Inclusion Compounds of Cyclotriveratrylene (2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15*H*-tribenzo[*a,d,g*]cyclononene) with Chlorinated Guests

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Inclusion compounds were formed between the host cyclotriveratrylene, H, (2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15H-tribenzo[a,d,g]cyclononene) and the guests carbon tetrachloride, 1,1,1-trichloroethane, 1,1,1-trichloropropane and 1,1,2-trichloroethane. 1 ($H \cdot CCl_4$) has guest molecules in channels alternating with channels of host molecules. 2 ($H \cdot C_2H_3Cl_3 \cdot C_3H_5Cl_3$) and 3 ($H \cdot 2C_2H_3Cl_3$) exhibit a slightly different packing arrangement with one guest molecule in the host cavity and the rest of the guest molecules in channels. The stability and reactivity of these inclusion compounds were investigated.
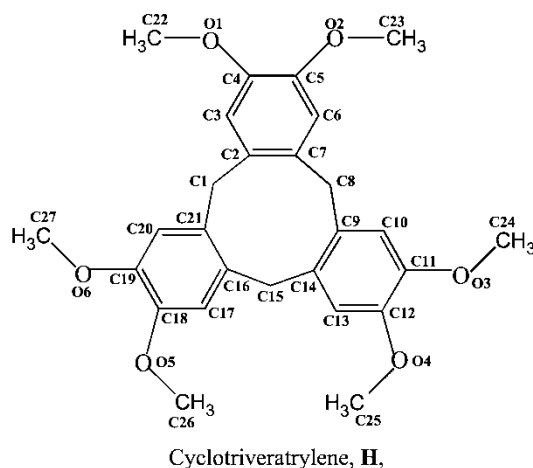
INTRODUCTION

The field of inclusion phenomena has grown dramatically in the last 20 years and host–guest compounds form an important aspect of supramolecular chemistry. There are several modern books and monographs available, culminating in the authoritative eleven-volume publication of *Comprehensive Supramolecular Chemistry*, which surveys the field up to 1996 [1–3]. While a great deal of effort has been expended in synthesizing novel host compounds and testing their enclathrating abilities, our laboratory has concentrated on examining their macro-properties in order to explore their possible application. This field, crystal engineering, is currently attracting attention and Braga [4] has pointed out the importance of solid-state reactivity, polymorphism, optical activity and the construction

of functional materials. Systems that can reversibly absorb and store guest molecules have received recent attention [5,6], while the question of host selectivity remains an important topic [7]. The physico-chemical properties of host–guest compounds have been reviewed [8]. Host molecules may be broadly classified into two main types: (i) those that form molecular complexes by fitting convex guests into the concave cavity of the host and (ii) those that form lattice inclusion compounds by packing in such a manner that spaces are left in the crystal structure to accommodate guest molecules. Cyclotriveratrylene (CTV) and related hosts exhibit behaviour common to both categories, and their chemistry and inclusion properties have been reviewed [9]. Complexation with a variety of small organic guests yield structures where columns of CTV molecules alternate with columns of guest molecules, whereas inclusion of spherical molecules such as C_{60} result in molecular complexes. Recent studies involve the synthesis and inclusion capabilities of metallocene-derivitized CTV molecules [10,11]. Here we present the structures of the cyclotriveratrylene host H = (2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15H-tribenzo[a,d,g]cyclononene) with a series of chlorinated guests: carbon tetrachloride, **1** = ($H \cdot CCl_4$); 1,1,1-trichloroethane and 1,1,1-trichloropropane, **2** = ($H \cdot C_2H_3Cl_3 \cdot C_3H_5Cl_3$); and 1,1,2-trichloroethane, **3** = ($H \cdot 2C_2H_3Cl_3$). The atomic numbering is shown in Scheme 1. We also report on their thermal stability, kinetics of desolvation and guest exchange.

