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Synthesis, electrochemical and magnetic properties of new acylic 'end-off' binuclear copper(II) complexes

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A series of nonbridged nitrito binuclear copper(II) complexes $[Cu_2L(NO_2)_2(H_2O)]$ $ClO_4 \cdot H_2O$ of 'end-off' Mannich base ligands have been synthesized. Cyclic voltammetry of these complexes revealed that the reduction process involved two successive one-electron transfer steps at different potentials.

$$Cu^{II}Cu^{II} \rightarrow Cu^{II}Cu^{I} \rightarrow Cu^{I}Cu^{I}$$

The conproportion constants K_{con} for the mixed valence $Cu^{II}Cu^{I}$ complex has been determined electrochemically. Cryomagnetic investigations (77–300 K) indicate an antiferromagnetic spin exchange between the copper(II) ions within the complex. Crystal structure analysis shows that the ligand is pentadentate, donating two nitrogens as well as a bridging oxygen to each copper. The most notable feature of the structure is that neither of the nitrito groups are bridging between the Cu ions but are bonded in an O-bonded, nonlinear arrangement to each copper resulting in an open m-phenolate structure. Perchlorates occupy the interstitial positions.