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Selectivity and structure of mixed guest clathrates†‡

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Received (in Durham, UK) 29th November 2007, Accepted 28th February 2008
First published as an Advance Article on the web 31st March 2008
DOI: 10.1039/b718397f

Downloaded by University of Belgrade on 01 January 2013
Published on 31 March 2008 on http://pubs.rsc.org | doi:10.1039/B718397F

This study investigates the selectivity of two organic host molecules towards pairs of guest molecules and in particular describes the crystal structures of the mixed guest clathrates obtained in selectivity studies. The diol organic host compounds 9,9′-(biphenyl-4,4′-diyl)difluoren-9-ol (**H1**) and 9,9′-(ethyne-1,2-diyl)difluoren-9-ol (**H2**) investigated in this study were found to show interesting selectivities (determined *via* competition experiments) towards THF *vs.* Et_2O and EtOH *vs.* MeCN, respectively. The crystal structures of the single guest inclusion compounds were elucidated and compared and in addition the crystal structures of the inclusion compounds containing mixed guests were studied and in each case could be correlated with the selectivity profiles.

Introduction

Systematic studies of clathrates with mixed guests are of great benefit in the field of crystal engineering.[1,2] In particular, investigation of the crystal structures of mixed guest clathrates is important, as building an understanding of the intermolecular interactions occurring in these compounds is an essential step towards eventually gaining control over the assembly of such compounds. If the ratio of guests in an inclusion compound, in which the guests differ in size, polarity and symmetry, can be varied, inclusion compounds with different properties may be obtained.[3,4]

Selective enclathration,[5,6] which is an important aspect of inclusion chemistry, has been investigated in numerous host–guest systems by conducting competition experiments,[7–10] with many successful results. Although many such selectivity studies have been performed, very little analysis of the structures corresponding to the crystals formed from the mixed guest solutions has been carried out.

In one such study previously conducted,[11] the selectivity of the diol host compound *trans*-9,10-dihydroxy-9,10-bis(*p-tert*-butylphenyl)-9,10-dihydroanthracene for mixtures of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) was investigated and the results show the formation of five distinct inclusion compounds in which the ratio of the two guests varies in discrete steps and is determined by the composition of the liquid guest mixture from which the inclusion compound is formed.

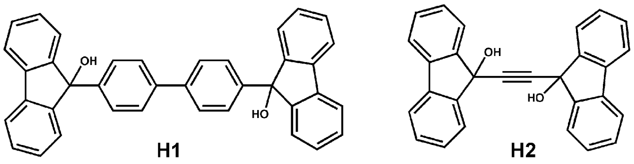
There are however few examples of such studies and here we carry out such a study, and have done so through investigation of two separate host–guest systems. The two hosts utilised in this work were 9,9′-(biphenyl-4,4′-diyl)difluoren-9-ol (**H1**)[12] and 9,9′-(ethyne-1,2-diyl)difluoren-9-ol (**H2**)[12] depicted in Scheme 1. These types of host molecules are well known and have been shown to be successful hosts, encapsulating a variety of guest molecules.[12,13] In the first set of experiments carried out the selectivity of **H1** for the guests THF *vs.* Et_2O was investigated and crystal structures of both the single and mixed guest inclusion compounds obtained were elucidated and compared to the competition experiment results. In the second set of experiments the selectivity of **H2** for the guests EtOH *vs.* MeCN was studied. In this case, these guests were chosen as with each of them the host forms different inclusion compounds (with different H : G ratios) at different temperatures. We thus wanted to investigate how the selectivity would be affected if the competition experiments were carried out at these different temperatures. A preliminary communication of these results has appeared.[14]

Experimental

Structure analysis

Crystallographic data, experimental and refinement parameters for all structures are given in Tables 1 and 2.

Suitable crystals of each of the inclusion compounds were grown by slow evaporation of a solution of the host in the relevant guest at 25 °C (with the exception of the structures of **H2** grown at −26 °C, which were crystallised in the freezer at that temperature). Cell dimensions for each inclusion



Scheme 1

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† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

‡ CCDC reference numbers 632726–632735, 679756 and 679757. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718397f

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Table 1 Crystal data, experimental and refinement parameters for inclusion compounds with **H1**

