

A LASER RAMAN, INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRAL STUDY OF COMPLEXATION OF METHYLMERCURY(II) THIOCYANATE BY IONIC THIOCYANATE

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SUMMARY

Aqueous alkali thiocyanate solutions containing dissolved methylmercury thiocyanate have been examined by laser Raman, infrared and nuclear magnetic resonance spectroscopy. The similarity of the observed Hg-S stretching frequency at ca. 280 cm^{-1} to the value for CH_3HgSCN in diglyme solution has been considered to favour a complex-ion model incorporating an essentially unperturbed CH_3HgSCN moiety. This conclusion is supported by the comparatively marginal displacement of the Hg-C and C-N stretching frequencies from their positions for CH_3HgSCN . The NMR coupling constant, $J(^{199}\text{Hg}-\text{C}-^1\text{H})$, observed for these solutions increases from 205.6 Hz for CH_3HgSCN to 212.5 Hz for a solution containing CH_3HgSCN and alkali thiocyanate in molar ratio 1/16. The magnitude of this change is also in accord with essentially unchanged hybridization of mercury after complexation. Coupling constant calculations using the extended Hückel method for a covalent species $\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$ predicted a lower coupling constant than that observed for CH_3HgSCN .

INTRODUCTION

It has been claimed that methylmercury can coordinate only one ligand¹. This generalization is based on dissociation studies², crystal structure determinations^{3,4} and spectroscopic investigations^{5,6} of methylmercury compounds. In apparent contradiction of this evidence are the numerous instances of complex formation between methylmercury compounds and neutral or ionic ligands⁷. Barbieri *et al.*^{8,9} investigating the ethylmercury thiocyanate/potassium thiocyanate system have concluded that negatively charged complexes of the general type, $\text{C}_2\text{H}_5\text{Hg}(\text{SCN})_n^{1-n}$ where n ranged from 1 to 3, are present. The stability of alkylmercury complexes has been found¹⁰ to decrease in the following order: $\text{CH}_3 < \text{C}_2\text{H}_5 < \text{C}_3\text{H}_7$. The formation of the following alkylmercury complexes has also been previously investigated: $\text{C}_2\text{H}_5\text{-HgBr}_2^-$, $\text{C}_2\text{H}_5\text{HgBr}_2^{2-}$ ¹¹, $(\text{R}_f)_2\text{HgI}^-$, $(\text{R}_f)_2\text{HgI}_2^{2-}$ where R_f is a fluoroalkyl ligand¹² (the existence of these complexes has been questioned by Downs¹³); $(\text{R}_f)_2\text{HgL}$ and

$(R_f)_2HgL_2$ where R_f is a fluoroalkyl or fluoroaryl ligand and L is pyridine, pyridine *N*-oxide and other ligands^{14,15}. A number of phenylmercury halide complexes with nitrogen donor atoms are also known¹⁶.

Two stereochemical configurations are possible for four coordinate species formed by the complexation of methylmercury thiocyanate by ionic thiocyanate:

(a) effective tetrahedral covalent coordination around mercury as is found¹⁷ for $Hg(SCN)_4^{2-}$ in the crystal; and

(b) distorted tetrahedral coordination in which the mercury-carbon bond and one mercury-thiocyanate bond are covalent bonds and remaining mercury-thiocyanate bonds are weaker interactions. This type of coordination configuration has been found¹⁸ for crystalline $Hg(CN)_2$.

The object of the present investigation was to distinguish between these possible arrangements for a case where covalent mercury-ligand bonding seemed a genuine possibility as evidenced by earlier related spectroscopic investigations^{19,20,21}. Polarographic investigations⁹ suggest that distinct complex formation of the type described above occurs for the thiocyanate and iodide systems, but not for the other halides.

EXPERIMENTAL

Preparation of compounds

*Methylmercury(II) iodide*²². Methyl iodide (40 g, 0.35 mole) and mercury (20 g, 0.10 mole) were exposed to sunlight for one week. The CH_3HgI was separated from the mixture using a Soxhlet extractor with absolute alcohol as solvent. The solution was cooled and methylmercury iodide was filtered off and recrystallized from hot ethanol (yield: 80%). The product (m.p. 151°, lit.²² 152°) was analysed. (Found: C, 3.44; H, 0.94; I, 37.02. CH_3HgI calcd.: C, 3.51; H, 0.88; I, 37.04%.)

