Supplementary Information

Solven-Solvent and Solvent-Solute Interactions in a 3D Chloroform Clathrate with Diorganotin Macrocycles in the Nano-sized Pores

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Available Information:

- Experimental procedure and spectroscopic characterization (including 1D and 2D NMR spectra and FAB^+ spectrum of the metal complex)
- TG curve
- Additional figure of the $[CDCl_3]_{10}$ cluster arrangements
- Supramolecular inclusion complex formed between the macrocycle and two $CDCl_3$ molecules
- Tables for intermolecular interactions

1. Experimental Procedure

N,N´-di(bicyclo[2.2.1]hept-2-yl)butane-1,4-diamine (0.200 g, 0.72 mmol), KOH (0.080 g, 1.44 mmol) and carbon disulfide (0.110 g, 1.44 mmol) were dissolved in methanol (5 mL) and stirred for 2 h, whereupon Me_2SnCl_2 (0.16 g, 0.72 mmol) dissolved in methanol (10 mL) was added to the solution. A white powder precipitated immediately, which was separated by filtration, washed with distilled water and dried with *n*-hexane. Crystals suitable for single-crystal X-ray diffraction analysis were grown from $CDCl_3$ within an NMR tube by slow evaporation of the solvent. Yield: 0.58 g (0.25 mmol), 68 %.

2. Instrumentation

NMR studies were carried out on a Varian Inova 400 instrument. Standards were TMS (internal, δ^1H = 0.00, δ^{13}C = 0.0 ppm) and $SnMe_4$ (external, δ^{119}Sn = 0.0 ppm). Two dimensional ^{1}H-^{1}H COSY and ^{13}C-^{1}H HSQC NMR experiments have been carried out in order to completely assign the ^{1}H and ^{13}C spectra. The FAB$^+$ mass spectrum was recorded on a Jeol JMS 700 equipment. The thermogravimetric analyses (TGA) wase accomplished with a TA SDT Q600 instrument. Approximately 5 mg of the solid sample were quickly placed in an alumina crucible and analyzed in the temperature range of 30-400 °C with a 10 °C/min heating rate, using a current of 50 mL/min of nitrogen as inert gas purge.

Single-crystal X-ray diffraction analysis

Single-crystal X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector ($\lambda_{\mathrm{Mo}K\alpha}$ = 0.71073 Å, monochromator: graphite). Frames were collected at T = 100 K via ω/ϕ-rotation at 10 s per frame (SMART).[1a] The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT).[1b] Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[1c,d] Non hydrogen atoms were refined anisotropically. C-H and C-D hydrogen atoms were placed in geometrically calculated positions using the riding model. Two of the five independent chloroform molecules were disordered: one over two sites (occ. 0.81 and 0.19) and the second over three sites (occ. 0.21, 0.33 and 0.46). For the latter DFIX, SAME and EADP instructions have been during the least squares refinement.

CCDC No. 841834.

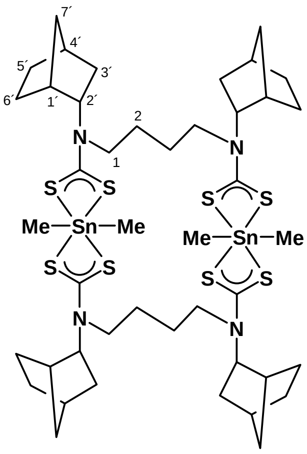
References

[1] (a) Bruker Analytical X-ray Systems. SMART: Bruker Molecular Analysis Research Tool, Versions 5.057 and 5 .618, 1997 and 2000. (b) Bruker Analytical X-ray Systems. SAINT + NT, Versions 6.01 and 6.04, 1999 and 2001. (c) Sheldrick, G. M. SHELX86, Program for Crystal Structure Solution; University of Göttingen: Germany, 1986. (d) Bruker Analytical X-ray Systems. SHELXTL-NT Versions 5.10 and 6.10, 1999 and 2000.

