

# Ground-State, Mode-Dependent Vibronic Coupling in Some Simple, Cyanide-Bridged Transition-Metal Donor–Acceptor Complexes

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Patterns of the shifts in bridging cyanide-stretching frequencies have been examined in several fully saturated,  $\mu$ -cyano, bi- or trimetallic transition-metal donor–acceptor (D/A) complexes. An earlier (Watzky, M. A.; et al. *Inorg. Chem.* **1996**, *35*, 3463) inference that the bridging ligand nuclear and the D/A electronic coordinates are entangled is unequivocally demonstrated by the  $32\text{ cm}^{-1}$  lower frequency of  $\nu_{\text{CN}}$  for  $(\text{NH}_3)_5\text{Cr}(\text{CNRu}(\text{NH}_3)_5)^{4+}$  than for the cyanopentaamminechromium(III) parent. This contrasts to the  $41\text{ cm}^{-1}$  increase in  $\nu_{\text{CN}}$  upon ruthenation of  $(\text{NH}_3)_5\text{RhCN}^{2+}$ . More complex behavior has been found for cis and trans trimetallic, donor–acceptor complexes. The symmetric combination of  $\text{CN}^-$  stretching frequencies in *trans*- $\text{Cr}^{\text{III}}(\text{MCL})(\text{CNRu}^{\text{II}}(\text{NH}_3)_5)^{5+}$  complexes (MCL = a tetraazamacrocyclic ligand) shifts  $100\text{--}140\text{ cm}^{-1}$  to lower frequency, and the antisymmetric combination shifts less than about  $30\text{ cm}^{-1}$ . This contrast in the shifts of the symmetric and the antisymmetric combinations of the CN stretches persists even in a trans complex with no center of symmetry. Two CN stretches have also been resolved in an analogous cis complex, and both shift to lower frequency by about  $60\text{ cm}^{-1}$ . The net shift, summed over all the CN-stretching frequencies, is about the same for the bis-ruthenates of related dicyano complexes. A simple, symmetry-adapted perturbation theory treatment of the coupled vibrations is employed to deal with the opposing effects of the “kinematic” shifts ( $\delta$ ) of  $\nu_{\text{CN}}$  to higher frequency, expected in the absence of D/A coupling, and shifts ( $\delta'$ ) of  $\nu_{\text{CN}}$  to lower frequency that occur when D/A coupling is large. The Rh(III)- and Cr(III)-centered complexes correspond to different limits of this model:  $\delta > \delta'$  and  $\delta < \delta'$ , respectively. When referenced by means of this model to complexes with Rh(III) acceptors, the shifts in trimetallic complexes, summed over the symmetric and antisymmetric combinations of CN stretches, are about twice those of bimetallic complexes. Similarly referenced and summed over all bridging CN frequencies, the shifts of  $\nu_{\text{CN}}$  to lower energies are proportional to the oscillator strength of the electronic, donor–acceptor charge-transfer transition. The simplest interpretation of this correlation is that the donor–acceptor coupling in these systems is a function of the nuclear coordinates of the bridging ligand. This behavior of these complexes is semiquantitatively consistent with expectation for  $\text{CN}^-$ -mediated vibronic (pseudo-Jahn–Teller) coupling of neighboring donors and acceptors, and the observed  $\text{Ru}^{\text{II}}/\text{CN}^-$  CT absorption parameters can be used in a simple, semiclassical vibronic model to predict shifts in  $\nu_{\text{CN}}$  that are in reasonable agreement with those observed.

## Introduction

Striking symmetry-dependent effects associated with the electronic coupling in some simple molecular complexes containing transition-metal donors (D) and acceptors (A) bridged by cyanide have been observed.<sup>1–3</sup> Symmetry dependent properties can yield information about the selection rules for D/A electronic coupling and, by inference, for electron transfer processes. In this paper we describe some remarkable symmetry dependencies observed for the mixing of the  $\text{CN}^-$  stretching vibrations and the D/A electronic coupling in cyanide-bridged transition-metal complexes.

The electronic coupling between electron transfer donors (D) and acceptors (A) is one of the most fundamental properties of reacting chemical systems and one of the most difficult to

systematically investigate.<sup>4–21</sup> The effect of electronic coupling on electron transfer reactivity is manifested in the electronic transmission coefficient,  $\kappa_{\text{el}}$ , which is a factor in the semiclassical

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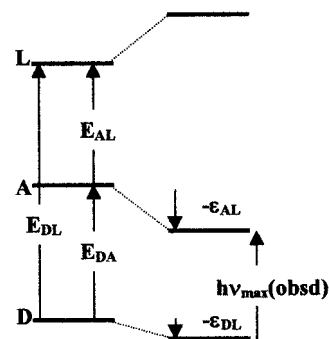
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description of electron transfer rate constants, eq 1.<sup>22,23</sup>

$$k_{\text{et}} = \kappa_{\text{el}} \kappa_{\text{nu}} \nu_{\text{nu}} \quad (1)$$

In addition, electronic coupling, usually represented by the matrix element  $H_{\text{DA}}$ , can also result in the modification of the physical properties of molecular ground states. It can give rise to (a) donor–acceptor charge transfer (DACT) bands whose oscillator strengths are proportional to  $H_{\text{DA}}^2$ ;<sup>4–11</sup> (b) variations in stability of the ground state<sup>4,6,7</sup> which are also proportional to  $H_{\text{DA}}^2$  (e.g., it may contribute to shifts in standard potentials<sup>10,11,24–32</sup>); or (c) changes in a number of other spectroscopic or thermodynamic properties.<sup>1–3,9,10,33</sup> The systematic variations in such properties in a series of related compounds might be used, in principle, to determine  $H_{\text{DA}}$ .

In practice, the manner in which the experimentally observed molecular properties vary with  $H_{\text{DA}}$  has sometimes been subjected to differing theoretical interpretations, and the evaluations of  $H_{\text{DA}}$  based on the analysis of different properties have sometimes led to significantly different conclusions.<sup>4–16,20,21,34–37</sup> Some of the conflicting views and much of the experimental challenge are consequences of (1) the difficulty in separating the effects of  $H_{\text{DA}}$  on ground-state properties from those which are the consequence of factors (nuclear reorganizational energy,  $\lambda_r$ ;  $\Delta G^\circ$ ; etc.) contributing to  $\kappa_{\text{nu}}$  that may also vary with the changes in molecular structure necessary to vary  $H_{\text{DA}}$ ; (2) the use of different approximate models in dealing with the complex issues of electronic coupling in different systems; and (3) the frequent assumption that some specific, simple models are equally useful in all systems. These problems are especially at issue when dealing with linked D/A systems, since the linker can play a major role in determining  $H_{\text{DA}}$ . Several theoretical studies,<sup>38–42</sup> recent experimental work with CN<sup>–</sup>-bridged D/A



**Figure 1.** Qualitative three-state energy level scheme in which a bridging ligand excited state (L) is configurationally mixed with ground (D) and excited (A) electron transfer states. The mixing results in a perturbational stabilization,  $\epsilon_{iL} = H_{iL}^2/E_{iL}$ , of the electron transfer states ( $i = D, A$ ).

complexes<sup>1–3,30–33</sup> and with oxo-bridged Fe<sup>II</sup>/Fe<sup>III</sup> complexes<sup>43,44</sup> have raised the possibility that in some systems  $H_{\text{DA}}$  may be a function of some specific nuclear coordinates. Such a dependence of  $H_{\text{DA}}$  on the nuclear coordinates implies that the separation of coordinates implicit in eq 1 is not always useful. This stands in contrast to the common assumption that electronic coupling is independent of the nuclear coordinates in electron transfer systems.

The most common approach for taking into account the role of the bridging ligand in mediating D/A coupling is in terms of the perturbational mixing of the electron transfer states with some higher energy electronic state involving the bridging ligand, typically a metal-to-ligand charge transfer (MLCT) state.<sup>4,5,8,10,12,45</sup> A typical mixing scheme is illustrated in Figure 1 and by eqs 2 ( $i = D, A$ ). This mixing gives rise to

$$\Psi_i = (\psi_i^\circ + \alpha_{iL}\psi_L^\circ)/(1 + \alpha_{iL}^2)^{1/2} \quad (2a)$$

$$\alpha_{iL} = H_{iL}/E_{iL} \quad (2b)$$

superexchange coupling in which the electronic matrix element is given by eqs 3<sup>8</sup>

$$H_{\text{DA}}^{\text{spx}} = H_{\text{DL}}H_{\text{LA}}/E_{\text{av}} \cong H_{\text{DL}}^2/E_{\text{av}} \quad (3a)$$

$$E_{\text{av}} = 2E_{\text{DL}}E_{\text{AL}}/(E_{\text{DL}} + E_{\text{AL}}) \quad (3b)$$

in which the parameters can be inferred from the MLCT spectra (vertical energies,  $E_{iL}$ , from absorption maxima and matrix elements,  $H_{iL}$ , from the oscillator strength).<sup>46</sup> This approach has been very successful when  $H_{\text{DA}}$  is small (typically less than 200 cm<sup>–1</sup>; e.g., see ref 45). However, in D/A systems with CN<sup>–</sup> linkers this model fails.<sup>1–3,30–33</sup> Most relevant to this work, the superexchange model does not easily accommodate the observed correlation between the CN<sup>–</sup> stretching vibrational frequency and the oscillator strength of the DACT transition<sup>1–3,32,33</sup> or the symmetry-dependent shifts of  $\nu_{\text{CN}}$  in the CN<sup>–</sup>-bridged complexes discussed in this paper. These experimental observations

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 (46)  $H_{ij} = (0.0205/r_{\text{DA}})[(\epsilon_{\text{max}})(\Delta\nu_{1/2})(h\nu_{\text{max}})]^{1/2}$  for a gaussian band,  $H_{ij}$  in cm<sup>–1</sup>,  $r_{\text{DA}}$  in Å;  $r_{\text{DA}}$  is the separation of centers of charge in the ground and excited states,  $\epsilon_{\text{max}}$  is the molar absorptivity at the band maximum,  $\Delta\nu_{1/2}$  is the band width at half-maximum, and  $h\nu_{\text{max}}$  is the energy of the band maximum.<sup>5–7</sup>

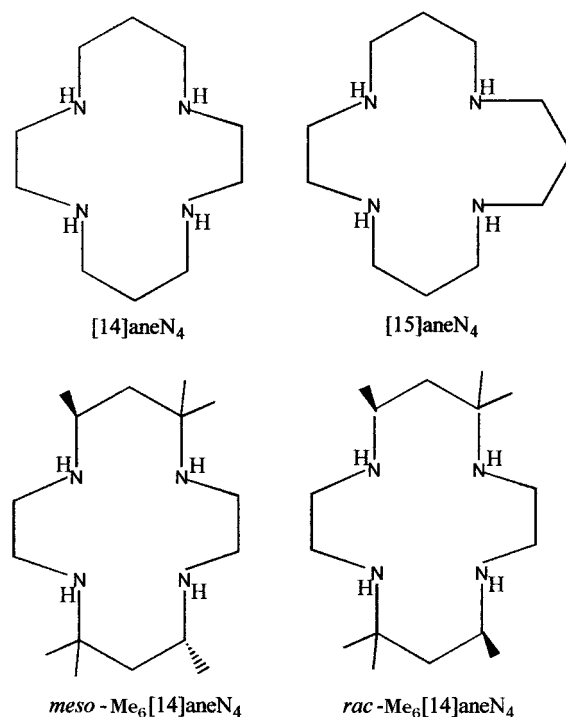
require that, in at least some systems, D/A “electronic” coupling is a function of the nuclear coordinates of the bridging ligand.

