

less than $E_f^\circ(\text{Pt}_2(\text{pop})_4\text{X}^{4-}/\text{Pt}_2(\text{pop})_4^{4-})$ or $E_f^\circ(\text{Pt}_2(\text{pop})_4^{3-}/\text{Pt}_2(\text{pop})_4^{4-})$, $\text{Pt}_2(\text{pop})_4\text{X}^{4-}$ and $\text{Pt}_2(\text{pop})_4^{3-}$ back-react with A^- (pathways 1 and 2 to regenerate the starting material, $\text{Pt}_2(\text{pop})_4^{4-}$, as observed when A is one of a number of osmium(III) complexes (vide infra). The fully oxidized species, $\text{Pt}_2(\text{pop})_4\text{X}_2^{4+}$, is produced (pathways 3 and 4 when $E^\circ(\text{A}/\text{A}^-)$ is greater than $E_f^\circ(\text{Pt}_2(\text{pop})_4\text{X}^{4-})$ or $E_f^\circ(\text{Pt}_2(\text{pop})_4^{3-}/\text{Pt}_2(\text{pop})_4^{4-})$, as observed for $\text{A} = \text{trans-Ru}(\text{en})_2\text{Cl}_2^+$ or O_2 and $\text{X} = \text{SCN}^-$).

It is difficult to estimate the E_f° value for the $\text{Pt}_2(\text{pop})_4^{3-}/\text{Pt}_2(\text{pop})_4^{4-}$ couple because the electrochemistry of $\text{Pt}_2(\text{pop})_4^{4-}$ is not reversible. The cyclic voltammograms of $\text{Pt}_2(\text{pop})_4^{4-}$ in HClO_4 (1.0 M) and NaX (0.1 M) solutions are characterized by an irreversible anodic wave, the potential (E_{pa}) of which decreases with increasing concentration and nucleophilicity of X^- (in 0.1 M NaX solutions, E° is 0.7, 0.5, and 0.4 V vs. SCE for $\text{X} = \text{Cl}, \text{Br},$ and SCN^- , respectively). However, as evidence for the thermal oxidation of $\text{Pt}_2(\text{pop})_4^{4-}$ by one-electron acceptors²⁰ such as Cyto-C^{3+} , $\text{Co}(\text{EDTA})^-$, $\text{Ru}(\text{NH}_3)_5\text{His}^{3+}$, and $\text{trans-Ru}(\text{NH}_3)_4\text{Cl}_2^+$ has not been found, it is likely that E_f° for $\text{Pt}_2(\text{pop})_4^{3-}/\text{Pt}_2(\text{pop})_4^{4-}$ is >0.15 V vs. SCE. This value is in reasonable agreement with that reported by Roundhill and co-workers.²¹

One-electron acceptors such as $\text{Co}(\text{EDTA})^-$, $\text{Ru}(\text{NH}_3)_5\text{His}^{3+}$, $\text{Co}(\text{ox})_3^{3-}$, $\text{trans-Os}(\text{NH}_3)_4\text{Cl}_2^+$, BSEP (BSEP = 1,1'-bis(α -sulfoethyl)-4,4-bipyridinium inner salt), O_2 , and $\text{trans-Ru}(\text{en})_2\text{Cl}_2^+$ have been found to quench the phosphorescence of $\text{Pt}_2(\text{pop})_4^{4-}$ efficiently.^{6a,20} The photoformation of $\text{Pt}_2(\text{pop})_4\text{X}_2^{4+}$ has been induced by $\text{trans-Ru}(\text{en})_2\text{Cl}_2^+$, whose thermal reaction with $\text{Pt}_2(\text{pop})_4^{4-}$ apparently does not proceed at room temperature.²⁰ With reagents such as $\text{trans-Os}(\text{NH}_3)_4\text{Cl}_2^+$, which possess very negative E_f° values, net photoformation of $\text{Pt}_2(\text{pop})_4\text{X}_2^{4+}$ was not observed upon steady-state irradiation. This is understandable in terms of rapid back-decay of photogenerated $\text{Pt}_2(\text{pop})_4^{3-}$ (or $\text{Pt}_2(\text{pop})_4\text{X}^{4-}$) to $\text{Pt}_2(\text{pop})_4^{4-}$ through pathway (1 or 2, because of the large driving force of the reaction).

With $\text{A} = \text{O}_2$, nucleophile-induced photooxidation of $\text{Pt}_2(\text{pop})_4^{4-}$ occurs with no observable degradation of the $\text{Pt}_2(\text{pop})_4$ unit. The E_f° of the O_2/O_2^- couple at 25 °C in water (pH 7) has been found to be -0.155 V vs. NHE.²¹ As the E_f° value for $\text{Pt}_2(\text{pop})_4^{3-}/\text{Pt}_2(\text{pop})_4^{4-}$ is <-1 V vs. NHE,^{6a} oxidative quenching of excited $\text{Pt}_2(\text{pop})_4^{4-}$ by O_2 is expected to be nearly diffusion-controlled, because of the large driving force of the reaction ($\Delta E^\circ > 0.8$ V). Experimentally, O_2 quenches the phosphorescence of $\text{Pt}_2(\text{pop})_4^{4-}$ efficiently ($\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$),^{6a,20} although energy as well as electron transfer may contribute significantly to the observed rate.

