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Guest exchange and competition in inclusion compounds

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The host 1,4-bis(9-hydroxyfluoren-9-yl)benzene forms isomorphous inclusion compounds with acetone and DMSO. The exchange process between these two guests has been monitored in detail and the selectivity of the host towards acetone, DMSO and propan-2-ol has been determined.

The compound **H** = 1,4-bis(9-hydroxyfluoren-9-yl)benzene is a versatile host molecule which conforms to Weber's host design specifications in that it is rigid and bulky and contains hydroxy moieties, which are good hydrogen-bond donors.[1] We have employed this host for the separation of lutidine (dimethylpyridine) isomers.[2]

While the synthesis, structure and thermal stability of organic inclusion compounds have been widely discussed,[3] the question of guest exchange has received little attention despite the fact that such processes are important for sensing and catalysis based on inclusion.[4–6] Recent studies on this subject include the study of single crystal to single crystal transformations induced by guest exchange in inclusion compounds of cholic acid.[7] Bulky hosts containing the fluorenyl moiety are responsive to volatile guests and the exchange of EtOH and n-PrOH has been monitored by X-ray powder diffraction.[8] A bisresorcinol derivative of anthracene has been shown to undergo guest exchange that is concomitant with structural adjustment while retaining its crystallinity.[9]

We have crystallised the host (**H**) with acetone, DMSO and propan-2-ol and elucidated the following structures: **1 H**·acetone; **2 H**·DMSO; **3 H**·MIX (MIX = 58% DMSO + 42% acetone as mole fractions) and **4 H**·2 Pr^{i}OH.

The crystals of **1** and **2** are isostructural and crystallise in space group $P\bar{1}$, and the guest molecules lie in channels running parallel to [100]. The projection of **1** is shown in Fig. 1(a) and 1(b), the latter with the guest molecules omitted and the host as a van der Waals representation, so that the channels are clearly evident. In both structures the guests are stabilised by two independent (Host)O–H···O(Guest) hydrogen bonds, details of which are given in Table 1. Complex **4** also crystallises in $P\bar{1}$ but is different in that the host–guest ratio is 1 : 2 and the channels in which the Pr^{i}OH guests are located are wider as shown in Fig. 2(a) and 2(b), which is viewed along [010]. Each Pr^{i}OH is stabilised by two independent H-bonds.

We have carried out selectivity experiments between all three pairs of guests by dissolving the host in mixtures of the guests in different proportions, allowing the inclusion compounds to crystallise and by analysing the guests in the crystals. The results are given in Fig. 3. These show that there is virtually no discrimination between acetone and DMSO [Fig. 3(a)] and that Pr^{i}OH is selected preferentially over both DMSO and acetone [Fig. 3(b) and 3(c)].

The result of the acetone/DMSO competition as well as the fact that their complexes are isostructural led us to attempt a guest exchange experiment. We preferred to work with powdered samples in order to avoid retardation of the process by diffusion barriers in large single crystals. We prepared the **H**·acetone compound by exposing a powdered specimen of the host to acetone vapour for 12 hours. The resulting inclusion compound is identical to structure **1**, as demonstrated by X-ray powder diffraction. The guest exchange was carried out by exposing **H**·acetone powder to DMSO vapour in a closed vessel at 25 °C. We sampled the resulting compound at regular intervals by DSC. The results are shown in Fig. 4 which displays the movement of the first endotherm from T_{on} = 81 °C, corresponding to pure acetone guest, to T_{on} = 197 °C for **2**. The second endotherm, T_{on} = 261 °C corresponds to the host melt, and remains constant throughout. The reaction is complete after 86 hours and the fact that we obtain a moving but single endotherm of guest release shows that a continuous solid solution of the mixed guests has been formed in the channels of the host.

