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CHARACTERISATION OF THE OXIDISED P-CLUSTERS IN THE MoFe PROTEIN OF Klebsiella pneumoniae NITROGENASE BY MCD SPECTROSCOPY


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Crystallographic studies of nitrogenase have confirmed earlier spectroscopic work from Hagan and Pierik [1] showing that this enzyme contains an unusual iron-sulphur cluster, called the P-centre, in which a pair of cuboids, [4Fe-4S], are linked by bridging sulphide ion and a pair of thiolate ligands. The P-cluster functions as a storage and transfer site for electrons en route from the electron donor, the iron protein, to the site of dinitrogen reduction, a hetero-atom iron-molybdenum-sulphur cluster. The magnetic and optical properties of the P-cluster have been studied using magnetic circular dichroism (MCD) spectroscopy in order to characterise its electronic properties. The MCD spectra of the MoFe protein, Klebsiella pneumoniae Kp1, at various poised potentials between -460 mV and +200 mV (vs. NHE) were measured at 4.2K and 5 Tesla. The P-cluster is oxidised at a mid-point potential of $E_{m} = -300$ mV by a two-electron process ($n = 2$) from a diamagnetic state to an integer spin state characterised by an EPR signal at $g \sim 12$ detected in the parallel mode, and by an intense MCD spectrum [2]. The MCD magnetisation properties, monitored at several wavelengths over a range of fields and temperature, have been successfully analysed for the first time. The EPR and MCD magnetisation results can be fitted to a ground electronic state, $S = 4$, with a negative, axial zero field splitting parameter $D = -2$ cm$^{-1}$.
