

## Electronic Coupling in Cyano-Bridged Ruthenium Polypyridine Complexes and Role of Electronic Effects on Cyanide Stretching Frequencies

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The spectroscopic and electrochemical properties of a series of polynuclear complexes containing cyano-bridged ruthenium polypyridine units are consistent with a valence-localized model. In all the Ru(II) forms, the lowest metal-to-ligand charge-transfer (MLCT) states are localized on N-bonded moieties. The photophysical properties at 298 and 77 K indicate that efficient intercomponent energy-transfer processes from C-bonded to N-bonded chromophoric units take place. The mixed-valence forms of these complexes show low-energy absorption bands which are assigned to metal-to-metal charge-transfer transitions involving C-bonded Ru(II) and N-bonded Ru(III) centers. The resonance Raman spectrum of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$  under near-resonance conditions with the Ru(II)  $\rightarrow$  Ru(III) charge-transfer band shows enhancement of the bridging cyanide stretching as expected for this type of electronic transition. In the infrared spectra the number of cyanide stretching bands supports the valence-localized model. For the representative  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$  complex, three CN stretches (one bridging, two terminal) are observed. Time-resolved infrared measurements for the MLCT excited state of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}]^+$  are reported. The excited-state IR spectrum shows features similar to those of the chemically prepared mixed-valence dimer,  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$ , strongly suggesting that valence delocalization is not significant in the excited state. The electronic factors affecting the frequency of the bridging cyanide are analyzed by examining the behavior of the mixed-valence ions  $[\text{M-Nc-M}'(\text{bpy})_2\text{-CN-M}]^{6+/4+}$  and  $[\text{NC-M}'(\text{bpy})_2\text{-CN-M}]^{3+/2+}$  ( $\text{M} = [\text{Ru}(\text{NH}_3)_5]^{2+/3+}$ ;  $\text{M}' = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}, \text{Re}^{\text{I}}$ ).

### Introduction

We have recently reported the spectroscopic, photophysical, and electrochemical properties of polynuclear ruthenium complexes of the type



where bpy is 2,2'-bipyridine or a related ligand.<sup>1,2</sup>

From the comparison of their electrochemical and photophysical properties with those of the mononuclear  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  complex as well as with the properties of other polynuclear complexes of the formula  $\text{M-Nc-Ru}(\text{bpy})_2\text{-CN-M}$  ( $\text{M}$  is a transition metal complex,<sup>3-5</sup>  $\text{H}^+$ ,<sup>6</sup> or  $\text{CH}_3^7$ ), the following conclusions were drawn: (i) In the polynuclear complexes, N-bonded Ru(II) units are easier to oxidize than C-bonded ones. (ii) The lowest MLCT state of the polynuclear complex is localized on the N-bonded Ru(II) unit. (iii) Intercomponent energy transfer from C-bonded to adjacent N-bonded units takes place with high efficiency. The lack of any emission from the corresponding mixed-valence species

was attributed to the occurrence of intramolecular electron-transfer processes from excited C-bonded units to N-bonded Ru(III) centers. An analysis of the absorption spectra of the mixed-valence ions in terms of equations derived by Hush<sup>8</sup> led these species to be classified as substantially valence-localized mixed-valence compounds.<sup>1</sup>

An alternative point of view has recently been taken by Cooper et al.<sup>9</sup> Their interpretation was largely based on the claim that in the infrared spectrum of the mixed-valence dimer  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$  only two cyanide stretches (one bridging, one terminal) instead of three stretches (one bridging, two terminal), as expected for a localized  $\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}$  species, were observed. They also noted that in the unoxidized polynuclear complexes no multiple transitions are present in the absorption spectra as expected for complexes in which metal sites are dissimilar. The slight hypsochromic shifts of the absorption spectra and appreciable bathochromic shifts of the emissions as compared to the monomers were suggested as an additional anomaly. They concluded that the mixed-valence dimer is delocalized and that some degree of delocalization in the emitting triplet metal-to-ligand charge-transfer (<sup>3</sup>MLCT) states of the unoxidized form is responsible for the photophysical behavior.

In order to better elucidate the degree of electronic interaction between metal centers in these systems, we report here additional photophysical and spectroscopic results. In particular, extensive comparisons are made between the infrared spectra of the mixed-valence forms of these polynuclear complexes and mixed-valence ions of general formula  $[\text{M-Nc-M}'(\text{bpy})_2\text{-CN-M}]^{6+/4+}$  and  $[\text{NC-M}'(\text{bpy})_2\text{-CN-M}]^{3+/2+}$  ( $\text{M}$  is  $[\text{Ru}(\text{NH}_3)_5]^{2+/3+}$  and  $\text{M}'$  is  $\text{Ru}^{\text{II}}, \text{Os}^{\text{II}},$  and  $\text{Re}^{\text{I}}$ ).

Resonance Raman spectra of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$  under near-resonance conditions with the intense

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Table I. Electrochemical, Spectroscopic, and Photophysical Properties of Mononuclear and Polynuclear Ruthenium Complexes

complex (solv)	$E_{1/2}^{ox}$ in V vs SCE			$\nu_{max}^{abs}$ , $cm^{-1}$ ( $\epsilon$ , L mol $^{-1}$ cm $^{-1}$ )	$\nu_{max}^{em}(298\text{ K})$ , $cm^{-1}$	$E_{0-0}(77\text{ K})^a$ , $cm^{-1}$	$\tau(298\text{ K})$ , ns	$\tau(77\text{ K})^b$ , $\mu s$
	(1)	(2)	(3)					
(2) (CH <sub>3</sub> CN)	0.86 <sup>c</sup>			20.3 (9500)	14.5 <sup>c</sup>	17.0 <sup>c</sup>	240 <sup>c</sup>	4 <sup>c</sup>
(2) (H <sub>2</sub> O)	0.90 <sup>c</sup>			23.3 (7500)				
(2') (CH <sub>3</sub> CN)	0.88 <sup>c</sup>			20.5 (11 400)	14.9 <sup>c</sup>	17.6 <sup>c</sup>	1200 <sup>c</sup>	12.5 <sup>c</sup>
(2'') (CH <sub>3</sub> CN)	0.73			20.3 (8400)	14.2		770 <sup>c</sup>	
(2'') (H <sub>2</sub> O)				22.0 (8200)				
(2,2) (CH <sub>3</sub> CN)	0.74 <sup>c</sup>	1.35 <sup>c</sup>		20.5 (15 400)	14.0 <sup>c</sup>	15.9 <sup>c</sup>	120 <sup>c</sup>	1.6 <sup>c</sup>
(2,2) (H <sub>2</sub> O)	0.64 <sup>c</sup>			22.5 (13 500)				
(2,2') (CH <sub>3</sub> CN)	0.75 <sup>c</sup>	1.34 <sup>c</sup>		20.7 (17 600)	14.3 <sup>c</sup>	16.9 <sup>c</sup>	400 <sup>c</sup>	4.6 <sup>c</sup>
(2,2') (H <sub>2</sub> O)	0.64 <sup>c</sup>			23.0 (15 500)				
(2,2,2) (CH <sub>3</sub> CN)	0.66 <sup>c</sup>	1.19 <sup>c</sup>	1.46 <sup>c</sup>	20.9 (21 600)	13.6 <sup>c</sup>	14.6 <sup>c</sup>	90 <sup>c</sup>	1.3 <sup>c</sup>
(2,2,2) (H <sub>2</sub> O)	0.53 <sup>c</sup>			22.5 (18 750); 20.1, sh				
(2,2'',2) (CH <sub>3</sub> CN)	0.54 <sup>d</sup>	1.24 <sup>d</sup>	1.58 <sup>d</sup>	20.6 (22 000)	13.9	14.1	140 <sup>c</sup>	
(2,2'',2) (H <sub>2</sub> O)				23.8 (19 500); 19.1 (13 400, sh)				

<sup>a</sup> From 77 K emission spectra in absolute ethanol. <sup>b</sup> Obtained in absolute ethanol. <sup>c</sup> From ref 1. <sup>d</sup> From ref 13. <sup>e</sup> Lifetimes determined on solutions that were freeze-pump-thaw degassed (five cycles with a pressure of 10<sup>-6</sup> Torr).

intervalence transfer band and the time-resolved infrared spectrum for the lowest <sup>3</sup>MLCT excited state of [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>+</sup> are presented.

