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Coordination Complexes of Mercury(II) Pseudo-halides. Preparation and Infrared Spectral Studies of the Complexes of Hg^{II} Pseudo-halides with 1,10-phenanthroline, 2,2'-bipyridine and Triphenylphosphine as Ligands

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New molecular addition compounds between 1.10-phenanthroline (Phen), 2.2'-bipyridine (Bipy) and triphenylphosphine (TPP) as Lewis bases and HgX_2 (where X=SCN, CN) as Lewis acids have been isolated and characterized by infrared spectrophotometry. Their empirical formulas are $Hg(SCN)_2$. Phen, $Hg(SCN)_2$. 2Phen, $Hg(SCN)_2$. Bipy, $Hg(SCN)_2$. 2TPP, $Hg(SCN)_2$. TPP, $Hg(CN)_2$. Phen, $Hg(CN)_2$. Bipy, $Hg(CN)_2$. 2TPP.

Introduction

Much of the interest in metal thiocyanato complexes developed with the discovery by Turco and Pecile,[1] that the presence of other ligands in the cordination sphere of a metal can affect the nature of the metal-thiocyanate bond. π-Electron acceptors, such as trialkylphosphines, can make the metal d-electrons less available for back donation to the thiocyanate, and thereby reduce the additional stability of the M—S bond and enhance the M—NCS type bonding.

Burmeister and Basolo[2] synthesized isomers of the thiocyanato group using triphenylarsine and 2.2'-bipyridine as ligands. Basolo *et al.*,[3] using tetraethyldiethylenetriamine, also demonstrated that steric factors can alter the nature of the thiocyanate bonding from Pd-SCN to Pd-NCS.

Our present investigations with $Hg(SCN)_2$ were undertaken to study the effects of the coordination of various ligands such as 1,10-phenanthroline, 2,2'-bipyridine and triphenylphosphine on the Hg—SCN bond and see if thiocyanato-bridged complexes, similar to the ones described by Chatt *et al.*,[4,5,6] could also be obtained. To make a comparative study among $Hg(SCN)_2$, $Hg(CN)_2$ and $HgCl_2$ as Lewis acids, complexes of the same ligands were prepared using $Hg(CN)_2$ and $HgCl_2$.

Experimental Section

Material and Manipulations. The chemical mercuric thiocyanate, mercuric cyanide mercuric chloride monohydrate, 1.10-phenanthroline (Phen), 2.2'bipyridine(Bipy) and triphenylphosphine (TPP) were obtained from commercial sources and used as such without further purification. The compounds were prepared by mixing the reactants in warm tetrahydrofuran (THF) solution as detailed below.

HgX_2 and Phen compounds. The compounds $Hg(SCN)_2$. Phen, $Hg(CN)_2$. Phen, and $HgCl_2$. Phen were obtained by slowly adding a warm solution of Phen in THF to a warm solution of the mercuric salt in the same solvent. The molar ratio of the reactants in each case was approximately (1:1). The compound $Hg(SCN)_2$. 2Phens was obtained by a method similar to the one described for the 1:1 adducts. In this case the solution of the reactants in THF were mixed in a 1:3 molar ratio and the solution of $Hg(SCN)_2$ was added to the solution of Phen under constant stirring. In each case, a colorless crystalline compound immediately precipitated, was filtered under reduced pressure on a sintered glass crucible, washed three times with a little THF and dried in vacuo for several hours.

Hg_2X and Bipy compounds. The method of preparation of these compounds was the same as the one described for the preparation of the Phen compounds. The colorless crystalline compounds were obtained from the reaction mixture.

HgX_2 and TPP compounds. The compounds were prepared by mixing the reactants in warm THF solution as described for the Phen compounds. The composition of the adducts obtained was determined by the molar ratio of the reactants. Thus, one-to-one and two-to-one colorless crystalline compounds were obtained from the warm reaction mixture by partially evaporating the solvent. The compounds were recrystallized from THF, filtered, washed with small portions of cold THF and dried in *vacuo* at room temperature.

