these narrow bands shifted (about 10 cm^{-1}) to higher energy upon metalation.

2. Visible-Ultraviolet Absorption Spectra. Solution spectra were determined at ambient temperatures by using either a Cary Model 14 or an HP 8452 diode array UV-vis spectrophotometer. Successive metalations resulted in shifts (about 20 nm) of the $\text{Ru}(\text{bpy})_2^{2+}$ MLCT absorption maxima to higher energies.

3. Electrochemistry. Cyclic voltammograms of acetonitrile solutions, containing about 10^{-3} M complex and 0.1 M TEAP, were run on a Princeton Applied Research 179 digital coulometer with PAR 175 programmer by using a saturated sodium calomel electrode (SSCE) as the reference, a platinum wire counter electrode, and either a platinum bead or a hanging mercury drop as the working electrode. Solutions were deaerated with ultrapure nitrogen gas passed through two chromous- HClO_4 scrubbers, a CaSO_4 drying column, and a stabilizer (containing DMF). The reference electrode was separated from the sample chamber by a two-compartment salt bridge. The compartment adjacent to the reference chamber contained 0.13 M TEAP in water, and the compartment adjacent to the sample chamber contained 0.1 M TEAP in acetonitrile. Data collection and output for scan rates greater than 50 mV/S were accomplished by using a Nicolet Model 20290-3C to digitize the signal and a Macintosh computer and local software for data analysis. Halfwave potentials for the $(\text{bpy})_2\text{Ru}(\text{III})-(\text{II})$ couple shifted 100–200 mV more positive with each metalation.

C. Luminescence Spectra and Lifetime Measurements. Luminescence spectra were recorded with a computerized (customized program from OLIS, Inc.) Princeton Applied Research OMA-1 with SIT vidicon by using a Molelectron UV1010 pumped DL-14 dye laser for excitation. Spectra were corrected for detector distortions. The apparatus and general procedures have been described in detail elsewhere.⁴⁰

Deaerated samples in 1-cm cuvettes were maintained at constant temperature (± 1)° in the 80 °C to –120 °C range in a PRA thermostated cell housing by using either isopropyl alcohol, ethylene glycol-water (1:1, v/v), or a stream of cooled nitrogen gas as coolant. Emission studies at 77 K were performed by using glassy samples in a cylindrical fluorescence cell (5-mm o.d. clear fused quartz, suprasil grade) mounted in an EPR quartz (suprasil) nitrogen dewar (Wilmad, Model Wg-850Q). Samples were dissolved and deaerated in $\text{DMSO-H}_2\text{O}$ (1:1, v/v) or DMF-CHCl_3 (3:1, v/v). Potassium chromate solution filters and/or optical glass filters were used to reduce scattered laser light.

Luminescence lifetimes were determined by deflecting the scattered light with a movable mirror through optical filters and an Instruments SA H100 monochromator onto a Hamamatsu 950 PM tube interfaced to a Gould-Biomation 4500 digital oscilloscope and Zenith ZW-158-43 computer.

Relative emission quantum yields were determined at room temperature by using $\text{Ru}(\text{bpy})_2(\text{CN})_2$ or $\text{Ru}(\text{bpy})_2^{2+}$ as the reference compound. The absorbances of the reference compound and the compound of interest were matched at a specified wavelength, the solutions were deaerated at least 30 min with deoxygenated N_2 and placed in the cell holder thermostated at 25 °C. Reference and sample emission spectra were collected in the OMA under identical conditions. The emission data were transferred to the Zenith computer, and the spectral intensities were integrated over the observation window.

D. Bimolecular Quenching Experiments. Experiments were performed at 25 ± 1 °C by using deaerated samples in 1-cm cuvettes and the apparatus described above for lifetime measurements. We used aqueous solutions, 1 M in NaCF_3SO_3 , for these experiments. Bimolecular rate constants were obtained from linear least-squares fits of pseudo-first-order plots decay rate constants vs quencher concentration.

(38) We have used the following guidelines in writing chemical formulas for the multinuclear complexes: (a) The donor complex is written on the left, the acceptor complex(es) on the right-hand side of the formula. (b) The acceptor is written as a ligand of the donor, with the bridging ligand interposed between the donor and acceptor. Abbreviations used are as follows: $\text{Ru}(\text{CNM})_3^{3+}$ for $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNM}(\text{NH}_3)_5)^{3+}$, $\text{Ru}(\text{CNMX})_2^{2+}$ for $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNM}(\text{NH}_3)_4\text{X})^{2+}$, and $\text{Ru}(\text{CNM})_2^{6+}$ for $(\text{bpy})_2\text{Ru}(\text{CNM}(\text{NH}_3)_5)_2^{6+}$. In all these compounds we have assumed that the Ru-CN bond does not isomerize on metalation. This is based on spectroscopic properties to be discussed elsewhere.

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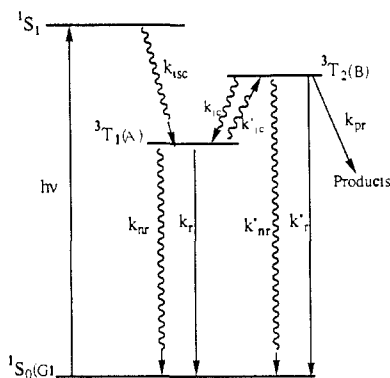
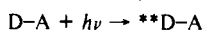


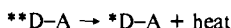
Figure 1. Jablonski diagram for a four-level system. Subscripts of the rate constants are as follows: nr = nonradiative, r = radiative, pr = photochemical reaction, ic = internal conversion, and isc = intersystem crossing.

E. Picosecond Flash Photolysis. These experiments were performed at the Notre Dame Radiation Laboratory, and Mr. C. Devadoss assisted with the use of the instrumentation. A mode-locked YAG laser (Quantel International) was used which had a pulse width of about 18 ps.⁴¹ Frequency-tripled (355 nm) pulses of about 1 mJ were used for excitation. Time delays were achieved by using optical fiber cables of different lengths.⁴¹ The spectral scan at each time delay was averaged over 100 pulses. Time delays were selected in a random sequence. The absorbance changes which were correlated to the sequence of time delays, but not to the actual time delay between the pump and probe pulses, were attributed to photodecomposition. Such photodecomposition of the Ru-(bpy)₂(CN)₂ metalates was usually associated with a red shift of the high energy bleaching in the transient spectra; such a red shift is expected for demetalation of these complexes. The excitation pulse intensity was varied for a few of the complexes with no qualitative changes in the observed behavior. We have used a flow cell to obtain picosecond transient spectra of the photoactive substrates. Flow rates were adjusted to ensure fresh solutions for each flash.

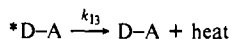
F. Transient Decay Kinetics. 1. Excited-State Relaxation Kinetics in Coupled Donor-Acceptor Systems. In the limit that donor and acceptor function largely as independent electronic systems, the photoinduced energy-transfer process can be described as a series of coupled first-order rate processes. Relaxation of the electronically excited system can then be treated as a straightforward eigenvalue problem.⁴² To simplify the discussion we have initially assumed that excitation



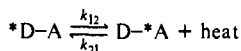
and vibrational equilibration among the donor centered excited states



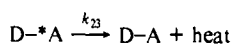
are very fast and efficient processes which are not coupled to the subsequent excited-state relaxation processes. Possible exceptions are noted in the Results and Discussion sections. This first metastable excited state (A), *D-A, can then relax to its ground state (G)



in competition with the population of an acceptor excited state (possibly by a thermally activated pathway)



where the reverse-energy-transfer step may be in competition with relaxation of the acceptor excited state in D-*A (hereafter designated B) to the ground state



This scheme is illustrated in Figure 1 based on the behavior of some of the Ru(bpy)₂(CN)₂-rhodium(III) adducts. The above kinetic parameters are related to those in Figure 1 as follows:

$$k_{13} = k_{nr} + k_r; \quad k_{12} = k'_{ic}; \quad k_{21} = k_{ic}; \quad k_{23} = k'_r + k'_{nr} + k_{pr}$$

The kinetic behavior of the electronically excited system ($[A \rightleftharpoons B] \rightarrow G$) may then be described by the rate equations

$$\frac{d[A]}{dt} = k_{21}[B] - (k_{13} + k_{12})[A]$$

$$\frac{d[B]}{dt} = k_{12}[A] - (k_{21} + k_{23})[B]$$

$$\frac{d[G]}{dt} = k_{13}[A] + k_{23}[B]$$

The resulting eigen equation can be solved in closed form.⁴² The solutions of interest for the Ru-Rh systems are of the form

$$2\lambda = (k_{11} + k_{22}) \pm [(k_{11} - k_{22})^2 + 4k_{21}k_{12}]^{1/2} \quad (1)$$

where $k_{11} = k_{12} + k_{13}$ and $k_{22} = k_{23} + k_{21}$. Two limiting cases are most useful to our discussion: (a) a "kinetic" limit following generation of the excited donor (formally for $k_{13} \ll (k_{12} + k_{21}) > k_{23}$ and for the positive root)

$$\lambda_1 \approx k_{12} + k_{21}$$

and (b) a limit appropriate to the net overall decay, obtained for a first-order Taylor's series expansion of (1)

$$\lambda'_2 \approx k_{13} + \frac{k_{12}(k_{13} + k_{12} - k_{23})}{(k_{13} + k_{12} - k_{21} - k_{23})} \quad (2)$$

When $k_{23} \gg (k_{12} + k_{13})$ and $k_{21} > k_{23}$, eq 2 reduces to

$$\lambda_2 \approx k_{13} + k_{23}K_{12} \quad (3)$$

where

$$K_{12} = k_{12}/k_{21}$$

When $(k_{12} - k_{23}) > k_{21}$ (k_{13} small), eq 2 reduces to $\lambda'_2 \approx k_{12}$.

2. Activation Parameters for the (³CT)Ru(bpy)₂²⁺ Excited-State Decays of Rh(NH₃)₅³⁺ Adducts. The temperature-dependent luminescence decays were monitored over approximately a 100 °C range in fluid DMSO-H₂O mixtures (1:1, v/v). Temperatures were determined to ± 1 °C. The temperature-dependent decays were fitted to simple Arrhenius expressions, and no attempt was made to determine if the small deviations from Arrhenius behavior were statistically significant. The (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ complex exhibited two distinctly different, thermally activated excited-state decay regimes above 220 K, and this behavior was fitted to a simple Arrhenius-type two-exponential expression

$$k_{\text{obsd}} = A_{\text{LT}} \exp(-E_{\text{a,LT}}/RT) + A_{\text{HT}} \exp(-E_{\text{a,HT}}/RT)$$

where LT and HT designate the low-temperature and high-temperature components, respectively.

G. Estimates of Donor and Acceptor Excited-State Energies. We have based our estimates of the energies of the various donor and acceptor excited states on small corrections of the energies of the parent (³CT)-Ru(bpy)₂(CN)₂ and M(NH₃)₆³⁺ or M(NH₃)₅X²⁺ excited-state energies. These corrections were based on different correlations for the donor and for the Rh and the Cr acceptors.

1. Donor Energies. The ³CT origin of Ru(bpy)₃²⁺ has been assigned at $17.80 \times 10^3 \text{ cm}^{-1}$ in a doped single crystalline matrix at 4 K.⁴³ Since the excited state involves some charge separation, the energy of the electronic origin is expected to be solvent dependent.⁴⁴ We have recently used the photoacoustic microcalorimetric technique⁴⁵⁻⁴⁷ to determine the ambient (³CT) Ru(bpy)₃²⁺ excited-state energy to be $16.83 \times 10^3 \text{ cm}^{-1}$ in ambient DMSO-H₂O solutions.⁴⁸ We have assumed that the relationships are similar between the ambient emission maxima and equilibrated excited-state energies of Ru(bpy)₃²⁺ and of the metalated complexes derived from Ru(bpy)₂(CN)₂. This leads to donor energies of 16.7×10^3 and $17.6 \times 10^3 \text{ cm}^{-1}$ for the mono- and bis-metalates (Rh(NH₃)₅³⁺), respectively, in the DMSO-H₂O solvent. For the metalates which have no ambient emission we have made small corrections of this estimate based on the observed variations in the Ru(III)-(II) reduction

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Table I. Characteristic Infrared Frequencies and Assignments of Selected Complexes

compound	band observed (cm ⁻¹)	assignment	
Ru(bpy) ₂ (CN) ₂	3070	ν_{C-H}	
	2072, 2060	ν_{CN^-}	
	1602	δ_{ring}	
	1463, 1444, 1422	$\nu_{C=C}, \nu_{C=N}$	
	767, 732	ρ_{ring}	
[Rh(NH ₃) ₅ O ₃ SCF ₃](CF ₃ SO ₃) ₂	3350, 3275	ν_{N-H}	
	[(bpy) ₂ (CN)Ru(CNRh(NH ₃) ₅)]-(PF ₆) ₃	3303, 3150	ν_{N-H}
		2924	ν_{CH}
	[(bpy) ₂ Ru(CNRh(NH ₃) ₅) ₂](PF ₆) ₆	2067, 2108	ν_{CN^-}
		1602	δ_{ring}
1467, 1477, 1421		$\nu_{C=C}, \nu_{C=N}$	
764, 732		ρ_{ring}	
3360, 3206		ν_{N-H}	
[(bpy) ₂ Ru(CNRh(NH ₃) ₅) ₂](PF ₆) ₆	2966	ν_{CH}	
	2124, 2105	ν_{CN^-}	
	1604	δ_{ring}	
	1467, 1444, 1421	$\nu_{C=C}, \nu_{C=N}$	
	764, 732	ρ_{ring}	

Table II. Absorption Maxima (and Extinction Coefficients) of Cyanide-Bridged Ru(bpy)₂(CN)₂M Complexes^a

M	H ₂ O	DMSO-H ₂ O (1:1)	DMF-CHCl ₃ (3:1)
<i>b</i>	428	457 (9.07)	498
Rh(NH ₃) ₅ ³⁺	415	430 (8.47)	457
[Rh(NH ₃) ₅] ₂ ⁶⁺	408	413 (8.16)	428
<i>trans</i> -Rh(NH ₃) ₄ CN ²⁺	418	430 (8.94)	455
<i>trans</i> -Rh(NH ₃) ₄ Br ²⁺	420	429 (10.4)	453
<i>trans</i> -Rh(NH ₃) ₄ I ²⁺	417	433 (11.7)	458
[Cr(NH ₃) ₅] ₂ ⁶⁺	379	390 (12.6)	408

^a λ_{max} in nanometers for solvents as indicated; $\epsilon/10^3$ in M⁻¹ cm⁻¹ in parentheses. ^b Ru(bpy)₂(CN)₂.

potentials and the observation that emission band maxima follow the same trend, in these complexes, as the reduction potentials.

