

Neutral Three-coordinate Complexes of Mercury(II) Involving Coordinated Cyano Groups

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1 : 1 Complexes of mercury(II) cyanide with 2-benzylpyridine, 4-picolyamine, 2-benzoylpyridine, 4-benzoylpyridine, 1,3-bis-(4-pyridyl) propane, quinoline, 6-methylquinoline; benzo(f)quinoline, isoquinoline, 3-methylisoquinoline, nicotinamide and N-methylnicotinamide have been synthesized. Molar conductances, molecular weight determinations and infrared spectral measurements down to 200 cm^{-1} show that all these compounds are neutral species having monomeric three-coordinated environments around mercury(II) in the solid state.

INTRODUCTION

The characteristic coordination numbers and stereochemical environments of mercury(II) are two-coordinate linear and four-coordinate tetrahedral.^{1,2} In addition to these, octahedral and five-coordination are also known.¹⁻⁵ Although coordination number three around mercury(II) is known in some systems, the species are, however, anionic or cationic; e.g., $[\text{SMe}_3][\text{HgI}_3]$ and $[\text{Nbu}_4^+][\text{HgI}_3]$, which have been established through X-ray structure determinations to contain discrete planar $[\text{HgI}_3]^-$ species.^{6,7} The salt $[\text{NMe}_4][\text{HgBr}_3]$, on the other hand, contains discretely pyramidal tribromomercurate ion $[\text{HgBr}_3]^-$ which is reported to get solvated to give four- or five coordinate species in polar solvents.⁸ The compounds $\text{Na}[\text{HgCl}_3]$, $\text{Na}[\text{HgCl}_3] \cdot 2\text{H}_2\text{O}$ and $[\text{NH}_4][\text{HgCl}_3]$ appear to have three-coordination around mercury(II), have in fact distorted octahedral species $[\text{HgCl}_6]^{4-}$ containing linear Cl-Hg-Cl skeletons with two Hg-Cl bonds shorter than the other four and the characteristic diagonal coordination around the mercury atoms is present.⁹ The compound $[\text{HgL}_2(\text{OCIO}_3)]\text{ClO}_4$, $\text{L} = \text{R}_3\text{P}$ or R_3As is considered to have three-coordinate environment around mercury(II) with one perchlorate coordinated to the metal as a monodentate ligand.¹⁰ X-ray analysis of the compound $[\text{NH}_4][\text{HgCl}_2(\text{SCN})]$ has shown that the metal atoms are basically three-coordinate.¹¹ Crystal structure determinations on $[\text{Hg}(\text{PR}_3)(\text{NO}_3)_2]$, where

R = 2,4,6-trimethylphenyl, have established that the bulky ligand forces mercury(II) to adopt a three-coordinate structure.¹²

It seems that three-coordinate mercury(II) complexes as neutral species involving coordinated cyano groups $\text{HgL}(\text{CN})_2$, where L = a monodentate ligand, are rather unknown. Some 1 : 1 complexes of mercury(II) cyanide with pyridine and ring substituted derivatives are known but these are 6-coordinate polymeric structures involving extensive bridging through cyano groups.¹³ Also, some 1 : 1 complexes of mercury(II) cyanide with pyridine N-oxide and its derivatives are known which have cyano-bridged dimeric tetrahedral structures involving terminally bonded pyridine N-oxide molecules and both terminal and bridging cyano groups.¹⁴ In the course of our investigations on the mercury(II) complexes with several nitrogen and/or oxygen donor ligands during the last few years in these laboratories, we have prepared some 1 : 1 mercury(II) cyanide complexes $\text{HgL}(\text{CN})_2$, where L = 2-benzylpyridine, 4-picolylamine, 2-benzoylpyridine, 4-benzoylpyridine, 1,3-bis-(4-pyridyl) propane, quinoline, 6-methylquinoline, benzo(f)quinoline, isoquinoline, 3-methylisoquinoline, nicotinamide and N-methylnicotinamide. These complexes have been characterized by analytical data, molar conductances, molecular weight determinations and infrared spectral measurements down to 200 cm^{-1} . It is shown that all these compounds are neutral species exhibiting coordination number three around mercury(II) involving coordinated cyano group in the solid state.

