Some Dimethyl Ether Adducts of Silyl and Germyl Halides

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The 1 : 1 adducts of dimethyl ether with silyl chloride, silyl bromide, and germyl chloride, which are stable only below their melting points, are reported. A single-crystal *X*-ray diffraction study of the silyl chloride adduct at 100 K shows that it contains simple, non-interacting adduct molecules, and the *X*-ray powder pattern of the silyl bromide adduct at 113 K shows it to be isostructural with the chloride adduct. The Raman and i.r. spectra of the solid adducts are described; they suggest that all three have similar structures. Assignments are suggested for the bands observed, including the M–O stretch. This appears at a very low frequency, which is consistent with the Si–O 'bond' in the silyl chloride adduct [227.24(12) pm] being much longer than normal Si–O single bonds. The bonding between the ether oxygen and silicon or germanium is discussed in terms of the involvement of valence-shell *d* and possibly M–X antibonding orbitals as acceptors.

It has been known for many years that four-co-ordinate silicon is able to form additional bonds with donor atoms; the SiF_6^{2-} anion is structurally well characterised,[1] and it is clear that many silatranes[2] have very short Si $\cdots$ N distances although, in terms of primary connectivity, the two atoms are separated by three or more bonds. A series of adducts of simple silyl halides (SiH_3X) with amines was studied[3] using vibrational spectroscopy, but it proved impossible to crystallise these materials, which formed intractable solids, probably polymeric in nature. It is also known[4] that silicon tetrahalides form discrete adducts with amines, and some reports of the formation of complexes with oxygen donors[5] have appeared. Rather less is known about the ability of germanium to form complexes with oxygen donors, though complexes of $GeCl_4$ with nitrogen donors have been prepared.[6] There do not appear to be any reports of discrete adducts of silyl or germyl halides with organic ethers, and we have investigated mixtures of these compounds using Raman, i.r., and *X*-ray methods to characterise the interactions between the oxygen donor and the acceptor. The present report concerns some simple 1:1 adducts formed when mixtures of dimethyl ether and silyl or germyl halides are cooled. A preliminary report, including full details of the determination of the *X*-ray crystal structure of the silyl chloride adduct, has already appeared.[7]

Experimental

Silyl bromide was prepared by the reaction of phenylsilane with liquid HBr at 195 K. Silyl chloride was prepared from silyl bromide by passing it over solid $HgCl_2$ in a vacuum line and purified by trap-to-trap distillation. Germyl chloride was prepared by the reaction of germane with $SnCl_4$. Dimethyl ether was a commercial sample. All samples were purifed and handled in vacuum apparatus to avoid hydrolysis or exposure to oxygen. In the course of purification we noticed that a mixture of silyl chloride and dimethyl ether formed a mass of long crystals at low temperature, and this encouraged us to study the mixture by *X*-ray methods.

Raman Spectra.—Samples were sealed in Pyrex glass capillaries, of about 1—1.5 mm internal diameter and 25 mm in length. These were cooled to controlled low temperatures using an Air Products CS-202 helium refrigerator by placing them in a groove cut in a copper plate attached to the cold station of the device. The cold station and sample tube were isolated from the atmosphere by a brass shroud provided with quartz windows that allowed a laser beam from an Omnichrome 543-MAP argon-ion laser (up to 150 mW power in the 514.5-nm line) to fall on the sample; the entire shroud could be moved on an x-y translator to allow perfect alignment of the laser beam and sample, and to allow different parts of the sample to be examined.

The silyl bromide adduct was studied initially using an all-glass cooling device in which nitrogen gas cooled by passing through a copper spiral immersed in liquid nitrogen was blown over the capillary sample tube; the temperature was monitored close to the sample using a thermocouple, and temperature control was achieved by altering the flow rate of the nitrogen gas. This allowed temperatures down to about 130 K to be attained. The Raman spectra recorded using this arrangement were as good as those using the refrigerator, but the use of the latter was preferred because of the lower temperatures that could be reached, and the improvement in temperature control. The silyl bromide adduct was later studied using the refrigerator to allow spectra to be obtained at temperatures comparable with those used for the other samples. As the spectra obtained at 20 K and at higher temperatures differed slightly both are given in the Table.

