SUPPLEMENTARY INFORMATION

SQUID Magnetometry As A Tool For Following a Clock Reaction in Solution

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1. METHODS AND MATERIALS

1.1 Materials

Sodium hydroxide, EDTA disodium salt, cobalt chloride and hydrogen peroxide (35 % by volume), all of ACS grade, were obtained from Aldrich and used without further purification. A 0.02 M $[Co(II)EDTA]^{2-}$ solution was made by dissolving equimolar quantities of EDTA and $CoCl_2$ in de-ionised water. The reacting solution used in all of the Cobalt experiments was a 9:1 by volume mixture of 0.02 M $[Co(II)EDTA]^{2-}$ and 35 % H_2O_2 solution at pH 3.9.

Sodium bromate, sulphuric acid, silver nitrate and malonic acid, all of A.C.S. grade, were obtained from Aldrich and used without further purification. A stock ferroin solution was produced by dissolving iron sulphate ($FeSO_4.7H_2O$) and 1, 10 – phenanthroline in de-ionised water to produce a 0.025 M solution. Both the iron sulphate and 1, 10 – phenanthroline were obtained from Aldrich and used without further purification.

1.2 Methods

1.2.1 pH Electrode Experiments

A pH electrode was connected directly to a computer using a PCI 9112 data acquisition card. A simple data acquisition program was written in Labview and the pH meter calibrated using buffer solutions (pH 4, 7 and 10). The measurement of pH was taken from 50 ml of reacting mixture in a small flask, with measurements of pH taken every 100 ms. The reacting mixtures were thermostatted at 25 ^{o}C using a water bath.

1.2.2 Absorption Spectroscopy Experiments

Ultraviolet/visible light absorption spectra were obtained for the reacting mixture in a Unicam UV-2 spectrometer. A thin path length (1 mm) cell was used as the absorption of the $[Co(III)EDTA]^{-}$ product was too high for the spectrometer to record accurately with longer path lengths. The clock reaction was followed in the spectrometer with full spectra of the solution in a 1 mm path length cell from 350 to 700 nm acquired at 4 minute intervals, and the absorption of the solution at given wavelengths against time taken from the full scans. The spectrometer could also record spectra at a given wavelength by recording the absorption at that wavelength every 125 ms. No temperature control of the reacting solutions was possible in the spectrometer.

1.2.3 NMR Relaxation Time Experiments

MRI experiments were conducted on a Bruker DMX-300 spectrometer equipped with a 7.0 T superconducting magnet, operating at a proton resonance of 300 MHz, and at 295 K. The reacting solution was prepared outside of the magnet and a 5 mm ID NMR tube was filled to a depth of a few centimetres of the reacting solution. The CPMG sequence recorded 64 echoes with a τ of 2 ms. CPMG measurements of the reacting sample were obtained at 30 s intervals

1.2.4 NMR Evans Method (Susceptibility) Experiments

The NMR experiments were performed using a Varian Unity INOVA 600 spectrometer, operating at a proton frequency of 599.8 MHz and a 5mm NMR tube with capillary insert. A 1% t-butanol in D_2O solution was used as the reference. The $[Co(II)EDTA]^{2-}$ solution was prepared as outlined above. Immediately after mixing, 400 µl of the mixed solution was put into the 5 mm NMR tube. The NMR measurement commenced 10 minutes after the mixing and the FID signal recorded sequentially at 40 second intervals. The acquired FID data was processed by home-written macro program on Igor Pro 6.04(Wavemetrics).

1.2.5 SQUID Experiments

The magnetic moment of the sample was measured using a Quantum Design MPMS5 magnetometer at 300 K. The SQUID magnetometer uses cgs units with the applied field measured in Oersteds, rather than Tesla, and the moment in emu, as opposed to A m^2. A field of 50000 Oe was used for all of the experiments, and was converted into the equivalent SI unit, A m^{-1}, for calculations (see flow chart, Fig. S2). The reaction was initiated outside of the SQUID magnetometer and a small, known mass (typically around 100 mg) of the reacting solution placed inside a 5 mm NMR tube which was then sealed. This sealed sample was loaded into a thin plastic tube and held in place with empty gelatine capsules lodged into position. A typical sample tube is shown in Fig. S1.

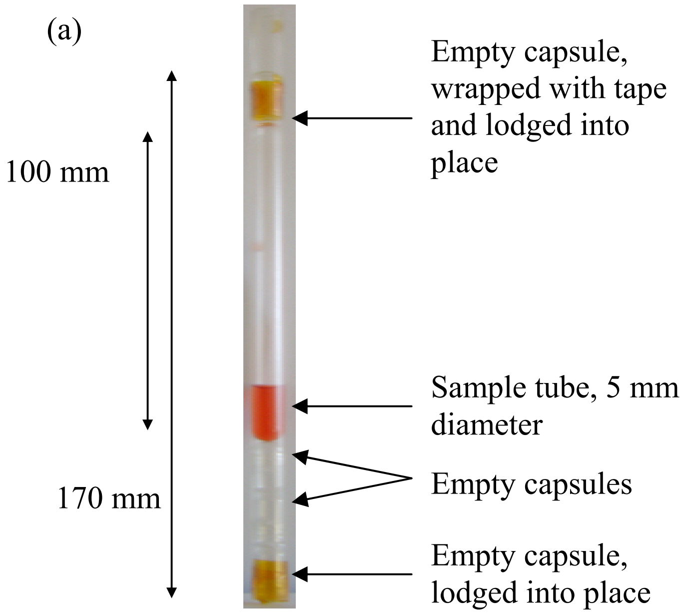

Fig. S1: Image of the sample tube.

The loaded tube was then inserted into the SQUID magnetometer. Before a measurement could be taken, the sample had to be centred within the coils of the SQUID magnetometer. This process would usually take at least 5 to 7 minutes. The SQUID magnetometer was programmed to take measurements at 1 s delays, with each measurement taking ~ 15 s. For the $[Co(II)EDTA]^{2-}/H_2O_2$ experiments, four measurements were taken and averaged for each data point. For the ferroin clock, only one measurement was taken at a time, allowing more measurements to be taken at a faster rate.

