

## Mercury(II) cyanide complexes with some bidentate ligands

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**Abstract.** Coordination compounds formed by the interaction of mercury(II) cyanide with some bidentate ligands—ethylenediamine, N,N-diethylethylenediamine, 1,3-propanediamine, 1,5-pentanediamine, 2,2'-bipyridylamine, 1,4-dioxane, morpholine, methylpyrazine, 4,4'-bipyridyl and 4,4'-bipyridyl N,N'-dioxide—have been prepared. Stoichiometries of the complexes have been established by metal, carbon and nitrogen estimations. The complexes isolated in the solid state have been characterized by IR spectroscopy down to  $200\text{ cm}^{-1}$  to elucidate the metal-ligand and metal-cyanide bonding modes. Tentative stereochemistries of the complexes in the solid state are discussed.

**Keywords.** IR spectra; mercury(II) cyanide; stereochemistry; coordination compounds; bidentate ligands.

### 1. Introduction

Coordination compounds formed by mercury(II) halides with nitrogen and oxygen donors have been subjected to extensive investigations (Dean 1978). The characteristic coordination numbers and stereochemical environments around the divalent mercury ion are two-coordinate linear, and four-coordinate tetrahedral. In addition to these, octahedral and five-coordination are also known (Dean 1978; Cotton and Wilkinson 1972). Three-coordination around Hg(II) is known in some systems (Eller *et al* 1977) but the species are mostly anionic (Fenn *et al* 1963) or cationic (Cheung *et al* 1965). Recently some neutral species exhibiting three-coordination around Hg(II) have been reported (Ahuja and Rao 1975; Ahuja *et al* 1978; Ahuja and Singh 1980a, b; Ahuja *et al* 1980a, b, c). The present communication describes the coordination compounds formed by the interaction of Hg(II) cyanide with ethylenediamine, N,N-diethylethylenediamine, 1,3-propanediamine, 1,5-pentanediamine, 2,2'-bipyridylamine, 1,4-dioxane, morpholine, methylpyrazine, 4,4'-bipyridyl and 4,4'-bipyridyl N,N'-dioxide. The ligands used in the present study possess more than one coordination site and can act as bidentate bridging or chelating ligands. IR spectroscopy has been used to distinguish the metal-ligand and metal-cyanide bonding modes and tentative stereochemistries of the complexes isolated in the solid state are discussed.

### 2. Experimental

The complexes were prepared by adding the Hg(II) cyanide to the respective ligand solution in hot ethanol. The complexes which formed immediately or crystallized out on cooling were suction-filtered, washed with ethanol and dried. The stoichiometry of the complexes was established by standard analytical methods and satisfactory analytical data (table 1) were obtained. IR spectra of the uncoordinated ligands and

Table 1. Analytical data.

Compound	Hg (%)		C (%)		N (%)	
	Observed	Theoretical	Observed	Theoretical	Observed	Theoretical
Hg(en)(CN) <sub>2</sub>	63.8	64.1	15.5	15.4	18.0	17.9
Hg(N,N-diethen)(CN) <sub>2</sub>	54.1	54.4	26.0	26.1	15.2	15.2
Hg(DAP)(CN) <sub>2</sub>	61.5	61.4	18.5	18.4	17.1	17.2
Hg(DAPP)(CN) <sub>2</sub>	56.5	56.5	23.5	23.7	15.9	15.8
Hg(BP)(CN) <sub>2</sub>	47.7	47.4	34.5	34.0	16.8	16.5
Hg(D)(CN) <sub>2</sub>	58.3	58.8	21.1	21.2	8.1	8.1
Hg(M)(CN) <sub>2</sub>	59.4	59.0	21.3	21.2	12.5	12.4
Hg(MP)(CN) <sub>2</sub>	60.0	60.2	21.6	21.7	16.8	16.9
Hg(4,4'-Bipy)(CN) <sub>2</sub>	48.5	49.0	34.8	35.3	13.4	13.7
Hg(4,4'-BipyO <sub>2</sub> )(CN) <sub>2</sub>	45.2	45.4	32.5	32.7	12.8	12.7

en = ethylenediamine; N,N-diethen = N,N-diethylethylenediamine; DAP = 1,3-propanediamine; DAPP = 1,5-pentanediamine; BP = 2,2'-bipyridylamine; D = 1,4-dioxane; M = morpholine; MP = methylpyrazine; 4,4'-Bipy = 4,4'-bipyridyl; 4,4'-BipyO<sub>2</sub> = 4,4'-bipyridyl N,N'-dioxide

their complexes were recorded in the rock salt and 650–200 cm<sup>-1</sup> regions as nujol mulls (neat in the case of liquid ligands) supported between sodium chloride plates and thin polythene sheets on a Perkin-Elmer 621 spectrophotometer equipped with caesium iodide optics. The observed frequencies due to coordinated CN groups, the mode of Hg(II)-ligand bonding and the tentative stereochemistry of each complex are listed in table 2.

