one-way photoisomerization. While the photostability of *Z*-**1** is clearly related to weak intramolecular hydrogen bonding in the ground state of *Z*-**1**, the role of the hydrogen bond in the nonradiative decay of the excited state remains to be elucidated.

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Supplementary Material Available: ORTEP representations, tables of atomic coordinates, thermal parameters, bond angles, and bond distances for *E*-**1** and *Z*-**1** (12 pages). Ordering information is given on any current masthead page.

Picosecond Infrared Study of Ultrafast Electron Transfer and Vibrational Energy Relaxation in a Mixed-Valent Ruthenium Dimer

Stephen K. Doorn,[†] Page O. Stoutland,[†] R. Brian Dyer,[*,‡] and William H. Woodruff[*,†]

Divisions of Inorganic and
Nuclear Chemistry, Mail Stop C-346, and Chemical and
Laser Sciences, Mail Stop J-567
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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Mixed-valent transition-metal dimers have become key systems for understanding many fundamental aspects of electron-transfer dynamics.[1] The mixed-valent dimer $[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^{1-}$ is an interesting member of this class. In this complex, the ruthenium centers are strongly coupled through a short cyanide bridge, but because the $[(NC)_5Ru^{III}CNRu^{II}(NH_3)_5]^{1-}$ state of this systems lies approximately 8000 cm^{-1} higher in energy, the odd electron is localized on the ruthenium cyanide center.[2] Optical excitation into the metal–metal charge-transfer (MMCT) band leads to reduction of the ruthenium ammine site. This state is highly unstable with respect to back electron transfer:

$$[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^{1-} \underset{ET}{\overset{h\nu}{\rightleftharpoons}} [(NC)_5Ru^{III}CNRu^{II}(NH_3)_5]^{1-}$$

The MMCT excitation is followed by back electron transfer, which may occur on very short time scales, allowing one to observe effects due to ultrafast reorganization processes, to discern excited state/ground state coupling phenomena, and to test modern electron-transfer theories. In this communication, we report a picosecond infrared study of the dynamics of $[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^{1-}$ following MMCT optical excitation.[3] We observe the terminal RuC≡N stretching vibrational frequency, which is sensitive to the oxidation state of the ruthenium cyanide center and also, because of anharmonicity, to the degree of vibrational excitation of this mode. Our observations allow us to observe unambiguously the formation and decay of the MMCT excited state and, by observing the energy flow out of this state, to address the more general issues of vibrational coupling and energy-transfer dynamics.

Ultrafast visible pump/infrared probe experiments were performed as described previously.[4] A visible pump pulse at 600 nm (2 ps, 50–100 μJ/pulse) is followed by an infrared probe pulse (2 ps, 10–100 nJ/pulse, FWHM 8 cm^{-1}) generated by difference frequency mixing of the visible pulse with a 532-nm pulse in a $LiIO_3$ crystal. Time resolution[5] is obtained by optical delay, and the infrared difference frequency is changed by tuning the frequency of the dye laser. The sodium salt of $[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^{1-}$ was synthesized by literature methods.[6] The visible spectrum consists of a broad (FWHM 4500 cm^{-1}) MMCT band centered at 683 nm (ϵ = 2800 M^{-1} cm^{-1}). In the ground state, the terminal RuC≡N stretch is observed at 2053 cm^{-1} (FWHM = 23 cm^{-1}, ϵ = 2500 M^{-1} cm^{-1}).[7]