### Experimental Section

**Materials.** All chemicals were reagent grade. Tetraethylammonium tetrafluoroborate, [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>](BF<sub>4</sub>), tetra-*n*-butylammonium chloride, [N(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>](Cl) (Aldrich), and hydrazine hydrate (Fluka) were used as purchased. Anhydrous acetonitrile (Aldrich, gold label) and *N,N*-dimethylformamide (DMF) (Aldrich) were used for the spectroscopic and electrochemical measurements.

**Complexes.** The following complexes were available from previous studies or prepared according to literature methods: Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>,<sup>10</sup> Ru(phen)<sub>2</sub>(CN)<sub>2</sub>,<sup>1</sup> (phen is 1,10-phenanthroline), Os(bpy)<sub>2</sub>(CN)<sub>2</sub>,<sup>11</sup> Re(phen)(CO)<sub>3</sub>(CN),<sup>12</sup> [Ru(bpy)<sub>2</sub>(NO)(CN)](PF<sub>6</sub>)<sub>2</sub>,<sup>1</sup> [NC-Ru(bpy)<sub>2</sub>-CN-Ru(bpy)<sub>2</sub>-CN](PF<sub>6</sub>)<sub>2</sub>,<sup>1</sup> [NC-Ru(bpy)<sub>2</sub>-CN-Ru(phen)<sub>2</sub>-CN](PF<sub>6</sub>)<sub>2</sub>,<sup>1</sup> [NC-Ru(bpy)<sub>2</sub>-CN-Ru(bpy)<sub>2</sub>-NC-Ru(bpy)<sub>2</sub>-CN](PF<sub>6</sub>)<sub>2</sub>,<sup>1</sup> (N(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>)<sub>2</sub>[NC-Ru(bpy)<sub>2</sub>-CN-Ru(dcb)<sub>2</sub>-NC-Ru(bpy)<sub>2</sub>-CN],<sup>13</sup> (dcb is 2,2'-bipyridine-4,4'-dicarboxylate), [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)](PF<sub>6</sub>)<sub>2</sub>,<sup>14</sup> [NC-M(bpy)<sub>2</sub>-CN-Ru(NH<sub>3</sub>)<sub>4</sub>(X)](PF<sub>6</sub>)<sub>3</sub>, and [Ru(NH<sub>3</sub>)<sub>4</sub>(X)-NC-M(bpy)<sub>2</sub>-CN-Ru(NH<sub>3</sub>)<sub>4</sub>(X)](PF<sub>6</sub>)<sub>6</sub> (X = NH<sub>3</sub>, py; M = Ru(II), Os(II)).<sup>15,16</sup>

[N(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>][Ru(dcb)<sub>2</sub>(CN)<sub>2</sub>]. A 0.15-g amount of [Ru(dcbH<sub>2</sub>)]-C<sub>2</sub>O<sub>4</sub><sup>13</sup> and 0.1 g of NaCN were refluxed in 25 mL of CH<sub>3</sub>OH. After 3 h, the solution was evaporated to 5 mL, filtered, and passed on a 2 × 20 cm silica gel column. The red fraction containing the complex was eluted with CH<sub>3</sub>OH, dried, and redissolved in water. Addition of HCl caused the precipitation of the neutral form of the complex near pH 2.5. The solid was filtered out, washed with cold water, and dried under vacuum. Anal. Calcd for Ru(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>)(CN)<sub>2</sub>·6H<sub>2</sub>O: C, 41.66, H, 3.76, N, 11.21. Found: C, 41.32, H, 3.80, N, 11.18. The neutral complex was converted to the anion (tetrabutylammonium salt) through ion-exchange chromatography.<sup>13</sup>

[Re(phen)(CO)<sub>3</sub>-CN-Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub>. This complex was prepared by reaction of stoichiometric amounts of Re(phen)(CO)<sub>3</sub>CN and [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)](PF<sub>6</sub>)<sub>2</sub>. In a typical preparation 0.1 g of Re(phen)(CO)<sub>3</sub>CN and 0.11 g of [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)](PF<sub>6</sub>)<sub>2</sub> were dissolved in 50 mL of methanol, under argon. After 2 h, oxygen was bubbled through the solution for 30 min. This solution was then loaded on a 2 × 15 cm neutral alumina column. The unreacted Re monomer was recovered by elution with methanol. The binuclear Re-Ru complex was collected by deactivating the column with water and then precipitated by addition of solid NH<sub>4</sub>PF<sub>6</sub>. The solid was recrystallized from a water/methanol

solution. Anal. Calcd for [Re(phen)(CO)<sub>3</sub>-CN-Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub>: C, 17.51; H, 2.11, N, 10.21. Found: C, 17.64, H, 2.08, N, 10.16.

**Mixed-Valence Compounds.** One-electron oxidized forms of the binuclear and trinuclear complexes for spectroscopic characterization were prepared by chemical oxidation in acetonitrile. The oxidized solutions were observed to be stable for several hours. Solid samples could also be obtained by precipitation with ether from acetonitrile solutions of the oxidized samples.

Oxidative titrations of [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN](PF<sub>6</sub>)<sub>2</sub>, [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>II</sup>(phen)<sub>2</sub>-CN](PF<sub>6</sub>)<sub>2</sub>, and [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>II</sup>(bpy)<sub>2</sub>-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN](PF<sub>6</sub>)<sub>2</sub> were performed by addition of aliquots of a standardized Br<sub>2</sub>/acetonitrile solution<sup>1</sup> to solutions 5 × 10<sup>-5</sup> to 1 × 10<sup>-4</sup> M in complex. Since the redox potential of Br<sub>2</sub> in CH<sub>3</sub>CN (1 V vs SCE)<sup>17</sup> is between the first and second oxidation step of these oligomers (see Table I), excess bromine did not result in further spectral changes. During these titrations the following isosbestic points were observed: [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-CN]<sup>2+</sup>, 381, 426, 670 nm; [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(phen)<sub>2</sub>-CN]<sup>2+</sup>, 414, 660 nm; [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>3+</sup>, 385, 440, 660 nm.

Solutions of the mixed-valence forms for FTIR and Raman measurements were obtained by addition of a slight excess of bromine to 10<sup>-2</sup>-10<sup>-3</sup> M CH<sub>3</sub>CN or DMF solutions of the polynuclear complexes. Despite the quantitative one-electron oxidation taking place in solution, solid samples precipitated by addition of ethyl ether were shown (by FTIR and electronic absorption spectra after redissolution) to contain 20-30% unoxidized form, presumably due to the presence of oxidizable impurities in the precipitating solvent.

**Apparatus and Procedures.** Cyclic voltammetric, spectroelectrochemical experiments, and controlled-potential electrolysis were performed in CH<sub>3</sub>CN in the presence of 0.1 M tetraethylammonium tetrafluoroborate with a Pt working electrode and a SCE reference electrode. The electrochemical, electronic absorption, emission, and lifetime experiments were performed as previously described.<sup>1,2,6,7</sup>

FTIR spectra were acquired with a Model IFS88 Bruker spectrophotometer. Since contact of acetonitrile or DMF solutions of the mixed-valence complexes with steel was observed to cause rapid decomposition, a modified Teflon front plate was used in the liquid IR measurements (Specac). Sample stability during the FTIR experiments was verified by measuring the electronic absorption spectra in the visible and near-infrared (NIR) regions before and after obtaining the IR spectrum. Subtraction of the CH<sub>3</sub>CN features in the 1700-2200-cm<sup>-1</sup> region was performed with reference to the 1826-cm<sup>-1</sup> CH<sub>3</sub>CN band which exhibited no overlap with IR bands of the complex.

Time-resolved infrared absorbance difference ( $\Delta A$ ) measurements were obtained using 250  $\mu$ J of 532-nm pulses from a frequency doubled Q-switched Nd:YAG (Spectra Physics DCR1) operating at 20 Hz. The IR absorbance of the excited volume was monitored with a tunable CW IR diode laser. The IR monitoring beam was calibrated by a monochromator. Absorbance changes were detected with a small-element nitrogen-cooled InSb detector and transient waveforms captured using a Tektronix Model 7912 HB digitizer. Computer control of the experiment was provided by a Mac II system.

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Each point of the  $\Delta A$  spectrum was calculated from the  $\Delta A$  changes 50 ns after excitation and was averaged for ca. 1000 shots. The ground-state depletion and the excited-state absorption signals were observed to decay with the same rate. The lifetimes measured by TRIR and emission were coincident.

