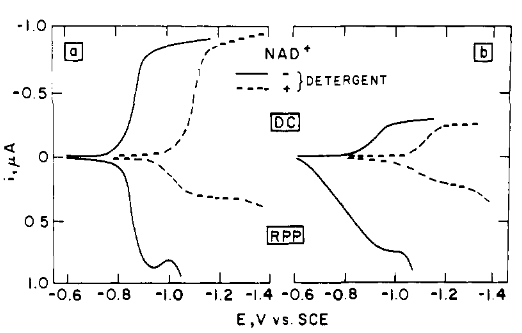


Figure 3. Direct current (DC) polarograms and reverse pulse polargrams (RPP) (constant E_p mode) of β-nicotinamide adenine dinucleotide (NAD^+). RPP: E_{in} plotted on the X axis (t = 0.5 s); E_p = −0.6 V (in absence of detergent), E_p = −0.8 V (in presence of 0.006% detergent, Triton X-100) (t_p = 0.8 ms). (a) β-NAD^+ (0.76 mM), 0.25 M $LiClO_4$–aqueous $NaHCO_3$–K_2CO_3, pH 9.2 buffer. (b) β-NAD^+ (0.76 mM) is 75% reduced to dimer electrochemically, making the resulting solution ca. 0.28 mM NAD· dimer and ca. 0.19 mM NAD^+.

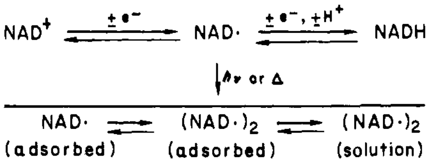
which the current was recorded. It may be seen from the results shown in Figure 1 that irradiating the electrode during the RPP experiment increases the current measured at the potential for radical oxidation, i.e., that light causes the conversion of dimers into radicals detectable within the diffusion layer. Scanning the wavelength range from 270 to 600 nm produces the photodissociation spectrum shown in the lower part of Figure 2 in which comparison is made to the independently determined absorption curve for the dimer.[1]

Irradiation of a solution of 1-ethyl-3-carbamidopyridinium ion in lithium perchlorate–carbonate buffer, pH 9.2, produces a small but well-defined increase in the current at the oxidation potential for the 3-substituted pyridinyl radicals. The wavelength dependence of the current increase bears a close resemblance to the absorption spectrum of the dimer as shown in the upper part of Figure 2 and is thus identified as a photodissociation spectrum of the dimer. Parallel observations have been made for 1-ethyl-3-carbomethoxypyridinium perchlorate in 0.25 M $LiClO_4/CH_3CN$, showing that the solvent does not alter the close resemblance between the photodissociation spectrum and the absorption spectrum of the pyridinyl radical dimer.

Irradiation with an N_2 pulse laser (100 kW/cm^2 per pulse, pulse width ca. 1.5 ns, 10–30 Hz) at 337 nm of NAD· dimer (produced from NAD^+[10] in aqueous buffer, pH 9.2, during RPP, E_{in} = 1.0 V vs. SCE, t = 2 s), gave rise to a transient current of radical oxidation in the course of a t_p (E_p = −0.6 V, t_p = 2 ms), the current being detected by an oscilliscope. The maximum current of the transient was 7 μA (a value limited by the rise time of the potentiostat). The transient decayed during 250–300 μs to the value of the current (2 μA) flowing in the absence of irradiation. (Transients were observed also for 2^+ and $(CONH_2)3^+$). We were unable, for lack of a suitable dye laser and the limitations imposed by the small magnitude of the current increase found, to obtain a reliable photodissociation spectrum for NAD· dimer. Other experiments, however, show that NAD· radicals form easily on the electrode surface from adsorbed NAD· dimer. Polarography of NAD^+ in aqueous buffer yields a current vs. voltage curve of the expected shape and position. However, RPP of such a "sample" reveals the presence of a substantial amount of adsorbed substance which has the oxidative properties of the NAD· radical. Addition of a detergent to the solution does not affect the polarographic wave height but sharply diminishes the amount of adsorbed radical,[3] as observed by the RPP E_p-constant mode technique (termed INPP by Cummings et al.[6]), seen in Figure 3a. (−0.6 V).

