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Coordination Complexes of Mercury(II) Pseudo-Halides Preparation and Infrared Spectra Studies of Hg^{II} Pseudo-Halides with N,N,N',N'-Tetramethylethylenediamine, 3-Cyanopyridine and Dimethylsulfoxide as Ligands

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Coordination compounds between N,N,N',N'-tetramethylethylenediamine, 3-cyanopyridine and dimethylsulfoxide as Lewis-bases and HgX_2 (where X = CN, SCN or Cl) as Lewis-acids have been prepared and characterized. The compounds have been examined spectrometrically in the infrared region 4000-200 cm^{-1} to establish the coordination sites and possible symmetries of the molecules. Assignments have been made for the Hg–X and Hg-ligand stretching vibrations.

Introduction

We have previously[1] investigated the complexing behaviour of HgX_2, (X = SCN or CN) with group IV halides where HgX_2 acted as Lewis bases. The present work was undertaken to study the behaviour of HgX_2 as Lewis acid with a well known chelating ligand, N,N,N',N'–tetramethylethylenediamine (TMen), 3-cyanopyridine (Cypy) which, though a bidentate ligand, cannot chelate due to its particular geometry and dimethylsulfoxide (DMSO), a monodentate ligand molecule with two donor atoms.

It was also considered of interest to compare the Lewis-acid character of the pseudo-halides of mercury with mercuric chloride towards the three types of ligands used in the present investigation.

The position of metal-halogen stretching frequencies ν(M–X) in the IR spectra of metal halides and their complexes is known to shift to a lower frequency region with increasing coordination number of the metal atom.[1,2] It was then considered interesting to investigate a similar effect on the ν(Hg–S) and ν(Hg–C) bands of $Hg(SCN)_2$ and $Hg(CN)_2$ on complex formation and compare the change with that of ν(Hg–Cl) vibration when $HgCl_2$ is involved in complex formation.

Experimental Section

Mercuric thiocyanate and mercuric chloride were Fisher certified grade and mercuric cyanide was Baker analyzed. The ligands were also obtained from commercial sources, *i.e.* 3-cyanopyridine (Cypy) from the K and K Laboratories Inc., N,N,N',N'-tetramethylethylene-diamine (TMen) and dimethylsufoxide (DMSO) from the Fisher Scientific Company. All the chemicals were used as such without further purification.

HgX_2 and TMen compounds. The compounds were prepared by mixing the reactants in warm tetrahydrofuran solution. In each case the molar ratio of the reactant was approximately 1:1. Crystalline compounds separated out on allowing the reaction mixture to stay overnight at room temperature. The colorless compounds so obtained were recrystallized from tetrahydrofuran solution, filtered and dried *in vacuo at room temperature.*

HgX_2 and Cypy compounds. The method of preparation of these compounds was the same as the one used to prepare the TMen compounds. The colorless crystalline compounds were obtained from the reaction mixture by partially evaporating tetrahydrofuran. The compounds were recrystallized from THF, filtered, washed with small portions of cold THF and dried *in vacuo* at room temperature.

HgX_2 and DMSO compounds. The compounds were prepared by dissolving HgX_2 in the minimum amount of warm DMSO. $Hg(CN)_2$ and $HgCl_2$ formed clear solutions but $Hg(SCN)_2$ formed turbid solution which had to be filtered warm. $Hg(SCN)_2$. 2DMSO and $Hg(CN)_2$. 2DMSO crystallized out from the respective reaction mixtures on standing overnight. $HgCl_2$. 2DMSO crystallized out on adding about 5 ml of absolute alcohol to the reaction mixture. The compounds were filtered out under suction and the excess DMSO removed under vacuo.

Micro elemental analyses and molecular weight determinations of the compounds were performed by Galbraith Laboratories Inc., Knoxville, Tennessee (U.S.A.). The analytical results are included in Table I. Conductivity measurements on these compounds in THF solution were made using Metrohm conductoscope, type E 365 B.

Infrared (IR) spectra were recorded on a Perkin-Elmer 621, grating spectrophotometer (4000-200 cm^{-1}).

