Molecular Structure of Dimeric Iron Trichloride in the Vapour Phase as determined by Electron Diffraction

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The molecular structure of the title compound has been determined by gas-phase electron diffraction, the vapour composition being obtained by quadrupole mass spectrometry. The experimental data can best be approximated by a model with a puckered four-membered ring (C_{2v} symmetry). This deviation from D_{2h} symmetry may be a consequence of large-amplitude vibrations around an imaginary axis connecting the two bridging chlorine atoms. The bond lengths and angles for the puckered-ring model are r_a(Fe–Cl) (terminal) 2.127(4), r_a(Fe–Cl) (bridge) 2.326(5) Å, Cl_t–Fe–Cl_t 124.3(7), and Cl_b–Fe–Cl_b 90.7(4)°. The bond lengths and force constants indicate that the terminal Fe–Cl bonds are considerably stronger than the bridging ones.

As part of our studies on the molecular structures of iron chlorides we have carried out an electron-diffraction study of dimeric iron trichloride. We recently reported on the structure of monomeric iron dichloride.[1] An earlier electron-diffraction study dealt with the structure of dimeric iron trichloride,[2] in which the molecular shape with bridging chlorines and D_{2h} symmetry was established, but the geometric parameters were reported with large uncertainties. Because of the importance of this structure, a new investigation was needed by up-to-date electron-diffraction techniques. Since far-i.r.[3] and Raman [4] spectroscopic studies have been done using the matrix-isolation technique, the present electron-diffraction analysis has been paralleled by a normal-co-ordinate analysis and subsequent calculations of the mean amplitudes of vibration.[5]

ANALYSIS

The electron-diffraction experiments were preceded by a mass spectrometric investigation of the vapour composition of iron trichloride as a function of the temperature. This was done with our combined electron-diffraction–quadrupole mass spectrometric equipment.[6] It was established that a nozzle temperature of 190 °C provides sufficient vapour pressure for the electron-diffraction experiment and the vapour consists of dimeric iron trichloride molecules. Details of the investigation of the variation of the vapour composition with temperature will be published elsewhere. The nozzle system used in this experiment was similar to the one described earlier.[7]

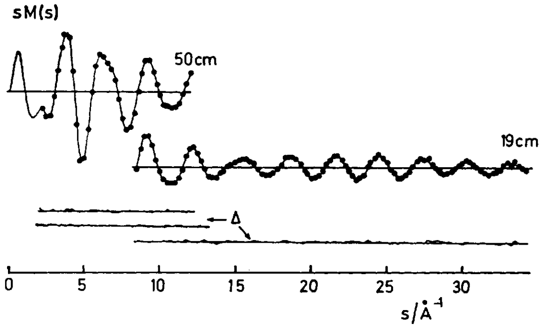

FIGURE 1 Experimental (●) and theoretical (—) molecular intensities and the difference curves (Δ) for Fe_2Cl_6. The theoretical curves correspond to the parameters of the C_{2v} model given in Table 1 (the experimental values are shown only for one of the averaged curves of 50 cm camera range)

The techniques used in the data treatment and structure analysis followed our usual procedure.[8] The coherent and incoherent electron-scattering amplitudes were taken from Cox and Bonham [9] and Tavard *et al.*,[10] respectively. The radial distributions were obtained according to expression (1) where $s = (4\pi/\lambda)\sin(\theta/2)$, λ is the electron wavelength,

$$f(r) = \sum_{s=0}^{34.25} sM(s)\exp(-0.002\,s^2)\sin sr\Delta s \qquad (1)$$

θ is the scattering angle, and $\Delta s = 0.25$ Å^{-1}. Theoretical molecular-intensity values have been used in the range of $0 < s \leqslant 2.0$ Å^{-1} to supplement the experimental data. The experimental molecular intensities and radial distributions are shown in Figures 1 and 2.

