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Time-Resolved Resonance Raman Spectroscopy at Low Temperature. The Excited-State Metal−Metal Stretching Frequency of $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-Dimethyl-2,5-diisocyanohexane)

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The time-resolved resonance Raman spectrum of the short-lived triplet ($d\sigma^*p\sigma$) excited state of $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) was obtained by lowering the temperature of a 3:1 ethanol/methanol solution until the excited-state lifetime became much greater than the width of the pulsed laser excitation source. The metal−metal stretching frequency is 151 cm^{-1} in the excited triplet state, as compared to 50 cm^{-1} in the ground state. The diatomic harmonic force constants derived from these frequencies are in a 9.12:1 ratio (excited state/ground state), consistent with the simple molecular orbital description that predicts that the Rh−Rh bond order is greater in the excited state than in the ground state. A comparison of $Rh_2(TMB)_4^{2+}$ and $Rh_2b_4^{2+}$ (b = 1,3-diisocyanopropane) Raman data indicates that the nature of the bridging ligand considerably affects the ground- and excited-state metal−metal stretching frequencies and that the population of the $p\sigma$ orbital may have very little effect on the bonding in the excited triplet state.

Introduction

Nanosecond time-resolved resonance Raman (TR^3) spectroscopy[1] is a powerful method that has been employed successfully in investigations of the excited electronic states of transition metal complexes.[2−9] Importantly, the TR^3 experiment can be performed on species in solution at room temperature, complementing the information obtained by other techniques that yield excited-state vibrational frequencies, such as low-temperature single-crystal absorption spectroscopy.[6]

Binuclear d^8−d^8 complexes display interesting spectroscopic and photochemical properties.[10,11] Indeed, the initial resonance Raman study[7] of "rhodium bridge" ($Rh_2b_4^{2+}$, b = 1,3-diisocyanopropane) established that the metal−metal bonding interaction was much stronger in the luminescent triplet $d\sigma^*p\sigma$ excited state (triplet excited-state metal−metal stretching frequency $\nu^*_{RhRh} = 144$ cm^{-1}, simple diatomic force constant $K^*_{diatomic} = 0.629$ mdyn/Å) than in the ground state ($\nu_{RhRh} = 79$ cm^{-1}, $K_{diatomic} = 0.189$ mdyn/Å). The excited-state Raman spectra of several potentially interesting members of this family, such as $M_2(dimen)_4^{2+}$ (M = Rh, Ir; dimen = 1,8-diisocyanomenthane),[12] could not be acquired with the TR^3 apparatus used in the $Rh_2b_4^{2+}$ investigation because the room-temperature excited-state lifetimes of these species in solution are shorter than the 7 ns pulse width of the Nd:YAG laser used to probe the excited-state vibrational spectrum.

To obtain an excited-state TR^3 spectrum, in general, the transient excited-state lifetime must be greater than the pulse width of the interrogating laser. If the excited-state lifetime is shorter than the laser pulse width, it is, of course, possible to use a faster pulsed laser; picosecond TR^3 and picosecond transient IR studies have been reported.[13,14] However, many transition metal complexes show a marked dependence of excited-state lifetime with temperature. Thus, another method to acquire excited-state TR^3 data for species with short room-temperature solution lifetimes is to cool a solution to a point where the lifetime is sufficiently long to permit acquisition of an excited-state TR^3 spectrum with a nanosecond laser system.

In the present study, the TR^3 spectrum of $Rh_2(TMB)_4^{2+}$ was measured at both room temperature and low temperature to show the utility of low-temperature nanosecond TR^3 spectroscopy. The $Rh_2(TMB)_4^{2+}$ complex has a relatively short triplet $d\sigma^*p\sigma$ ($^3A_{2u}$) excited-state lifetime at room temperature in fluid solution ($\tau_{RT} \approx 25$ ns in CH_3CN), but this lifetime exhibits a dramatic temperature dependence such that the excited-state lifetime is ∼20 μs at 77 K.[15] The spectrum of the triplet excited state of

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$Rh_2(TMB)_4^{2+}$ exhibits an absorption band at 490 nm,[16] assigned to a $d\sigma^* \rightarrow p\sigma$ transition analogous to the one that causes large intensity enhancement of the metal−metal stretching mode in the $^3A_{2u}$ $Rh_2b_4^{2+}$ TR^3 spectrum.[7] These properties make the $Rh_2(TMB)_4^{2+}$ complex an excellent one for exploring low-temperature nanosecond TR^3 spectroscopy.