The behavior of the  $\text{CN}^-$ -linked complexes has led us to describe the electronic coupling between two metals bridged by  $\text{CN}^-$  in terms of a semiclassical vibronic, or pseudo-Jahn–Teller model.<sup>1–3,33</sup> We have also reported<sup>1</sup> a preliminary observation that the shift of  $\nu_{\text{CN}}$  in a *trans*-trimetallic complex, in which the three metals were bridged by two cyanides, was predominately in the symmetric combinations,  $\nu_s$ , of  $\text{CN}^-$  stretches and much less in the antisymmetric combination,  $\nu_a$ . This observation is very remarkable. We initially attributed it to a symmetry selection rule.<sup>1</sup> Alternatively, this large difference in the shifts of  $\nu_s$  and  $\nu_a$  might arise from some delocalized electronic interactions that were not incorporated in the semiclassical, pseudo-Jahn–Teller model that we employed in our earlier studies. Further investigation, reported here, of  $\text{CN}^-$ -bridged complexes has demonstrated that this mode specific vibronic coupling is characteristic of *trans* but not *cis* complexes.

## Experimental Procedures

**A. Synthesis of Complexes.** A large number of *cis* and *trans* complexes were synthesized for this study. Most of the parent [*cis*- and *trans*-M(MCL)(CN)<sub>2</sub>]X complexes have been reported previously (X = Cl<sup>-</sup> or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>):<sup>47</sup> *trans* complexes with MCL = [14]aneN<sub>4</sub> and M = Cr, Co, Rh;<sup>1,30,48–50</sup> *trans* complexes with MCL = *ms*-Me<sub>6</sub>[14]aneN<sub>4</sub> and M = Cr, Co, Rh;<sup>1,30,48–50</sup> [*trans*-Cr([15]aneN<sub>4</sub>)(CN)<sub>2</sub>]CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>;<sup>48</sup> [*cis*-Rh([14]aneN<sub>4</sub>)(CN)<sub>2</sub>]Cl;<sup>51</sup> *cis* complexes with MCL = *rac*-Me<sub>6</sub>[14]aneN<sub>4</sub> and M = Cr, Co, Rh.<sup>1,48,50,51</sup> The synthesis and characterization of many of the corresponding ruthenated complexes have also been reported (usually as PF<sub>6</sub><sup>-</sup> salts): *trans*-(MCL)M(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>5+</sup> with M = Cr, Co, Rh and MCL = [14]aneN<sub>4</sub> and *ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>; *cis*-(MCL)Cr(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>5+</sup>; *cis*-(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)-(CN)Cr(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>3+</sup>.<sup>1–3,30–32,52</sup> The skeletal structures of the macrocyclic ligands are illustrated in Figure 2. Literature syntheses were also followed for [Cr(NH<sub>3</sub>)<sub>5</sub>CN]X<sub>2</sub>,<sup>53</sup> [Ru(NH<sub>3</sub>)<sub>5</sub>Cl](Cl)<sub>2</sub>,<sup>54</sup> and [Ru(NH<sub>3</sub>)<sub>5</sub>O<sub>3</sub>SCF<sub>3</sub>](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>.<sup>55</sup> [Rh<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] was synthesized by first converting [Rh<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub><sup>55</sup> to [Rh<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>(O<sub>3</sub>SCF<sub>3</sub>)](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> in concentrated HO<sub>3</sub>SCF<sub>3</sub> at 110 °C for 3 h. The triflate product was mixed with an excess of NaCN in water and refluxed for 6 h. The cyano complex product was precipitated by the addition of NaClO<sub>4</sub>. The perchlorate salt was converted to the chloride by anion-exchange chromatography (Dowex 1X8; Cl<sup>-</sup> form). UV–vis and IR spectra were used to characterize the product<sup>57</sup> (yield, 30–40%).

***cis*- and *trans*-[Rh([15]aneN<sub>4</sub>)Cl<sub>2</sub>]Cl.** These complexes were synthesized in the same manner as *cis*- and *trans*-[Rh([14]aneN<sub>4</sub>)Cl<sub>2</sub>]Cl.<sup>50</sup> A solution of RhCl<sub>3</sub>·3H<sub>2</sub>O (1.0 g, 3.8 mmol) and [15]aneN<sub>4</sub> (0.86 g, 4.0 mmol) in 50 mL of methanol was refluxed for approximately 5 min. After cooling to room temperature, the yellow precipitate (*cis* complex) was collected by vacuum filtration, washed with ethanol and ether, and then dried in vacuo (yield, 35%). Any unreacted ligand (as well as any remaining *cis* isomer) was precipitated by means of the



**Figure 2.** Skeletal structures of the tetraazamacrocyclic ligands (see ref 37 for formal names).

addition of 10 mL of concentrated HCl to the filtrate. The solution was vacuum filtered, and the yellow filtrate was evaporated to dryness. The yellow residue (*trans* complex) was recrystallized from 20 mL of 3 M HCl, collected by vacuum filtration, washed with acetone and ether, and air dried (yield, 45%). The UV–vis spectra of the isolated materials were compared to the corresponding *cis/trans*-Rh(Me<sub>6</sub>[14]aneN<sub>4</sub>)Cl<sub>2</sub><sup>+</sup><sup>50,51</sup> and *cis/trans*-Rh(Me<sub>6</sub>[14]aneN<sub>4</sub>)Cl<sub>2</sub><sup>+</sup> complexes in order to establish the complex geometry.

***cis*- and *trans*-[Rh(MCL)(CN)<sub>2</sub>]Cl (MCL = *ms*-Me<sub>6</sub>[14]aneN<sub>4</sub> (*trans* Isomer), *rac*-Me<sub>6</sub>[14]aneN<sub>4</sub> (*cis* Isomer), [15]aneN<sub>4</sub> (*cis* and *trans* Isomers)).** These complexes were synthesized by a procedure analogous to the synthesis of *cis/trans*-Rh<sup>III</sup>([14]aneN<sub>4</sub>)(CN)<sub>2</sub><sup>+</sup>.<sup>50,51</sup> A solution consisting of [Rh(MCL)Cl<sub>2</sub>]Cl (0.300 g, 0.61 mmol) and ground NaCN (1.50 g, 30.5 mmol) in 30 mL of water was refluxed for approximately 4 h. The solution was cooled to room temperature, excess NaClO<sub>4</sub> was added, and the resulting solution then chilled to 0 °C for 2 h. The white precipitate was collected by vacuum filtration and washed with ice-cold water, acetone, and ether, and then it was dried in vacuo. The product was recrystallized from a minimal amount of hot water. The perchlorate salt was converted to the chloride salt by anion exchange chromatography using Dowex 1X8, Cl<sup>-</sup> form (yield, 60%).

The UV–vis and infrared spectra of the isolated complexes were compared to those of the previously characterized *cis*- and *trans*-[Rh(MCL)(CN)<sub>2</sub>]<sup>+</sup> complexes.<sup>50,51</sup>

***trans*-[Co(*ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CN)<sub>2</sub>](O<sub>3</sub>SCF<sub>3</sub>).** A solution of *trans*-[Co(*ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>)Cl<sub>2</sub>]Cl<sup>57</sup> (1.0 g, 2.2 mmol) and ground NaCN (0.54 g, 11 mmol) in 30 mL of water was stirred at 70 °C for ~3 h, at which point the color changed from green to orange and, finally, to yellow. When the solution was cooled to room temperature, a white precipitate formed and this was removed by vacuum filtration. The volume of the filtrate was reduced to approximately half then chilled to 0 °C overnight. The yellow product was collected and recrystallized from warm water and precipitated from solution with excess Na(O<sub>3</sub>SCF<sub>3</sub>). We found that a minimum of three recrystallizations were required to remove excess cyanide (yield, 45%).

**Preparation of the Cyanoruthenates.** We have previously discussed the general ruthenation procedures.<sup>1,30,33</sup> Owing to the need to identify the  $\text{CN}^-$  stretches in this study, we have had to take greater care and to repeat each preparation several times. The ruthenates must be synthesized from the pentaammineruthenium(II) (most often from the

(47) Macrocyclic ligand abbreviations: [14]aneN<sub>4</sub> = 1,4,8,11-tetraazacyclotetradecane; *ms*-Me<sub>6</sub>[14]aneN<sub>4</sub> = 5,12-*ms*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; [15]aneN<sub>4</sub> = 1,4,8,12-tetraazacyclopentadecane; *rac*-Me<sub>6</sub>[14]aneN<sub>4</sub> = 5,12-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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triflate complex in a nonaqueous solvent) under anaerobic conditions, shielded from light. We used a Cr<sup>2+</sup>-scrubbed Ar stream to purge all solutions. The crucial step in the synthesis of the ruthenates was the purification of the parent dicyano complex. Because large excesses of cyanide were used in their synthesis, removal of any remaining cyanide usually required a minimum of three recrystallizations. Any remaining free cyanide resulted in the formation of the [(H<sub>3</sub>N)<sub>3</sub>Ru-CN-Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> complex which has an intense absorption centered around 900 nm,<sup>1,33,52</sup> the same spectral region in which the M<sub>4</sub>M<sub>2</sub>CT (terminal metal-to-terminal metal charge transfer) bands were observed in all the complexes. Once formed, this complex proved virtually impossible to separate from the desired ruthenated complex. This impurity has been independently characterized.<sup>52</sup> Purification of the ruthenated complexes proved to be challenging since we needed clean and reproducible infrared spectra, with no more than two CN<sup>-</sup> stretches, and all the ruthenated complexes were, to differing degrees, air and light sensitive. In most cases (the exceptions were Ru and Os centered) the complexes were too unstable to be readily purified by ion-exchange chromatography and we employed multiple recrystallizations. After each stage of purification the products were characterized by UV-Vis, FT-IR, cyclic voltammetry, elemental, and/or ICP analysis methods. The solid Cr(III) ruthenates were relatively stable in an Ar atmosphere, shielded from light, and refrigerated; they could be so stored (in the solid state) for a month or two. The Co(III) and Rh(III) ruthenates were much less stable. These complexes could typically be stored for a maximum of 2 weeks under the same conditions. Because of the relative instability of the Rh(III) complexes, they were freshly synthesized prior to any experimental study. The monoruthenates of Cr(III) and Rh(III) (macrocycles and pentaammines) exhibited the same trends in stability. Generally, all the CN-bridged ruthenates exhibited enough stability in the solid state that they could be handled for weighing, transferring, etc. However, in solution, the CN-bridged ruthenates were very oxygen and light sensitive. Elemental analyses of these compounds can be found in Table S1.<sup>58</sup> The colors and yields of the compounds prepared are summarized in the Supporting Information.<sup>58</sup>

