

Dalton Transactions

An international journal of inorganic chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: L. Baklouti and J. Harrowfield, *Dalton Trans.*, 2025, DOI: 10.1039/D5DT01784J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

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

View Article Online
DOI: 10.1039/D5DT01784J

Lassaad Baklouti^{a,b} and Jack Harrowfield^c

^aDepartment of Chemistry, Faculty of Sciences of Sfax, University of Sfax

^bLaboratory of Applied Chemistry and Natural Substances

Resources and Environment, Faculty of Sciences of Bizerte, University of Carthage, Tunisia. E-mail: lassaad.baklouti@fss.usf.tn

^cISIS, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France. E-mail: harrowfield@unistra.fr

ABSTRACT: 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 in particular of 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 as to the identity of such factors.

1. Introduction

Two important steps in the development of metal ion coordination chemistry were those of the distinction of « *inert* » and « *labile* » complex ion species first proposed by Henry Taube^{1,2} and the subsequent quantification for 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 for metal aqua ions as reference species rate constants for water ligand exchange 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 of mixing of the reagents while inert complexes required observably longer periods remains of practical importance in designing syntheses. 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 recognition of many other factors surveyed, for example, in references 6-22. The terms « solvothermal » and « hydrothermal », the latter limited to cases where water is the sole solvent present, qualify 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 sub-critical solvothermal synthesis of metal ion complexes, both because 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.

View Article Online

DOI: 10.1039/D5DT01784J

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. Where 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 where a metal ion source and a ligand are dissolved, by heating if necessary, under ambient pressure, in a solvent and efforts 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 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 place.* »¹⁴ Crystallisation of the product is not just desirable to establish its purity but more importantly to enable an 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 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.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 hydroxylic 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 known⁵⁰ 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 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 mix 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^{29,30,65,66,67} but again they have been in the main focussed 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 (CH₃)₂NH (dimethylamine), a reaction exploited in organometallic carbonylation reactions,⁷¹ and suggested to be the reason for the facility of the synthesis of crystalline [(CH₃)₂NH₂]₃[Ln(dipic)₃] complexes (Ln = lanthanide(III); dipic = pyridine-2,6-dicarboxylate) by simply boiling a solution of hydrated LnCl₃ with dipicH₂ 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, the latter 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 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. Figure 1 provides an illustration of how solvent fragments may influence the complete structure, an influence which diverts that 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 by 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



study of the reaction and its possible metal ion catalysis under these conditions would 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



produces a medium of significant buffering capacity which, on the basis of the approximate expression $\text{pH} = (\text{pK}_1 + \text{pK}_2)/2$ would be expected to give this medium a room-temperature pH of ~ 7.2 . Although reaction mixture pH values have not been reported systematically, since most ligand sources are added as the conjugate acid (e.g. carboxylic acids, 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/H₂O 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 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 synthesis⁹⁷ but that a U(VI)Cu(I) complex is obtained with a very similar dicarboxylate and Cu(II) reactant when DMF/H₂O is the solvent⁹⁸ indicates 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 reductant and has been deliberately employed as a reactant (in 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 frameworks¹⁰¹ but the present authors have avoided its use following some explosive reactions. A long-recognised drawback to 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 CO₂ attributed to the very low solubility of its neodymium(III) complex. While dissolved oxygen was considered to have some role in the oxidation, nitrate counterions from metal salt reactants were obvious possible oxidants¹⁰² and it has recently been shown¹⁰³ 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 through to oxalate,¹⁰⁴ and 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 the phosphine oxide.¹⁰⁵ Evidence that in 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 by 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 the time conventionally assigned to reaction and, with product applications in mind, considerable research has been devoted to find ways of shortening 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 and the quest for "greener" methods continuing.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 literature¹¹¹⁻¹¹⁴ 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 determinations? 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 ion, that formation of a solution occurs readily but that 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 that of crystal formation, it does have the disadvantage that 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 established⁹ 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 MOFs⁶⁷), 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 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 for this and thus there is a need to know how much if there is a desire to optimise yields. Ligands may also show particular chemical reactivity, susceptibility to oxidation having already been discussed, and a wide variety of other reactions,⁶² many metal-ion induced, are known and some 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 reactions¹¹⁹ has been a necessary concern but only in a single case¹²⁰ has some evidence for one such reaction, H-atom abstraction, 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 model¹²² 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 printing¹²³ 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 to 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 shown⁶⁵ to be valuable in following the stepwise decomposition and redox reactions of 2,3-pyrazinedicarboxylate under solvothermal conditions. Ligand isomerisation and oligomerisation reactions¹⁵ 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.

