

Directional 1-D inclusion networks: self-assembly of unsymmetrical koilands into directional koilates in the crystalline phase †

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Received 7th June 2000, Accepted 13th July 2000

First published as an Advance Article on the web 21st September 2000

An unsymmetrical koiland **5** based on the double fusion of two different calix[4]arenes by two silicon atoms has been prepared and structurally characterised. Using *p*-xylene and phenylpropyne as symmetrical unsymmetrical connectors, respectively, directional 1-D inclusion networks have been obtained and structurally characterised by X-ray diffraction methods on single crystals. In both cases, the 1-D networks were packed in a parallel fashion. However, the linear arrays were oriented in opposite directions, thus leading to non-directional systems.

Introduction

Non-covalent molecular networks are infinite architectures formed by the self-assembly of molecular units possessing in their structure the assembling algorithm which may be coded within building blocks using energy and geometry criteria. The driving force leading to the formation of molecular networks lies on the construction of specific interaction patterns which may be termed assembling nodes and their translation into one (1-D), two (2-D) or three (3-D) directions of space. The design of the assembling node may be based on molecular recognition processes between the complementary molecular building blocks composing the system. For the self-assembly processes, in principle, any type of reversible interaction may be used. We have previously reported molecular networks based on the use of van der Waals interactions,¹ hydrogen bonding combined with electrostatic charge/charge interactions² and coordination bonds.³

Dealing with 1-D networks based on a single translation of the assembling node, the control of directionality is an important and rather challenging issue. In particular, such control is crucial for the exploitation of directional physical properties such as dipolar interactions.

In the present contribution we report the design and structural characterisation of two directional 1-D inclusion networks.

The formation of inclusion complexes between concave and convex molecules has been investigated over the last three decades. We have extended the concept of inclusion to the construction of inclusion networks in the solid state.¹ The proposed strategy was based on the design of koilands^{4–12} (from Greek *koilos*: hollow) which are defined as multicavity systems bearing at least two receptor cavities arranged in a divergent fashion (Fig. 1). The ability of koilands to form discrete binuclear complexes with molecular units acting as stoppers [Fig. 1(a)] has been demonstrated.^{4,7,9,11,12} Since each individual cavity is designed to form inclusion complexes with convex molecules,

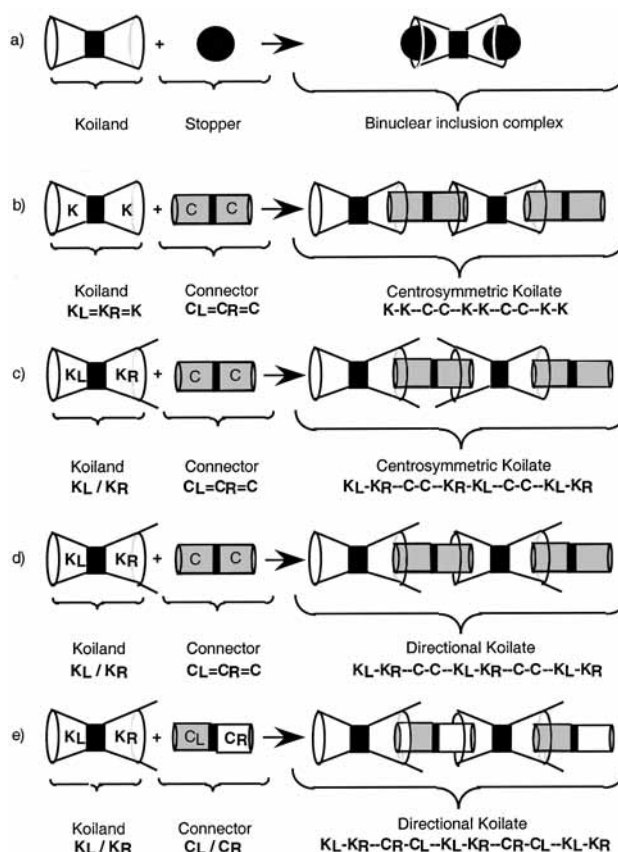


Fig. 1 Schematic representation of discrete binuclear inclusion complexes which may be formed between koilands and stopper molecules (a) and of koilates (1-D inclusion networks) which may be obtained in the presence of connector molecules. The 1-D networks may be non-directional (b, c) or directional (d, e).

