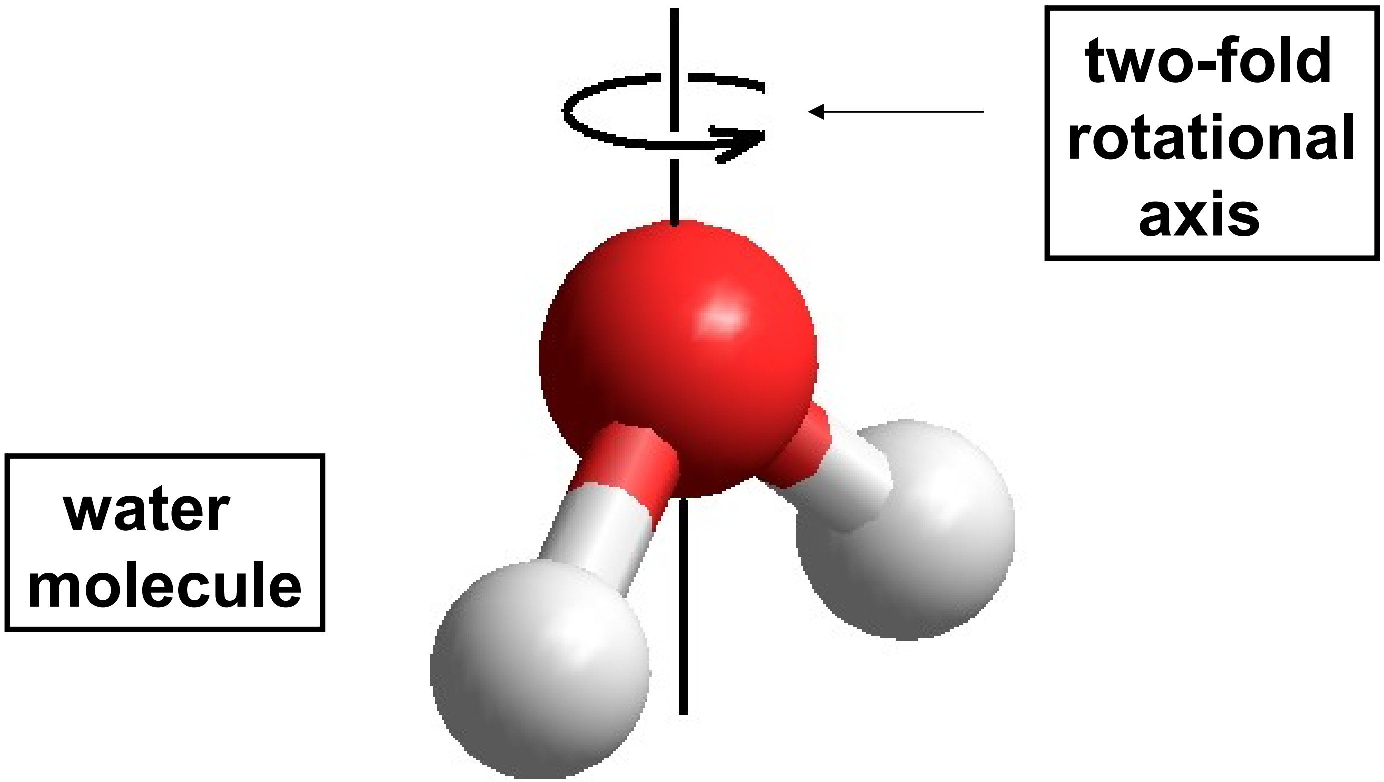
GOVT JST PG

Presented By:- Manika Choubey
Asst.Professor in Chemistry

PRESENTATION ON-

GROUP THEORY AND SYMMETRY

Group Theory and Symmetry.

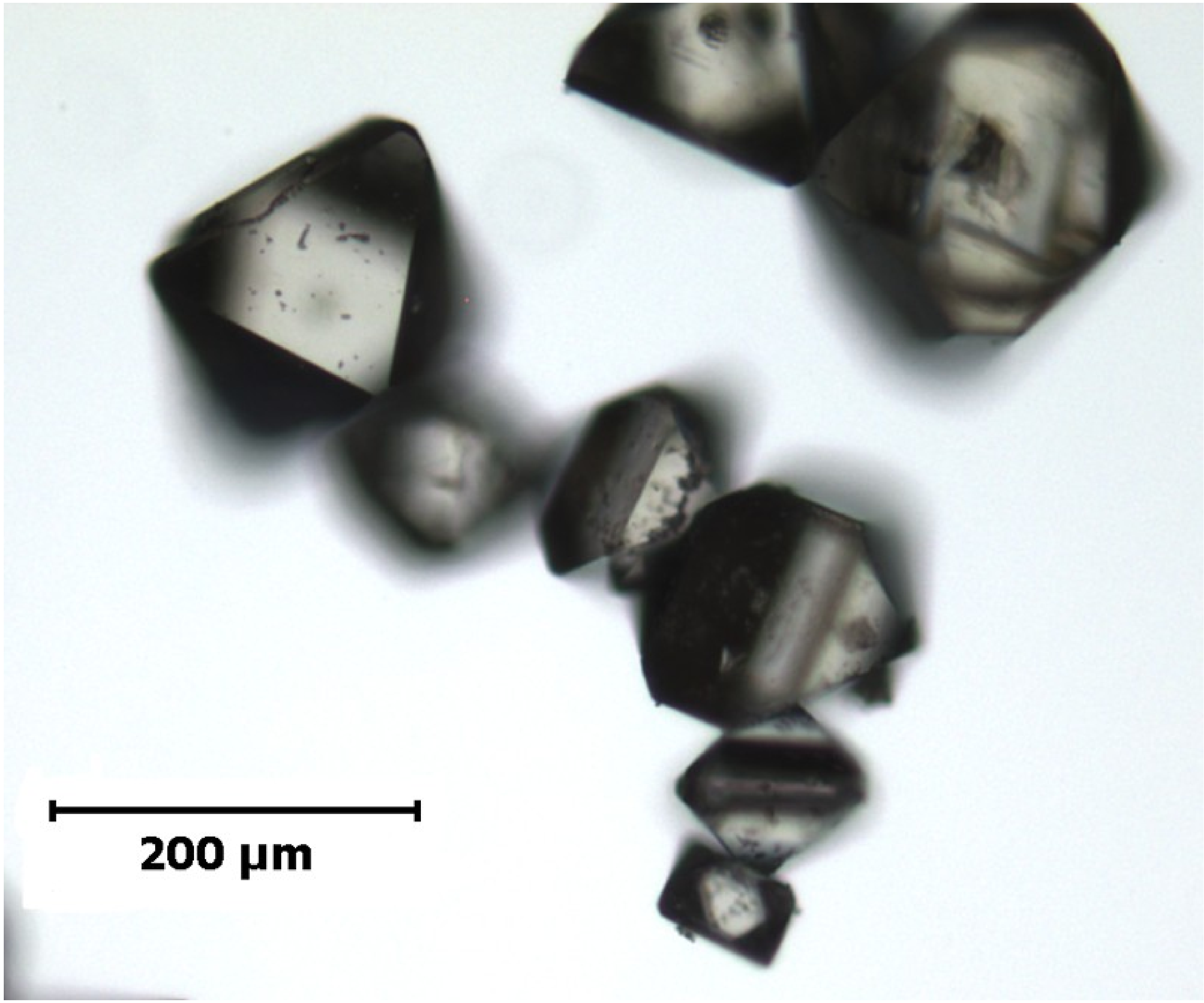


Molecular Structure:

The most powerful idea in chemistry is the idea of the three-dimensional structures of molecules. Two techniques have been invaluable in this regard. One is NMR (Nuclear Magnetic Resonance), and the other is X-ray crystallography. X-ray crystallography has been intensively developed as a technique, which involves the ideas of symmetry of molecules. Understanding NMR also involves an understanding of symmetry. Group theory is also vital in understanding and predicting infra-red and Uv-visible (electronic) spectra.