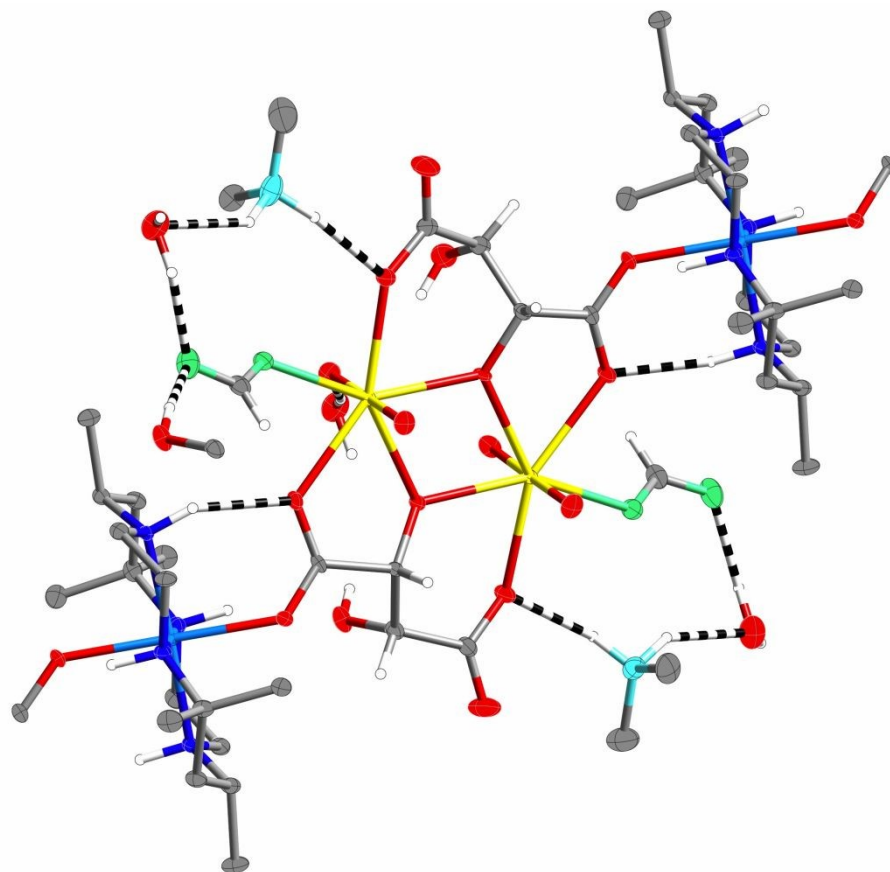


Figure 1

A fragment within the structure of $[(\text{CH}_3)_2\text{NH}_2]_2[(\text{UO}_2)_2(\text{HTRT})_2(\text{HCO}_2)_2\text{Ni}(\text{R,S-Me}_6\text{cyclam})]\cdot 2\text{H}_2\text{O}$ (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, 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.)

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



| Metal(s) | Ligand(s) | Solvent(s) | T _r /°C ^a | t _r ^b | T _{coll} ^c | n ^d | Ref |
|---|---|--|---------------------------------|-----------------------------|--------------------------------|----------------|-----|
| Cu(I) | 4,4'-bipyridine | H ₂ O | 140 | 2 d | RT | 1 | 32 |
| Co(II), Cu(II), Zn(II) | 5-diacetatoamino- isophthalate | CH ₃ OH/H ₂ O (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 ₂ O | 180 | 14 d | RT | 6 | 35 |
| Pb(II) + K(I), Rb(I), or Cs(I) | isophthalate, 4,4'-biphenyldisulfonate | DMF ^f /CH ₃ OH (2:1) | 150 | 3 d or 3 h | RT | 5 | 36 |
| Bi(III) | pyridine-2,6-dicarboxylate | DMF, CH ₃ OH or C ₂ H ₅ OH | 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 ₂ O or DMF/H ₂ O | | | | | 39 |
| Zn(II) | 5-((4-tert-butyl)- phenylazo)isophthalate, 1,2-di(4-pyridyl)ethene) | C ₂ H ₅ OH/H ₂ O (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 ₂ O | 200 or 150 | 3 d | RT | 7 | 41 |
| Ln(III) Y(III) | F- | ethyleneglycol/H ₂ O various ratios | 190 | 12 h | RT | 3 | 42 |
| U(VI) | Zwitterionic and anionic dicarboxylates | H ₂ O/CH ₃ CN (3:1) or H ₂ O/DMA ^h (3:1) | 140 | 1 - 14 d | 140 | 7 | 43 |
| Sc(III) | thiophenedicarboxylate, nitrate | CH ₃ CN/H ₂ O (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.

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 lettering) are found.



| Metal | Crystal composition ^a | Solvent | Refcode | Ref |
|---------|---|-------------------------|---------|-----|
| Cu(II) | $[(\text{CH}_3)_2\text{NH}_2]_3[(\text{Cu}_4\text{Cl})_3(\text{BTC})_8] \cdot 9\text{DMA}$ | DMA | ABEMIF | 75 |
| Co(II) | $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Co}_2\text{Cl}_2(\text{BTC})_{4/3}]$ | DMA/AN | ABAYIO | 76 |
| Cd(II) | $[(\text{CH}_3)_2\text{NH}_2]_4[\text{Cd}_2(\text{TTCA})_2\text{Cl}_2] \cdot 7\text{DMF} \cdot 2\text{Diox} \cdot 6\text{H}_2\text{O}$ | DMF/Dioxan | ADEGEY | 77 |
| Fe(II) | $[(\text{CH}_3)_2\text{NH}_2][\text{Fe}^{\text{II}}_3(\text{OH})(\text{BPTC})_{1.5}(\text{DMSO})_3]$ | DMA/DMSO | BAZBIQ | 78 |
| Bi(III) | $[(\text{CH}_3)_2\text{NH}_2]_4[\text{Bi}_2(\text{PDC})_2(\text{HPDC})_2] \cdot 2\text{DMF} \cdot \text{NH}(\text{CH}_3)_2$ | DMF | AHEZEV | 79 |
| Eu(III) | $[(\text{CH}_3)_2\text{NH}_2]_4[\text{Eu}_4(\text{DDAC})_3(\text{HCO}_2)(\text{OH}_2)_2] \cdot 8\text{DMF} \cdot 9\text{H}_2\text{O}$ | DMF/H ₂ O | AZOXUL | 80 |
| Y(III) | $[(\text{CH}_3)_2\text{NH}_2][\text{Y}(\text{BTEC})(\text{H}_2\text{O})]$ | DMF/H ₂ O | ABUMUJ | 81 |
| U(VI) | $[\text{UO}_2(\text{ADDC})(\text{DMF})]$ | DMF/H ₂ O | ZOZCEY | 82 |
| U(VI) | $[(\text{CH}_3)_2\text{NH}_2]_4[(\text{UO}_2)_4(\text{ADDC})_6]$ | DMF/H ₂ O | ZOZCIC | 82 |
| U(VI) | $[(\text{CH}_3)_2\text{NH}_2]_2[(\text{UO}_2)_2(\text{ADDA})_3] \cdot 3\text{H}_2\text{O}$ | DMF/H ₂ O | IHOGIX | 83 |
| U(VI) | $[(\text{CH}_3)_2\text{NH}_2]_2[(\text{UO}_2)_2(\text{KTA})_3]$ | DMA/H ₂ O | QUKLAL | 84 |
| U(VI) | $[\text{UO}_2\text{Pb}(\text{BTA})(\text{HCO}_2)(\text{phen})]$ | DMF/H ₂ O | OSOMOA | 85 |
| U(VI) | $[\text{PPh}_4][\text{UO}_2(\text{R-CHDC})(\text{HCO}_2)]$ | DMF/H ₂ O | COVSOY | 86 |
| U(VI) | $[\text{NH}_4]_2[\text{PPh}_4]_2[(\text{UO}_2)_4(\text{ADDA})_6]$ | DMF/AN | YEXDAJ | 87 |
| U(VI) | $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})][\text{UO}_2(\text{CAM})(\text{HCO}_2)_2]$ | DMF/H ₂ O | JIVBAV | 88 |
| U(VI) | $[\text{PPh}_3\text{Me}]_3[\text{NH}_4]_3[(\text{UO}_2)_6(\text{CAM})_9]$ | DMF/AN/H ₂ O | JIVBOI | 88 |
| U(VI) | $[\text{UO}_2(1,2\text{-PDA})] \cdot \text{CH}_3\text{CN}$ | AN/H ₂ O | FUDNOK | 89 |
| U(VI) | $[\text{C}(\text{NH}_2)_3][(\text{CH}_3)_2\text{NH}_2]_2[(\text{UO}_2)_3(\text{TDC})_4(\text{HCO}_2)]$ | DMF/H ₂ O | EWIQEJ | 90 |
| U(VI) | $[\text{UO}_2(\text{ADP})(\text{HCO}_2)_2\text{Cu}(\text{R,S-Me}_6\text{cyclam})] \cdot 2\text{H}_2\text{O}$ | DMF/H ₂ O | YAPSUH | 91 |
| U(VI) | $[(\text{CH}_3)_2\text{NH}_2]_2[(\text{UO}_2)_2(\text{HTRT})_2(\text{HCO}_2)_2\text{Ni}(\text{R,S-Me}_6\text{cyclam})] \cdot 2\text{H}_2\text{O}$ | DMF/H ₂ O | VEXPEX | 92 |
| U(VI) | $[\text{Hquin}^b][(\text{UO}_2)_2(\text{TRT})(\text{CH}_3\text{CO}_2)]$ | 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-tetraazacyclotetradecane; TRT = *R,R*-tartrate dianion.