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Cyclotriveratrylene, **H**,

(2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15-tribenzo[*a,d,g*]cyclononene)

carbon tetrachloride   1,1,1-trichloroethane   1,1,1-trichloropropane   1,1,2-trichloroethane

SCHEME 1
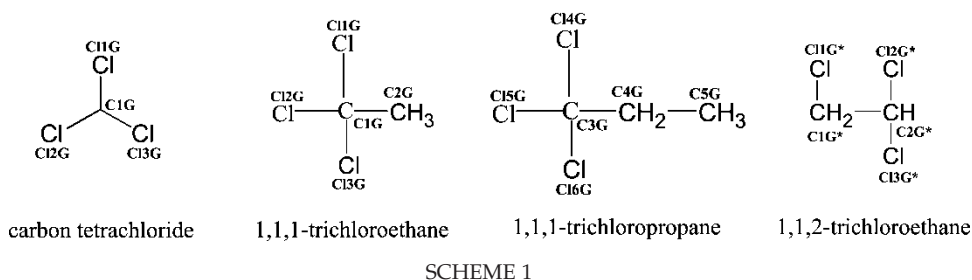
EXPERIMENTAL

Structure Determination and Refinement

Suitable crystals of all three compounds were grown by slow cooling of dilute solutions of the host in the liquid guests at elevated temperatures, typically at 55°C. The resultant crystals tended to be of poor quality and crumbled when taken out of the mother liquor. Unit cell dimensions were determined on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. The strategies for the data collections were evaluated using the COLLECT [12] software. The data were scaled and reduced using DENZO-SMN [13]. The crystal data and important experimental details of the data collections are given in Table I. All three structures were solved by direct methods using SHELXS-97 [14] and refined employing full-matrix least-squares with the program SHELXL-97 [15] refining on F^2. The non-hydrogen atoms were treated anisotropically and the hydrogens were geometrically constrained with a common temperature factor.

Compound **1** crystallized in the space group *Pnma* with $Z = 4$. Both the host and guest molecules are situated on mirror planes at Wyckoff position c. The following atoms were placed with a site occupancy factor of 0.5: C1, C1G, Cl1G and Cl3G.

Compound **2** was grown unexpectedly from a solution of 1,1,1-trichloroethane contaminated with trace amounts of 1,1,1-trichloropropane. The struc-

ture was solved in the monoclinic space group $P2_1/c$ with $Z = 4$. Both the host and guest molecules were found in general positions.

Compound **3** crystallized in the space group $P\bar{1}$ with $Z = 4$. The asymmetric unit consists of two independent host molecules and four independent guest molecules. Three of the guest molecules have a similar geometry with the chlorine atoms staggered. The fourth guest molecule is distorted with two of the chlorine atoms in an eclipsed position. One of the C—Cl bond distances for this guest refined to 2.26(2) Å, compared to the average value which varied from 1.73(1) to 1.84(2) Å. A residual electron density of 1.664 eÅ^{-3} found near one of the guests could not be modelled. All these factors contributed towards the final *R*-factor of 0.1241 obtained for this structure. Crystallographic data for compounds **1** to **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC no. 222548 (**1**), 222549 (**2**) and 222550 (**3**). Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk)

Thermal Analysis

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a Perkin-Elmer PC7-series system. TG analyses were used to determine accurate host:guest ratios, while DSC

