

Molecular structure of monomeric scandium trichloride by gas electron diffraction and density functional theory calculations on ScCl_3 and Sc_2Cl_6 †

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The molecular structures of monomeric and dimeric scandium trichloride were optimised by DFT calculations with basis sets of valence shell TZ + P quality, and the molecular force fields and normal vibrational modes calculated. Optimisation of ScCl_3 yielded an equilibrium geometry of D_{3h} symmetry and bond distance Sc–Cl 228.5 pm. Optimisation of a model of the dimer with double Cl bridges indicated an equilibrium geometry of D_{2h} symmetry, the terminal and bridging bond distances Sc–Cl_t 226.0 and Sc–Cl_b 247.5 pm, and the valence angles Cl_t–Sc–Cl_t 114.9 and Cl_b–Sc–Cl_b 86.6°. Synchronous gas electron diffraction (GED) and mass spectrometric (MS) data were recorded with the effusion cell kept at 900 ± 10 K. The gas was found to consist of $92 \pm 2\%$ monomer and $8 \pm 2\%$ dimer. Least-squares refinement of a trigonal pyramidal (C_{3v}) model of the monomer yielded the bond distance $r_g(\text{Sc–Cl}) = 229.1(3)$ pm and a valence angle α Cl–Sc–Cl $119.8(5)^\circ$. The concentration of the dimer was too low for the GED data to give accurate structure parameters for this species. Bond energies for both monomer and dimer were calculated from thermochemical data in the literature and compared to corresponding energies in MCl_3 and M_2Cl_6 , M = Al, Ga or In.

The monomeric scandium trihalides, ScX_3 , have been the subject of several studies aiming towards the establishment of the molecular structure, *i.e.* the determination of the Sc–X bond distance and the molecular shape; is the equilibrium geometry trigonal pyramidal, symmetry C_{3v} , or planar, symmetry D_{3h} ?

The first investigation of ScF_3 by gas electron diffraction (GED) dates back to 1961.¹ Diffraction data recorded at an unspecified temperature were found to be consistent with a monomer concentration of 100% and D_{3h} symmetry. This, of course, is the symmetry indicated by a spherical ion model, by the VSEPR model. It is also consistent with a hybridisation model since sd^2 hybrid orbitals formed from the 4s, $3d_{xy}$ and $3d_{x^2-y^2}$ atomic orbitals on Sc have major lobes pointing in the appropriate directions. (Hybridisation of the 4s, $3d_{xz}$ and $3d_{yz}$ orbitals would, however, yield hybrids favorable for a trigonal pyramidal co-ordination geometry.) Three reports on the IR absorption spectra of ScF_3 in rare gas matrices were published in the 60s or early 70s.^{2–4} Since the symmetric Sc–F stretching frequency (ν_1) could not be found, it was concluded that the molecule must be planar or near-planar. The electric deflection of molecular beams, on the other hand, indicated a polar, *i.e.* non-planar structure,⁵ and a second investigation by GED yielded a F–Sc–F valence angle of $110(2.5)^\circ$.⁶

Finally a third, careful analysis of GED data recorded with a nozzle temperature of 1750 K yielded a Sc–F bond distance of $r_g = 184.7(2)$ pm and a non-bonded F···F distance which, after correction for thermal vibration, differed from that calculated for a planar model by $0.0(15)$ pm;⁷ the molecule is clearly planar or very nearly so. Equilibrium geometries of D_{3h}

symmetry are also indicated by *ab initio* calculations at the CISD(Q) level⁸ and by DFT calculations at the same level as those described below for ScCl_3 .⁹ It would seem that the question about the equilibrium structure of ScF_3 has been settled for the time being!

