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Thermally induced reversible conformational changes in the host–guest adduct of *meso*-tetramethyltetrakis(ethyl)calix[4]pyrrole

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Abstract—The binding of methanol, ethanol, and *N*,*N*-dimethylformamide to *meso*-tetramethyltetrakis(ethyl)calix[4]pyrrole (**1**) was investigated in both solid and solution with the exhibition of multi-fashion hydrogen bonding as shown by X-ray crystallography. The thermodynamic stability of these host–guest inclusion complexes were determined by exploiting TGA and DTA. An unexpected conformational change in **1**·2EtOH occurred by thermal induction.

Calix[4]pyrroles are a long-known important class of macrocycles owing to their interesting anion,[1] metal ion,[2] and neutral molecule[3,4] binding ability. Recently, reports on the synthesis and anion binding properties of N-confused calix[4]pyrroles have been reviewed.[5] Since the pioneering synthesis by Baeyer,[6] numerous studies have been made on its synthesis,[7] properties, and reactivities including fluorescent,[8] colorimetric,[9] and electrochemical sensing.[10] Some theoretical studies have shown that these macrocycles can adopt a variety of conformations according to the following stability order: 1,3 alternate > partial cone > 1,2 alternate > cone; both in the gas phase and also in solvents like dichloromethane.[11] The diverse mode of binding of short-chain alcohols, mono-amides, and other solvent molecules to calix[4]pyrroles have been studied in the solid state by X-ray crystallography and in solution by NMR titrations.[4] A thermodynamic approach for halide recognition was reported recently.[12] However, the stability pattern and the cause of the diverse conformations of those neutral host–guest adducts were not very clear. In addition, the possibility of intra-structural convertibility of these adducts remained unexplored. In this communication we report the formation and relative thermal stability of neutral inclusion complexes of a calix[4]pyrrole, which display multipoint hydrogen bonding interactions. Intra-structural conversion of the intact host–guest molecule by thermal means was showed by thermogravimetry.

meso-Tetramethyltetrakis(ethyl)calix[4]pyrrole (**1**) was recrystallized successively from methanol/water, ethanol/water and dimethylformamide/water at 4 °C.[13] Solution ^{1}H NMR spectra showed that these adduct molecules retain their respective guest molecules intact in solution phase.[14] From their solid state structures, **1**·2EtOH and **1**·2DMF were found to adopt the 1,2 conformation as shown by X-ray crystallography.[15,16] Two molecules of the guest were symmetrically situated above and below each host molecule (Fig. 1). The corresponding crystals of **1**·2MeOH showed some disordering problems in its X-ray structure but its tetragonal space group *I*-4 could be identified. However, the presence of methanol in the solid was verified by IR spectroscopy and the presence of two methanols per host was computed by ^{1}H NMR and this was confirmed by thermogravimetric analysis (TGA).[†] Interestingly, the reported Me$_8$-calix[4]pyrrole·2MeOH[4] exists as the 1,3 conformer with an identical space group to the **1**·2MeOH adduct.[14] The presence of π–π stacking in the DMF adduct was proposed earlier for the stability of the 1,2 host–guest adduct,[4] but the reason for **1**·2EtOH to exist as the 1,2 conformer is different owing to the absence of any π stacking group. From the solid state structure, it was seen that along with the primary

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Keywords: *meso*-Tetramethyltetrakis(ethyl)calix[4]pyrrole; TGA; DTA; Powder XRD; X-ray structure.

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[†] Thermogravimetric experiments were performed at a heating rate 10 °C/min in the temperature range 35–350 °C under a nitrogen flow of 20 ml/min. A silica crucible was used as sample holder.

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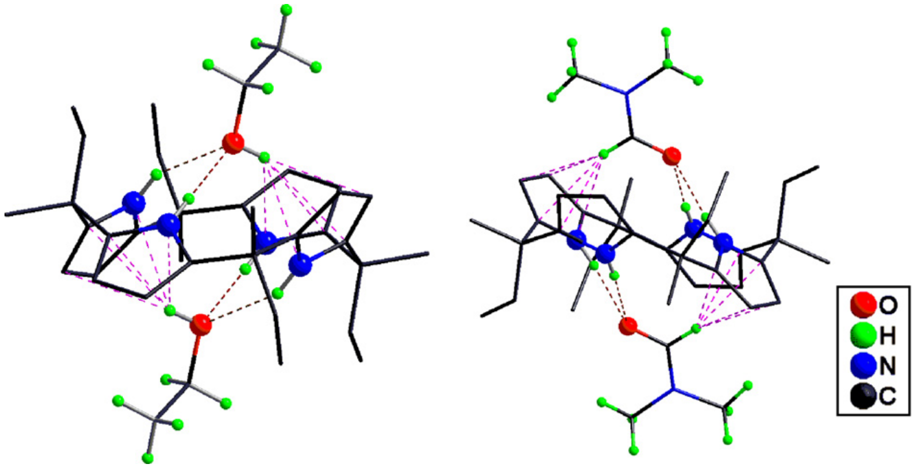

