

## A THREE-COORDINATE COMPLEX OF MERCURY(II) CYANIDE WITH 4-PICOLYLAMINE

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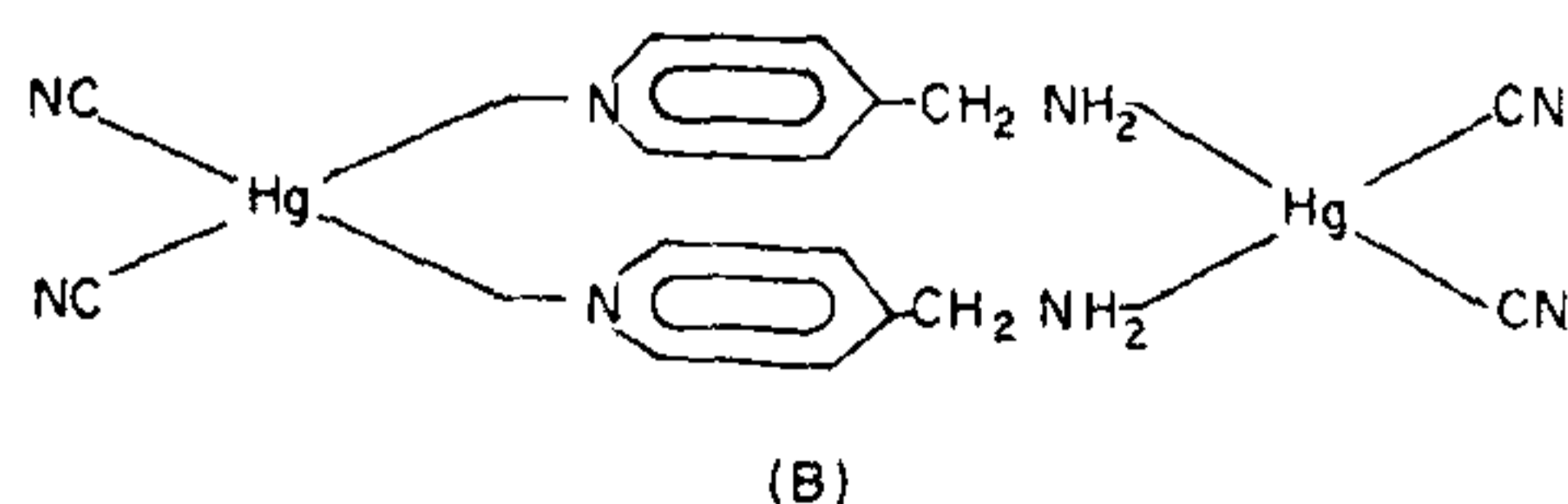
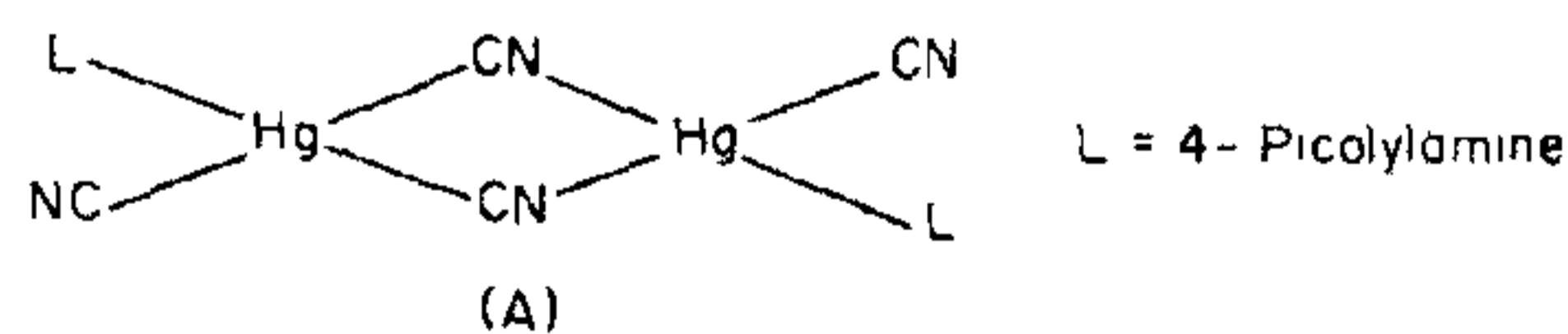
BIVALENT mercury ion,  $\text{Hg}^{2+}$ , is known to have a strong tendency for complex formation and the characteristic coordination numbers and stereochemical arrangements are two coordinate linear and four coordinate tetrahedral. In addition to these, six and five coordinations are also known<sup>1</sup>. Three coordination around mercury(II) is known in some systems but the species are anionic or cationic<sup>2</sup>. Some 1:1 complexes, e.g.,  $\text{Ph}_3\text{P HgX}_2$ ,  $\text{PyHgX}_2$  and  $\text{PyOHgX}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{Py} =$  pyridine or its ring substituted alkyl or dialkyl derivative,  $\text{PyO} =$  pyridine N-oxide or its ring substituted derivative) are known but these are halogen-bridged dimeric tetrahedral structures in the solid state<sup>3-5</sup>.  $\text{Ph}_3\text{AsO HgCl}_2$ , however, has an oxygen-bridged dimeric structure<sup>6</sup>. The present communication describes the isolation of a 1:1 complex of mercury(II) cyanide with 4-picolylamine (a potentially bidentate ligand). This is considered as a monomeric neutral species exhibiting coordination number three with a trigonal planar environment of one nitrogen, from pyridine ring of 4-picolylamine molecule, and two carbon atoms (of the terminally bonded cyano groups), around the mercury(II) in the solid state.