**B. Spectroscopic Measurements.** Most of the experimental procedures have been described in detail previously.<sup>1-3,33</sup> Ultraviolet, visible, and near-infrared spectra of the ruthenated complexes were obtained in distilled water on an OLIS-modified Cary-14 spectrophotometer controlled by a Gateway 486/33 PC. Spectral deconvolutions were performed using SpectraCalc.<sup>59</sup> The molar absorptivities of the M<sub>4</sub>M<sub>2</sub>CT absorption bands were determined from the spectroscopic changes which followed addition of 10- $\mu$ L aliquots of standardized oxidant to the reduced forms of the ruthenated complexes dissolved in Ar-degassed, distilled water. Oxidant solutions were either 0.10 M Ce<sup>4+</sup> in 1.0 M H<sub>2</sub>SO<sub>4</sub> or 0.10 M Fe<sup>3+</sup> in 1.0 M HCl (Ar-degassed). Prior to each redox "titration", the ruthenated complexes were either (a) stirred over Zn/Hg (in Ar-deaerated solutions and shielded from light for the ruthenated polypyridyl complexes) for approximately 1/2 h or (b) reacted with an equimolar amount of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> (Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> reduced over Zn/Hg for 1/2 h anaerobically and shielded from light) for the ruthenated macrocyclic ligand complexes.

Infrared spectra were obtained as KBr pellets using a Nicolet 760SX FT-IR and/or a Nicolet 680 DSP Workstation. We obtained a minimum of 20 accumulations for each IR spectrum recorded. Spectral grade KBr used for all pellets was obtained from Aldrich and used without further purification.

## Results

**A. Cyanide-Stretching Region in the Infrared.** The spectral region in which the cyanide frequencies of the complexes discussed in this report appear (1950–2200 cm<sup>-1</sup>) is typically free of any interfering bands, making identification of the cyanide stretches unequivocal. Furthermore, these complexes contain only one or two cyanides so that the shift in frequency to lower energy when CN<sup>-</sup> bridges a strongly coupled donor and acceptor (i.e., when there is a relatively low-energy, intense

DACT absorption) is clear and unequivocal in these systems.<sup>1-3,60-68</sup> A comparison of the CN-stretching frequencies in the (H<sub>3</sub>N)<sub>5</sub>M<sup>III</sup>(CNRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>)<sup>4+</sup> complexes synthesized in this study nicely illustrates the point: for M = Cr the CN stretch shifts to lower energy than in the parent Cr(NH<sub>3</sub>)<sub>5</sub>CN<sup>2+</sup> complex by 32 cm<sup>-1</sup> while in the M = Rh analog the shift is to higher energies by 41 cm<sup>-1</sup>. The results of monoruthenation of the dicyano complexes with Co(III), Cr(III), and Rh(III) centers were generally more equivocal. The infrared spectra of these complexes exhibited one, relatively broad intense band and several weaker bands that often appeared as shoulders on the side of the intense band. The fragility of the complexes precluded rigorous purification. Subject to some reservations, the IR spectra of these complexes were qualitatively consistent with the pattern of shifts noted above. Tables 1–3 summarize the IR and DACT spectra.

In general, the intensities of the CN<sup>-</sup> stretches increase upon ruthenation. The increase is most dramatic for Cr-centered complexes. The increases appear to be as large as 20-fold in some of the CN stretches of Cr(III) centered complexes and 2–4-fold for the Rh(III)-centered complexes (see Table S2<sup>58</sup>). The frequencies and the intensities of the CN<sup>-</sup> stretching vibrations varied slightly with the counter ion. The cis complexes generally exhibited two cyanide-stretching frequencies of nearly equal intensities, Figure 3, or a single, broad CN stretching band. The *trans*-dicyano parent complexes and their bis-ruthenates usually exhibited two cyanide stretching frequencies of unequal intensities, Figure 4 (see also Figures 1S and 2S<sup>58</sup> and ref 2). The ratio of the intensities of these two bands averaged about 10/1 for the Rh(III)-centered *trans*-dicyano complexes. The apparent ratio for the analogous Cr(III)-centered complexes was about 2/1; however, the CN stretches in the parent Cr(III) complexes are so weak that signal-to-noise and baseline issues render this ratio uncertain. On the other hand, the intensity ratio of these two CN stretches in the bis-ruthenates does appear to be appreciably larger for Cr than for Rh-centered complexes. In the ruthenates, the corresponding ratios are about 10/1 for Cr(III)- and 6/1 for Rh(III)-centered complexes. These observations are only qualitatively useful since the range of intensities is so large and obviously complicated by issues of

(60) We have observed no exceptions to this pattern among mono- and dicyano complexes. It is frequently assumed that only the kinematic effect, represented by  $\delta$  in our treatment, will alter  $\nu_{\text{CN}}$  for a bridging cyanide<sup>61-65</sup> (an exception is sometimes made when  $d\pi/p\pi$  mixing results in a weakened CN bond<sup>66,67</sup>). For example, the high frequency CN<sup>-</sup> stretch of M<sup>II</sup>(CN)<sub>6</sub>Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub><sup>-</sup> complexes has commonly been assigned to the bridging cyanide. Thus, a recent report<sup>68</sup> assigned two resonance Raman bands at 2098 and 2014 cm<sup>-1</sup> as the bridging and *trans*-axial CN stretches, respectively, and a "band" at 2050 cm<sup>-1</sup>, observed in the infrared, as the *cis*-CN stretch. In the C<sub>4v</sub> symmetry of this complex, one expects four IR-allowed bands (both axial CN stretching combinations, which have a<sub>1</sub> symmetry, and the two *cis*-CN stretching combinations with a<sub>1</sub> and e symmetry). The large number of normal CN stretching vibrational modes in such systems makes them much more difficult to treat than the mono- and dicyano complexes that we have used.

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**Table 1.** Spectroscopic Properties of [*trans*-M(MCL)(NC)<sub>2</sub>]<sub>2</sub>X {Parent} and [*trans*-M<sup>III</sup>(MCL)(CNRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub>]<sub>2</sub>X<sub>5</sub> {M<sup>III</sup>(Ru<sub>2</sub>)} Complexes

M(III)	MCL <sup>a</sup>	X	Ru <sub>t</sub> → M <sub>c</sub> <sup>III</sup> MMCT		
			λ <sub>max</sub> (ε <sub>max</sub> )[Δν <sub>1/2</sub> ] <sup>b</sup>	ν <sub>CN</sub> (cm <sup>-1</sup> ) <sup>c</sup>	
				ν <sub>s</sub>	ν <sub>a</sub>
Cr (parent)	[14]aneN <sub>4</sub>	PF <sub>6</sub> <sup>-</sup>		2135 (vw)	2094 (w)
<b>Cr (Ru<sub>2</sub>)</b>	<b>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>500(7.6)[4.9]</b>	<b>1996 (w)</b>	<b>2077 (s)</b>
Cr (parent)	[14]aneN <sub>4</sub>	BF <sub>4</sub> <sup>-</sup>		2139 (vw)	2093 (w)
<b>Cr (Ru<sub>2</sub>)</b>	<b>[14]aneN<sub>4</sub></b>	<b>BF<sub>4</sub><sup>-</sup></b>		<b>1997 (w)</b>	<b>2074 (s)</b>
Cr	[14]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2135 (vw)	2093 (w)
Cr (parent; <sup>13</sup> CN <sup>-</sup> )	[14]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2091 (w)	2055 (w)
<b>Cr (Ru<sub>2</sub>; <sup>13</sup>CN<sup>-</sup>)</b>	<b>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>		<b>1971 (w)</b>	<b>2033 (s)</b>
Cr (parent)	<i>ms</i> -Me <sub>6</sub> [14]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2136 (vw)	2094 (w)
<b>Cr (Ru<sub>2</sub>)</b>	<b><i>ms</i>-Me<sub>6</sub>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>515(6.4)[5.2]</b>	<b>1992 (w)</b>	<b>2061 (s)</b>
Cr (parent)	[15]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2136 (vw)	2091 (w)
<b>Cr (Ru<sub>2</sub>)</b>	<b>[15]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>515(7.1)[4.6]</b>	<b>2012 (w)</b>	<b>2075 (s)</b>
Co (parent)	<i>ms</i> -Me <sub>6</sub> [14]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2130 (w)	2090 (w)
<b>Co (Ru<sub>2</sub>)</b>	<b><i>ms</i>-Me<sub>6</sub>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>513(1.4)[6.0]</b>	<b>2094 (w)</b>	<b>2132 (s)</b>
Rh (parent)	[14]aneN <sub>4</sub>	PF <sub>6</sub> <sup>-</sup>		2142 (w)	2124 (m)
<b>Rh (Ru<sub>2</sub>)</b>	<b>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{342(0.8)[6.01]}<sup>d</sup></b>	<b>2156 (w)</b>	<b>2114 (s)</b>
Rh (parent)	<i>ms</i> -Me <sub>6</sub> [14]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2143 (w)	2123 (m)
<b>Rh (Ru<sub>2</sub>)</b>	<b><i>ms</i>-Me<sub>6</sub>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{330(0.85)[5.9]}<sup>d</sup></b>	<b>2160 (w)</b>	<b>2094 (s)</b>
Rh (parent)	[15]aneN <sub>4</sub>	Cl <sup>-</sup>		2143 (w)	2126 (s)
<b>Rh (Ru<sub>2</sub>)</b>	<b>[15]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{340(0.90)[6.1]}<sup>d</sup></b>	<b>2159 (w)</b>	<b>2118 (s)</b>

<sup>a</sup> Tetraazamacrocyclic ligand abbreviations.<sup>47</sup> Ruthenated complexes in bold for clarity. <sup>b</sup> λ<sub>max</sub> in nm; (ε<sub>max</sub> in cm<sup>-1</sup> M<sup>-1</sup>)/10<sup>3</sup>; (Δν<sub>1/2</sub> in cm<sup>-1</sup>)/10<sup>3</sup>. <sup>c</sup> Relative intensities in parentheses: s = strong; m = medium; w = weak; vw = very weak. <sup>d</sup> Probably mixed with Ru<sup>II</sup>/CN<sup>-</sup>(π\*) MLCT.<sup>33</sup>

**Table 2.** Spectroscopic Properties of [*cis*-M(MCL)(NC)<sub>2</sub>]<sub>2</sub>X {Parent} and [*cis*-M<sup>III</sup>(MCL)(CNRu<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub>]<sub>2</sub>X<sub>5</sub> {M<sup>III</sup>(Ru<sub>2</sub>)} Complexes

