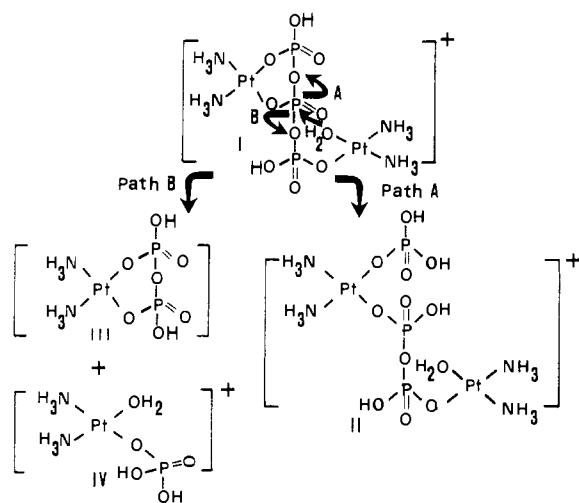Scheme I

upfield component of the doublet A. The phosphorus-31 NMR spectrum of the blue product isolated at the end of the reaction exhibits the same two signals, H and J, as were observed at the end of the reaction in solution.

A plausible assignment can be made for the initial small peaks D–F to the intermediate I shown in Scheme I. The agreement of the coupling constants in the two doublets D (4.16 ppm, J = 20.8 Hz) and E (0.02 ppm, J = 21.0 Hz) and the doublet of doublets F (−8.51 ppm, J = 20.8, 21.0 Hz) and the parallel rate of disappearance of the three sets of peaks support the argument that the peaks arise from the same species. The two doublets are 7.0 and 11.0 ppm downfield, respectively, from the doublet of free triphosphate ion (A), and the doublet of doublets is 10.6 ppm downfield from the triplet of free triphosphate ion (B). The large downfield shifts of all of these resonances indicate that all three phosphates are bound to the platinum.[8] Since *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ has only two labile sites, a dinuclear platinum(II) species must be formed initially. The observed chemical shifts are consistent with the structure I shown in Scheme I. The formation of I from the respective reactants requires a series of events such as monodentate coordination, chelation, and coordination to a second platinum atom. The failure to observe any monodentate species during the reaction suggests that monodentate coordination is the rate-limiting step followed by rapid reactions leading to dinuclear complexation. This sequence of events is consistent with the kinetic results that the formation of the intermediate follows a second-order rate law, first order with respect to each of the reactants.

The decay of intermediate I to yield hydrolyzed products may proceed by two pathways as shown in Scheme I. In path A, attack by the coordinated aquo or hydroxo group on the β-phosphorus atom and cleavage of the phosphorus–oxygen bond (indicated by A) should result in the formation of a transient intermediate, which upon hydrolysis yields product II. Alternatively, cleavage of the phosphorus–oxygen bond at the position indicated by B would result in complexes III and IV. The two peaks H and J are 1.5 and 1.4 ppm downfield relative to the peaks for othophosphate and pyrophosphate, respectively. These two peaks can readily be interpreted as originating from product II. The singlet H is assigned to the monodentate orthophosphate ligand and peak J to the bridging pyrophosphate ligand. The two phosphate groups in the py-

rophosphate ligand are nearly equivalent in structure II; the small difference in chemical shifts between the two phosphate groups may contribute to the broadness of peak J as compared to that of H. The phosphorus-31 NMR spectrum (at pH 8.0) of the pyrophosphato chelate, III, has been shown[9] to give a singlet about 8 ppm downfield from free pyrophosphate with two satellites originating from the 33.7% abundant platinum-195 nucleus (I = $^1/_2$). The absence of a peak at this position confirms that path A in Scheme I is the predominant path for formation of products at pH 4.0. At pH 6 and above, the peak due to the pyrophosphato chelate (III) was observed, indicating a possible contribution from path B.

The phosphorus-31 NMR spectra of pyrophosphate ion in the presence of *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$]$^{2+}$ at various time intervals exhibit the same two signals, G and H, as observed in the triphosphate reaction, with peak G decreasing and peak H increasing with time. The peak G, about 12 ppm downfield from free pyrophosphate ion, is attributed to a dinuclear species with pyrophosphate bridging between the two platinum atoms. Upon hydrolysis this dinuclear species would produce orthophosphate ions (peak H) bound to platinum.

