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Structural study of the cyclic chlorosiloxanes and chlorosilathianes†

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Crystal structures of the cyclic $(OSiCl_2)_3$ and $(OSiCl_2)_4$ molecules showed that the bonding around silicon remains close to tetrahedral in each case, with varying oxygen angles providing for cyclisation. The trimer ring is planar, but the tetramer ring is buckled, with valence angles at O of 170.7 and 148.5°. HF/6-31G* and MP2/6-31G* calculations on the $(OSiCl_2)_n$, $(SSiCl_2)_n$, $(OSiH_2)_n$ and $(SSiH_2)_n$ polymer series were performed. Silicon shows a strong tendency towards retention of regular tetrahedral bonding throughout. For the oxo- and thio-chloride series, calculated energies of formation expressed relative to the monomer are in line with preparative experience. The non-appearance of a four-membered oxo ring, as would be required in a dimer $(OSiCl_2)_2$, is attributable to too great a charge separation within a small structure, but reduction of these unfavourable factors permits the formation of a four-membered ring in the thio series to give $(SSiCl_2)_2$. Features of ring development in the oxo series can be correlated with structures shown by silicates.

The preparation of chlorosiloxanes and chlorosilathianes dates from the mid 1800s with identification of products from the high-temperature reactions of silicon tetrachloride with oxygen[1] and with hydrogen sulfide.[2] The products formed in largest quantity are hexachlorodisiloxane Si_2OCl_6 and trichlorosilanethiol $SiCl_3SH$ respectively, but in each case other less volatile products arise. Successive investigations assisted identification of various chlorosiloxanes.[3] Then it became well established from work in this laboratory, now some 40 years ago, that the high-temperature reaction with oxygen yields series of both open-chain compounds $Si_nO_{n-1}Cl_{2n+2}$ and presumably cyclic derivatives $(OSiCl_2)_n$ with $n = 3,4\ldots$, but no dimer was found.[4] The products from the hydrogen sulfide reaction were again found to comprise open-chain and cyclic members, but now with the dimer $Si_2S_2Cl_4$ prominent.[5]

No structural work directly on the cyclic oxo- or thio-halides appears to have been done over the intervening years, although there are studies on related cyclic molecules. There have been X-ray and electron diffraction structure determinations on dimethylsilicones $(OSiMe_2)_n$[6] and an X-ray determination on $(SSiMe_2)_2$.[7] Then of particular relevance to our present approach there is a theoretical study of the (experimentally inaccessible) $OSiH_2$ molecule and its cyclic polymers.[8]

Samples of the crystalline $(OSiCl_2)_3$ and $(OSiCl_2)_4$ products remained from our earlier work;[4] so in re-entering this field we first determined the molecular structures of these chlorides by X-ray analysis, and then tested the free-molecule structures as calculated from *ab initio* theory against the well refined experimental results. For the trimer there was a very good match of both molecular parameters and vibrational frequencies. The tetramer showed an interesting deviation due to ring folding in the crystalline phase. Extension of the theoretical approach to the thio series served to provide information on the way in which comparative charge distribution and the valence angle preferences of oxygen and sulfur influence the development of the thio- and oxo-ring systems. Theoretical coverage of the two hydride series $(OSiH_2)_n$ and $(SSiH_2)_n$ consolidates work on the former[8,9] and gives comparative information on the latter.

The crystals remaining from our 1960 work[4] which had been stored in sealed containers were used for the crystal structure determination.

Experimental Procedures and Data Collection

Crystal structure determination

With usual dry-box handling of these highly moisture-sensitive compounds, crystals of $(OSiCl_2)_3$ and $(OSiCl_2)_4$ were covered in silicone oil on a microscope slide. A crystal was quickly mounted in the cold nitrogen stream of the diffractometer. At 130 K there was no hydrolytic decomposition or other crystal decay. Check reflections were steady within ±2%. Details of experimental conditions are included in Table 1.

