Experimental and computational evidence for a stabilising Cl(lone-pair)···π(chelate-ring) interaction

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ESI Table S1 Crystal data and refinement details for the crystal of **1** at 100, 150, 200, 250, 273 and 298 K.[a]

Parameter	100 K	150 K	200 K	250 K	273 K	298 K
a (Å)	10.12941(5)	10.15307(7)	10.18020(9)	10.20882(12)	10.22154(11)	10.23633(14)
b (Å)	16.43674(9)	16.49930(13)	16.57028(17)	16.6674(2)	16.7214(2)	16.7834(3)
c (Å)	13.38681(7)	13.41809(10)	13.45064(12)	13.48201(16)	13.49259(15)	13.50677(18)
β (º)	96.9574(5)	97.0345(7)	97.0780(8)	97.0862(11)	97.0519(11)	97.0002(13)
V (Å^3)	2212.42(2)	2230.86(3)	2251.68(4)	2276.50(5)	2288.68(5)	2303.17(6)
D_x (g cm^{-3})	1.662	1.648	1.633	1.615	1.606	1.596
μ (mm^{-1})	14.311	14.193	14.062	13.898	13.834	13.747
no. reflections	26819	27048	27294	27688	27792	28001
no. unique reflections	3946	3980	4018	4064	4076	4108
no. reflections with						
$I \geq 2\sigma(I)$	3863	3859	3777	3708	3657	3567
R (obs. data)	0.022	0.023	0.025	0.027	0.028	0.032
a and *b* in						
weighting scheme	0.037; 1.248	0.037; 1.201	0.041; 0.910	0.044; 0.795	0.044; 0.769	0.049; 0.534

R_w (all data)	0.057	0.058	0.066	0.072	0.075	0.086
Max. and min. residual peaks (e Å^{-3})	0.39; 1.62	0.38; 1.52	0.39; 1.32	0.48; 0.99	0.50, 0.88	0.53, 0.81

a Each crystal has the molecular formula $C_{19}H_{22}Cl_3NS_2Sn$, $M = 553.53$, monoclinic, $P2_1/n$ and $Z = 4$.

ESI Table S2 A listing of the electrostatic potential charge deviation ($\Delta|V_{ESP}|$) for selected intermolecular interactions in the crystals of **1** obtained at 100 and 298 K, as identified through the Hirshfeld surface analysis.

Contact	V_{ESP} (kcal/mol)					
	100 K			298 K		
	H-donor	H-acceptor	$\Delta\|V_{ESP}\|$	H-donor	H-acceptor	$\Delta\|V_{ESP}\|$
Cl2···Cg(Sn,S1,S2,C1)^{ii}	10.69	-12.11	22.80	9.03	-9.91	18.94
Cl3···Cg(Sn,S1,S2,C1)^{iii}	9.91	-9.54	19.45	8.10	-8.28	16.38
Cg(C8-C13)·· Cg(C14-C19)^{ii}	-9.48	-9.85	0.37	-8.41	-8.68	0.27
H7c···Cg(C14-C19)^{i}	34.01	-9.48	43.49	32.19	-8.68	40.87
H6c···Cl3^{ii}	32.82	5.27	27.55	32.50	4.71	28.33
H12···Cl1^{iv}	22.46	-23.78	46.24	18.39	-23.72	42.11
S2···Cl2^{ii}	4.27	-12.11	16.38	3.99	-9.91	13.90
Cl3^{ii}···S2	4.08	-9.54	13.62	3.11	-8.28	11.39

