Nucleation-Controlled Crystallization of a New, Spontaneously Resolved Solvate of $[Ru(bpy)_3](PF_6)_2$ and its Desolvation Reaction**

Josef Breu,* Wolfgang Seidl, Dominikus Huttner, and Florian Kraus[a]

Abstract: Simply by increasing the supersaturation level, racemic $[Ru(bpy)_3](PF_6)_2$ no longer crystallises as the well-known true racemate (β-modification; $P\bar{3}c1$, $a = 10.6453(5)$, $c = 16.2987(9)$ Å, $Z = 2$). Rather, it spontaneously resolves and forms a conglomerate of pure Λ- and pure Δ-crystals with a so far unknown structure type. This new modification actually is a solvate ($[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,CH_3COCH_3$; δ-type; $P32$, $a = 13.8133(7)$ Å, $c = 11.6523(7)$ Å, $Z = 2$). By a solution-mediated equilibration the new modification is shown to be the metastable (Ostwald) product, which is formed based on nucleation kinetics. Upon desolvation the solvate transforms into a second enantiomorphic crystal structure (γ-type; $P3_1$, $a = 10.3809(4)$, $c = 26.2576(13)$ Å, $Z = 3$). The latter could previously only be obtained by chemical resolution prior to crystallisation, but could not be accessed directly from racemic solutions. However, the new δ-modification can now be utilised for optical resolution by the so-called method of "resolution by entrainment". This example emphasises the potential that both kinetically controlled crystallisation and desolvation of solvates bear with respect to crystal engineering.

Keywords: chiral recognition · conglomerate crystallisation · molecular recognition · nucleation · polymorphism

Introduction

The existence of more than one crystal structure for the same molecular compound (i.e., polymorphism) is a frequently occurring phenomenon[2] that is both of fundamental academic and economical interest. On the one hand, polymorphs are the result of the same cohesive forces and, therefore, they provide more comprehensive information on the intermolecular interactions than any singular crystal packing. Especially concomitant polymorphs are of great value in improving our understanding of molecular recognition and self-assembly.[3] On the other hand, polymorphic modifications of the same compound may differ markedly in chemical and physical properties (shelf life, solubility, bioavailability, morphology, etc.), which at a practical level makes polymorphism a potentially important issue across a wide range of industries including pharmaceuticals, healthcare, agrochemicals, pigments, dyestuffs and foods. The prominent problem cases of Abbot Laboratories' HIV drug Ritanovir® and of Glaxo Wellcome's anti-ulcer drug Zantac® are potent reminders of the importance of molecular solid-state chemistry.[4]

Despite this, our ability to consistently and reproducibly "synthesise" one or the other already known polymorph is still limited. Polymorphs apparently come and go in unpredictable ways.[5–7] The design of crystallisation approaches that would grant us access to the multitude of theoretical polymorphs which are predicted to exist within a narrow energy range for almost any given molecular compound appears even more utopian.[8–11]

Two polymorphs can only be at thermodynamic equilibrium at the p,T conditions of the transition point at which the ΔG curves cross. Therefore, it is evident that the vast majority of polymorphism incidences are based on the kinetics and energetics of nucleation, which unfortunately are poorly understood and difficult to study. The matter is complicated by the fact that flexible molecules frequently accept different conformations in the different crystal structures (*conformational polymorphism*). This requires a balanced treatment of inter- and intramolecular interactions. Even a controlled variation of solvents designed to influence—and possibly control—the intermolecular interaction patterns is hampered by the inadvertent and unpredictable inclusion of solvent molecules.

Observation of polymorphism for a rigid molecule at the same p,T conditions and in the same solvent is a comparatively rare phenomenon. This is unfortunate, since with such a system the complex matter would be simplified a great deal and it would be better suited to study nucleation in a more systematic way. Such a system is reported in this paper, namely $[Ru(bpy)_3](PF_6)_2$.

