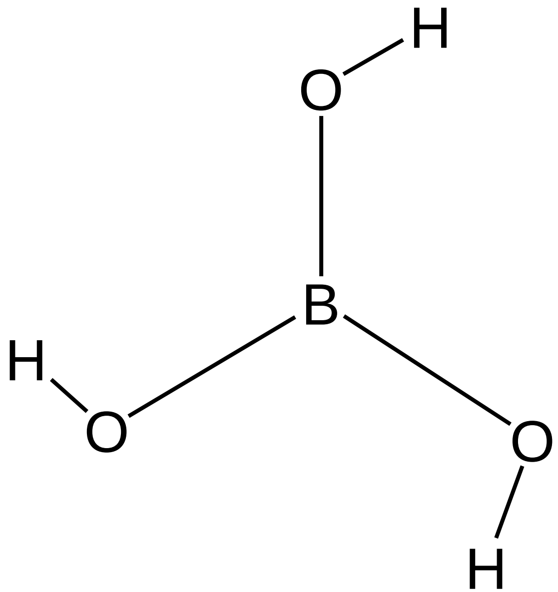
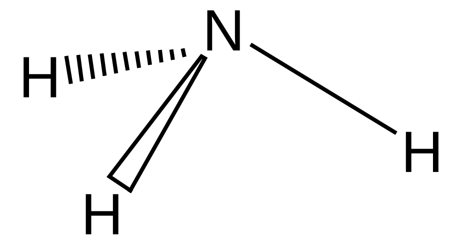
Point Groups

C_1 : no symmetry
C_s : only a plane of symmetry
C_k : only a k rotational axis
C_i : only an inversion center
C_{kh} : a k rotational axis and σ_h
C_{kv} : a k rotational axis and k σ_v
D_k : only C_k and k C_2 rotational axes
D_{kh} : operations of D_k and σ_h which implies k σ_v
D_{kd} : operations of D_k and k σ_d which bisect the angles of C_2
S_k : only the improper rotation S_k
T_d : tetrahedral
O_h : octahedral



C_{3h}



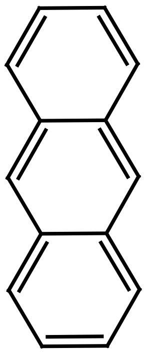
C_{3v}

Point group representations

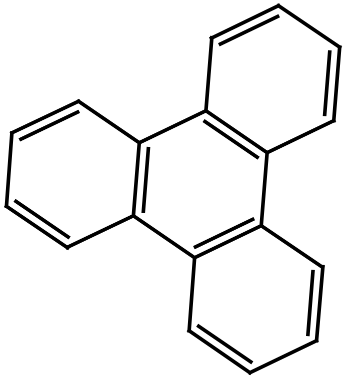
A point group representation is a basis set in which the irreducible representations are the basis vectors. Shown below is the C2v point group. It has four dimensions. The dimensions are the symmetry operations. There are four basis vectors, which are also known as irreducible representations.

C_{2v}		Symmetry elements for the group				Spectroscopy active component		
		E	C_2	sv (xz)	sv' (yz)	Microwave	IR	Raman
Symmetry label	A_1	1	1	1	1		z	x^2, y^2, z^2
	A_2	1	1	-1	-1	R_z		xy
	B_1	1	-1	1	-1	R_y	x	xz
	B_2	1	-1	-1	1	R_x	y	yz

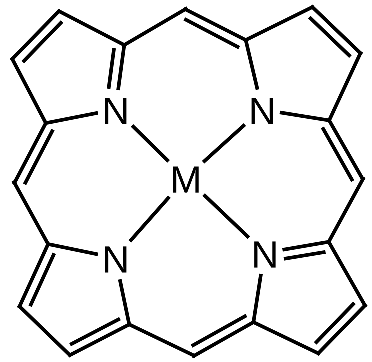
D_{kh} point groups



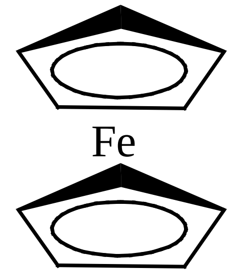
D_{2h}



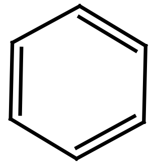
D_{3h}



D_{4h}

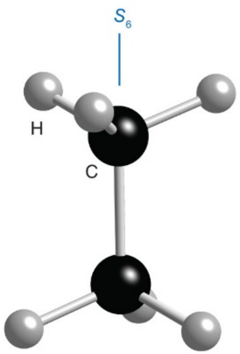


D_{5h}



D_{6h}

D_{kd} point groups



D3d

D_{kh} character table

The D_{4h} point group is a second example. It has 16 dimensions. Note that the symmetry operations are listed by class. A class refers to a given type of operation, e.g. reflection, inversion, rotation, etc.

