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The role of short-range diffusion in solvent-assisted mechanochemical synthesis of metal complexes†

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The role of short-range diffusion in solvent-assisted mechanochemical synthesis is demonstrated in studies of a polymorphic transition and a ligand dissociation reaction involving copper(I) thiocyanate complexes.

There is considerable current interest in the subject of solvent-free synthetic chemistry.[1–3] The main basis for this interest is the potential reduction in environmental contamination and the increased convenience associated with the elimination of solvent from synthetic reactions.[1,2] One method of achieving this is by grinding the solid reactants together (mechanochemistry), and this has shown promise as a solvent-free synthetic method for the preparation of a variety of metal complexes.[1,2] The possible benefit of including a minor amount of solvent in such reactions has been reported,[4] and we have recently shown that this can result in a dramatic increase in the rate of formation of product in the reaction of metal compounds with ligands to form metal coordination compounds.[5]

Little is known about the mechanisms of mechanochemical reactions. In the case of a reaction involving two or more reactants, it seems obvious that grinding the reactants together produces a mixture in which the reactants are in more intimate contact, hence facilitating reaction between them. However, this does not shed any light on the detailed mechanisms of the reactions involved. In order to examine this question further, we have examined the mechanochemistry of two kinds of reaction in which there is only one reactant, so that improved intimacy of contact between different reactants by grinding is not a factor. The two kinds of reaction that we have studied are polymorphic transitions and ligand dissociation reactions. In the first of these a single compound is converted to a different polymorph of the same compound while in the second a single compound dissociates into two different compounds. The systems chosen for study involve complexes of copper(I) thiocyanate with triphenylphosphine and pyridine. The use of thiocyanate as a ligand provides a useful probe to follow the reactions *via* infrared spectroscopy, by monitoring changes in the ν(CN) vibrations.

As an example of a polymorphic transition we have used the complex $[CuSCN(PPh_3)_2]_2$. The structure of this compound as crystallized from dichloromethane solution shows that it is a centrosymmetric doubly thiocyanate-bridged dimer.[6] We have found that crystallization of this compound from pyridine produces a different polymorph in which the molecular structure is closely similar to the one previously determined,[6] but is not centrosymmetric. The X-ray crystal structure of this polymorph is shown in Fig. 1.‡ The IR spectrum of this compound in the ν(CN) region (Fig. 2(a)) shows two bands at 2082, 2104 cm^{-1}, consistent with the presence of two inequivalent thiocyanate groups. Grinding of the dry crystals produced no change in the IR spectrum. However, addition of a very small amount of acetonitrile, just sufficient to allow the formation of a paste during grinding, followed by a few minutes standing of the product in air to allow evaporative removal of the acetonitrile from the resulting paste of product, resulted in the complete conversion of the compound to the symmetrical polymorph. The IR spectra recorded after three such treatments carried out successively on the same sample show that this did not occur to any perceptible extent with one such treatment (Fig. 2(b)), but that the conversion to the centrosymmetric polymorph was complete after three treatments, resulting in a single ν(CN) band at 2095 cm^{-1} (Fig. 2(d)).§

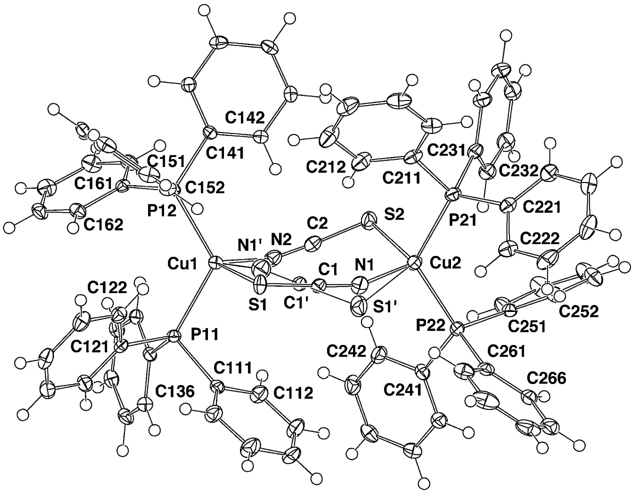

Fig. 1 Structure of the unsymmetrical polymorph (monoclinic $P2_1/c$) of $[CuSCN(PPh_3)_2]_2$. Cu(1)–P(11,12),S(1),N(2,1′) are 2.2665, 2.2569(5), 2.4389(7), 2.018(2), 1.99(1); Cu(2)–P(21,22),S(2,1′),N(1) are 2.2714, 2.2636(5), 2.4746(5), 2.561(4), 1.945(2) Å.

