Use of EPR Spectroscopy in Elucidating Electronic Structures of Paramagnetic Transition Metal Complexes

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Electronic structure is an important concept in many areas of chemistry such as inorganic, physical, materials, and biophysical. However, undergraduate students often receive limited opportunities for hands-on exploration of the theory (1). Among the many techniques for describing electronic structure, electron paramagnetic resonance (EPR) spectroscopy is unique in its ability to selectively probe paramagnetic molecules (2). In fact, EPR spectroscopy can provide a wealth of information about the electronic structure of paramagnetic molecules, including those involving metal ions (3). In this paper I describe how EPR spectroscopy can be utilized to understand the electronic structure of metal complexes of tetraphenyl porphyrins (TPP).

Porphyrs are among the most extensively studied biological chromophores. The interest in metalloporphyrins spans from their unique structural and physical properties to their ability to show a variety of chemical reactivities (4). The practical aspects of these molecules include their catalytic properties, biomedical applications, and development of new materials. Thus, there is an inherent interest in porphyrin chemistry. The “rigid” ligand framework of porphyrin imparts a stable conformation. In addition, a wealth of information is already available on porphyrins and their metal complexes. These features prompted an examination of the electronic structure of metalloporphyrin complexes using EPR spectroscopy. I have chosen two $S = 1/2$ complexes, oxo-molybdenum(V) (d$^1$) and copper(II) (d$^9$) porphyrin complexes, as examples.

This paper introduces the application of EPR spectroscopy of transition metal complexes along with crystal field theory.

Background

Electrons have a magnetic dipole moment due to their intrinsic angular momentum (or spin). For a spin angular momentum, $S$, the associated magnetic moment ($\mu$) is

$$\mu = -g_e \mu_B S$$

where $g$ is a dimensionless quantity called the electron $g$-factor, $\mu_B$ is the Bohr magneton and is equal to $e\hbar/4\pi mc = 9.2731 \times 10^{-24}$ J/T ($e$ and $m$ are the charge and mass of the electron, respectively, $h$ is Planck’s constant, and $c$ is the speed of light). The interaction of an applied magnetic field $B_0$—usually along the z axis—with the magnetic moment of an electron can be described by a Hamiltonian, $\mathcal{H} = g_e\mu_B B_0 \mathcal{S}$, where $\mathcal{S}$ is the angular momentum operator. For spin angular momentum $S$, $2S + 1$ nondegenerate energy states can be obtained. Thus, for $S = 1/2$ systems, two nondegenerate energy levels are obtained with $M_s = -1/2$ and $M_s = +1/2$. This loss of degeneracy upon application of a magnetic field is called the electronic Zeeman effect. It should be pointed out that systems with multiple unpaired electrons are complicated by zero field splitting. In this paper the discussion is limited to $S = 1/2$ systems.

The energies of different spin manifolds are proportional to the strength of the magnetic field ($B_0$) (5). In EPR spectroscopy, a transition is induced between the two $M_s$ levels by applying a suitable electromagnetic radiation $\nu$ (10–1000 J/mol, microwave region) that satisfies the resonance condition $\hbar \nu = g_e \mu_B B_0$ (Fig. 1). For free electrons the value of the constant $g$ is 2.0023; however, in molecules whose unpaired electron is
no longer free, its value varies considerably. Orbital motion, introduced as a result of spin–orbit coupling, leads to a departure from the free electron $g$ value. This is particularly important for transition metal ions, where the orbital angular momentum is never completely absent. The energy due to spin–orbit coupling is comparatively smaller than the energy of the electron–field interaction. Thus, for transition metal ions, the spin–orbit coupling effect alters $g$ values from those of the free electrons. This effect is very important for second- and third-row transition metals, whose spin–orbit coupling constant is large.

Several other factors such as nuclear Zeeman effect and quadrupole interaction can alter the energy levels. Nuclei possessing spin angular momentum exhibit additional splitting due to the nuclear Zeeman effect. Thus, nuclear spin of $I$, when interacting with the electronic spin, perturbs the energy of the system in such a way that each electronic state is split into $2I+1$ sublevels. Since the nuclear magneton is about 1000 times smaller than the Bohr magneton, nuclear magnetic interactions are weak, so the energy separations between sublevels are small. Transition involving these states gives rise to hyperfine splitting in a well-resolved spectrum and is designated by “$A$”. Similarly, when ligand nuclei with spin angular momentum are involved, they give rise to nuclear superhyperfine structure and are designated by “$a$”. Both of these interactions can be seen clearly in the present case. Thus, $n$ nuclei of spin $I$ can give rise to $2nI+1$ resonances. In this article discussion is limited to nuclear interaction.