Compound	**H1**·2THF	**H1**·2Et$_2$O	**H1**·1.35THF·0.65Et$_2$O	**H1**·1.15THF·0.85Et$_2$O	**H1**·0.9THF·1.1Et$_2$O
Molecular formula	$C_{38}H_{26}O_2 \cdot 2(C_4H_8O)$	$C_{38}H_{26}O_2 \cdot 2(C_4H_{10}O)$	$C_{38}H_{26}O_2 \cdot 1.35(C_4H_8O) \cdot 0.65(C_4H_{10}O)$	$C_{38}H_{26}O_2 \cdot 1.15(C_4H_8O) \cdot 0.85(C_4H_{10}O)$	$C_{38}H_{26}O_2 \cdot 0.9(C_4H_8O) \cdot 1.1(C_4H_{10}O)$
Host : guest ratio	1 : 2	1 : 2	1 : 1.35 : 0.65	1 : 1.15 : 0.85	1 : 0.9 : 1.1
M_r/g mol^{-1}	658.80	662.83	660.81	660.81	660.81
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	15.8094(5)	7.5658(2)	15.1601(6)	15.1157(3)	15.0708(5)
b/Å	14.9432(4)	32.1197(8)	15.2878(6)	15.2709(4)	15.2736(5)
c/Å	15.5776(4)	15.3726(5)	15.7069(7)	15.7497(4)	15.8003(6)
β/°	103.219(1)	99.269(1)	101.288(2)	100.986(1)	100.415(1)
V/Å^3	3582.6(2)	3686.9(2)	3569.9(3)	3568.9(2)	3577.1(2)
Z	4	4	4	4	4
μ(Mo-Kα)/mm^{-1}	0.077	0.075	0.077	0.077	0.077
T/K	113	113	113	113	103
Range scanned, θ/°	2.14–27.09	2.97–26.34	3.04–27.09	3.00–27.11	2.46–27.11
Index ranges, hkl	−20–18; −17–19; ±19	±9; ±39; ±19	±19; ±19; −20–19	±19; ±19; ±20	−19–18; −19–17; ±19
No. reflections collected	20794	13168	14223	14794	13596
No. unique reflections	7625	7260	7653	7794	7458
R_{int}	0.0686	0.1205	0.0510	0.0537	0.0588
No. reflections with $I > 2\sigma I$	4148	3033	4348	4283	4524
Data/restraints/parameters	7625/0/459	7260/0/464	7653/0/425	7794/0/457	7458/0/468
Final R indices ($I > 2\sigma I$)	$R_1 = 0.0495$	$R_1 = 0.0646$	$R_1 = 0.0690$	$R_1 = 0.0518$	$R_1 = 0.0654$
	$wR_2 = 0.1047$	$wR_2 = 0.1148$	$wR_2 = 0.1652$	$wR_2 = 0.1269$	$wR_2 = 0.1492$
R indices (all data)	$R_1 = 0.1244$	$R_1 = 0.2121$	$R_1 = 0.1397$	$R_1 = 0.1218$	$R_1 = 0.1207$
	$wR_2 = 0.1264$	$wR_2 = 0.1581$	$wR_2 = 0.1959$	$wR_2 = 0.1523$	$wR_2 = 0.1743$
$\Delta\rho_{max, min}$/e Å^{-3}	0.339; −0.303	0.292; −0.282	0.635; −0.473	0.576; −0.385	0.486; −0.232

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Table 2 Crystal data, experimental and refinement parameters for inclusion compounds with **H2**