Methylmercury(II) thiocyanate. CH_3HgI (5 g, 15 mmole) and silver thiocyanate (2.5 g, 15 mmole) were shaken in ethanol (25 ml) for three hours. The silver iodide and excess silver thiocyanate were filtered off and the filtrate was evaporated to dryness under a vacuum. The product obtained was then recrystallized from benzene and white platelets were obtained (yield, 90%; m.p. 125°, lit.² 125.5°) and were analysed. (Found: C, 8.82; H, 1.00; S, 11.5. C_2H_3HgNS calcd.: C, 8.79; H, 1.10; S, 11.72%.) Various other methods of preparation and purification were attempted. Preparation by the addition of alkali thiocyanate to a solution of $CH_3HgOOCCH_3$ resulted in a product from which it was difficult to completely eliminate impurities. Recrystallization of CH_3HgSCN from water or acetone resulted in partial decomposition. Infrared spectra of CH_3HgSCN after recrystallization from these solvents included a peak at ca. 2060 cm^{-1} which may have been due to traces of free thiocyanate. Attempted purification by sublimation resulted in partial decomposition.

The methylmercury(II) acetate was a Pfaltz & Bauer laboratory reagent. The lithium thiocyanate was a B.D.H. laboratory reagent and the potassium thiocyanate a B.D.H. analytical reagent. Both alkali thiocyanates were dried by storing them in a vacuum over P_2O_5 . Other reagents were of analytical reagent grade.

The following series of solutions were investigated by the techniques indicated: (1) $CH_3HgSCN/LiSCN$ in CH_3OH (IR, Raman, NMR); (2) $CH_3HgSCN/KSCN$ in H_2O (IR, Raman); (3) $CH_3HgSCN/KSCN$ in D_2O (NMR); (4) $CH_3HgSCN/LiSCN$

in CH_3NO_2 (NMR); (5) $\text{CH}_3\text{HgSCN}/\text{CH}_3\text{HgClO}_4$ in CH_3NO_2 (NMR).

These solutions were prepared by weighing into a test-tube exact quantities of CH_3HgX and alkali salt and subsequent addition of solvent. Because of the toxicity of the organomercurials, solutions were prepared on a small scale (typically 2 ml). For this reason while molar ratios tabulated are accurate, the concentrations given are only approximate. Methylmercury perchlorate (0.2 M) was prepared in 10 ml of nitromethane [solution (5)] by the reaction of CH_3HgI (0.68 g, 2 mmole) with silver perchlorate (0.42 g, 2 mmole). Silver iodide was filtered off. The isolation of methylmercury perchlorate was not attempted due to its explosive nature. Solution (5) was prepared by the addition of methylmercury thiocyanate (0.96 g, 0.35 mmole) to 2 ml of the $\text{CH}_3\text{HgClO}_4$ solution. Evidence for the formation of the complex $(\text{CH}_3\text{Hg})_2\text{-SCN}^+$ has been reported by Schwarzenbach *et al.*².

Several attempts were made to isolate $\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$ as the potassium, cesium, ammonium, tetramethylammonium and barium salts. These attempts in all cases resulted in the formation, as evidenced by infrared spectra, of a mixture of $\text{K}_2\text{Hg}(\text{SCN})_4$, KSCN and another component. The third component exhibited infrared absorptions at 2129 s(sharp), 2076 s(broad), 773 m(broad) and 529 w(sharp) cm^{-1} .

Microanalyses of C, H and S were carried out by the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

Spectra

Raman spectra were recorded using a Perkin-Elmer LR-1 spectrometer with an 8 mW laser source (He/Ne, 632.8 nm).

Infrared spectra were recorded on expanded scale using an Hitachi EPI-G2 infrared spectrometer (covering the region 4000 to 400 cm^{-1}). Spectra were also recorded on a Perkin-Elmer 225 infrared spectrometer (4000–200 cm^{-1}) and a Jasco IR-F spectrometer (700–200 cm^{-1}). Solid spectra were recorded as nujol or fluorolube mulls supported by KBr, ultrapure silicon* or polyethylene supports. Spectra of solutions were recorded with samples supported by thin polyethylene sheets.

The infrared spectrum of methylmercury(II) thiocyanate was recorded at 293° and at 77°K using a standard low-temperature infrared cell^{23,24}, with liquid nitrogen as coolant. The only change in the spectrum was a splitting of a band at 2990 cm^{-1} in the room temperature spectrum into components at 2994, 2975 and 2918 cm^{-1} in the spectrum recorded at 77°K. The failure to observe any significant change in the C–N stretching frequency (2185 cm^{-1} at 293°K; 2188 cm^{-1} at 77°K) which would be expected to be sensitive to major structural change (for example, changes in mercury coordination) indicates that no such structural change occurs between 293° and 77°K.