Experimental Section

$Rh_2(TMB)_4(PF_6)_2$ was synthesized following published procedures.[17] CH_3CN (Burdick and Jackson spectrograde) was dried over 3 Å molecular sieves. Methanol (Aldrich spectrograde) and absolute ethanol were taken from freshly opened bottles. Solutions of $Rh_2(TMB)_4(PF_6)_2$ in either CH_3CN (for room-temperature TR^3 experiments) or 3:1 ethanol/methanol (for low-temperature TR^3 measurements) were prepared with an absorbance of ca. 0.6−0.8 per mm path length at the ground-state absorption maximum of 516 nm, degassed by five freeze−pump−thaw cycles on a high vacuum line and flame-sealed in 5 mm NMR tubes.

A "one-color" TR^3 experiment was performed, in which a single laser pulse both creates the transient excited-state population and excites the resonance Raman spectrum of the triplet state that is the predominant molecular species in the illuminated sample volume. A Lambda-Physik XeCl excimer-pumped dye laser system with Coumarin 102 dye was the photon source in the TR^3 experiments; the dye laser pulse width was ca. 30 ns and the pulse energy was 4−5 mJ/pulse. Scattered light was analyzed using a SPEX model 1403 scanning double monochromator and detected with a cooled Hamamatsu R928 photomultiplier tube. The PMT signal was processed with a Stanford Research Systems model SR250 gated integrator and sent to a personal computer for analysis. In all spectra, the excimer dye laser wavelength was 490 nm, the spectral slit width of the monochromator was 4 cm^{-1}, the PMT high voltage was −900 V and the gated integrator averaged 10 laser pulses. The monochromator shutter was automatically closed while scanning the region from $\Delta\nu = -25$ to $+25$ cm^{-1}.

For the low-temperature TR^3 experiments, the sample solution in a short flame-sealed NMR tube was mounted on a home-built copper sample holder which was attached to the coldfinger of an Air Products Displex closed cycle helium cryostat. The sample temperature was monitored with a silicon diode temperature probe attached to the sample holder with Crycon grease.

Results

The TR^3 spectra of $Rh_2(TMB)_4^{2+}$ at room temperature in CH_3CN solution and at 150 K[18] in 3:1 ethanol/methanol mixture (just above the glass temperature of the solvent) are shown in Figures 1 and 2, respectively. The room-temperature TR^3 spectrum shows a weak, but distinct, feature at 151 cm^{-1}, much higher in frequency than the ground-state band at 50 cm^{-1} which was observed in previous continuous-wave laser excited resonance Raman spectra in CH_3CN solution. (The 50 cm^{-1} band is obscured by the solvent Rayleigh scattering in Figure 1.) No overtones based on the 151 cm^{-1} band were observed, yet the 151 cm^{-1} band also is observed in the anti-Stokes portion of the room-temperature spectrum, eliminating the possibility that it is a spectral artifact. In the 150 K TR^3 spectrum, the 151 cm^{-1} band is much more prominent relative to wings of the Rayleigh scattering peak. Additionally, at least two overtones of the 151 cm^{-1} band are clearly observed (although the second overtone overlaps with a solvent band from ethanol). The 50 cm^{-1} ground-state feature also appears as a weak feature in both the Stokes and anti-Stokes spectra.

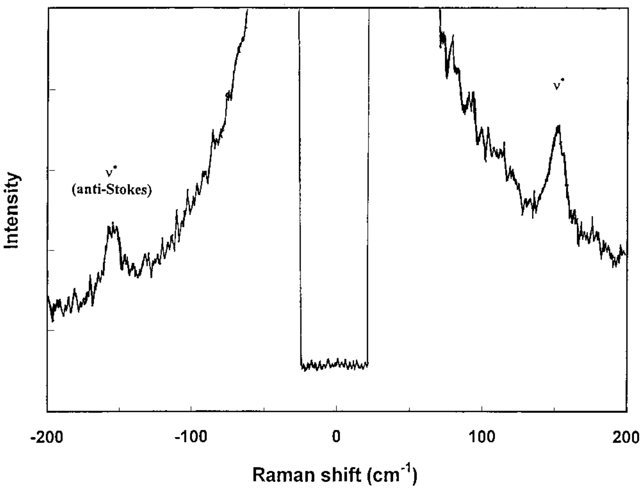

Figure 1. TR^3 spectrum of $Rh_2(TMB)_4^{2+}$ at room temperature in CH_3CN solution; $\lambda_{exc} = 490$ nm, 4.8 mJ/pulse; two co-added scans.