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(1) S. C. Jain and R. Rivest, *Can. J. Chem.*, *47*, (1969).
(2) R. J. H. Clark, *Spectrochim. Acta*, *21*, 955 (1965).

The spectra of solids were taken in Nujol mulls using sodium chloride plates (4000-600 cm^{-1}) and caesium iodide plates or polyethylene discs (600-200 cm^{-1}). To examine the possible dissociation in the solutions, the spectra of some of the compounds were also recorded in THF solution using NaCl cells. The infrared spectra results in the normal and the far infrared regions are tabulated in the Tables II, III and IV.

Results and Discussion

System HgX_2 . TMen. Although ethylenediamine (*en*) is known to be a typical bidentate chelating ligand in coordination chemistry, its bridging behaviour has also been reported in many cases.[3,4,5] In such cases a model of the bridge structure has been shown where *en* is bonded in the trans form

Table I. Analytical results

Compounds	Color	Melting point °C	Hg% Cal. Found	C% Cal. Found	H% Cal. Found	N% Cal. Found	S% Cal. Found	Cl%	Mol. Weight Found Cal.	Nature of Adduct
$Hg(CN)_2$. TMen	Colourless	176-7	54.39 54.2	26.03 26.0	4.34 4.4	15.19 15.3	—		368.8 354	1:1
$Hg(SCN)_2$. TMen	Colourless	110-11	46.33 46.4	22.18 22.5	3.70 3.7	12.93 12.7	14.78 14.7		432.8 400	1:1
$HgCl_2$. TMen	Colourless	153-5	— —	18.57 18.7	4.12 4.0	7.22 7.1	— —		387.6 397	1:1
$Hg(CN)_2$. 2Cypy	Colourless	111-12	43.59 43.2	36.51 36.6	1.74 1.7	18.24 18.4	—		460.6 150	1:1
$Hg(SCN)_2$. Cypy	Colourless	137-8	47.69 47.5	22.82 22.1		13.31 12.6	15.22 14.9		420.6 220	1:1
$HgCl_2$. 2Cypy	Colourless	118-9		30.04 30.4	1.67 1.7	11.68 11.6	— —		479.6 176	1:2
$Hg(CN)_2$. 2DMSO	Colourless	96-7		17.60 17.7	2.93 2.9	6.85 6.9	15.65 15.8		408.9 213	1:2
$Hg(SCN)_2$. 2DMSO	Colourless	88-9		15.22 15.2	2.53 2.1	5.92 6.1	27.06 27.1		473 230	1:2
$HgCl_2$. 2DMSO	Colourless	112-13	46.90 47.1	— —	— —	— —	— —	16.58 16.4	— —	1:2

Table II. Infrared spectra results in Nujol mulls: System HgX_2 and TMen (cm^{-1})

TMen Neat	$Hg(SCN)_2$. TMen	$Hg(CN)_2$. TMen	$HgCl_2$. TMen	Band Assignments (8-14)
	2110 s	2168 s	—	ν(C≡N)
1410 m	1408 m	1408 m	1410 m	—CH_2 bending
1330 m	1338 sh	1345 s	1355 sh	—N—CH_3 deformation
1280 m	1292 m	1292 s	1292 s	CH_2 wagging
1265 s	1245 m	1253 s	1250 s	
1178 sh	1190 m	1187 m	1187 m	CH_2 twisting
1158 s	1164 s	1163 m	1164 m	
1136 s	1130 s	1131 s	1131 s	ν(C—C)
1096 s	1062 m	1072 s	1068 s	ν(C—N)
1032 s	1040 m	1034 s	1036 s	
—	1020 s	1016 s	1015 s	
931 m	955 s	948 s	951 s	CH_2 rocking
868 m	928 sh	930 s	929 s	
830 m	840 mw	—	885 sh	
782 m b	792 s	785 sh	785 s	
—	770 s	770 s	769 s	
—	703 s	—	—	ν(C—S)
—	699 s	—	—	
	587 m s	584 m s	584 m	ν(Hg—N)
492 w	450 s	458 s	467 s	ligand
445 w	437 s	430 s	432 s	
	476 s	—	—	δ(S—C≡N)
	419 s	—	—	
		430 s*		ν(Hg—C)
		411 s		
397 m	376 w	367 m	373 m	ligand
—	—	355 w	—	δ(Hg—C≡N)
—	—	317 m	—	
—	—	—	300 v s	ν(Hg—Cl)
—	—	—	270 v s	
—	296 sh	—	—	ν(Hg—S)
338 w	258 m	263 m	255 sh	—C—C—N bending (ligand)

* Since the band at about 430 cm^{-1} is observed for all the $Hg(CN)_2$ complexes, the ligand band and the ν(Hg—C) bands may be considered as overlapping in this case. v = very, s = strong, m = medium, w = weak, sh = shouler, b = broad.