By assuming that the only change in moment is due to the change in the oxidation state of the metal, a maximum or minimum value can be subtracted to give a change in magnetic moment due to the reaction. As the diamagnetic susceptibility is related to the atomic number of an atom, the change in moment due to any change in metal oxidation state can be assumed to be a result of changes in the number of unpaired electrons. The next steps are conversion to SI units to give a moment in A m^2 and then division by the volume of material, in m^3, to give a volume magnetisation in A m^{-1}. The volume magnetic susceptibility is then calculated by dividing the volume magnetisation by the magnetic field applied. Volume, mass and molar susceptibilities can be interconverted using the density and concentrations of the material, and from the molar susceptibility, the number of unpaired electrons per metal atom can be estimated from the spin-only formula for magnetic susceptibility (see below). A flow chart showing the series of calculations required is depicted in Fig. S2.

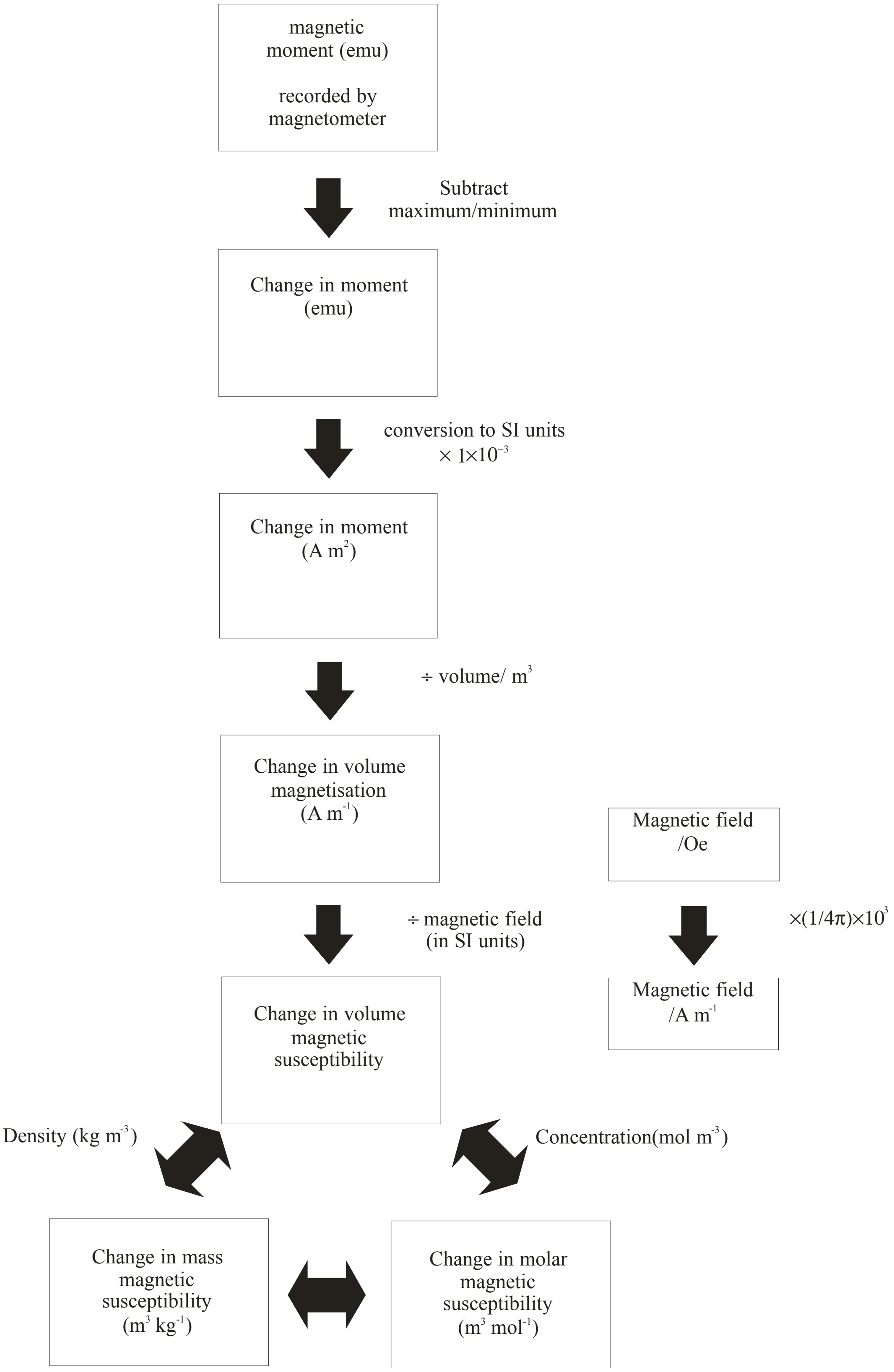

Fig. S2: Flow chart detailing the calculations required to convert magnetic data recorded by SQUID into a measurement of magnetic susceptibility.

1.2.6 Analysis

In order to compare the various methods of following the reaction described above, some methods of quantifying the features of the reaction are needed. One of the distinctive features of autocatalysis in a reaction is a period of slow reaction rate (sometimes known as the ‘induction period’) followed by one where the reaction rate increases to a maximum value before slowing down again. This behaviour is colloquially known as ‘clocking’, given that the reaction changes rapidly from unreacted to reacted after a period of time. Fig. S3 is reproduced here, with the rate of reaction added, in order to illustrate the behaviour and terms used.