Figure 1. Crystal structures of (a) **1**·2EtOH and (b) **1**·2DMF. All hydrogens in the rings except for the pyrrole N–H are omitted for clarity. Brown dashes represents N–H···O hydrogen bonding and pink dashes represent secondary π–H interactions involving pyrrole rings with the hydrogens of O–H in alcohol and H in DMF forming a cone-like motif.

N–H···O_{guest} hydrogen bonding, a weak, secondary hydrogen bonding interaction was present between O–H···$C_{pyrrole}$ and C–H···$C_{pyrrole}$ in the ethanol and DMF adducts, respectively. This creates a cone-like motif in both cases, which may be the reason for stabilizing the EtOH adduct in the 1,2 conformation (Fig. 1). The average N–H_{host}···O_{guest} distance was found to be ~2.1–2.2 Å and the C–H···O_{guest}/C_{guest} distance was ~2.8 Å, well below the sum of the van der Waals radii of H and C. The N–H···O angle lies in between 148° and 168°. As pyrrole is an aromatic system, it can form π–H hydrogen bonds as displayed in Figure 1. A list of selected bond distances and angles is given in Table 1.

The relative thermodynamic stability of the three adducts was investigated by thermogravimetric experiments. Analyses were performed in the temperature range 35–350 °C with a heating rate of 10 °C/min under a constant nitrogen atmosphere of 20 ml/min using an autosampler fitted with a silica crucible as sample holder. The TGA curve showed a stability order of **1**·2DMF > **1**·2MeOH ≈ **1**·2EtOH. In the case of the ethanol adduct, the TGA curve showed an ill-defined wide zone of mass loss in the temperature range 80–110 °C (Fig. 2a). A multi-step process involved 16% mass loss throughout the region. The result is consistent with the 15.95% calculated for the loss of ethanol. The first derivative TGA plot confirmed the multi-step behavior as shown in the inset (Fig. 2a). Surprisingly, the differential thermal analysis (DTA) curve showed a broad endothermic peak around 55–60 °C without any mass loss (Fig. 2b). The enthalpy change in this process was approximately 94 J/g where it was 47 J/g at 97 °C for the initiation of mass loss and 24 J/g for melting at 160 °C. The first enthalpy change may be a signature of the structural modification in **1**·2EtOH corresponding to a change from 1,2 to some other conformation keeping the host–guest molecule intact. The thermogravimetric data are tabulated in Table 2. The change occurring in the solid state by thermal means was found to be preserved even in solution. The ^{1}H NMR signal of the pyrrole N–H of **1**·2EtOH (1,2) was shifted upfield (7.09–6.99 ppm) in thermostatically heated **1**·2EtOH (60 °C, 2 h). Such thermal changes could even be induced in solution and when **1**·2EtOH was allowed to precipitate from a hot ethanolic solution at 60 °C, the upfield shift of the pyrrole N–H at rt remained the same. The IR spectrum showed the retention of ethanol in the adduct and identical elemental analyses of the two conformers ruled out loss of any fragment from the heated sample. We tried to obtain the structure of the heated sample by single crystal X-ray study after thermostatically heating the 1,2 conformer at 60 °C for 2 h under ethanolic vapor. Unfortunately, the crystals diffracted weakly preventing structural characterization of the transformed species. However, the powder X-ray diffraction pattern (XRD) of this conformer was recorded, which differed from that of the starting **1**·2EtOH (1,2). As a comparison, crude **1** was also subjected to XRD. As the enthalpy change without any mass loss around 60 °C is presumed to be due to the change in the bonding of ethanol with **1**, an attempt was made to crystallize **1** from water/ethanol at 60 °C. The microcrystalline solid isolated in this process was not crystalline enough for X-ray analysis but did show the presence of ethanol as an adduct with identical elemental analysis. Powder XRD of this material matched the XRD obtained from thermally heated **1**·2EtOH (1,2) at 60 °C. All the recorded XRD curves are presented in Figure 3. Recrystallization of the heated sample under ambient conditions led to the isolation of