The gas-phase IR spectra of monomeric ScCl_3 , ScBr_3 and ScI_3 have been recorded by Selivanov.¹⁰ No symmetric Sc–X stretching frequencies (ν_1) could be assigned. The IR spectrum of matrix-isolated ScBr_3 has also been reported; ν_2 , ν_3 and ν_4 could be assigned, but ν_1 was not found.¹¹ Neither the trichloride nor the tribromide appears to have been studied by GED up to the present, but Ezhov *et al.*¹² have recently published the results of a GED study of gaseous ScI_3 at 1050 K. The molecular beam was found to contain both monomeric and dimeric species with mole fractions of 21(3) and 79(3)% respectively. Least-squares refinement of the molecular structures of both monomer and dimer yielded a monomer bond distance of 262(1) pm and a monomer valence angle of $117(2)^\circ$: the concentration of the monomer is obviously too small to allow a distinction to be made between planar and pyramidal models.

In this article we report the results of density functional theory (DFT) calculations on both monomeric and dimeric scandium trichloride and a GED investigation which shows that monomeric ScCl_3 is trigonal planar or very nearly so.

Density Functional Theory Calculations

The original plan was to optimise the molecular structures of both ScCl_3 and Sc_2Cl_6 by DFT calculations using the program system GAUSSIAN 94¹³ with the Becke exchange¹⁴ and the Perdew–Wang correlation functional¹⁵ (BPW 91). Optimisation of a trigonal planar (D_{3h}) model of ScCl_3 with the standard effective core potential (ECP) basis LanL2DZ¹³ converged to a bond distance of 229.1 pm. The dimer was assumed to have a diborane-like structure with two bridging chlorine atoms (see

† Supplementary data available: experimental conditions for the synchronous GED/MS. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/2787/>, otherwise available from BLDSC (No. SUP 57406, 2 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

Table 1 Structure parameters of ScCl₃ and Sc₂Cl₆ obtained by density functional theory calculations or gas electron diffraction. Interatomic distances (*r*), root-mean-square vibrational amplitudes (*l*), perpendicular amplitude correction coefficients (*K*) and shrinkages (δ) in pm, angles in °^a

	DFT ^b			GED	
	<i>r_e</i>	<i>l</i>	<i>K</i>	<i>r_g</i>	<i>l</i>
ScCl ₃					
Mole fraction 93(3)%					
Interatomic distances					
Sc–Cl	228.5	7.8	3.6	229.1(3)	7.6(2) ^d
Cl···Cl	395.7	23.6	0.6	390.8(11)	23.3(10) ^d
Shrinkage					
$\delta(\text{Cl}\cdots\text{Cl})^c$	6.1			6.0(16)	
Valence angle					
Cl–Sc–Cl	120.0			119.8(5)	
Sc ₂ Cl ₆					
Mole fraction 7(3)%					
Interatomic distances					
Sc–Cl _t	226.0	7.7	27.6	227.5(10) ^d	7.6(2) ^d
Sc–Cl _b	247.5	11.7	8.8	246(2)	[11]
Cl _b ···Cl _b	339.5	15.5	3.5	325(6)	[15.5]
Sc···Sc	360.1	14.0	2.1	349(4)	[14.0]
Cl _b ···Cl _t	394.9	37.2	26.0	404(2)	37.6(10) ^d
Cl _t ···Cl _t	380.4	25.5	42.4	412(2)	[25.5]
Sc···Cl _t	517.8	64.4	8.3	501(3)	[45.0] ^d
Cl _t ···Cl _t	603.0	165.2	4.3	543(3)	[51.0] ^d
Cl _t ···Cl _t	713.1	39.0	1.1	691(3)	[39]
Valence angles					
Cl _t –Sc–Cl _t	114.9			[114.9]	
Cl _b –Sc–Cl _b	86.6			86(2)	
Sc–Cl _b –Sc	93.4			94(2)	
<i>R</i> factor ^e				0.053	

^a Estimated standard deviations in parentheses in units of the last digit. Non-refined parameters in square brackets. ^b The calculations on ScCl₃ have been carried out with the ADF program and the TZ + P basis set IV, that on Sc₂Cl₆ with GAUSSIAN 94 and a 6-311G* basis set. See comment in Density Functional Theory Calculations. ^c The shrinkage is defined as $\delta(\text{Cl}\cdots\text{Cl}) = \sqrt{3} r_g(\text{Sc–Cl}) - r_g(\text{Cl}\cdots\text{Cl})$. ^d See comment in Structure refinements. ^e $\sqrt{[\sum w(I_{\text{obs}} - I_{\text{calc}})^2] / \sum w(I_{\text{obs}})^2}$.

sketch in Contents). Optimisation of a model of *D*_{2h} symmetry with the LanL2DZ basis yielded the terminal and bridging bond distances Sc–C_t 227.5 and Sc–Cl_b 251.2 pm.