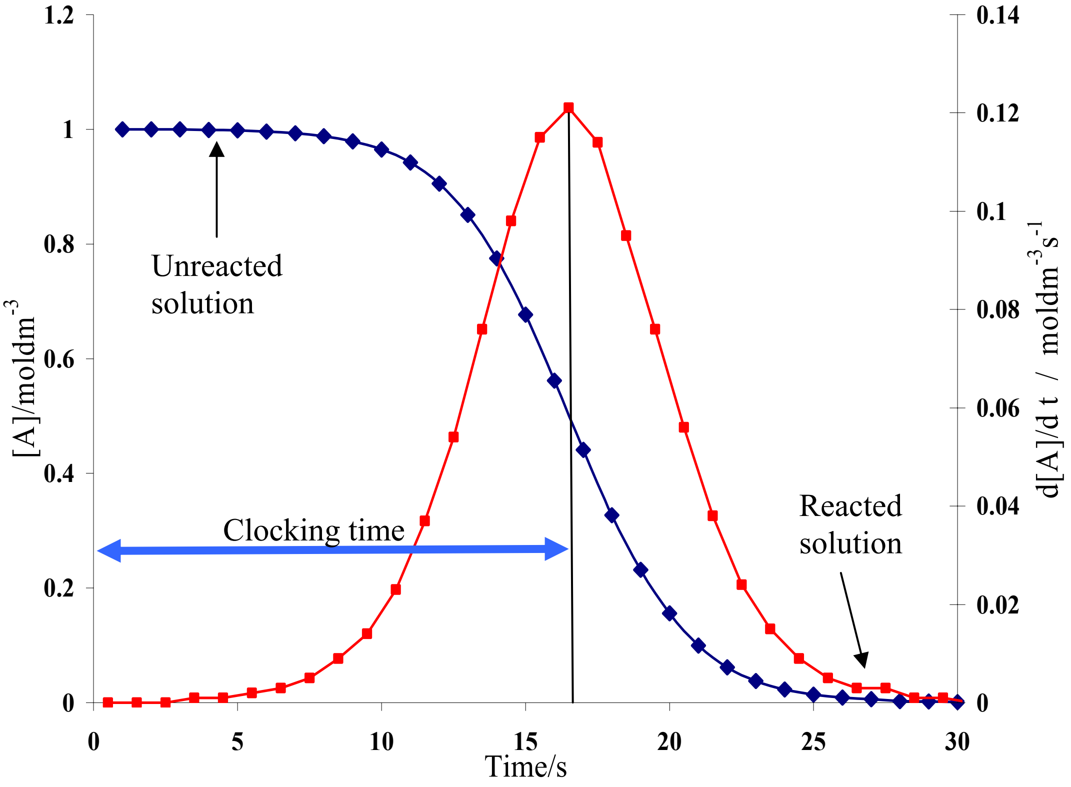

Fig. S3: The fall in [A] for the simple, quadratic autocatalytic reaction A + B → 2 B.

Various features of the reaction could be chosen to be the indicator required, as long as its use is consistent. The induction period is not a well-defined measure as it can be hard to determine the state of the reaction and whether the reaction is slow or not. Likewise, there is rarely a clear point when the reaction can be said to be finished. A first derivative of the data with respect to time will show when the reaction reaches its maximum rate, as shown in Fig. S3. This is the parameter used in this work to quantify the clock reactions depicted in the next chapter and will be referred to as the 'clocking time'. This measurement can also be used for every set of data. Assigning the clocking time to some maximum or minimum value of the data may work for some methods but not all methods produce convenient sets of data. Certainly, in some of the experiments depicted below, the end of the reaction is often not clear as there are further reactions of hydrogen peroxide in an alkali transition metal solution, as well as the presence of intermediate species. The maximum value of the first derivative should correspond to the same point for all of the experimental methods used.

2 RESULTS

2.1 Study of the $[Co(II)EDTA]^{2-}/H_2O_2$ Reaction

2.1.1 Absorption Spectroscopy Experiments

Fig. S4 shows absorption spectra for 0.018 M solutions of $[Co(II)EDTA]^{2-}$ and $[Co(III)EDTA]^{-}$ between 350 nm and 700 nm. The $[Co(III)EDTA]^{-}$ solution was produced by letting a 9:1 by volume mixture of $[Co(II)EDTA]^{2-}$ and H_2O_2 react overnight. To check that the reaction has proceeded to completion, two spectra were recorded several minutes apart, showing no further change in the absorption of the reacted solution.

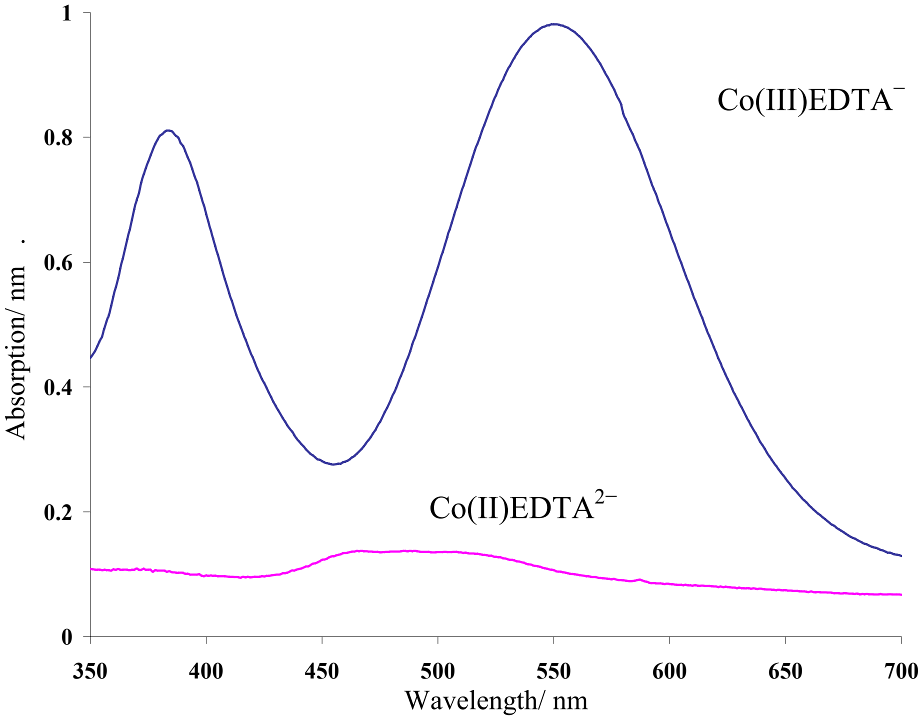

Fig. S4: Absorption spectra from 350 nm to 700 nm for 0.018 M $[Co(II)EDTA]^{2-}$ (pink) and 0.018 M $[Co(III)EDTA]^{-}$ (blue) solutions.

The spectra in Fig. 5 of the main paper can be used to follow the concentrations of Co(II) and Co(III) species. The total absorption measured at a given wavelength, λ, would be given by:

$$A_{\mathrm{tot},\,\lambda} = (\varepsilon_{\mathrm{Co(II)EDTA},\lambda}\times[\mathrm{Co(II)EDTA}]^{2-} + \varepsilon_{\mathrm{Co(III)EDTA},\lambda}\times[\mathrm{Co(III)EDTA}]^{-}) \qquad (1)$$

ε are absorption coefficients for the given species at a given wavelength. The path length is constant throughout and can be ignored. The wavelength chosen is the isosbestic point of the two Co(III) species (ie, the fully reacted complex and the proposed peroxo-dicobalt(III)) species involved, 578 nm, so that the formation of the intermediate does not complicate matters. Finally, we take into account that the total cobalt concentration, $[\mathrm{Co(III)EDTA}]^{-} + [\mathrm{Co(II)EDTA}]^{2-}$, is constant throughout.