Compound	1.5**H2**·2EtOH	**H2**·2EtOH	**H2**·MeCN·H_2O	**H2**·2MeCN	1.5**H2**·EtOH·MeCN	1.5**H2**·1.07EtOH·0.93MeCN	1.5**H2**·1.41EtOH·0.59MeCN
Molecular formula	$1.5(C_{28}H_{18}O_2)\cdot 2(C_2H_6O)$	$C_{28}H_{18}O_2\cdot 2(C_2H_6O)$	$C_{28}H_{18}O_2\cdot C_2H_3N\cdot H_2O$	$C_{28}H_{18}O_2\cdot 2(C_2H_3N)$	$1.5(C_{28}H_{18}O_2)\cdot C_2H_6O\cdot C_2H_3N$	$1.5(C_{28}H_{18}O_2)\cdot 1.07(C_2H_6O)\cdot 0.93(C_2H_3N)$	$1.5(C_{28}H_{18}O_2)\cdot 1.41(C_2H_6O)\cdot 0.59(C_2H_3N)$
Host : guest ratio	1.5 : 2	1 : 2	1 : 1 : 1	1 : 2	1.5 : 1 : 1	1.5 : 1.07 : 0.93	1.5 : 1.41 : 0.59
M_r/g mol^{-1}	671.77	478.56	447.51	468.53	666.76	666.76	666.76
Crystal symmetry	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.5245(2)	9.755(2)	11.176(2)	9.9567(1)	9.7084(2)	9.6894(1)	9.6310(2)
b/Å	11.534(2)	10.638(2)	18.325(4)	10.8079(2)	11.562(2)	11.558(2)	11.548(2)
c/Å	16.275(3)	24.811(5)	23.185(5)	11.9167(2)	16.045(3)	16.063(3)	16.154(3)
α/°	99.20(3)			79.455(1)	80.21(3)	80.29(3)	80.54(3)
β/°	91.61(3)	91.77(3)	97.89(3)	88.281(1)	87.41(3)	87.53(3)	87.79(3)
γ/°	90.19(3)			83.363(1)	89.34(3)	89.42(3)	89.66(3)
V/Å^3	1764.2(6)	2573.5(9)	4703.6(2)	1252.21(3)	1772.9(6)	1771.4(6)	1770.8(6)
Z	2	4	8	2	2	2	2
μ(Mo-Kα)/mm^{-1}	0.081	0.080	0.081	0.078	0.079	0.079	0.079
T/K	173	173	173	173	173	173	173
Range scanned, θ/°	2.80–27.07	2.52–24.47	2.15–27.87	2.68–27.87	3.58–27.85	3.58–27.85	4.15–27.85
Index ranges, hkl	±12; ±14; ±20	±11; ±12; ±28	±14; ±24; ±30	−12–13; ±14; ±15	±12; −15–14; −21–20	−12–11; −14–15; ±20	±12; −15–14; −21–20
No. reflections collected	14087	7587	17961	10505	15234	14887	14997
No. unique reflections	7628	4220	10473	5768	8256	8142	8198
R_{int}	0.0230	0.0713	0.0478	0.0143	0.0310	0.0361	0.0329
No. reflections with $I > 2\sigma I$	5753	2123	5761	4525	5423	4951	5429
Data/restraints/ parameters	7628/0/481	4220/0/345	10473/0/639	5768/0/335	8256/0/478	8142/0/477	8198/0/475
Final R indices ($I > 2\sigma I$)	$R_1 = 0.0410$ $wR_2 = 0.0945$	$R_1 = 0.0762$ $wR_2 = 0.1885$	$R_1 = 0.0465$ $wR_2 = 0.1067$	$R_1 = 0.0382$ $wR_2 = 0.0918$	$R_1 = 0.0415$ $wR_2 = 0.0909$	$R_1 = 0.0452$ $wR_2 = 0.1071$	$R_1 = 0.0468$ $wR_2 = 0.1142$
R indices (all data)	$R_1 = 0.0630$ $wR_2 = 0.1025$	$R_1 = 0.1596$ $wR_2 = 0.2210$	$R_1 = 0.1125$ $wR_2 = 0.1321$	$R_1 = 0.0546$ $wR_2 = 0.1002$	$R_1 = 0.0819$ $wR_2 = 0.1017$	$R_1 = 0.0970$ $wR_2 = 0.1218$	$R_1 = 0.0868$ $wR_2 = 0.1290$
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.454; −0.327	0.381; −0.419	0.427; −0.227	0.229; −0.250	0.236; −0.208	0.473; −0.289	0.380; −0.547

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compound were established from the intensity data measurements on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo-Kα radiation, and an Oxford Cryostream cooling system (Oxford Cryostat) was used to control the temperature. The strategy for the data collections was evaluated using the COLLECT[15] software and, for all structures, data were collected using the standard ϕ- and ω-scan techniques, and were scaled and reduced with DENZO-SMN[16] software. The structures were solved by direct methods using SHELX-86[17] and refined by least-squares with SHELX-97[18] refining on F^2. The program X-Seed[19] was used as a graphical interface for structure solution and refinement using SHELX, and the program PovRay, included in the graphical interface X-Seed, was used to produce the packing diagrams.

For each structure non-hydrogen atoms were refined anisotropically, with the exception of disordered atoms which were refined with isotropic temperature factors. The hydroxyl hydrogen atoms were located in difference electron density maps and allowed to refine independently, while all remaining hydrogens were placed in geometrically constrained positions with isotropic temperature factors. Hydrogens were not placed on disordered atoms.

In all cases of disorder, the temperature factors of the two partial atoms were forced to refine to the same value. This value was then fixed and the site occupancy factors were allowed to refine to give a total site occupancy factor of one. The refined site occupancy factors were then fixed and the isotropic temperature factors of the two partial atoms were allowed to refine independently.

Competition experiments

Competition experiments were carried out by preparing a series of mixtures of two guests such that the mole fraction of a given guest varied from 0 to 1. The host compound (0.050 g) was then added to these mixtures, with a total guest : host molar ratio of at least 125 : 1 and dissolved by heating and stirring the solutions. The solutions were filtered through 0.5 μm syringe filters and either left to evaporate slowly at 25 °C (or in the case of the competition experiments carried out at −26 °C, the solutions were sealed and placed in the freezer at this temperature), resulting in the formation of crystals. These crystals were then filtered, surface dried, dissolved in nitrobenzene and the resulting solutions analysed by gas chromatography using a Varian 3900 gas chromatograph equipped with a Varian fused silica column (30 m length, 0.32 mm diameter).

Results and discussion

In the first investigation the host **H1** was found to form inclusion compounds with tetrahydrofuran (**H1**·2THF) and diethyl ether (**H1**·2Et_2O). The stoichiometries of the two inclusion compounds were analysed by thermal gravimetry (TG), and the structures of **H1**·2THF and **H1**·2Et_2O were elucidated by single-crystal X-ray diffraction methods at low temperature.