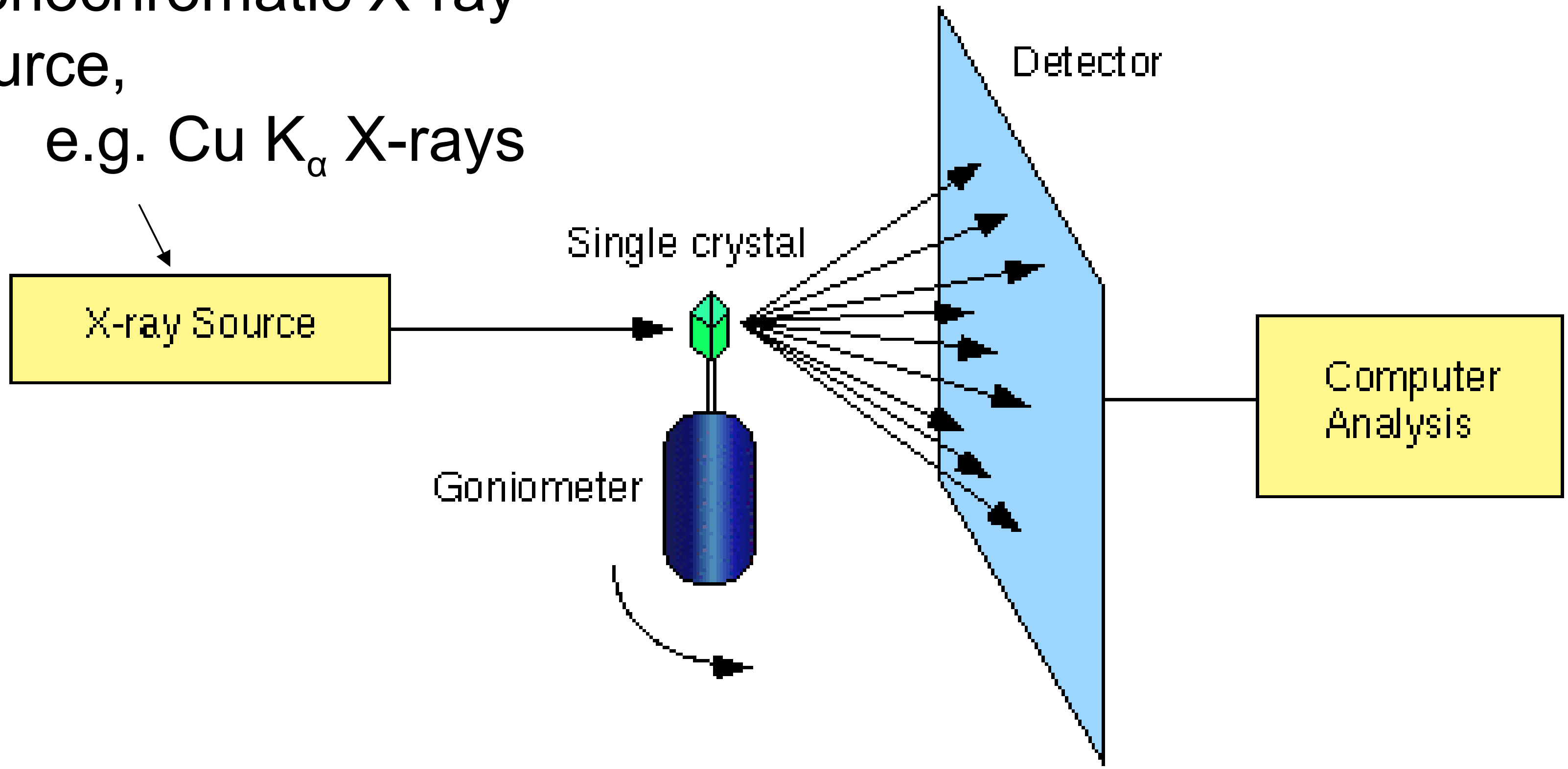
On the next two slides are structures of complexes of metal ions determined by X-ray crystallography. These are shown simply to illustrate the power of X-ray crystallography in determining molecular structure. Determining such structures relies heavily on a knowledge of symmetry and group theory.

Crystals of $[Cd(DPP)_2](ClO_4)_2$ (viewed through a microscope)

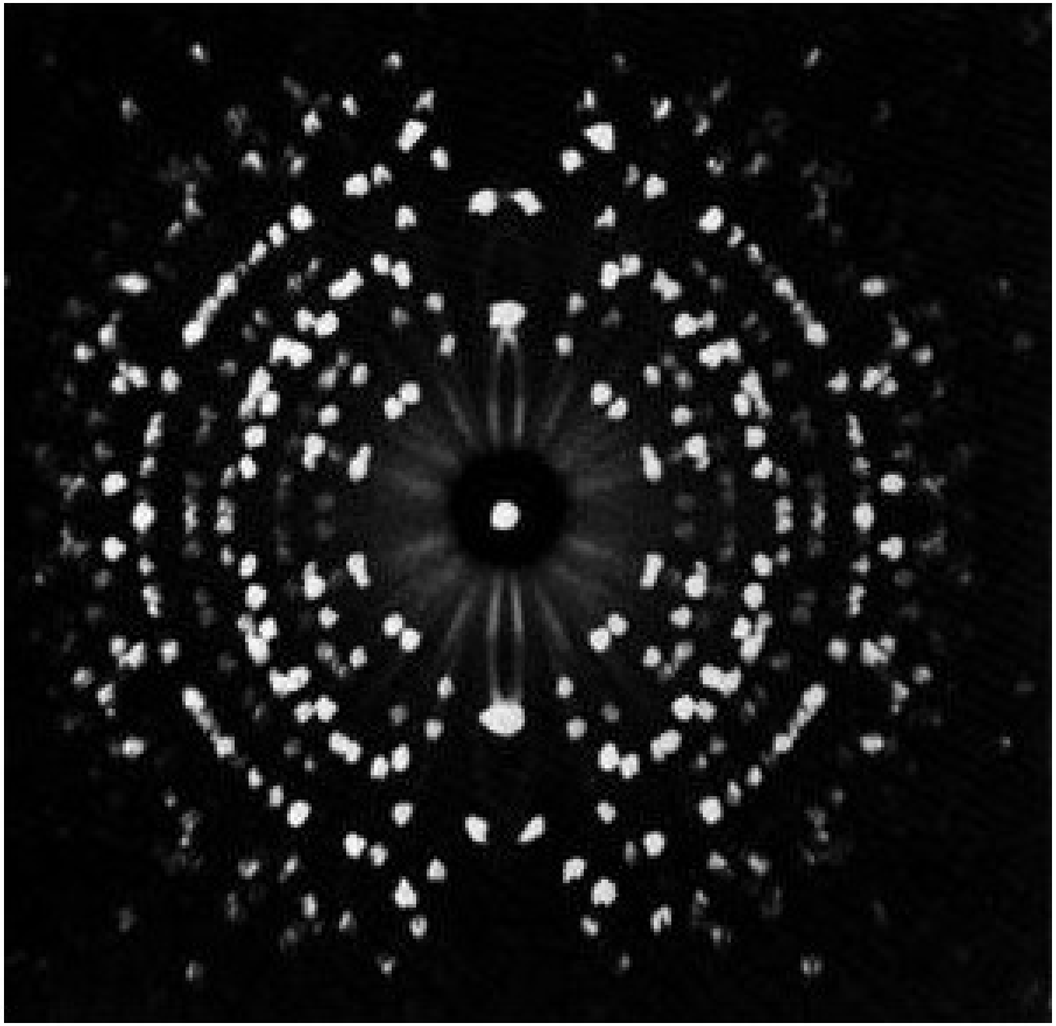


X-ray diffractometer:

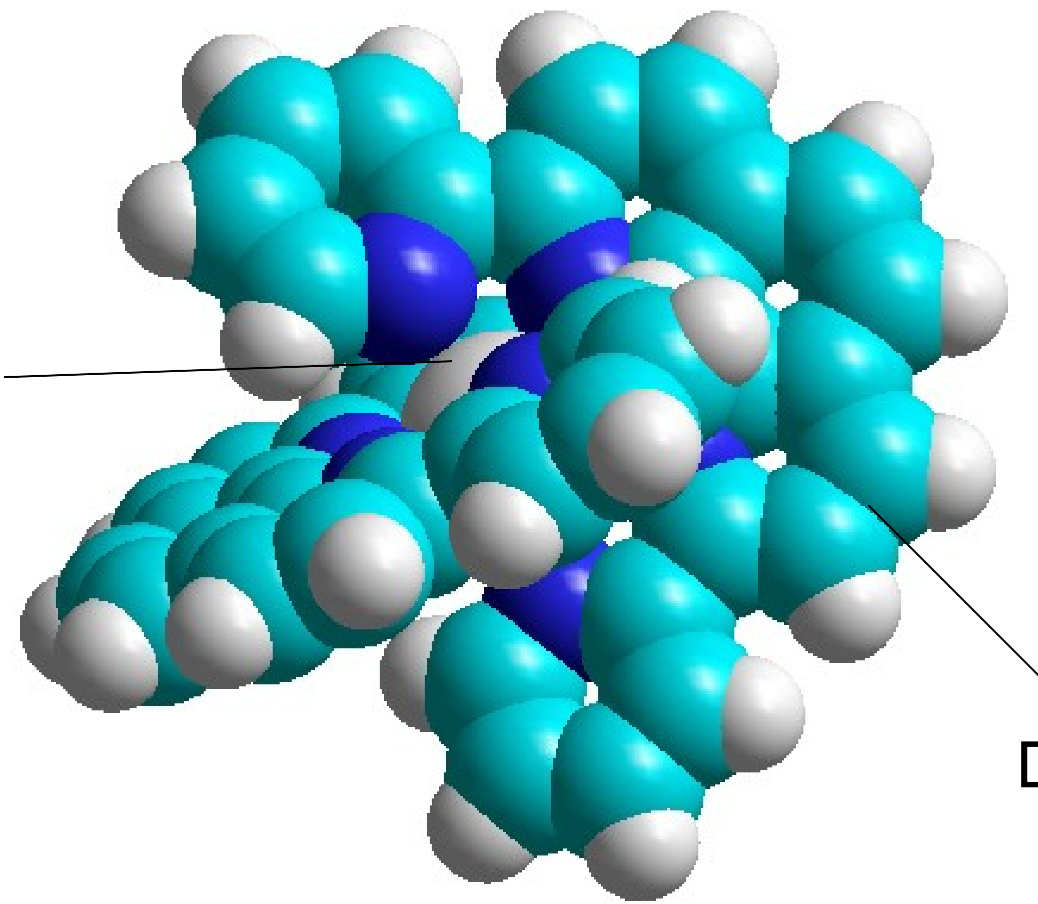
Monochromatic X-ray source,
e.g. Cu K_α X-rays

