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# An investigation of the complexation of host *N*,*N'*-bis(9-phenyl-9-thioxanthenyl)ethylenediamine with dihaloalkane guests

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Abstract Two wheel-and-axle host compounds were synthesized and assessed for their host ability. After growing crystals of N,N'-bis(9-phenyl-9-thioxanthenyl)ethylenediamine from various alkyl halide solvents, we discovered that this host is highly proficient for the enclathration of these guest types. However, the novel compound N,N'bis(9-phenyl-9-xanthenyl)-1,6-hexamethylenediamine, bearing the more flexible axle, showed no inclusion ability whatsoever. Competition experiments where the title host compound was recrystallized from equimolar binary and ternary mixtures of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>I<sub>2</sub> showed this host to have a selectivity in the order  $CH_2Br_2 > CH_2I_2 > CH_2Cl_2$  for these guests. Varying the molar ratios of guests in these mixtures beyond equimolar revealed that the host remained selective for the bromine derivative whenever it was present, even at low dibromomethane concentrations. Single crystal X-ray diffraction data and, more specifically, host-guest interactions in the crystal, were used to explain the selectivity order; lattice energies were also considered in this context. The relative thermal stabilities of the three complexes, obtained from thermal experiments, showed that the selectivity order and these thermal stabilities are unrelated.

**Keywords** Host–guest chemistry · Inclusion · Complexes · Selectivity · Alkyl halides · X-ray crystallography · Supramolecular chemistry

#### Introduction

Our research team has recently spent much time studying the behaviour of various host compounds when these are recrystallized from mixtures of related guests, isomeric or not. As an example, (R,R)-(-)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol **1** has an affinity for the xylenes and shows discriminatory behaviour when recrystallized from various equimolar binary and ternary mixtures of these guests [1].

Weber et al. [2] synthesized a family of novel wheeland-axle hosts **2** over 20 years ago. These compounds have a rigid basic framework, bulky substituents, functional groups in strategic positions and symmetry relations. Various aromatic axle moieties (Ar) were incorporated into the structure, including benzene and biphenyl, and parts of the wheels (Ar<sup>1</sup> and Ar<sup>2</sup>) were also either benzene or biphenyl but also naphthalene. These researchers found that the functional group X had to be the hydroxyl functionality for the compound to display any host ability since X=H produced compounds with no host ability at all.

We subsequently synthesized our own family of what may also be regarded as wheel-and-axle hosts **3–6** and reported on their efficient host abilities [3–5]. The wheel component of these compounds are also bulky while the axles show far less rigidity than the compounds of Weber and his team, ours being based on an ethano linkage. Furthermore, the NH functional groups are expected to increase the ability of these compounds as hosts through hydrogen bonding with suitable guests. At that time, we reported that compound **6** formed complexes with  $CH_2Cl_2$ and  $CHCl_3$ , and also other non-halogen-containing species, but no further work was conducted in this regard [5].

We have recently discovered that 6 has, in fact, a high affinity for the haloalkanes, and here we report on this

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behaviour. Our primary focus is to gain an understanding of the reasons for any discriminatory behaviour displayed by the host when in the presence of mixtures of related halogencontaining guests, more specifically the three dihalomethanes CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>I<sub>2</sub>. Selected complexes were further analysed utilizing single crystal X-ray diffraction, differential scanning calorimetry and thermogravimetric analyses in order to investigate the reasons for any preferences shown by this host. Lattice energy calculations were also considered here.

Furthermore, we synthesized the novel hexamethylene derivative 7 in order to compare its host ability with that reported for the ethylenediamine derivative 3 [3].

we grew crystals of **6** from the potential guest solvent, and allowed the solvent to evaporate off over time at ambient conditions. The crystals that formed were collected using vacuum filtration, washed thoroughly with petroleum ether and dried, also using vacuum filtration. <sup>1</sup>H-NMR spectros-copy experiments then showed whether inclusion of the guest had occurred or not, and the host:guest (H:G) ratio was obtained by the integration of relevant host and guest resonances on the spectra.

The host ability of novel compound **7** was investigated in a similar fashion. A wide range of potential guests was used in the recrystallization experiments, ranging from alcohols to amines, ketones, alkanes, cycloalkanes, aromatics, alkyl



#### **Results and discussion**

Compounds **6** and **7** were readily synthesized by first treating the appropriate xanthenyl derivative **8** with perchloric acid. The perchlorate salt **9** that so-formed was reacted either with ethylenediamine or hexamethylenediamine to afford **6** and **7**, respectively, in good yield (90–99%) (Scheme 1).