Table 1. List of selected bond distances and angles of **1**·2EtOH and **1**·2DMF

Calix[4]pyrrole	$N_{pyrrole}$–H···O distance (Å) (primary)	$N_{pyrrole}$···O distance (Å)	$N_{pyrrole}$–H···O angle (°)	O–H···$C_{pyrrole}$ interacting distance (Å) (secondary)	Dihedral angle (1,2 and 1,3 pyrrole plane) (°)
1·2EtOH	2.20	3.01	168.2/148.2	2.81	70/0
1·2DMF	2.12	2.93	167.9/167.9	2.80	71/0

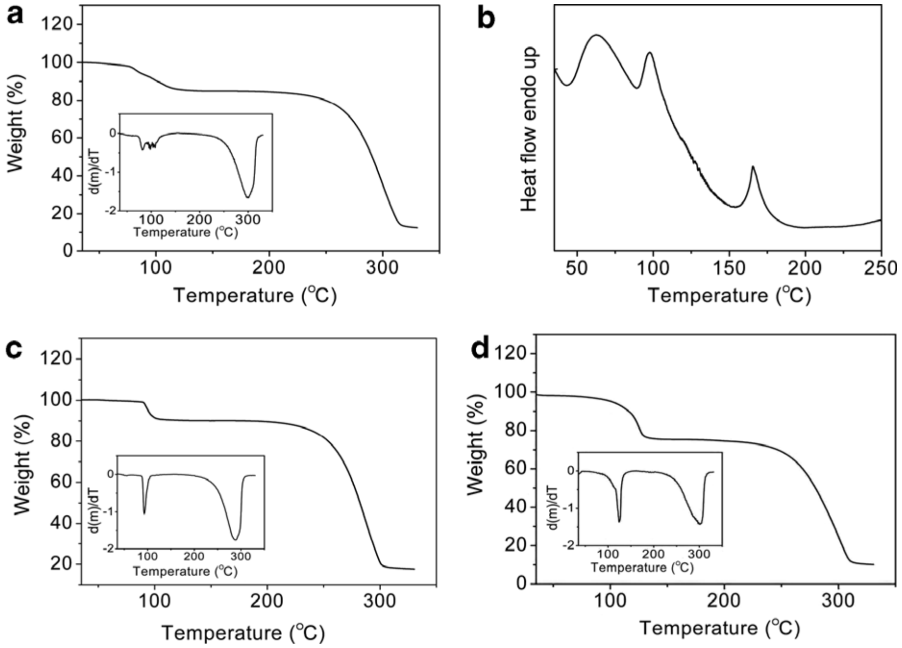

Figure 2. (a) TGA profile of **1**·2EtOH, (b) DTA of **1**·2EtOH, (c) TGA of **1**·2MeOH and (d) TGA of **1**·2DMF. Inset pictures show the first derivative plots of respective TGA curves. Of the two inflections, the first one is responsible for mass loss and the second one is for decomposition. In the DTA plot, all the peaks are endothermic in nature. A peak around 55 °C represents a conformational change; a peak around 90 °C corresponds to mass loss and that around 160 °C to melting.

Table 2. List of TGA/DTA data of **1**·2MeOH, **1**·2EtOH, **1**·2DMF and **1**·(CRUDE)

Calix[4]pyrrole (**1**)	TGA peak (temp range) (°C)	1st derivative point of TGA (°C)	Weight loss (%)		DTA peak (°C)		
			Calculated	Found	1st	2nd	3rd
1·2MeOH	90–100	97	11.66	11.75	x	96.8	154.8
1·2EtOH	83–100	82–100	15.95	16.0	60	97.0	160.0
1·2DMF	100–135	125	23.14	23.10	x	128.0	155.0
1·(CRUDE)	x	x	x	x		150	

x = not available.