The amount of radical generated at different initial potentials (−0.6 to −1.4 V) is measured by the current flowing during a pulse applied in the potential range for the oxidation of the radical (−0.6 V). (The effect of surfactants such as tetraethylammonium ion on the adsorption of NAD^+ and its reduction products have been discussed by Elving and co-workers.[3]) If 75% of the NAD^+ is reduced electrochemically to the NAD· dimer, the polarographic current is correspondingly reduced as expected, but the quantity of adsorbed radicals detected by RPP remains unexpectedly high in concentration. Addition of detergent to the "prereduced" solution again diminishes the NAD· radical present on the surface, as illustrated in Figure 3b.

Many of the apparently conflicting results concerning the electrochemistry of NAD^+, as summarized by Elving,[3] can be understood as the result of photodissociation or thermal dissociation of NAD· dimer, either adsorbed or in solution. The scheme for electrochemical NAD^+ reduction should thus be written as in eq 1. The one-electron reduction potential estimated for NAD^+ from pulse radiolysis results (−1.19 V vs. SCE) should not be subject to the complications introduced by adsorption,[11] and is in reasonable agreement with the result estimated for zero dimer interference on the basis of present work in detergent solution. (See Figure 3). Stabilization of NAD· radicals by combination with the coenzyme binding sites of enzymes has been demonstrated by using pulse radiolysis to generate the NAD· radicals.[12]



(1)

The present results contribute strongly to our understanding of the nature of the electronic transitions in unstable radical dimers and provide an important element of knowledge for the understanding of the behavior of NAD· radicals. The RPP technique seems to be a convenient and useful way of obtaining photodissociation spectra of many radical dimers.

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Metal–Metal Interactions in Binuclear Rhodium Isocyanide Complexes. Polarized Single-Crystal Spectroscopic Studies of the Lowest Triplet ← Singlet System in Tetrakis(1,3-diisocyanopropane)dirhodium(2+)

Steven F. Rice and Harry B. Gray*

Contribution No. 6325
from the Arthur Amos Noyes Laboratory
California Institute of Technology
Pasadena, California 91125

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The description of the electronic structures of systems containing relatively weak metal–metal bonds between square planar d^8 units is a problem that has received much attention.[1] Our own efforts in this area have centered around several well-defined rhodium(I) isocyanide oligomers, the prototypal complex being $Rh_2b_4^{2+}$ (b = 1,3-diisocyanopropane).[2,3] The lowest triplet excited state of $Rh_2b_4^{2+}$ is of particular interest, owing to its rich photophysical and photochemical properties.[4-6] We have now obtained the

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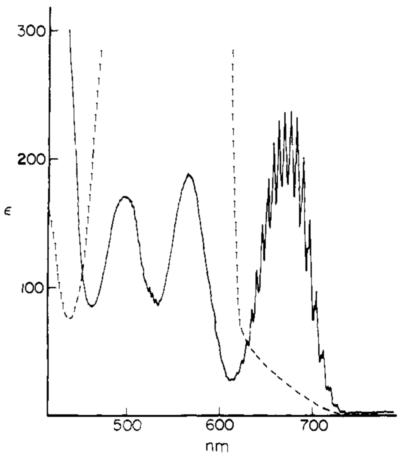

Figure 1. Absorption spectra (400–800 nm) of a single crystal of $(Rh_2b_4)(BPh_4)_2$ at 5 K: solid line, perpendicular polarization; dashed line, parallel polarization.

Table I. Absolute Energies and Spacings of the Vibronic Components for the $E_u(^3A_{2u}) \leftarrow {}^1A_{1g}$ Absorption System in $(Rh_2b_4)(BPh_4)_2$ at 5 K

v^a	E_v, cm^{-1}	Δ^b	$E_v - E_{v-1}$	n	E_v, cm^{-1}	$E_v - E_{v-1}$
0	13306			11	14906	142
	13369	63		12	15046	140
1	13455		149	13	15187	141
	13513	58		14	15333	146
2	13607		152	15	15473	140
	13661	54		16	15613	140
3	13752		145	17	15754	141
	13805	53		18	15895	141
4	13897		145	19	16033	138
	13948	51		20	16176	143
5	14040		143	21	16308	132
	14094	54				
6	14188		148			
	14232	44				
7	14331		143			
	14376	45				
8	14479		148			
	14513	34				
9	14619		140			
	14662	43				
10	14764		145			

[a] The assigned a_{1g}(Rh–Rh) vibrational quantum number.
[b] Spacing between the principal peaks in the progression and secondary (unassigned) peaks.

low-temperature single-crystal polarized absorption spectrum of $(Rh_2b_4)(BPh_4)_2$ in the region of the lowest triplet ← singlet transition. Analysis of these spectroscopic data has provided reasonably detailed information about several aspects of the geometric and electronic structure of this important triplet.

