1005. *Spectroscopic Studies of Bistrifluoromethylmercury in Solution.*

By A. J. Downs.

From the observed Raman and infrared spectra of bistrifluoromethylmercury in various solvents a virtually complete vibrational assignment has been made on the basis of a linear C–Hg–C skeleton; change of solvent has little effect on the vibrational frequencies. Raman spectra of solutions containing bistrifluoromethylmercury and a mercuric halide or nitrate show that no exchange occurs at temperatures below 100°. Investigation of the reaction of the trifluoromethyl compound with ionic halides fails to support the postulated formation of complex anions containing the trifluoromethyl group.

In its comparatively high melting point (163°),[1] ready solubility in many solvents, including water,[1,2] and reluctance to undergo exchange with inorganic halides,[2] bistrifluoromethylmercury is unlike its simple methyl analogue. With halide ions, it has been reported,[3] the trifluoromethyl compound forms complex anions of the type $[Hg(CF_3)_2X]^-$ and $[Hg(CF_3)_2X_2]^{2-}$ (X = Cl, Br, or I), the evidence being based on conductometric titrations and the isolation of solid adducts containing large cations. In certain respects, therefore, bistrifluoromethylmercury apparently resembles dimethylmercury less than a mercuric halide. To examine this analogy more closely we have observed the Raman and infrared spectrum of the trifluoromethyl compound dissolved in water, methanol, benzene, diethyl ether, acetone, acetonitrile, and pyridine.

X-Ray data[1] for solid bistrifluoromethylmercury indicate a linear C–Hg–C skeleton.

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[1] Emeléus and Haszeldine, *J.*, 1949, 2953.

[2] Lagowski, Ph.D. Thesis, Cambridge, 1959.

[3] Emeléus and Lagowski, *J.*, 1959, 1497.

In solutions of benzene and water the compound has a normal molecular weight, and the complication of appreciable association or dissociation can be neglected. The small apparent dipole moment in benzene and carbon tetrachloride[4] is probably due, not to permanent deformation of the molecule, but to an anomalously high atom polarisation.[5,6] Since the infrared spectra of the compound in the solid phase and in solution are very similar, and since the Raman and infrared frequencies associated with the skeletal Hg–C stretching modes do not coincide, it is concluded from the present work that the molecule retains its linear shape in solution. Without exception, the vibrational frequencies vary only slightly with change of solvent. This is surprising, particularly in the case of the symmetrical Hg–C stretching mode; the corresponding frequency of the mercuric halides[7] or bis(trifluoromethylthio)mercury, $Hg(S{\cdot}CF_3)_2$,[8] is markedly solvent-dependent as a result of either solvation or complex-formation. The insensitivity of the vibrational frequencies of bistrifluoromethylmercury to change of solvent suggests that the compound does not readily form adducts with donor molecules, a conclusion difficult to reconcile with the reported formation of anionic complexes.[3]

The Raman spectra of mixtures of bistrifluoromethylmercury with mercuric chloride, bromide, or iodide in methanol and with mercuric nitrate in water, at temperatures up to 100°, consist merely of superpositions of the spectra of the pure components; there is no evidence of an exchange, $Hg(CF_3)_2 + HgX_2 \rightleftharpoons 2CF_3HgX$ [cf. the behaviour of bis(trifluoromethylthio)mercury[8] and bispentafluorophenylmercury[6]]. In this reluctance to react with mercuric salts bistrifluoromethylmercury behaves neither like a dialkylmercury nor like a mercuric halide; the combination of bulk and electrophilic character peculiar to the trifluoromethyl group may well be responsible.