^b quin = quinuclidine = 1-azabicyclo[2.2.2]octane.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Dedicated to Dr Pierre Thuéry on the occasion of his retirement.



References

View Article Online
DOI: 10.1039/D5DT01784J

1. H. Taube, *Rates and Mechanisms of Substitution in Inorganic Complexes in Solution*. *Chem. Rev.* 1952, **50**, 69-126.
2. C. Creutz, P. C. Ford, T. J. Meyer, *Henry Taube: Inorganic Chemist Extraordinaire*. *Inorg. Chem.* 2006, **45**, 7059-7068.
3. M. Eigen, Nobel Prize Lecture, *Immeasurably Fast Reactions*, Nobel Foundation 1967.
4. L. Helm, A. E. Merbach, *Inorganic and Bioinorganic Solvent Exchange Mechanisms*. *Chem. Rev.* 2005, **105**, 1923-1959.
5. S. F. Lincoln, *Mechanistic Studies of Metal Aqua Ions: A Semi-Historical Perspective*. *Helv. Chim. Acta* 2005, **88**, 523-545.
6. M. Viciano-Chumillas, X. Liu, A. Leyva-Pérez, D. Armentano, J. Ferrando-Sorio, E. Pardo. *Mixed-component metal-organic frameworks: Heterogeneity and complexity at the service of application performances*. *Coord. Chem. Rev.* 2022, **451**, 214273.
7. W. Gong, Z. Chen, J. Dong, Y. Liu, Y. Cui. *Chiral Metal-Organic Frameworks*. *Chem. Rev.* 2022, **122**, 9078-9144.
8. K. Lv, S. Fichter, M. Gu, J. März, M. Schmidt. *An updated status and trends in actinide metal-organic frameworks (An-MOFs): from synthesis to application*. *Coord. Chem. Rev.* 2021, **446**, 214011.
9. R. I. Walton. *Perovskite Oxides Prepared by Hydrothermal and Solvothermal Synthesis: A Review of Crystallisation, Chemistry and Compositions*. *Chem. Eur. J.* 2020, **26**, 9041-9069.
10. E. A. Dolgoplova, O. A. Ejagbavwo, C. R. Martin, M. D. Smith, W. Setyawan, S. G. Karakalos, C. H. Henager, H-C. zur Loye, N. B. Shustova. *Multifaceted Modularity: A Key for Stepwise Building of Hierarchical Complexity in Actinide Metal-Organic Frameworks*. *J. Am. Chem. Soc.* 2017, **139**, 16852-16861.
11. C. R. Kim, T. Uemura, S. Kitagawa. *Inorganic nanoparticles in porous coordination polymers*. *Chem. Soc. Rev.* 2016, **45**, 3828-3845.
12. Y. Zhao, K. Li, J. Li. Review: *Solvothermal Synthesis of Multifunctional Coordination Polymers*. *Z. Naturforsch. B* 2014, **65**, 976-998.
13. P. H. Mutin, A. Vioux. *Recent advances in the synthesis of inorganic materials via non-hydrolytic condensation and related low temperature routes*. *J. Mater. Chem. A* 2013, **1**, 11504-11512.
14. N. Stock, S. Biswas. *Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites*. *Chem. Rev.* 2012, **112**, 933-969.