TABLE I   Crystal data, experimental and refinement parameters

	1	2	3
Compound	$C_{27}H_{30}O_6 \cdot CCl_4$	$C_{27}H_{30}O_6 \cdot C_2H_3Cl_3 \cdot C_3H_5Cl_3$	$C_{27}H_{30}O_6 \cdot 2C_2H_3Cl_3$
M_w, g mol^{-1}	604.32	731.32	717.30
Temperature, K	173(2)	173(2)	173(2)
Crystal system,	Orthorhombic	Monoclinic	Triclinic
Space group	$Pnma$	$P2_1/c$	$P1$
a, Å	9.7120(19)	20.429(4)	14.403(3)
b, Å	16.778(3)	12.335(3)	15.147(3)
c, Å	17.544(4)	14.220(3)	15.347(3)
α, °	90	90	98.94(3)
β, °	90	102.27(3)	91.56(3)
γ, °	90	90	92.31(3)
V, Å^3	2859(1)	3501(1)	3303(1)
Z	4	4	4
Absorption coefficient, mm^{-1}	0.454	0.532	0.562
$F(000)$	1256	1520	1488
Crystal size, mm	0.47 × 0.09 × 0.05	0.55 × 0.35 × 0.07	0.39 × 0.50 × 0.40
Index ranges	h: − 11,8; k: − 16,20; l: − 17,21	h: − 24,25; k − 14, 11; l: − 17,15	h: − 11,18; k: − 18,19; l: − 13,17
Reflections collected/unique	10629/2539	13437/6326	13479/11444
Data/restraints/Parameters	2539/0/181	6326/0/405	11444/0/787
Goodness-of-fit	1.044	1.061	1.242
ρ_{calc}/g cm^{-3}	1.404	1.387	1.443
Final R indices [I > 2σ(I)]	$R_1 = 0.0447$, w$R_2 = 0.0850$	$R_1 = 0.0773$, w$R_2 = 0.2169$	$R_1 = 0.1241$, w$R_2 = 0.3410$
R indices (all data)	$R_1 = 0.0937$, w$R_2 = 0.1028$	$R_1 = 0.1207$, w$R_2 = 0.2500$	$R_1 = 0.1961$, w$R_2 = 0.3831$
Largest difference peak and hole, eÅ^{-3}	0.269 and − 0.441	0.721 and − 0.977	1.669 and − 0.741

measurements yielded the onset temperatures of guest release and allowed the monitoring of any phase changes that may occur in the structures during heating. Crystals were blotted dry and crushed before analysis. Experiments were performed over a temperature range of 30 to 200°C at a heating rate of 10 K min^{-1} with a purge of dry nitrogen at 40 ml min^{-1}.

DISCUSSION

For compound **1** the bowl-shaped host molecules lie in channels parallel to [100] with each molecule in the cavity of the other. Alternating columns have the host cavity facing in opposite directions (Fig. 1). The guest molecules lie in channels parallel to [100]. This is in agreement with other structures involving host H and small organic guests [9]. The channels were mapped using the program SECTION [16] and were found to vary in size from approximately 3.7 × 6.6 to 7.5 × 7.3 Å. Very weak intermolecular contacts of the form (Host)-C—H···Cl(Guest) exist with the shortest C···Cl distance 3.376(4) Å.

Structure **2** also has the host molecules stacked in columns with adjacent columns in an antiparallel relationship, parallel to [001]. Interestingly, the host molecules are separated from each other by one molecule of 1,1,1-trichloroethane situated in the host cavity, its methyl group directed towards the centroid of the host cavity at an angle of 151.6°. Guests 1,1,1-trichloropropane occupy channels of approximate size 5.5 × 10.7 Å, parallel to
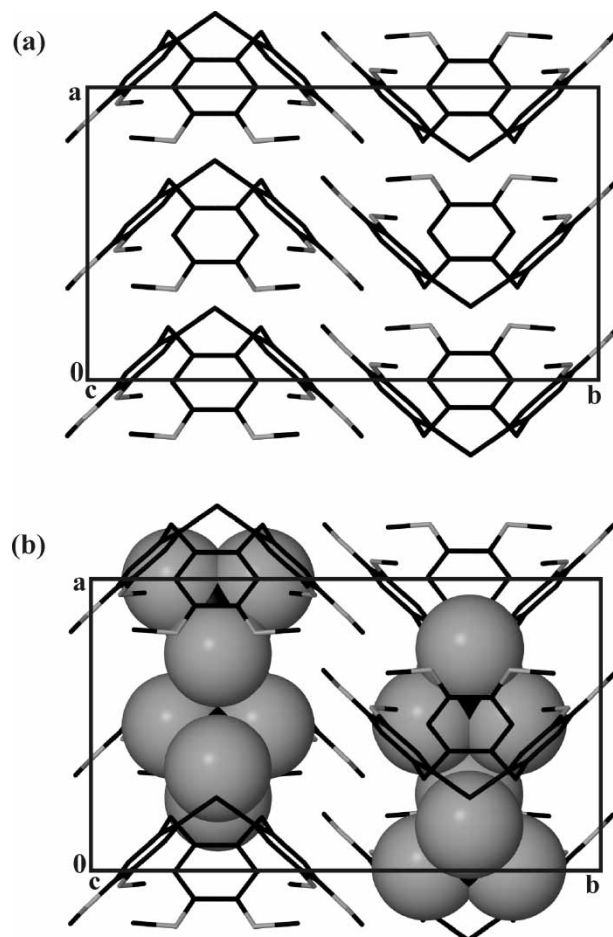

