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Review

Multi-frequency, high-field EPR as a powerful tool to accurately determine zero-field splitting in high-spin transition metal coordination complexes

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Contents

Abstract

Electron paramagnetic resonance at multiple, high frequencies (95–700 GHz) and at correspondingly high magnetic fields (up to 25 T), known as HFEPR, is a relatively new technique. There have been an increasing number of applications of HFEPR, such as in organic radical chemistry and in materials science. The focus of this review, however, is on the application of HFEPR to transition metal coordination chemistry, in particular

Abbreviations: acac, anion of 2,4-pentanedione; bpea, *N*,*N*-bis(2-pyridylmethyl)-ethylamine; btz, 2,2′-bi-2-thiazoline; BWO, backward wave oscillator; cor, dianion of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole; cyclam, 1,4,8,11-tetraazacyclotetradecane; dbm, dianion of 1,3-diphenyl-1,3-propanedione (dibenzoylmethane); dmb, 3,3-dimethyl-1-butanol; dmiz, 1,2-dimethylimidazole; DOTA, tetraazacyclododecanetetraacetic acid; DPDME, dianion of deuterioporphyrin IX dimethyl ester; DTPA, trianion of diethylenetriaminepentaacetic acid; EDTA, dianion of ethylenediaminetetraacetic acid; en, ethylenediamine; EPR, electron paramagnetic resonance; EtL, anion of 2-oxypropiophenone oxime; FDMRS, frequency-domain magnetic resonance spectroscopy; Gu, guanidinium; HFEPR, high-frequency and -field EPR; HIM2-py, 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-hydroxy; hmpH, 2-hydroxymethylpyridine; HS, high-spin; INS, inelastic neutron scattering; Im, imidazole; LS, low-spin; MCD, magnetic circular dichroism; NCTPP, trianion of 5,10,15,20-tetraphenyl-*N*-confused porphyrin; Pc, dianion of phthalocyanine; OEP, dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; Ph, phenyl; py, pyridine; taa, trianion of tris(1-(2-azolyl)-2-azabuten-4-yl(amine); TBP_8Cz, trianion of octa-*tert*-butylphenyl corrolazine; terpy, 2,2′:6′,2″-terpyridine; thf, tetrahydrofuran; SOC, spin–orbit coupling; SOD, superoxide dismutase; tpfc, trianion of 5,10,15-tris(pentafluorophenyl)corrole; TPP, dianion of 5,10,15,20-tetraphenylporphyrin; VTVH–MCD, variable temperature and field MCD; zf, zero-field; zfs, zf splitting

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to mononuclear complexes, as opposed to clusters that are relevant to single-molecule magnets. There are many complexes of paramagnetic transition metal ions for which conventional EPR (fields below 2 T, frequencies not exceeding 35 GHz) is less than ideal. Primarily, such systems are high-spin (i.e., $S > 1/2$), wherein the effects of zero-field splitting can make the complex either "EPR-silent" using conventional EPR, or make the EPR spectrum not particularly informative. Examples of the former are many integer-spin (non-Kramers) ions such as Mn(III) and Fe(II), while the latter case is exemplified by high-spin Fe(III). We will review here the use of HFEPR to study high-spin transition metal complexes, generally of the first row. For half-integer high-spin systems, we will review only those where the large magnitude of zero-field splitting necessitates the use of HFEPR. We will generally not discuss systems in which the zero-field splitting is in most cases very small and conventional EPR is extensively employed. The experimental and analytical methods for the accurate determination of zero-field splitting and other spin Hamiltonian parameters from HFEPR studies of these systems will be described. Comparison with other physical methods such as magnetometry, magnetic circular dichroism (MCD), and Mössbauer effect spectroscopy will also be made. We will further give selected examples how ligand-field theory can be used to provide information on chemical bonding and geometry, based on analysis of the spin Hamiltonian parameters well established by HFEPR.

