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INFRARED, RAMAN AND FORCE FIELD STUDIES OF TETRAKIS(ANIONOMERCURI)METHANES

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Summary

In order to throw light on the nature of the Hg–C bond in permercurated methanes, the infrared and Raman spectra of solid tetrakis(anionomercuri)methanes, $C(HgX)_4$ ($X = CN^-$, $HCOO^-$, CH_3COO^- and CF_3COO^-) have been assigned in the range $4000\text{--}40\text{ cm}^{-1}$. For these four as well as for other molecules of this type ($X = F^-$, Cl^- , Br^- , I^- and SCH_3^-) the force fields for the CHg_4 tetrahedron have been calculated. The Hg–C force constants are 18 to 28% lower than in the related $Hg(CH_3)X$ compounds; since the Hg–C bond lengths are approximately the same in both linear and tetrahedral configuration, this can be explained in terms of the nonbonded interactions between mercury atoms.

Introduction

A number of tetrakis(anionomercuri)methanes of the $C(HgX)_4$ type has been synthesized by Matteson and coworkers [1], Grdenić and coworkers [2,3], and Breitingner and coworkers [4,5]. X-ray structural studies for $X = CN^-$ [6], CH_3COO^- [2,7] and CF_3COO^- [2,8] showed a nearly tetrahedral arrangement of four metal atoms around the carbon atom. The main structural data of the CHg_4 tetrahedra are listed in Table 1. The $Hg \cdots Hg$ distances in the tetrahedra are larger than the Van

TABLE 1
MAIN X-RAY STRUCTURAL DATA FOR CHg₄ TETRAHEDRON

Molecule	Space group	Z	Mean CHg distance (pm)	Range of HgCHg bond angles (°)	O...N or O...O distance (pm)	Ref.
C(HgCN) ₄ ·H ₂ O	P2 ₁ /n	4	205.3(3.0)	105(3)–114(3)	277 ^a	6
C(HgOCOCH ₃) ₄ ·2H ₂ O	P2 ₁ /c	4	205(2)	104.6(1.0)–113(1.0)	279 ^b	7
C(HgOCOCF ₃) ₄	P4 ₂ /n	2	204.2(4.0)	108.04(2)–112.36(2)	–	8

^a N...HO distance. ^b O...HO distance.

der Waals distance of Hg^{II} (which is expected to be about 300 pm) but lower than the second Hg...Hg distance of 346.6 pm in solid mercury. The CHgX valence angles are distorted by about 2–5° from linearity.

The solid state vibrational spectra of tetrakis(methylthiomercuri)methane C(HgSCH₃)₄, μ -dithiotetramercurimethane CHg₄S₂ [4] and tetrakis(halomercuri)methanes C(HgX)₄ (X = F, Cl, Br, I) [5] have been assigned by Bretinger and coworkers. The tetrakis(methylmercuri)methane C(HgCH₃)₄ has also been prepared and structural studies are currently in hand [10]. Only for C(HgX)₄ with X = F, Cl, Br and I have force constant calculations been undertaken, and they were of a very simple nature [5]. It seemed important, therefore, to examine the vibrational spectra of other molecules having the CHg₄ tetrahedral structure. Here we present our attempt to interpret the infrared and Raman spectra of C(HgX)₄ with X = CN⁻, HCOO⁻, CH₃COO⁻ and CF₃COO⁻, and using also the experimental data on the other tetrakis(anionomercuri)methanes [4,5], to calculate force constants using a simplified model for C(HgX)₄ type molecules.

Experimental

The infrared spectra were recorded on a Digilab FTS-20C and Digilab FTS-14 infrared interferometers. Far infrared spectra were measured in the range 400–40 cm⁻¹ on a Beckman FS-720 and Grubb-Parsons IRIS interferometers using 6 μ m polyethylene terephthalate beamsplitters. Solid samples were studied as mulls in Nujol and vaseline mixture or as polyethylene pellets. Raman spectra were recorded with a Jobin-Yvon RAMANOR HG-25 holographic grating double monochromator spectrometer using the excitation from Carl Zeiss (DDR) argon- and krypton-ion lasers. Solids were studied as ground-up powders in capillary tubes. Solutions were measured in a glass cell.

Tetrakis(cyanomercuri)methane hydrate was prepared as previously described [6]. Tetrakis(acetoxymercuri)methane dihydrate and tetrakis(trifluoroacetoxymercuri)methane were prepared by dissolving Hofmann's base in acetic acid or trifluoroacetic acid [2]. The syntheses of tetrakis(carboxymercuri)methanes C(HgX)₄ (X = HCOO⁻, CH₃COO⁻ and CF₃COO⁻, as well as carboxy derivatives of other carboxylate anions) will be fully described in a separate paper [3b]. All chemicals used in preparations of the compounds were reagent grade.

