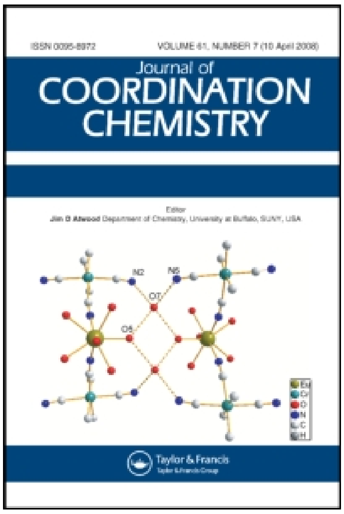

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Some Three-coordinate Complexes of Mercury(II)

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SHORT COMMUNICATION
Some Three-coordinate Complexes of Mercury(II)

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INTRODUCTION

Nicotinic acid, nicotinamide and N-methylnicotinamide – pyridine derivatives with a carboxyl or amido group in the β-position in the ring – possess two potential donor sites, (i) pyridine ring nitrogen, and (ii) carbonyl oxygen in the case of nicotinamide and N-methylnicotinamide or carboxyl oxygen in nicotinic acid. As monodentate ligands bonding may occur through any one of these sites. One cannot rule out the possibility of the two coordination sites bonding to different metal ions (bidentate bridging ligand) resulting in polymeric structures. It should be possible to distinguish between the likely modes of metal–ligand bonding by i.r. spectroscopy. Except for the complexes of mercury(II) chloride and bromide with nicotinamide[1] there is no report on those of mercury(II) halides and pseudohalides with these ligands. The present communication describes the coordination compounds formed by the interaction of mercury(II) chloride, bromide, cyanide and thiocyanate with nicotinic acid, nicotinamide and N-methylnicotinamide. The complexes isolated have been characterized by molecular conductance, molecular weight and infrared spectral measurements down to 200 cm^{-1} to elucidate the mode of metal–ligand bonding and the tentative stereochemistries of the complexes. Most of the complexes isolated have 1:1 stoichiometry (metal:ligand) and are considered to have monomeric, three-coordinated structures in the solid state.

All the mercury(II) chloride, bromide and cyanide complexes with the ligands investigated were obtained by mixing together the respective mercury(II) salt and a solution of the ligand in ethanol. Preparation of mercury(II) thiocyanate complexes needed boiling of a suspension of the metal thiocyanate in ethanol with an excess of the ligand. The stoichiometry of the complexes isolated was checked by metal and halogen halogen/pseudohalogen estimations. Conductivity measurements were made on freshly prepared ~1 mM solutions in absolute methanol at 25°C with a Phillips conductivity bridge Model PR 9500. The i.r. spectra of the uncoordinated ligands and of the mercury complexes were recorded as NUJOL mulls on Perkin-Elmer 621 (rock salt region) and P.E. 225 (700–200 cm^{-1}) spectrophotometers. Molecular weight determinations were carried out by the Rast method in camphor.

RESULTS AND DISCUSSION

The complexes isolated in the present study and their analytical data are listed in Table I. They are quite stable, have sharp melting points and are insoluble in most of the common organic solvents except for methanol and dimethylformamide in which most of them are soluble. Molar conductance of ~10^{-3} M solutions in absolute methanol indicate them to be non-electrolytes ($\Lambda_m \sim 10$ mho cm^2 mole^{-1}). Characteristic i.r. bands in uncoordinated nicotinic acid, nicotinamide and N-methylnicotinamide and in the complexes are listed in Table II.

Significant absorption bands due to the amido group in nicotinamide and N-methylnicotinamide are νNH, νCO and νCN (Table II). In complexes of amides and other carbonyl donors[2] a significant negative shift of the carbonyl frequency takes place because of coordination through the carbonyl oxygen. The νNH, νCO and νCN of the uncoordinated nicotinamide and N-methylnicotinamide remain either unperturbed or undergo slight positive shifts in the mercury(II) complexes studied here. These features clearly indicate that the amido group is inert towards coordination in both these ligands. The

TABLE I
Analytical data

Compound	M.P. (°C)	Molecular weight		Metal(%)		Anion(%)	
		Found	Calc.	Found	Calc.	Found	Calc.
$Hg(N)_2Cl_2$	220	505	517	38.5	38.7	13.5	13.7
$Hg(N)Br_2$	175	459	483	41.1	41.4	33.1	33.1
$Hg(N)_4(SCN)_2$	195	(£)		24.3	24.7	14.1	14.4
$Hg(NA)_2Cl_2$	236	(£)		38.8	38.8	13.4	13.8
$Hg(NA)Br_2$	210	431	482	41.0	41.5	33.5	33.2
$Hg(NA)(CN)_2$	220	insol.		53.3	53.5	–	–
$Hg(NA)(SCN)_2$	105	(£)		45.9	45.6	26.5	26.5
$Hg(MNA)Cl_2$	221	367	407	49.4	49.0	17.2	17.4
$Hg(MNA)Br_2$	205	486	497	40.2	40.2	32.2	32.2
$Hg(MNA)(CN)_2$	196	insol.		51.2	51.2	–	–
$Hg(MNA)(SCN)_2$	144	(£)		44.0	44.2	25.4	25.6