EXPERIMENTAL

Mercury(II) cyanide and all the ligands used were purchased from M/s Ega Chemie, West Germany and used as such. The complexes were prepared by mixing together hot solutions of the mercury(II) cyanide (10 mmol in 20 ml ethanol) and the respective ligand (20 mmol in 10 ml ethanol). The complexes which crystallized out on cooling were suction-filtered, washed with ethanol and dried in an air oven at *ca.* 60°C . Stoichiometries of the compounds isolated were checked by metal, C, H and N estimations. Mercury was estimated by dissolving the complex in dilute hydrochloric acid and completing the estimation gravimetrically as mercury(II) sulphide. C, H and N were determined by microanalysis.

Conductivity measurements were made on freshly prepared *ca.* 10^{-3} M solutions in distilled ethanol or dimethylformamide at 25°C with a Philips conductivity bridge Model PR 9500. Infrared spectra of the uncoordinated ligands and their complexes with mercury(II) cyanide were recorded as Nujol mulls supported between sodium chloride plates (rock salt region) on a Perkin-Elmer spectrophotometer Model 783. The $650\text{--}200\text{ cm}^{-1}$ region infrared spectra were recorded as Nujol mulls held between CsI plates or thin polyethylene sheets on a Perkin-Elmer 621 spectrophoto-

meter equipped with caesium iodide optics. Molecular weight measurements were carried out by the Rasts' method in camphor or on a Mechrolab Inc. Vapour Pressure Osmometer Model 301 A using absolute alcohol as the solvent at 37°C. Calibrations were carried out by using acetanilide in the range 0.005–0.010 M. Δ_R readings were recorded at intervals of 3 minutes each. The solutions were approximately 0.005 M. Reported values (Table 1) are the means of three determinations.

TABLE 1
ANALYTICAL DATA AND IR-DATA OF COORDINATED
CYANO MODES (cm⁻¹)

Compound	M.pt. (°C)	Mole- cular weight	% Found (Calcd.)				ν (CN)	ν (Hg-C)	δ Hg C N
			Hg	C	H	N			
Hg(2-BP)(CN) ₂	146	—	47.7 (47.5)	40.0 (39.8)	2.51 (2.61)	10.0 (9.97)	2185	417	323
Hg(4-PA)(CN) ₂	—	—	55.8 (55.5)	26.8 (26.6)	2.25 (2.22)	15.7 (15.5)	2180	425	330
Hg(2-BOP)(CN) ₂	239	376 (435)	46.2 (46.0)	38.4 (38.6)	2.10 (2.07)	10.1 (9.96)	2180	423	328
Hg(4-BOP)(CN) ₂	80	459 (435)	46.2 (46.0)	38.8 (38.6)	2.10 (2.07)	10.0 (9.96)	2181	422	329
Hg(DPP)(CN) ₂	245	470 (450)	44.6 (44.4)	40.1 (40.0)	3.10 (3.10)	12.5 (12.4)	2160	415	308
Hg(Q)(CN) ₂	195	430 (381)	52.3 (52.5)	35.0 (34.6)	1.85 (1.83)	11.2 (11.0)	2180	422	316
Hg(6-MQ)(CN) ₂	167	400 (395)	51.0 (50.6)	36.8 (36.5)	2.31 (2.28)	10.5 (10.6)	2182	420	315
Hg(BfQ)(CN) ₂	215	419 (431)	46.5 (46.4)	42.2 (41.8)	2.12 (2.09)	10.0 (9.9)	2183	421	327
Hg(IQ)(CN) ₂	206	371 (381)	52.6 (52.5)	34.9 (34.6)	1.81 (1.83)	11.0 (11.0)	2185	422	316
Hg(3-MIQ)(CN) ₂	150	370 (395)	51.0 (50.6)	36.8 (36.5)	2.30 (2.28)	11.0 (10.6)	2183	413	318
Hg(NA)(CN) ₂	220	—	53.3 (53.5)	25.5 (25.7)	1.64 (1.60)	15.3 (15.0)	2183	425	323
Hg(NMNA)(CN) ₂	196	—	51.2 (51.5)	28.0 (27.8)	2.10 (2.06)	14.6 (14.4)	2180	430	322