fusing, in a rigid framework, two or more such cavities has been shown to lead, in the presence of appropriate connectors, to a non-covalently assembled inclusion network termed a *koilate*. For example, linear koilates (one-dimensional linear molecular arrays) were obtained in the solid state using mainly van der Waals interactions between rigid koilands possessing

† Based on the presentation given at Dalton Discussion No. 3, 9–11th September 2000, University of Bologna, Italy.

Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See <http://www.rsc.org/suppdata/dt/b0/b0045381/>

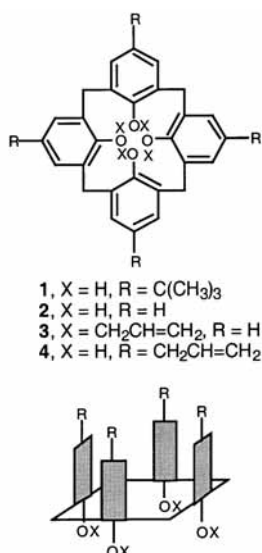


Fig. 2 Calix[4]arene derivatives (top) and a schematic representation of their cone conformation (bottom).

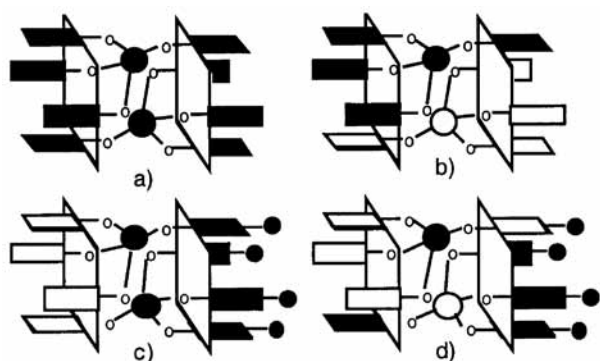


Fig. 3 Schematic representation of symmetrical (a) and unsymmetrical koilands (b, c, d). Electronically differentiated koilands may be formed by a double fusion of two identical calix[4]arenes by two different elements (b) whereas geometrically differentiated koilands may be based on the double fusion of two different calix[4]arenes by two identical fusing elements (c). Unsymmetrical koilands may also show both electronic as well as geometrical differentiation (d).

two divergent cavities with an angle of 180° between them and linear connectors, possessing two extremities each capable of being included within the cavities of the direceptor [Fig. 1(b)].

The design of koilands may be based on calix[4]arene derivatives¹³ since these molecules in cone conformation offer a preorganised and tuneable pocket surrounded by four aryl moieties as well as four hydroxy groups for further functionalisation (Fig. 2). Furthermore, the calix[4]arene backbone offers the possibility of tuning both the entrance and the depth of the preorganised cavity *via* the nature of the substituents R located at the *para* position. Linear koilands were obtained upon fusion of two calix[4]arenes derivatives in the cone conformation by two silicon atoms (Fig. 3).¹ Examples of fused calix[4]arenes using titanium(IV), niobium(V), aluminium(III) and, more recently, zinc have been reported.¹⁴ Using thiacalix[4]arene derivatives for which the CH₂ groups are replaced by S atoms^{15,16} koilands based on fusion of such units by Cu(II),¹⁷ Zn(II) or Co(II)¹⁸ atoms have been obtained and structurally characterised in the solid state by X-ray analysis.

