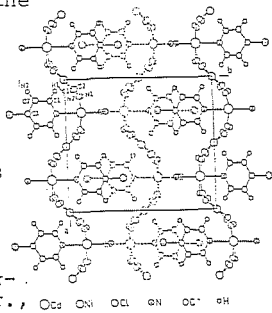


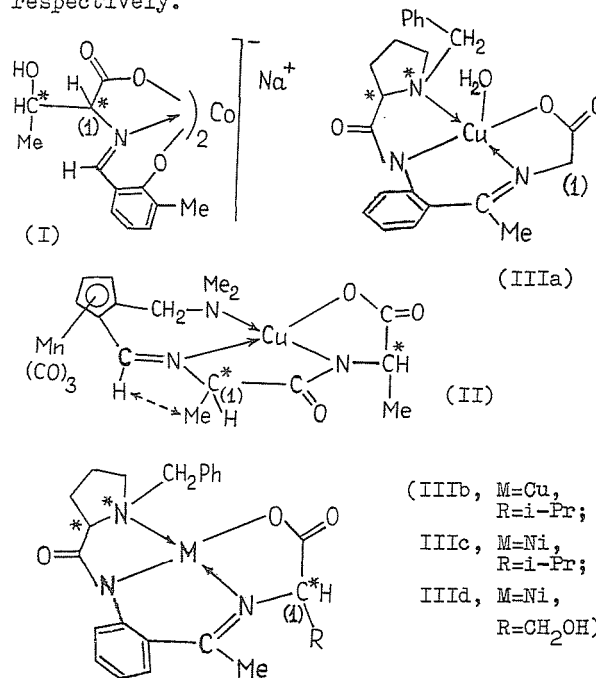
09.4-3 THE STRUCTURE OF 4-CHLOROPYRIDINE AMMINIC CADMIUM TETRACYANO-NICKELATE. By O. Büyükgüngör, D. Ülkü, Physics Department, Hacettepe University, Beytepe Ankara, Turkey.

The crystal structure of  $\text{Cd}(\text{NH}_3)(4\text{-Clpy})\text{Ni}(\text{CN})_4$  was determined from three dimensional intensity data measured with  $\text{MoK}\alpha$  radiation on a manual GE-diffractometer. The crystals are orthorhombic, space group  $\text{Ima}2$  with  $a=12.490(3)\text{\AA}$ ,  $b=14.238(8)\text{\AA}$ ,  $c=7.705(5)\text{\AA}$  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  $2.35\text{\AA}$ . A sixth nitrogen belonging to an ammonia group at  $2.27\text{\AA}$  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 complexes" (D. Ülkü, Z. Kristallogr., *Opz* **1975**) 271-280).



09.4-5 ON THE STRUCTURE OF INTERMEDIATES AND THE ORIGIN OF ENANTIOSELECTIVITY IN ASYMMETRIC SYNTHESIS OF AMINO ACIDS. By Yu.T. Struchkov, Yu.N. Belokon', V.M. Belikov and A.S. Bat-sanov, Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow, USSR.

Highly enantioselective reactions of asymmetric synthesis and racemization 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 ( $\Lambda$ -configuration), S-disubstituted cyanamrenyl moiety and N-benzyl-S-prolyne unit, respectively.



09.4-4  $\text{NiBr}_2$  COMPLEXES WITH TRIPHENYLARSINE OXIDE (tpaso). By G. Uliva, E.E. Castellano, J. Zukerman-Schpector and A.C. Massabni. Instituto de Física e Química de São Carlos. 13560 - São Carlos-SP-Brazil.

In an attempt to produce tetrahedrally coordinated Ni(II) complexes with tpaso as a ligand, Goodgame and Cotton (JACS, **82**, 5774, 1960) obtained in the same chemical reaction, blue, orange and green solids. The orange and green ones have been crystallized and their structures determined.

$\text{NiBr}_2 \cdot 4\text{tpaso} \cdot 8\text{H}_2\text{O}$  (green):  $M_r = 1650.2$ ,  $P2_1/c$ ,  $a = 13.731(2)$ ,  $b = 16.267(3)$ ,  $c = 17.647(2)\text{\AA}$ ,  $\beta = 112.04(1)^\circ$ ,  $V = 3651\text{\AA}^3$ ,  $Z = 2$ ,  $D_x = 1.50 \text{ Mgm}^{-3}$ ,  $\text{CuK}\alpha$ ,  $\lambda = 1.54184\text{\AA}$ ,  $\mu = 38.67 \text{ cm}^{-1}$ ,  $R = 0.039$ , 3741 unique reflections, 3203 with  $I > 3\sigma(I)$ .

$\text{NiBr}_2 \cdot 4\text{tpaso} \cdot \frac{3}{2}(\text{C}_6\text{H}_5\text{CH}_3) \cdot \text{H}_2\text{O}$  (orange):  $M_r = 1663.7$ ,  $P\bar{1}$ ,  $a = 12.647(8)$ ,  $b = 13.953(5)$ ,  $c = 22.853(6)\text{\AA}$ ,  $\alpha = 90.91(3)$ ,  $\beta = 96.70(4)$ ,  $\gamma = 111.16(4)^\circ$ ,  $V = 3727\text{\AA}^3$ ,  $Z = 2$ ,  $D_x = 1.48 \text{ Mgm}^{-3}$ ,  $\text{MoK}\alpha$ ,  $\lambda = 0.71073\text{\AA}$ ,  $\mu = 30.48 \text{ cm}^{-1}$ ,  $R = 0.087$ , 8600 unique reflections, 4293 with  $I > 3\sigma(I)$ .

In the green complex the Ni(II) ion is sited on a center of symmetry and is octahedrally coordinated to six water molecules which are hydrogen bonded to the tpaso molecules and to the bromide anions forming a second coordination sphere in a nearly octahedral arrangement.

In the orange complex the cation is pentacoordinated with the four oxygen atoms of the tpaso ligands forming the basis of a tetragonal pyramid and with a Br anion in the apical position.

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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 acetaldehyde to the anionic C(1) centre from the *re* side is hindered by the methyl substituent in benzene cycle of another ligand, while an attack from the *si* side is not hindered. In complex II the S-configuration of C(1) is more favourable than the R-configuration, in which the substituent at C(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 C(1) have higher conformational energies than corresponding diastereomers with the S-configuration. Therefore in all three cases the formation of S-AA is more favourable on the steric 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.