15. W. L. Leong, J. J. Vittal. *One-dimensional coordination polymers: complexity and diversity in structures, properties and applications*. *Chem. Rev.* 2011, **111**, 688–764. View Article Online
DOI: 10.1039/D5DT01784J
16. D. Zhao, D. J. Timmens, D. Yuan, H.-C. Zhou. *Tuning the Topology and Functionality of Metal-Organic Frameworks by Ligand Design*. *Acc. Chem. Res.* 2011, **44**, 123-135.
17. W. Lin, W. J. Rieter, K. M. L. Taylor. *Modular Synthesis of Functional Nanoscale Coordination Polymers*. *Angew. Chem. Int. Ed.* 2009, **48**, 650-658.
18. G. Férey. *Hybrid porous solids: past, present and future*. *Chem. Soc. Rev.* 2008, **37**, 191-214.
19. O. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim. *Reticular synthesis and the design of new materials*. *Nature* 2003, **423**, 705-714.
20. R. I. Walton. *Subcritical solvothermal synthesis of condensed inorganic materials*. *Chem. Soc. Rev.* 2002, **31**, 230–238.
21. C. Mellot-Draznieks, S. Girard, G. Férey, J. C. Schön, Z. Cancarevic, M. Jansen. *Computational Design and Prediction of Interesting Not-Yet-Synthesised Structures of Inorganic Materials by Using Building-Unit Concepts*. *Chem. Eur. J.* 2002, **8**, 4102-4113.
22. J. C. Bailar, Jr. *Coordination polymers*, in *Preparative Inorganic Reactions*; Jolly, W. L., Ed.; Wiley Interscience: New York, 1964; Vol. 1, pp 1-27.
23. Y. Huo, S. Xiu, L.-Y. Meng, B. Quan. *Solvothermal synthesis and applications of micro/nano carbons: A review*. *Chem. Eng. J.* 2023, **451**, 138572.
24. S. Efe, C. Schauerte, K. Merz. *Crystal engineering under hydro-thermal conditions: cocrystals and reactions of 3-cyanopyridine with glutaric acid*. *Cryst. Growth Des.* 2022, **22**, 2272–2278.
25. L. Liu, S. Wang, G. Jiang, B. Zhang, J. Yang, J. Wang, W. Liu, Y. Li. *Solvothermal synthesis of zirconia nanomaterials: Latest developments and future*. *Ceramics International* 2022, **48**, 32649-32676.
26. M. H. Mruthunjayappa, N. S. Kotrappanavar, D. Mondal. *New prospects on solvothermal carbonisation assisted by organic solvents, ionic liquids and eutectic mixtures – A critical review*. *Progr. Mater. Sci.* 2022, **126**, 100932.
27. S. P. Sasikala, P. Poulin, C. Aymonier. *Advances in subcritical hydro-/solvothermal processing of graphene materials*. *Adv. Mater.* 2017, **29** (22), 1605473.
28. J. Lai, W. Niu, R. Luque, G. Xu. *Solvothermal synthesis of metal nanocrystals and their applications*. *Nano Today* 2015, **10**, 240-267.
29. G. Demazeau. *Solvothermal processes: definition, key factors governing the involved chemical reactions and new trends*. *Z. Naturforsch.* 2010, **65**, 999–1006.



30. G. Demazeau. *Solvothermal reactions: an original route for the synthesis of novel materials*. *J. Mater. Sci.* 2008, **43**, 2104–2114. View Article Online
DOI: 10.1039/D5DT01784J
31. A. Rabeneau. *The Role of Hydrothermal Synthesis in Preparative Chemistry*. *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 1026-1040.
32. O. M. Yaghi, H. Li. *Hydrothermal Synthesis of a Metal-Organic Framework containing Large Rectangular Channels*. *J. Am. Chem. Soc.* 1995, **117**, 10401-10402.
33. Y. Xu, D. Yuan, B. Wu, L. Han, M. Wu, F. Jiang, M. Hong. *1D Tube, 2D Layer, and 3D Framework Derived from a New Series of Metal(II)-5-Aminodiacetic Isophthalate Coordination Polymers*. *Cryst. Growth Des.* 2006, **6**, 1168-1174.
34. A. L. Willis, Z. Chen, J. He, Y. Zhu, N. J. Turro, S. O'Brien. *Metal Acetylacetonates as General Precursors for the Synthesis of Early Transition Metal Oxide Nanomaterials*. *J. Nanomater.* 2007, **2007**, 14858.
35. P. Thuéry. *Uranyl Ion Complexes with Cucurbit[n]urils (n = 6, 7 and 8): A New Family of Uranyl-Organic Frameworks*. *Cryst. Growth Des.* 2008, **8**, 4132-4143.
36. X.-Q. Li, H.-B. Zhang, S.-T. Wu, J.-D. Lin, P. Lin, Z.-H. Lia, S.-W. Du. *Synthesis, structures and luminescent properties of new Pb(II)/M(I) (M = K, Rb and Cs) frameworks based on dicarboxylic acids: a novel icosahedral Pb₆-M₆ SBU*. *CrystEngComm* 2012, **14**, 936-944.
37. A. Thirumurugan, W. Li, A. K. Cheetham. *Bismuth 2,6-pyridinedicarboxylates: Assembly of molecular units into coordination polymers, CO₂ sorption and photoluminescence*. *Dalton Trans* 2012, **41**, 4126-4134.
38. H.-L. Jiang, D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen, H.-C. Zhou. *An Exceptionally Stable Porphyrinic Zr Metal-Organic Framework Exhibiting pH-Dependent Fluorescence*. *J. Am. Chem. Soc.* 2013, **135**, 13934-13938.
39. C. Falaise, J.-S. Charles, C. Volkringer, T. Loiseau. *Thorium Terephthalates Coordination Polymers Synthesised in Solvothermal DMF/H₂O System*. *Inorg. Chem.* 2015, **54**, 2235-2242.
40. J. S. Caddy, T. B. Faust, I. M. Walton, J. M. Cox, J. B. Benedict, M. B. Solomon, P. D. Southon, C. J. Kepert, D. M. D'Alessandro. *Photoactive and Physical Properties of an Azobenzene-Containing Coordination Framework*. *Aust. J. Chem.* 2017, **70**, 1171–1179.
41. R. Zhao, L. Mei, K.-Q. Hu, M. Tian, Z.-F. Chai, W.-Q. Shi. *Bimetallic Uranyl Organic Frameworks Supported by Transition-Metal-Ion-Based Metalloligand Motifs: Synthesis, Structure Diversity and Luminescence Properties*. *Inorg. Chem.* 2018, **57**, 6084–6094.
42. C. Sun, M. Schäferling, U. Resch-Genger, M. Gradzielski. *Solvothermal Synthesis of Lanthanide-doped NaYF₄ Upconversion Crystals with Size and Shape Control: Particle Properties and Growth Mechanism*. *ChemNanoMat* 2021, **7**, 174-183.