### 3. Results and discussion

The techniques of electronic absorption spectroscopy and magnetic susceptibility measurements yield unambiguous structural information about transition metal compounds. However, these could not be studied for the Hg(II) complexes because of the closed shell of valence electrons. Stereochemistry of the compounds now studied has been arrived at by comparing the Hg(II)-ligand and Hg(II)-cyanide bonding modes with similar modes in complexes whose structures are known through x-ray crystallography and/or magnetic susceptibility and IR spectral studies.

#### 3.1 Diamine complexes

Infrared spectra of the 1:1 mercury(II) cyanide complexes with ethylenediamine, N,N-diethylethylenediamine, 1,3-propanediamine and 1,5-pentanediamine show significant differences from the IR spectra of metal(II) halide complexes with these ligands which have been shown by IR, Raman spectral and/or x-ray structural studies to have *trans* configuration of the diamine acting as a bridge between two metal atoms (Brodersen 1959; Powell and Shepherd 1959; Newman and Powell 1961; Krishnan and Plane 1966; Iwamoto and Shriver 1971; Nakamoto 1977). On the other hand, IR spectra of the complexes studied here exhibit multiplicity of bands and closely resemble those of the metal(II)-ethylenediamine complexes in which the *cis* or chelating form of ethylenediamine has been established (Horby and Torrible 1965; Earnshaw *et al* 1969; Berg and Rasmussen 1973; Nakamoto 1977). It is thus clear that the diamines used act as

Table 2. IR spectral data ( $\text{cm}^{-1}$ ) and stereochemistry.

Compound	Coordinated CN frequencies			Mode of Hg(II)-ligand bonding	Tentative stereochemistry
	$\nu\text{CN}$	$\nu\text{Hg-C}$	$\delta\text{Hg-CN}$		
Hg(en)(CN) <sub>2</sub>	2172	386	300	Bidentate chelating	Monomeric tetrahedral
Hg(N,N-diethen)(CN) <sub>2</sub>	2159	380	290	Bidentate chelating	Monomeric tetrahedral
Hg(DAP)(CN) <sub>2</sub>	2158	385	320	Bidentate chelating	Monomeric tetrahedral
Hg(DAPP)(CN) <sub>2</sub>	2152	365	290	Bidentate chelating	Monomeric tetrahedral
Hg(BP)(CN) <sub>2</sub>	2178	400	300	Bidentate chelating	Monomeric tetrahedral
Hg(D)(CN) <sub>2</sub>	2185	445-430	338	Bidentate bridging	Polymeric 4-coordinate
Hg(M)(CN) <sub>2</sub>	2185	420	333	Bidentate bridging	Polymeric 4-coordinate
Hg(MP)(CN) <sub>2</sub>	2185	440-430	340-330	Bidentate bridging	Polymeric 4-coordinate
Hg(4,4-Bipy)(CN) <sub>2</sub>	2170	423	315	Bidentate bridging	Polymeric tetrahedral
Hg(4,4'-BipyO <sub>2</sub> )(CN) <sub>2</sub>	2180	430	330	Bidentate bridging	Polymeric tetrahedral
Hg(CN) <sub>2</sub>	2193	442	341		Polymeric

bidentate chelating ligands in their complexes with Hg(II) cyanide and lead to the formation of 5-membered rings in the case of the first two ligands and as 6- and 8-membered rings with 1,3-propanediamine and 1,5-pentanediamine, respectively. In general, IR spectra of complexes with *trans* or bridging diamines, being more symmetrical, exhibit fewer absorption bands (9 to 10) in the region  $1600\text{--}650\text{ cm}^{-1}$  while the *cis* or chelating form being less symmetrical gives a multiplicity of bands (20 to 22) in the same region.

The observed frequencies associated with  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{Hg-CN}$  modes suggest the exclusive presence of terminally bonded CN groups (Jain and Rivest 1969, 1970; Ahuja and Garg 1971a, b; 1972) in the 1:1 Hg(II) cyanide complexes with the diamines studied. From a consideration of the bidentate chelating nature of the diamines and the terminal CN groups the 1:1 Hg(II) cyanide complexes with ethylenediamine, N,N-diethylethylenediamine, 1,3-propanediamine and 1,5-pentanediamine are considered to have monomeric, four-coordinated structures with tetrahedral environments around the Hg(II) ions in the solid state.