Optimisation of a *C*_{2v} model of the dimer (*i.e.* a model in which the central Sc₂Cl₂ ring is non-planar) with the standard all-electron (AE) basis set 6-311G*¹³ converged to *D*_{2h} symmetry (planar Sc₂Cl₂ ring). Interatomic distances and valence angles are listed in Table 1. The normal vibrational modes are listed in Table 2. The molecular force field was transferred to the program ASYM 40 for calculation of root-mean-square vibrational amplitudes, *l*, and perpendicular amplitude correction coefficients *K*¹⁶ (see Table 1).

After several attempts to optimise the structure of the monomer at the BPW91/6-311G* level had failed to converge, we turned to the Amsterdam Density Functional (ADF) program.¹⁷ Calculations were carried out with the Vosko–Wilk–Nusair parametrisation,¹⁸ the gradient correction of Becke¹⁴ for exchange and of Perdew¹⁹ for correlation. A standard basis set of TZ + P quality (IV) was used,¹⁷ with the atomic cores of Sc and Cl up to and including the 2p AOs frozen in their atomic shape. Structure optimisation of a *C*_{3v} model of ScCl₃ now converged nicely to yield a structure of *D*_{3h} symmetry. The vibrational modes are listed in Table 2, the bond distance, root mean square (r.m.s.) vibrational amplitudes and perpendicular amplitude correction coefficients are listed in Table 1.

Experimental

A sample of ScCl₃·*x*H₂O with a stated purity of 99.99% was purchased from Aldrich Chemical Company. The anhydrous trichloride was obtained by heating the sample under reflux with thionyl chloride as described in ref. 20.

Table 2 Normal mode frequencies (cm⁻¹) of ScCl₃ and Sc₂Cl₆ obtained by DFT calculations

Symmetry	Mode	ω	Symmetry	Mode	ω
ScCl ₃ (<i>D</i> _{3h})					
A ₁	1	341	E	2	468
E	3	86	A ₂	4	79
Sc ₂ Cl ₆ (<i>D</i> _{2h})					
A _g	1	438	A _g	2	287
A _g	3	151	A _g	4	71
B _{1g}	5	237	B _{1g}	6	81
B _{2g}	7	465	B _{2g}	8	58
B _{3g}	9	73	A _u	10	36
B _{1u}	11	474	B _{1u}	12	109
B _{1u}	13	12	B _{2u}	14	319
B _{2u}	15	56	B _{3u}	16	412
B _{3u}	17	273	B _{3u}	18	94

Gas electron diffraction and mass spectrometry

Synchronous MS and GED experiments were carried out on the modified EMR-100/ApdM-1 unit in Ivanovo. The nickel oven containing the sample was kept at the lowest possible temperature at which sufficient vaporisation took place, about 900 K, corresponding to a vapour pressure of about 0.025 Torr (Torr \approx 133 Pa).²¹ The ratio of evaporation surface to the nozzle orifice was approximately 400. The length to diameter ratio of the diffusion nozzle was optimised to keep equilibrium concentrations of the monomer and dimer in the vapor and a negligibly small scattering volume.²² Other experimental

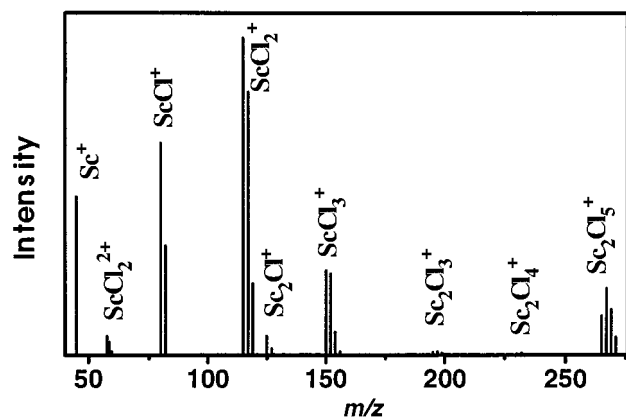


Fig. 1 A portion of the mass spectrum of scandium trichloride under the conditions of the gas electron diffraction experiment. The ionising potential is 50 V