To investigate the anionic complexes $[Hg(CF_3)_2X]^-$ and $[Hg(CF_3)_2X_2]^{2-}$ reported previously,[3] we have studied the Raman spectra of aqueous and methanolic solutions containing various proportions of bistrifluoromethylmercury and halide ions. In most cases some decomposition occurred during irradiation by the Raman mercury arc-light source, with the production of fluoroform and the corresponding tetrahalogenomercurate ion, HgX_4^{2-}:

$$Hg(CF_3)_2 + 4X^- + 2H_2O \longrightarrow HgX_4^{2-} + 2CHF_3 + 2OH^-$$

The only species detectable in solution by the Raman effect were bistrifluoromethylmercury and (after several hours) the HgX_4^{2-} ion;[9] no lines attributable to the ions $[Hg(CF_3)_2X]^-$ and $[Hg(CF_3)_2X_2]^{2-}$ were observed. Unchanged bistrifluoromethylmercury was detected even in the presence of a large excess of halide ions; hence, if trifluoromethylmercury complex ions exist under these conditions, they must be relatively unstable to dissociation according to an equation such as $[Hg(CF_3)_2X_2]^{2-} \rightleftharpoons Hg(CF_3)_2 + 2X^-$. A slight reduction (~3%) in the frequency of the symmetric Hg–C stretching mode of the mercury compound (comparable with that observed when pyridine replaces water as a solvent) may reflect some weak association between the $Hg(CF_3)_2$ molecules and halide ions. A much larger frequency change would be expected to accompany the formation of a complex anion such as $[Hg(CF_3)_2X]^-$, together with the appearance of a new band associated with the Hg–X stretching vibration; no such band was observed.

Though the Raman effect is not sufficiently sensitive to rule out the possibility of the formation of small amounts of trifluoromethylmercury complexes in solution, the implications of these experiments are supported by fluorine-resonance and ultraviolet-absorption measurements. Change of solvent or the addition of a potassium halide to a solution of the

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[4] Sawatzky and Wright, *Canad. J. Chem.*, 1958, **36**, 1555.

[5] Finn, Hampson, and Sutton, *J.*, 1938, 1254; Coop and Sutton, *J.*, 1938, 1269; Armstrong, Le Fèvre, and Le Fèvre, *J.*, 1957, 371.

[6] Chambers, Coates, Livingstone, and Musgrave, *J.*, 1962, 4367.

[7] Allen and Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1786; Downs, unpublished work.

[8] Downs, Ebsworth, and Emeléus, *J.*, 1961, 3187.

[9] Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

mercury compound has but a small effect on the chemical shift and on the appropriate coupling constants in the fluorine resonance spectrum. By contrast, the ^{199}Hg–F and, especially, the F–F coupling constants of heptafluoropropylmercuric iodide, C_3F_7HgI, have recently been observed [10] to vary appreciably with environment, serving in this case as a relatively sensitive index to molecular behaviour. The ultraviolet absorption spectra of aqueous solutions containing varying proportions of bistrifluoromethylmercury and potassium iodide gave no indication of interaction, although over a period of weeks slow decomposition occurred with the formation of the HgI_4^{2-} ion, identified by its characteristic ultraviolet spectrum.[11] In analogous conditions, the spectrum of mercuric chloride and potassium iodide shows unambiguous evidence of immediate interaction.

To summarise, the spectroscopic information obtained does not support the postulated formation of complex anionic derivatives of bistrifluoromethylmercury in solution. Some form of weak association between the mercury compound and halide ions is, however, indicated by slight modifications in the Raman and fluorine resonance spectra; more definite evidence of this has been derived from cryoscopic measurements, details of which will be published subsequently.

RESULTS

Vibrational Spectra of Bistrifluoromethylmercury.—The observed frequencies of the infrared and Raman spectra of pure bistrifluoromethylmercury are given in Table 1, together with the relative intensities and states of polarisation of the bands.

TABLE 1.

Infrared and Raman spectra of bistrifluoromethylmercury (frequencies in cm.$^{-1}$).