43. Y. H. Lee, Y. Atoini, S. Kusumoto, S. Hayami, Y. Kim, J. Harrowfield, P. Thuéry, *Mixed-ligand uranyl ion complexes with two flexible, pyridinium-based dicarboxylate zwitterions and simple anionic dicarboxylates*. *CrystEngComm* 2025, **27**, 1034-1043. DOI: 10.1039/D5DT01784J
44. Y. Gao, X. Yang, J. Su, L. Li. *A stable scandium(III) metal-organic framework with introduced nitrate ion enhancing selectivity in the separation of MTO products*. *Chin. J. Struct. Chem.* 2025, **44**, 100576.
45. S. Huh, S.-J. Kim, Y. Kim. *Porphyrinic metal-organic frameworks from custom-designed porphyrins*. *CrystEngComm* 2016, **18**, 345-368.
46. Q. Zha, X. Rui, T. Wei, Y. Xie. *Recent advances in design strategies for porphyrin-based coordination polymers*. *CrystEngComm* 2014, **16**, 7371-7384.
47. M. Inoue in *Chemical Processing of Ceramics*, 2nd edition, CRC Press, Taylor and Francis Group, New York, 2005, chapter 2, "Solvothermal Synthesis".
48. C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li, C.-D. Wu. *A Multifunctional Organic-Inorganic Hybrid Structure based on Mn(III)-Porphyrin and Polyoxometallate as a Highly Effective Dye Scavenger and Heterogeneous Catalyst*. *J. Am. Chem. Soc.* 2012, **134**, 87-90.
49. A. J. Parker. *The effects of solvation on the properties of anions in dipolar aprotic solvents*. *Quart. Rev. Chem. Soc.* 1962, **16**, 163-187.
50. A. J. Parker. *Protic-Dipolar Aprotic Solvent Effects on Rates of Bimolecular Reactions*. *Chem. Rev.* 1969, **69**, 1-32.
51. P.L. Goggin. *Sulphoxides, Amides, Amine Oxides and related ligands* in: G. Wilkinson, J.A. McCleverty, R.D. Gillard (Eds.), *Comprehensive Coordination Chemistry*, vol. 2, Pergamon Press, Oxford, 1987, **Chapter 15.8**, p. 487.
52. S. Funahashi, Y. Inada. *Solvation Structures and Solvent Exchange Reactions of Metal Ions in Various Coordinating Solvents*. *Bull. Chem. Soc. Jpn* 2002, **75**, 1901-1925.
53. Y. He, Y. Zhu, N. Wu. *Mixed solvents: a key in solvothermal synthesis of KTaO₃*. *J. Solid State Chem.* 2004, **177**, 2985-2990.
54. D. Xu, Z. Liu, J. Liang, Y. Qian. *Solvothermal synthesis of CdS nanowires in a mixed solvent of ethylenediamine and dodecanethiol*. *J. Phys. Chem. B* 2005, **109**, 14344-14348.
55. M.-G. Ma, F. Deng, K. Yao. *Solvothermal synthesis and characterisation of LaPO₄ with hierarchical nanostructure in mixed solvents of ethanol and water*. *Mater. Lett.* 2014, **124**, 173-176.
56. A. Nohara, S. Takeshita, T. Isobe. *Mixed-solvent strategy for solvothermal synthesis of well-dispersed YBO₃:Ce³⁺, Tb³⁺ nanocrystals*. *RSC Adv.* 2014, **4**, 11219-11224.
57. K.-Q. Hu, X. Jiang, C.-Z. Wang, L. Mei, Z.-N. Xie, W.-Q. Tao, X; X.-L. Zhang, Z.-F. Chai, W.-Q. Shi. *Solvent-Dependent Synthesis of Porous Anionic Uranyl-Organic Frameworks*



Featuring a Highly Symmetrical ctn or bor Topology for Selective Dye Adsorption. *Chem. Eur. J.* 2017, **23**, 529-532. View Article Online
DOI: 10.1039/D5DT01784J