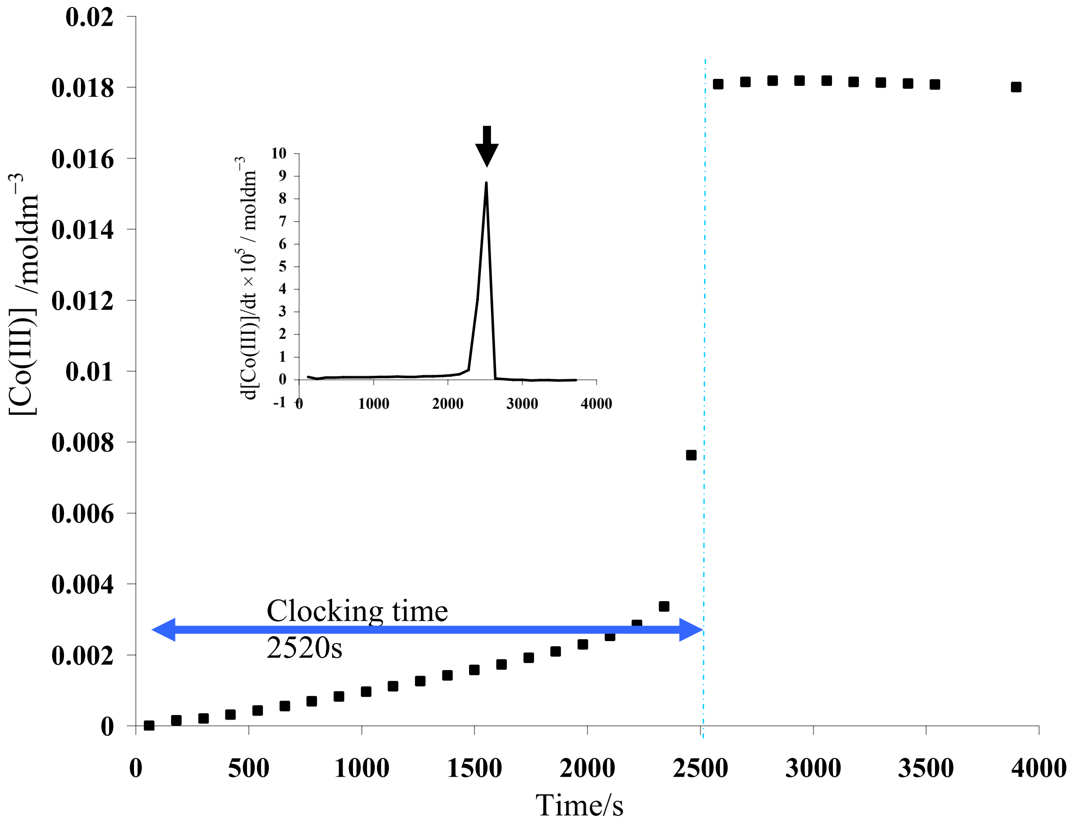

Fig. S5: Time-dependent changes in the concentration of Cobalt(III) species, calculated from the absorption data shown in Fig. 4 (main paper). Insert shows the rate of change of concentration of Co(III) with clocking time (maximum in d[Co(III)EDTA]$^-$/dt) identified.

The clock behaviour displayed in Fig. S5 is striking. The clocking time, 2520 s is easily observed in the rate data although the precision of the value is limited by the time taken to record an individual spectrum, 30 s.

Finally, the absorption at one given wavelength was recorded every 625 ms. Fig. S6 shows one such measurement, following the reaction at 600 nm. The clock behaviour of the reaction is exhibited as expected.

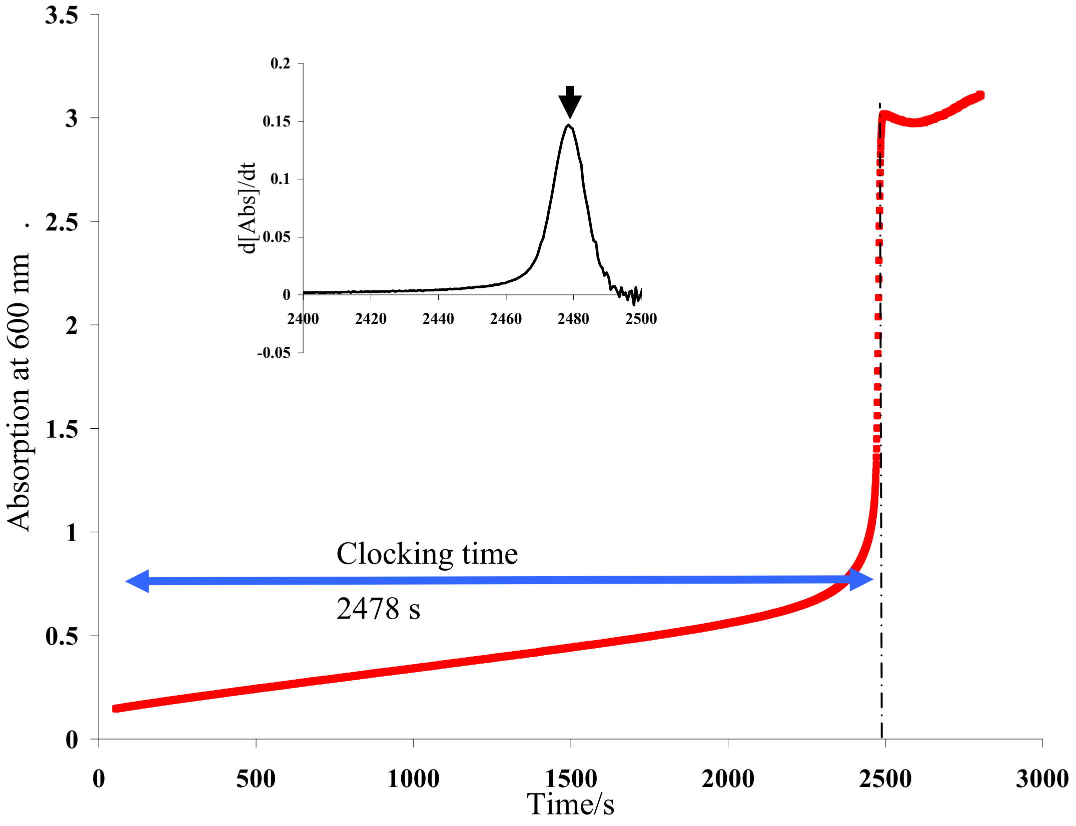

Fig. S6: The time–dependent absorption for a typical reaction of [Co(II)EDTA]$^{2-}$ with H_2O_2 at 600 nm. Measurements of absorption taken every 625 ms. The inset highlights the rate of change in

