Inorganic Chemistry Laboratory

Analysis of the Electron Spin Resonance Spectra of Copper(II) and Silver(II) Picolinate

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Here is a procedure for calculating the g–value and the spin-only magnetic moment from X–band ESR spectra of the $M(pic)_2$ (M = Cu, Ag). The spectra were acquired from solid-state samples in a quartz tube and at room temperature at Western Michigan University. A JOEL JES–TE100 ESR spectrometer was the instrument used. Note that the spectra are a plot of magnetic field strength **B** (abscissa, vector quantity in millitesla (mT)) vs. the first derivative of the absorption intensity (ordinate, dimensionless).

There are two features you need to notice about these spectra. First two bands appear in each spectrum, and in this case the observation is consistent with an axially symmetric electronic structure. The weaker feature is designated $g_{||}$ and corresponds to unpaired electron spin density in the electronic z direction (defined to be parallel to the external magnetic field direction) while the stronger band is assigned to $g_{\perp}$ and arises from the approximately degenerate x and y directions (perpendicular to the applied field).

The spectra can be analyzed quantitatively to give the spectroscopic splitting factor (g–value, dimensionless). The g-value is found from this relationship:

$$g = h\,\nu_{MW}/\mu_B\,\mathbf{B}$$

The microwave frequency ν_{MW} is given on each spectrum in units of gigahertz GHz (10^9 s^{-1}). You must find the value of the magnetic field strength **B** such that it is the center of the maximum of the $g_{||}$ band and at the zero intensity observed for the $g_{\perp}$ signal; use the original spectral data in the Excel file to find these values. Calculate $g_{||}$ and $g_{\perp}$ using Planck's constant h as 6.626×10^{-34} J s and the Bohr magneton μ_B as 9.274×10^{-24} J T^{-1}. Both g–values should be ~2, but report them to three significant figures.

Once you have values for $g_{||}$ and $g_{\perp}$, you should calculate the average g–value as follows:

$$g_{avg} = 1/3\; g_{||} + 2/3\; g_{\perp}$$

From g_{avg} you can determine the spin-only magnetic moment μ_{SO} for copper in $Cu(pic)_2$.

$$\mu_{SO} = g_{avg}\,[S(S+1)]^{1/2}\,\mu_B$$ (μ_B is reported as the unit for μ_{SO})

where S is the total spin angular momentum: $S = \Sigma s$; $s = ½$ for each unpaired electron. Compare your calculated μ_{SO} value with those listed the *Inorganic Chemistry* textbook.

From your analysis you should be able to confirm the number of unpaired electrons present on each metal atom and the oxidation state for copper and silver in the picolinate compounds and their axial electronic symmetry.