[a] Priv. Doz. Dr. J. Breu, W. Seidl, D. Huttner, F. Kraus
Institut für Anorganische Chemie der Universität Regensburg
93040 Regensburg (Germany)
Fax: (+49) 941-9434523
E-mail: josef.breu@chemie.uni-regensburg.de

[**] Chiral Recognition among Trisdiimine-Metal Complexes, Part 8. For Part 7, see ref. [1].

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Results and Discussion

Due to its photochemical and photophysical properties[12] $[Ru(bpy)_3](PF_6)_2$ has been intensively investigated over the last decades. From racemic solutions under "standard" crystallisation conditions, for instance slow evaporation from acetone solutions, a true racemate, the β-modification, is formed ($P\bar{3}c1$, $a = 10.6453(5)$, $c = 16.2987(9)$ Å, $Z = 2$).[13–15] Furthermore, since $[Ru(bpy)_3]^{2+}$ is inert towards racemisation an enantiomorphic γ-type[15] ($P3_1$, $a = 10.3809(4)$, $c = 26.2576(13)$ Å, $Z = 3$) can be "forced" upon $[Ru(bpy)_3](PF_6)_2$ by chemical resolution prior to crystallisation. Enantiomerically pure $[Ru(bpy)_3](PF_6)_2$ can no longer crystallise in the centrosymmetric β type, but must crystallise in an enantiomorphic structure with a space group that contains no improper symmetry operations. However, γ type never forms spontaneously from racemic solutions.

Certainly, racemic $[Ru(bpy)_3](PF_6)_2$ has been crystallised many times worldwide from probably any common solvent.[13–18] Nevertheless, by simply raising the supersaturation level, we were able to find a so far unknown enantiomorphic modification. When starting again with a racemic solution in acetone, but speeding up evaporation by a modest flow of nitrogen, spontaneous resolution occurs. Instead of the true racemate, β, a conglomerate of pure Λ and pure Δ crystals of a new enantiomorphic modification is obtained.

This new modification actually is an acetone solvate ($[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,CH_3COCH_3$) and may be called a pseudopolymorph.[19, 20] However, since both the β modification and this new solvate may be obtained from the very same solvent with only the level of supersaturation deciding between the two, they should actually be regarded siblings. We feel that the usage of "pseudo" overemphasises the differences by focusing on the composition. From the point of genesis (nucleation) the two are indeed closely related. Accordingly, we will refer to this new solvate in short as δ modification.

Crystal structure: Similar to the β and γ type (compare Figures 3 and 4 in ref. [15]), the δ modification consists of layers of complex cations (Figure 1). The unit cell contains only one layer, which is enantiomerically pure. In the *ab* plane a honeycomb-like hexagonal pattern is visible (Figure 2). Note, that adjacent complex cations are displaced along the *c* axis by 2.311 Å (Figure 3), hence the layer is corrugated. The

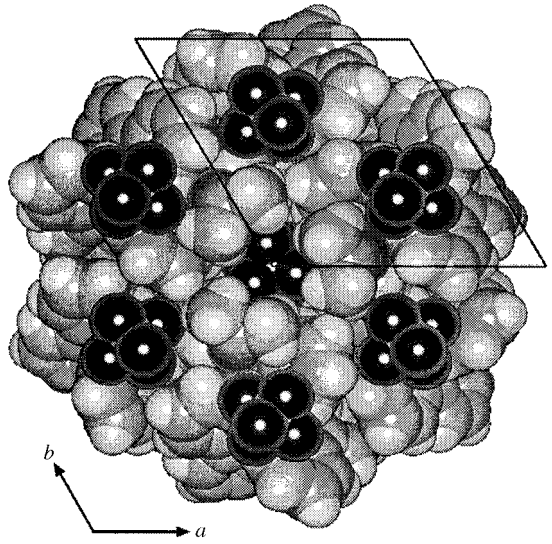

Figure 2. Space-filling packing diagram of complex cation layer in δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$.