#### Assessment of the host potential of 6 and 7

#### Complex formation

The host ability of compound **6** has been reported before [5]. In addition to the described complexes with  $CH_2Cl_2$  and  $CHCl_3$  in that report, we also investigated the affinity of this host for other alkyl halides. In order to achieve this,

halides, cyclic ethers, cyclic amines and amides, and not one of these was included. Host 3, where the hexamethylene axle has been replaced by an ethylene one, showed efficient host ability, on the other hand [3]. An obvious conclusion to the difference in behaviour is the lack of rigidity in the axle region of 7 compared with 3, thus preventing close crystal packing and, consequently, any possible significant host–guest interactions, thus affecting a reduction of enclathration potential for compound 7.

Table 1 is a summary of the potential alkyl halide guests investigated in the recrystallization experiments using host 6 as well as the H:G ratios of complexes successfully formed as obtained from proton NMR spectra.

It is clear from this table that **6** has an affinity for a number of haloalkanes. The preferred H:G ratio is consistently 1:1, and whether the guest is included or not appears to





depend on its relative size: all guest molecules bearing one or two halogen atoms are included by **6**, namely  $CH_2Cl_2$ ,  $CH_2Br_2$ ,  $CH_2I_2$ ,  $BrCH_2Cl$  and  $CH_3I$  whilst only the smallest of the three haloforms used,  $CHCl_3$ , formed a complex with **6**. The molecules  $CHBr_3$  and  $CHI_3$ , having three large halogen atoms bonded to the central carbon atom, were not enclathrated by this host.

Table 1 Host: guest (H:G) ratios of complexes formed by host  ${\bf 6}$  with haloalkanes

Guest (G)	H:G
CH <sub>2</sub> Cl <sub>2</sub>	1:1
CH <sub>2</sub> Br <sub>2</sub>	1:1
CH <sub>2</sub> I <sub>2</sub>	1:1
CHCl <sub>3</sub>	1:1
CHBr <sub>3</sub>	a
CHI <sub>3</sub>	a
CH <sub>3</sub> I	1:1
BrCH <sub>2</sub> Cl	1:1

Determined using <sup>1</sup>H-NMR spectroscopy using CDCl<sub>3</sub> as solvent <sup>a</sup>No inclusion occurred

Competition studies using equimolar solvent mixtures

Since host **6** includes all three of the dihalomethanes  $(CH_2Cl_2, CH_2Br_2 \text{ and } CH_2I_2)$ , competition experiments were carried out in order to determine if this host shows discriminatory behaviour when in the presence of some or all of these guests. Therefore **6** was dissolved in a variety of combinations of the halides where these were present in equimolar quantities. Here crystallization was conducted in closed vials that were kept at approximately 0 °C to ensure that the amount of guests present remained equimolar. The crystals that resulted were then treated in an identical manner to those obtained from the single solvent experiments. The H:G ratios, obtained from the proton NMR spectra, are given in Table 2, where the preferred guest is shown in bold italic font face for ease of analysis.

Notable from Table 2 is that the overall H:G ratio remains approximately constant at 1:1, the same as the preferred ratio in the single solvent experiments. Furthermore, host **6** certainly shows discriminatory behaviour under competition experiment conditions. Whether in the presence of equimolar binary  $(CH_2Cl_2/CH_2Br_2, CH_2Br_2/CH_2I_2)$ 

CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Br <sub>2</sub>	CH <sub>2</sub> I <sub>2</sub>	Guest ratios	Overall H:G ratio
x	x		0.22: <b>0.77</b>	~1:1
х		x	0.32: <b>0.65</b>	~1:1
	x	Х	<b>0.63</b> :0.35	~1:1
x	x	х	0.16: <b>0.46</b> :0.38	~1:1

Table 2 Results of competition experiments using 6 and various equimolar mixtures of the dihalomethanes

Ratios determined using <sup>1</sup>H-NMR spectroscopy

Experiments were conducted in duplicate for confirmation purposes and an average value is provided here

or ternary (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Br<sub>2</sub>/CH<sub>2</sub>I<sub>2</sub>) solutions, this host is selective for the dibromo derivative whenever it is present (77 and 63% is extracted in the two binary experiments, respectively, and 46% in the ternary experiment). When this dihalide is absent, the host discriminates against CH<sub>2</sub>Cl<sub>2</sub> in favour of CH<sub>2</sub>I<sub>2</sub> (32%:65%). The selectivity order of this host compound for these guests therefore increases in the order CH<sub>2</sub>Cl<sub>2</sub> < CH<sub>2</sub>I<sub>2</sub> < CH<sub>2</sub>Br<sub>2</sub>.

# Competition studies using mixtures of solvents with varying molar ratios

In the previous section, we only considered equimolar mixtures of the guests in competition experiments. What would happen if the molar amount of each of the guests in binary competition experiments was not equivalent? Would the selectivity of the host change? In order to answer these questions, we set up binary competition experiments as before but in each case we sequentially changed the relative ratios of the two guests in competition.

