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The usefulness of EPR spectroscopy in the study of compounds with metal–metal multiple bonds

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Electronic Supporting Information (ESI)

Some Basic EPR Principles

Only enough theoretical background will be provided to allow a senior-level chemistry student to appreciate and understand the experimental results. For additional insight on the technique the reader is referred to classic EPR textbooks.[1] The foundation of EPR spectroscopy is the resonant absorption of microwave radiation caused by electron spins in paramagnetic species when they are placed in a homogeneous magnetic field. This phenomenon is akin to that which provides the basis for the widely used nuclear magnetic resonance (NMR) spectroscopy. The main difference is that in NMR spectroscopy the resonance absorption is by nuclear- instead of electron-spins. Importantly routine NMR is most often used to aid characterization of diamagnetic compounds while EPR is most useful for paramagnetic species. Unfortunately, because EPR instrumentation is not as common as NMR instrumentation, it is not unusual for chemists not to follow up on paramagnetic complexes. For common magnetic fields such as those found in most laboratories the energy gap between the resonance states is in the microwave region of the electromagnetic spectrum (GHz) whereas in NMR it is in the radiofrequency (MHz) range. Another aspect where EPR and NMR spectroscopies differ is the way the experiments are done. In EPR the frequency is typically held constant while the magnetic field strength is varied whereas in NMR the field is usually held constant while the radio frequency is varied.

EPR is a very sensitive technique—requiring samples smaller by two or three orders of magnitude than those needed for NMR under comparable conditions—since the magnetic moment of the electron is that much larger (by a factor of ~ 650) than that of even the most sensitive nucleus, ^{1}H. Moreover, EPR sensitivity as well as resolution increases dramatically as the microwave frequencies increase.[2] Because of this, the high-field magnets at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida provide a very useful setting. Measurements in high magnetic fields (strength of many teslas (T)) often provide much clearer fingerprints for transition metal complexes, which afford fundamental data for testing theoretical electronic structure and bonding models.

Importantly the high-field EPR (HF-EPR) instrumentation makes it possible to study compounds that are 'silent' under standard (low-field) EPR measurements, say, for example, due to a very large Zero-field splitting (*vide infra*).

Let's now have a small parenthesis to better understand the data provided in the manuscript. It is important to emphasize that our focus has been on the study of isolated paramagnetic units, i. e., a dimetallic cation or anion, rather than collections of molecules such as those in ferromagnetic or antiferromagnetic materials, in which there is a strong intermolecular magnetic coupling that leads to various magnetic phases. In an isolated paramagnetic species the unpaired electrons have quantized energy levels. In most cases, the microwave resonant absorption condition can be expressed[6] by a spin Hamiltonian operator, $\hat{H}$:

$$\hat{H} = \beta_e\, B\cdot g\cdot\hat{S} + \hat{S}\cdot D\cdot\hat{S} + \hat{I}\cdot A\cdot\hat{S} - g_n\beta_n B\cdot\hat{I} + \hat{I}\cdot Q\cdot\hat{I} \qquad \text{Eq. 1}$$

In Eq. 1 B is the applied magnetic field, and $\hat{S}$ and $\hat{I}$ are the electron spin and nuclear spin operators, respectively. In this equation, g is the Lande g-matrix ,with three principal components g_x, g_y and g_z, where the x, y and z directions usually coincide with the molecular symmetry axes. Because in solutions the paramagnetic entities are generally randomly oriented, an average value, $g_{av} = (g_x + g_y + g_z)/3$, is obtained. The term A represents the electron-nuclear hyperfine matrix for a given metal atom. Again there are components along the principal axes A_x, A_y and A_z, that averages to the corresponding isotropic value $(A_x + A_y + A_z)/3$ in a fluid solution. D is the (electronic) spin-spin splitting tensor, generally made up of two parameters D and E. The axial Zero-field splitting, D, represents the spin-spin interaction component along the principal symmetry axis while E is the so-called rhombic splitting. By definition $E < D/3$, and zero for a molecule with axial symmetry–for which the x and y directions are equivalent. In Eq. 1, Q is the electric quadrupole tensor, and β_e and β_n are the electronic and nuclear Bohr magnetons.