absorption for the time period 2400 to 2500 s after initiation of the reaction, with clocking time identified by an arrow.

Figs. S5 and S6 illustrate the reproducibility of the experiments performed in the UV/vis spectrometer, with only a 42 s difference between the two clocking times. This technique is clearly reliable in reproducing both the details of the peaks, such as that assigned to an intermediate and the timings of the $[\text{Co(II)EDTA}]^{2-}/\text{H}_2\text{O}_2$ reaction.

2.1.2 SQUID Experiments

The change in the number of unpaired spins can be calculated from the flow chart (Fig. S2) and Fig. 1 in the main paper, and the results are summarised below:.

Δmagnetic moment/emu = 5.50×10^{-4}

Δmagnetic moment/A m^2 = 5.50×10^{-7}

Δvolume magnetisation/A m^{-1} = 6.14

Δvolume magnetic susceptibility = 1.54×10^{-6}

Δmolar magnetic susceptibility/m^3 mol^{-1} = 8.57×10^{-8}

From this change in molar susceptibility, the number of unpaired spins can be estimated from the spin-only formula for susceptibility.

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 (S(S+1))}{3kT} \qquad (2)$$

For the data presented in Fig. 1 of the main paper, the change in the number of unpaired spins = 3.15, slightly higher than the expected value of 3, but an error of only 5%. It is likely that there is some contribution to the susceptibility of the $[Co(II)EDTA]^{2-}$ solution due to orbital contributions that arise from the $d^7(t_{2g}^5\,e_g^2)$ configuration of the ion. These effects are largest when there is an unoccupied orbital of a similar energy to a singly occupied orbital present in the ion (such as d^1 and d^2 configurations). The electron configuration here should have an orbital magnetic contribution and such contributions has been observed in some Co(II) complexes[1]**.** The $[Co(II)EDTA]^{2-}$ complex is likely to have a higher magnetic moment than predicted by a simple spin-only model, so the change in susceptibility as it reacts to form the $[Co(III)EDTA]^{-}$ complex (t_{2g}^6 configuration so no orbital contribution) should be larger than predicted.

We interpret the later rise in recorded magnetic moment (as observed both by the SQUID and the Evans methods) as arising from the formation of paramagnetic O_2 from the disproportionation of excess H_2O_2 in the final reacted solution:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (3)$$

This reaction is catalysed by transition metals and is also more rapid in solutions where pH > 7 (compare Fig. 2 of the main paper). The maximum amount of O_2 produced by the reaction can be estimated by considering the amount of H_2O_2 present in a small reacting sample, and assuming that all of it decomposes to form O_2. For a typical reacting sample of 0.1 ml, there are 1.4×10^{-4} moles of hydrogen peroxide present in the sample, and this will decompose to form 7×10^{-5} moles of oxygen.

Is this gas responsible for the rise in magnetic moment of the sample after the reaction has clocked? Assuming that all of the gas remains in the sample space, the magnetic moment of this volume of O_2 can be calculated using the volume susceptibility of the gas, 1.83×10^{-6} [2]. This gives a potential rise in magnetic moment, in emu, at 50 kOe of 8.74×10^{-3}. This is far larger than that seen in Fig. 1 of the main paper. However, the formation of bubbles shows clearly that not all of the gas does remain in the sample. The saturation concentration of oxygen in water (standard conditions) is $\sim 0.2 \times 10^{-3}$ mol dm^{-3}. Given a molar susceptibility of O_2 of 4.3×10^{-8} m^3 mol^{-1}, this gives rise to an increase in the magnetic moment of the 0.1 ml sample of reacting solution, in a field of 50 kOe, of 6.84×10^{-6} emu, approximately a power of ten smaller than that seen in the figure. The higher value observed soon after the reaction (in both the SQUID and the NMR-Evans method experiments) has clocked is likely to be due to a rapid production of O_2 and bubble formation. Then, as the gas escapes from the solution and out of the measured region of the sample, the magnetic moment of the sample falls towards that expected of a saturated O_2 solution. Not all of the oxygen that can be produced from the reactions of H_2O_2 will be released at the moment the reaction clocks. Instead, bubbles of gas are observed in the reaction many hours after the oxidation to $[Co(III)EDTA]^-$ is complete. Obviously, as the pressure in the sealed tube increases, the saturation concentration of oxygen (and hence the magnetic moment) will increase.

The reproducibility of the reaction in the SQUID magnetometer needs to be considered. In earlier experiments with this reaction, a larger amount (0.3182 g) of reacting solution was measured, and the clock times were in the order of hours, rather than the expected 40 minutes. With smaller samples (< 0.1 g), the timings were much closer to those obtained using the more traditional methods. However, the reproducibility between experiments is still worse than that observed in the three other employed methods (pH, NMR, UV/vis) with a standard deviation of 340 s (in four consecutive experiments) equalling almost 15 % of the clocking time.

Finally, Fig. S7 displays a comparison of the SQUID and the electronic absorption data which show gratifying similarities in shape and clocking times.

