

## Models to Maquettes to Metalloproteins: Cobalt as a Spectroscopic Probe of Zinc Biochemistry

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The use of Co(II) as a spectroscopic surrogate for Zn(II) is a well-established protocol in metallobiochemistry, and the potential wealth of available information is reflected in the rich spectroscopy of the high-spin (*hs*) Co(II) ion. However, interpretation of spectroscopic observations in terms of structure and bonding is often hampered by complicated electronic structure. We will present here a systematic investigation of a growing library of model compounds, encompassing 4-, 5- and 6-coordination, utilizing simple chemical substitutions to interrogate individual hyperfine interactions. Our integrated approach to paramagnetic resonance, simultaneously applying EPR (X- and Q-band), ENDOR (X- and Q-band), NMR (100-500 MHz) and NMR dispersion (NMRD,  $\nu_H = 1 - 80$  MHz) offers unparalleled access to the molecular spin system. Correlation of native, Zn and Co-substituted enzyme studies is provided by x-ray absorption spectroscopy (XAS). Results on a series of metalloproteins maquettes and several Zn enzymes involved in bacterial proliferation, will also be presented.