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Investigation of the solid state reaction of $FeSO_4{\cdot}7H_2O$ with 1,10-phenanthroline †

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Received 11th June 2002, Accepted 9th July 2002
First published as an Advance Article on the web 19th August 2002

Solid-state reaction of $FeSO_4{\cdot}7H_2O$ and 1,10-phenanthroline in a 1 : 1 molar ratio was investigated by time-resolved *in-situ* energy dispersive X-ray diffraction (EDXRD), DSC, TG/DTA, Mössbauer and IR spectroscopy. The reaction of these solids takes place rapidly at around 70 °C and initially produces an intermediate crystalline phase, $Fe(phen)_3SO_4{\cdot}5H_2O$ before cleanly converting to $Fe(phen)(H_2O)_3SO_4$. This is in contrast to the product of the reaction of $FeSO_4{\cdot}7H_2O$ with 1,10-phenanthroline in aqueous solution which produces $[Fe(phen)_3{}^{2+}][SO_4{}^{2-}]$. All the spectral data suggest that the final product is a neutral Fe(II) complex. The coordination sphere around the Fe(II) ions is thought to be octahedral consisting of a unidentate sulfate ligand, a bidentate 1,10-phenanthroline ligand and three aquo ligands.

Introduction

Solid–solid reactions that take place at low temperature can offer the potential for preparing phases that cannot be prepared in solution.[1–6] For example, Toda's group have reported that organic solid state reactions could produce products very efficiently, even stereoselectively;[6–8] Mallouk's group have addressed the importance of turning down the heat to produce kinetic products;[5,9,10] Xin's group has reported many new structures prepared by using solid-state reactions at temperatures from room temperature up to around 100 °C.[2–4]

Some of us have previously studied the solid-state reaction between transition metal salts and a variety of ligands.[11–18] In some cases it was shown that coordination of the ligands takes place in a stepwise manner with sequential substitution of coordinated water in hydrated salts. This could be used to produce complexes that cannot easily be obtained in solution phase.[12,16–18] We also showed that the water molecules present in the hydrated salts have a significant effect on the rates of these reactions.[3,4]

Reaction of iron(II) ion and phenanthroline in aqueous solution produces the stable deep blood-red complex cation, $[Fe(phen)_3]^{2+}$. $[Fe(phen)_3]^{2+}$ has a low spin $(t_{2g})^6$ configuration, which has the greatest crystal field stabilisation energy compared to the possible high spin $(t_{2g})^4(e_g)^2$ species, such as $[Fe(phen)(H_2O)_4]^{2+}$ and $[Fe(phen)_2(H_2O)_2]^{2+}$. In order to obtain complexes with interesting electronic properties, such as those that exhibit spin crossover phenomena, one has to devise means of synthesis other than the conventional solvent-mediated routes, such as pyrolysis or leaching the ligands in organic solvents.[19] We have found it is possible to synthesise metal complexes conveniently by mixing stoichiometric amounts of starting materials in the solid state at low temperatures (less than 100 °C).[12]

The solid-state reaction between $FeSO_4{\cdot}7H_2O$ and *o*-phenanthroline is different from some of the previously studied reactions. Unusually, crystalline $FeSO_4{\cdot}7H_2O$ contains water in which six molecules act as donor ligands while the remaining water molecule is present as occluded water of crystallisation.

Results and discussion

When solid $FeSO_4{\cdot}7H_2O$ and 1,10-phenanthroline are ground together in a 1 : 1 molar ratio in a pestle and mortar and heated to over 70 °C ligand substitution reactions take place to give a new red crystalline phase in high purity. Fig. 1 shows the X-ray powder diffraction pattern of the red solid product, together with the XRD patterns of the starting materials and $Fe(phen)_3SO_4{\cdot}5H_2O$. $Fe(phen)_3SO_4{\cdot}5H_2O$ is the sole product that crystallises if this reaction is carried out in aqueous solution. The diffractogram of the final red product contains no Bragg reflections assignable to either of the starting materials or to $Fe(phen)_3SO_4{\cdot}5H_2O$. All the Bragg reflections in the XRD pattern shown in Fig. 1c can be indexed on a monoclinic cell ($a = 13.707$, $b = 10.075$, $c = 11.914$ Å, $\beta = 111.6°$). The systematic absences are consistent with the space group $P2_1/a$. Assuming a formulation of $Fe(phen)(H_2O)_3SO_4$ (*vide infra*) and $Z = 4$ the unit cell volume gives a calculated density of 1.68 g cm^{-3}. We have tried to determine the structure from the powder diffraction data using direct methods. Unfortunately, we cannot measure the intensity of sufficient unique reflections for a structure solution. However, we are still investigating real-space/Monte-Carlo structure solution methods.