A plot of the mole fraction of guest A present in the crystal after recrystallization of the host from a mixture of guests A and B ( $Z_A$ ) against the mole fraction of A in the liquid mixture of A and B ( $X_A$ ) can provide one of three general selectivity curves (Fig. 1) [6]. Plot **a** would be obtained if there was no selectivity displayed by the host, and the amount of A and B included depended on the ratio of A and B present in the mixture. Plot **b** represents the case where the host shows selectivity for one guest (A in this example) over the entire concentration range, and more of A is included by the host compared with the percentage of A present in the liquid mixture, and plot **c** is an example of the host selectivity being dependent on the guest concentration, and changes as the molar ratios of the two guests change in the liquid mixture.

The selectivity constant [6] may be given by

 $K_{A:B} = Z_A / Z_B \times X_B / X_A,$ 

where  $X_A + X_B = 1$ .

Clearly, if no selectivity is shown by the host (plot **a**), then  $K_{A:B} = 1$ .



Fig. 1 General selectivity curves

We considered each of the  $CH_2Br_2/CH_2Cl_2$ ,  $CH_2Br_2/CH_2L_2$   $CH_2I_2$  and  $CH_2I_2/CH_2Cl_2$  binary competition experiments here. Various known molar amounts of the two guests in each experiment were mixed together and the vials treated in an identical manner to the equimolar experiments, and the crystals and mother liquor analyzed using <sup>1</sup>H-NMR spectroscopy to obtain values for the mole fractions ( $X_{CH2X2}$  and  $Z_{CH2X2}$  where X = halogen). These data provided the plots given in Fig. 2a ( $CH_2Br_2/CH_2Cl_2$ ), 2b ( $CH_2Br_2/CH_2I_2$ ) and 2c ( $CH_2I_2/CH_2Cl_2$ ).

From both Fig. 2a and b, it is clear that host **6** is selective for  $CH_2Br_2$  over the entire concentration range used, even at low concentrations of this guest. (Note that plot **b** in each of the three figures is obtained experimentally, while plot **a**, where K = 1, has been inserted for reference purposes.) In the absence of dibromomethane (Fig. 2c), however, the host initially shows selectivity for diiodomethane at low diiodomethane concentrations, extracting 44% of this guest from a 72%:28%  $CH_2Cl_2:CH_2I_2$  mixture. From a 34%:66%  $CH_2Cl_2:CH_2I_2$  mixture, the host extracts exactly 66% of the diiodomethane, and it is at this point that  $K_{CH2Cl2:CH2I2} =$ 1. Beyond this point, the selectivity is for dichloromethane: a 14%:86%  $CH_2Cl_2:CH_2I_2$  mixture saw the host extracting



Fig. 2 Selectivity curves for a  $CH_2Br_2/CH_2Cl_2$ , b  $CH_2Br_2/CH_2I_2$  and c  $CH_2I_2/CH_2Cl_2$ 

76% of the diiodomethane (which is a smaller percentage than what was present in the mixture) and the data point therefore dips below the  $K_{CH2CI2:CH2I2} = 1$  straight line here.

We subsequently conducted single crystal X-ray diffraction (SCXRD) experiments to determine which intermolecular forces were responsible for retaining the guest in each crystal and also which factors might explain the selectivity order of this host compound.

# Single crystal X-ray crystallographic analyses of host 6 alone and its complexes with the three dihalides

These experiments were conducted at 200 K using a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.71073 Å). APEXII and SAINT were used for data collection, and cell refinement and data reduction, respectively [7]. SHELXT-2014 [8] was used to solve the structures, and refined by least-squares procedures using SHELXL-2014 [8] together with SHELXLE [9] as a graphical interface. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were added in idealized geometrical positions in a riding model while nitrogen-bound hydrogen atoms were located on the difference Fourier map. Data were corrected for absorption effects using the numerical method implemented in SADABS [7]. [CCDC reference numbers 1533422 ( $\mathbf{6}\cdot CH_2CI_2$ ), 1533423 ( $\mathbf{6}\cdot CH_2Br_2$ ), 1533424 ( $\mathbf{6}\cdot CH_2I_2$ ) and 1540116 (host  $\mathbf{6}$  alone)].