Structure determination followed our usual procedures[10] using a Siemens R3M diffractometer. Cell parameters were derived from 25 well centred reflections. Structure solutions were by direct methods and all atoms were refined anisotropically. Absorption corrections from ψ scans were applied. With use of the SHELXL 93 package[11] the quantity minimised in refinement was $\Sigma w(|F_o|^2 - |F_c|^2)$ with $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + g_2P]$ where $P = (\frac{1}{3})[\max|F_o|^2 + 2|F_c|^2]$, and g_1, g_2 are variable weighting coefficients.

Bond lengths and angles obtained from the refinements are given in Table 2, which refers to the molecular structures shown in Figs. 1 and 2.

CCDC reference number 186/1040.

See http://www.rsc.org/suppdata/dt/1998/2697/ for crystallographic files in .cif format.

Quantum chemical calculations

All calculations were done using various versions of the GAUSSIAN program.[12–14] The geometries of all species were optimised at the HF/6-31G* level of theory and harmonic vibrational frequencies calculated. Uncorrected vibrational frequencies for $Si_3O_3Cl_6$ and $Si_4O_4Cl_8$ are included in Table 3. All geometries were reoptimised at the MP2 = Full/6-31G* level of theory. In calculating the thermal corrections, a factor of 0.893 was applied to the HF/6-31G* frequencies.

For most classes of compounds the observed distances and angles lie between the HF and MP2 values. For this reason both values are given.

Vibrational spectra

Infrared spectra were run to 280 cm^{-1} using Nujol mulls prepared in a dry-box and mounted between cesium iodide plates. Reproductibility of spectra from successive runs showed there to be no significant decomposition.

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† Dedicated to Professor Warren Roper F. R. S., University of Auckland on the occasion of his 60th birthday.

Raman spectra were recorded using polycrystalline samples sealed into glass tubes. The excitation radiation, provided by a Spectra-Physics 2045E argon ion laser, was filtered with an Anaspec 300S laser filter monochromator to remove plasma lines before the radiation reached the sample. Scattered light was collected at 90° to the incident beam, dispersed by a Spex 1403 double monochromator and detected by a thermoelectrically cooled RCA 31034 photomultiplier tube. The signal was processed by a pulse-height discriminator and photon-counting electronics, and the resulting data were accumulated by computer. Spectra were measured as Stokes shifts from 50 to 1200 cm^{-1} from the Rayleigh line, using an incident power of 100 mW and spectral resolution of ≈ 1 cm^{-1}. To be sure that argon-plasma or sample emission lines were not inadvertently assigned to Raman scattering, data were obtained using two excitation wavelengths (476.5 and 457.9 nm); the resultant spectra were essentially identical and gave the same Raman shifts to within ±2 cm^{-1}. The observed vibrational frequencies are given in Table 3.

Discussion

For ease of reference the four series of compounds are designated O/Cl, O/H, S/Cl and S/H according to the ring and external substituent atoms. Bonding discussions centre on variations in ring geometry, since these were found to exert little effect on the exocyclic Si–H or Si–Cl linkages.

The match of the calculated structure (Table 4) and vibrational frequencies (Table 3) with experimental values for $Si_3O_3Cl_6$ and $Si_4O_4Cl_8$ confirms the applicability of both HF/6-31G* and the MP2/6-31G* quantum chemical calculations as providing reliable values for the oxo compounds. There is still a close accord between calculated and experimental values for the tetramer despite the chair folding of the molecule within the crystal. The same level of theory has already been used for the O/H series.[8] While no corresponding check is available against an experimentally determined structure for the thio series, the calculated molecular parameters for $Si_2S_2Cl_4$ (Fig. 3) are in line with expectations based on the known crystal structures of SiS_2[16] and $Si_2S_2Me_4$,[7] and the free-molecule structure of Me_2SiCl_2.[17] The use of the HF/6-31G* basis set throughout thus provides both internal consistency and wider comparability.