In each case the scattered light was collected by a lens and focused onto the entrance slit of a Spex Ramalab double monochromator spectrometer. The spectrometer scan motor was controlled by a BBC Master microcomputer, which also collected data from the final output stage of the spectrometer amplifier, through an analogue-to-digital converter, and displayed the spectrum on the screen. After collection, each spectrum could be transferred to a floppy disk and plotted on a Plotmate A4 plotter. Peaks were located, using programs written for the purpose, with a precision of ± 1 cm^{-1}

Infrared Spectra.—Infrared spectra of cold mixtures of silyl or germyl halide and dimethyl ether were recorded on a Perkin-Elmer 598 spectrophotometer after spraying a gaseous mixture onto the central window of a conventional cold cell, cooled with liquid nitrogen. The coolant was then removed and the spectrum monitored until annealing occurred. The coolant was then replaced and the full spectrum recorded.

X-*Ray Diffraction.*—Full details of the single-crystal study of the silyl chloride adduct have been given in a preliminary

Table. Raman and i.r. bands of 1 : 1 adducts of dimethyl ether and silyl chloride, silyl bromide, and germyl chloride

$SiH_3Cl·Me_2O$		$SiH_3Br·Me_2O$			$GeH_3Cl·Me_2O$		Me_2O	SiH_3Cl	SiH_3Br	GeH_3Cl	
I.r. 77 K	Raman 15 K	I.r. 77 K	Raman 20 K	Raman 130 K	I.r. 77 K	Raman 14 K	I.r. 77 K	Raman 15 K	Raman 120 K	Raman 120 K	Suggested assignment
3 005		3 005	3 007	3 007							
					2 980		2 980				
2 961		2 968	2 975	2 973							
2 935	2 925	2 926	2 940	2 944	2 920		2 920				C–H stretches
2 904											
2 861		2 859	2 870	2 871	2 855		2 865				
2 823		2 820		2 829	2 809		2 817				
		2 230			2 162						
2 224	2 229	2 218	2 224	2 230	2 146	2 150		2 220	2 222		Asymmetric
	2 215	2 190	2 210	2 218	2 139	2 143		2 217	2 209	2 145	M–H stretches
2 196	2 193	2 182	2 181	2 188	2 113	2 118		2 194	2 191	2 120	Symmetric
1 482					1 473		1 480				
				1 467	1 467		1 465				
1 461	1 450	1 460	1 460	1 461	1 458		1 459				Asymmetric CH deformations
1 459		1 450	1 450	1 453	1 448						
			1 440	1 447			1 446				
1 248		1 246		1 256	1 247		1 246				Symmetric CH deformations
1 181		1 176		1 180	1 178		1 177				
1 153		1 153	1 145	1 143	1 157		1 161				Asymmetric C–O stretch
1 065		1 050	1 065	1 060	1 080		1 090				Symmetric C–O stretch
998		978	970		915	915	915				Methyl rock
910	920	912	914	914	851	845		930	927		
	894	890	896	896							
880	880			872	832	832		924	920	850	MH deformations
	867	860	862	857							
850	850		848	845	712	727		683	658	628	MH rock
840	833	830	836	832	698	716		670	640		
		410			423	430	423				COC deformation
427	431	310	295	295				515	410	385	M–X stretch
	399	280	249	256	340	326		494	393	348	
300		448	445		270	285					M–O stretch

publication,[7] but it is worth recalling here that the silicon atom in the adduct is five-co-ordinate and the O–Si–Cl angle is nearly linear. Atomic co-ordinates have been deposited with the Cambridge Crystallographic Data Centre. The Figure shows packing diagrams, drawn using PLUTO,[8] which illustrate the isolation of the molecular adduct units.

