

Templated crystal nucleation: mixed crystals of very different copper(II) N,N',N'' -trimethyltriazacyclononane complexes

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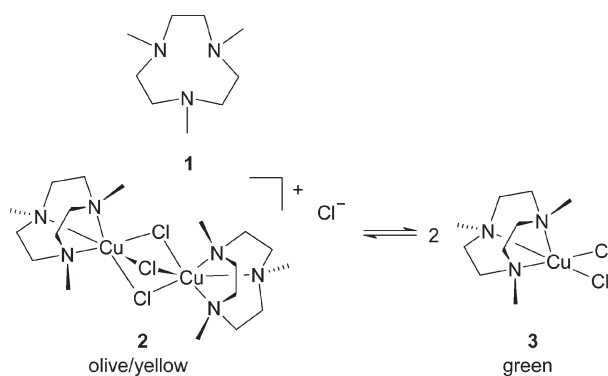
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Templation of a daughter phase by a parent crystal results from an equilibrating mixture of two very different copper(II) N,N',N'' -trimethyltriazacyclononane complexes.

It is now well established that, despite their often beautiful appearance, crystalline substances are frequently not pure compounds. Indeed, impurities within crystalline lattices are responsible for an enormous range of interesting and useful properties such as p- and n-type semiconductivity, the colour of minerals such as Lapis Lazuli¹ and the formation of 'hourglass inclusions' with potential non-linear optical applications.² Crystals containing more than one compound were also responsible for the controversy over bond stretch isomerism in the late 1980s,³ and there is now significant interest in the study of such compounds, which have been termed 'molecular alloys'.^{4–10} It has been shown to be possible to use single crystals of materials to template the epitaxial growth of a daughter phase of an isostructural or nearly isostructural compound to produce composite crystals with well-defined zones.^{4,5,10} Generally, both the inclusion of impurities within a regular crystal lattice and the templation of a daughter phase might be expected to require a match between the size, shape or distribution of key functionalities, such that the boundary region does not generate severe stress within the resulting composite solid.^{6,11} The use of one material to template the growth of a daughter phase, in the production of designer materials containing technologically useful vectorial junctions between ordered domains, is potentially a highly important procedure by analogy with layered inorganic solids. Template nucleation effects are also of great interest in answering fundamental questions such as the origin of biological chirality (the 'Adam' effect).^{12,13} Moreover, they can give profound insights into the nucleation process, as in the inclusion of indigo at the twin boundary of saccharin crystals.^{14,15} We now report the preparation of two interconverting but non-isostructural Cu(II) complexes that form single co-crystals containing well defined, templated domains.

The reaction of N,N',N'' -trimethyltriazacyclononane (**1**) with copper(II) chloride in polar solvents such as ethanol or THF results in the formation of a crystalline olive-yellow binuclear species of formula $[\{Cu(\mathbf{1})\}_2(\mu-Cl)_3]Cl \cdot 4H_2O$ (**2**) (Scheme 1). Complex **2**



Scheme 1 Solution equilibrium between the bi- and mononuclear Cu(II) complexes of N,N',N'' -trimethyltriazacyclononane.

adopts a distorted octahedral geometry at the Cu(II) centre, but because of the operation of the Jahn–Teller effect in Cu(II), readily loses an axial bridging chloride ligand to give the bright green monomeric complex $[Cu(\mathbf{1})Cl_2]$ (**3**), which possesses a distorted square-pyramidal Cu(II) centre. The equilibrium between complexes **2** and **3** is highly dependent upon the solvent, with neutral, monomeric **3** being the predominant species in non-coordinating solvents such as CH_2Cl_2 . Complexes **2** and **3** may be crystallised individually (**3** as the CH_2Cl_2 hemisolvate), and their X-ray crystal structures have been determined (Fig. 1 and Table 1).[†]

Crucially, the coordination geometry about each individual Cu(II) centre in **2** is almost identical to that in **3**, except for the additional axial chloride interaction (which results in a dimer with crystallographic two-fold symmetry). Viewed from the triazacyclononane side, the complexes are essentially indistinguishable (Fig. 2). This close similarity in size and shape results in particularly interesting crystal deposition behaviour in solvent media, in which both **2** and **3** co-exist in equilibrium. So, while slow evaporation of a solution of **2** in polar solvents gives pure crystalline **2** as a monoclinic form (Table 1), crystals grown from CH_2Cl_2 /hexane (1 : 1, v/v) are orthorhombic needles containing bright green **3** as well as olive-yellow **2** (Fig. 3). This co-crystallisation of two related species can be ascribed to a shift in the solution equilibrium as the crystallisation proceeds, such that crystals of binuclear **2** begin to deposit as the solution becomes more concentrated as a result of CH_2Cl_2 evaporation. However, this does not explain the enclosure of zones of **3** by **2**, indicating that both species are being deposited from solution simultaneously and suggesting that in the orthorhombic form, each is capable of templating the growth of the other. Usually however, it is