The resonance Raman spectra were obtained on two separate instruments. In one experiment excitation of 676.4 nm was provided by a Coherent INNOVA 90K Kr<sup>+</sup> laser. The scattered radiation was collected 90 deg to the incident light into a Jobin Yvon U1000 double monochromator (Instruments SA). The Raman signal was detected by a Hamamatsu R943 cooled photomultiplier tube and processed by a Spectra Link photon-counting system (Instruments SA). In the second apparatus, excitation of 720 nm was provided by a Spectra Physics Model 3900 Ti:sapphire laser pumped by a 2045 Ar<sup>+</sup> laser (Spectra Physics). The scattered radiation was dispersed by a Spex 1877D triple spectrograph and detected with a liquid-nitrogen-cooled Photometrics PN12CCD.

## Results and Discussion

**Spectroscopic and Photophysical Properties of Unoxidized Compounds.** A summary of redox, spectroscopic, and photophysical properties of mononuclear and polynuclear ruthenium complexes is given in Table I. In the table and in the text, the following abbreviations are used for unoxidized and corresponding mixed-valence complexes: Ru<sup>II</sup>(bpy)<sub>2</sub>(CN)<sub>2</sub>, (2); Ru<sup>II</sup>(phen)<sub>2</sub>(CN)<sub>2</sub>, (2'); [Ru<sup>II</sup>(dcb)<sub>2</sub>(CN)<sub>2</sub>]<sup>4-</sup>, (2''); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-CN]<sup>+</sup>, (2,2); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-CN]<sup>2+</sup>, (2,3); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(phen)<sub>2</sub>-CN]<sup>+</sup>, (2,2'); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(phen)<sub>2</sub>-CN]<sup>2+</sup>, (2,3'); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>2+</sup>, (2,2,2); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>3+</sup>, (2,3,2); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(dcb)<sub>2</sub>-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>2-</sup>, (2,2'',2); [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(dcb)<sub>2</sub>-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>+</sup>, (2,3'',2).

The visible absorption bands for the polynuclear complexes were assigned to additive contributions of MLCT  $d\pi(\text{Ru}) \rightarrow \pi^*(\text{L})$  (L is bpy, phen, or dcb) transitions originating from different component subunits.<sup>1,13</sup> This assignment is consistent with the small shift of band energy and increase of band intensities observed in going from model monomers to polynuclear complexes.<sup>1</sup> This assignment is also consistent with energy shifts and changes in band shape for spectra of (2,2,2) and (2,2'',2) when the solvent is changed from CH<sub>3</sub>CN to H<sub>2</sub>O (Table I).<sup>18-23</sup>

The fact that the spectra of these oligomers are not resolved into multiple MLCT transitions in CH<sub>3</sub>CN has been interpreted by Cooper et al. as a consequence of bridge-mediated electronic delocalization between Ru(II) centers or degeneracy between <sup>1</sup>MLCT transitions localized on -Ru<sup>II</sup>(bpy)<sub>2</sub>- subunits.<sup>9</sup> These interpretations, however, are not consistent with changes in emission and absorption energies between mononuclear and polynuclear complexes (Table I). Furthermore, the differences

in stabilization energies of  $d\pi$  orbitals of the bridged metals due to the asymmetry of the CN bridge are not considered.

On the basis of the electrochemical results (Table I), energy differences of the order of 1000 cm<sup>-1</sup> are estimated for -NC-Ru-CN compared to -CN-Ru-CN (cf. (2), (2,2) and (2'), (2,2'), Table I) and 1600 cm<sup>-1</sup> for -NC-Ru-CN- compared to CN-Ru-NC (cf. (2), (2,2,2) and (2''), (2,2'',2); Table I). These energy differences explain the observed trend in emission energies and indicate that no structure should be expected in the visible absorption spectra of the polynuclear complexes because of the small energy shifts and large bandwidth of MLCT transitions. These conclusions are further confirmed by the properties of two linkage isomers, [(phen)(CO)<sub>3</sub>Re-NC-Ru(bpy)<sub>2</sub>-CN]<sup>+</sup> and [(phen)(CO)<sub>3</sub>Re-CN-Ru(bpy)<sub>2</sub>-CN]<sup>+</sup>, recently prepared in our laboratory.<sup>24</sup> In CH<sub>3</sub>CN,  $E_{1/2}(\text{Ru(III)}/\text{II}) = +1.10$  V, MLCT(Ru  $\rightarrow$  bpy) absorption is  $21.74 \times 10^3$  cm<sup>-1</sup>, and the emission maximum is  $17.58 \times 10^3$  cm<sup>-1</sup> for the Re-NC-Ru-CN isomer compared to 0.94 V,  $20.74 \times 10^3$  cm<sup>-1</sup>, and  $16.61 \times 10^3$  cm<sup>-1</sup> for the Re-CN-Ru-CN isomer. No structure is observed upon summing the absorption spectra of these two isomers. The spectral shifts of the polynuclear ruthenium complexes with respect to the parent mononuclear species can be interpreted on the basis of these results. The red shift of emission maxima of the polynuclear species is a result of the asymmetry of the bridge which makes the energy of the N-bonded chromophore lower than that of the monomer. The very small blue shift observed in absorption spectra is then due to the superimposition of the red-shifted MLCT band of the N-bonded unit together with a blue-shifted MLCT band of the C-bonded unit. The N-bonded unit is lowered in energy by the asymmetry of the bridge, while the C-bonded unit is raised by the presence of the additional metal center to which it is attached.

Our conclusions concerning the localized nature of the complexes and the occurrence of photoinduced intramolecular energy transfer from the chromophore bound by the carbon of the cyanide to the one bound to the nitrogen are supported by the photophysical data. The decrease of the emission lifetimes along the series (2), (2,2), (2,2,2); (2'), (2,2'); and (2''), (2,2'',2) labels the emitting excited states as belonging to the N-bonded chromophore. In going from the binuclear Re-NC-Ru-CN complex to the linkage isomer Re-CN-Ru-CN, the lifetime of the Ru(bpy)-based emission decreases from 835 to 422 ns.<sup>24</sup> These changes suggest that thermal activation from <sup>3</sup>MLCT states localized on the N-bonded chromophoric unit to d-d states is lower than that from <sup>3</sup>MLCT states localized on the C-bonded ones. The decrease in emission energy observed upon going from mononuclear to polynuclear complexes is maintained from 298 to 77 K (Table I). This observation precludes the possibility that conformational changes about the bridging cyanide may influence the results.<sup>9</sup>

**Cyanide Stretching in Polynuclear Complexes.** Cyanide stretching frequencies and relative band intensities of the various complexes are reported in Table II. In polynuclear complexes, bridging cyanide frequencies ( $\nu(\text{CN}b)$ ) have generally been observed at higher energy with respect to those of terminal cyanides ( $\nu(\text{CN}t)$ ).<sup>3,25,26</sup> Dows et al.<sup>25</sup> have shown that this frequency increase is associated largely with kinematic coupling, i.e. the motion of the bridging CN being constrained by the second metal center. For example, the bands observed for [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN]<sup>+</sup> at 2098 and 2069 cm<sup>-1</sup>, with an intensity ratio of 1:2, can be assigned to  $\nu(\text{CN}b)$  and to two degenerate, terminal stretching modes, respectively, by comparison with  $\nu(\text{CN})$  of 2053 and 2067 cm<sup>-1</sup> for Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>.<sup>3</sup>

FTIR spectra in acetonitrile solution of (2,3) and (2,3,2) are compared to those of (2,2) and (2,2,2) in Figure 1. These spectra