Calculated values for bond lengths and angles within the rings are listed in Table 4, and the Mulliken charge distributions over the ring atoms in Table 5. While any charge distribution such as the Mulliken population analysis is arbitrary, there is undoubtedly a large charge transfer from the Si atom to the O or S atoms. Differences in the degree of charge transfer between different polymers should be reliable. The charge transfer increases significantly on polymerisation. Comparative energies of formation per monomeric unit (as for example per $OSiCl_2$) for the dimer, trimer and tetramer are in Table 6. The correspondence of results given by the chloro- and hydrido-series will be apparent from these Tables.

Molecular structure of the trimer

The molecular structure from the X-ray analysis is shown in Fig. 1. The molecule is not using its otherwise trigonal symmetry towards the packing in the crystal, and therefore the positions of all its atoms were refined independently. The consequent deviations from strict D_{3h} symmetry are slight (Table 2). With O–Si–O and Si–O–Si angles all close to 107.6 and 132.3° respectively, it is evident that the Si atoms impose their preference towards regular tetrahedral co-ordination on the bridging O atoms. It is the same situation as with the cyclic free molecule $(OSiMe_2)_3$.[6] Oxygen angles as low as 132° develop only through the 'inwards' strain from the six-membered ring. For comparison, the angle in the non-cyclic $Cl_3SiOSiCl_3$ molecule[18] is 146°, and bridging oxygen preferences in silica and silicates are in the range 140–145°, although angles from 120 to 180° are found.[19a] The longer 'thermal ellipsoid' axes of the O atoms are oriented almost perpendicular to the ring plane (Fig. 1), but this is not necessarily a consequence of the ring strain. With its disparate O and Si angles the ring geometry of $(OSiCl_2)_3$ contrasts with that of the isoelectronic dichlorophosphazene trimer, $(NPCl_2)_3$, in which the angles at N (121.4°) and P (118.3°) are almost equal.[20]

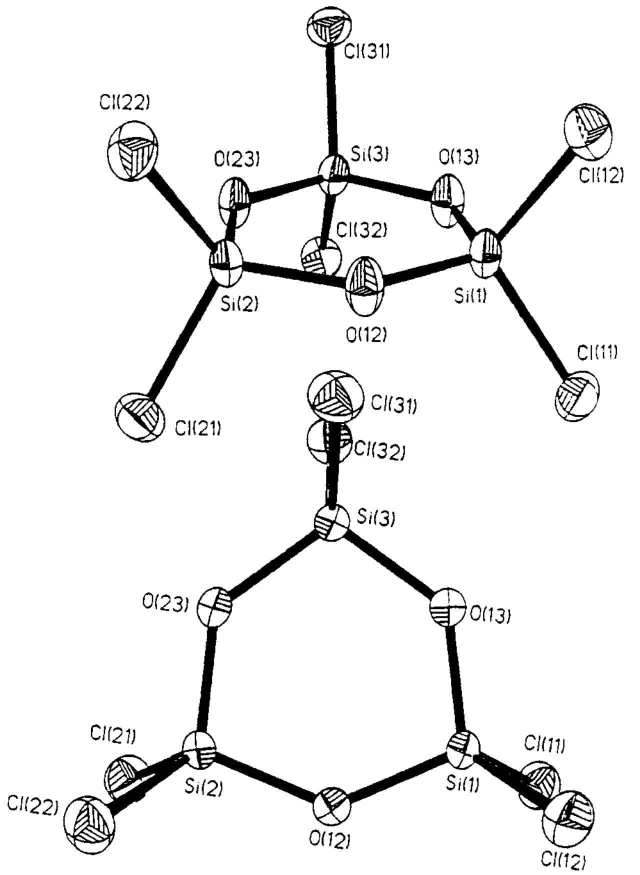

Fig. 1 Lower: a view of the $(OSiCl_2)_3$ molecule looking along the trigonal axis. The disparity of the O and Si angles is apparent. Upper: an oblique view showing the thermal ellipsoids at 50% probability extending across the ring plane