2. The Rh(III) Acceptor Energies in Metalated Complexes. The acceptor excited states of the Rh(NH₃)₅³⁺ cyanometalates were presumed to be very similar in energy to those of Rh(NH₃)₆³⁺.^{28,49} We have used simple ligand field approaches^{29,50} to estimate these splittings. In doing this we have assumed that the M-NC bonding interaction is roughly comparable to nitrile or isothiocyanate interactions.⁵¹ The results of these calculations are listed in Table VII.

3. The Cr(III) Acceptor Energies in Metalated Complexes. The (²E)Cr(III) energy was determined from the emission spectra. The higher energy excited states have been presumed to be similar to the energies of the corresponding states in Cr(NH₃)₆³⁺. Once again the excited states of pentaammine complexes are presumed to be split, and the splitting energies were estimated by using ligand field approaches.^{29,50}

Results

A. Synthesis and Characterization. Most of the rhodium(III)-ammine adducts were relatively straightforward to synthesize and purify. The chromium(III) adducts were much more difficult, owing to their photosensitivity, and we were unable to isolate pure samples of (bpy)₂(CN)Ru(CN)Cr(NH₃)₅³⁺. Rather this complex was always obtained in combination with the bis-metalated complex. Analytical data are summarized in Table S-I.⁵²

Typical infrared frequencies are listed in Table I. The C-N stretching frequencies were most useful in characterizing the metalated complexes since these bands shifted to higher energies with metalation as indicated in Table I.

The metal-to-ligand charge-transfer (MLCT) absorption maxima of the Ru(bpy)₂ moiety shifted progressively to the blue

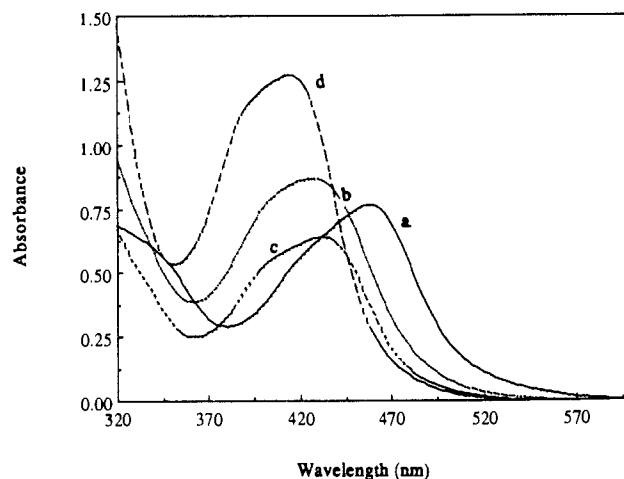


Figure 2. Electronic absorption spectra of (a) Ru(bpy)₂(CN)₂, (b) (bpy)₂(CN)Ru(*trans*-CNRh(NH₃)₄Br)²⁺, (c) (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺, and (d) (bpy)₂Ru(CNRh(NH₃)₅)₂⁶⁺. All complex concentrations approximately 10⁻⁴ M in 1:1 DMSO-H₂O solution.

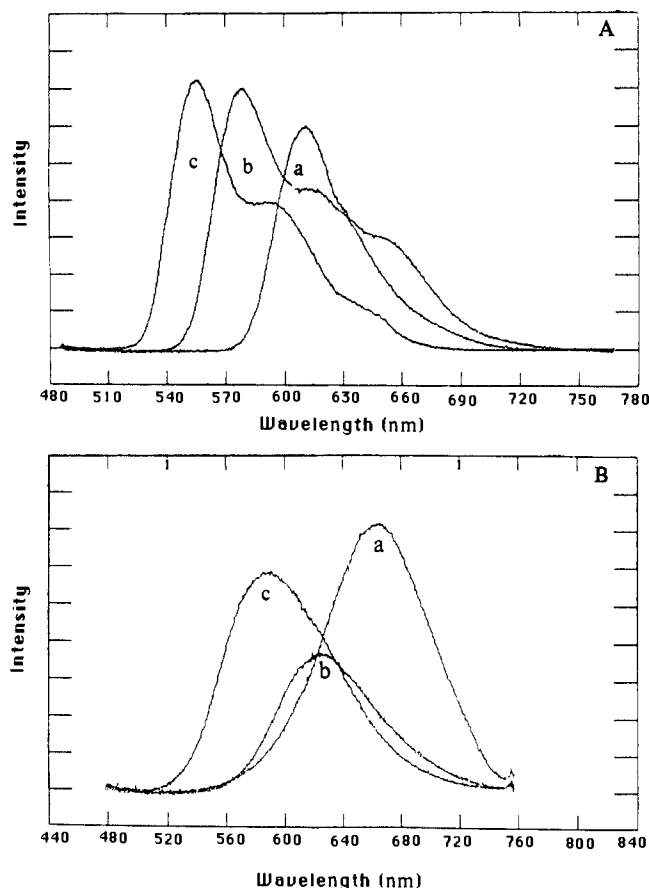


Figure 3. Emission spectra of (a) Ru(bpy)₂(CN)₂, (b) (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺, and (c) (bpy)₂Ru(CNRh(NH₃)₅)₂⁶⁺ in DMF-CHCl₃ (3:1, v/v) solutions at (A) 77 K and (B) 298 K.

on successive metalation (Figure 2). These MLCT absorption bands were solvent sensitive (Table II), most strongly for the mono- and unmetalated complexes. The blue shifts of the MLCT absorptions paralleled the pattern of shifts of the Ru(III)-Ru(II) reduction potentials upon metalation (Table III).

B. Luminescence Behavior. The (³CT)Ru(bpy)₂²⁺ emission maxima shift to higher energy with each successive Rh(III) metalation of coordinated cyanide (Figure 3 and Table IV). The emission band maxima are solvent dependent, but the solvent dependencies (for absorption as well as emission) are greatly diminished in those complexes with both cyanides metalated (Table IV). Spectroscopic and lifetime determinations of the Cr(NH₃)₅³⁺

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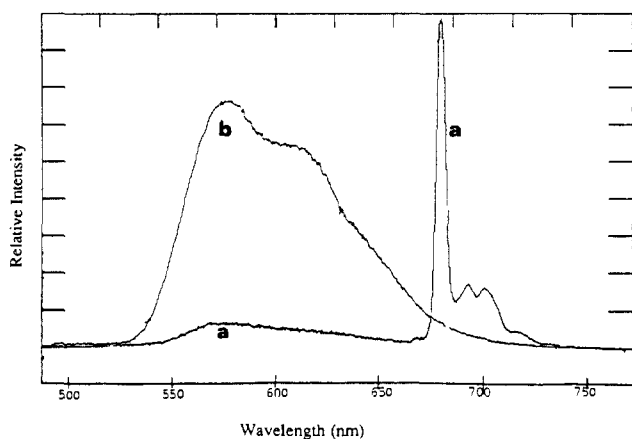
(51) Note that comparable M-N vibrational frequencies have been reported for M-NC-Ru,^{51a} M-NC-R,^{51b} and M-NCS:^{51b} (a) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 1142. (c) Ferraro, J. R. *Low-Frequency Vibrations of Inorganic and Coordination Compounds*; Plenum: New York, 1971.

(52) Supplementary material. See paragraph at the end of this paper.

Table III. Summary of Cyclic Voltammetry on Cyanometalates of Ru(bpy)₂(CN)₂

metalate	$E_{1/2}$, V(ΔE_p , mV) ^a		
	Ru(III) → Ru(II) ^b	bpy → bpy ^{-c}	bpy(bpy ⁻) ₂ ^c
Ru(bpy) ₂ (CN) ₂ ^d	0.719 ± 0.002 (70)	-1.669 (76)	-1.896 (81)
Ru(bpy) ₃ ²⁺ ^d	1.21 ± 0.01 (70) ^e	-1.378 (68)	
Cr(NH ₃) ₅ ³⁺	1.05 ± 0.02 (65)		
[Cr(NH ₃) ₅ ³⁺] ₂	1.338 ± 0.002 (80)		
Rh(NH ₃) ₅ ³⁺	1.002 ± 0.002 (79)	-1.695 (84)	-1.931 (87)
[Rh(NH ₃) ₅ ³⁺] ₂	1.188 ± 0.003 (74)	-1.695 (84)	-1.931 (88)
Rh(NH ₃) ₄ I ²⁺	0.923 ± 0.01 (88)		

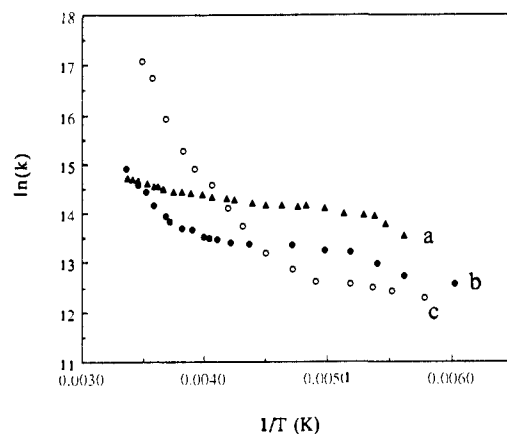
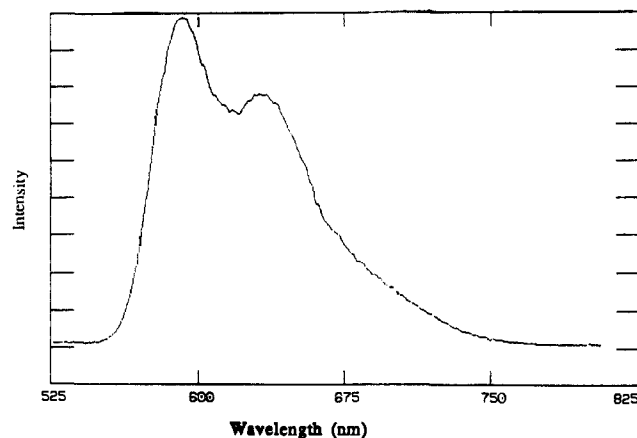
^a Using either a Pt bean or HMD working electrode with a saturated sodium-calomel reference; 25 °C; 1 × 10⁻³ M complex in acetonitrile; 0.1 M TEAP supporting electrolyte. ^b Average ($E_{1/2}$ in V) and standard deviation for scan rates of 50, 100, 200, 500, 1000, and 2000 mV/s. ^c Scan rate of 500 mV/s. ^d Mononuclear complexes. ^e Average and standard deviation for scan rates of 50, 500, and 1000 mV/s.

**Figure 4.** Emission spectra of (bpy)Ru(CN)Cr(NH₃)₂⁶⁺ in DMSO-H₂O glass at 77 K (a), contrasted to the spectrum of the (³CT)Ru(bpy)₂(CN)₂ parent (b). Excitations at 400 nm.

and the *trans*-Rh(NH₃)₄X²⁺ (X = I or Br) metalates were complicated by photodecomposition of the metalated substrates, and this often resulted in the presence of small amounts of the strongly emitting Ru(bpy)₂(CN)₂ parent. This feature is illustrated in Figure 4 (note that the emission yield from the Ru(bpy)₂(CN)₂ parent is at least 10 times greater than that of the typical ²E emission of a Cr(III) pentaammine) and noted in Table IV. To monitor for the possibility of increased Ru(bpy)₂(CN)₂ contamination of the spectra obtained by repetitive pulsing for signal averaging, we compared the averaged spectra (and lifetimes) to those obtained from single pulse excitation of the complexes. The Ru(bpy)₂(CN)₂ emission was also identified by its emission lifetime and the solvent dependence of the spectrum and lifetime.