Results

Vibrational assignments

The infrared and Raman spectra of $C(HgX)_4$ ($X = HCOO^-$, CH_3COO^- , CF_3COO^-) molecules are quite complex, because of the group frequencies of X anions.

For an "isolated" CHg_4 skeleton with the tetrahedral structure (T_d point group) four fundamental modes are predicted: two infrared and Raman active ($2 f_2$) and two Raman active only (a_1 and e). For the totally symmetric CHg_4 stretching mode the four heavy mercury atoms are moving and a strong Raman band is expected at a

TABLE 2
INFRARED AND RAMAN FREQUENCIES OF $C(HgCN)_4 \cdot H_2O$ (cm^{-1})

IR ^a (solid)	RAMAN (solid)	Assignment
3550s,b 3450s,b 2176sh 2171m	2171vs 2121vw	} $\nu(H_2O)$, OH str $\nu(^{12}CN)$, a_1 , and f_2 , CN str $\nu(^{13}CN)$
2029vvw 1623vw,sh 1608m 1591vw,sh	930vw,b 790vw,b	
737sh 723m 674m	721vw 687vw 668vw 603w	} $\nu_a(CHg_4)$, f_2 , CHg_4 asym str
580vvw 560vvw 530vvw	500vvw 404s a_1	
395s,b 365s,b	} f_2 321s } 306s } e	} $\delta(HgCN)$, HgCN def
292m	f_2 147vvs	
120sh	120sh 109sh	} $\delta_f(CHg_4)$, f_2 , CHg_4 def
99s 67m	100s 67vvs 63sh	
55sh	42sh	

^a Nujol and voltaef mull and polyethylene pellets.

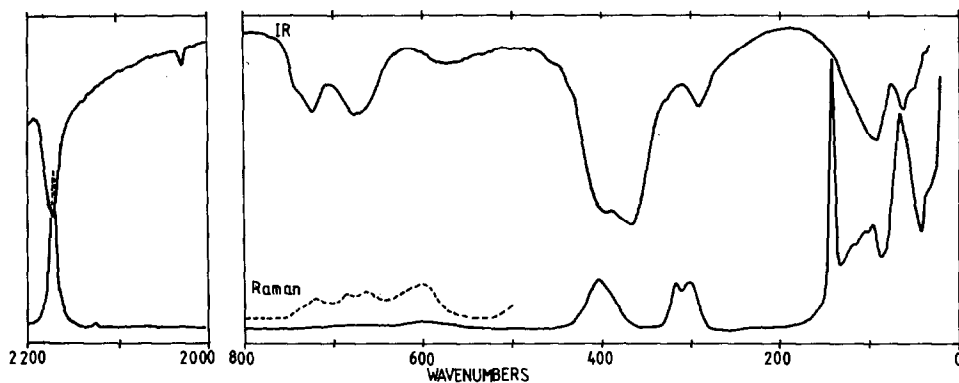


Fig. 1. Infrared and Raman spectra of solid $C(HgCN)_4 \cdot H_2O$.

very low frequency ($\sim 130 \text{ cm}^{-1}$). The asymmetric CHg_4 stretching mode can be described as a vibration of the central carbon atom among the four mercury atoms; a strong infrared and a weak Raman band is expected at much higher wavenumbers ($\sim 670 \text{ cm}^{-1}$). In solid samples this triply degenerate asymmetric stretching mode appears as a complex feature. According to Breiter's data for tetrakis(halomercuri)methanes [5] the band splittings are the three components of the degeneracy, caused by lattice forces. The slight distortion from the exact tetrahedral geometry also gives rise to some splittings of degenerate modes. The symmetric stretching mode a_1 may be unambiguously identified in Raman spectra of solutions if it gives rise to a detectably polarised band. In addition to these considerations results of assignments for related molecules [4,5,10] have been used.

The infrared and Raman spectra of $C(HgCN)_4 \cdot H_2O$ are shown in Fig. 1, and frequencies listed in Table 2. The medium intensity infrared bands near 700 cm^{-1} are assigned to the asymmetric CHg_4 stretching mode and the strong Raman line at 147 cm^{-1} to the symmetric one. The strong Raman band at 67 cm^{-1} is reasonably assigned to the doubly degenerate deformation mode, while the complex infrared and Raman band near 100 cm^{-1} is assigned to the triply degenerate deformation

