

The Determination of the Geometry of Cu(II) Complexes

An EPR Spectroscopy Experiment

Eugenio Garribba* and Giovanni Micera**

Department of Chemistry, University of Sassari, I-07100 Sassari, Italy; *garribba@uniss.it **micera@uniss.it

Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool in the study of the structures and environments of species that contain unpaired electrons, such as transition-metal ions, organic free radicals, and electronically excited states. It is the electronic analog of NMR spectroscopy that probes the nuclear spin of molecules.

For an inorganic chemist it is of primary importance to utilize instrumental techniques to understand and to evaluate the electronic structure of metal complexes. In the framework of an inorganic chemistry laboratory, it can be very useful to present a resonance spectroscopy, such as EPR spectroscopy, to infer details about the structure of complexes formed by paramagnetic metal ions.

An easy application of EPR spectroscopy uses the Cu(II) ion (electronic configuration $3d^9$), a particularly favorable example of a metal ion that exhibits a wide range of stereochemistries (tetra-, penta-, and hexa-coordinated) with a variety of intermediate situations. The geometry of the complex affects the electronic properties of the Cu(II) ion, establishes the order of the energy levels of the d orbitals, and, consequently, the ground state for a particular arrangement.

For coordination geometries corresponding to an elongated octahedron, a square pyramid and square planar, the ground state is $d_{x^2-y^2}$. When the coordination around copper ion is a compressed octahedron or a trigonal bipyramid, the ground state is d_{z^2} . EPR spectroscopy can distinguish the ground states $d_{x^2-y^2}$ and d_{z^2} on the basis of the principal values of the g tensor in the anisotropic spectra.

The value of g is the primary empirical parameter that characterizes the response of a paramagnetic molecule and is loosely analogous to the chemical shift in NMR spectroscopy (1). It provides a quantitative measure of the molecule's magnetic moment and is sensitive to the changes in the molecule's electronic structure. Its measurement and meaning have been already presented in this *Journal* (2–4). With this experiment students find that the g factors for the metal complexes are quite different from the g factor of a free electron ($g_e = 2.0023$) and, furthermore, that they can be smaller or larger than g_e . The shifts in the g value are caused by the influence of spin-orbit coupling and the students could be asked to explain these trends.

Background

For a gaseous metal ion, the g factor corresponds to the Landé factor:

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (1)$$

where J is the total angular momentum, L is the orbital angular momentum, and S is the spin angular momentum. The

perturbing effect of the ligands quenches the orbital angular momentum ($L = 0$), so there exists only a spin angular momentum ($J = S$) and the g factor should be close to that of the free electron ($g \approx 2$) (5).

The spin-orbit interaction between the ground state, $|0\rangle$, and the excited states, $|n\rangle$, reintroduces a little orbital contribution and the g value deviates from 2,

$$g_i = g_e + 2\lambda \sum_{n=1,2,\dots} \left(\frac{\langle 0 | \hat{L}_i | n \rangle \langle n | \hat{L}_i | 0 \rangle}{E_0 - E_n} \right) \\ = 2.0023 + 2\lambda \sum_{n=1,2,\dots} \left(\frac{\langle 0 | \hat{L}_i | n \rangle \langle n | \hat{L}_i | 0 \rangle}{E_0 - E_n} \right) \quad (2)$$

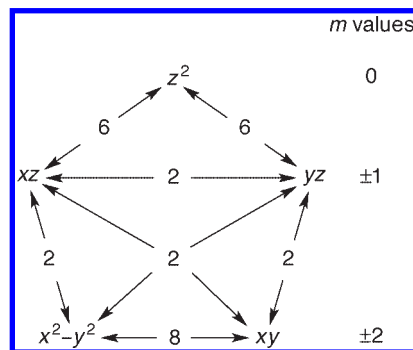
where $i = x, y, \text{ or } z$, λ is the spin-orbit coupling constant, E_0 and E_n are the energies of the ground and the excited states, respectively. The sum is over all the excited states.