Luminescence lifetimes were temperature dependent for all the emitting complexes. We have found that the temperature dependencies of the (³CT)Ru(bpy)₂²⁺ excited-state lifetimes in the Rh(NH₃)₅³⁺ metalates were complex (Figure 5) but instructive. Both Ru(CNRh)³⁺ and Ru(CNRh)₂⁶⁺ had more strongly temperature-dependent lifetimes in fluid solution than did the Ru(bpy)₂(CN)₂ parent. At temperatures above the glassy region (i.e., with $T \geq 220$ K) of the DMSO-H₂O solvent system, the very shallow temperature dependence of the Ru(bpy)₂(CN)₂ complex could be fitted with an Arrhenius activation energy of $E_a \approx 1.0$ kcal mol⁻¹.⁵³ The bis-metalated Ru(CNRh)₂⁶⁺ complex was reasonably well-represented throughout the same temperature regime by $E_a \approx 8$ kcal mol⁻¹ but with a 10⁶-fold greater preexponential factor than that of the parent ($A \approx 1.5 \times 10^{13}$ and 1.5×10^7 s⁻¹, respectively). In this same temperature regime and

(53) The lifetime of this complex increased systematically by about a factor of 2 between 210 and 298 K in the fluid DMSO-H₂O solutions. The uncertainties in these measurements preclude any evaluation of deviations from simple Arrhenius behavior.

**Figure 5.** Temperature-dependent lifetimes of (a) Ru(bpy)₂(CN)₂, (b) (bpy)₂(CN)Ru(CNRh(NH₃)₃)³⁺, and (c) (bpy)₂Ru(CNRh(NH₃)₃)₂⁶⁺ in DMSO-H₂O (1:1, v/v).**Figure 6.** Emission spectrum of (bpy)₂(CN)Ru(CNRh(NH₃)₄I)²⁺ in DMF-CHCl₃ glass (3:1, v/v) at 77 K.

medium, the monometalated Ru(CNRh)³⁺ complex exhibited both kinds of behavior (Figure 5): (a) $E_a \approx 1$ kcal mol⁻¹ and $A \approx 0.6 \times 10^7$ s⁻¹ for $270 \geq T/K \geq 220$ and (b) a steeper slope for $T > 270$ K which corresponded to $E_a \approx 5$ kcal mol⁻¹. Approximate deconvolution of the two components leads to larger values of E_a in the high-temperature regime, with uncertainties on the order of 15% in E_a . These Arrhenius-fitting parameters are summarized in Table IV.

The determinations of relative radiative yields were much less susceptible to spurious Ru(bpy)₂(CN)₂ emissions, and these measurements demonstrate that the systems in which such spurious emissions were found were all systems in which the Ru chromophore emission was largely quenched. We have used the measured lifetimes and relative quantum yields to obtain estimates of the variations in radiation rates, $k_r = \eta_r \tau^{-1}$. Our observations, summarized in Table V, indicate that Rh(III) metalation of the cyanides increases the radiative rates, k_r , for (³CT)Ru(bpy)₂(CN)₂. However, bis-metalation with either Cr(NH₃)₅³⁺ or Rh(NH₃)₅³⁺ effectively quenches the ambient (³CT)Ru(bpy)₂(CN)₂ luminescence. For the chromium(III) metalates, we have observed the characteristically sharp and long-lived (²E)Cr(III) luminescence at 77 K (Figure 4).

Anomalous emissions were found for several Ru-Rh complexes, and, as noted above, these could usually be ascribed to small amounts of Ru(bpy)₂(CN)₂ impurities. These effects dominated the behavior in DMSO-H₂O mixtures, even at 77 K, of the Rh(NH₃)₄I²⁺ metalate. Somewhat cleaner emissions were found for the Ru(CNRhBr)²⁺ complex in DMSO-H₂O glasses at 77 K. The 77 K emission spectrum obtained from Ru(CNRhI)²⁺ was very peculiar even in the DMF-CHCl₃ glass (Figure 6). The two emission maxima observed were at 590 and 635 nm. These emission maxima are each red shifted from the expected emission maxima of Ru(CNRhX)²⁺ ($\lambda_{max} = 577$ nm) and Ru(bpy)₂(CN)₂

Table IV. Emission Maxima, Lifetimes, and Activation Parameters for Excited-State Decays of Metalates of Ru(bpy)₂(CN)₂^a

metalate	DMSO-H ₂ O (1:1)				DMF-CHCl ₃ (3:1)			
	298 K	77 K	Ru-centered (<i>k</i> _{RuCN})		Rh-centered (<i>k</i> _{Rh})		298 K	77 K
			<i>A</i>	<i>E</i> _a	<i>A</i>	<i>E</i> _a		
<i>b</i>	634 (0.43)	573 (4.3)	1.5 × 10 ⁷	1.0			672 (0.225)	610 (4.2)
Rh(NH ₃) ₅ ³⁺	604 (0.31)	556 (5.7)	0.6 × 10 ⁷ ^c	10 ^c	10 ¹² ^c	8 ^c	626 (0.61)	577 (6.1)
[Rh(NH ₃) ₅] ₂ ⁶⁺	576 (0.04)	543 (8.4)	<i>d</i>	<i>d</i>	1.5 × 10 ¹³	8	589 (0.05)	553 (7.6)
<i>trans</i> -Rh(NH ₃) ₄ CN ²⁺	606 (0.40)	556 (6.0)					630 (0.63)	578 (6.25)
<i>trans</i> -Rh(NH ₃) ₄ Br ²⁺	620 (0.04, 0.22) ^e	554 (5.0)					632 (0.22)	577 (5.8)
<i>trans</i> -Rh(NH ₃) ₄ I ²⁺	[631 (0.35)] ^f	572 (3.9) ^f					650 (0.06)	590 (5.3)
Cr(NH ₃) ₅ ³⁺		738 ^g						
[Cr(NH ₃) ₅] ₂ ⁶⁺	<i>h</i>	680 ⁱ (78)					(≤0.04)	680 (78) ⁱ

^a λ_{max} in nanometers for solvents indicated; lifetimes, μs in parentheses; activation energies in kcal mol⁻¹ for fluid solution; *A* in s⁻¹. ^b Ru(bpy)₂(CN)₂. ^c Approximate resolution of two-term rate law: *k*_{Ru} + *k*_{Rh}. The components were resolved in different temperature regimes. ^d Not resolved in fluid solution. ^e Components of biphasic decay. ^f Weak emission, probably Ru(bpy)₂(CN)₂; a short-lived decay (≤40 ns) was also observed. ^g Minor component (~30%) of preparative mixture. ^h Not detected. ⁱ Narrow band emission due to (²E)Cr(III).

Table V. Relative Radiative Rate Constants (*k*_r) and Emission Quantum Yields (η) (25 °C DMSO-H₂O (1:1), Deaerated Solutions)

metalate of Ru(bpy) ₂ (CN) ₂ ⁻	<i>k</i> _r (complex)/ <i>k</i> _r (parent)	η(complex)/η(parent)	λ _{excitation}
(parent)	1.00	1.00	
<i>trans</i> -Rh(NH ₃) ₄ CN ²⁺	1.27	1.20	421
Rh(NH ₃) ₅ ³⁺	1.44	1.12	421
[Rh(NH ₃) ₅] ₂ ⁶⁺	2.00	0.16	421
<i>trans</i> -Rh(NH ₃) ₄ Br ²⁺		≤0.26	417
<i>trans</i> -Rh(NH ₃) ₄ I ²⁺		≤0.09	421
[Cr(NH ₃) ₅] ₂ ⁶⁺		0.00	421

(λ_{max} = 610 nm), and we resolved a single (4 μs) decay component from the 77 K luminescence. This contrasts to the ambient solution behavior of Ru(CNRhBr)²⁺, under conditions where partial photodecomposition occurred (emission maximum in DMSO-H₂O at 620 nm, compared to 604 nm for the Rh(NH₃)₅³⁺ metalate and 631 nm for the unmetalated Ru(bpy)₂(CN)₂ parent). We resolved two luminescence decay components in these ambient DMSO-H₂O solutions of Ru(CNRhBr)²⁺. Two decay components and the observed emission maximum are the expected results of partial photodemetalation in fluid solutions. The Ru(CNRhI)²⁺ emission in DMF-CHCl₃ at 77 K is not as readily attributable to a combination of metalate and parent emissions. Rather it appears different from the expectation for either. Although the signal-to-noise was poor for small numbers of accumulations, we could find no significant differences in the spectra obtained after 1–3 accumulations and those which resulted from multiple accumulations of the Ru(CNRhI)³⁺ emission. Perdeuteration, to form (bpy)₂(CN)Ru(*trans*-CNRh(ND₃)₄X)²⁺, increased the 77 K emission lifetime of the iodo complex metalate by about 20% (with a somewhat broader emission spectrum) and had smaller effects on the (³CT)Ru decay lifetimes of the Rh(ND₃)₅³⁺ metalated complexes.

C. Picosecond Flash Photolysis Studies. We have examined some of the binuclear complexes for fast relaxation processes at 25 °C by using a 18-ps pulse and time-delayed absorption spectroscopy. Strong bleaching of the ground-state MLCT absorption was observed when the metalated complexes were irradiated at 355 nm. The ground-state absorption spectrum was recovered in time periods ranging from less than 25 ps (for metalation with Ru(NH₃)₅³⁺^{28b}) to tens of nanoseconds or longer. Most of the polypyridyl-ruthenium(II) complexes that we have examined exhibit small changes in the intensities and energies of their absorption bands during the first 25–100 ps after the pulse. The small changes observed in the transient spectrum of Ru(CNRhCN)²⁺ (Figure 7A) are reasonably typical of such small amplitude absorbance changes. These features may be attributable to the resolution of the MLCT excited state.⁵⁴ We consider here only the larger amplitude, usually slower changes in the transient absorption spectrum. At the time of our experiments, the detection

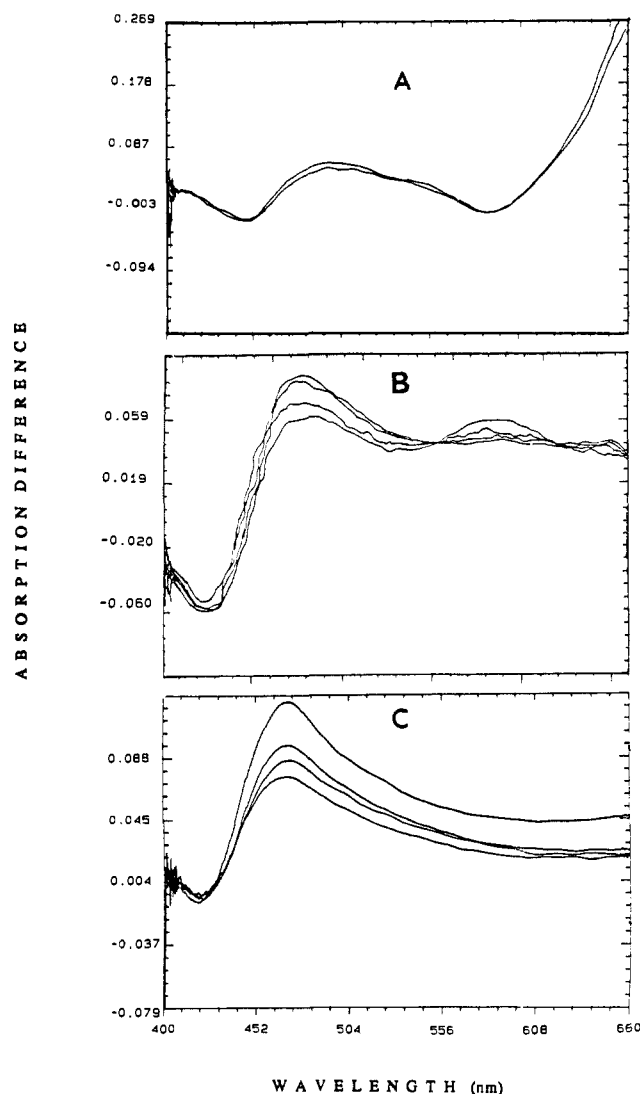


Figure 7. (A) Difference spectra of (bpy)₂(CN)Ru(*trans*-CNRh(NH₃)₄CN)²⁺ for 0 and 20 ns delays following picosecond excitation (top and bottom spectra, respectively). (B) Difference spectra of (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ at various time delays following picosecond excitation: top to bottom for λ < 500 nm; 0, 5, 10, 20 ns (opposite order for λ > 600 nm). (C) Difference spectra of (bpy)₂Ru(CNRh(NH₃)₅)²⁺ at various time delays following picosecond excitation: from top to bottom, 0, 5, 10, 20 ns.

sensitivity was poor in the 400–450-nm region. This resulted in very noisy signals when there was appreciable substrate MLCT bleaching, and transient changes in absorption in this region were rarely useful.