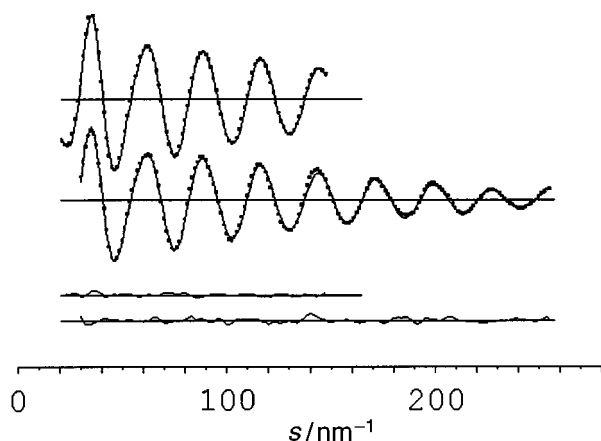


Fig. 2 Calculated (full lines) and experimental (squares) modified molecular intensity curves of ScCl_3 with difference curves shown below

conditions are summarised in SUP 57406. A portion of the mass spectrum is given in Fig. 1. For analysis of the gas composition we assumed that the ions ScCl_n^+ , $n = 1$ to 3, are formed from the monomer, that the ions Sc_2Cl_n^+ , $n = 1$ to 5, are formed from the dimer, and that the ratio of the ionisation cross-sections of dimer to monomer is equal to 2.

Atomic electron scattering factors were taken from ref. 23 and backgrounds were drawn as smooth least-squares adjusted polynomials to the difference between experimental and calculated molecular intensities.

Structure refinements

Structure refinement of the monomer was based on a geometrically consistent r_u model of C_{3v} symmetry. The mole fraction of monomer in the molecular beam, the Sc–Cl bond distance, the non-bonded Cl \cdots Cl distance and the Sc–Cl and Cl \cdots Cl r.m.s. vibrational amplitudes were refined as independent parameters. The asymmetry constant of the Sc–Cl bond distance (and of the terminal Sc–Cl distance in the dimer) was estimated from $\kappa = (1/6)l^4/[8\pi^2c\omega_e x_e \mu/h]$. Molecular constants taken from the scandium monochloride molecule²⁴ yielded $\kappa = 7.24 \times 10^{-6} \text{ pm}^3$.

Structure refinement of the dimer was based on a geometrically consistent r_u model of D_{2h} symmetry. Such a model is characterised by four independent structure parameters, e.g. the terminal and bridging Sc–Cl_t and Sc–Cl_b bond distances and the valence angles α Cl_t–Sc–Cl_t and Cl_b–Sc–Cl_b. Since the amount of dimer in the molecular beam was less than 10% we were unable to refine these four parameters without divergence, and the valence angle α Cl_t–Sc–Cl_t was fixed at the value obtained by the DFT calculations. The difference between the

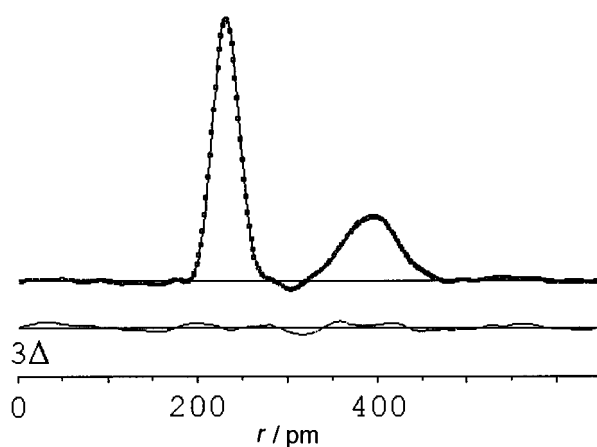


Fig. 3 Calculated (full line) and experimental (squares) radial distribution curves of a mixture of ScCl_3 (92%) and Sc_2Cl_6 (8%). Artificial damping constant $k = 25 \text{ pm}^2$. The two peaks at about 230 and 390 pm represent the Sc–Cl bond distance and the non-bonded Cl \cdots Cl distance in the monomer. Below: difference curve