Micro elemental analyses and molecular weight determinations of the compounds were carried out by

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(2) J. L. Burmeister and F. Basolo, *Inorg. Chem.,* 3, 1587 (1964).
(3) F. Basolo, W. H. Baddley, and J. L. Burmeister, *Inorg. Chem.,* 3, 1202 (1964).
(4) J. Chatt, L. A. Duncanson, *Nature, 178,* 997 (1956).
(5) J. Chatt, L. A. Duncanson, F. A. Hart, and P. G. Owston, *Nature, 181,* 43 (1958).
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Table I. Analytical Results

Compounds	Melting Point °C	Hg% Calcd. Found	C% Calcd. Found	H% Calcd. Found	N% Calcd. Found	S% Calcd. Found	P% Calcd. Found	Cl% Calcd. Found	Molecular weight
$Hg(SCN)_2$. Phen	205-06	40.4	33.8	1.6	11.3	12.9	—	—	
		40.7	33.8	1.6	11.1	12.7	—	—	240
$Hg(SCN)_2$. 2(Phen)	244-5	29.6	46.1	2.4	12.4	9.4	—	—	
		29.9	45.9	2.2	12.2	9.7	—	—	142
$Hg(CN)_2$. Phen	~355 D	46.3	38.9	1.8	12.9	—	—	—	
		46.1	38.9	1.9	12.8	—	—	—	209
$HgCl_2$. Phen*	~375 D	44.5	31.9	1.8	6.2	—	—	16.0	
		44.3	31.9	1.6	6.2	—	—	16.0	—
$Hg(SCN)_2$. Bipy	183-5	42.4	30.4	1.7	11.8	13.6	—	—	—
		42.2	30.5	1.8	11.8	13.6	—	—	—
$Hg(CN)_2$. Bipy	235-7	49.1	35.2	2.0	13.7	—	—	—	
		49.1	35.3	2.0	13.4	—	—	—	324
$HgCl_2$. Bipy*	316-7	46.9	28.1	1.9	5.6	—	—	16.6	
		46.4	28.3	1.9	5.6	—	—	16.9	—
$Hg(SCN)_2$. TPP	110-11		41.4	2.6	4.8	—	5.3	—	
			41.6	2.7	4.7	—	5.3	—	452
$Hg(SCN)_2$. 2TPP	190-91		54.2	3.6	3.3	7.6	7.4	—	
			54.6	3.6	3.4	7.7	7.4	—	457
$Hg(CN)_2$. 2TPP	239-40	25.8	58.7	3.9	3.6	—	—	—	
		25.7	59.1	3.9	3.3	—	—	—	272
$HgCl_2$. TPP**			40.5	2.8				13.3	
			40.8	2.9				13.6	

* Previously prepared by Sutton[30]. ** Previously prepared by Evans *et al.*[20]. D, decomposed.

Table II. Infrared Spectral Results (cm^{-1} in Nujol mulls): HgX_2 and Phen Compounds