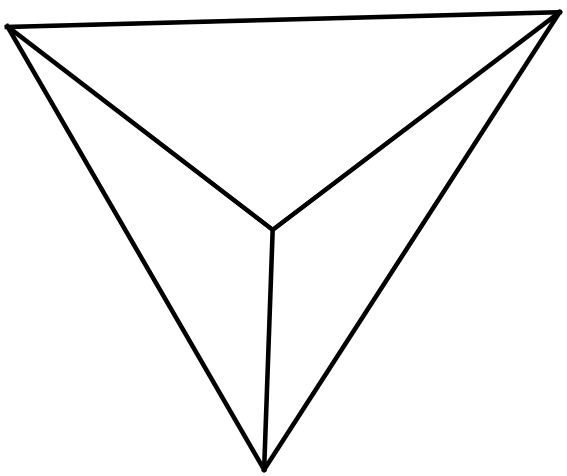
D_{4h}	Symmetry elements for the group										Spectroscopy active component		
Symmetry label	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	s_h	$2s_v$	$2s_d$	Microwave	IR	Raman
A_{1g}	1	1	1	1	1	1	1	1	1	1			x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z		
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1			x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1			xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)		(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1			
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1			
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1			
E_u	2	0	-2	0	0	-2	0	2	0	0		(x, y)	

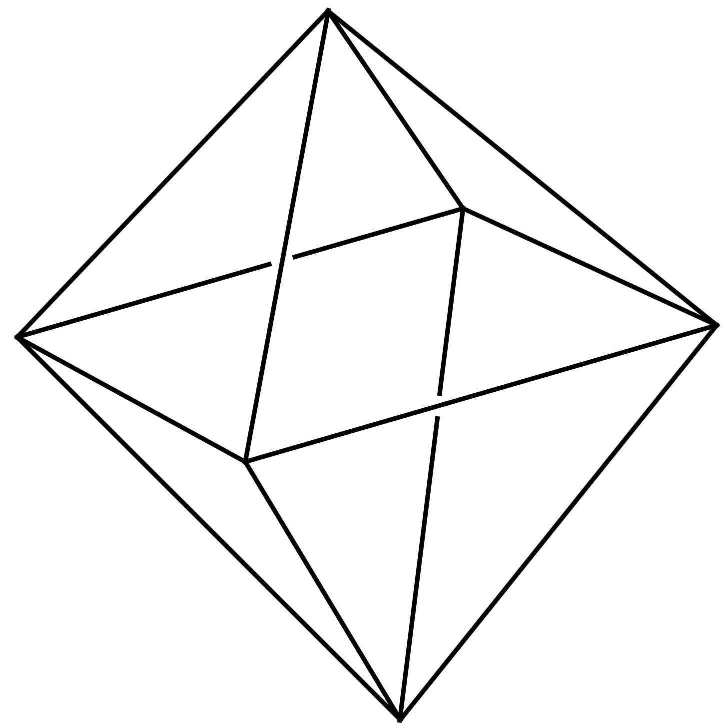
D_{kh} character table

The D_{6h} point group is a third example. The molecule benzene belongs to this point group.

D_{6h}		Symmetry elements for the group												Spectroscopy active component		
		E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	s_h	$3s_d$	$3s_v$	Microwave	IR	Rama
Symmetry label	A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1			x^2+y^2 z^2
	A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z		
	B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1			
	B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1			
	E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)		(xz, y
	E_{2g}	2	-1	1	2	0	0	2	-1	-1	2	0	0			$(x^2-y^2$ xy)
	A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1			
	A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1		z	
	B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1			
	B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1			
	E_{1u}	2	1	-1	-2	0	0	-2	-1	1	-2	0	0		(x, y)	
	E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0			

High symmetry point groups: Tetrahedral and octahedral





Tetrahedron (T_h) **Octahedron (O_h)**

The tetrahedral point group

The T_d point group is a high symmetry group. Many transition metal complexes belong to this group, but also molecules such as methane, CH_4.

