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# PHOTOPHYSICAL PROPERTIES OF THE LOWEST ELECTRONIC EXCITED STATES OF BINUCLEAR RHODIUM(I) ISOCYANIDE COMPLEXES

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CONTENTS

## A. INTRODUCTION

Some years ago the authors discovered [1] that square planar rhodium(I) isocyanide complexes (e.g. $Rh(CNPh)_4^+$) aggregate in solution. The binuclear species are intensely colored, owing to a strong visible absorption system attributable to an allowed $\sigma^*(d_{z^2}) \rightarrow \sigma(p_z, \pi^*CNR)$ transition associated with the direct Rh(I)–Rh(I) interaction [1,2]. Early in our research on these oligomeric species, Lewis and Mann employed binucleating diisocyanides (e.g. 1,3-diisocyanopropane, which we call "bridge", or b) to prepare discrete binuclear Rh(I) complexes for detailed studies [3–15]. The authors have found that $Rh_2b_4^{2+}$ and certain related complexes possess rich photophysical and photochemical properties, and it is the former area that will be reviewed in the sections that follow.

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## B. POLARIZED ABSORPTION SPECTRA OF $Rh_2b_4^{2+}$

The authors absorption spectroscopic measurements in the 400–800 nm region on a single crystal of $(Rh_2b_4)(BPh_4)_2$ at 5 K showed that the intense 550 nm band is $z$-polarized, as predicted for the $^1A_{2u} \leftarrow {}^1A_{1g}(d\sigma^* \rightarrow p\sigma)$ transition assignment; these experiments also revealed a vibronically structured system at longer wavelengths ($\lambda_{max} \sim 670$ nm) that is polarized perpendicular to the Rh–Rh axis [13]. The observed polarization of the 670 nm band accords with the assignment $E_u(^3A_{2u}) \leftarrow {}^1A_{1g}$; $E_u(^3A_{2u})$ presumably acquires singlet character by mixing with the $^1E_u$ state associated with the allowed $^1E_u \leftarrow {}^1A_{1g}$ transition at 318 nm ($\epsilon$ 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. 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 [14]. We associate this frequency with the totally symmetric Rh–Rh stretching motion because the dominant distortion in $^3A_{2u}$ should be along the Rh–Rh bond axis, as the state is derived from $^1A_{1g}$ by $1a_{2u}(d\sigma^*) \rightarrow 2a_{1g}(p\sigma)$ excitation, and all other vibrations that could couple significantly to $^3A_{2u} \leftarrow {}^1A_{1g}$ (i.e. the $a_{1g}$(Rh–C–N) bend and the $a_{1g}$(Rh–C) 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) [16] and 79 $cm^{-1}$ ($CH_3CN$ solution) [14]]. Our analysis of the band shape of the absorption system also showed that the excited state is greatly distorted from the ground state along the Rh–Rh coordinate; specifically, we found that there is a large (~0.3 Å) Rh–Rh contraction in the $^3A_{2u}$ excited state (2.94 Å estimated for $^3A_{2u}$, as compared to 3.24 Å for the ground state) [13].

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 $1a_{1g}(d\sigma)$ and $1a_{2u}(d\sigma^*)$ orbitals are occupied. The relatively weak Rh–Rh bond in the ground state presumably results from the stabilization of the filled $1a_{1g}(d\sigma)$ and $1a_{2u}(d\sigma^*)$ levels derived from configurational mixing with unoccupied orbitals of appropriate symmetries [$2a_{1g}(p\sigma)$ and $2a_{2u}(p\sigma^*)$]. Our spectroscopic results showed clearly that the $2a_{1g}$ orbital is strongly $\sigma$ bonding, as the Rh–Rh frequency in the $^3A_{2u}$ state falls squarely in the range displayed by single M–M bonds [17]

Our analysis of the crystal absorption spectrum also allowed 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, $\chi_e$, was estimated as 0.38 $cm^{-1}$ from the spectrum. A Birge–Sponer extrapolation ($D_e = \omega_e^2/4\chi_e$) gave 42 kcal $mol^{-1}$ for the Rh–Rh bond dissociation energy in the $^3A_{2u}$ excited state.

## C. LUMINESCENCE SPECTRUM OF $Rh_2b_4^{2+}$

The binuclear cation ($Rh_2b_4^{2+}$) exhibits pronounced luminescence at slightly longer wavelengths than the singlet and triplet absorption features. The luminescence consists of two broad bands separated by about 2000 $cm^{-1}$ ($\lambda_{max}$ ~660 and 830 nm). The energies of the origins of these two emission bands are precisely coincident with the origins of the $^1A_{2u}$ and $^3A_{2u}$ absorptions. The lower energy band can be quenched by oxygen, whereas the intensity of the higher energy feature is insensitive to the presence of air. It is apparent from these and other observations [16] that the two bands are attributable to transitions from the singlet ($^1A_{2u}$) and triplet ($^3A_{2u}$) excited states derived from the $(d\sigma)^2(d\sigma^*)^1(p\sigma)^1$ electronic configuration. The observed lifetimes are 1.1 ns [8,18] for the fluorescence and 8.5 $\mu$s for the phosphorescence of $(Rh_2b_4)(BPh_4)_2$ in acetonitrile solution at room temperature.