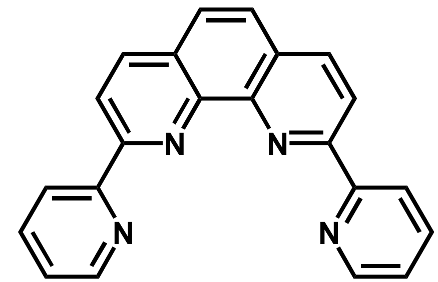


X-ray diffraction pattern:



The actual structure of the $[Cd(DPP)_2]^{2+}$ complex cation:

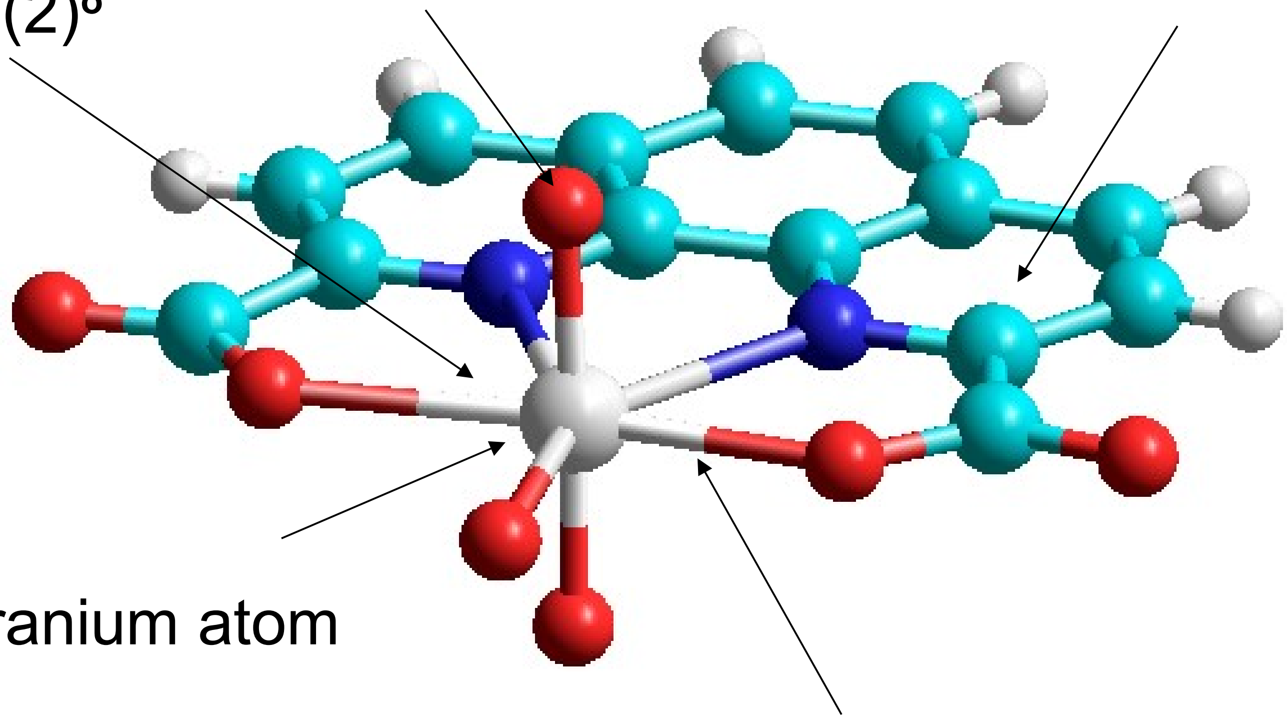




DPP

G. M. Cockrell, R. D. Hancock, D. G. VanDerveer, G. Zhang, R. P. Thummel, *J. Am. Chem. Soc.*, **2008**, *130*, 1420.

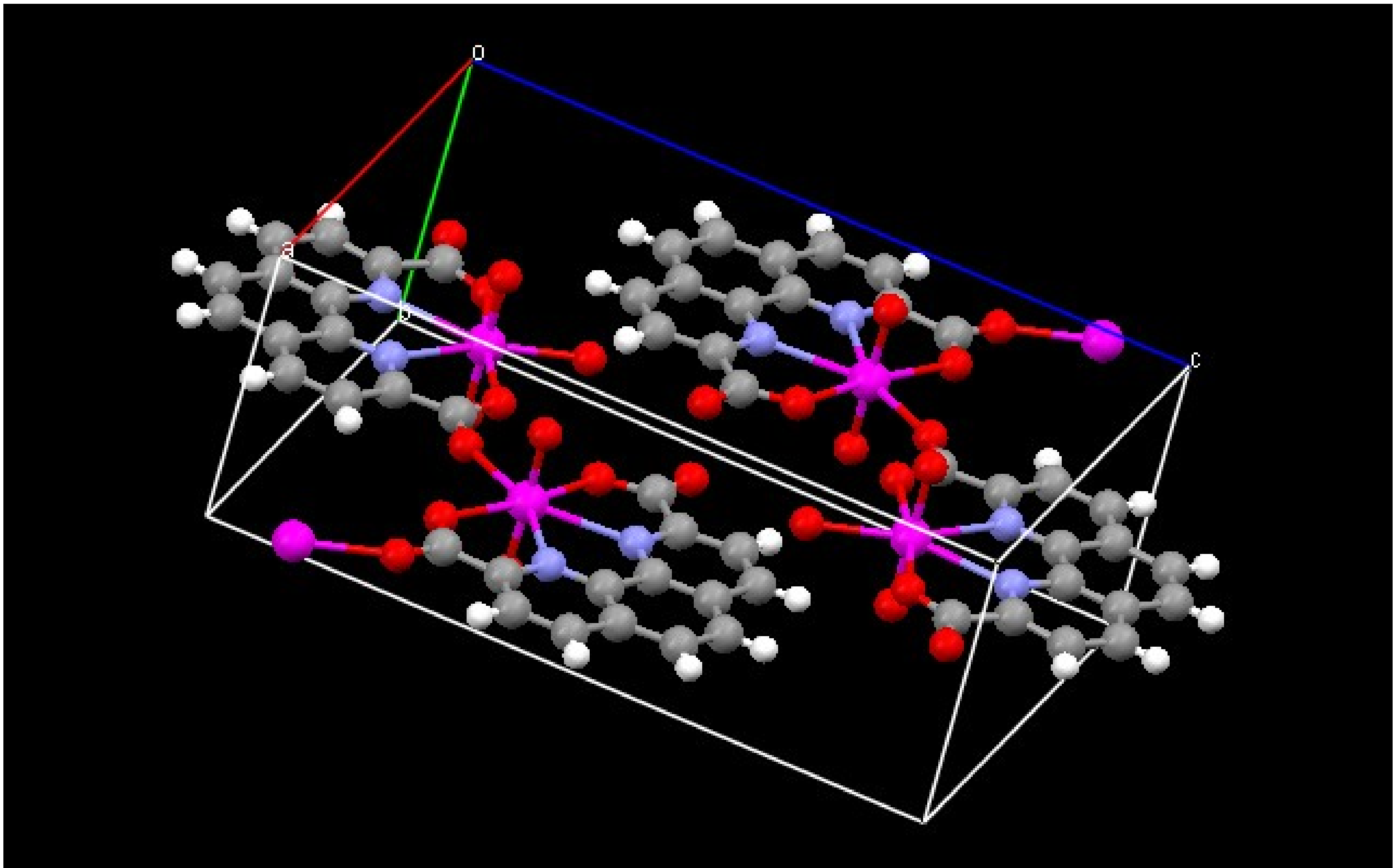
Importance of X-ray crystallography



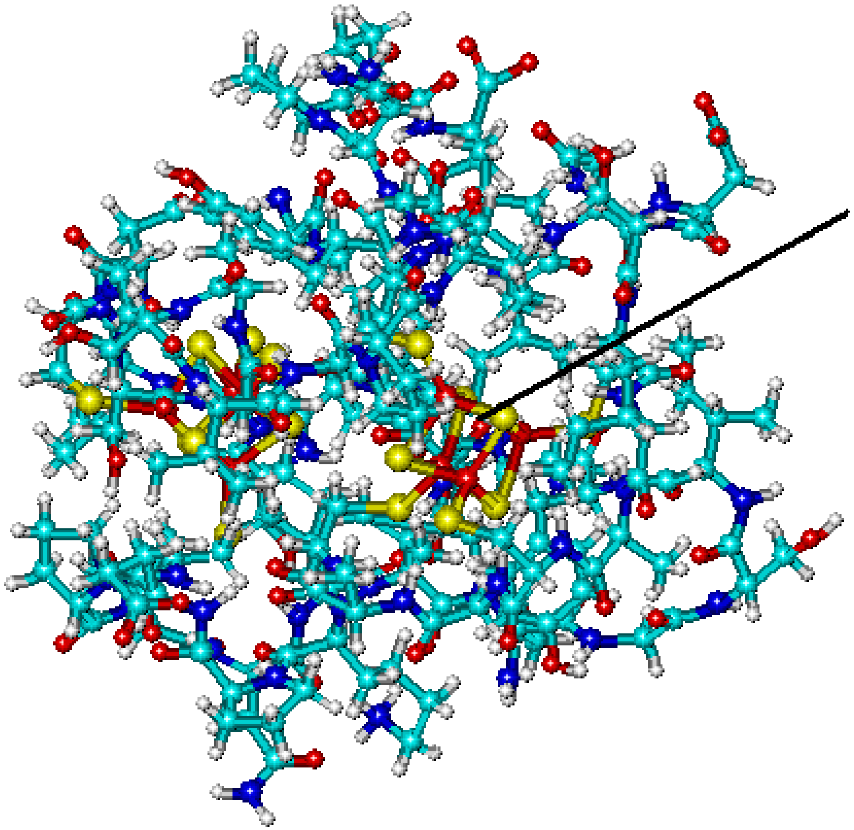
Structure of [UO_2(PDA)] determined by X-ray crystallography

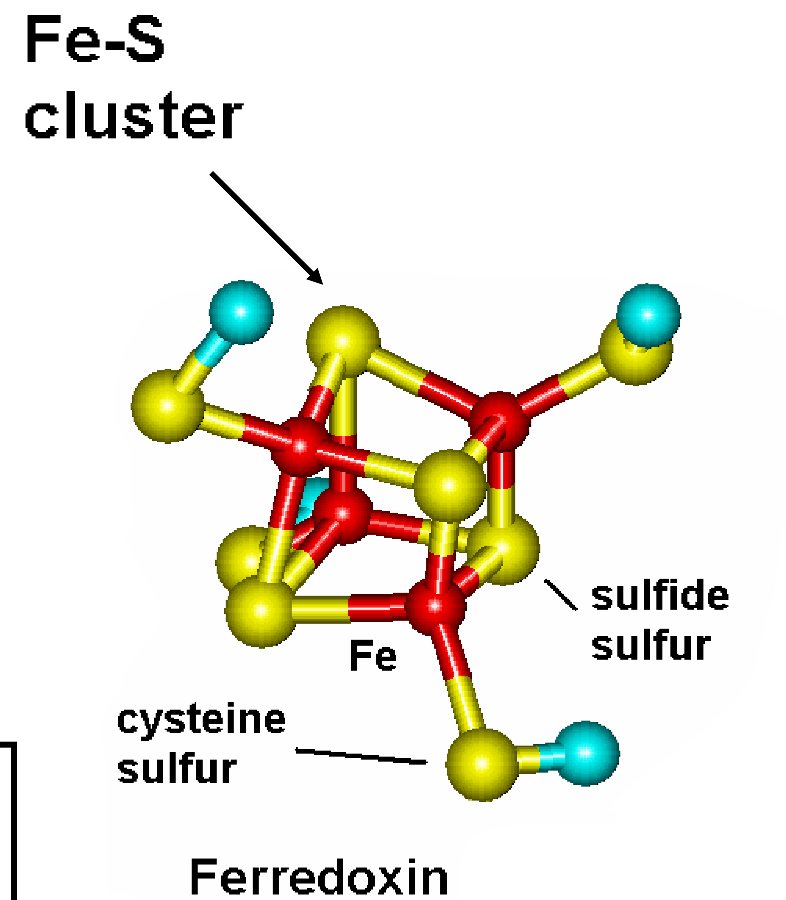
Nolan E. Dean, R. D. Hancock, M Frisch, C. Cahill, *Inorg. Chem.*, **2008** in the press.

Unit cell of $[UO_2(PDA)]$



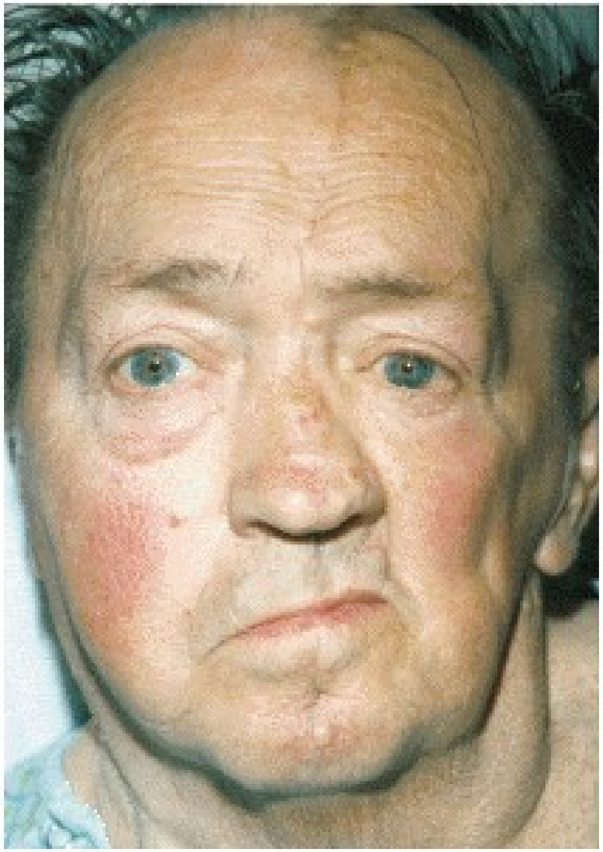
Structures of proteins.





Ferredoxin. Fe-containing protein used for electron transport in bacteria.