Phen	$Hg(SCN)_2$. Phen	$Hg(SCN)_2$. 2Phen	$Hg(CN)_2$. Phen	$HgCl_2$. Phen	Band Assignments
	2115 vs	2088 s	2158 m	—	$\nu(C{\equiv}N)$
1610 s, 1580 s	1615 m, 1585 m	1617 m, 1584 m	1624 m, 1586 m	1618 s, 1592 s	Ring vibrations
1558 m, 1490 s	1568 m, 1505 m	1568 m, 1505 s	1568 m, 1510 s	1574 s, 1514 s	
1415 s, 1512 s	1420 s	1421 s	1426 s	1428 s	
848 s	856 sh, 845 s	855 sh, 848 s	856 m, 842 s	861 s, 849 s	Out-of-plane hydrogen deformation
735 s	775 s, 725 s	772 m, 728 s	774 m, 724 s	841 s, 770 s	
—	700 sh	705 sh	—	—	$\nu(C—S)$
685 v, s, b	695 s	700 s	715 s	720 vs	
622 m	635 ms	632 ms	632 m	631 s	Ligand
508 m	510 w	510 w	512 w	512 w	
—	495 w, 470 m	490 w, 469 m	493 w, 470 m	471 w, 430 w	
—	446 m	446 m, 434 m	—	—	$\delta(S—C{\equiv}N)$
408 s	421 s	417 s	418 m	420 s	Ligand
—	—	—	402 s, 380 sh	—	$\nu(Hg—C)$
—	—	—		—	$\delta(Hg—C{\equiv}N)$
—	296 w	298 m	—	—	$\nu(Hg—S)$
—	—	—	—	270 vs	$\nu(Hg—Cl)$
—	—	—	—	240 s	
239 s	239 m	240 m	244 m	224 m	Ligand

s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad.

Galbraith Laboratories Inc., Knoxville, Tennessee (U. S. A.). The analytical results are included in Table I. Conductivity measurements on the Phen complexes were carried out in dimethylsulfoxide solutions using a Metrohm conductoscope, type E 365B equipped with an immersion cell.

Infrared (IR) spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer. In the normal range (4000-600 cm^{-1}) the spectra were taken using sodium chloride optics. In the far infrared region (600-200 cm^{-1}) caesium iodide plates or polyethylene discs were used. The IR results are included in Tables II, III, and IV.

Infrared Spectra and Structural Discussion

Complexes of HgX_2 with Phen and Bipy. Near infrared region. Schilt and Taylor[7] have studied the IR or a number of Phen and Bipy metal complexes. On the basis of IR results they were able to distinguish between a coordinated and a free base. Our IR results are consistant with the presence of coordinated Phen and coordinated Bipy.[7,8,9]

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(7) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, *9*, 211 (1959).

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Table III. Infrared Spectral Results (cm^{-1} in Nujol mulls): HgX_2 and Bipy Compounds

2,2′-Bipy	$Hg(SCN)_2$. Bipy	$Hg(CN)_2$. Bipy	$HgCl_2$. Bipy	Band Assignments
	2112 s	2170 m	—	$\nu(C\equiv N)$
1580 s	1598 m	1597 sh	1598 s	Ring
1558 m	1590 s	1588 s	1589 s	frequency
1540 sh	1574 m	1572 sh	1578 m	
1522 sh	1562 sh	1568 m	1570 m	
750 vs	768 vs	768 vs, 758 s	764 vs	Out-of-plane ring hydrogen vibrations
	732 s	735 m	731 s	
—	700 sh	—	—	$\nu(C–S)$
650 m	650 ms	650 m	648 s	ligand
620 s	628 m	628 m	626 m	
—	449 m	—	—	$\delta(S–C\equiv N)$
—	430 m	432 w	445 mw	
400 vs	421 m, 410 s	415 sh, 407 s	428 w, 414 s	ligand
	—	399 s	—	$\nu(Hg–C)$
	—	320 w	—	$\delta(Hg–C\equiv N)$
	300 w	—	—	$\nu(Hg–S)$
	—	—	269 s	$\nu(Hg–Cl)$
	—	—	245 sh	
255 vw	260 vw	268 vw	269 vw	ligand

s, strong; m, medium; w, weak; v, very; sh, shoulder.