The infrared spectrum of a CsI disc of CH_3HgSCN in the region 700–200 cm^{-1} indicated that partial thiocyanate displacement by iodide had occurred as evidenced by the appearance of absorptions at 527 cm^{-1} (similar to an absorption of CH_3HgI)⁵ and at 485 and 474 cm^{-1} (ionic thiocyanate bands) as well as bands at 552, 441 and 233 cm^{-1} . The spectrum of CH_3HgSCN as a nujol mull between ultrapure silicon supports included only these latter three features.

* The ultrapure silicon (99.999999% pure) was supplied by Alfa Inorganics as a one inch diameter rod. The rod was cut into thin sections and polished to give blanks of ca. 1 mm thickness.

Nuclear magnetic resonance

NMR spectra were recorded using a Perkin-Elmer R-20 spectrometer and employing sodium 3-(trimethylsilyl)propanesulphonate (δ 0.02 ppm) as internal standard for the methanol and D₂O solutions and the solvent resonance at δ 4.29 ppm as internal standard for the nitromethane solutions.

Extended Hückel calculations

In the one electron MO approximation, the Fermi contact contribution, $J(A-B)$, to the coupling of nuclei A and B is given by the following equation originally derived by Pople and Santry²⁵.

$$J(A-B) = -(128/9)\pi \cdot h \cdot \beta^2 \cdot \gamma_A \cdot \gamma_B \cdot \sum_i^{\text{occ}} \cdot \sum_j^{\text{unocc}} \\ (E_j - E_i)^{-1} \cdot \sum_{\mu\nu\lambda\sigma} C_{i\mu} \cdot C_j \cdot C_j \cdot C_{i\sigma} \\ \langle \phi_\lambda | \delta(r_A) | \phi_\mu \rangle \cdot \langle \phi_\nu | \delta(r_B) | \phi_\sigma \rangle$$

The authors use of the above equation was modified by including not only one center integrals over *s* orbitals but all multicenter integrals over valence shell orbitals subject to the one restriction that the origin for orbitals ϕ_λ and ϕ_μ must lie within 3 Å of atom A and similarly for atom B.

One electron wave functions and energies were computed according to the extended Hückel theory, using the following valence orbital ionization potentials (VOIP's) for the diagonal elements of the Hamiltonian matrix (*H*; in eV's):

$$\begin{aligned} H(H_{1s}) &= -13.60, & H(C_{2s}) &= -19.41 \\ H(C_{2p}) &= -10.64, & H(N_{2s}) &= -25.56 \\ H(N_{2p}) &= -13.19, & H(S_{3s}) &= -20.66 \\ H(S_{3p}) &= -11.58, & H(Hg_{5d}) &= -15.66 \\ H(Hg_{6s}) &= -10.44, & H(Hg_{6p}) &= -5.00 \quad (\text{ref. 26a-c}). \end{aligned}$$

All overlaps were included and are calculated using Clementi's double zeta functions²⁷ for all atoms except mercury where the Herman and Skillman²⁸ functions for mercury(I) were employed. This ensures at least approximately correct behavior of the valence orbitals at all nuclei.

The off diagonal elements were approximated using the Cusach's expression:

$$H_{\mu\nu} = 0.5 S_{\mu\nu} \cdot (2 - |S_{\mu\nu}|) \cdot (H_{\mu\mu} + H_{\nu\nu})$$

which was handled so as to retain invariance to rotation^{29,30}.

For these calculations the geometry of the H₃CHg⁺ ion was held fixed with $R_{\text{CH}} = 1.095$ Å, $R_{\text{CHg}} = 2.06$ Å³¹ and tetrahedral angles. Other distances and angles are taken from ref. 32 or are as listed in Table 6.

RESULTS AND DISCUSSION

The spectroscopic parameters employed in the present investigation to distin-

* All terms are defined in the original reference.

guish between a covalent and an ionic model for the ion, $\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$, are the metal–ligand vibrational frequencies, the carbon–nitrogen stretching frequencies and the NMR coupling constants, $J(^{199}\text{Hg}-\text{C}-^1\text{H})$.

The Hg–S stretching frequency of methylmercury(II) thiocyanate would be anticipated to undergo a substantial decrease if additional thiocyanate ligands were covalently bonded to mercury (see Table 1)^{19,33,34}. In contrast the mercury–sulphur stretching frequency would be anticipated to be only marginally displaced relative to the neutral molecule if the complex were of an anion-dipole type. Such a result was found in the case of the complex, $\text{Hg}(\text{CN})_2\text{Cl}_2^{2-}$, where the evidence indicated³⁵ that the mercury–chloride bonds were essentially ionic. The dependence of the Hg–C stretching frequencies of several RHgX compounds on the nature of X suggests that this parameter may also be sensitive to further changes in the covalent coordination of mercury^{5,6,36}.