Facial symmetry



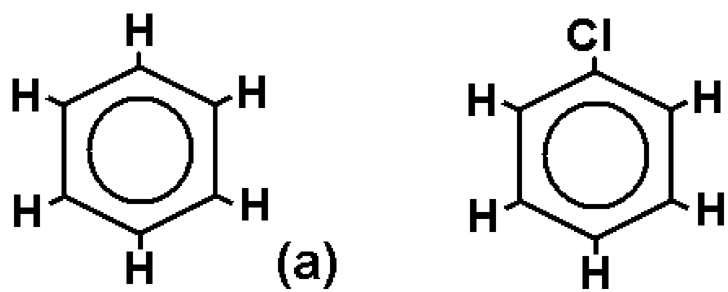
Photograph: Scott

Invariance to transformation as an indicator of facial symmetry:

Mirror image

Symmetry

Symmetry is a very important aspect of chemistry, and an understanding of it is important in spectroscopy, crystallography, and molecular orbital calculations. An example of this is seen in comparing the two molecules below:

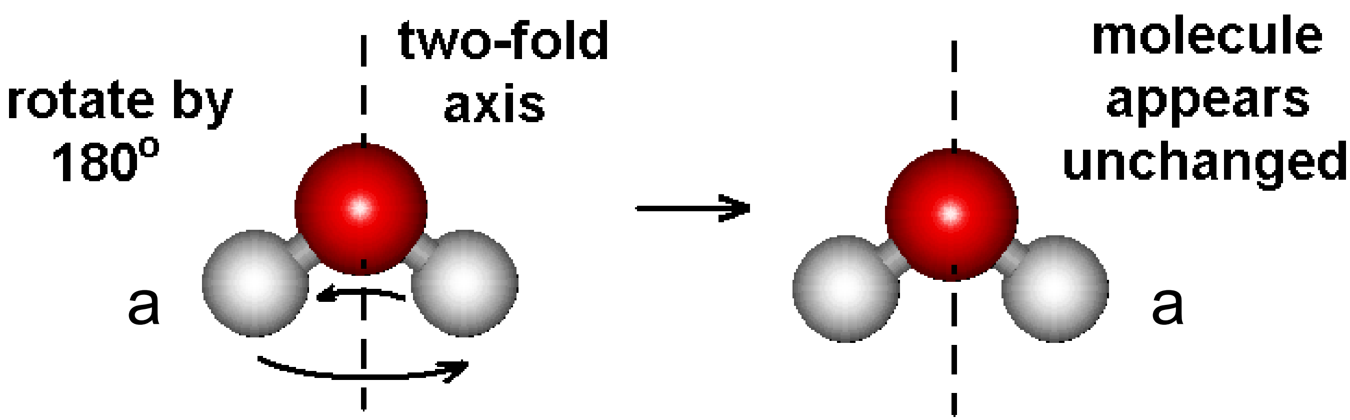


(a) (b)

We can all see at a glance that (a) is more symmetric than (b), and that (a) will have only a single peak in the ^{1}H NMR, while (b) will have three. In more complicated situations it may be more difficult to work out such things, and an analysis of symmetry allows us to predict such things as spectra following mathematical rules.

