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What goes on in sub-critical solvothermal synthesis of metal ion complexes?

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The remarkable success of solvothermal methods in providing an extraordinary range of new materials has somewhat obscured the fact that much of the underlying chemistry remains ill-understood. This is true, particularly in sub-critical solvothermal syntheses yielding coordination polymers and frameworks, making product selection and optimisation of yields a matter of empirical variations in reactant mixtures and reaction conditions. There are, however, many indications within known observations of the operation of factors that could be better understood by their independent direct study under solvothermal conditions. This article provides some suggestions to identify such factors.

1. Introduction

Two important steps in the development of metal ion coordination chemistry were the distinction of "*inert*" and "*labile*" complex ion species first proposed by Henry Taube[1,2] and the subsequent quantification of labile species of this distinction initiated by Manfred Eigen[3,4] and expanded in particular for the lanthanides by André Merbach.[4] Although there is not a simple dichotomy, and rate constants for water ligand exchange in metal aqua ions as reference species at room temperature vary over a range of nearly 10^{20} s^{-1},[5] Taube's simple differentiation of labile complexes as those where ligand substitution occurred within the time it takes to mix the reagents, while inert complexes required observably longer periods, remains practically important in synthesis design. It is not, of course, the only consideration, and the development of the procedures referred to as "solvothermal" synthesis of coordination complexes, polymers and frameworks has depended on the recognition of many other factors surveyed, for example, in ref. 6–22. The terms "solvothermal" and "hydrothermal", with the latter limited to cases where water is the sole solvent present, qualify the syntheses of a huge variety of materials other than metal ion complexes and involve conditions, in particular of temperature and pressure, that can also vary over a great range.[23–31] The following discussion is, however, limited to that of the sub-critical solvothermal synthesis of metal ion complexes, as it has become a standard technique of materials chemistry and because there are fundamental aspects which warrant further study in order to be fully exploited.

Solvothermal methods in general[29,30] are characterised by the fact that they are conducted in closed vessels under autogenous pressure at temperatures which are close to or considerably exceed the boiling point of the solvent, very commonly a mixture of liquids with quite different solvation capacity. When the temperature is below the critical temperature of the solvent, the method can be termed "sub-critical solvothermal synthesis".[20] Its application in metal ion coordination chemistry can be seen as a first logical step beyond "classical" procedures in which a metal ion source and a ligand are dissolved, by heating if necessary, under ambient pressure, in a solvent, and efforts are then made to isolate any product, most simply by cooling the reaction mixture. Such simple and familiar procedures work particularly well for labile metal ion complexes of unit or low nuclearity but are of limited utility for the synthesis of polymers and frameworks where, for example, rapid precipitation at relatively low temperatures leads to amorphous or heterogeneous products or where polymer formation depends on relatively slow assembly processes such as hydrolytic condensation.[9] In effect, sub-critical solvothermal synthesis provides a simple means of extending the temperature range of solution reactions, ideally a range in which decomposition of organic reagents can be ignored. Table 1 provides an indication of the diversity of systems and a range of experimental details known for this method.[32–44] It is a method largely compatible with what has been said of metal–organic (coordination) framework (MOF) synthesis that "The main goal in MOF synthesis is to establish the synthesis conditions that lead to defined inorganic building blocks without decomposition of the organic linker. At the same time, the kinetics of crystallisation must be appropriate to allow nucleation and growth of the desired phase to take

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Table 1 A representative selection of the conditions employed in the sub-critical hydro/solvothermal syntheses of coordination complexes