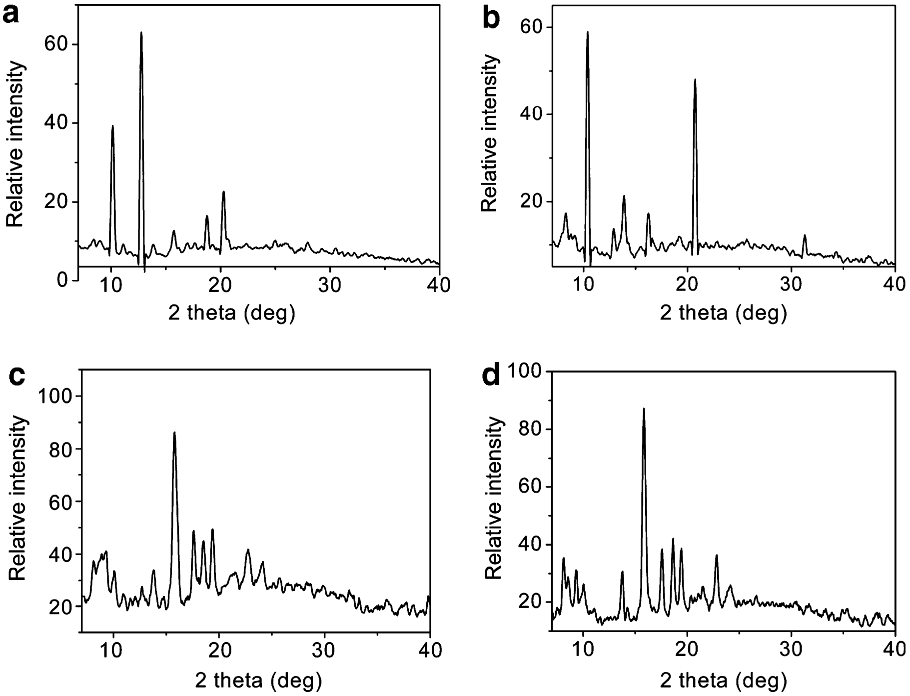

Figure 3. Powder XRD patterns of (a) crude **1**, (b) **1**·2EtOH, (c) **1**·2EtOH after heating at ~60 °C and (d) 1 recrystallized from ethanol/water ~60 °C. Patterns shown in (c) and (d) are similar.

diffraction quality crystals whose cell parameters matched with those of the original **1**·2EtOH adduct (1,2). This suggests that the forms are interchangeable. The Me_8-calix[4]pyrrole, on crystallization in the presence of ethanol in DCM, yielded pure Me_8-calix[4]pyrrole and its X-ray structure[17] was found to be identical to that crystallized from acetone.[4] In contrast, the DMF adducts of both the calix[4]pyrroles (octamethyl and tetratmethyltetraethyl derivatives) occurred as the common 1,2 conformer but crystallized differently and unlike the identical space groups for methanol adducts of both derivatives, the reported DMF adduct[4] crystallized with triclinic symmetry whereas the present DMF adduct has a monoclinic system. All these differences thwarted our attempts to identify the conformer formed from **1**·2EtOH (1,2) at 60 °C.

1·2MeOH and **1**·2DMF showed normal behavior in both TGA and DTA (Figs. 2c and 2d). The bound MeOH and DMF were lost at 95 °C and at 125 °C with ~12% and ~23% mass loss as expected. The DTA study of **1**·2MeOH and **1**·2DMF did not show any unexpected results. Characterization data are provided.[14]

In conclusion, we have shown that the binding of simple alcohols and DMF to a calix[4]pyrrole exhibit primary and weak secondary hydrogen bonding. The relative thermal stabilities of these host–guest adducts were examined by thermogravimetry and differential thermal analysis. An unusual interconversion, presumably due to the change in primary hydrogen bonding of the guest ethanol with the host **1**, was observed on heating. Such a change is reversible and is operative both in the solid state and in solution. In the absence of single crystal X-ray data we were unable to establish the type of conformer present in thermally heated **1**·2EtOH (1,2). Diverse modes of binding of the guests with some pyrrole β-substituted calix[4]pyrrole and N-confused calix[4]pyrrole hosts and their thermal interconversion are being investigated and will be communicated later.

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13. **1** was synthesized by a modified and eco-friendly procedure reported by us.[7] **1**·2EtOH and **1**·2MeOH were crystallized by slow diffusion of water into ethanol or methanol solutions of **1** upon standing for 2 days at 4 °C under aerobic conditions. **1**·2DMF was crystallized by slow diffusion of water into a DMF solution containing **1** at 4 °C for 3 days under aerobic conditions. **1** was found to be fairly soluble in paraffin oil, hence single crystals for X-ray diffraction were mounted for data collection only after coating with heavier Paratone-N.
14. Characterization of **1**·2EtOH (1,2) ($C_{36}H_{56}N_4O_2$): C, H, N (%); Calcd C, 74.87; H, 9.70; N, 9.71. Found: C, 74.99; H, 9.61; N, 9.69. FAB-MS: Molecular ion peak (m/z) at 484 corresponding to free ligand and is indicative that two solvent molecules are lost during measurement. FT-IR (KBr pellet, cm^{-1}): 3435 (s, pyrrole N–H), 3348 (bs,