We have so far been unsuccessful in our attempts to grow single crystals of the dimethyl ether adduct with silyl bromide. Since we had been able to identify the presence of phase changes as the reason why we could not stabilise single crystals of silyl chloride or bromide,[9] we recorded powder patterns over the temperature range 233—113 K. A sample of the silyl bromide adduct was sealed in a 0.5-mm diameter Pyrex capillary tube and patterns photographed using a Guinier-Simon powder camera equipped with a low-temperature device. Temperatures were monitored and controlled using a Pt 100 thermoresistor.

No evidence of phase transformations was found, but the patterns recorded at 113 K are very similar to those simulated by LAZY PULVERIX [10] from the single-crystal results for the silyl chloride adduct. We therefore conclude that these adducts are isostructural.

The melting point of the silyl bromide adduct was found to be 214 ± 2 K, rather higher than the freezing point found for the silyl chloride adduct in the single-crystal study, 190 ± 2 K.

Results

When the liquid mixture of silyl chloride and dimethyl ether (1 : 1) is cooled the Raman spectrum of the solid initially formed is quite different from that of silyl chloride.[11] In particular, the silyl deformation modes, which give a strong doublet above 920 cm^{-1} in the Raman spectrum of solid silyl chloride, are replaced by a set of bands between 830 and 900 cm^{-1}, and the band due to the rocking mode, near 675 cm^{-1} for the chloride, is absent in the spectrum of the adduct. The strong bands near 500 cm^{-1}, due to the Si–Cl stretch in solid silyl chloride, shift to near 400 cm^{-1} for the adduct. In the SiH stretching region, near 2 200 cm^{-1}, the differences are less clear, but small shifts in band positions do occur. The Raman spectrum of dimethyl ether is much weaker than that of silyl chloride, and it is not possible to identify many bands due to the donor molecule in the spectrum of the adduct. A broad band near 1 450 cm^{-1} and a sharp band at 2 925 cm^{-1} are probably due to the CH_3 deformation and CH stretching modes respectively of the complexed ether.

