09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

Since the inter-bond angles at the iron atom are close to 90° the coordination at iron is better described as octahedral not tetrahedral. The relative configuration of the new chiral centre in 1a and 1b, and the prochiral centre in 1c is established. The carbon monoxide ligand is in each compound anti to the carbon oxygen bond. If this anti conformation is preferred in the enolate (X = C=CHR) the approach of an electrophile will occur on the face of the enolate which is not shielded by a phenyl group of the phosphine ligand thus determining the stereochemistry.

References

09.4-1 CRYSTAL AND MOLECULAR STRUCTURE OF DICYANO-COBYRINIC ACID HEXAMETHYLS.T.

by J.C.A. Boeyens, A.J. Markwell and M.S. Shaikjee
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The crystal and molecular structure of the vitamin B₂ derivative, dicyano-cobyrinic acid heptamethyl ester, has been determined. The structure was solved (4270 independent reflections measured on a diffractometer) using standard Fourier methods, with initial phasing of the cobalt atom, to an R-factor of 0.1068. The space group is P1 with Z = 2; unit cell dimensions, a = 16.332, b = 13.252, c = 14.4758; α = 90.0, β = 109.75, and γ = 90.0°. The two cyanide ligands are bonded in a linear fashion to the cobalt, the one in the lower position being H-bonded to an isopropanol molecule. There are no significant differences between the two crystallographically independent molecules, except for their orientations in the unit cell.

09.4-2 DEVELOPMENT OF KNOWLEDGE OF THE LIGAND TRANS-STRENGTHENING. By L.A. Aslanov, Chemistry Department, Moscow State University, Moscow, USSR.

In development of the earlier investigation (O.A.Reutov et al., Coordinationnaya Khimia (1982) 8, 1161 (Russ.)) the ligand trans-strengthening in octahedral complexes of tin (IV) was studied by the X-ray crystallography methods. This type of interaction is apparent in iodine complexes, e.g. SnI₄·H₂O (I) (HMPTA=hexamethylphosphorotriamide). It can be described as a shortening of the Sn-I trans interatomic distance 2,634(2) Å in trans-position to Et-group. This distance is shorter than Sn-I in SnI₄·Dipy (ii), SnI₄·2TPPO (iii) (Dipy=2,2’-dipyridyl, TPPO=triphenylphosphinoxide) 2,782(2)-2,819(2) Å, and even shorter than Sn-I in SnI₄·2,69(2) Å (F.Meller, I.Fan-Vuchen, Acta Cryst. (1955) 8, 343). Such anomalous shortening of Sn-I trans inspite of the increase of coordination number from 4 to 6 is found first. It can be explained by the electron-donating Et-ligand influence and is observed simultaneously with displacement of the equatorial ligands from equatorial plane to trans. Cis-weakening of Sn-I cis bonds in (i) in comparison with Sn-I in (ii) and (iii) is relatively smaller (3,8%) than trans-strengthening (5,8%). These facts show that trans-strengthening is a special phenomenon, which determines together with cis-weakening the structures of octahedral tin(IV) complexes. The single crystals without statistical distribution of alkyl groups and halogen atoms (L.A. Aslanov et al. Organometal. Chem. (1978) 144, 39) were grown for compounds Alk Sn R’-HO (Ligand trans-Cl) (Hal=I becomes moderate. The Sn-Br bond distances give no information about trans-strengthening, but the trans-strengthening was found by IR- and Raman-spectroscopy both in chloride and bromine complexes. The shortening of Sn-Br trans distances in bromine complexes is smaller in comparison with Sn-Cl bonds in iodine complexes. The Alk Sn HaI₄·2L (Alk=Et, Bu; n=0,1; Hal=Cl, Br; L=TPPO, HMPTA etc.). The Sn-Cl bond distances do not show any information about trans-strengthening, but the trans-strengthening was found by IR- and Raman-spectroscopy both in chloride and bromine complexes. The shortening of Sn-Cl trans bonds in comparison with Sn-Br trans bonds in iodine complexes is in progress.