The **H1**·2THF structure crystallises in the space group $P2_1/c$, with $Z = 4$, and with the asymmetric unit consisting of one host and two guest molecules, with both host and guest molecules located on general positions. The guest molecules are located in restricted channels along [001] and the structure is stabilised by two (Host)–O–H···O(Guest) hydrogen bonds, with the hydrogen bonding details given in Table 3.

H1·2Et_2O also crystallises in the space group $P2_1/c$, with $Z = 4$, and the host and guest molecules located on general positions, but the cell dimensions are different from those of **H1**·2THF with the *a*-axis being half the length and the *b*-axis double the length. However, the packing of the structure is similar to that of **H1**·2THF with the host molecules packing to form the same channels along [001] in which the guest molecules are located. The packing pattern, viewed along [001], is depicted in Fig. 1. The structure is stabilised by the same hydrogen bonding pattern, with the hydrogen bonding details given in Table 3.

Competition experiments were carried out in order to determine whether the host would selectively include either THF or Et_2O. The typical general results obtained from such competition experiments are displayed in Fig. 2. The results of these competition experiments are displayed in Fig. 3, with the diagonal line representing zero selectivity. From these results it can be seen that the host **H1** shows a preference for THF over the whole concentration range. In addition to carrying out these competition experiments, the structures of the inclusion compounds crystallized from three of the mixed guest solutions were elucidated and the H : G ratios obtained from the crystal structures were found to correlate with the mole fractions obtained from the competition experiment analysis by gas chromatography.

The solution with $X_{THF} = 0.55$ gave crystals with Z_{THF}(GC) = 0.73 and the refined crystal structure yielded **H1**·1.35(1)THF·0.65(1)Et_2O, corresponding to $Z_{THF} = 0.68$. Similarly the solution with $X_{THF} = 0.32$ gave crystals with Z_{THF}(GC) = 0.60 with crystal structure refinement yielding **H1**·1.15(1)THF·0.85(1)Et_2O, which corresponds to $Z_{THF} = 0.58$. The solution with $X_{THF} = 0.12$ gave Z_{THF}(GC) = 0.45 and refinement of the crystal structure refinement yielded **H1**·0.90(1)THF·1.10(1)Et_2O, corresponding to $Z_{THF} = 0.45$. Thus in all three cases the selectivity demonstrated by the competition experiments correlates with the H : G ratios obtained from the crystal structures.

The inclusion compounds with mixed guests all crystallise in the space group $P2_1/c$ and are isostructural to **H1**·2THF. In each case the H : G_{TOTAL} = 2 with one whole molecule on one of the guest sites and two partial molecules superimposed on the other guest site, with some atoms sharing common sites. The changes which occur in the positions of the guest molecules are summarised in Fig. 4 and the hydrogen bonding details of each of the structures are given in Table 3.

Fig. 4(a) shows the structure of **H1**·2THF, in which there is one whole THF guest molecule on each guest site. Fig. 4(b) and (c) show the structures of **H1**·1.35(1)THF·0.65(1)Et_2O and **H1**·1.15(1)THF·0.85(1)Et_2O, respectively. In both of these structures there is a whole, ordered THF molecule on one guest site and on the other guest site, the two superimposed partial molecules are a partial THF and a partial Et_2O molecule with site occupancies of 0.35 and 0.65, respectively for **H1**·1.35(1)THF·0.65(1)Et_2O (Fig. 4(b)) and site occupancies of 0.15 and 0.85, respectively for **H1**·1.15(1)THF·

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Table 3 Hydrogen bonding details