Dealing with 1D-networks, the control of the directionality remains an important and challenging issue. In particular, for all cases of koilates obtained so far,^{7,9,11,12} owing to the symmetrical nature of koilands and connectors used, no particular directionality or orientation could be obtained [Fig. 1(b)]. In order to control the directionality of koilates, one may take advantage of molecular recognition processes governing the

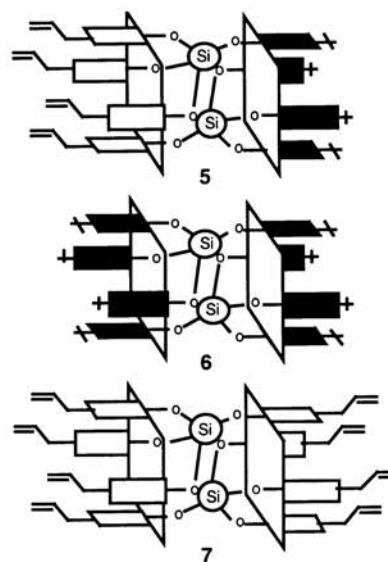


Fig. 4 Schematic representation of the unsymmetrical koiland **5** obtained upon fusion of compounds **1** and **4** by two Si atoms (top) and of symmetrical koilands **6** and **7** resulting from the homofusion of calix **1** or **4** by two silicon atoms, respectively.

formation of inclusion networks through the recognition of the connector by the cavity of the koiland. Thus, by using appropriate sets of cavities and connectors, one should be able to design directional koilates using unsymmetrical molecular units. In principle, using unsymmetrical koilands and symmetrical connectors, one may obtain either non-directional [Fig. 1(c)] or directional koilates [Fig. 1(d)], whereas using unsymmetrical koilands and connectors, only the formation of directional koilates may be expected [Fig. 1(e)].

The design of unsymmetrical koilands may be based on either electronic or geometric differentiation of the two cavities (Fig. 3). Electronic differentiation [Fig. 3(b)] may be achieved using two different fusing atoms with the same oxidation state IV such as Si and Ti.⁵ The unsymmetrical nature of the Si–Ti heterobinuclear koiland is based on the induced difference between the two calix units by their coordination to two different metals with different electronegativities. Indeed, one of the calix units is triply coordinated to a Si atom whereas the other unit is triply coordinated to a Ti atom.

Geometric differentiation [Fig. 3(c)] may be accomplished, while keeping the same fusing element such as Si, by connecting two different calix units.¹⁰ Finally, one may use both electronic and geometrical differentiation to design unsymmetrical koilands [Fig. 3(d)].

As an unsymmetrical koiland, compound **5** based on the double fusion of two different calix derivatives **1** and **4** by two Si atoms was designed. The rationale behind the choices of compound **1** and **4** was based on our previous observations.^{7,9,12} Indeed, it has been demonstrated by X-ray structural analysis in the crystalline phase that whereas the koiland **6** composed of two *p*-*tert*-butylcalix[4]arenes formed a koilate in the presence of hexadiyne,⁷ the other symmetrical koiland **7** based on two *p*-allylcalix[4]arenes formed another koilate in the presence of *p*-xylene.⁹

The general strategy for the synthesis of koilands was based on treatment of calix derivatives with NaH in dry THF followed by addition of SiCl₄.⁴ The desired compounds are usually obtained after chromatography on silica or by crystallisation. The same type of procedure was employed for the preparation of unsymmetrical koiland **5** (Fig. 4). Upon treatment of an equimolar mixture of two different calix[4]arenes **1**¹⁹ and **4**²⁰ with NaH as base in dry THF followed by addition of SiCl₄, as expected, the reaction affords, in addition to the desired unsymmetrical koiland **5** composed of both compounds **1** and **4** [**1–4**] in 12% yield, two other symmetrical koilands **6** [**1–1**] and **7**