Infrared		Raman	
Solid	C_6H_6 soln.	Aq. soln.	Assignment
2930w			$\left\{\begin{array}{l}\nu_5 + \nu_6 + \nu_{11}\ (E_u)\\ \quad\text{or } \nu_1 + \nu_6 + \nu_8\ (E_u)\end{array}\right.$
2850w			$2 \times \nu_5 + \nu_6$ (A_{2u})
2300w			$\nu_8 + \nu_{11}$ (A_{2u}, E_u)
2230w, br			$\nu_5 + \nu_8$ (E_u)
2130w			$\nu_1 + \nu_5$ (A_{2u})
1883w			$\nu_6 + \nu_8$ (E_u)
1660w, br			$\nu_9 + \nu_{11}$ (A_{2u}, E_u)
1570w, br			$\nu_1 + \nu_{12}$ (E_u)
1430vw			$\nu_2 + \nu_6$ (A_{2u})
$\left.\begin{array}{l}1238\\1228\end{array}\right\}$ w	$\left.\begin{array}{l}1239\\1230\end{array}\right\}$ w		$\nu_2 + \nu_{12}$ (E_u) $\nu_6 + \nu_9$ (E_u)
		1160s, depol.	ν_8 (e_g)
1143vs	1138vs		ν_{11} (e_u)
1072vs	1078vs		ν_5 (a_{2u})
1049vs		1052mw, pol.	ν_1 (a_{1g})
716m	714m		ν_6 (a_{2u})
		713s, pol.	ν_2 (a_{1g})
524mw	529mw		ν_{12} (e_u)
		515w, depol.	ν_9 (e_g)
274s	273s		ν_7 (a_{2u})
		261vw?	ν_{10} (e_g)?
264s	260ms		ν_{13} (e_u)
		226s, pol.	ν_3 (a_{1g})

The vibrational spectrum of dimethylmercury has been interpreted satisfactorily [12,13] in terms of a linear C–Hg–C skeleton with free rotation of the methyl groups. Bauman [14] has concluded that the effective point group in such cases is D_{3d}, though deviations from the normal

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[10] Clase and Ebsworth, unpublished work.

[11] Fromherz and Lih, *Z. phys. Chem.* (*Leipzig*), 1933, *A*, **167**, 103.

[12] Gutowsky, *J. Chem. Phys.*, 1949, **17**, 128.

[13] Boyd, Thompson, and Williams, *Discuss. Faraday Soc.*, 1950, **9**, 154; Goggin and Woodward, *Trans. Faraday Soc.*, 1960, **56**, 1591.

[14] Bauman, *J. Chem. Phys.*, 1956, **24**, 13.

D_{3d} selection rules may sometimes occur. The modes of vibration for bistrifluoromethylmercury and their symmetry species and selection rules are shown in Table 2. The rules permit six Raman lines (three polarised) and seven infrared bands due to fundamentals, no vibration being active in both spectra. Vibrational assignments have been based on these rules, with the help of analogies from the spectra of other simple trifluoromethyl compounds.[15]

The three polarised Raman lines are confidently assigned to ν_1, ν_2, and ν_3, the a_{1g} modes. The depolarised Raman lines at ~1160 and ~515 cm.$^{-1}$ are also readily ascribed to ν_8 and ν_9, respectively. There is some doubt about the existence of a very weak line at ~260 cm.$^{-1}$; if real, this probably represents ν_{10}, the Raman-active CF_3 rocking mode. The Raman spectrum of dimethylmercury [12,13] also contains a low-frequency line which can only be attributed to the " forbidden " skeletal bending frequency ν_{14}; since no comparable scattering is observed in the present case, this frequency cannot be determined for bistrifluoromethylmercury.

The infrared spectrum of bistrifluoromethylmercury in solution (over the range 200—4000 cm.$^{-1}$) contains six bands attributable to fundamentals, which have been assigned primarily by comparison with similar modes in the spectra of dimethylmercury [12] and the trifluoromethyl halides.[15] The antisymmetric skeletal stretching and CF_3 rocking modes, ν_7 and ν_{13}, respectively, have very similar frequencies (~270 and ~260 cm.$^{-1}$), and there is some uncertainty about which band is due to which fundamental. The higher frequency is favoured as ν_7 by analogy with the spectra of trifluoromethyl iodide [15] and trifluoromethylmercuric halides, CF_3HgX,[16] and by calculations based on simple valence force field theory.