## D. TEMPERATURE EFFECTS ON EXCITED STATE LIFETIMES [19]

The authors initiated a detailed study of the temperature dependence of the luminescence of several binuclear rhodium(I) isocyanides after discovering that the room-temperature phosphorescence from $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-diisocyanohexane) is barely observable: indeed, we found that the triplet ($d\sigma^* p\sigma$) lifetime for this complex is dramatically shorter at 300 than at 77 K (25 ns versus 20 $\mu$s), in sharp contrast to the behavior of the $^3A_{2u}$ state of $Rh_2b_4^{2+}$ [the triplet lifetime of the latter complex in poly(methylmethacrylate) changes very little from 294 (9 $\mu$s) to 77 K (16 $\mu$s)]. The results that will be discussed here come from measurements of emission intensities as a function of time after a 10 ns laser pulse. In most of the experiments, monophasic exponential decay of the emission was not observed; rather, the decay appeared to be biphasic and the amount contributed to the overall intensity by each of the two decay components varied with temperature.

The biphasic emission is puzzling. One explanation is that there are two non-thermally-equilibrated states that are populated by a temperature-dependent intersystem crossing mechanism; these states could be the two spin-orbit components of the *dσ*pσ* triplet. Another possibility is that there are two (or possibly more) conformations of the binuclear species that have different lifetimes. The relative concentrations of these conformations could vary with temperature and environment, thereby accounting for the observed behavior. Of course, we recognize that the origin of the biphasic emission may be much less interesting; it could simply signal partial photodecomposition of the sample.

The matter of principal interest here is the impressive temperature variation of the emission lifetimes for certain binuclear Rh(I) complexes (in each case the fast and slow components follow each other; that is, the ratio of their lifetimes does not change significantly throughout the temperature range). Arrhenius plots for the slow components of three binuclear Rh(I) complexes are shown in Fig. 1. For $[Rh_2(TMB)_4](PF_6)_2$ and [Rh(CN-

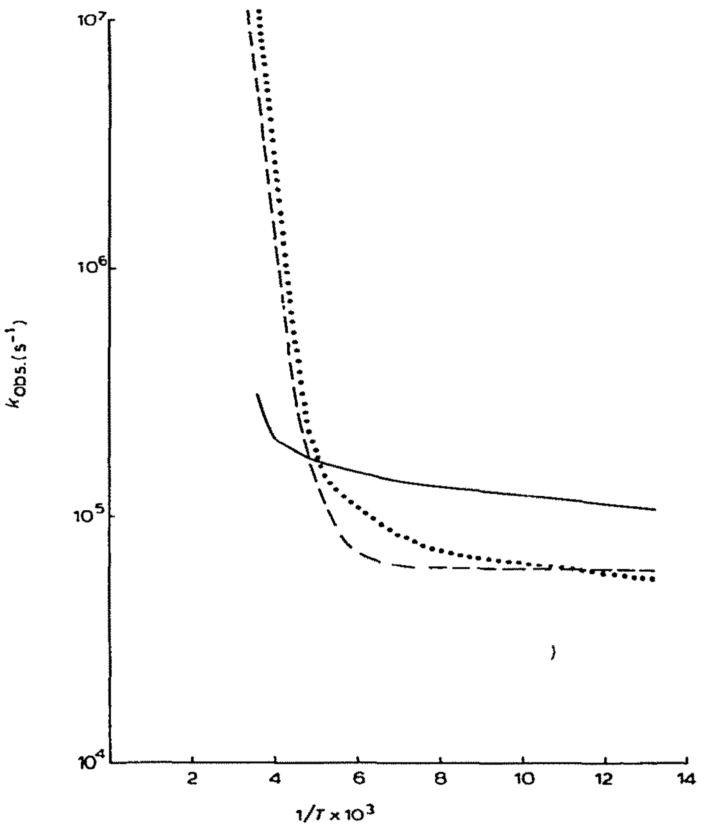

Fig. 1. Variation of the rate constant for decay of binuclear Rh(I) *dσ*pσ* triplets (slow component) with temperature (————, $(Rh_2b_4)(BPh_4)_2$; - - - - - -, $[Rh_2(TMB)_4](PF_6)_2$; · · · · · ·, $[Rh(CN\text{-}cHx)_4]_2(BF_4)_2$).

cHx)$_4$]$_2$(BF$_4$)$_2$, the plots are linear and steep in the high temperature region, but they curve sharply and tend to level off at lower temperatures. The results can be expressed analytically as follows: $k_{\rm obs.} = k_0 + A_{\rm e}^{-E_a/RT}$ (plus small extra terms to account for the curvature between the low and high temperature limits), with $E_a = 2250$ and 2480 cm$^{-1}$ for the Rh$_2$(TMB)$_4^{2+}$ and [Rh(CN–cHx)$_4$]$_2^{2+}$ compounds, respectively. Because the yield and lifetime of the phosphorescence follow the same trend, it was presumed that excited state decay occurs by a temperature-dependent non-radiative pathway.

At this time we can only speculate on the mechanism of non-radiative decay of the $d\sigma^*p\sigma$ triplet states of Rh$_2$(TMB)$_4^{2+}$ and [Rh(CN–cHx)$_4$]$_2^{2+}$. A reasonable possibility is that each triplet is thermally activated to a *d–d* excited state whose equilibrium geometry is $D_{2d}$-distorted about each Rh(I) center. There is ample evidence that certain *d–d* excited states of $d^8$ square planar complexes are distorted in this way (toward a tetrahedral geometry) [20,21], and that such states undergo very rapid non-radiative decay to the ground state. Because population of the critical *d–d* excited state involves a $D_{2d}$ distortion at each Rh(I) center, the process could be prohibitively energetic for Rh$_2$b$_4^{2+}$, whose Rh(I) atoms are more rigidly locked in a square planar environment.

In view of the above hypothesis, it will be interesting to examine the $d\sigma^*p\sigma$ triplet lifetime behavior of binuclear $d^8$ complexes with relatively more energetic *d–d* excited states. Iridium(I) and platinum(II) complexes are obvious candidates for such investigations, and data now being collected by T.P. Smith, C.-M. Che, and L. Butler will be reported in due course.

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