^{57}Fe Mössbauer spectroscopy is a very sensitive probe of the electronic structure of iron-containing compounds.[20–22] The room temperature ^{57}Fe Mössbauer spectrum of the final red product is shown in Fig. 2. The spectrum exhibits mainly a doublet with an isomer shift of 1.16 mm s^{-1} with a quadruple splitting of 2.84 mm s^{-1} in addition to a low intensity singlet at 0.51 mm s^{-1}. The singlet is indicative of the presence of a small amount of an unknown Fe(III) impurity, which may come from either impurities in the starting material, or aerial oxidation during the reaction course. The major doublet resonance is typical of a high spin iron(II) complex, which exhibits parameters between $FeSO_4{\cdot}7H_2O$ ($\Delta = 3.22$, $\delta = 1.26$)[23] and high spin iron

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† Electronic supplementary information (ESI) available: powder XRD data for $Fe(phen)SO_3{\cdot}3H_2O$. See http://www.rsc.org/suppdata/dt/b2/b205625a/

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DOI: 10.1039/b205625a

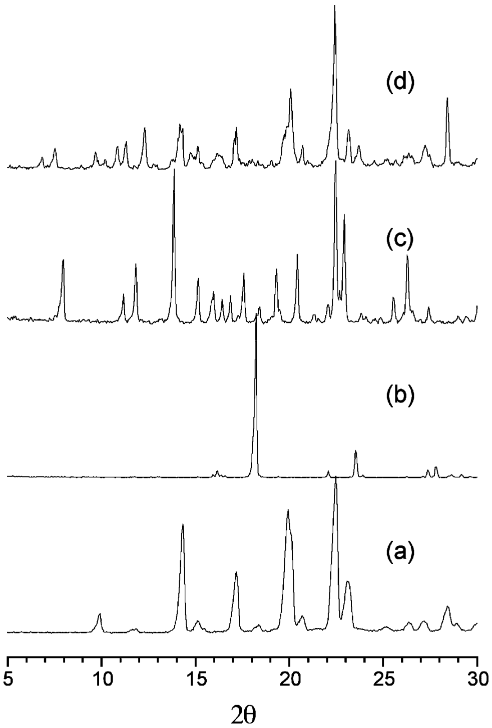

Fig. 1 Powder X-ray diffraction patterns of (a) 1,10-phenanthroline; (b) $FeSO_4 \cdot 7H_2O$; (c) $Fe(phen)(H_2O)_3SO_4$; (d) $Fe(phen)_3SO_4 \cdot 5H_2O$.

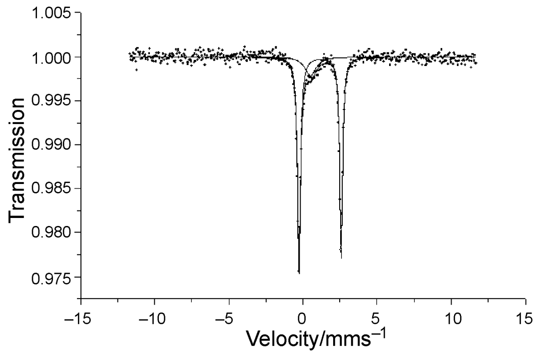

Fig. 2 Room temperature ^{57}Fe Mössbauer spectrum of $Fe(phen)(H_2O)_3SO_4$.