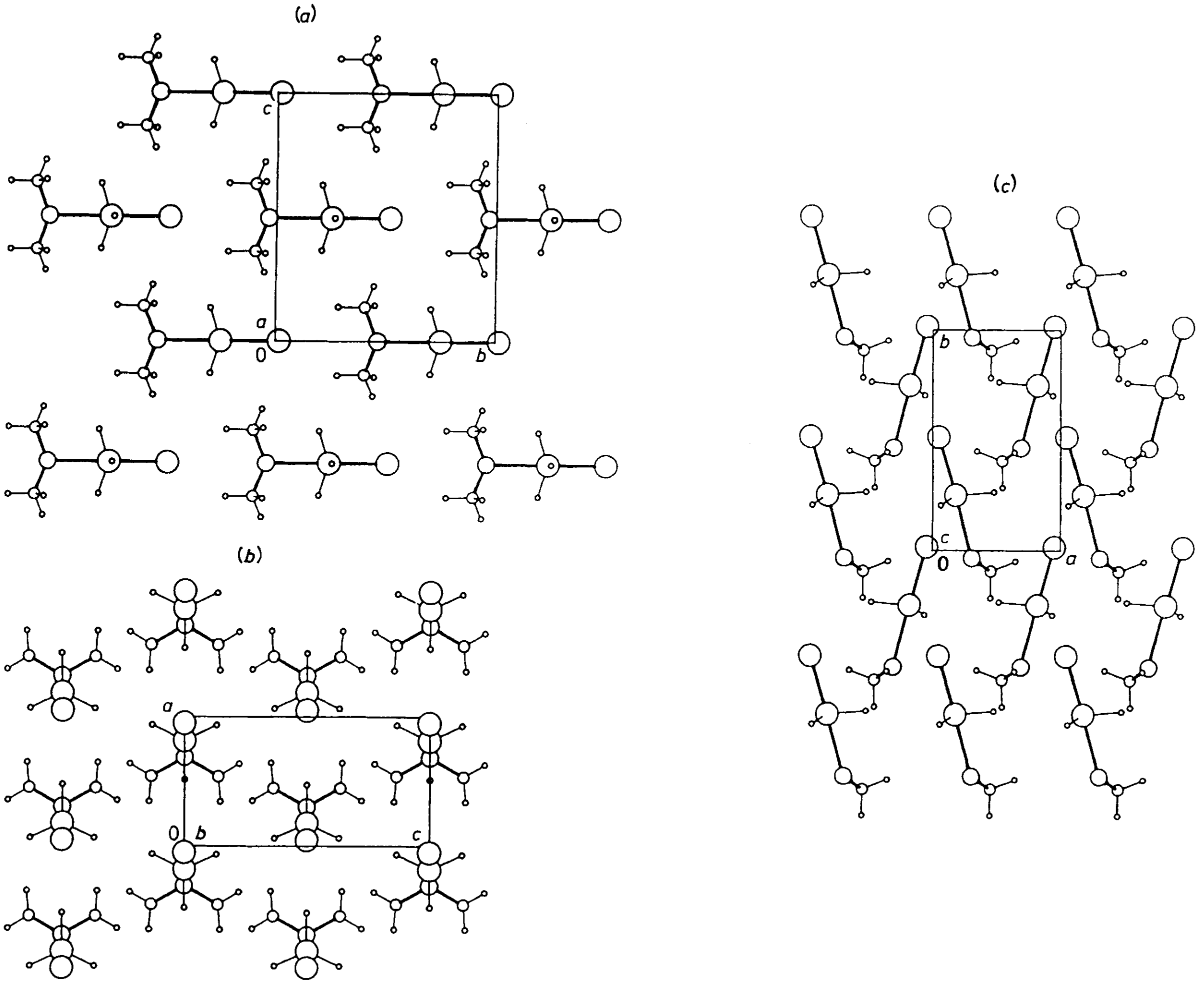

Figure. Packing diagrams (PLUTO) showing views along the *a* (*a*), *b* (*b*), and *c* (*c*) axes

Mixtures with other ratios of silyl chloride:dimethyl ether were studied, but no bands due to any species other than the presumed 1:1 adduct were observed, except in mixtures containing a large excess of silyl chloride, when the spectrum of solid silyl chloride itself was found.

The silyl bromide–dimethyl ether and germyl chloride–dimethyl ether mixtures showed similar behaviour in the Raman study. There were some minor differences, but the bands found are sufficiently similar for it to be very probable that the solid adducts have similar structures (Table). One notable difference in the germyl chloride case was that the germyl deformation modes appeared as two groups, two or three at higher frequencies and two at lower, which is reminiscent of the separation of the modes into HMH deformations and rocking modes in the simple silyl and germyl halides.

A more significant difference appears in the Si–Br mode of the silyl bromide–dimethyl ether adduct, which shows two strong bands in the Raman, at 256 and 295 cm^{-1}, much reduced from the simple silyl bromide solid frequencies near 400 cm^{-1}. This may indicate a stronger interaction between the two molecules of adduct in the primitive cell (see below).

Cooling and warming the solid adducts led to no significant changes in the Raman spectra. Thus there is no evidence for any phase changes, or for the necessity for annealing when the adduct forms from a liquid mixture. The Raman spectrum was recorded at the lowest attainable temperature (*ca.* 15 K for the chloride adducts) to minimise linewidths, which were typically 4–5 cm^{-1} for strong bands of the sample, compared with a spectral slitwidth of 2 cm^{-1}. The silyl bromide adduct was also studied at a higher temperature (see above) and some bands, particularly those assigned to the Si–Br stretching mode, were considerably broader than those of the chloride adducts.