### 3.2 2,2'-Bipyridylamine complex

Rock salt as well as low frequency region IR spectrum of the 1:1 Hg(II) cyanide-2,2'-bipyridylamine complex indicates clearly that the bipyridylamine is bonded through the two pyridyl ring nitrogens (Gill *et al* 1961) to the same metal ion (bidentate chelating ligand) resulting in the formation of 6-membered rings (Ahuja and Singh

1973a, b). The observed frequencies of  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{Hg-CN}$  modes suggest the exclusive presence of terminally bonded CN groups. The complex may thus be assigned a monomeric, four-coordinated structure with a tetrahedral environment of two terminally bonded CN groups and two pyridyl ring nitrogens of the bidentate chelating 2,2'-bipyridylamine molecule around the Hg(II) ions in the solid state.

### 3.3 1,4-Dioxane complex

Except for some intensity changes and the slightly lower frequencies of some absorption bands (particularly the asymmetric C-O-C at  $1125\text{ cm}^{-1}$  and the symmetric stretching vibrations at  $880\text{ cm}^{-1}$  in the complex which provides good evidence for the absence of free ligand, the IR spectrum of the 1:1 Hg(II) cyanide complex with 1,4-dioxane is almost superimposable on the spectra of its constituent molecules. This close similarity in the IR spectra of the complex and the free constituent molecules was earlier observed for  $\text{Hg}(1,4\text{-dioxane})\text{Cl}_2$  (Mikawa *et al* 1966). X-ray structure determinations (Hassel and Hvoslef 1954) on  $\text{Hg}(1,4\text{-dioxane})\text{Cl}_2$  have shown the Hg(II) chloride and dioxane molecules to be linked together by weak O-Hg-O bonds to make a planar chain and that the two constituent molecules retain essentially similar configurations to those in their free molecules (Mikawa *et al* 1966). This close similarity of the IR spectra of the 1:1 Hg(II) cyanide complex with 1,4-dioxane to that of its constituent molecules strongly suggests that the interaction between dioxane and the Hg(II) cyanide molecules is almost of the same order as in  $\text{Hg}(1,4\text{-dioxane})\text{Cl}_2$ . However, if the coordinated dioxane molecules had a boat rather than a chair configuration in its complex with Hg(II) cyanide the IR spectrum would be expected to have a multiplicity of absorption bands owing to the increased number of IR active fundamentals. It has been pointed out (Ramsay 1947) that for 1,4-dioxane 17 IR active fundamentals in the region  $1500\text{--}750\text{ cm}^{-1}$  are permitted for the boat structure while only 7 are allowed for the chair form. Since the fundamental frequencies due to coordinated CN groups (table 2) in this complex do not suffer any significant shift, it is suggested that the planar chain arrangement of the two oxygens and the two chlorines (two C-bonded CN groups in the cyanide complex) surrounding the Hg(II) in  $\text{Hg}(1,4\text{-dioxane})\text{Cl}_2$  is retained in the 1:1 Hg(II) cyanide-dioxane complex as well.

### 3.3 Morpholine complex

Besides the shift of the N-H stretching vibration to lower frequencies ( $\nu(\text{NH})$  uncoordinated morpholine  $3440\text{ cm}^{-1}$ ; present complex  $3252\text{ cm}^{-1}$ ) the C-O-C stretching mode suffers a significant negative shift in the 1:1 Hg(II) cyanide-morpholine complex. The C-O-C stretching vibration at  $1095\text{ cm}^{-1}$  in uncoordinated morpholine occurs at  $1031\text{ cm}^{-1}$  in this complex. This decrease in the C-O-C stretching mode may be attributed to a change in the nature of the C-O-C bond as a result of oxygen-to-metal coordination. The morpholine is thus considered to coordinate through both its donor sites and act as a bidentate ligand bridging two metal ions in its 1:1 complex with Hg(II) cyanide and in this respect may be compared with the bidentate bridging nature of 1,4-dioxane in the  $\text{Hg}(1,4\text{-dioxane})\text{Cl}_2$  complex. The metal-ligand interaction in the Hg(II) cyanide-morpholine complex seems to be a little stronger (than dioxane in  $\text{Hg}(\text{dioxane})\text{Cl}_2$ ) as the fundamental frequencies of the Hg(II) cyanide suffer significant shifts in the complex. Frequencies of  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{Hg-CN}$  modes are consistent with terminally bonded cyano groups.

### 3.4 Methylpyrazine and 4,4'-bipyridyl complexes

Pyrazine and 4,4'-bipyridyl may be considered as pyridine derivatives, replacement of one of the CH group *para* to nitrogen by a nitrogen resulting in pyrazine, and that of a proton in the *para* position by a pyridyl group resulting in 4,4'-bipyridyl. Whereas pyrazine is known to act as a monodentate ligand as well as a bidentate bridging ligand, 4,4'-bipyridyl acts predominantly as a bidentate bridging ligand and complexes exhibiting the monodentate behaviour of 4,4'-bipyridyl are relatively few (Poller and Toley 1967; Carmichael and Edwards 1972). Geometries of both these ligands, however, rule out their acting as bidentate chelating ligands.