FIGURE 1   Packing diagram of **1** down [001] with the host represented in stick form and (a) guests omitted and (b) guests represented in van der Waals radii.
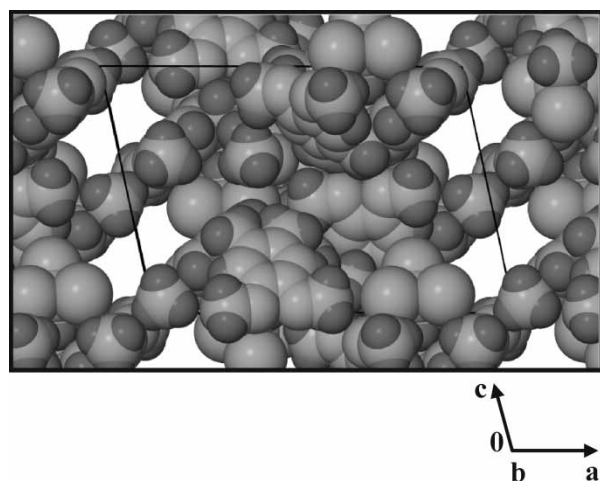
FIGURE 2 Space-filling projection of **2** along [010] with guest 1,1,1-trichloropropane omitted, showing the open channels.

FIGURE 4 Thermal analysis results for **2**.

[010]. A space filling projection with the guests 1,1,1-trichloropropane omitted is shown in Fig. 2. There are weak C—H···π hydrogen bonding interactions between 1,1,1-trichloroethane and the host with the shortest distances: C(2G)···C(16) 3.727(1) Å and C(2G)···C(17) 3.741(1) Å. These are slightly longer than those reported by Hancock and Steed [17] where the shortest C—H···π distance in a rhodium (I) complex of cyclotriveratrylene was 3.431(14) Å.

A similar packing of host molecules is observed for structure **3** with the host molecules parallel to [010], (Fig. 3). Again, each host cavity is occupied by one guest molecule with the rest of the guest molecules in channels parallel to [100]. These channels are constricted and vary in size from approximately 3.7 × 4.9 to 6.6 × 5.6 Å. Again the structure is stabilized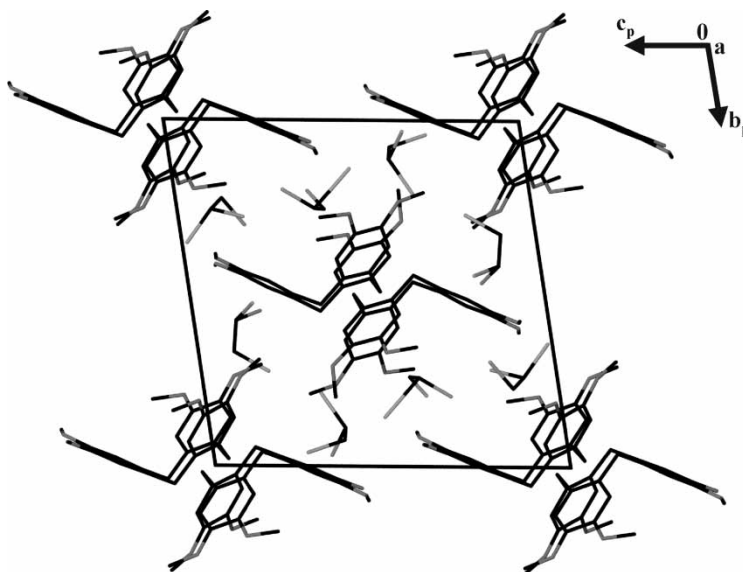 by weak C—H···π hydrogen bonding interactions between the guest in the host cavity and the aromatic rings of the host molecule. These C—H···π distances lie in the range 3.501(1) to 3.859(1) Å.