Structure of the tetramer

Here, with an eight-membered ring, the Si–O–Si angle is no longer restricted to a low value. A careful early crystal structure determination for octamethylcyclotetrasiloxane $(OSiMe_2)_4$ showed the molecule to be puckered with Si and O angles 109 and 142.5°.[21] The present chloro-tetramer differs in assuming a C_i centrosymmetric chair configuration through bending about molecular vectors through Si(1) $\cdots$ Si(2) and Si(1a) $\cdots$ Si(2a) to give bond angles at O(1) of 170.7° and O(2) of 148.5° (see Fig. 2). An approximate two-fold axis passes through the atoms O(1) and O(1a). All four Si and the two O(1) atoms are coplanar, with O(2) and O(2a) lying 0.1130 Å respectively above and below this central plane, the 'chair' dihedral angles being 164.9° [between planes Si(1)Si(2)O(2) and Si(1)Si(2)Si(1a)Si(2a)]. It is a configuration recalling the chair form of the isoelectronic dichlorophosphazene tetramer $P_4N_4Cl_8$,[22] although in that case the chair bending is about vectors through P and N atoms.

The appearance of a configuration with such differing Si–O–Si angles within the same molecule reflects the ease with which the angle can vary to meet particular structural needs imposed merely by molecular packing in the crystal lattice. The calculated structure for the free molecule constrained to D_{4h} planarity still gives an O–Si–O angle as low as the tetrahedral value

Table 1 Crystal data, experimental conditions and refinements *

	$Si_3O_3Cl_6$	$Si_4O_4Cl_8$
M	344.97	459.96
Crystal size/mm	1.02 × 1.01 × 0.68	0.65 × 0.59 × 0.23
a/Å; α/°	6.388(2); 77.77(5)	5.982(1); 77.43(2)
b/Å; β/°	8.646(5); 77.58(3)	8.088(2); 81.18(2)
c/Å; γ/°	11.155(4); 72.93(4)	8.156(2); 72.68(1)
Z	2	1
U/Å^3; D_c/g cm^{-3}	567.8(4); 2.018	366.02(14); 2.087
F(000)	336	224
μ(Mo-Kα)/cm^{-1}	17.95	18.56
ω Scan, 2θ range/°	5 to 50	5 to 55
Range *h*,*k*,*l*	0 to 7, −9 to 10, −12 to 13	0.to 5, −9 to 10, −10 to 10
Reflections collected	2156	1505
Reflections used (R_{int})	1962 (0.0326)	1346 (0.0453)
Transmission range	0.985–0.463	1.000–0.650
Parameters refined	109	73
Residual density/e Å^{-3}	0.594, −0.385	0.269, −0.501
S	1.109	1.223
R (*wR*) [$I > 2\sigma(I)$]	0.0334 (0.0897)	0.0255 (0.0693)
(all data)	0.0360 (0.0937)	0.0261 (0.0697)

* Details in common: triclinic, space group $P\bar{1}$; 130 K.

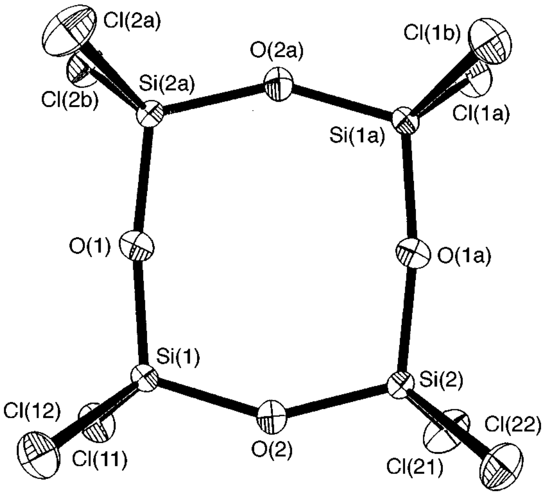

Fig. 2 The $(OSiCl_2)_4$ molecule seen perpendicular to the main ring of the chair structure. Atoms O(1) and O(1a) are in the plane containing the four Si atoms, O(2) and O(2a) lie respectively 0.113 Å above and below the ring plane with Si–O–Si angles 148.5°