58. B. Tan, Y. Luo, X. Liang, S. Wang, X. Gao, Z. Zhang, Y. Fang. *Mixed Solvothermal Synthesis of MIL-101(Cr) and Its Water Adsorption/Desorption Performance.* *Ind. Eng. Chem. Res.* 2019, **58**, 2983-2990.
59. S. K. Dey, P. Mitra, A. Mukherjee. *Influence of Solvent in Solvothermal Syntheses: Change of Nuclearity in Mixed-Valence Co^{II/III} Complexes of an O-Donor-Rich Schiff Base Ligand.* *Cryst. Growth Des.* 2015, **15**, 706-717.
60. O. A. El Seoud. *Solvation in pure and mixed solvents: Some recent developments.* *Pure Appl. Chem.* 2007, **79**, 1135-1151.
61. W. E. Waghorne. *Thermodynamics of solvation in mixed solvents.* *Chem. Soc. Rev.* 1993, **22**, 285-292.
62. S. Kusumoto, Y. Koide, S. Hayami, Y. Kim, J. Harrowfield, P. Thuéry. *Synthesis of uranyl ion coordination polymers with zwitterionic carboxylate ligands: comparing solvothermal and ambient conditions.* *J. Incl. Phenom. Macrocyclic Chem.* 2025, **105**, 167-174.
63. Y. Hao, P. Kegler, T. E. Albrecht-Schmitt, S. Wang, Q. Dong, E. V. Alexseev. *Two-Dimensional Uranyl Borates: From Conventional to Extreme Synthetic Conditions.* *Eur. J. Inorg. Chem.* 2020, 407-416.
64. E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese. *Zn(II) coordination polymers, metallohexacycles and metallocapsules - do we understand self-assembly in metallocupramolecular chemistry: algorithms or serendipity ?* *CrystEngComm* 2011, **13**, 6864-6870.
65. K. E. Knope, H. Kimura, Y. Yasaka, M. Nakahara, M. B. Andrews, C. L. Cahill. *Investigation of in Situ Oxalate Formation from 2,3-Pyrazinedicarboxylate under Hydrothermal Conditions using Nuclear Magnetic Resonance Spectroscopy.* *Inorg. Chem.* 2012, **51**, 3883-3890.
66. K. M. O. Jensen, C. Tyrsted, M. Bremholm, B. B. Iversen. *In-situ Studies of Solvothermal Synthesis of Energy Materials.* *ChemSusChem* 2014, **7**, 1594-1611.
67. P. Mahata, M. Prabu, S. Natarajan. *Role of Temperature and Time in the Formation of Infinite -O-M-O- Linkages and Isolated Clusters in MOFs: A Few Illustrative Examples.* *Inorg. Chem.* 2008, **47**, 8451-8463.
68. Y. Kim, Sa. Lee, Y.-P. Chen, B. Lee, Su. Lee, J. Park. *Partial-Interpenetration-Controlled UiO-Type Metal-Organic Framework and its Catalytic Activity.* *Small* 2024, **20**, 2305999.
69. A. Ferguson, L. Liu, S. J. Tapperwijn, D. Perl, F-X. Coudert, S. Van Cleuvenbergen, T. Verbiest, M. A. van der Veen, S. G. Telfer. *Controlled partial interpenetration in metal-*



organic frameworks. *Nature Chem.* 2016, **8**, 250-257.

View Article Online

DOI: 10.1039/D5DT01784J

70. J. Muzart. *N,N*-dimethylformamide: much more than a solvent. *Tetrahedron* 2009, **65**, 8313-8323.
71. B. Panda, G. Albano. *DMF as a CO Surrogate in Carbonylation Reactions: Principles and Applications to the Synthesis of Heterocycles. Catalysis* 2021, **11**, 1531-1555.
72. T. J. Mooibroek, P. Gamez, A. Pevec, M. Kasunic, B. Kozlevcar, W.-T. Fu, J. Reedijk. *Efficient, stable, tunable, and easy to synthesize, handle and recycle luminescent materials: [H₂NMe₂]₃[Ln(III)(2,6-dipicolinate)₃] (Ln = Eu, Tb, or its solid solutions). Dalton Trans* 2010, **39**, 6483-6487.
73. D. A. Buckingham, J. M. Harrowfield, A. M. Sargeson. *Metal Ion Activation in the Base Hydrolysis of amides. Hydrolysis of the Dimethylformamidopentaaamminecobalt(III) Ion. J. Am. Chem. Soc.* 1974, **96**, 1726-1729.
74. T. Cottineau, M. Richard-Plouet, J.-Y. Mevellec. *Hydrolysis and Complexation of N,N-Dimethylformamide in New Nanostructured Titanium Dioxide Hybrid Inorganic Sols and Gels. J. Phys. Chem. C* 2011, **115**, 12269-12274.
75. Y.-X. Tan, Y.-P. He, J. Zhan. *Pore partition effect on gas sorption properties of an anionic metal-organic framework with exposed Cu²⁺ coordination sites. Chem. Commun.* 2011, **47**, 10647-10649.
76. S.-J. Liu, C. Cao, F. Yang, M.-H. Yu, S.-L. Yao, T.-F. Zheng, W.-W. He, H.-Xi. Zhao, T.-L. Hu, X.-H. Bu. *High Proton Conduction in Two Co^{II} and Mn^{II} Anionic Metal–Organic Frameworks Derived from 1,3,5-Benzenetricarboxylic Acid {[M₂Cl₂(BTC)_{4/3}]·(Me₂NH₂)⁺₂·4/3H₂O}_n (M = Co (1) and Mn (2)). Cryst. Growth Des.* 2016, **16**, 6776-6780.
77. Y.-N. Gong, S.-Y. Zhang, P. Xiong, Y.-R. Xie, Z.-Y. Du, D.-C. Zhong. *A two-fold interpenetrating porous metal–organic framework with a large solvent-accessible volume and selective sensing of nitroaromatic explosives. J. Coord. Chem.* 2016, **69**, 996-1004.
78. J.-W. Zhang, M.-C. Hu, S.-N. Li, Y.-C. Jiang, Q.-G. Zhai. *Ligand Torsion Triggered Two Robust Fe-Tetrapic Carboxylate Frameworks with Enhanced Gas Uptake and Separation Performance. Chem. Eur. J.* 2017, **23**, 6693-6700.
79. L. Senior, A. Linden. *Coordination polymers incorporating Bi(III) and 2,4,6-pyridine tricarboxylic acid and its derivatives: Synthesis, structure and topology. Polyhedron* 2020, **184**, 114564.
80. H. Chen, Z. Zhang, T. Hu, X. Zhang. *An NH₂-modified {Eu^{III}}₂-organic framework for the efficient chemical fixation of CO₂ and highly sensitive sensing of 2,4,6-trinitrophenol. Inorg. Chem. Front.* 2021, **8**, 4376-4385.