Several transient absorption changes were observed following MLCT excitation of (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ (Figure

(54) Winkler, J. R.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 3470.

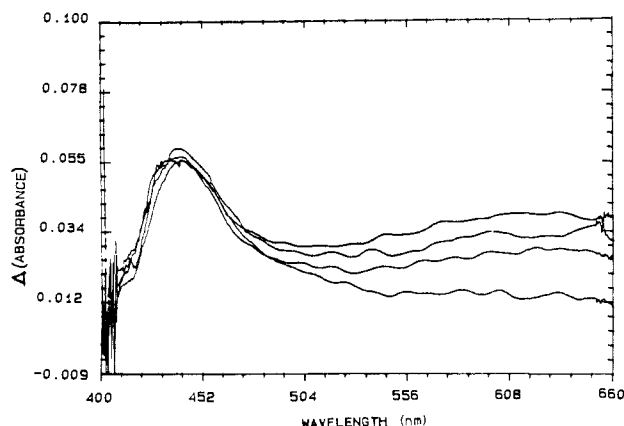


Figure 8. Difference spectra of $(\text{bpy})_2\text{Ru}(\text{CN}(\text{Cr}(\text{NH}_3)_5)_2)^{6+}$ at various time delays following picosecond excitation: from top to bottom at 550 nm, 0, 250, 700, and 3×10^3 ps.

7B). The absorbance at $\lambda > 450$ nm increased during excitation, and an apparent absorption maximum developed at 480 nm in 0–25 ps. The actual absorption maximum is probably at higher energy⁵⁵ than indicated by the difference spectra in Figure 8 since the difference spectra are distorted by strong substrate bleaching in this region. The 480-nm absorbance decreased (about 5–25%) rapidly during the first 1000 ps and then much more slowly over a period of more than 10 ns. Nearly parallel with the initial rapid decrease of the 480-nm absorbance, a new absorption band grew in at 585 nm. This new band decayed in concert with all other transient absorbances and bleachings over a time period greater than 10 ns.

Our initial observations on the $(\text{bpy})_2\text{Ru}(\text{CNRh}(\text{NH}_3)_5)_2^{6+}$ complex suggested rather complicated transient behavior. However, some of the absorbance changes did not correlate with the time delay between picosecond pump and probe, and we inferred that this complex photodecomposes in the spectrometer. On the other hand, transient absorbance changes determined by using a flow cell (Figure 7C) decayed monotonically with a lifetime of about 50 ns, in good agreement with the results of our luminescence measurements.

The transient spectrum obtained from $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_4\text{CN})^{2+}$ showed a remarkably strong near infrared absorption (Figure 7A). This spectrum did not decay significantly in 20 ns (note that our luminescence studies indicate that the lowest energy excited state of this complex has a 400-ns ambient lifetime), and there was no evidence of photodecomposition.

The $\text{Ru}(\text{CNRhBr})^{2+}$ and $\text{Ru}(\text{CNRhI})^{2+}$ complexes were so photosensitive that not much of their value could be obtained from our picosecond studies. All the transient spectra obtained from $\text{Ru}(\text{CNRhI})^{2+}$ were indistinguishable from the picosecond spectra of $\text{Ru}(\text{bpy})_2(\text{CN})_2$. There were suggestions of a genuine short nanosecond transient obtained upon excitation of $\text{Ru}(\text{CNRhBr})^{2+}$, but we have been unable to verify this owing to the limited amounts of compound available.

The picosecond transient spectra of $\text{Ru}(\text{CNCr}(\text{NH}_3)_5)_2^{6+}$ were also complicated by photodemetalation. Only when we used a flow cell did we obtain a reasonably consistent set of transient spectra (Figure 8). These spectra indicated that the substrate bleaching at 413 nm and a new absorbance at $\lambda \leq 438$ nm (maximum uncertain owing to overlap with the bleached region) persisted after 20 ns. Since the $(^3\text{CT})\text{Ru}(\text{bpy})_2$ excited state is apparently greater than 99% quenched under these conditions, these features would seem to be associated with product formation. The positive absorbance ($\lambda \leq 438$ nm) is consistent with formation of $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNCr}(\text{NH}_3)_5)^{3+}$ ($\lambda_{\text{max}} = 430$ nm) but not with the parent ($\lambda_{\text{max}} = 457$ nm). We were unable to resolve any systematic time dependence of the spectral changes ($\leq 20\%$) in

Table VI. Summary of Rate Constants for Bimolecular Quenching of $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2^a$

acceptor	$k_q \times 10^{-9}$ ($\text{M}^{-1} \text{s}^{-1}$)	acceptor	$k_q \times 10^{-9}$ ($\text{M}^{-1} \text{s}^{-1}$)
$\text{Rh}(\text{NH}_3)_5\text{Br}^{2+}$	0.157	<i>trans</i> - $\text{Rh}(\text{NH}_3)_4\text{Br}_2^+$	0.890
$\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$	0.338	<i>trans</i> - $\text{Rh}(\text{NH}_3)_4\text{I}_2^+$	3.063
<i>trans</i> - $\text{Rh}(\text{NH}_3)_4\text{Cl}_2^+$	0.156		

^aOn the basis of donor lifetime measurements at 298 K in 1.0 M NaCF_3SO_3 .

this wavelength region ($\lambda < 450$ nm). This suggests that there is substantial demetalation during the 18-ps excitation pulse. In view of the small transient absorbance changes in the wavelength region (< 450 nm) characteristic of absorption by the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore, we found surprising the substantial transient absorption changes in the long wavelength region. At very short times there was a very broad absorption feature which had a maximum at about 610 nm. This feature decayed with a rate constant of about $1 \times 10^7 \text{ s}^{-1}$. It seems most likely that this absorption feature should be assigned to either the decay (without much demetalation) of a $(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)(\text{CN}(^2\text{E})\text{Cr}(\text{NH}_3)_5)^{6+}$ species or to the relaxation of some other intermediate Cr(III) species. These possibilities will be examined in greater detail elsewhere.⁵⁶

D. Bimolecular Quenching of $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$. Several haloamminerhodium(III) complexes have been found to be efficient quenchers of $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$, with $1 \times 10^8 < (k_q \text{M}^{-1} \text{s}^{-1}) \leq 3 \times 10^9$. The results of these determinations are listed in Table VI.

E. Excited-State Electronic Structures of Donor and Acceptor Centers. When the donor-acceptor electronic coupling is sufficiently small, estimates of the energies of the lowest donor and acceptor excited states can be based on appropriate monomer complexes. Since we have employed pentaammine and tetraammine acceptors, the acceptor energy states can be based on perturbational corrections of the corresponding $\text{M}(\text{NH}_3)_6^{3+}$ energies. Similarly, the donor energies can be based on perturbational corrections of the excited-state energies of $\text{Ru}(\text{bpy})_2(\text{CN})_2$. This approach is undoubtedly best for the lowest energy excited states, and it provides logical basis for the detailed consideration of excited-state processes in these systems. It is important to note that none of the quenchers employed here have significant absorptions (absorptivities are less than $1 \text{ M}^{-1} \text{ cm}^{-1}$) in the spectral region of the $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ emissions in the metalated compound. This qualitatively demonstrates that the spin-allowed electronic transitions of the acceptors occur at relatively high energy. In the $\text{M}(\text{NH}_3)_6^{3+}$ monomers these are typical Laporte forbidden metal centered d-d absorptions (absorptivities less than $100 \text{ M}^{-1} \text{ cm}^{-1}$) for $\text{Cr}(\text{NH}_3)_6^{3+}$, $\lambda_{\text{max}} = 452$ nm, while for $\text{Rh}(\text{NH}_3)_6^{3+}$, $\lambda_{\text{max}} = 305$ nm. In the cyanometalate complexes these d-d absorptions are masked by the much more strongly allowed ($^1\text{A}_1 \rightarrow ^1\text{CT}$) $\text{Ru}(\text{bpy})_2(\text{CN})_2$ transitions (absorptivities about $10^4 \text{ M}^{-1} \text{ cm}^{-1}$; see Table II).

The acceptor energies estimated for the $(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)_2^{6+}$ complex are summarized in Figure 9. The energy of the lowest ^2E excited state is based on the observed emission; higher energy states are based on $\text{Cr}(\text{NH}_3)_6^{3+}$. An excited-state, metal-to-metal, ($^1\text{A}_1$) $\text{Ru}(\text{II}) \rightarrow (^2\text{E})\text{Cr}(\text{III})$, charge-transfer transition is expected at about $12 \times 10^3 \text{ cm}^{-1}$ above the energy of the ^2E excited state, based on simple considerations.^{57,58} It is clear that the ($^4\text{T}_2$) $\text{Cr}(\text{NH}_3)_5^{3+}$ acceptor state and the $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ donor state of $(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)_2^{6+}$ have

(56) Buranda, T.; Endicott, J. F. Work in progress.

(57) (a) Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777. (b) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301. (c) Endicott, J. F.; Tamilarasan, R.; Brubaker, G. R. *Ibid.* **1986**, *108*, 5193.

(58) Estimate based on an excited state, ($^2\text{E})\text{Cr}(\text{III}) \rightarrow \text{Cr}(\text{II})$, reduction potential of about 0.7 V⁴⁰ compared to about 0.1 V for the pentaammine-rhenium(III)-(II) couple. This difference in potentials would contribute a $5 \times 10^3 \text{ cm}^{-1}$ red shift of the $\text{Ru} \rightarrow \text{Cr}$ MMCT transition (compared to the analogous $\text{Ru} \rightarrow \text{Ru}$ transition^{21a}).

(55) Excited-state absorption maxima have been reported for $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$ at 430 nm: (a) Benasson, R.; Salet, C.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 3722. (b) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

Table VII. Excited-State Properties of Some Metalates of Ru(bpy)₂(CN)₂^a

metallate	ν_{\max} , cm ⁻¹ /10 ³ ³ CT emission (77 K)	ν_o , cm ⁻¹ /10 ³ ³ CT donor ^b	ν_o , cm ⁻¹ /10 ³ acceptor ^c	* $E_{1/2}(D^+/*D)$, ^d V vs SSCE	$\delta\Delta E_{DA}$, ^e kcal mol ⁻¹	10 ⁻⁶ k_{nr} , ^f s ⁻¹
<i>g</i>	17.45	16.0 ^e		1.26		
Rh(NH ₃) ₅ ³⁺	17.98	16.8 ^e	19.7	1.09	8	44
[Rh(NH ₃) ₅] ₂ ⁶⁺	18.42	17.6 ^e	19.7	0.99	6	44
<i>trans</i> -Rh(NH ₃) ₄ CN ²⁺	17.98	17.6 ^e	23.6		17	
<i>trans</i> -Rh(NH ₃) ₄ Br ²⁺	18.05	17.6 ^e	16.4		-3	60
<i>trans</i> -Rh(NH ₃) ₄ I ²⁺	(16.95) ^h	16.8 ⁱ	15.3	1.16	-4	150
Cr(NH ₃) ₅ ³⁺	<i>j</i>	18.3 ⁱ	13.55 ^k [18.5] ^l	1.22		
[Cr(NH ₃) ₅] ₂ ⁶⁺	<i>j</i>	18.9 ⁱ	14.71 ^k [18.5] ^l	1.01		

^aDMSO-H₂O. ^bEstimate based on photoacoustic measurements of (³CT)Ru(bpy)₂²⁺ excited-state energy (ref 48) adjusted for variations of ambient emission maxima. ^c(³T₁)Rh and (⁴T₁)Cr(III) energies based on ligand field splittings expected on M(NH₃)₆³⁺ spectrum from substitution of NH₃ by NCRu assuming Dq(CNRu) ≈ Dq(NCS⁻). (²E)Cr(III) energies based on observed emission. ^dEstimates based on $E_{1/2}(D^+/D) - E(^3CT)$. Entropy contributions might make these couples less reducing by as much as 0.1 V. ^e $E_{DA} = E(\nu_o, \text{acceptor}) - E(\nu_o, \text{donor})$. ^fNonradiative rates (k_{nr}) in H₂O based on pentaammine (or hexaammine) analogues (refs 30, 36, and 40). ^gRu(bpy)₂(CN)₂. ^hNo emission observed in DMSO-H₂O (emission in DMF-CHCl₃). ⁱEstimate corrected for variation of $E_{1/2}$. ^jNo (³CT)Ru(II) emission resolved for the metallate. ^kObserved (²E)Cr(III) emission. ^lEstimated excited-state quartet origin.