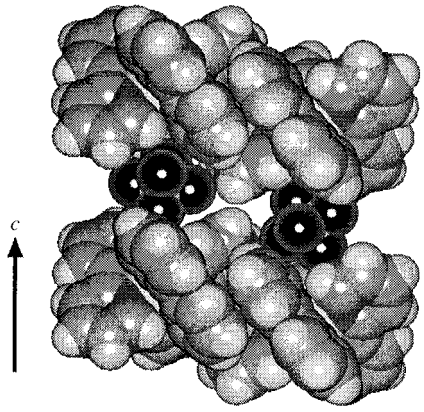

Figure 3. Space-filling packing diagram of complex cation columns running along *c* in δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$ displaying the interlocking of adjacent cations.

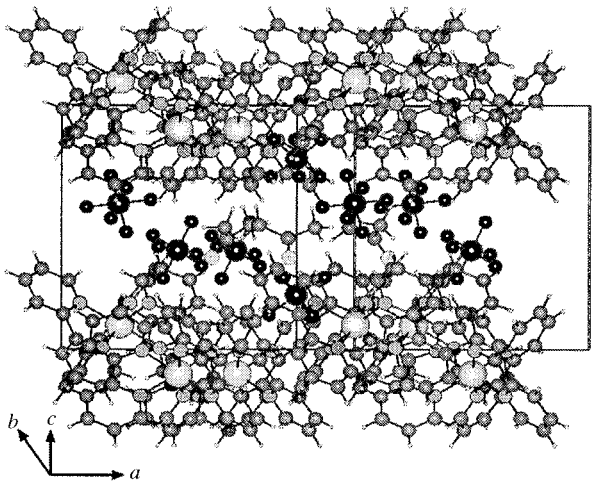

Figure 1. Crystal-packing diagram of δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$.

intermolecular distances may be discussed on the basis of the Ru···Ru distances. Within the layer they amount to 8.3031(4) Å and are much shorter than the in plane distances in the β and the γ modifications (10.6453(5) Å and 10.3873(5) Å, respectively). Along the *c* axis the layers are stacked without displacement (orthogonally) on top of each other. The layer distance corresponds to the *c* axis (11.6523(7) Å). While in β and γ direct contacts between cations along the stacking direction exist (8.1494(5) Å and 8.7601(6) Å, respectively), in the δ form the layers are separated by one of the two PF_6^- sites. In summary, the intermolecular contacts and the packings are quite different in the three modifications. In β and γ, the closest contacts between cations are between layers, while in δ they are found within the layer. Also, with δ modification the $\pi-\pi$ interaction patterns between neighbouring ligands (Figure 3) are

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neither of the T-shaped (as observed with β) nor of the shifted π stack (as observed with γ) type. The intermolecular pattern observed with the δ form has been named "orthogonal quadruple aryl embrace".[21]

The cavity at the centre of the honeycomb hosts the second anion site (Wyckoff position 2*c* at 0,0,*z*). However, there is extra space in this void that is filled by three acetone molecules to achieve efficient packing.

Relative stability of the three (pseudo-)polymorphs: Macroscopic thermodynamics dictates that the crystalline phase formed in a supersaturated solution should be the one with the lowest free energy. Given that both the β and δ modifications may be obtained at the very same p,T conditions from the same solution, the two polymorphs either are incidentally at (or at least close to) thermodynamic equilibrium at the conditions chosen for crystallisation, or one of them is a metastable structure that is formed based on Ostwald's[22] step rule. Formulated in 1897 this rule states that the crystal phase nucleating from the melt or solution does not have to be the thermodynamically most stable one, but as Stranski and Totomanow[23] argued some time later, the nucleating phase is the one with the lowest free-energy barrier of formation. A solution may be supersaturated because the route to a more stable (crystalline) phase takes place through the formation of a supercritical nucleus.[24] The free energy of a nucleus is determined not only by the difference in chemical potential in solution and in the crystalline phase, which drives nucleation, but also by the surface free energy. Classical nucleation theory (CNT) assumes that the nuclei are compact, spherical objects of radius *r* with no reference to any details of the atomic (molecular) structure[25, 26] and the free energy of these clusters (c) is given by Equation (1):

$$\Delta G_c(r) = \frac{4\pi r^2\gamma - 4/3\pi r^3}{\nu k_B T \ln(\sigma + 1)} \quad (1)$$

where γ is the surface free energy, ν is the molar volume of the nucleus, k_B the Boltzmann factor and σ the relative supersaturation. While γ is always positive because of the work that has to be done to create an interface between solution and nucleus, the volume term is always negative. Initially, with small aggregates the surface term dominates and the free energy of the aggregate increases with size. Only when the nucleus has reached a certain "critical" size does the volume term take over and the free energy decrease. The height of the nucleation barrier can easily be obtained as Equation (2).