2-BP = 2-benzylpyridine, 2-BOP = 2-benzoylpyridine, 4-BOP = 4-benzoylpyridine,
BPP = 1,3-bis-(pyridyl) propane, Q = quinoline, 6-MQ = 6-methylquinoline,
BfQ = benzo(f)quinoline, IQ = isoquinoline, 3-MIQ = 3-methylisoquinoline,
NA = nicotinamide, NMNA = methylnicotinamide, 4-PA = 4-picolylamine.

RESULTS AND DISCUSSION

Analytical data of the mercury(II) cyanide compounds isolated (Table 1) indicate 1:1 stoichiometry (metal:ligand). The compounds studied are quite stable and are soluble in absolute alcohol or dimethylformamide in which solvents they behave as non-electrolytes.¹⁵ Comparison of the infrared spectra of the mercury(II) compounds with the corresponding uncoordinated ligand spectrum facilitated the assignment of bands due to coordinated cyano groups. Infrared frequencies due to coordinated cyano groups are listed in Table 1. No absorption bands were observed in the infrared spectra of these compounds which could be attributed to water or ethanol thus establishing them to be anhydrous and free from coordinated or lattice water/ethanol.

The techniques of electronic absorption spectroscopy and magnetic susceptibility measurements yield unambiguous structural information of transition metal compounds. Because of the closed shell of valence electrons these could not be studied for the mercury(II) compounds. Stereochemistries of the compounds studied herein have been arrived at by comparing the mercury(II)-ligand and mercury(II) cyanide bonding modes with similar modes in compounds whose structures are known through X-ray crystallography and/or magnetic susceptibility and infrared spectral studies.

Mode of mercury(II)-ligand bonding

Benzylpyridine: Infrared spectrum of the 1:1 mercury(II) cyanide-2-benzylpyridine complex shows absorption bands due to the benzyl group at almost the same positions as in the uncoordinated ligand. However, appreciable changes take place in the fundamental vibrations of the pyridine moiety on coordination. The $\nu_{\text{C}\equiv\text{C}}$ and $\nu_{\text{C}\equiv\text{N}}$ observed at 1590 and 1551 cm^{-1} , respectively, and the pyridine ring vibrations observed at 996, 602 and 403 cm^{-1} in the uncoordinated 2-benzylpyridine suffer significant position shifts on complexation indicating coordination of the benzylpyridine via its pyridine ring nitrogen atom.¹⁶

Picolylamine: 4-Picolylamine possesses two potential donor sites: (i) pyridine ring nitrogen, and (ii) amino nitrogen of the $-\text{CH}_2\text{NH}_2$ group. Infrared spectrum of 1:1 mercury(II) cyanide complex with this ligand suggests that the picolylamine is bonded via its pyridine ring nitrogen to mercury(II). This is evident from the fact that the fundamental pyridine ring vibrations at 998, 584 and 390 cm^{-1} in the uncoordinated amine suffer significant positive shifts and occur at 1025, 600 and 405 cm^{-1} , respectively, in this complex. The ν_{NH} modes (of the $-\text{CH}_2\text{NH}_2$ group) in the uncoordinated picolylamine at 3350 and 3280 cm^{-1} absorb at almost the same frequencies in the mercury(II) cyanide

complex thus ruling out coordination through the amino group. It is thus clear that 4-picolyamine is bonded exclusively through its pyridine ring nitrogen¹⁶ to the mercury(II) and that it acts as a terminally bonded monodentate ligand in this complex.