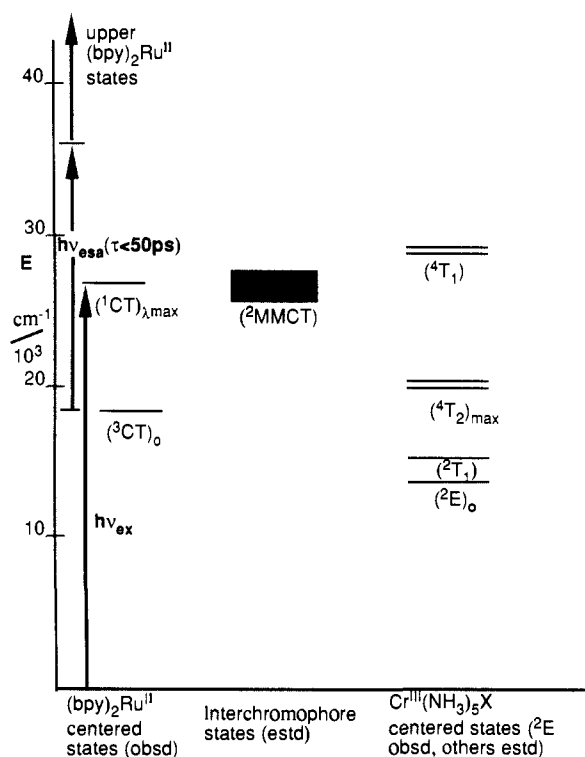


Figure 9. Relative energies (calculated and observed) of donor and acceptor electronic states in (bpy)₂Ru(CN)Cr(NH₃)₅⁶⁺. Subscripts: max = absorption maximum, 0 = electronic origin, and esa = excited state absorption (range of spectral observations indicated by arrows). See text for details of estimates.

very similar energies. In fact, our estimates of the origin of this acceptor excited state, based on typical absorption band widths of Cr(III) complexes^{30,40} and assuming that the ⁴T₂ excited state of Ru(CN)Cr(NH₃)₅³⁺ is well approximated by (⁴T_{2g})Cr(NH₃)₆³⁺, indicate 400-cm⁻¹ lower energy for the (⁴T_{2g})Cr(NH₃)₅³⁺ acceptor than for the (³CT)Ru(bpy)₂²⁺ donor state. The origin of the ²E state is about 5160 cm⁻¹ lower than the donor energy.

The structured, 4.2 K Rh(NH₃)₆³⁺ emission data of Hakamata et al.⁴⁹ suggest that the lowest energy triplet excited state of this complex has an electronic origin of slightly more than 20 × 10³ cm⁻¹. This is approximately 2.9 × 10³ cm⁻¹ (8 kcal mol⁻¹) higher than our estimate of the (³CT)Ru(bpy)₂²⁺ donor energy in (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺. The relatively low energy (²E)Cr(III) emissions observed in the Cr(NH₃)₅³⁺ metalates indicates that the RuCN ligand is a very good π-acceptor, analogous to imine or nitrile ligands. We have therefore assumed that RuCN is as effective in promoting d-orbital splittings as are imine ligands, and we tentatively place the electronic origin of the (³T₁)Rh(NH₃)₅³⁺ acceptors at 19.7 × 10³ cm⁻¹. The energies of the Rh(NH₃)₄X²⁺ acceptor excited state (in metalated complexes)

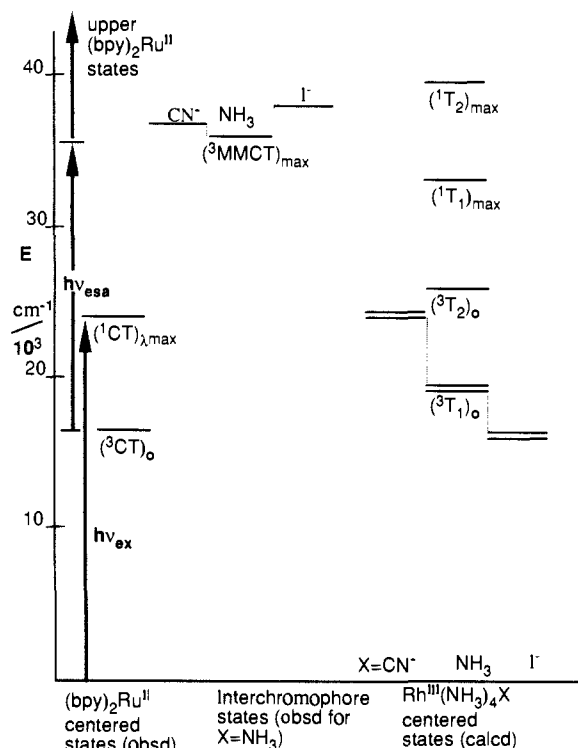


Figure 10. Relative energies (calculated and observed) of donor and acceptor electronic states in (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺. Subscripts, etc., are the same as in Figure 9. The direction of changes in energy of the acceptor state are indicated for (bpy)₂(CN)Ru(CNRh(NH₃)₄CN)²⁺ and (bpy)₂(CN)Ru(CNRh(NH₃)₄I)²⁺.

can be estimated, relative to (³T₁)Rh(NH₃)₅³⁺, based on the differences in the ligand field parameters of X and NH₃. Thus we estimate a decrease of 4.4 × 10³ cm⁻¹ in the acceptor state energy when NH₃ is replaced by I⁻ and an increase of 3.9 × 10³ cm⁻¹ when NH₃ is replaced by CN⁻. This approach may overestimate these energy differences, but one can be confident that the relative ordering of excited-state energies and that even the approximate magnitudes of the variations (i.e., about (1–4) × 10³ cm⁻¹) are correct.

We have assigned an excited-state absorption, observed in the (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ complex, as a metal-to-metal, (¹A₁)Ru(II) → (³T₁)Rh(III), charge-transfer (MMCT) absorption based on analogy to the ground-state MMCT absorption in the analogous Ru(NH₃)₅³⁺ metalates^{21a} since both (²T₂)Ru(III) and (³T₁)Rh(III) each have one partly occupied nonbonding t_{2g} orbital.

Our energy estimates for Rh(III) monometalates are summarized in Figure 10.

We have found no good basis for estimating the energies of the metal-centered, d-orbital excited states of the Ru(bpy)₂(CN)₂ donor. These states have been implicated in the nonradiative

relaxation behavior of $(^3\text{CT})\text{Ru}(\text{bpy})_3^{2+}$.⁵⁹ They will certainly be higher in energy in $\text{Ru}(\text{bpy})_2(\text{CN})_2$ than in $\text{Ru}(\text{bpy})_3^{2+}$. We have found no evidence that the metal-centered donor states play a significant, direct role in the behavior of the cyanometalates reported in this paper.

Discussion

This study has employed techniques, concepts, and materials which have evolved during the past couple of decades to examine the problem of energy transfer in covalently linked donor–acceptor systems. The complexes studied were selected because the acceptor electronic structures and chemistries are well understood, and because it is possible to make critical comparisons between photophysical processes in the covalently linked systems and in their mononuclear components. This study has shown that even though the $(^3\text{CT})\text{Ru}(\text{II})$ donor and the $\text{M}^{\text{III}}(\text{NH}_3)_4\text{X}$ acceptors are “strongly coupled” by means of a cyanide-bridged ligand, they do often function nearly as expected for the independent donor and acceptor systems. The extent of electronic coupling and independence of the donor and acceptor centers are major issues explored below.

There are several possible relaxation pathways for the “localized” $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ excited state in these multinuclear complexes. These may be briefly summarized as (a) charge transfer to the covalently linked acceptor, (b) the normal donor (radiative and nonradiative) relaxation channels, and (c) energy transfer to the covalently linked acceptor.

The excited-state reduction potentials are negative enough that some consideration must be given to the possibility of excited-state donor–acceptor electron transfer, although this process is most likely thermodynamically unfavorable for the Cr(III) acceptors and only marginally possible for most of the Rh(III) acceptors ($\text{Ru}(\text{CNRh})^{2+}$ is a possible exception). We note that the transient absorption spectra in Figure 7 are qualitatively similar to the comparable spectra generated from $\text{Ru}(\text{bpy})_2(\text{CN})_2$ and $\text{Ru}(\text{bpy})_3^{2+}$ in the short wavelength region ($\lambda \leq 500$ nm; there are differences of detail, of course) and are in contrast to the transient spectra generated by excitation of the related $\text{Ru}(\text{CNRu})^{3+}$ and $\text{Ru}(\text{CNCr})^{3+}$ complexes, in which efficient “electron transfer” appears to occur.⁶⁰ We have found that transient spectra of the electron-transfer systems lack the positive absorption feature at about 450 nm (which seems to be a $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ -centered absorption),⁵⁵ exhibit their strongest substrate bleaching between 440 and 460 nm, and exhibit a characteristic broad and intense absorption at the red end of the spectrum ($\text{Ru}(\text{III})?$). In addition there is no correlation between observed transient behavior and $*E_{1/2}(\text{D}^+/\text{D})$, while transient behavior does correlate with ΔE_{DA} in the Ru–Rh and Ru–Cr systems, and the products of photo-reaction have the spectral characteristics of substitutional rather than redox products. This latter point is even true of $(\text{bpy})_2\text{-(CN)Ru}(\text{CNRh}(\text{NH}_3)_4\text{I})^{2+}$ (products observed in picosecond flash photolysis studies), although we would be reluctant to rule out electron transfer only on this basis.

It is clear (e.g., from emission spectra) that some of the electronically excited Ru–Rh complexes do decay predominantly by means of the Ru-centered excited-state relaxation channels. However, when the acceptor has electronic excited states lower in energy than the energy of the $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ donor, the characteristic Ru-centered decays are quenched. We ascribe the excited-state behavior of the Ru–Cr and Ru–Rh complexes to donor–acceptor energy transfer. Transfer of energy to the $\text{M}^{\text{III}}(\text{NH}_3)_4\text{X}$ center can be followed by (a) back transfer to $\text{Ru}(\text{bpy})_2^{2+}$, (b) nonradiative or radiative relaxation of $\text{M}^{\text{III}}(\text{NH}_3)_4\text{X}$, and (c) substitution into the M^{III} coordination sphere. The resulting scheme is summarized in Figure 1.

The energy-transfer processes which are important here involve dipole forbidden ground-state excited-state transitions at the donor and acceptor chromophores (no significant acceptor absorbance in the region of donor emission). Consequently the Förster

mechanism^{11,23,61–63} of energy transfer is inefficient, and the transfer processes are mediated by an exchange mechanism.²⁴ The theoretical formalisms describing the exchange pathway²⁴ have many general features in common with those describing electron-transfer pathways.¹¹ Thus such energy-transfer processes can be treated formally in much the same way as simple chemical reactions, and this class of energy-transfer processes are being increasingly used to examine some aspects of the electronic constraints on elementary processes.^{1,7c,7d,9c,11,57} Our observation of a simple stepwise equilibration between donor and acceptor excited states in the $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_5)^{3+}$ complex is a gratifying demonstration that energy transfer in such a system does have many features of a simple chemical process. However, since some general features of the cyanometalate systems are simpler with the $\text{Cr}(\text{NH}_3)_5^{3+}$ adducts, these complexes are discussed first.

A. Energy Transfer in Cyano-Bridged Ru–Cr Complexes. The observation of sensitized luminescence from $(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)^{6+}$, following excitation of the $\text{Ru}(\text{bpy})_2^{2+}$ chromophore (at 77 K), clearly demonstrates the intramolecular energy-transfer process.⁶⁴ Provided the donor and acceptor function reasonably independently, at least three possible energy-transfer pathways can be distinguished: (i) $(^3\text{CT})\text{Ru} \rightarrow (^2\text{E})\text{Cr}(\text{III})$, (ii) $(^3\text{CT})\text{Ru} \rightarrow (^4\text{T}_2)\text{Cr}(\text{III})$, and (iii) pathways involving higher donor excited states. We will only consider the lower energy donor pathways. Population of either the ^2E - or $^4\text{T}_2\text{Cr}(\text{III})$ excited states appears to be energetically favorable for energy transfer from the bis-metalated $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ donor (see Figure 11). Comparison with the bimolecular $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2 \rightarrow (^2\text{E})\text{Cr}(\text{NH}_3)_6^{3+}$ energy-transfer process⁶⁵ would lead one to expect⁶⁵ $k_{12}(\text{Cr}) \geq 2 \times 10^8 \text{ s}^{-1}$ in the metalated complexes for direct $(^3\text{CT})\text{Ru} \rightarrow (^2\text{E})\text{Cr}(\text{III})$ energy transfer. However, the picosecond flash photolysis results indicate that most of the demetalation of the electronically excited, bis-metalated complex occurs in less than 25 ps. This observation is reminiscent of the “prompt” photochemical processes which are characteristic of the population of $^4\text{T}_2$ excited states of Cr(III) ammine complexes.⁶⁶ The $(^4\text{T}_{2g})\text{Cr}(\text{NH}_3)_6^{3+}$ excited state is appreciably distorted along Cr–N skeletal modes⁶⁷ (with respect to the O_h ground state), and such distortions are presumed characteristic of the $(t_{2g}^2e_g)$ metal orbital population of the lowest energy quartet states of Cr(III) amines.⁶⁷ As a consequence the $(^3\text{CT})\text{Ru} \rightarrow (^4\text{T}_2)\text{Cr}(\text{III})$ energy-transfer process can be described as a semiclassical surface crossing for which the rate constant is given by^{26,57}

$$k_{\text{en}} = \kappa_{\text{el}}\kappa_{\text{nu}}\nu_{\text{nu}}\Gamma \quad (4)$$

where κ_{el} and κ_{nu} are the electronic and nuclear transmission coefficients (or retardation factors), ν_{nu} is the mean frequency of

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(62) Yardley, J. T. *Introduction to Molecular Energy Transfer*; Academic Press: New York, 1980.