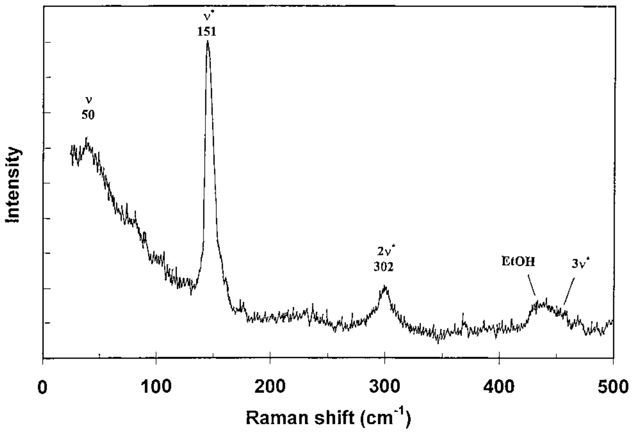

Figure 2. TR^3 spectrum of $Rh_2(TMB)_4^{2+}$ in a 3:1 ethanol/methanol solution at a nominal temperature of 150 K; $\lambda_{exc} = 490$ nm, 4.0 mJ/pulse; three co-added scans. The vertical scale is 5 times that of Figure 1.

The room-temperature TR^3 spectrum corresponds to the situation in which the laser pulse width is approximately equal to the excited-state lifetime, which is essentially the minimum condition for obtaining excited-state TR^3 spectra, while the 150 K TR^3 spectrum corresponds to the situation in which the laser pulse width is small compared to the excited-state lifetime (which is several μs at 150 K[15]). The obviously higher quality of the low-temperature TR^3 spectrum results from increased population of the triplet excited-state resulting from the laser pulse width being much shorter than the triplet lifetime.

Discussion

It is interesting to note how the conformational flexibility of the bridging ligand affects the ground- and excited-state Rh−Rh frequencies, ν and ν^*. The ν for $Rh_2(TMB)_4^{2+}$ (50 cm^{-1}) is lower than that of $Rh_2b_4^{2+}$ (79 cm^{-1}) in CH_3CN solution, while the ν^* is higher for $Rh_2(TMB)_4^{2+}$ (151 cm^{-1}) than for $Rh_2b_4^{2+}$ (144 cm^{-1}). The TMB ligand imposes less constraint on the binuclear metal unit in the ground state than does the b (1,3-diisocyanopropane) ligand, resulting in a larger Rh−Rh bond distance[17] and a lower ν. This observation correlates with

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Table 1. Metal-Metal Stretching Frequencies, Force Constants, and Bond Distances for the d^8-d^8, d^7-d^8, and d^7-d^7 Binuclear Rhodium Complexes

	$Rh_2L_4^{2+}$ ($^1A_{1g}$)		$Rh_2L_4^{2+}$ ($^3A_{2u}$)		$Rh_2L_4Cl_2^{2+\,a}$	
	bridge	TMB	bridge	TMB	bridge	TMB
ν (cm^{-1})	79	50	144	151	283	288
K (mdyn/Å)	0.189	0.076	0.629	0.691	0.948	1.141
r_{RhRh} (Å, exptl)	3.243	3.262	2.93^b	−	2.837	2.770
r_{RhRh} (Å, calc)^c	3.175	3.237	2.964	2.933	2.832	2.760

[a] Data from ref 21; the force constants were calculated using a linear, four-atom force field. [b] Rh−Rh distance computed from a Franck−Condon analysis of the electronic absorption spectrum (Rice, S. F.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1988**, *27*, 4704). [c] Rh−Rh distances calculated from Woodruff's bond distance/force constant correlation (ref 19).

the MO prediction of a zero bond order in the ground state of each of these complexes. The higher value of ν_{RhRh} for $Rh_2(TMB)_4^{2+}$ in the $^3A_{2u}$ excited state reflects the greater conformational freedom of TMB to accommodate the predicted excited-state Rh−Rh bond. The ratios of the simple metal−metal harmonic force constants in the two electronic states (K_{exc}/K_{gd}) are 3.32 for $Rh_2b_4^{2+}$ and 9.12 for $Rh_2(TMB)_4^{2+}$ (see Table 1), reflecting the importance of the structure of the bridging ligand on the binuclear metal environment.