As an example of a ligand dissociation reaction we have used the complex $[CuSCN(PPh_3)(py)_2]$ (py = pyridine). This is a yellow compound formed in the reaction of CuSCN with PPh_3 in a 1 : 1

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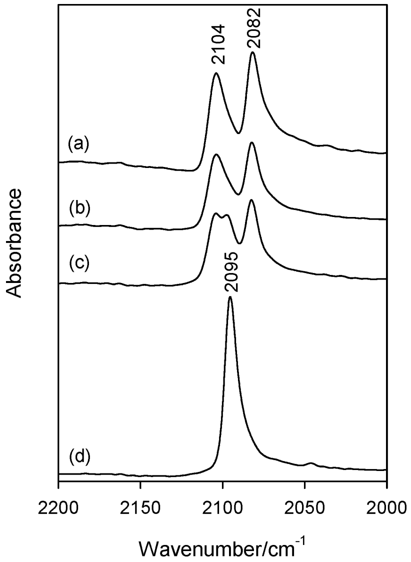

Fig. 2 IR spectra in the CN stretching region of the unsymmetrical polymorph (monoclinic $P2_1/c$) of $[CuSCN(PPh_3)_2]_2$ (a) untreated, and (b)–(d) after successive treatments with acetonitrile and grinding.

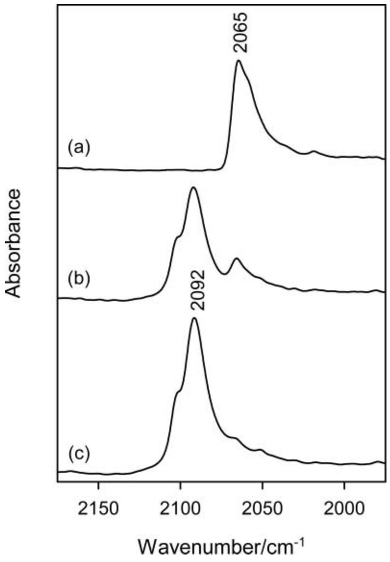

Fig. 3 IR spectra in the CN stretching region of $[CuSCN(PPh_3)(py)_2]$ (a) untreated, and (b), (c) after successive treatments with acetonitrile and grinding.

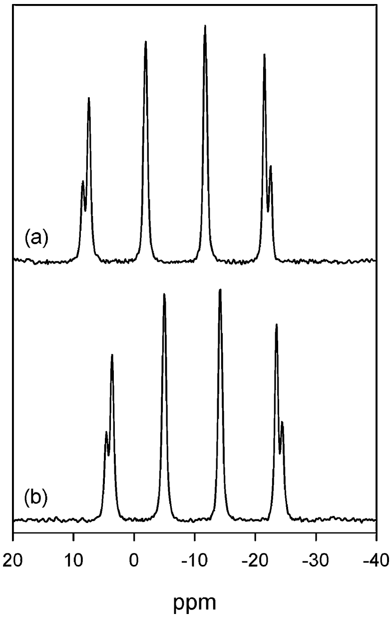

Fig. 4 ^{31}P CPMAS NMR spectrum of $[CuSCN(PPh_3)(py)_2]$ (a) after dry grinding, and (b) after grinding with acetonitrile.

mole ratio in pyridine, and is a four-coordinate mononuclear complex.[7] It can also be prepared from a 1 : 2 vol/vol mixture of pyridine and acetonitrile, and washing of the product with acetonitrile causes no change in the composition of the compound. However, addition of a very small amount of acetonitrile, just sufficient to allow the formation of a paste during grinding, followed by a few minutes standing of the product in air to allow evaporative removal of acetonitrile and pyridine from the resulting paste of product, results in the complete conversion of the compound to the colourless complex $[CuSCN(PPh_3)(py)]$ with loss of 1 mole of pyridine.§ This was confirmed by IR spectroscopy, and by gravimetric and elemental analysis. The IR spectra recorded after two such treatments carried out successively on the same sample (Fig. 3) show that most of the conversion occurs after the first treatment, and that it is complete after the second treatment. The ^{31}P CP MAS NMR spectrum of the final product (Fig. 4(b)) shows that it is a pure, homogeneous phase with a single copper environment. An attempt to prepare the same compound by recrystallization of $[CuSCN(PPh_3)(py)_2]$ from hot acetonitrile was unsuccessful, and heating of $[CuSCN(PPh_3)(py)_2]$ to 120 °C resulted in the loss of both pyridine molecules and the formation of a mixture of symmetrical $[CuSCN(PPh_3)_2]_2$ and CuSCN, identified by IR spectroscopy. Thus it appears that the solvent-assisted mechanochemical reaction readily yields a product that is not easily obtainable by other synthetic methods, a point that we have already noted in a previous study.[5]

It is clear from the results in Fig. 2 and 3 that both reactant and product phases are present in the reaction mixture at intermediate stages of the reaction, so material has to physically move from the reactant phase to the product phase during the reaction. We propose that the reactions involve dissolution of the reactant in the solvent and subsequent precipitation of the product within the voids between the particles of reactant. The two possible mechanisms of mass transport from the reactant to the product phase are convection and diffusion. However, convection requires movement of the liquid relative to the solid phase, and this is minimized by the very small amount of solvent used in our experiments. Also, the movement of solvent relative to a solid is zero at the solid/liquid interface, so that mass transport across the interface can only occur by diffusion. This clearly focuses attention on the importance of molecular diffusion in the reaction mechanism.