- (18) The appearance of electronic structures in the absorption spectra of (2,2,2) and (2,2'',2) in polar solvents are expected on the basis of known specific solvent interactions,<sup>19-23</sup> which mainly affect redox and spectroscopic properties of ruthenium polypyridine complexes containing terminal cyanides. The pronounced shoulder on the low-energy side of the visible spectra with half of the intensity with respect to the higher energy band is confidently assigned to MLCT transitions originating on the central chromophoric units, protected by a direct solvent interaction.<sup>1,13</sup> The blue shifts, in polar solvents, of the MLCT transitions localized on the external Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> units of these trinuclear complexes, are consistent with previous observations on the mononuclear dicyano complex.<sup>21-23</sup> The electronic origin of these effects can be described, by means of a perturbative approach, in terms of an energy lowering of the  $\pi^*$  CN orbitals followed by  $d\pi$  metal orbital stabilization, as well as in terms of a decreased  $\sigma$ -donor ability of CN which should cause an increase of the nuclear effective charge at the ruthenium center.
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Table II. Cyanide Stretching Frequencies (cm<sup>-1</sup>) of Mononuclear and Polynuclear Complexes<sup>a</sup>

complex	$\nu(\text{CN}t)$	$\nu(\text{CN}b)$
Ru <sup>II</sup> (bpy) <sub>2</sub> (CN) <sub>2</sub>	2058 (1), <sup>f</sup> 2076 (1) <sup>f</sup> 2053 (1), <sup>b</sup> 2067 (1) <sup>b</sup>	
[Zn <sup>II</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Zn <sup>II</sup> ] <sup>4+</sup>		2095 (1), <sup>b</sup> 2107 (1) <sup>b</sup>
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-CH <sub>3</sub> ] <sup>+</sup>	2085 (1) <sup>b</sup>	2164 (3) <sup>b</sup>
[CH <sub>3</sub> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-CH <sub>3</sub> ] <sup>2+</sup>		2184 (1), <sup>b</sup> 2211 (1) <sup>b</sup>
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Pt <sup>II</sup> (dien)] <sup>2+</sup>	2058 (1) <sup>b,f</sup>	2108 (1) <sup>b,f</sup>
[(dien)Pt <sup>II</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Pt <sup>II</sup> (dien)] <sup>4+</sup>		2108 (1), <sup>b,f</sup> 2129 (1) <sup>b,f</sup>
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>4</sub> (py)] <sup>3+</sup>	2084 (1) 2078 (1) <sup>b</sup>	2001 (3) 2014 (2) <sup>b</sup>
[Zn <sup>II</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>4</sub> (py)] <sup>5+</sup>		2015 (3), 2105 (1)
[(py)(NH <sub>3</sub> ) <sub>4</sub> Ru <sup>III</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>4</sub> (py)] <sup>6+</sup>		2030 (br)
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>4</sub> (py)] <sup>2+</sup>	2076 (2) <sup>c</sup>	2090 (1) <sup>c</sup>
[(py)(NH <sub>3</sub> ) <sub>4</sub> Ru <sup>II</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>4</sub> (py)] <sup>4+</sup>		2092 (3), <sup>c</sup> 2143 (1) <sup>c</sup>
[(NH <sub>3</sub> ) <sub>5</sub> Ru <sup>III</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>6+</sup>		2035 (br)
[(NH <sub>3</sub> ) <sub>5</sub> Ru <sup>II</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>4+</sup>		2014 (1), <sup>b</sup> 2059 (1) <sup>b</sup>
Os(bpy) <sub>2</sub> (CN) <sub>2</sub>	2062 (1), 2074 (1) 2052 (1), <sup>b</sup> 2067 (1) <sup>b</sup>	2090 (2), <sup>c</sup> 2130 (1) <sup>c</sup>
[NC-Os <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>3+</sup>	2072 (1) 2063 (1) <sup>b</sup>	1998 (4) 1995 (4) <sup>b</sup>
[NC-Os <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>	2065 (1) <sup>c</sup>	2078 (1) <sup>c</sup>
[(Cl)Os <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>		1993 <sup>e,g</sup>
[Zn <sup>II</sup> -NC-Os <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>5+</sup>		2006 (2), (2089) (1)
(phen)(CO) <sub>3</sub> Re <sup>I</sup> (CN)	2123 ( $\nu(\text{CO}) = 1916, 1926, 2024$ ) 2120 <sup>b</sup> ( $\nu(\text{CO}) = 1909, 1938, 2018$ ) <sup>b</sup>	
[(phen)(CO) <sub>3</sub> Re <sup>I</sup> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>3+</sup>		2141 ( $\nu(\text{CO}) = 1927, 1948, 2033$ )
[(phen)(CO) <sub>3</sub> Re <sup>I</sup> -CN-Ru <sup>III</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>3+</sup>		2137 <sup>b</sup> ( $\nu(\text{CO}) = 1926$ (br), 2029) <sup>b</sup>
[(phen)(CO) <sub>3</sub> Re <sup>I</sup> -CN-Ru <sup>II</sup> (NH <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>		2110 ( $\nu(\text{CO}) = 1918, 1928, 2025$ )
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN] <sup>+</sup>	2079 (2) 2079 (2) <sup>b</sup>	2104 (1) 2102 (1) <sup>b</sup>
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (bpy) <sub>2</sub> -CN] <sup>+</sup>	2098 (2), 2110 (1) 2097, <sup>d</sup> 2108 <sup>d</sup>	2015 (10) 2017 <sup>d</sup>
[Zn <sup>II</sup> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (bpy) <sub>2</sub> -CN-Zn <sup>II</sup> ] <sup>5+</sup>	2120, 2146	2027
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>II</sup> (bpy) <sub>2</sub> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN] <sup>2+</sup>	2078 (1) 2078 <sup>d</sup>	2099 (1) 2099 <sup>d</sup>
[NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN-Ru <sup>III</sup> (bpy) <sub>2</sub> -NC-Ru <sup>II</sup> (bpy) <sub>2</sub> -CN] <sup>3+</sup>	2092 (1) 2092 <sup>d</sup>	2001 (20) 2000 <sup>d</sup>

<sup>a</sup> CH<sub>3</sub>CN solutions unless otherwise noted. In parentheses are reported the approximate intensities of  $\nu(\text{CN})$  for the observed doublets. <sup>b</sup> KBr pellets. <sup>c</sup> CH<sub>3</sub>CN solutions in the presence of NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O. <sup>d</sup> DMF solutions. <sup>e</sup> Water solution. <sup>f</sup> Data taken from ref 3. <sup>g</sup> Data taken from ref 38.

were measured on unoxidized and oxidized samples of the same concentration so that the intensity changes are relevant. The (2,2) and (2,2,2) species exhibit the expected two CN stretches. In (2,2) one  $\nu(\text{CN}b)$  is expected along with one  $\nu(\text{CN}t)$  for the two terminal CN, while one  $\nu(\text{CN}b)$  and one  $\nu(\text{CN}t)$  should be present for (2,2,2) for the degenerate terminal and bridging cyanides.<sup>1</sup> The spectrum of (2,3) consists of three well-resolved bands at 2110, 2098, and 2015 cm<sup>-1</sup>, while the spectrum of (2,3,2) shows two bands at 2092 and 2001 cm<sup>-1</sup>. In both cases, the lowest energy band is the most intense. IR spectra of freshly prepared DMF solutions of (2,3) give comparable results with bands at 2108, 2097, and 2017 cm<sup>-1</sup>. It should be stressed that these results refer to solutions of the mixed-valence forms, where oxidation is complete and no decomposition takes place (see Experimental Section). In solid samples obtained from solutions of the mixed-valence complexes, in spite of the presence of a substantial amount of unoxidized species (see Experimental Section), the intense bands at 2010 cm<sup>-1</sup> for (2,3) and 2000 cm<sup>-1</sup> for (2,3,2) were still observed.<sup>27</sup> These observations clearly contrast with the claim by Cooper et al. that only two bands at 2096 and 2108 cm<sup>-1</sup> are present in a sample of (2,3) obtained by electrochemical oxidation of (2,2) in 0.1 M KBr/DMF.<sup>9</sup> The reasons for this contradiction are unclear.