$$\Delta G_c^* = \frac{16\pi\nu^2\gamma^3}{3k_B^2T^2\ln^2(\sigma + 1)} \quad (2)$$

CNT does not consider the atomic structure of the nucleus explicitly, but rather this is subsumed in the surface term. Unfortunately, structural details of precritical aggregates can not be accessed experimentally. However, for polymorphic systems it is assumed that intermediary aggregates of different structural types corresponding to the distinct crystal structures are formed.[27] Corresponding with the individual structure of "polymorphic" aggregates, the free energies and, hence, the nucleation barriers differ. With polymorphic nucleation the free energy barrier is governed by the two competitive factors of surface free energy and relative supersaturation, both of which are highly dependant on the polymorphic modifications.

According to Boltzmann statistics the number of aggregates that are in the state ΔG_c^* is proportional to $\exp(-\Delta G_c^*/k_BT)$, and nucleation shows Arrhenius-like behaviour. The homogenous nucleation rate can be written as Equation (3):[26]

$$J = A\exp(-\Delta G_c^*/k_BT) \quad (3)$$

in which A is a pre-exponential frequency factor. All exponential factors except for T depend on the polymorph. When we assume for the sake of simplicity that the pre-exponential factor is common to the two polymorphs in a dimorphic system, then the nucleation kinetics of the polymorphs are determined by the two factors of supersaturation and of surface free energy (Figure 4). Low temperature and

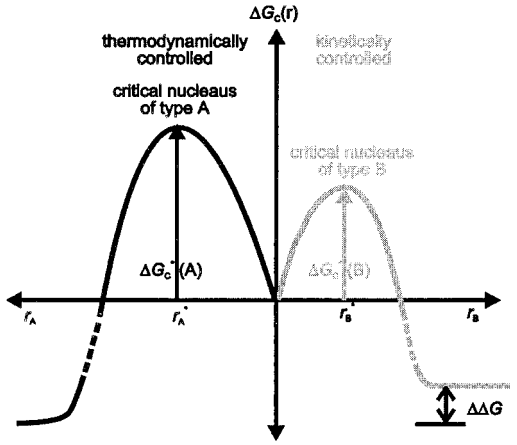

Figure 4. Schematic representation of the reaction coordinate for nucleation in a dimorphic system to show the nucleation (activation) barriers for the formation of polymorphs A and B.

increasing supersaturation gives rise to preferred nucleation of the metastable form.[28] Actually J may show sharp maxima[26] and at a given set of nucleation parameters, it may well be that only the metastable form nucleates. If at the same conditions, supercritical nuclei of the metastable form also are able to grow at a significant rate, macroscopic crystals (detectable by diffraction) may be produced as a single phase .

In summary, the rate of nucleation for different polymorphs and solvates is dependant on the volume term (corresponding to the lattice energy), the structure of the critical nucleus (corresponding to the crystal structures), temperature of nucleation, the degree of supersaturation and possibly the activity of solvent molecules to be included. Since the nucleation barrier in a first approximation is equivalent to the activation energy in molecular reactions,[29] it bears, in principle, some potential for crystal engineering: It opens the path to a kinetic product control that consequently will give access to a broader area of crystal phase space.

For instance, by increasing the supersaturation, nucleation may then be controlled by the lowest nucleation barrier and we might end up with the metastable instead of the

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thermodynamically stable crystalline phase. In our case, by increasing the supersaturation, we no longer obtain the thermodynamic stable β modification, but instead the metastable δ modification (see next paragraph).

