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AN ELECTRON DIFFRACTION DETERMINATION OF THE MOLECULAR STRUCTURES OF SILYL- AND GERMYL-MANGANESE PENTACARBONYL IN THE GAS PHASE

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Summary

The molecular structures of the title compounds have been determined by gas phase electron diffraction methods. The Si—Mn and Ge—Mn bond lengths are 240.7 ± 0.5 and 248.7 ± 0.2 pm respectively and the C—Mn—C angles in the silyl and germyl cases are 94.5 ± 2° and 97 ± 2° respectively. Comparisons are made with the reported structure of $CH_3Mn(CO)_5$ and He^I photoelectron spectra of these compounds in an attempt to determine the extent of $d \rightarrow d$ π-bonding in the Si—Mn or Ge—Mn bonds.

Introduction

In silyl- and germyl-transition metal complexes there exists the possibility of multiple bonding between the silicon, or germanium, atom and the transition metal atom, involving unoccupied silicon or germanium *d* orbitals. It is therefore of interest to determine the molecular structures of some of these complexes to see whether there is any stereochemical evidence for multiple bonding. However up to the present the only compound of this type whose gas phase structure has been determined is silylcobalt tetracarbonyl [1], so we have determined the gas phase structures of silylmanganese pentacarbonyl and germylmanganese pentacarbonyl by electron diffraction.

From a multiple bonding point of view the most important parameters are the silicon—manganese and germanium—manganese bond lengths. These will be compared with the (methyl)carbon—manganese bond length in methylmanganese pentacarbonyl [2] where there is no possibility of such multiple bonding.

It is also interesting to find out whether these structures bear out the conclusions from the He^I photoelectron spectra of these compounds [3] that

TABLE 1

WEIGHTING FUNCTIONS, CORRELATION PARAMETERS AND SCALE FACTORS

Compound	Camera height (mm)	dols (nm^{-1})	s_{min}	s_1	s_2	s_{max}	P/h	Scale factor
$SiH_3Mn(CO)_5$	250	4	68	108	250	280	0.4448	1.056 ± 0.038
	500	2	36	60	135	155	0.4763	1.168 ± 0.029
	1000	1	10	17.5	62.5	70	0.4920	0.900 ± 0.047
$GeH_3Mn(CO)_5$	250	4	68	108	248	288	0.4207	1.007 ± 0.033
	500	2	28	53	130	150	0.2475	0.007 ± 0.020
	1000	1	12	20	65	73	0.4587	0.851 ± 0.030

$d \rightarrow d$ π-bonding is not important in the silicon—manganese and germanium—manganese bonds and that the main effect in changing from methyl to germyl to silyl is an increase in the strength of the σ bond.

Experimental

Samples of silylmanganese and germylmanganese pentacarbonyl were prepared by reacting silyl iodide or germyl bromide with sodiummanganese pentacarbonyl in diethyl ether [4, 5]. The products were collected at 77 K and purified by fractional condensation. Purities were checked spectroscopically.

Scattering intensities were recorded photographically using a Balzers KDG2 gas diffraction apparatus and were digitised on a Joyce Loebl microdensitometer. During exposures the samples were kept at 323 K [$SiH_3Mn(CO)_5$] and 328 K [$GeH_3Mn(CO)_5$] and the nozzle at 333 K. Three nozzle to plate distances were used (1000, 500 and 250 mm) giving data over a range of the scattering variable, s, of about 10-300 nm^{-1}.

Calculations were carried out on an IBM 370/155 computer at the Edinburgh Regional Computing Centre with data reduction and least squares refinement programs previously described [6, 7].

Table 1 shows weighting points (used to set up the off diagonal weight matrix), correlation parameters and scale factors. The complex scattering factors of Cox and Bonham [8] were used and all distances are r_a. The electron wavelength used was determined by direct measurement of the accelerating voltage and from the diffraction pattern of powdered thallous chloride.