Except for slight shifting and/or splitting of some absorption bands and the appearance of weak bands at  $\approx 990$  and  $1250 \text{ cm}^{-1}$  [which indicate that the ligand is bonded through both the ring nitrogens, and that the complex has a short chain length polymeric structure (Lever *et al* 1961, 1962, 1963, 1964; Ahuja and Rastogi 1970)], the IR spectrum of the 1:1 Hg(II) cyanide complex with methylpyrazine studied herein is almost superimposable on the spectra of the constituent molecules and may be compared with the bidentate bridging nature of 1,4-dioxane in the Hg(1,4-dioxane)Cl<sub>2</sub> complex (Mikawa *et al* 1966). It is thus concluded that the interaction between methylpyrazine and Hg(II) cyanide is almost of the same order as in Hg(1,4-dioxane)Cl<sub>2</sub> and that methylpyrazine acts as a bidentate bridging ligand and that the complex has a short chain polymeric structure. Moreover, the fundamental frequencies due to the CN groups do not suffer significant shifts or splitting in this complex. The evidence provided points to the fact that the 1:1 Hg(II) cyanide complex with methylpyrazine has a planar chain arrangement of the two nitrogens (bridging methylpyrazine) and the two terminally bonded CN groups around Hg(II) in the solid state.

Infrared spectrum of the 1:1 Hg(II) cyanide complex with 4,4'-bipyridyl indicates that both the nitrogens of the bipyridyl are bonded to metal(II) ions and that 4,4'-bipyridyl is bridged between two Hg(II) ions. Steric position of the two nitrogen atoms in 4,4'-bipyridyl precludes chelation but favours coordination to different metal ions. Further, the IR spectrum of coordinated 4,4'-bipyridyl exhibits fewer absorption bands as compared to the spectrum of the uncoordinated ligand. This is due to a change from non-planarity (Almenningen and Bastiansen 1959; Cumper *et al* 1962) to planarity upon coordination. The observed IR frequencies due to  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{Hg-CN}$  modes suggest the exclusive presence of only terminally bonded cyano groups and the complex is considered to have a polymeric chain structure with a tetrahedral environment of the two N-atoms of the bridging 4,4'-bipyridyl and the two C-atoms of the terminally bonded CN groups around the Hg atoms in the solid state.

### 3.5 4,4'-Bipyridyl N,N'-dioxide complex

The IR spectrum of the 1:1 Hg(II) cyanide complex with this ligand shows clearly that both the oxygens of the dioxide are coordinated and that the ligand bridges the two Hg(II) ions. The steric position of the two oxygen atoms in this ligand precludes chelation but favours coordination to different metal ions thus resulting in polymeric chain structures. Normal modes of the 4,4'-bipyridyl N,N'-dioxide that are likely to be affected the most on coordination are the NO stretching and bending vibration frequencies (Simpson *et al* 1963; Vinciguerra *et al* 1963; Ahuja and Singh 1973b; Ahuja 1974; Ahuja *et al* 1980b, c). The  $\nu\text{NO}$  which appears as a strong doublet at 1249 and

1234  $\text{cm}^{-1}$  in the uncoordinated dioxide in the solid state (nujol mull) suffers a significant negative shift (1229, 1170  $\text{cm}^{-1}$ ) in this complex. This lowering of the  $\nu$ NO frequencies is attributed to a decrease in the  $\pi$ -bond character of the NO bond as a result of oxygen-to-metal coordination. The NO bending vibration appearing as strong absorptions at 848 and 834  $\text{cm}^{-1}$  in the IR spectrum of uncoordinated 4,4'-bipyridyl N,N'-dioxide is observed with almost similar intensity but shifted slightly to lower frequencies in this complex. In addition to the ligand bands the IR spectrum of this complex shows strong absorption bands at 2170, 420 and 315  $\text{cm}^{-1}$  which are identified as  $\nu$ CN,  $\nu$ Hg-C and  $\delta$  Hg-CN modes consistent with the presence of only terminally bonded cyano groups. From a consideration of the bidentate bridging nature of 4,4'-bipyridyl N,N'-dioxide and terminal CN groups the 1 : 1 Hg(II) cyanide complex with this ligand is tentatively assigned to have a four-coordinate polymeric chain structure with a tetrahedral environment of the two O-atoms of the bridging dioxide and the two C-atoms of the terminally bonded CN groups around the Hg atoms in the solid state.

The tentative stereochemistries and the isomorphous nature of the Hg(II) cyanide complexes reported herein have been derived from a comparison of the Hg(II)-ligand and the Hg(II)-cyanide bonding modes with those of compounds of established structures. However, x-ray and Raman studies would lend more conclusive support for the structures of these complexes.

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