1,10-phenanthroline complexes ($\Delta = 2.1\sim3.0$, $\delta = \sim1.0$).[24–28] The Mössbauer parameters are also significantly different from the values obtained for $[Fe(phen)_3]^{2+}$ complexes ($\Delta = 0.15–0.58$, $\delta = 0.18–0.3$).[24,25,28,29]

The infrared spectrum in the region below 1300 cm^{-1} is particularly useful in probing the coordination of the sulfate ions. Free pyramidal sulfate anions exhibit only ν_3 and ν_4 infrared active vibrations, while coordinated sulfate ions show all four fundamental vibrations.[30] Fig. 3a shows the spectrum of final product, $Fe(phen)(H_2O)_3SO_4$, which exhibits all the four normal vibrations of coordinated SO_4^{2-} at 986 (ν_1), 472 (ν_2), 1042–1173 (ν_3, split) and 618 cm^{-1} (ν_4), which is consistent with a unidentate sulfate ligation. In contrast, the spectrum of $Fe(phen)_3SO_4 \cdot 5H_2O$ (Fig. 3b) shows that there are absorptions only at 1114 (ν_3) and 616 cm^{-1} (ν_4), which is consistent with the fact that the sulfate ions are not coordinated to the metal centre.

There are two more bands at 808 and 640 cm^{-1} compared to that of $Fe(phen)_3SO_4 \cdot 5H_2O$, which can be assigned to coordinated water molecules, because they have IR bands at around 800 (ρ_r) and 600 cm^{-1} (ρ_w) in addition to other common bands.[30]

The TG/DTA data show that the final red product does not lose weight up to 100 °C (Fig. 4). We then observe a one-step 12.6% weight loss between 100 and 180 °C caused by loss of the three water molecules (calculated value is 14.0%), which is supported by the thermal analysis of a similar compound, $[Ni(phen)(H_2O)_2(C_6H_5O_4)]$[31] further weight loss is caused by decomposition of the compound and combustion of the phenanthroline ligand above 300 °C, which is considerably higher than compared with the bis- or tris-phenanthroline complexes, which occur at 160~400 °C.[32–35] The total weight loss found (78.1%) is in accordance with the calculated value (79.2%, Fe_2O_3 as the final product).

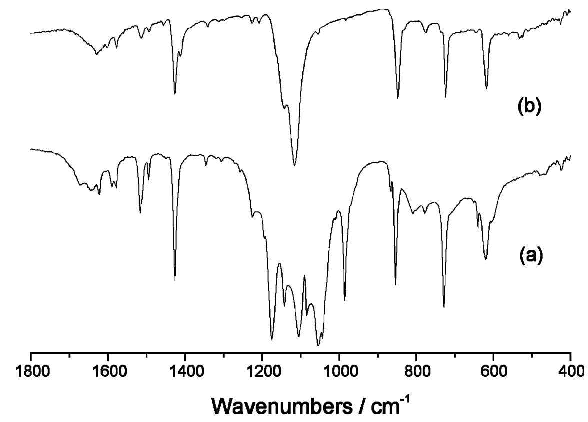

Fig. 3 Infrared spectra of: (a) $Fe(phen)(H_2O)_3SO_4$ and (b) $Fe(phen)_3SO_4 \cdot 5H_2O$.

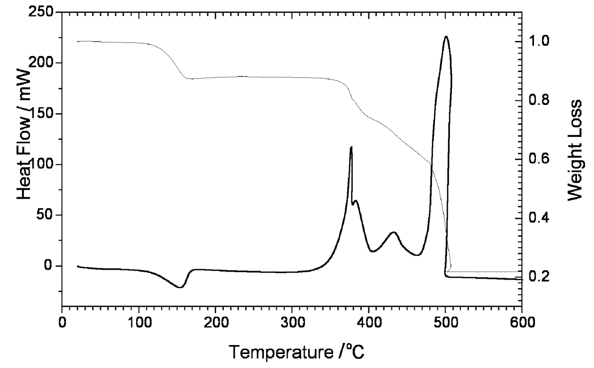

Fig. 4 TG/DTA data for $Fe(phen)(H_2O)_3SO_4$.

Taking all the data into consideration we believe that the final red product of the reaction is best formulated as $Fe(phen)(H_2O)_3SO_4$. All spectroscopic data suggest that this compound is a neutral molecule containing an octahedrally coordinated Fe(II) ions, in which the SO_4^{2-} anion acts as a unidentate ligand, and three water molecules and one 1,10-phenanthroline molecule occupy the other five coordination sites.