81. F. M. Amombo Noa, M. Abrahamsson, E. Ahlberg, O. Cheung, C. R. Göb, C. J. McKenzie, L. Öhrström. *A unified topology approach to dot-, rod- and sheet-MOFs*. *Chem (Cell Press)* 2021, **7**, 2491-2512. DOI: 10.1039/D5DT01784J
82. P. Thuéry, E. Rivière, J. M. Harrowfield. *Uranyl- and Uranyl-3d-Block-Cation Complexes with 1,3-adamantanedicarboxylate: Crystal Structures, Luminescence and Magnetic Properties*. *Inorg. Chem.* 2015, **54**, 2838-2850.
83. P. Thuéry, J. M. Harrowfield. *Solvent effects in solvo-hydrothermal synthesis of uranyl ion complexes with 1,3-adamantanediacetate*. *CrystEngComm* 2015, **17**, 4006-4018.
84. P. Thuéry, J. M. Harrowfield. *Two-dimensional assemblies in f-element ion (UO_2^{2+} , Yb^{3+}) complexes with two cyclohexyl-based polycarboxylates*. *Polyhedron* 2015, **98**, 5-11.
85. P. Thuéry, J. M. Harrowfield. *Modulation of the Structure and Properties of Uranyl Ion Coordination Polymers Derived from 1,3,5-Benzenetriacetate by Incorporation of Ag(I) or Pb(II)*. *Inorg. Chem.* 2016, **55**, 6799-6816.
86. P. Thuéry, Y. Atoini, J. Harrowfield. *Uranyl–Organic Coordination Polymers with trans-1,2-, trans-1,4- and cis-1,4-Cyclohexanedicarboxylates: Effects of Bulky PPh_4^+ and PPh_3Me^+ Counterions*. *Cryst. Growth Des.* 2018, **18**, 2609-2619.
87. P. Thuéry, Y. Atoini, J. Harrowfield. *Closed Uranyl-Dicarboxylate Oligomers: A Tetranuclear Metallatricycle with Uranyl Bridgeheads and 1,3-Adamantanedicarboxylate Linkers*. *Inorg. Chem.* 2018, **57**, 7932-7939.
88. P. Thuéry, Y. Atoini, J. Harrowfield. *Chiral Discrete and Polymeric Uranyl Ion Complexes with (1R,3S)-(+)-Camphorate Ligands: Counterion-Dependent Formation of a Hexanuclear Cage*. *Inorg. Chem.* 2019, **58**, 870 - 880.
89. P. Thuéry, Y. Atoini, J. Harrowfield. *Structure-directing effects of coordinating solvents, ammonium and phosphonium counterions in uranyl ion complexes with 1,2-, 1,3- and 1,4-phenylenediacetates*. *Inorg Chem.* 2020, **59**, 2503-2518.
90. P. Thuéry, J. Harrowfield. *2,5-Thiophenedicarboxylate: an Interpenetration-Inducing Ligand in Uranyl Chemistry*. *Inorg. Chem.* 2021, **60**, 9074-9083.
91. P. Thuéry, J. Harrowfield. *Contrasting Networks and Entanglements in Uranyl Ion Complexes with Adipic and trans,trans-Muconic Acids*. *Inorg. Chem.* 2022, **61**, 2790-2803.
92. P. Thuéry, J. Harrowfield. *(R,R)-Tartrate as a polytopic ligand for UO_2^{2+} : mono- and dipericodic coordination polymers including di- and tetranuclear subunits*. *Polyhedron* 2023, **235**, 116346.
93. L. A. Borkowski, C. L. Cahill. *Topological Evolution in Uranyl Dicarboxylates: Synthesis and Structures of One-Dimensional $\text{UO}_2(\text{C}_6\text{H}_8\text{O}_4)(\text{H}_2\text{O})_2$ and Three-Dimensional $\text{UO}_2(\text{C}_6\text{H}_8\text{O}_4)$* . *Inorg. Chem.* 2003, **42**, 7041-7045.



94. P. F. S. Cartwright, E. J. Newman, D. W. Wilson. *Precipitation from homogeneous solution. A Review. The Analyst* 1967, **92**, 663-679. View Article Online
DOI: 10.1039/D5DT01784J
95. J.-F. Qian, W.-J. Tian, S. Yang, Z.-H. Sun, L. Chen, M.-J. Wei, Z. Wu, M.-Y. He, Z.-H. Zhang, L. Mei. *Auxiliary-Ligand Dependent Adaptive Regulation of Uranyl Coordination in Mixed-Ligand Uranyl Compounds of Flexible Benzenetetracarboxylic Acid. Inorg. Chem.* 2020, **59**, 17659-17670.
96. J. Harrowfield, Y. Atoini, P. Thuéry. *Plumbing the uncertainties of solvothermal synthesis involving uranyl ion carboxylate complexes. CrystEngComm* 2022, **24**, 1475-1484.
97. P. Thuéry, J. Harrowfield. *Uranyl Ion Complexes with all-cis-1,3,5-Cyclohexanetricarboxylate: Unexpected Framework and Nanotubular Assemblies. Cryst. Growth Des.* 2014, **14**, 4214-4225.
98. P. Thuéry, J. Harrowfield. *Structural Consequences of 1,4-Cyclohexanedicarboxylate Cis/Trans Isomerism in Uranyl Ion Complexes: From Molecular Species to 2D and 3D Entangled Nets. Inorg. Chem.* 2017, **56**, 13464-13481.
99. Z. Weng, Z.-H. Zhang, T. Olds, M. Sterniczuk, P. C. Burns. *Copper(I) and Copper(II) Uranyl Heterometallic Hybrid Materials. Inorg. Chem.* 2014, **53**, 7993-7998.
100. E. H. Gamage, J. K. Clark, M. Yazbak, H.-P. Cheng, M. Shatruk, K. Kovnir. *Solvothermal Synthesis of $[Cr_7S_8(en)_8Cl_2]Cl_3 \cdot 2H_2O$ with Magnetically Frustrated $[Cr_7S_8]^{5+}$ Double-Cubes. Chem. Eur. J.* 2022, **28**, e202103761.
101. S.-X. Wang, M. Chrzanowski, W.-Y. Gao, L. Vojtas, Y.-S. Chen, M. J. Zaworotko, S. Ma; *Vertex-directed self-assembly of a high-symmetry supramolecular building block using a custom-designed porphyrin. Chem. Sci.* 2012, **3**, 2823-2827.
102. M. B. Andrews, C. L. Cahill. *In situ oxalate formation during hydrothermal synthesis of uranyl hybrid materials. CrystEngComm* 2011, **13**, 7068-7078.
103. D. E. Felton, T. A. Kohlgruber, Z. D. Tucker, E. M. Gulotty, B. L. Ashfeld, P. C. Burns. *Utilising ionic liquids as bifunctional reagents for the ionothermal synthesis of uranyl compounds. Cryst. Growth Des.* 2023, **23**, 8311-8318.
104. P. Thuéry, Y. Atoini, J. Harrowfield. *Crown Ethers and their Alkali Metal Ion Complexes as Assembler Groups in Uranyl–Organic Coordination Polymers with cis-1,3-, cis-1,2- and trans-1,2-Cyclohexanedicarboxylates. Cryst. Growth Des.* 2018, **18**, 3167-3177.
105. P. Thuéry, Y. Atoini, J. Harrowfield. *Triple-armed aliphatic tricarboxylic acids as sources of ligands for uranyl ion: influence of bridgehead functionalization. CrystEngComm* 2023, **25**, 3904-3915.
106. A. R. Katritzky, D. A. Nichols, M. Siskin, R. Muragan, M. Balasubramanian. *Reactions in High-Temperature Aqueous Media. Chem. Rev.* 2001, **101**, 837-892.