Compound	D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H–A/°
H1·2THF	O9–H9···O1G	0.94(3)	1.78(3)	2.726(2)	177(2)
	O22–H22···O5G	0.94(3)	1.81(3)	2.752(2)	176(2)
H1·2Et$_2$O	O9–H9···O1G	0.96(4)	1.95(4)	2.907(3)	175(3)
	O22–H22···O5G	1.01(5)	1.86(5)	2.855(3)	171(4)
H1·1.35THF·0.65Et$_2$O	O9–H4···O1G	0.90(3)	1.87(3)	2.766(3)	175(3)
	O22–H1···O5G	0.91(4)	1.90(4)	2.812(3)	174(3)
H1·1.15THF·0.85Et$_2$O	O9–H9···O1G	0.89(3)	1.88(3)	2.762(2)	177(2)
	O22–H22···O5G	0.92(2)	1.91(2)	2.830(2)	175(2)
H1·0.9THF·1.1Et$_2$O	O9–H9···O1G	0.85(3)	2.00(3)	2.845(2)	177(3)
	O22–H22···O5G	0.90(4)	1.87(4)	2.769(3)	175(3)
1.5**H2**·2EtOH	O9–H9···O1G	0.90(2)	1.79(2)	2.675(2)	167(2)
	O12–H12···O3G	0.95(2)	1.76(2)	2.705(2)	173(2)
	O29–H29···O9	0.91(2)	1.91(2)	2.816(2)	173(2)
	O3G–H3G···O29	0.93(2)	1.86(2)	2.780(2)	170(2)
H2·2EtOH	O9–H9···O1G	0.92(1)	1.84(2)	2.700(4)	156(5)
	O12–H12···O3G	0.96(1)	1.73(2)	2.652(4)	160(4)
	O1G–H1G···O12	0.96(1)	1.77(1)	2.736(4)	178(6)
	O3G–H3G···O9	0.96(1)	1.77(2)	2.728(4)	173(9)
H2·MeCN·H$_2$O	O9–H9···O1G	0.97(2)	1.65 (3)	2.607(2)	173(2)
	O12–H12···O2G	0.94(2)	1.76(2)	2.693(2)	176(2)
	O29–H29···O12	0.91(2)	1.77(2)	2.678(2)	177(2)
	O32–H32···O9	0.95(2)	1.75(2)	2.690(2)	168(2)
	O1G–H1GA···O29	0.98(3)	1.84(3)	2.827(2)	176(2)
	O2G–H2GA···O32	0.81(2)	1.96(2)	2.765(2)	169(2)
H2·2MeCN	O9–H9···N1G	0.87(2)	2.04(2)	2.913(1)	172(2)
	O12–H12···O9	0.90(2)	1.98(2)	2.868(1)	173(2)
1.5**H2**·EtOH·MeCN	O9–H9···N1G	0.90(2)	1.86(2)	2.747(2)	165(2)
	O12–H12···O3G	0.98(2)	1.74(2)	2.717(2)	178(2)
	O29–H29···O9	0.90(2)	1.84(2)	2.734(2)	174(2)
	O3G–H3G···O29	0.97(2)	1.78(2)	2.745(2)	172(2)
1.5**H2**·1.07EtOH·0.93MeCN	O9–H9···N1G	0.94(2)	1.82(2)	2.736(2)	165(2)
	O12–H12···O3G	1.02(3)	1.70(3)	2.713(2)	175(2)
	O29–H29···O9	0.92(2)	1.82(2)	2.738(2)	175(2)
	O3G–H3G···O29	0.93(2)	1.82(2)	2.748(2)	174(2)
1.5**H2**·1.41EtOH·0.59MeCN	O9–H9···O1G	0.91(2)	1.83(2)	2.738(4)	173(2)
	O9–H9···N3G	0.91(2)	1.84(2)	2.706(4)	159(2)
	O12–H12···O5G	0.96(2)	1.75(3)	2.712(2)	174(2)
	O29–H29···O9	0.98(2)	1.79(2)	2.766(2)	173(2)
	O5G–H5G···O29	0.93(2)	1.83(2)	2.756(2)	170(2)

0.85(1)Et$_2$O (Fig. 4(c)). In both structures these two partial molecules share a common oxygen atom.

The structure of **H1**·0.90(1)THF·1.10(1)Et$_2$O is shown in Fig. 4(d). In this structure there is one whole, ordered Et$_2$O molecule on one guest site and on the other guest site there are two superimposed partial guest molecules including a partial Et$_2$O molecule with site occupancy 0.1 and a partial THF molecule with site occupancy 0.9. These two partial molecules share a common oxygen atom as well as two common carbon atoms on either side of the oxygen atom. In addition, the remaining two carbon atoms of the partial THF molecule are both disordered over two positions, with site occupancies of 0.4 and 0.5.

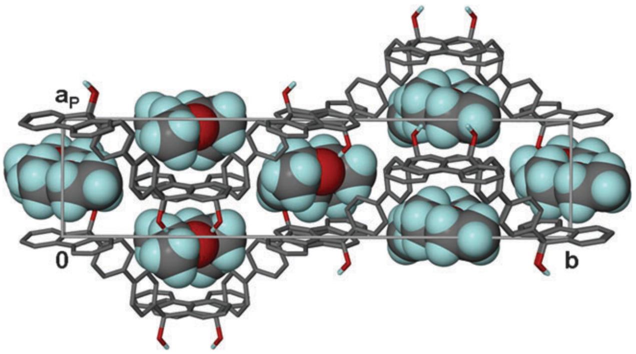

Fig. 1 Packing of **H1**·2Et$_2$O viewed along [001] with guest molecules represented with van der Waals radii.

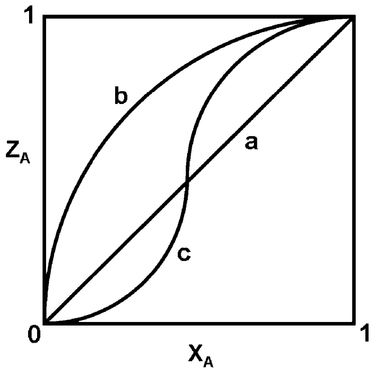

Fig. 2 Typical selectivity curves obtained from competition experiments. Each graph shows the mole fraction X of one of the guests in the initial solution *vs.* the mole fraction Z of the same guest included in the crystal, displaying (a) no selectivity, (b) good selectivity and (c) concentration dependent selectivity.