The evaluation of the matrix elements gives the general formula (6):

$$g_i = 2.0023 \pm \frac{k\lambda}{E_0 - E_n} \quad (3)$$

where k defines the degree of orbital mixing. Since λ is greater than 0 for the electronic configurations d^1 – d^4 and is less than 0 for the configurations d^6 – d^9 and since $E_0 - E_n$ is always less than 0, the plus sign applies to the cases of more-than-half-filled electronic configurations and the minus sign to the cases of less-than-half-filled configurations. Thus, the g factor for Cu(II) (d^9 system, $S = 1/2$) complexes is higher than 2.0023, while the g factor for vanadium(IV) (d^1 system, $S = 1/2$) species is less than 2.0023.

The value of k can be extracted from the “magic pentagon”, shown in Scheme I (6). It is constituted by three rows



Scheme I. The magic pentagon used to find the value of k .

corresponding to the three different values of the magnetic quantum number of the d orbitals, $m = 0, \pm 1, \pm 2$. It allows the evaluation of k values along the three principal axes. In eq 2, the spin-orbit coupling along z axis is operating only between orbitals with $\Delta m = 0$ and that along x and y axes between orbitals with $\Delta m = \pm 1$, since $\hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2$ and $\hat{L}_y = (\hat{L}_+ - \hat{L}_-)/2i$.

EPR Spectra of Cu(II) complexes

In *regular situations*, when the ground state is the $d_{x^2-y^2}$ or d_{z^2} orbital, the EPR spectra are axial, with equivalent x and y axes and two g values, g_{\parallel} (g_z) and g_{\perp} ($g_x = g_y$). When the geometry is elongated octahedral, square pyramidal or square planar, the ground state is the $d_{x^2-y^2}$ orbital:

$$g_{\parallel} = g_z = 2.0023 \pm \frac{8\lambda}{E(d_{x^2-y^2}) - E(d_{xy})} \quad (4)$$

$$\begin{aligned} g_{\perp} = g_x = g_y &= 2.0023 \pm \frac{2\lambda}{E(d_{x^2-y^2}) - E(d_{xz})} \\ &= 2.0023 \pm \frac{2\lambda}{E(d_{x^2-y^2}) - E(d_{yz})} \end{aligned} \quad (5)$$

where λ is the spin-orbit coupling constant for Cu(II) ion and E are the orbital energies. In these cases, the relation $g_{\parallel} > g_{\perp} > 2.0023$ is expected (*normal spectrum*).

When the geometry is compressed octahedral or trigonal bipyramidal, the ground state is the d_{z^2} orbital and the perpendicular and parallel components of the g tensor can be described by the following equations:

$$g_{\parallel} = g_z = 2.0023 \quad (6)$$

$$\begin{aligned} g_{\perp} = g_x = g_y &= 2.0023 \pm \frac{6\lambda}{E(d_{z^2}) - E(d_{xz})} \\ &= 2.0023 \pm \frac{6\lambda}{E(d_{z^2}) - E(d_{yz})} \end{aligned} \quad (7)$$

An EPR spectrum of this type is characterized by $g_{\perp} > g_{\parallel} = 2.0023$ (*inverse spectrum*).

In *intermediate situations*, a "rhombic" spectrum, exhibiting three g values, is observed. For instance, if the geometry is intermediate between the square pyramid and the trigonal bipyramid, the ground state is a linear combination of the $d_{x^2-y^2}$ and d_{z^2} orbitals,

$$\Psi_{\text{gs}} = c_1 |d_{z^2}\rangle + c_2 |d_{x^2-y^2}\rangle \quad (8)$$

where c_i are the coefficients of linear combination. For complexes of this type, a parameter R can be indicative of the predominance of the d_{z^2} ($c_1 > c_2$) or $d_{x^2-y^2}$ orbital ($c_2 > c_1$) in the ground state (7),

$$R = \frac{g_y - g_z}{g_x - g_y} \quad (9)$$

with $g_x > g_y > g_z$. If $R > 1$, the greater contribution to the ground state arises from d_{z^2} orbital; if $R < 1$, the greater contribution to the ground state arises from $d_{x^2-y^2}$ orbital.