Table IV. Infrared Spectral Results (cm^{-1} in Nujol mulls): HgX_2 and TPP compounds

TPP	$Hg(SCN)_2$. TPP	$Hg(SCN)_2$. 2TPP	$Hg(CN)_2$. 2TPP	Band Assignment
—	2121 s	2104 s	2184 vw	$\nu(C\equiv N)$
—	2084 s	—	—	
—	710 s, m	711 m	—	$\nu(C–S)$
617 m	614 m	614 w	616 m	ligand
512 s	521 vs	520 s	524 s	
488 vs	501 vs	500 vs	502 vs	
—	487 vs	486 s	486 vs	$\nu(Hg–P)$
—	440 sh	445 m	—	$\delta(S–C\equiv N)$
428 m	434 ms	425 m	432 s	ligand
—	—	—	395 sh	$\nu(Hg–C)$
—	—	—	308 ms	$\delta(Hg–C\equiv N)$
—	299 w	295 w	—	$\nu(Hg–S)$

s, strong; m, medium; w, weak; sh, shoulder; v, very.

For the Phen complexes, the 900-1400 cm^{-1} region does not change on coordination but the 700-900 cm^{-1} region does.[9] Two strong bands observed for free Phen at 735 cm^{-1} and 848 cm^{-1} respectively and associated with the out of plane hydrogen deformation vibrations; split as a result of coordination. Coordination also causes a general shift towards higher frequencies of the bands in the 1400-1600 cm^{-1} region which are attributed to ring vibrations.[10] Since the infrared spectra observed for $Hg(SCN)_2$. Phen and $Hg(SCN)_2$. 2Phen in these two regions are quite comparable to those obtained by Schilt and Taylor[7] for $[Hg(Phen)_3](ClO_4)_2$, but different from $PhenHClO_4$ reported by the same authors, it seems that in both compounds Phen act as a bidentate ligand.

Similar to the Phen complexes, the IR spectra of the Bipy complexes also show no marked difference from the IR spectrum of the ligand in the region 800-1500 cm^{-1}. The strong band at 750 cm^{-1} of the free ligand, which is associated with the out of plane deformation vibration of the two equivalent sets of four adjacent hydrogen atoms,[11] is split on coordination. The ring vibration bands which appear in the region 1522-1580 cm^{-1} for the free ligand move to higher frequencies on coordination.

In addition to the ligand bands the $Hg(SCN)_2$ complexes with Phen and Bipy also exhibit bands due to the thiocyanato groups. These bands can yield three valuable pieces of information and they have been used:

1. To determine whether both bridging and terminal thiocyanates are present by counting the number of $\nu(CN)$ bands. If only one $\nu(CN)$ band is observed only one type of pseudohalide is present. This was found to be the case for these complexes.

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(10) D. H. Bush and J. C. Bailar, *J. Am. Chem. Soc.*, *78*, 1137 (1956).

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2. To differentiate between a coordinated thiocyanate and an ionic one.[12] The ionic thiocyanate absorbs below 2100 cm^{-1} and at 750 cm^{-1}. On the basis of the ν(CN) and ν(C–S) which appear above 2100 cm^{-1} and at about 700 cm^{-1} we conclude that the SCN groups remain covalently bonded to mercury.

3. To determine whether a thiocyanato group is S-bonded or N-bonded to the metal atom.[1] The symmetrical ν(C–S) occurs between 690 and 720 cm^{-1} for the M–SCN bonded compounds and we observe the ν(C–S) bands at about 700 cm^{-1}. This strongly suggests a mercury-sulfur bond in the complexes with Phen and Bipy.

Far infrared region. Apart from the ligand bands we would expect to observe ν(Hg–S), δ(SCN), ν(Hg–C), δ(Hg–CN), and ν(Hg–Cl) bands in this region[13] for the $Hg(SCN)_2$, $Hg(CN)_2$, and $HgCl_2$ complexes. Tentative assignments of these bands are reported in the IR Tables II and III.

a. *HgX_2 and Phen compounds.* The bands located at 622 cm^{-1} and at 408 cm^{-1} in free Phen move to a higher frequency region upon coordination. Ferraro *et al.*[8] also observed a similar effect on the positions of the bands at 620 cm^{-1} and 404 cm^{-1} for the Phen and rare earth complexes. They have attributed this effect to the chelation of the ligand molecule.

