Ienvirokent around Hg(II) in the solid state. Tentative stereochemistries of the complexes are discussed. It has been prepared and characterized. The (4-benzylpyridine)CN, and Hg(4-benzylpyridine)(SCN) complexes isolated in the solid state in order to elucidate the mode coordination of the benzylpyridines via their pyridine ring nitrogen atoms.8

Some Three-coordinated Complexes of Mercury(II)
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Complexes of Hg(II) cyanide and thiocyanate with 2- and 4-benzylpyridines have been prepared and characterized. The complexes prepared are: Hg(2-benzylpyridine)(CN)2, Hg(4-benzylpyridine)CN, and Hg(4-benzylpyridine)(SCN). IR spectra down to 200 cm⁻¹ have been recorded for the complexes isolated in the solid state in order to elucidate the mode of coordination of the benzylpyridines and cyanide/thiocyanate bonding. Tentative stereochemistries of the complexes are discussed. It is shown that Hg(4-benzylpyridine)CN has a neutral, monomeric four-coordinated tetrahedral structure. Hg(2-benzylpyridine)(CN)2 and Hg(4-benzylpyridine)(SCN)2 are neutral species exhibiting coordination number three with trigonal planar environment around Hg(II) in the solid state.

The divalent mercury ion, Hg²⁺, is known to have a strong tendency for complex formation and its characteristic coordination numbers are 2 and 4 and stereochemical arrangements are linear and tetrahedral. Octahedral and five-coordinated geometries are also known in some cases.8 Besides these some 1:1 complexes of the type Ph₃P·Hg·X₂ (X = Cl or Br)8 and Hg·PyX₂ or Hg·PyOX₂ (Py = pyridine, PyO = pyridine N-oxide or their ring substituted alkyl or dialkyl derivatives)8 are known and are considered as halogen-bridged dimeric tetrahedral structures in the solid state. Hg₃AsOCl₉, however, has an oxygen-bridged dimeric structure9. Coordination number three is rather rare for mercury(II). Although three coordination around mercury(II) is reported in some systems, the species are anionic e.g. [Me₄N][HgCl₆] [Me₄S][HgCl₆]. We now report 1:1 complexes of mercury(II) cyanide and thiocyanate with 2- and 4-benzylpyridines which are considered as neutral species exhibiting coordination number three with trigonal planar environment around mercury(II) in the solid state.

Mercury(II) cyanide complexes were prepared by adding an excess of the ligand to an ethanolic solution of the metal cyanide. Mercury(II) thiocyanate complexes were 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.

Hg(2-benzylpyridine)(CN)₂ : [Found: Hg, 47.7. Calc. : Hg, 47.5 %].

Hg(4-benzylpyridine)CN : [Found: Hg, 34.1. Calc. : Hg, 33.9 %].

Hg(4-benzylpyridine)(SCN)₂ : [Found: Hg, 41.5; SCN, 24.3. Calc. : Hg, 41.2; SCN, 23.9 %].

IR spectra of the uncoordinated benzylpyridines and mercury(II) complexes were recorded in nujol on Perkin-Elmer 621 (rock salt region) and P.E. 225 (700-200 cm⁻¹) spectrophotometers.

Mercury(II) cyanide gave a 1 : 1 complex with 2-benzylpyridine and a 1 : 2 complex with 4-benzylpyridine while mercury(II) thiocyanate formed a 1 : 1 complex with 4-benzylpyridine only. IR spectra of these complexes show bands due to the benzyl groups at almost the same positions as in the uncoordinated 2- and 4-benzylpyridines. However, appreciable changes take place in the fundamental vibrations of the pyridine moiety on complexation. The vC=N, vC–C and vC–C–N observed at 1600 and 1560 cm⁻¹, respectively, and the pyridine ring vibrations observed at ~995, 605 and 405 cm⁻¹ in the uncoordinated benzylpyridines suffer significant positive shifts on complexation indicating coordination of the benzylpyridines via their pyridine ring nitrogen atoms.