M(III)	MCL <sup>a</sup>	X	Ru <sub>t</sub> → M <sub>c</sub> <sup>III</sup> MMCT		
			λ <sub>max</sub> (ε <sub>max</sub> )[Δν <sub>1/2</sub> ] <sup>b</sup>	ν <sub>CN</sub> (cm <sup>-1</sup> ) <sup>c</sup>	
				ν <sub>1</sub>	ν <sub>2</sub>
Cr (parent)	<i>rac</i> -Me <sub>6</sub> [14]aneN <sub>4</sub>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2131 (w)	2126 (w)
<b>Cr (Ru<sub>2</sub>)</b>	<b><i>rac</i>-Me<sub>6</sub>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>525(8.2)[5.1]</b>	<b>2077 (s)</b>	<b>2075 (s)</b>
Rh (parent)	[14]aneN <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>		2132 (m)	2125 (m)
<b>Rh (Ru<sub>2</sub>)</b>	<b>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{340(0.3)}<sup>d</sup></b>	<b>2161 (s)</b>	<b>2132 (s)</b>
Rh (parent)	<i>rac</i> -Me <sub>6</sub> [14]aneN <sub>4</sub>	PF <sub>6</sub> <sup>-</sup>		2123 (m)	2126 (m)
<b>Rh (Ru<sub>2</sub>)</b>	<b><i>rac</i>-Me<sub>6</sub>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{345(0.4)}<sup>d</sup></b>	<b>2161 (s)</b>	<b>2132 (s)</b>
Rh (parent)	[15]aneN <sub>4</sub>	Cl <sup>-</sup>		2145 (m)	2126 (m)
<b>Rh (Ru<sub>2</sub>)</b>	<b>[15]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{343(0.39)}<sup>d</sup></b>	<b>2159 (s)</b>	<b>2118 (s)</b>

<sup>a-d</sup> See notes to Table 1.

**Table 3.** Spectroscopic Properties of Monoruthenates of Some Cyanoam(m)ine Complexes

M(III)	nonbridging ligand(s) <sup>a</sup>	X	Ru <sub>t</sub> → M <sub>c</sub> <sup>III</sup> MMCT		
			λ <sub>max</sub> (ε <sub>max</sub> )[Δν <sub>1/2</sub> ] <sup>b</sup>	ν <sub>CN</sub> (cm <sup>-1</sup> ) <sup>c</sup>	
				ν <sub>1</sub>	ν <sub>2</sub>
Cr (parent)	[14]aneN <sub>4</sub> <sup>e</sup>	PF <sub>6</sub> <sup>-</sup>		2135 (vw)	2094 (w)
<b>Cr (Ru)</b>	<b>[14]aneN<sub>4</sub>, CN<sup>-</sup></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>525(8.2)[5.1]</b>	<b>2078<sup>f</sup> (s)</b>	
Cr (parent)	(NH <sub>3</sub> ) <sub>5</sub> <sup>g</sup>	(NO <sub>3</sub> ) <sub>2</sub>		2140 (vw)	
<b>Cr (Ru)</b>	<b>(NH<sub>3</sub>)<sub>5</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>462(3.1)[5.7]</b>	<b>2108 (s)</b>	
Rh (parent)	<i>rac</i> -Me <sub>6</sub> [14]aneN <sub>4</sub> <sup>e,h</sup>	PF <sub>6</sub> <sup>-</sup>		2123 (m)	2126 (m)
<b>Rh (Ru)</b>	<b><i>rac</i>-Me<sub>6</sub>[14]aneN<sub>4</sub>, CN<sup>-</sup><sup>h</sup></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{345(0.4)}<sup>d</sup></b>	<b>2167 (w)</b>	<b>2128 (m)</b>
Rh (parent)	<i>ms</i> -Me <sub>6</sub> [14]aneN <sub>4</sub> <sup>g</sup>	O <sub>3</sub> SCF <sub>3</sub> <sup>-</sup>		2143 (w)	2123 (m)
<b>Rh (Ru)</b>	<b><i>ms</i>-Me<sub>6</sub>[14]aneN<sub>4</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{343(0.39)}<sup>d</sup></b>	<b>2132 (s)</b>	<b>2097 (w)</b>
Rh (parent)	(NH <sub>3</sub> ) <sub>5</sub> <sup>g</sup>	PF <sub>6</sub> <sup>-</sup>		2122 (m)	
<b>Rh (Ru<sub>2</sub>)</b>	<b>(NH<sub>3</sub>)<sub>5</sub></b>	<b>PF<sub>6</sub><sup>-</sup></b>	<b>{391(0.7)[6.4]}<sup>d</sup></b>	<b>2163 (s)</b>	

<sup>a-d</sup> See notes to Table 1. <sup>e</sup> *trans*-M(MCL)(CN)<sub>2</sub><sup>+</sup>. <sup>f</sup> Only one band was resolved. <sup>g</sup> M(NH<sub>3</sub>)<sub>5</sub>CN<sup>2+</sup>. <sup>h</sup> *cis*-M(MCL)(CN)<sub>2</sub><sup>+</sup>.

the relaxation of selection rules,<sup>69-71</sup> differences in changes of dipole moment and differences in signal-to-noise.

On the basis of the usual dipole selection rules, the weaker of the two bands observed in the *trans* complexes has been assigned as the symmetric combination of the cyanide stretching and the stronger band as the antisymmetric combination.

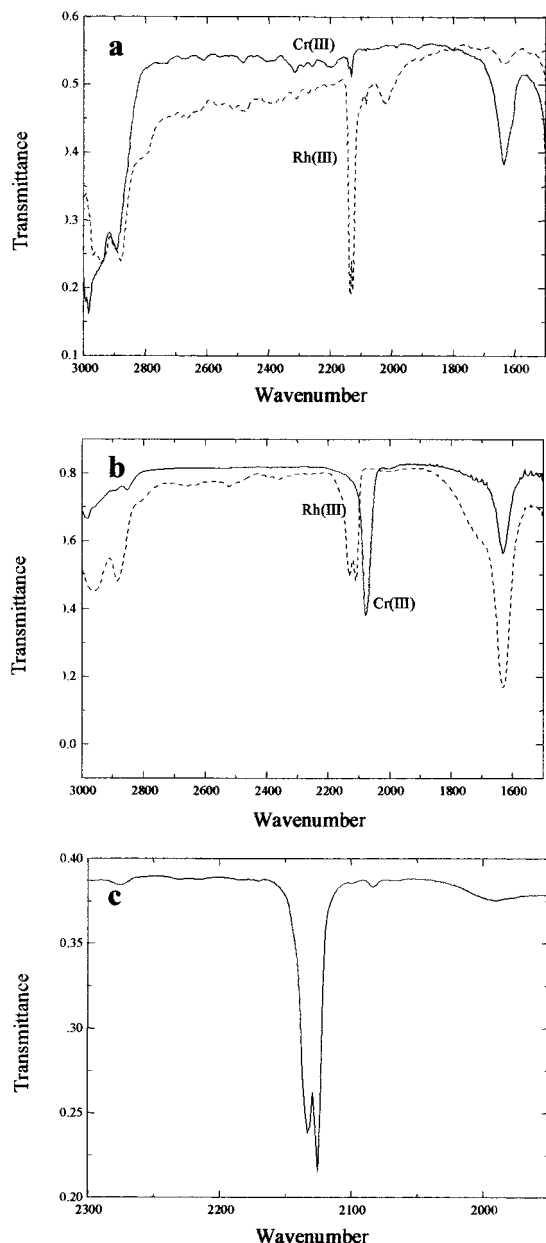
Because of the relative weakness of these stretches in the Cr<sup>III</sup>-centered parent dicyano complexes, several batches of each complex were synthesized with differing counter ions. The band energies and relative intensities varied some with the counter ion, as noted in Table 1, but the observed bands were generally reproducible to within about 6 cm<sup>-1</sup>.

The observed differences in the energies of the bands that we have assigned as ν<sub>s</sub> and ν<sub>a</sub> in the parent *trans*-M(MCL)-(CN)<sub>2</sub><sup>+</sup> complexes are very consistent for each metal. For M = Cr(III), ν<sub>s</sub> - ν<sub>a</sub> = 43 ± 2 (averaged over the different salts), 42, and 45 cm<sup>-1</sup> for MCL = [14]aneN<sub>4</sub>, *ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>, and [15]aneN<sub>4</sub>, respectively. The splitting is significantly smaller in the complex with enriched in <sup>13</sup>CN<sup>-</sup>, 39 cm<sup>-1</sup>; this is the consequence of the smaller isotopic shift observed for ν<sub>a</sub> than

(69) Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders: Orlando, FL, 1992.

(70) The slight relaxation of the dipole selection rules in the complexes of C<sub>2h</sub> symmetry is probably a consequence of small molecular distortions (e.g., M-C≡N angles in many transition-metal complexes average (176 ± 2)°; see footnote 41 in ref 48) and/or lower site symmetry. Deviations from axial linearity are common<sup>67</sup> but not universal<sup>71</sup> in cyanometalates.

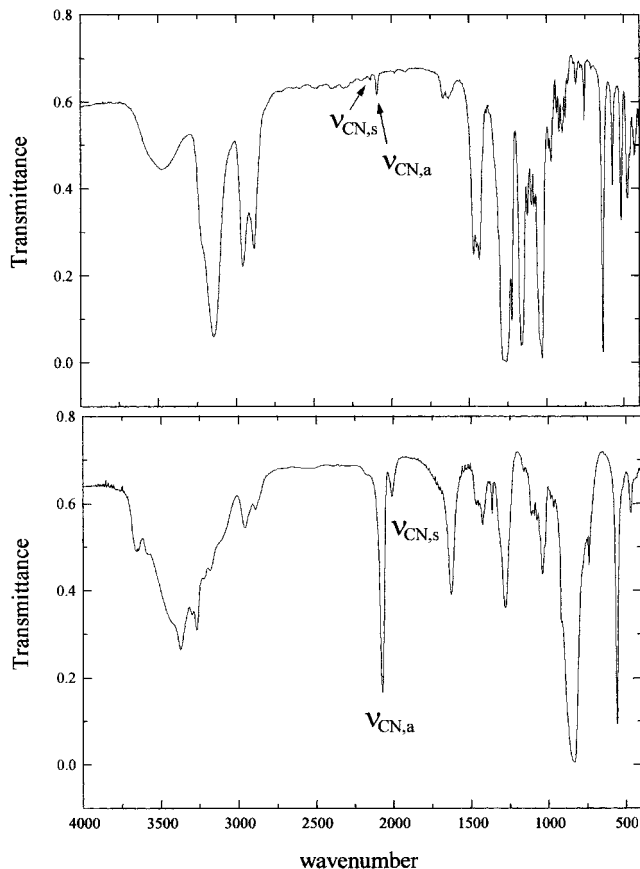
(71) Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1995**, *34*, 3600.