Table 3 shows relevant experimental data for these SCXRD experiments. The three complexes crystallize in the monoclinic crystal system and  $P2_1/n$  space group, and all guests are disordered over two positions. In fact, upon close inspection of the X-ray data, it is clear that these three crystal structures are isostructural. We therefore wondered whether, perhaps, the host alone would have the same crystal packing as in the complexes, and therefore whether this

Table 3 Crystallographic data for 6·CH<sub>2</sub>Cl<sub>2</sub>, 6·CH<sub>2</sub>Br<sub>2</sub> and 6·CH<sub>2</sub>I<sub>2</sub>, and also for host 6 alone

	6·CH <sub>2</sub> Cl <sub>2</sub>	<b>6</b> ·CH₂Br₂	<b>6</b> ·CH₂I₂	Host 6 alone
Chemical formula	$C_{40}H_{32}N_2S_2 \cdot CH_2Cl_2$	$C_{40}H_{32}N_2S_2 \cdot CH_2Br_2$	$C_{40}H_{32}N_2S_2 \cdot CH_2I_2$	C <sub>40</sub> H <sub>32</sub> N <sub>2</sub> S <sub>2</sub>
Formula weight	689.72	778.62	872.62	604.80
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> /n	<i>P</i> 2 <sub>1</sub> /n	$P2_1/n$	<i>P</i> -1
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	0.349	2.539	1.939	0.205
a (Å)	10.1138(8)	10.2014(5)	10.5803(7)	9.0912(5)
b (Å)	13.3589(10)	13.3548(6)	13.3472(8)	12.3688(7)
c (Å)	25.0909(17)	25.0025(16)	24.9308(17)	14.9416(8)
Alpha (°)	90	90	90	77.362(2)
Beta (°)	92.771(3)	92.864(3)	92.337(3)	82.375(2)
Gamma (°)°	90	90	90	70.793(2)
$V(\text{\AA}^3)$	3386.1(4)	3402.0(3)	3517.7(4)	1544.81(15)
Z	4	4	4	2
F(000)	1440	1584	1728	686
Temp. (K)	200	200	200	200
Restraints	6	7	8	0
Nref	8332	8458	8736	7386
Npar	448	460	454	405
R	0.0503	0.0470	0.0642	0.0391
wR2	0.1462	0.1358	0.1979	0.1043
S	1.01	1.02	1.03	1.03
θmin-max (°)	1.6, 28.4	2.1, 28.3	1.6, 28.3	1.8, 27.9
Tot. data	47,384	47,750	49,817	39,535
Unique data	8332	8458	8736	7386
Observed data [I > 2.0 sigma(I)]	6934	6471	6779	6497
R <sub>int</sub>	0.025	0.022	0.021	0.017
Dffrn measured fraction $\theta$ full	1.000	0.999	1.000	0.999
Min. resd. dens. (e/ Å <sup>3</sup> )	-1.18	-1.01	-2.13	-0.78
Max. resd. dens. (e/ $Å^3$ )	0.88	1.29	4.77	0.5

host has some zeolite character where the voids remain intact whether guest is present or not. We thus recrystallized the host from *m*-xylene, a solvent it does not include, and obtained suitable crystals for SCXRD analysis. Figures of the four unit cells are provided in Fig. 3a–d. It is clear that, under these conditions, the crystal packing of the host collapses in the absence of guest: the host crystallizes in a different crystal system (triclinic) and space group (*P*-1) when it is alone, compared with when it is in the presence of guest (monoclinic,  $P2_1/n$ ).

The X-ray data were analysed closely and, more specifically, we considered appropriate host-guest and guest-guest intermolecular contacts obtained from the X-ray data, and these are summarized in Table 4. Here we sought to determine whether any significant interactions between host and guest could be pinpointed to explain the observed selectivity order.

Since the guest molecules have no aromatic groups,  $\pi$ - $\pi$  stacking interactions are only observed between host species, as expected (Table 4). Furthermore, these guests are devoid of any common hydrogen bond donating and accepting capability, and so no classic hydrogen bonding is observed between host and guest. Also noticeable is that there are no (guest)C-H··· $\pi$ (host) contacts present at all. Other short host-guest contacts number two (for the CH<sub>2</sub>Cl<sub>2</sub> complex), three (CH<sub>2</sub>Br<sub>2</sub>) and three (CH<sub>2</sub>I<sub>2</sub>). One must not lose sight of the fact that, due to the isostructurality of the host packing in the three complexes, the dichloromethane molecule, since it has the smallest volume of the three guests, probably experiences more spacious accommodation than the dibromomethane molecules, and the diiodomethane guests are likely to be the more "cramped" of the three. Interactions of any importance are more likely the less spacious the accommodation since the guests find themselves in closer contact with the host. The diiodomethane molecules even experience a guest–guest interaction since the lack of space allows for two of these to be close enough in proximity to interact favourably with one another [C<sub>8</sub>–I<sub>81</sub>···I<sub>81</sub>–C<sub>8</sub>, 3.789(4) Å, 27.7(6)°].