Molecular model

For the purposes of least squares refinements it was assumed for each molecule that the manganese pentacarbonyl group had local C_{4v} symmetry, the MH_3 group had local C_{3v} symmetry and all the manganese—carbon and carbon—oxygen bonded distances were equal; since there is a twelve fold barrier to rotation about the M—Mn bond, free rotation about this bond was assumed. These assumptions allowed the molecule to be described uning the 4 bonded distances and the following angles: H—M—H, $Mn—C_{eq}—O_{eq}$ and $C_{ax}—Mn—C_{eq}$.

The assumption that the manganese—carbon distances are equal for axial and equatorial carbons might have proved to be unjustified, but it is unlikely that the difference will be greater than the 4 pm found in methylmanganese pentacarbonyl and may be around 2 pm as in manganese pentacarbonyl hydride, or even less. Such small differences within the molecule would be very difficult to determine reliably by electron diffraction. There is no evidence for any asymmetry of the Mn—C peak in the radial distribution curves nor are the experimental Mn—C or Mn ... O amplitudes of vibration significantly greater than values found in other manganese pentacarbonyl derivatives.

Refinements

Silylmanganese pentacarbonyl

The silicon—manganese, manganese—carbon, and carbon—oxygen bonded

TABLE 2. MOLECULAR PARAMETERS FOR $MH_3Mn(CO)_5$

	$SiH_3Mn(CO)_5$		$GeH_3Mn(CO)_5$		
	Distance	Amplitude	Distance	Amplitude	Shrinkage correction
a. Independent distances					
r_1(C—O)	113.2 (0.3)	4.2 (0.8)	113.9 (0.2)	4.3 (0.8)	
r_2(Mn—C)	184.7 (0.2)	7.5 (0.6)	184.9 (0.2)	6.8 (0.6)	
r_3(Mn—M)	240.7 (0.5)	7.4 (0.9)	248.7 (0.2)	5.7 (0.6)	
r_4(M—H)	149.0 (fixed)	8.5 (fixed)	153.5 (fixed)	12.0 (fixed)	
b. Dependent distances					
d_5(Mn···O_{ax})	297.4 (1.0)	8.2 (0.6)	298.2 (1.0)	6.8 (0.6)	0.59
d_6(Mn···O_{eq})	297.4 (1.0)		298.2 (1.0)		0.59
d_7(C_{eq}···O_{eq})	474.2 (1.7)	11.5 (1.4)	478.2 (1.5)	8.5 (1.3)	2.27
d_8(O_{eq}···O_{eq})	590.6 (2.0)		590.0 (2.0)		3.42
d_9(C_{eq}···C_{eq})	367.0 (1.1)		365.9 (1.1)		1.33
d_{10}(C_{eq}···C_{eq})	271.2 (0.6)	10.7 (1.4)	276.3 (0.6)	15.9 (fixed)	0.25
d_{11}(C_{eq}···C_{ax})	260.1 (0.7)		259.4 (0.7)		0.25
d_{12}(O_{eq}···O_{eq})	436.0 (0.7)	28.7 (3.6)	445.5 (1.4)	27.7 (fixed)	1.40
d_{13}(O_{eq}···O_{ax})	418.6 (1.4)		418.1 (1.4)		1.40
d_{14}(C_{eq}···O_{eq})	362.0 (0.7)	18.4 (0.9)	368.8 (0.7)	19.3 (fixed)	0.82
d_{15}(C_{ax}···O_{eq})	362.0 (0.7)		368.8 (0.7)		0.82
d_{16}(C_{eq}···O_{ax})	348.8 (1.0)		348.4 (1.0)		0.82
d_{17}(M···C_{ax})	424.0 (1.1)	19.4 (7)	432.2 (1.0)	7.1 (1.5)	1.43
d_{18}(M···O_{ax})	536.3 (1.5)	21.7	545.1 (1.4)	7.9	2.38
d_{19}(M···C_{eq})	291.3 (1.4)	25.0 (fixed)	291.9 (0.8)	15.5 (1.0)	0.28
d_{20}(M···O_{eq})	367.0 (1.8)	36.0	364.5 (1.4)	19.4	0.00
d_{21}(H···Mn)	322.9 (0.9)	12.0 (fixed)	333.3 (1.0)	12.0 (fixed)	0.59
d_{22}(H···C_{ax})	494.3 (1.1)	15.0 (fixed)	504.8 (1.3)	15.0 (fixed)	2.27
d_{23}(H···O_{ax})	602.6 (1.8)	18.0 (fixed)	613.6 (1.7)	18.0 (fixed)	3.42
d_{24}(H···H)	242.4 (0.2)	10.0 (fixed)	240.7 (0.7)	10.0 (fixed)	0.07
(H···C_{eq})	Between 282.0 and 423.4		Between 286.0 and 427.7		
(H···O_{eq})	Between 313.7 and 508.5		Between 309.7 and 510.5		
c. Independent angles					
< 1 (H—M—H)		110° (fixed)		110° (fixed)	
< 2 (C_{ax}—Mn—C_{eq})		94.5° (2°)		97° (2°)	
< 3 (Mn—C_{eq}—O_{eq})		180° (fixed)		180° (fixed)	