The IR spectra of the complexes display two new bands in the region of 470-495 cm^{-1}. No definite assignment can be made to these bands. They are quite close to some pure ligand bands and may result from a small displacement of these bands due to complex formation. It is very unlikely that they are due to Hg–N stretching since this band would rather be expected to be lower than 300 cm^{-1}.[14,15] Since there is a strong ligand band at 239 cm^{-1} it is very possible that a weak band in this range could not be seen.

It is interesting to note that, as previously observed,[16] the ν(Hg–C) and the ν(Hg–Cl) of $Hg(CN)_2$ and $HgCl_2$ move to a lower position on complex formation while the ν(Hg–S) of $Hg(SCN)_2$ remains almost unaffected.

b. *HgX_2 and Bipy complexes.* Ferraro *et al.*[8] report the effect of chelation of Bipy on its three main IR bands. The bands at 655 cm^{-1} and 624 cm^{-1} have been reported to undergo a slight shift but the band at 405 cm^{-1} has been found to move to a higher position and split as a result of chelation. In our present investigation we observe the corresponding bands at 650 and 620 cm^{-1} for the free ligand which show very little change on coordination but the strong band at 400 cm^{-1} does shift to 420 cm^{-1} region and split on complex formation.

The assignments of the ν(Hg–S), δ(SCN), ν(Hg–C), δ(Hg–CN), and ν(Hg–Cl) bands are in good agreement with the assignments made for the corresponding vibrations in the previous section. The (Hg–N) bands being probably located in a lower region than 250 cm^{-1} were not observed.

The infrared spectra yield three pieces of information which can be of some use to assign a structure to these complexes:

(i) The ligands are coordinated as bidentates;

(ii) There is only one type of cyano group in any particular complex;

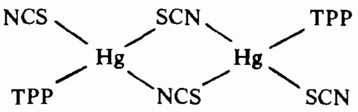
(iii) In the thiocyanato complexes SCN is covalent and S-bonded.

Additional information on these complexes was sought by trying to determine their conductivities and their molecular weights. They are not soluble in non polar solvents, so that polar solvents like dimethylsulfoxide and N,N-dimethylformamide had to be used. In such solvents, the IR spectra indicate dissociation. The absence of conductivity is then meaningless and as expected the values obtained for the molecular weights and reported in Table I are low compared to the theoretical monomeric values.

It is then impossible to assign definite structures to the prepared compounds. However, the information obtained from the IR spectra measurements permit certain hypothesis. For the 1:1 adducts, a tetrahedral structure where mercury has a coordination number of 4 is the most reasonable. A bridged structure where all the pseudohalides would be bridging would give a linear polymer where mercury has a coordination number 6.

For the 1:2 adducts, if one accepts that the ligands are bidentate and that the SCN groups are covalent and non bridging only two structures are possible where mercury has a coordination number of 6 and where the SCN groups can be either *cis* or *trans* to each other. A coordination number of six for mercury has previously been suggested by Sinha and O'Brien.[17,18] Grdenic in a review on mercury compounds[19] mentions that in covalent compounds the highest known coordination number is 4, but that for ionic compounds a coordination number 6 is «probable but not established yet». He also reports that in some ionic compounds mercury has a cordination number of 8.

Complexes of HgX_2 with TPP. With $Hg(SCN)_2$ and TPP we obtained two types of compounds *i.e.* $Hg(SCN_2$. TPP and $Hg(SCN_2$. 2TPP. These two classes of compounds have also been reported by Evans *et al.*[20] for adducts formed from mercury halides and tertiary phosphines and arsines. The one-to-one adducts, in fact, have been found to be bridged dimers. On the basis of the crystallographic analyses the dimeric compounds have been given a *trans*-symmetric structure of the type:



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The possibility of such a thiocyanato-bridged structure has been confirmed by Chatt *et al.*[5,6] through X-Ray crystallography. The IR spectra of these compounds have been reported to display two cyano stretching bands.[4] The ν(CN) band appearing at a higher wave number has been assigned to the bridging SCN group and the one appearing at a lower wave number assigned to the terminal SCN group.