In general, EPR transitions involve change of only the electron spin, and not the nuclear spin. Because of this, the EPR transitions are fairly insensitive to the nuclear Zeeman term (fourth term in Eq. 1), as well as the quadrupole (fifth) term. Therefore for most applications the fourth and fifth terms from Eq (1) can hence be dropped.

In this account a few situations where EPR has provided unique chemical information are examined:

(a) Is An Unpaired Electron In A Metal- or Ligand-based Molecular Orbital?

In general, unpaired electrons can be in metal-based molecular orbitals (MOs) or ligand-based MOs. This determination is not always trivial in coordination complexes that involve organic ligands. In a simplistic way, one can think of what happens to a neutral complex to which an electron is added (reduced) or removed (oxidation). Because different metal centers or ligands are more or less prone to redox processes, it is relevant to ask the question of where the resulting unpaired electron is preferentially located. This question has been investigated using a number of techniques by a large number of groups as demonstrated by a large volume of literature in the field of non-innocent ligands,[3] i. e., those that can be oxidized or reduced preferentially over the metal centers. In this context it is important to keep in mind that for organic radicals with one unpaired electron, the standard X-band EPR spectra generally produce signals that are often sharp and narrow with g values close to that of the free electron (g_e) of about 2.0023. However, the g values for species having an unpaired electron residing on a metal center are often different because such electrons can gain or lose angular momentum. As an example, for a species with a d^1 electron the g-values are related to the spin-orbit coupling constant of the metal, λ, and the metal level involved via the relation:

$g_\parallel = g_e$; but $g_\perp = g_e - 2\lambda/\Delta$, where Δ is the energy difference between the metal levels involved in the spin-orbit interaction, $g_\parallel$ is the g value along the principal axis and $g_\perp$ is the g value along the component perpendicular to that direction. Because this component is directly proportional to λ, it becomes more and more significant as one moves down a group of the periodic table, say going from Cr to Mo to W. Below there are EPR data that helped to provide significant conclusions on this topic, especially on Cr–Cr, Mo–Mo and W–W bonded complexes.

(b) **Hyperfine Interaction *A*: How many or which metal atoms are directly bonded?**

By now it should now be apparent that while the *g*-factor provides direct information on whether the unpaired electron(s) is (are) metal- or ligand-centered, this technique provides little information on the number of nuclei in the molecule. This is akin to the chemical shift in NMR which directly identifies the NMR signal with the resonating nucleus, but there is no basic structural information until an analysis of the J-coupling and the accompanying multiplet intensity pattern (given by the binomial distribution) is carried out. In EPR spectroscopy, the hyperfine coupling, *A*, plays the role of J in NMR. In both techniques the signal multiplet intensity follows a similar pattern. Therefore the number of peaks in a multiplet is given by $2nI+1$, where n is the number of equivalent nuclei and I is the nuclear spin of the metal nuclei. For example, if the EPR sample is a dirhenium complex where the Re atom has an $I = 5/2$, one would expect an 11-line multiplet (# peaks = $2nI+1 = (2\text{x}2\text{x}2.5)+1 = 11$), with a relative (binomial) intensity distribution ratio of 1:2:3:4:5:6:5:4:3:2:1. An example of a dirhenium complex with a Re–Re multiple bond is given in the manuscript. Table 1 provides a convenient comparison of the EPR and NMR techniques.

Table 1. A comparison of EPR and NMR techniques.

	EPR	NMR
Sensitivity	manograms	milligrams
Main parameter measured	*g*-value	chemical shift, δ
Energy-related information	Zero-field splitting, D,E	dipolar coupling
Coupling	hyperfine coupling , *A*	J-coupling
Peak multiplicity	multiplet intensity given by Pascal Triangle for s = ½, and binomial distribution for s >1/2	same for a first-order multiplet
Line widths	~ 100s of MHz for transition metal ions ~ 10 MHz for organic radicals	1–100 Hz in solutions; many MHz for solids
Relaxation time	T_1 and T_2 (nano second)	nuclear T_1 and T_2 (milli-nanosec)
Spectral widths	~ 10 MHz (2-3 gauss)	Hz – kHz
Time scale	10^{-12} – 10^{-3} s	10^{-10} – s

(c) Clearing Ambiguities by Use of High-Field EPR (HF-EPR) Including 'EPR –Silent' Compounds

When higher fields are used splitting of signals may occur, even for carbon- or nitrogen- or oxygen-centered electron for which *g* for the unpaired electron is very nearly g_e at X-band. An example is provided by a phenoxy radical in a W-band (ν of 95 GHz) field but even in these cases the spread of *g* values is very small (2.0067 – 2.0022 = 0.0045).[4,5] However, the splitting is significantly more common and larger for species containing transition metal atoms.

