Spectral parameters are compared for several acetates in Table I.

However, praseodymium is not unique in providing usable spectra. That (1) high resolution in the solid is not only possible for the paramagnetic ions. In some cases the resonances of carbon atoms closest to the metal center are unobservable, in other cases the electron and nucleus may differ. The resolution cannot improve coupling to quadrupole nuclei, the magic angle directions for the Zeeman direction. Fortunately however, a very short electron $T_1$ should average the nuclear dipole–dipole interaction considerably. Mechanical spinning may not eliminate all the residual inhomogeneous broadening because, as in the case of coupling to quadrupole nuclei, the magic angle directions for the electron and nucleus may differ. The resolution cannot improve without bound, however, since increasing the magnetic field strength may be accompanied by an increase in the electron $T_1$.

Acknowledgment. This work was supported by the National Institutes of Health (GM-29428).

Registry No. Praseodymium acetate, 6192-12-7; europium acetate, 1184-63-0.

The chemical shift dispersion gained in the paramagnetic complex may not appear very great when compared with the increase in line width observed at this magnetic field strength. However, the absence of molecular tumbling to modulate the chemical shift anisotropy in the solid should eliminate the usual broadening associated with a paramagnetic shift reagent at higher magnetic field strengths, which limits to some extent their utility in solution-phase studies. Thus, the 35-ppm line width for the methyl resonance of the europium compound will probably drop to 7 ppm or less in a 300-MHz proton field, making the shift 10 times the broadening. It should be noted that for an electron–nuclear dipolar interaction modified by the anisotropy of the $g$ factor and zero-field splittings, the axis of quantization of the electron magnetization will be tipped away from the nuclear Zeeman direction. Fortunately however, a very short electron $T_1$ should average the nuclear dipole–dipole interaction considerably. Mechanical spinning may not eliminate all the residual inhomogeneous broadening because, as in the case of coupling to quadrupole nuclei, the magic angle directions for the electron and nucleus may differ. The resolution cannot improve without bound, however, since increasing the magnetic field strength may be accompanied by an increase in the electron $T_1$.

Table I. Carbon-13 Chemical Shifts in Lanthanide Acetates

<table>
<thead>
<tr>
<th></th>
<th>Carboxyl</th>
<th>Methyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid</td>
<td>Solid</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>185.1</td>
<td>185</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>174.4</td>
<td>211</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>253.3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ ppm with respect to external Me$_2$Si. Here liquid-state shifts were measured in saturated solutions in $^2$H$_2$O at ambient temperature.

Metal–Metal Interactions in Binuclear Platinum(II) Diphosphite Complexes. Resonance Raman Spectra of the $^{13}$A$_{1g}(d^6\sigma^*)^2$ and $^{3}$A$_{2u}(d^6\sigma^*\pi\rho)$ Electronic States of Pt$_2$(P$_2$O$_7$)$_4$$^{4-}$

Chi-Ming Che,$^{1a}$ Leslie G. Butler,$^{1a}$ Harry B. Gray,$^{1a}$ R. M. Crooks,$^{1b}$ and William H. Woodruff,$^{1b}$

**Contribution No. 6819, Arthur Amos Noyes Laboratory California Institute of Technology Pasadena, California 91125 and Department of Chemistry University of Texas at Austin Austin, Texas 78712 Received April 1, 1983**

Recent spectroscopic studies have established that certain binuclear $d^8$ complexes exhibit substantial metal–metal bonding interactions in their ground and lowest electronic excited states.$^{2,3,4}$

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A useful model for Pt-Pt interactions of this sort is provided by Table the binuclear diphosphite-bridged complex, Pt$_2$(pop)$_4^{4-}$ (pop = HOOPOOH$^{-}$).$^{8,9}$ Vibrionally resolved absorption and emission spectra of this complex suggest that its electronic properties are similar to those of several binuclear rhodium(I) species that have been studied extensively in our laboratories.$^{9}$

Here we report the results of time-resolved resonance Raman (TR$^3$) spectroscopic measurements on Pt$_2$(pop)$_4^{4-}$ that confirm that the Pt-Pt bonding in the $^2$A$_{2u}$(do$^*$$\pi$po) excited state is much stronger than that in the ground state.