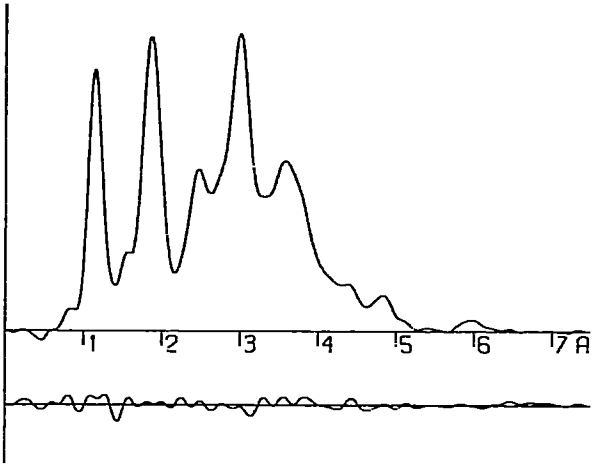

Fig. 1. Radial distribution curve, $P(r)/r$, and final deviations between experimental and theoretical curves for $SiH_3Mn(CO)_5$. Before Fourier inversion the data were multiplied by $s.\ \exp(-0.0025\ s^2)/(Z_{Mn}-F_{Mn})(Z_O-F_O)$.

distances and their amplitudes of vibration all refined satisfactorily, as did the Mn—C—O and C—Mn—C angles. The overlapping of large numbers of peaks in the radial distribution curve (Fig. 1) necessitated the refinement of certain groups of vibrational amplitudes as single parameters (see Table 2). Most groups, other than those involving hydrogen atoms, refined satisfactorily; the amplitudes of vibration of the silicon to axial carbon and silicon to axial oxygen being the only exceptions. These amplitudes along with all parameters involving hydrogen were set at fixed values.

The final *R* factor was 0.16. Table 3 shows the least squares correlation matrix, and final molecular scattering intensity and difference curves are shown in Fig. 2. The intensity data or uphill curves may be obtained from the authors on request.

Germyl manganese pentacarbonyl

The refinements were very similar to those of silylmanganese pentacarbonyl. The germanium—manganese, carbon—manganese and carbon—oxygen bonded distances and their amplitudes of vibration and the Mn—C—O and C—Mn—C angles all refined satisfactorily.

Here also there is considerable overlapping in the radial distribution curve (Fig. 3) which necessitated the constraint of certain groups of amplitudes (Table 2). Amplitudes of vibration involving right angled carbon···carbon, carbon···oxygen and oxygen···oxygen distances did not refine, nor did any parameters involving hydrogen. These parameters were set at fixed values. The final *R* factor was 0.13.

Table 4 shows the least squares correlation matrix, and final molecular scattering intensity and difference curves are shown in Fig. 4. The intensity data or uphill curves can be obtained from the authors on request.

Shrinkage corrections applied were the same as those applied in the structure determination of pentacarbonyl(trifluorophosphine)molybdenum [7].

