

# Molecular Symmetry

## Some Applications of Group Theory & Graph Theory

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### Introduction

This practical is designed to introduce you to elementary concepts of **symmetry** and **group theory**. *Symmetry operations* are defined, and a systematic procedure for specifying molecular symmetry in terms of *point groups* described, in a reasonably detailed Appendix, providing all the theory you will need. Models of the molecules whose point groups you are asked to identify are available, and virtual molecular models are available at the Chemistry website (<http://www.chem.ox.ac.uk/vrchemistry/sym/splash.html>).

*(Molecular models may NOT be taken out of the laboratory!)*

- You should complete both **Parts I** and **II** of the schedule below.
- Study carefully the content of the Appendix, and make sure you are thoroughly familiar with the examples given there, before you embark on the questions posed.
- The questions in **Part I** concern the identification of specific symmetry operations and the subsequent assignment of point groups to a range of inorganic molecules (*i.e.* applied **group theory**). If you have already attended Dr Vallance's lectures, you should find this material familiar & straightforward!
- The material of **Part II** additionally involves the application of elementary ideas of **graph theory** to polyhedral molecules. This will be unfamiliar to all of you, so study the Appendix carefully – it contains all the theory you will need to tackle the problems, and relevant worked examples.
- It's probably best to read through the appropriate part of the Appendix a *couple of times* before tackling the questions.





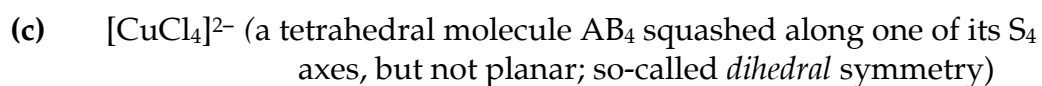
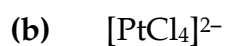




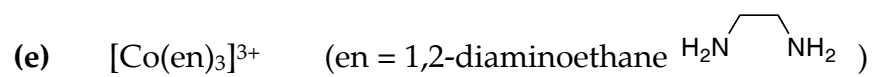
- (3) On a diagram, or diagrams, of the molecule depict the symmetry elements and hence assign a *point group* to each of the following molecules:

**Hints:** • Use the flow chart in Figure 8 of the Appendix to identify the point group.

- Use the list of symmetry elements constituting each point group, which is given in Table 2 of the Appendix, to make sure you miss any symmetry elements in your diagrams.
- Follow the worked example of H<sub>2</sub>O which is presented in the Appendix.





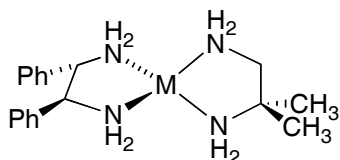
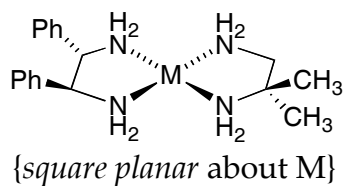
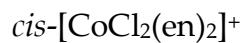
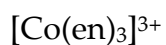




- (4) (a) What symmetry-based criteria must a molecule obey in order to potentially be optically-active?

**Hint:** • Symmetry aspects of optical activity are considered at the end of Part I of the Appendix.

- (b) Which of the following molecules cannot be optically active?



{*tetrahedral* about M}

- (5) Establish the *point group* of the isopolyanion,  $[\text{Nb}_6\text{O}_{19}]^{8-}$ , in the compound  $\text{K}_8\text{Nb}_6\text{O}_{19}$  (the Lindquist structure).

The related species  $[\text{W}_4\text{Nb}_2\text{O}_{19}]^{4-}$  can exist in *two* isomeric forms. Identify the *point group* of each isomer.

What is the point group of the ion  $[\text{TeMo}_6\text{O}_{24}]^{6-}$  ?

## Part II

(1) Using the models provided establish the *point groups* of the regular (triangular) *Platonic solids*, and indicate (drawings or words) how the symmetry elements relate to the polyhedron

(i) tetrahedron

(ii) octahedron

(iii) cube

(iv) dodecahedron



(v) icosahedron

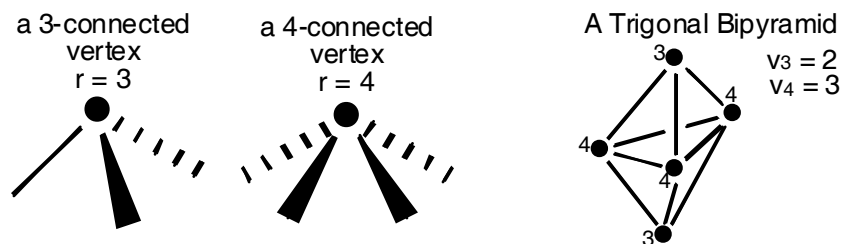
(2) Models of the polyhedral boranes  $[\text{B}_8\text{H}_8]^{2-}$ ,  $[\text{B}_9\text{H}_9]^{2-}$ ,  $[\text{B}_{10}\text{H}_{10}]^{2-}$  are provided.

