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On the Diamagnetic Susceptibility of some Group IVB Organometallic Halides

H. WILLEMEN, D. F. VAN DE VONDEL and G. P. VAN DER KELEN*

Laboratory for General and Inorganic Chemistry-B, University of Ghent, Krijgslaan 271, B-9000 Ghent, Belgium

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The diamagnetic susceptibility of a series of methyl–group IVB halides has been measured. By the method of Dorfman the pure Langevin diamagnetic contribution (χ_M^d) and the temperature independent paramagnetic contribution (χ_M^p) could be separately determined. This greatly improved the information obtainable from these data. The χ_M^p term could be interpreted in terms of steric hindrance, (p–d)π bonding and polymerisation effects.

Introduction

The metal–halogen bond in methyl–group IVB halides has been studied since many years in our laboratory. In this paper we report the results obtained from diamagnetic susceptibility measurements for the compounds with the general formula $(CH_3)_{4-n}MeX_n$, where Me = Si, Ge or Sn and X = Cl, Br and I. For the sake of simplicity all the susceptibility data are multiplied by -10^6 and expressed in c.g.s. units.

Experimental

The preparation and purification of the compounds was done by well known methods [1–3]. In order to prevent hydrolysis and the presence of molecular oxygen, all manipulations were carried out under a nitrogen atmosphere.

The susceptibilities were measured by the Faraday method, using a Brucker B-E 15C 8 electromagnet and a Cahn R.G. 2050 electrobalance. Carefully purified benzene ($\chi_g = 0.702$) [4] was used as a standard for the measurements. For cyclohexane ($\chi_g = 0.7868$) [5] we obtained $\chi_g = 0.7925$, for water saturated with air ($\chi_g = 0.719$) [6] $\chi_g = 0.7195$ and for $(nbut)_4Sn$ ($\chi_g = 0.6642$) [7] $\chi_g = 0.6655$. From these data we can trust that our results are accurate to better than 1%. The molecular refraction data were determined with a Pulfrich refractometer.

TABLE I. $-\chi_M \times 10^6$ for the Methyl Halogen Compounds of Group IVB Elements in c.g.s. Units.

Compound	X = Cl	X = Br	X = I
$(CH_3)_4Si$ [8]	74.9	74.9	74.9
$(CH_3)_3SiX$ [8]	79.0	91.3	104.1
$(CH_3)_2SiX_2$ [8]	81.3	–	131.8
$(CH_3)SiX_3$ [8]	87.45	115.5	–
SiX_4 [8]	87.4	123.3	186.2
$(CH_3)_4Ge$	84.5	84.5	84.5
$(CH_3)_3GeX$	90.3	98.5	–
$(CH_3)_2GeX$	91.6 [7]	107.0	138.2
$(CH_3)GeX_3$	95.1	120.5	158.25
GeX_4	99.0	129.2	170.9
$(CH_3)_4Sn$	100.1 [7]	100.1	100.1
$(CH_3)_3SnX$	101.1	112.5	130.7
$(CH_3)_2SnX_2$	102.8	121.3	153.5
$(CH_3)SnX_3$	107.7	129.8	172.1
SnX_4	117.3	148.8	195.6

Results

The molar susceptibilities for the germanium and tin compounds measured in this work are given in Table I, together with the results from M. W. Lister and R. Marson [8] for the silicon analogues. No measurement was performed for $(CH_3)_3GeI$, due to the instability of this compound.

Discussion

The diamagnetic susceptibility is often interpreted in terms of an additivity scheme. P. Pascal [10] expressed the susceptibility as a sum of atomic contributions and corrections due to structural characteristics of the molecule. Pacault and Hoarau [1] selected values for the atomic contributions. Through a linear regression analysis we obtained a linear rela-

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*Author to whom correspondence should be addressed.

