

### Three-coordinate Complexes of Mercury(II) Pseudo-halides with Benzo(f)quinoline

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The divalent mercury ion,  $\text{Hg}^{2+}$ , is known to have a strong tendency for complex formation and the characteristic coordination numbers and stereochemical arrangements are two-coordinate linear and four-coordinate tetrahedral. Octahedral and five-coordinate species are also known [1] but coordination number three is rather rare for mercury(II) [2]. Three coordination around mercury(II) is known in some systems but the species are anionic [2], e.g.,  $[\text{SMe}_3][\text{HgI}_3]$ ,  $\text{Na}[\text{HgCl}_3]$ ,  $\text{Na}[\text{HgCl}_3] \cdot 2\text{H}_2\text{O}$ ,  $[\text{NH}_4][\text{HgCl}_3]$ ,  $[\text{NMe}_4][\text{HgBr}_3]$ . The present communication describes 1:1 complexes formed by the interaction of mercury(II) cyanide and thiocyanate with benzo(f)quinoline which are shown, from molecular weight, molar conductance and i.r. spectral studies, to be monomeric neutral species exhibiting coordination number three with trigonal planar environment around mercury(II) in the solid state.

Benzo(f)quinoline was obtained from Koch–Light Laboratories Limited and used as such. The mercury(II) cyanide complex was prepared by adding an excess of the ligand to a hot ethanolic solution of the metal cyanide. Mercury(II) thiocyanate complex was obtained by boiling a suspension of the metal thiocyanate in ethanol with an excess of the ligand and the mixture was filtered hot. The complexes which crystallized out on cooling were suction-filtered, washed with ethanol and dried. The stoichiometry of the complexes isolated was established by standard analytical methods and satisfactory analytical data were obtained.  $\text{Hg}(\text{Benzo(f)quinoline})(\text{CN})_2$ . Found: Hg, 46.2; Calc.: Hg, 46.4%.  $\text{Hg}(\text{Benzo(f)quinoline})(\text{SCN})_2$ . Found: Hg, 40.3; SCN, 23.2. Calc.: Hg, 40.4; SCN, 23.4%.

Conductivity measurements of the mercury(II) cyanide complex were made on freshly prepared  $\sim 1$  mM solutions in purified DMF at 25 °C with a Philips conductivity bridge model Pr 9500. Molecular weight measurements of the mercury(II) cyanide complex were made on a Mechrolab Inc. Vapour Pressure Osmometer Model 301 A using absolute ethanol as the solvent. Infrared spectra of the uncoordinated benzo(f)quinoline and of

the mercury(II) complexes were recorded as nujol mulls held between sodium chloride plates (rock salt region) and thin polythene sheets ( $650\text{--}200\text{ cm}^{-1}$ ) on a Perkin-Elmer 621 spectrophotometer.

Mercury(II) cyanide and thiocyanate gave 1:1 complexes with benzo(f)quinoline. The mercury(II) cyanide complex is soluble in DMF and molar conductance in this solvent indicates that the complex is essentially non-electrolyte. Benzo(f)quinoline, like pyridine and quinoline molecules, possesses only one coordination site. Absorption bands due to the benzo group in uncoordinated benzo(f)quinoline appear at almost the same frequencies in the i.r. spectra of the mercury(II) cyanide and thiocyanate complexes with this ligand. However, appreciable perturbations are observed in the fundamental frequencies of the pyridine moiety. Absorption bands at  $\sim 1585$  and  $1550\text{ cm}^{-1}$ , due to  $\text{C}\cdots\text{C}$  and  $\text{C}\cdots\text{N}$  stretching modes, respectively, in uncoordinated benzo(f)quinoline shift to higher frequencies in the i.r. spectra of mercury(II)–benzo(f)quinoline complexes. Moreover, the pyridine ring vibrations of the uncoordinated ligand at  $\sim 990$ ,  $605$  and  $405\text{ cm}^{-1}$  also undergo significant positive shifts in the spectra of complexes. These features are consistent with coordination of the benzo(f)quinoline via its pyridine ring nitrogen atom [3] to the mercury(II).

In addition to the ligand bands modified slightly on account of coordination, the i.r. spectrum of the 1:1 mercury(II) cyanide–benzo(f)quinoline complex shows absorption bands at  $2183$ ,  $421$  and  $327\text{ cm}^{-1}$  due to  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  modes, respectively. The frequencies of these modes are significantly 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 [4] and absorbs at  $2193$ ,  $442$  and  $341\text{ cm}^{-1}$  due to  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  modes [5], respectively. The frequency of  $\nu\text{CN}$  suffers a significant negative shift when the cyano bridges break down and mercury(II) cyanide complexes with terminal cyano groups absorb at lower frequencies [6] than pure mercury(II) cyanide while bridging cyano groups absorb at higher energies [7] ( $>2200\text{ cm}^{-1}$ ). Furthermore, complexes having both terminal and bridging cyano groups exhibit two bands in each of the  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  regions – the one appearing at higher wavenumbers is assigned to the bridging cyanide groups while the lower energy bands to the terminal cyanide groups [8]. With benzo(f)quinoline acting as a monodentate ligand the 1:1 mercury(II) cyanide–benzo(f)quinoline complex is, therefore, tentatively assigned a monomeric, neutral three-coordinated trigonal planar

structure with two terminal cyano groups and a nitrogen of the organic ligand around the mercury atoms in the solid state. Moreover, molecular weight determinations in absolute ethanol (observed 419; calculated 431) is also consistent with a neutral, monomeric three-coordinated environment around mercury(II). Cyano-bridged dimeric tetrahedral structure with both terminal and bridging cyanide groups or six-coordinated polymeric octahedral structure with only bridging cyanide groups could also be postulated. However, such structures are ruled out as the i.r. spectrum of the compound under investigation indicates the exclusive presence of terminal cyano groups.

Infrared spectrum of the 1:1 mercury(II) thiocyanate-benzo(f)quinoline complex shows absorption bands at 2120, 2100, 708 and 432  $\text{cm}^{-1}$ . These bands are assigned to  $\nu\text{CN}$  (2120, 2100  $\text{cm}^{-1}$ ),  $\nu\text{CS}$  (708  $\text{cm}^{-1}$ ) and  $\delta\text{SCN}$  (432  $\text{cm}^{-1}$ ) due to coordinated thiocyanate groups and their frequencies are consistent with those normally associated with terminally S-bonded SCN groups [9]. From a consideration of the frequencies due to coordinated thiocyanate groups and the terminally bonded benzo(f)quinoline molecule the 1:1 mercury(II) thiocyanate-benzo(f)quinoline complex is tentatively assigned a monomeric neutral three-coordinated structure around mercury(II) in the solid state. One could postulate a thiocyanato-bridged dimeric four-coordinated tetrahedral structure with both terminal and bridging thiocyanate groups or six-coordinated polymeric octahedral structure with only bridging thiocyanate groups in this complex. However, such structures are ruled out as the fundamental vibrations due to coordinated thiocyanate groups suggest the

exclusive presence of terminally S-bonded thiocyanate groups in the solid state i.r. spectrum of this complex. The tentative stereochemistries of the compounds studied herein have been arrived at from a comparison of their metal-ligand frequencies with those of compounds with established structures. However, unambiguous characterization of these compounds should be based on complete crystal structure determinations.

## References

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