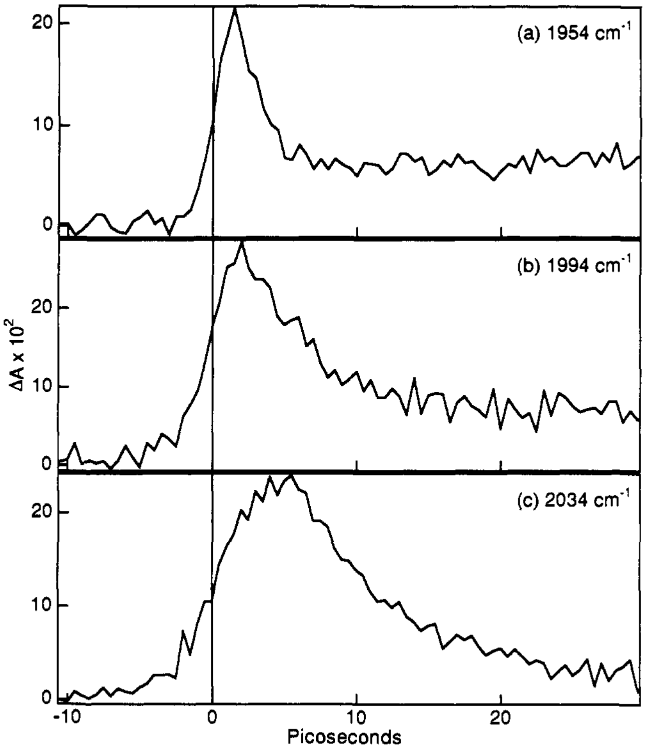

Figure 1. Transient decays obtained at (a) 1954, (b) 1994, and (c) 2034 cm^{-1} from 0.04 M dimer in D_2O. See Table I for appropriate rise and decay times. Offsets remaining at long times are due to thermal transients and do not affect the fits obtained.

Table I. Rise and Decay Times for the Best Fit to Data from 1954 to 2060 cm^{-1} [a]

wavelength (cm^{-1})	rise time (ps)	fall time (ps)
1954	0.1	0.7
1974	0.3	1.9
1994	0.6	3.6
2014	0.7	4.6
2034	1.4	5.9
2060[b]	0.0	6.9

[a] Values given correspond to the best fit obtained when convolving the instrument response (typically a 3–4 ps FWHM sech^2 function) with a biexponential function; estimated relative error is ±0.5 ps. [b] Ground-state bleach.

Upon excitation at 600 nm, we observe an ultrafast (instrumentally limited, $\tau < 0.5$ ps) decrease in the RuC≡N absorbance for the ground state at 2053 cm^{-1}. The recovery is fit by convolving the instrument response with a 6 ± 1 ps exponential. Simultaneous

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[†] Division of Inorganic and Nuclear Chemistry.

[‡] Division of Chemical and Laser Sciences.

(1) See, for example: (a) *Mixed-Valence Compounds*; Brown, D. B., Ed.; D. Reidel: Dordrecht, The Netherlands, 1980. (b) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(2) Estimated from redox potentials for the appropriate monomer pairs; see: Haim, A. *Inorg. Chem.* **1985**, *14*, 113.

(3) The photophysics of a related molecule, $[(NC)_5Fe^{2+}CNRu^{3+}(NH_3)_5]^{1-}Na^+$, have recently been investigated using femtosecond visible spectroscopy: Walker, G. C.; Barbara, P. F.; Doorn, S. K.; Dong, Y.; Hupp, J. T. *J. Phys. Chem.* **1991**, *95*, 5712.

(4) Dyer, R. B.; Peterson, K. A.; Stoutland, P. O.; Woodruff, W. H. *J. Am. Chem. Soc.* **1991**, *113*, 6276.

(5) Using deconvolution techniques we estimate that we can resolve ca. 500 fs events, given typical signal to noise ratios.

(6) Vogler, A.; Kisslinger, J. *J. Am. Chem. Soc.* **1982**, *104*, 2311.

(7) In C_{4v} symmetry there should be more than one band in this region. Compounds of this type, however, often show only one IR-active MC≡N stretching vibration, perhaps because of their closeness to O_h symmetry (see for example: Siddiqui, S.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1987**, *26*, 3101). The bridging cyanide stretch is observed at 2118 cm^{-1} and is ca. 50 times weaker than the terminal stretch.

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with the ground-state bleach, we observe a new absorption centered at 2110 cm^{-1}, which decays with $\tau < 0.5$ ps. Subsequently, we observe a broad feature extending from 1950 to 2040 cm^{-1}. Shown in Figure 1 are three kinetic traces taken throughout the region 1950–2040 cm^{-1}. While the rise times of the transients at the low-energy end of the band are instrument limited, they become progressively slower when moving to the high-energy side of the band and in fact correspond to the *decay* times found for the lower energy transients (Table I). Additionally, the decay times of the transients change from <1 ps at 1954 cm^{-1} to 6 ps at 2034 cm^{-1}, matching the recovery time of the ground-state band (6 ± 1 ps).[8]