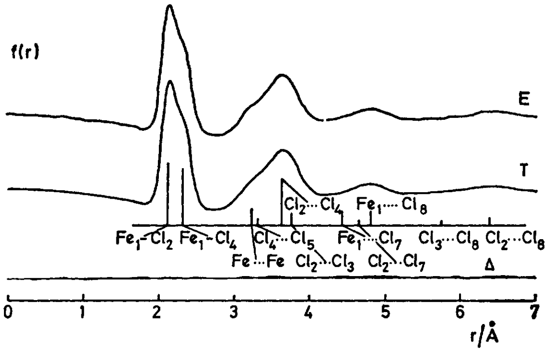

FIGURE 2 Experimental and theoretical radial distributions and the difference curves for the two models of Fe_2Cl_6. The positions and relative weight of the interatomic distances are also indicated

Our analysis was based on two models, one of D_{2h} symmetry (planar four-membered ring) and the other C_{2v} symmetry (puckered ring), see Figure 3. The latter may appear as a result of the electron-diffraction structure analysis even if the equilibrium structure has D_{2h} symmetry: large amplitude vibrations around an imaginary axis connecting the two bridging chlorine atoms will lead to average distances between atoms on opposite ends of the molecule less than those predicted from the bond lengths and the symmetry. Similar large-amplitude torsional motion has been observed by Shen and Hedberg [11] in dimeric aluminium trichloride and its analogues.

The calculated mean amplitudes of vibration (see Table 1) for both models were used in the initial parameter sets. The force fields for these calculations were constructed taking into consideration the experimental frequencies.[3,4] The latter seem to be rather uncertain in the low-frequency

TABLE 1

Geometrical parameters for dimeric iron trichloride

	C_{2v} model			D_{2h} model		
	r_a/Å	l_a/Å	$l_{calc.}$/Å	r_a/Å	l_a/Å	$l_{calc.}$/Å
(Fe–Cl)$_{av.}$	2.227(4)			2.227(5)		
Δ(Fe–Cl)	0.199(1)			0.199(1)		
Fe(1)–Cl(2)	2.127(4)	0.059(1)	0.057	2.127(4)	0.059(2)	0.057
Fe(1)–Cl(4)	2.326(5)	0.084(2)	0.074	2.326(5)	0.084(2)	0.075
Fe(1) · · · Fe(6)	3.234(8)	0.143(6)	0.142	3.207(8)	0.129(8)	0.140
Cl(4) · · · Cl(5)	3.310(8)	0.141 [a]	0.140	3.372(8)	0.127 [a]	0.136
Cl(2) · · · Cl(4)	3.632(7)	0.170(5)	0.196	3.639(8)	0.178(5)	0.196
Cl(2) · · · Cl(3)	3.761(9)	0.154 [b]	0.156	3.723(12)	0.162 [b]	0.160
Fe(1) · · · Cl(7)	4.425(11)	0.316(29)	0.272	4.628(11)	0.312(13)	0.237
Fe(1) · · · Cl(8)	4.809(11)	0.190(11)	0.210			
Cl(2) · · · Cl(7)	4.655(20)	[0.530]	0.530	5.267(19)	[0.470]	0.470
Cl(3) · · · Cl(8)	5.750(16)	[0.420]	0.420			
Cl(2) · · · Cl(8)	6.396(14)	0.212(20)	0.232	6.450(15)	0.211(24)	0.216
	Angle (°)			Angle (°)		
Cl(2)–Fe(1)–Cl(3)	124.3(7)			122.1(11)		
Cl(4)–Fe(1)–Cl(5)	90.7(4)			92.9(3)		
ψ	16.7(10)			[0]		
R (%)	5.04			6.16		

The average Fe–Cl bond length, Δ(Fe–Cl), and the three angles were used as independent geometrical parameters in the refinements. Values in parentheses are total errors referring to the last digital unit. Values in square brackets were not allowed to vary in the refinement. The assumed amplitudes are values from the spectroscopic calculations.[5] $R = [\Sigma W(I_{obs.} - I_{calc.})^2/\Sigma W I_{obs.}^2]^{\frac{1}{2}}$.

[a] Refined together with Fe(1) · · · Fe(6). [b] Refined together with Cl(2) · · · Cl(4).

region. The spectroscopically calculated mean amplitudes for the Cl(2) · · · Cl(7) and Cl(3) · · · Cl(8) interactions were assumed throughout the analysis.