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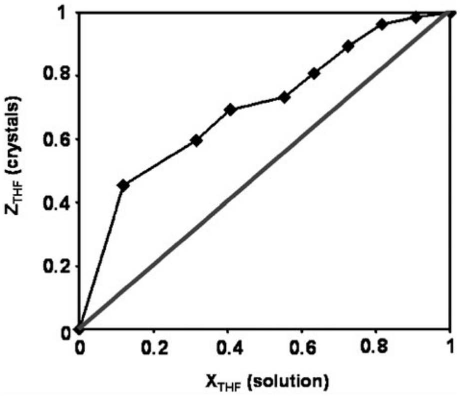

Fig. 3 Results of the THF *vs.* Et_2O competition experiments, in which THF is preferentially enclathrated over the whole concentration range.

In the second investigation the host **H2** was found to form inclusion compounds with ethanol (1.5**H2**·2EtOH and **H2**·2EtOH) and acetonitrile (**H2**·MeCN·H_2O and **H2**·2MeCN). Inclusion compounds 1.5**H2**·2EtOH and **H2**·MeCN·H_2O were formed by crystallisation at 25 °C, while inclusion compounds **H2**·2EtOH and **H2**·2MeCN were formed by crystallisation at −26 °C. The stoichiometries of the four inclusion compounds were analysed by TG and the structures were elucidated by single-crystal X-ray diffraction methods at low temperature. The hydrogen bonding details of each of the structures are displayed in Table 3.

The 1.5**H2**·2EtOH structure crystallises in the space group $P\bar{1}$ with $Z = 2$, with the asymmetric unit consisting of one and a half host molecules and two EtOH guest molecules. The whole host molecule and the guest molecules are located on general positions, with the half host molecule located on a centre of inversion at Wyckoff position *c*. The host molecules pack to form rows of cavities along [010] with each cavity containing four guest molecules.

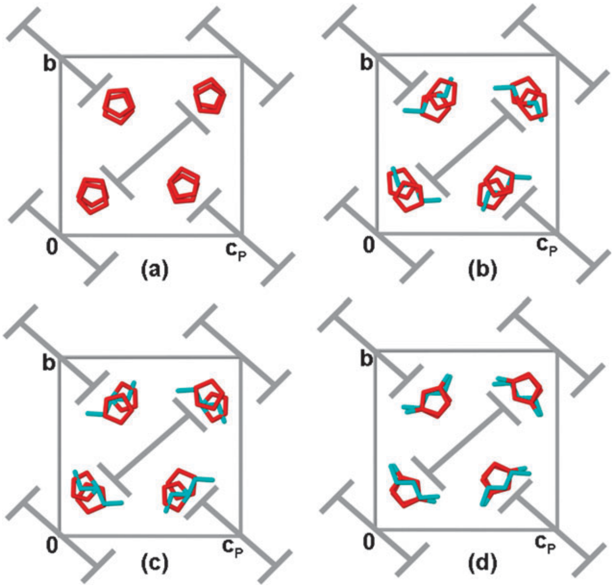

Fig. 4 Schematic diagram summarising the differences between the **H1**·2THF structure and the mixed guest inclusion compound structures, with the THF guests shown in red and the Et_2O guests shown in blue.

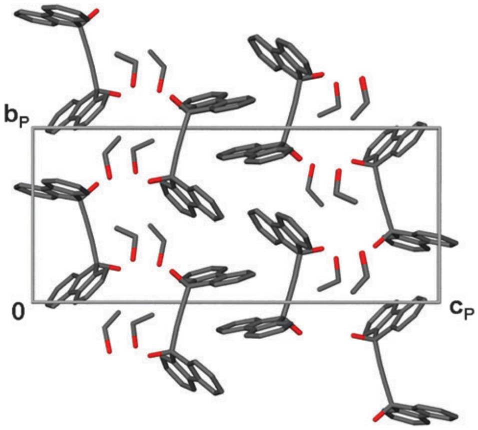

Fig. 5 Packing diagram of **H2**·2EtOH viewed along [100].

H2·2EtOH crystallises in the space group $P2_1/n$ with $Z = 4$, with one host molecule and two guest molecules in the asymmetric unit, with both host and guest molecules located on general positions. The guest molecules are located in undulating channels along [010] and Fig. 5 shows the crystal packing viewed along [100]. The differences in the host···guest interactions in 1.5**H2**·2EtOH and **H2**·2EtOH are displayed in Fig. 6.