Mechanistic studies

We were interested in investigating the mechanism of this solid-state reaction, particularly as $[Fe(phen)_3]^{2+}[SO_4^{2-}]$ is the exclusive product in aqueous solution due to the high CFSE of the low spin $(t_{2g})^6$ Fe(II) configuration. The time-resolved, *in-situ* energy-dispersive X-ray diffraction (EDXRD) technique provides us with a powerful means to investigate solid-state reactions, since data can be obtained in short periods from large quantities (grams) of reacting solids in laboratory-sized reaction vessels. Fig. 5a shows a three-dimensional plot of the *in-situ* EDXRD data measured during the reaction at 70 °C. The reaction appears to begin immediately on mixing the solid reagents at room temperature, as evidenced by a colour change from pale green to red and indeed the time-resolved, *in situ* diffraction data shows no characteristic Bragg reflections of the crystalline starting materials (it should be noted that it takes ~2 minutes between mixing the reagents and commencing EDXRD data collection). At 70 °C the *in-situ* EDXRD data clearly show that the crystallisation is complete after 10 minutes. All the observed Bragg reflections in the final EDXRD spectrum can be indexed

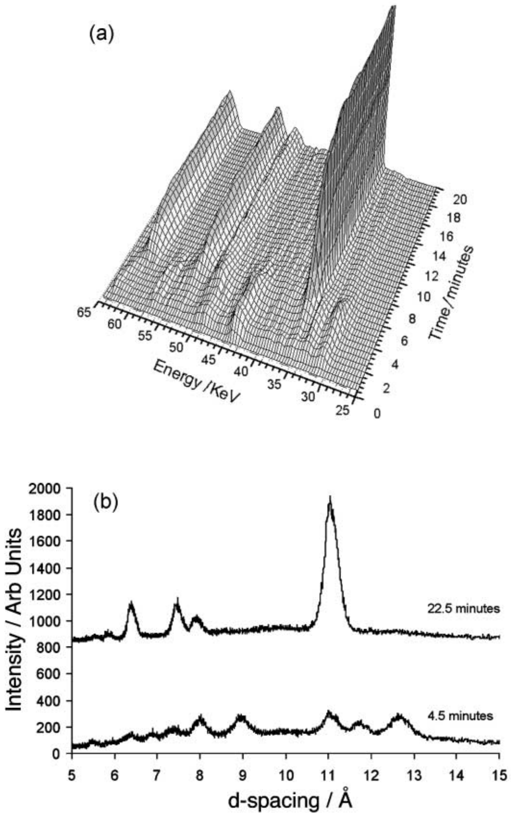

Fig. 5 (a) *In-situ* EDXRD patterns recorded during the reaction of $FeSO_4·7H_2O$ and 1,10-phenanthroline in the ratio 1 : 1 at 70 °C. (b) EDXRD spectrum taken after 4.5 minutes, and then after 22.5 minutes.

on the unit cell parameters of $Fe(phen)(H_2O)_3SO_4$. However, at the early stages of the reaction the EDXRD spectra show a series of Bragg reflections of a transient intermediate crystalline phase. Fig. 5b shows the EDXRD spectrum after 4.5 minutes, which is the point at which the integrated intensity of the Bragg reflections of the intermediate phase reaches their maximum, and after 22.5 minutes after which the EDXRD patterns show no further change. All of these diffraction features appear simultaneously and grow and decay at the same time, suggesting that they are all due to a single phase. The Bragg reflections of the intermediate may be indexed using the unit cell parameters of $Fe(phen)_3SO_4·5H_2O$, in addition the spectrum contains a few low intensity Bragg reflections that may be assigned to the final product. It should be noted that the relative intensities of the Bragg reflections in the EDXRD data and the *ex-situ* angular-dispersive measurements do not match, since the former data are affected by the energy profile of the incident white beam X-rays, absorption and the latter by preferred orientation effects.

In order to confirm that $Fe(phen)_3SO_4·5H_2O$ is in fact a precursor to $Fe(phen)(H_2O)_3SO_4$, the reaction between the former compound and $FeSO_4·7H_2O$ was investigated. 2 mmol of $FeSO_4·7H_2O$ was mixed with 1 mmol of $Fe(phen)_3SO_4·5H_2O$, finely ground and heated at 70 °C for 2 hours. Powder X-ray diffraction data (Fig. 6) show that $Fe(phen)(H_2O)_3SO_4$ is the final product.