The blue color for the hydrolyzed product is consistent with a redox titration using cerium(IV), which reveals that the average oxidation state of platinum in the blue species is 2.3 ± 0.2. A reasonable description of the blue species would be the combination of two dinuclear species (product II in Scheme I) through an axial platinum–platinum bond with one platinum(III) for every three platinum(II) ions. The broader line widths of peaks H and J compared to line widths previously reported[6] for coordinated phosphates are consistent with the fact that the blue species is paramagnetic and EPR active. The different average oxidation state also accounts for the different coordination chemical shift observed for the platinum blue.

(9) Bose, R. N.; Cornelius, R. D., submitted for publication.

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Observation of an Intervalence Charge-Transfer Band in a Mixed-Valence Ruthenium Dimer Bridged by a Nonconjugated Nitrogen Donor Ligand

Sir:

We wish to communciate the synthesis, spectra, and electrochemistry of a new ruthenium dimer containing the nonconjugated bridging ligand 1,4-cyclohexanedione dioximate (1) and the observation of an intervalence charge-transfer band upon generation of the Ru(II)–Ru(III) dimer.
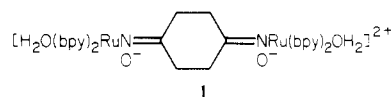
(8) The phosphorus-31 NMR spectra of the two isomeric chelates, the α,γ and β,γ isomers, show 5–9 ppm downfield coordination chemical shifts for only the coordinated phosphate groups. The uncomplexed phosphate groups, namely the β-phosphate in the α,β isomer and the α-phosphate in the β,γ isomer show 1–2 ppm upfield changes in chemical shifts.[6]

Table I. Visible and Near-Infrared Absorption Spectral Properties of $Ru_2(bpy)_4(OH_2)_2(\mu\text{-}1,4\text{-cyclohexanedione dioximato})^{n+}$ Complexes in 0.2 M DCl/D_2O^a

complex	λ_{max}, nm $(\epsilon, M^{-1} cm^{-1})^b$
(2,2)	491 (3800), 339 (3500)
(2,3)	910 (42), 481 (2600), 477 (2200), 342 (2900)
(3,3)	591 (3100), 433 (1500), 350 (2300)

^{a} PF_6^- salts: $n = 2$, (2,2); $n = 3$, (2,3); $n = 4$, (3,3). Spectra were obtained over the 325-2200-nm range. ^{b} ϵ values are reported to $\pm 5\%$.

The (2,2)[1] dimer is synthesized by refluxing 2 equiv of *cis*-(bpy)₂RuCl₂·2H₂O[2] with 1 equiv of 1,4-cyclohexanedione dioxime[3] in 80:20 (v/v) ethanol/H₂O under argon in the dark. After 9 h, the volume is reduced by two-thirds and aqueous KPF_6 added to precipitate a crude deep purple product. Alumina chromatography (2:7 CH₃CN/benzene) and recrystallization from acetone/diethyl ether yields the (2,2) dimer.[4] The (2,2) dimer is converted in situ to the (2,3) and (3,3) dimers by addition of 1 and 2 equiv, respectively, of Ce(IV) in 0.2 M DCl/D₂O. It is particularly important to show that 1 equiv of Ce(IV) produces purely the (2,3) dimer without production of the (3,3) dimer (with residual (2,2) dimer remaining). Evidence that this is indeed the case is found in electronic absorption spectral properties of the three species (Table I). Only the (3,3) dimer has a band in the vicinity of 591 nm. The absence of this peak in the spectrum of the (2,3) dimer shows that solutions of the (2,3) dimer are devoid of the other two species.