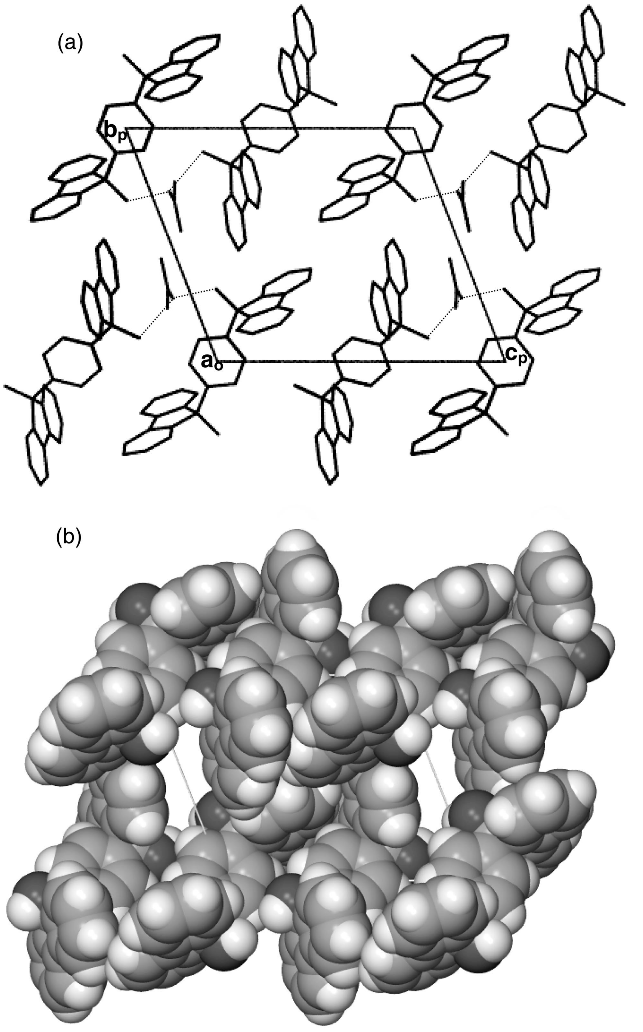

Fig. 1 (a) Projection of **1** along [100], H-bonds are shown by dotted lines; (b) space-filling projection of **1** along [100] with guest molecules omitted, showing the open channels.

We also grew single crystals with mixed guests. GC analysis showed that these contained 58% DMSO and 42% acetone (as

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Table 1 Hydrogen-bonding parameters

Compound	Donor (D)	Acceptor (A)	D–H/Å	D···A/Å	D···H–A/°
1	O9A	O1G	0.93(2)	2.866(2)	172(2)
	O9B	O1G	0.90(2)	2.870(2)	171(2)
2	O9A	O1G	0.91(2)	2.791(2)	173(2)
	O9B	O1G	0.95(2)	2.785(2)	171(2)
3	O9A	O1G	0.93(3)	2.795(2)	170(2)
	O9B	O1G	0.94(3)	2.798(2)	167(3)
4	O9	O1G	0.98(2)	2.722(2)	166(2)
	O1G[a]	O9	0.93(2)	2.840(2)	167(2)

[a] $-x, 1-y, 1-z$.

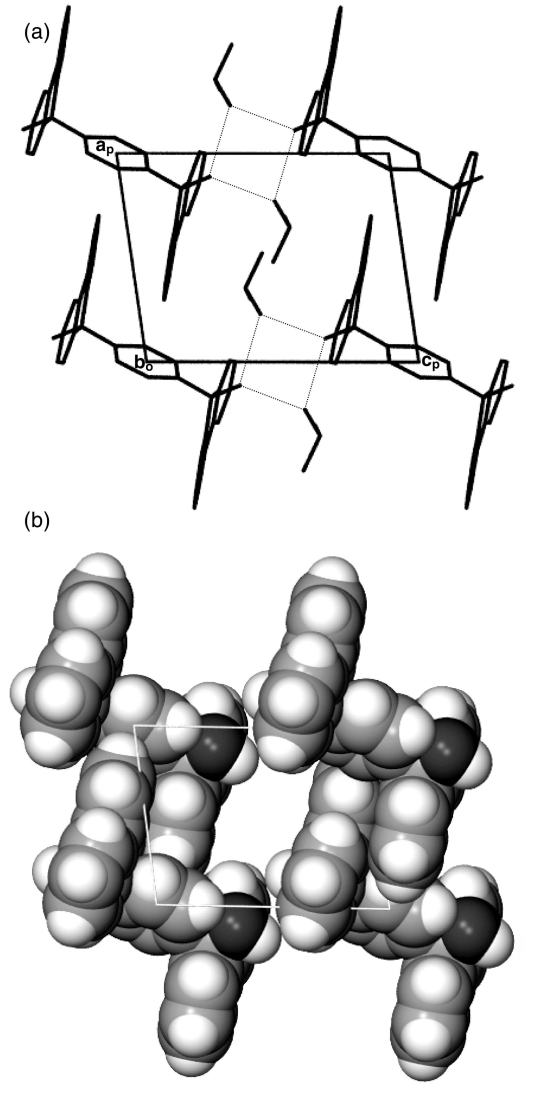

Fig. 2 (a) Projection of **4** along [010], H-bonds are shown by dotted lines; (b) space-filling projection of **4** along [010] with guest molecules omitted, showing the open channels.

mole percentages). We elucidated the structure of this compound, **3** (**H·**MIX), which is isostructural with **1** and **2**. However, the difference electron density map obtained after the host structure had been refined could only be interpreted as a severely disordered guest, averaging DMSO and acetone. The packing of **3**, however, is essentially the same as that of **1** and **2**. We have carried out similar structure analysis of an inclusion compound with mixed guests, when the host 1,1-bis(dihydroxyphenyl)cyclohexane was shown to enclathrate a mixture of 2,3-xylenol and 3,5-xylenol.[10]