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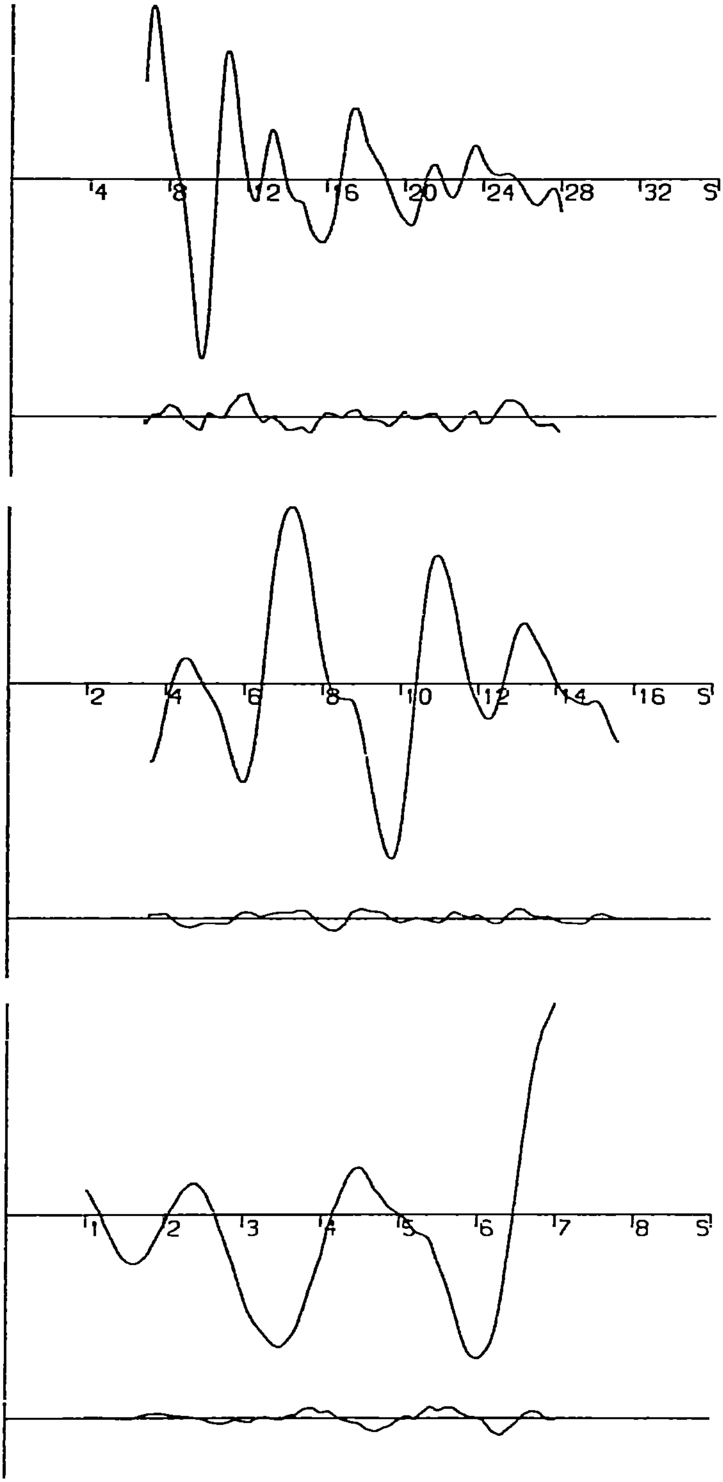

Fig. 2. Observed and final weighted difference molecular intensities for $SiH_3Mn(CO)_5$ for data sets obtained with nozzle-to-plate distances of 250, 500 and 1000 mm.

