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Molecular Force Fields and Bonding in Methylchlorogallate and Methylchloroindate Ions: $|R_{4-n}M^{III}Cl_n|^-$; $R=CH_3$ or CD_3; $M^{III}=Ga$ or In; $n=0-4$

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The infrared and Raman spectra of the deutero-methylchlorometallates $|(CH_3)_4As||(CD_3)_{4-n}M^{III}Cl_n|$; $M^{III}=Ga$ or In and $n=1$ to 3 have been recorded for the solid state and interpreted on the basis of C_{3v} or C_{2v} symmetry for the metallate ions. Simple valence molecular force fields for the series have been determined by least squares calculations on these spectra and the spectra of the undeuterated analogues previously reported. Both M – Cl and M – C stretching force constants increase markedly and monotonically with increasing chlorine substitution across the series $|(CH_3)_{4-n}M^{III}Cl_n|^-$; $n=0$ to 4. These variations are correlated with observed changes in M – Cl and M – C bond distances, and rationalized as a combination of inductive and resonance effects.

The preparation and the vibrational spectra of the solid compounds $[(CH_3)_4M^V][(CH_3)_{4-n}M^{III}Cl_n]^-$, where $M^V=As$ or Sb, $M^{III}=Ga$ or In and $n=0$, 1, 2, 3 or 4 have been described by us some years ago.[1] A number of these compounds have also been studied by X-ray crystallography,[2-7] and the average bond distances and valence angles of the anions are listed in Table 2. As pointed out by Hausen and coworkers,[4-6] the average M – Cl bond distance in the anions decreases monotonically with increasing Cl substitution: The decrease on going from $[(CH_3)_3MCl]^-$ to $[MCl_4]^-$ is about 0.21 Å when M = Ga and about 0.22 Å when M = In. The variation of the M – C bond distances is less clear, both because the error limits of the M – C bond distances are larger, and because the variation of the M – C bond distances with increasing Cl substitution is smaller. But comparison of the structures of the ions $[(CH_3)_4In]^-$ and $[(CH_3)InCl_3]^-$ suggests that the total change of the M – C bond distance across the series is about 0.06 Å.

We have previously carried out normal coordinate analysis of the isoelectronic species $[(CH_3)_4M^{III}]^-$, $M^{III}=Al$, Ga and In, $(CH_3)_4M^{IV}$, $M^{IV}=Si$, Ge and Sn and $[(CH_3)_4M^V]^+$, $M^V=P$, As and Sb[8] and discussed variations in the force fields. We were now interested in investigating how the force fields vary across the series $[(CH_3)_{4-n}M^{III}Dl_n]^-$ and have supplemented the IR and Raman spectra quoted in Ref. 1 with spectra of the fully deuterated species before carrying out normal coordinated analysis.

EXPERIMENTAL

The deuterated starting materials $(CD_3)_3Ga\cdot O(C_2H_5)_2$ and $(CD_3)_3In$ were prepared by Grignard reactions from CD_3I and Ga/Mg or In/Mg alloys in diethyl ether. Both compounds were purified by vacuum distillation. Reaction of these deuterated derivatives with stoichiometric amounts of $GaCl_3$ or $InCl_3$ yielded $(CD_3)_2GaCl$ or $(CD_3)_2InCl$ of high purity.

The deuterated methylchlorometallates were prepared by the following reactions as described in Ref. 1:

$$(CH_3)_3AsCl_2+(CD_3)_2M^{III}Cl\rightarrow [(CH_3)_3As(CD_3)]^+[(CD_3)M^{III}Cl_3]^-$$

$$(CH_3)_4AsCl+(CD_3)_2M^{III}Cl\rightarrow [(CH_3)_4As]^+[(CD_3)_2M^{III}Cl_2]^-$$

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$(CH_3)_4AsCl + (CD_3)_3In \rightarrow$
$[(CH_3)_4As]^+[(CD_3)_3InCl]^-$
$(CH_3)_4AsCl + (CD_3)_3Ga \cdot O(C_2H_5)_2 \rightarrow$
$[(CH_3)_4As]^+[(CD_3)_3GaCl]^- + O(C_2H_5)_2$
$M^{III} = Ga,\ In$

The products were purified by one recrystallization from CH_2Cl_2.