Table 1 X-Ray data^a

	5·3CH ₂ Cl ₂	5·2C ₈ H ₁₀	5·2C ₉ H ₈
Chemical formula	C ₈₄ H ₈₈ O ₈ Si ₂ ·3CH ₂ Cl ₂	C ₈₄ H ₈₈ O ₈ Si ₂ ·2C ₈ H ₁₀	C ₈₄ H ₈₈ O ₈ Si ₂ ·2C ₉ H ₈
<i>M</i>	1536.60	1494.14	1514.13
<i>a</i> /Å	11.4684(5)	12.7530(6)	15.3269(5)
<i>b</i> /Å	17.5630(7)	14.5330(6)	17.4756(6)
<i>c</i> /Å	20.4767(5)	25.010(1)	19.0824(6)
<i>a</i> ^o	97.489(2)	100.191(5)	65.355(5)
<i>β</i> ^o	101.974(2)	98.867(5)	72.286(5)
<i>γ</i> ^o	97.733	106.834(5)	64.786(5)
<i>V</i> /Å ³	3944.3(5)	4261.7(9)	4152.84(5)
Crystal dimensions/mm	0.20 × 0.16 × 0.10	0.20 × 0.15 × 0.15	0.20 × 0.20 × 0.14
<i>μ</i> /mm ⁻¹	0.305	0.098	0.102
No. of data measured	30386	57465	18973
No. of data with <i>I</i> > 3σ(<i>I</i>)	10852	10123	11390
<i>R</i>	0.063	0.088	0.056
<i>R</i> _w	0.092	0.11	0.065

^a Details in common: radiation: Mo-Kα (graphite monochromated) ($\lambda = 0.71073$ Å); diffractometer: KappaCCD; triclinic, space group $P\bar{1}$, *Z* = 2; colourless crystals; *T* = 173 K.

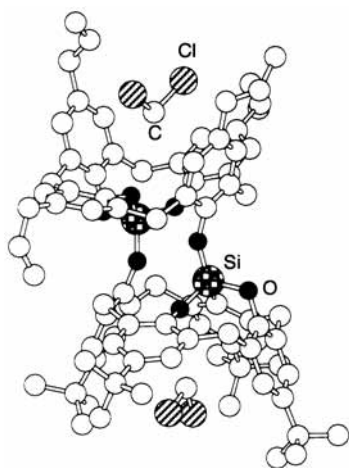


Fig. 5 Structure of the binuclear complex 5·3CH₂Cl₂ obtained from koiland **5** and CH₂Cl₂. H atoms and the third solvent molecule omitted for clarity.

[4–4] resulting from the homo coupling of the two different calix units in 65 and 7% yields, respectively. Both koilands **6**⁴ and **7**⁹ have been previously obtained and fully characterised.

The starting compounds for the synthesis of **5** were the *p*-*tert*-butylcalix[4]arene **1** which was prepared according to the published procedure¹⁹ and the calix **4** which was synthesised in three steps from compound **1** following reported procedures.²⁰

For compound **5**, as expected for unsymmetrical heterodimers, ²⁹Si NMR studies in CHCl₃ revealed the presence of two signals at δ –111.73 and –112.78, whereas for the symmetrical koilands **6** and **7** unique signals at δ –111.95 and –112.94, respectively, were observed.

In the solid state, the structure of compound **5** was confirmed as its CH₂Cl₂ binuclear inclusion complex (Fig. 5). X-Ray analysis data on a single crystal of 5·3CH₂Cl₂ is provided in Table 1. As expected from its design, compound **5**, composed of two different calix units in cone conformation, indeed contains two geometrically different cavities oriented in a divergent manner. The fusing Si atoms show tetrahedral geometry (average O–Si–O angle of *ca.* 109.5°) with an average Si–O distance of *ca.* 1.61 Å, whereas the distance between the two Si atoms is 3.68 Å. These values are similar to those previously observed for compounds **6**⁴ and **7**.⁹ In the lattice, in addition to the koiland **5**, three CH₂Cl₂ molecules are present. Among these, two are located within the two cavities (each cavity contains one CH₂Cl₂ molecule), thus acting as stoppers, whereas the third CH₂Cl₂ molecule is disordered and localised between discrete binuclear complexes thus occupying empty spaces.