TABLE 1

MERCURY–SULPHUR STRETCHING FREQUENCIES ($\Delta\bar{\nu}$, cm^{-1})

Species	$\nu(\text{Hg}-\text{S})$
HOHgSCN	299 ^a
CH_3HgSCN	283 ^b
$\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$	276 ^c
$\text{Hg}(\text{SCN})_2$	278 ^b
$\text{Hg}(\text{SCN})_2^{2-}$	239 ^b
$\text{Hg}(\text{SCN})_x\text{I}_y^{-(x+y-2)}$	221 ^d

^a Ref. 21. ^b Ref. 19. ^c This work. ^d Ref. 20.

The carbon–nitrogen stretching frequency of the thiocyanate anion is 2068 cm^{-1} , and of CH_3HgSCN in methanol, 2138 cm^{-1} ¹⁹. The C–N stretching frequency of a complex thiocyanate anion of methylmercury would be expected¹⁹ to be observable between 2068 and 2138 cm^{-1} .

As the *s* character of C–Hg bonds of CH_3HgX molecules increases the numerical value of the NMR coupling constant, $J(^{199}\text{Hg}-\text{C}-^1\text{H})$ increases^{37,38,39}. For compounds of the type R_2Hg , electron donating substituents increase the electron-density in the carbon–mercury bond by increasing *p* character and thus decreasing the *s* character of the bond. On the other hand, electron withdrawing substituents increase the *s* character of the carbon–mercury bond and so increase the coupling constants. The *s* character of the carbon bonds when the carbon is bonded to mercury remains practically constant. The change in $J(^{199}\text{Hg}-\text{C}-^1\text{H})$ could therefore be attributed to changes in *s* character of the valence orbitals of mercury³⁷.

In addition to hybridization changes at mercury, the electron donating substituents will lead to a decrease in the effective nuclear charge for the mercury 6s orbital and the concomitant decrease in the density of this orbital at the mercury nucleus will also contribute to a decrease in the coupling constant³⁸.

(a). *Mercury–ligand vibrational frequencies.* The significant data derived from the Raman and infrared spectra of $\text{CH}_3\text{HgSCN}/\text{KSCN}/\text{H}_2\text{O}$ and $\text{CH}_3\text{HgSCN}/\text{LiSCN}/\text{CH}_3\text{OH}$ solutions are summarized in Tables 2 and 3.

TABLE 2

FREQUENCIES FOR THE SYSTEM $\text{CH}_3\text{HgSCN}/\text{MSCN}/\text{SOLVENT}$ FOR THE REGION $600\text{--}200\text{ cm}^{-1}$ IN THE RAMAN SPECTRUM

Concn. (M), CH_3HgSCN	Concn. (M), MSCN	Molar ratio ($\text{CH}_3\text{HgSCN}/\text{MSCN}$)	Raman shifts ($\Delta\bar{\nu}$, cm^{-1})			
0.5	0.5 (Li) ^a	1/1 (CH_3OH)	540 s(p)	519 w ^b	285 m(p) ^c	238 w(p)
0.5	1.0 (Li)	1/2 (CH_3OH)	540 s(p)	516 w	283 m(p)	238 w(p)
0.5	4.0 (Li)	1/8 (CH_3OH)	537 s(p)	516 w	278 m(p)	238 w(p)
0.25	10.0 (K)	1/40 (H_2O)	540 s(p)	^d	276 m(p)	
	CH_3HgSCN		540 (p) ^e			
	$(\text{CH}_3)_2\text{Hg}$			515 ^f		
	$\text{Hg}(\text{SCN})_4^{2-}$					239 (p) ^e

^a Alkali cation in alkali thiocyanate. ^b Polarization measurements inconclusive. ^c (p) = polarized. ^d No line observed. ^e Ref. 19. ^f Ref. 36.