The *in-situ* EDXRD experiments were also performed at 50, 60 and 80 °C. Fig. 7 shows the data obtained by integrating the relevant Bragg reflections belonging to crystalline $Fe(phen)_3SO_4·5H_2O$ and $Fe(phen)(H_2O)_3SO_4$ respectively. At 50 °C it can be seen that $Fe(phen)_3SO_4·5H_2O$ crystallisation is complete after one hour, but the second step of crystallisation of $Fe(phen)(H_2O)_3SO_4$ has not yet commenced. However, as the reaction temperature is increased, both steps are completed after 40 minutes at 60 °C, 10 minutes at 70 °C and 6 minutes at 80 °C respectively, the intermediate $Fe(phen)_3SO_4·5H_2O$ is present for shorter and shorter times as the temperature is raised.

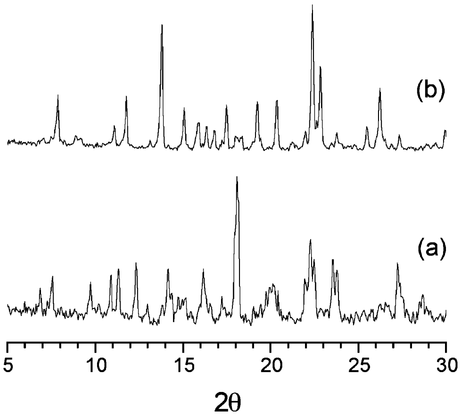

Fig. 6 Powder XRD patterns for: (a) a mixture of $FeSO_4·7H_2O$ and $Fe(phen)_3SO_4·5H_2O$ in a 2 : 1 molar ratio at rt and (b) after heating at 70 °C for 2 hours.

DSC measurements have also been recorded on this solid–solid reaction, in order to provide complementary data about the course of the reaction. Fig. 8a shows the DSC data when finely ground $FeSO_4·7H_2O$ with 1,10-phenanthroline are heated in a 1 : 1 molar ratio. The reaction exhibits two heat flows between 50 and 59 °C, followed by a sharp endothermic peak at 63.5 °C. There are no other thermal processes observed on further heating or cooling. Since $FeSO_4·7H_2O$ loses water at around 68 °C (Fig. 8b), we believe that the endothermic peak is due to dehydration and the two exothermic features from the two successive reactions forming $Fe(phen)_3SO_4·5H_2O$ and $Fe(phen)(H_2O)_3SO_4$ respectively. The DSC data shows no other thermal events after the endothermic process: this is also in accordance with the TG/DTA data (Fig. 4).

An interesting point is why does $Fe(phen)_3SO_4·5H_2O$ crystallise first rather than $Fe(phen)(H_2O)_3SO_4$ as might be expected from a stepwise reaction? $Fe(phen)_3SO_4·5H_2O$ may be the kinetic product as the Fe(II) centre in $FeSO_4·7H_2O$ is coordinated by only aquo ligands and these may be more readily displaced in the solid state by other neutral *o*-phenanthroline ligands. Other reaction pathways would require significant anion mobility.[16–18] In fact, this trend has already been employed to prepare some $Fe(phen)_2X_2$ complexes.[32,34,36] For example, significantly higher temperatures are required for the decomposition of $Fe(phen)_3X_2$ (X = Cl, Br) complexes.

Conclusions

Solid $FeSO_4·7H_2O$ and 1,10-phenanthroline react rapidly in the solid-state to produce crystalline $Fe(phen)(H_2O)_3SO_4$. The spectroscopic data suggest that $Fe(phen)(H_2O)_3SO_4$ is an octahedral Fe(II) complex containing a unidentate sulfate, and the other five coordination sites are taken by a bidentate 1,10-phenanthroline ligand and three water molecules.

The *in situ* EDXRD data and DSC studies highlight the rapidity of the reaction, and show that $Fe(phen)(H_2O)_3SO_4$ is produced after crystallisation of $Fe(phen)_3SO_4·5H_2O$. Surprisingly, $Fe(phen)(H_2O)_3SO_4$ appears to be the thermodynamically favoured phase in the solid state while $Fe(phen)_3SO_4·5H_2O$ is the thermodynamic product in solution.