Fig. 6 A portion of the X-ray structure of the inclusion network formed between the koiland **5** and *p*-xylene showing the assembling core composed of two consecutive koilands **5** encapsulating a *p*-xylene molecule which acts as the connector. H atoms are omitted for clarity.

Turning to the connectors, *p*-xylene which was previously shown to form a koilate with compound **7** was used as a symmetrical connector while phenylpropyne appeared to be an interesting candidate as an unsymmetrical connector. The choice of the latter was again based on our previous observations on koiland **6** which was found to form a koilate in the presence of hexadiyne.⁷

Using koiland **5**, the formation of directional 1-D networks was investigated using either *p*-xylene as a symmetrical connector or phenylpropyne as a directional connector. Upon slow diffusion of isopropyl alcohol into a solution of **5** in *p*-xylene as solvent, colourless crystals of 5·2C₈H₁₀ were obtained. X-Ray diffraction data on a single crystal thus obtained are provided in Table 1. As in the case of 5·3CH₂Cl₂, 5·2C₈H₁₀ crystallises in the triclinic crystal system with space group $P\bar{1}$; of the two *p*-xylene molecules present, one acts as a connector by bridging through inclusion processes consecutive koilands so leading to the formation of the koilate, whereas the other did not participate in the formation of the koilate but instead occupies the empty space between them. For the koiland **5**, the coordination geometry around the fusing Si atoms is again tetrahedral (average O–Si–O angle of *ca.* 109.46°) with an average Si–O distance of *ca.* 1.62 Å, whereas the distance between the two Si atoms is 3.82 Å similar to those for 5·3CH₂Cl₂. For the koilate, the assembling core which leads to the 1-D network by a single translation is defined by the encapsulation of a *p*-xylene molecule by two consecutive koilands **5** in an unsymmetrical manner (Fig. 6). In other words, one methyl group of *p*-xylene is included within the cavity of **5** bearing *p*-allyl groups, whereas the other methyl group penetrates the cavity of a consecutive koiland **5** bearing *tert*-butyl groups. The shortest distance between the connector and cavities of koilands ranges from 3.5 to 3.7 Å. For the Me group of *p*-xylene included within the cavity bearing the allyl groups, two van der Waals contacts of *ca.* 3.7 Å are observed, whereas for the other methyl group included within the cavity bearing the *tert*-butyl groups, eight van der Waals contacts (<3.7 Å) are observed. Furthermore, two van der Waals contacts of *ca.* 3.7 Å between consecutive

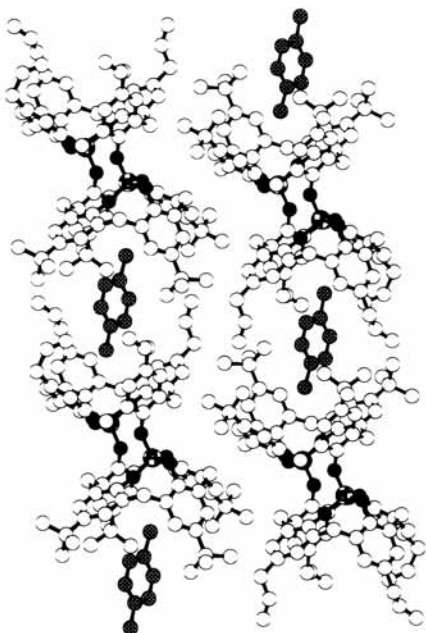


Fig. 7 A portion of the X-ray structure of two parallel linear inclusion networks formed by connection through inclusion of consecutive koilands **5** by *p*-xylene showing the packing in opposite directions of the linear arrays. H atoms and solvent molecules are omitted for clarity.

koilands, *i.e.* C...C distance between allyl and *tert*-butyl groups, are observed. Owing to the unsymmetrical nature of the assembling core, upon translation, a 1-D directional koilate is obtained (Fig. 7). The directional linear koilates are positioned in a parallel fashion, however the packing is symmetrical, *i.e.* consecutive linear koilates are oriented in opposite directions, thus generating centres of symmetry. Consequently, the overall system is non-directional. The centrosymmetric packing of directional koilates may be due to cancellation of dipolar moments.