TABLE 3

LEAST SQUARES CORRELATION MATRIX MULTIPLIED BY 1000 FOR $SiH_3Mn(CO)_5$

R_1	R_2	R_3	<2	U_1	U_2	U_3	U_5	U_7	U_{10}	U_{12}	U_{14}	U_{17}	K_1	K_2	K_3
1000	−23	−114	−635	11	70	6	71	19	60	77	108	30	27	142	84
	1000	−15	−481	9	33	−11	38	2	19	20	−79	52	46	−7	−30
		1000	47	−33	−94	195	53	−57	272	23	−18	1	−49	−97	−40
			1000	−78	−141	16	−87	−6	50	−150	−268	−19	−145	−160	−30
				1000	459	109	374	124	−69	16	188	1	586	438	52
					1000	39	467	152	−113	17	230	0	682	589	104
						1000	228	89	542	28	1	0	195	123	−52
							1000	146	258	19	59	7	602	502	104
								1000	−23	472	3	−422	188	199	86
									1000	22	−170	11	−106	−116	−16
										1000	167	−756	33	12	−25
											1000	−137	292	260	−56
												1000	14	−27	−74
													1000	572	72
														1000	52
															1000

TABLE 4

LEAST SQUARES CORRELATION MATRIX MULTIPLIED BY 1000 FOR $GeH_3Mn(CO)_5$

R_1	R_2	R_3	< 2	U_1	U_2	U_3	U_5	U_7	U_{17}	U_{19}	K_1	K_2	K_3
1000	51	25	−606	8	85	54	42	83	16	−95	18	101	96
	1000	−59	−615	38	112	134	107	48	59	50	113	122	85
		1000	−120	−65	−181	−28	−36	−44	−29	−224	−92	−146	−178
			1000	−83	−177	−156	−46	−89	−30	−132	−150	−225	−140
				1000	445	335	259	117	100	318	530	511	157
					1000	410	338	151	124	384	624	656	247
						1000	176	118	104	344	579	496	135
							1000	161	113	−131	480	369	86
								1000	−65	−3	199	172	92
									1000	49	180	136	5
										1000	438	542	293
											1000	636	227
												1000	258
													1000

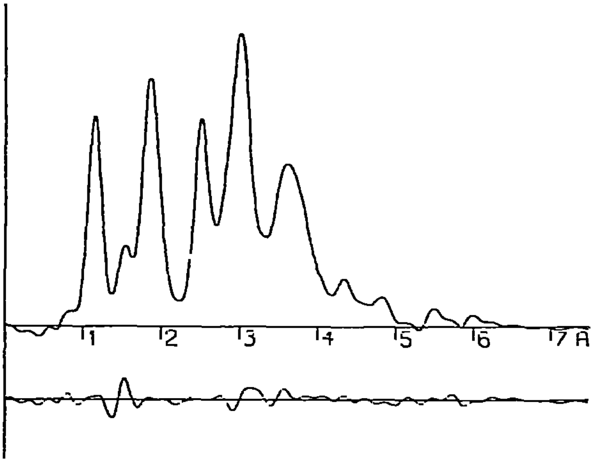

Fig. 3. Radial distribution curve, P(r)/r, and final differences between experimental and calculated curves for $GeH_3Mn(CO)_5$. Before Fourier inversion the data were multiplied by $s.\ \exp(0.0025\ s^2)/(Z_{Mn}-F_{Mn})(Z_O-F_O)$.

Discussion

In methylmanganese pentacarbonyl the covalent radius of manganese has been found to be 141.8 pm [2]. Using this, and taking the covalent radii of silicon and germanium to be 110.0 and 117.8 pm respectively (calculated from bond lengths between tetrahedrally coordinated atoms in ethane [9], methylsilane [10] and methylgermane [11]), we would expect the silicon—manganese bond length to be 251.9 pm and the germanium—manganese bond length to be 259.6 pm. In fact these two bond lengths turn out as 240.7 and 248.7 pm respectively.

These two bond lengths could be taken to indicate that multiple bonding does exist between the manganese and silicon or germanium atoms in these compounds. This multiple bonding would involve the π 3*d* orbitals of manganese and the 3*d* (or 4*d*) π-orbitals of silicon (or germanium). However, He^I photoelectron spectra of these compounds [3] indicate that the main change in going from a methyl to a silyl to a germyl substituent on manganese pentacarbonyl is a σ effect, and that silyl is a slightly better σ acceptor than germyl which is a much better σ acceptor than methyl; that is, silyl is slightly more electropositive than germyl which is very much more electropositive than methyl. This theory would also lead to similar results to those we have found here. We intend to make further studies to find out more about these effects.