ethanol O–H), 3110 (s, pyrrole aromatic C–H), 2969, 2929, 2873, 1209, 767. ^{1}H NMR: ($CDCl_3$, 400 MHz, 298 K, ppm) 7.09 (bs, 4H, N–H, C_4H_2N), 5.82 (d, 8H, β-H, C_4H_2N, $J = 2.2$ Hz), 3.62–3.57 (q, 4H, CH_2, ethanol, $J = 7.08$ Hz), 1.79 (d, 8H, CH_2, ethyl, $J = 7.08$ Hz), 1.39 (ws, OH, ethanol), 1.33 (t, 12H, CH_3, ethyl, $J = 3.16$ Hz), 1.17–1.13 (t, 6H, CH_3, ethanol, $J = 7.08$ Hz), 0.63–0.61 (t, 12H, CH_3 of methyl, $J = 5.84$ Hz). TGA/DTA: From the TGA curve it was observed that at around 80 °C, mass loss in terms of ethanol starts and completed around 100 °C. The total mass loss (16%) is in good agreement with the calculated (15.9%). Melting point was to be ~160 °C. Over 250 °C, the compound decomposes. In DTA, an endothermic peak occurred at ~60 °C with no practical mass loss. Two more endothermic peaks appeared at about 97 °C and 160 °C for mass loss and melting, respectively. Characterization of **1**·2EtOH ($C_{36}H_{56}N_4O_2$) after heating at about 60 °C for 2 h: FAB-MS: Molecular ion peak (*m/z*) at 484. C, H, N values are as previous. FT-IR (KBr pellet, cm^{-1}): 3436 (s, pyrrole N–H), 3349 (bs, ethanol O–H), 3110 (s, pyrrole aromatic C–H), 2969, 2929, 2873, 1209, 767. ^{1}H NMR: ($CDCl_3$, 400 MHz, 298 K, ppm) 6.99 (bs, 4H, N–H, C_4H_2N), 5.81 (d, 8H, β-H, C_4H_2N, $J = 2.2$ Hz), 3.65-3.60 (q, 4H, CH_2, ethanol, $J = 7.08$ Hz), 1.79 (d, 8H, CH_2, ethyl, $J = 7.08$ Hz), 1.40 (ws, OH, ethanol), 1.35–1.31 (t, 12H, CH_3, ethyl, $J = 4.16$ Hz), 1.18–1.14 (t, 6H, CH_3, ethanol, $J = 7.08$ Hz), 0.64–0.61 (t, 12H, CH_3 of methyl, $J = 7.32$ Hz). **1**·2MeOH ($C_{34}H_{52}N_4O_2$): M.W. 548, large colorless prisms from methanol/water. FAB-MS: Molecular ion peak (*m/z*) at 484 corresponding to free ligand. C, H, N (%): Calcd C, 74.45; H, 9.49; N, 10.22. Found: C, 74.54; H, 9.59; N, 10.02. FT-IR (KBr pellet, cm^{-1}): 3439 (s, pyrrole N–H), 3337 (bs, methanol O–H), 3110 (s, pyrrole aromatic C–H), 2969, 2929, 2873, 1209, 767. ^{1}H NMR: ($CDCl_3$, 400 MHz, 298 K, ppm) 7.07 (bs, 4H, N–H, C_4H_2N), 5.83 (d, 8H, β-H, C_4H_2N, $J = 2.68$ Hz), 3.36 (s, 3H, Me, methanol), 1.79 (d, 8H, CH_2, ethyl, $J = 4.8$ Hz), 1.35 (t, 12H, CH_3, ethyl, $J = 3.4$ Hz), 1.19 (s, 6H, CH_3, methanol), 0.63 (t, 12H, CH_3, methyl, $J = 1.24$ Hz). Methanol O–H was not very clear. Though disordered, we were able to obtain the lattice parameters from the X-ray study: Colorless block, space group *I*-4, $a = 10.813$, $b = 10.813$, $c = 13.672$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 1598.54 Å^3. TGA/DTA: From the TGA curve it was observed that at ~95 °C, 12% mass loss occurred and the compound starts decomposing at ~250 °C. Two endothermic peaks were found to appear between ~97 °C and 155 °C in DTA corresponding to the loss of two methanol molecules and melting of the compound. **1**·2DMF ($C_{38}H_{58}N_6O_2$): M.W. 630, colorless blocks from DMF/water. C, H, N (%): Calcd C, 72.26; H, 9.19; N, 13.31. Found: C, 72.51; H, 9.01; N, 13.39. FAB-MS: (*m/z*) at 484 and can be explained as previous. FT-IR (KBr pellet, cm^{-1}): 3430 (s, pyrrole N–H), 3110 (aromatic C–H, pyrrole), 2969, 2929, 2873, 1696 (C=O stretching, DMF), 1209, 767. ^{1}H NMR: ($CDCl_3$, 400 MHz, 298 K, ppm) 7.95 (s, 1H, $HCONMe_2$), 6.99 (bs, 4H, N–H, C_4H_2N), 5.80 (d, 8H, β-H, C_4H_2N, $J = 2.68$ Hz), 2.89 (s, 3H, Me, $HCONMe_2$), 2.82 (s, 3H, Me, $HCONMe_2$) 1.79 (d, 8H, CH_2, ethyl, $J = 3.76$ Hz), 1.33–1.31 (t, 12H, CH_3, ethyl, $J = 4.4$ Hz), 0.63 (t, 12H, CH_3, methyl, $J = 5.84$ Hz). TGA/DTA: Mass loss was found to start at ~120 °C and was found to be 23% as per calculated. From DTA, two endothermic peaks were found to occur at around 128 °C and 155 °C for mass loss and melting of the compound, respectively. Here also decomposition occurred around 250 °C.