As stated above, another alternative for the preparation of directional linear koilates may be based on the use of unsymmetrical koiland **5** and phenylpropyne as an unsymmetrical connector [Fig. 1(e)]. Again, upon slow diffusion of isopropyl alcohol into a solution of **5** in phenylpropyne as solvent, colourless crystals were obtained. X-Ray diffraction data on a single crystal of $5 \cdot 2C_8H_8$ thus obtained are provided in Table 1. As in the above two examples, $5 \cdot 2C_8H_8$ crystallises in the triclinic crystal system with space group $P\bar{1}$. Again, one of the two phenylpropyne molecules present acts as a connector leading to the formation of the koilate by bridging consecutive koilands through inclusion processes, whereas the other occupies the empty space between koilates. For the koiland **5**, the coordination geometry around the fusing Si atoms is again tetrahedral (average O–Si–O angle of *ca.* 109.45°) while the average Si–O distance is *ca.* 1.61 Å, whereas the distance between the two Si atoms is 3.78 Å. These values are similar to those for the koilate using *p*-xylene. The assembling core is again defined in terms of the encapsulation of a phenylpropyne molecule by two consecutive koilands **5** (Fig. 8). Whereas the propyne moiety of the connector is included within the cavity of **5** bearing *tert*-butyl groups with five van der Waals contacts being observed, the phenyl moiety penetrates the cavity of a consecutive koiland **5** bearing *p*-allyl groups leading to fifteen van der Waals contacts. The shortest distance between the connector and cavities of koilands is *ca.* 3.34 Å. Again, due to the unsymmetrical nature of the assembling core, upon translation, a 1-D directional koilate is obtained (Fig. 9). However, as for $5 \cdot 2C_8H_{10}$, the directional linear koilates are positioned in a parallel fashion but with opposite orientation, thus leading to a non-directional packing.



Fig. 8 A portion of the X-ray structure of the inclusion network formed between koiland **5** and phenylpropyne showing the assembling core composed of two consecutive koilands **5** encapsulating a phenylpropyne molecule which acts as the connector. H atoms are omitted for clarity.

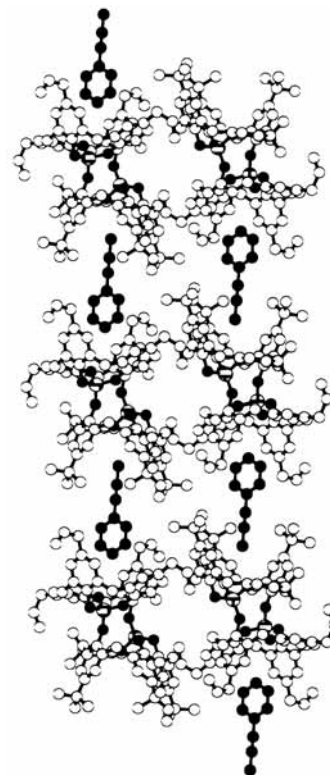


Fig. 9 A portion of the X-ray structure of two parallel linear inclusion networks formed by connection through inclusion of consecutive koilands **5** by phenylpropyne molecules showing the packing in opposite directions of the linear arrays. H atoms and solvent molecules are omitted for clarity.

In conclusion, the unsymmetrical koiland **5** based on the double fusion of two different calix[4]arenes by two silicon atoms has been prepared and structurally characterised. Using *p*-xylene and phenylpropyne as symmetrical and unsymmetrical connectors, respectively, directional 1-D inclusion networks were obtained and structurally characterised by X-ray diffraction methods on single crystals. In both cases, the 1-D networks were packed parallel with each other. However, owing to the opposite orientation of the linear arrays, a non-directional arrangement was obtained in both cases. The possibility of controlling both the directionality of 1-D inclusion networks as well as their unsymmetrical packing is currently under investigation using chiral calix[4]arene derivatives.