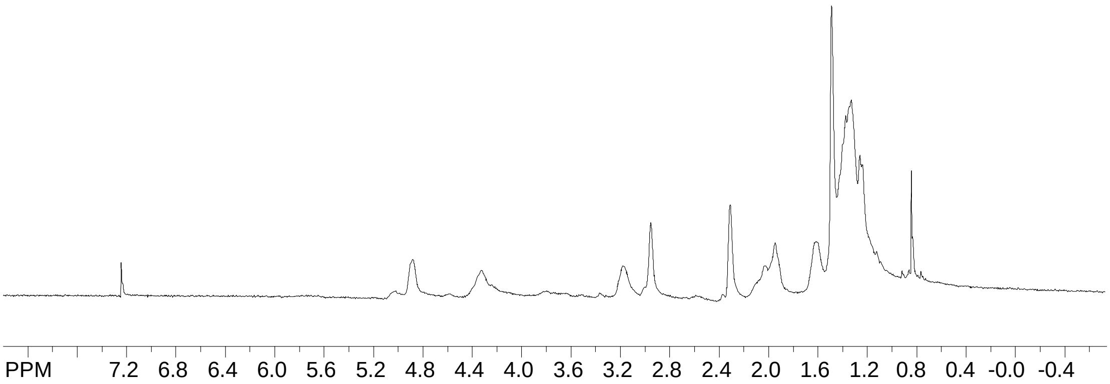
3. Spectroscopic data

^{1}H NMR (400 MHz, CDCl$_3$, 20 °C, TMS): δ = 1.26-1.39 (br, H2, H3´$_{endo}$, H5´$_{endo}$, H6, H7), 1.47 (br, Sn-Me), 1.62 (br, H5´$_{exo}$), 1.95 (br, H3´$_{exo}$), 2.31 (br, H4´), 2.95 (br, H1’), 3.18 and 4.33 (br, ABX$_2$ system, H1), 4.88 (br, H2´$_{exo}$) ppm. **^{13}C NMR** (100 MHz, CDCl$_3$, 20 °C, TMS): δ = 15.2 (Sn-Me), 22.9 (C6’), 25.2 (C2), 29.6 (C5’), 33.3 (C3’), 37.2 (C4’), 38.2 (C7’), 40.6 (C1’), 51.6 (C1), 65.8 (C2’), 200.6 (CS$_2$) ppm. **^{119}Sn NMR** (75 MHz, CDCl$_3$, 20 °C, SnMe$_4$) δ = –332 ppm.

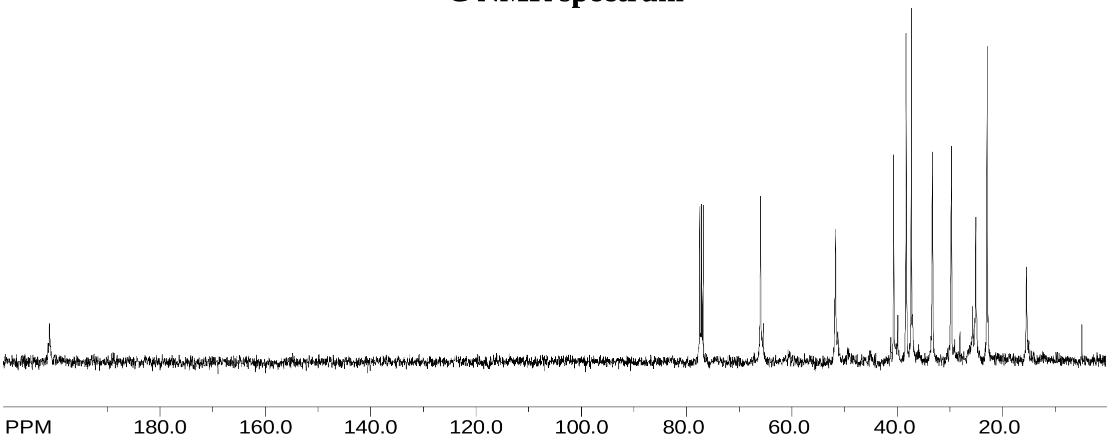
MS (FAB$^+$): *m/z* (%): 1150 (M, 1.3), 1135 (M-Me, 3).