(a) Show that these polyhedra conform to the equations given in the manual for triangulated polyhedra

(namely that  $\sum v_r (6 - r) = 12$  and that  $\sum v_r = V$ ).

(b) What are the *point groups* of these three molecules?

**Hints:** •  $v_r$  is the number of vertices that are composed of  $r$  edges, and  $V$  is the total number of vertices.



•  $\sum v_r (6 - r) = 12$  expands as:

$$3v_3 + 2v_4 + v_5 (+ 0v_6) - v_7 - 2v_8 - 3v_9 \dots = 12$$

# we start with  $r = 3$  because it is the least number of edges required to form a three dimensional vertex.

# the expansion goes up to the number of vertices in the polyhedron - 1 (*i.e.*  $V - 1$ ).

*e.g.* for  $[\text{B}_8\text{H}_8]^{2-}$  we expand as far as the " $v_7$  term".



- (3) Structural and NMR studies have established that the polyhedral frameworks in  $[\text{B}_7\text{H}_7]^{2-}$  and  $\text{Os}_7(\text{CO})_{21}$  have triangular faces exclusively.
- (a) Use Euler's equations to generate *possible polyhedral structures* for these molecules and use the additional information given below to identify the *actual structures* and the *point groups* of the molecules.
- The  $^{11}\text{B}$  NMR spectrum of  $[\text{B}_7\text{H}_7]^{2-}$  has two types of resonance with intensities in the ratio 5:2.
  - The  $^{13}\text{C}$  NMR spectrum of  $\text{Os}_7(\text{CO})_{21}$  has three resonances with intensities in the ratio 3:3:1.

**Hint:** follow the example for 8-vertex polyhedra given below.

- By trial and error find solutions to the simultaneous equations given by Euler's rules:

$$3v_3 + 2v_4 + v_5 - v_7 = 12 \quad \text{and} \quad v_3 + v_4 + v_5 + v_6 + v_7 = 8$$

- Present the solutions in a matrix:

$v_3$	$v_4$	$v_5$	$v_6$	$v_7$	<i>triangulated polyhedron</i>
	6		2		hexagonal bipyramid
	4	4			dodecahedron
1	3	3	1		capped pentagonal bipyramid
2		6			bicapped octahedron (capped faces not linked)
2	2	2	2		bicapped octahedron (capped faces edge-linked)
2	1	4	1		bicapped octahedron (capped faces vertex-linked)
3	1	1	3		Tricapped trigonal bipyramid
4			4		Tetra-capped tetrahedron

- Take note of any structural evidence:

*e.g.* If the NMR spectrum of vertex atoms has two peaks of equal intensity, this suggests a dodecahedron

but two peaks in the intensity ratio 3:1 suggests a hexagonal pyramid or a capped octahedron

- (i) Possible Euler's Rule solutions for 7-vertex triangulated polyhedra

$v_3$	$v_4$	$v_5$	$v_6$	<i>triangulated polyhedron</i>

- (ii) Geometry and point group of chosen polyhedron for  $[B_7H_7]^{2-}$

- (iii) Geometry and point group of chosen polyhedron for  $Os_7(CO)_{21}$



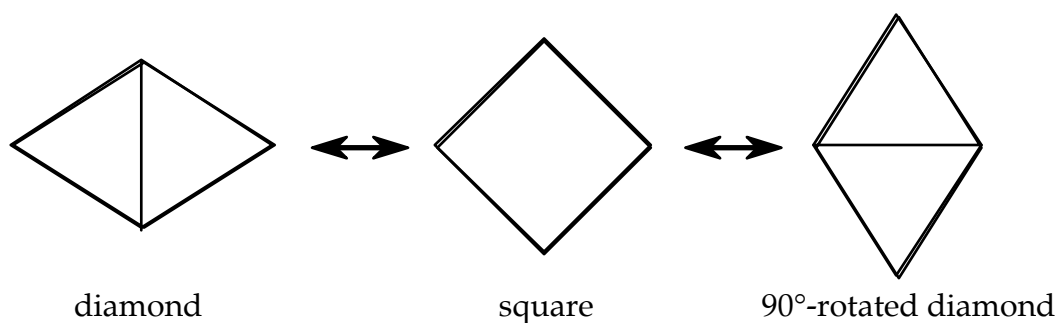
- (4) The structures of the borane anions  $[B_nH_n]^{2-}$  in solution have been studied using  $^{11}\text{B}$  NMR spectroscopy.