Table 2 Experimentally determined bond lengths (Å) and angles (°)

Trimer

Si(1)–O(12)	1.616(2)	Si(2)–O(23)	1.615(2)
Si(1)–O(13)	1.615(2)	Si(3)–O(23)	1.619(2)
Si(2)–O(12)	1.622(2)	Si(3)–O(13)	1.617(2)
Si(1)–Cl(11)	2.011(2)	Si(2)–Cl(22)	1.998(1)
Si(1)–Cl(12)	2.002(1)	Si(3)–Cl(31)	1.998(2)
Si(2)–Cl(21)	1.998(1)	Si(3)–Cl(32)	1.996(1)
Si(1)–O(12)–Si(2)	132.5(1)	Cl(11)–Si(1)–Cl(12)	109.3(1)
Si(2)–O(23)–Si(3)	132.2(1)	Cl(21)–Si(2)–Cl(22)	109.8(1)
Si(3)–O(13)–Si(1)	132.2(2)	Cl(31)–Si(3)–Cl(32)	109.7(1)

Calculated values: HF, Si–O 1.627, Si–Cl 2.021 Å; Si–O–Si 134.0, Cl–Si–Cl 110.4°; MP2, Si–O 1.649, Si–Cl 2.015 Å; Si–O–Si 132.4°, Cl–Si–Cl 110.6°

Tetramer

Si(1)–O(1)	1.587(2)	Si(1)–Cl(11)	1.998(1)
Si(1)–O(2)	1.597(2)	Si(1)–Cl(12)	1.999(1)
Si(2)–O(1)	1.590(2)	Si(2)–Cl(21)	1.996(1)
Si(2)–O(2)	1.593(2)	Si(2)–Cl(22)	1.994(1)
O(1)–Si(1)–O(2)	110.2(1)	Cl(11)–Si(1)–Cl(12)	109.26(4)
O(1a)–Si(2)–O(2)	109.4(1)	Cl(21)–Si(2)–Cl(22)	109.68(4)
Si(1)–O(1)–Si(2)	170.7(1)	Si(1)–O(2)–Si(2a)	148.5(1)

Calculated values: HF, Si–O 1.611, Si–Cl 2.023 Å; O–Si–O 109.1, Si–O–Si 160.9, Cl–Si–Cl 110.5°; MP2, Si–O 1.629, Si–Cl 2.017 Å; O–Si–O 110.1, Si–O–Si 159.9, Cl–Si–Cl 110.7°

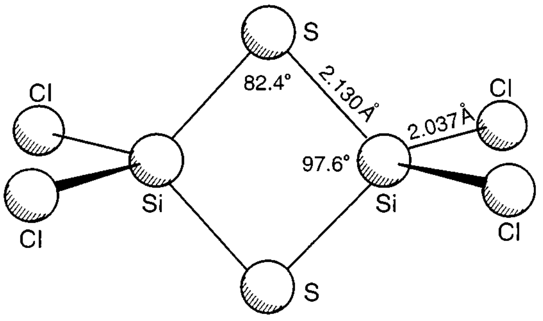

Fig. 3 The HF/6-31G* calculated structure of the centrosymmetric $S_2Si_2Cl_4$ molecule. For comparison, MP2/6-31G* gives: Si–S 2.122, Si–Cl 2.035 Å; Si–S–Si 79.8, S–Si–S 100.2°

of 109.1°, and Si–O–Si accordingly at 160.9°. The calculations did not initially assume equivalent O atoms. At the same time the calculated HF/6-31G* energies (kcal mol^{-1}, cal = 4.184 J) required to produce bending to the chair configuration are low, *viz.* bending by 10°, 0.32; 20°, 1.26; 25°, 1.96; 30°, 2.81. These calculations used the optimised structural parameters, varying only the out of plane parameter for the two O atoms. Anisotropic displacement parameters for both O(1) and O(2) remain quite low; so there is again no evidence of ring strain.