Keywords: Coordination chemistry; Electron paramagnetic resonance; EPR; High-frequency and -field EPR; Magnetic resonance; Transition metal ions; Zero-field splitting

1. Introduction

It is well known that the electronic structure of metal complexes determines their magnetic properties. The reverse is also true to a certain extent—i.e., knowing the magnetic properties of a given complex may give us insight into its electronic structure, and sometimes its geometric structure as well. Knowledge of the magnetic properties of transition metal complexes is thus paramount in understanding various phenomena characteristic for them, such as catalytic activity. More recently, magnetism of such complexes have become of increased interest since it is relevant for the properties of "single-molecule magnets", which are polynuclear clusters assembled from mononuclear coordination complexes.

Transition ion complexes are often paramagnetic, since they have partly occupied d orbitals, and thus possess unpaired electron spins. The paramagnetism of such species makes them amenable to the electron paramagnetic resonance (EPR) experiment, which has been one of the most successful tools in investigating their magnetic properties [1]. From the point of view of coordination chemistry, octahedral d^4–d^7 transition metal complexes can be either low-spin (LS) or high-spin (HS). The former have the maximum number of paired electrons yielding spin ground states $S = 0$, 1/2, or 1 (respectively for d^6, $d^{5,7}$, d^4), and the latter have the maximum number of *un*paired electrons yielding $S = 3/2$, 2, or 5/2 (respectively for d^7, $d^{4,6}$, d^5) [2]. However, from the practical point of view of an EPR spectroscopist, *all* transition metal complexes can also be divided into two classes: low-spin (LS) and high-spin (HS), but in this context, LS means $S = 1/2$ (as $S = 0$ is diamagnetic and useless for EPR), while HS is any $S > 1/2$. HS complexes in turn can be segregated into half-integer spin numbers ($S = 3/2, 5/2$, etc.) and integer-spin numbers ($S = 1, 2$, etc.). As we will see below, the EPR properties of these three categories are distinctly different and each warrants a different experimental approach.

The main difference between the LS and HS complexes as defined for EPR lies in the phenomenon of zero-field splitting (zfs), which appears only for $S \geq 1$, i.e., in high-spin states. The admixture of excited electronic states to the ground state causes the different M_S spin sublevels to split in the absence of a magnetic field in conditions of low symmetry. Zfs is mediated by spin–orbit coupling (SOC), and since the latter's magnitude varies strongly between different metal ions, and because of a variety of possible geometries, the zfs magnitudes vary accordingly, from very small values for highly symmetric complexes of Mn(II), where it is of the order of 10^{-2} cm^{-1} to octahedral complexes of Co(II), where it is known to reach values of the order of 10^2 cm^{-1}. While zfs of the magnitude lying at the lower end of the above range is usually easy to measure by conventional EPR, that approaching and exceeding the conventional EPR quantum energies ($\sim$0.3 cm^{-1} for X-band and $\sim$1.2 cm^{-1} for Q-band) is very difficult, and often impossible to determine using conventional methods, for reasons illustrated in Section 2.1. In view of this difficulty, most information on the magnetism of such problematic ions has been traditionally obtained from bulk magnetic susceptibility/magnetization measurements [1]. The accuracy of this bulk technique in determining spin Hamiltonian parameters in general, and zfs in particular, is, however, inferior to that of EPR, a resonance technique.

The recent decade has seen an impressive development in the extension of traditional EPR into high frequencies and fields (HFEPR) [3]. There are several excellent reviews of HFEPR in the literature; for the technical aspects we refer the reader to the review by Smith and Riedi [4]. For a review more relevant to the current topic, we refer to the paper of Hagen [5]. Compared to the latter, we will limit ourselves to HS transition ion complexes, although we will greatly expand the number of discussed systems due to the extensive progress in this technique since 1999. Of those, we will emphasize complexes where the large magnitude of zfs necessitates the use of HFEPR; non-Kramers (integer spin) species with very small zfs are left out, and so are those Kramers (half-integer spin) ions where the purpose of experiment has not been the measurement of zfs parameters. We note that zfs parameters can be determined by physical methods other than HFEPR. These range from well-known and widely applied magnetometric techniques, as mentioned above (e.g., variable temperature dc magnetic susceptibility) [6], to the very powerful, but less commonly used magneto-optic technique, magnetic circular dichroism (MCD) [7], to the rather exotic (for chemists) method, inelastic neutron scattering (INS) [8,9]. We also refer to the extensive review by Boča that lists zfs parameters for a wide range of transition metal