Elemental analysis for C, H and Cl were performed by usual methods, the Ga or In content was determined by titration with Titriplex III. The yields listed in Table 1 refer to the alkyl metal component. IR spectra were taken of Nujol or Hostaflon mulls, pressed as capillary films between CsBr plates, and recorded with a Perkin-Elmer PE 283 spectrometer. Raman spectra were measured on a PH O spectrophotometer of Coderg, Inc.; for excitation, the bluegreen (4880 Å) line of an Argon laser was employed.[9]

NORMAL COORDINATE ANALYSIS

For each of the species under consideration a valence force field was defined using the pertinent members of the following set: Stretching force constants $f(M-C)$ and $f(M-Cl)$ and stretch/stretch interaction force constants $f(MC/MC')$, $f'(MC/MCl)$ and $f'(MCl/MCl')$; Bending force constants $f(CMC)$, $f(CMCl)$ and $f(ClMCl)$; Methyl group force constants $f(C-H)$ (stretch), $f(MCH)$ and $f(HCH)$ (bend) and $f'(MCH/MCH')$ (interaction). The framework bond distances and valence angles are listed in Tables 2a and 2b. All C–H bond distances were fixed at 1.08 Å and all M–C–H angles were assumed to be tetrahedral.

Normal coordinate analysis was carried out using a program written by Hilderbrandt[10] which allows the force constants to be refined by least-squares calculations on the observed vibrational frequencies by an iterative procedure. The best values for the force constants are listed in Tables 2a and 2b, and observed and calculated frequencies are compared in Tables 3a and 3b. In Tables 2a and 2b we also include the values for the force constants previously obtained for the species $[(CH_3)_4M]^-$,[8] and the force constants obtained for $[GaCl_4]^-$ and $[InCl_4]^-$ using the observed frequencies of Chemouni[11] and Contreras and Tuck.[12]

DISCUSSION

Inspection of the M–Cl and M–C stretching force constants in Tables 2a and 2b, reveals that the

Table 1. Preparation and elemental analysis data.

Starting materials $(CD_3)_2M^{III}Cl$ or $(CD_3)_3M^{III}$ g (mmol)	$(CH_3)_3AsCl_2$ or $(CH_3)_4AsCl$ g (mmol)	Product	Yield (%)	Elemental analysis, found (calc.) (%) Metal	C	H+ 1/2D	Cl
0.46 (3.26)	0.62 (3.25)	$[(CH_3)_3AsCD_3][CD_3GaCl_3]$	92	21.22 (20.99)	18.01 (18.08)	4.60 (4.55)	31.95 (32.01)
0.57 (3.06)	0.58 (3.04)	$[(CH_3)_3AsCD_3][CD_3InCl_3]$	88	30.1 (30.43)	16.01 (15.92)	4.08 (4.01)	28.21 (28.19)
0.44 (3.11)	0.52 (3.05)	$[(CH_3)_4As][(CD_3)_2GaCl_2]$	80	22.41 (22.36)	23.30 (23.11)	5.86 (5.82)	22.81 (22.74)
0.68 (3.65)	0.62 (3.64)	$[(CH_3)_4As][(CD_3)_2InCl_2]$	84	31.98 (32.17)	20.28 (20.19)	5.11 (5.08)	19.9 (19.87)
1.12[a] (5.65)	0.90 (5.28)	$[(CH_3)_4As][(CD_3)_3GaCl]$	68	23.91 (23.68)	28.17 (28.56)	6.98 (7.19)	11.92 (12.04)
1.06 (6.27)	1.07 (6.27)	$[(CH_3)_4As][(CD_3)_3InCl]$	74	33.6 (33.82)	24.81 (24.76)	6.30 (6.23)	10.56 (10.44)

[a] As $(CD_3)_3Ga \cdot O(C_2H_5)_2$.

Table 2a. Bond distances (in Å), stretching force constants (in mdyn/Å), valence angles (in deg) and bending force constants (in mdyn Å) for the ions $|(CH_3)_{4-n}GaCl_n|^-$.[a]

	$[(CH_3)_4Ga]^-$[2,8]	$[(CH_3)_3GaCl]^-$[1]	$[(CH_3)_2GaCl_2]^-$[3]	$[CH_3GaCl_3]^-$[3]	$[GaCl_4]^-$[4]
R(Ga−C)	2.2(2)	2.053(23)	1.980(13)	1.934(8)	
f(Ga−C)	1.87	2.24	2.56	2.80	
R(Ga−Cl)		2.381(8)	2.277(4)	2.222(3)	2.172(2)
f(Ga−Cl)		0.74	1.16	1.51	1.96
∠(CGaC)	109.5	115.2(10)	125.3(6)		
f(CGaC)	0.10	0.18	0.09		
∠(CGaCl)		102.9(10)	107.2(4)	114.3(6)	
f(CGaCl)		0.65	0.45	0.46	
∠(ClGaCl)			99.7(1)	104.3(2)	109.5
f(ClGaCl)			0.48	0.47	0.54
f′(GaC/GaC′)	0.12	0.14	0.12		
f′(GaC/GaCl)		0.17	0.16	0.12	
f′(GaCl/GaCl′)			0.11	0.18	0.18
f(C−H)	4.75	4.72	4.75	4.82	
f(HCH)	0.45	0.38	0.39	0.39	
f(GaCH)	0.28	0.35	0.36	0.38	
f′(GaCH/GaCH′)	−0.0045	−0.003	−0.0008	−0.011	