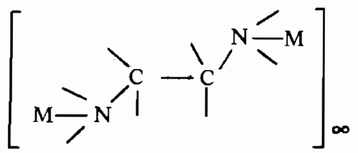
Table III. Infrared spectral results: System HgX_2 and Cypy (cm^{-1})

Cypy Nujol	Cypy THF	$Hg(SCN)_2$. Cypy Nujol	$Hg(SCN)_2$. Cypy THF	$Hg(CN)_2$. 2Cypy Nujol	$Hg(CN)_2$. 2Cypy THF	$HgCl_2$. 2Cypy Nujol	$HgCl_2$. 2Cypy THF	Band assignments (21, 25)
2231 s	2232 s	2233 m	2233 m	2234 s	2233 sh	2233 s	2233 s	$\nu(C\equiv N)$ ligand
		2120 s	2125 s	2182 m	2185 m	—	—	$\nu(C\equiv N)$ Lewis acid
		2075 sh	—	—	—	—	—	
1585 s	1585 s	1598 m	1586 s	1598 s	1585 s	1596 s	1586 m	ring stretching frequencies
1555 s	1562 s	1571 m	1560 m	1570 s	1562 m	1570 s	1560	
1415 s	1406 s	1423 s	—	1418 sb	1404 sh	1420 s	—	
1209 m		1207 w		1205 m		1208 sh		C—H in plane deformation
1200 m		1200 w		—		1202 m		
1183 m		1190 m		1184 s		1185 s		
1220 w		1122 m		1122 s		1123 m		
1055 w		1059 m		1058 s		1060 m		
1030 m		1041 s		1039 s		1040 s		ring sketeral vibrations
1018 s		1028 m		1026 s		1028 s		
778 m		789 m		782 m		785 m		C—H out of plane vibration
—		730 sh		—		—		$\nu(C—S)$
—		722 m		—		—		
695 s		689 s		693 s		693 s		ring bending
631 s		645 s		637 s		660 m		
—		628 m		—		640		
552 s		554 s		556 s		556 s		ligand
—		471 m		473 m		472 m		$\nu(Hg—N)$
—		460 m		—		—		$\delta(S—C\equiv N)$
—		432 m		—		—		
—		—		424 s		—		$\nu(Hg—C)$
394 s		398 m		398 s		397 m		ligand
352 m		350 w		354 m		356 m		
—		—		—		328 s		$\nu(Hg—Cl)$
—		—		—		387 m		
—		—		323 m		—		$\delta(Hg—CN)$
—		—		320 sh				
—		298 w		—		—		$\nu(Hg—S)$

Table IV. Infrared spectra results: System HgX_2 and DMSO (cm^{-1})

DMSO Neat	$Hg(SCN)_2$. 2DMSO Nujol	$Hg(CN)_2$. 2DMSO Nujol	$HgCl_2$. 2DMSO Nujol	Band assignments (25, 33, 34)
—	2120 s	2184 m	—	$\nu(C\equiv N)$
1435 m	1440 s	1440 s	1434 s	Asym CH_3 deformation
1415 sh	1410 sh	—	1406 s	
1404 m	1400 m	1405 m	1400 sh	Sym CH_3 deformation
1309 m	1312 m	1310 m	1316 m	
1290 sh	1292 sh	1295 sh	1298 m	
1045 s	1020 s	1030 sb	1032 s	$\nu(S=O)$
1026 sh			992 sb	
952 m	952 m	900 s	943 sb	CH_3 rocking
926 m	935 m	930 m	—	
890 w	900 w	895 w	900 m	
—	720 sh	—	—	$\nu(C—S)$ for Hg(SCN)
698 ms	705 m	702 m	712 m	ν asym (C—S) ligand
664 m	670 w	669 m	675 w	ν sym (C—S)
—	458 m	—	—	$\delta(SCN)$
—	—	430 s	—	$\nu(Hg—C)$
—	424 m	422 ms	410 m	$\nu(Hg—O)$
381 m	390 m	385 ms	390 m	$\delta(C—S—O)$
332 m	332 m	331 ms	335 m	
—	—	328 sh	—	$\delta(Hg—C\equiv N)$
—	—	315 w	—	
—	—	—	313 vs	$\nu(Hg—Cl)$
—	—	—	280 s	
	295 m			$\nu(Hg—S)$
	275 w			