Metal(s)	Ligand(s)	Solvent(s)	$T_r{}^a$/°C	$t_r{}^b$	$T_{coll}{}^c$	n^d	Ref.
Cu(I)	4,4′-Bipyridine	H_2O	140	2 d	RT	1	32
Co(II), Cu(II), Zn(II)	5-Diacetatoamino-isophthalate	CH_3OH/H_2O (1 : 1)	90	3 d	RT	3	33
Cr(III), Mn(III)	O^{2-}	Acetone	200	3 d	RT	2	34
U(VI)	CB6, CB7, CB8,^{e} aliphatic dicarboxylates	H_2O	180	14 d	RT	6	35
Pb(II) + K(I), Rb(I), or Cs(I)	Isophthalate, 4,4′-biphenyldisulfonate	DMF^f/CH_3OH (2 : 1)	150	3 d or 3 h	RT	5	36
Bi(III)	Pyridine-2,6-dicarboxylate	DMF, CH_3OH or C_2H_5OH	100 and 125	3 d	RT	6	37
Zr(IV)	Tetrakis(4-carboxyphenyl)-porphyrin	DEF^g	120	12 h	RT	2	38
Th(IV)	Terephthalate	DMF, H_2O or DMF/H_2O					39
Zn(II)	5-((4-*tert*-Butyl)-phenylazo)isophthalate, 1,2-di(4-pyridyl)ethene	C_2H_5OH/H_2O (1 : 1)	120	24 h	RT	1	40
U(VI) + Co(II), Cu(II), Zn(II), or Cd(II)	2,2′-Bipyridine-4,4′-dicarboxylate	H_2O	200 or 150	3 d	RT	7	41
Ln(III) Y(III)	F^-	Ethylene glycol/H_2O various ratios	190	12 h	RT	3	42
U(VI)	Zwitterionic and anionic dicarboxylates	H_2O/CH_3CN (3 : 1) or H_2O/DMA^h (3 : 1)	140	1–14 d	140	7	43
Sc(III)	Thiophenedicarboxylate, nitrate	CH_3CN/H_2O (1 : 1)	100	3 d	RT	1	44

[a] T_r = reaction temperature. [b] t_r = period of heating at T_r. [c] T_{coll} = temperature at which products were collected (not necessarily that at which crystallisation first occurred). [d] n = number of different products prepared. [e] CB = cucurbituril. [f] DMF = dimethylformamide. [g] DEF = diethylformamide. [h] DMA = dimethylacetamide.

place".[14] Crystallisation of the product is not just desirable to establish its purity but more importantly to enable X-ray crystal structure determination, crucial to an understanding of the product properties, and this of course is also the case for molecular complexes and coordination polymers (CPs).

In practice, the use of sub-critical solvothermal synthesis of metal ion complexes, CPs and MOFs in particular, has been associated principally with two needs. One is that of obtaining a homogeneous solution of both a metal ion source and a ligand (or a ligand source) and the other is that of producing a crystalline product suitable for structure determination by X-ray methods. The former is important in achieving the latter but neither step is free of complications.

2. Influence of the solvent used in sub-critical solvothermal reactions

The importance of both the physical and chemical properties of the solvent employed in solvothermal syntheses in general has been discussed in several reviews.[9,14,15,20,23,31,45,46] One physical property that is unlikely to be of significance in sub-critical syntheses is the solvent vapour pressure. This determines the actual pressure, usually simply defined as "autogenous", inside the container being heated and this is also determined by the fraction of the container volume occupied by the liquid reaction mixture.[20,31] While this occupancy factor is not always explicitly noted in reports of sub-critical syntheses, where it is (*e.g.* ref. 35), it is well below full, meaning that pressures would typically be ~1 MPa, well below values (~GPa) that might have a significant influence on chemical equilibria or kinetics.[31,47] What is a critical solvent property, of course, is the capacity to form a solution of the chosen reactants from which the desired reaction product can be precipitated. It is quite commonly the case that metal ion and ligand sources have very different solubility characteristics, a perhaps extreme example being found in the formation of coordination polymers involving porphyrins and polyoxometallates.[48] The capacity to dissolve a wide range of compounds of greatly different polarity is a characteristic of dipolar aprotic solvents[49,50] such as dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), acetonitrile (AN), *N*-methylpyrrolidinone (NMP) and tetrahydrofuran (THF), all of which are Lewis bases and have a well-explored coordination chemistry,[51,52] certainly one factor favouring their capacity to dissolve metal ion sources. Significantly, such solvents are also water-miscible, meaning it is possible to mix an aqueous solution of a metal ion source with a dipolar aprotic solvent solution of a ligand source without phase separation resulting, and mixtures of water or hydrolytic species such as alcohols with dipolar aprotic solvents are the most common media employed in sub-critical solvothermal syntheses. This adds a level of complexity to synthesis design, since it has long been known[50] that different mixtures of the same two solvents can have quite different properties and indeed systematic variation of the solvent mixture composition used in sub-critical solvothermal syntheses has been shown to give rise to quite different products in a variety of different systems.[9,39,42,53–58] This work, however, has proceeded in an essentially empirical manner,[59] since the study of solvation in mixed solvents has been largely limited to temperatures and pressures below those employed in solvothermal syntheses.[60,61]