Benzoylpyridines: 2- and 4-Benzoylpyridines possess two potential donor sites each: (i) pyridine ring nitrogen, and (ii) oxygen of the carbonyl group. The CO stretching vibration of the uncoordinated benzoylpyridines at *ca.* 1655 cm^{-1} remains either unperturbed or undergo slight positive shifts in the 1:1 mercury(II) cyanide complexes with these ligands. On the other hand, infrared spectra of both these complexes exhibit appreciable perturbations in the fundamental frequencies of the pyridine part of the molecule and indicate conclusively that coordination of the 2- and 4-benzoylpyridines takes place via their pyridine ring nitrogen atoms only.¹⁶⁻¹⁸

1,3-Bis-(4-pyridyl) propane: This ligand consists of two pyridyl groups both bonded in γ -position to the two terminal carbon atoms of propane. Molecular models show considerable free rotation about the carbon-carbon bonds of propane. The two donor sites may coordinate to the same metal ion leading to 12-membered ring formation or to two different metal ions resulting in polymeric chain structures. Infrared spectroscopy has proved very useful in distinguishing the bridging (trans) and chelating (cis) forms of the same ligand. The trans form being more symmetrical gives rise to fewer absorption bands while the multiplicity of bands indicates the less symmetrical cis or chelating configuration.¹⁹ Molecular weight measurements of the 1:1 mercury(II) cyanide complex with this ligand (as determined by the Råst's method in camphor, found 470, calcd. 450) suggest that the ligand is acting as a monodentate one bonding via only one of the pyridyl nitrogens to mercury(II).

Quinoline, isoquinoline and their derivatives: Infrared spectra of the mercury(II) cyanide complexes with these ligands show appreciable perturbations in the fundamental frequencies of the pyridine moiety. Absorption bands at *ca.* 1585 and 1550 cm^{-1} due to C=C and C=N stretching modes, respectively, in the uncoordinated quinolines shift to higher frequencies in the infrared spectra of the mercury(II) cyanide complexes. Moreover, the pyridine ring vibrations of the uncoordinated ligands at *ca.* 990, 605 and 405 cm^{-1} also undergo significant positive shifts in the spectra of these complexes. These features are consistent with coordination of the quinolines²⁰ via their pyridine ring nitrogen atom to mercury(II).

Nicotinamide and N-methylnicotinamide: These ligands are pyridine derivatives with an amido group in the β -position on the ring. Each of these ligands possesses two potential donor sites: (i) pyridine ring nitrogen, and (ii) the carbonyl oxygen. As monodentate ligands bonding may occur through any one of these sites. One cannot rule out the possibility of the

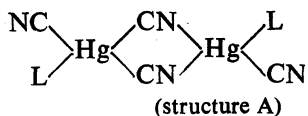
two coordination sites bonding to different metal ions (bidentate bridging ligand) resulting in polymeric structures. It should be possible to distinguish between the likely modes of metal-ligand bonding using infrared spectroscopy. Significant absorption bands due to the amido group in nicotinamide and N-methylnicotinamide are νNH , νCO and νCN . These fundamental modes of the uncoordinated ligands at *ca.* 3330, 3120 (νNH), *ca.* 1680 cm^{-1} (νCO) and *ca.* 1120 cm^{-1} (νCN) remain either unperturbed or undergo slight positive shifts in the mercury(II) cyanide complexes indicating thereby that the amido group is inert towards coordination in both these ligands. On the other hand, infrared spectra of these complexes exhibit appreciable perturbations in the fundamental frequencies of the pyridine part of these molecules. Absorption bands at *ca.* 990, 605 and 405 cm^{-1} undergo significant positive shifts indicating conclusively that coordination of both these ligands takes place via their pyridine ring nitrogen^{16, 21-23} only to mercury(II). Because of the electron releasing nature of the methyl group the amide nitrogen in N-methylnicotinamide is more basic than that of the nicotinamide. However, the present studies show conclusively that N-methylnicotinamide also bonds via its pyridine ring nitrogen only.