T_d		Symmetry elements for the group					Spectroscopy active component		
		E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Microwave	IR	Raman
Symmetry label	A1	1	1	1	1	1			$x^2+y^2+z^2$
	A2	1	1	+1	-1	-1			
	E	2	-1	2	0	0			$(2z^2-x^2-y^2, x^2-y^2)$
	T_1	3	0	-1	1	-1	(R_x, R_y, R_z)		
	T_2	3	0	-1	-1	1		(x, y, z)	(xy, xz, yz)

Examples of point group assignment

Determining the point group to which a molecule belongs will be the first step in a treatment of the molecular orbitals or spectra of a compound.

It is important that this be done systematically. The flow chart in the figure is offered as an aid, and a few examples should clarify the process.

Systematic assignment of a molecule to a point group

Symmetry properties are used to determine the molecular orbitals and spectral features of a molecule. It is important to have a systematic approach to assignment of the point group.

The scheme gives a systematic series of questions that lead to the point group assignment.

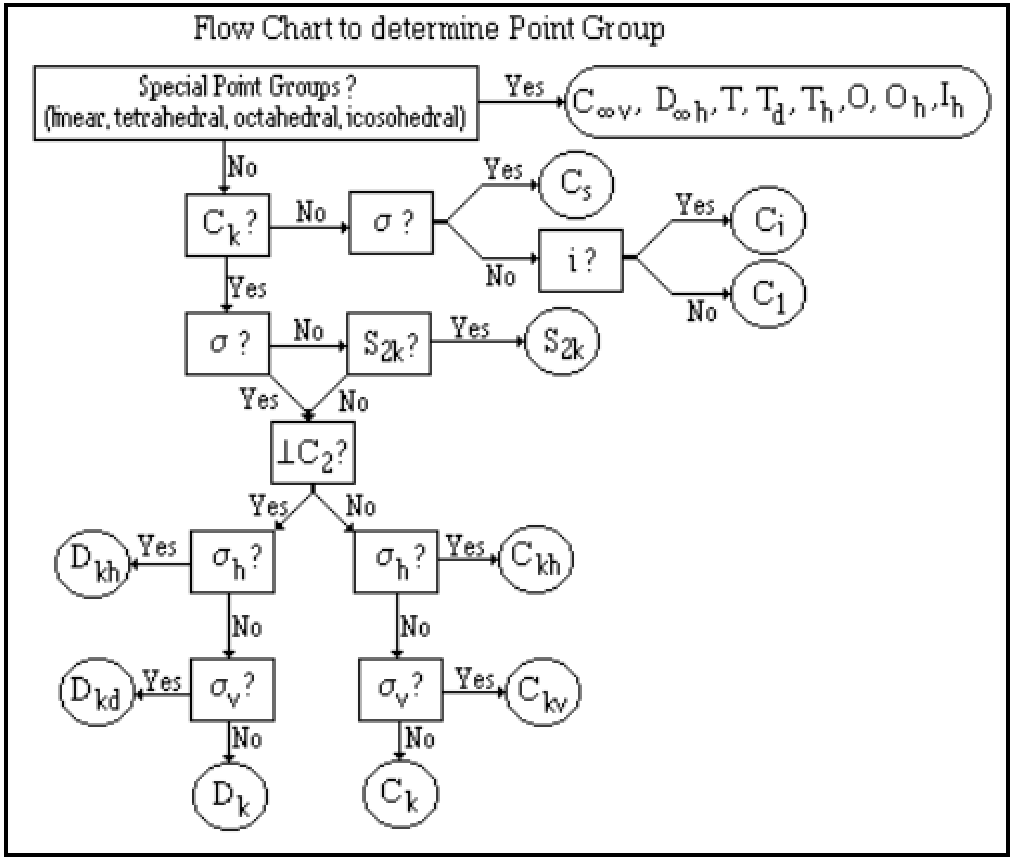
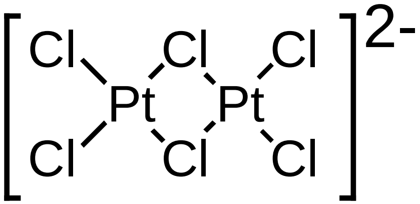
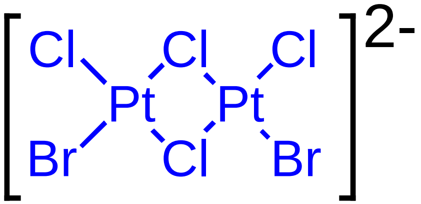


Figure 1-6. Flow chart for the determination of molecular point groups

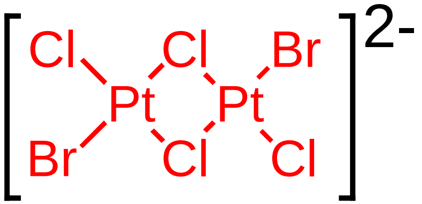
What are the point groups for the following Pt(II) ions?