The g values can be easily determined by comparison with an internal or external reference such as diphenylpicrylhydrazyl (DPPH). The students could measure the magnetic field strength for each absorption band of the sample, B_{sample} (B_{\parallel} and B_{\perp} in systems with axial symmetry or B_x , B_y , and B_z in systems with rhombic symmetry), and for DPPH, B_{DPPH} . By knowing the g factor of DPPH ($g_{\text{DPPH}} = 2.0036$), it is easy to extract the g value of the sample (g_{\parallel} and g_{\perp} in systems with axial symmetry or g_x , g_y , and g_z in systems with rhombic symmetry).

$$g_{\text{sample}} = g_{\text{DPPH}} \frac{B_{\text{DPPH}}}{B_{\text{sample}}} = 2.0036 \frac{B_{\text{DPPH}}}{B_{\text{sample}}} \quad (10)$$

Experiment

The experiment has been tested during the course of the inorganic chemistry laboratory. To provide a suitable framework for students, the EPR technique has been discussed in two prelab lectures. The complete set of experiments needs two 3-hour laboratory sessions: synthesis of the complexes in the first session, followed by recording and interpreting the EPR spectra in the second session. We report the results from eleven compounds, but suggest synthesizing only three complexes to demonstrate the three cases of a normal, an inverse, and an intermediate (rhombic) EPR spectrum. Alternatively, the students could work in groups and each group could prepare two or three compounds. A detailed description of the experiment is reported in the Supplemental Material.^W

Hazards

Ethylenediamine causes burns, is flammable and harmful in contact with skin and if swallowed. 1,10-Phenanthroline and 2,2'-bipyridine are toxic if swallowed; moreover, 1,10-phenanthroline is very toxic to aquatic organisms and may cause long term adverse effects in the aquatic environment. MeOH and EtOH are highly flammable and must be kept away from sources of ignition. MeOH is toxic by inhalation, in contact with the skin, and if swallowed. Copper and potassium salts can be harmful if swallowed and are irritating to eyes, respiratory system, and skin. All the chemicals must be handled under a fume hood and the students must wear suitable protective clothing, gloves, and eye or face protection.

Table 1. EPR Parameters of the Cu(II) Complexes

Compound	g_x	g_y	g_z	R	Ground State	Geometry
[Cu(en) ₂ (ClO ₄) ₂]	2.049	2.049	2.198	0	$d_{x^2-y^2}$	Elongated octahedron
[Cu(en) ₂ (BF ₄) ₂]	2.050	2.050	2.178	0	$d_{x^2-y^2}$	Elongated octahedron
[Cu(en) ₂ (NO ₃) ₂]	2.065	2.065	2.169	0	$d_{x^2-y^2}$	Elongated octahedron
[Cu(phen) ₂ (H ₂ O)](NO ₃) ₂	2.214	2.148	2.007	2.14	$c_1 d_{z^2}\rangle + c_1 d_{x^2-y^2}\rangle$	Intermediate SP-TBP
[Cu(phen) ₂ (H ₂ O)](BF ₄) ₂	2.258	2.119	2.018	0.73	$c_1 d_{z^2}\rangle + c_2 d_{x^2-y^2}\rangle$	Intermediate SP-TBP
[Cu(bpy) ₂ Cl]ClO ₄	2.211	2.132	2.010	1.54	$c_1 d_{z^2}\rangle + c_2 d_{x^2-y^2}\rangle$	Intermediate SP-TBP
[Cu(phen) ₂ Cl]ClO ₄	2.170	2.170	2.005	∞	d_{z^2}	Trigonal bipyramid
[Cu(phen) ₂ Br]ClO ₄	2.164	2.164	2.013	∞	d_{z^2}	Trigonal bipyramid
[Cu(phen) ₂ I]ClO ₄	2.155	2.155	2.030	∞	d_{z^2}	Trigonal bipyramid
[Cu(bpy) ₂ Br]ClO ₄	2.169	2.169	2.011	∞	d_{z^2}	Trigonal bipyramid
[Cu(bpy) ₂ I]ClO ₄	2.157	2.157	2.030	∞	d_{z^2}	Trigonal bipyramid

NOTE: SP is square pyramid and TBP is trigonal bipyramid.

