



Cobalt(II) “Scorpionate” Complexes as Models for Cobalt-Substituted Zinc Enzymes:

Electronic Structure Investigation by High-Frequency and -Field Electron Paramagnetic Resonance Spectroscopy

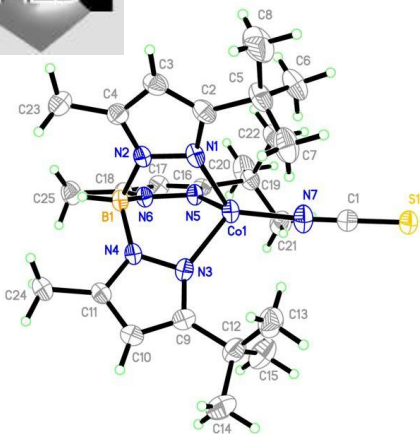


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Many metalloenzymes contain a zinc(II) ion in the active site. However, Zn(II) is spectroscopically “silent” with respect to both paramagnetic resonance and electronic absorption techniques. As a result, cobalt(II) is often substituted for Zn(II), which yields enzyme that can be studied by EPR and UV-Visible spectroscopies, while retaining enzyme activity. In this project, synthetic models for these active sites are studied by HF-EPR and UV-Vis-NIR spectroscopy and by x-ray crystallography (see structure at upper left). These model compounds contain the trispyrazolylborate ligand, known as a “scorpionate” due to its mode of binding, which models the tris histidine motif found in many Zn enzymes. The series of complexes studied showed very similar molecular structures and UV-Vis-NIR spectra, however, HF-EPR spectra (see figure at lower left) showed significant differences among these complexes. This finding suggests that enzyme activity can be controlled by very subtle effects.

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