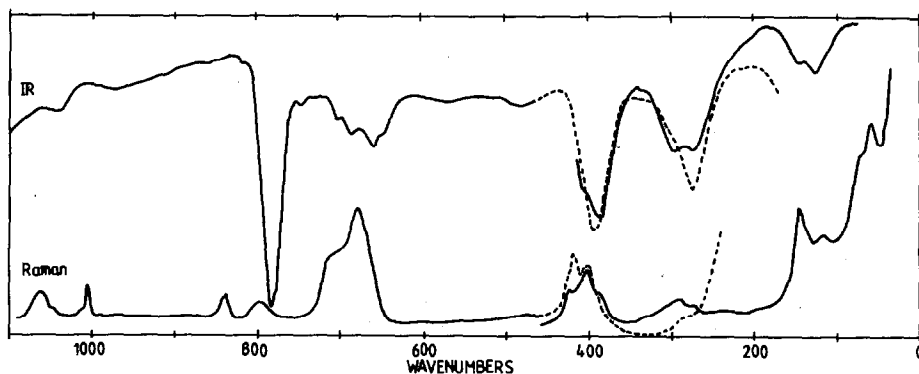


Fig. 2. Infrared spectra recorded in solid state and Raman spectra of $HCOOH/H_2O$ solution for $C(HgCOOH)_4$ (Broken lines refer to solution spectra).

TABLE 3
 INFRARED AND RAMAN FREQUENCIES OF $C(HgCOOH)_4$ (cm^{-1})

IR		Raman ^a	Assignment
Solid	Solution ^c		
3430s,b			} $\nu(H_2O)$, OH str ^b
3260sh			
3150sh			
		2956vs(0.2)	$\nu(CH)$, CH str
		2780w,b(dp?)	
		1738sh(dp?)	
1692w		1677vs(0.1)	$\nu_a(COO)$, COO <i>asym</i> str ^d
1620s,sh			$\delta(H_2O)$, H ₂ O def ^b
1595vvs	1590vs		$\nu_a(COO)$, COO <i>asym</i> str
1368m	1360m	1400s(0.4)	$\delta(CH)$, CH i.p. def
1265vs	1295m	1360m(p)	$\nu_s(COO)$, COO <i>sym</i> str
		1207w,b(0.2)	$\gamma(CH)$, CH o.p. def
1176sh	1180 ^e	1162w	
1045vw		1062vww,b	
975vww,b		840vww	
817vww		800vww,b	$\delta(OCO)$, OCO i.p. def
785vs			} $\nu_a(CHg_4)$, f_2 , CHg ₄ , <i>asym</i> str
743vww		710m,sh(0.6)	
709sh		681m(0.5)	
685m,sh			
658m			
645sh			
558vww		427m(p)	$\nu_s(HgO)$, a_1 , HgO <i>sym</i> str
488vww		408s,sh(dp)	} $\nu_a(HgO)$, f_2 , HgO <i>asym</i> str
410sh			
394s			
388s		298m,b	$\rho(OCO)$, OCO o.p. def
302m		277m	$\nu_s(CHg_4)$, a_1 , CHg ₄ <i>sym</i> str
149w,sh		147s	
130m		115m,b	} $\delta_f(CHg_4)$, f_2 , CHg ₄ def
104sh		83w,sh	
		74w,sh	
		69w,sh	
		63s	} $\delta_e(CHg_4)$, e , CHg ₄ def
		58s	

^a Raman spectrum in HCOOH/H₂O solution, below 400 cm^{-1} solid state Raman spectrum. ^b The solid sample contained some H₂O. ^c Solution in HCOOH/H₂O measured in a CaF₂ cell with subtraction of solvent bands. ^d Mainly HCOOH band. ^e Overlapping with HCOOH band.

mode. The assignment of the bands for HgCN groups and for the crystalline H₂O is also included in Table 2. The coincidence of CN stretching modes in the infrared and Raman spectra indicates an absence of vibrational coupling between CN groups. The carbon-mercury stretching mode for Hg-CN shows two features in the

infrared and one in the Raman spectra, indicating a weak vibrational coupling between symmetric and asymmetric motions. Three bands were found for HgCN deformation modes (see Table 2).

The formate anions are planar and asymmetric, and their relative orientation in the dissolved state influences the symmetry of the $C(HgOCOH)_4$ molecule as a whole. The infrared and Raman spectra of tetrakis(formatomercuri)methane are presented in Fig. 2; the wavenumbers and assignments of these bands are listed in Table 3. The depolarised Raman lines near 700 cm^{-1} can be attributed to the asymmetric CHg_4 stretching mode. In the Raman spectrum of solid $C(HgOCOH)_4$ the symmetric stretching mode appears at 147 cm^{-1} as a strong single line. It is difficult to locate the triply degenerate deformation mode of the CHg_4 skeleton but a number of bands was found below 115 cm^{-1} , and the weak shoulders near 70 cm^{-1} can probably be attributed to this mode. Unfortunately the far infrared spectrum is very poor in this region. The low frequency Raman doublet around 60 cm^{-1} can be assigned as the doubly degenerate deformation mode of CHg_4 .

The infrared and Raman bands – as far as the $HCOO^-$ fundamental modes are concerned – very similar to those of other metal formates (see e.g. [11]). As a result of vibrational coupling between HgO stretching modes a polarised Raman line is observed at 427 and a depolarised one at 408 cm^{-1} referring to the symmetric (a_1) and to the symmetric mode (f_2), respectively.