Ring development and molecular structures generally

By way of background the following points can first be noted. (i) There is a much higher polarity of the Si–O than the Si–S bond (electronegativity differences 1.7 and 0.7, corresponding to 51 and 12% 'ionic character' on Pauling's scale[23]). (ii) Arising from this polarity, the bridging O valence angles to Si are highly variable[19b] and accommodate the strong preference of Si towards tetrahedral co-ordination. (iii) Two-covalent S prefers a lower valence angle than does O.

The calculated ring angles for each of the three dimer, trimer and tetramer pairs within the O/Cl and O/H series (Table 4) are closely matching, showing that the substituent has little influence on ring development. With the trimer pair $(OSiCl_2)_3$ and $(OSiH_2)_3$ the molecules remain planar, but folding occurs with the thio pair $(SSiCl_2)_3$ and $(SSiH_2)_3$. This ring buckling to a trigonally symmetrical C_{3v} crown provides for the requirement of a lower valence angle at S (and Si). For the $(OSiCl_2)_4$ and $(OSiH_2)_4$[8] tetramers, planarity was imposed, because with the flexibility of the eight-membered rings bending to unpredictable configurations could be expected in the crystalline compound *e.g.* to a chair or to a crown as in $(OSiMe_2)_4$.[21]

As regards the four-membered ring dimer formation, identified only with sulfur, the bond angles and charge transfer are relevant. Calculated angles for an oxo ring are 91.4 (O) and 88.6° (Si). For the thio ring corresponding values are 82.4 and 97.6°, through the lower sulfur angle preference reducing ring straining. Charge transfer within the Si–S bond is much lower than in Si–O (Table 5), so that electrostatic repulsive forces across the ring are reduced, especially with the larger ring size. However, apart from the present series, cyclodisiloxane molecules have been found to arise from rearrangement of disiladioxetones bearing suitable substituents.[24] It has been suggested that in this case, where Si···Si falls to only 2.35 Å, there may be stabilising bonding between the Si atoms.

Evidence of possible dimer *vs.* trimer formation can be extracted from calculated polymerisation energies of mono-

Table 3 Vibrational wavenumbers (cm^{-1}) for chlorosiloxanes $Si_3O_3Cl_6$ and $Si_4O_4Cl_8$

Trigonal symmetric $Si_3O_3Cl_6$[a]

	Calculated		Observed		
Mode	wavenumber	activity[b]	IR	Raman	Ratio obs./calc.[c]
E′	140	I_{vw}, R_m		133s	0.95
A_1′	154	R_{ms}		146s	0.95
E″	181	R_{ms}		168ms	0.93
E′	312	I_w, R_{vw}	297mw	—	0.95
A_1′	377	R_{vs}		351s	0.93
A_2′	425	I_w	398w		0.94
E′	555	I_{ms}, R_{vw}	512s	—	0.94
A_1′	635	R_s		573s	0.90
E″	675	R_m		620mw	0.92
A_2′	716	I_s	656s		0.92
A_1′	794	R_m		745mw	0.94
E′	817	I_w, R_w	774vw		0.95
E′	1136	I_{vs}, R_w	1064s	1051w	0.93

Centrosymmetric $Si_4O_4Cl_8$[a]

	Calculated		Observed		
Mode	wavenumber	activity[b]	IR	Raman	Ratio obs./calc.[c]
B_{2g}	107	R_m		102m	0.95
A_{1g}	153	R_{ms}		149s	0.96
E_g	158	R_{ms}			
B_{1g}	175	R_m		170m	0.97
E_u	367	I_m	340m		0.93
A_{1g}	367	R_{vs}		368s (br)	1.00
E_g	371	R_m			
A_{2u}	422	I_m	395m		
A_{1g}	489	R_m		445w	0.91
E_u	513	I_s	488s		0.95
B_{2g}	559	R_m		517w	0.93
E_g	679	R_{ms}		612, 618w	0.91
A_{2u}	711	I_{vs}	630m, 652s		0.92
E_u	746	I_{mw}	724m		0.97
A_{1g}	767	R_{ms}		712m	0.93
E_u	1234	I_{vs}	1132s (br)		0.92