The results of the least-squares refinement based on the molecular intensities are presented in Table 1 for both models. The r_a parameters were not converted into r_α values since the low frequencies are either missing or rather uncertain, and the perpendicular-vibration correction terms (K values) showed considerable sensitivity to even relatively small changes in the assumed values of the low frequencies.

DISCUSSION

The parameters obtained are in general agreement with the structure of similar halogen-bridged dimers as shown in Table 2. The difference between the terminal and bridging Fe–Cl bond lengths is *ca.* 0.2 Å which is a fairly constant value in this series of molecules and suggests a considerable difference in the strength of the terminal and bridging bonds. The stretching force constants of the terminal Fe–Cl bond are 2.127,[3] 2.237,[12] or 2.185 mdyn Å^{-1},[4,*] and for the bridging bond 1.217,[3] 1.222,[12] or 1.28 mdyn Å^{-1},[4] according to three different normal-coordinate analyses. This suggests that the terminal are considerably stronger than the bridging bonds.

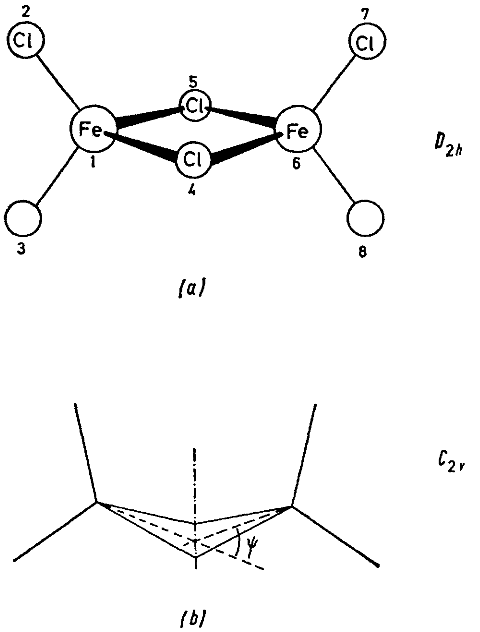

FIGURE 3 Molecular models for Fe_2Cl_6. The numbering of atoms is also shown

TABLE 2

Geometrical parameters for some M_2Cl_6 metal halide dimers

	Fe_2Cl_6 [a]	Al_2Cl_6 [b]	Ga_2Cl_6 [b]
$r(M-X)_t$/Å	2.127(4)	2.065(3)	2.099(2)
$r(M-X)_b$/Å	2.326(5)	2.252(3)	2.300(3)
X_t–M–X_t/°	124.3(7)	123.4(16)	124.6(18)
X_b–M–X_b/°	90.7(4)	91.0(16)	88.3(8)
ψ/°	16.7(10)	23.4(60)	20.5(33)
Δ[$(M-X)_t - (M-X)_b$]/Å	0.199	0.187	0.201
$(M-X)_t/(M-X)_b$	0.91	0.92	0.91

[a] Present work. [b] Ref. 11.

As to the symmetry of the molecule, the electron-diffraction results give better agreement with the C_{2v} than with the D_{2h} model. However, a planar equilibrium structure cannot be excluded for reasons stated above.

It is supposed that the deviation from planarity is the result of the large-amplitude bending of the two distorted $FeCl_4$ tetrahedra around their common edge. There is a puckering, 16.7° on average, of the Fe_2Cl_2 ring. This corresponds to the ring-puckering mode which has the smallest frequency in this type of compound (*e.g.* for Fe_2Cl_6 it is 24.3 cm^{-1} in an argon matrix [3]). In consequence of the large bending (rocking) of the two terminal $FeCl_2$ groups, the corresponding Fe · · · Cl and especially the Cl · · · Cl distances will be spread over a

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[*] Throughout this paper: 1 dyn = 10^{-5} N.

considerable range of the f(r) curve. The spectroscopically calculated amplitudes[5] for these chlorine–chlorine distances, in consequence of the very small values of the corresponding mode, are unusually large l[Cl(2) $\cdots$ Cl(7)] = 0.530 and l[Cl(3) $\cdots$ Cl(8)] = 0.420 Å for the C_{2v} model, and l[Cl(2) $\cdots$ Cl(7)] = l[Cl(3) $\cdots$ Cl(8)] = 0.470 Å for the D_{2h} model.

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