Details of the TR$^3$ technique have been described previously.$^{5,10} Aqueous solutions of Pt$_2$(pop)$_4^{4+}$ (10$^{-3}$ M) were deaerated prior to the Raman experiments. The laser excitation sources for the cw Raman and TR$^3$ experiments were the 356.4-nm line of a Spectra-Physics 171 Kr$^+$ laser and the 354.7-nm third harmonic of a Quanta-Ray DCR-1A Nd:YAG oscillator/amplifier, respectively. The transient absorption spectrum of the $^2$A$_{2u}$(do$^*$$\pi$po) state of Pt$_2$(pop)$_4^{4+}$ exhibits an intense peak at 325 nm and a broad shoulder at 400-500 nm.$^7$ The 325-nm system has been assigned$^7$ to the do$\rightarrow$ do$^*$ transition of the $^2$A$_{2u}$(do$^*$$\pi$po) excited state of Pt$_2$(pop)$_4^{4+}$. Excitation of Pt$_2$(pop)$_4^{4+}$ at 354.7 nm results in fluorescence (410 nm, $^2$A$_{2u}$, t $<$ 2 ns) and phosphorescence (520 nm, $^2$A$_{2u}$, t $>$ 10 µs) with $I_{250} > I_{410}$. Thus, during our 7-nsec Nd:YAG laser pulse, the major species present is the $^2$A$_{2u}$(do$^*$$\pi$po) state of Pt$_2$(pop)$_4^{4+}$. Decay of this excited state to the ground state is complete in the 100 ms between laser pulses. The $^2$A$_{1g}$ and $^2$A$_{2u}$ resonance Raman spectra of Pt$_2$(pop)$_4^{4+}$ are shown in Figure 1. The ground-state spectrum (lower trace) shows an intense peak at 118 cm$^{-1}$ with two evident overtones, whereas the excited-state TR$^3$ spectrum of the same solution (upper trace) exhibits an intense peak at 156 cm$^{-1}$ with one overtone. The 118-cm$^{-1}$ band is assigned to the Pt-Pt stretching motion of the $^2$A$_{1g}$ state of Pt$_2$(pop)$_4^{4+}$ on the basis of its large enhancement in resonance with the do$^*$$\pi$po electronic transition and the overtone progression. The 156-cm$^{-1}$ band is attributed to the excited-state (do$^*$$\pi$po) Pt-Pt stretch. The fact that the intensity of the 156-cm$^{-1}$ ground-state peak increases as the laser pulse energy increases confirms our assignment. An examination of the overtones of the Pt-Pt stretch in the ground-state resonance Raman spectrum of Pt$_2$(pop)$_4^{4+}$ shows small anharmonicity (ca. 1 cm$^{-1}$ per progression member). The single overtone observed for $^2$A$_{2u}$(do$^*$$\pi$po) suggests similarly small anharmonicity in the excited state.