Results

Normal Spectra: $g_{||} > g_{\perp} > g_e$

The powdered EPR spectra of a series of bis(ethylenediamine)copper(II) complexes, [Cu(en)₂X₂] with X = ClO₄⁻, BF₄⁻, and NO₃⁻, are proposed (Table 1). They indicate normal tetragonal Cu(II) environment giving rise to two g values ($g_{||}$ and g_{\perp} , both higher than free electron g value). The spectrum of [Cu(en)₂(ClO₄)₂] is shown in Figure 1. The molecular structure of [Cu(en)₂(ClO₄)₂], [Cu(en)₂(BF₄)₂], and [Cu(en)₂(NO₃)₂] has been discussed previously and shows the presence of square planar [Cu(en)₂]²⁺ cations with the anions occupying definite positions along the tetragonal axis (8). The weak coordination of the anions that imposes an octahedral elongated structure, as suggested by IR spectra, is intermediate between those for the free and the fully coordinated species (8).

Inverse Spectra: $g_{\perp} > g_{||} \approx g_e$

For penta-coordinated Cu(II) complexes with [Cu(phen)₂X]ClO₄ and [Cu(bpy)₂X]ClO₄ stoichiometry, where X = Cl⁻, Br⁻, or I⁻, two alternative geometries are con-

ceivable: one approaches the limit of the square pyramid and another to the trigonal bipyramid. The EPR spectroscopy distinguishes between the two situations. The spectra of [Cu(phen)₂Cl]ClO₄ (9, Figure 2), [Cu(phen)₂Br]ClO₄ (9), [Cu(phen)₂I]ClO₄ (9), [Cu(bpy)₂Br]ClO₄ (this work) and [Cu(bpy)₂I]ClO₄ (9) support the latter geometry and show an axial symmetry with two g values ($g_{\perp} > g_{||}$) and with the g factor corresponding to the higher symmetry axis ($g_{||}$) practically coincident with g_e (Table 1). This indicates a d_{z^2} ground state and a pentacoordinate arrangement strongly shifted toward the trigonal bipyramid, with a X⁻ (Cl⁻, Br⁻, I⁻) ion and two nitrogen atoms of two different molecules of 1,10-phenanthroline or 2,2'-bipyridine in the equatorial plane and the other two aromatic nitrogens in axial position.

Intermediate Spectra: $g_x > g_y > g_z$

The EPR spectra of [Cu(phen)₂(H₂O)](NO₃)₂, [Cu(phen)₂(H₂O)](BF₄)₂, and [Cu(bpy)₂Cl]ClO₄, recorded on the polycrystalline samples, are characterized by three g values. Generally, the higher value is indicated as g_x and the lower as g_z (Table 1). This suggests that the ground state is a combination of the d_{z^2} and $d_{x^2-y^2}$ orbitals (see above). The

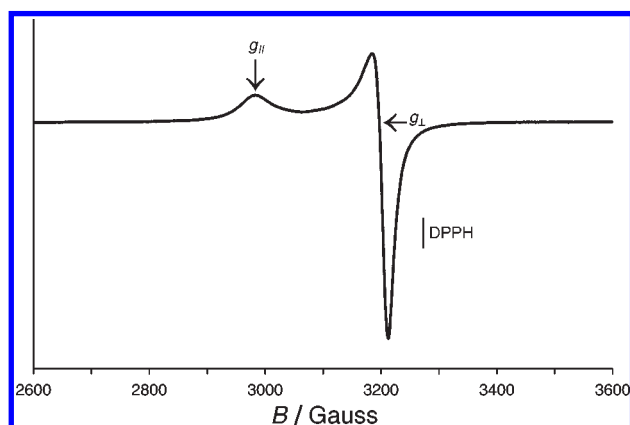


Figure 1. EPR spectrum of [Cu(en)₂(ClO₄)₂].

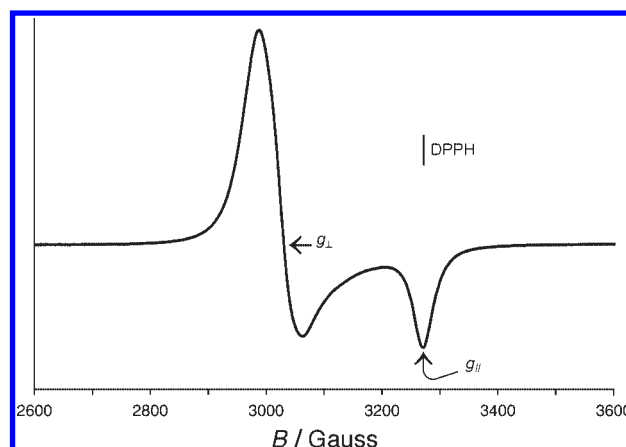


Figure 2. EPR spectrum of [Cu(phen)₂Cl]ClO₄.