TABLE 2.

Vibrational modes, symmetry species, and selection rules for $Hg(CF_3)_2$ (effective point group D_{3d}).

	Symmetry species					
Type of vibration	a_{1g}	a_{1u}	a_{2g}	a_{2u}	e_g	e_u
CF_3 stretch (antisym.)					ν_8	ν_{11}
CF_3 stretch (sym.)	ν_1			ν_5		
CF_3 deform. (antisym.)					ν_9	ν_{12}
CF_3 deform. (sym.)	ν_2			ν_6		
CF_3 rock					ν_{10}	ν_{13}
HgC_2 stretch (antisym.)				ν_7		
HgC_2 stretch (sym.)	ν_3					
HgC_2 bend						ν_{14}
(CF_3 torsion *)		(ν_4 *)				
Activity	R, pol.			I.R.	R, depol.	I.R.

* Absent for free rotation.

Abbreviations: R = Raman-active; I.R. = infrared-active; pol. = polarised; depol. = depolarised.

The infrared spectrum of bistrifluoromethylmercury in the solid state is very similar to that of the material in solution; an additional intense band at ~1050 cm.$^{-1}$ may be due to the " forbidden " symmetric C–F stretching frequency, ν_1, the appearance of which is attributed to a lowering of symmetry through intermolecular interactions in the crystal lattice. The remaining weak bands in the spectrum can be ascribed to suitable combinations of the fundamentals. Significantly, as required by the D_{3d} selection rules, no first overtones are observed in the infrared spectrum; the symmetry species of the observed combinations are consistent with infrared activity on the basis of these rules (see Table 1).

The general simplicity of the infrared and Raman spectra strongly supports the linear-skeleton model for the $Hg(CF_3)_2$ molecule. If the skeleton were appreciably bent, the point group would be C_{2v}, the selection rules for which would permit all 21 fundamentals (or 19 with free CF_3 rotation) in both the Raman and infrared spectra, seven of the Raman lines being polarised. For the D_{3d} model there should be no coincidences between Raman and infrared fundamental frequencies. The two near-coincidences observed (at ~520 and ~710 cm.$^{-1}$) are explained by the near-degeneracy of the appropriate Raman- and infrared-active modes; comparison with the vibrational spectra of dimethylmercury [12,13] suggests that there should be

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[15] Plyler and Benedict, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 2245; Edgell and May, *J. Chem. Phys.*, 1954, **22**, 1808.

[16] Coates, unpublished work.

little difference in frequency between ν_2 and ν_6 (~710 cm.$^{-1}$), ν_9 and ν_{12} (~520 cm.$^{-1}$), and ν_{10} and ν_{13} (~260 cm.$^{-1}$) when CH_3 is replaced by the much heavier CF_3 group. There is less ambiguity about the two Hg–C stretching modes (ν_3 and ν_7), the activities of which are consistent with a centrosymmetric molecule.

The frequencies of the three strongest Raman lines for a series of solutions of bistrifluoromethylmercury are listed in Table 3. Change of concentration does not affect the position of the lines for solutions up to 3M. Slight frequency changes in the Raman spectra of solutions containing bistrifluoromethylmercury and an excess of an alkali metal halide are indicated in Table 4.

Fluorine Resonance Spectra.—The fluorine resonance spectrum of the mercury compound in solution consists of a single line with two sets of satellites due to ^{199}Hg–F and ^{13}C–F coupling; the appropriate parameters for solutions in benzene, methanol, and pyridine are contained in Table 5. The addition of a mercuric halide to a solution of bistrifluoromethylmercury has no effect on the spectrum. For potassium iodide and the mercury compound (1 : 1) in methanolic solution, $\phi(^{19}F)$ [17] is observed to be $+35{\cdot}7 \pm 0{\cdot}2$ p.p.m. and $J(^{199}HgF)$ $1312{\cdot}2 \pm 0{\cdot}3$ c./sec., representing slight changes in the same direction as those observed when pyridine is used as a solvent.