How can the relative thermodynamic stability of the three known (pseudo-)polymorphs be established? When different crystal forms are possible for a substance each form has a certain solubility value under a fixed set of conditions: solvent composition, temperature and pressure. The solubility of different polymorphs is different.[28] Thus, even if crystals of two forms have been produced concomitantly, the system will always tend to produce only the less soluble (more stable) of different modifications eventually. Of course, the time it takes to express this tendency depends on kinetic factors and may be quite variable.[30] Three mechanisms can occur through rather different pathways: solid-state transformation, melt-mediated transformation and solution-mediated transformation.[28] Since an enantiotropic or monotropic phase transition between a true racemate and an enantiomorphic structure is impossible and since $[Ru(bpy)_3](PF_6)_2$ decomposes before melting, the thermodynamic relation between the modifications has to be established by the last method. The solution-mediated transformation includes the mass-transfer process in solution, that is, when the solution concentration is between the solubility of the metastable and the stable form, the stable form precipitates through dissolution of the less stable form. Two processes are involved in that transformation: growth of supercritical nuclei (and larger crystals) of the stable form and dissolution of the less stable form. Of course, since $[Ru(bpy)_3]^{2+}$ will not racemise in solution the enantiomorphic modifications, δ and γ, have to be supplied as 1:1 mixtures (conglomerates) of Λ and Δ crystals in a solution-mediated equilibration with the true racemate β (Figure 5). The γ

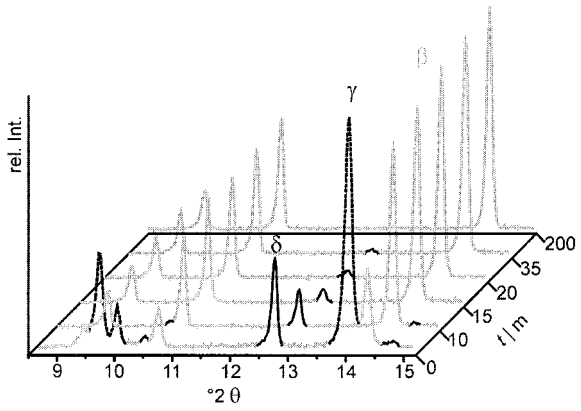

Figure 5. Time-resolved XRD-monitoring of the solution-mediated equilibration of known crystalline phases of $[Ru(bpy)_3](PF_6)_2$.

modification, which previously could only be obtained after chemical resolution prior to crystallisation, was included in the experiment for the sake of completeness.

When immersing a blend of the three different crystalline modifications of $[Ru(bpy)_3](PF_6)_2$ in a saturated solution in acetone, the thermodynamically unstable conglomerate of the γ modification is gone before the capillary can be mounted on the diffractometer. This is fully in line with calculated lattice energy differences,[1] which showed γ to be clearly less stable than β. Moreover, the metastable δ modification is converted within minutes to the thermodynamically stable β modification. Thus, the solution-mediated equilibration unequivocally proves the β form to be the most stable among the three known modifications.

Furthermore, the speed of this solution-mediated phase transformation explains why the δ modification has been overlooked to date, despite the multitude of crystallisations performed worldwide. In crystallising a compound from solution two stages have to be distinguished: 1) the formation of a critical nucleus, as discussed above, and 2) its subsequent growth. The fields of maximum nucleation rates and maximum crystal growth rates may or may not overlap (Figure 6).

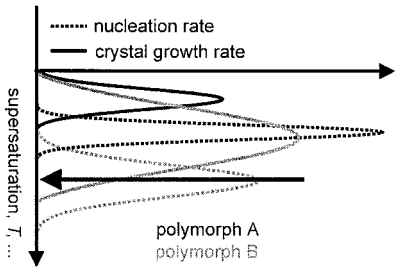

Figure 6. Schematic representation of nucleation and crystal growth in a dimorphic system.