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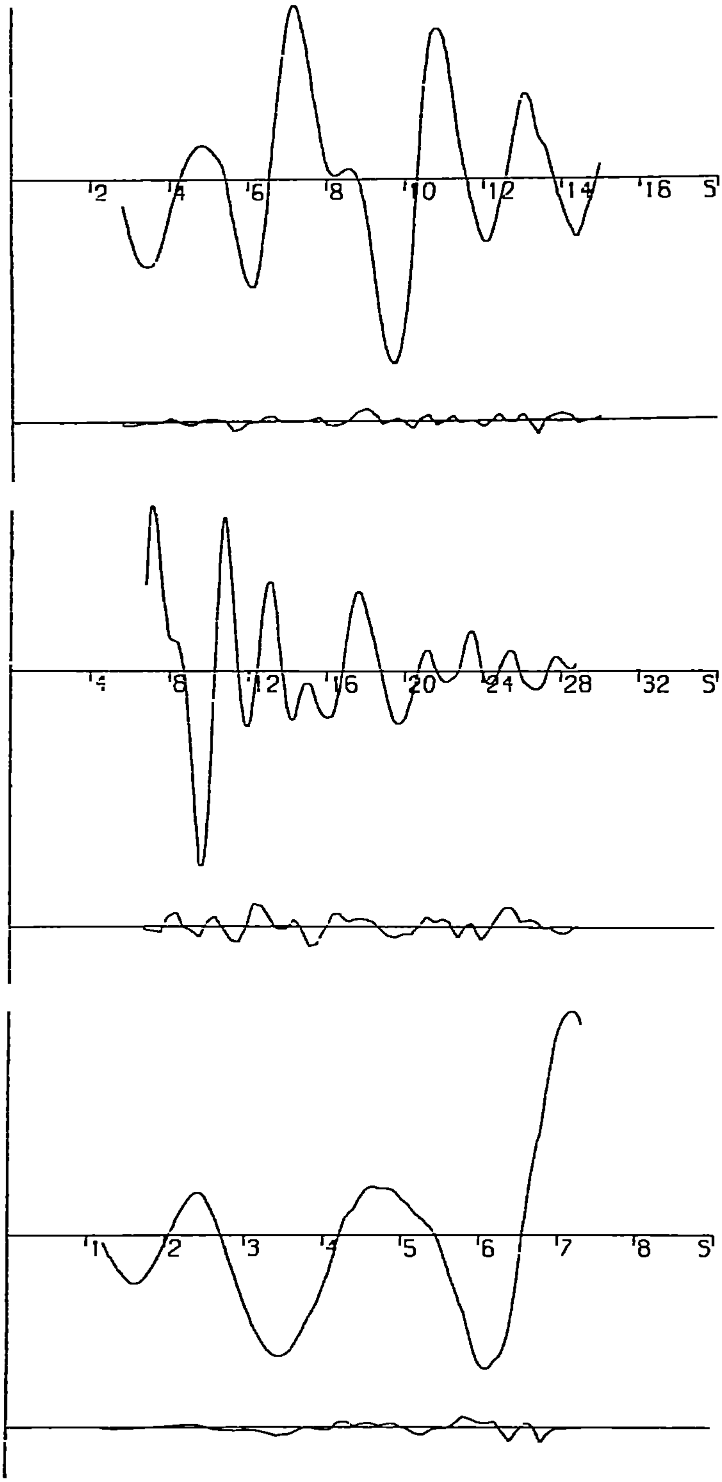

Fig. 4. Observed and final weighted difference molecular intensities for $GeH_3Mn(CO)_5$ for data sets obtained with nozzle-to-plate distances of 250, 500 and 1000 mm.

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