(63) Tamilarasan, R.; Endicott, J. F. *J. Phys. Chem.* **1986**, *90*, 1027.

(64) (a) Scandola and co-workers^{64b} have very recently reported a similar sensitized luminescence in the closely related $(\text{bpy})_2\text{Ru}(\text{NCCr}(\text{CN})_5)_2^{4+}$ complex. (b) Bignozzi, C. A.; Indelli, M. T.; Scandola, F. *J. Am. Chem. Soc.* **1989**, *111*, 5192.

(65) It has been argued elsewhere⁶⁵ that the bimolecular $\text{Cr}(\text{NH}_3)_6^{3+}$ quenching of $(^3\text{CT})\text{Ru}(\text{bpy})_2$ ($k_{\text{bi}} = 6.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)⁶⁵ is exchange allowed with a rate given by^{24,63} ($k_{\text{en}} = (H_{\text{RP}})^2(\text{FC})\gamma$, where $k_{\text{en}} = k_{\text{bi}}/K_0$, K_0 is an association constant (estimated⁶⁵ to be $K_0 \approx 1.2 \text{ M}^{-1}$) for bringing the reactants into van der Waals contact, γ is a collection of constants, (FC) is a Franck–Condon (or nuclear reorganizational) factor, and H_{RP} is the appropriate electronic matrix element (see also eq 4). H_{RP} is expected to be strongly distance dependent,^{7–12,24} $H_{\text{RP}} \approx J_{\text{RP}} \exp(-\alpha r_{\text{DA}})$, where α is an inverse mean orbital radius characteristic of the donor–acceptor system, r_{DA} is the donor–acceptor separation, and the coupling constant J_{RP} is a constant characteristic of the donor–acceptor system. This factor alone predicts a more rapid energy-transfer process in the cyano-bridged than in the outer-sphere reaction system. For the $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2\text{Cr}(\text{NH}_3)_6^{3+}$ reaction, the closest approach gives $r_{\text{DA}} \geq 6 \text{ \AA}$ (average $r_{\text{DA}} \approx 8 \text{ \AA}$), while for the RuCNCr complexes $r_{\text{DA}} \approx 5 \text{ \AA}$. An earlier study⁵⁷ found that $\alpha \approx 0.55 \text{ \AA}^{-1}$ when eq 5 was fitted to the observations on $(^2\text{E})\text{Cr}(\text{III})\text{-(}^1\text{A}_1)\text{Co}(\text{III})$ energy-transfer reactions. On the basis of these various estimates of r_{DA} and α , we would expect $k_{12}(\text{Cr}) \geq 2 \times 10^8 \text{ s}^{-1}$ (or $k_{12}(\text{Cr}) \sim 10^{10} \text{ s}^{-1}$ based on the average value of r_{DA} for the bimolecular reaction).

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(59) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 339.

(60) Lei, Y.; Buranda, T.; Endicott, J. F. Work in progress.

correlated nuclear motions, and Γ is a nuclear tunneling correction factor. Since low-frequency vibrational modes are involved $\nu_{\text{nu}} \sim 10^{13} \text{ s}^{-1}$, so that $\Gamma \sim 1$ and

$$-RT \ln \kappa_{\text{nu}} \cong (\lambda/4)(1 + \Delta G^\circ/\lambda)^2 \quad (5)$$

where $\lambda = (\lambda_{\text{Cr}} + \lambda_{\text{Ru}})/2$, λ_{Cr} and λ_{Ru} are nuclear reorganizational parameters which can be obtained from the respective Stokes shifts (here, $\lambda_{\text{Cr}}^{68} \sim 5 \times 10^3$ and $\lambda_{\text{Ru}}^{69} \sim 1.6 \times 10^3 \text{ cm}^{-1}$), and ΔG° is the free energy difference between the initial and final states. For $-\Delta G^\circ$ in the range of $(0.5-1) \times 10^3 \text{ cm}^{-1}$ and $\kappa_{\text{el}} \sim 1$, k_{en} is thus estimated to be approximately 10^{12} s^{-1} . These parameters indicate that the activation barrier for $(^3\text{CT})\text{Ru} \rightarrow (^4\text{T}_2)\text{Cr}(\text{III})$ energy transfer in the bis-metalated complexes is very small (in the range of $500 \pm 200 \text{ cm}^{-1}$), which is consistent with the very efficient donor quenching in this system at all temperatures ($k_{\text{en}}(\text{calcd}) \sim 10^9 \text{ s}^{-1}$ compared to our experimentally determined lower limit of $\geq 10^7 \text{ s}^{-1}$).^{70,71} Our observations on this complex do not yet provide any information about the magnitude of the donor-acceptor coupling. Additional studies of covalently linked Ru-Cr complexes are in progress.⁵⁶

B. Energy Transfer in Cyano-Bridged Ru-Rh Complexes. The excited-state lifetimes of rhodium(III)-ammine complexes tend to fall in the range of $(1-50) \times 10^{-9} \text{ s}$ in solutions at ambient temperatures,^{31,72} and we have found that am(m)ine complexes of Rh(III) can be very efficient bimolecular quenchers of $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ (Table V). Thus we were initially surprised that most of the cyano-bridged Ru-Rh complexes exhibited characteristic $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ emissions. This apparent reversal of the reactivity order expected, and that found for Ru-Cr systems (see above), for comparable cyano-bridged and bimolecular Rh(III) quenching of $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ excited states, turns out to have its origin in the combined effect of the relatively fast equilibration of the Ru and Rh excited states, the diffusional separation of the products in the bimolecular reactions, and the details of the energetics and kinetics of these processes.

Our studies of the $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_5)^{3+}$ and $(\text{bpy})_2\text{Ru}(\text{CNRh}(\text{NH}_3)_5)^{6+}$ complexes can be readily interpreted in terms of the kinetic scheme outlined in the Experimental Section and summarized in Figure 1. The excited-state relaxation behavior of the monometalate near or just below ambient temperature suggests that eq 3 is an appropriate limit for excited-state relaxation of this complex; i.e., the $(^3\text{CT})\text{Ru}$ and $(^3\text{T}_1)\text{Rh}$ excited states are in labile equilibrium, and the excited-state lifetime is determined by an equilibrium-weighted combination of relaxation processes characteristic of the Ru center with those characteristic of the Rh center. The excited-state relaxation behavior of electronically excited $(\text{bpy})_2\text{Ru}(\text{CNRh}(\text{NH}_3)_5)^{6+}$ appears to conform to the same formal limit (i.e., eq 3), but now with $k_{23}K_{12} > k_{13}$. Our observation that a new absorbing species develops in the excited-state absorption spectrum of $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_5)^{3+}$ following picosecond excitation demonstrates the center-to-center migration of excitation energy in a polynuclear complex. The vibronic relaxation through molecular excited states immediately after light absorption by heavy metal complexes normally produces a vibrationally equilibrated distribution of the lowest energy excited states within a few picoseconds. The thermally promoted population of a higher energy state over a 1-ns time period implies that this new state was electronically isolated from the light-absorbing chromophore. There are closely related reports of photoinduced energy transfer in covalently linked donor-acceptor systems, including the observation of acceptor excitation concomitant with donor quenching,^{22d} but this is the

first direct observation of donor and acceptor equilibration in a system with only partial donor quenching. In order to proceed further with this analysis it is necessary to consider the temperature dependence of the excited-state decays in these complexes.

The data in Table IV indicate that cyanometalation of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ tends to increase the donor lifetime and that this increase in lifetime is about the same (approximately 2 μs at 77 K) for each metalation. This is probably clearest for the studies in the DMF- CHCl_3 glasses, but the only exceptions to this behavior are found in the relatively equivocal observations on the $\text{Rh}(\text{NH}_3)_4\text{Br}^{2+}$ (in DMSO- H_2O) and $\text{Rh}(\text{NH}_3)_4\text{I}^{2+}$ metalates. This observation is important since it indicates that under conditions which favor vibronic trapping of the excitation at the donor a major $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ relaxation pathway involves the CN^- ligands and that this excited-state relaxation pathway can be blocked by metalating the ligands.⁷³ This pattern persists into high-temperature regimes; however, an additional, thermally activated pathway for relaxation contributes to the high-temperature photophysics of the rhodium(III) metalates. Thus, within the limits of reasonable experimental uncertainty and some specific interpretations, the temperature dependencies of the $(^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ excited-state lifetimes of the $\text{Ru}(\text{CNRh})^{3+}$ and $\text{Ru}(\text{CNRh})_2^{6+}$ complexes are in good accord with the expectation based on eq 3, where the variations in excited-state lifetimes of these complexes are reasonably well fitted to an equation of the form

$$(\tau)^{-1} \cong k_{\text{Ru}} + (2-n)k_{\text{RuCN}} + nk_{\text{Rh}} \quad (6)$$

where n is a degeneracy factor equal to the number of metalated cyanides ($n = 0, 1, \text{ or } 2$), $2k_{\text{RuCN}}$ is the relaxation rate constant for the unmetalated $\text{Ru}(\text{bpy})_2(\text{CN})_2$ parent, and k_{Rh} and k_{Ru} are relaxation rate constants⁷⁴ for the rhodium-mediated pathway and for the $\text{Ru}(\text{bpy})_2^{2+}$ center, respectively, in the metalated complexes. The observations indicate that $k_{\text{Ru}} \ll 2k_{\text{RuCN}}$ and that k_{Rh} are nearly independent of the extent of metalation (i.e., whether $n = 1$ or 2). Equation 3 suggests that for the k_{Rh} term, $E_{\text{a}} = [E(^3\text{dd}^\circ) - E(^3\text{CT}^\circ) + E_{\text{a,nr}}]$, where the first two terms give the energy difference between donor-acceptor and the third is the activation barrier for relaxation of $(^3\text{dd})\text{Rh}(\text{III})$. The experimental activation energies suggest that the acceptor energies are a little higher than the donor energy, consistent with our estimates (Table VII and Figure 10). Even the preexponential factors are qualitatively in accord with expectation⁷⁵ for the simple scheme proposed: (a) Nonradiative relaxation of $(^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ is a forbidden process involving nuclear and electronic tunneling, and the forbiddenness is manifested in the small preexponential coefficient (i.e., a small value of the electronic matrix element for the nonradiative crossing between nested excited-state and ground-state potential energy surfaces). (b) The relaxation of a $(^3\text{dd})\text{Rh}(\text{III})$ center involves large changes in Rh-N bond lengths and is more nearly a classical surface crossing with very little, if any, electronic retardation.

An alternative to $(^3\text{CT})\text{Ru}$ relaxation by means of energy transfer to a neighboring Rh(III) center, as discussed in the preceding paragraphs, is relaxation by means of population of a $(^3\text{dd})\text{Ru}(\text{II})$ ligand field excited state. The metalation of the cyanide ligands should make them better π -acceptors and worse σ -donors, and the resulting systematic changes in the $(^3\text{CT})\text{Ru}$ - $(^3\text{dd})\text{Ru}$ energy might be postulated as the origin of the change in the relaxation pathway. However, the positive shift of $E_{1/2}$ for $\text{Ru}(\text{III})$ - (II) upon metalation is most consistent with π -stabilization of the $\text{Ru}(\text{II}) t_{2g}$ orbitals,³¹ and since we estimate the

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(69) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275.

(70) A similar semiclassical estimate of the rate constant for $(^3\text{CT})\text{Ru}(\text{II}) \rightarrow (^2\text{E})\text{Cr}(\text{III})$ would result in $k_{\text{en}} \sim 1 \text{ s}^{-1}$ since $\lambda_{\text{Cr}} \sim 0$. However, the nominal value of $|\Delta G^\circ|$ is so large for this process that one would expect much of the excess energy to appear as N-H vibrational excitation. This would have the effect of reducing $|\Delta G^\circ|$ and increasing the rate constant⁷¹ for this process to 10^{10} - 10^{12} s^{-1} (i.e., $\Gamma \gg 1$ in eq 4).

(71) Kestner, N. R.; Jortner, J.; Logan, J. J. *Phys. Chem.* **1974**, *78*, 2148.

(72) Lei, Y.; Buranda, T.; Endicott, J. F. Work in progress.

(73) It is plausible to speculate that this CN^- -mediated relaxation pathway couples the $(^3\text{CT})\text{Ru}(\text{II})$ excited state to the solvent, providing a relatively efficient route for energy disposal.