The Rh−Rh stretching frequencies may be empirically related to the corresponding bond distances through one of several correlations. For $Rh_2(TMB)_4^{2+}$, Woodruff's correlation[19] for 4d diatomics gives a ground-state bond distance of 3.237 Å (crystal structure value = 3.262 Å[17]) from the observed frequency of 50 cm^{-1}; it predicts a bond distance of 2.933 Å, corresponding to a 0.304 Å shortening, in the $^3A_{2u}$ excited state. This Rh−Rh shrinkage for $Rh_2(TMB)_4^{2+}$ is larger than the calculated decrease of 0.211 Å in the excited state of $Rh_2b_4^{2+}$ (relative to the ground state). Harvey's correlation for binuclear rhodium complexes[20] does less well for ground-state $Rh_2(TMB)_4^{2+}$ (calculated bond distance = 3.520 Å from the 50 cm^{-1} ground-state metal−metal frequency) and predicts a shortening of 0.634 Å in the excited state. Importantly, both correlations indicate a greater contraction of the Rh−Rh distance (as compared to $Rh_2b_4^{2+}$) upon formation of the $^3A_{2u}$ excited state of $Rh_2(TMB)_4^{2+}$.

A picture of the relative importance of d and p orbitals in the formation of the metal−metal bond in bridged Rh_2 complexes emerges from the resonance Raman and TR^3 experiments. Table 1 summarizes the results for the d^8-d^8 ($^1A_{1g}$ ground-state dimer), d^7-d^8 ($^3A_{2u}$ excited-state dimer) and d^7-d^7 (ground-state axially ligated dimer)[21] Rh_2 species with both b and TMB bridging ligands, along with diatomic harmonic force constants and bond distances (both from X-ray crystallographic data and from Woodruff's bond distance/force constant correlation[19]). The data in Table 1, along with the corresponding plot in Figure 3, show that the formal p_z-p_z orbital contribution to the Rh−Rh bond in the excited state is not very significant,[22] since the force constant for the metal−metal stretching mode in the $^3A_{2u}$ excited state (d^7-d^8) for $Rh_2b_4^{2+}$ and $Rh_2(TMB)^{2+}$ is only a little more than the average of the $^1A_{1g}$ ground state (d^8-d^8) and axially ligated d^7-d^7 $Rh_2b_4Cl_2^{2+}$ and $Rh_2(TMB)Cl_2^{2+}$ force constants; the latter is presumably somewhat less than it would be for a nonaxially ligated d^7-d^7 case, according to the trans effect.[11,23,24] This situation is consistent with electronic spectroscopic data for other types of d → p_z excited states of d^8-d^8 compounds.[25] Thus, we conclude that the proposed picture of the excited dσ*pσ triplet state of the bridged Rh(I) dimers as a diradical tethered by a single metal−metal bond,[26] [•M−M•]*, is only partially correct. A better description of the $^3A_{2u}$ state is one in which there is a bonding electron in the overlapping d_{z^2} orbitals (Rh−Rh bond order = $^1/_2$), with the other unpaired spin located in a diffuse, largely nonbonding, p_z-derived orbital.[25,27] This bonding proposal could be tested by examining the resonance Raman spectra of radical d^7-d^8 ground-state species;[28,29] to date, however, these spectra have not been reported.

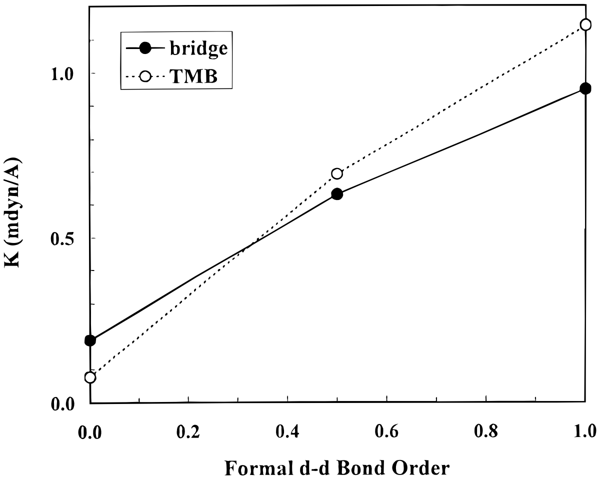
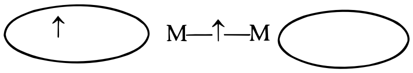


Figure 3. Correlation of calculated diatomic Rh_2 force constants for Rh_2^{2+} (d^8-d^8), Rh_2^{2+}* (d^7-d^8), and Rh_2^{4+} (d^7-d^7) species with the formal $d_{z^2}-d_{z^2}$ bond order.



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