[a] Frequencies calculated as being only weakly active and found unobservable are omitted. The qualitative match of observed and calculated intensities (strong, medium, weak) is apparent. [b] I = Infrared, R = Raman. [c] For many molecules this ratio of observed/calculated frequencies is commonly given as 0.89.[15]

Table 4 The HF/6-31G* molecular parameters (Å and °), with MP2/6-31G* values in parentheses

Molecule	Si–O/Si–S	Si–Cl/Si–H	Si–O–Si/Si–S–Si	O–Si–O/S–Si–S	Cl–Si–Cl/H–Si–H
$OSiCl_2$	1.488 (1.533)	2.008 (2.012)	— —	— —	109.1 (108.3)
$(OSiCl_2)_2$	1.657 (1.687)	2.015 (2.011)	91.4 (89.6)	88.6 (90.4)	110.2 (110.3)
$(OSiCl_2)_3$	1.627 (1.649)	2.021 (2.015)	134.0 (132.4)	106.0 (107.6)	110.4 (110.6)
$(OSiCl_2)_4$	1.611 (1.629)	2.023 (2.017)	160.9 (159.9)	109.1 (110.1)	110.5 (110.7)
$SSiCl_2$	1.920 (1.932)	2.021 (2.024)	— —	— —	107.1 (107.0)
$(SSiCl_2)_2$	2.130 (2.122)	2.037 (2.035)	82.4 (79.8)	97.6 (100.2)	107.6 (107.7)
$(SSiCl_2)_3$	2.136 (2.127)	2.032 (2.029) 2.038 (2.034)[a]	108.1 (105.0)	114.1 (114.6)	109.1 (109.3)
$OSiH_2$	1.498 (1.545)	1.469 (1.483)	— —	— —	111.1 (111.5)
$(OSiH_2)_2$	1.671 (1.699)	1.466 (1.478)	91.5 (89.9)	88.5 (90.1)	110.7 (110.7)
$(OSiH_2)_3$	1.641 (1.663)	1.466 (1.477)	133.5 (132.1)	106.5 (107.9)	110.8 (111.2)
$(OSiH_2)_4$	1.626 (1.645)	1.467 (1.478)	159.6 (158.7)	110.4 (111.3)	110.8 (111.4)
$SSiH_2$	1.935 (1.948)	1.469 (1.483)	— —	— —	109.9 (110.2)
$(SSiH_2)_2$	2.150 (2.140)	1.468 (1.482)	83.3 (81.2)	96.7 (98.8)	109.5 (109.2)
$(SSiH_2)_3$	2.148 (2.139)	1.463 (1.477) 1.470 (1.485)[a]	102.9 (98.9)	106.5 (113.9)	112.1 (112.2)

[a] For differentiated bonds in the crown structure.

meric $OSiCl_2$ and $SSiCl_2$ species (Table 6), as also for the parallel $OSiH_2$ and $SSiH_2$. While such energies are specifically of idealised thermodynamic significance, they recall aspects of the original preparative experience. Thus the more negative energy for $(OSiCl_2)_3$ than for $(OSiCl_2)_2$ would seemingly underscore the non-appearance of the latter.[4] There is no such difference between $(SSiCl_2)_3$ and $(SSiCl_2)_2$, where the latter molecule does appear.[5] Then further, when this crystalline dimer is melted, the liquid does not recrystallise, but gives time-dependent molecular weight values,[5] corresponding to an equilibrating mixture of interconverting dimer, trimer and tetramer. Our calculations suggest that the polymerisation energies for these species should be similar.