In most crystallisation attempts, the supersaturation necessary to induce nucleation is generated by precipitation through addition of a second solvent, in which the solute is less soluble, by slow evaporation or by supercooling. It is likely that in some of the preparations of $[Ru(bpy)_3](PF_6)_2$ reported in the literature, initially a supersaturation level was reached whereby nucleation of the δ-phase would have occurred. However, since no precautions were taken to keep the supersaturation level constant, through subsequent crystal growth of the δ-nuclei the supersaturation continuously decreased down to the level at which nucleation of the thermodynamically stable β phase was initiated (see Figure 1.11 in ref. [30]). Once supercritical nuclei of β were present, even macroscopic crystals of the δ-polymorph would have been converted within minutes completely to β through a solution-mediated phase transition. Only when the supersaturation throughout the crystallisation is kept at a level high enough to promote both nucleation and crystal growth of the δ-modification, while nucleation of β is cut off, a pure δ-batch may be obtained (indicated by an arrow in Figure 6).

Formation of γ-$[Ru(bpy)_3](PF_6)_2$ from δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$ (desolvation): With respect to crystal engineering, solvent-containing modifications like δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$ imply additional potential. Alternatively, these compounds may be viewed as clathrates (host–guest compounds), which are formed by the inclusion of guest (solvent) molecules by a host component. This view might actually reflect a realistic picture of nucleation of the δ modification. There is no specific interaction of the acetone molecules evident in the packing of δ. Rather, the role of the solvent

molecules seems to be that of a filler. This suggests that during nucleation the intermolecular interactions between solute molecules favour, among others, a precritical aggregate structure related to the δ structure, but that would not lead to an efficient, dense packing. Only when the appropriate guests are present to fill the voids, may this structure develop into a macroscopic three-dimensional periodic crystal structure.

Such clathrates may easily be decomposed, leading to new crystalline phases.[31, 32] With δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$ desolvation actually is a spontaneous process that occurs at ambient temperature. This pseudomorphosis is a relatively slow reaction that can easily be monitored by X-ray powder diffraction (Figure 7). The transformation can also be followed under the microscope, since upon desolvation the crystals turn cloudy at the reaction front. The conversion of individual crystals even of similar size is quite non-uniform. At the same time, entirely unchanged crystals are present next to completely desolvated crystals. Most likely, the nucleation barrier of the desolvated phase is responsible for this induction period. The volume decrease accompanying the loss of the solvent molecules is considerable ($\Delta V = 15\,\%$). Therefore, it is not surprising that the transformation is not single crystal to single crystal, but instead when starting with a δ crystal a microcrystalline powder is obtained, albeit in the shape of the starting single crystal (pseudomorphosis). The reaction is not topotactic. When monitoring the desolvation of an oriented single crystal on a precession camera no preferred orientation of the microcrystals formed can be observed.

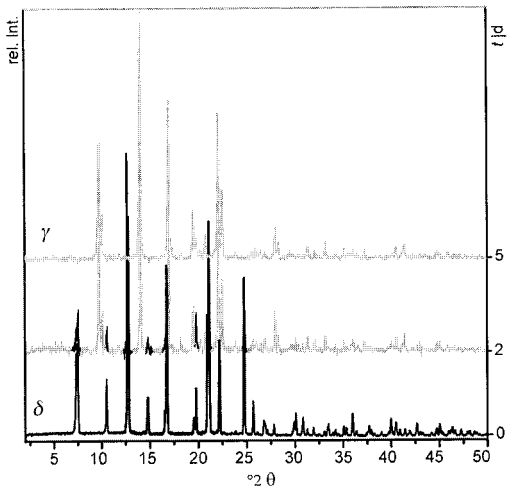

Figure 7. Pseudomorphosis of γ-$[Ru(bpy)_3](PF_6)_2$ after δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$.

Structure solution of the pseudomorph formed from after δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$ is simple. The desolvation product is the second enantiomorphic structure type known, the γ modification. As outlined above, the packing patterns of δ and γ phases are quite different. Thus, there is no simple reaction coordinate evident for the transformation.

