

# Syntheses, Structures and Vibrational Spectroscopy of Some Adducts of Silver(I) Cyanide with (Oligo-)Pyridine Bases

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 70<sup>th</sup> birthday*

Crystalline materials obtained by the crystallization of silver(I) cyanide from/with a variety of (oligo-)pyridine bases, L, of various bulk, have been characterized by room temperature single crystal X-ray structure determination. From L = quinoline (= 'quin'), AgCN : quin (1:2), is obtained, the structure being a single-stranded polymer, the successive silver atoms located on two-fold axes linked by linearly bridging cyanide groups and four-coordinate, the other two coordination sites being occupied by symmetry related quinoline nitrogen atoms. From L = 2,4,6-trimethylpyridine ('collidine'  $\equiv$  'coll') AgCN : coll (1:1) is obtained; it is similarly a one-dimensional polymer with bridging cyanide linkages, but now with three-coordinate silver(I), the one ligand nitrogen being coordinated. The adduct for L = pyridine (= 'py'), is of novel AgCN : py (10:9) stoichiometry; it also is a one-dimensional polymer, with three-coordinate silver(I) atoms also coordinated by pyridine nitrogen, but with periodic 'errors' in a wave-like array (similar to that recently reported for 'LT-CuCN'), here associated with the incorporation of occasional two-coordinate silver(I) lacking the pyridine – an unusual coordination complex example of a 'modulated' structure?

1:1 adducts are obtained with L = 2,2'-bipyridine, 'bpy', 1,10-phenanthroline, 'phen', and 2,9-dimethylphenanthroline, 'dmp', the latter two adducts being 'solvated' with additional moles of phen and pyridine respectively. AgCN : bpy (1:1) is a single-stranded polymer with four-coordinate silver atoms linearly bridged by cyanides. The complex components of AgCN : phen (1:2) ( $\equiv$  AgCN : phen (1:1). phen) and AgCN : dmp (: py) (1:1(:1)) are both mononuclear 1:1 species, [LAgCN], with three-coordinate metal atoms. With 2,2':6',2"-terpyridyl, 'tpy', a pyridine solvated adduct of AgCN : tpy : py (8:2:1) stoichiometry is found, the pyridine being incorporated in the one-dimensional polymer which comprises an ...Ag'(NCAgCN)Ag'(NCAgCN)Ag'... spine, with (tpy)Ag(NCAgCN)Ag' and Ag'(NCAg(py)CN)(tpy) units pendant to either side at alternate three-coordinate Ag'. In all of the oligodentate ligand complexes, the molecular packing is of interest, being dominated by the usual interleaving and perpendicular aromatic planar moieties.

The IR spectra of the one-dimensional polymers show bands that are assigned to vibrations of the extended AgCN chains in these complexes:  $\nu(\text{CN})$ ,  $\nu(\text{AgC/N})$  (the AgC/AgN stretching mode, involving vibration of the CN group between its two neighbouring Ag atoms),  $\delta(\text{AgCN})$  (the restricted rotation of the CN group), and  $\delta(\text{NAgC})$  (the counter-vibration of the Ag substructure against the CN substructure). The  $\nu(\text{CN})$  and  $\nu(\text{AgC/N})$  bands in AgCN : py (10:9) occur in the ranges 2096 – 2154 and 360 – 460  $\text{cm}^{-1}$  respectively, and show splittings that can be attributed to the unusual structure of this complex in the solid state. The Raman spectra of the py complex in the solid state and in solution are also discussed. In the other two unidentate ligand complexes, single bands are observed for the  $\nu(\text{CN})$  and  $\nu(\text{AgC/N})$  modes at 2140, 392 (AgCN : coll (1:1)) and 2140, 422  $\text{cm}^{-1}$  (AgCN : quin (1:2)) respectively. The monomeric AgCN : bidentate ligand complexes AgCN : phen (1:1) and AgCN : dmp (1:1) show lower  $\nu(\text{CN})$  and  $\nu(\text{AgC/N})$  frequencies than the polymeric AgCN : bpy (1:1), despite the fact that the Ag-C/N distances in the former are shorter than that in the latter, in agreement with previously observed trends in AgCN/ER<sub>3</sub> compounds.

**Key words:** Silver Cyanide, Pyridine, Structure, Infrared Spectroscopy, Raman Spectroscopy