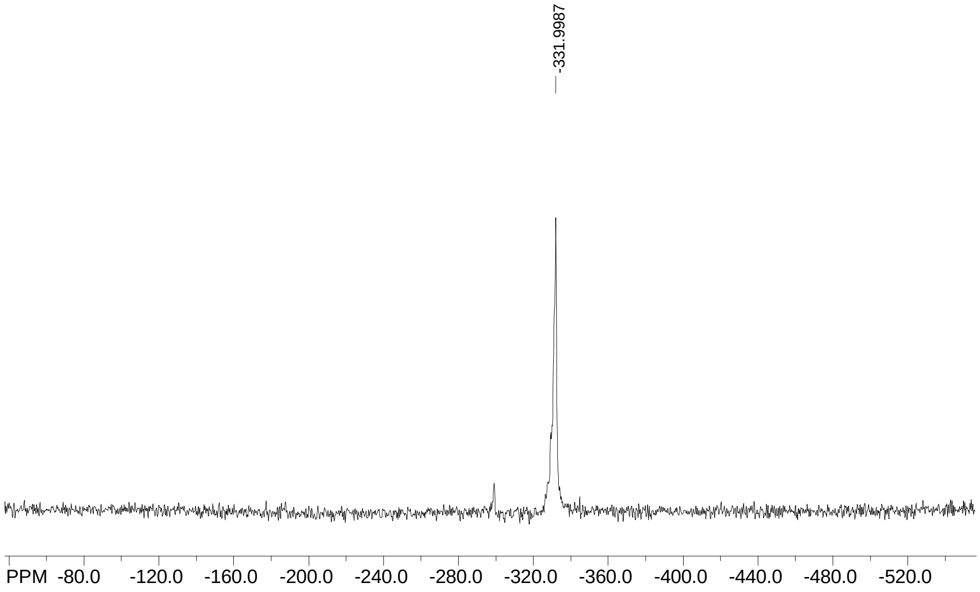
^{1}H-NMR spectrum



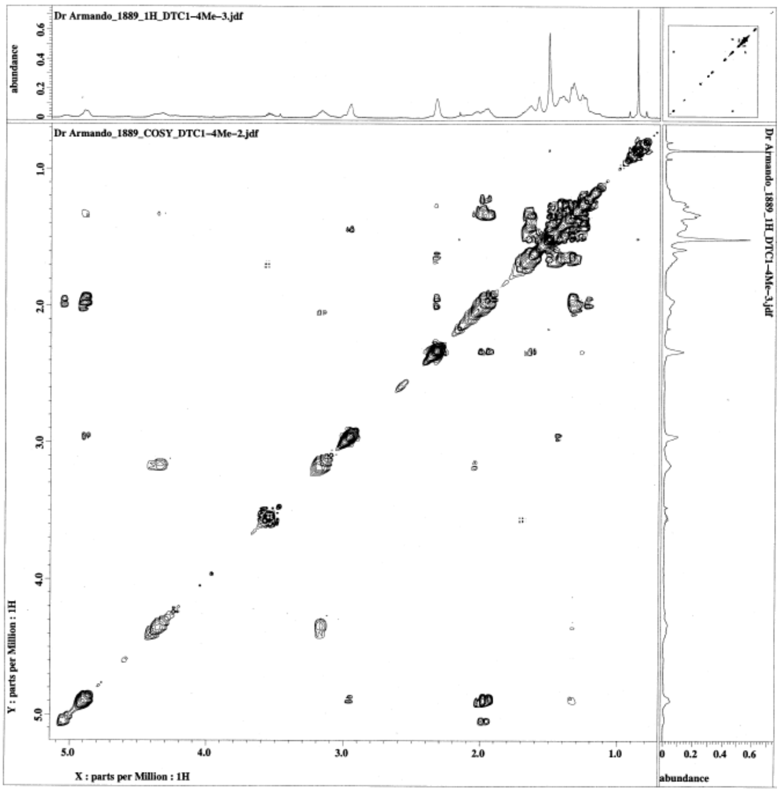
^{13}C NMR spectrum



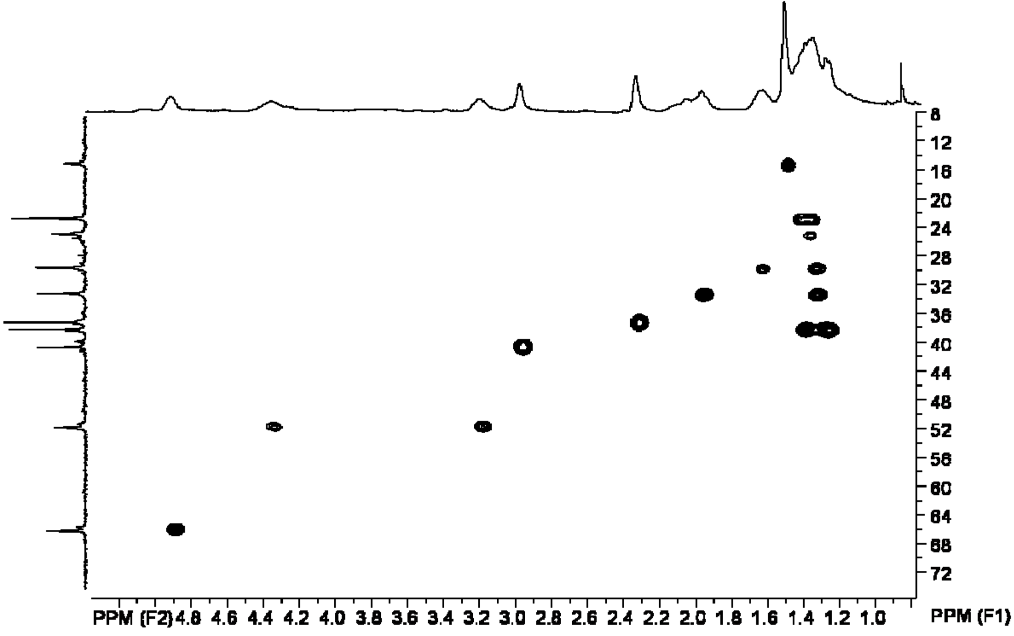
^{119}Sn NMR spectrum



^{1}H-^{1}H COSY



^{13}C-^{1}H HSQC NMR spectrum



FAB$^+$ Mass spectrum

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[ Mass Spectrum ]
Data  : JGA025                       Date : 25-Feb-2011 00:09