Spectroscopic measurements in the 400–800-nm region on a single crystal of $(Rh_2b_4)(BPh_4)_2$ at 5 K reveal a vibronically structured band ($\lambda_{max} \sim 670$ nm) that is polarized perpendicular to the Rh–Rh axis (Figure 1). The observed polarization requires that the system be assigned to $E_u(^3A_{2u}) \leftarrow {}^1A_{1g}$; presumably, $E_u(^3A_{2u})$ acquires singlet character by mixing with the ^1E_u state associated with the allowed $^1E_u \leftarrow {}^1A_{1g}$ transition at 318 nm (ϵ 31 500; CH_3CN solution). We have not positioned the symmetry-forbidden $A_{1u}(^3A_{2u}) \leftarrow {}^1A_{1g}$ transition, as it does not contribute significantly to the absorption spectrum.

A progression in a vibrational frequency of about 150 cm^{-1} is built on the 670-nm band (Table I). This vibrational frequency accords well with the 144-cm^{-1} value assigned to the a_{1g}(Rh–Rh) fundamental of the $^3A_{2u}$ excited state from resonance Raman spectroscopic experiments performed on $Rh_2b_4^{2+}$ in CH_3CN solution.[7] We associate this frequency with the totally symmetric Rh–Rh stretching motion for two reasons: (1) the dominant distortion in $^3A_{2u}$ should be along the Rh–Rh bond axis, as the state is derived from $^1A_{1g}$ by $1a_{2u}(4d_{z^2}\sigma^*) \rightarrow 2a_{1g}(5p_z\sigma)$ excitation and (2) all other vibrations that could couple significantly to $^3A_{2u} \leftarrow {}^1A_{1g}$ (i.e., the a_{1g} MCN bend and the a_{1g} MC stretch) should exhibit higher energies.

The most striking result obtained from these experiments is that the Rh–Rh stretching frequency is dramatically higher in the $^3A_{2u}$ state of $Rh_2b_4^{2+}$ than in the ground state [values for the $^1A_{1g}$ state from resonance Raman spectroscopy are 85 cm^{-1} (crystal)[8] and 79 cm^{-1} (CH_3CN solution)[7]]. Analysis of the band shape of the absorption system also reveals that the excited state is greatly distorted from the ground state along the Rh–Rh coordinate; specifically, we find that there is a large (~0.3 Å) Rh–Rh contraction in the $^3A_{2u}$ excited state (2.94 Å estimated[9] for $^3A_{2u}$ as compared to 3.24 Å for the ground state).[3]

The Rh–Rh contraction in $^3A_{2u}$ is predicted by simple molecular orbital theory. If $4d_{z^2}$–$5p_z$ mixing is neglected, the Rh–Rh bond order in the ground state of $Rh_2b_4^{2+}$ is zero, because both the $1a_{1g}(4d_{z^2}\sigma)$ and $1a_{2u}(4d_{z^2}\sigma^*)$ orbitals are occupied.[10] The relatively weak Rh–Rh bond in the ground state presumably results from the stabilization of the filled $1a_{1g}(4d_{z^2}\sigma)$ and $1a_{2u}(4d_{z^2}\sigma^*)$ levels derived from configurational mixing with unoccupied orbitals of appropriate symmetries [$2a_{1g}(5p_z\sigma)$ and $2a_{2u}(5p_z\sigma^*)$]. Our spectroscopic results show clearly that the $2a_{1g}$ orbital is strongly σ bonding, as the Rh–Rh frequency in the $^3A_{2u}$ state is very near to the value expected for a single M–M bond.[11] Most important, our results mean that the $^3A_{2u} \leftarrow {}^1A_{1g}$ transition in binuclear Rh(I) isocyanide complexes does not possess the degree of Rh → CNR charge-transfer character that is present in the otherwise analogous transition in monomeric parent complexes.[12,13]

The crystal spectrum also allows certain conclusions to be drawn with regard to the overall potential surface of the $^3A_{2u}$ state of $Rh_2b_4^{2+}$. In the excited-state Rh–Rh vibrational progression there is a significant albeit small deviation from harmonic behavior. The anharmonicity parameter, χ_e, may be estimated as 0.38 cm^{-1} from the spectrum. A Birge–Sponer extrapolation ($D_e = \omega_e^2/4\chi_e$)[14] gives 42 kcal/mol for the Rh–Rh bond dissociation energy in the $^3A_{2u}$ excited state.[15]