The vibrational spectra of tetrakis(acetoxymmercuri)methane and tetrakis(trifluoroacetoxymmercuri)methane are more complex, because of the more complicated CH_3COO^- and CF_3COO^- vibrations. The vibrational spectra and tabulated frequencies for $C(HgOCOCH_3)_4 \cdot 2H_2O$ and $C(HgOCOCF_3)_4$ are presented in Figs. 3 and 4, and Tables 4 and 5. Three skeletal modes for CHg_4 are easily assigned by analogy with the formate molecule. The triply degenerate deformation mode $\delta_f(CHg_4)$ presents similar difficulties in identification. The symmetric and asymmetric HgO stretching modes are attributed to the bands near 300 cm^{-1} . An approximate assignment of CH_3COO^- and CF_3COO^- internal vibrations is also given; this is generally in accordance with more elaborate assignments for other metal acetates [12] and trifluoroacetates [13].

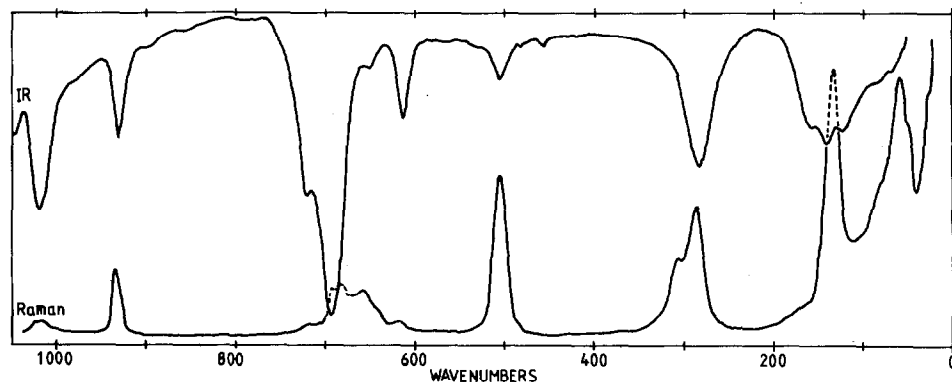


Fig. 3. Infrared and Raman spectra of $C(HgOCOCH_3)_4 \cdot 2H_2O$ in solid state.

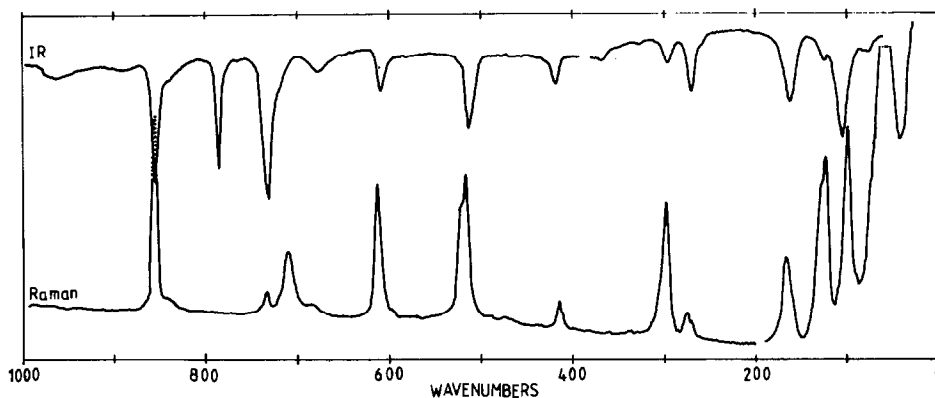


Fig. 4. Infrared and Raman spectra of $C(HgOCOCF_3)_4$ in solid state.

Force constant calculation

For the normal coordinate calculations, tetrahedral angles about carbon atom and a five point masses simplified model have been used. The weight used for mercury includes the molecular or atomic weight of the X anions. The CHg bond lengths have been taken from the available X-ray [2,6-9] (see Table 1) or microwave data from similar molecules [14]. The standard GF matrix method has been applied [15]. The procedures used for calculating the G matrix and refining the force constants have been outlined previously [16,17]. The F_{11} and F_{22} values are readily obtained from the relation $F_{ii} = \lambda_{exp}/G_{ii}$, where λ_{exp} is the experimental eigenvalue, but F_{33} , F_{34} and F_{44} are interdependent and, because there are only four observable skeletal frequencies, the problem cannot be solved without further assumptions. In most cases $F_{34} = 0$ has been assumed, but for molecules with complicated X anions it was not successful. For these molecules $F_{44} = 1.3 \times 10^2 \text{ N m}^{-1}$ has been constrained and F_{33} and F_{34} have been refined. The results presented in Table 7 reproduced the observed frequencies from Table 6. The internal coordinate force constants are tabulated in Table 8.