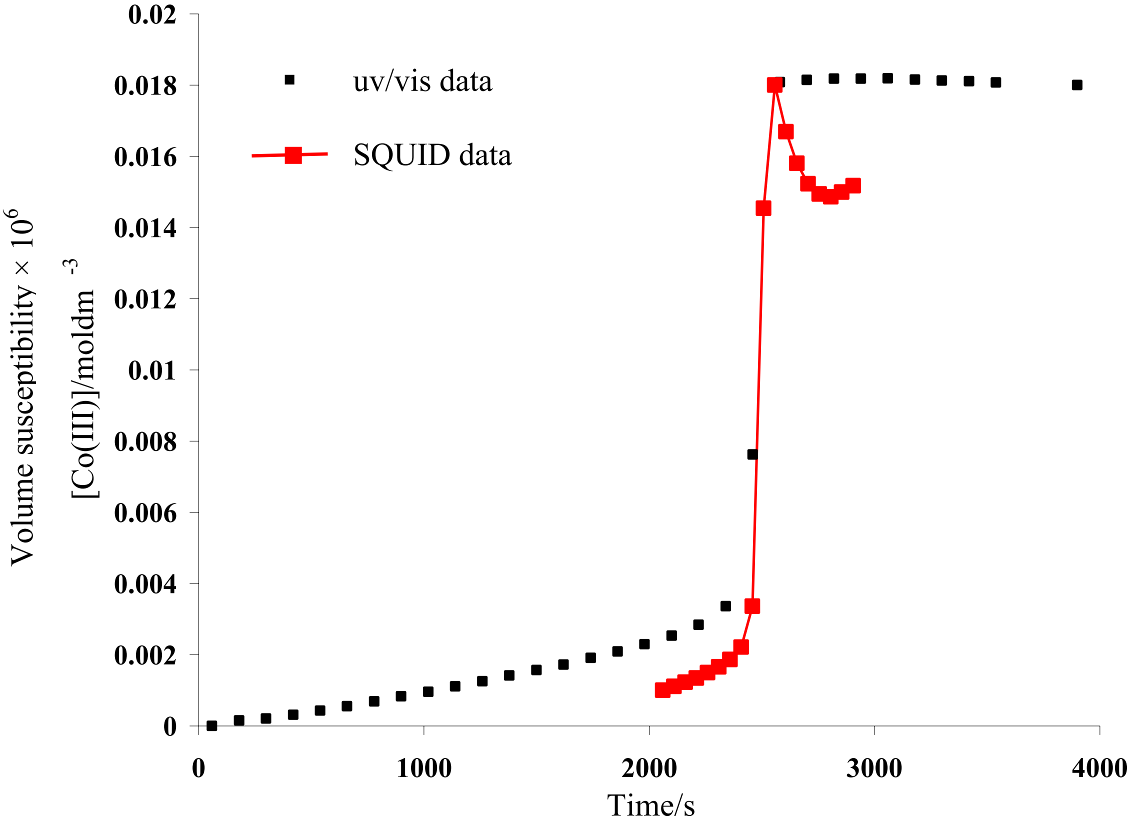

Fig. S7: A comparison of [Co(III)EDTA]$^-$ data obtained from typical absorption spectroscopy (black squares) and SQUID magnetometry (red squares and line) experiments.

2.1.3 Evans Method

This technique is based on the frequency shift of an NMR signal of a co-dissolved compound, typically t-butyl alcohol, by the magnetic field due to an accompanying paramagnetic species. A coaxial double NMR tube is used and the inner, capillary tube contains the t-butyl/D_2O alcohol mixture (2:98). The solution containing the paramagnetic solution to be measured and a 1 % t-butyl alcohol is situated in the outer tube. The paramagnetic metal species produces a relative frequency shift in the alcohol signal, for a superconducting solenoid magnet, of :

$$\frac{\Delta\nu}{\nu} = \frac{\Delta\chi}{3} \qquad (4)$$

where $\Delta\chi = \chi - \chi_o$ and χ and χ_0 are the volume magnetic susceptibilities of the sample and reference solution, respectively. For $\Delta\nu / \nu = 0.505 ppm$, we obtain a change in volume magnetic susceptibility of 1.515×10^{-6} (cf, 1.54×10^{-6} from the SQUID measurement).

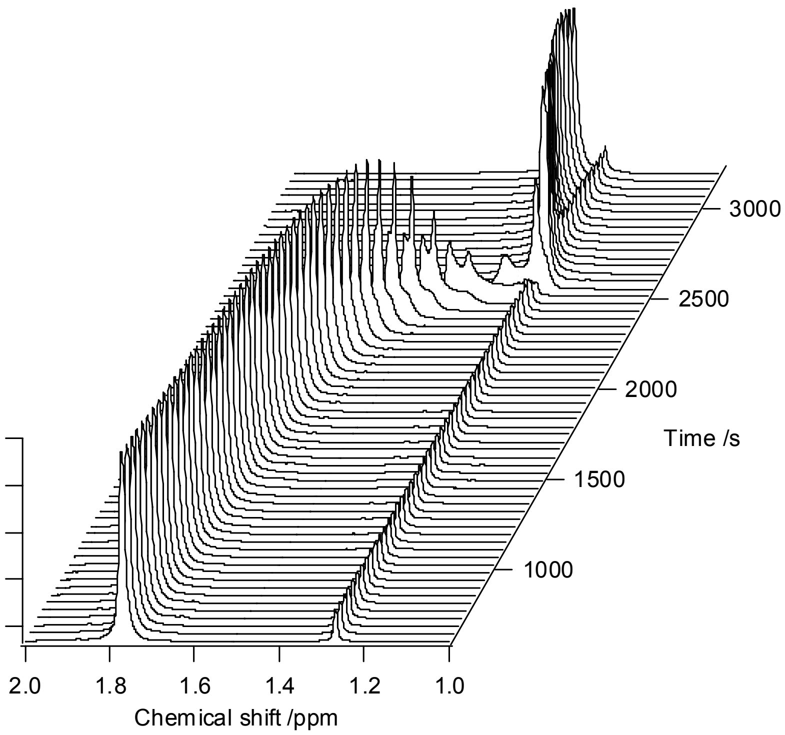

Fig. S8: NMR spectra recorded for the reacting solution of $[Co(II)EDTA]^{2-}$ and H_2O_2 (following the Evans method, reaction is initiated at time = 0 s). Only the t-butyl resonances are depicted. The signal at 1.267 ppm corresponds to that of the t-butyl alcohol in the absence of any paramagnetic substances (and hence, is the signal from the standard mixture in the capillary). The large signal situated at 1.772ppm at time t = 0 corresponds to t-butyl alcohol in the Cobalt solution. Fig. 2 in the main paper portraits this spectrum as a contour plot.