TABLE II. Bond Distances and Mutual Distortions in $(CH_3)_{4-n}MeX_n$ Compounds.[a]

Bond	r_{Me-L} [16]	δ_{L-L}	ω_{L-L}	δ_{R-X}	ω_{R-X}
Si–C	1.85	3.01	0.99		
Si–Cl	2.02	3.29	0.31	3.16	0.64
Si–Br	2.16	3.52	0.38	3.28	0.67
Si–I	2.44	3.98	0.32	3.52	0.63
Ge–C	1.94	3.16	0.84		
Ge–Cl	2.10	3.42	0.18	3.30	0.50
Ge–Br	2.30	3.75	0.15	3.43	0.52
Ge–I	2.48	4.04	0.26	3.62	0.53
Sn–C	2.16	3.52	0.48		
Sn–Cl	2.33	3.80	−0.20	3.31	0.49
Sn–Br	2.46	4.00	−0.10	3.78	0.17
Sn–I	2.69	4.38	−0.08	3.97	0.18

[a] L = methyl (R) or halogen (X); van der Waals radius of Cl = 1.80, Br = 1.95, I = 2.15 and CH_3 = 2.00 [17].

tion between the χ_M values and the degree of substitution n for all series except for the $(CH_3)_{4-n}SnCl_n$ compounds.

$(CH_3)_{4-n}SiCl_n : \chi_M = 75.3 + 3.4\,n$
$(CH_3)_{4-n}SiBr_n : \chi_M = 77.05 + 12.1\,n$
$(CH_3)_{4-n}SiI_n : \chi_M = 75.7 + 27.1\,n$
$(CH_3)_{4-n}GeCl_n : \chi_M = 85.3 + 3.5\,n$
$(CH_3)_{4-n}GeBr_n : \chi_M = 85.6 + 11.1\,n$
$(CH_3)_{4-n}GeI_n : \chi_M = 88.3 + 22.1\,n$
$(CH_3)_{4-n}SnBr_n : \chi_M = 99.56 + 11.5\,n$
$(CH_3)_{4-n}SnI_n : \chi_M = 103.92 + 23.2\,n$

The coefficients of n should equal the difference in the atomic contribution of the methyl group *versus* that of the halogen atom. According to Pacault and Hoarau the difference in contribution to χ_M between a CH_3 group and a halogen (X) is equal to 4.55, 14.15 and 29.75 respectively for X = Cl, Br and I. These values exceed those found by us. Moreover these coefficients should also be independent of the central metal for a given halogen atom which is also not found. As we shall see a little further this last condition can be better fulfilled.

Another additivity rule [12] considers, besides atomic contributions, also bond contributions and bond–bond interactions. A third approach to the problem of additivity is based on the theoretical calculation [13] of three separate contributions: 1) from the inner electron shells of each atom present, 2) from the bonding electrons in each bond and 3) from the nonbonding lone-pair electrons present in the outer shells. None of these rules proved to yield consistent results in the case of the methyl–group IVB halides studied by us [14].

For CX_4 compounds with X = halogen, P. Pascal [15] derived a relation between Δ, the diamagnetic anomaly (= difference between the calculated molar susceptibility using his simple additivity rule, and the observed molar susceptibility), α, the polarisability of the halogen atoms and ω, the mutual distortion of geminal atoms:

$$9.48\cdot\alpha\cdot\omega = \Delta\cdot 10^{-20} \tag{1}$$

The distance $\delta_{LL'}$ between the centre of two ligands bonded to the central metal can be easily calculated:

$$\delta^2_{LL'} = r^2_{Me-L} + r^2_{Me-L'} - 2r_{Me-L}r_{Me-L'}\cos 109°28' \tag{2}$$

with r_{Me-L} the metal–ligand bond length. The mutual distortion $\omega_{L,L'}$ can be calculated as:

$$\omega_{L,L'} = r_L + r_{L'} - \delta_{LL,} \tag{3}$$

with r_L the vander Waals radius of the ligand. The different mutual distortions that should be considered in $(CH_3)_{4-n}MeX_n$ compounds are summarized in Table II.

The data from Table II show clearly the importance of the methyl groups, since the interaction between either two methyl groups or between a halogen atom and a methyl group is much more pronounced that between two halogens.