In the i.r. spectrum of mixtures of silyl chloride and dimethyl ether we are less sure that the mixing ratio is exactly 1:1 but the behaviour of the spectrum on annealing shows that the initial solid contains a mixture of complexed and uncomplexed species, and that annealing leads to a solid composed at least mainly of adduct. The strong bands due to SiH stretching were not well resolved, and give no definite information about the species present, but many weaker bands due to dimethyl ether are very sharp and show distinct shifts compared with those of solid dimethyl ether itself. In addition to these, and the bands seen also in the Raman spectrum, new moderately strong i.r. bands appear on annealing which have no counterpart in the i.r. spectra of either component of the mixture, or in the Raman spectrum of the silyl chloride–dimethyl ether mixture. Weak lines in the same region appear in the Raman spectrum of the silyl bromide–dimethyl ether mix, and the Raman spectrum of the germyl chloride–dimethyl ether mix shows a clear line close to the position of the 'new' i.r. band.

The bands observed, together with data for solid halides and dimethyl ether, are listed in the Table. It should be noted that the solid silyl halides show changes in their Raman spectra [11] as the temperature is altered which are attributable to phase changes. The spectra listed here are the simplest in each case, to provide a clear-cut basis for comparison with the spectra of the adducts. In particular, both silyl bromide and germyl chloride have a phase which has a much more complex pattern in the M–H stretching region than the simple spectra of the adducts and the 'simple' phases of all three halides reported here. A full description of the spectra and other evidence relating to the low-temperature behaviour of the three halides will be published separately.

Discussion

It is clear from the *X*-ray results reported earlier[7] that the vibrating unit in the solid is likely to be the single adduct molecule, $SiH_3Cl{\cdot}Me_2O$. It is possible that some interactions between units may occur, leading to splitting of bands, but the packing diagrams (Figure) show no signs of any close contacts that could suggest strong intermolecular interactions. We shall discuss the spectra of all three adducts in the light of the known structure of the silyl chloride adduct.

The adduct molecule has eight atoms, if we ignore the methyl hydrogens, so there should be a total of 18 ($3N - 6$) normal modes. The highest symmetry possible is C_s, in which case the vibrations separate as $11a' + 7a''$ modes. Distinction between the two symmetry species is impossible in the absence of *polarisation* information (inevitable given the polycrystalline nature of the sample) and the lack of any facility for altering the orientation of a crystalline sample relative to the laser beam. All modes are allowed to be active in both Raman and i.r. spectra. The primitive unit cell contains two molecules of adduct, and in the absence of inversion centres this could lead to a doubling of any mode in either spectrum.

More likely as a cause of splitting in the spectrum is the phenomenon of longitudinal–transverse splitting of the optical modes,[12] which in the case of a polar (non-centric) biaxial crystal, as here, can lead to up to *three* components for each unit-cell mode, rather than the two components arising in the cases of cubic or uniaxial crystals. The magnitude of the effect depends on the mode concerned, and the effect seems to be obvious only in the Si–Cl stretching bands in the present case, as in the spectra of solid silyl chloride itself.[11]

The local (site) symmetry of the adduct molecule (C_s) formally distinguishes between a unique hydrogen and a symmetry-related pair of hydrogen atoms on silicon or germanium, but the M–H stretching region of the Raman spectra of the adducts does not appear to reflect this. Instead, it seems that the MH_3 group continues to vibrate as a unit with effective three-fold symmetry, so that we have a strong totally symmetric stretch at lower frequency, and an antisymmetric mode, which is split into two components by the absence of true three-fold symmetry, giving a weaker band at higher frequency, just as in the simple silyl chloride solid, where the local symmetry is thought to be C_s also. The frequencies of the bands are as noted very similar to those in the solid halides themselves, showing that the formation of the adduct has very little effect on the strength of the M–H bonds, and thus does not involve M–H antibonding orbitals.