Although, the γ phase for $[Ru(bpy)_3](PF_6)_2$ could be synthesised previously through chemical resolution prior to crystallisation, the general potential of such desolvation reactions of clathrates is evident. From racemic solutions γ is not accessible directly by any kind of crystallisation conditions (Figure 8). However, it can now be synthesised indirectly through the desolvation of δ-$[Ru(bpy)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$. The kinetically controlled crystallisation of the δ polymorph implies a spontaneous resolution. Thus, this route could also be utilised for optical resolution by the so-called method of "resolution by entrainment".[33]

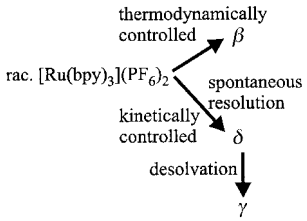

Figure 8. Schematic representation of the relative stability of known crystalline phases of racemic $[Ru(bpy)_3](PF_6)_2$.

Conclusion

Crystal engineering implies the control over the design and the preparation of desired crystal structures. Currently, most approaches rely on relatively strong and directive intermolecular interactions, such as dative or hydrogen bonding. These are explored in a systematic way by identifying *supramolecular synthons* that can then be used to construct predefined architectures.[34, 35] In this approach the focus is on the molecular entity, which is designed with the supramolecular entity (crystal) in mind. This strategy is in some respect similar to approaches taken in the synthesis of large molecules. However, the main key to the versatility of molecular synthesis is the mature knowledge about the structure of transition states. With the right choice of reagents, catalysts and solvents it is usually possible to proceed along the desired direction of the reaction coordinate. On the basis of this profound knowledge deliberate and reproducible kinetic product control is feasible.

For crystals, the critical nucleus corresponds to a transition state. Unfortunately, more than a hundred years after Ostwald formulated his step rule we still have little structural information on critical nuclei. Even for homogeneous nucleation the influence of temperature, supersaturation and solvent on the "activation energy" for different types of nuclei in a polymorphic system is unclear. In reality, the situation is yet more complex because the nucleation is most likely to be heterogeneous. The catalytic role of the substrates, the surface of impurities or the flask, or biopolymers in the case of biomimetic synthesis, is still more dubious.

As a consequence, kinetically controlled crystallisation currently relies on the empirical exploration of the appropriate nucleation conditions in a trial and error approach and its strict repetition. As with any kinetically controlled experiment, if the set of initial parameters is not recorded with scrutiny or is not complete, such metastable polymorphs may "disappear".[5–7]

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However, with respect to crystal engineering, nucleation promises some potential. The first attempts to develop strategies for ensuring maximum diversity of isolated crystal forms on that basis have been reported.[36] With the right choice of crystallisation (nucleation) parameters it should, in principle, be possible to synthesise a great deal more of the many predicted, but so far experimentally unknown, low-energy polymorphs. It is expected, that experimentalists will increasingly take up the challenge presented by the "structure prediction" community.[10, 37–42] The more we learn about the structure and the activation energy of possible transition states, the more deliberately may we choose the right nucleation parameters. Experimental setups that allow control of the supersaturation level at a given temperature will be particularly useful. Atomistic models of the critical nuclei may be contributed by computer simulations.[43–48]

Additionally, the formation of clathrates may assist in a more thorough exploration of crystal-phase space. Desolvation, especially if the reaction is topotactic, may in general yield crystal packing patterns that are not accessible otherwise,[49] but which may display appealing properties. The possible inclusion of solvents might even be explored in a kind of combinatorial crystallisation from solvent mixtures.

$[Ru(bpy)_3](PF_6)_2$ appears to be an ideal candidate to study the above strategies in a more systematic way, both experimentally and through simulations using classical potentials. Experimentally the higher diffraction power of this organometallic compound is advantageous. Additionally, by chemical resolution the crystallisation of the thermodynamically stable β modification may be completely suppressed. This way three (pseudo-)polymorphs are accessible in a single solvent. For simulations it is reassuring to have a validated force field available;[1] the rigid nature of the molecular ions minimises the number of variables and the ionic character of the building blocks should provoke aggregation.