[a] The bond distances and valence angles have been averaged to yield species of T_d ($[(CH_3)_4Ga]^-$ and $[GaCl_4]^-$), C_{3v} ($[(CH_3)_3GaCl]^-$ and $[CH_3GaCl_3]^-$) and C_{2v} symmetry ($[(CH_3)_2GaCl_2]^-$). The estimated standard deviations listed are the average e.s.d's of crystallographically independent bond distances and valence angles.

Table 2b. Bond distances (in Å), stretching force constants (in mdyn/Å), valence angles (in deg) and bending force constants (in mdyn Å) for the ions $|(CH_3)_{4-n}InCl_n|^-$.[a]

	$[(CH_3)_4In]^-$[5,8]	$[(CH_3)_3InCl]^-$[1]	$[(CH_3)_2InCl_2]^-$	$[CH_3InCl_3]^-$[6]	$[InCl_4]^-$[7]
R(In−C)	2.239(3)	2.23(3)	(2.20)[b]	2.183(16)	
f(In−C)	1.57	1.94	2.19	2.41	
R(In−Cl)		2.551(7)	(2.45)[b]	2.400(3)	2.33(2)
f(In−Cl)		0.66	0.98	1.38	1.78
∠(CInC)	109.5	116.4(10)	(135)[b]		
f(CInC)	0.06	0.12	0.09		
∠(CInCl)		101.0(10)	(105.9)[b]	116.3	
f(CInCl)		0.58	0.45	0.36	
∠(ClInCl)			(99.0)[b]	102.0	109.5
f(ClInCl)			0.50	0.54	0.39
f(InC/InC′)	0.09	0.09	0.08		
f′(InC/InCl)		0.12	0.11	0.09	
f′(InCl/InCl′)			0.13	0.15	0.12
f(C−H)	4.75	4.78	4.76	4.77	
f(HCH)	0.45	0.35	0.36	0.36	
f(InCH)	0.25	0.33	0.34	0.38	
f′(InCH/InCH′)	−0.050	−0.003	−0.007	−0.078	

[a] See comments Table 2a. [b] Estimated values, see also data for $[(CH_3)_4As][(CH_3)_2InBr_2]$ in Ref. 13.

Table 3a. Observed and calculated frequencies (in $\mathrm{cm^{-1}}$) for the ions $[(CH_3)_{4-n}GaCl_n]^-$ and $[(CD_3)_{4-n}GaCl_n]^-$ with $n=1$, 2 or 3.

$[(CH_3)_4As]^+$ $[(CH_3)_3GaCl]^-$		$[(CH_3)_4As]^+$ $[(CD_3)_3GaCl]^-$ [a]		$[(CH_3)_4As]^+$ $[(CH_3)_2GaCl_2]^-$		$[(CH_3)_4As]^+$ $[(CD_3)_2GaCl_2]^-$		$[(CH_3)_4Sb]^+$ $[CH_3GaCl_3]^-$		$[(CH_3)_3AsCD_3]^+$ $[CD_3GaCl_3]^-$		Assignment (C_{3v} or C_{2v})
obs.[1,22]	calc.	obs.[9]	calc.	obs.[1,22]	calc.	obs.[9]	calc.	obs.[1]	calc.	obs.[9]	calc.	
2950	2976	2208	2213	2959	2986	2212	2221	2990	3003	2238	2234	$\nu_{as}CH_3(CD_3)$
2846	2862	2115	2056	2891	2871	2110	2063	2894	2887	2118	2076	$\nu_{s}CH_3(CD_3)$
1182 1178	1236 to 1164	943	933 to 892	1206 1200	1245 to 1171	950 (925)	948 to 898	1212 1204	1258 to 1189	943	967 to 908	$\delta_{s}CH_3(CD_3)$
734 724	723 to 713	539	545 to 530	740 725	744 to 738	568 545	560 to 551	758 740	761	598 578	573	$\rho CH_3(CD_3)$
541	547	490	481	582	591	532	518	591	598	535	522	ν GaC, A_1
513	525	n.o.	452	547	551	482	476					$\nu_{as}GaC_3(GaC_2)$,
242	238	230	234									$\nu_{s}GaC_3(GaC_2)$, νGaCl, A_1
				286	291	285	289	328	333	339	331	$\nu_{as}GaCl_3(GaCl_2)$
				301	292	289	291	334	331	333	329	$\nu_{s}GaCl_3(GaCl_2)$
172	170 E	n.o.	157	165	157 B	153	148	162	163 E	152	149	δ CGaC
148	147 A_1	n.o.	135	144	148 A_2 145 B	127	136 132	130	139 A_1	125	138	δ CGaCl
118	118 E	n.o.	105	133 119 107	122 A_1 111 A_1	107 95	114 106	118	115 E	119	115	δ ClGaCl

