Hyperpolarisation of Salypr Ligands and Their Associated Zn(II) and Cu(II) Complexes.

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Signal Amplification By Reversible Exchange (SABRE) is a hyperpolarisation technique that is typically used to polarise small N-heterocyclic molecules. The hyperpolarisation of multidentate ligands and their respective complexes by SABRE has received little attention. Schiff bases, in particular those derived from a salen motif, are therefore of interest. A range of salpyr ligands (Schiff base molecules bearing a pyridyl ring), which have reported biological activity, were synthesised. Ultimately, it was desired to establish how structural complexity affected hyperpolarisation by SABRE. Complexation of the half- and full-salpyr ligands (L1 and L2 respectively) to Cu(II) and Zn(II) further enabled the effect of diamagnetic and paramagnetic metal centres upon polarisation transfer to be measured. These ligands and complexes were analysed by SABRE alongside 3,4-diaminopyridine (DAP). The overall enhancements observed for 3,4-DAP and L1 were 484-fold and 133-fold respectively when analysed in d4-MeOH using a magnetic field of 65 G for polarisation transfer. When d4-MeOH is exchanged for d2-DCM, L1 and L2 yielded 26.7- and 13-fold overall enhancements respectively. Comparison of L1 and [ZnL1] was achieved in a 2:1 mixture of d4-MeOH and d6-DMSO and yielded enhancements of 15-fold and 15.2-fold respectively. [CuL1] did not show any enhancement; this is presumed to be due to increased relaxation rate of the hyperpolarised state due to the paramagnetic Cu(II) ion. The structural differences from 3,4-DAP to the full-salpyr L2 yield significant reductions to SABRE activity, however, coordination to Zn(II) did not change the observed enhancements. The half-salpyr L1 can be used in the synthesis of a range of asymmetric salen ligands, and the structure-activity relationship of SABRE may be further investigated.