Advances in Cobalt-59 Solution NMR: Studies of Cobalt Tetrpyrroles

$^{59}$Co solution NMR spectroscopy has been developed to study cobalt(III) tetrpyrroles including, but not limited to, the naturally occurring cob(III)alamins. This spectroscopy offers unique insight into the Co 3d electronic structure of the species; the electronic structure provides unique information regarding the reactivity of the cobalt (III) and cobalt (I) tetrpyrroles, such as organometallic Co–C bond strengths and Co(I) nucleophilicity. $^{59}$Co NMR spectra have been acquired diverse library of cobalt tetrpyrroles. The $^{59}$Co NMR shifts are influenced by both axial and equatorial ligand identity. Challenges in collecting $^{59}$Co NMR spectra of these species can be attributed to the efficient relaxation pathways; the $I=7/2$ character of the nuclei often causes the $^{59}$Co resonances to widen beyond detection. In the past, adequate signal-to-noise ratios were achieved by collecting a large number of scans over several days of saturated solutions. Development of a novel $^{59}$Co pulse sequence has resulted in more efficient data collection; the $^{59}$Co resonance can be seen in less than 20 minutes for a 3 mM sample, which is a significant improvement over previous reports for Co(III) tetrpyrroles. $^{59}$Co chemical shifts were indirectly referenced to [Co(CN)$_6$]$^{3-}$ via the residual water resonance. Also distinct from previous reports, these experiments were carried out in buffered aqueous solution at a physiological-relevant pH, which required a judicious choice of buffer salts. The spectral data were paired with density functional theory (DFT) calculations to further understand the electronic structures. Future work includes expanding beyond the diamagnetic Co(III) species to the highly nucleophilic Co(I) oxidation state tetrpyrrole species. Development of this $^{59}$Co solution NMR library will draw interest from bioinorganic, organometallic, and environmental chemists due to as the variety of the applications for cobalt tetrpyrroles relevant to these fields.