to different metal atoms.



In the present investigations to avoid any additional side interaction through hydrogen bonding in the complexes between the nitrogen atom of the *en* molecule and the halogen atom of the metal halide[6,7]

(3) V. K. Brodersen, *Z. anorg. u. allgem. Chem.*, *298*, 142 (1959).
(4) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 3089 (1959).
(5) G. Newman and D. B. Powell, *J. Chem. Soc.*, 477 (1961).

we used N, N, N′, N′-tetramethylethylenediamine (TMen). As shown in Table I, in each case we obtained HgX_2 . TMen (X = Cl, SCN or CN) type one to one adducts. The molecular weight determined in tetrahydrofuran (THF) and the non-electrolyte nature of these compounds in the same solvent strongly suggest that they are monomers. In each case the mercury atom seems to exhibit a coordination number four.

Infrared Spectra. Infrared spectral studies have been found useful to distinguish between the *trans*, the *cis* and the *gauche* configurations of rotational isomers of the type $R–CH_2–CH_2–R$[8,11] where R is a functional group. Working with coordination complexes, Baldwin[10] and Iwamoto[11] were able to determine. using IR spectra, the configuration of ethylene-diamine in these complexes.

An attempt to differentiate the *cis* from the *gauche* configuration of the coordinated *en* molecule by nuclear magnetic resonance spectroscopy was made by Powell and Sheppard.[12] But, because of the mobility of the ring in the gauche form, the method was found unsuitable. The IR spectroscopic studies, however, have been found quite useful for such a differentiation. On the basis of the IR results the metal-ethylene-diamine complexes have been divided into two groups depending on the *gauche* and the *cis* configuration of the chelated ethylenediamine molecule.[12] It has also been pointed out that the complexes with ligands in the *gauche* form are more stable than those of the same ligand in the *cis* form.

In our present investigation we do not observe any IR bands in the region 735-750 cm^{-1} (Table II) where the CH_2 rocking vibrations of the *trans* form have been assigned.[9,13] However, we do observe strong bands in the region 800-1050 cm^{-1} which usually is the region where the CH_2 rocking vibrations for the *gauche* form appear in the IR spectra.

Baldwin[10] has indicated that the IR bands in the region 1460-900 cm^{-1} remain unaffected by deuteration of the amino hydrogen of the *en* molecule and therefore can safely be assigned to the vibration of the CH_2 groups. He assigned a sharp and strong band at 1050 cm^{-1} to the stretching vibration of either the C–N or the C–C band. We observed two bands in this region for the free ligand. One at 1096 cm^{-1} was assigned to the ν(C–N) which in the complexes is shifted to a lower frequency by about 25 cm^{-1}. An other band at 1136 cm^{-1} which remains unaffected on coordination was assigned to the ν(C–C).

Sweeny *et al.*[13] and Mizushima *et al.*[9] have shown that the position of the IR peaks in the region 750-950 cm^{-1} are characteristic of the CH_2 rocking frequencies associated with the molecule type $R–(CH_2)_2–R$. The spectra of the ligand TMen and its complexes (Table II) reveal the presence of strong medium bands in the region 830-1032 cm^{-1} indicating that in the free state as well as in the coordinated form the ligand molecules most probably are in the *gauche* configuration.