The preference order  $(CH_2Br_2>CH_2I_2>CH_2Cl_2)$  may be explained by considering these numbers of contacts, where the dibromo- and diiodo- complexes experience more of these contact types compared with the dichloromethane complex. However, perhaps more significant is the fact that all of the complexes experience one non-classical H-bond, a (guest)C–H···S–C(host) interaction, and the strongest of these is between the host and dibromomethane (2.78 Å, 142°), the preferred guest. These host–guest interactions therefore explain the selectivity order that was observed earlier.



Fig. 3 Unit cells for  $\mathbf{a} \cdot \mathbf{6} \cdot \mathbf{CH}_2 \mathbf{Cl}_2$ ,  $\mathbf{b} \cdot \mathbf{6} \cdot \mathbf{CH}_2 \mathbf{Br}_2$ ,  $\mathbf{c} \cdot \mathbf{6} \cdot \mathbf{CH}_2 \mathbf{I}_2$  and  $\mathbf{d}$  host  $\mathbf{6}$  alone; host molecules are shown in ball-and-stick representation and guests in space-fill form; all guests display disorder over two positions; the crystals of the three complexes are isostructural but different to pure host  $\mathbf{6}$ 

Non-covalent interaction	<b>6</b> ·CH <sub>2</sub> Cl <sub>2</sub>	6-CH <sub>2</sub> Br <sub>2</sub>	6·CH <sub>2</sub> I <sub>2</sub>	Symmetry operator
$\pi - \pi$ (host–host only)	4.304(1)–5.780(1) Å	4.270(1)–5.786(1) Å	4.253(2)–5.949(2) Å	
CH··· $\pi$ (host–guest)	None present	None present	None present	
H-bonding	Non-classical	Non-classical	Non-classical	
Short contacts (host/guest a	nd guest/guest) <sup>a,b</sup>			
$C_7 - H_{7A} - C_{53} - C_{52}$	2.79 Å, 152° (<)			2 - x, 1 - y, 1 - z
$C_8 - H_{8B} - C_{12}$	2.82 Å, 140° (<)			x, y, z
$C_7 - H_{7A} - C_{53} - C_{52}$		2.87 Å, 148° (<)		1 + x, y, z
$C_8 - H_{8A} - C_{12}$		2.78 Å, 142° (<<)		1 - x, 1 - y, 1 - z
$C_8 - Br_{82} - C_{52} - S_2$		3.397(2) Å, 159.4(2)° (<)		1 + x, y, z
$C_{32}$ - $H_{32}$ ··· $I_{81}$ - $C_8$			3.14 Å, 116° (<)	1/2 + x, $1/2 - y$ , $1/2 + z$
$C_{13} - H_{13} - C_7$			3.17 Å, 145° (<)	1/2 - x, -1/2 + y, 1/2 - z
$C_7 - H_{7A} - C_{12}$			2.83 Å, 145° (<)	1/2 + x, $1/2 - y$ , $1/2 + z$
$C_8 - I_{81} \cdots I_{81} - C_8$			3.789(4) Å, 27.7(6)° (<)	1 - x, 1 - y, -z

Table 4 Crystallographic data for 6·CH<sub>2</sub>Cl<sub>2</sub>, 6·CH<sub>2</sub>Br<sub>2</sub> and 6·CH<sub>2</sub>I<sub>2</sub>

<sup>a</sup>Distances denoted by < are contacts that measure less than the sum of the van der Waals radii of the atoms involved while those denoted by << is this sum minus 0.2 Å

<sup>b</sup>Atomic numbering is as follows:



#### Lattice energies

A freely available online software package written by Angelo Gavezzotti [10] was used to calculate the lattice energies of the three complexes and also for the free host using the SCXRD data. Lattice energy is a measure of how much energy is released into the surrounds when one mole of the crystals is formed from the gas phase: the more energy that is released, the more exothermic is complex formation. Table 5 summarizes the results of these calculations.

For host 6, lattice energies (in kJ mol<sup>-1</sup>) are in the order diiodomethane  $\approx$  dibromomethane < dichloromethane ane < host alone. These results imply that complexation

Table 5 Calculated lattice energies for  $6{\cdot}CH_2Cl_2,\ 6{\cdot}CH_2Br_2$  and  $6{\cdot}CH_2I_2$ 

Sample	Lattice energies (kJ mol <sup>-1</sup> )
Host 6 alone	-115.4
6.Dichloromethane	-265.4
6.Dibromomethane	-275.2
6.Diiodomethane	-277.4

with diiodomethane and dibromomethane are the most exothermic processes (-277.4 and -275.2 kJ mol<sup>-1</sup>, respectively) of the three complexations assessed. Due

to the comparability of the lattice energies for these two complexations, these energy considerations alone cannot be used to explain the observed selectivity of this host for  $CH_2Br_2$  in competition experiments. Nevertheless, comparisons of these lattice energies do explain the discrimination of host **6** against  $CH_2Cl_2$ : the associated energy release upon complexation of this guest is considerably less (-265.4 kJ mol<sup>-1</sup>) than for the other two complexes. Also, these energies explain why complexation of these halogeno guests is a favourable process for host **6** since crystallization of the host alone is accompanied by a much smaller energy release (-115.4 kJ mol<sup>-1</sup>) compared with the three complexes.