N = Nicotinic acid; NA = Nicotinamide; MNA = N-methylnicotinamide. (£) = reacts with camphor.

carboxyl group vibrations of the nicotonic acid remain almost unperturbed in the i.r. spectra of mercury(II)-nicotinic acid complexes thus excluding the metal-to-oxygen coordination in these complexes. On the other hand, i.r. spectra of the complexes exhibit appreciable perturbations in the fundamental frequencies of the pyridine part of the molecule. Absorption bands at ~1590 and 1550 cm^{-1} due to C$\overset{\cdots}{-}$C and C$\overset{\cdots}{-}$N stretching modes, respectively, in uncoordinated nicotinic acid, nicotinamide and N-methylnicotinamide shift to higher frequencies in the i.r. spectra of the mercury(II) complexes studied here. Moreoever, the pyridine ring vibrations of these ligands at ~990, 605 and 405 cm^{-1} also undergo significant positive shifts. These frequency shifts (Table II) indicate conclusively that coordination of the ligands investigated here takes place via the pyridine ring nitrogen[1,3] only to the mercury(II) ions studied. Because of the electron releasing nature of methyl group the amide nitrogen in N-methyl-nicotinamide is more basic than that of the nicotinamide. However, the present studies show that N-methylnicotinamide bonds through its pyridine nitrogen only.

Molecular weight determinations show that the 1:2 mercury(II) chloride-nicotinic acid complex is a monomer in the solid state. Strong band at 297 cm^{-1} in the low frequency i.r. spectrum of this complex is in fair agreement with the frequency normally associated with tetrahedral mercury(II)-chlorine stretching mode.[4] From a consideration of the molecular weight and νHg-Cl mode the complex is tentatively assigned a monomeric, four-coordinated tetrahedral structure in the solid state. Absence of a band at ~300 cm^{-1} assignable to νHg-Cl mode in the 1:2 mercury(II) chloride–nicotinamide suggests that the chlorines are bridging and the complex is considered to have a six-coordinated polymeric octahedral structure with only bridging chlorines and terminal nicotinamide molecules around the mercury atoms.

The 1:1 mercury(II) chloride-N-methylnicotinamide and the 1:1 mercury(II) bromide complexes with nicotinic acid, nicotinamide and N-methylnicotinamide are shown by molecular weight determinations as monomeric in the solid state. The mercury-halogen stretching modes are also in agreement with only terminally bonded halogens.[4,5] These complexes are thus considered to have monomeric three-coordinate environment about the mercury atoms in the solid state.

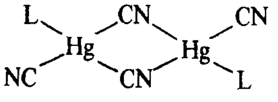
In addition to the ligand bands modified slightly on account of coordination i.r. spectra of the 1:1 cyanide complexes with nicotinamide and N-methylnicotinamide studied here show absorption bands at ~2180, 425 and 325 cm^{-1} due to νCN, νHg–C and δHg C N modes, respectively. The frequencies of these modes are lower than those of the corresponding modes in mercury(II) cyanide in the solid state. Mercury(II) cyanide has a linear cyanide-bridged polymeric chain structure in the solid state[6] and absorbs[7] at 2193, 442 and 341 cm^{-1} due to νCN, νHg–C and δHg C N modes, respectively. The frequency of νCN suffers a significant negative shift when the cyanide bridges break down and mercury(II) cyanide complexes with terminal cyanide groups absorb at lower frequencies[8] than pure mercury(II)

TABLE II
Characteristic infrared bands (4000–200^{-1})

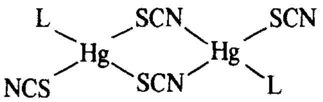
Compound	νNH	νCO (*)	$\nu C\overset{..}{-}C$ $\nu C\overset{..}{-}N$	νCN	Ring vibrations	Other bands
N		1685 s	1585 m		989 m	
			1545 m		610 m, 387 m	
$Hg(N)_2Cl_2$		1687 s	1627 m		1025 s	
			1592 s		630 ms, 423 m	νHg–Cl 297 ms
$Hg(N)Br_2$		1690 s	1625 m		1025 m	
			1596 s		625 m, 426 m	νHg–Br 215 m
$Hg(N)_4(SCN)_2$		1695 sh	1605 m		1036 m	νCN 2135 s;
			1591 m		625 m, 426 m	νCS 697 ms;
						δSCN 450 w, 435 m
						νHg–SCN 305 m
NA	3330 s	1680 m	1580 m	1120 m	990 m	
	3120 m		1570 m		605 m, 396 m	
$Hg(NA)_2Cl_2$	3389 s	1700 s	1624 m	1110 m	1018 s	
	3184 m		1609 s		640 s, 408 m	
$Hg(NA)Br_2$	3433 s	1703 s	1615 s	1115 m	1042 s	
	3267 s		1596 s		627 m, 430 m	νHg–Br 230 s
$Hg(NA)(CN)_2$	3417 s	1700 s	1617 s	1113 s	1034 s	νCN 2183 ms;
	3329 m		1591 s		624 m	νHg–C 425 s;
						δHg C N 323 m
$Hg(NA)(SCN)_2$	3380 m	1702 s	1600 m	1115 m	1026 m	νCN 2125 s, 2108 s
	3320 m		1575 m		620 m, 428 m	νCS 700 m;
						δSCN 465 m, 445 m;
						νHg–SCN 285 m
MNA	3330 s	1648 s	1599 s	1130 m	1000m	
					607 m, 399 m	
$Hg(MNA)Cl_2$	3350 s	1660 s	1600 s	1125 m	1028 m	νHg–Cl 290 ms
					632 m, 430 m	
$Hg(MNA)Br_2$	3358 m	1645 s	1600 s	1110 m	1030 m	νHg–Br 230 ms
					630 m, 423 m	
$Hg(MNA)(CN)_2$	3360 m	1630 s	1595 s	1120 m	1027 s	νCN 2180 m;
					624 m, 415 m	νHg–C 430 s;
						δHg C N 327 m
$Hg(MNA)(SCN)_2$	3350 m	1640 s	1596 s	1115 m	1030 m	νCN 2136 s;
					631 m, 420 m	νCS 695 m;
						δSCN 455 m;
						νHg–SCN 300 m