Sample: DTC1-4Me                          Operator name Ing.Victoria Labastida
Note : Dr.Jorge Guerrero/Iran  Centro de Investigaciones Quimicas UAEM
Inlet : Direct                       Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.12 min           Scan# : (1,3)
BP : m/z 307.0000       Int.   : 100.00
Output m/z range : 538.0884 to 1205.0236      Cut Level : 0.00 %
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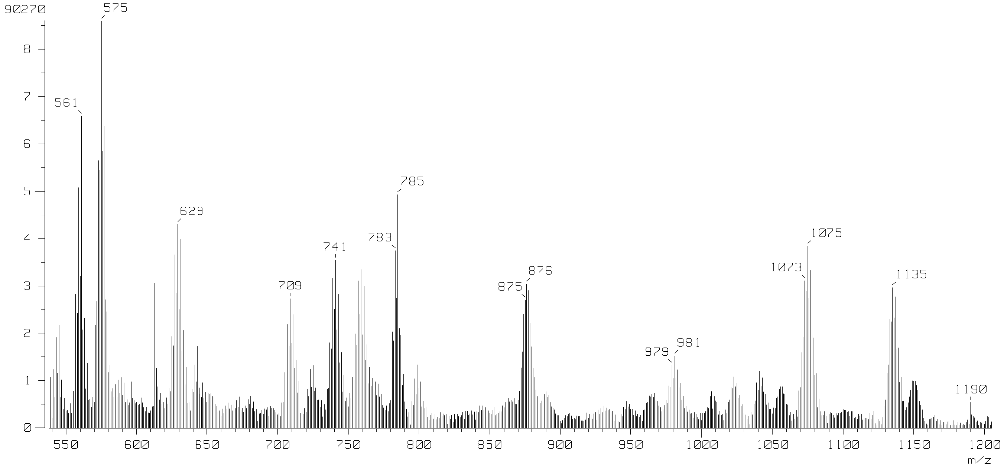