TABLE 3

VIBRATIONAL FREQUENCIES FOR THE SYSTEM $\text{CH}_3\text{HgSCN}/\text{MSCN}/\text{SOLVENT}$ IN THE REGION $2000\text{--}2200\text{ cm}^{-1}$

Concn. (M), CH_3HgSCN	Concn. (M), MSCN	Molar ratio ($\text{CH}_3\text{HgSCN}/\text{MSCN}$)	Raman ($\Delta\bar{\nu}$, cm^{-1})	Infrared (ν , cm^{-1})
0.5	0.5 (Li) ^a	1/1 (CH_3OH) ^b	2124 (p) ^c	2133
0.5	1.0 (Li)	1/2 (CH_3OH) ^b	2124 (p)	2130
0.5	4.0 (Li)	1/8 (CH_3OH) ^b	2123 (p)	2126
0.25	10.0 (K)	1/40 (H_2O) ^b	2119 (p)	^d

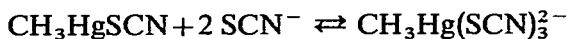
^a Alkali cation in alkali thiocyanate. ^b Frequencies attributable to ionic thiocyanate were observed at 2060 cm^{-1} in the Raman spectra of all the solutions and at 2061 cm^{-1} in the infrared spectra of all the solutions. ^c (p) = polarized. ^d Shoulder.

For all of the solutions studied the Hg–C stretching frequency was observed at ca. 540 cm^{-1} in the Raman spectrum. The position of this band did not change significantly with increasing thiocyanate concentration. The band was in all cases intense and polarized. The profile of the 540 cm^{-1} line was symmetrical for spectra of the aqueous solutions while for the methanolic solutions the profile was asymmetric on the lower frequency side. A sub-band analysis assuming only two components revealed a weak sub-band centred at ca. 516 cm^{-1} . This band coincides with the carbon–mercury symmetric stretching vibration of dimethylmercury (514 cm^{-1})^{40,41}. On the basis of this evidence it would appear that an equilibrium of the type:



exists in these solutions and is further to the right in the methanol solutions than it is in the aqueous solutions. Disproportionation reactions of this type have been discussed by Dessy and Lee⁴².

The bands observed at ca. 278 cm^{-1} for the methanol solutions and 276 cm^{-1} for the aqueous solutions are only slightly displaced from the Hg-S stretching frequency for CH_3HgSCN in methanol (283 cm^{-1})¹⁹. In the aqueous solution all CH_3HgSCN is presumed to be present in the form of a complexed anion as CH_3HgSCN is insoluble in water at room temperature. Therefore the sole Hg-S stretching frequency observed for that solution (276 cm^{-1}) is attributed to the complex ion $\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$. This frequency has a counterpart in the spectra of the methanol solutions which decreases from 285 to 278 cm^{-1} with increasing concentration of lithium thiocyanate. This shift is considered to indicate that in solutions containing a ratio of $\text{CH}_3\text{HgSCN}/\text{LiSCN}$ of $1/1$ the predominant species is uncomplexed CH_3HgSCN , while in the $1/8$ solution the equilibrium:



is sufficiently far to the right that $\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$ is the predominant species.

Confirmation of the existence of the symmetrization equilibrium described earlier is found for the methanol solutions in the Hg-S stretching region where two polarized bands (278 and 238 cm^{-1} for a solution having a $\text{CH}_3\text{HgSCN}/\text{LiSCN}$ ratio of $1/8$) have been observed. The 238 cm^{-1} line coincides with the Hg-S stretching frequency of $\text{Hg}(\text{SCN})_4^{2-}$ ¹⁹. The assignment to this species rather than to a covalent $\text{CH}_3\text{Hg}(\text{SCN})_3^{2-}$ species is indicated by the approximately constant ratio

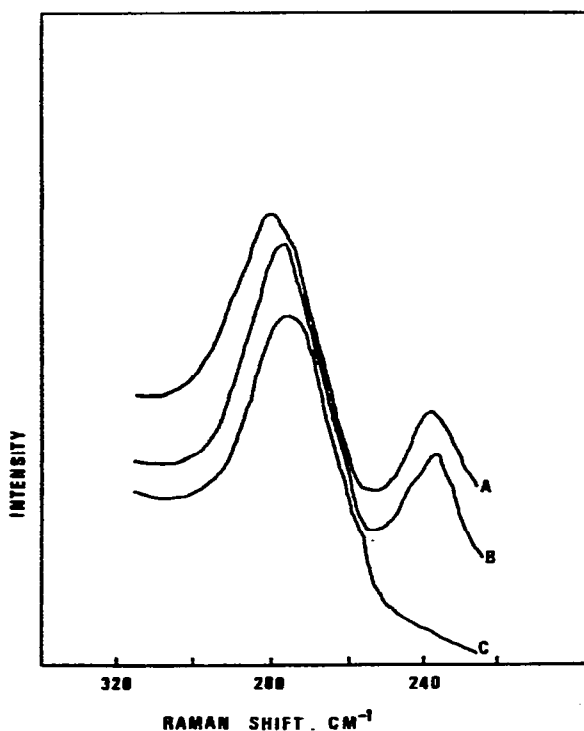


Fig. 1. Raman spectra of $\text{CH}_3\text{HgSCN}/\text{MSCN}/\text{Solvent}$ in the region from 220 to 320 cm^{-1} . Spectrum A: $1\text{ M CH}_3\text{HgSCN}$, 2 M LiSCN in CH_3OH ; Spectrum B: $1\text{ M CH}_3\text{HgSCN}$, 8 M LiSCN in CH_3OH ; Spectrum C: $1\text{ M CH}_3\text{HgSCN}$, 20 M KSCN in H_2O .