According to Van Vleck the molar susceptibility should be considered as the sum of two contributions – a pure diamagnetic term and a temperature independent paramagnetic contribution:

$$\chi_M = \chi^d_M + \chi^p_M \tag{4}$$

Following Dorfman [5] we have calculated the diamagnetic contribution χ^d_M from the expression:

TABLE III. The Diamagnetic and Paramagnetic Terms ($\times -10^6$) for the Methyl–Halogen Compounds of Group IVB According to the Dorfman Method.

Compound	χ_M	R_M	$\alpha \times 10^{24}$	χ^d_M	$-\chi^p_M$
$(CH_3)_4Si$	74.9	30.21 [21]	11.99	76.16	1.3
$(CH_3)_3SiCl$	79.0	29.90 [19]	11.87	81.60	2.6
$(CH_3)_2SiCl_2$	81.3	29.60 [22]	11.75	86.61	5.3
CH_3SiCl_3	87.45	29.10 [22]	11.55	90.92	3.5
$SiCl_4$	87.40	29.00 [23]	11.51	95.54	8.1
$(CH_3)_3SiBr$	91.3	33.00 [24]	13.10	98.13	6.8
$(CH_3)_2SiBr_2$	–	35.88 [24]	14.24	118.53	–
CH_3SiBr_3	115.5	38.17 [24]	15.15	136.95	21.45
$SiBr_4$	123.3	40.82 [25]	16.21	155.36	32.06
$(CH_3)_4Ge$	84.5	32.070	12.73	91.5	7.0
$(CH_3)_3GeCl$	90.5	31.20 [1]	12.39	95.4	4.9
$(CH_3)_2GeCl_2$	91.6	32.52 [1]	12.91	102.4	10.8
$(CH_3)GeCl_3$	95.1	32.16 [1]	12.77	106.6	11.5
$GeCl_4$	99.0	31.598 [18]	12.54	110.1	11.1
$(CH_3)_3GeBr$	98.5	36.6 [19]	14.53	114.94	16.4
$(CH_3)_2GeBr_2$	107.0	37.31 [3]	14.81	131.1	24.1
CH_3GeBr_3	120.5	39.58 [3]	15.71	148.9	28.4
$GeBr_4$	129.9	44.421 [18]	17.64	171.3	42.1
$(CH_3)_4Sn$	100.1	36.861	14.63	110.3	10.2
$(CH_3)_3SnCl$	101.1	39.02 [2]	15.49	118.7	17.6
$(CH_3)_2SnCl_2$	102.8	39.20 [2]	15.56	123.9	21.1
CH_3SnCl_3	107.7	39.42 [2]	15.65	129.0	21.3
$SnCl_4$	117.3	35.228 [18]	13.99	126.4	9.1
$(CH_3)_3SnBr$	112.5	36.73 [2]	14.58	125.7	13.2
$(CH_3)_2SnBr_2$	121.3	40.17 [2]	15.95	145.9	24.6
CH_3SnBr_3	129.8	45.39	18.00	168.97	39.2
$SnBr_4$	148.8	48.633 [2]	19.31	188.4	39.6
$(CH_3)_3SnI$	130.7	39.47 [2]	15.67	140.4	9.7
$(CH_3)_2SnI_2$	153.5	52.10 [2]	20.68	186.6	33.1
CH_3SnI_3	172.1	55.53 [2]	22.04	215.6	43.5
SnI_4	195.6	80.50 [20]	31.96	256.0	60.4

$$\chi^d_M = -3.11 \times 10^6 \sqrt{\alpha k} \qquad (5)$$

k is the number of electrons present in the molecule; α is the polarisability, which can be calculated from the experimentally determined molecular refraction:

$$R_M = \frac{4\pi N}{3}\alpha \qquad (6)$$

Using equations 4, 5, 6 and the values from Table I for χ_M, one obtains χ^p_M. The values for R_M, α, χ_M, χ^d_M and χ^p_M for $(CH_3)_{4-n}MeX_n$ compounds are collected in Table III.