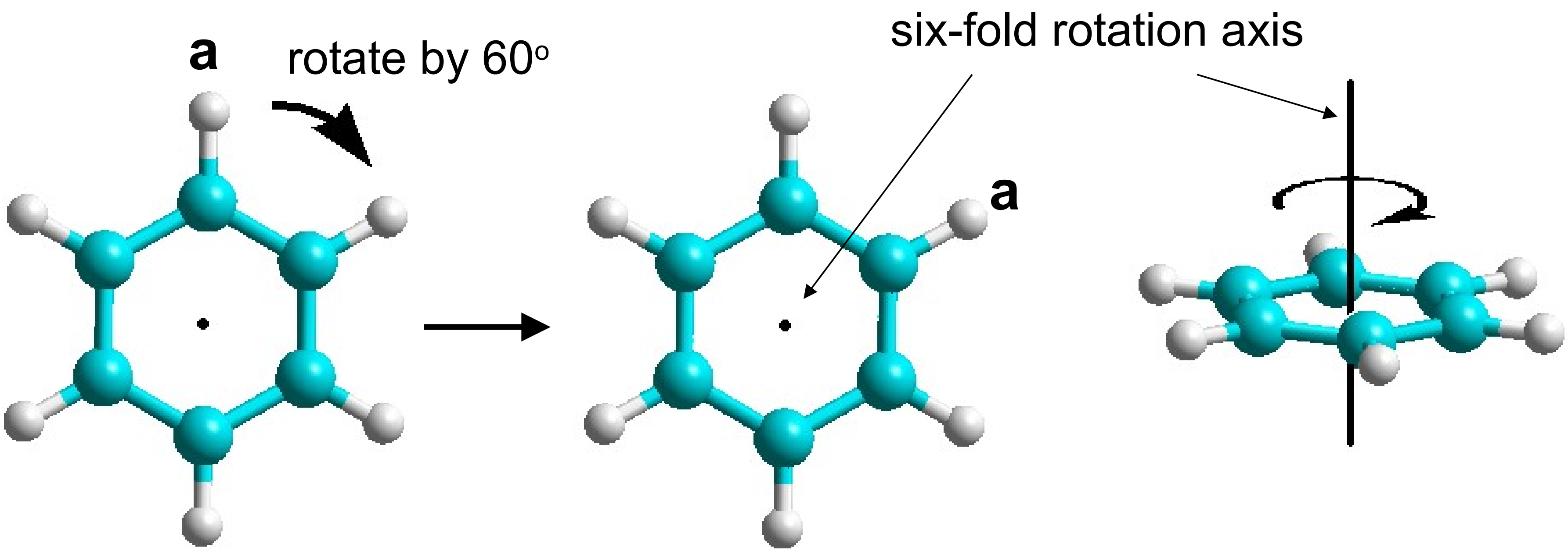
Symmetry Elements

Symmetry is defined as invariance to transformation. What this means in simple terms is that if we perform a symmetry operation on a molecule, it should not appear to have changed. Thus, if we rotate a water molecule by 180° about its two-fold axis of symmetry, it should not appear to have changed:



Transformations of the benzene molecule:

The presence of a symmetry element is identified by the fact that we can carry out a symmetry operation without the molecule appearing to have changed. Thus, for the benzene molecule, rotation by 60° about the six-fold rotation axis does not change its appearance:



The rotation axis is a six-fold rotation axis because we can repeat the operation six times before we get back to the original orientation of the benzene molecule

The symmetry operations form a *group*, which is to say that
1) any two of them carried out must have the same effect as one other operation in the group, and
2) One element of the group must do nothing, i.e. is the identity (E).

The symmetry elements considered in group theory in relation to molecules are

1) Axis of rotation (C_n)
2) Mirror planes (σ)

} the two most important symmetry elements

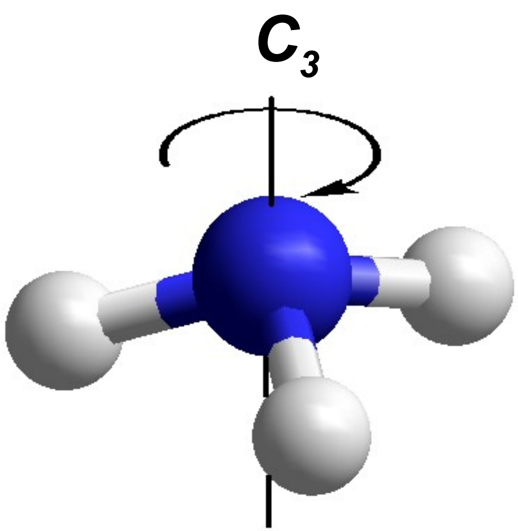
3) Center of symmetry (i)
4) Improper Rotation (S_n)
5) Identity (E)

One needs to be able to identify the symmetry present in molecules, as discussed below:

Axis of Rotation (C_n).

An object has axial symmetry when it is invariant to rotation by some fraction of 360°. It is said to have an *n*-fold axis of symmetry, or a C_n axis, when it is invariant to rotation by 360°/*n*. Conventionally rotation is clockwise.

Some examples of rotational symmetry are:

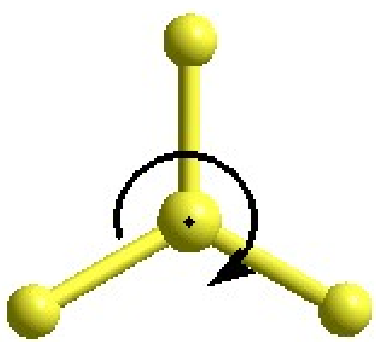


C_3 or three-fold rotational axis of the ammonia molecule. If we rotate the ammonia molecule by 360/3 or 120º about this axis, its appearance is unchanged.

Rotational axes of BF_3

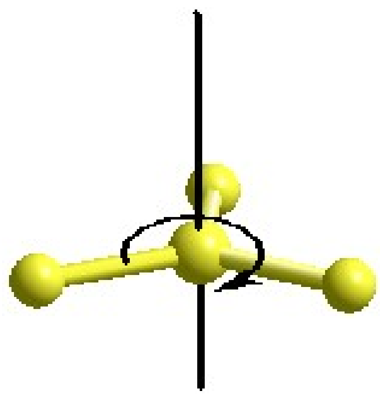
principal axis
(highest value of C_n)

C_3



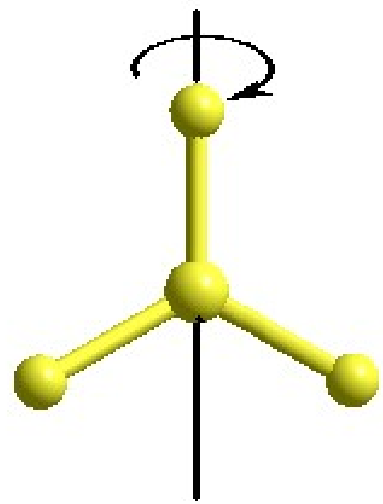
three-fold axis viewed from above

C_3



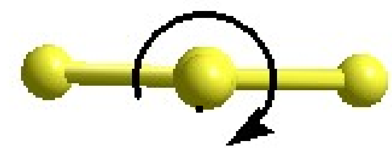
three-fold axis viewed from the side

C_2



two-fold axis viewed from the side

C_2

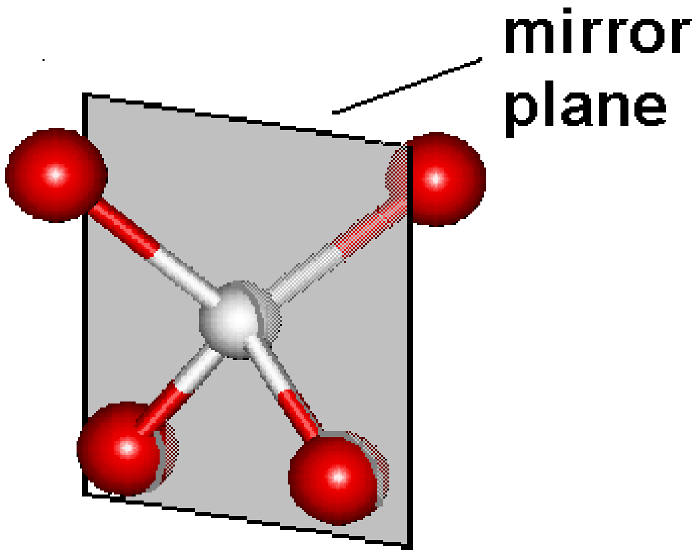


two-fold axis viewed from above

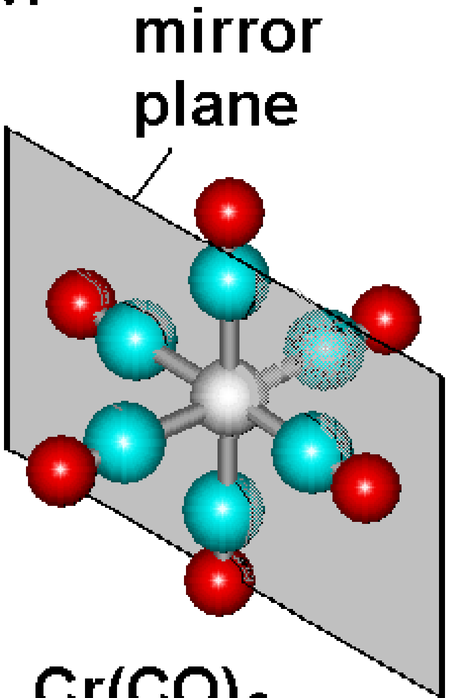
Note: there are 3 C_2 axes

1) Mirror Planes.