The sensitivity of solvothermal synthesis to variations in the mixing ratio of two solvents in the whole reaction mixture is mirrored in its sensitivity to changes in one component (usually the dipolar aprotic solvent).[6–22] In many instances, this can be considered as simply a consequence of the incorporation (or not) of the solvent in the product crystals through direct coordination or weak interactions such as H-bond acceptance, thus giving materials with different compositions and therefore different structures. In many other instances, this is but part of the story. The fact that the product of a solvothermal synthesis is not necessarily the same as the product obtained from the same reactants under other conditions[9,62,63] is an indication of the special nature of solvothermal synthesis. It is rather difficult, however, to define why it is special because in the majority of instances only the crystal structure of the product is available as a guide to the chemistry leading to it and this can result, as noted early on,[64,65] in reports which are purely speculative. This is not to say that efforts to follow reaction during solvothermal treatment are unknown[29,30,65–67] but again they have been mainly focused on product formation and not upon any changes in the supernatant solution chemistry. Nonetheless intriguing examples of the former concern monitoring of the gradual formation of interpenetrated crystal structures,[68,69] interpenetration being a common feature of CP and MOF structures influencing their potential applications.[8,14,15,45]

To illustrate the difficulties involved in unravelling the many roles of the solvent in sub-critical solvothermal synthesis, it is convenient to consider the commonly employed (co)solvent *N*,*N*-dimethylformamide, DMF.[70] DMF is known to undergo reaction near its boiling point (153 °C) to give CO and $(CH_3)_2NH$ (dimethylamine), a reaction exploited in organometallic carbonylation reactions,[71] and suggested to be the reason for facilitating the synthesis of crystalline $[(CH_3)_2NH_2]_3[Ln(dipic)_3]$ complexes (Ln = lanthanide(III); dipic = pyridine-2,6-dicarboxylate) by simply boiling a solution of hydrated $LnCl_3$ with $dipicH_2$ in DMF for 1 hour.[72] DMF is also known to undergo rapid metal ion catalysed base hydrolysis,[73] though the reaction is relatively slow under acidic conditions.[74] The difference is that hydrolysis can be considered to give rise formally to dimethylammonium ion and formate, with the latter being a good ligand for metal ions in the higher oxidation states involved in most solvothermal syntheses. Consideration of the very large number of crystal structures involving dimethylammonium cations in the Cambridge Structural Database (CSD) shows that a large fraction involves crystal structures of CPs and MOFs produced in sub-critical solvothermal syntheses where DMF (or, in fewer cases, DMA) was used as a cosolvent. This could be taken in a positive sense as indicating that the utility of DMF (and other amides formed by dimethylamine) includes its capacity to provide a cation well-suited to the crystallisation of anionic CPs and MOFs, but the more important point to note presently is that, although the number of cases is a relatively small proportion of the total, there are instances where both formate and dimethylammonium are present in the isolated crystals and even some where formate is present without dimethylammonium. On this point, Table 2 refers to a selection of structures,[75–92] encompassing a wide range of metal ions and illustrating the range of compositions that can be observed for a single cation (uranyl ion), with some examples for DMA and AN as well as DMF. Fig. 1 provides an illustration of how solvent fragments