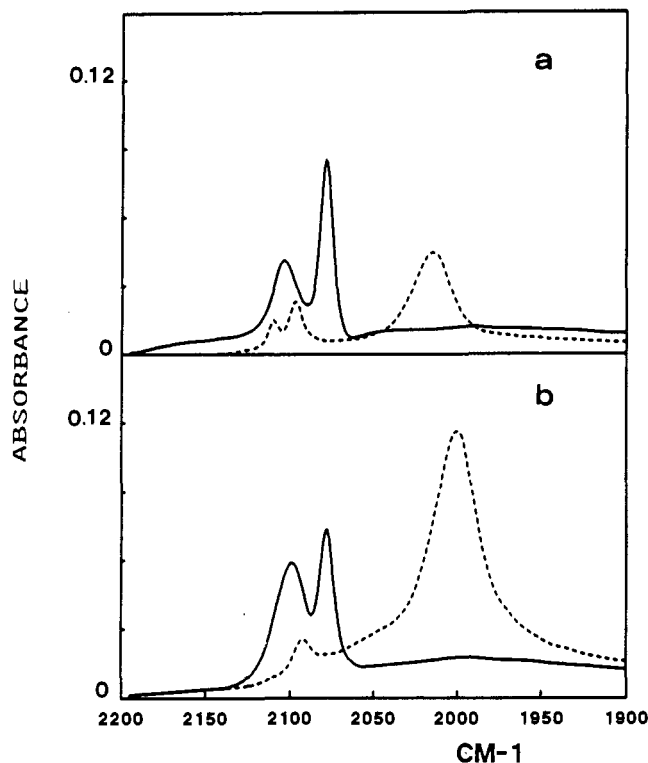
A valence-localized mixed-valence dimer [NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-Ru<sup>III</sup>(bpy)<sub>2</sub>-CN]<sup>2+</sup> is expected to exhibit three different cyanide stretching frequencies including  $\nu(\text{CN}b)$  and  $\nu(\text{CN}t)$  linked to Ru(II) and  $\nu(\text{CN}t)$  bound to Ru(III). In assigning

these modes the comparison between (2,3) and (2,3,2) is informative. In (2,3,2), two external NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-units are bonded to a central Ru(III). In the (2,3,2) spectrum the band at 2092 cm<sup>-1</sup> can be assigned to two equivalent  $\nu(\text{CN}t)$  bands which are comparable to  $\nu(\text{CN}t)$  at 2099 cm<sup>-1</sup> in (2,2,2). The more intense band at 2001 cm<sup>-1</sup> remains to be assigned to the two  $\nu(\text{CN}b)$  bonded through the nitrogen to Ru(III). These assignments imply that for (2,3) the 2110-cm<sup>-1</sup> band is  $\nu(\text{CN}t)$  bound to Ru(III), the band at 2098 cm<sup>-1</sup> is  $\nu(\text{CN}t)$  of the Ru(II) unit, and  $\nu(\text{CN}b)$  is the band at 2015 cm<sup>-1</sup>. These assignments are consistent with the shifts to higher energy of  $\nu(\text{CN}t)$  in the presence of Zn<sup>2+</sup> ions. Acetonitrile solutions of (2,3) in the presence of 3-fold excess of Zn<sup>2+</sup> exhibited cyanide stretches at 2146, 2120, and 2027 cm<sup>-1</sup>. In comparison KBr pellets of Ru<sup>II</sup>(bpy)<sub>2</sub>(CN)<sub>2</sub>-Zn<sup>II</sup> adducts<sup>28</sup> show bands at 2107 and 2095 cm<sup>-1</sup>.

In order to gain some general insight into the factors that affect the stretching frequency of bridging cyanides we have examined the IR spectra of a series of binuclear and trinuclear species. The complexes include M-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN, M-NC-Ru<sup>II</sup>(bpy)<sub>2</sub>-CN-M, M-NC-Os<sup>II</sup>(bpy)<sub>2</sub>-CN, and (phen)-(CO)<sub>3</sub>Re<sup>I</sup>CN-M (M = [Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>2+/3+</sup> and/or [Ru(NH<sub>3</sub>)<sub>4</sub>(py)]<sup>2+/3+</sup>). The cyanide frequencies from the IR spectra are reported in Table II. The assignments of bridging versus terminal cyanides for the binuclear ruthenium compounds are based on the comparison between Ru(bpy)<sub>2</sub>(CN)<sub>2</sub> and the related trinuclear

(27) The IR spectra of the solid mixed-valence complexes showed an increasing amount of unoxidized species from NaCl to KBr pellets. No indication of decomposition, under these experimental conditions, was obtained by absorption spectra analysis after dissolution of the KBr pellets in water.

(28) The stoichiometry of this adduct was not investigated. Ru-Zn adducts can be easily obtained by addition of an excess of Zn<sup>2+</sup> ions to CH<sub>3</sub>CN solutions of Ru(bpy)<sub>2</sub>(CN)<sub>2</sub>. The higher energy of  $\nu(\text{CN})$  with respect to those exhibited by the dicyanide complex suggest that both CN groups are bound to Zn<sup>2+</sup>.



**Figure 1.** FTIR spectra in  $\text{CH}_3\text{CN}$  solutions: (a)  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}]^+$  (continuous line),  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$  (dashed line); (b)  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{II}}(\text{bpy})_2\text{-NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}]^{2+}$  (continuous line),  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN}]^{3+}$  (dashed line).

species. For the binuclear  $[\text{NC-Os}(\text{bpy})_2\text{-CN-Ru}(\text{NH}_3)_5]^{3+}$   $\nu(\text{CN}t)$  and  $\nu(\text{CN}b)$  are assigned on the basis of the effect observed upon  $\text{Zn}^{2+}$  addition (Table II) and on the comparison with  $[\text{Os}(\text{bpy})_2(\text{Cl})\text{-CN-Ru}(\text{NH}_3)_5]^{3+}$  (Table II). These assignments are also confirmed by resonance Raman studies; vide infra.

For the dimers and trimers based on  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  and  $\text{Ru}(\text{II})$  ammine moieties, cyanide stretching frequencies are typically observed at  $30\text{--}60\text{ cm}^{-1}$  higher frequency than  $\nu(\text{CN})$  of the  $\text{Ru}(\text{II})$  monomer. These changes are consistent with those of the previously investigated  $\text{Ru-Pt}$  complexes (Table I).<sup>3</sup> With N-bonded  $\text{Ru}(\text{III})$  ammine units  $\nu(\text{CN}b)$  shifts in the opposite direction decreasing with respect to  $\nu(\text{CN})$  of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  by  $50\text{--}60\text{ cm}^{-1}$ . For all the cyano-bridged species an increase in the intensity of  $\nu(\text{CN}b)$  is observed for the oxidized compared to the reduced complex. This observation can be understood by the larger change in dipole moment experienced by the CN stretch by being bound by  $\text{Ru}(\text{II})$  and  $\text{Ru}(\text{III})$  instead of two  $\text{Ru}(\text{II})$  units. This general trend is also observed for the binuclear  $\text{Os-Ru}$  complexes but with a lesser increase in frequency as compared to the osmium monomer.

The exception to this trend is observed in dimers containing  $\text{Re}(\text{I})$  (Table II). The opposite shifts occur with  $\nu(\text{CN}b)$  decreasing by  $13\text{ cm}^{-1}$  for  $[(\text{phen})(\text{CO})_3\text{Re-CN-Ru}^{\text{II}}(\text{NH}_3)_5]^{2+}$  with reference to the CN stretch of  $(\text{phen})(\text{CO})_3\text{Re}^{\text{I}}\text{CN}$ . In  $[(\text{phen})(\text{CO})_3\text{Re}^{\text{I}}\text{CN-Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$ ,  $\nu(\text{CN}b)$  is  $2141$  or  $18\text{ cm}^{-1}$  greater than in the  $\text{Re}(\text{I})$  monomer.

The effect of bridge formation on the cyanide stretching frequency is clearly a complex one. The results can be analyzed by considering the combined effects of three factors:<sup>29,30</sup> (i) kinematic coupling; (ii) back-bonding from the C-bonded metal; (iii) back-bonding from the N-bonded metal.

(i) Kinematic coupling is defined as the simple mechanical constraint on the CN motion imposed by the presence of the

second metal center. This effect is expected to always be present and to shift  $\nu(\text{CN})$  to higher frequency upon bridge formation.<sup>25</sup>

(ii) A certain amount of back-bonding from the metal bound to the carbon of the cyanide may be present before bridge formation. This back-bonding is dependent on the nature of the metal and other ligands present as potential competitors. The back-bonding is expected to be enhanced by the withdrawal of charge from the CN which accompanies coordination to the second metal. A weakening of the CN bond is predicted with a shift to lower frequency of  $\nu(\text{CN})$  with the formation of the bridge.

(iii) Back-bonding to a bridging cyanide from the metal bound to the nitrogen is not generally considered. However, when a metal in a low oxidation state with strong donating ligands is present at this position and the C-bonded center does not act as a strong  $\pi$ -donor, this effect may become relevant. This effect is then similar to what has been observed with coordinated nitriles.<sup>31,32</sup> In such a case, back-bonding at the nitrogen end may represent a source of bond weakening resulting in a shift of  $\nu(\text{CN})$  to lower frequency upon bridge formation.