Mirror symmetry means invariance to reflection, as shown for the molecules below:



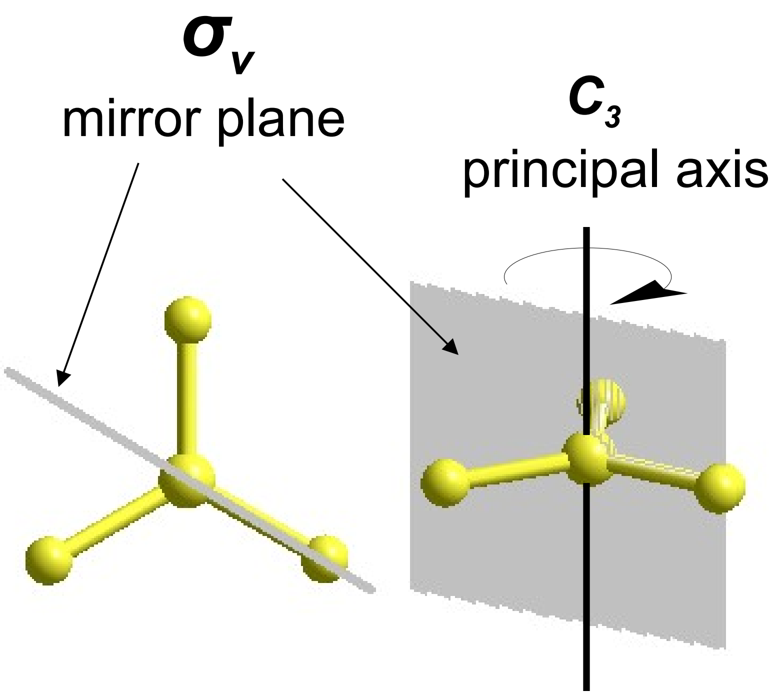
$[ZnI_4]^{2-}$



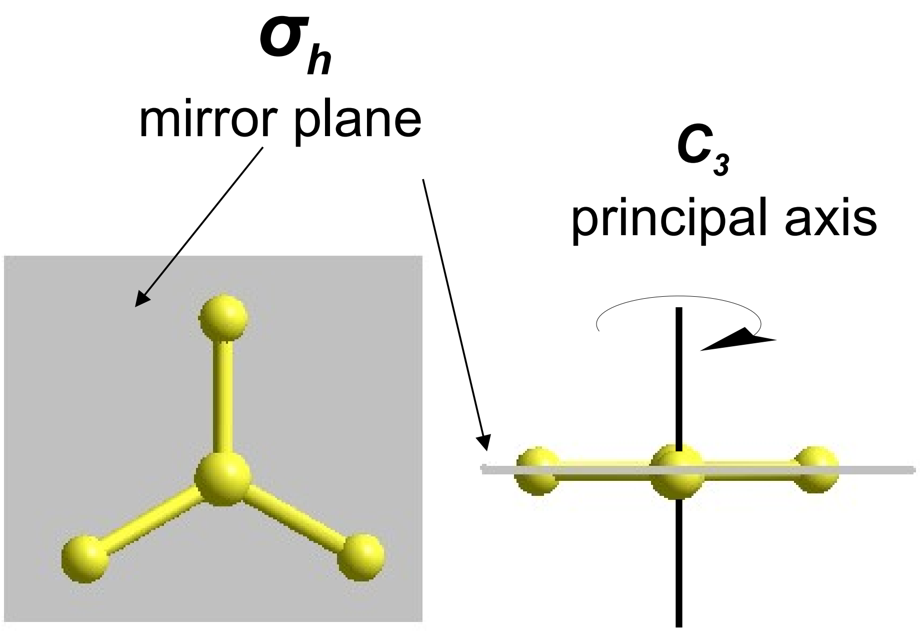
$Cr(CO)_6$

Mirror planes (σ) of BF_3:

Mirror planes can contain the principal axis (σ_v) or be at right angles to it (σ_h). BF_3 has one σ_h and three σ_v planes: (v = vertical, h = horizontal)



σ_v mirror plane
contains the C_3 axis

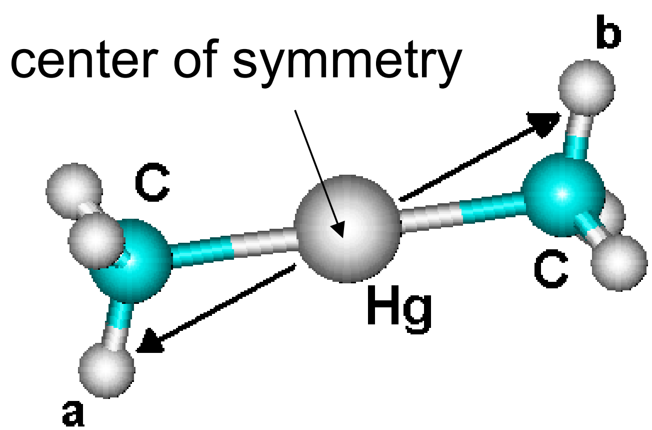


σ_h mirror plane
is at right angles to the C_3 axis

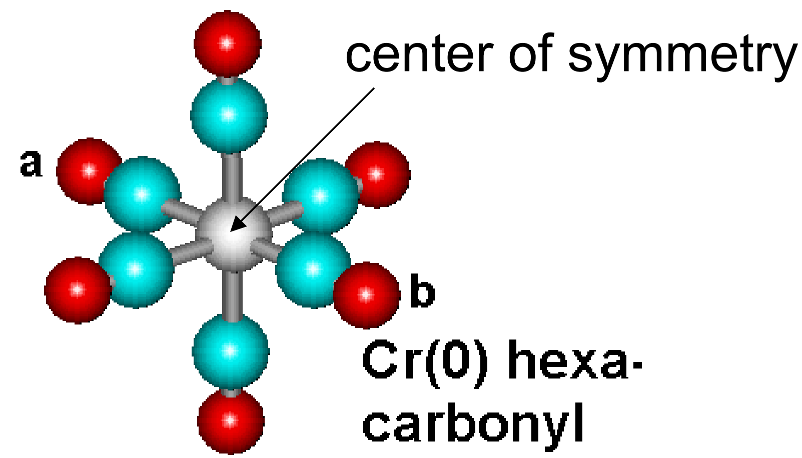
2) Center of Symmetry (*i*)

The inversion operation takes a point through the center of symmetry of the molecule to an equal distance on the other side.

Examples of molecules with a center of symmetry are:



dimethyl mercury

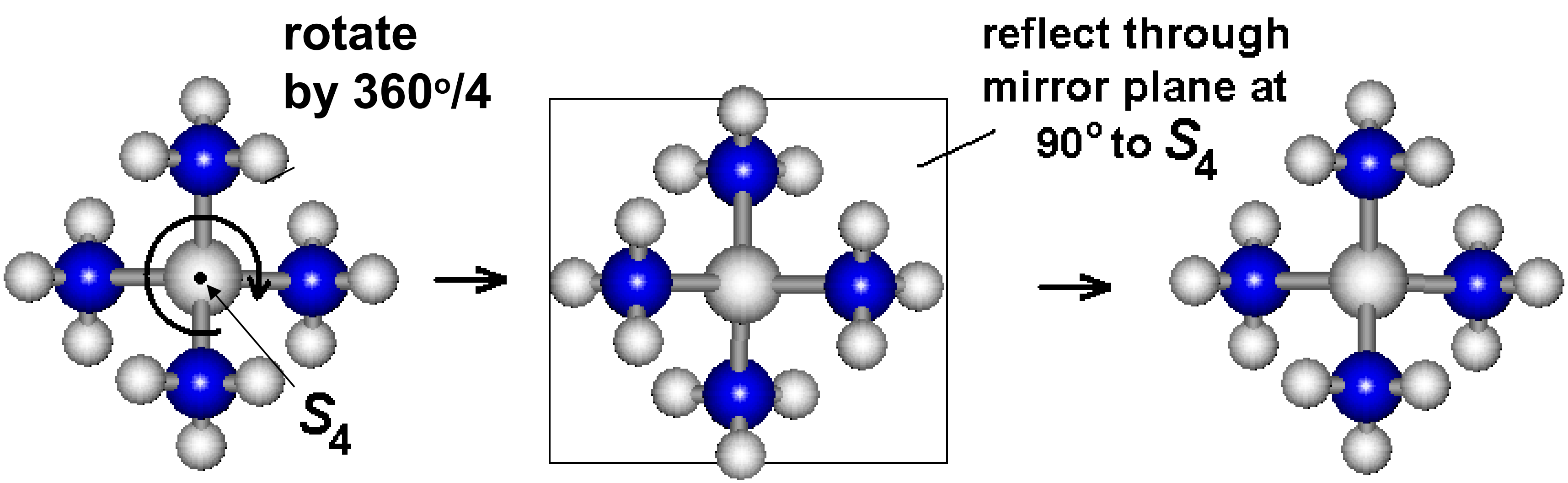


for every atom, as with the 'a' atoms above, reflection through the center gives an identical atom at b