Some of the borane anions, e.g.  $[B_8H_8]^{2-}$  and  $[B_{11}H_{11}]^{2-}$ , are found to be "stereochemically non-rigid" and the boron atoms appear to be equivalent in the NMR experiment, despite their solid state structures indicating several distinct boron environments.

Other boranes, e.g.  $[B_7H_7]^{2-}$  and  $[B_9H_9]^{2-}$ , are "stereochemically rigid" and their NMR spectra reflect the different boron chemical environments observed in the solid state.

Non-rigidity has been attributed to low energy rearrangement pathways.

It has been proposed by William Lipscomb (Nobel prize: 1976) that stereochemically non-rigid polyhedral molecules rearrange by a *diamond*  $\rightarrow$  *square*  $\rightarrow$  *diamond* mechanism involving four adjacent vertices as shown:



Using the models provided, for each borane anion in turn, identify a 'diamond' arrangement.

In a **thought experiment** make it undergo interconversion by breaking a B–B bond to create a square, which then reforms a B–B bond to give a 90° rotated diamond.

Confirm that for  $[B_5H_5]^{2-}$ ,  $[B_8H_8]^{2-}$  and  $[B_9H_9]^{2-}$  this process leads to a topologically identical polyhedron.

- (a) Does the rearrangement lead to a *pseudo-reflection* or a *rotation* of these molecules?

(b) What happens when you perform a single diamond  $\rightarrow$  square  $\rightarrow$  diamond rearrangement on  $[\text{B}_6\text{H}_6]^{2-}$  and  $[\text{B}_7\text{H}_7]^{2-}$  ?

(c) Propose a rule for identifying those polyhedra which undergo successful rearrangements in terms of criteria for the connectivities of the vertices defining the diamond.

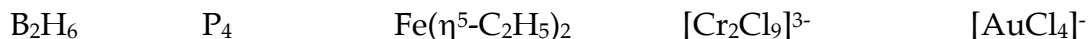
(The answer is in R.B. King, *Inorganica Chimica Acta*, 1981, **49**, 237)

## References

1. C. Vallance, **Symmetry I**, Lecture Course Michaelmas Term  
The practical will inevitably be much easier if you have attended these lectures
2. P. Walton, **Beginning Group Theory in Chemistry**, OUP, 1998  
A bit pedestrian, but work through it if you find this subject hard
3. A. Vincent, **Molecular Symmetry and Group Theory**, 2<sup>nd</sup> ed., Wiley, 2001  
Another programmed approach, taking you through the mechanics step-by-step
4. G.E. Davidson, **Group Theory for Chemists**, Macmillan, 1991  
Learn group theory with a one-time BBC Mastermind champion
5. F.A. Cotton, **Chemical Applications of Group Theory**, 3<sup>rd</sup> ed., Wiley, 1990  
The classic book on the subject – very elegant!

## Questions from Past Exam Papers

1. Depict the symmetry elements and hence identify the point group of *ONE* of the following:

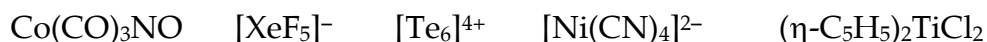


[2006]

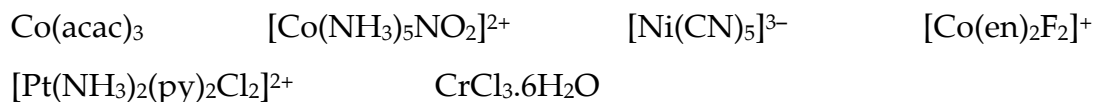
2. (a) Which of the following are square planar ?



- (b) Depict the symmetry elements and hence identify the point group of *ONE* of the following:



- (c) Discuss the possibilities of isomerism in *THREE* of the following:



[2007]

3. Depict the symmetry elements and hence identify the point group of *ONE* of the following:



[2008]