In addition to the ligand bands, IR spectrum of the 1:1 mercury(II) cyanide complex with 2-benzylpyridine shows bands at 2185, 417 and 323 cm⁻¹ assigned to vCN, vHg–C and $vHgCN$ modes, respectively, due to coordinated cyano groups. 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 cyanide-bridged polymeric chain structure in the solid state and absorbs at 2193, 442 and 341 cm⁻¹ due to vCN, vHg–C and $vHgCN$ modes, respectively. These modes suffer significant negative shifts when the cyano bridges break down because mercury(II) cyanide complexes with terminal cyano groups absorb at lower energies than pure mer-
cury(II) cyanide while bridging cyanide groups absorb at higher energies. Furthermore, complexes having both terminal and bridging cyano groups exhibit two bands in each of the νCN, νHg-C and δHgCN regions; the one appearing at higher wave numbers is assigned to the bridging cyanide groups while the lower energy band is assigned to the terminal cyanide groups. With 2-benzylpyridine acting as a monodentate ligand, the 1:1 mercury(II) cyanide-2-benzylpyridine complex is, therefore, tentatively assigned a monomeric, three-coordinated trigonal-planar structure with two terminal cyanato groups and a nitrogen of the 2-benzylpyridine around the mercury atom in the solid state. 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 IR spectrum of the compound under investigation indicates the exclusive presence of terminal cyano groups.

IR spectrum of the 1:2 mercury(II) cyanide-4-benzylpyridine complex shows bands at 2123, 419 and 327 cm⁻¹ due to νCN, νHg-C and δHgCN modes, respectively, consistent with the presence of terminally bonded cyano groups. From a consideration of the frequencies due to coordinated cyano groups and the terminally bonded 4-benzylpyridine molecules, a four-coordinated monomeric tetrahedral stereochemistry is suggested for the 1:2 mercury(II) cyanide-4-benzylpyridine complex.

Mercury(II) thiocyanate gives a 1:1 complex with 4-benzylpyridine. IR spectrum of this compound shows bands at 2107, 710, 425 and 263 cm⁻¹ which are assigned to νCN, νCS, δSCN and νHg-SCN modes, respectively, due to coordinated thiocyanate groups. The frequencies of these modes are consistent with terminally S-bonded thiocyanate groups. From a consideration of the frequencies due to coordinated thiocyanate groups and the terminally bonded 4-benzylpyridine molecule the 1:1 mercury(II) thiocyanate-4-benzylpyridine complex is tentatively assigned a monomeric three-coordinated structure in the solid state. One could postulate a thiocyanate-bridged four-coordinated structure with both terminal and bridging thiocyanate groups or six-coordinated polymeric structure with only bridging thiocyanate groups for 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 IR spectrum of this compound. The tentative stereochemistries of the compounds reported 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 can be done only on the basis of complete crystal structure determinations.

References


Amperometric Determination of Fe(III), Co(II) & Ag(I) Using Benzylmercaptoacetic Acid & Its Complexes with Fe(II), Co(II), Ni(II), Cu(II) & Ag(I)

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Benzylmercaptoacetic acid has been used for the amperometric determination of Fe(III), Co(II) and Ag(I) in the concentration ranges 5.58-139.60, 11.70-117.86 and 21.57-215.70 ppm respectively with an accuracy of ±0.5%. The interference due to a large number of foreign ions has also been studied. Complexes of Fe(III), Co(II), Ni(II) and Cu(II) have been isolated in the solid form and characterised on the basis of analytical data, conductance, magnetic moment and IR studies.

Mercaptoacetic acid has been used as an analytical reagent for the colorimetric determination of a number of metal ions but no report on the metal complexes of benzylmercaptoacetic acid has appeared. The present note describes the preparations and characterisation of the solid complexes of Fe(III), Co(II), Ni(II) and Cu(II) with benzylmercaptoacetic acid and its use for the amperometric determination of Fe(III), Co(II) and Ag(I).

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