In the present case the IR spectrum of $Hg(SCN)_2 . TPP$ displays two bands in the ν(CN) region, while the IR spectrum of $Hg(SCN)_2 . 2TPP$ shows only one ν(CN) band. The two ν(CN) bands for the 1:1 adducts seem to indicate the presence of two types of thiocyanato groups in the compound,[21] *i.e.* the bridging and the terminal thiocyanato groups. Chatt and Duncanson[4] for the bridged compound $[(PBu_3^n)Pd(SCN)_2]_2$ have reported two ν(CN) bands, 2162 cm^{-1} and 2120 cm^{-1}. The difference of 42 cm^{-1} between the positions of the bridging SCN (2162 cm^{-1}) and the terminal SCN (2120 cm^{-1}) for the Pd compounds is quite comparable to the observed difference of 37 cm^{-1} for the compound $Hg(SCN)_2 . TPP$ (Table IV).

Since the IR spectra of the free ligand and its complexes with HgX_2 do not show any marked difference in the region 1450-1435 cm^{-1} and 1005-995 cm^{-1} which is characteristic of the P-phenyl linkage,[22] it seems that the coordination of the phosphorus atom of TPP to the mercury atom does not effectively change the electron distribution of the P-phenyl linkage. Identification of the ν(C–S) band, which is known to be diagnostic of metal-sulfur or metal-nitrogen linkages,[23] is made difficult by the presence of a number of ligand bands in the 690-850 cm^{-1} region. Since we do not observe any new band between 750-850 cm^{-1} for the complexes it seems that the Hg–SCN band remains unchanged in the complexes. In Table IV we report only the ν(CN) bands in the normal range.

With $Hg(CN)_2$ and TPP we obtained only 1:2 adducts. The IR spectrum of this compound showed a very weak ν(CN) band at 2184 cm^{-1} unlike the ν(CN) of the thiocyanato compounds which appeared as strong bands. From our previous experience with nitrile compounds[24] we know that a coordinated cyano group displays a stronger ν(CN) band than an uncoordinated cyano group. $Hg(CN)_2$ in the pure state exists in a polymeric form where the cyano groups are known to bridge two mercury atom.[25] As a result of complex formation between $Hg(CN)_2$ and TPP, it seems that the cyano bridges break down and cause the ν(CN) band to appear much weaker and 16 cm^{-1} lower than the ν(CN) for $Hg(CN)_2$.

An attempt to determine the molecular weights of these compounds in THF solution indicated strong dissociation in THF. Since the THF solutions of the complexes were found to be non-conducting it seems that the compounds dissociate to form neutral species.

Far infrared spectra results: (600-200 cm^{-1}). In addition to the bands due to the ligand, one would expect the Hg–P stretching vibration to appear in this region for all the HgX_2 and TPP complexes. We observe one new band in the region 480 cm^{-1} which seems to result from Hg–P bonding. Taylor *et al.*[26] assign ν(Pt–P) at 436 cm^{-1} for the $(PtCl_2 . TPP)_2$ compound. Gogging and Goodfellow[27] also report ν(Pt–P) bands in the range 442-427 cm^{-1}. Infrared active bands for TPP in the region 600-200 cm^{-1} have been discussed by several authors.[26,28,29] It is easy to differentiate these ligand bands from the ν(Hg–S) and δ(SCN) bands for the $Hg(SCN)_2 . TPP$ compounds: and from ν(Hg–C) and δ(Hg–CN) bands for the Hg(CN) . 2TPP compound. Tentative assignments for the ν(Hg–S), δ(SCN), ν(Hg–C), and δ(Hg–C≡N) bands have been given in Table IV. These assignments are in good agreement with the assignments made for the respective bands in the first section of the discussion.

Acknowledgment. The authors gratefully acknowledge the continued finnancial assistance from the National Research Council of Canada.

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