(*) νOCO in case of nicotinic acid.

cyanide while bridging cyanide groups absorb at higher energies.$^{9, 10}$ Furthermore, νHg–C shifts to higher frequencies in complexes containing bridging cyanide groups and this positive shift may be attributed to coupling of νHg–C with νCN in the Hg C N part of the molecule. Since terminal cyanide groups absorb at lower energies than pure mercury(II) cyanide the terminal νHg–C and δHg C N modes would also be expected to absorb at lower energies. Moreover, complexes having both terminal and bridging cyanide groups display two bands in each of the νCN, νHg–C and δHg C N regions^{10} – the one appearing at higher wave numbers being assigned to the bridging cyanide groups while the other at lower wave numbers to the terminal cyanide groups. The observed frequencies of νCN (~2180 cm^{-1}), νHg–C (~430 cm^{-1}) and δHg C N (~330 cm^{-1}) in the 1:1 mercury(II) cyanide complexes with nicotinamide and N-methylnicotinamide studied here strongly suggest the presence of only terminal cyanide groups. With nicotinamide and N-methylnicotinamide acting as monodentate ligands bonding through their pyridine ring nitrogens only (*vide supra*) both these complexes are, therefore, tentatively assigned as monomeric, three-coordinated structures with terminal cyanide groups and a nitrogen of the organic ligand around the mercury atoms in the solid state. One could postulate cyanide-bridged dimeric structures (A) or six-coordinated polymeric octahedral structures with only bridging cyanide groups for these complexes. However, such structures are ruled out as the i.r. spectra of the compounds under investigation indicate the presence of only terminal cyanide groups.



(A)



(B)

Mercury(II) thiocyanate gave a 1:4 complex with nicotinic acid but 1:1 with nicotinamide and N-methylnicotinamide. The i.r. spectra of these complexes show absorption bands at ~2130 cm^{-1} (νCN), ~700 cm^{-1} (νCS), ~450, 430 cm^{-1} (δ SCN) and ~300 cm^{-1} (νHg–SCN) due to coordinated thiocyanate groups. The frequencies of these bands are consistent with those normally associated with terminally S-bonded SCN groups.[11] With terminally pyridine ring nitrogen bonded nicotinic acid, nicotinamide and N-methylnicotinamide and terminally S-bonded thiocyanate groups the 1:4 mercury(II) thiocyanate–nicotinic acid complex is considered as a six-coordinated, monomeric octahedral structure and the 1:1 complexes with nicotinamide and N-methylnicotinamide as monomeric, three-coordinated structures in the solid state. Thiocyanate-bridged dimeric[10] structures (B) or six-coordinated polymeric octahedral structures with only bridging thiocyanate groups for these 1:1 complexes are ruled out as the fundamental vibrations due to coordinated thiocyanate groups show the presence of only terminally S-bonded SCN groups.[10,11] It may be pointed out that the frequency of νHg–S of Hg(SCN)$_2$[12] suffers only a small negative shift in the mercury(II) thiocyanate complexes studied here. This may be attributed to the fact that there are two sets of antibonding π-orbitals localized on the sulphur atom which along with the vacant d-orbitals of the sulphur atom can accept electron density from the filled nonbonding d-orbitals of the mercury atom thus resulting in strengthening of the Hg–S bond.

Metal-pyridine stretching modes have been assigned in the range 287–200 cm^{-1} in some metal(II) halide complexes with pyridine.[13] However, no absorption band insensitive to change of halogen/pseudohalogen was observed above 200 cm^{-1} which could be assigned to νHg–N mode in the present study. The tentative stereochemistries of the compounds reported herein have been derived from a comparison of their metal–ligand frequencies with those of compounds of established structures. However, unambiguous characterization of these compounds should be based on complete crystal structure determinations.

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