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(9) The excited-state geometrical distortion was obtained from a detailed Franck–Condon analysis of the absorption spectrum for the $^3A_{2u} \leftarrow {}^1A_{1g}$ transition. The total absorption band was fitted to the predicted intensities for the individual vibronic components of the progression by employing the following expression (Ballhausen, C. J. "Molecular Electronic Structures of Transition Metal Complexes"; McGraw-Hill: New York, 1979; p 112):

$$\frac{\langle\chi_0|\chi_{v'}\rangle}{\langle\chi_0|\chi_0\rangle} = \left(\frac{1}{2^{v'}v'!}\right)^{1/2}\left(\frac{\alpha''-\alpha'}{\alpha''+\alpha'}\right)^{v'/2} H_{v'}\left[\frac{\alpha''}{\alpha''+\alpha'}\left[\frac{\alpha'(\alpha''+\alpha')}{\alpha''-\alpha'}\right]^{1/2}\Delta\xi\right]$$

The intensities of the individual vibronic lines are proportional to the squares of the overlap. α'' and α' are related directly to the ground-state and excited-state vibrational frequencies of the distorting mode. $H_{v'}$ is a Hermite polynomial of v' order. $\Delta\xi$, a normal coordinate distortion, is the value that is adjusted to fit the absorption band. $\Delta\xi$ can then be related to a change in the Rh–Rh internal coordinate through the use of the diatomic approximation, which assumes that the effective reduced mass of the system is simply that of the two rhodium atoms.

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We are now in position to estimate the ground-state Rh–Rh bond energy in $Rh_2b_4^{2+}$ from the following relationship: $D_e(^1A_{1g}) = E_t^d(^3A_{2u} \leftarrow {}^1A_{1g}, Rh_2^{2+}) - E_t^m(^3A_{2u} \leftarrow {}^1A_{1g}, Rh^+) + D_e(^3A_{2u})$. From the spectrum of $Rh(CNR)_4^+$ we take E_t^m = 62 kcal/mol[8] and E_t^d for $Rh_2b_4^{2+}$ = 38 kcal/mol. Thus for $D_e(^3A_{2u})$ = 42 kcal/mol, the ground-state Rh–Rh bond energy is about 18 kcal/mol. Because the 0–0 energies of the triplet ← singlet transitions are known quite accurately, any error in $D_e(^1A_{1g})$ must come from the Birge–Sponer value for $D_e(^3A_{2u})$. Accordingly, we consider 18 kcal/mol as an upper limit for the ground-state Rh–Rh bond energy, as it is likely that the Birge–Sponer extrapolation overestimates[14] $D_e(^3A_{2u})$ for $Rh_2b_4^{2+}$. We intend to study the temperature dependence of the dissociation of $Rh_2(CNR)_8^{2+}$ complexes in various solvents, which should provide additional information on this point.

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(15) Because the bridging ligands will prevent Rh–Rh dissociation, the estimated D_e is for the $^3A_{2u}$ state of a strictly analogous unbridged complex, $Rh_2(CNR)_8^{2+}$. Interestingly, the Birge–Sponer plot [E_v/v vs. v (Clark, R. J.; Franks, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 2763)] exhibits a significant curvature, suggesting that the decrease in vibrational frequency per vibrational quantum begins to level off. It is our opinion that this curvature represents mixing of ligand bending character into the Rh–Rh stretching wave function for high a_{1g} vibrational quanta. The value of χ_e was obtained from fitting only the first 10 vibrational quanta to a straight line, thereby approximating an unbridged Rh–Rh bond.

Metal–Metal Interactions in Binuclear Rhodium Isocyanide Complexes. Resonance Raman Spectra of the $^1A_{1g}$ and $E_u(^3A_{2u})$ Electronic States of Tetrakis(1,3-diisocyanopropane)dirhodium(I)

Richard F. Dallinger,[1a] Vincent M. Miskowski,[1b]
Harry B. Gray,[1b] and William H. Woodruff*[1c]

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712
and Contribution No. 6324
from the Arthur Amos Noyes Laboratory
California Institute of Technology
Pasadena, California 91125