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[a] In the case of $[(CH_3)_4As][(CD_3)_3GaCl]$ only the IR spectra could be measured.

Table 3b. Observed and claculated frequencies (in cm^{-1}) for the ions $[(CH_3)_{4-n}InCl_n]^-$ and $[(CD_3)_{4-n}InCl_n]^-$ with $n=1$, 2 or 3.

$[(CH_3)_4As]^+$ $[(CH_3)_3InCl]^-$			$[(CH_3)_4As]^+$ $[(CD_3)_3InCl]^-$		$[(CH_3)_4Sb]^+$ $[(CH_3)_2InCl_2]^-$			$[(CH_3)_4As]^+$ $[(CD_3)_2InCl_2]^-$		$[(CH_3)_4Sb]^+$ $[CH_3InCl_3]^-$			$[(CH_3)_3AsCD_3]^+$ $[CD_3InCl_3]^-$		Assignment (C_{3v} or C_{2v})
obs.[1]	calc.		obs.[9]	calc.	obs.[1]	calc.		obs.[9]	calc.	obs.[1]	calc.		obs.[9]	calc.	
2965	2995		2218	2226	2976	2988		2210	2222	2980	2995		2208	2226	$\nu_{as}CH_3(CD_3)$
2891	2875		2120	2068	2880	2873		2098	2064	2885	2875		2121	2069	$\nu_sCH_3(CD_3)$
1150 1140	1191 to 1121		885	893 to 860	1166 1156	1206 to 1132		904 898	910 to 871	1159 1155	1202 to 1145		898	924 to 866	$\delta_sCH_3(CD_3)$
685	694 to 689		517	519 to 511	704	714 to 711		549 512	533 to 529	741	757		557	566	$\rho CH_3(CD_3)$
										530	537		481	469	νInC, A_1
480	487		436	431	522	525		468	462						$\nu_{as}InC_3(InC_2)$
467	480		421	417	490	501		442	435						$\nu_sInC_3(InC_2)$,
215	205		197	204											ν_sInCl, A_1
					241	239		235	238	293	288		290	287	$\nu_{as}InCl_3(InCl_2)$
					257	258		252	258	308	308		307	307	$\nu_sInCl_3(InCl_2)$
144	146	E	135	136	134	136 135	B_1 A_2	130	129 124	130	129	A_1	123	122 118	δ ClInC
130	128	A_1	119	115	128	125	B_2	114	114	120	122	E			δ ClInCl
					116	112	A_1	96	104						
n.o.	90	E	n.o.	80	106	101	A_1	86	96	110	108	E	106	108	δ ClInCl

decrease of M – Cl and M – C bond distances with increasing Cl substitution is accompanied by a monotonic *increase* of the M – Cl and M – C force constants. And just as the decrease of M – Cl bond distances across the series is more than twice as large as the decrease of the M – C bond distances (0.20 Å *versus* about 0.06 Å), so the f(M – Cl) force constants are found to increase by a factor of about 2.6, while the f(M – C) force constants increase with a factor of about 1.5. Closer inspection shows that f(M – Cl) change with nearly constant steps of 0.32 to 0.42 mdyn Å^{-1} across both series, while the change in f(M – C) is particularly large when the first Cl atom is introduced into $[(CH_3)_4M]^-$, 0.40 and 0.37 mdyn Å^{-1}, while the two following Cl atoms bring about changes ranging from 0.21 to 0.29 mdyn Å^{-1}.