In the region between 1 500 and 1 000 cm^{-1} we expect two bands due to C–O stretches of the complexed ether unit (as well as CH_3 deformation modes). The two strong bands in the i.r. spectrum of solid dimethyl ether, at 1 161 and 1 090 cm^{-1}, may be assigned to the antisymmetric and symmetric COC stretching modes respectively. They move down by 4–40 cm^{-1} in the spectra of the adducts (Table). The larger shift of the symmetric mode is consistent with a shift of bonding electrons into an orbital formerly lone pair in character, now bonding to silicon, but the fact that both modes shift to lower frequency on formation of the adduct shows that other changes, including changes in bond angle, may also be involved. The bond angle found in the crystalline silyl chloride adduct, 111.02(12)°, is only very slightly less than that reported in the gas phase, 111.7(3)°, but the bond length, 143.3(2) pm in the crystal, is distinctly larger than the gas-phase value, 141.0(3) pm (r_s).[13]

The changes in the SiH deformation and rocking modes of silyl chloride on formation of the adduct are most striking. The five modes of the free molecule (a_1 and e deformations, and e rocking) become five deformation modes of the adduct. One of these involves in-phase changes in the ClSiH bond angles, as in the symmetric deformation of the free molecule; we may call it the symmetric deformation. Two correspond to the two components of the antisymmetric deformation mode, with changes in the HSiH bond angles but not in the ClSiH angles, and two correspond to the two components of the rock, which may now be viewed as a tilt of the H_3 unit against the ClSiO axis about one of two mutually perpendicular axes. All five modes seem to have rather similar frequencies, giving rise to a group of bands in both i.r. and Raman spectra between 820 and 920 cm^{-1}. The spectra of the silyl bromide adduct contain a very similar group of bands.

There is also a strong band in the i.r. spectrum of the silyl chloride adduct near 1 000 cm^{-1} that we assign to a methyl rocking mode of the complexed ether, significantly increased in frequency from the free molecule. In the i.r. spectrum of the silyl bromide adduct this band appears at 970 cm^{-1}, showing that the methyl rock is also strongly perturbed in this case.

The germyl chloride adduct shows a rather different pattern, with two groups of bands, a doublet at about 720 cm^{-1} and two or three bands near 840 cm^{-1}. These seem to correspond more closely to the separate rocking and deformation bands found for the simple halides, suggesting that the perturbation of the halide by the ether is less in this case. Correspondingly, the shift of the methyl rock of the ether is very small.

In the M–X stretching regions the Raman spectra of the three samples differ considerably, but all three i.r. spectra are similar, with very strong broad bands considerably lower in frequency than those of the simple solid halides. The drop in frequency is least for germyl chloride (about 30 cm^{-1}) and greatest for silyl bromide (about 130 cm^{-1}). The breadth of the bands in the i.r. spectra, which were recorded at liquid-nitrogen temperature in each case, means that we cannot be sure whether the Raman and i.r. frequencies are compatible, especially as the two spectra will be affected differently by reflection and biaxial effects.

The 'new' band in the i.r. spectrum of the silyl chloride adduct, at 300 cm^{-1}, is identified with the expected Si–O stretching mode. It is much lower in frequency than bands assigned to Si–O modes in more conventional molecules,[14] but this is consistent with the very long 'bond' (227 pm, compared with around 170 pm for normal Si–O single bonds) and the weakness of the interaction, which only appears to lead to discrete adduct units in the solid state. There is no counterpart to this mode in the Raman spectrum. This band may be compared with that observed in the i.r. spectrum, but not in the Raman, for $SiCl_4{\cdot}NMe_3$, at 280 cm^{-1}, which has been tentatively assigned to the Si–N stretch.[15]

For the silyl bromide adduct the corresponding band appears above the Si–Br stretches, at about 450 cm^{-1}, and it is seen weakly in the Raman spectrum as well. The higher frequency argues that the strength of the interaction is greater than in the silyl chloride adduct, which is consistent with the fact that other modes are also more perturbed. For the germyl chloride adduct the Ge–O stretch is assigned at about 280 cm^{-1}, appearing in both the Raman and i.r. spectra.