Table 2 Examples of the composition of structurally characterised complexes obtained by sub-critical solvothermal syntheses in which dipolar aprotic solvents and solvent fragments (bold letters) are found

Metal	Crystal composition[a]	Solvent	Refcode	Ref.
Cu(II)	$[\mathbf{(CH_3)_2NH_2}]_3[(Cu_4Cl)_3(BTC)_8]\cdot 9\mathbf{DMA}$	DMA	ABEMIF	75
Co(II)	$[\mathbf{(CH_3)_2NH_2}]_2[Co_2Cl_2(BTC)_{4/3}]$	DMA/AN	ABAYIO	76
Cd(II)	$[\mathbf{(CH_3)_2NH_2}]_4[Cd_2(TTCA)_2Cl_2]\cdot 7\mathbf{DMF}\cdot 2Diox\cdot 6H_2O$	DMF/dioxane	ADEGEY	77
Fe(II)	$[\mathbf{(CH_3)_2NH_2}][Fe^{II}_3(OH)(BPTC)_{1.5}(DMSO)_3]$	DMA/DMSO	BAZBIQ	78
Bi(III)	$[\mathbf{(CH_3)_2NH_2}]_4[Bi_2(PDC)_2(HPDC)_2]\cdot 2\mathbf{DMF}\cdot\mathbf{NH(CH_3)_2}$	DMF	AHEZEV	79
Eu(III)	$[\mathbf{(CH_3)_2NH_2}]_4[Eu_4(DDAC)_3(\mathbf{HCO_2})(OH_2)_2]\cdot 8\mathbf{DMF}\cdot 9H_2O$	DMF/H$_2$O	AZOXUL	80
Y(III)	$[\mathbf{(CH_3)_2NH_2}][Y(BTEC)(H_2O)]$	DMF/H$_2$O	ABUMUJ	81
U(VI)	$[UO_2(ADDC)(\mathbf{DMF})]$	DMF/H$_2$O	ZOZCEY	82
U(VI)	$[\mathbf{(CH_3)_2NH_2}]_4[(UO_2)_4(ADDC)_6]$	DMF/H$_2$O	ZOZCIC	82
U(VI)	$[\mathbf{(CH_3)_2NH_2}]_2[(UO_2)_2(ADDA)_3]\cdot 3H_2O$	DMF/H$_2$O	IHOGIX	83
U(VI)	$[\mathbf{(CH_3)_2NH_2}]_2[(UO_2)_2(KTA)_3]$	DMA/H$_2$O	QUKLAL	84
U(VI)	$[UO_2Pb(BTA)(\mathbf{HCO_2})(phen)]$	DMF/H$_2$O	OSOMOA	85
U(VI)	$[PPh_4][UO_2(R\text{-}CHDC)(\mathbf{HCO_2})]$	DMF/H$_2$O	COVSOY	86
U(VI)	$[\mathbf{NH_4}]_2[PPh_4]_2[(UO_2)_4(ADDA)_6]$	DMF/AN	YEXDAJ	87
U(VI)	$[Ni(R,S\text{-}Me_6cyclam)][UO_2(CAM)(\mathbf{HCO_2})_2]$	DMF/H$_2$O	JIVBAV	88
U(VI)	$[PPh_3Me]_3[\mathbf{NH_4}]_3[(UO_2)_6(CAM)_9]$	DMF/AN/H$_2$O	JIVBOI	88
U(VI)	$[UO_2(1,2\text{-}PDA)]\cdot\mathbf{CH_3CN}$	AN/H$_2$O	FUDNOK	89
U(VI)	$[C(NH_2)_3][\mathbf{(CH_3)_2NH_2}]_2[(UO_2)_3(TDC)_4(\mathbf{HCO_2})]$	DMF/H$_2$O	EWIQEJ	90
U(VI)	$[UO_2(ADP)(\mathbf{HCO_2})_2Cu(R,S\text{-}Me_6cyclam)]\cdot 2H_2O$	DMF/H$_2$O	YAPSUH	91
U(VI)	$[\mathbf{(CH_3)_2NH_2}]_2[(UO_2)_2(HTRT)_2(\mathbf{HCO_2})_2Ni(R,S\text{-}Me_6cyclam)]\cdot 2H_2O$	DMF/H$_2$O	VEXPEX	92
U(VI)	$[Hquin^b][(UO_2)_2(TRT)(\mathbf{CH_3CO_2})]$	AN/H$_2$O	VEXPIB	92