Linear regression of χ^d_M *versus* n gives the following equations:

$(CH_3)_{4-n}SiCl_n$: $\chi^d_M = 76.55 + 4.81\,n$

$(CH_3)_{4-n}SiBr_n$: $\chi^d_M = 77.58 + 19.72\,n$

$(CH_3)_{4-n}GeCl_n$: $\chi^d_M = 91.52 + 4.84\,n$

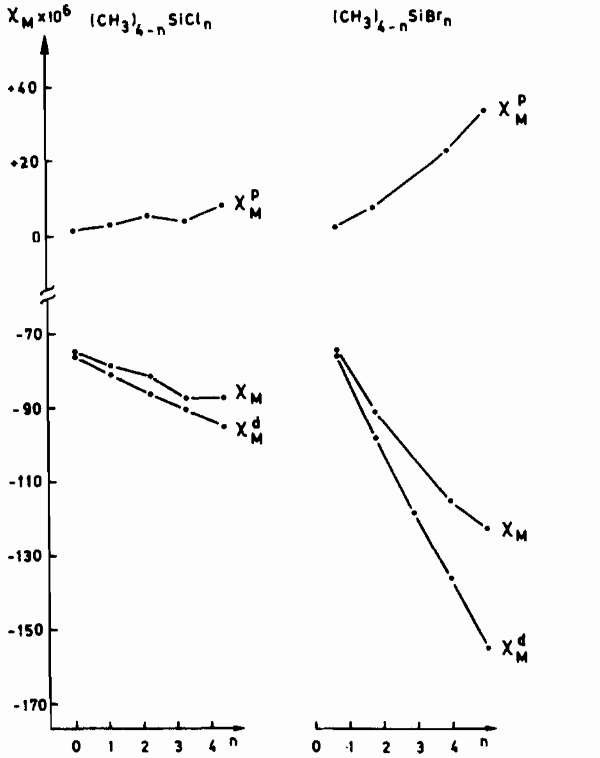

Fig. 1. χ_M, χ_M^d and χ_M^p as a function of n for the series $(CH_3)_{4-n}SiX_n$ with X = Cl or Br.

Fig. 2. χ_M, χ_M^d and χ_M^p as a function of n for the series $(CH_3)_{4-n}GeX_n$ with X = Cl or Br.

$(CH_3)_{4-n}GeBr_n$: $\chi_M^d = 92.84 + 19.36\,n$

$(CH_3)_{4-n}SnBr_n$: $\chi_M^d = 107.96 + 19.95\,n$

$(CH_3)_{4-n}SnI_n$: $\chi_M^d = 108.46 + 36.66\,n$

From the coefficients of n it is clear that the diamagnetic contribution is additive, except for the $(CH_3)_{4-n}SnCl_n$ series. The additivity seems now to hold even irrespective of the central metal atom.

A loss of electron symmetry results, according to Dorfman, in an increased Van Vleck paramagnetism. In this respect the non negligible paramagnetic term found for the tetramethyl derivates which increases on going from silicon to tin is remarkable and could tentatively be ascribed to steric effects. In this case, however, it should decrease from Si to Sn as follows from the ω_{L-L} (L = R) values from Table II. On the other hand, P. Pascal suggested that an increasing polarisability of the halogen atoms results in an increased diamagnetic anomaly (see equation 1), with the assumption that the polarisability of the carbon atom is negligible. For the group IVB metals the polarisability increases with increasing atomic number. The increase in χ_M^p for the tetramethyl derivates on going from Si to Sn may therefore be attributed to the change in polarisability of the central metal.

Substitution of a methyl group by a halogen atom should decrease χ_M^p. This is the case for only two compounds, $(CH_3)_3GeCl$ and $(CH_3)_3SnI$. For the other compounds, instead, χ_M^p increases on further halogen substitution. This can be explained by accepting a (d–p)π bonding between the central metal and the halogen atom. The lowering of the C_∞ symmetry for a σ bond to the C_{2v} symmetry for a double bond, results in an increasing Van Vleck paramagnetism. From Figures 1, 2 and 3 it is clear that this double bonding occurs for the series $(CH_3)_{4-n}GeCl_n$ and $(CH_3)_{4-n}SnI_n$ from n = 2, and for the other series from n = 1. Moreover this effect is stronger in the iodides than in the bromides and rather small in the chlorides.