Received October 10, 1980

The unique photophysical and photochemical properties of binuclear rhodium(I) isocyanide complexes have received much recent attention.[2-9] There is some Rh–Rh bonding interaction in the ground state ($^1A_{1g}$) of the prototypal complex, $Rh_2b_4^{2+}$ (b = 1,3-diisocyanopropane), in spite of the fact that simple theory suggests that the Rh–Rh bond order is zero (filled $4d_{z^2}\sigma$ and $4d_{z^2}\sigma^*$ orbitals).[9] Greatly enhanced Rh–Rh bonding is predicted for the lowest triplet and singlet excited states, owing to the promotion of a $4d_{z^2}\sigma^*$ electron to a $5p_z\sigma$ orbital.[2] Measurement of the Rh–Rh vibrational frequencies in the ground and excited electronic states in question should reveal whether or not the Rh–Rh bonding is stronger in the latter. We report the results of such a study of the $^1A_{1g}$ and $E_u(^3A_{2u})$ states of $Rh_2b_4^{2+}$, using time-resolved resonance Raman (TR^3) spectroscopy.

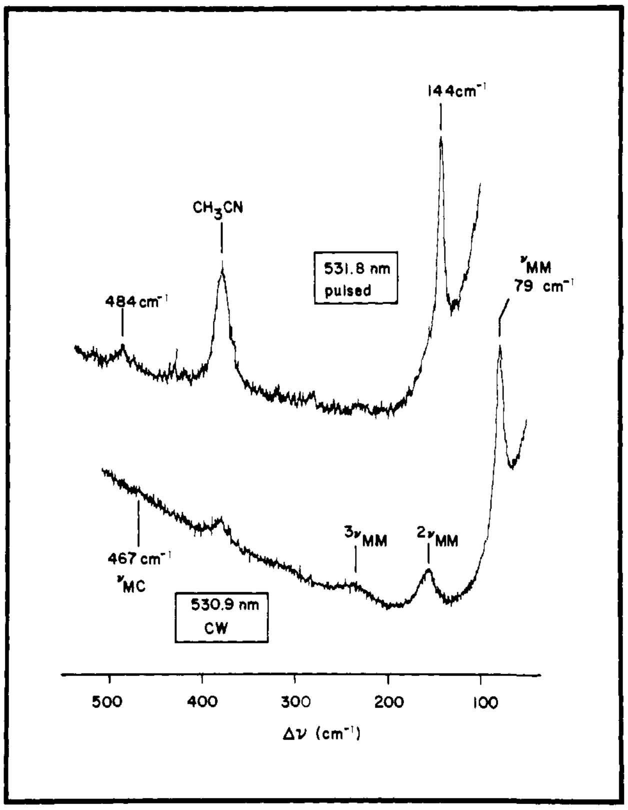

Figure 1. Lower trace: ground-state resonance Raman spectrum of $Rh_2b_4^{2+}$ obtained by continuous-wave excitation at 530.9 nm (Kr laser). Conditions: laser power, 75 mW at the sample; $[Rh_2b_4^{2+}] = 5 \times 10^{-4}$ M in CH_3CN solvent. The acetonitrile was filtered through activated charcoal, then deaerated by bubbling nitrogen followed by three cycles of freeze–pump–thaw. Upper trace: excited-state resonance Raman spectrum of $Rh_2b_4^{2+}$ obtained by pulsed excitation with the second harmonic of the Q-switched Nd:YAG laser, 531.8 nm. The solution sample was the same as used for the ground-state spectrum. Excitation conditions: pulsed excitation at 531.8 nm, pulse duration 7 ns, per pulse energy 5 mJ, pulse repetition frequency 10 Hz, average (C.W. equivalent) power 50 mW.

The TR^3 technique[10] has been successfully applied to several excited-state transients.[11-13] The experiment involves the creation of the desired excited state by optical or radiolytic excitation, with simultaneous or subsequent interrogation of the resonance Raman spectrum by using a pulsed laser. Acetonitrile solutions of $Rh_2b_4^{2+}$ (ca. 5×10^{-4} M) were deaerated with nitrogen prior to the pulsed Raman experiments. The laser excitation sources for the CW and pulsed resonance Raman experiments were the 530.9-nm line of a Spectra Physics 171 Kr^+ laser and the 531.8-nm second harmonic of a Quanta-Ray DCR-1A Nd:YAG oscillator/amplifier, respectively. In both cases a spining cell following the Shriver design was employed.[14]

The transient absorption difference spectrum of $Rh_2b_4^{2+}$ shows broad features [400–550-nm region, ϵ(calcd) $\sim 10^4$ M^{-1} cm^{-1}] to the blue of the ground-state absorption (553 nm) and prompt

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