4. Additional figures

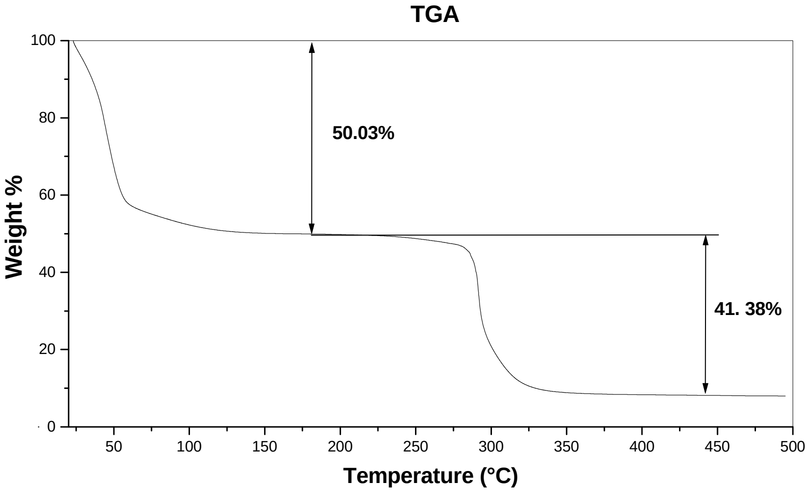

Figure S1. TGA graph of $[\{Me_2Sn(1,4\text{-bisdtc})\}_2]\cdot 10CDCl_3$

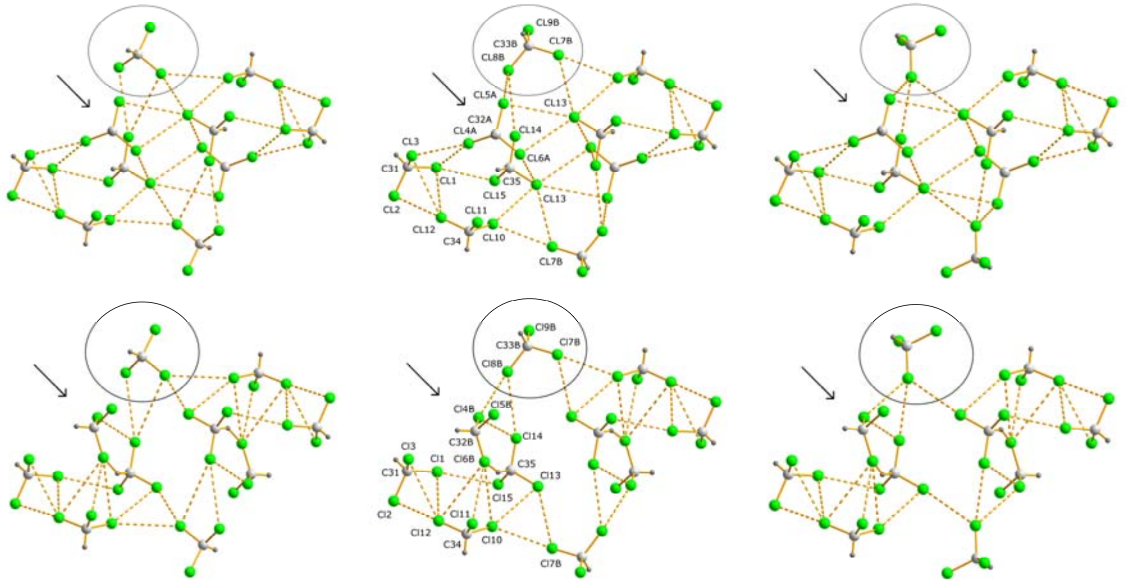

Figure S2. The disorder of two of the five independent $CDCl_3$ molecules gives rise to two series of different cluster arrangements. The disordered deuterochloroform molecules are marked by circles ($CDCl_3$ disordered over three sites) and arrows ($CDCl_3$ disordered over two sites). The threefold disordered $CDCl_3$ molecules generate “snapshots of clusters, whose differences consist in a gradual outward-rotation of the molecule marked by the circle.