A typical thermal analysis result is shown in Fig. 4. In all three compounds the TG shows a single desolvation step corresponding to guest release. There is good agreement between the experimental and calculated host:guest ratios, with host:guest ratio 1:1 for compound **1**, 1:1:1 for compound **2** and 1:2 for compound **3**. The DSC curves show two endotherms, which we attribute to the loss of guest and the host melt respectively. A summary of the thermal analysis results is given in Table II where we compare T_{on}, the endotherm onset temperature with T_b, the normal boiling point for each guest.

Kinetics

For all three compounds we analysed the kinetics of desolvation by carrying out a series of isothermal TG experiments. The mass-time curves for compounds

FIGURE 3 Packing diagram of **3** down [100] with the hydrogen atoms omitted for clarity.

TABLE II   Thermal analysis data

Inclusion compound		1	2	3
H:G ratio		1:1	1:1:1	1:2
TG results	Calc. % mass loss	25.5	37.4	37.2
	Exp. % mass loss	25.7	35.4	37.4
DSC results	T_{on} (K) A*	348.2	342.3	373.5
	B*	501.5	502.0	501.7
Normal boiling points T_b (K)		349.7	347.1	386.5
T_{on}/T_b		0.996	0.986	0.966
E_a (isothermal kinetics)		171(11)	113(1)	84(7)

*A and B refer to the endotherms as indicated in Fig. 3.

1 and **2** were deceleratory and fitted the first-order rate law,

$$-\ln(1 - \alpha) = kt$$

where α is the extent of the reaction and k is the rate constant [18]. TG experiments were carried out between 85 and 100°C for compound **1** and 60 and 80°C for compound **2**. The corresponding Arrhenius plots are shown in Figs. 5(a) and 5(b). Activation energies of 171(11) and 113(1) kJ mol^{-1} were obtained for compounds **1** and **2**, respectively.

The mass–time curves for compound **3** also yielded deceleratory curves but these followed the diffusion-controlled model R3:

$$1 - (1 - \alpha)^{\frac{1}{3}} = kt$$

and the corresponding Arrhenius plot, drawn over a temperature range of 70–90°C yielded an activation energy of 84(7) kJ mol^{-1} (Fig.5(c)).

We also used a non-isothermal method of desorption for compound **3** [19]. We recorded the TG mass loss curves under differing heating rates varying from 1 to 20 K min^{-1}. This allowed us to plot the log of the heating rate *versus* reciprocal temperature for various degrees of decomposition. The results, shown in Fig. 6, yielded activation energies which vary from 73(3) to 80(5) kJ mol^{-1}, in good agreement with those obtained by the isothermal method. We note that there is good correlation between the T_{on}/T_b ratios and the activation energies obtained for the desolvation reactions.