of integrated intensities of the band at ca. 280 cm^{-1} to that of the band at 238 cm^{-1} , for substantially different ratios of CH_3HgSCN to LiSCN considered (see Fig. 1). The failure to observe a Raman line at ca. 240 cm^{-1} in spectra of the aqueous solution system correlates with the failure to detect the Hg-C stretching frequency for $(\text{CH}_3)_2\text{-Hg}$ in the same solutions.

The similarity of the Hg-S stretching frequencies for the aqueous solution to that observed for methylmercury thiocyanate in solution is considered to unambiguously favour the ion-dipole complex formulation. This conclusion is further substantiated by the observation that the Hg-C stretching frequency for the aqueous solution system coincides with that observed for CH_3HgSCN in methanol¹⁹.

(b). *Thiocyanate frequencies.* The Raman line observed at 2119 cm^{-1} in the spectrum of the aqueous solution was assigned to the C-N stretching frequency of a covalently bonded SCN ligand of the ion-dipole complex $\text{CH}_3\text{Hg}(\text{SCN})_2^-$. The C-N stretching frequencies in the Raman spectra of the methanolic solutions were intermediate between the corresponding frequencies observed for CH_3HgSCN (2138 cm^{-1})¹⁹ and the ion-dipole complex (2119 cm^{-1}) and consequently the band profiles in these cases are considered to incorporate contributions from both complexed and uncomplexed CH_3HgSCN . The similarity of the frequencies for complexed CH_3HgSCN to that for uncomplexed CH_3HgSCN supports the contention that the CH_3HgSCN entity remains essentially unperturbed in the anion complex. The C-N stretching frequencies of the ionic thiocyanate ligands are not distinguishable from the Raman line (2060 cm^{-1}) due to ionic thiocyanate.

The only observable infrared absorptions for the $\text{CH}_3\text{HgSCN}/\text{LiSCN}$ methanol solutions (other than those due to solvent) are assigned to carbon-nitrogen stretching. The feature at ca. 2130 cm^{-1} was attributed to covalently bonded thiocyanate. The absorption maximum shifted from 2135 to 2126 cm^{-1} with increasing concentration of alkali thiocyanate. The observation of the ionic thiocyanate absorption at $2061 \pm 1.5\text{ cm}^{-1}$ in all of the solutions examined confirmed that the displacement in the absorption due to covalent thiocyanate was real. This shift in frequency is considered to arise from a breakdown in marginal intermolecular interaction in solution of the same type as that which caused splitting of the $\text{C}\equiv\text{N}$ stretching frequencies (observed at 2131 and 2181 cm^{-1}) for crystalline CH_3HgSCN ¹⁹. The breakdown in intermolecular interaction would result from coordination of thiocyanate anions. The C-N stretching vibration for the aqueous solution species appeared as a shoulder on the free thiocyanate absorption. The observation of the weak C-S stretching frequency in both Raman and infrared spectra of these solutions was not observed because of the intensity and breadth of the overlapping methyl rocking mode at 792 cm^{-1} .

(c). *Nuclear magnetic resonance spectra.* The significant data from the nuclear magnetic resonance investigation of the $\text{CH}_3\text{HgSCN}/\text{LiSCN}/\text{CH}_3\text{OH}$ and the $\text{CH}_3\text{HgSCN}/\text{KSCN}/\text{D}_2\text{O}$ systems are given in Tables 4 and 5. The concentration of LiSCN was varied so that the ratios of CH_3HgSCN (0.5 M) to LiSCN were 1/1, 1/2, 1/4, 1/6, 1/8 and 1/16 for the methanol solutions. Spectra of some of these solutions were also recorded in nitromethane. The results were not significantly different. In the aqueous (D_2O) solutions the ratios of CH_3HgSCN (0.25 M) to KSCN were 1/20 and 1/40.