[a] Ligand abbreviations: BTC = benzene-1,3,5-tricarboxylate; TTCA = triphenylene-2,6,10-tricarboxylate; BPTC = 3,3′,5,5′-biphenyl-tetracarboxylate; PDC = pyridine-2,4,6-tricarboxylate; DDAC = aminoterphenyl-pentacarboxylate; BTEC = benzene-1,2,4,5-tetracarboxylate; ADDC = 1,3-adamantane-dicarboxylate; ADDA = 1,3-adamantane-diacetate; KTA = Kemp's triacetate = *cis*,*cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylate; phen = 1,10-phenanthroline; RCHDC = *R*,*R*-*trans*-1,2-cyclohexane-dicarboxylate; CAM = 1*R*,3*S*-camphorate; PDA = phenylene diacetate; TDC = thiophene-2,5-dicarboxylate; ADP = adipate = 1,6-hexanedioate; cyclam = 1,4,8,11-tetra-azacyclotetradecane; TRT = *R*,*R*-tartrate dianion. [b] Quin = quinuclidine = 1-azabicyclo[2.2.2]octane.

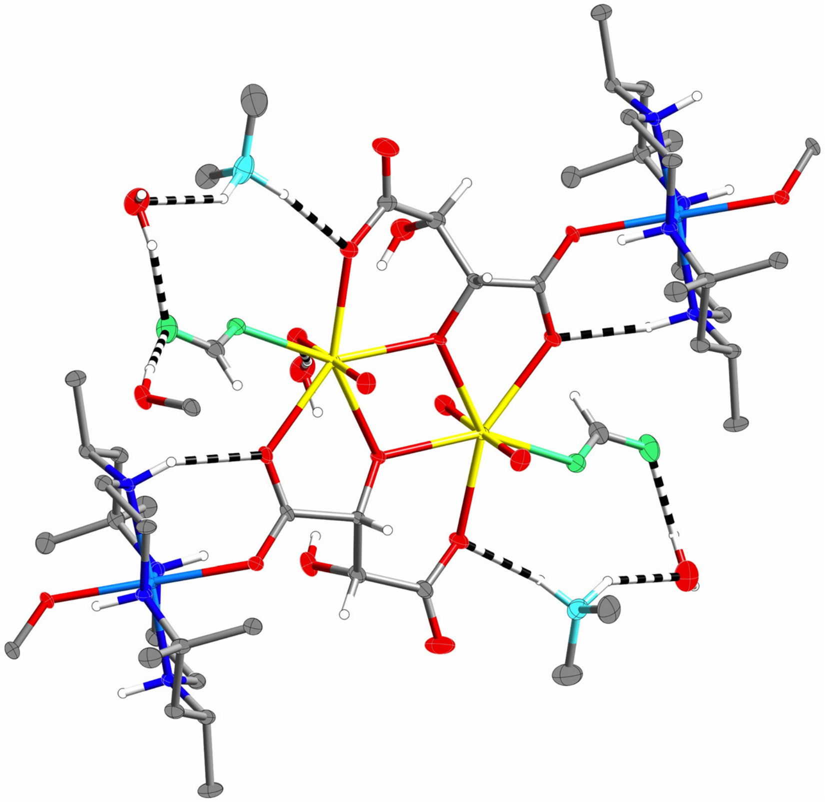

Fig. 1 A fragment within the structure of $[(CH_3)_2NH_2]_2[(UO_2)_2(HTRT)_2(HCO_2)_2Ni(R,S\text{-}Me_6cyclam)]\cdot 2H_2O$ ($HTRT^-$ = hydrogentartrate)[92] showing the part of the intricate network of hydrogen bonds (dashed lines) that link dimethylammonium counterions, water and coordinated formate. For clarity, CH atoms are shown only on the coordinated tartrate and formate units, with formate oxygen shown in green and dimethylammonium nitrogen in pale blue. Otherwise U = yellow, Ni = sky blue, N = dark blue, and O = red, H = white spheres with an arbitrary radius of 0.1 Å, with other atom displacement ellipsoids shown at the 80% level (figure prepared using CrystalMaker 11.5 from CrystalMaker Software Ltd).