The structure of **4** is distinctly different from those of **1**, **2** and **3**. We therefore considered the problem of structure change as the ratio of Pr^{i}OH–acetone and Pr^{i}OH–DMSO was increased systematically. We therefore obtained X-ray powder diffraction (XRPD) patterns from powders with mixed guests and found that for the acetone–Pr^{i}OH series the structure adopted is that of **1** for $x_{\mathrm{Pr^iOH}} \leq 0.3$, after which it changes to that of **4**. In the case of DMSO–Pr^{i}OH, however, structure **2** prevailed throughout. The XRPD patterns for **1** and **4** are shown in Fig. 5. We have demonstrated similar effects with the structures of 1,1,2,2-tetraphenylethane-1,2-diol with mixtures of 2,6-lutidine and 3,5-lutidine.[11]

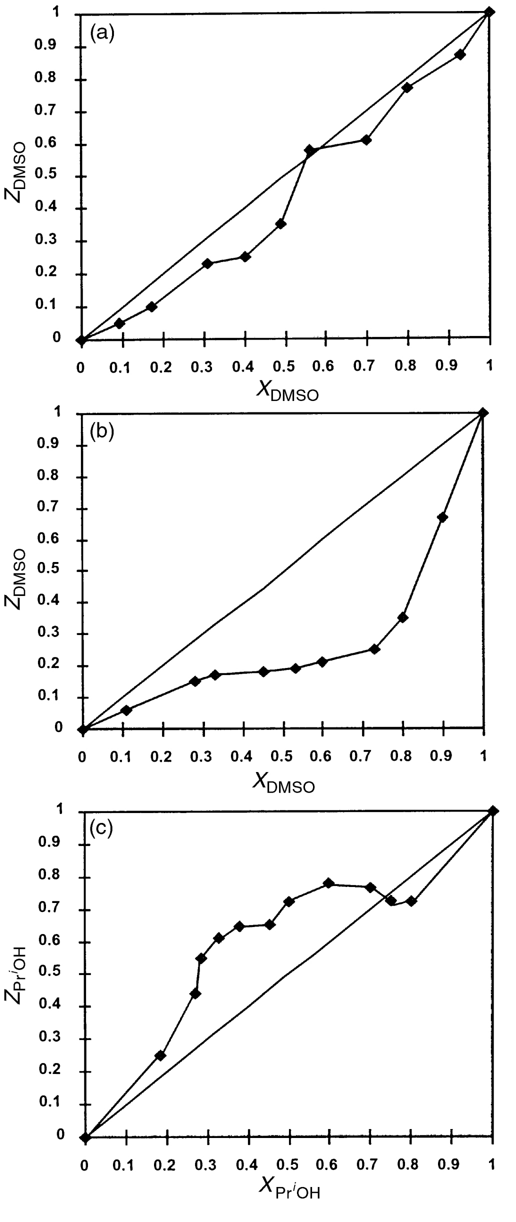

Fig. 3 Results of the competition experiments: (a) DMSO *versus* acetone; (b) DMSO *versus* Pr^{i}OH; (c) Pr^{i}OH *versus* acetone. X_{guest} is the mole fraction of guest in the liquid mixture; Z_{guest} is the mole fraction of this guest in the crystal.

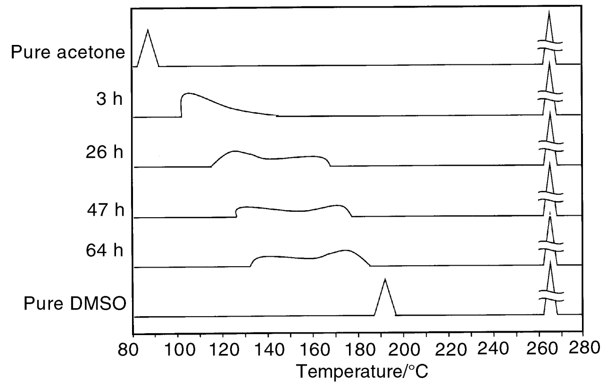

Fig. 4 Migration of the desorption endotherm as a function of time for the guest exchange experiment (**H**·acetone + DMSO→**H**·DMSO + acetone).