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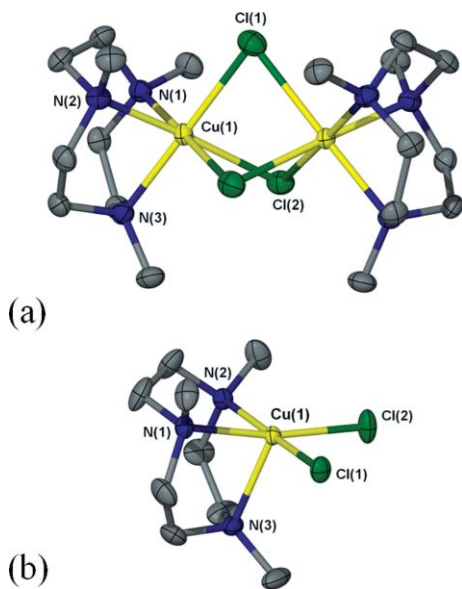


Fig. 1 X-Ray molecular structures of (a) $[\{\text{Cu}(1)\}_2(\mu\text{-Cl})_3]\text{Cl}\cdot 4\text{H}_2\text{O}$ (**2**) and (b) $[\text{Cu}(1)\text{Cl}_2]\cdot \text{CH}_2\text{Cl}_2$ (**3**) (ellipsoids are shown at the 30% level).

Table 1 Crystal parameters for **2** and **3**

	2	3
Formula	$\text{C}_{18}\text{H}_{42}\text{Cl}_4\text{Cu}_2\text{N}_6\cdot 4\text{H}_2\text{O}$	$\text{C}_9\text{H}_{21}\text{Cl}_2\text{CuN}_3\cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pbcn$
$a/\text{\AA}$	13.7720(14)	13.7910(3)
$b/\text{\AA}$	13.5920(14)	14.5310(2)
$c/\text{\AA}$	8.5480(8)	15.0530(4)
$\alpha/^\circ$	90	90
$\beta/^\circ$	101.364(3)	90
$\gamma/^\circ$	90	90
$V/\text{\AA}^3$	1568.7(3)	3016.58(11)
Z	2	8
R indices	$R1$ 0.0444 $wR2$ 0.1285	0.0371 0.1039

apparently the bright green **3** that is deposited first, with the olive-yellow **2** forming as a daughter phase as the solution becomes more concentrated.

Attempts to break up the mixed crystals resulted in the isolation of stable crystals of bright green **3** (confirmed by X-ray crystallography), however the templated form of **2** proved to be highly unstable. This is in contrast to the monoclinic crystals obtained

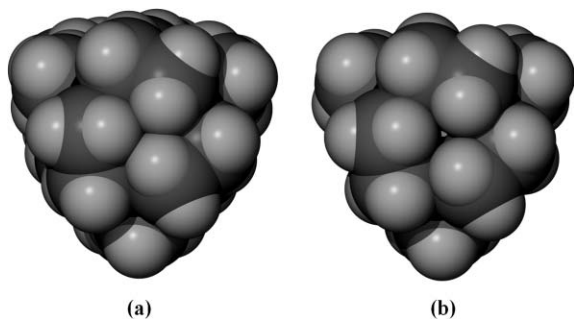


Fig. 2 Space-filling views of (a) **2** and (b) **3** from the triazacyclononane side of each complex.

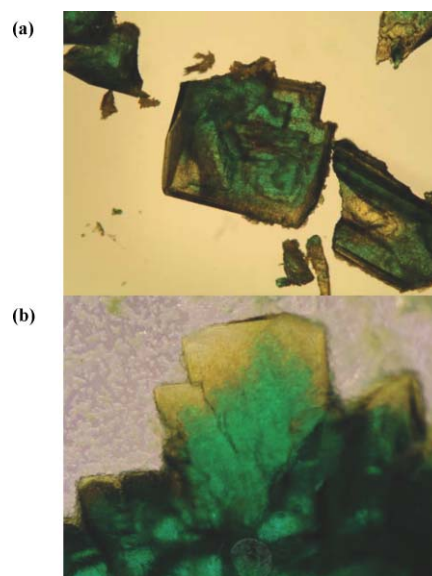


Fig. 3 Photographs of mixed crystals of **2** (yellow) and **3** (green) showing (a) mutual templation and (b) templation of **2** by **3**.

from polar solvents, indicating that orthorhombic **3** is the stable lattice that templates the formation of an unstable phase of **2**. In the absence of **3**, compound **2** is deposited in the much more stable monoclinic form. Attempts to characterize the templated daughter phase of **2** by single crystal X-ray diffraction were unsuccessful because of the fragility of the crystals, although Bragg peaks were observable.

