

Mercury(II) Cyanide Complexes with 4,4'-Bipyridine and 4,4'-(Propane-1,3-diyl)bipyridine

Ishar Singh Ahuja and Raghuvir Singh

Chemistry Department, Banaras Hindu University,
Banaras-5, India.

Abstract

1 : 1 Coordination complexes formed by mercury(II) cyanide with 4,4'-bipyridine and 4,4'-(propane-1,3-diyl)bipyridine have been prepared and characterized by molar conductance, molecular weight and infrared spectral measurements down to 200 cm^{-1} in the solid state. The 4,4'-bipyridine complex is shown to have a polymeric chain structure with a tetrahedral environment of two nitrogen atoms of bridging 4,4'-bipyridine and two carbon atoms of the terminally bonded cyano groups about the mercury atoms. The 4,4'-(propane-1,3-diyl)bipyridine complex is suggested to have a monomeric three-coordinate structure with only terminally bonded 4,4'-(propane-1,3-diyl)bipyridine and cyano groups.

Known coordination compounds of mercury(II) cyanide with bidentate nitrogen donor ligands have the stoichiometry $\text{LHg}(\text{CN})_2$ ($\text{L} = 1,10\text{-}o\text{-phenanthroline}$, $2,2'\text{-bipyridine}$, $2,2'\text{-bipyridylamine}$, ethylenediamine, $N,N\text{-diethylethylenediamine}$, propane-1,3-diamine or pentane-1,5-diamine) and are monomeric with chelation of L and four-coordinate mercury.¹⁻⁵ We now report a study of the preparation and structure of the mercury(II) cyanide complexes with 4,4'-bipyridine and 4,4'-(propane-1,3-diyl)bipyridine.

Experimental

4,4'-Bipyridine and 4,4'-(propane-1,3-diyl)bipyridine were obtained from Koch-Light Laboratories and Reilly International Chemicals Inc., respectively, and used as such. The complexes were prepared by mixing together the mercury(II) cyanide and the respective ligand solutions 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 isolated was established by standard analytical methods and satisfactory analytical data were obtained. The complexes are fairly soluble in $N,N\text{-dimethylformamide}$ and methanol but insoluble in ethanol, acetone, benzene, dichloromethane and dichloroethane. Conductivity measurements were made on freshly prepared $c. 0.001\text{ M}$ solutions in purified dimethylformamide at 25°C ($\pm 0.5^\circ\text{C}$) with a Philips conductivity measuring bridge PR 9500. Molecular weight determination of the 4,4'-(propane-1,3-diyl)bipyridine complex was carried out by the Rast method in camphor (found 470, calc. 450). The 4,4'-bipyridine complex is too

¹ Jain, S. C., and Rivest, R., *Inorg. Chim. Acta*, 1970, 4, 291.

² Ahuja, I. S., and Singh, R., *Inorg. Chim. Acta*, 1973, 7, 565.

³ Ahuja, I. S., and Singh, R., *Inorg. Nucl. Chem. Lett.*, 1973, 9, 289.

⁴ Ahuja, I. S., and Singh, R., *Inorg. Nucl. Chem. Lett.*, 1974, 10, 421.

⁵ Ahuja, I. S., and Singh, R., *J. Coord. Chem.*, 1975, 4, 181.

insoluble in camphor. Infrared spectra were recorded as Nujol mulls supported between sodium chloride plates (rock salt region) and thin polythene sheets (15–50 μm) on a Perkin-Elmer 621 spectrophotometer equipped with caesium iodide optics.

4,4'-Bipyridine complex, m.p. $>290^\circ\text{C}$ (Found: C, 34.8; H, 1.9; Hg, 48.0; N, 13.4. Calc. for $\text{C}_{12}\text{H}_8\text{HgN}_4$: C, 35.3; H, 1.9; Hg, 49.0; N, 13.7%). Λ_m in dimethylformamide $14.1 \text{ S mol}^{-1} \text{ cm}^2$. $\nu(\text{CN})$ 2120, $\nu(\text{Hg}-\text{C})$ 423, $\delta(\text{HgCN})$ 315 cm^{-1} .

4,4'-(Propane-1,3-diyl)bipyridine complex, m.p. 245°C (Found: C, 40.1; H, 3.1; Hg, 44.6; N, 12.5. Calc. for $\text{C}_{15}\text{H}_{14}\text{HgN}_4$: C, 40.0; H, 3.1; Hg, 44.4; N, 12.4%). Λ_m in dimethylformamide $4.7 \text{ S mol}^{-1} \text{ cm}^2$. $\nu(\text{CN})$ 2160, $\nu(\text{Hg}-\text{C})$ 415, $\delta(\text{HgCN})$ 308 cm^{-1} .

Results and Discussion

Analytical data show that mercury(II) cyanide forms 1 : 1 complexes with 4,4'-bipyridine and 4,4'-(propane-1,3-diyl)bipyridine and molar conductivities in dimethylformamide demonstrate that both these complexes are essentially non-electrolytes.

The infrared spectrum of the 1 : 1 mercury(II) cyanide–4,4'-bipyridine complex and the insolubility of the compound in camphor suggest the bidentate bridging nature of 4,4'-bipyridine and the polymeric nature of the complex. Further, the infrared spectrum of coordinated 4,4'-bipyridine exhibits fewer absorption bands compared with the spectrum of the uncoordinated ligand. This is due to a change from non-planarity⁶ to planarity on coordination. The observed infrared frequencies of $\nu(\text{CN})$ 2120, $\nu(\text{Hg}-\text{C})$ 423 and $\delta(\text{HgCN})$ 315 cm^{-1} strongly suggest the presence of only terminal cyano groups^{1–5} and the complex is considered to have a polymeric chain structure with a tetrahedral environment of two nitrogen atoms of the bridging 4,4'-bipyridine and two carbon atoms of the terminally bonded cyano groups around the mercury atoms.

Infrared bands associated with the cyano groups, $\nu(\text{CN})$ 2160, $\nu(\text{Hg}-\text{C})$ 415 and $\delta(\text{HgCN})$ 308 cm^{-1} , are lower than the corresponding values⁷ [$\nu(\text{CN})$ 2193 cm^{-1} , $\nu(\text{Hg}-\text{C})$ 442 cm^{-1} and $\delta(\text{HgCN})$ 341 cm^{-1}] for mercury(II) cyanide (cyano-bridged polymeric structure).⁸ This is indicative of terminal CN groups in the 1 : 1 mercury(II) cyanide–4,4'-(propane-1,3-diyl)bipyridine complex. Since the compound is monomeric as indicated by its molecular weight and the ligand cannot chelate, the compound must contain three-coordinate mercury⁹ and unidentate 4,4'-(propane-1,3-diyl)bipyridine. However, the possibility of a polymer \rightarrow monomer breakdown in hot camphor is not completely ruled out.

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⁷ Jones, L. H., *J. Chem. Phys.*, 1957, **27**, 665.

⁸ Hvoslef, J., *Acta Chem. Scand.*, 1958, **12**, 1568.

⁹ Ahuja, I. S., and Sambasivarao, K., *J. Inorg. Nucl. Chem.*, 1975, **36**, 586.