Solvent-Guest Control of Two Extremely Similar Tetrohydrofuran Inclusion Structures

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SUPPLEMENTARY MATERIAL

Analysis of the tetrahydrofuran (THF) guest molecules in the two crystal structures.

S1. Compound $(1)_4$·THF from THF and methanol

In compound $(1)_4$·THF, the difference Fourier showed peaks (~ 1.5 eÅ^{-3}) which were assigned to THF molecules (each of occupancy 0.25) in two positions surrounding a centre of symmetry. The strongest peak (~ 1.8 e Å^{-3}) was assigned to the oxygen atom of the guest. This resulted in the C-H···π and O-H···O contacts that are illustrated in Figure 5a. The guest was refined using instruction PART -1 and restraining the geometry to idealised values using DFIX and thermal parameters with SIMU. The difference Fourier also contained additional peaks around these positions with slightly lower heights (~ 1 e Å^{-3}) and shown in yellow in Figure S1. These indicated rotational flexibility of the guest keeping the centre of mass unchanged. However, these minor sites were not modelled or included in the refinement.

Figure S1. Peaks in the difference Fourier included (grey & red), and not included (yellow), in the refinement.

Output from SQUEEZE/PLATON

```
Void  X(av) Y(av) Z(av) Volume Ang^3 El-Count (e-) Vol/Electron Vol/Atom
========================================================================
   1  0.500-0.008 0.500          202       22               9.3       75
   2  0.500-0.035 0.000          202       22               9.3       75

Total (Positive) Electron Count in Voids/Cell =    43
Total (Fo-Fc)map Electron Count in  Unit Cell =    43
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S2. Compound $(1)_2$·THF from pure THF

In compound $(1)_2$·THF, the difference Fourier contained four peaks (heights ~ 3 e Å^{-3}) and two further peaks (~ 2 e Å^{-3}). These were modelled as THF in the envelope conformation disordered over two positions, with four carbon atoms in common (sof of 0.5) and the envelope flap oxygen atom taking up two separate positions (sof of 0.25 each). This assignment gave the favourable C-H···O and O-H···O host-guest contacts shown in Figure 5b. The difference Fourier also contained additional peaks of heights just over 1 e Å^{-3}, which were close to the modelled THF molecule. These peaks (yellow spheres in Figure S2) indicate alternative orientations of the THF guest having lower occupancies. These were not modelled or included in the refinement. The residual densities alerted in both cif are solely due to exclusion of the low occupied sites of THF in the two crystal structures.

Figure S2. Peaks in the difference Fourier included (grey & red), and not included (yellow), in the refinement.

Output from SQUEEZE/PLATON

```
Void  X(av) Y(av) Z(av) Volume Ang^3 El-Count (e-) Vol/Electron Vol/Atom
=========================================================================
   1  0.500-0.010 1.000          241       37               6.4       51
   2  0.500-0.024 0.500          241       37               6.4       51

Total (Positive) Electron Count in Voids/Cell =    75
Total (Fo-Fc)map Electron Count in  Unit Cell =    74
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