Far infrared spectra (*700-200 cm^{-1}*). The absorption observed from 600 to 450 cm^{-1} may arise either from skeletal bending modes of the ligand molecule, or from Hg–N stretching vibrations. We observe two strong to medium bands in this region and assign them to the ν(Hg–N) bands. Powell and Sheppard[14] also assign metal-nitrogen stretching bands in this region.

Other IR bands in addition to the ones due to the ligand and the ν(Hg–N) are those of ν(C–S), δ(SCN) and ν(Hg–S) for the $Hg(SCN)_2$. TMen complex; ν(Hg–C) and δ(HgCN) for the $Hg(CN)_2$. TMen complex; and ν(Hg–Cl) for the $HgCl_2$. TMen complexes. Tentative assignments have been made to those bands in the table.

$Hg(SCN)_2$. TMen. Due to the fact that the SCN group forms both M–SCN and M–NCS bonded complexes depending on the other ligands present,[15] the compound $Hg(SCN)_2$. TMen needs special comments. Basolo *et al.*[16] have shown that due to the steric factors $(C_2H_5)_2N–(CH_2)_2–N(C_2H_5)_2$ causes Pd–SCN bond to change into Pd–NCS type bonding. It is also well established that in all cases in which thiocyanate is present both as ion and as coordinated group, the two species can be differentiated on the basis of their IR spectra. The ionic thiocyanate absorbs below 2100 cm^{-1} and at 750 cm^{-1}.[17]

On the basis of the ν(CN) and the ν(C–S) in the spectra of $Hg(SCN)_2$. TMen, which appear at 2116 cm^{-1} and ~700 cm^{-1} respectively, we can conclude that the SCN group remains Hg–SCN bonded in the complex. For the isothiocyanate type of bonding (Hg–NCS), the ν(C–S) would have been found at a higher frequency.[18]

Compounds HgX_2 . $(Cypy)_n$. 3-cyanopyridine molecule has two strong coordinating groups but due to fixed orientation in space both the groups can not coordinate to the same metal atom. As a bidentate ligand the Cypy molecule can, however, coordinate to two different metal atoms. As a monodentate it can either coordinate via the pyridine nitrogen or via the cyano-nitrogen depending on their relative ligating strength.

As detailed in Table I we prepared three compounds of Cypy with $Hg(SCN)_2$, $Hg(CN)_2$ and $HgCl_2$. In the case of $Hg(SCN)_2$ we could obtain only 1:1 adduct even when the reaction was performed in an excess of the ligand. $Hg(CN)_2$ and $HgCl_2$, however, gave 1:2 adducts. To determine the coordination sites we recorded the IR spectra.

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(6) J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 2712 (1956).
(7) S. C. Jain and R. Rivest, *J. Inorg. Nucl. Chem.*, *31*, 399 (1969).
(8) I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, *21*, 2195 (1953).
(9) S. Mizushima, I. Ichishima, I. Nakagawa and J. V. Quagliano, *J. Phys. Chem.*, *59*, 293 (1955).
(10) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).
(11) T. Iwamoto, *Inorg. Chim. Acta*, *2*, 269 (1968).
(12) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).
(13) D. M. Sweeny, S. Mizushima and J. V. Quagliano, *J. Am. Chem. Soc.*, *77*, 6521 (1955).
(14) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, *17*, 68 (1961).
(15) A. Turco and C. Pecile, *Nature*, *191*, 66 (1961).
(16) F. Basolo, W. H. Baddley and J. L. Burmeister, *Inorg. Chem.*, *3*, 1202 (1964).
(17) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, *81*, 6412 (1959).
(18) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, *22*, 1081 (1966).

Gill *et al.*[19] during the course of the IR spectra studies of a number of pyridine complexes observed only small shifts in the spectrum of pyridine as a result of coordination to a metal atom. Bicelli[20] also found the IR spectrum of coordinated pyiridine differed very little from the spectrum of pyridine itself. Greenwood and Wade,[21] however, reported that the IR spectrum of the pyridine molecule is considerably modified when the non-bonding pair of electrons on the nitrogen atom is donated to a Lewis acid.

From our previous work with dinitriles[22] cyanoethylacetate[23] and cyanoacetamide[24] we know that when a cyano group coordinates to a Lewis acid through its free electron the cyano stretching frequency ν(CN), shows a positive shift in the IR spectrum. Thus a coordinated CN group can be easily differentiated from the uncoordinated one.