Discussion

On the basis of the crystal structure of $C(HgCN)_4 \cdot H_2O$ [6], which has four molecules in the unit cell, the factor group analysis gives

$$\Gamma_{int} = 30a_g + 30b_g + 33a_u + 33b_u$$

$$\Gamma_T = 3a_g + 3b_g + 2a_u + b_u$$

$$\Gamma_R = 3a_g + 3b_g$$

for the internal, translatory and rotatory modes, respectively. The water molecule was not taken into account. The species $C(HgOCOCH_3)_4 \cdot 2H_2O$ [7] should have identical lattice modes (Γ_T and Γ_R), but for internal modes of a simplified $C(HgO \cdots)_4$ unit we have:

$$\Gamma_{int} = 21a_g + 21b_g + 24a_u + 24b_u.$$

The $C(HgOCOCF_3)_4$ has a different crystal structure [2,8] with two molecules per

TABLE 4

VIBRATIONAL FREQUENCIES OF $C(HgOCOCH_3)_4 \cdot 2H_2O$ AND $Hg(OCOCH_3)_2$ (cm^{-1})

$C(HgOCOCH_3)_4 \cdot 2H_2O$		$Hg(OCOCH_3)_2$	Assignment
IR solid (Nujol)	Raman solid (powder)	IR solid (Nujol)	
3010vs	3010w		$\nu_a(CH)$, CH <i>asym</i> str
2982vw	2984w-m		$\nu_a(CH)$, CH <i>asym</i> str
2928vw	2930m-s		$\nu_s(CH)$, CH <i>sym</i> str
	2842vw		
1698vw			
	1663vw		
1625s	1624vw	1619vs	} $\nu(C=O)$, C=O str
1590sh	1595w	1600vs	
1575vw	1580vw,sh	1565vs,br	
	1441sh		
1430s	1430w	1448s	$\delta_a(CH_3)$, CH_3 <i>asym</i> def
1378vs	1374vw	1377vs	} $\delta_s(CH_3)_2$, CH_3 <i>sym</i> def
	1365vw		
1327vs	1318w	1319vs	} $\nu(C-O)$, CO str
	1312w	1302vs	
1240sh	1230	1240sh	
1170w	1172w		
	1124w		
1048m		1049m	} $\rho(CH_3)$, CH_3 rock
	1023vw	1029m	
1018s	1014vw	1018m	
975sh		975 sh	} $\nu(C-C)$, CC str
929m	933s	936m	
		927m	
719m	720w	703s	} $\delta(CCO)$, CCO def
		684m	
693vs	693s		} $\nu_a(CH_3)_4, f_2, CH_3$ <i>asym</i> str
	684s		
	670m,sh		
650w	660s	656w	$\delta(OCO)$, OCO i.p. def
615m	620w	613m-s	$\gamma(OCO)$, OCO wag
509m	509vs	528m	$\rho(OCO)$, OCO o.p. def
457w			
	310m,sh	315s	} $\nu(HgO)$, HgO str
287s	290s		
	170sh	198vs	$\tau(CH_3)$, CH_3 torsion (?)
162m			} $\nu_s(CH_3)_4, a_1, CH_3$ <i>sym</i> str
145m	136vs		
125m			
90vw	90vw		$\delta_\gamma(CH_3)_4, f_2, CH_3$ def
70vw			} $\delta_e(CH_3)_4, e, CH_3$ def
	59vs		
	51sh		

unit cell (see Table 1), and the distribution of internal and lattice modes becomes:

$$\Gamma_{int} = 5a_g + 7b_g + 5e_g + 6a_u + 5b_u + 5e_u$$

$$\Gamma_T = b_g + e_g$$

$$\Gamma_R = a_g + e_g + b_u + e_u$$

(Continued on p. 213)

TABLE 5
 INFRARED AND RAMAN FREQUENCIES OF $C(HgOCOFC_3)_4$ (cm^{-1})