A

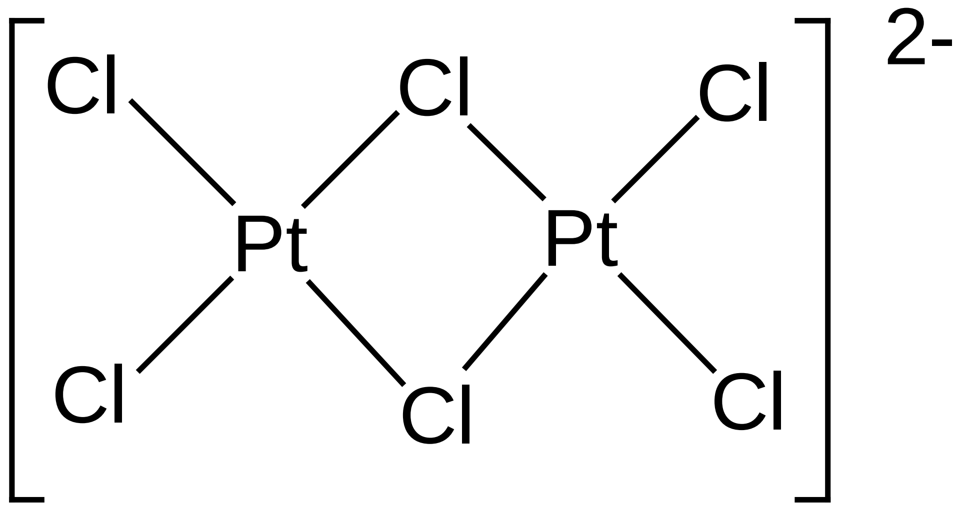


B

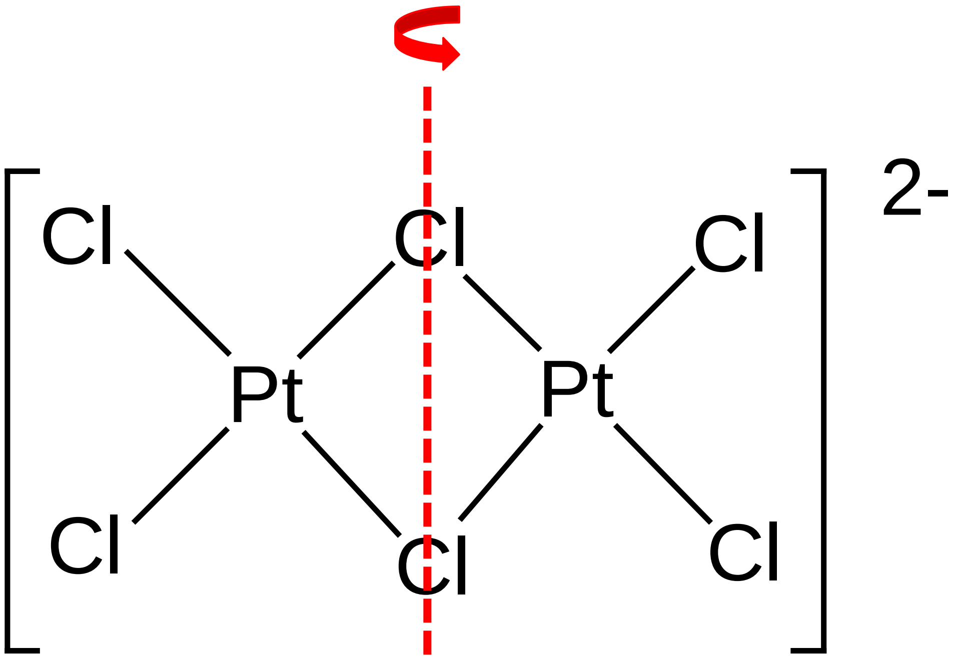


C

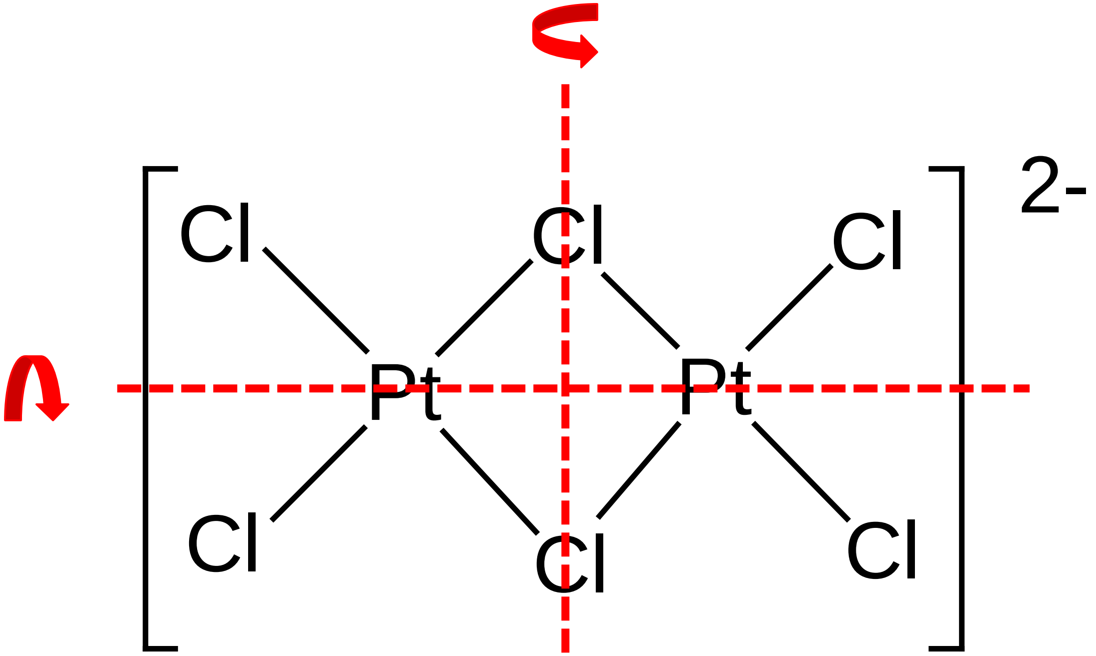
