Syntheses, Structures and Vibrational Spectroscopy of Some Adducts of Copper(I) Cyanide with Pyridine Bases

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Synthetic and room temperature single crystal X-ray structural characterizations are recorded for adducts of copper(I) cyanide formed by crystallization of copper(I) cyanide from (unidentate) pyridine ('py') bases L, of 1:2 (L = py; new phase), 1:1.5 (L = 2-methylpyridine, '2mp') and 1:1 (L = quinoline, 'quin') stoichiometries. All are single-stranded polymers, with successive copper atoms linked by single linear cyanide bridges (C,N disordered, individual components not resolved), with four- or three-coordinate N₂Cu(CN)₂ or NCu(CN)₂ copper environments in the 1:2 and 1:1 adducts, these alternating in the 1:1.5 (2:3) adduct. The present and previous related studies providing a basis for a systematic survey of their vibrational spectroscopy. The IR spectra of the infinite polymers show bands that are assigned to vibrations of the CuCN chains in these complexes: v(CN), v(CuC/N) (the CuC/CuN stretching mode, involving vibration of the CN group between its two neighbouring Cu atoms), $\delta(CuCN)$ (the restricted rotation of the CN group), and $\delta(NCuC)$ (the counter-vibration of the Cu substructure against the CN substructure). Gravimetric and vibrational spectroscopic studies following loss of the base molecules from these complexes show that ligand removal occurs in several stages via a series of well-defined adducts, some of which have unusual stoichiometries and structures. Conversely, solid CuCN may be "activated" towards adduct formation by prior reaction with pyridine bases.

Key words: Copper Cyanide, Pyridine, Structure, Infrared Spectroscopy, Raman Spectroscopy