IR ^a (solid)	IR ^b (solution)	Raman (solid)	Raman ^c (solution)	Assignment
1800w,b	1792m,sh			
1714sh			1712w,b(p)	
1672vs	1695vs	1676m		$\nu_a(COO)$, COO <i>asym</i> str
			1607w(dp)	
1422s	1425w,b	1424m,s		$\nu_s(COO)$ COO <i>sym</i> str
1365vw			1362m(p)	
1206sh				
1190vvs,b	1205vs	1190vvw		$\nu_s(CF_3)$, CF ₃ <i>sym</i> str
1160vs,b	1184m			$\nu_a(CF_3)$, CF ₃ <i>asym</i> str
	1176m		1155m(0.1)	
	1132m,s			
1070vvw				
1044vvw			1042w(dp)	
			1009m,s(0.1)	
970vw,b				
895vw,b				
856s		858s	856vs(0.1)	$\nu(CC)$, CC str
840sh		844vw,sh		
	799w			
788s	789s			$\delta_s(CF_3)$, CF ₃ <i>sym</i> def
763vw			754m(0.26)	} $\nu_a(CHg_4)$, f_2 , CHG ₄ <i>asym</i> str
736s	721m	737w	720w(dp)	
		713m		
684a		686w,m	684vw,b(dp)	$\delta_a(CF_3)$, CF ₃ <i>asym</i> def
615w,m	612m	618s	619s(0.4)	$\delta(OCO)$, OCO i.p. def
		530sh		
520m	517s	525s	524s(0.5)	$\rho(COO)$, COO rock
425w		424w		
		370vw		
304m,v		306s	311s(0.4)	$\nu_s(HgO)$, a_1 , HgO <i>sym</i> str
279s		284w	284w(dp)	$\nu_a(HgO)$, f_2 , HgO <i>asym</i> str
172s		175s	167w(p)	$\rho(CF_3)$, CF ₃ rock
		138sh		
132w		132vs		$\nu_s(CHg_4)$, a_1 , CHG ₄ <i>sym</i> str
113vs		108vs		$\delta_f(CHg_4)$, f_2 , CHG ₄ def
84sh		82sh		
		74sh		
		66vs		} $\delta_e(CHg_4)$, e CHG ₄ def
57vw				
		46vvw		} lattice modes
		38sh		
		30sh		
		25sh		

^a In Nujol, voltaef mull or polyethylene pellets. ^b Solution in CH₃CN and CD₃CN. ^c Solution in CH₃CN.

TABLE 6

VIBRATIONAL FREQUENCIES (cm^{-1}) OF $\text{C}(\text{HgX})_4$ TYPE MOLECULES USED FOR FORCE CONSTANTS CALCULATION

Compound	$\nu_3(\text{CHg}_4)$ $\nu_1(a_1)$	$\delta_e(\text{CHg}_4)$ $\nu_2(e)$	$\nu_a(\text{CHg}_4)$ $\nu_3(f_2)$	$\delta_f(\text{CHg}_4)$ $\nu_4(f_2)$	Remarks	References
$\text{C}(\text{HgF})_4$	164.5	54.5	689.5	88	^a	5
$\text{C}(\text{HgCl})_4$	139	51	665	73	^a	5
$\text{C}(\text{HgBr})_4$	117	42	647	55.5	^a	5
$\text{C}(\text{HgI})_4$	98	36	623	49	^a	5
$\text{C}(\text{HgCN})_4 \cdot \text{H}_2\text{O}$	147	67	698	99.5	^a	This work
$\text{C}(\text{HgOCOCH}_3)_4 \cdot 2\text{H}_2\text{O}$	135	60.5	693	83	^a	This work
$\text{C}(\text{HgOCOCF}_3)_4$	132 ^a	66 ^a	720 ^b	105 ^b		This work
$\text{C}(\text{HgOCOH})_4$	147 ^a	60 ^a	695.5 ^b	97 ^a		This work
$\text{C}(\text{HgSCH}_3)_4$	129	63	632	68	^a	4

^a Mean values from solid state spectra. ^b Solution data.

TABLE 7

FORCE CONSTANTS OF $\text{C}(\text{HgX})_4$ TYPE MOLECULES IN SYMMETRY COORDINATE REPRESENTATION

Compound	$F_{11}(a_1)$ ^a	$F_{22}(e)$ ^b	$F_{33}(f_2)$ ^a	$F_{34}(f_2)$ ^c	$F_{44}(f_2)$ ^b
$\text{C}(\text{HgF})_4$	3.50	0.54	1.43	0	1.11
$\text{C}(\text{HgCl})_4$	2.83	0.54	1.56	0	0.76
$\text{C}(\text{HgBr})_4$	2.26	0.42	1.65	0	0.56
$\text{C}(\text{HgO})_4$	1.85	0.36	1.65	0	0.40
$\text{C}(\text{HgCN})_4$ ^d	2.89	0.85	1.88	0.29	(1.30)
$\text{C}(\text{HgSCH}_3)_4$	2.43	0.82	1.42	0	0.70
$\text{C}(\text{HgOCOH})_4$ ^e	3.13	0.73	1.02	-0.05	(1.30)
$\text{C}(\text{HgOCOCH}_3)_4$	2.79	0.78	1.43	0.08	(1.30)
$\text{C}(\text{HgOCOCF}_3)_4$ ^e	3.10	1.09	1.21	0.17	(1.30)

^a 10^2 N m^{-1} , ^b $10^{-18} \text{ N m rad}^{-2}$, ^c $10^{-8} \text{ N rad}^{-1}$, ^d With one H_2O , ^e With two H_2O ; bracketed values were constrained.