2.2 Other Reactions

The clock reaction between $[Co(II)EDTA]^{2-}$ and H_2O_2 is not the only reaction that can be followed using SQUID magnetometry. In theory, any reaction that displays a change in magnetic susceptibility can be followed using a SQUID magnetometer. Reactions involving the transition metals that feature changes in the oxidation state of the metal species are particularly attractive candidates for such a study. There are further considerations that limit the number of potential reactions for study. The time taken between initiation of the reaction (which, at present, has to occur outside the SQUID as the sample tube must be sealed before being placed inside the SQUID) and the first measurement of the sample limits possible reactions to those which are slow, or those which are slow at the start of the reaction. Autocatalysis, such as that observed in the $[Co(II)EDTA]^{2-}$ reaction, leads to kinetics for which the reaction is slow at initiation. Important details of the reaction, such as the clocking time, occur much later on and make these reactions suitable for observation by SQUID magnetometry.

2.2.1 Ferroin Clock Reaction

One group of reactions that is also suitable for study by this technique is based on the Belousov-Zhabotinsky (BZ) reaction. This reaction features the autocatalytic oxidation of a metal ion, such as Mn(II), Ce(III) or ferroin (iron(II) phenanthroline) by acidified bromate, with the regeneration of the original metal ion by the reaction of the oxidised ion with an organic species, such as malonic acid. A more detailed description of this reaction can be found in Oscillations, Waves and Chaos in Chemical Kinetics by S. K. Scott[3]. With the organic species present, the reaction displays oscillations while a clock reaction, exhibiting the autocatalytic oxidation of the ferroin to ferriin without the regeneration of the metal catalyst, can be prepared by removing the organic species[4]. As this reaction exhibits both a change in oxidation state and an induction period due to the autocatalytic nature of the reaction, it can be studied conveniently by this technique.

The ferroin-catalysed reaction shows different reaction mechanisms depending on different relative concentrations of ferroin and bromate ions. At concentrations of ferroin, so that $[\text{ferroin}] < [BrO_3^-]$, the key step is the autocatalytic oxidation of ferroin. However, as the concentration of ferroin is increased, a second reaction pathway, the dissociation of ferroin, becomes increasingly important. The overall stoichiometry of the reaction is:

$$4\ \text{ferroin} + BrO_3^- + 5\ H^+ \rightarrow 4\ \text{ferriin} + HOBr + 2\ H_2O \qquad (5)$$

and does not reveal the autocatalytic nature of the reaction. The key sequence of steps in the reaction is the same as for the BZ reaction. It assumed that there are small initial concentrations of $HBrO_2$ and Br^- present in the reaction mixture.

$$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons Br_2O_4 + H_2O \qquad (6)$$

$$Br_2O_4 \rightleftharpoons 2\ BrO_2^{\cdot} \qquad (7)$$

$$BrO_2^{\cdot} + M^{n+} + H^+ \rightleftharpoons M^{(n+1)+} + HBrO_2 \qquad (8)$$

This set of reactions show that an autocatalytic species, $HBrO_2$, is present. There is autocatalytic oxidation of the metal ion in the same manner as observed in the BZ reaction. When the ratio, [ferroin]/[BrO_3^-] reaches a certain value, a second pathway becomes important[4].

$$[Fe(phen)_3]^{2+} \rightleftharpoons [Fe(phen)_2]^{2+} + phen \qquad (9)$$

$$[Fe(phen)_2]^{2+} \rightarrow \text{products} \qquad (10)$$

Körös *et al.*[4] observed this change in pathway as a change in behaviour of the reaction. The reaction would start with normal, autocatalytic behaviour, but then switch to a first order oxidation of ferroin. UV/vis studies of the reaction were significantly hindered by the tendency of the reaction to initiate somewhere in the sample and a travelling wave to form and propagate through the reacting solution. Similar behaviour was observed in reactions performed in NMR tubes.

Fig. S9 shows the magnetic moment data for the reaction of ferroin with acidified bromate, with 1.875 × 10^{-3} M ferroin and 5.2 × 10^{-3} M $NaBrO_3$ at pH 2.1. 0.2353 g of reacting solution was used at 300 K.

