Syntheses, Structures and Vibrational Spectroscopy of Some Mixed Pyridine/Triphenylphosphine Adducts of Copper(I) Cyanide

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

Single crystal room temperature X-ray structure determinations are described for three adducts formed between copper(I) cyanide, pyridine ('py') and triphenylphosphine of (p : q : r =) 1:1:1, 1:1.5:0.5 and 1:0.5:2 (plus py hemisolvate) stoichiometry. The latter is binuclear [(Ph₃P)₂(py)Cu(μ -CN)Cu(PPh₃)₂(CN)]. py; the others are linear polymers with ...Cu(μ -NC)Cu(μ -NC)Cu... spines with four-coordinate copper atoms, the coordination sphere of every copper atom in the first being completed by pendant py and Ph₃P ligands, while the second has those of alternate copper atoms coordinated by a pair of py ligands. Assignment of bridging CN in all cases is crystallographically ambiguous. The IR spectra of the infinite polymeric complexes show bands that are assigned to vibrations of the CuC chains in the complexes: v(CN), v(CuC/N) (the CuC/N stretching mode, involving vibration of the CN group between its two neighbouring Cu atoms), δ (CuCN) (the restricted rotation of the CN group) and δ (NCuC) (the counter vibration of the Cu substructure against the CN substructure). The v(CN) and v(CuC/N) frequencies show correlations with the Cu-C/N bond lengths that are similar in form to those recently established for a range of AgCN complexes.

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