In general, these three effects are expected to operate simultaneously with the magnitude and direction of the frequency shift depending on their relative importance.

In complexes of the general formula  $\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-M}$ ,  $\nu(\text{CN}b)$  shifts to higher energy when M is a poor Lewis acid group such as  $\text{Zn}^{\text{II}}$ , a  $\text{Pt}(\text{II})$  unit,  $\text{Ru}^{\text{II}}(\text{NH}_3)_5$ , or a  $\text{Ru}^{\text{II}}(\text{bpy})_2$  unit (Table II). In such a case, it is likely that no substantial enhancement of the back-bonding from the  $-\text{Ru}(\text{bpy})_2-$  center to the cyanide is caused by coordination to M. The strength of the bridging cyanide bond is not significantly altered, and therefore, the kinematic coupling effect predominates. When M is a strong Lewis acid such as a  $\text{Ru}^{\text{III}}(\text{NH}_3)_5$  or  $\text{Ru}^{\text{III}}(\text{bpy})_2$ , a shift to lower frequency is observed. This is consistent with strong enhancement of  $\pi$  back-bonding upon forming the bridge. The kinematic coupling effect is then no longer predominant, and the increase in  $\nu(\text{CN}b)$  intensity is consistent with enhanced back-bonding.<sup>33,34</sup>

With complexes of the form  $(\text{phen})\text{Re}^{\text{I}}(\text{CO})_3\text{CN-M}$  (M is  $[\text{Ru}(\text{NH}_3)_5]^{2+/3+}$ ), the opposite behavior is observed when M is changed from  $\text{Ru}(\text{II})$  to a  $\text{Ru}(\text{III})$  ammine fragment. This effect is most likely related to the fact that in the mononuclear  $(\text{phen})\text{Re}^{\text{I}}(\text{CO})_3\text{CN}$  complex, the carbonyl groups act as strong  $\pi$ -acceptors, as demonstrated by the low  $\nu(\text{CO})$  (Table II) and very positive  $\text{Re}(\text{II})/(\text{I})$  potential ( $E_{\text{p,a}}$  in  $\text{CH}_3\text{CN}$  ( $100\text{ mV/s}$ ) =  $1.6\text{ V}$  vs SCE). Thus  $\pi$  back-bonding to the cyanide is very small due to this competition, as demonstrated by the high  $\nu(\text{CN}b)$ . It is likely that in this situation  $\pi$  donation to the bridging cyanide from nitrogen-bonded  $\text{Ru}(\text{II})$  ammine unit can be significant. This effect leads to a significant weakening of the bridging cyanide resulting in a small shift of  $\nu(\text{CN}b)$  toward lower frequency. When M is a  $\text{Ru}(\text{III})$  ammine fragment, the predicted increase in  $\pi$  back-bonding from  $\text{Re}(\text{I})$  to the cyanide (with a corresponding decrease in back-bonding to the carbonyls, as witnessed by the observed increase in their stretching frequency; Table II) is evidently not sufficient to counterbalance the kinematic coupling effect. This then leads to an overall small shift of  $\nu(\text{CN}b)$  to higher frequency.

The above analysis shows that the total molecular environment contributes to the frequency changes of the cyanide stretch upon bridge formation. Thus, unless very homogeneous classes of compounds are considered, generalizations must be taken with great caution.

**Time-Resolved Infrared Spectroscopy.** The time-resolved infrared technique provides a vibrational probe of the metal oxidation state in the excited states of polynuclear complexes.

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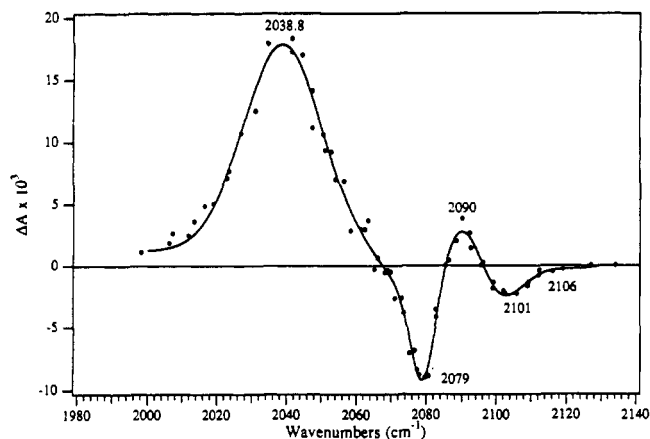
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(34) Schilt, A. A. *Inorg. Chem.* **1964**, *9*, 1323.

(29) These factors seem to be particularly relevant in the present case. Other factors, such as  $\sigma$  effects, should be considered in a general case.<sup>30</sup>

(30) Sarapu, A. C.; Fenske, R. S. *Inorg. Chem.* **1975**, *14*, 247.

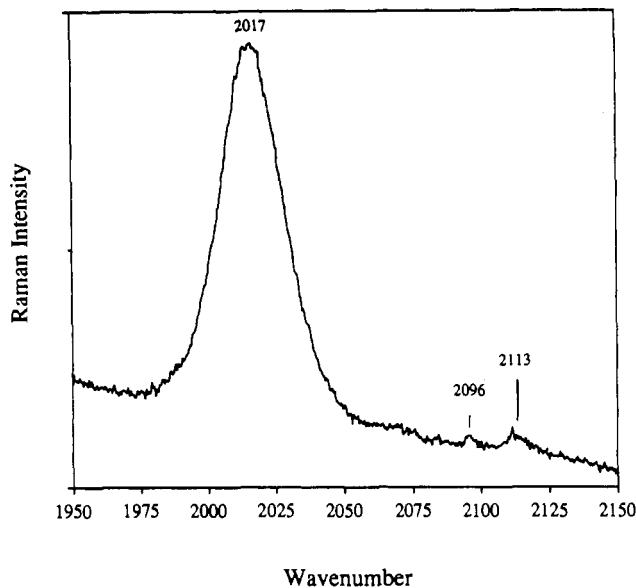


**Figure 2.** Time-resolved IR absorbance difference ( $\Delta A$ ) spectrum of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^+$  in  $\text{CH}_3\text{CN}$ , generated with 532-nm pulsed excitation and 300  $\mu\text{J}$  per pulse. The sample concentration is ca. 2 mM in a 0.2 mm path length cell.

The IR  $\Delta A$  spectrum for the MLCT excited state of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^+$ , (2,2\*), is shown in Figure 2. Depletion signals are observed at 2079 and 2101  $\text{cm}^{-1}$ , which correspond to the ground-state CN vibrations of (2,2) at 2079 and 2104  $\text{cm}^{-1}$ . Excited-state bands clearly appear at 2039 and 2090  $\text{cm}^{-1}$ . The presence of a third excited-state absorption at 2106  $\text{cm}^{-1}$  can be inferred from a multi-Gaussian fit of the  $\Delta A$  spectrum (solid line of Figure 2) that takes into account the spectral parameters of the ground state. Comparison of the excited-state spectrum with that of the chemically produced mixed-valence dimer (2,3) permits band assignments to be made. The intense 2039- $\text{cm}^{-1}$  feature is the  $\text{CN}_b$  stretch shifted down in frequency from 2104 in the ground-state (2,2) complex. The 2090- $\text{cm}^{-1}$  band is assigned to the  $\text{Ru}^{\text{II}}(\text{CN}_t)$  stretch. This band is at 2079  $\text{cm}^{-1}$  in the ground-state (2,2) complex and shifts to 2098  $\text{cm}^{-1}$  in (2,3). Finally, the band at 2106  $\text{cm}^{-1}$  is assigned as the  $\text{Ru}^{\text{III}}(\text{CN}_t)$  stretch, which occurs in the (2,3) complex at 2110  $\text{cm}^{-1}$ .