(74) The subscripts in eq 6 are chosen to emphasize the centers giving rise to each component of the relaxation time. This notation is readily related to that of the general kinetic scheme of the Experimental Section and to the photophysical parameters emphasized in Figure 1 as follows: $(\tau)^{-1} = \lambda$; $k_{13} = (k_{\text{nr}} + k_{\text{r}}) = (k_{\text{Ru}} + (2-n)k_{\text{RuCN}})$; $nk_{\text{Rh}} = k_{23}K_{12} = K_{\text{ic}}(k'_{\text{nr}} + k'_{\text{r}} + k_{\text{p}})$. Note that k_{Ru} and k_{RuCN} both have radiative and nonradiative components.

(75) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *J. Phys. Chem.* **1987**, *91*, 1095.

(³dd)Ru(II) excited-state energy to be $3.5 \times 10^3 \text{ cm}^{-1}$ greater than the energy of (³CT)Ru(bpy)₂(CN)₂, it does not appear that the ligand field excited states of Ru(II) can provide a competitive relaxation pathway. However, this pathway for excited-state relaxation might become important in bis-metalated complexes if acceptor energies at the metalate center (M(NH₃)₅) were sufficiently large. The k_{Ru} term in eq 6 allows for this possibility.

Substitution of CN⁻, Br⁻, or I⁻ for NH₃ coordinated to Rh(III) can be used to “fine tune” the energy of the (³dd)Rh(III) excited state (see Figure 10). One expects both K_{12} and k_{23} to increase through this series, in reasonable accord with observations. Thus for the respective complexes in solutions at ambient temperatures, the Rh(NH₃)₄CN²⁺ metalate has the longest (³CT)Ru(bpy)₂²⁺ lifetime (three times longer than the parent in DMF–CHCl₃), the Rh(NH₃)₅³⁺ metalate has a slightly shorter lifetime, and the Rh(NH₃)₄Br²⁺ is much shorter lived, and we were unable to detect any metalated complex emissions from the Rh(NH₃)₄I²⁺ metalate under ambient conditions. This order for the quenching efficiencies of the Rh(III) center in the metalated complexes is supported by similar order of relative (³CT)(bpy)₂(CN)Ru(CNRh(NH₃)₄X)²⁺ emission quantum yields (1.2, 1.1, ≤ 0.26 and ≤ 0.09 , respectively, Table V) and by the marked increase in photosensitivity through this series (i.e., the Rh(NH₃)₄CN²⁺ metalate is the least and the Rh(NH₃)₄I²⁺ metalate is the most photosensitive). These observations do not permit us to distinguish between the contributions of k_{23} and K_{12} , although the calculated donor–acceptor energy differences point to a very large contribution from K_{12} .

The picosecond transient absorptions (TA) spectra of (bpy)₂(CN)Ru(CNRh(NH₃)₄(CN)²⁺ (Figure 7A) exhibit an intense near-red absorption. The picosecond TA spectra of the other Rh(III) metalates have only very weak absorbances in this region. The contrast can be plausibly interpreted in terms of the blue shift expected of the ligand field bands in the cyano complex; thus, one would expect components of the (³T₂)Rh(III) excited state to have absorption maxima (¹A₁ → ³T₂) at approximately 300–330 nm (see Figure 10), and the strong red absorption in Figure 7A can be attributed to the high energy tail of a (³CT)Ru(bpy)₂²⁺ → (³T₂)Rh(NH₃)₄CN²⁺ absorption whose maximum is at 700–800 nm. There are several possible assignments of the apparent 530-nm shoulder on the 490-nm (³CT)Ru(bpy)₂²⁺ TA of this complex, e.g., it could originate from a similar transition to a higher energy Rh(III) ligand field state, a MMCT absorption, or possibly some mixed-metal state.

We were unable to resolve any distinct absorption feature attributable to a MMCT state, or any fast relaxation of the (³CT)Ru(bpy)₂²⁺ excited state in (bpy)₂Ru(CNRh(NH₃)₅)⁶⁺, comparable to those striking features in the picosecond TA of (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ (Figure 7B). This contrast probably arises from the combined effects of the very rapid overall excited-state decay of the bis-metalate and the more rapid energy-transfer rate expected in this complex, since small amplitude absorption changes would be correspondingly difficult to detect. There does appear to be appreciable (unresolved) transient absorbance throughout the long wavelength visible region of the bis-metalate.

There are two points in regard to the *bimolecular* Ru–Rh energy-transfer reactions that require further comment. First, the apparent efficiencies can be attributed to the contribution of diffusive separation (k_{-d} ; thus, $k_{23} = k'_{\text{nr}} + k'_r + k_{-d}$) of the reaction products. Secondly, much of the apparent variation of energy-transfer rates with the donor–acceptor energy difference can be ascribed to the expected variations in back-energy-transfer rate with this energy difference (ΔE_{DA}): assuming similar values of λ , eqs 3–5 indicate that k_{21} should increase about 400-fold as ΔE_{DA} decreases over the range $0 \geq \Delta E_{\text{DA}} \geq -2.5 \times 10^3 \text{ cm}^{-1}$, and we observed a 20-fold variation in k_{21} ,⁷⁶ the quenching rates appear to be nearly diffusion limited in the limit that back energy transfer is energetically prohibitive. Thus, the bimolecular quenching

(76) Note that the behavior discussed here approaches the limit in which eq 1 reduces to $\lambda_2 \approx (k_{23} - k_{21})$. The diffusional contribution k_{23} is likely to differ a little for the +1 and +2 ions.

studies indicate that *both* forward and back energy transfer, (³CT)Ru ⇌ (³dd)Rh, are very rapid.

A detailed analysis of the behavior of the metalated systems indicates that our estimates of the donor and acceptor energies, the estimated nuclear reorganizational barrier to energy transfer ($\lambda/4$), the observed photophysical behavior of the metalated complexes, and the weak coupling model are almost but not quite compatible. For example, for (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ $\lambda \sim 4.5 \times 10^3 \text{ cm}^{-1}$ ⁷⁷ so that even for isoergonic energy transfer $\Delta G^*(\text{calcd}) \approx 3 \text{ kcal mol}^{-1}$ in the weak coupling limit (i.e., based on eq 5 with $\Delta G^0 = 0$). For the estimated donor–acceptor energy difference, $\Delta G^*(\text{calcd}) \approx 9 \text{ kcal}$, which is close to the observed activation barrier of 8 kcal mol^{-1} (for τ^{-1}), but when combined with $\nu_{\text{eff}} \sim 10^{13} \text{ s}^{-1}$ (see eq 4), these estimates result in $k_{12}/k_{\text{el}} = (0.5\text{--}1.5) \times 10^7 \text{ s}^{-1}$, which is appreciably smaller than the observed relaxation rate of about 10^9 s^{-1} . Thus, the estimated excited-state parameters and the weak donor–acceptor coupling model are most consistent with $\tau^{-1} \approx k_{\text{RuCN}} = k_{12}$ but would require that the very rapid excited-state relaxation in Figure 7B is some sort of artifact. On the other hand, the very rapid equilibration between excited states would be possible if the estimated parameters were slightly in error (e.g., if ΔE_{DA} were overestimated by about $2.5 \text{ kcal mol}^{-1}$) or if there were appreciable donor–acceptor mixing so that donor and acceptor properties cannot be accurately based on the properties of the mononuclear component complexes. Unfortunately, the discrepancies are not sufficiently outside the range of uncertainties where a clear choice between the possibilities is obvious. The overall behavior of these systems leads us to suspect that donor–acceptor coupling is very strong.⁷⁸ We expect that current studies^{56,60} will provide more substantial information about donor–acceptor coupling cyanide-bridged systems.

Overall, the excited-state relaxation in the cyano-bridged Ru–Rh systems considered here is adequately described, by the simple sequence of (a) excitation and vibronic relaxation within donor electronic manifolds to generate the lowest energy donor excited state, followed by (b) energy transfer from donor to acceptor in competition with relaxation of the donor excited state to the ground state, and finally (c) relaxation of the acceptor excited state to the ground state or to products in competition with back energy transfer. Thus, in terms of the kinetic scheme developed in the Experimental Section, the observation that k_{obsd} was slightly greater than k_{13} for (bpy)₂(CN)Ru(CNRh(NH₃)₅)³⁺ indicates that $K_{12}k_{23} \sim k_{13}$. If $k_{13} \approx 1 \times 10^6 \text{ s}^{-1}$,⁷⁸ then $K_{12}k_{23} \sim 2 \times 10^6 \text{ s}^{-1}$; i.e., if $K_{12} \sim 0.1$, $k_{23} \sim 2 \times 10^7 \text{ s}^{-1}$, which is comparable in magnitude to the excited-state relaxation rates of several rhodium pentaammines investigated by Ford and co-workers,^{31,72} while $k_{21} \approx 2 \times 10^9 \text{ s}^{-1} \gg k_{23}$.

C. Concerning the Electronic Independence of the Metal Centers in the (bpy)₂(CN)Ru(CNM(NH₃)₅)³⁺ Complexes. A major element in understanding the dynamical behavior of multinuclear systems is evaluation of the electronic coupling between donor and acceptor centers. With no coupling, $\kappa_{\text{el}} = 0$, and no transfer occurs. Information about the center-to-center, Ru–M, electronic coupling may, in principle, be obtained from spectroscopic observations or more indirectly (and equivocally) from the rate of the center-to-center energy- (or electron-) transfer process. In practice, even the spectroscopic information can be misleading since the extent of coupling is expected to depend on the electronic configurations of the states involved, and the implicated states are not generally the same for the observed spectroscopic and relaxation processes. It is easiest to begin a discussion of the coupling between donor and acceptor centers by describing each

(77) On the basis of the Stokes shift inferred for Rh(NH₃)₆³⁺,⁴⁴ a Stokes shift of $1.6 \times 10^3 \text{ cm}^{-1} = 2\lambda_{\text{Ru}} \text{ for } (\text{bpy})_2\text{Ru}^{2+}$ ⁶⁹ and $\lambda = (\lambda_{\text{Rh}} + \lambda_{\text{Ru}})/2$.

(78) Among the observations which suggest that significant donor–acceptor mixing does occur in the RuCNM complexes we note the following: (a) very fast (<25 ps) regeneration of the ground state following picosecond excitation of the Ru(NH₃)₅³⁺ metalates⁶⁰; (b) the failure to detect a transfer step (k_{12}) in (bpy)₂Ru(CN)Cr(NH₃)₂⁶⁺ even during the excitation pulse (Figure 8); (c) the significant variations of $E_{1/2}$ for the Ru(III)–(II) couple when the metal center of the metalate is changed (e.g., note the 150-mV difference in $E_{1/2}$ for bis-metalates with Cr(NH₃)₅³⁺ and Rh(NH₃)₅³⁺ in Table III).

center with a wave function, ${}^{\circ}\psi_i$, characteristic of the electronic state i in the equivalent mononuclear complex j . The mixing terms can then be introduced as perturbations of the parent electronic configurations. In the weak coupling limit, the mixing perturbations can be roughly classified as "exchange" or "superexchange". The exchange interaction has its origin in the indistinguishability of the donor and acceptor electrons.

The most important superexchange couplings are likely to arise from the configurational mixing of the ${}^{\circ}\psi_i$ wave functions with the zero-order wave functions of low-energy charge-transfer (CT) excited states,^{11,55,80} since the induced dipole moment resulting from such mixing would tend to have a finite component along the donor-acceptor axis resulting in appreciable polarization of the zero-order wave functions (see discussion in refs 11 and 57) in the region of their greatest overlap. The contributions of such perturbations will be inversely proportional to the energy difference between the donor (or acceptor) excited state and the perturbing CT state.

These perturbations will result in modified wave functions for the donor and acceptor excited states; e.g., for a Ru-Rh system

$$\psi_{3CT}^D \cong {}^{\circ}\psi_{3CT}^D + a_{\text{exch}} {}^{\circ}\psi_{3dd}^A + b_{\text{sxch}} \psi_{\text{MMCT}} \quad (7)$$

and

$$\psi_{3dd}^A \cong {}^{\circ}\psi_{3dd}^A + a'_{\text{exch}} {}^{\circ}\psi_{3CT}^D + b'_{\text{sxch}} \psi_{\text{MMCT}} \quad (8)$$

where we have used the subscripts ${}^3\text{CT}$, ${}^3\text{dd}$, and MMCT to designate the $({}^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$, $({}^3\text{dd})\text{Rh}(\text{III})$, and the $({}^1\text{A}_1)\text{Ru} \rightarrow ({}^3\text{dd})\text{Rh}$ MMCT excited states, respectively, and where the mixing coefficients are of the form $a_{\text{exch}} \cong a^{\circ}/|E_{3dd} - E_{3CT}|$, $b_{\text{sxch}} \cong b^{\circ}/(E_{3CT} - E_{\text{MMCT}})$, etc. The electronic couplings result in an electronic matrix element of the form

$$H_{\text{RP}} \cong H_{\text{exch}} + H_{\text{sxch}} \quad (9)$$

The H_{exch} term will tend to dominate eq 9 when the donor and acceptor orbitals are largely unmixed but have very similar energies. The H_{sxch} term will tend to be most important in systems in which there are excited states (usually charge-transfer states) with energies near those of the donor and acceptor.