#### Nature of guest accommodation

In order to determine the nature of the accommodation experienced by each guest, that is, whether discrete cavity or channel occupation is prevalent, these guests were omitted from the packing calculation using the Mercury CSD 3.5.1 software package, and the resultant voids computed; these are illustrated in Fig. 4a–c. Upon close analyses of these X-ray data, it is clear that discrete cavities are present, and two guests are found in each of these. Discrete cavity occupation has been associated with complexes that have higher relative thermal stabilities compared with those in which the guests reside in channels, whether slightly constricted or open [11].

Thermal analyses experiments were then conducted on the three isostructural complexes to ascertain their relative thermal stabilities.

# Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of complexes of host **6** with the three dihalides

These experiments were carried out by heating the complexes at 10 °C/min in open ceramic pans. The so-obtained DSC and TG traces are provided in Fig. 5a–c.

The guest release process in each case is rather uneventful as witnessed by the DSC, TG and derivative of the TG traces in these figures. It is clear that the guest release initiates prior to the host melt as observed by the two endotherms in each DSC trace.

The term  $(T_{on} - T_b)$  data has been reported to be a measure of the relative thermal stabilities of isostructural host–guest complexes [12];  $T_{on}$  is the onset temperature for



Fig. 4 Voids showing that guests occupy discrete cavities in the crystals of  $\mathbf{a} \ \mathbf{6} \cdot \mathrm{CH}_2 \mathrm{Cl}_2$ ,  $\mathbf{b} \ \mathbf{6} \cdot \mathrm{CH}_2 \mathrm{Br}_2$  and  $\mathbf{c} \ \mathbf{6} \cdot \mathrm{CH}_2 \mathrm{I}_2$ ; two guests are accommodated in each void; the isostructurality in these three complexes can readily be observed here too



Fig. 5 Traces of the DSC, TG and derivative of the TG obtained after thermal experiments conducted on a  $6 \cdot CH_2Cl_2$ , b  $6 \cdot CH_2Br_2$  and c  $6 \cdot CH_2I_2$ , respectively

the guest release process (obtained from the lower derivative curve in Fig. 5a–c) and  $T_b$  is the boiling point of pure liquid guest. The more positive this value, the more thermally stable is the complex. These data are summarized in Table 6, and also the percentage mass loss experienced and theoretically expected for each of the 1:1 complexes.

The expected mass loss upon complete guest removal through heating is in close agreement with that theoretically expected for all three complexes (Table 6).

The onset temperature for guest release  $(T_{on})$  decreases as the size of the dihalide increases (76.8, 70.8 and 67.7 °C for complexes with CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>I<sub>2</sub>, respectively). Since the boiling point of these pure guests  $(T_b)$ increases in the same order, the relative thermal stability order, as given by  $(T_{on} - T_b)$  data, may therefore be written as CH<sub>2</sub>Cl<sub>2</sub>>CH<sub>2</sub>Br<sub>2</sub>>CH<sub>2</sub>I<sub>2</sub> (37.2, -26.2 and -114.3 °C, respectively). It is clear that, in this case, these data are unrelated to the preference order noted before. However, the peak temperatures of the endotherms representing the guest release process (where guest release is most rapid) do decrease according to this preference order, where these temperatures for complexes **6**·CH<sub>2</sub>Br<sub>2</sub> > **6**·CH<sub>2</sub>I<sub>2</sub> > **6**·CH<sub>2</sub>Cl<sub>2</sub>(124 > 123 > 110 °C).

**Table 6** Thermal properties of complexes formed by  $\mathbf{6}$  with the dihalomethanes

Guest (G)	$T_{\rm on}$ (°C)	$T_{\rm b}$ (°C)	$(T_{on} - T_b)$ (°C)	Mass loss expected (%)	Actual mass loss meas- ured (%)
CH <sub>2</sub> Cl <sub>2</sub>	76.8	39.6	37.2	12.3	12.6
CH <sub>2</sub> Br <sub>2</sub>	70.8	97.0	-26.2	22.3	21.6
$CH_2I_2$	67.7	182.0	-114.3	30.7	30.3