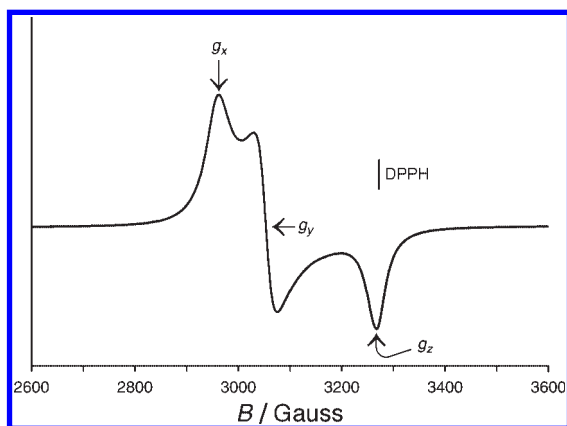


Figure 3. EPR spectrum of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{NO}_3)_2$.

spectrum of $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{NO}_3)_2$ is shown in Figure 3. Spectra with three g values are clearly indicative of a penta-coordination about Cu(II) ion with a geometry intermediate between the trigonal bipyramid and the square pyramid. The values of R for $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{NO}_3)_2$ and $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{ClO}_4$ are higher than 1 (2.14 and 1.54, respectively), while that for $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{BF}_4)_2$ is lower than 1 (0.73). Therefore, for $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{NO}_3)_2$ (10) and $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{ClO}_4$ (11) the geometry is closer to the trigonal bipyramid with a water molecule or a chloride ion and two aromatic nitrogen atoms as equatorial ligands and two nitrogen atoms in axial position. For $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})](\text{BF}_4)_2$ (12) the geometry is closer to the square pyramidal limit with the four nitrogen atoms of the two phenanthroline ligands on the equatorial plane and the water molecule in the axial site.

Conclusions

This article describes an experimental approach for teaching the electronic structure of complexes formed by paramagnetic transition-metal ions, such as Cu(II). The analysis of the EPR spectra provides a direct and convenient way to understand the variations of the Cu(II) complex geometry through the concepts of crystal field, ground state, and g value of the species examined. This work allows the student to learn how to extract chemical information from the EPR spectra and how to discriminate between various structures that, to a first approximation, should seem very similar.

In the classroom it should be noted that three ligands (en, phen, and bpy), characterized by analogous donor set (N, N) and by the possibility of forming five-membered chelated rings, show very different chemical behavior. Ethylenediamine forms essentially elongated octahedron complexes with the four nitrogen atoms on the equatorial plane and the presence of a, more-or-less weak, monodentate anion in the apical position. With 2,2'-bipyridine and 1,10-phenanthroline the formation of penta-coordinate structures with geometries ranging from the trigonal bipyramid to the square pyramid is favored.

As a consequence of the plasticity effect of Cu(II) ion (11), attempts to predict the stereochemistry of unknown compounds usually fail, as for the series $[\text{Cu}(\text{bpy})_2\text{Cl}]\text{ClO}_4$, $[\text{Cu}(\text{bpy})_2\text{Br}]\text{ClO}_4$, $[\text{Cu}(\text{bpy})_2]\text{ClO}_4$. Although one would expect three similar structures that are close to the trigonal bipyramid for $[\text{Cu}(\text{phen})_2\text{Cl}]\text{ClO}_4$, $[\text{Cu}(\text{phen})_2\text{Br}]\text{ClO}_4$, and $[\text{Cu}(\text{phen})_2\text{I}]\text{ClO}_4$, the first complex shows an intermediate geometry, while the last two are characterized by a trigonal bipyramidal arrangement.

Supplemental Material

A detailed description of the experiment, including the background of EPR spectroscopy and the details of the experiment, is available in this issue of *JCE Online*.

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