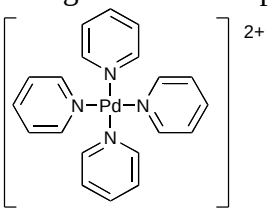
Symmetry and Group Theory

1. For each of the following molecules or ions:
   i) describe their shape and draw their structure,
   ii) identify the important symmetry elements on the drawing,
   iii) identify the point group.

ethyne, ethene, *trans*-1,2-dichloroethene, CH_3I, CH_2I_2, CHI_3, $[MnO_4]^-$, $[CO_3]^{2-}$, $[PtCl_4]^{2-}$, benzene, pyridine, ammonia.

2.
   i) Draw all the geometric isomers of $[Fe(CN)_4Cl_2]^{3-}$
   ii) Identify the symmetry elements present on the drawings of both isomers and assign them to point groups
   iii) Draw the isomers of $[Fe(CN)_3Cl_3]^{3-}$
   iv) Identify the key symmetry elements on the drawings and assign point groups to the isomers

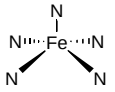
3.
   i) Why does CH_3OH belong to a different point group than CH_3O^-?



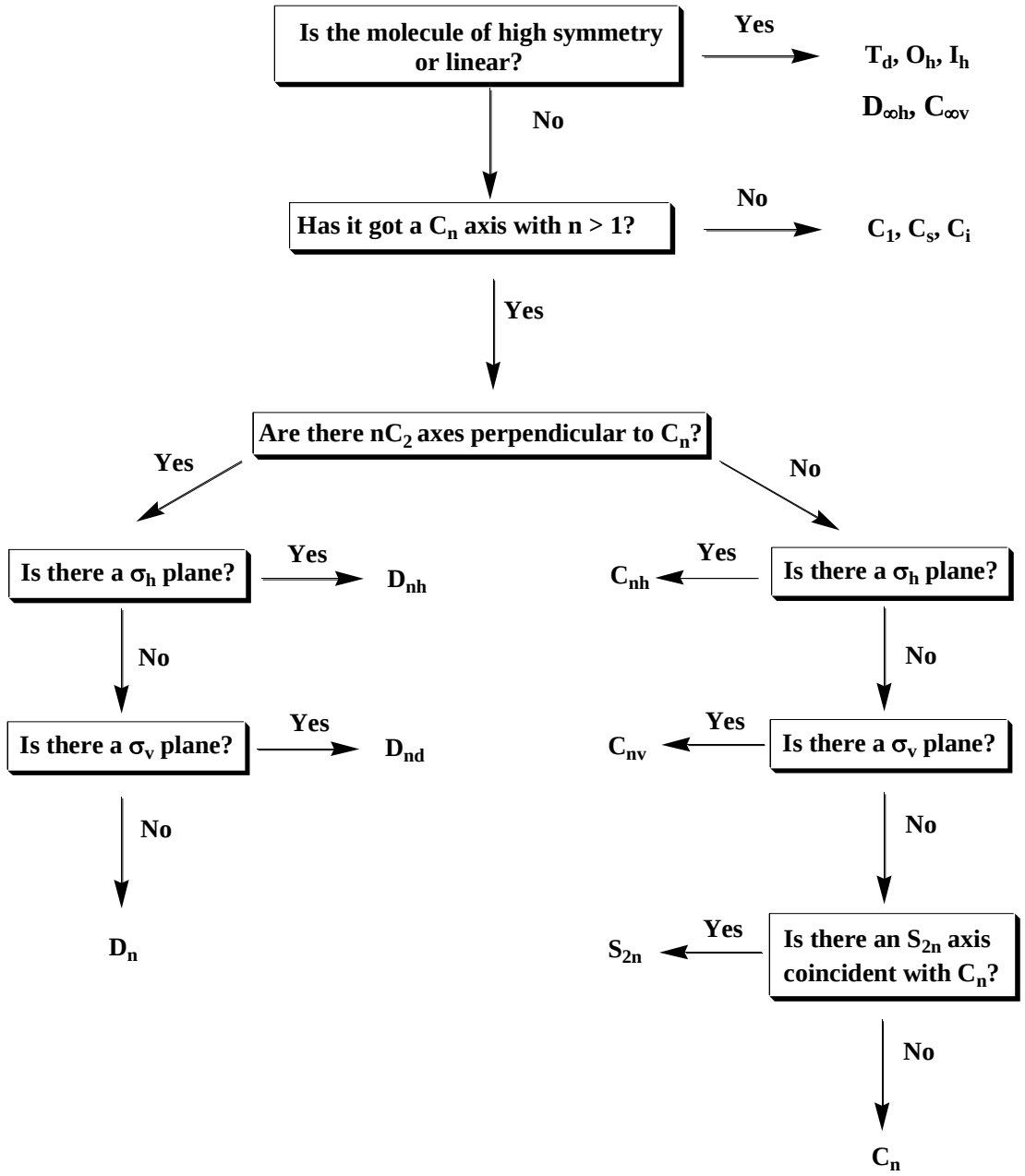
   ii) Why can $[Pd(py)_4]^{2+}$ (above) belong to more than one point group?
   iii) Draw structures for $[Pd(py)_4]^{2+}$ in (a) D_{4h} and (b) D_{2h} point symmetry.
   iv) To which point group does Al_2Cl_6 belong? Draw the structure and include the key symmetry elements to help you to decide.

4. A. CH_3I reacts with CN^- to form CH_3CN *via* an S_N2 pathway
   i) Draw the transition state.
   ii) To which point group does the transition state belong?
   B. $BrCH_2CN$ also reacts with cyanide in a similar way.
   i) What is the point group of the transition state in this case?
   ii) What is the point group of the final product?

5. Haemoglobin is an oxygen carrier protein. The structure of the free active site approximates to that shown below (a square-based pyramid). Which point group best describes the active site?



Flowsheet for assigning point groups:



SYMMETRY ELEMENTS:

E = the identity, provides a "do nothing" operation
C_n = rotation axis (proper), by 360/*n* degrees, applied *n* times (C_n^n) completes a full circular rotation

σ_h = horizontal mirror plane, perpendicular to the principal rotation axis
σ_v = vertical mirror plane, contains the principal rotation axis, usually cuts through atoms
σ_d = dihedral mirror plane, also vertical, but usually bisects bonds
i = inversion centre, move every point in a molecule through the centre of inversion and get exactly the same molecule back afterwards
S_n = improper axis of rotation, rotate about a C_n axis, <u>followed by</u> reflection in a mirror plane perpendicular to the axis; $S_{n=odd}$ must be applied 2*n* times to return to the starting point, *i.e.* S_n^{2n}.

Notes:
Tetrahedral (T_d), octahedral (O_h) and icosahedral (I_h) geometries are considered as high symmetry
Linear molecules have an infinite-fold axis
Planar molecules must possess a mirror plane
$S_1 \equiv \sigma$, $S_2 \equiv i$; an S_n operation performed once (S_n^1) changes handedness/chirality