**Figure 3.** Infrared spectra of *cis*-M(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CN)<sub>2</sub><sup>+</sup> complexes and their bis-ruthenates (solid lines for M = Cr; dotted lines for M = Rh): (a) *cis*-M(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CN)<sub>2</sub><sup>+</sup>; (b) *cis*-M(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>5+</sup>; (c) expanded and higher resolution spectrum for the CN-stretch region of *cis*-Cr(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>5+</sup>.

for  $\nu_s$ , 38 and 44 cm<sup>-1</sup>, respectively. This is qualitatively consistent with the assignment since the mass of the central metal would contribute to  $\nu_a$  but not to  $\nu_s$ ; therefore, the isotopic substitution would make a larger percentage contribution to the latter. For the complexes with M = Rh(III),  $\nu_s - \nu_a = 20 \pm 3$  cm<sup>-1</sup> (the same series of MCL ligands); for M = Co(III) a splitting of about 40 cm<sup>-1</sup> was observed for MCL = *ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>. Bis-ruthenation of the *trans* complexes resulted in a larger splitting,  $53 \pm 7$  cm<sup>-1</sup>, for the Rh(III)-centered complexes and, as noted above, a reversal of the order of  $\nu_a$  and  $\nu_s$  for the Cr(III) complexes. This contrast in behavior is illustrated in Figure 5 (compare also Figures 3 and 4).

Table 2 summarizes the IR spectra found in this study for the *cis*-M(MCL)(CN)<sub>2</sub><sup>+</sup> and *cis*-(MCL)M(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>5+</sup> complexes. We have no basis for assigning the symmetric and antisymmetric stretching combinations when two bands were



**Figure 4.** Infrared spectra of *trans*-Cr([15]aneN<sub>4</sub>)(CN)<sub>2</sub>O<sub>3</sub>SCF<sub>3</sub> (top) and *trans*-Cr([15]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub>(PF<sub>6</sub>)<sub>5</sub> (bottom).

resolved. The energy differences of these vibrational components were usually small, and often we were unable to resolve them. As expected, when two bands were resolved, they were nearly equal in intensity.

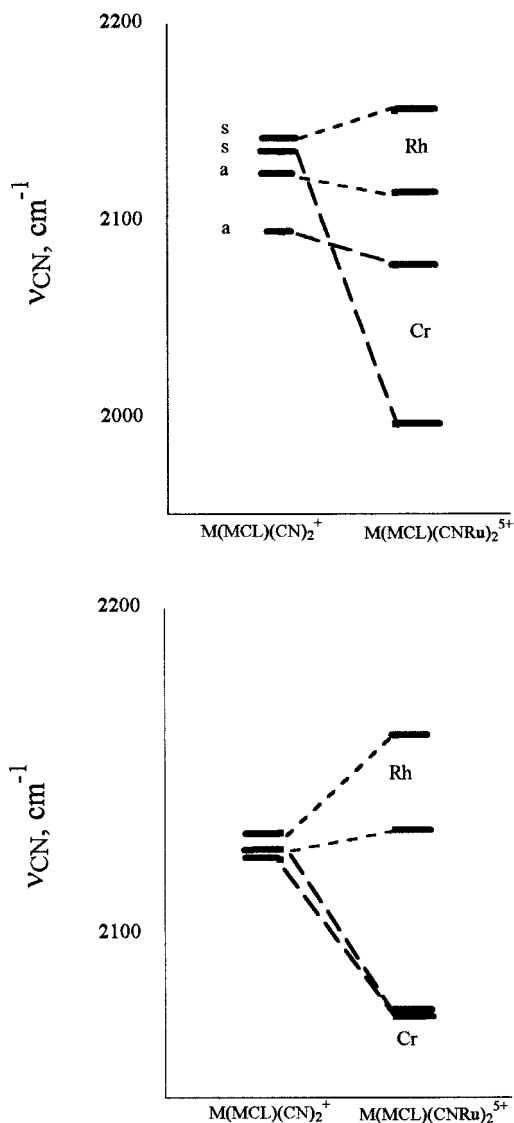
Table 3 summarizes our observations of the shifts in  $\nu_{CN}$  for monocyano complexes. Owing to the large increase in intensity of the CN stretch for ruthenated Cr<sup>III</sup> complexes we often resolved only one band for the monoruthenates of dicyanochromium(III) complexes. Monoruthenation of Rh(MCL)(CN)<sub>2</sub><sup>+</sup> complexes resulted in two CN stretching bands of different intensities. Both bands in these monoruthenates were shifted from those of the parent (especially in the *trans* complex). These shifts suggest that the coupling between the CN stretches (see Discussion) is not eliminated by ruthenation.

**B. Possibility of Isomerism in the M<sub>c</sub>(CN<sup>-</sup>)M<sub>t</sub> Linkage.**<sup>72</sup> Linkage isomerism is well documented in CN<sup>-</sup>-bridged systems.<sup>66</sup> If linkage isomerization were to occur in the compounds reported here, it would complicate the interpretation of our observations. The most detailed information about linkage isomerization induced by cyanometalation is for the Hg<sup>2+</sup> and Ag<sup>+</sup> metalates of cyano-Cr(III) complexes.<sup>73,74</sup> These appear to be fairly slow processes, with half-lives ranging from minutes for the pentaquo complex<sup>73</sup> to many hours for *cis*-Cr(en)<sub>2</sub>(CN)<sub>2</sub><sup>+</sup>.<sup>74</sup> The isocyanide linkage isomers, Cr<sup>III</sup>-(NC<sup>-</sup>)-M<sup>n+</sup>, appear to dissociate relatively rapidly into Cr(III) hydrolysis products.<sup>72-74</sup> The Cr<sup>III</sup>-(CN<sup>-</sup>)-Ru<sup>II</sup> complexes discussed here

(72) (a) Recent discussions with Prof. H. Taube led us to put together these observations. (b) Pouloupoulou, V. G.; Taube, H.; Nunes, F. S. *Inorg. Chem.* **1999**, *38*, 2844.

(73) Espenson, J. H.; Bushey, W. R. *Inorg. Chem.* **1971**, *10*, 2457.

(74) Heatherton, A.; Oon, J. M.; Vargas, R.; Kane-Maguire, N. A. P. *Inorg. Chim. Acta* **1980**, *94*, L279.



**Figure 5.** Schematic representations of the shifts in the cyanide-stretching frequencies which occur upon ruthenation of cyanide in  $M(\text{MCL})(\text{CN})_2^+$  complexes (based on observations for *trans*-[14]ane $\text{N}_4$  and *cis-rac*- $\text{Me}_6[14]\text{aneN}_4$  complexes): (top) *trans* complexes; (bottom) *cis* complexes.

are reasonably stable materials that can be reproducibly synthesized and characterized, and they show no spectroscopic signs of decomposition in deaerated solutions for periods of an hour or so. We have previously noted that  $\text{CN}^-$ -stretching region of the IR spectrum is a good indication of the quality of the cyanoruthenate. We have observed a qualitative contrast in the behavior of the  $\text{Cr}(\text{NH}_3)_5^{3+}$  metalate of  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ . This material exhibits a well defined, sensitized ( $^2\text{E}$ ) $\text{Cr}^{\text{III}}$  emission at 77 K,<sup>75</sup> but we have found it to be a very difficult material to synthesize, characterize, and manipulate.<sup>76</sup> Related ruthenates of  $\text{Cr}([\text{14}]\text{aneN}_4)(\text{CN})_2^+$  have been reported to undergo linkage isomerization in the solid state when heated for 1 h or more.<sup>77</sup> It may also be relevant that the  $\text{Cr}^{\text{III}}(\text{CN}^-)\text{Ru}^{\text{III}}$  forms of the compounds discussed here do “decompose” in solution in times of the order of hours, and that attempts to isolate solid products

from these oxidations have always resulted in samples with “extra”  $\text{CN}$ -stretching bands (suggesting the presence of several compounds). The relative instability of the  $\text{Co}(\text{III})$  and  $\text{Rh}(\text{III})$  centered complexes, even in the solid state, could be related to linkage isomerization. It is likely that there is a significant loss of  $\text{M}_1\text{M}_2\text{CT}$  stabilization energy in  $\text{Cr}^{\text{III}}(\text{CN}^-)\text{Ru}^{\text{II}}$  complexes upon linkage isomerization, and this may be a factor contributing to their relative stability. All the complexes discussed here had simple, “clean” solid state IR spectra and well-defined and stable solution visible spectra, within the limits noted above. As a consequence we formulate the  $\text{CN}^-$ -bridging linkages based on cyanide coordination in the monometallic, parent cyano complexes.

**C. UV-Vis-NIR Absorption Spectroscopy.** The relatively intense UV-visible absorption bands of the cyanide-bridged, ruthenated complexes and their variations in intensity and energy with the oxidation state of the terminal  $\text{Ru}(\text{NH}_3)_5$  moieties have been discussed in detail.<sup>1-3,33</sup> The DACT ( $\text{Ru}^{\text{II}}/\text{M}_1$ ) absorption parameters relevant to this study are summarized in Table 2.

## Discussion

We have synthesized and compared the spectra of a substantial number of compounds in order to address issues raised by our earlier observation<sup>1-3</sup> of the apparent symmetry dependence of shifts of the  $\text{CN}$  stretch in the *trans*-([14]ane $\text{N}_4$ ) $\text{Cr}(\text{CNRu}(\text{NH}_3)_5)_2^{5+}$  complex. The mode-dependent shifts of the  $\text{CN}$  stretch are apparently a characteristic property of *trans*- $\text{CN}^-$ -bridged trimetallic complexes. However, the  $\text{CN}$  vibrational mode which couples with the D/A electronic transition is not dictated by the overall molecular symmetry since similar behavior is observed in the *trans*-([15]ane) $\text{Cr}(\text{CNRu}(\text{NH}_3)_5)_2^{5+}$  complex which has no more than the  $\text{C}_2$  symmetry of the *cis* complexes. In all these *trans*- $\text{Cr}^{\text{III}}(\text{MCL})(\text{CNRu}^{\text{II}}(\text{NH}_3)_5)_2^{5+}$  complexes, the vibration identified as the symmetric combination of  $\text{CN}$  stretches shifts far more than the antisymmetric combination. This is in striking contrast to observations on the  $\text{Rh}(\text{III})$  analogs, but it is consistent with the inferences in our earlier work<sup>1-3</sup> in the sense that we correlated the shifts in  $\nu_{\text{CN}}$  with a vibronic stabilization energy,  $\epsilon_s = (H_{\text{DA}}^{\text{v}})^2/E_{\text{DA}}$ , which is proportional to the oscillator strength of the DACT absorption. The inferred  $\text{Ru}^{\text{II}}/\text{Rh}^{\text{III}}$  DACT absorption is weaker (by at least a factor of 8) and at higher energy than the corresponding absorption band of the  $\text{Cr}(\text{III})$ -centered complexes.<sup>33</sup> A different pattern is observed for the *cis*-( $\text{L}$ ) $\text{Cr}^{\text{III}}(\text{CNRu}^{\text{II}}(\text{NH}_3)_5)_2^+$  complexes ( $\text{L}$  = polypyridyl<sup>1-3</sup> or *rac*- $\text{Me}_6[14]\text{aneN}_4$ ). These complexes characteristically exhibit a broad  $\text{CN}$  stretching band with about one half of the shift of  $\nu_{\text{CN}}$  that we find for the symmetric combination in the *trans* analogs. For  $\text{L} = \text{rac-Me}_6[14]\text{aneN}_4$  we have been able to resolve this band into two, nearly degenerate components (Figure 3). With a proper choice of reference, the sum of the variations of  $\nu_{\text{CN}}$  that accompany ruthenation do correlate with  $\epsilon_s$  for both the *trans* and *cis* (assuming that  $\nu_{\text{CN}}$  for the latter corresponds to two nearly degenerate stretches; Figure 3) complexes. A simple, symmetry adapted vibronic model, with  $H_{\text{DA}} = H_{\text{DA}}^{\circ} + bQ_{\text{CN}}$  (where  $bQ_{\text{CN}}$  represents the  $\text{CN}$  nuclear coordinates), can qualitatively account for these observations.