may influence the complete structure and divert the structure from one anticipated for a simple metal-ion/ligand complex. The relatively infrequent occurrence of formate and acetate binding, in general, is quite possibly just a reflection of competition from multidentate carboxylates present in many reaction mixtures. Note also that intact DMF, either coordinated or as a solvate molecule, can be found in many structures, indicating that the hydrolysis reaction may in fact attain an equilibrium. Overall, the evidence appears to favour hydrolysis as the reaction undergone by DMF under solvothermal conditions, but a study of the reaction and its possible metal ion catalysis under these conditions would be necessary to establish this as a true conclusion. The same can be said for solvents such as DMA and AN, also well known to be susceptible to hydrolytic cleavage.

While the chemical effects of solvent hydrolysis on product composition just described are readily understood, others are perhaps less obvious. Thus, the hydrolysis of DMF

$$(CH_3)_2NCHO + H_2O \\ \rightarrow (CH_3)_2NH + HCO_2H = (CH_3)_2NH_2{}^+ + HCO_2{}^-$$

produces a medium of significant buffering capacity, which, on the basis of the approximate expression $pH = (pK_1 + pK_2)/2$ would be expected to give this medium a room-temperature pH of ~7.2. Reaction mixture pH values have not been reported systematically, since most ligand sources are added as the conjugate acid (*e.g.* carboxylic acids and phosphonic acids) initial values would be expected to be low, as indeed observed where such measurements have been made.[93] As initial DMF concentrations in the reaction mixtures typically greatly exceed those of the metal ions and ligands, the buffer created by gradual hydrolysis should dominate the mixture pH, meaning that the success in using DMF/H_2O to provide crystalline products could be due to progressive deprotonation resulting in a form of "homogeneous precipitation".[94] Gradual basification of an initially acid reaction mixture does seem, in any case, to be important in that the addition of NaOH or KOH to the initial reaction mixture is known to sometimes result in product contamination with amorphous solids.[40,95] Like DMF, both DMA and AN undergo hydrolysis under solvothermal conditions and thus could also control crystallisation rates. There is no evidence in the nature of isolated products that the cyclic amide NMP undergoes detectable ring opening under solvothermal conditions, although these products do contain deprotonated acids.[96] Once again, some basic kinetic studies could clarify the situation.

Redox chemistry is an intentional aspect of solvothermal syntheses of mixed metal oxides[9,20,30] but in the synthesis of coordination polymers and frameworks, its occurrence is rather incidental and not always of obvious origin. The facts that heterometallic U(VI)Cu(II) complexes of a saturated tricarboxylate ligand can be obtained through hydrothermal synthesis[97] but a U(VI)Cu(I) complex is obtained with a very similar dicarboxylate and Cu(II) reactant when DMF/H_2O is the solvent[98] indicate that the reducing power of DMF may be operative, but in other systems hydrothermal syntheses also result in reduction of Cu(II) to Cu(I).[32,99] Unlike DMF, DMSO can be both an oxidant and a reductant and has been deliberately employed as a reactant (in the ethylenediamine solvent) for solvothermal syntheses where it provides a source of sulfide.[100] As a single solvent, DMSO has been used in the synthesis of porphyrin-derived frameworks[101] but the present authors have avoided its use following some explosive reactions. A long-recognised drawback of solvothermal syntheses with organic ligands is the oxidative degradation of such ligands ultimately to oxalate,[65,102] a reaction which has been followed in detail for 2,3-pyrazinedicarboxylate,[65] where numerous intermediates were identified and the termination at oxalate rather than at CO_2 attributed to the very low solubility of its neodymium(III) complex. While dissolved oxygen was considered to play some role in the oxidation, nitrate counterions from metal salt reactants were obvious possible oxidants[102] and it has recently been shown[103] that the substitution of triflate for nitrate is an effective means of inhibiting ligand oxidation. Crown ethers are ligands which appear to be particularly sensitive to oxidation to oxalate,[104] and the removal of nitrate would presumably eliminate this reaction but it also must be asked whether a better understanding of the oxidation reactions might enable a better choice of reaction time to be made. As noted above, steps in the oxidation of 2,3-pyrazinedicarboxylate can be distinguished, and in the case of tris(carboxyethyl)phosphine, oxidation is even terminated at the stage of phosphine oxide.[105] Evidence that in a purely aqueous solution an oxidation process having no effect on the isolated product composition may still occur is provided by a pH increase (indicative of an oxidation reaction consuming acid) observed in a hydrothermal synthesis.[93] While superheated water can attack organic molecules in several ways including oxidation,[106] such reactions involve temperatures and pressures well above those of sub-critical solvothermal synthesis.