The excited-state complex (2,2\*) involves the promotion of an electron from a  $d\pi$  orbital on one of the metals to a  $\pi^*$  ligand-based orbital. The formula for the excited state may be written as  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})(\text{bpy})\text{-CN}]^+$ , with the N-bonded chromophore being the lower energy excited state. The distribution of electron density about the metal centers is similar for the (2,3) and (2,2\*) species. Both species show a significant shift down in the frequency for the  $\text{CN}_b$  stretch from the (2,2) complex. For the (2,3) the shift is 90  $\text{cm}^{-1}$  compared to 65  $\text{cm}^{-1}$  for (2,2\*). Both species show an upshift in frequency relative to the (2,2) spectrum for the  $\text{Ru}^{\text{II}}(\text{CN}_t)$  stretch at 2079  $\text{cm}^{-1}$ . For the (2,3) compound this shift is to 2098  $\text{cm}^{-1}$  as compared to 2090  $\text{cm}^{-1}$  for (2,2\*). The significant downshift in  $\text{CN}_b$  frequency and the presence of three excited-state absorptions supports a valence-localized model.

The magnitude of the frequency shift is less for (2,2\*) than (2,3) relative to (2,2). This indicates that the difference in electron density about the metal centers is less in the photochemically prepared mixed-valence dimer (2,2\*) than for the chemically prepared species (2,3). It has been shown using time-resolved resonance Raman spectroscopy that in many metal complexes the MLCT excited states do not completely transfer electron density from the metal  $d\pi$  orbital to the  $\pi^*$  ligand orbital,<sup>35</sup> since the electron donor and acceptor orbitals involved in the transition are coupled. The extent of charge transfer is less than 1 electron



**Figure 3.** Raman spectrum of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^{2+}$  in  $\text{CH}_3\text{CN}$  with laser excitation of 720 nm. The spectrum was obtained under near-resonance conditions with the intense intervalence band at 1300 nm. The spectrum was measured immediately after oxidation of  $[\text{NC-Ru}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{bpy})_2\text{-CN}]^+$  by  $\text{Br}_2$  vapor and is the result of 16 1-min integrations.

unit. The smaller shifts for (2,2\*) than (2,3) are consistent with this explanation.

**Resonance Raman Spectroscopy.** The resonance Raman technique is useful in uncovering the nature of the electronic transitions since intensity enhancement of modes associated with the absorbing chromophore are expected. In dimeric complexes which possess intervalence transfer (IT) transitions, enhancement of vibrations associated with the bridging ligand as well as metal-ligand stretches and deformations are observed when in resonance with these absorptions.<sup>36</sup> The first such example of this type of experiment utilized  $[(\text{CN})_5\text{Ru}^{\text{II}}\text{-CN-Ru}^{\text{III}}(\text{NH}_3)_5]^-$ . The most intense Raman peak is assigned to the bridging cyanide stretch at 2118  $\text{cm}^{-1}$ . Enhancement is also observed for the terminal cyanide stretch (2077  $\text{cm}^{-1}$ ) along with the various metal-ligand stretches and deformations in the low-frequency region of the spectrum.<sup>37</sup>

Recently, this technique has been extended to the binuclears  $[\text{NC-Os}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$  and  $[(\text{Cl})\text{Os}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$ . In these complexes excitations of 647.1, 676.4, and 752.4 nm are in resonance with the  $\text{Os}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$  charge-transfer band near 800 nm.<sup>38</sup>  $\nu(\text{CN}_b)$  is identified as the intense peak at 1995  $\text{cm}^{-1}$ , while  $\nu(\text{CN}_t)$  is attributed to the weak band at 2055  $\text{cm}^{-1}$  in the spectrum of  $[\text{NC-Os}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$ . These assignments are verified by the comparison of these two species, as the 2055- $\text{cm}^{-1}$  peak is not present for  $[(\text{Cl})\text{Os}^{\text{II}}(\text{bpy})_2\text{-CN-Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$ .

In near-resonance conditions with the near-infrared absorption band of (2,3),<sup>1</sup> Raman spectra are expected to demonstrate an intense peak due to the bridging cyanide as well as two weaker terminal CN stretches between 1900 and 2300  $\text{cm}^{-1}$ . Excitation of 720 nm results in the Raman spectrum in Figure 3. The spectrum shows a relatively intense peak at 2017  $\text{cm}^{-1}$  with two very weak features at 2096 and 2113  $\text{cm}^{-1}$ . The same features are observed with excitation of 676.4 nm but with weaker Raman peaks as expected when the exciting laser line is further removed from the absorption band. No peaks are observed for the corresponding (2,2) species in this region in analogous experiments. The intense peak at 2017  $\text{cm}^{-1}$  in (2,3) can then be assigned

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**Table III.** Spectroscopic Parameters of the Mixed-Valence Complexes

complex (solv)	$\nu_{\max}(\text{MLCT}), 10^3 \text{ cm}^{-1}$ ( $\epsilon, \text{ L mol}^{-1} \text{ cm}^{-1}$ )	$\nu_{\max}(\text{IT}), 10^3 \text{ cm}^{-1}$ ( $\epsilon, \text{ L mol}^{-1} \text{ cm}^{-1}$ )	$\Delta\nu_{1/2}, 10^3 \text{ cm}^{-1}$	$\alpha^2$	$\Delta\nu_{1/2}(\text{calcd}),^a$ $10^3 \text{ cm}^{-1}$	$\Delta\nu_{1/2}(\text{calcd}),^b$ $10^3 \text{ cm}^{-1}$
(2,3) (CH <sub>3</sub> CN)	25.4 (9900)	7.69 (10 200)	3.4	0.07	3.9	2.5
(2,3) (D <sub>2</sub> O)	26.3 (7900) <sup>c</sup>	8.0 (9000) <sup>c</sup>	3.6	0.06	4.0	
(2,3') (CH <sub>3</sub> CN)	25.6 (10 500)	7.58 (10 500)	3.4	0.07	3.9	2.5
(2,3') (D <sub>2</sub> O)	26.7 (9800) <sup>c</sup>	7.90 (10 900) <sup>c</sup>	3.3	0.07	4.0	
(2,3,2) (CH <sub>3</sub> CN)	23.6 (17 000)	7.25 (11 700)	4.9	0.12	3.6	2.6
(2,3,2) (D <sub>2</sub> O)	24.8 (15 900) <sup>c</sup>	8.2 (9500) <sup>c</sup>	5.1	0.09	3.9	
(2,3'',2) (D <sub>2</sub> O)	25.1 (15 000)	7.5 (9500)	4.8		3.7	

<sup>a</sup> Calculated for  $\Delta E = 1000 \text{ cm}^{-1}$  (binuclear) and  $\Delta E = 1600 \text{ cm}^{-1}$  (trinuclear). <sup>b</sup> Calculated for  $\Delta E = E_{1/2}(2) - E_{1/2}(1)$ . <sup>c</sup> From ref 1.

as to the bridging CN stretch in confirmation of the IR result. Furthermore, the two weak features are at the frequency expected for the terminal stretches from IR data.

**Electronic Spectra of Mixed-Valence Compounds.** Relevant spectral parameters for (2,3), (2,3'), (2,3,2), and (2,3'',2) are reported in Table III. The absorption bands in the visible region can be assigned to  $d\pi\text{Ru(II)} \rightarrow \pi^*(\text{bpy})$  (MLCT) transitions. As expected for MLCT bands which are localized on electronically independent moieties, the band intensities are proportional to the number of Ru(II) centers. The energy increases, with respect to the isoivalent species, are of comparable magnitude with those observed for adducts of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  with Lewis acids.<sup>3-7</sup> Furthermore the band maxima shift to higher energy by changing the solvent from acetonitrile to water, which is expected for MLCT bands for complexes of this type.<sup>18-23</sup>

An alternative interpretation has been forwarded by Cooper et al.,<sup>9</sup> who proposed the assignment of a ligand-to-metal charge-transfer (LMCT) transition for (2,3) in this region. This assignment was based on the comparison with an electronic absorption spectrum, obtained upon oxidation of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CN})_2$  in  $\text{CH}_3\text{CN}$  solution, supposedly belonging to  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{CN})_2]^+$  ( $\nu_{\max} = 22 \times 10^3 \text{ cm}^{-1}$ ,  $\epsilon$  ca. 9000).<sup>39</sup> However, the spectrum does not correspond to that of  $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{CN})_2]^+$ . The electrochemical oxidation of  $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CN})_2$  is indeed very complicated. No isosbestic points are observed in spectroelectrochemical experiments (controlled-potential electrolysis (CPE) at +0.95 V vs SCE), but spectral variations occur showing an initial bleaching of the  $\text{Ru}^{\text{II}}(\text{bpy})$  MLCT absorption ( $\lambda_{\max} = 495 \text{ nm}$ ). This bleach is followed by spectral changes which are independent of the applied potential and lead to a final spectrum with  $\lambda_{\max} = 460 \text{ nm}$ . Cyclic voltammetric measurements taken at different points of the CPE show the appearance of a new wave at about 1.2 V vs SCE. The spectral features of the solvent complex  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CN})(\text{CH}_3\text{CN})]^+$ <sup>40</sup> ( $\epsilon = 9000$ ,  $\nu_{\max} = 22 \times 10^3 \text{ cm}^{-1}$ ) are coincident with the final spectrum obtained for CPE of acetonitrile solutions of  $[\text{Ru}(\text{bpy})_2(\text{CN})_2]$ . Furthermore,  $E_{1/2}$  of the Ru(III)/(II) couple for the solvent complex is 1.18 V vs SCE. The spectrum reported by Cooper et al. is therefore likely that of  $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CN})(\text{CH}_3\text{CN})]^+$ , and the band at  $22 \times 10^3 \text{ cm}^{-1}$  should be then ascribed to a MLCT transition.