Relationships to silicate structures

A conceptual link between the chlorosiloxanes and rock-forming silicates is provided *via* the silicones, whose Si–O bonding features in common with those of silicates have been examined.[9] Over the whole silicate field, Si shows the usual preferences towards tetrahedral co-ordination, which can be interpreted as arising from the tendency towards equilisation of repulsions between the charge-bearing O atoms. Accumulated experimental evidence shows that, as with the chlorosiloxanes, this tetrahedral preference is accommodated by the widely varying O_b bridging angles. As the Si–O_b–Si angle decreases the Si–O_b bond lengthens. The effect is slight over the range 180–150°, but thereafter becomes progressively more marked,[19] seemingly through electrostatic repulsions. It is possibly discernible in the O/Cl tetramer as between the Si–O(1) and Si–O(2) lengths, and is apparent in the trimer with the Si–O length increased by 0.025(2) Å. This is also evident in the calculated structures (Table 4). An O_b angle 130–120° seems to represent a lower limit of stability, since six-membered silicate rings are rare while eight-membered rings of varied conformations are common. Edge-sharing of tetrahedra to give four-membered rings is unknown excepting a very reactive non-mineral form of silicon dioxide.[25] Features of ring development as determined by angle preferences are thus common to both the ionic silicates and the present chlorosiloxanes.

Table 5 Mulliken charges from HF/6-31G* calculations

Compound	q(Si)	q(O)/q(S)	q(Cl)/q(H)
$OSiCl_2$	1.068	−0.623	−0.223
$(OSiCl_2)_2$	1.265	−0.774	−0.246
$(OSiCl_2)_3$	1.330	−0.816	−0.257
$(OSiCl_2)_4$	1.333	−0.789	−0.272
$SSiCl_2$	0.736	−0.318	−0.209
$(SSiCl_2)_2$	0.759	−0.302	−0.229
$(SSiCl_2)_3$	0.775	−0.322	−0.211[a]
			−0.241[a]
$OSiH_2$	0.940	−0.680	−0.130
$(OSiH_2)_2$	1.159	−0.841	−0.159
$(OSiH_2)_3$	1.110	−0.819	−0.146
$(OSiH_2)_4$	1.200	−0.843	−0.178
$SSiH_2$	0.610	−0.413	−0.099
$(SSiH_2)_2$	0.695	−0.479	−0.108
$(SSiH_2)_3$	0.648	−0.459	−0.088[a]
			−0.101[a]

[a] For the differentiated atoms in a crown structure.

Table 6 Polymerisation energies, kcal per monomer unit. Values from HF/6-31G* (MP2/6-31G* in parentheses)[a]

Compound	E/kcal	Compound	E/kcal
$(OSiCl_2)_2$	−62.7 (−57.2)	$(OSiH_2)_2$	−60.6 (−53.4)
$(OSiCl_2)_3$	−79.9 (−72.4)	$(OSiH_2)_3$	−77.0 (−68.3)
$(OSiCl_2)_4$[b]	−82.3 (−74.0)	$(OSiH_2)_4$[b]	−79.2 (−70.1)
$(SSiCl_2)_2$	−34.1 (−36.9)	$(SSiH_2)_2$	−34.5 (−34.5)
$(SSiCl_2)_3$[c]	−33.9 (−38.3)	$(SSiH_2)_3$[c]	−37.6 (−38.9)

[a] Over the O/Cl and O/H oxo series MP2/6-31G* gives consistently lower values than HF/6-31G*, but the polymer increments given by the two sets are similar. Thermal energy corrections including zeropoint energies have been included. [b] For D_{4h} planar molecules. [c] For crown-shaped molecules.

Conclusion

This work provides a more definitive examination of the factors influencing ring development than could have been inferred from the original preparative evidence. The computational approach has been particularly useful in showing not only the relevance of the bond angle preferences of Si and O or S (Table 4) but also effects arising from comparative charge transfer values (Table 5). There is quantitative evidence on ring stabilities and the likelihood of folding as the rings become larger (Table 6). Our understanding of ring development in mineral silicates is advanced by what we have observed in the bonding and structure within these molecules.

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