The involvement of O_2 as a one-electron acceptor also may be inferred from the dramatic increase in Φ_{ox} with increasing acidity of the solution (Table I). Increasing the concentration of H^+ , which tends to remove O_2^- by protonation to $^*\text{HO}_2$, can inhibit the back-reaction of O_2^- with $\text{Pt}_2(\text{pop})_4^{3-}$ (or $\text{Pt}_2(\text{pop})_4\text{X}^{4-}$) and also lead to the formation of $\text{Pt}_2(\text{pop})_4\text{X}_2^{4+}$ through $^*\text{HO}_2$ oxidation. The increase in Φ_{ox} with increasing concentration and nucleophilicity of X^- is in accord with the corresponding increase in the concentration of $\text{Pt}_2(\text{pop})_4\text{X}^{4-}$ in the photooxidation process.

In irradiated $\text{Cyto-C}^{3+}/\text{Pt}_2(\text{pop})_4^{4-}/\text{NaX}$ (0.1 M) solutions,²² decay of photogenerated Cyto-C^{2+} to Cyto-C^{3+} is much slower for $\text{X} = \text{Cl}$ than for $\text{X} = \text{H}_2\text{PO}_4$, thereby indicating that the back-reaction can be inhibited by axial-ligand binding. With a better nucleophile, SCN^- , the back-decay of Cyto-C^{2+} is strongly inhibited. Such inhibition is important, because it means that

$\text{Pt}_2(\text{pop})_4^{4-}$ can be used as an efficient photoreduction initiator of intramolecular electron-transfer reactions in multisite proteins and protein complexes.²³ Replacement of the standard $\text{Ru}(\text{bpy})_3^{2+}/\text{EDTA}$ photoreducing system² with $\text{Pt}_2(\text{pop})_4^{4-}/\text{SCN}^-$ will facilitate certain types of transient absorption spectroscopic measurements, because the binuclear Pt^{II} complex does not absorb as strongly as $\text{Ru}(\text{bpy})_3^{2+}$ at wavelengths above 400 nm.

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Registry No. $\text{Pt}_2(\text{pop})_4^{4-}$, 80011-25-2; $\text{Pt}_2(\text{pop})_4(\text{H}_2\text{O})_2^{2-}$, 99546-98-2; $\text{Pt}_2(\text{pop})_4\text{Cl}_2^{4-}$, 87355-26-8; $\text{Pt}_2(\text{pop})_4\text{Br}_2^{4-}$, 87374-25-2; $\text{Pt}_2(\text{pop})_4(\text{SCN})_2^{4-}$, 102133-43-7; $\text{trans-}[\text{Ru}(\text{en})_2\text{Cl}_2]\text{ClO}_4$, 56172-97-5; HClO_4 , 7601-90-3; HCl , 7647-01-0; NaCl , 7647-14-5; NaBr , 7647-15-6; KNCS , 333-20-0; cytochrome c, 9007-43-6.

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Use of NMR Chemical Shifts To Study the Bonding in Mixed-Ligand-Metal Complexes

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In our previous studies of mixed chelates (MXY, where X and Y are bidentate ligands), the properties of the metal ion such as the ionization potentials, optical spectra, and electron spin resonance spectra were reported.¹⁻³ In general, the above metal properties turned out to be the average of the properties observed for the two nonmixed chelates, MX_2 and MY_2 . In order to determine the effects on the ligands themselves, proton and carbon nuclear magnetic resonance can be used. Although the chemical shifts are sensitive to small changes in bonding, the interpretation of the changes is not always straightforward. In this paper, molecular orbital calculations are utilized to interpret the experimental NMR data of platinum(II) acetylacetonate type complexes.

Experimental Section

The calculation procedure was to use the INDO method⁴ to determine the geometry of the complexes and then to use the CNDO5 method as modified by Rajzmann and Francois⁵ to calculate the atomic charges and chemical shifts. A standard program with no reparameterization was utilized so that the results would be as universally applicable as possible. Due to program size limitations H and F atoms were used to place of CH_3 and CF_3 groups, respectively. Also, Be was used in place of the actual metal atom in the calculations. Because of these approximations, only the methine position would be expected to have a high theoretical-experimental correlation. The experimental platinum(II) proton and carbon chemical shift data were taken from a recent paper.⁶ This paper reported data for both the palladium(II) and platinum(II) complexes. The correlation coefficient between the two sets of complexes is 0.9998 for the proton data and 0.9997 for the carbon data. Thus, our conclusions