Another area for which HF-EPR can be useful is for the study of paramagnetic compounds with a large D (Zero-field splitting) that are either EPR-silent or yield a very poor EPR-fingerprint if their spin-spin (Zero-field) splitting is larger in frequency than that of the commonly commercially available microwave frequency, X-band (9.5 GHz). This can be seen from the simple equation for resonance (neglecting hyperfine and quadruple coupling):

$B_{reson} = [h\nu - D\,(2M_s + 1))]\,/g_e\beta_e$, where M_s is again the electron spin quantum number.

It is important to note that the above equation assumes a first-order perturbation regime where the Zeeman term is much larger than the other terms. Here the Zero-field split resonances spread to both positive and negative values of the resonance field defined by the Zeeman term. So if there is a negative number, there will also be a positive number of the same magnitude. Because the number of observed peaks in an EPR spectrum for a given set of oriented molecules is equal to $2\,M_S$, it is possible to simply count the number of peaks to obtain the number of unpaired electrons on the complex. This in turn yields information on the oxidation state of the dimetal moiety.

On the other hand, assuming again that the D term is a perturbation on the Zeeman term, as is usually the case in HF-EPR, B_{reson} is not a positive number if $h\nu < D\,(2M_S + 1)$, hence there is no real field value that can satisfy the resonance condition. Under these conditions there will be no EPR signal; such compounds are termed ‘EPR silent’. One must be cautious to check the compound again by using a higher microwave frequency, such that the microwave photon energy, $h\nu$, becomes significantly larger than the D value, $h\nu >> D(2M_S + 1)$.

References and notes

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(1) For example, see: (a) Electron Paramagnetic Resonance: Elemental Theory and Practical Applications, J. A. Weil and J. R. Bolton, 2nd ed. John Wiley & Sons, Inc. New York. 2007. (b) EPR: Instrumental Methods, C. J. Bender and L. J. Berliner, Eds., Springer-Verlag, Inc. New York, 2012. (c) Principles of pulse electron paramagnetic resonance**,** A. Schweiger and G. Jeschke, Oxford University Press, Oxford, 2001.

(2) In this respect, EPR spectroscopy again resembles NMR spectroscopy where resolution is greatly increased as the field strength increases, for example from 300 to 800 MHz and so on. In EPR the various fields are often referred to by letters. The most common are X-band (9.5–10 GHz), Q-band (35 GHz) and other less common such as W-band (95 GHz), J-band (285 GHz) or S-band (3 GHz).

(3) For example, see: (a) C. C. Lu, E. Bill, T. Weyhermüller, E. Bothe and K. Wieghardt, *J. Am. Chem. Soc*. 2008, **130**, 3181. (b) M. R. Ringerberg, S. L. Kokatam, Z. M. Heiden and T. B. Rauchfuss, *J. Am. Chem. Soc***.** 2008, **130**, 788. (c) D. Das, B. Sarkar, T. K. Mondal, S. M. Mobin, J. Fiedler, W. Kaim and G. K. Lahiri, *Inorg. Chem*. 2011, **50**, 7090.

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(5) For other examples on the use of high-field spectroscopy in systems of biological interest, see: (a) C. W. Kay, R. Bittl, A. Bacher, G. Richter and S. Weber, *J. Am. Chem. Soc.* 2005, **127**, 10780. (b) K. K. Anderson, P. P. Schmidt, B. Katterle, K. R. Stand, A. E. Palmer, S-K. Lee, E. I. Solomon, A. Gräslund and A.-L. Barra, *J. Biol. Inorg. Chem.* 2003, **8**, 235. (c) S. Un, C. Gerez, E. Elleingand and M. Fontecave, *J. Am. Chem. Soc.* 2001, **123**, 3048.