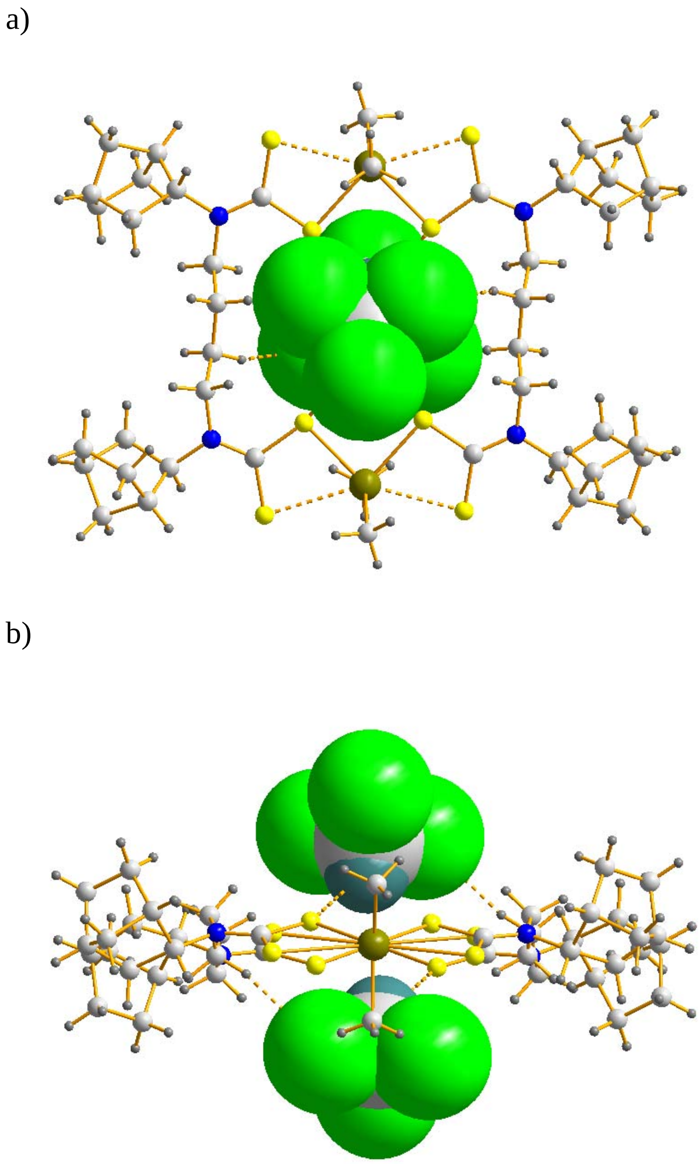

Figure S3. Supramolecular inclusion complex formed between the diorganotin macrocycle and two $CDCl_3$ molecules, which are embedded in the cavities above and below the macrocycle plane. a) top view; b) lateral view.

5. Tables for the description of the intermolecular connectivity

Table S1. Intermolecular contacts between the diorganotin macroycle and $CDCl_3$ molecules in the crystal structure of $[\{Me_2Sn(1,4\text{-bisdtc})\}_2]\cdot 10CDCl_3$.

Note: For the case of the disordered $CDCl_3$ molecules the analysis includes only those having the highest occupancy (C32A and C33B).

Contact	**C–X [Å]**	**X···Y [Å]**	**∠CXY [°]**	**Symmetry code**
C31-Cl2···H8	1.743(5)	2.81	155	+x+1,+y,+z
C31-Cl2···H13B	1.743(5)	2.95	137	+x+1,+y,+z
C31-Cl3···H20A	1.747(5)	3.03	98	-x,+y-½,-z+½
C31-D31···S3	1.00	2.55	161	-x+1,+ y+½,-z+½
C32A-Cl5A···H21B	1.743(6)	2.95	113	+x,+y,+z
C32A-Cl5A···S1	1.743(6)	3.63	161	+x,+y,+z
C32A-Cl6A···H16B	1.745(7)	2.87	96	-x+1,+ y-½,-z+½
C33B-Cl7B···H4B	1.724(11)	3.10	129	+x,-y+½,+z-+½
C33B-D33B···S2	1.00	2.97	141	-x+1, +y-½,-z+½
C34-Cl11···H20A	1.748(4)	3.08	154	+x,- y+½,+z+½
C34-D34···S4	1.00	2.69	161	+x,+y,+z
C35-Cl15···H10A	1.752(6)	3.00	116	+x,+ y,+z

Table S2. Intermolecular Cl···Cl contacts between $CDCl_3$ molecules in the crystal structure of $[\{Me_2Sn(1,4\text{-bisdtc})\}_2]\cdot 10CDCl_3$. Note: The analysis includes only the clusters given in Figure 2.