Experimental

Synthesis

$Fe(phen)(H_2O)_3SO_4$. $FeSO_4·7H_2O$ and 1,10-phenanthroline, were purchased from Aldrich and used after being ground and passed through a 120 μm sieve. 1 mmol each of the starting materials were weighed accurately and mixed thoroughly in a

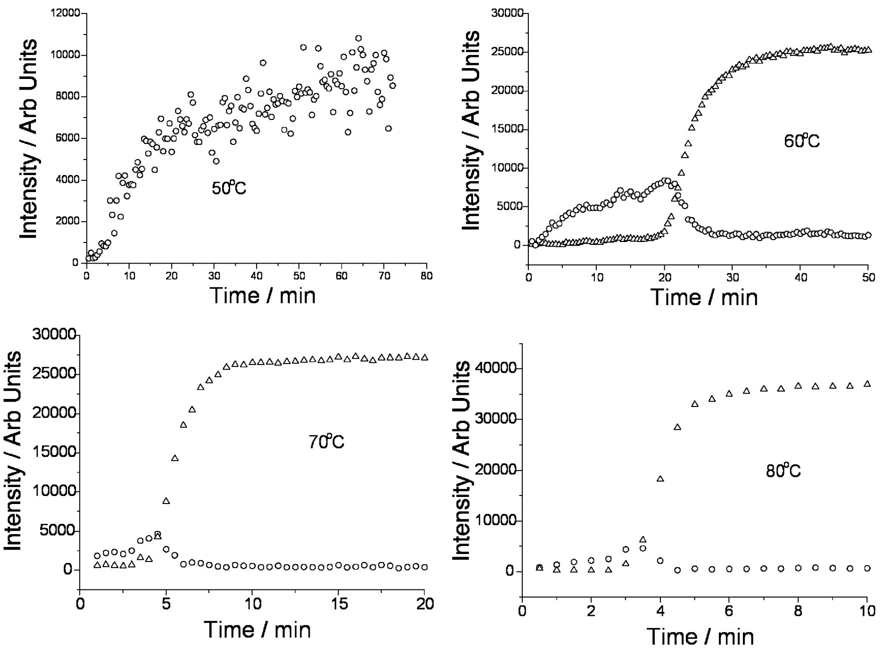

Fig. 7 Time dependence of the integrated intensity of the 001 Bragg reflection of $Fe(phen)_3SO_4{\cdot}5H_2O$ (○) and $Fe(phen)(H_2O)_3SO_4$ (△) at 50, 60, 70 and 80 °C.

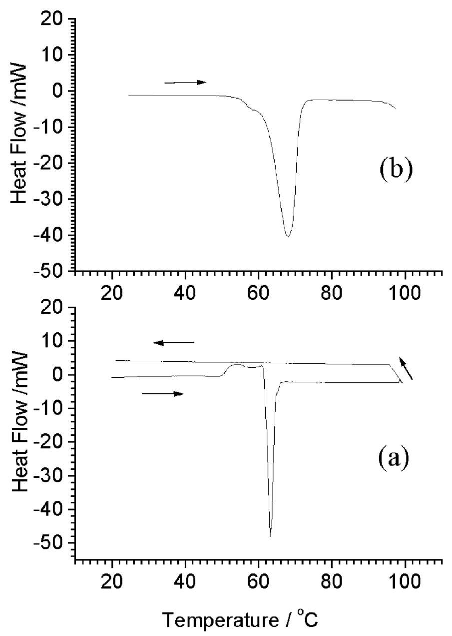

Fig. 8 DSC curves obtained for: (a) 1 : 1 mixture of finely ground solid $FeSO_4{\cdot}7H_2O$ and 1,10-phenanthroline and (b) solid $FeSO_4{\cdot}7H_2O$.

mortar with a pestle. The mixture was transferred into a tube with a cover, and placed in an oven maintained at a set temperature until the reaction was verified to be complete by powder X-ray diffraction measurements on small samples of the reaction mixture. The palely coloured starting materials (green $FeSO_4{\cdot}7H_2O$ and colourless 1,10-phenanthroline) were observed to form a red crystalline product. Although the reaction took place at room temperature, temperatures of 60–80 °C were necessary for the reactions to reach completion. Microanalysis was performed to estimate the water content in the compound. Found(calculated) for $Fe(phen)(H_2O)_3SO_4$ were: Fe: 14.18(14.46); C: 37.23(37.32); H: 3.62(3.65); N: 7.21(7.25)%.