The instability of the  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  complex toward oxidation as well as the observed instability of this unit in  $\text{M}-\text{NC}-\text{Ru}(\text{bpy})_2-\text{CN}-\text{M}$  adducts is consistent with carbon coordination of CN to the metal.<sup>1,2</sup> In contrast, the stability in solution of oxidized polynuclear complexes in which the nitrogen is bound to Ru(III) polypyridine units is consistent with the high  $\sigma$ -donor ability of the nitrogen end of CN.<sup>41</sup>

In the weak coupling limit, Hush equations can be applied in the analysis of IT bands.<sup>8</sup> Table III reports the spectroscopic parameters of the IT bands, obtained in water and acetonitrile

solutions of various mixed-valence complexes, and  $\alpha^2$  values.<sup>42</sup> The sensitivity of the IT bands to solvent changes is lower than that of the residual MLCT absorption bands in all the complexes examined, suggesting strong electronic delocalization. It should be noted, however, that the specific solvent interactions<sup>18-23</sup> which cause an increase of the MLCT energy in the mixed-valence complexes may also be responsible for some compensation of the expected increases in the IT energy upon going from  $\text{CH}_3\text{CN}$  to water. By correction of the  $E_{1/2}$  value of the Ru(III)/(II) couples obtained in water solution<sup>1</sup> for a liquid junction potential of 0.19,<sup>43</sup> the thermodynamic energy contributions to the IT transition result in comparable magnitudes in the two solvents. Considering also the differences in the dielectric functions ( $1/D_{\text{op}} - 1/D_s$ ), 0.53 in acetonitrile and 0.55 in water, no substantial IT band shift is expected in these two solvents.

The  $\alpha^2$  values are of the order of 0.07–0.1 (Table III), indicating some departure from complete localization of the odd electron in these species. Half-widths of these bands are, however, wider than those observed for typical class III mixed-valence compounds.<sup>44</sup> The width at half-height of the IT band ( $\Delta\nu_{1/2}$ ) is related to the band maximum ( $\nu_{\max}$ ) and to the internal energy difference between the two oxidation state isomers ( $\Delta E$ ) by eq 1.

$$\Delta\nu_{1/2} = [2310(\nu_{\max} - \Delta E)]^{1/2} \quad (1)$$

For asymmetric mixed-valence compounds, application of this equation requires the knowledge of  $\Delta E$ , which is not readily available.<sup>44</sup> An upper limit for  $\Delta E$  is represented by  $\Delta E_{1/2}$ . For example, for (2,3), the difference between the redox potential of the (3,3)/(2,3) and (2,3)/(2,2) couples may be used.<sup>45,46</sup> The lower limit is obtained when all the different factors affecting the constant of the comproportionation equilibrium are taken into account.<sup>42,47</sup> This limit is given by the contribution of the electronic asymmetry of the bridging ligand. As shown in Table III, the calculated  $\Delta\nu_{1/2}$  values are in the range 10% higher to 30% lower than that observed.<sup>42,48</sup> Since it is unrealistic to consider the redox asymmetry as the only term contributing to  $\Delta E$ , these spectral features can also be considered consistent with an essentially trapped-valence description of a mixed-valence complex.

## Conclusions

The results reported in this paper support a localized picture of the binuclear and trinuclear cyano-bridged Ru–polypyridine complexes. Infrared spectra of the mixed-valence  $[\text{NC}-\text{Ru}^{\text{II}}$

(39) It should be noted that for an LMCT transition,  $\pi(\text{bpy}) \rightarrow d\pi(\text{RuIII})$ , the energy maximum should shift to lower energy by increasing the polarity of the solvent, allowing for the lower energy difference between filled  $\pi(\text{bpy})$  and  $d\pi^*(\text{RuIII})$  orbitals.

(40) The  $[\text{Ru}(\text{bpy})_2(\text{CN})(\text{CH}_3\text{CN})]^+$  complex was prepared by stoichiometric addition of  $\text{NaN}_3$  to an acetonitrile solution of  $[\text{Ru}(\text{bpy})_2(\text{CN})(\text{NO})]^{2+}$ .

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(44) Creutz, C. *Prog. Inorg. Chem.* 1983, 30, 1.

(45) A substantial contribution to the high peak splitting ( $E_{1/2}(2) - E_{1/2}(1)$ ) observed for these polynuclear species, ca. 0.6 V, may result from electrostatic effects as discussed for  $[(\text{bpy})_2\text{RuCl}]_2^{+}$ .<sup>46</sup>

(46) Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* 1978, 8, 2211.

(47) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* 1984, 23, 3002.

(48) It is well-known that for fully delocalized systems calculated  $\Delta\nu_{1/2}$  values exceed the experimental ones.<sup>44</sup>



$(bpy)_2-CN-Ru^{III}(bpy)_2-CN]^{2+}$  complex demonstrate three cyanide stretching bands indicative of a valence-localized model of these species. The lack of resolved multiple absorption bands and different shifts in absorption and emission need *not* to be explained by a delocalized model as these observations are consistent with overlapping absorption bands of several chromophores and small interchromophoric energy differences.

All the experimental results (IR, resonance Raman, time-resolved infrared, electronic absorption and emission spectra) on the fully reduced and mixed-valence forms can be consistently interpreted in terms of a substantially localized model for the complexes. In this model, the metal-metal interaction, mediated by the bridging cyanide(s), is sufficiently small (relative to vibronic trapping energies) that *oxidation states* and *electronic excitation* are essentially localized on the various metal-containing fragments but strong enough to allow mutual *perturbation* of the fragments. In other words, each molecular fragment retains its identity (with individual redox sites and electronically excited states) in the polynuclear complex, although the energetics associated with each fragment (redox potentials and excitation energies) may shift somewhat depending on the nature and oxidation state of the other metal centers. An inherent energetic asymmetry is associated with the asymmetry of the cyanide bridge, favoring by ca.  $1 \times 10^{-3} \text{ cm}^{-1}$  the electronic excitation (and by ca. 0.15 V the oxidation) of an N-bonded Ru(II) center relative to an equivalent C-bonded one. The photophysical behavior of the fully reduced species, characterized by efficient intercomponent energy transfer and emission from the lowest energy chromophore, is also fully consistent with such a model.

Some interesting general conclusions concerning the effect of

bridge formation on cyanide stretching frequencies have been drawn, based on the comparison of a wide variety of cyano-bridged complexes. The effect appears to be a complex function of kinematic coupling and  $\pi$ -back-bonding effects. When changes in  $\pi$ -back-bonding upon bridge formation are negligible, as when the additional metal center is a poor Lewis acid (like Ru(II)), the C-N bond order is not altered and kinematic coupling dominates resulting in a shift to higher frequency. On the other hand, when a good Lewis acid (like Ru(III)) binds to the nitrogen end of a cyanide already bound to a good  $\pi$ -donor center,  $\pi$ -back-bonding to the cyanide is strongly enhanced causing substantial weakening of the C-N bond. In this case, the kinematic effect can be overcome and shifts to lower frequency may result.

Finally, these results demonstrate that the transient IR technique has great potential for characterization of the metal oxidation state in the MLCT excited state of polynuclear complexes. Experiments of this type can provide important information on the degree of metal-metal coupling and on its effect on the photophysical properties.

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