The **H2**·MeCN·H_2O structure crystallises in the space group $P2_1/c$ with $Z = 8$, with the asymmetric unit consisting of two host molecules, two MeCN guest molecules and two water molecules and with both host and guest molecules located on general positions. The host molecules pack to form undulating restricted channels along [001] in which the guest molecules are located.

H2·2MeCN crystallises in the space group $P\bar{1}$ with $Z = 2$, with one host and two guest molecules in the asymmetric unit and with both host and guest molecules located on general positions. The host molecules pack to form two sets of intersecting channels: one set of channels is located along [100] and contains one of the unique guest molecules and the second set, consisting of highly restricted channels, is located along [010] and contains the other unique guest molecule. These channels can be clearly seen in Fig. 7, which shows the crystal packing viewed along [001].

Competition experiments were carried out at both 25 °C and at −26 °C in order to determine the selectivity of this host for

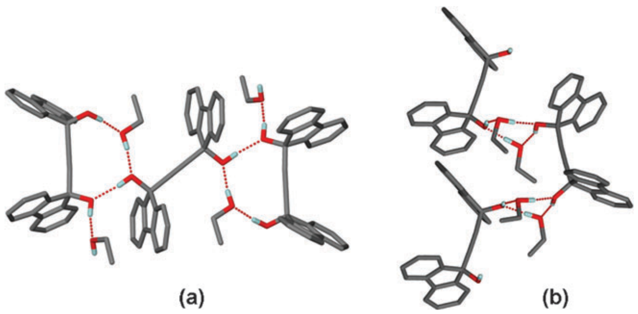

Fig. 6 Differences in host···guest hydrogen bonding in (a) 1.5**H2**·2EtOH and (b) **H2**·2EtOH.

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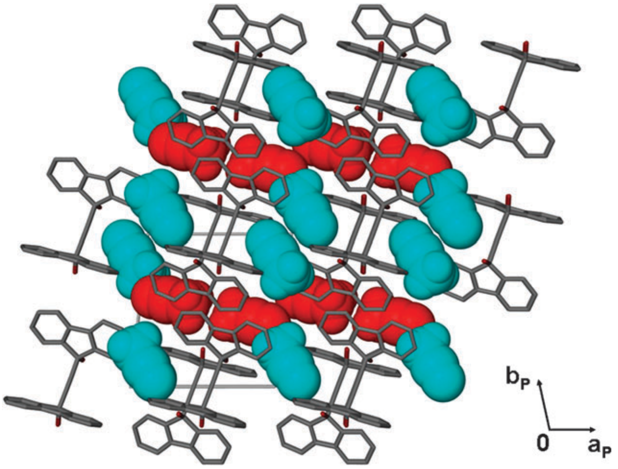

Fig. 7 Packing of **H2**·2MeCN viewed along [001] with guest molecules represented with van der Waals radii and one set of unique guest molecules shown in red, and the second set shown in blue.

the two guests, and also to examine whether the selectivity would be affected by crystallisation at different temperatures. The results of these competition experiments are illustrated in Fig. 8 with the diagonal line representing zero selectivity, the grey dots representing the results obtained at 25 °C and the black diamonds representing the results obtained at −26 °C.

It can be clearly seen from these results that this system does not behave in any of the typical ways previously observed in such selectivity studies (Fig. 2), but instead shows a very interesting and unusual selectivity profile, indicating a unique type of molecular recognition.

At −26 °C the host forms an inclusion compound with Z_{EtOH} = 0.56 irrespective of the initial ratio of the two guests. At room temperature, although the same compound is not formed in each case, only a small range of mole fractions are observed, varying between $Z_{\mathrm{EtOH}} \sim 0.5$ and $Z_{\mathrm{EtOH}} \sim 0.7$, with Z_{EtOH} increasing slightly with X_{EtOH}.

The crystal structures of the compounds formed at 25 °C from solutions with X_{EtOH} = 0.10, X_{EtOH} = 0.60 and X_{EtOH} = 0.89 were elucidated and yielded 1.5**H2**·EtOH·MeCN (corresponding to Z_{EtOH} = 0.5), 1.5**H2**·1.07(1)EtOH·0.93(1)MeCN (corresponding to Z_{EtOH} = 0.53) and 1.5**H2**·1.41(1)EtOH·0.59(1)MeCN (corresponding to Z_{EtOH} = 0.70), respectively. Thus, once again, the crystal structures were in good agreement with the mole fractions obtained from the competition experiments.