**Experimental Procedure**

The ligand, tetraphenyl porphyrin (H$_2$TPP, 1), and its molybdenum and copper complexes were synthesized according to published procedures (6).

EPR spectra of two metalloporphyrin complexes, Cu(TPP) and MoO(TPP)Cl, were recorded in toluene solutions (Figs. 2–4), in a Bruker ESP 300 E X-band spectrometer at room temperature under nonsaturating microwave conditions. The $g$ values were calculated using the formula $g = h
\nu/\mu_B B_0$, where $h = 6.626 \times 10^{-34}$ J s, $\mu_B = 9.274 \times 10^{-24}$ J/T, $\nu$ is the microwave frequency, and $B$ is the field position where the $g$ values are measured. Thus, the $g$ value at a field 3498 G (349.8 mT), the field position of the central resonance of the room-temperature spectrum of MoOCl(TPP), is calculated to be 1.971.

**Results and Discussion**

The EPR spectra of the complexes show several important features. The room temperature spectrum of MoO(TPP)Cl solution has one strong central peak and six satellite peaks
using the relationship
value is more for copper ($\text{MoO(TPP)Cl}$ is less. The deviation from the free electron is more than the free electron value of 2.0023, that for
pattern in Cu(TPP) complicates the evaluation of anisotropic with the porphyrin nitrogen atoms. The complex spectral exhibits a rich superhyperfine structure due to interactions could be detected. (Fig. 4). No nitrogen superhyperfine coupling for
nuclear gyromagnetic ratio of the two
values ($\gamma_{\text{I}} = 5/2, 15.72%$; $\gamma_{\text{I}} = 5/2, 9.46%$; and $I = 0$ isotopes, 74.82%) give rise to this characteristic and unique pattern for Mo(V).
The large central line is due to $I = 0$ isotopes, which account for 75% of the integrated intensity. Isotopes with $I = 5/2$ spin give rise to six satellite peaks ($2nI + 1 = 2 \times 1 \times 5/2 + 1 = 6$) around the central signal. The nuclear gyromagnetic ratio of the two $I = 5/2$ isotopes ($\gamma_{\text{I}} = 5/2$) are $+2.2233$ and $+2.3817$. Under the experimental conditions employed the two isotopes could not be differentiated.

For both compounds, the room-temperature spectra were used to estimate the average metal hyperfine coupling. The average metal hyperfine constant for Cu(TPP) is 95 G; that for MoO(TTP)Cl is 48 G. This difference in magnitude is primarily due to the larger magnetic moment of the copper nucleus. Both room- and low-temperature spectra exhibit rich ligand superhyperfine structure (see below).

The $g$ values obtained from the room temperature spectra of Cu(TPP) and MoO(TTP)Cl exhibit resonance at $g = 2.117$ and 1.971, respectively. While the $g$ value of the Cu(TPP) is more than the free electron value of 2.0023, that for MoO(TTP)Cl is less. The deviation from the free electron value is more for copper ($\Delta g = |g - g_e| = 0.1147$) and less for molybdenum ($\Delta g = |g - g_e| = 0.0313$). The frozen toluene solution spectrum of MoO(TTP)Cl showed only one peak for $I = 0$ isotopes, indicating that anisotropy is too small to be detected (Fig. 4). No nitrogen superhyperfine coupling could be detected.

Interestingly, the frozen solution spectrum of Cu(TPP) exhibits a rich superhyperfine structure due to interactions with the porphyrin nitrogen atoms. The complex spectral pattern in Cu(TPP) complicates the evaluation of anisotropic $g$ values ($g_{||} = 2.195$, $g_{\perp} = 2.078$). Fortunately, two well-resolved low-field transitions allowed us to evaluate the $g_{||}$ component. The $g_{||}$ component was evaluated from the average $g$ values using the relationship $g_{\perp} = g_{||} + 2g_{LL}$. The anisotropic $g$ values were used to understand the electronic structure of the metal ion in Cu(TPP).