**A. Reference Systems for the Shifts of  $\nu_{\text{CN}}$ .** We previously chose to reference the shifts in the observed  $\text{CN}$  stretching frequencies to those of the parent complex,  $\Delta\nu_{\text{CN}} = [\nu_{\text{CN}}(\text{parent}) - \nu_{\text{CN}}(\text{complex})]$ .<sup>1-3</sup> This choice provides a convenient basis for the discussion of the general trends in these frequencies, but it does not correlate well with the magnitudes of the shifts observed in mono- and *trans*-bis-ruthenates. In principle, the

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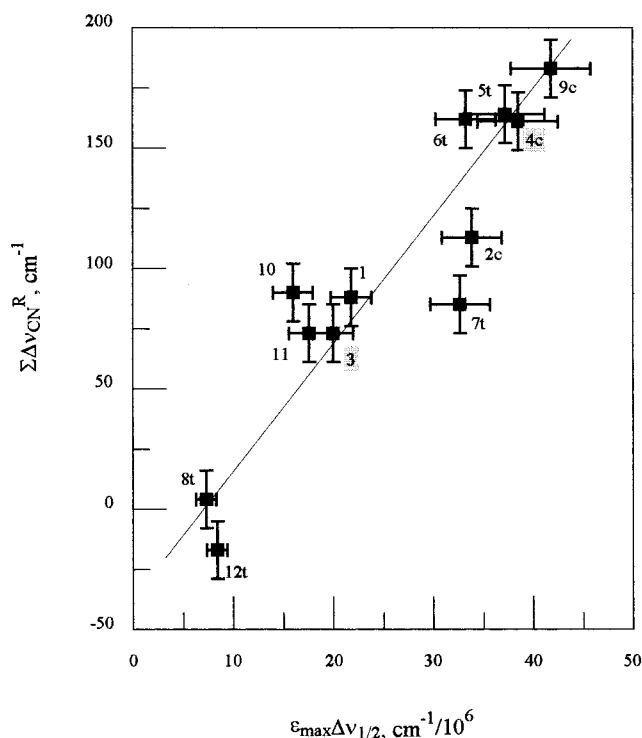
(77) Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Scandola, F. *J. Chem. Soc., Dalton Trans.* **1994**, 2391.

proper reference should be the value of  $\nu_{\text{CN}}$  in a ruthenated complex with the same charge type, but in which there is no donor-acceptor coupling. Such a reference may be impossible to find.<sup>77</sup> Since the shifts of  $\nu_{\text{CN}}$  have been observed to vary with  $\epsilon_s^{1-3}$  and since this quantity appears to be very small for Rh(III) ruthenates,<sup>33</sup> we have chosen these complexes as reference systems. An additional consideration is that the charge distribution within the molecule should be as similar as possible in the reference and in the compound of interest. The significance of this consideration is illustrated by considering the possible  $\text{Ru}(\text{bpy})_2(\text{CNRh}(\text{NH}_3)_5)_2^{6+}$  and  $\text{Rh}(\text{bpy})_2(\text{CNRu}(\text{NH}_3)_5)_2^{5+}$  references for the values of  $\Delta\nu_{\text{CN}}$  reported for  $\text{Ru}(\text{bpy})_2(\text{CNRu}(\text{NH}_3)_5)_2^{6+}$ .<sup>1-3</sup> The values of  $\sum\Delta\nu_{\text{CN}}$  summed over the observed frequencies reported<sup>1</sup> for these potential references are  $-64$  and  $+5$   $\text{cm}^{-1}$ , respectively, per  $\sum\Delta\nu_{\text{CN}}$ . These references would lead to values of  $161$  and  $54$   $\text{cm}^{-1}$ , respectively, for  $\sum\Delta\nu_{\text{CN}}^{\text{R}} = [\sum\nu_{\text{CN}}(\text{ref}) - \sum\nu_{\text{CN}}(\text{complex})]$ . This contrast can be most simply rationalized as an electric field or internal Stark effect since the  $\text{CN}^-$  dipole is aligned with the electric field of the  $\text{Ru}^{2+}$  and  $\text{Rh}^{3+}$  ions in the first of the proposed references and opposed in the second. Since the internal electric field direction and approximate amplitude should be the same in the  $\text{Ru}^{\text{II}}(\text{CN}^-)\text{Rh}^{\text{III}}$  and the  $\text{Ru}^{\text{II}}(\text{CN}^-)\text{Ru}^{\text{III}}$  complexes, we have chosen the first reference. Similarly, we have chosen  $\text{Rh}^{\text{III}}(\text{CN}^-)\text{Ru}^{\text{II}}$  references for the  $\text{M}^{\text{III}}(\text{CN}^-)\text{Ru}^{\text{II}}$  complexes.

**B. Correlation of  $\Delta\nu_{\text{CN}}$  with D/A Electronic Coupling.** Previous work has demonstrated a correlation between  $\Delta\nu_{\text{CN}} = \nu_{\text{CN}}(\text{MCN}) - \nu_{\text{CN}}(\text{MCNRu})$  and the ground-state stabilization that results from D/A mixing.<sup>1-3,33,79</sup> Since the DACT oscillator strength is roughly twice as large for the bis-ruthenates as for the mono-ruthenates, the inferred correlation suggests that  $\Delta\nu_{\text{CN}}$  should increase similarly. Yet  $\Delta\nu_{\text{CN}} = 39$   $\text{cm}^{-1}$  for  $\text{Cr}(\text{NH}_3)_5(\text{CNRu}(\text{NH}_3)_5)^{4+}$  and  $139$   $\text{cm}^{-1}$  for just the shift of the symmetric combination of stretches in *trans*-([14]aneN<sub>4</sub>)Cr(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>. The ratio of these shifts is 1:4 rather than the 1:2.5 based on the respective oscillator strengths. This contrast is mostly a consequence of the choice of the parent cyano complexes as reference systems. If instead one takes the  $\text{CN}^-$  stretches of the corresponding Rh(III)-centered complexes

(78) This choice of reference corresponds to an approximate, experimental correction for  $\delta$  in eqs 5. In Figure 5 we have used  $\Delta\nu_{\text{CN}}^{\text{R}} = \Delta\nu_{\text{CN}}(\text{Rh}_c) - \Delta\nu_{\text{CN}}(\text{M}_c)$ , where possible, to correct for small differences in the coupling between  $\nu_{\text{CN}}$  and  $\nu_{\text{MC}}$ . Since the corresponding references for the "parent"  $\text{M}(\text{NC})(\text{NH}_3)_5^{3+}$  complexes were not available for Ru(II) centered complexes, we used values of  $\Delta\nu_{\text{CN}}^{\text{R}} = [\nu_{\text{CN}}(\text{Rh}_c) - \nu_{\text{CN}}(\text{Ru}_c)]$  for  $\text{Ru}(\text{bpy})_2(\text{CN})(\text{CNRu}(\text{NH}_3)_5)^{3+}$  and  $\text{Ru}(\text{bpy})_2(\text{CNRu}(\text{NH}_3)_5)_2^{6+}$  in Figure 5.

(79) In eq 11,  $a$  is a linear vibronic parameter resulting from the mixing of the ground state with MLCT and LMCT excited states. Assuming that the MLCT and LMCT states make comparable contributions, and based on a first-order Taylor's series expansion of the stabilization energies, we found<sup>1-3,33</sup> that  $a \approx 4\alpha_{\text{CT}}[\lambda_{\text{CT}}k/2]^{1/2}$ , where  $\alpha_{\text{CT}} = H_{\text{CT}}/E_{\text{CT}}$ ,  $\lambda_{\text{CT}}$  is the correlated vibrational reorganizational energy, and  $k$  is the correlated force constant. Since the  $\text{CN}^-/\text{Cr}(\text{III})$  LMCT mixing is expected to be relatively weak, we use  $a \approx 3\alpha_{\text{CT}}[\lambda_{\text{CT}}k/2]^{1/2}$  in the estimates below. Equation 11 is based on a model<sup>1,32,33</sup> in which local (e.g.,  $d\pi/p\pi$ ,  $\text{M}^{\text{II}}/\text{CN}^-$ ) interactions stabilize the ground and excited electron transfer states while distorting (e.g., as a consequence of electron delocalization) the C-N bond. These interactions are represented in terms of the corresponding MLCT (and/or LMCT) parameters. Since the MCLT and electron transfer states have different nuclear coordinates ( $Q_{\text{nu}}$ ) at their potential energy (PE) minima, the stabilization energies contain a term that is first order in the nuclear coordinates ( $aQ_{\text{nu}}$ ). An electron transfer matrix element of the type  $H_{\text{DA}} = (H_{\text{DA}}^{\circ} + bQ_{\text{nu}})$  results in a secular equation that is second order in energy. Minimization of the resulting ground state PE function,  $V_a$ , permits solution for the amplitude of the ground state displacement in  $Q_{\text{nu}}$ . The second derivative ( $d^2V/dQ_{\text{nu}}^2$ ) gives an effective force constant,  $k_{\text{eff}}$ . This can be combined with  $H_{\text{DA}} = H_{\text{DA}}^{\circ} + b(Q_{\text{nu}})_{\text{min}}$  to obtain eq 11.