The IR spectrum of the isolated (2,2) dimer shows a C=N oxime stretch (1629 cm⁻¹) that is shifted from the free oxime value (1679 cm⁻¹).[5] Use of ¹⁵N-labeled dioxime ($\nu_{C=^{15}N}$ = 1655 cm⁻¹) yields a complex with $\nu_{C=N}$ at 1611 cm⁻¹. The shift in the 1629-cm⁻¹ band upon isotopic substitution confirms the identification of that band as the oxime C=N stretch; the shifts in $\nu_{C=N}$ to lower frequencies upon addition of (bpy)₂RuCl₂ verifies the coordination of the oxime nitrogen to ruthenium.

A cyclic voltammogram of the (2,2) salt (CH₃CN, 0.1 M tetra-*n*-butylammonium hexafluorophosphate) displays two reversible waves with $E_{1/2}$ = 0.927 and 0.457 V vs. NHE. The presence of H₂O bound to Ru(II) was confirmed by cyclic voltammetry.[6]

The most interesting spectral property of these complexes is the broad transition centered at 910 nm (ϵ = 42 M⁻¹ cm⁻¹) seen upon generation of the mixed-valence (2,3) species. On the basis of the width and intensity of this peak, we ascribe it to an intervalence (IT) transition.[7] In addition, neither the (2,2) nor the (3,3) species shows absorption at such long wavelength. The extent of delocalization (α^2) of the exchanging electron can be calculated from the properties of the IT band by using eq 1,[8] where d is the Ru–Ru separation (in

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon_{max}\tilde{\nu}_{1/2}}{\tilde{\nu}_{max}d^2} \quad (1)$$

Å), ϵ_{max} is the molar absorptivity at $\tilde{\nu}_{max}$, and $\tilde{\nu}_{1/2}$ is the bandwidth at half-height. Using the experimental values of d = 4.60 Å,[9] $\tilde{\nu}_{max}$ = 1.10 μm⁻¹, $\tilde{\nu}_{1/2}$ = 1.69 μm⁻¹, and ϵ_{max} = 42 M⁻¹ cm⁻¹ gives a value of α^2 = 1.3 × 10⁻³, only slightly smaller than for $(NH_3)_5Ru(pyrazine)Ru(bpy)_2Cl^{4+}$ in CH₃CN (α^2 = 2.6 × 10⁻³).[8]

In the 1,4-cyclohexanedione dioximato Ru(II)–Ru(II) dimer, the chair ⇌ twisted-boat ⇌ boat equilibria may be operative with the two ruthenium centers closest together in the boat conformer. The unligated 1,4 dioxime crystallizes in the twisted-boat form.[9] However, the steric requirements for the metal-bound boat conformer are great and it is doubtful that a significant percentage resides in this form.

The use of alkyl dioxime ligands provides a new protocol for the preparation of bimetallic complexes containing predominately saturated bridging ligands for electron-transfer studies. In addition, the potential of Ru–oxime complexes can be varied by deprotonation of the oxime hydroxyl.[10] The synthesis of ruthenium complexes with rigid bridging dioxime ligands is currently in progress.

(1) Abbreviations used: bpy, 2,2'-bipyridine; (2,2), the 2+ ion; (2,3), the 3+ ion; (3,3), the 4+ ion; IT, intervalence charge-transfer transition.

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(4) Yield ~40%. Anal. Calcd for C₄₆H₄₄N₁₀O₄P₂F₁₂Ru₂: C, 42.73; H, 3.42; N, 10.83. Found: C, 42.88; H, 3.25; N, 10.74 (Robertson Laboratory, Florham Park, NJ).

(5) The remainder of the IR spectrum displays bands common to Ru-(II)–bpy complexes and PF₆⁻ salts: Inskeep, R. G. *J. Inorg. Nucl. Chem.* **1962**, *24*, 763. IR (Nujol mull, cm⁻¹): 2835 (m), 2730 (w), 1629 (w), 1600 (m), 1210 (m), 1160 (w), 1020 (m), 965 (vw), 840 (vs), 760 (s), 725 (s), 660 (vs).

(6) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 42. The cyclic voltammogram of the complex in CH₃CN shows a shift to more positive potentials as CH₃CN replaces H₂O as a ligand. The possibility exists that the oximato oxygen and not H₂O weakly occupies the sixth coordination site. This would still be consistent with our analytical data, given the fact that H₂O frequently cocrystallizes with Ru–bpy complexes.

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