15. Crystal data for **1**·2EtOH: Molecular formula: $C_{36}H_{56}N_4O_2$, $M = 576.85$, large colorless rectangular blocks, $0.20 \times 0.10 \times 0.08$ mm^3, triclinic, space group *P*-1, $a = 10.220(5)$, $b = 10.301(5)$, $c = 16.250(5)$ Å, $\alpha = 77.829(5)°$, $\beta = 88.626(5)°$, $\gamma = 85.603(5)°$, $V = 1667.3(13)$ Å^3, $Z = 2$, $D_c = 1.149$ Kg/m^3, $F(000) = 632$, Bruker SMART APEX, Mo-Kα radiation, $\lambda = 0.71069$ Å, $T = 100(2)$ K, ($2.00 \leqslant \theta \leqslant 28.34°$), 11202 Reflections collected, 7969 unique, $R(\text{int}) = 0.0346$, Final GooF = 1.029, $R_1 = 0.1108$, $wR_2 = 0.2771$, R indices based on 7969 reflections with $I > 2\sigma(I)$ (Refinement on F^2), 385 parameters, 3 restraints, absorption corrections empirical, $\mu = 0.070$ mm^{-1}.
16. Crystal data for **1**·2DMF: Molecular formula: $C_{38}H_{58}N_6O_2$, $M = 630.90$, colorless prisms, $0.20 \times 0.20 \times 0.08$ mm^3, monoclinic, space group *P*21/*n*, $a = 11.728(5)$, $b = 12.065(5)$, $c = 12.976(5)$ Å; $\alpha = 90°$, $\beta = 96.742(5)°$, $\gamma = 90°$, $V = 1823.4(13)$ Å^3, $Z = 2$, $D_c = 1.149$ Kg/m^3, F(000) = 688, Bruker SMART APEX, Mo-Kα radiation ($\lambda = 0.71069$ Å), $T = 100(2)$ K, ($2.21 \leqslant \theta \leqslant 28.28°$), 11972 Reflections collected, 4496 unique, $R(\text{int}) = 0.0679$, Final GooF = 0.993, $R_1 = 0.1006$, $wR_2 = 0.2392$, R indices based on 4496 reflections with $I > 2\sigma(I)$, (Refinement on F^2), 212 parameters, 0 restraints, absorption corrections empirical, $\mu = 0.092$ mm^{-1}. Crystallographic data for **1**·2EtOH and **1**·2DMF have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 635032 and 635033. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.
17. Attempts to crystallize Me_8-calix[4]pyrrole with ethanol as adduct failed in ethanol/dichloromethane medium as unsolvated Me_8-calix[4]pyrrole as the 1,3 conformer was isolated similar to that from crystallization in acetone.[4] Lattice parameters and space group: Tetragonal, space group *P*-1, $a = 10.251$, $b = 10.251$, $c = 23.924$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 2514$ Å^3.