**Figure 6.** Correlation of the shifts in the  $\text{CN}^-$  stretch,  $\Delta\nu_{\text{CN}}^{\text{R}}$ , with the oscillator strength of the donor-acceptor electronic transition. Points for the bisruthenates are labeled c for *cis* and t for *trans*; shaded backgrounds indicate Ru(II)-centered complexes. Key to points: (1) *cis*-Cr(CN)(bpy)<sub>2</sub>(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>3+,1a</sup>; (2) *cis*-Cr(bpy)<sub>2</sub>(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+,1a</sup>; (3) *cis*-Ru(CN)(bpy)<sub>2</sub>(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>3+,1a</sup>; (4) *cis*-Ru(bpy)<sub>2</sub>(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>2+,1a</sup>; (5) *trans*-Cr([14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>; (6) *trans*-Cr(*ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>; (7) *trans*-Cr([15]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>; (8) *trans*-Co(*ms*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>; (9) *cis*-Cr(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>; (10) *cis*-Cr(*rac*-Me<sub>6</sub>[14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>; (11) Cr(NH<sub>3</sub>)<sub>5</sub>(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>4+</sup>; (12) *trans*-Co([14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>. All points referenced to Rh(III) analogs as described in the text.

as the reference, then the ratio of the shifts,  $\Delta\nu_{\text{CN}}^{\text{R}}$ , is 1:2.2, very nearly as expected (the respective values of  $\Delta\nu_{\text{CN}}^{\text{R}}$ , summed over all the CN stretches, are  $73$  and  $164$   $\text{cm}^{-1}$ ). Figure 6 is a strictly empirical correlation of  $\Delta\nu_{\text{CN}}^{\text{R}}$  with the oscillator strengths of the electronic DACT transitions observed in the *cis*- and *trans*-M<sup>III</sup>(MCL)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>5+</sup>, the Cr(NH<sub>3</sub>)<sub>5</sub>(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sup>4+</sup> and the polypyridyl complexes from our earlier work for which we have information on the appropriate Rh(III) reference compounds.<sup>78</sup> The *cis*- and *trans*-bis-ruthenates (of Cr(III)- and Ru(II)-centered complexes) are all at the upper right hand side of the figure, the mono-ruthenates are in the middle and the Co(III) centered complexes are at the lower left. This correlation demonstrates that the values of  $\Delta\nu_{\text{CN}}^{\text{R}}$  are comparable for the *cis*- and *trans*-bis-ruthenates despite the fact that the shifts of the CN stretches are mostly in the symmetric combination of stretching frequencies for the *trans*-complexes but nearly equally distributed over the symmetric and antisymmetric combinations for the *cis*-complexes.

**C. Interpretation of the Complex Geometry Dependence of the Shifts in  $\nu_{\text{CN}}$ .** Our experimental observations, described above, have found an unexpected dependence of the pattern of shifts in the cyanide stretching frequency on the complex geometry in bis-cyanometalates. This contrasting behavior of the *cis* and *trans* complexes, illustrated schematically in Figure 5 can be largely accommodated in terms of a simple vibronic model. Before we consider that model we need to consider some general points about shifts of the CN stretch.



**1. Perturbational Approach to Shifts in  $\nu_{\text{CN}}$ .** Since the CN stretch is much higher energy than the coupled MC and  $M'N$  stretching frequencies, the issues are most easily approached using simple perturbation theory arguments. First, we consider simple bimetallic systems of the type  $M\text{-CN-}M'$ . In such systems, there will be some coupling energy,  $\mathcal{E}$ , between the  $M'-N$  and the  $C-N$  stretches (a necessary result of a normal coordinate analysis; we have incorporated the MC/CN vibrational coupling into  $\nu_{\text{CN}}^\circ$ , the CN stretch of the parent  $M\text{-CN}$  complex). If this coupling does not result in changes in the CN stretching force constant, the perturbationally corrected vibrations are of the form in eqs 4 (additional details in the supporting information). For simplicity, we set  $\mathcal{E}^2/h^2(\nu_{\text{CN}} - \nu_{M'N}) = \delta$ .

$$\nu_1 = \nu_{\text{CN}}^\circ + \mathcal{E}^2/h^2(\nu_{\text{CN}}^\circ - \nu_{M'N}) \quad (4a)$$

$$\nu_2 = \nu_{M'N} - \mathcal{E}^2/h^2(\nu_{\text{CN}}^\circ - \nu_{M'N}) \quad (4b)$$

The two nominally degenerate CN vibrations of dicyano complexes must be treated as symmetric and antisymmetric combinations of the "local"  $\nu_1$  vibrations. If the local,  $\nu_1$ , vibrations are coupled with a resulting interaction energy,  $h\gamma$ , then the symmetric and antisymmetric combinations of the frequencies are given by eqs 5. If some additional perturbational

$$\nu_s = \nu_{\text{CN}}^\circ + \delta + \gamma = \nu_1 + \gamma \quad (5a)$$

$$\nu_a = \nu_1 - \gamma \quad (5b)$$

coupling decreases  $\nu_{\text{CN}}^\circ$ , either by means of a decrease of the stretching force constant and/or an increase in the anharmonicity, then  $\nu_1$  takes the form in eq 6,

$$\nu_1' = \nu_{\text{CN}}^\circ + \delta - f \quad (6)$$

where  $f$  is the change in stretching frequency (per ruthenate). Symmetry adaptation of the local  $\nu_1'$  contributions results in eqs 7.

$$\nu_s' = \nu_{\text{CN}}^\circ + \delta - f_s \quad (7a)$$

$$\nu_a' = \nu_{\text{CN}}^\circ + \delta - f_a \quad (7b)$$

Several mechanisms have been proposed that can give rise to the  $f_i$  contributions; examples are delocalization of electron density between the metal  $M'$  and cyanide (as in "back-bonding" interactions) and anharmonicities induced by pseudo-Jahn-Teller, vibrational/electronic coupling. In effect the coupling corrections  $\gamma$  are the result of three-center (NC)-M-(CN) interactions, while the  $f_i$  corrections arise from "local" M-(CN)- $M'$  vibronic interactions. In terms of this treatment, the difference in the shifts of  $\nu_{\text{CN}}$  observed for two complexes, as in  $\Delta\nu_{\text{CN}}^{\text{R}} = \nu_{\text{CN}}(\text{M}) - \nu_{\text{CN}}(\text{M}')$ , is equal to  $(f_{M'} - f_M)$ . This is a basis for the correlation in Figure 6.

Based on the previous discussion, the  $f_i$  are proportional to the stabilization energies that result from the pseudo-Jahn-Teller-like coupling of the bridging ligand nuclear coordinates with the DACT electronic coordinates<sup>1-3,33</sup> (see also the Supporting Information). If we now allow for the perturbational coupling,  $\gamma'$ , between  $\nu_s'$  and  $\nu_a'$ , then the resulting second-order secular equation has the roots given by eq 8

$$\nu_{\pm} \cong \nu_1 - 1/2(f_s + f_a) \mp 1/2[\Delta^2 + 4\gamma'^2]^{1/2} \quad (8)$$

( $\Delta = f_s - f_a$ ; additional details in the Supporting Information). The two limiting solutions for eq 8 correspond to the condi-

tions: (a)  $\Delta^2 \ll 4\gamma'^2$ ; and (b)  $\Delta^2 \gg 4\gamma'^2$ . These are the limits in which (a)  $H_{\text{DA}}$  is small and the observed frequencies are dominated by the kinematic effect,  $\delta$ , and coupling between the CN oscillators,  $\gamma$ , and (b)  $H_{\text{DA}}$  is very large and vibronic coupling effects,  $f_i$ , dominate the shifts in  $\nu_{\text{CN}}$ . The first of these limits seems most appropriate for the Rh(III)-centered complexes. Thus, ruthenation of the *trans*-Rh([14]aneN<sub>4</sub>)(CN)<sub>2</sub><sup>+</sup> results in an increase of 20 cm<sup>-1</sup> in  $(\nu_s + \nu_a)/2$ , an increase in  $(\nu_s - \nu_a)$ , and no change in the relative ordering of the CN stretches. This is consistent with limit a, eqs 9, and  $\gamma' \sim 2\gamma$  and  $(f_s + f_a) = 2f \sim 2\delta - 40$  cm<sup>-1</sup>.

$$\nu_s = \nu_1' - 1/2(f_s + f_a) + \gamma' + \Delta^2/8\gamma' \quad (9a)$$

$$\nu_a = \nu_1' - 1/2(f_s + f_a) - \gamma' - \Delta^2/8\gamma' \quad (9b)$$

The values of  $\nu_{\text{CN}}$  for Rh(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> and its ruthenate imply that  $(\delta - f) \cong 40$  cm<sup>-1</sup>. The average of  $(\delta - f) \sim 30 \pm 10$  cm<sup>-1</sup> for these Rh(III)-centered complexes is consistent with the expected small values of  $\epsilon_s$  (estimated to be about 96 cm<sup>-1</sup>)<sup>33</sup> and  $f$  (see also the discussion below), as well as the uncertainties of the measurements and the approximations in the model used.

The properties of the Cr(III) centered complexes with *trans* geometries seem most consistent with limit b of eq 8. This leads to eqs 10. The origin of the larger red shift of  $\nu_s$  than  $\nu_a$  for the

$$\nu_a \cong \nu_1' - f_a + 2\gamma'^2/\Delta \quad (10a)$$

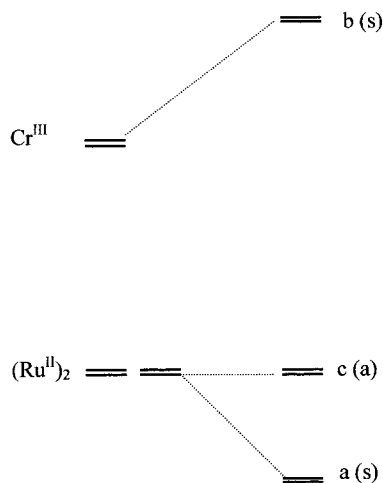
$$\nu_s \cong \nu_1' - f_s - 2\gamma'^2/\Delta \quad (10b)$$

*trans*-Cr(III)-centered complexes is discussed below. The quantity that we propose as an experimental measure of the total shift in  $\nu_{\text{CN}}$  (summed over all CN stretches) can be written  $\Sigma\Delta\nu_{\text{CN}}^{\text{R}} \cong 2f_{\text{Cr}} - 2f_{\text{Rh}}$  (the subscripts indicate the different central metals). The intercept of  $-26 \pm 18$  cm<sup>-1</sup> in Figure 6 is in reasonable accord with the estimate of  $-2(\delta - f)_{\text{Rh}} \cong -60 \pm 20$  cm<sup>-1</sup> based on the [14]aneN<sub>4</sub> complex (above). The apparent value of  $f_{\text{Rh}} \sim 13$  cm<sup>-1</sup> suggests that  $\delta \sim 48$  cm<sup>-1</sup>. This detailed agreement indicates that the simple perturbation theory approach is at least internally consistent. We now examine the physical interpretation of these parameters.