4-Picolylamine was obtained from M/s. Reilly Tar & Chemicals Corporation, U. S. A., and used as such. The mercury(II) cyanide complex was prepared by adding an excess of the ligand to an ethanolic solution of the metal cyanide. The complex which crystallized out on cooling was filtered and washed with ethanol and dried. Stoichiometry of the complex was established by metal, carbon and nitrogen estimations which agree with the 1:1 formula. Infrared spectra of the uncoordinated ligand (neat) and the mercury(II) cyanide complex (nujol mull) were recorded on a Perkin-Elmer 621 spectrophotometer.

4-Picolylamine possesses two potential donor sites: (i) pyridine nitrogen, and (ii) amino nitrogen of the  $-\text{CH}_2\text{NH}_2$  group. Infrared spectrum of the 1:1 mercury(II) cyanide complex with this ligand suggests that the organic amine is bonded through its pyridine nitrogen to mercury(II). This is evident from the fact that the fundamental pyridine ring vibrations at 998, 584 and  $390\text{ cm}^{-1}$  in the free 4-picolylamine show significant positive shifts at 1025, 600 and  $405\text{ cm}^{-1}$ ,

respectively. The  $\nu\text{NH}$  modes (of the  $-\text{CH}_2\text{NH}_2$  group) in the free picolylamine at 3350 and  $3280\text{ cm}^{-1}$  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 the 4-picolylamine is bonded exclusively through its pyridine nitrogen<sup>7</sup> to the mercury(II) ions and that it acts as a terminally bonded monodentate ligand in this complex.

In addition to the ligand bands indicating coordination of the 4-picolylamine via its pyridine nitrogen, infrared spectrum of this complex shows absorption bands at 2180, 425 and  $330\text{ cm}^{-1}$  which are identified as  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  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 which has a linear cyanide-bridged polymeric chain structure in the solid state<sup>8</sup> and absorbs at 2193, 422 and  $341\text{ cm}^{-1}$  due to  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  modes, respectively. Mercury(II) cyanide complexes with terminal cyano groups, absorb at lower frequencies<sup>10</sup> than pure mercury(II) cyanide while bridging cyano groups absorb at higher wave numbers ( $> 2200\text{ cm}^{-1}$ )<sup>11</sup>. Furthermore,  $\nu\text{Hg-C}$  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  $\nu\text{CN}$  in the  $\text{HgCN}$  part of the molecule<sup>12</sup>. Since terminal cyano groups absorb at lower energies than pure mercury(II) cyanide, the terminal  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  modes would also be expected to absorb at lower energies. Moreover, complexes having both terminal and bridging cyano groups exhibit two bands for each of the  $\nu\text{CN}$ ,  $\nu\text{Hg-C}$  and  $\delta\text{HgCN}$  modes<sup>13</sup> the bands appearing at higher wave numbers being assigned to the bridging cyano groups and the bands at



Structures A and B for the complex

lower energies to the terminal cyano groups. The observed frequencies of  $\nu_{\text{CN}}$  ( $2180\text{ cm}^{-1}$ ),  $\nu_{\text{Hg-C}}$  ( $425\text{ cm}^{-1}$ ) and  $\delta_{\text{HgCN}}$  ( $330\text{ cm}^{-1}$ ) in the 1:1 mercury(II) cyanide complex with 4-picolyamine strongly suggest the exclusively terminally bonded cyano groups. From a consideration of pyridine nitrogen bonded monodentate behaviour of 4-picolyamine molecule and the presence of terminally bonded cyano groups, the 1:1 complex of mercury(II) cyanide with 4-picolyamine is assigned a monomeric three coordinate structure with a planar environment of one nitrogen atom and two carbon atoms around mercury(II) in the solid state and rule out structures A and B for the complex.

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## THE DETERMINATION OF THE ATMOSPHERIC RATIOS OF ThC TO ThB USING Ge(Li) SPECTROMETERS

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THE relative concentrations of thoron daughters ThC (Bi-212) and ThB (Pb-212) in the atmosphere are of interest in several geophysical and health physics problems<sup>1-3</sup>. The main difficulty in estimating their individual concentrations is the simultaneous presence of the short-lived radon daughter products in the atmosphere in concentrations higher by an order of magnitude or more. This makes the conventional decay analysis impossible, as by the time radon daughter products have decayed, ThC and ThB are in radioactive equilibrium<sup>1-3</sup>. However, the ThC/ThB ratios can be determined in the presence of radon daughters by delayed coincidence techniques using liquid scintillators<sup>2</sup> or by unscrambling the complex gamma spectrum of radon and thoron daughters<sup>3</sup>. The former method needs complicated electronic equipments while the latter requires the spectra of RaB, RaC, ThB and ThC. This requires the rapid radiochemical separation and counting of the above radionuclides of short half-lives<sup>3</sup>. (Delayed separation and counting of the above isotopes would distort the spectral shapes due to ingrowth of daughter products). Here we give a simpler method which can be used with the Ge(Li) spectrometers currently available in several laboratories. In this method, advantage is taken of the high resolution of the Ge(Li) spectrometers which enables the accurate estimation of closely overlapping photopeaks.

The atmospheric particulates for these studies were collected on Hollingsworth and Vose H-70 filters at a height of 18 m on the terrace of the Modular Laboratories, Bhabha Atomic Research Centre, Trombay, Bombay. To increase the counting efficiency, three blowers, each drawing 1200 lit per min, were run simultaneously through filters of dimensions  $30 \times 15$  cm. each. The three filters, after collection, were pressed together in a hydraulic press into pellets of 1 cm thickness and 6 cm. diameter. They were then counted in a 80 cc Ge(Li) detector coupled to a 1024 channel analyser. A time delay was allowed for the decay of short-lived radon daughters. The collection and counting times were optimized by trial and