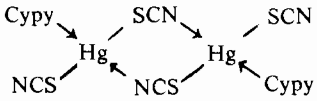
In our present investigations with the Cypy complexes of mercury we observe in Table III, that the ν(CN) of the ligand remains almost unchanged in the IR spectra of its complexes. This strongly suggests that the cyano group of the ligand does not participate in coordination thereby indicating that the pyiridine nitrogen of the Cypy molecule is more basic than the cyano nitrogen towards mercury.

Since we now know the coordination site, it is interesting to compare the IR spectrum of the ligand to its complexes. Coordinated pyridine is readily distinguished from the free base by a positive shift in the position of the strong band at 1578 cm^{-1} to 1600 cm^{-1}.[19] In the case of free Cypy (Table III) we observe two strong bands at 1585 cm^{-1} and 1555 cm^{-1} which we assign to ring stretching frequencies.[25] In the IR spectra of the complexes these bands appear at 1598 cm^{-1} and 1570 cm^{-1}.

For the bands appearing between 990 and 1217 cm^{-1} in the IR spectra of pyridine, Greenwood[21] and Gill[19] have some disagreement in their assignments. In the present case for Cypy we observe five bands between 1055 and 1210 cm^{-1} which remain unshifted in the spectra of the complexes. Two bands at 1030 cm^{-1} and 1018 cm^{-1} for Cypy, however, move to a higher position (1040 and 1028 cm^{-1}) for the complexes. These two bands we assign to ring skeletal vibration.

In the lower region we observe three bands at 778, 695 and 631 cm^{-1} for free Cypy. The 778 band which we assign to C–H out of plane vibration moves to a higher position in the IR of the complexes. Out of the remaining two, probably due to ring bending, the one at 631 cm^{-1} also shifts to higher positions in the spectra of the complexes.

The compound Hg(SCN)$_2$. Cypy needs special comments. The IR spectrum of this compound in the ν(CN) region shows three bands, one of which at 2234 cm^{-1} is due to the ligand and the remaining two at 2120 cm^{-1} and 2075 cm^{-1} due to the SCN groups. The fact that the ligand in this compound acts as a monodentate, coordinating only through pyridine nitrogen leads us to believe that either the mercury atom in this compound exhibits a coordination number three or it is a binuclear compound with bridging thiocvanate groups as shown below:



In a similar compound [P(Bu^n)$_3$. Pd(SCN)$_2$]$_2$ Chatt and Duncanson[26] have reported two ν(CN) bands: one at 2162 cm^{-1} for the bridging SCN group and another one at 2120 for the terminal SCN group. The difference of 42 cm^{-1} between the two ν(CN) bands is quite comparable to 45 cm^{-1} observed for [Hg(SCN)$_2$. Cypy]$_2$ compound in the present case. The existence of such a bridged structure has also been confirmed by Chatt *et al.*[27,28] through X-ray crystallography for similar compounds. An attempt to determine molecular weight in tetrahydrofuran solution gave a value of 220 against the calculated value of 840 for the dimer. This shows complete dissociation of the dimer into four species in the solution. The IR spectra recorded in THF for all the HgX$_2$ and Cypy complexes (Table III) display original bands for the free ligand thereby showing strong dissociation. Since the solutions of these compounds in THF were found non conducting this shows the dissociation of the complexes in neutral species, *i.e.*:

$$[Hg(SCN)_2 . Cypy]_2 \longrightarrow 2Hg(SCN)_2 + 2Cypy$$

Furthermore, the presence of the two ν(CN) and two ν(C–S) bands in the infrared spectrum of [Hg(SCN)$_2$. Cypy]$_2$ indicates two types of thiocyanate groups,[29] the one at a higher position due to bridging –SCN– and the another one at a lower position due to terminal –SCN groups.

