Optical Detection of Zero Field Magnetic Resonance in the Triplet State of Chlorophyll b

Sir:

We have observed the zero-field magnetic resonance transitions of the lowest triplet state of chlorophyll b in *n*-octane solution at 2°K by triplet absorption detection of magnetic resonance (TADMR).[1,2] Chlorophyll b exhibits very weak phosphorescence[3] but strong triplet–triplet (T–T) absorption maximizing at about 500 nm,[4] and the TADMR method is particularly well suited for obtaining its triplet state zero field epr spectra.[2] Further, it has been reported that at temperatures below 77°K *n*-octane serves as a Shpolskii-type matrix for chlorophyll, exhibiting sharp line absorption and fluorescence spectra.[5] Using a 4-W argon ion laser as the photoexcitation source, two microwave-induced T–T absorption signals were observed for polycrystalline samples of chlorophyll in *n*-octane with maxima at frequencies of 1000 ± 5 and 870 ± 5 MHz. Both transitions correspond to an increase in T–T absorption intensity (see Figure 1).

The 870-MHz transition consists of several overlapping peaks spread across ~40 MHz. These peaks probably arise from several inequivalent sites in the Shpolskii matrix.[5] The two zero field transitions could also be detected as microwave-induced changes in the fluorescence intensity at 2°K when observing the fluorescence at 647 nm.[6] The third transition was too weak to be detected under present experimental conditions. The observed transitions correspond to ~1% decrease in the fluorescence intensity at 647 nm. The signals disappeared as the sample was warmed above 4°K. The zero field transitions correspond to triplet spin Hamiltonian parameters of $|D| = 0.0312$ cm^{-1} and $|E| = 0.0022$ cm^{-1}.[7]

Both triplet absorption detection and fluorescence detection of magnetic resonance arise from the same effect—a change in the overall steady state population in the triplet state by microwave saturation of the zero field transitions. An increase in the overall triplet state population will cause an increase in the T–T absorption intensity and a decrease in the fluorescence intensity (depletion of the ground state).

From previous TADMR work a microwave-induced increase in T–T absorption will be observed for two of the zero-field transitions when the rates of population and decay for one of the triplet spin sublevels dominates in the intersystem crossing.[2] This dynamical situation would be consistent with both the fluorescence and T–T absorption intensity changes observed for chlorophyll b in the present experiments. It is also consistent with dynamical studies of a similar π-electron system, the Zn porphin triplet state, whose population and decay occurs preferentially through the Z (out-of-plane) spin sublevel.[8] The intersystem crossing rate constants can
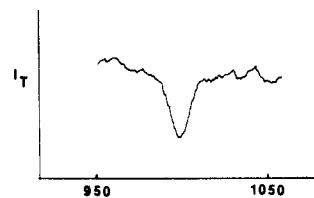

Figure 1. Zero field magnetic resonance signal of the triplet state of chlorophyll b in *n*-octane at 2°K detected by the microwave-induced change in the triplet–triplet absorption intensity. The signal corresponds to an increase in triplet–triplet absorption intensity (decrease in transmitted light, I_T) at 488 nm. The frequency scale is in megahertz.

be measured directly for each of the triplet spin sublevels by observing the changes in either fluorescence intensity or T–T absorption intensity as a function of time after turning on a saturating microwave field;[9] such experiments are in progress to elucidate the triplet state intersystem crossing mechanisms of chlorophyll b.

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Solution Behavior of Triphenylphosphine Complexes of Ruthenium(II)

Sir:

$RuCl_2L_3$ and $RuCl_2L_4$ (L = PPh$_3$) are catalytically active complexes[1,2] which have been widely used for the synthesis of Ru(II) complexes.[3,4] The variable phosphine content is an intriguing feature reminiscent of the $PtL_3–PtL_4$ system.[5] With the exception of molecular weight measurements, the solution behavior of these two complexes is uncharacterized. This is due in part to the lack of commonly used spectral probes (*e.g.*, CO or hydride ligands.) We report here a variable-temperature ^{31}P nmr study of these complexes which shows their solution behavior to be complex yet readily interpretable.

The proton-decoupled Fourier transform ^{31}P nmr spectrum of $RuCl_2L_4$ in CHCl$_3$ (Figure 1a) consists of two resonances in an intensity ratio of 3:1 at 30°. The less intense resonance falls at the chemical shift of PPh$_3$. The ^{31}P nmr spectrum of $RuCl_2L_3$ in CHCl$_3$ at 30° (Figure 1b) exhibits a strong signal coincident with the

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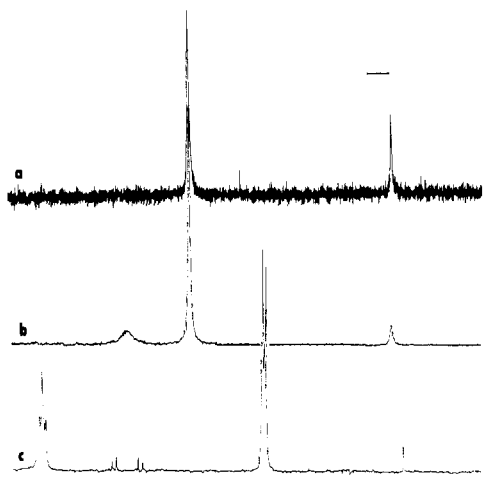
Figure 1. The 40.5-MHz ^{31}P nmr spectra of (a) RuCl$_2$(PPh$_3$)$_4$ in CHCl$_3$ at 30°, (b) RuCl$_2$ (PPh$_3$)$_3$ in CHCl$_3$ at 30°, and (c) RuCl$_2$ (PPh$_3$)$_3$ in CHCl$_3$ at −90°. Horizontal bar extends from 0 to +5 ppm.

