# Supplementary Material (ESI) for Chemical Communications

**Electronic Supplementary Information.**

All the iron atoms appear to be five-coordinate, with square pyramidal coordination patterns. The outer Fe(1) atoms have the carbonyl ligand of C(4) in the apical site, with two carbonyl and two thiolate sulfur atoms in the base plane. The central Fe(2) atoms have S(3) in the apical site (this bridges to the other Fe(2) atom) and three S atoms and one carbonyl ligand in the base plane. If one extends the O(4)-C(4)-Fe(1) and S(3)-Fe(2) lines, which both lie close to the plane which bisects the S(1) and S(2) vector and passes through Fe(1) and Fe(2), the lines intersect at a point X in that plane. If we assume that X lies on a bent Fe-X-Fe bond, then the coordination at each iron atom becomes six-coordinate with a pattern approaching octahedral. The octahedra of Fe(1) and Fe(2) now share a face, with the ligating atoms S(1) and S(2) and the point X at its vertices. In contrast, in the planar $Fe_2S_2$ group about the centre of symmetry, the mean Fe(2)...Fe(2') distance is substantially longer at 2.651(9) Å, and the octahedra of these iron atoms share the edge between S(3) and S(3'). Intermolecular contacts are at normal van der Waals' distances.

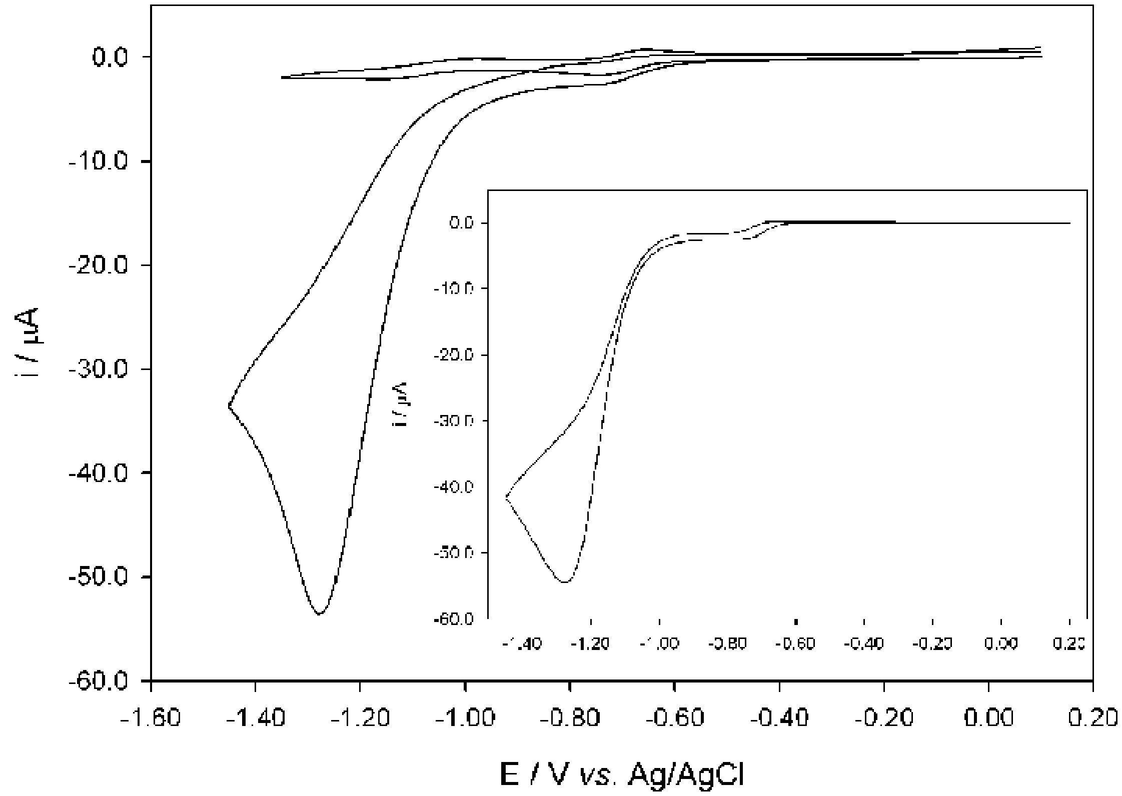

**Figure 4.** *Experimental and simulated (Digisim, Version 2.0.0.1) cyclic voltammograms of 1.5 mM of* **C** *in the presence 33 mM* $LutH^+$ *at 100 mV* $s^{-1}$. *The experimental diffusion coefficient of* **C** *was found to be 2.65 ** $10^{-6}$ *cm* $^2$ $s^{-1}$ *and this value was used for all iron species in the simulation; the diffusion coefficient used in the simulation for* $LutH^+$ *was 2.1 ** $10^{-5}$ *cm* $^2$ $s^{-1}$. *Thermodynamic and kinetic parameters used in the simulation are given in the Scheme. The experimental curve obtained in the absence of* $LutH^+$ *is also shown.*