An examination of Table 1 reveals that the orthorhombic and monoclinic forms of these compounds are somewhat related by similar a unit cell dimensions, although b is *ca.* 7% different and c in monoclinic **2** is rather more than half that of orthorhombic **3**. Comparison of the crystal packing in **2** and **3**, viewed along the crystallographic c axis, reveals that while a and b dimensions are similar, in fact the packing arrangement is rather different. The epitaxial growth must therefore proceed on a molecular basis by the inclusion of the very similar triazacyclonane end of one molecule into the lattice of orthorhombic **3** to give a highly unstable polymorph of **2**. The growth of granddaughter regions of **3** are also possible. This hypothesis is supported by inspection of the boundary region between the yellow and green zones, which visually suggests the presence of a mixture of both compounds.

In conclusion, we have demonstrated that epitaxial growth of one phase by another can proceed at a molecular level without significant matching of the unit cell dimensions of the stable phases of the two materials. Similarities in one portion of the molecule result in its inclusion on the growing face of the crystal of another and *vice versa*.

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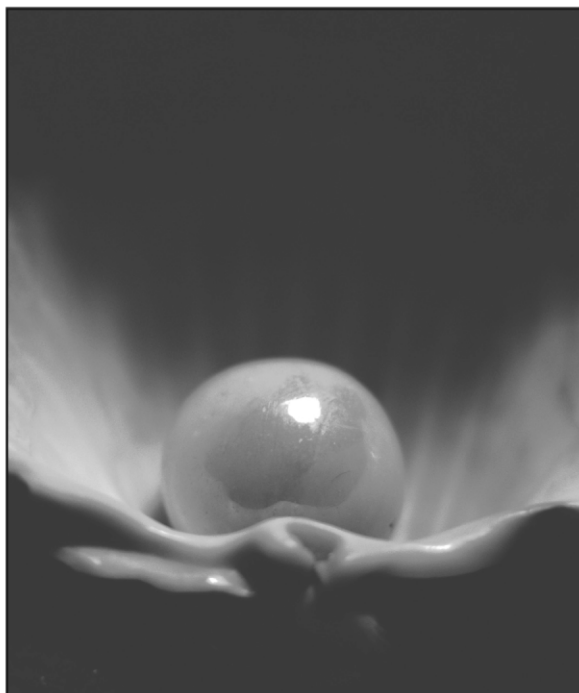
Notes and references

† Crystal data for **2**: $\text{C}_{18}\text{H}_{50}\text{Cl}_4\text{Cu}_2\text{N}_6\text{O}_4$, $M = 683.52$, $0.20 \times 0.10 \times 0.10$ mm, yellow prism, monoclinic, space group $P2_1/c$ (no. 13), $a = 13.7720(14)$, $b = 13.5920(14)$, $c = 8.5480(8)$ \AA , $\beta = 101.364(3)^\circ$, $V = 1568.7(3)$ \AA^3 , $Z = 2$, $D_c = 1.447$ g cm^{-3} , $F_{000} = 716$, KappaCCD, Mo-K α

radiation, $\lambda = 0.71073 \text{ \AA}$, $T = 298(2) \text{ K}$, $2\theta_{\text{max}} = 52.0^\circ$, 2876 unique reflections. Final GoF = 1.048, $R1 = 0.0444$, $wR2 = 0.1223$, R indices based on 2558 reflections with $I > 2\sigma(I)$ (refinement on F^2), 164 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.729 \text{ mm}^{-1}$ CCDC 622422. Crystal data for **3**: $\text{C}_{9,50}\text{H}_{22}\text{Cl}_3\text{CuN}_3$, $M = 348.19$, $0.4 \times 0.2 \times 0.1 \text{ mm}$, green block, orthorhombic, space group *Pbcn* (no. 60), $a = 13.7910(3)$, $b = 14.5310(2)$, $c = 15.0530(4) \text{ \AA}$, $V = 3016.58(11) \text{ \AA}^3$, $Z = 8$, $D_c = 1.533 \text{ g cm}^{-3}$, $F_{000} = 1440$, KappaCCD, Mo- K_α radiation, $\lambda = 0.71070 \text{ \AA}$, $T = 293(2) \text{ K}$, $2\theta_{\text{max}} = 50.0^\circ$, 33372 reflections collected, 2580 unique ($R_{\text{int}} = 0.0410$). Final GoF = 1.031, $R1 = 0.0371$, $wR2 = 0.1008$, R indices based on 2397 reflections with $I > 2\sigma(I)$ (refinement on F^2), 151 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.961 \text{ mm}^{-1}$. CCDC 622423. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b614043b

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