107. H. Kaur, N. Devi, S. Singh Siwal, W. F. Alsanie, M. K. Thakur, V. K. Thakur, *Metal-Organic Framework-Based Materials for Wastewater Treatment: Superior Adsorbent Materials for the Removal of Hazardous Pollutants. ACS Omega* 2023, **8**, 9004-9030. DOI: 10.1039/D5DT01784J
108. Z. Ni, R. I. Masel. *Rapid Production of Metal-Organic Frameworks by Microwave-Assisted Solvothermal Synthesis. J. Am. Chem. Soc.* 2006, **128**, 12394-12395.
109. H. M. L. Robert, F. Kunderat, E. Bermudez-Ureña, H. Rigneault, S. Monneret, R. Quidant, J. Polleux, G. Baffou. *Light-Assisted Solvothermal Chemistry using Plasmonic Nanoparticles. ACS Omega* 2016, **1**, 2-8.
110. D. Sud, G. Kaur. *A comprehensive review on synthetic approaches for metal-organic frameworks: From traditional solvothermal to greener protocols. Polyhedron* 2021, **193**, 114897.
111. Z. Kovács, C. Molnár, U. L. Štanger, V-M. Cristea, Z. Pap, K. Bernadi, L. Baia. *Optimization Method of the Solvothermal Parameters Using Box-Behnken Experimental Design - The Case Study of ZnO Structural and Catalytic Tailoring. Nanomaterials* 2021, **11**, 1334.
112. Z.-X. Xu, Y. Xiao, Y. Kang, L. Zhang, J. Zhang. *Homochiral Cluster-Organic Frameworks Constructed from Enantiopure Lactate Derivatives. Cryst. Growth Des.* 2015, **15**, 4676-4686.
113. H. Kohlmann. *Looking into the Black Box of Solid-State Synthesis. Eur. J. Inorg. Chem.* 2019, 4174-4180.
114. Y. Huang, B. Yan, M. Shao. *Solvothermal synthesis, crystal structure and characterizations of three quaternary lanthanide homophthalate coordination polymers. Solid State Sci.* 2008, **10**, 1132-1138.
115. H. M. Felmy, K. T. Bennett, S. B. Clark. *The impact of mixed solvents on the complexation thermodynamics of Eu(III) by simple carboxylate and amino carboxylate ligands. J. Chem. Thermodynamics* 2017, **114**, 83-92.
116. L. Rao, G. Tian, P. Di Bernardo, P-L. Zanonato. *Hydrolysis of Plutonium(VI) at Variable Temperatures (283-343 K). Chem. Eur. J.* 2011, **17**, 10985-10990.
117. P-L. Zanonato, P. Di Bernardo, A. Bismondo, G. Lui, X. Chen, L. Rao. *Hydrolysis of Uranium(VI) at Variable Temperatures (10-85 °C). J. Am. Chem. Soc.* 2004, **126**, 5515-5522.
118. X.-M. Chen, M.-L. Tong. *Solvothermal in Situ Metal/Ligand Reactions: A New Bridge between Coordination Chemistry and Synthetic Organic Chemistry. Acc. Chem. Res.* 2007, **40**, 162-170.



119. H. D. Burrows, T. J. Kemp. *The Photochemistry of the Uranyl Ion. Chem. Soc. Rev.*, 1974, **3**, 139-165. View Article Online
DOI: 10.1039/D5DT01784J
120. P. Thuéry, J. Harrowfield. *Stepwise Introduction of Flexibility into Aromatic Dicarboxylates Forming Uranyl Ion Coordination Polymers: a Comparison of the Phthalate Relatives 2-Carboxyphenylacetate and 1,2-Phenylenediacetate. Eur. J. Inorg. Chem.* 2021, 2182-2192.
121. L. Carlucci, G. Ciani, J. M. Garcia-Ruiz, M. Moret, D. M. Proserpio, S. Rizzato. *Crystallisation Behaviour of Coordination Polymers. 1. Kinetic and Thermodynamic Features of 1,3-Bis(4-pyridyl)propane/MCl₂ Systems. Cryst. Growth Des.* 2009, **9**, 5024-5034.
122. S. L. James. *Tackling a difficult question: how do crystals of coordination polymers form ? IUCrJ* 2015, **1**, 263-264.
123. J. Hengsteler, K. A. Kanes, L. Khasanova, D. Momotenko. *Beginner's Guide to Micro- and Nanoscale Electrochemical Additive Manufacturing. Ann. Rev. Anal. Chem.* 2023, **16**, 71-91.
124. M. J. Van Vleet, T. Wang, X. Li, J. R. Schmidt. *In Situ, Time-Resolved and Mechanistic Studies of Metal-Organic Framework Nucleation and Growth. Chem. Rev.* 2018, **118**, 3681-3721.



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

[View Article Online](#)
DOI: 10.1039/D5DT01784J