## Conclusions

Two wheel-and-axle host compounds were synthesized and assessed for their host ability. N,N'-bis(9-phenyl-9thioxanthenyl)ethylenediamine was found to be highly efficient especially for the enclathration of alkyl halides, including six of the eight potential guests investigated with a preferred host:guest ratio of 1:1. N,N'-Bis(9-phenyl-9xanthenyl)-1,6-hexamethylenediamine, on the other hand, showed no host ability whatsoever, and this is most likely due to the loss of rigidity in the molecule owing to the long, flexible C6 bridging axle unit. Competition experiments using equimolar binary and ternary mixtures of  $CH_2Cl_2$ ,  $CH_2Br_2$  and  $CH_2I_2$  showed that the title host compound has an overwhelming preference for the dibromo guest. The host's selectivity was thus ascertained to be in the order  $CH_2Br_2 > CH_2I_2 > CH_2Cl_2$ . Further selectivity experiments in which two guests were mixed together in varying molar ratios showed that, whenever dibromomethane was present, the host showed selectivity for this guest over the entire concentration range investigated, even at low concentrations of this guest in the mixture ( $CH_2Br_2/CH_2Cl_2$  and  $CH_2Br_2/CH_2I_2$ ). Experiments using varying amounts of  $CH_2I_2$  and  $CH_2Cl_2$  showed that the selectivity of the host was dependent on the relative molar amounts of these two guests in the mixtures.

Data from single crystal X-ray diffraction experiments provided explanations for the observed selectivity order: the dibromo and diiodo guests both experience more short host–guest contacts than the dichloro equivalent. Furthermore, each of the three guests experience a non-classical hydrogen bond with the host [(guest)C–H···S–C(host)], and the most preferred guest,  $CH_2Br_2$ , experiences the strongest of these. These data also showed that the three complexes are isostructural and that the host packing collapses when guest is not present, crystallizing in a different crystal system and space group.

Lattice energy calculations showed that the exothermicity of the crystallization process decreases in the order  $CH_2I_2 \approx CH_2Br_2 > CH_2CI_2 >$  host alone. These energy considerations do not fully explain why the bromine-containing guest is most preferred in competition experiments, but do explain the discrimination observed against dichloromethane.

All three guests are accommodated in discrete cavities, with each cavity enclosing two guest molecules.

Thermal experiments revealed that the relative thermal stabilities of the complexes, using  $(T_{on} - T_b)$  data, increases in the order  $CH_2I_2 < CH_2Br_2 < CH_2Cl_2$  which could not be related to the observed selectivity order of this host. However, the guest-release endotherm peak temperatures correlate directly with this selectivity order, decreasing in the order **6**·CH<sub>2</sub>Br<sub>2</sub> > **6**·CH<sub>2</sub>I<sub>2</sub> > **6**·CH<sub>2</sub>Cl<sub>2</sub>.

## Experimental

#### **General methods**

Melting points were recorded on an Electrothermal IA9000 Series digital melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 Series Fourier Transform Infrared spectrometer, and <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra on a Varian Gemini 200 spectrometer. Thermal experiments were conducted using a TA SDT Q600 Module system and analysed using TA Universal Analysis 2000 data analysis software. Samples were placed in open ceramic pans with an empty ceramic pan functioning as a reference. High purity nitrogen gas was used as purge gas in both cases.

## Synthesis of *N*,*N'*-bis(9-phenyl-9-thioxanthenyl) ethylenediamine 6

## 9-Phenylthioxanthen-9-ol 8 (Y = S)

This compound was synthesized using a Grignard reaction according to a published procedure [13, 14]. The crude material was recrystallized from dichloromethane/ petroleum ether to afford **8** (Y=S) in a 96% yield, mp 106 °C (lit. [14], mp 105–106 °C);  $\nu_{max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3601 (sharp, free OH), 3385 (br, H-bonded OH) and 1583 (Ar);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 3.28 (1H, s, OH), 7.00–7.70 (11H, m, Ar) and 8.07 (2H, d, *J* 7.5, Ar);  $\delta_{\rm C}$ (CDCl<sub>3</sub>)/ppm 79.13 (COH), 128.39 (Ar), 128.64 (Ar), 128.76 (Ar), 129.18 m(Ar), 129.45 (Ar), 129.88 (Ar), 130.20 (Ar), 133.63 (quaternary Ar), 142.11 (quaternary Ar) and 145.47 (quaternary Ar).

### 9-Phenylthioxanthen-9-ylium perchlorate 9 (Y = S)

The salt **9** (Y = S) was prepared using a similar procedure to that given by Goosen et al., [15] precipitating out of solution as a red/brown solid in a yield of 83%, mp 230–235 °C [lit. [16], mp 239 °C (decomp.)];  $\nu_{max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1590 (Ar);  $\delta_{H}$ (CDCl<sub>3</sub>)/ppm 7.20–9.00 (13H, multiplets, Ar).