Over distances of the order of centimetres, typical of the size of reaction vessels used in conventional solution-based chemical synthesis, diffusion is slow and quite ineffective relative to convection, hence the need for stirring to dissolve substances, for example. However, in mechanochemical synthesis, the diffusion takes place within the inter-particle voids, whose size is comparable to the particle size when the amount of solvent is sufficiently small to form a paste. Assuming a typical value for the diffusion coefficient of a molecule in solution ($D = 0.5 \times 10^{-9}$ m^2 s^{-1}), and a mean diffusion path length of the order of the particle size (say d = 0.1 mm), the diffusion time ($t = d^2/2D$) is 10 s. This is clearly compatible with the short reaction times that we have observed in our present and previous studies.[5]

The factors that determine the rate of mass transport by diffusion, and hence the reaction rate, are as follows:

(1) Diffusion medium. Addition of a small amount of solvent in which the reactant is soluble provides a clearly identifiable medium in which diffusion can take place. The transport rate will increase with increasing solubility of the reactant in the solvent.

(2) Surface area. Since diffusion takes place from the surface of the solid, an increase in surface area results in an increase in transport rate. Reduction of the particle size d (by grinding) increases the solid surface area, and it can easily be shown that the surface area of a given amount of a powdered substance is proportional to $1/d$.

(3) Diffusion path length. The rate of diffusion is inversely proportional to the square of the diffusion path length, so that a reduction in the diffusion path length results in a large increase in diffusion rate. The diffusion path length is reduced by using the minimum amount of solvent and by reducing the particle size (by grinding). The kinetics of diffusion are such that the diffusion rate is proportional to the inverse square of the diffusion path length[8] and hence, according to the above, to $1/d^2$.

Combining factors (2) and (3) leads to a very strong ($1/d^3$) dependence of transport rate on paticle size, which provides an explanation for the dramatic increase in conversion with successive periods of grinding that is suggested by the IR data in Fig. 2(b)–(d). The dramatic increase in reaction rate that we observe upon addition of a very small amount of a suitable solvent and reducing the reactant particle size by grinding is clearly consistent with the key role played by diffusion in the reaction mechanism.

Further consideration of factor number (1) above raises the question of the relevance of the diffusion mechanism in "dry" (solvent-free) mechanochemical reactions. Diffusion can take place in solids as well as in fluids, but the diffusion rate under normal conditions is negligible. The diffusion coefficient can however be increased by increasing the temperature, and an increase in temperature can be caused by frictional heating of the solid during high energy mechanical milling in a ball mill. This has been suggested before,[9] and provides a possible explanation for the role of frictional heating in dry mechanochemical synthesis, where a number of mechanisms involving mass transport have been suggested in cases where the heating is insufficient to cause melting.[1,2,10]

It is also possible that enhancement of diffusion by frictional heating is not necessary in some of the previously reported solvent-free mechanochemical reactions, because the enhancement may be caused by the presence of small amounts of adventitious solvent, *i.e.* they are actually solvent-assisted reactions. A case in point is the reaction between nickel(II) nitrate hexahydrate and phenanthroline;[1,2,11] this reaction produces water as a by-product, and this can act in the same way as added solvent. It is interesting to note that the reported very short reaction time (2 min) is similar to the times that we have observed in our solvent-assisted reactions.

The above arguments clearly indicate the need for a clearer focus on the role of molecular diffusion in mechanochemical reactions. This allows an understanding of observations that are otherwise difficult to comprehend, and suggests ways in which the scope of mechanochemistry can be considerably extended.

Acknowledgements

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Notes and references

‡ Crystal data: $C_{74}H_{60}Cu_2N_2P_4S_2$, M = 1292.3. Monoclinic, $P2_1/c$, a = 23.6170(4), b = 13.5021(2), c = 20.1922(3) Å, β = 105.453(2)°, V = 6206 Å^3, T *ca.* 100 K. 26401 unique CCD reflections ($R_{\text{int}} = 0.058$; 14188 > $2\sigma(I)$), $R1 = 0.041$, $wR2 = 0.103$. A disordered component was resolved for SCN(1), major, minor site occupancies refining to 0.828(2) and complement; no disorder was discernible elsewhere in the structure. The phase is isomorphous with its azide counterpart.[12]

§ About 0.1 mmol of compound was ground using an agate mortar and pestle of the type normally used to prepare samples for IR spectroscopy. For the solvent-assisted reactions 1 drop of solvent was added using a small pipette. The solvent was removed after grinding for about two minutes by allowing the mixture to stand for a few minutes in air at ambient temperature. No reaction was observed if large crystals of the reactant were treated with solvent without grinding. IR spectra were recorded on dry powders using a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a Universal ATR sampling accessory. The ^{31}P CPMAS NMR data were acquired at 9.4 T on a Bruker MSL-400 spectrometer operating at a ^{31}P frequency of 161.92 MHz.

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