The coupling constant, $J(^{199}\text{Hg}-\text{C}-^1\text{H})$, for CH_3HgSCN was found to in-

TABLE 4

NUCLEAR MAGNETIC RESONANCE DATA FOR THE SYSTEM:
CH₃HgSCN/MSCN/SOLVENT

Concn. (M), CH ₃ HgSCN	Concn. (M), MSCN	Molar ratio (CH ₃ HgSCN/MSCN)	Solvent	$J(^{199}\text{Hg}-\text{C}^{-1}\text{H})$ (Hz)
0.50			CH ₃ OH	205.6 ^b
0.25	0.25 (Li) ^a	1/1	CH ₃ OH	205.9
0.50	0.50 (Li)	1/1	CH ₃ OH	206.2
1.00	1.00 (Li)	1/1 ^c	CH ₃ OH	207.1
0.50	1.00 (Li)	1/2	CH ₃ OH	208.6
1.00	2.00 (Li)	1/2	CH ₃ OH	208.7
2.00	4.00 (Li)	1/2	CH ₃ OH	210.9
1.00	4.00 (Li)	1/4	CH ₃ OH	209.2
0.50	3.00 (Li)	1/6	CH ₃ OH	210.8
0.50	4.00 (Li)	1/8	CH ₃ OH	211.3
0.50	8.00 (Li)	1/16	CH ₃ OH	212.5 ^b
0.25	10.00 (K)	1/40	D ₂ O	219.4 ^b
0.25	~20 (K)	1/80	D ₂ O	222.7 ^b

^a Cation of the alkali thiocyanate. ^b The chemical shift [$\delta(^{200}\text{Hg}-\text{C}^{-1}\text{H})$] varied from 1.01 ppm for CH₃HgSCN in methanol to 1.19 ppm for the 1/16 solution (methanol), and was constant at 1.12 ppm for both the 1/40 and 1/80 solutions (D₂O). ^c A 1/1 solution of CH₃HgSCN/KSCN in CH₃OH exhibited a coupling constant of 208.5 Hz. A 1/1 solution of CH₃HgSCN/LiSCN in CH₃NO₂ exhibited a coupling constant of 206.0 Hz.

TABLE 5

CALCULATED AND EXPERIMENTAL COUPLING CONSTANTS FOR METHYLMERCURY THIOCYANATE COMPLEXES

Species	Coupling constant [$J(^{199}\text{Hg}-\text{C}^{-1}\text{H})$] (Hz)	
	Calcd.	Experimental ^a
CH ₃ HgSCN	-138	(-)205.6
CH ₃ Hg(SCN) ₂ ⁻	-118 ^b	(-)220.0
(CH ₃ Hg) ₂ SCN ⁺	-151	(-)239.9 ^c

^a The sign of the experimental constant is presumed to be negative. ^b Covalent. ^c The chemical shift [$\delta(^{200}\text{Hg}-\text{C}^{-1}\text{H})$] was 1.16 ppm measured relative to nitromethane (4.29 ppm).

crease while the chemical shift changed marginally as the alkali thiocyanate concentration increased. Dimethylmercury was detected in the spectra of the methanol solutions but not in the spectra of the aqueous solutions.

The small increase in coupling constant of methylmercury(II) thiocyanate on complexation (ca. 7 Hz estimated from the limiting upper value of a coupling constant vs. concentration plot: Fig. 2) suggests that no appreciable change in hybridization of the mercury has occurred. This small increase contrasts with the coupling constant decrease observed with covalent complex formation between dimethyltin (IV) and chloride^{4,3}.