#### N,N'-Bis(9-phenyl-9-thioxanthenyl)ethylenediamine 6

This compound was prepared according to a procedure devised in our laboratories [5]. The residue so-formed was crystallized and recrystallized from chloroform/petroleum ether to afford a 1:1 **6**:CHCl<sub>3</sub> inclusion complex in a 90% yield, mp 174–176 °C [lit. [5], 174–175 °C (decomp.)];  $\nu_{max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3347 (weak, NH) and 1587 (Ar);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 2.42 (2H, br s, N<u>H</u>), 2.50 (4H, s, C<u>H</u><sub>2</sub>) and 7.10–7.80 (26H, m, Ar);  $\delta_{\rm C}$ (CDCl<sub>3</sub>)/ppm 46.41 (CH<sub>2</sub>), 68.21 (PhCNH), 127.84 (Ar), 128.07 (Ar), 128.89 (Ar), 128.99 (Ar), 130.00 (Ar), 131.83 (Ar), 133.60 (quaternary Ar), 139.89 (quaternary Ar) and 148.53 (quaternary Ar).

# Synthesis of *N*,*N'*-bis(9-phenyl-9-xanthenyl) hexamethylenediamine 7

9-Phenylxanthen-9-ol 8 (Y=O)

Alcohol 8 (Y=O) was prepared by using the procedure of Glover et al. [17] The residue that formed was recrystallized from benzene/petroleum ether to afford **8** (Y=O) in a 55% yield, mp 160–162 °C (lit. [17], mp 161–162 °C);  $\nu_{max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3588 (free OH), 3380 (br, H-bonded OH) and 1602 (Ar);  $\delta_{\rm H}$ (CDCl<sub>3</sub>)/ppm 2.73 (1H, s, OH) and 7.00–7.90 (13H, m, Ar);  $\delta_{\rm C}$ (CDCl<sub>3</sub>)/ppm 72.46 (PhCOH), 118.45 (Ar), 125.60 (Ar), 128.27 (Ar), 128.78 (Ar), 129.25 (quaternary Ar), 130.02 (Ar), 131.09 (Ar), 150.05 (quaternary Ar) and 151.71 (quaternary Ar).

#### 9-Phenylxanthen-9-ylium perchlorate 9 (Y = O)

The solid **9** (Y=O) was prepared in the same fashion as salt **9** (Y=S) [15]. An orange solid precipitated out of the solution with a yield of 80%, mp 283–286 °C (lit. [15], 280–281 °C);  $\nu_{max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1601 (Ar);  $\delta_{H}$ (CDCl<sub>3</sub>)/ ppm 7.75–8.60 (13H, multiplets, Ar).

# *N,N'*-Bis(9-phenyl-9-xanthenyl)-1,6-hexamethylenedia mine 7

This novel compound was prepared in the same manner as host 6 but substituting ethylenediamine for hexamethylenediamine. The residue crystallized and recrystallized from chloroform/petroleum ether to furnish compound 7 in 99% yield, mp 184–186 °C;  $\nu_{max}$ (CHCl<sub>3</sub>)/  $cm^{-1}$  3600–3100 (br, NH) and 1601 (Ar);  $\delta_{H}$ (CDCl<sub>3</sub>)/ppm 1.15 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.38 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.80 (2H, s, NH), 2.10 (4H, t, J 6.7, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) and 6.90–7.60 (26 H, m, Ar);  $\delta_{\rm H}(\rm CDCl_3)/\rm ppm~29.00~(\rm CH_2CH_2CH_2CH_2CH_2CH_2),$ 32.47 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 45.08 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH-<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 62.20 (Ph<u>C</u>NH), 118.13 (Ar), 125.24 (Ar), 128.01 (quaternary Ar), 128.51 (Ar), 129.27 (Ar), 130.02 (Ar), 130.09 (Ar), 130.85 (Ar), 151.74 (quaternary Ar) and 153.42 (quaternary Ar); m/z 628 (M<sup>+</sup>, 0.4%), 181 (M-371-76, 5.4%), 196 (M-432, 1.6%), 257 (M-371, 100%) and 371 (M-257, 0.4%). [Found: C, 83.9; H, 6.4; N, 4.5. C<sub>44</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub> requires C, 84.0; H, 6.4; N, 4.5%].

## Supplementary data

CCDC-1533422 ( $6\cdot$ CH<sub>2</sub>Cl<sub>2</sub>), 1533423 ( $6\cdot$ CH<sub>2</sub>Br<sub>2</sub>), 1533424 ( $6\cdot$ CH<sub>2</sub>I<sub>2</sub>) and 1540116 (host 6 alone) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam. ac.uk/data\_request/cif.

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