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PARTIAL HYDROLYSIS OF A SCHIFF BASE LIGAND COORDINATED TO COPPER(II)

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The polyamine ligand, tris(4-(2-pyridyl)-3-aza-3-butenyl) amine, tren-py$_3$, has been prepared by the Schiff base reaction between tren and pyridine-2-aldehyde and the crystal structures of its complexes with Mn^{II}, Fe^{II}, Co^{II}, Cu^{II} and Zn^{II} have been determined as the tetrafluoroborate salts and the Ni^{II} complex as the hexafluorophosphate salt. In all six crystals, the three imine nitrogen atoms and the three pyridine nitrogen atoms surround the metal ion in a somewhat distorted octahedral configuration with the amine nitrogen atom forming a "cap" on the triangular face defined by the imine nitrogen atoms, but with a considerably longer M–N distance In all except the copper complex, the complex is only slightly distorted from trigonal symmetry In the copper complex, however, a strong Jahn–Teller distortion of the octahedron is observed, such that the Cu–N bond distances are 2 05, 2 09 and 2 19 Å for the imine nitrogen atoms and 2 05, 2 16 and 2 31 Å for the pyridine nitrogen atoms, with the two longest Cu–N bonds *trans*

The copper complex is further unique in its susceptibility to hydrolysis When an aqueous solution of the copper complex is shaken with chloroform, pyridine-2-aldehyde is extracted into the chloroform, the color of the aqueous solution changes from apple-green to blue, the visible spectrum changes from one characteristic of 6-coordinate Cu^{II} to one characteristic of 5-coordinate Cu^{II}, and crystals of [(4-(2-pyridyl)-3-aza-3-butenyl)bis(2-aminoethyl)amine] copper(II) tetrafluoroborate may be obtained by evaporation of the aqueous solution Aqueous solutions of the complexes of the other five metal ions show no evidence of hydrolysis of the ligand under similar conditions

The crystal structure of the hydrolysis product shows the copper(II) ion to have a distorted trigonal bipyramidal coordination, with the tertiary amine nitrogen atom and the pyridine nitrogen atom at the apices Thus it appears that the strong tendency for copper(II) to form five-coordinate complexes has caused the rather unusual partial hydrolysis of the coordinated tren-py$_3$ ligand to form the ligand tren-py$_1$