Sc–Cl bond distance in the monomer and the terminal distance in the dimer, $r_g(\text{Sc–Cl}) - r_t(\text{Sc–Cl}_t)$, was fixed at the value obtained by DFT calculations with LanL2DZ basis (1.6 pm). (The estimated standard deviation obtained for the Sc–Cl_t bond distance was expanded from 0.3 to 1.0 pm to include the uncertainty due to this constraint.) The vibrational amplitudes of the two bond distances were refined with a constant difference, as were the amplitudes of the Cl \cdots Cl distance in the monomer and of the Cl_b \cdots Cl_t distance in the dimer which turned out to be very similar. The calculated vibrational amplitudes of the non-bonded Sc \cdots Cl_t distance at about 500 pm and the non-bonded Cl_t \cdots Cl_t distance at about 540 pm were 64 and 165 pm respectively. These amplitudes were varied stepwise to minimise the square-error sum. The best fit was obtained for the values 45 and 51 pm respectively. Other amplitudes were fixed at their calculated values.

The structures were refined by a modified version of the program KCED 25 originally written by H. M. Seip. The refinements converged to yield the best values listed in Table 1. Since the refinements were carried out with diagonal weight matrices the listed estimated standard deviations have been multiplied by a factor of 2.0 to include the uncertainty due to data correlation and expanded to include an estimated scale uncertainty of 0.1%. Experimental and calculated molecular intensity curves are compared in Fig. 2, radial distribution curves in Fig. 3.

Results and Discussion

The composition of the molecular beam

The mass spectra recorded simultaneously with the GED diagrams indicated that the mole fractions of monomers and dimers in the molecular beam were 92 ± 2 and $8 \pm 2\%$ respectively, while the amount of trimer or higher species was negligible. These mole fractions are in good agreement with the less accurate values obtained by analysis of the electron diffraction data, 93(3) and 7(3)% respectively. The high concentration of the monomer allows an accurate determination of its molecular structure, while the concentration of the dimer was too low for the GED diagrams to contain much information about the molecular structure of Sc_2Cl_6 .

The molecular structure of ScCl_3

Least-squares structure refinement of a molecular model of C_{3v} symmetry to the GED data yielded a Cl–Sc–Cl valence angle

of 119.8(5)° while structure optimisation by DFT calculations with an all-electron basis of TZ + P quality yielded an equilibrium structure of D_{3h} symmetry; calculations and experiment agree that the molecule is planar or very nearly so. A planar equilibrium structure is also indicated by the gas phase IR spectra since the symmetric Sc–Cl stretching mode (ν_1) could not be detected.¹⁰ The calculated Sc–Cl bond distance is 228.5 pm in good agreement with experimental (r_g) distance of 229.1(3) pm.

Before going on to discuss the molecular structures of the monomeric trichlorides of the heavier Group 3 metals, yttrium and lanthanum, we pause to note that while the bond distances in the Group 13 trichlorides MCl_3 , $M = Al, Ga$ or In , are 6 to 11 pm shorter than the bond distance in the monochlorides MCl ,²⁵ the bond distance in $ScCl_3$ is 6 pm longer than in $ScCl$, 222.9 pm.²⁶

An early GED investigation of YCl_3 indicated that the equilibrium structure is planar.²⁷ More recently, Konings and Boonj²⁸ have recorded the infrared spectrum of gaseous YCl_3 and assigned the four normal modes under the assumption that the structure is pyramidal. This assignment has been challenged by Marsden and Smart²⁹ who optimised the structure at the MP2 level with a ECP basis of DZ quality and obtained an equilibrium structure of D_{3h} symmetry. Finally, a reinvestigation by a combination of GED and DFT calculations has shown that the structure is indeed planar or very nearly so.³⁰

The equilibrium structure of monomeric $LaCl_3$ is still not definitely established. Two relatively recent investigations of $LaCl_3$ by GED led to the conclusion that the equilibrium geometry is pyramidal,^{31,32} while quantum chemical calculations at various levels indicate that it is planar.^{33–36}

The molecular structure of Sc_2Cl_6

Density functional theory calculations on the dimer with a 6-311G* basis converged to a model of D_{2h} symmetry. Bond distances and valence angles are listed in Table 1.