$Fe(phen)_3SO_4{\cdot}5H_2O$. Was synthesised both in the solid state and in solution. The solid-state synthesis was similar to the synthesis of $Fe(phen)SO_4{\cdot}3H_2O$, but a molar ratio of 1 : 3 was used for the salt to ligand. The solution method was performed as follows: 10 mmol of $FeSO_4{\cdot}7H_2O$ were dissolved in 5 ml of deionised water, and 30 mmol of 1,10-phenanthroline were added to the solution. The solution was then stirred on a hot plate stirrer maintained at 70 °C until all the phenanthroline dissolved. To this was added 10 ml of acetone and the precipitate formed was filtered and washed with acetone and dried in air. The XRD patterns and the microanalysis showed that the products from both methods were the same and in accordance with $Fe(phen)_3SO_4{\cdot}5H_2O$. Found(calculated): C: 55.57(55.25); H: 4.56(4.38); N: 10.83(10.74); Fe: 7.13(7.14); S: 4.14(4.10) for the solid method; C: 55.58(55.25); H: 4.57(4.38); N: 11.10(10.74); Fe: 6.76(7.14); S: 4.24(4.10)% for the solution method.

Characterisation

Powder X-ray diffraction data were measured using a Philips PW1710 diffractometer using Cu-Kα radiation ($K_{\alpha 1}$ = 1.5406 Å and $K_{\alpha 2}$ = 1.5444 Å) in Bragg–Bretano geometry. Materials were finely ground and pressed into a flat aluminium sample holder. Diffraction data were recorded over the angular range 2θ = 5–70° with a step of 0.02°. A ^{57}Fe Mössbauer spectrum of the powdered sample of $Fe(phen)SO_4{\cdot}3H_2O$ was recorded in transmission geometry using a *ca.* 50 mCi $^{57}Co/Rh$ source with a multiscaler of 512 channels in constant acceleration mode at the Open University, UK. All the isomer shift data are quoted relative to the centroid of the metallic iron spectrum at room temperature. Thermogravimetric analysis was performed using a STA-1500H thermal analyser in a static air, over the temperature range 25 to 1000 °C and with a heating ramp of 2 °C min^{-1}. Infrared spectra were recorded on a Nicolet FTIR-170sx spectrometer in the range 400–4000 cm^{-1}, from samples pressed into KBr discs. Elemental analysis was performed by the analytical services at the Inorganic Chemistry Laboratory, Oxford. A Sataram micro-DSC was used to observe *in situ* DSC curves with sealed cells, Al_2O_3 as reference. The reaction mixture in a sealed cell of 1 cm^3 heated at 1 °C min^{-1} to 100 °C then back (the calorimeter can only be operated between 0 and 100 °C). The data were collected every 30 seconds. 0.5 mmol each of $FeSO_4{\cdot}7H_2O$ and 1,10-phenanthroline were used. *In-situ* energy-dispersive X-ray diffraction experiments were performed on the Station 16.4 of the SRS at the Daresbury Laboratory, UK. Station 16.4 receives X-ray continuous in the energy range 10–120 keV, and is designed for experiments that require white-beam X-rays. In the energy-dispersive X-ray diffraction experiment the diffracted X-ray beam is measured by a fixed-angle solid-state germanium detector; this allows rapid data accumulation (of the order of seconds), and for data to be collected from large volumes of sample.[37,38] The station is equipped with a heating apparatus so that data may be collected from reacting materials at elevated temperature.[39] In the current work, mixtures of 1 mmol each of $FeSO_4 \cdot 7H_2O$ and 1,10-phenanthroline were finely ground and placed in a Pyrex tube with 1 mm thick walls. Temperatures of around 70 °C were chosen for the reactions studied here; this meant that reactions reached completion in a reasonable amount of time, but that there was sufficient time to record representative spectra at each stage of reaction. Spectra were recorded every 30 seconds.

Acknowledgements

The authors would like to thank Professor F. J. Berry at The Open University, UK, who measured the Mössbauer spectrum of the iron compound, the National Natural Science Foundation of China for financial support, and the EPSRC for provision of synchrotron beam time at Daresbury Laboratory, UK. L. L. also thanks the Royal Society for the award of an FCO Chevening Fellowship.

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