MMCT excitation should lead to a complex in which the ruthenium cyanide center has formally changed from a 2+ to a 3+ oxidation state, resulting in a shift of the $\mathrm{RuC{\equiv}N}$ stretch from the ground-state value of 2053 cm^{-1} to ca. 2120 cm^{-1}.[9] We can thus unambiguously assign the short-lived transient at 2110 cm^{-1} to the MMCT excited state. The features between 1950 and 2040 cm^{-1} are consistent with vibrationally hot ground-state molecules formed following the back electron transfer. Metal–cyanide stretches exhibit anharmonicities of ca. 14 cm^{-1},[10] leading to vibrationally excited states that are shifted to lower energy from the ground-state band. The frequencies observed correspond to population of the vibrationally excited states $v = 1$–7.[11]

Data taken throughout the band from 1950 to 2040 cm^{-1} show that there is a steady progression of rate constants, with the higher vibrational states relaxing more quickly (see Table I). This is consistent with the expectation based on existing evidence[12] that higher vibrational states typically have larger cross sections for energy transfer. In the present case, relaxation can take place either through an intramolecular mechanism (i.e., IVR) or through transfer of the excess energy to the surrounding solvent molecules. Little is known about IVR rates in inorganic molecules; the available evidence suggests that such rates may be slower than observed in organic systems (typically <1 ps) due to large frequency mismatches, which lead to poor coupling between modes, particularly across M–L linkages.[13] Transfer of energy to the solvent from excited inorganic molecules is generally found to be much slower than we observe[14] and is typically solvent dependent. We are presently preparing to perform picosecond Raman experiments to directly observe low-frequency modes to address this question.

These findings demonstrate that the back electron transfer[15] from the MMCT state is ultrafast ($\tau < 0.5$ ps). The infrared frequency observed for the MMCT state suggests that nearly a full charge transfer occurs. More intriguing, however, is that upon return to the ground electronic state large amounts of energy (up to 14 000 cm^{-1}) are placed into a single vibration: the terminal $\mathrm{RuC{\equiv}N}$ stretching mode.[16] The large energy difference[2] (ca. 8000 cm^{-1}) between the $\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ and the $\mathrm{Ru^{III}}$–$\mathrm{Ru^{II}}$ species potentially allows the deposition of large amounts of energy into selected vibrational modes of the product of the thermal back electron transfer. The efficiency and selectivity of this process in the present case is, however, quite remarkable.[17] Vibrationally excited products following electron transfer have been observed in the gas phase, but to our knowledge this is the first direct observation in the solution phase.[18] Moreover, the relative rates observed for electronic and vibrational relaxation in $[\mathrm{(NC)_5Ru^{II}CNRu^{III}(NH_3)_5}]^{1-}$ suggest that activated modes in the excited state remain so on the time scale of electron transfer, holding important consequences for electron-transfer theories and for fast electron-transfer processes such as charge separation in photosynthesis. Studies of related systems are in progress in our laboratories in order to discern how modifications to the system may affect electron transfer and energy relaxation dynamics.

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(8) No differences were seen when the solvent was changed from D_2O to H_2O.

(9) We base this on comparison to model compounds, for example $[\mathrm{(NC)_6Fe^{III}}]^{3-}$ (2118 cm^{-1}) and $[\mathrm{(NC)_6Fe^{II}}]^{4-}$ (2044 cm^{-1}); similar behavior is expected for the analogous ruthenium complexes. See: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 273.

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(15) As was noted by a referee, the term "thermal back electron transfer" may not be appropriate to describe the fast reaction following MMCT excitation. Our results make it clear that the electronically excited MMCT state does not have time to thermalize. This suggests that attempts to model such fast electron-transfer reactions using theories that assume vibrational equilibration are inappropriate. However, the description of this process as a "back electron transfer", albeit from vibrationally hot states, is accurate as demonstrated by the typical $\mathrm{Ru^{III}C{\equiv}N}$ frequency observed in the MMCT transient.

(16) The results of Barbara et al. (ref 3) showed a 1–2-ps transient, which was initially assigned to the back electron transfer. Our results show that the back electron transfer is much faster and that subsequent events on the 500-fs to 6-ps time scale are actually vibrational relaxation.

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Enantioselective Total Synthesis of (−)-Calicheamicinone

A. L. Smith, C.-K. Hwang, E. Pitsinos, G. R. Scarlato, and K. C. Nicolaou*

Department of Chemistry
The Scripps Research Institute
10666 North Torrey Pines Road
La Jolla, California 92037
Department of Chemistry
University of California, San Diego
La Jolla, California 92093

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Calicheamicin $\gamma_1{}^1$[1] is a prominent member of the enediyne class of anticancer antibiotics[2] possessing phenomenal anticancer

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