more intense resonance of RuCl$_2$L$_4$. In addition, free PPh$_3$ is present. Finally, an extremely broad resonance is observed at − 57.3 ppm with intensity twice that of the PPh$_3$ signal. These spectra are consistent with the following reactions[6]

$$RuCl_2L_4 \longrightarrow RuCl_2L_3 + L \tag{1}$$

$$RuCl_2L_3 \rightleftharpoons \text{“RuCl}_2L_2\text{”} + L \tag{2}$$
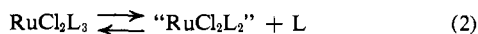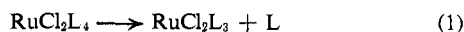
RuCl$_2$L$_4$ dissociates essentially completely to RuCl$_2$L$_3$, which produces the resonance at −41.1 ppm. This five-coordinate unsaturated complex then further dissociates to some extent to produce what might be a 14-electron species (eq 2).

The solid-state structure of RuCl$_2$L$_3$ is unusual.[7] While MX$_2$L$_3$ species are usually trigonal bipyramidal with all phosphines equatorial,[8] RuCl$_2$L$_3$ is square pyramidal with two trans basal phosphines and the third phosphine apical. The apical phosphorus-ruthenium bond is 0.16 Å (20σ) shorter than the average basal Ru–P bond length. Since the ^{31}P spectrum at 30° is not the AX$_2$ pattern expected for square pyramidal RuCl$_2$L$_3$, the question of structural change on dissolution immediately arises. Alternatively, square pyramidal geometry may persist in solution; bending motions even more subtle than those required for Berry pseudorotation might render the phosphines time-average equivalent. Finally, equivalence could result from intermolecular exchange.

The ^{31}P nmr spectrum of RuCl$_2$L$_3$ at −90° in CH$_2$Cl$_2$ (Figure 1c) shows that the phosphine ligands are inequivalent in solution. The major peaks constitute an AX$_2$ pattern with $J_{P-P'}$ = 30 Hz. The population-weighted average of the two chemical shifts is −41.2 ppm. Although o-phenyl hydrogen interactions have been discussed,[7] we believe that the square pyramidal geometry observed in solution is determined by electronic requirements of the d^6 configuration. Low-spin d^6 complexes are predicted to be square pyramidal using second-order Jahn–Teller arguments.[9]

(6) All solutions were approximately 0.1 M.
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The low temperature spectrum of RuCl$_2$L$_3$ (0.1 M) also shows about 5 mol % of "RuCl$_2$L$_2$." The AB pattern observed for this species is inconsistent with a 14-electron monomer. Tetrahedral or cis or trans planar species would show a ^{31}P singlet. A halide bridged dimer, [RuCl$_2$L$_2$]$_2$ (below), accounts for the observed spectrum. This dimer maintains square pyramidal geometry about ruthenium.
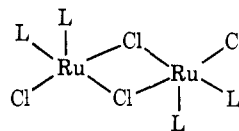
These results explain the interchangeability of RuCl$_2$L$_3$ and RuCl$_2$L$_4$ in synthetic procedures. Moreover, the equilibria underlying the production of L$_2$ClRu(Cl)$_3$-Ru(N$_2$)L$_2$ from RuCl$_2$L$_4$ by reverse osmosis[10] are now demonstrated directly. In fact, an elementary procedure suffices to remove phosphine from RuCl$_2$L$_3$. If RuCl$_2$L$_3$ is slurried in refluxing ethanol the solid darkens. The solvent extracts triphenylphosphine, leaving a solid of formula RuCl$_2$L$_2$ which is insoluble in CHCl$_3$.[11] The behavior of the Ru(II)–PPh$_3$ system is similar to that of the RhCl(PPh$_3$)$_3$–Rh$_2$Cl$_2$(PPh$_3$)$_4$ equilibrium.[12] Although the dimer observed here differs structurally from the Ru$_2$Cl$_3$L$_6$$^+$ cations formed by mixed aryl alkyl phosphines,[13] there is a clear tendency for Ru(II) phosphine complexes to form halogen bridges.

Although phosphorus-phosphorus coupling simplifies identification of species present in solution, it must be noted that most resonances observed here are exchange broadened. We are presently attempting to obtain thermodynamic and kinetic data for all inter- and intramolecular processes.[14]

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Synthesis of 1,2-Dithiosquarate Salts and X-Ray Crystal Structure of Potassium Bis(dithiosquarato)nickelate(II)

Sir:

The oxocarbon anions have been recognized as an aromatic series,[1] and a nitrogen analog (2) of the squarate dianion (1) has been reported.[2] Our interest

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(2) S. Hünig and H. Pütter, Angew. Chem., Int. Ed. Engl., 12, 149 (1973).