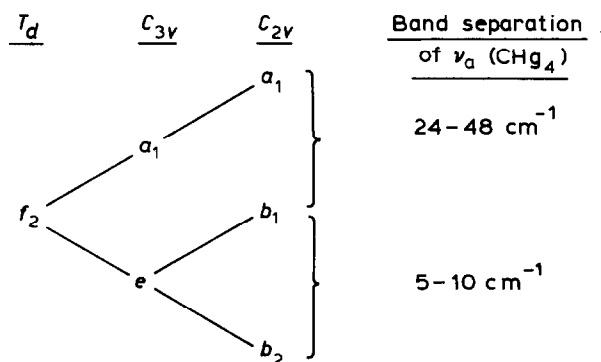
TABLE 8

INTERNAL COORDINATE FORCE CONSTANTS OF $\text{C}(\text{HgX})_4$ TYPE MOLECULES (10^2 N m^{-1})

Compound	f_r	f_{rr}	$f_\alpha - f_{\alpha\alpha}$	$f_{\alpha\alpha} - f'_{\alpha\alpha}$	$f_{r\alpha} - f'_{r\alpha}$	$R(\text{CHg})$ ^a (pm)
$\text{C}(\text{HgF})_4$	1.95	0.52	0.20	0.07	0	205
$\text{C}(\text{HgCl})_4$	1.88	0.32	0.15	0.03	0	206
$\text{C}(\text{HgBr})_4$	1.80	0.15	0.12	0.02	0	207
$\text{C}(\text{HgI})_4$	1.70	0.05	0.09	0.005	0	209
$\text{C}(\text{HgCN})_4$	2.13	0.25	(0.25)	(0.05)	0.10	206
$\text{C}(\text{HgSCH}_3)_4$	1.67	0.25	0.19	-0.014	0	205
$\text{C}(\text{HgOCOH})_4$	1.68	0.48	(0.24)	(0.07)	-0.02	205
$\text{C}(\text{HgOCOCH}_3)_4$	1.77	0.34	(0.25)	(0.06)	0.03	205
$\text{C}(\text{HgOCOCF}_3)_4$	1.68	0.47	(0.28)	(0.03)	0.06	204

^a Bond distances used for calculation; bracketed values originated from refined F_{33} and constrained F_{44} .

where Γ_{int} refers to a $C(\text{HgO} \cdots)_4$ simplified model. In the experimental spectra the alternation of external modes was actually observed in all cases, but the absence of the great number of internal modes and their alternation suggest a very weak coupling between neighbouring molecules in the lattice. The splitting of f_2 modes into three or more components could be caused only partly by the lattice effects. This can be attributed rather to the distortion of the exact tetrahedron. The correlations between point groups are:



With regard to the asymmetric stretching modes, the C_{2v} skeletal symmetry can be suggested, which refers to one well separated (a_1) and two closely spaced (b_1 and b_2) features. The separation of these bands could be a spectroscopic measure of the extent of distortion from the regular tetrahedron.

Force constants of methylmercury(II) halides [18] and cyanide [19] are well known. It is interesting to compare force constants and other properties between methylmercury derivatives and the corresponding tetrakis(anionomercuri)methanes. For the cyanide derivatives the HgC stretching force constant is lower by 13% for $C(\text{HgCN})_4$ than for $[\text{Hg}(\text{CH}_3)\text{CN}]$ [19] (see Table 9). The lowering of the HgC stretching force constant is surprising because the bond length is lowered by 3.2 pm.

TABLE 9

COMPARISON OF INTERATOMIC DISTANCES, FORCE CONSTANTS AND CHARACTERISTIC FREQUENCIES OF MERCURY CYANIDE DERIVATIVES

Parameters	[$\text{Hg}(\text{CH}_3)\text{CN}$]	$C(\text{HgCN})_4$	$\text{Hg}(\text{CN})_2$
Bond length (pm)			
Hg-CN	205(1) ^a	205 ^{b,c}	201.5(3) ^d
Hg-C	208(2) ^a	205 ^{b,c}	-
Force constants (10^2 N m^{-1})			
$K(\text{CN})$	17.27 ^e	17.15 ^g	1762 ^f
$K(\text{Hg-CN})$	2.38 ^e	2.50 ^g	2.61 ^f
$K(\text{Hg-C})$	2.45 ^e	2.13 ^g	-
Stretching frequencies (cm^{-1})			
$\nu(\text{CN})$	2179 ^e	2171 ^e	2194 ^f
$\nu(\text{Hg-CN})$	378 ^e	388 ^{c,g}	412,442 ^f
$\nu(\text{Hg-C})$	559 ^e	147,698 ^{c,g}	-

^a Ref. 20. ^b Ref. 6. ^c Mean values. ^d Ref. 21. ^e Ref. 19. ^f Ref. 22. ^g This work.