Experimental

Synthesis of compound **5**

Compound **4**²⁰ (270 mg, 4.6×10^{-4} mol) and NaH (123 mg, 5.1×10^{-3} mol) were added under argon to a suspension of compound **1**¹⁹ (300 mg, 4.6×10^{-4} mol) in dry THF (40 ml). The reaction mixture was stirred for 24 h at room temperature

(r.t.) and a 1 M solution of SiCl_4 (1.5 ml) in CH_2Cl_2 , then added and the mixture stirred for 3 h at r.t. After the removal of solvents *in vacuo*, CHCl_3 (50 ml) was added to the solid residue and the solid filtered off. Upon chromatography [solid deposition of the mixture, SiO_2 ; CH_2Cl_2 -Hexane (2:8)], the desired heterodimer **5** (12%) and the two possible homodimers **6**⁴ (65%) and **7**⁹ (8%) were isolated. Both compounds **6** and **7** were identified from previously obtained data. For **5**: δ_{H} (CDCl_3 , 300 MHz, 25 °C) 1.12 (s, CH_3 , 9H), 1.19 (s, CH_3 , 9H), 1.26 (s, CH_3 , 18H), 3.09–3.44 (m, ArCH_2CH , 8H; ArCH_2Ar , 8H), 4.44–4.59 (m, ArCH_2Ar , 8H), 4.93–5.12 (m, $\text{H}_2\text{C}=\text{CH}$, 8H), 5.78–6.04 (m, $\text{CH}=\text{CH}_2$, 4H), 6.71–7.08 (s, H arom, 16H); δ_{C} (CDCl_3 , 50.32 MHz, 25 °C) 31.27, 31.37, 31.46, 33.27, 33.92, 34.22, 34.87, 39.20, 39.53, 39.59, 115.1, 115.61, 116.04, 125.02, 125.12, 126.13, 126.46, 128.30, 128.43, 129.44, 129.57, 130.13, 130.26, 132.33, 132.88, 133.51, 133.93, 135.64, 137.47, 137.64, 137.83, 145.51, 145.87, 146.42, 146.65, 148.16, 148.88; δ_{Si} (CDCl_3 , 59.63 MHz, 25 °C): –111.73, –112.78. Calc. for $\text{C}_{84}\text{H}_{88}\text{O}_8\text{Si}_2 \cdot 0.5\text{H}_2\text{O}$: C, 78.16; H, 6.95. Found: C, 78.13; H, 7.33%.

Crystallisation

5· $3\text{CH}_2\text{Cl}_2$. Upon slow diffusion at r.t. of MeOH (3 ml) into a solution of compound **5** (1.5 mg) in CH_2Cl_2 (0.5 ml), suitable single-crystals were obtained after several weeks.

5· $2\text{C}_8\text{H}_{10}$. Upon slow diffusion at r.t. of isopropyl alcohol (2.5 ml) into a solution of compound **5** (4 mg) and *p*-xylene (1 ml) as solvent, suitable colourless single-crystals were obtained after several weeks.

5· $2\text{C}_8\text{H}_8$. Upon slow diffusion at r.t. of isopropyl alcohol (3 ml) into a solution of compound **5** (2.5 mg) and phenylpropyne (0.5 ml) as solvent, suitable colourless single-crystals were obtained after several weeks.

Details of X-ray data collection and refinement for **5**· $3\text{CH}_2\text{Cl}_2$, **5**· $2\text{C}_8\text{H}_{10}$ and **5**· $2\text{C}_8\text{H}_8$ are provided in Table 1.

CCDC reference number 186/2088.

See <http://www.rsc.org/suppdata/dt/b0/b0045381/> for crystallographic files in .cif format.

Acknowledgements

We thank the CNRS and the Institut Universitaire de France (IUF) for financial support.