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(22) Flash photolysis of a sample containing 50 μM cytochrome c in 0.1 M Na_2HPO_4 solution (11% reduced) gives a prompt signal that decays on a millisecond time scale following excitation. The magnitude of the prompt signal was studied at constant laser power between 500 and 600 nm, where the platinum complexes have little absorption. The spectrum thus obtained agrees closely with that predicted from the difference spectra of $\text{Cyto-C}^{3+}/\text{Cyto-C}^{2+}$, indicating that the prompt signal corresponds to the photoinduced reduction of the protein. In 0.1 M NaCl , the rate of decay of the signal (or the back-reaction) decreases by more than tenfold. In 0.1 M NaSCN , the prompt signal remains relatively constant over 200 ms, indicating that essentially no back-decay of Cyto-C^{2+} to Cyto-C^{3+} takes place in this time interval.

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Table I. Calculated and Experimental^a Methine H and C Data^b

	M(acac)(tfac)		<i>trans</i> -M(tfac) ₂	<i>cis</i> -M(tfac) ₂	M(acac)(hfac)		M(acac) ₂
$\delta^{\text{H}}_{\text{exptl}}$	5.96	5.58	6.01	6.01	6.30	5.63	5.54
$\delta^{\text{H}}_{\text{calcd}}$	6.31	5.65	6.28	6.25	6.96	5.80	5.54
$q^{\text{H}}_{\text{calcd}}$	0.019	0.002	0.020	0.019	0.035	0.003	0.001
$\delta^{\text{C}}_{\text{exptl}}$	99.5	103.1	99.4	99.4	95.8	103.1	102.9
$\delta^{\text{C}}_{\text{calcd}}$	106.4	105.9	102.3	102.3	111.4	109.8	102.9
$q^{\text{C}}_{\text{calcd}}$	-0.133	-0.138	-0.130	-0.132	-0.125	-0.137	-0.140
$\angle \text{C}-\text{C}-\text{C}$, deg	118.49	115.39	115.41	115.83	118.76	112.99	118.46

^aData from ref 6. ^b q = atomic charge, δ = chemical shift.

are not dependent on our choice of the platinum data set. The abbreviations used are acac for $\text{CH}_3\text{COCHCOCH}_3^-$, tfac for $\text{CF}_3\text{COCHCOCH}_3^-$, and hfac for $\text{CF}_3\text{COCHCOCF}_3^-$.

Results and Discussion

The calculated data are given in Table I. To facilitate comparisons with the experimental data, the calculated chemical shift values have been adjusted by a constant value chosen so that the experimental and calculated chemical shift values in $\text{M}(\text{acac})_2$ are equal. This shift of the absolute magnitude does not affect the values of the correlation coefficients.

As discussed by Fliszar et al.,⁷ one would expect a correlation between the atomic charges and the chemical shifts for closely related atoms. The present results support this. For the methine protons the correlation coefficient between the experimental proton chemical shifts and the calculated proton atomic charges is 0.996. For the methine carbons the correlation coefficient between the experimental carbon chemical shifts and the calculated carbon atomic charges is -0.968. A high correlation coefficient (0.984) also exists between the experimental methine proton chemical shifts and the charges of the attached carbon atoms.

Since the correlations are satisfactory, it appears that the approximations used in the calculations are vindicated and that the calculated charges are meaningful. The decrease in electron density of the methine protons and carbons from acac to tfac to

hfac is consistent with the known basicity of the three ligands. Of particular interest is the change in the methine position charge density as a function of the basicity of the second ligand in the mixed complexes. In $\text{M}(\text{acac})_2$ the methine protons are almost neutral, $q = 0.001$, and the methine carbons have the largest negative charge, $q = -0.140$. In the mixed $\text{M}(\text{acac})(\text{tfac})$ the acac is a better electron donor than tfac, the acac methine proton positive charge increases to 0.002, and the carbon negative charge decreases to -0.138. When the opposing group is an even weaker electron donor, hfac, the acac group loses even more electron density: $q^{\text{H}} = 0.003$ and $q^{\text{C}} = -0.137$. Thus, the present results give quantitative support to the model that, in a mixed complex, the more basic ligand will be a better electron donor than in the corresponding bis complex.

The results for the calculated chemical shifts were mixed. A good correlation (0.986) exists between the experimental and calculated proton chemical shifts, but a poor correlation (-0.26) exists between the calculated and experimental carbon chemical shifts. The poor carbon correlation may be due to a change in hybridization of the methine carbon across the series. This interpretation is supported by the calculated changes in C-C-C bond angles given in Table I. The calculated decrease in C-C-C bond angle from acac to hfac is consistent with our X-ray determined values⁸ for $\text{Cu}(\text{acac})(\text{hfac})$; in acac the angle is 124.1°, and in hfac the angle is 121.3°.

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