

### SELF-ASSEMBLED COORDINATION COMPLEXES BY SOLID-STATE REACTIONS

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Coordination polymers and 0-D frameworks, built up of metal centres linked by organic ligands, have been extensively studied in recent years with especial interest in their utility for molecular recognition, non-linear optical properties or for catalytic purposes(1). We have recently shown that the symmetrical bipodal N',N'',N''',N''''-tetraalkyl-N,N-phenylenedicarbonylbis(thioureas) readily form 2:2 and 3:3 metallamacrocyclic complexes of platinum(II) and nickel(II) in high yields (2,3).

The structure of the metallamacrocyclic complexes seem to depend only on the relative (para vs meta) substitution position of the two carbonylthiourea moieties linked through the phenylene ring. We have also recently reported(4) on two related coordination polymers [ZnBr<sub>2</sub>(pyz)<sub>2</sub>],1 and [ZnBr<sub>2</sub>(pyz)<sub>2</sub>],2. The solid-state reaction of 1 with pyrazine yields 2, and 2 in its turn is readily converted to 1 by heating. The activation energy of the latter has been determined as 99.8 kJmol<sup>-1</sup>. Coordination polymers of these types, and the inclusion compounds they form, may be prepared by means of solid-solid or solid-gas reactions. Some examples will be presented.

#### References

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### A NOVEL FREE-MOUNTING SYSTEM FOR PROTEIN CRYSTALS: IMPROVEMENT OF DIFFRACTION POWER BY ACCURATELY CONTROLLED HUMIDITY CHANGES

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The protein crystal itself is one of the bottlenecks in structural genomics. Post-growth crystal treatment in particular crystal dehydration, can help to improve crystal order by crystal shrinkage. New crystal contacts can be formed especially hydrogen bonds. Here we describe a novel device for capillary-free mounting of protein crystals. A controlled stream of air allows an accurate adjustment of the relative humidity (r.h.) at the crystal. The crystal is held on the tip of a micropipette. With a video system (CCD), the two-dimensional shadow projections of crystals can be recorded for optical analysis. Instead of the micropipette, a standard loop can also be used. Experiments and results for different crystal systems demonstrate the general use of this method, also in combination with shock-freezing, to improve crystal order. In some cases the number of unique reflections was increased up to 6-fold. Additionally the system allows the test of arbitrary gaseous or volatile substances by adding them simply to the mainstream. Systematic post-growth crystal treatment monitored online optically and by X-rays becomes reality in protein crystallography.

**Keywords:** POST-GROWTH CRYSTAL TREATMENT HUMIDITY CONTROL CRYSTAL IMPROVEMENT

### STRUCTURAL DIVERSITY IN CO-ORDINATION POLYMERS WITH AN ANGULAR DIPYRIDYL LIGAND

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There are many factors which are of significance in the design of co-ordination frameworks, including the metal centre, the anion, the ligand and the solvent system. The ligand bis(4-pyridyl)-1,3,5-triazine (dpt), which has peripheral N-donors fixed at an angle of 120 degrees, has been reacted with a number of metal salts to yield a variety of different structures which range from simple monomeric units through one- and two-dimensional polymers to a three-dimensional network. By using the same ligand throughout, it has been possible to observe the effects that other factors have on co-ordination polymer growth. In the case of the zinc nitrate system changing the solvent system led to the formation of a pair of polymorphs, while simply changing the cadmium nitrate:ligand ratio yielded two very different compounds: one is a discrete monomeric compound in which only one N-donor is coordinated while the other is a parallel interpenetrated two-dimensional network. The reaction of CuSCN with dpt gave two distinct products from the same reaction mixture. Although these products have the same chemical formula they are polymorphs, one of which adopts a one-dimensional ribbon structure and the other a three-dimensional framework arrangement.

**Keywords:** DESIGN COORDINATION FRAMEWORKS POLYMORPH

### TUNING POLARITY BY SOLID SOLUTIONS OF MOLECULAR CRYSTALS

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Application of a general principle of polarity formation in molecular crystals<sup>1</sup> has become a base to elaborate theoretical and synthetic concepts to grow polar materials. In this respect, organic solid solutions H<sub>1-x</sub>G<sub>x</sub> co-crystallized by use of a host (H) and a guest compound (G) offer a broad range for tuning properties, including effects of polarity. Most effectively, polar properties may arise for components representing donor/acceptor [(A)/(D)] disubstituted  $\pi$ -systems (H: D- $\pi$ -D, A- $\pi$ -A, G: D- $\pi$ -A, or vice versa), which show synthon interactions in corresponding crystal structures. In H<sub>1-x</sub>G<sub>x</sub> crystals, polar effects can arise irrespective of a centric crystal structure of H and G. In order to facilitate solid solution formation and a near to parallel alignment of compounds, extended linear  $\pi$ -systems were inserted between the D/A terminal groups. Solid solution formation over the entire range of composition x was found for 4,4'-dinitrostilbene (DNS, H) and 4-chloro-4'-nitrostilbene (CNS, G) crystallizing in P21/c. CNS is showing a 50:50 % site occupation for both orientations of the dipole moment. In these structures weak CH...Cl and CH...O<sub>2</sub>N hydrogen bonding is made responsible for polarity formation during crystal growth. Solid solution formation was observed for the entire range of composition. All H<sub>1-x</sub>G<sub>x</sub> mixtures were showing a SHG effect. The relative response was increasing with x, reaching its maximum at x = 1. Phase sensitive SH-microscopy<sup>2</sup> has revealed 180° domain formation, a twinning mechanism typical for Markov-type grow-in polarity.

#### References

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