Examples of point group assignment



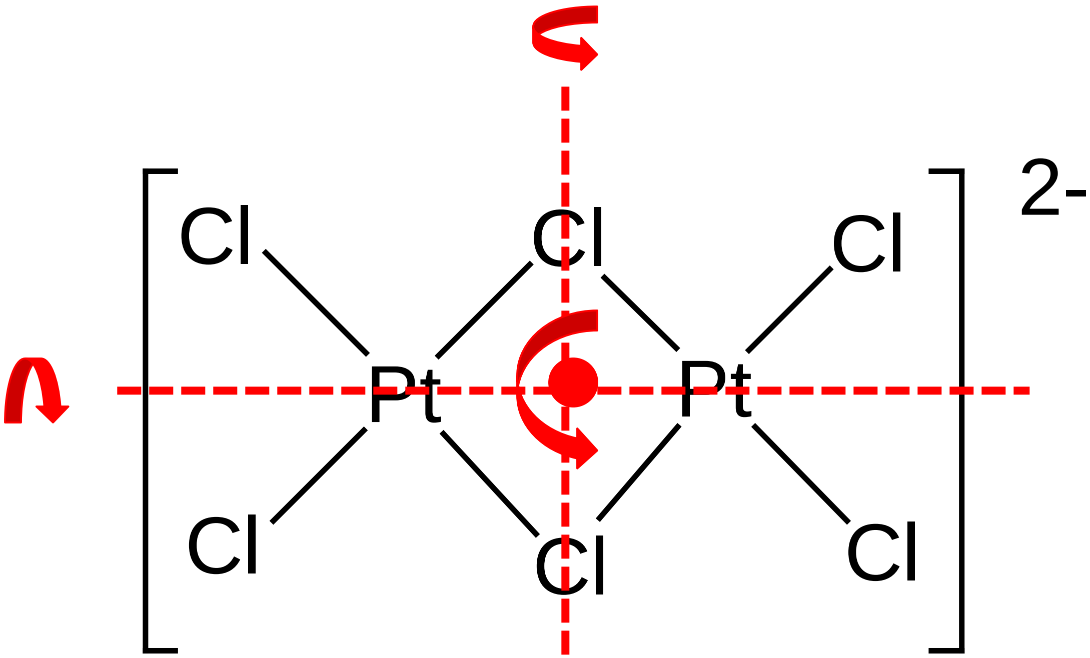
Examples of point group assignment



Examples of point group assignment