No assignments have been made in the lattice region, below about 150 cm^{-1}, though some bands were seen in the Raman spectra. The lattice spectrum is expected to be simple, with three translational and three librational modes, corresponding to the two molecular units in the primitive cell, but there must also be torsional and bending modes of the 'skeleton' in the low-frequency region. In particular, the X–M–O bends are expected to occur at a very low frequency (the corresponding bend of the axial F–P–F group in PF_5 is found[16] at about 175 cm^{-1}, and the masses in the present cases are larger). A band at 156 cm^{-1} in the Raman spectrum of the silyl chloride adduct could be due to one component of this mode, which is not necessarily degenerate in the absence of three-fold symmetry, but there are several other possibilities at lower frequencies.

The overall impression given by the vibrational spectra is of a simple vibrating unit composed of a single adduct molecule, which shows the bands expected from its composition, though the low-frequency bends and the torsion of one portion against the other are not assigned. The changes in the bands of the ether moiety are small, as are the changes in the MH stretches, but the deformations of the MH_3 group are profoundly modified by the interaction, and a new band assigned to the M–O stretch is seen in the i.r. spectrum.

The bonding of the ether oxygen to silicon or germanium clearly involves donation of a lone pair on oxygen into a suitable acceptor orbital on the Group 4 atom. The geometry at silicon in the silyl chloride adduct, which is tending towards trigonal bipyramidal, is not conclusive evidence for any particular bonding scheme, but is certainly consistent with the use of a single 3*d* orbital to supplement the 3*s* and 3*p* valence shell orbitals in the complex. The fact that the MH stretches are almost unaltered in frequency by the formation of the adduct is evidence that the MH antibonding orbitals are not involved as acceptor orbitals, though it is clear from the lower M–X stretching frequency that the M–X antibonding orbital could be involved. The fact that the new Si–O bond stretch is assigned below the lowered Si–Cl stretching mode in the silyl chloride adduct guarantees that the lowering in frequency is not due to any mechanical coupling between the modes in this case. Indeed, it might be argued that the higher frequency is more likely to be the Si–O stretch as we have assigned in the silyl bromide adduct, but this is contradicted by the very long Si–O bond, and the comparatively small lengthening of the Si–Cl bond.

We conclude, then, that the acceptor orbital on Si or Ge probably involves the M–X antibonding orbital and some 3*d* or 4*d* character as well, as if only the antibonding orbital were involved the Si–Cl bond would probably be weakened more than enough to cause a lengthening of only 5%

It is clear that germyl chloride interacts much less strongly with the ether oxygen than either silyl halide, and it seems that the silyl bromide adduct is more strongly bound than the silyl chloride adduct, as the perturbations of the M–X stretching mode are greatest in the latter case. These differences may reflect an intrinsically greater ability of silicon to form bonds with first-row donor atoms. It is harder to see why the bromide forms a stronger adduct than silyl chloride, and it may well be simply that the mechanical coupling between the two colinear bonds (O–M and M–X) in the adduct molecule causes the Si–Br stretch to appear at a lower frequency and the Si–O stretch to appear at a higher frequency. This would also explain the very different Si–O stretching frequencies of the two silyl adducts; in the chloride case it is pushed down by the Si–Cl stretch at higher frequency, in the bromide it is pushed up by the Si–Br stretch at a lower frequency.

The packing diagrams show that the molecular adducts pack without any sign of additional specific interactions between them. The molecules may be expected to have two opposed dipolar bonds each (Si–Cl and Si–O), but there is no sign that such bonds in neighbouring molecules are aligned or closer to each other than is required by the simple packing at van der Waals distances.

We have shown that Raman spectroscopy is an extremely powerful tool in the study of weakly interacting systems. The spectra recorded below the melting points of the adducts show unequivocally that a change in the chemical composition has taken place, and the details of the spectra allowed us to form sensible hypotheses about the nature of the change before the *X*-ray evidence was available. There is clearly much more work to be done with similar systems, and Raman spectroscopy will certainly be an invaluable method in any further investigation.

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