The $(CH_3)_{4-n}SnCl_n$ series shows a different pattern for χ_M^p as a function of n. It is however known [26] that tin can adopt 5 or 6 coordination through polymerization in these compounds, resulting in a lower symmetry than the tetrahedral $(CH_3)_4Sn$ or $SnCl_4$ compounds.

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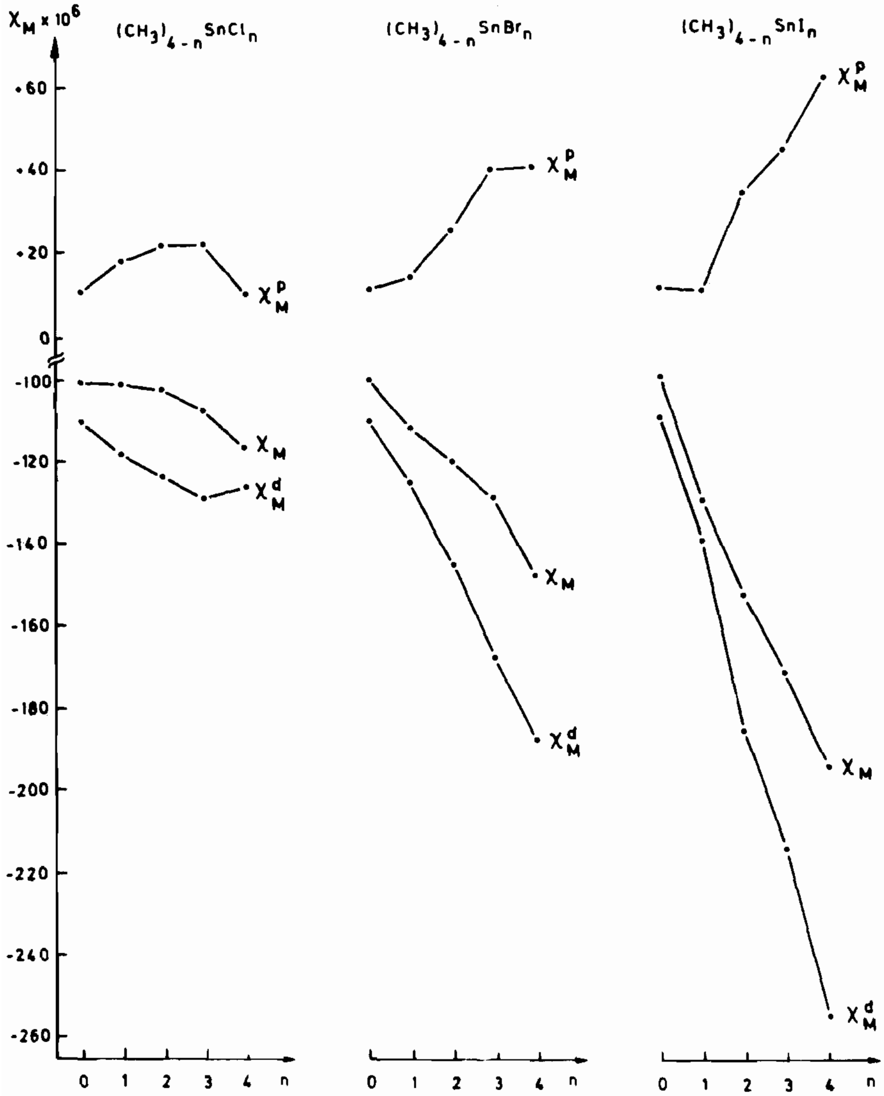

Fig. 3. χ_M, χ_M^d and χ_M^p as a function of n for the series $(CH_3)_{4-n}SnX_n$ with X = Cl, Br or I.

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