Mode of mercury(II) cyanide bonding and stereochemistry

In addition to the ligand bands modified slightly on account of coordination, infrared spectra of all the 1:1 mercury(II) cyanide complexes with the ligands investigated herein show absorption bands at *ca.* 2170, 420 and 320 cm^{-1} . These bands are assigned as νCN (*ca.* 2170 cm^{-1}), $\nu\text{Hg-C}$ (*ca.* 420 cm^{-1}) and $\delta\text{Hg CN}$ (*ca.* 320 cm^{-1}) modes due to coordinated cyano groups. The frequencies of these modes are significantly lower than those of the corresponding modes in mercury(II) cyanide which has been shown to have a cyano-bridged polymeric chain structure²⁴ in the solid state and absorbs²⁵ at 2193, 442 and 341 cm^{-1} due to νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ modes, respectively. The νCN of the free cyanide ion (KCN) absorbs at 2080 cm^{-1} . Upon coordination to a metal ion this frequency suffers a significant positive shift and occurs in the range 2200–2000 cm^{-1} . The cyanide ion acts as a σ -donor by donating electrons to the metal and also as a π -acceptor by accepting electrons from the metal. Whereas σ -bonding tends to raise this frequency, π -bonding decreases this frequency. Cyanide ion is, however, a better σ -donor and a poor π -acceptor. The frequency of νCN is thus generally higher in metal complexes than the value for ionic cyanides. Furthermore, the frequency of νCN suffers a negative shift when the cyano bridges break down and mercury(II) cyanide complexes with terminal cyano groups absorb at lower frequencies²⁶ than pure mercury(II) cyanide while bridging cyano groups absorb at higher energies^{19, 27} ($> 2200 \text{ cm}^{-1}$). Moreover,

$\nu\text{Hg-C}$ shifts to higher frequencies in complexes containing bridging cyano groups and this positive shift may be attributed to coupling of $\nu\text{Hg-C}$ with νCN in the HgCN part of the molecule.¹³ Since terminal cyano groups absorb at lower energies than pure mercury(II) cyanide, the terminal $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ modes would also be expected to absorb at lower energies. It may be pointed out that complexes having both terminal and bridging cyano groups exhibit¹⁴ two bands in each of the νCN , $\nu\text{Hg-C}$ and $\delta\text{Hg C N}$ regions—the one appearing at higher wavenumbers being assigned to the bridging cyano group while the other at lower energies to the terminal groups.

The observed frequencies of νCN (ca. 2170 cm^{-1}), $\nu\text{Hg-C}$ (ca. 415 cm^{-1}) $\delta\text{Hg CN}$ (ca. 320 cm^{-1}) in practically all the 1 : 1 mercury(II) cyanide complexes with the ligands investigated here strongly suggest the exclusive presence of terminally bonded cyano groups. From a consideration of the terminally pyridine ring nitrogen bonded nature of all the ligands investigated and the presence of exclusively terminally bonded cyano groups, all these complexes are assigned neutral monomeric three-coordinated structures with two terminally bonded cyano groups and a nitrogen of the organic amine around mercury(II) in the solid state. Molecular weight determinations are also consistent with monomeric three-coordinate environments about mercury(II) in all these complexes. One would postulate cyano-bridged dimeric 4-coordinate tetrahedral structures (A) with both terminal and bridging cyano group, or six coordinated polymeric



L = pyridine ring nitrogen bonded organic amine

octahedral structures with only bridging cyano groups for these complexes. However, such structures are ruled out as the infrared frequencies due to coordinated cyano groups indicate the exclusive presence of terminally bonded cyano groups in all these compounds.

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