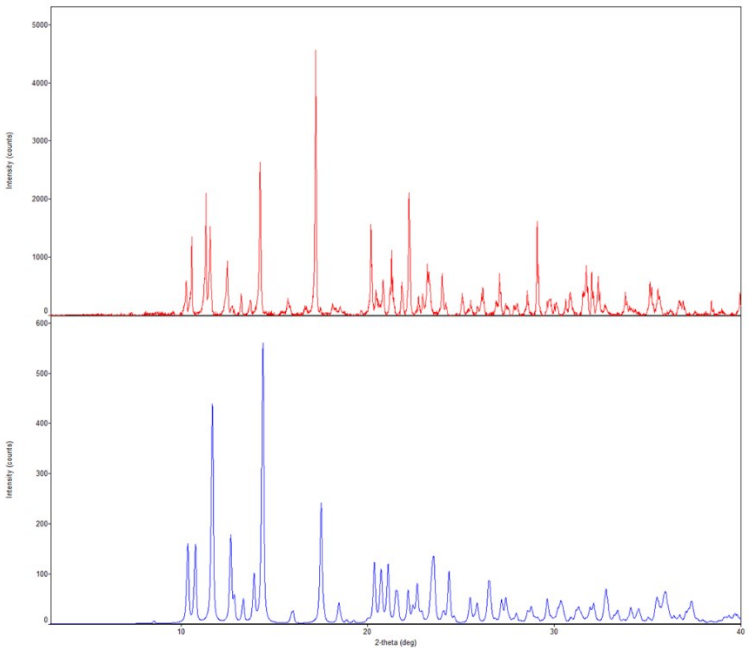
Symmetry element: (i) -1+*x*, *y*, *z*; (ii) 1½-*x*, ½+*y*, ½-*z*; (iii) 1½-*x*, -½+*y*, ½-*z*; (iv) 2-*x*, 1-*y*, 1-*z*.

ESI Table S3 The percentage contributions of various interatomic contacts to the Hirshfeld surface for **1** at 100 and 298 K

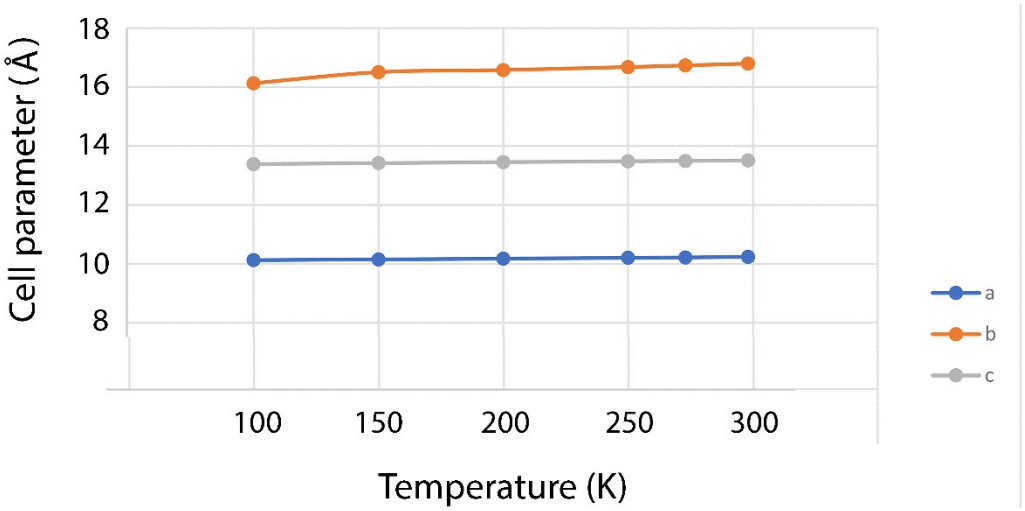
Contact	100 K	298 K
H···H	40.6	41.1
H···Cl/ Cl···H	27.4	28.1
H···C/ C···H	16.9	16.4
H···S/ S···H	6.2	6.0
Cl···C/ C···Cl	4.1	4.0
C···C	3.0	2.8
Cl···S/ S···Cl	1.6	1.5
N···Cl/ Cl···N	0.2	0.1
Cl···Cl	0.1	–

ESI Table 4. Corrected interaction energies (kcal/mol) for all close contacts present at 298 K obtained from the CE-B3LYP/DGDZVP model. Scale factors of 1.057, 0.740, 0.871 and 0.618 were applied to $E_{electrostatic}$ ($E_{electro}$), $E_{polarisation}$ (E_{polar}), $E_{dispersion}$ (E_{dis}) and $E_{repulsion}$ (E_{rep}).