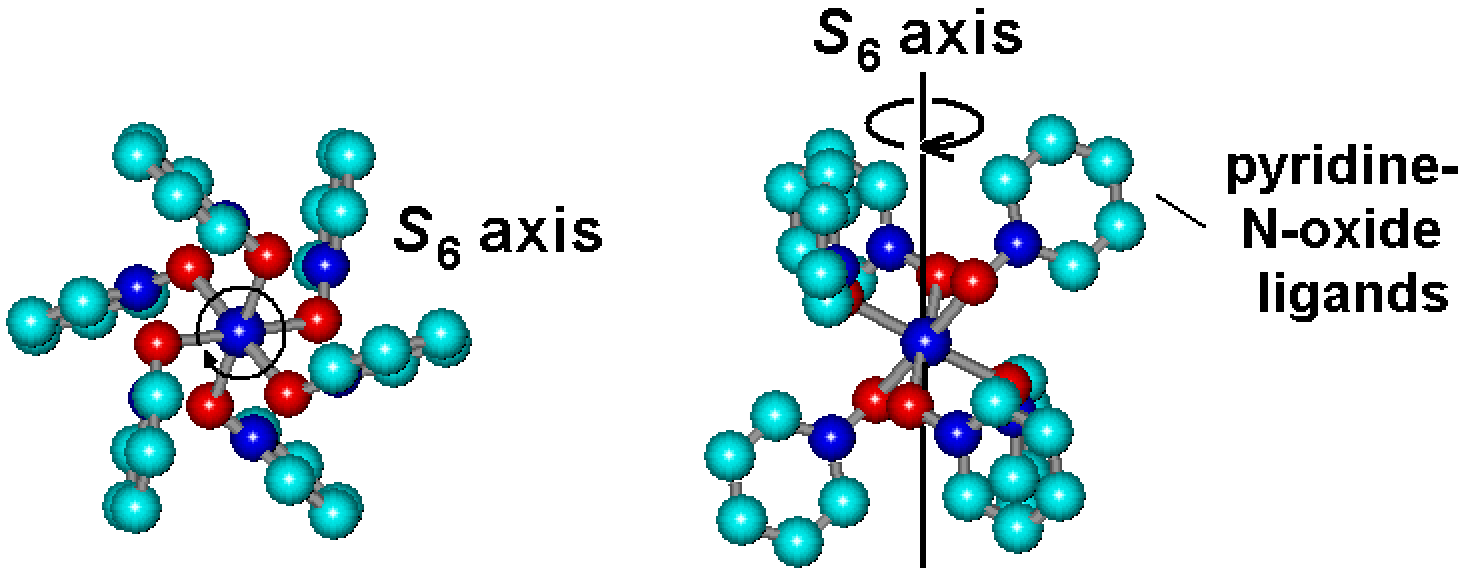
(Note: The center of symmetry is important in deciding whether orbitals are *g* or *u* (lecture 2.))

4) Improper Rotation Axis (S_n)

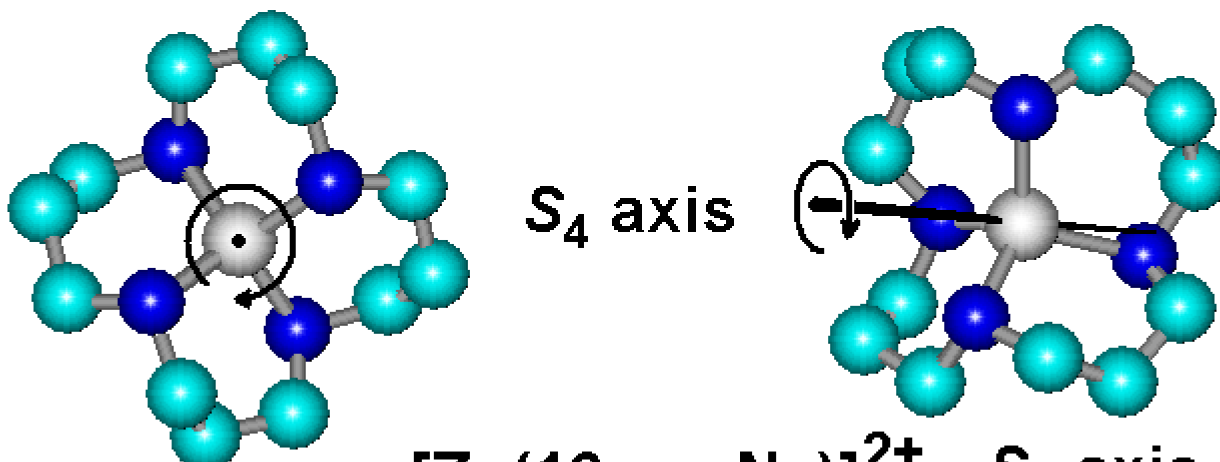
The improper rotation axis is invariant to rotation by $2\pi/n$, followed by reflection through a plane at right angles to the rotation axis. This symmetry element is less important than the others, and is necessary to create the complete group. Most rotation axes that can be identified are also proper rotation axes. Examples of improper rotation axes are shown below:



The S_4 improper rotation axis here is also a C_2 axis

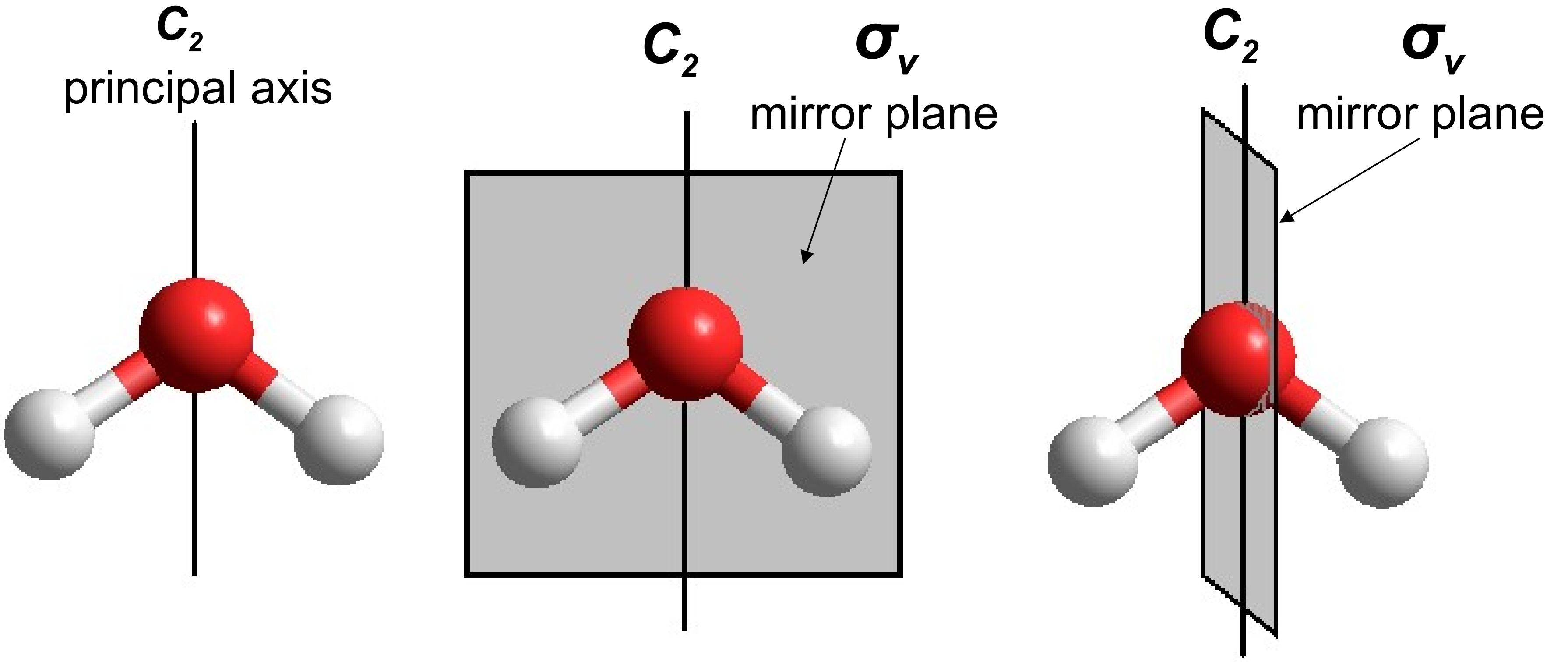


$[Co(O\text{-}NC_5H_5)_6]^{2+}$ S_6 axis ≡ C_3 axis



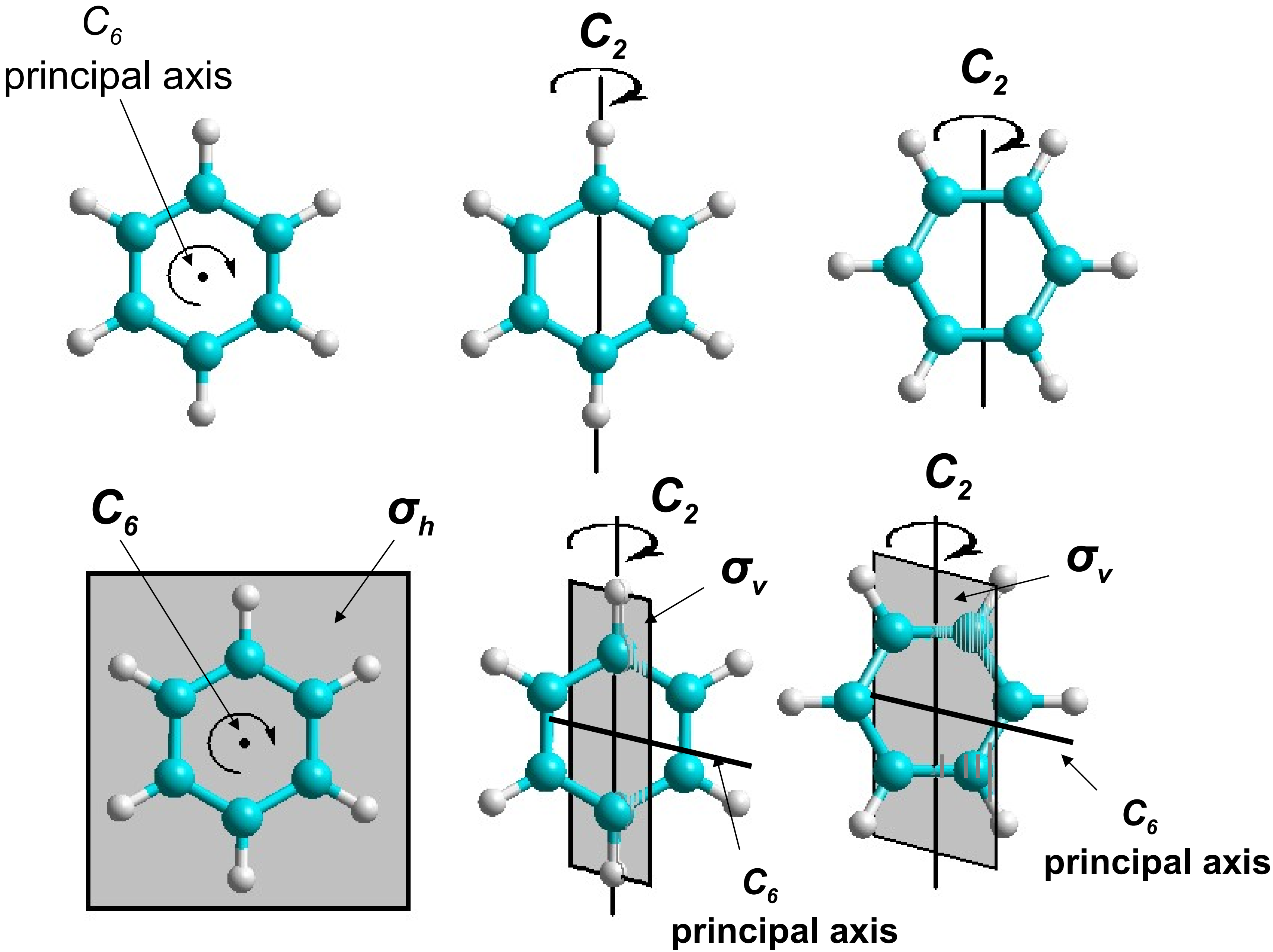
$[Zn(16\text{-}aneN_4)]^{2+}$ S_4 axis ≡ C_2 axis

Rotational axes and mirror planes of the water molecule:

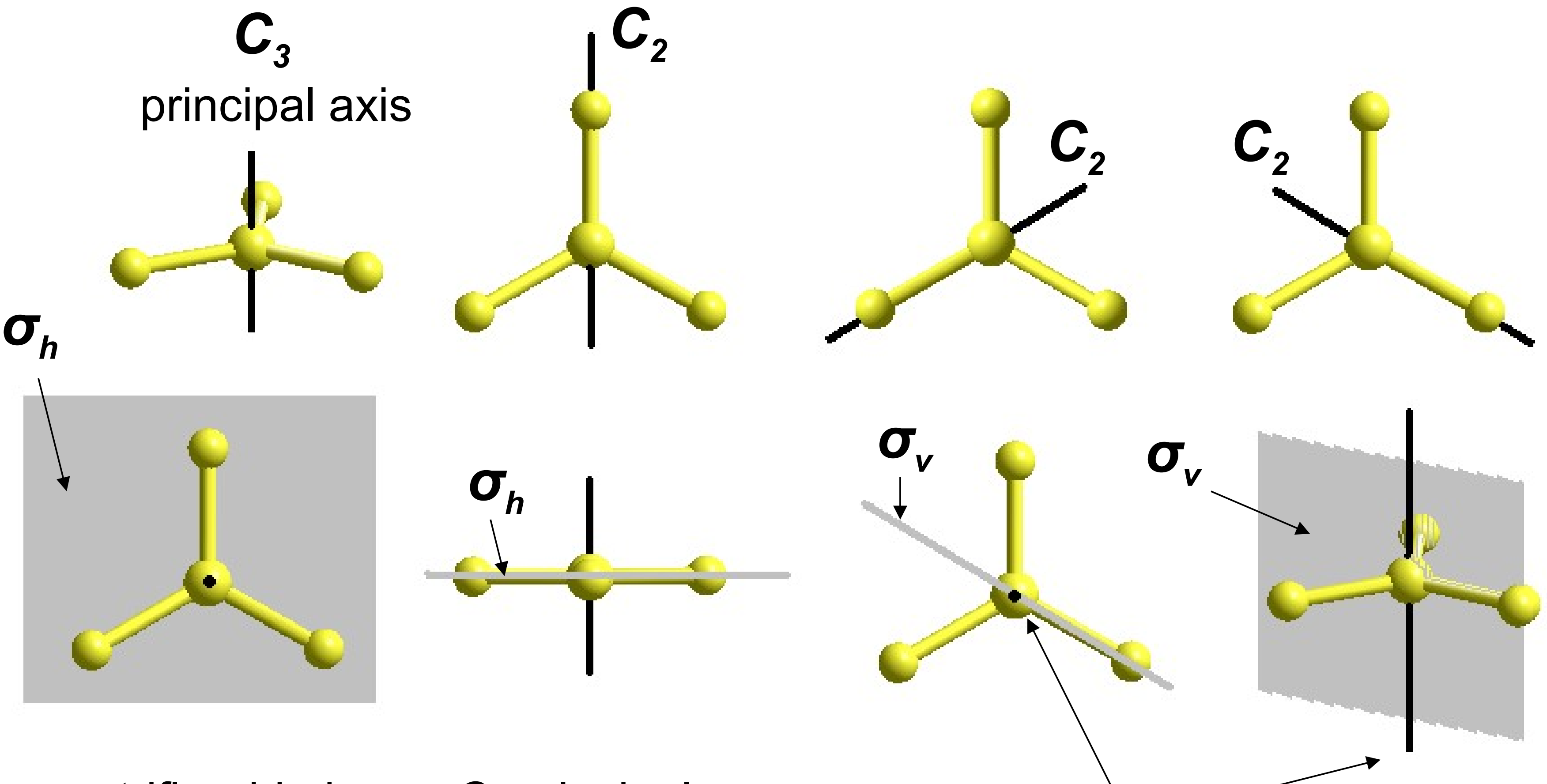


The water molecule has only one rotational axis, its C_2 axis, which is also its principal axis. It has two mirror planes that contain the principal axis, which are therefore σ_v planes. It has no σ_h mirror plane, and no center of symmetry.

Rotational axes and mirror planes of benzene



Rotational axes and mirror planes of boron trifluoride



boron trifluoride has a C_3 principal axis and three C_2 axes, a σ_h mirror plane three σ_v mirror planes, but no center of inversion

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THANKS