Guest Exchange

The question of guest-exchange in organic inclusion compounds has received little attention, despite the fact that this process is important in sensing and in catalysis [20,21]. The exchange between dimethyl sulphoxide and acetone in the inclusion compounds with the host 1,4-bis(9-hydroxyfluoren-9-yl) benzene has been studied by DSC [22]. The mechanism of tetrahydrofuran and thiophene exchange in the inclusion compounds formed with the host 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol has been elucidated by infra-red spectroscopy, showing that this
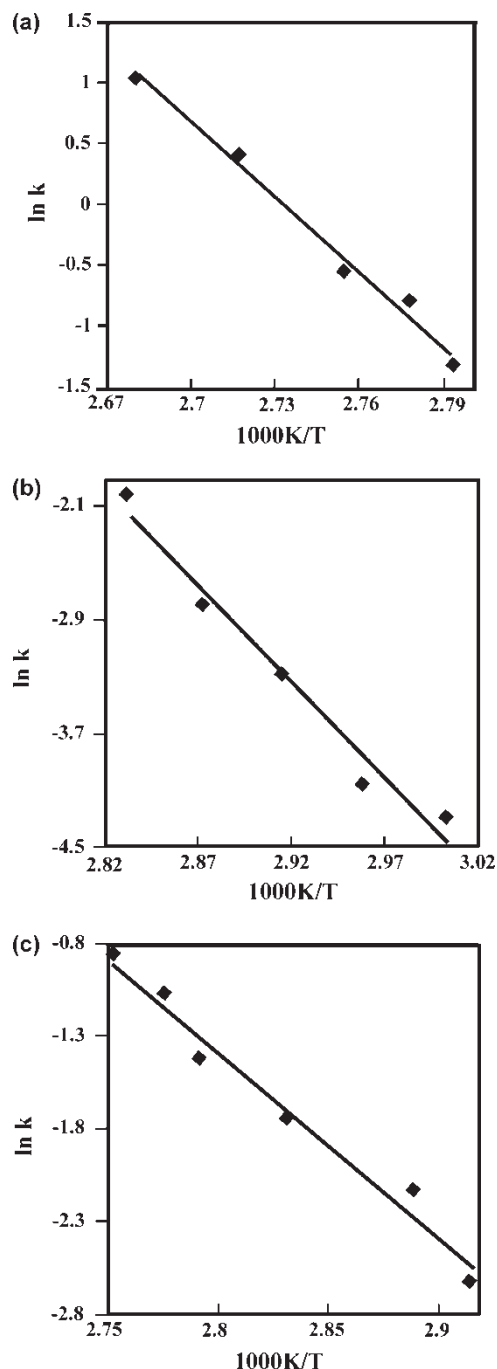

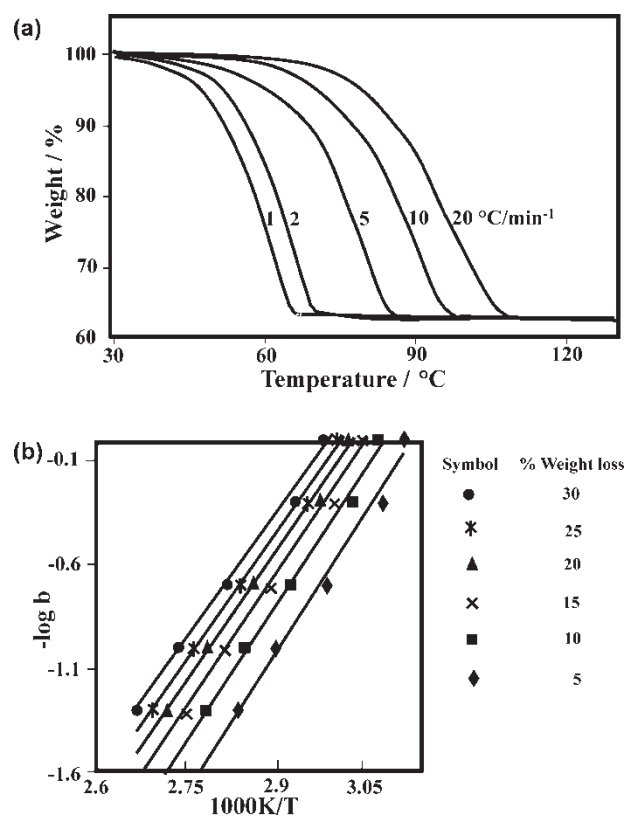FIGURE 5   Arrhenius plots for the desolvation of (a) **1**, (b) **2** and (c) **3**.

(a)

(b)

FIGURE 6 (a) TG curves indicating the desolvation of **2** at heating rates 1, 2, 5,10 and 20 K min^{-1}. (b) Plot of $-\log \beta$ *vs* $1/T$ for **2**.

exchange proceeds via a recrystallisation step of the apohost [23].