Compounds HgX$_2$. 2DMSO. Dimethylsulfoxide has two coordination sites and can coordinate to the mercury atom either through the sulfur atom or through the oxygen atom. Cotton and Francis[30] prepared a large number of complexes of DMSO and elucidated their structures. On the basis of infrared spectra evidence was presented that in all the cases except Pd^{II} oxygen was the donor atom. In the case of PdCl$_2$. 2DMSO, however, bonding through sulfur (Pd←S) was suggested. During the course of reactions of sulfoxides with some group III and IV halides, Lappert and Smith[31] observed that DMSO underwent two types of reactions: (a) giving simple molecular addition compounds and (b) giving

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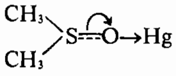
[19] N. S. Gill, R. H. Nutall, D. E. Scaife and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, *18*, 79 (1961).
[20] L. Bicelli, *Nuovo Cim.*, *9*, 148 (1958).
[21] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).
[22] S. C. Jain and R. Rivest, *Can. J. Chem.*, *41*, 2130 (1963).
[23] S. C. Jain and R. Rivest, *Can. J. Chem.*, *42*, 1079 (1964).
[24] S. C. Jain and R. Rivest, *Can. J. Chem.*, *45*, 139 (1967).
[25] C. N. R. Rao, « Chemical Absorptions of Infrared Spectroscopy » Academic Press, New York, p. 324, 1963.
[26] J. Chatt and L. A. Duncanson, *Nature*, *178*, 997 (1956).
[27] J. Chatt, L. A. Duncanson, F. A. Hart and P. G. Owston, *Nature*, *181*, 43 (1958).
[28] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1416 (1961).
[29] R. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).
[30] F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, *82*, 2986 (1960).
[31] M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 3224 (1961).

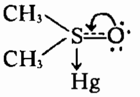
chlorosubstituted sulfides or their derivatives. Langer[32] and Tanaka[33] have recently reported the preparation of several DMSO complexes with group (IV) organometallic compounds.

The analytical results (Table I) indicate that in the case of HgX_2, (X = Cl, CN or SCN) DMSO forms simple 1:2 type moleculars adducts. To determine the possible coordination site we recorded the infrared spectra in the region 4000-2000 cm^{-1} and assigned various bands (Table IV).

Infrared spectra. The S=O bond has a partial double bond character, a coordination through the oxygen therefore, should result in lowering this S–O bond order. In the IR spectra this effect would be demonstrated by a bathochrome effect on the S–O stretching frequency (νS–O). A coordination through the sulfur, on the other hand would be expected to raise the ν(S–O). These effects can be visualized as below:



Bathochrome effect



Hypsochrome effect

The infrared spectra (Table IV) show that all the $HgX_2 . 2DMSO$ compounds display a lowering of the ν(S–O) bands as a result of coordination indicating the involvement of the oxygen in coordination. A lowering of the ν(S–O) was also observed by Cotton *et al.*[34] for a number of halide compounds which indicated that oxygen and not sulfur was the donor atom.

The IR spectra in the ν(C≡N) region for $Hg(SCN)_2 . 2DMSO$ and $Hg(CN)_2 . 2DMSO$ compounds display sharp bands at 2120 cm^{-1} and 2184 cm^{-1} for pure $Hg(SCN)_2$ and $Hg(CN)_2$. This shows that the SCN and CN groups are also covalently bonded to mercury in the complexes. If the SCN and CN groups were ionic in the compounds they would have displayed ν(C≡N) bands in a much lower region.[35]

Molecular weight determination of these compounds in THF solution show strong dissociation of these compounds. Solutions of these compounds in THF were found non conducting. Langer and Blut[32] also noticed strong dissociation of a variety of DMSO complexes in solutions.

The behaviour of the ν(C–S) bands of the ligand have been reported to be dependent on whether the ligand is O-bonded or S-bonded.[34] The appearance of two bands in the region 712-669 cm^{-1} (Table IV) normally assigned to ν_{asym} (C–S) and ν_{sym} (C–S) further supports bonding through the oxygen atom.