TABLE 10

COMPARISON OF METAL-CARBON STRETCHING FORCE CONSTANTS ($K(\text{CHg})$) AND METAL-HALIDE STRETCHING FREQUENCIES ($\nu(\text{HgX})$)

X	$K(\text{CHg}) (10^2 \text{ N m}^{-1})$		$\nu(\text{HgX}) (\text{cm}^{-1})$	
	$[\text{Hg}(\text{CH}_3)\text{X}]$	$\text{C}(\text{HgX})_4^a$	$[\text{Hg}(\text{CH}_3)\text{X}]$	$\text{C}(\text{HgX})_4^a$
CN	2.45 ^b	2.13	378	388 ⁺
F	2.66 ^h	1.95	482,414 ^e	496 ⁺ ^f
Cl	2.55 ^c	1.88	336 ^c	315 ⁺ ^f
Br	2.43 ^c	1.80	228 ^c	218 ⁺ ^f
I	2.33 ^c	1.70	181 ^c	171 ^f
SCH ₃	2.33 ^d	1.67	329 ^d	323 ^g

^a This work. ^b Ref. [19]. ^c Ref. [18]. ^d Ref. [25]. ^e Ref. [26]; correlation splitting in solid sample spectra. ^f Ref. [4]. ^g Ref. [5]. ^h Approximate calculation; + = mean values.

The slightly weaker HgC bond in the tetrahedron of $\text{C}(\text{HgCN})_4$ leads to the increased Hg-CN force constant, the value was lying between those for $[\text{Hg}(\text{CH}_3)\text{CN}]$ and $\text{Hg}(\text{CN})_2$. This same sequence applies to the Hg-CN stretching frequencies. The CN stretching force constants and frequencies are not very sensitive to the bonding of mercury in $[\text{Hg}(\text{CH}_3)\text{CN}]$ and $\text{C}(\text{HgCN})_4$ molecules, but they are considerably higher in $\text{Hg}(\text{CN})_2$. It is noteworthy that the mercury cyanide derivatives, namely $\text{C}(\text{HgCN})_4$, $\text{Hg}(\text{CN})_2$ [22] and $[\text{Hg}(\text{CN})_4]^{2-}$ [23], having multiple CN groups, showed very weak or no coupling between vibrations of different CN groups. Other heavy metal cyano complexes, e.g. $\text{K}_2[\text{Pt}(\text{CN})_4]$ [24], show three CN stretching bands in the range 2168–2133 cm^{-1} .

The HgC stretching force constants were found to be 18–28% lower for $\text{C}(\text{HgX})_4$

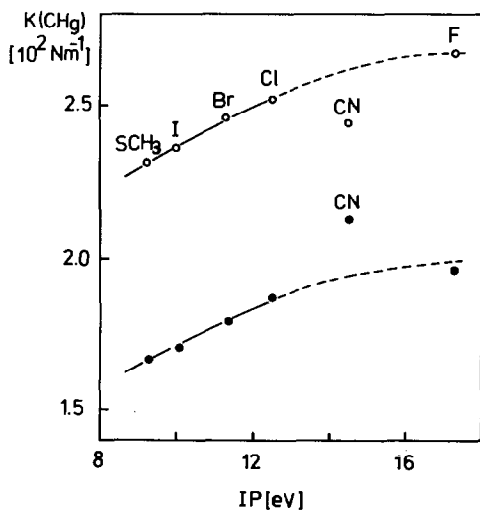
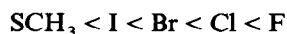


Fig. 5. Relationship of HgC stretching force constants to the first ionisation potential of X in $[\text{Hg}(\text{CH}_3)\text{X}]$ (upper) and in $\text{C}(\text{HgX})_4$ (lower) molecules.

compounds than for methylmercury(II) derivatives (Table 10). However, the HgC stretch–stretch interaction force constant around the central carbon atom is higher by an order of magnitude for $C(HgX)_4$ compounds than the same interaction term across the heavy mercury atom in $[Hg(CH_3)X]$ molecules (cf. Table 8 and ref. [18]). The HgC stretch–stretch interaction force constant for formate, acetate and trifluoroacetate derivatives is similar to the “light” F and Cl derivatives of the $C(HgX)_4$ type.

Table 10 also shows that there are no big differences between HgX stretching modes in the two systems. This means that the HgX bonding is not much affected by the number of metal atoms attached to carbon. As expected [27] the dependence of the HgC stretching force constant on the first ionization potential of X shows the following sequence:



This dependence is shown in Fig. 5, where the data for the corresponding $Hg(CH_3)X$ molecules are also presented.

Although the main HgC bond distances in $C(HgX)_4$ compounds may not be essentially different [6,28] from those in $[Hg(CH_3)X]$ [14], the force constants are significantly smaller in mercury methanes. It could be concluded that the type of bonding to the central carbon atom for $C(HgX)_4$ molecules is slightly different from those in $[Hg(CH_3)X]$ molecules, which could be explained in terms of the considerably strong $Hg \cdots Hg$ interactions in the tetrahedrally arranged metal skeleton.

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