One of the most revealing features of the spectra of Figures 3 and 4 is the rich superhyperfine structure. The superhyperfine structure is due to the interaction of the unpaired electron with the nitrogen atoms of the porphyrin macrocycle. The most abundant isotope of natural nitrogen ($^{14}\text{N}$, 99.63%) has a spin of 1. The nuclear magnetic moment of $^{14}\text{N}$ (+0.4038) is smaller than that of copper or molybdenum. Thus, the magnitude of the interaction with a nitrogen isotope is small compared to that with a Mo or a Cu nucleus. Because there are four nitrogen atoms and all of them can interact with the unpaired electron, one could potentially observe $2 \times 4 \times 1 + 1 = 9$ resonances. The room-temperature EPR spectrum of Cu(TPP) exhibits 9 distinct lines due to the coupling with the porphyrin nitrogen atoms (Fig. 3). In contrast, the first-derivative spectrum of MoO(TTP)Cl does not clearly show 9 resonances (Fig. 2, top), although 9 resonances can be observed in the second derivative spectrum (Fig. 2, bottom). The superhyperfine structure indicates that all four nitrogen atoms are interacting with the unpaired electron.

The average $\alpha_{3d}$ for Cu(TPP) is 14 G, and that for MoO(TTP)Cl is 2.7 G. The half-filled 4d orbital of molybdenum is more diffuse than the half-filled 3d orbital of copper. Keeping other factors constant, this should lead to better interaction with the nitrogen nucleus, which in turn should lead to a larger nitrogen superhyperfine constant for MoO(TTP)Cl. This difference can be explained from the shape of the d orbitals. Crystal field theory predicts that the unpaired electron in Cu(TPP) should reside on the metal 3d$_{x^2-y^2}$ orbital, which points directly toward the nitrogen atoms positioned along $Y$ and $Y$ axes (Fig. 5). In contrast, the half-filled 4d$_{xy}$ orbital in MoO(TTP)Cl points in between the nitrogen atoms. As a result, the interaction of the unpaired electron with the nitrogen atoms in MoO(TTP)Cl is smaller compared to that in Cu(TPP). Interestingly, no nitrogen superhyperfine splitting can be detected in the X-band CW-EPR spectrum of VO(TPP), where the unpaired electron resides on the 3d$_{xy}$ orbital of vanadium. This illustrates that the 4d orbitals are

![Figure 4. EPR spectra of MoOCl(TPP) in toluene. Top: room temperature (297 K) spectrum; bottom: low-temperature (77 K) spectrum.](image)

![Figure 5. Half-filled orbitals for Cu(II) and Mo(V).](image)
more diffuse than their 3d counterparts. Thus, nitrogen superhyperfine structure provides direct information about the electronic structure of the metal ions.

The \(g\) value deviation (\(\Delta g\)) from the free electron (\(g_0\)) along any direction can be explained by applying a simplified theory described in eq 1

\[
g = g_0 \pm \frac{n\lambda}{\Delta E}
\]

where \(n\) defines the amount of orbital mixing, \(\lambda\) is the ground state spin–orbit coupling constant, and \(\Delta E\) is the transition energy. The plus sign applies to the case of mixing with a filled orbital and the minus sign to the empty orbital. Thus, the \(g\) value for copper(II) (more-than-half-filled \(d^9\) system, \(S = 1/2\)) would be more than the free electron value, whereas that for molybdenum(V) (less-than-half-filled \(d^1\) system, \(S = 1/2\)) complex would be less than the free electron value. This feature has been observed experimentally. Therefore, from the first approximation, the \(g\) value for less-than-half-filled configurations such as Mo(V) should be \(<2.0023\) and that for molybdenum(V) system is larger than that of the molybdenum(V) system.

**Summary**

This report describes an experimental approach to teaching the electronic structure of the paramagnetic transition metal–porphyrin complex. The EPR spectra provide a direct and convenient way to teach the concept of crystal field theory, shapes of orbitals, and isotopic abundance and their influence on the spectra. In addition, students can learn how to extract chemical information from EPR spectra.

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**Note**

1. The \(g\) value is further influenced by a charge-transfer transition involving metal and ligand orbitals; however, the CT transition is not invoked in the present discussion.

**Literature Cited**