**2. Estimates of the Magnitude of the Shift Parameters Based on a Semiclassical Vibronic Model.** An important remaining issue is whether the ratio  $f/\epsilon_s$  is in accord with expectation based on the vibronic coupling model. We have shown elsewhere<sup>1-3,33</sup> that a semiclassical, pseudo-Jahn-Teller model can describe the entanglement of vibrational and electronic parameters as in eq 11.<sup>1,79</sup> The parameter  $\nu_{\text{eff}}$  in eq 11

$$H_{\text{DA}} \cong H_{\text{DA}}^\circ + a[\Delta\nu_{\text{CN}}E_{\text{DA}}^\circ/k\nu_{\text{eff}}]^{1/2} + H_{\text{DA}}^\circ(\Delta\nu_{\text{CN}}/\nu_{\text{eff}}) \quad (11)$$

arises from the contributions of all nuclear displacement coordinates to the ground-state potential energy surface, and it is presumed to be a composite of the contributions of all the relevant displacement coordinates.<sup>1</sup> Reasonable correlations of the observations are possible for  $H_{\text{DA}}$  with  $[\Delta\nu_{\text{CN}}E_{\text{DA}}]^{1/2}$  or with  $\Delta\nu_{\text{CN}}$ ,<sup>32</sup> corresponding to the second and third right-hand-side terms, respectively, of eq 11. Thus, if we assume  $\Delta\nu_{\text{CN}} \propto \epsilon_s = (H_{\text{DA}})^2/E_{\text{DA}}$  (based on the second rhs term of eq 11), then the parameters  $f(\text{Rh}) = \Delta\nu(\text{Rh}) = 13$  cm<sup>-1</sup> (obtained in the preceding section) and  $\epsilon_s(\text{Rh}) = 96$  cm<sup>-1</sup><sup>33</sup> combined with  $\epsilon_s(\text{Cr}) = 1400$  cm<sup>-1</sup> imply that  $\Delta\nu(\text{Cr}) = 183$  cm<sup>-1</sup>. This is in good agreement with  $\Delta\nu(\text{Cr}) = 160$  cm<sup>-1</sup> observed for *trans*-Cr([14]aneN<sub>4</sub>)(CNRu(NH<sub>3</sub>)<sub>5</sub>)<sub>2</sub><sup>5+</sup> (summed over both frequen-



**Figure 7.** Qualitative effects of three-center coupling on metal  $d\pi$  orbitals of a trimetallic system based on eqs 13. Letters in parentheses indicate symmetric (s) or antisymmetric (a) combinations.

cies; Table 1). However, this limit of eq 11 requires that  $H_{DA}^{\circ} = 0$ . This may not be correct.

Rather than assuming that one or another term of eq 11 may be neglected, we have iteratively fitted our observations for the  $(\text{NH}_3)_5\text{M}(\text{CNRu}(\text{NH}_3)_5)^{4+}$  complexes,  $\text{M} = \text{Cr}(\text{III})$  and  $\text{Rh}(\text{III})$ . For  $\Delta\nu_{\text{CN}}(\text{Rh}) \cong 7 \text{ cm}^{-1}$  and  $\Delta\nu_{\text{CN}}(\text{Cr}) \cong 80 \text{ cm}^{-1}$  the contributions of electronic entanglement to the respective shifts, we obtain  $H_{DA}^{\circ} \sim 850 \text{ cm}^{-1}$  and  $\nu_{\text{eff}} \sim 180 \text{ cm}^{-1}$ . An assumption implicit in this analysis, and in the correlation in Figure 6, is that the  $\text{Rh}(\text{III})$ - and  $\text{Cr}(\text{III})$ -centered complexes have similar values of  $\nu_{\text{eff}}$  and  $H_{DA}^{\circ}$ . A literal interpretation of these parameters suggests that  $\nu_{\text{eff}}$  would be larger for Rh while  $H_{DA}^{\circ}$  would be larger for Cr(III) since the DACT transitions are  $d\pi/d\sigma$  and  $d\pi/d\pi$ , respectively. Such a literal or any more detailed interpretation does not seem justified at this time.

**3. Three-Center Interpretation of the Dependence of the Coupled Vibrational Modes on the Complex Geometry.** In the present report, we are only interested in the properties of the ground state. In the vibronic argument, the vibrational modes which contribute to the mixing of the D/A wavefunctions should be the same modes which contribute to the stabilization of the ground state and which are as a result shifted to lower energies. We will use a simple Hückel-like molecular orbital approach to explore further the  $f_i$  contributions to the ground state. The discussion of the trans complexes can be developed in terms of a set of coplanar  $d\pi$  orbitals and an idealized linear geometry. We assume that the three metals are coupled by means of the antibonding  $\pi^*$  orbitals of the bridging cyanides, but we will construct our discussion based on the properly symmetrized sets of metal orbitals (the symmetry required for this argument is  $C_2$ , with the  $C_2$  axis perpendicular to the  $\text{M}-\text{CN}$  axis). The resulting combinations of metal orbitals are analogous to the molecular orbitals in three-center bonding models,<sup>80</sup> eqs 12 (the metal centers are numbered sequentially). Figure 7 illustrates

$$\psi_a = [(d\pi_1 + d\pi_3)/2^{1/2} + \alpha_{12}d\pi_2]/(1 + \alpha_{12}^2)^{1/2} \quad (12a)$$

$$\psi_b = [\alpha_{21}(d\pi_1 + d\pi_3)/2^{1/2} - d\pi_2]/(1 + \alpha_{21}^2)^{1/2} \quad (12b)$$

$$\psi_c = (d\pi_1 - d\pi_3)/2^{1/2} \quad (12c)$$

the corresponding orbital diagram for a Cr(III) centered complex.

The resulting electronic states are symmetric (ground and DACT) and antisymmetric (DACT') corresponding to partly filled  $\psi_1$ ,  $\psi_2$ , and  $\psi_3$  orbitals, respectively. If we assume that the stabilization,  $\epsilon_{ij} = \alpha_{ij}^2/E_{ij}$ , arises from local vibronic interactions, then the symmetry-adapted vibronic mixing coefficients,  $\alpha_{ij}$ , in eqs 12 must give rise to stabilization energies of the form  $Q_k(\partial E_g/\partial Q_k)$  (from the first-order Taylor's expansion of the ground-state potential energy around the perturbing nuclear coordinate). For the symmetrical ground state, the differential term can be rewritten  $\partial E_g/\partial Q_s = (\partial E_g/\partial r_{12} + \partial E_g/\partial r_{32})$ , where the  $r_{ij}$  are the local (CN-stretching) nuclear coordinates. If each of these local vibronic interactions contributes an amount  $\epsilon_s/2$  (or  $\epsilon_s^{\text{th}}/\text{Ru}(\text{II})$ , in the notation of ref 32) to the stabilization energy then the net ground state stabilization is  $\epsilon_s$ . The corresponding treatment of the antisymmetric mode results in  $\partial E_g/\partial Q_a = (\partial E_{12}/\partial r_{12} - \partial E_{32}/\partial r_{32})$  and the antisymmetric mode will not contribute to the ground state stabilization. Of course, the total stabilization energy depends on the interactions of two sets of  $d\pi$  orbitals at each metal in the trans complexes, but the symmetry aspects of the argument are not changed by the generalization (the orbitals corresponding to those in eqs 12 would have  $e_g$ ,  $e_g$ , and  $e_u$  symmetry in  $D_{4h}$ ).

The cis complexes present a different set of problems. We can again use three-center perturbation theory reasoning, but several different orbital symmetry species contribute to the ground-state stabilization. In  $C_{2v}$  symmetry the important symmetry-adapted species are (a) CN vibrations ( $a_1$  and  $b_2$ ); (b) central atom  $d\pi$  orbitals ( $a_1$  in the  $\text{M}_t\text{M}_c\text{M}_t$  plane;  $a_2$  and  $b_1$  out of plane); and (c) terminal atom  $d\pi$  orbitals ( $a_1$  and  $b_2$  in plane;  $a_2$  and  $b_1$  out of plane). The complexes that we have examined have only  $C_2$  symmetry, and this somewhat simplifies the treatment. The symmetric combination of CN vibrations will promote nearest-neighbor interactions for three-center combinations of the a-symmetry orbitals ( $a_1$  and  $a_2$  orbitals in  $C_{2v}$ ). This will result in contributions of  $\epsilon_s$  to the ground state stabilization, similar to those in the trans complexes discussed above. However, the three-center vibronic coupling argument applied to the combinations of b orbitals ( $b_1$  orbitals in  $C_{2v}$ ) requires that the antisymmetric vibrational mode give rise to contributions of  $\epsilon_a$  to the stabilization energy. If all these orbital combinations were equally weighted in the ground-state stabilization, then one would expect that the symmetric vibrational mode would be shifted more than the antisymmetric mode (by  $\sim 2/1$ ). Such equal weighting is apparently not the case in most of our systems (Ru(II)-centered complexes may be an exception<sup>1</sup>).

## Conclusions

We have found that trimetallic complexes containing Cr(III) acceptors  $\text{CN}^-$ -bridged to Ru(II) donors exhibit different patterns of shifts to lower energy of the  $\text{CN}^-$  stretching vibrations depending on whether the complex geometry is trans (much larger shift of the symmetric than the antisymmetric mode) or cis (similar shifts in both modes). The behavior of the trans complexes was found to be independent of the presence of a molecular center of symmetry. When referenced to the corresponding Rh(III)-centered complexes and summed over both modes, the amplitudes of these shifts are proportional to the oscillator strengths of the donor-acceptor electronic transitions, and they correlate with the behavior of related tri- and bimetallic D/A complexes.

A first-order perturbation theory treatment has been used to separate the opposed effects on the CN stretch of (a) the mechanical coupling between the high frequency CN stretch and the low frequency  $\text{M}-\text{N}$  and  $\text{M}'-\text{C}$  stretches (the "kine-

(80) Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed.; Wiley: New York, 1990.

matic" effect),  $\delta$ , and the coupling between the in-phase and out-of-phase CN stretches,  $\gamma$ ; from (b) the entanglement of the donor–acceptor electronic coupling with the CN nuclear coordinates ("vibronic" coupling),  $\zeta$ . When  $\gamma > \zeta$  in trans complexes, the perturbation theory argument predicts an enhanced splitting of the symmetric and antisymmetric stretches, compared to the parent, without changing their order. This corresponds to the behavior observed for the Rh(III)-centered complexes. When  $\gamma < \zeta$  the order of the symmetric and antisymmetric vibrations can be reversed, as observed for Cr(III)-centered complexes. The effects of electronic mixing with the nuclear coordinates,  $\zeta$ , can be interpreted in terms of a previously proposed vibronic (or pseudo-Jahn–Teller) model in which  $H_{DA} = H_{DA}^{\circ} + bQ_{CN}$  (for  $bQ_{CN}$  the vibronic coupling term). This model, which does not take explicit account of variations of the electronic structure of donor and acceptor, implies that  $|H_{DA}^{\circ}| < |bQ_{CN}|$  for the CN<sup>−</sup>-bridged complexes. The CN<sup>−</sup>-bridged complexes clearly define a limit in which such vibronic coupling between donor and acceptor is very important.

This behavior contrasts to the prevailing assumption that electronic coupling is independent of the nuclear coordinates in electron transfer systems. The conditions under which the bridging ligand nuclear coordinates might be entangled with D/A coupling in other bridged electron transfer systems are under investigation.

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**Supporting Information Available:** Summary of synthesis of ruthenates, a table of elemental analyses, a table of relative intensities of vibrational bands, IR spectra, and some perturbation theory details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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