Table I. Structural and Spectroscopic Parameters for Binuclear Platinum and Rhodium Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>state</th>
<th>d(M-M), Å</th>
<th>$\nu$(M-M), cm$^{-1}$</th>
<th>k(M-M), mdy A$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_2$(pop)$_4^{4-}$</td>
<td>$^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>2.925$^a$</td>
<td>156$^c$</td>
<td>1.80$^a$</td>
</tr>
<tr>
<td>Pt$_2$(pop)$_4^{4-}$</td>
<td>$^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>2.71$^b$</td>
<td>156$^c$</td>
<td>1.40$^b$</td>
</tr>
<tr>
<td>Rh$_2$(pop)$_4^{4-}$</td>
<td>$^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>2.695$^c$</td>
<td>156$^c$</td>
<td>2.08$^d$</td>
</tr>
<tr>
<td>Rh$_2$(pop)$_4^{4-}$</td>
<td>$^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>3.242$^d$</td>
<td>79$^e$</td>
<td>0.19$^d$</td>
</tr>
<tr>
<td>Rh$_2$(pop)$_4^{4-}$</td>
<td>$^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>2.94$^f$</td>
<td>134$^g$</td>
<td>0.63$^f$</td>
</tr>
<tr>
<td>[Rh(CNPh)$_2$(pop)]$^4-</td>
<td>$ $^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>3.193$^f$</td>
<td>60$^e$</td>
<td>0.11$^f$</td>
</tr>
<tr>
<td></td>
<td>$^2$A$_{1g}$(do$^*$$\pi$po)</td>
<td>162$^e$</td>
<td>0.80$^e$</td>
<td></td>
</tr>
</tbody>
</table>


Figure 1. Lower trace: ground-state resonance Raman spectrum of Pt$_2$(pop)$_4^{4+}$ obtained by continuous excitation at 356.4 nm. Upper trace: excited-state resonance Raman spectrum using pulsed Nd:YAG laser at 354.7 nm. So $= ^2$A$_{1g}$ $^1$T$^1$ $= ^2$A$_{2u}$.

Shoulders at 102 and 128 cm$^{-1}$ are evident on the 118-cm$^{-1}$ ground-state peak (Figure 1).
series,11 and, in the ground state, it has a 4-fold greater restoring force than Rh2b2+.12

The variation in metal–metal bond distances among the bi-nuclear platinum and rhodium complexes is informative (Table I). We infer from the ~0.3 Å shorter ground-state M–M bond distance that diphosphite is substantially more constraining than the bridging isocyamide. As a result, the decrease in bond length upon excitation or oxidation is larger for Rh2b2+ than for Pt2-(pop)4+. In each case, however, the structural and spectroscopic properties of the M–M bond in the triplet excited state closely approximate those of the corresponding dichloro (da)2(d2d2) species, thereby attesting to the utility of the (da)2(dσ*πe) formulation (i.e., single M–M bond) formulation of 3A2u. Important additional information about M–M interactions in these binuclear complexes should be obtained from studies now underway on the products of the excited-state electron-transfer quenching reactions.

Acknowledgment. We thank Vince Miskowski for helpful discussions. This research was supported by National Science Foundation CHE-81-20419 (C.-M.C., L.G.B., and H.B.G.) and CHE-81-09541 (R.M.C. and W.H.W.).

Synthesis of Conduritol A from Benzoquinone Using 9-[(Benzyloxy)methoxy]anthracene as a Protecting and Directing Group

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Received March 28, 1983

As part of our efforts2 to synthesize aminocyclitol antibiotics3 from non-carbohydrate starting materials, we considered the conversion of benzoquinone (1) to the (±)-fortamines 2,4,5 Compound 1 has carbonyl groups at C-3 and C-6 (fortimicin numbering), which might be reduced to the cis,3,6-dihydroxy functionality. Formal oxygenation and hydroxyaminolysis of the C=C bonds of 1 would complete the functionalization. In order to implement these ideas we chose to preserve the enedione part structure of 1 by protecting one C=C bond. The protecting agent

(4) Compounds 2a (fortamine), 2b (2-deoxyfortamine), and 2c (2-deoxy-1-epifortamine) are the aminocyclitol portions of the antibiotics fortimicin A, istamycin A, and sporaricin A, respectively, among others. For isolation and structures see: (a) Mitscher, L. A.; et al. J. Antibiot. 1977, 30, 552. (b) Okami, Y.; et al. Ibid. 1979, 32, 964. (c) Deushi, T.; et al. Ibid. 1979, 32, 187.