Experimental Section

Synthesis: $[Ru(bpy)_3](PF_6)_2$ was obtained by metathesis of the corresponding chloride, which was prepared in turn according to literature procedures.[50]

δ-$[Ru(bpy)_3](PF_6)_2$ may be reproducibly crystallised from dry acetone by the following procedure: an Erlenmeyer (50 mL) flask was charged with a saturated solution (approx. 20 mL) and then steadily evaporated by purging a smooth flow of nitrogen through the flask. The nitrogen flow was set to roughly 50 $cm^3 min^{-1}$ by adjusting the valve at the outlet. During crystallisation the flask was thermostated by ice water. To prevent solvent loss during data collection, suitable crystals were immediately immersed in perfluoroether RS 3000.[51]

Crystal structure analyses: Crystal data were collected with a Stoe IPDS diffractometer equipped with a graphite monochromator. The data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods applying SIR97[52] and refined with the SHELX-97 program package.[53] SHELX refines against F^2 and all data were used in the full-matrix least-squares. H atoms were placed in idealised positions and refined with fixed isotropic displacement parameters of 1.2 U_{eq} (parent C). All other atoms were refined anisotropically. The weighting scheme recommended by the program was used and refinement was continued until complete convergence (maximum shift/esd < 0.001) was achieved. The absolute structure was assigned on the basis of the Flack x parameter.[54] x is the fractional contribution of the inverted component of a "racemic twin". It is expected to be zero for the correct structure, unity for the inverted structure. Graphics and geometrical parameters were prepared using the PLATON package.[55]

Crystal data: $[Ru(C_{10}H_8N_2)_3](PF_6)_2 \cdot 1.5\,C_3H_6O$, $M_r = 945.23$, trigonal, $P32$ (Nr. 150), $a = 13.8133(7)$, $c = 11.6523(7)$ Å, $V = 1925.47(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.630$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $\mu = 0.59$ mm^{-1}, $T = 200(2)$ K, orange, hexagonal prism ($0.30 \times 0.30 \times 0.20$ mm). Data collection: 8346 reflections collected, 2305 independent reflections, $R_{int} = 0.0340$, 2176 observed reflections [$I_o > 2\sigma(I_o)$], $\theta_{max} = 25.2°$, $h = -15 \rightarrow 16$, $k = -16 \rightarrow 12$, $l = -13 \rightarrow 13$. Refinement: $wR(F^2) = 0.0723$, $R(F) = 0.0287$, $S = 1.032$, Flack parameter[54] $= -0.01(4)$, $(\Delta/\sigma)_{max} < 0.001$, $\Delta\rho_{max} = 0.409$ e Å^{-3}, $\Delta\rho_{min} = -0.284$ e Å^{-3}.

Bond lengths and angles are within the expected range and compare well with literature data.[13–16] The PF_6^- site separating the cations stacked along c, resides on a crystallographic C_3 axis. However, the electron density found at this site is much better represented by aligning the octahedron with its pseudo-C_4 axis along the threefold axis and accepting this anion site to be disordered around the crystallographic C_3 axis. Static and dynamic disorder is a well-documented phenomenon with the almost spherical hexafluorophosphate anion.

Furthermore, for the sake of an efficient packing the solvate molecules can not be oriented to fit the crystallographic C_2 axis and are disordered around this twofold axis; this is also a frequent observation in solvates.[56]

CCDC-180251 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk).

Solution-mediated equilibration: A mixture of three approximately equal amounts of β crystals, Λ and Δ crystals (1:1) of the δ modification and Λ and Δ crystals (1:1) of the γ modification was prepared and filled into a glass capillary. A Stoe Stadi P diffractometer equipped with a Ge-monochromator and a point sensitive detector was used to record powder diffraction traces by using $Cu_{K\alpha 1}$ radiation ($\lambda = 1.54060$ Å) between 8.57–15.18° 2θ, the range in which characteristic reflections are observed for all three modifications. The detector was kept stationary during data collection (counting time 5 min). Then a saturated solution of $[Ru(C_{10}H_8N_2)_3](PF_6)_2$ in acetone was added and diffraction traces were recorded at given time intervals. The same equipment was used for recording the powder diffraction patterns discussed in the pseudomorphosis section. However, then the detector was moved with a step size of 0.2° min^{-1} and a counting time of 120 s.

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