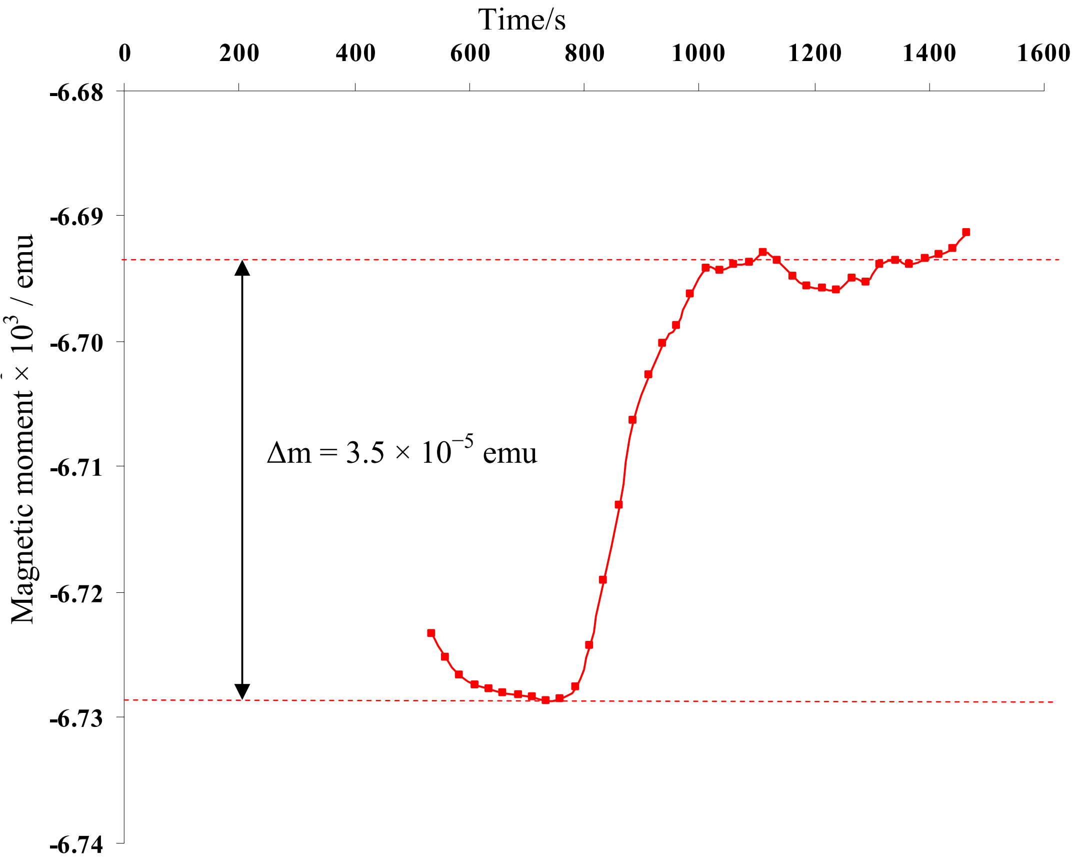

Fig. S9: A typical set of raw magnetic moment data acquired from the SQUID magnetometer for the clock reaction between ferroin and acidified BrO_3^-. Concentrations and conditions specified in the text.

The clock reaction is observable in the SQUID magnetometer. The change in magnetic moment, shown by the black arrow in Fig. S9 is 3.5×10^{-5} emu.

$$\Delta\text{magnetic moment/emu} = 3.50 \times 10^{-5}$$

$$\Delta\text{magnetic moment/A m}^2 = 5.50 \times 10^{-8}$$

$$\Delta\text{volume magnetisation/A m}^{-1} = 0.149$$

$$\Delta\text{volume magnetic susceptibility} = 3.74 \times 10^{-8}$$

$$\Delta\text{molar magnetic susceptibility/m}^3\text{ mol}^{-1} = 1.99 \times 10^{-8}$$

The molar magnetic susceptibility can be related to the amount of unpaired spin per metal atom in the same way as for the cobalt reaction. For the data presented in Fig. S9, the change in the number of unpaired spins = 1.17. This is approximately the same as that expected for the one-electron oxidation of ferroin to ferriin. A larger magnetic moment of the oxidised complex, ferriin, is expected given that there is an orbital contribution from the $t_{2g}^5 e_g^0$ ground state[1]. As expected there is also a change in behaviour as [ferroin] is increased. Fig. S10 shows the change in magnetic moment for the clock reaction with 1.875×10^{-2} M ferroin and 5.2×10^{-3} M $NaBrO_3$ at pH 2.1. 0.2290 g of reacting solution was used at 300 K.

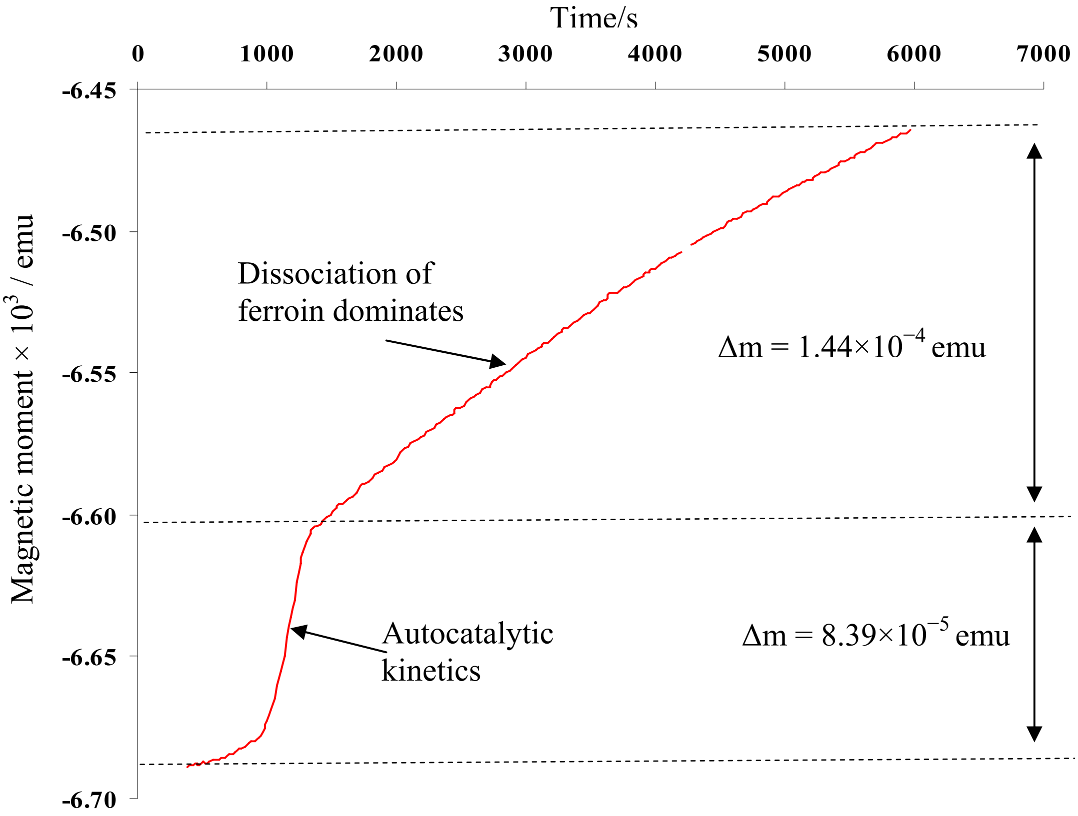

Fig. S10: A typical set of raw magnetic moment data acquired from the SQUID magnetometer for the clock reaction between ferroin and acidified BrO_3^-. Ferroin is 10 times more concentrated in this experiment than in Fig. S9. Concentrations and conditions specified in the text.

The shape of the curve certainly suggests that the reaction is behaving as expected. The first part of the curve resembles a clock, with an induction period and then a sharp rise in the magnetic moment. After the ‘clock’ behaviour, there is still an increase. This behaviour was as predicted by Körös *et al.*[4]. The reaction has not been followed to completion, but the change observed can still used to give an idea of what has happened during the reaction. The total change in magnetic moment, Δm = 2.28 × 10^{-4} emu, corresponds to the change in 1 unpaired electron per atom in a 1.56 × 10^{-2} M solution, which is only just short of the concentration of ferroin used in the reaction.

References

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4: Körös. E., Burger, M. and Kris, A., *React. Kinet. Catal. Lett.*, 1974, **1**, 475-480.