3. Duration of the reaction time in sub-critical solvothermal reactions

Another well-known disadvantage of solvothermal synthesis is the length of time conventionally assigned to the reaction, and, with product applications in mind, considerable research has been devoted to finding ways to shorten reaction times, microwave heating being one approach that has proved quite successful,[23,107,108] with "light-assisted" solvothermal synthesis in open vessels being a novel recent development.[109] The quest for "greener" methods continues.[110] Determination of the optimal reaction time can be a difficult issue, largely because of the very nature of the solvothermal method. There are occasional references in the literature[111–114] to the method as a "black box" procedure because of the enclosure of the reaction mixture or filled reaction vessel within a stainless steel autoclave, meaning that visual observation of the reaction's progress is not possible. What goes in is known, what comes out can be characterised but what happens in between is often unclear. Is a homogeneous solution of the reactants formed immediately on attaining the temperature desired or is dissolution of the least soluble component a limiting factor? If a homogeneous solution forms at some stage, does product crystallisation begin to occur shortly thereafter or only after final cooling of the apparatus? If crystals do form rapidly, is an extended period of heating required in order that they attain a size suitable for X-ray structure determination? Is it possible that crystals deposited at the reaction temperature are not the same as those deposited at room temperature? These are questions that arise independently of whether time is also required for reactions (discussed above) other than that of metal ion to ligand coordination to occur. Partial responses are provided by studies, *e.g.*[35,43,62,82–92,96–98,104,105] using transparent glass reaction vessels and these show, at least for polycarboxylate complexes of uranyl ions, that the formation of a solution occurs readily but any deposition of crystals at the reaction temperature occurs in time periods ranging from hours to several weeks. In many cases, precipitation of crystalline or even amorphous material does not occur at all, though both can be induced by cooling. Although crystallisation at the reaction temperature precisely defines the conditions of crystal formation, it has the disadvantage that the yields of CPs and MOFs are often low, a handicap in relation to any application. In these cases, it is essentially unknown whether the crystallisation temperature has a significant influence on the nature of the product, while in contrast for mixed-metal oxides, where yields are high and formation rapid, it is well established[9] that it does. For CPs and MOFs where a reaction temperature dependence of products, isolated at room temperature, has been demonstrated (*e.g.* for Mn(II) carboxylate MOFs[67]), there is thus some uncertainty as to how it arises.