Far infrared spectra. We observe new bands in the 400-450 cm^{-1} region for all the three compounds which we are left with after eliminating the bands due to the ligand. $Hg(SCN)_2 . 2DMSO$ and $Hg(CN)_2 . 2DMSO$ are also expected to show δ(SCN) (bending) and ν(Hg–C) (stretching) bands in this region. Since pure $Hg(SCN)_2$ displays a strong δ(SCN) band at 427 cm^{-1} and $Hg(CN)_2$ displays a strong ν(Hg–C) band at 442 cm^{-1}, we can easily differentiate these bands from the ν(Hg–O) bands. A medium band at 410 cm^{-1} in the IR spectrum of $HgCl_2 . 2DMSO$ can be assigned to ν(Hg–O) with fair certainty. This assignment is in agreement with the assignment of Tanaka.[33] Tentative assignments to ν(Hg–S), δ(Hg–SCN) and ν(Hg–C) bands are given in Table IV.

Relative donor ability of the ligands and the effects of increasing coordination number of mercury on ν(Hg–Cl), ν(Hg–S) and (Hg–C) bands. Since the metal-halogen stretching bands are known to be sensitive to coordination number of the metal atom and the strength of the metal ligand bond,[2] in the present work we have investigated the effect of increasing coordination number of mercury on the ν(Hg–Cl), ν(Hg–S) and ν(Hg–C) for $HgCl_2$, $Hg(SCN)_2$ and $Hg(CN)_2$

In the pure $HgCl_2$ the ν(Hg–Cl) appear at 373 cm^{-1} as a very strong band. The IR spectra of the complexes exhibit this band, as expected, at a lower region (328-280 cm^{-1}). Metal-halogen stretching bands are usually very strong and are easily identified. It can be seen (Table V) that the ν(Hg–Cl) of the Cypy complex is the highest in the series, implying a weaker interaction of this ligand with $HgCl_2$. On the basis of the lowering of the ν(Hg–Cl) we can place TMen > DMSO > Cypy in their decreasing basicity towards $HgCl_2$. This strongly suggests that the presence of the electron withdrawing cyano group on the pyridine ring markedly reduces the donor ability of the pyridine nitrogen.[36]

It is interesting to note that similar to the ν(Hg–Cl) band the ν(Hg–C) band of ν$Hg(CN)_2$ is also lowered on complex formation. The position of the ν(Hg–S) band of $Hg(SCN)_2$ seems to be least effected by complex formation and remains almost unchanged.

If we compare the magnitudes of lowering of the ν(Hg–Cl) and the ν(Hg–C) on complex formation, we find that the shift for the ν(Hg–Cl) is greater than the ν(Hg–C) in similar compounds. From this observation one could be tempted to conclude that $HgCl_2$ is a stronger Lewis acid than $Hg(CN)_2$. But such a comparison and conclusion can be wrong due to the following facts:

(a) $Hg(CN)_2$ in the solid state is polymeric in nature where the cyano groups are bridging between two Hg atoms. The mercury atom, therefore, is already tetracoordinated in the pure $Hg(CN)_2$.

(b) The electron feeding character of the mercury atom to the cyano group through π bonding[29] gives additional strength to the $\text{Hg} \underset{\pi}{\overset{\sigma}{\rightleftarrows}} \text{C}{\equiv}\text{N}$ bond.

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Table V. Change of ν(Hg–X) with the change of the coordination of Hg

ν(Hg–Cl)		ν(Hg–S)		ν(Hg–C)	
$HgCl_2$	373 v s	$Hg(SCN)_2$	301 m	$Hg(CN)_2$	442 v s
$HgCl_2$. TMen	300 v s 270 v s	$Hg(SCN)_2$. TMen	296 sh	$Hg(CN)_2$. TMen	430 s
$HgCl_2$. 2DMSO	313 v s 280 s	$Hg(SCN)_2$. 2DMSO	295 m	$Hg(CN)_2$. 2DMSO	430 sh
$HgCl_2$. 2Cypy	328 s 287 m	$Hg(SCN)_2$. Cypy	300 w 298 w	$Hg(CN)_2$ 2Cypy	424 v s

v = very; w = weak; s = strong; sh = shouler; m = medium

The reason why the ν(Hg–S) of $Hg(SCN)_2$ remains almost unchanged on complex formation may be attributed to the fact that there are two sets of antibonding π-orbitals localized on the sulfur atom, which, along with the vacant d-orbitals of the sulfur atom, can accept electron density from the filled non-bonding d-orbitals of the mercury atom, resulting in additional stability of the Hg-S bond.[15]

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