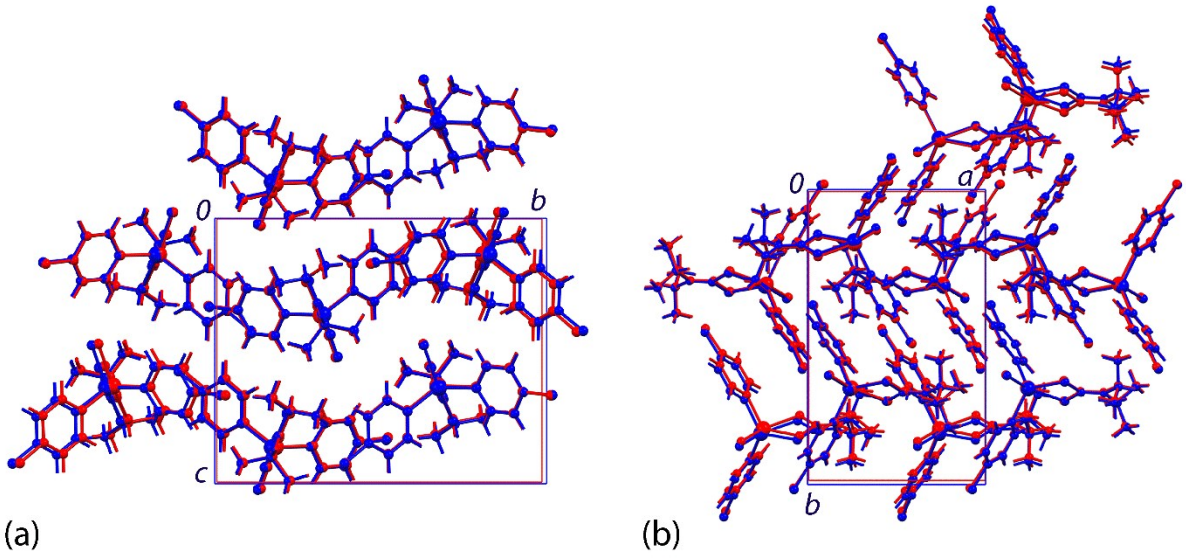
Contact	$E_{electro}$	E_{polar}	E_{dis}	E_{rep}	E_{total}	Symmetry operation
C6–H6c···Cl3^{ii} + Cg(C8-C13)···Cg(C14-C19)^{ii} + Cl2···π(chelate-ring)^{ii} + Cl3^{ii}···π(chelate-ring) + Cl2···S2^{ii} + Cl3^{ii}···S2	-5.83	-0.72	-12.21	7.98	-10.78	1½-*x*, ½+*y*, ½-*z*
C7–H7c···C17^{i} + C7···π(C14-C19)^{i}	-4.40	-0.65	-9.66	4.47	-10.24	-1+*x*, *y*, *z*
C12–H12···Cl1^{iv} (× 2)	-2.68	-0.57	-3.32	2.63	-3.94	2-*x*, 1-*y*, 1-*z*



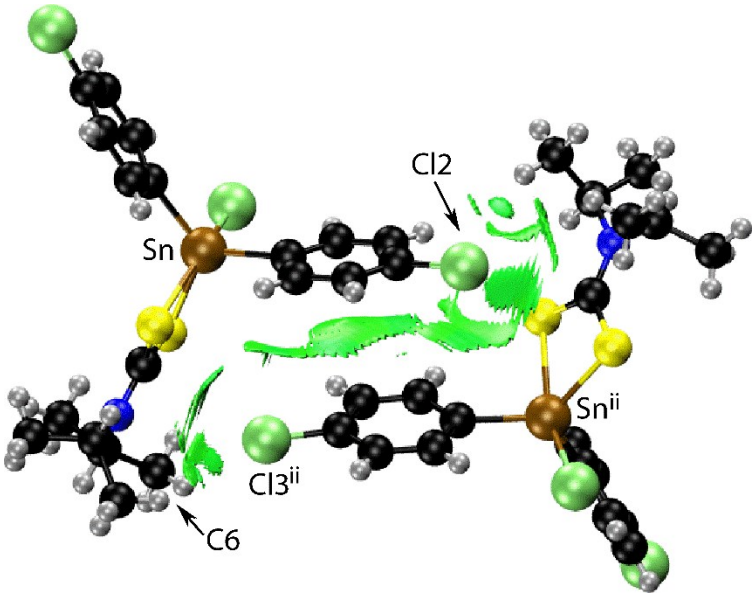
ESI Figure 1. Experimental (293 K; red trace) and theoretical (based on single crystal data measured at 100 K) PXRD traces for **1** confirming the homogeneity of the sample and the absence of phase change in the bulk material.



