THE STRUCTURE OF 4-CHLOROPYRIDINE AMMONIUM CADMIUM TRIPPYCYANO-NICKELATE. By O. Büyükgüngör, D. Nikit, Physics Department, Hacettepe University, Beytepe Anahare, Turkey.

The crystal structure of Cd(NH₃)₂(4-Cl-Cpy)Ni(CN)₄ was determined from three dimensional intensity data measured with MoKα radiation on a manual GE-diffractometer. The crystals are orthorhombic, space group Im2 with a=12.490(3)Å, b=14.238(8)Å, c=7.705(5)Å and Z=4. The parameters obtained from Patterson and Fourier synthesis were full-matrix least-squares refined to an R value of 0.04 for 604 independent reflections. The structure consists of corrugated polymeric two-dimensional networks made up of tetracyano-nickelate ions coordinated to cadmium. The nearest neighbours of cadmium involve four cyanide nitrogens and the nitrogen of a 4-chloropyridine. The average distance from the cadmium atom to these five neighbours is 2.35Å.

A sixth nitrogen belonging to an ammonia group at 2.27Å completes a slightly distorted octahedron. The 4-chloropyridine and the ammonia molecules bound to cadmium in trans positions project from both sides of the network. The projections of one network fit into the spaces of the other, so that the layers are arranged as closely as possible. This compound has a structure closely related to but distinct from that of the "Hoffmann pyridine complex" (D. Wilh. Z. Kristallogr., 1976, 271-280).


Highly enantioselective reactions of asymmetric synthesis and retroreacomisation of amino acids (AA) proceed through intermediates representing metal complexes of the Schiff bases of AA. Such complexes possess their own chirality, independent of the chirality of AA involved. Thus, this inherent chirality in I, II and III is caused by asymmetric metal chelation (4-configuration), S-disubstituted symmetrical moiety and S-benzyl-5-pyrrole unit, respectively.

In attempts to elucidate the mechanism of these stereospecific reactions we performed X-ray structural studies and force field calculations of the complexes I-III. It is shown that in the carbanionic precursor of I approaching of acetaldheyde to the anionic (C) centre from the R side is hindered by the methyl substituent in benzene cycle of another ligand, while an attack from the s side is not hindered. In complex II the S-configuration of O(1) is more favourable than the R-configuration, in which the substitutant at O(1) is involved in a short intramolecular contact with the aldimine hydrogen (see the scheme). The diastereomers of the complexes III with the R-configuration of O(1) have higher conformational energies than corresponding dia stereomers with the S-configuration. Therefore in all three cases the formation of S-AA is more favourable on the sterio grounds. These structural results are in a full agreement with experimental data on the stereospecificity observed. Absolute configuration of I-III has been determined by X-ray method.

Work supported by CAPES, CNPq, FAPESP and FINEP.