TABLE 3.

Strong lines (± 2 cm.$^{-1}$) in the Raman spectrum of bistrifluoromethylmercury in various solvents.

Mode	H_2O	MeOH	C_6H_6	Et_2O	$COMe_2$	MeCN	Pyridine
ν_8	1160	1155	1149	1154	1156	1157	1151
ν_2	713	713	713	714	712	713	708
ν_3	226	225	223	224	224	223	219

TABLE 4.

Strong Raman lines (± 2 cm.$^{-1}$) of bistrifluoromethylmercury in the presence of an excess of halide ions.

Halide	Solvent	ν_8	ν_2	ν_3
KCl *	H_2O	1154	712	222
KBr *	H_2O	1152	711	220
KI *	H_2O	1158	710	221
LiBr	MeOH	1152	712	219

* System decomposed slowly during irradiation.

TABLE 5.

Fluorine resonance spectrum of bistrifluoromethylmercury.

Solvent	$\phi(^{19}F)$ * (p.p.m. $\pm$ 0·1) ($CCl_3F = 0$)	$J(^{199}HgF)$ (c./sec. $\pm$ 0·2)	$J(^{13}CF)$ † (c./sec.)
Benzene	+36·4	1324·5	356·3 $\pm$ 0·2
Methanol	+36·6	1312·1	—
Pyridine	+33·85	1259·9	358·4 $\pm$ 0·4

* No significant variation in chemical shift as a function of concentration is observed. † The ^{13}CF satellites consist of quartets with a splitting of 5·3 $\pm$ 0·1 c./sec. (benzene solution), or 3·8 $\pm$ 0·3 c./sec. (pyridine solution).

EXPERIMENTAL

Bistrifluoromethylmercury was prepared by reaction of trifluoromethyl iodide with cadmium amalgam at room temperature; [1] it was purified as described by Emeléus and Haszeldine.[1]

The Raman effect was examined with solutions of the pure compound at concentrations ranging from 0·3M to 3M; the solutions were centrifuged and filtered through a fine glass sinter to obtain clear samples (~5 ml.). Solutions containing mercuric salts or ionic halides were

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[17] Filipovich and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.

approximately molar with respect to bistrifluoromethylmercury. The spectra were reproduced directly by means of a pen recorder coupled to a Hilger E612 spectrometer. The light source was a commercial unit (Hilger FL1) comprising four mercury discharge lamps, or a spiral Toronto-arc arrangement; in both cases the spectra were excited by the 4358 Å mercury line. The observed frequencies were calibrated from the position of appropriate strong bands in the spectra of pure carbon tetrachloride, benzene, and acetone, and are correct within ± 2 cm.$^{-1}$ for all but the weak and diffuse bands.

Infrared spectra over the range 400—4000 cm.$^{-1}$ were recorded with a Perkin-Elmer model 21 double-beam spectrometer, fitted with either a sodium chloride or potassium bromide prism; the range 200—400 cm.$^{-1}$ was investigated with a Grubb-Parsons DB3/DM2 double-beam grating spectrometer. Solid bistrifluoromethylmercury was examined as a mull with Nujol or hexachlorobutadiene, and in a KBr disc.

Fluorine resonance spectra were recorded at 40 Mc./sec. with a Varian Associates V-4300B high-resolution nuclear magnetic resonance spectrometer with flux stabiliser, by the sample-spinning technique. The samples were contained in Pyrex tubing of 5 mm. external diameter. The ^{13}C–F and ^{199}Hg–F coupling constants of the mercury compound were measured for the most concentrated solutions obtainable (3—4M); chemical shifts were determined for dilute solutions (~0·3M) containing a drop of trichlorofluoromethane as internal standard. Ultraviolet spectra were recorded at wavelengths between 190 and 390 mμ on a Perkin-Elmer model 137 UV spectrophotometer.

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DEPARTMENT OF INORGANIC CHEMISTRY, THE UNIVERSITY,
NEWCASTLE UPON TYNE 1.

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