In addition to a lack of any knowledge of the dependence of product solubility on temperature, there is essentially no information on possible solution equilibria in mixed solvents at elevated temperatures. Available data, such as those for Eu(III) interactions with carboxylate ligands,[115] are typically limited to 298 K and show a complicated dependence of equilibrium constants, including those for solvent autoionisation, on solvent composition. Thus, while there are at least some data for the temperature dependence of aqua ion acidity in a single solvent, for example,[116,117] they are of little direct value. For labile metal ions of the transition, lanthanide and actinide series, however, complexation equilibria should be established essentially immediately upon dissolution of the reagents at the temperatures employed in sub-critical solvothermal syntheses, so what need there is for extended heating after this point is unclear unless it is simply to maintain crystal formation. Of course, if product formation is dependent upon reactions such as solvent hydrolysis, time will be required, and thus it is important to know how much time is needed if there is a desire to optimise yields. Ligands may also show particular chemical reactivity; susceptibility to oxidation has already been discussed, and a wide variety of other reactions,[62] many of them metal-ion induced, are known and some of these have been deliberately exploited in crystal engineering.[15,118] In our own work on uranyl ion CP and MOF species formed by hydro/solvothermal syntheses in transparent vessels, the possibility of photocatalysed uranyl ion reactions[119] has been a necessary concern but only in a single case,[120] some evidence for one such reaction, H-atom abstraction, has been obtained. All these reactions complicate the choice of reaction time in solvothermal processes but any basis for this choice is largely empirical. If there is a desire to adhere to the "main goal in MOF synthesis"[14] referred to earlier, knowledge of how to avoid complications is essential.

4. The nature of crystals deposited in sub-critical solvothermal syntheses

While kinetic control of crystal formation cannot be excluded,[121] presuming that the conditions of sub-critical solvothermal synthesis are such as to ensure equilibrium, then it is solubility which determines the nature of the crystals deposited at the reaction temperature. Thus, their nature does not necessarily reflect that of the dominant species in solution, so any analysis of structures simply in terms of metal-ion-ligand coordination is speculative and while it may be said to be supported by, say, DFT calculations, any species for which comparison might be made is unknown in the absence of a detailed understanding of the solution equilibria. The question as to how crystals of CPs and MOFs may form has been described as "difficult",[122] and the formation of partially interpenetrated crystal structures[68,69] is an illustration of just how complicated it may be. A simple model[122] for systems involving labile metal ions is that small cyclic oligomers may first form a crystal and that this is followed by ring-opening polymerisation in the solid state, but again the limited data on solution speciation renders this uncertain as a general mechanism. Some form of molecular 3D printing[123] is perhaps an alternative mechanism. Regardless of this issue, another sometimes unexpected feature of sub-critical solvothermal synthesis is that the composition of the product in terms of metal : ligand ratio often does not match that of the initial reaction mixture. Purely empirical procedures have been followed to optimise yields without it being clear whether kinetic or thermodynamic factors are the more important.

5. Conclusions

A short answer to the question posed in the title of this manuscript is "Quite a lot". It would seem that even under the relatively mild conditions of sub-critical solvothermal synthesis, a variety of other reactions may accompany that of metal-ion-ligand coordination and that these reactions can determine the yield and nature of the product. The success of solvothermal methods in general in providing materials with a remarkable range of properties and uses has, however, left obscure much of the basic chemistry leading to these products. While formation and crystallisation of coordination complexes in mixed solvents at elevated temperatures are processes perhaps outside the comfort zone for kinetic and thermodynamic measurements, there are opportunities for basic studies to considerably clarify the nature of the "black box" in solvothermal synthesis. NMR spectroscopy is one technique clearly suited to the study of solvent hydrolysis in mixed aqueous systems and has already been shown[65] to be valuable in following the stepwise decomposition and redox reactions of 2,3-pyrazinedicarboxylate under solvothermal conditions. Ligand isomerisation and oligomerisation reactions[15] are further examples of processes that could be readily studied by this and other spectroscopic methods such as the measurement of infra-red and circular dichroism spectra. These reactions are those occurring in homogeneous solutions but of course there are reactions of major importance involved in crystal formation and growth, and this is an area where methods for their direct study in sealed vessels have recently undergone important development.[124] The sophisticated techniques involved here offer, amongst other things, the capacity to study surface interactions of small species possibly produced by homogeneous solution reactions and thus elaborate in remarkable detail the nature of solvothermal synthesis in general.

Conflicts of interest

There are no conflicts to declare.

Data availability

No new data were used in the preparation of this article.

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