Interaction site	**Motif**	**Contact**	**Cl···Cl [Å]**	**θ_1 [°]**	**θ_2 [°]**	**Symmetry code**
Cluster I	III	C31-Cl1···Cl4A	4.0838(8)	87	147	+x,-y+1+½,+z-½
	IV	C31-Cl1···Cl12	4.0664(5)	73	122	-x+1,+y-½,-z+½
	I	C31-Cl1···Cl15	3.4081(6)	166	95	-x+1,+y-½,-z+½
	V	C31-Cl1···Cl15	3.4081(6)	166	127	-x+1,+y-½,-z+½
	IV	C31-Cl2···Cl12	3.5433(7)	90	158	-x+1,+y-½,-z+½
	II	C31-Cl3···Cl11	3.4107(5)	150	144	+x-1,-y+1+½,+z-½
	IV	C31-Cl3···Cl12	3.7090(7)	84	141	-x+1,+y-½,-z+½
	III	C31-Cl3···Cl4A	3.2776(5)	117	169	+x,-y+1+½,+z-½
	II	C32A-Cl5A···Cl8B	3.8493(5)	131	112	+x,+y,+z
	III	C32A-Cl5A···Cl13	4.0133(7)	96	147	+x,+y,+z
	III	C32A-Cl6A···Cl13	3.6569(6)	109	110	+x,+y,+z
	VI	C32A-Cl6A···Cl13	3.6472(5)	134	109	-x+1,-y+2,-z+1
	V	C33B-Cl7B···Cl10	3.4323(5)	171	123	+x,+y,+z
	II	C33B-Cl8B···Cl14	3.5635(8)	135	159	-x+1,-y+2,-z+1
	V	C33B-Cl9B···Cl1	3.6132(5)	173	127	-x+1,-y+1,-z+1
	V	C34-Cl10···Cl13	3.6192(6)	157	123	+x,+y,+z
	VI	C35-Cl13···Cl6A	3.6569(6)	110	75	+x,+y,+z
	V	C35-Cl13···Cl7B	3.9887(6)	135	82	+x,+y,+z
	V	C35-Cl15···Cl9B	3.4475(7)	156	95	+x,-y+1+½,+z-½
Cluster II	IV	C31-Cl1···Cl12	4.066(2)	73	122	-x+1,+y-½,-z+½
	I	C31-Cl1···Cl15	3.408(2)	166	95	-x+1,+y-½,-z+½
	V	C31-Cl1···Cl15	3.408(2)	166	127	-x+1,+y-½,-z+½
	IV	C31-Cl2···Cl12	3.543(2)	90	158	-x+1,+y-½,-z+½
	V	C31-Cl3···Cl6B	3.72(1)	142	150	-x,+y-½,-z+½
	IV	C31-Cl3···Cl12	3.709(2)	84	141	-x+1,+y-½,-z+½
	--	C32B-Cl5B···Cl12	3.54(1)	76	129	+x-1,+y,+z
	--	C32B-D32B···Cl12	2.77(3)	134	--	+x-1,+y,+z
	V	C32B-Cl6B···Cl11	3.56(1)	144	93	-x+1,-y+2,-z+1
	V	C32B-Cl4B···Cl8B	3.54(2)	149	125	+x,+y,+z
	V	C33B-Cl7B···Cl10	3.433(5)	171	123	+x,+y,+z
	II	C33B-Cl8B···Cl14	3.563(5)	135	141	-x+1,-y+2,-z+1
	V	C33B-Cl9B···Cl1	3.613(6)	173	127	-x+1,-y+1,-z+1
	IV	C34-Cl10···Cl6B	3.721(9)	84	158	1-x,2-y,1-z
	IV	C34-Cl11···Cl6B	3.56(1)	89	144	1-x,2-y,1-z
	IV	C34-Cl12···Cl6B	4.09(1)	73	125	1-x,2-y,1-z
	V	C34-Cl10···Cl13	3.619(2)	157	123	+x,+y,+z
	V	C34-Cl11···Cl3	3.411(2)	144	89	+x+1,-y+1+½,+z+½
	V	C35-Cl13···Cl7B	3.989(6)	135	82	+x,+y,+z
	V	C35-Cl14···Cl4B	3.26(2)	159	97	-x+1,-y+2,-z+1
	V	C35-Cl15···Cl9B	3.447(7)	156	95	+x,-y+1+½,+z-½
	--	C35-D35···Cl6B	2.96	147	--	-x+1,-y+2,-z+1