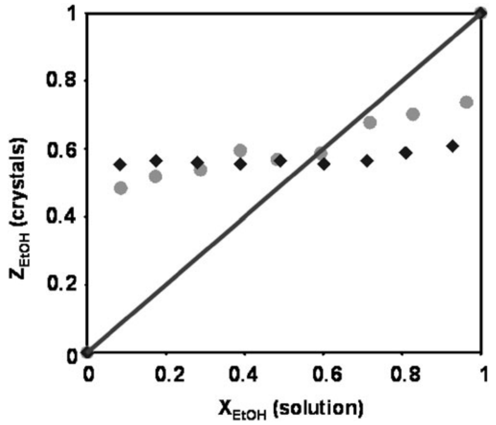

Fig. 8 Results of the EtOH *vs.* MeCN competition experiments, with unusually invariant mole fractions of EtOH included in the crystals. Irrespective of the initial ratio of the two guests in solution (X_{EtOH}), only a very small range of mole fractions are observed in the inclusion compounds formed (Z_{EtOH}).

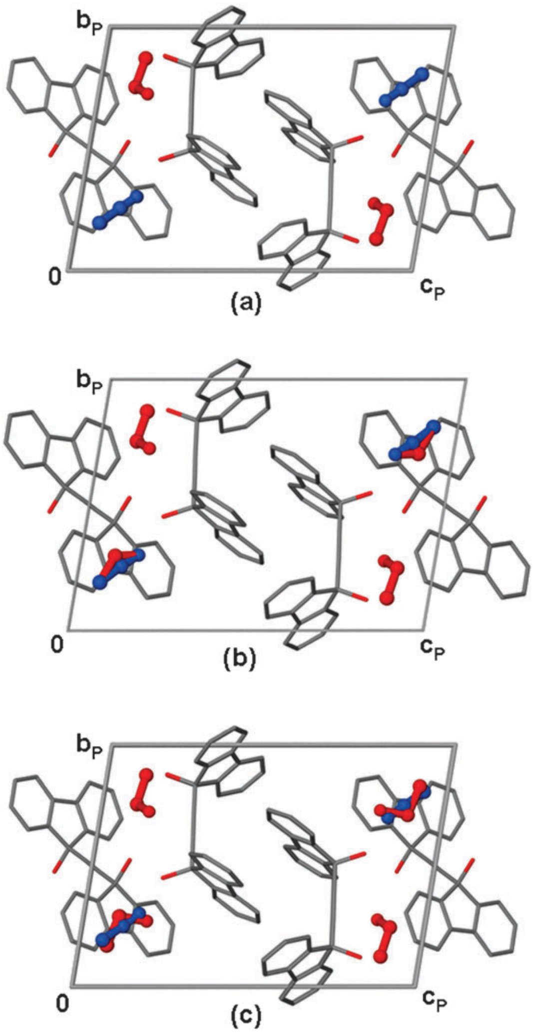

Fig. 9 Packing diagrams of (a) 1.5**H2**·EtOH·MeCN, (b) 1.5**H2**·1.07(1)EtOH·0.93(1)MeCN and (c) 1.5**H2**·1.41(1)EtOH·0.59(1)MeCN viewed along [100] with EtOH guests depicted in red and MeCN guests depicted in blue.

All three structures crystallise in the space group $P\bar{1}$ with H : G_{TOTAL} = 1.5 : 2 and are isostructural to 1.5**H2**·2EtOH in terms of packing of the host molecules. Packing diagrams of each of these mixed guest inclusion compounds are illustrated in Fig. 9, viewed along [100]. The hydrogen bonding details for each of the structures are presented in Table 3.

In the 1.5**H2**·1.07(1)EtOH·0.93(1)MeCN structure the partial EtOH and MeCN molecules share a common carbon atom and in addition the O atom of the EtOH molecule and the N atom of the MeCN molecule share a common site. In the structure of 1.5**H2**·1.41(1)EtOH·0.59(1)MeCN the two partial guest molecules are located on the same guest site, but without atoms overlapping on the same site.

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The cell dimensions of the compounds formed at −26 °C were determined and it was found that in each case the cell dimensions were the same as those of 1.5**H2**·2EtOH, the inclusion compound formed with EtOH at 25 °C. This is an extremely interesting result as, despite the fact that the host forms different inclusion compounds with either EtOH or MeCN when crystallised at −26 °C, when given any mixture of the two at −26 °C, it forms neither of these two structures, but rather always forms the same structure as the 25 °C EtOH inclusion compound structure.

Conclusions

In summary, two investigations of selectivity were carried out *via* competition experiments, with analysis by gas chromatography, giving mole fractions of two guests included by a particular host from solutions of varying mole fractions of the two guests. In both studies, the structures of a number of the mixed guest clathrates were elucidated and were shown to have H : G ratios which correlated with the mole fractions obtained in the competition experiments. This demonstrates that the guest ratios observed in the selectivity profile correspond to each crystal formed from the mixed guest solution, rather than representing mixtures of crystals. These novel results give new insight into clathrates with mixed guests, which thus far have not been studied extensively from both a selectivity and structural perspective.

In addition to this new insight obtained, these studies display some interesting and unique selectivity profiles, not previously seen in similar studies which is extremely interesting in terms of the molecular recognition processes occurring in these systems.

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