In addition to their contributions to H_{RP} , the exchange and superexchange interactions result in a spin-spin coupling between the metal centers of these multinuclear complexes. As a result, there may be several spin components of each electronic state considered, and some excited-state decay pathways which are spin forbidden in the mononuclear parent complexes may be spin allowed in the multinuclear complexes. This is not a concern in the singly excited cyano-bridged Ru-Rh complexes, but it is an important concern in the Ru-Cr analogues. For example, there are potentially seven spin components of the ground electronic state of $(\text{bpy})_2\text{Ru}(\text{CNCr}(\text{NH}_3)_5)_2^{6+}$ and nine spin components of its $({}^3\text{CT})\text{Ru}(\text{II})-\text{Cr}(\text{III})$ excited state. Although the role of spin-spin coupling in these systems is not yet clear, the $({}^2\text{E})\text{Cr}(\text{III})$ lifetime observed for the $\text{Ru}(\text{CNCr})_2^{6+}$ complex falls in the range generally found for mononuclear chromium-pentammines^{30,40b,c} indicating that the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition remains spin forbidden in the trinuclear complex. This suggests that while nearest neighbor spin-spin coupling (in these complexes between $({}^3\text{CT})\text{Ru}(\text{bpy})_2^{2+}$ and $({}^4\text{A}_2)\text{Cr}(\text{III})$) may be important, next nearest neighbor couplings ($\text{Cr}(\text{III})-\text{Cr}(\text{III})$ in the bis-metalated complexes) are not an important factor. This is reminiscent of the pattern of spin-spin couplings in $\text{Mn}^{2+} + \text{Ti}^{2+} + \text{Mn}^{2+}$ clusters which have been elegantly documented by Güdel and co-workers.⁸¹

In view of the above discussion it is likely that H_{RP} will be different for Ru-M ground state and for $({}^3\text{CT})\text{Ru}-(^*\text{dd})\text{M}$ excited-state couplings. For example, an intense MMCT transition in the potential electron-transfer system $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRu}-$

$(\text{NH}_3)_5)^{3+21a}$ implies that $H_{\text{RP}} \cong 1800 \text{ cm}^{-1}$ for the $({}^1\text{A}_1)\text{Ru}(\text{II})-({}^2\text{T}_1)\text{Ru}(\text{III})$ coupling,^{21a} but this does not provide direct information about the $({}^3\text{CT})\text{Ru}(\text{II})-({}^2\text{T}_1)\text{Ru}(\text{III})$ coupling.

The most pertinent observation on the systems which we have studied is the transient absorption that developed at 585 nm subsequent to picosecond excitation of $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_5)^{3+}$. The rise of this absorbance was accompanied by a decrease in the $({}^3\text{CT})\text{Ru}(\text{II})$ absorbance. Since the 585-nm absorbance increase was of a similar magnitude as the excited-state $({}^3\text{CT})\text{Ru}$ absorbance decrease, this transition is much more intense than expected for a ligand field absorbance, and it most likely arises from an excited-state $({}^1\text{A}_1)\text{Ru}(\text{II}) \rightarrow ({}^3\text{dd})\text{Rh}(\text{III})$ MMCT transition similar to that found at 695 nm for the ground state of the $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRu}(\text{NH}_3)_5)^{3+}$ complex^{21a} (note that the MMCT transitions are orbitally similar in the $({}^1\text{A}_1)\text{Ru}(\text{II})-({}^2\text{T}_1)\text{Ru}(\text{III})$ and the $({}^1\text{A}_1)\text{Ru}(\text{II})-({}^3\text{dd})\text{Rh}(\text{III})$ systems). Consequently, the absorbance at 585 nm is most likely assigned as an absorbance characteristic of the electronically excited Rh(III) center. This assignment implies⁸² $H_{\text{RP}} \geq 10^3 \text{ cm}^{-1}$ for $({}^1\text{A}_1)\text{Ru}(\text{II})-({}^3\text{dd})\text{Rh}(\text{III})$ coupling in this complex. Strong, cyanide-mediated coupling of the filled (t_{2g}) $d\pi$ orbitals of Ru(II) and the partly vacant $d\pi$ orbital of the $({}^3\text{dd})\text{Rh}(\text{III})$ acceptor is very likely. However, the ruthenium center of the $({}^3\text{CT})\text{Ru}(\text{II})$ excited state is more like Ru(III) than Ru(II), so that such strong, cyanide-mediated donor-acceptor couplings are not expected in the singly excited Ru-Rh complex, and this system can appropriately be described as two mostly isolated electronic configurations, weakly coupled through perturbations as sketched in eqs 2-4. Owing to the similar energies of the $({}^3\text{CT})\text{Ru}(\text{II})$ and $({}^3\text{dd})\text{Rh}(\text{III})$ configurations H_{exch} is expected to make a substantial contribution to H_{RP} in the Ru-Rh complexes. Owing to the relatively low-energy MMCT transition of the $({}^1\text{A}_1)\text{Ru}(\text{II})-({}^3\text{dd})\text{Rh}(\text{III})$ excited state, there may also be a contribution from H_{sxch} .

A relatively cruder, but strictly empirical, criterion for the electronic integrity of the donor and acceptor of the cyanide-bridged complexes can be based on their spectroscopic properties and the extent to which these properties differ from those of their mononuclear equivalents. This cannot be a very precise criterion for these complexes because cyanide metalation of $\text{Ru}(\text{bpy})_2(\text{CN})_2$ increases the Ru(III)-(II) reduction potential, so that metalation alone is expected to result in alteration of the MLCT energetics even without strong donor-acceptor coupling. The absorption and emission band shapes are very little altered by metalation (e.g., see Figures 2 and 3). The MLCT absorption maxima (and most of the MLCT emission maxima) follow simple patterns based on minimal mixing [λ_{max} for DMSO-H₂O ambient solutions (absorption maxima for DMF-CHCl₃ solutions in parentheses): $\lambda_{\text{max}} = 431 \pm 2 \text{ nm}$ for RhCNRhX ($X = \text{NH}_3, \text{CN}^-, \text{Br}^-, \text{I}^-$) ($456 \pm 2 \text{ nm}$); $\lambda_{\text{max}} = 412 \pm 2 \text{ nm}$ for $\text{Ru}(\text{CNM})_2$ ($M = \text{Rh}(\text{NH}_3)_5^{3+}, \text{Cr}(\text{NH}_3)_5^{3+}, \text{Co}(\text{NH}_3)_5^{3+28b}$) ($416 \pm 16 \text{ nm}$)] in contrast to the absorption of the $\text{Ru}(\text{bpy})_2(\text{CN})_2$ parent at 457 nm (498 nm). The emission maxima at 77 K average $555 \pm 1 \text{ nm}$ in DMSO-H₂O ($577 \pm 1 \text{ nm}$ in DMF-CHCl₃) for RuCNRhX ($X = \text{NH}_3, \text{CN}, \text{Br}$) compared to 573 nm (610 nm), for the $({}^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ parent. The $(\text{bpy})_2(\text{CN})\text{Ru}(\text{trans-CNRh}(\text{NH}_3)_4\text{I})^{2+}$ complex is the exception in this series of compounds with a significantly altered emission spectrum.

Thus the spectroscopic observations indicate that the $(\text{bpy})_2(\text{CN})\text{RuCN}$ and $\text{CNM}(\text{NH}_3)_5$ metal centers of most of the complexes considered here are usefully considered to be nearly electronically independent, with strong perturbational coupling. Only for the $(\text{bpy})_2(\text{CN})\text{Ru}(\text{trans-Rh}(\text{NH}_3)_4\text{I})^{2+}$ complex is there any spectroscopic evidence for appreciable donor-acceptor mixing.

Summary and Conclusions

This study has demonstrated that dipole forbidden energy transfer can be very rapid in cyanide-bridged multinuclear complexes. In these complexes, the donor and acceptor electronic

(79) Estimated magnitude of the relaxation rate constant of a mono-metalated $({}^3\text{CT})\text{Ru}(\text{bpy})_2(\text{CN})_2$ excited state when the metalate acceptor energy states cannot be populated by the donor. The temperature-dependent lifetimes and eqs 4 and 5 imply that k_{13} (monometalate) $\cong 0.5k_{13}$ (parent).

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systems can be regarded as electronically independent at least when a large difference in nuclear coordinates accompanies the migration of energy and when the acceptor and donor state differ significantly in energy. Under these circumstances there is first vibrational equilibration among the donor excited states, followed by an equilibration of excitation energy between the donor and acceptor. In only one complex, $(\text{bpy})_2(\text{CN})\text{Ru}(\text{CNRh}(\text{NH}_3)_4\text{I})$ in which the donor energy was greater than or equal to the acceptor energy, did we find spectroscopic characteristics which might suggest that the lowest energy excited state has mixed donor and acceptor character. At 77 K the lowest energy excited states of the cyanide bridged Ru–Cr complexes behave like typical $(^2\text{E})\text{-Cr}(\text{III})$ excited states, presumably because the donor–acceptor energy difference is too great for appreciable mixing of their electronic configurations. One expects similar factors to contribute to donor–acceptor coupling in electron transfer and dipole forbidden energy-transfer systems. We have examined a few electron-transfer systems in which similar general features seem to be exhibited. This work will be reported elsewhere.⁶⁰ The cyano-bridged Ru–Rh complexes provide some unique insights into the “normal” relaxation pathways of $(^3\text{CT})\text{Ru}$ -polypyridyl excited

states, since a tunable ^3dd relaxation pathway is introduced by the Rh(III) center. The observations are qualitatively in accord with the expectation that the $^3\text{CT} \rightarrow ^3\text{dd}$ relaxation pathways will be characterized by large Arrhenius frequency factors ($A \approx 10^{13} \text{ s}^{-1}$) and activation energies that reflect both the donor–acceptor energy gap and the reorganizational energy for the relaxation of the ^3dd excited state.

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Supplementary Material Available: Table of elemental analyses for cyanide-bridged complexes (1 page). Ordering information is given on any current masthead page.

Reaction Aspects of a μ -Peroxo Binuclear Copper(II) Complex

Nobumasa Kitajima,* Takayuki Koda, Yusaku Iwata, and Yoshihiko Moro-oka*

Contribution from the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan. Received September 25, 1989

Abstract: The reactivity of a μ -peroxo binuclear copper(II) complex $[\text{Cu}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)]_2(\text{O}_2)$ (**1**) toward a variety of substrates is described. PPh_3 and CO are not oxidized by **1**; they generate mononuclear copper(I) complexes $\text{Cu}(\text{L})(\text{HB}(3,5\text{-Me}_2\text{pz})_3)$ ($\text{L} = \text{CO}, \text{PPh}_3$) via displacement reactions. Cyclohexene is oxidized to oxygenated products such as 2-cyclohexen-1-ol only under aerobic conditions, and labeling experiments established that the oxygen atoms incorporated into the products come from the exogenous dioxygen, not from the peroxide ion in the μ -peroxo complex. Phenols and a catechol are oxidatively coupled under anaerobic conditions, while under a dioxygen atmosphere, both oxidatively coupling and oxygenation to give benzoquinones are observed. On the basis of kinetic results, a mechanism is proposed for the oxygenation reactions in which homolytic cleavage of the O–O bond in the μ -peroxo complex is followed by free radical chain reactions with dioxygen.

Introduction

Tyrosinase is a monooxygenase in which the active site contains a binuclear copper center that is known to bind dioxygen as a peroxide.¹ A similar binding mode is found in hemocyanin, a ubiquitous oxygen transport protein for invertebrates. Although tyrosinase was the first discovered monooxygenase,² few of its mechanistic details have been elucidated to date.³ Currently increasing interest in the activation of dioxygen by monooxygenases prompted several groups to study oxidations using biomimetic copper complexes.⁴ Valentine et al. reported catalytic epoxidations of olefins with iodosobenzene as an oxidant and suggested that a high-valent oxocopper species might be involved.⁵ Recently, dioxygen was reported to effect the hydroxylation of certain CH bonds in the ligands of copper(I) complexes.⁶ These oxidations

are supposed to proceed via peroxocopper intermediates. However, there has been no stoichiometric oxidation of an externally added substrate by a well-characterized peroxo copper complex, except for the oxo-transfer reactions recently reported by Karlin et al. In these studies, three structurally distinctive types of μ -peroxo binuclear copper(II) complex were synthesized,⁷ and two of these classes (one having an unsymmetric peroxo ligand and a μ -phenoxo group, and the other having a trans μ -1,2-peroxo) were demonstrated to be effective for oxo-transfer reaction to triphenylphosphine after protonation or acylation of the peroxo complexes.^{8,9}

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