We carried out guest vapour exchange by placing crystals of compound **1** in a closed system saturated with 1,1,1-trichloroethane vapour at 25°C. The solid compound was sampled by TG at selected intervals over a period of 2 h. The results are shown in Fig. 7, which displays three representative curves taken at (a) $t = 0$, (b) $t = 65$ min and (c) $t = 120$ min, the latter representing complete reaction. Further work needs
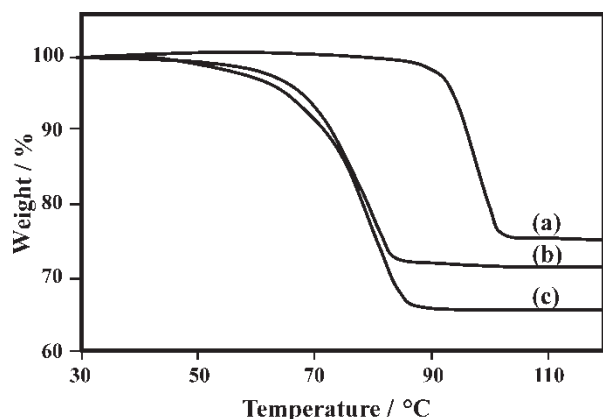

FIGURE 7   TG curves for the exchange reaction at time = (a) 0 min, (b) 65 min and (c) 120 min.

to be carried out to establish the mechanism of the guest exchange, as the velocity of the reaction is dependent on a number of parameters which include temperature, crystallite size distribution, vapour pressure of the incoming guest and the geometry of the apparatus. In our case we simply monitored the final mass loss of the exchanged inclusion compound which showed a first mass loss of 25.7%, corresponding to the initial **H**·CCl$_4$, to 33.6%, corresponding to the final **H**·2C$_2$H$_3$Cl$_3$.

CONCLUSION

The inclusion capabilities of the cyclotriveratrylene host compound with chlorinated guests have been investigated. Both 1,1,1- and 1,1,2-trichloroethane possess C—H bonds capable of weak interactions with the aromatic rings of the host. This results in the preferential inclusion of these guests in the host cavity, which is not observed with carbon tetrachloride. The thermal stability, kinetics of desolvation and guest exchange of the resultant compounds were established.

References

[1] Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, 1991.
[2] Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, 2001.
[3] Atwood, J. L.; Davies, J. E. D; MacNicol, D. D; Vögtle, F. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, **1996**; Vols 1–11.
[4] Braga, D.; Humphrey, J. Editorial *Crystallogr. Eng. Commun.* **2003**, *5*, 1.
[5] Biradha, K.; Fujita, M. *J. Chem. Soc. Dalton Trans.* **2000**, 3805.
[6] Torminaga, M.; Tashiro, S.; Aoyagi, M.; Fujita, M. *Chem. Commun.* **2002**, 2038.
[7] Nassimbeni, L. R.; Su, H. *New J. Chem.* **2002**, *6*, 989.
[8] Nassimbeni, L. R. *Acc. Chem. Res.* **2003**, *36*, 631.
[9] Collet, A. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Chapter 9.
[10] Ahmad, R.; Hardie, M. J. *Crystal Growth Des.* **2003**, *3 and 4*, 493.
[11] Knaust, J. M.; Inman, C.; Keller, S. W. *Chem. Commun.* **2004**, 492.
[12] COLLECT, data collection software, Nonius, Delft, Netherlands, **1998**.
[13] Otinowski, Z.; Minor, W. In *Methods in enzymology. Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1997; 276, pp 307–326.
[14] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
[15] Sheldrick, G. M. *SHELX-97, A Program for Crystal Structure Determination*; University of Göttingen: Germany, 1997.
[16] Barbour, L. J. J. *Appl. Crystallogr.* **1999**, *32*, 353.
[17] Hancock, K. S. B.; Steed, J. W. *Chem. Commun.* **1998**, 1409.
[18] Brown, M. E. *Introduction to Thermal Analysis*; Chapman and Hall: New York, 1988; Chapter 13.
[19] Flynn, J. H.; Wall, L. A. *Polymer Lett.* **1966**, *4*, 323.
[20] Weber, E. *Kirk–Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1995; 14, p 122.
[21] Bell, D. A.; Anslyn, E. V. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996; Vol. 2, Chapter 14, p 439.
[22] Caira, M. R.; Nassimbeni, L. R.; Vujovic, D.; Weber, E. *J. Chem. Soc. Perkin Trans. 2*, **2001**, 861.
[23] Caira, M. R.; Nassimbeni, L. R.; Toda, F.; Vujovic, D. *J. Chem. Soc. Perkin Trans. 2*, **2001**, 2119.