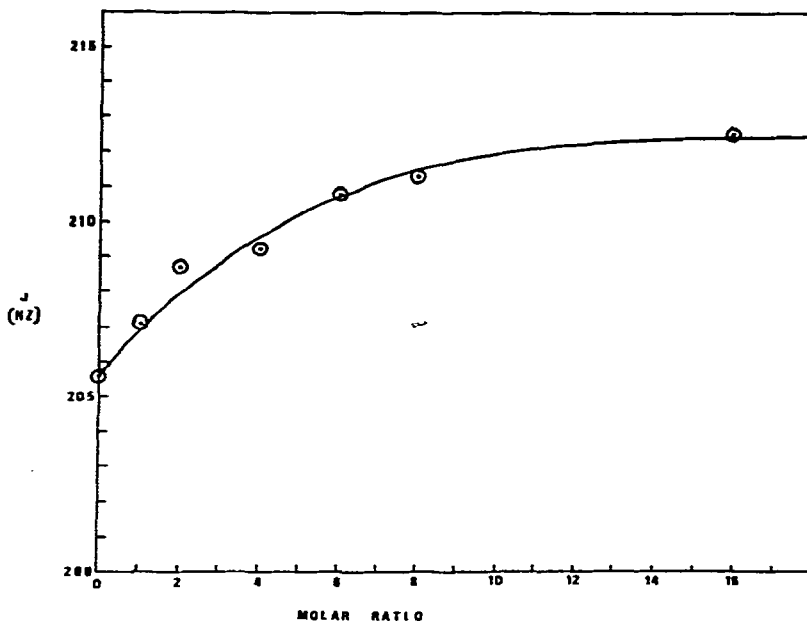


Fig. 2. Variation of $J(^{199}\text{Hg}-\text{C}^{-1}\text{H})$ with molar ratio of LiSCN to CH_3HgSCN . For molar ratios of 1, 2 and 4, $M(\text{CH}_3\text{HgSCN})=1.0$ and for ratios 6, 8 and 16, $M(\text{CH}_3\text{HgSCN})=0.5$.

Calculated and experimental values of the coupling constants of methylmercury(II) thiocyanate complexes are given in Table 5. The sign of the calculated coupling constants was found to be negative. Double resonance studies of dimethylmercury by *McLauchlan et al.*⁴⁴ have shown that the geminal coupling constant $J(^{199}\text{Hg}-\text{C}^{-1}\text{H})$ has a negative sign. It would therefore be anticipated that the sign of the coupling constants in Tables 4 and 5 should be negative.

Although the magnitudes of the calculated coupling constants are somewhat small they vary linearly with the experimental values³⁸. A least squares treatment for eight CH_3HgX systems*, including CH_3HgSCN , gave a good linear fit;

$$J_{\text{exp}} = +215.4 - 2.7308 J_{\text{calcd.}}$$

with an average deviation of 4 Hz and an index of determination of 0.973. It was found that the calculated value for the coupling constant of the cation $(\text{CH}_3\text{Hg})_2\text{-SCN}^+$ (151 Hz) was greater than the calculated value for the coupling constant of methylmercury(I) thiocyanate (138 Hz). This is in accordance with the experimental results (see Table 4). The calculated value of the coupling constant of the covalent methylmercury(II) thiocyanate anion, $\text{CH}_3\text{Hg}(\text{SCN})_2^-$ (118 Hz) was less than the calculated value for the coupling constant of methylmercury(II) thiocyanate (138 Hz). The experimental coupling constant of CH_3HgSCN increased with increasing alkali thiocyanate concentration.

According to the calculations the major contributing factor to the change in $J(^{199}\text{Hg}-\text{C}^{-1}\text{H})$ with changes in substituents is the change in effective nuclear charge

* For which both calculated and experimental coupling constants are available.

TABLE 6

ASSUMED MOLECULAR PARAMETERS FOR METHYLMERCURY THIOCYANATE SPECIES

(a). *Methylmercury thiocyanate*^a

d(Hg-S)	2.50 Å	θ (HgSC)	120°
d(S-C)	1.58 Å	θ (SCN)	180°
d(C-N)	1.21 Å	θ (SHgC)	180°

(b). *The covalent anion complex, CH₃Hg(SCN)₃²⁻ (as for CH₃HgSCN except)*

θ (HgSC)	109° 28'
θ (SHgS)	109° 28'

(c). *The cation complex, (CH₃Hg)₂SCN⁺ (as for CH₃HgSCN except)*

θ (HgSC)	135°, 90°
θ (HgSHg)	90°

^a Assumed bond distances and angles taken from refs. 3 and 32 with the exceptions of θ (HgSC), θ (SHgS) and θ (HgSHg) which were chosen to simplify molecular geometry.

of mercury. In CH₃Hg(SCN)₃²⁻ with three thiocyanate anions covalently bound to CH₃Hg⁺ the transfer of electron density is significantly larger than in CH₃HgSCN and the lower net positive charge on mercury leads to a lower density of the 6s orbital at the nucleus and a smaller coupling constant. In (CH₃Hg)₂SCN⁺ the opposite is true.

These results are also compatible with a change in hybridization at the mercury. An increase in the number of thiocyanate anions covalently bound to mercury should reduce the s character of the mercury hybrid directed to carbon. In an ion-dipole complex it is expected that the covalent bonding to the unique thiocyanate might be relaxed slightly in the presence of the two ionic thiocyanates and their negative charges, thus increasing the s character in the mercury-carbon bond^{37,39}.

Thus the coupling constant data further supports the formulation of the species, CH₃Hg(SCN)₃²⁻, as an ion-dipole complex rather than a predominantly covalent species.

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