Attempts to refine the four independent structure parameters characterising a D_{2h} model, viz. the terminal and bridging Sc–Cl_t and Sc–Cl_b bond distances and the valence angles α Cl_t–Sc–Cl_t and Cl_b–Sc–Cl_b, to the GED data failed to converge. The difference between the Sc–Cl bond distance in the monomer and the terminal distance in the dimer, $r_g(\text{Sc–Cl}) - r_t(\text{Sc–Cl}_t)$, was therefore fixed at the value obtained by DFT calculations with LanL2DZ basis (1.6 pm), and Cl_t–Sc–Cl_t at the value obtained by the all-electron calculations on the dimer. The best values obtained for the two structure parameters that could be refined without constraints $r_b(\text{Sc–Cl}_b) = 246(2)$ pm and α Cl_b–Sc–Cl_b 86(2)° are not significantly different from their calculated values. In the following we base our discussion of the dimer on the calculated structure parameters.

The compound Sc_2Cl_6 appears to be similar to the Group 13 analogues M_2Cl_6 , $M = Al$,³⁷ Ga ^{37,38} or In ,³⁸ insofar as the bridging M–Cl distance is about 20 pm longer than the terminal and the Cl_b–Sc–Cl_b angle is close to 90°, but to differ from the Group 13 analogues by having a Cl_t–Sc–Cl_t less than 120°: Cl_t–Al–Cl_t 123.6(16),³⁷ Cl_t–Ga–Cl_t 124.7(18)³⁷ and Cl_t–In–Cl_t \approx 130°.³⁸

The crystal structure of $ScCl_3$ is constructed from $ScCl_6$ octahedra, each Cl atom bridges two Sc atoms at a distance, 252 pm, about 5 pm longer than the Sc–Cl_b distance in the gaseous dimer.³⁹

Bond energies

The mean bond energy of monomeric $ScCl_3$ at 298 K may be calculated from the standard enthalpy of formation:²⁴ $MBE(\text{ScCl}_3) = \{\Delta H_f^\circ[\text{Sc}(\text{g})] + 3\Delta H_f^\circ[\text{Cl}(\text{g})] - \Delta H_f^\circ[\text{ScCl}_3(\text{g})]\}/3 = 478(3)$ kJ mol⁻¹. Similarly the mean bond energy of gaseous $LaCl_3$ calculated from the standard enthalpy of formation⁴⁰ is

found to be 509 kJ mol⁻¹. Both the Sc–Cl and La–Cl MBEs are larger than those of the Group 13 analogues, MCl_3 , $M = B, Al, Ga$ or In , which range from 456 to 327 kJ mol⁻¹.²⁵ While the MBEs of the Group 13 trichlorides decrease as the group is descended, those of the Group 3 trichlorides appear to increase.

Since the terminal Sc–Cl bond distance in Sc_2Cl_6 is very close to the bond distance of the monomer, we assume the bond energies to be equal; $BE(\text{Sc–Cl}_t) = MBE(\text{ScCl}_3)$. The mean energy of the bridge bonds may then be estimated from the dimerisation enthalpy,⁴¹ $\Delta H_d^\circ = -199$ kJ mol⁻¹ where $\Delta H_d^\circ = 2 BE(\text{Sc–Cl}_t) - 4 BE(\text{Sc–Cl}_b)$ or $BE(\text{Sc–Cl}_b) = 289$ kJ mol⁻¹. The M–Cl_b bond is thus stronger in Sc_2Cl_6 than in Al_2Cl_6 , Ga_2Cl_6 or In_2Cl_6 .³⁸ The ratio between terminal and bridging bond energies is however 1.7 ± 0.1 for both Sc and the Group 13 metals.³⁸

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