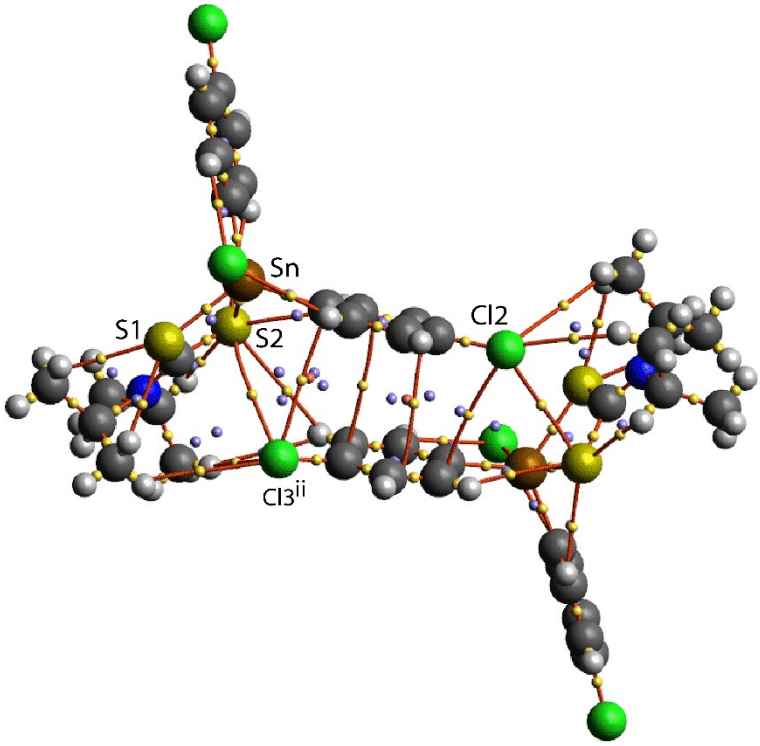
ESI Figure 2. A plot of the variation in the unit cell dimensions *a*, *b* and *c* (Å) in **1** with temperature.



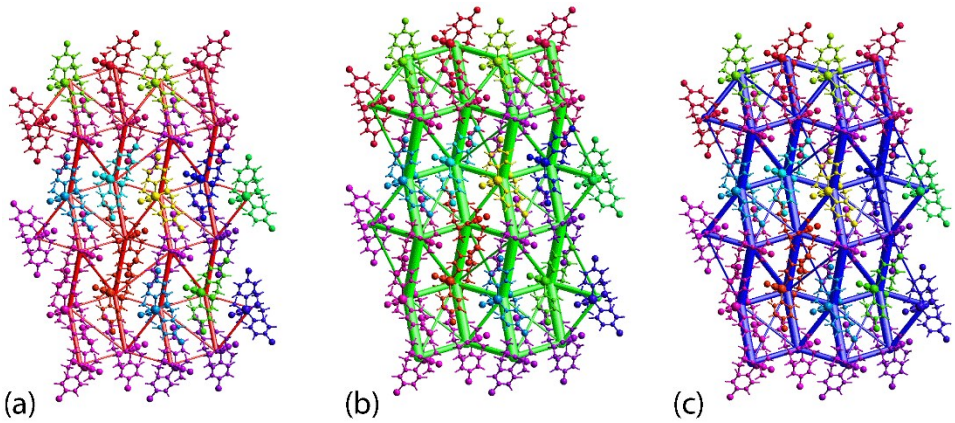
ESI Figure 3. A comparison of the molecular packing of **1** measured at 100 K (red) and 298 K (blue) viewed along the *a*- and *c*-axes, respectively.



ESI Figure 4. Image of the non-covalent interaction plot for **1** measured at 298 K, highlighting the weakly attractive: (a) Cl2(lone-pair) ··π(chelate-ring)^{ii}, π(chlorophenyl) ··π(chlorophenyl)^{ii} and Cl3^{ii}···H6c–C6 interactions. Symmetry operation: (ii) 1½-*x*, ½+*y*, ½-*z*.



ESI Figure 5. An image of Quantum Theory of Atoms in Molecule (QTAIM) analysis for **1** measured at 298 K. Symmetry operation: (ii) 1½-*x*, ½+*y*, ½-*z*.



ESI Figure 6. Simulated energy framework for **1** measured at 298 K within 2 × 2 × 2 unit-cells, showing the decomposed frameworks delineated into (a) electrostatic or coulombic potential (red), (b) dispersion force (green) and (c) overall energy framework. The frameworks are drawn at a scale of 150 with an energy cut-off of 1.91 kcal/mol.