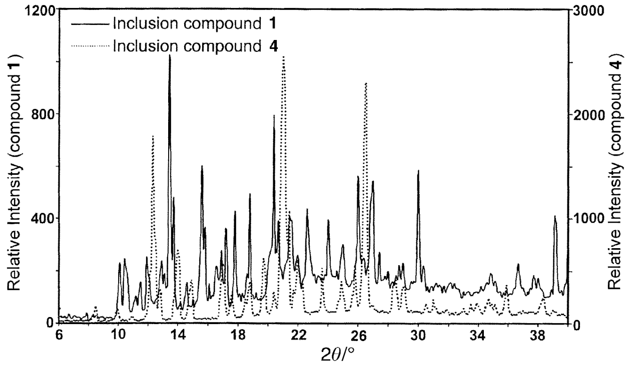

Fig. 5 Experimental XRPD traces of **1** (solid line) and **4** (dotted line).

Lattice energy calculations were performed for **1**, **2** and **4** using the atom–atom potential method. We employed the program EENY,[12] using a force field of the type

$$V(r) = a \exp(-br) - c/r^6$$

where r is the interatomic distance and the coefficients a, b and c are those given by Gavezzotti.[13] We incorporated a hydrogen bonding potential that is a simplified version of that given by Vedani and Dunitz[14] and is formulated as

$$V(\text{H-bond}) = (A/R^{12} - C/R^{10}) \cos^2 \theta$$

where R is the distance between the hydroxy hydrogen and the O acceptor, θ is the O–H · · · O angle, and the $\cos^2 \theta$ term is the energy penalty paid by the bond to take into account non-linearity. We obtained the following values for the lattice energies: **1**, −533.6 kJ mol^{-1}, **2**, −533.4 kJ mol^{-1} and **4**, −540.6 kJ mol^{-1}. The lattice energy values show the stabilities of the inclusion complexes to be in the order **4** > **2** ≈ **1**. This is in agreement with the results obtained from the competition experiments where the host compound shows no discrimination between acetone and DMSO while Pr^{i}OH is selected preferentially over both acetone and DMSO. The contributing factor for this is the additional hydrogen bonding which occurs in the Pr^{i}OH structure. In inclusion compounds lattice energy calculations are only strictly valid for host–guest systems which have the same stoichiometry and where the guests are isomeric. The values obtained are therefore only offered as a guideline.

Crystal data †

Compound **1**: $C_{35}H_{28}O_3$, $M = 496.57$, triclinic, $a = 8.6441(5)$, $b = 12.3085(8)$, $c = 13.7443(9)$ Å, $\alpha = 109.514(3)°$, $\beta = 94.460(3)°$, $\gamma = 104.182(3)°$, $V = 1315.79(14)$ Å^3, $T = 171$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 0.079 mm^{-1}, 6393 reflections measured, 4887 unique ($R_{int} = 0.0348$), $wR(F^2) = 0.1356$ (all data), $R_1 = 0.0538$ (observed data).

Compound **2**: $C_{34}H_{28}O_3S$, $M = 516.66$, triclinic, $a = 8.5651(3)$, $b = 12.4402(4)$, $c = 13.8939(3)$ Å, $\alpha = 109.148(2)°$, $\beta = 93.849(2)°$, $\gamma = 104.620(1)°$, $V = 1334.90(7)$ Å^3, $T = 175$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 0.155 mm^{-1}, 8926 reflections measured, 4771 unique ($R_{int} = 0.0206$), $wR(F^2) = 0.1463$ (all data), $R_1 = 0.0506$ (observed data).

Compound **3**: $C_{34.42}H_{28}O_3S_{0.58}$, $M = 508.24$, triclinic, $a = 8.5652(2)$, $b = 12.4265(3)$, $c = 13.8868(3)$ Å, $\alpha = 109.155(2)°$, $\beta = 93.853(3)°$, $\gamma = 104.601(1)°$, $V = 1332.83(5)$ Å^3, $T = 172$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 0.155 mm^{-1}, 7226 reflections measured, 4794 unique ($R_{int} = 0.0175$), $wR(F^2) = 0.1901$ (all data), $R_1 = 0.0701$ (observed data).

Compound **4**: $C_{38}H_{38}O_4$, $M = 558.72$, triclinic, $a = 8.348(1)$, $b = 9.227(1)$, $c = 10.369(2)$ Å, $\alpha = 96.095(8)°$, $\beta = 96.159(8)°$, $\gamma = 106.679(7)°$, $V = 752.77(19)$ Å^3, $T = 173$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, μ(Mo-Kα) = 0.078 mm^{-1}, 3460 reflections measured, 2517 unique ($R_{int} = 0.0265$), $wR(F^2) = 0.1211$ (all data), $R_1 = 0.0512$ (observed data).

For **2** and **3** the sulfur atom of DMSO is found to be disordered over two positions without altering the position of the oxygen that is an acceptor of a hydrogen bond.

Notes and references

† CCDC reference numbers 161745–161748. See http://www.rsc.org/suppdata/p2/b0/b009446n/ for crystallographic files in .cif or other electronic format.

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