It is well known that increased halogen substitution in derivatives of Group IV elements of the type $(CH_3)_{4-n}M^{IV}Cl_n$ leads to a shortening of the bond distances. In the present context it is pertinent to recall the bond distances obtained for the series with M^{IV} = Sn, which is isoelectronic with the series $[(CH_3)_{4-n}InCl_n]^-$:

	R(M – C)m(Å)	R(M – Cl) (Å)
$(CH_3)_4Sn$[14]	2.144(3)	
$(CH_3)_3SnCl$[15]	2.106(6)	2.351(2)
$(CH_3)_2SnCl_2$[16]	2.109(9)	2.327(4)
$(CH_3)SnCl_3$[15]	2.104(16)	2.304(3)
$SnCl_4$[17]		2.281(4)

The M – Cl bond distance is seen to decrease monotonically down the series, though the total change (0.07 Å) is only about one third of that observed for the isoelectronic ions $[(CH_3)_{4-n}InCl_n]^-$. The variation of the M – C distances is again less clear, but the total change appears to be about 0.04 Å, not very different from that found for the Group III complex ions.

Donor – acceptor bonds in complexes formed by derivatives of Group III and V elements are, however, known to be very sensitive to inductive effects. Thus the Ga – N bond distance in $(CH_3)_3GaN(CH_3)_3$ is 2.20(3) Å,[18] in $H_3GaN(CH_3)_3$ 2.111(2) Å[19] and in Cl_3GaNH_3 2.057(11) Å.[20] The Ga – P bond distance in $(CH_3)_3GaP(CH_3)_3$ is 2.52(2) Å[18] and in $Cl_3GaP(CH_3)_3$ 2.353(2) Å,[21] a change of 0.17 Å.

We have previously described the anionic complexes $[(CH_3)_3MCl]^-$ as donor acceptor complexes between $(CH_3)_3M$ and Cl^-: $(CH_3)_3M \leftarrow Cl^-$.[22] This description seems reasonable when the Ga – Cl bond distance in this complex is compared to the Ga – P bond distance in $(CH_3)_3GaP(CH_3)_3$: 2.38 *versus* 2.52 Å. It is also in agreement with the similarity of the Ga – C stretching force constant in the complex ion and in free $(CH_3)_3Ga$:[23] 2.27 *versus* 2.29 mdyn Å^{-1}.

The structure of the ion $[GaCl_4]^-$ may be discussed in terms of four resonance structures of the type $Cl_3Ga \leftarrow Cl^-$. The three "normal", "covalent" Ga – Cl bonds should then be similar to the Ga – Cl bonds in $Cl_3GaP(CH_3)_3$ which are 2.17 Å long.[21] The donor acceptor bond would be expected to be about 0.17 Å shorter than in the complex $[(CH_3)_3GaCl]^-$, that is about 2.21 Å. Resonance between the four canonical forms gives a tetrahedral ion when each Ga – Cl bond distance is equal to $(3/4)\cdot 2.17$ Å $+ (1/4)\cdot 2.21$ Å $= 2.18$ Å.

The structure of $[(CH_3)_2GaCl_2]^-$ may be rationalized in terms of two resonance structures of the type $(CH_3)_2ClGa \leftarrow Cl^-$. By analogy with the series $(CH_3)_{4-n}SnCl_n$ the presence of two methyl groups is expected to increase the covalent Ga – Cl bond with about 0.04 to 2.21 Å, and the donor acceptor bond by $(2/3)\cdot 0.17$ Å from 2.21 to 2.32 Å. The average bond distance obtained by resonance is $(1/2)\cdot 2.21$ Å $+ (1/2)\cdot 2.32$ Å $= 2.27$ Å. A similar argument applied to $[(CH_3)GaCl_3]^-$ leads to a predicted average Ga – Cl bond distance of 2.22 Å, again in agreement with the experimental value.

In our discussion of M – Cl bonding we have implicitly assumed that the M – C bonds in the species $[(CH_3)_3MCl]^-$, $[(CH_3)_2MCl]^-$ and $[(CH_3)MCl_3]^-$ are essentially normal covalent bonds. These bonds would be expected to change with increasing Cl substitution much in the same way as the Sn – C bond distances in the series $(CH_3)_{4-n}SnCl_n$, that is with 0.01 or 0.02 Å per Cl atom.

The structure of the ions $[(CH_3)_4M]^-$ must be discussed in terms of resonance structures of the type $(CH_3)_3M \leftarrow CH_3^-$. Each M – C bond would then be 75 % covalent and 25 % dative. We would therefore expect the largest change in M – C bond distance on going from $[(CH_3)_3MCl]^-$ to $[(CH_3)_4M]^-$. Unfortunately the M – C bond distances have not been determined with sufficient accuracy to allow these predictions to be tested. But it is gratifying that the greatest increase in M – C stretching force constants occurs on going from $[(CH_3)_4M]^-$ to $[(CH_3)_3MCl]^-$.

Finally we wish to point out that the largest angle bend force constants are found for the species $[(CH_3)_3MCl]^-$ which are the only ones that we have described in terms of a single resonance structure.

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