References

- 1 M. W. Hosseini and A. De Cian, *Chem. Commun.*, 1998, 727.
- 2 M. W. Hosseini, R. Ruppert, P. Schaeffer, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1994, 2135; G. Brand, M. W. Hosseini, R. Ruppert, A. De Cian, J. Fischer and N. Kyritsakas, *New J. Chem.*, 1995, **19**, 9; M. W. Hosseini, G. Brand, P. Schaeffer, R. Ruppert, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1996, **37**, 1405; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 102; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 1755; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 1933; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *New J. Chem.*, 1997, **21**, 285; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *New J. Chem.*, 1998, **22**, 1389; W. Jaunky, M. W. Hosseini, J.-M. Planeix, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1999, 2313; O. Félix, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 2000, 281.

- 3 C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. H. White, *Angew. Chem., Int. Ed.*, 1998, **37**, 920; G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1998, 2545; M. Loi, M. W. Hosseini, A. Jouaiti, A. De Cian and J. Fischer, *Eur. J. Inorg. Chem.*, 1999, 1981; M. Loï, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 1999, 603; C. Klein, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 2000, 239.
- 4 X. Delaigue, M. W. Hosseini, A. De Cian, J. Fischer, E. Leize, S. Kieffer and A. van Dorrselaer, *Tetrahedron Lett.*, 1993, **34**, 3285.
- 5 X. Delaigue, M. W. Hosseini, E. Leize, S. Kieffer and A. van Dorrselaer, *Tetrahedron Lett.*, 1993, **34**, 7561.
- 6 X. Delaigue, M. W. Hosseini, R. Graff, J.-P. Kintzinger and J. Raya, *Tetrahedron Lett.*, 1994, **35**, 1711.
- 7 F. Hajek, E. Graf, M. W. Hosseini, X. Delaigue, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1996, **37**, 1401.
- 8 F. Hajek, E. Graf and M. W. Hosseini, *Tetrahedron Lett.*, 1996, **37**, 1409.
- 9 F. Hajek, M. W. Hosseini, E. Graf, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1760.
- 10 F. Hajek, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1997, **38**, 4555.
- 11 F. Hajek, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Mater. Res. Bull.*, 1998, **33**, 79.
- 12 J. Martz, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas and J. Fischer, *J. Mater. Chem.*, 1998, **8**, 2331.
- 13 C. D. Gutsche, *Calixarenes Revisited, Monographs in Supramolecular Chemistry, No. 1*, ed. J. F. Stoddart, Royal Society of Chemistry, Cambridge, 1998.
- 14 M. M. Olmstead, G. Sigel, H. Hope, X. Xu and P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 8087; F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1990, 1083; J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1992, 1349; J. L. Atwood, P. C. Junk, S. M. Lawrence and C. L. Raston, *Supramol. Chem.*, 1996, **7**, 15; A. Bilyk, J. M. Harrowfield, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1997, 4251 and references therein.
- 15 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama and S. Miyano, *Tetrahedron Lett.*, 1997, **38**, 3971; T. Sone, Y. Ohba, K. Moriya, H. Kumada and K. Ito, *Tetrahedron Lett.*, 1997, **38**, 10689.
- 16 H. Akdas, L. Bringel, E. Graf, M. W. Hosseini, G. Mislin, J. Pansanel, A. De Cian and J. Fischer, *Tetrahedron Lett.*, 1998, **39**, 2311.
- 17 G. Mislin, E. Graf, M. W. Hosseini, A. Bilyk, A. K. Hall, J. McB Harrowfield, B. W. Skelton and A. H. White, *Chem. Commun.*, 1999, 373.
- 18 A. Bilyk, A. K. Hall, J. M. Harrowfield, M. W. Hosseini, G. Mislin, B. W. Skelton, C. Taylor and A. H. White, *Eur. J. Inorg. Chem.*, 2000, 823.
- 19 C. D. Gutsche and M. Iqbal, *Org. Synth.*, 1989, **68**, 234.
- 20 C. D. Gutsche and J. A. Levine, *J. Am. Chem. Soc.*, 1982, **104**, 2652.