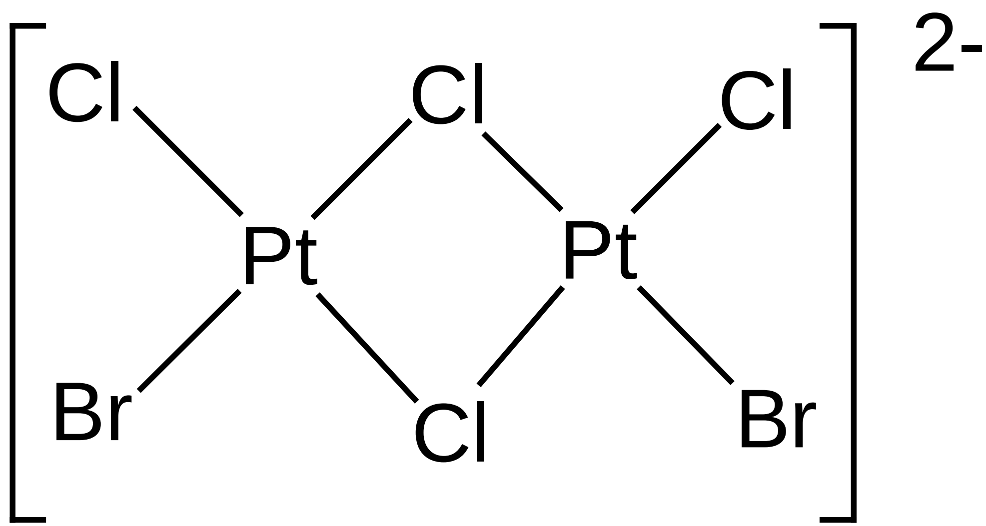


Examples of point group assignment

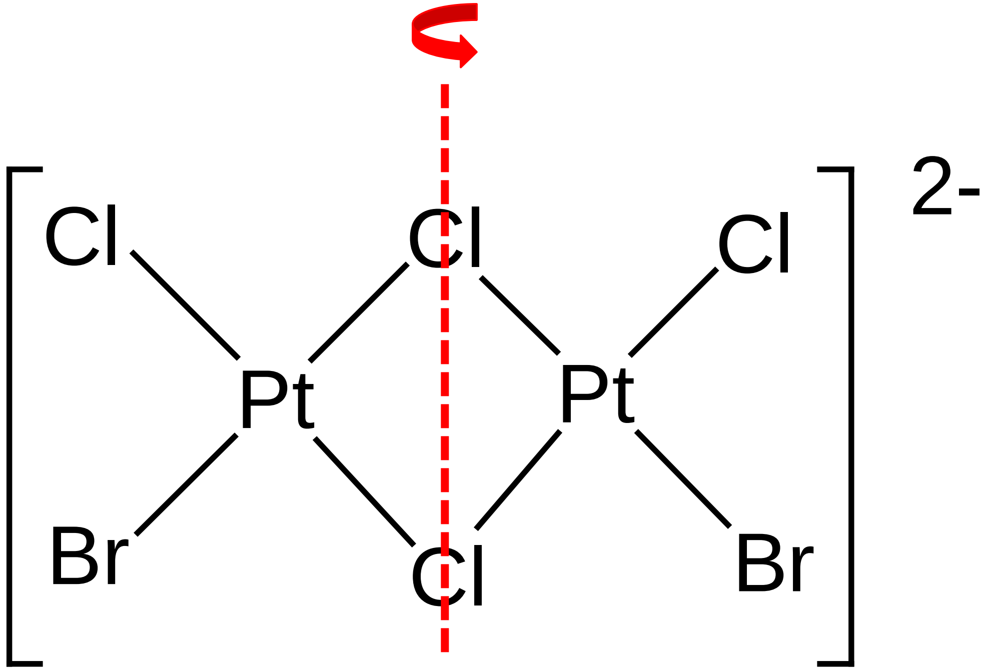


D_{2h}

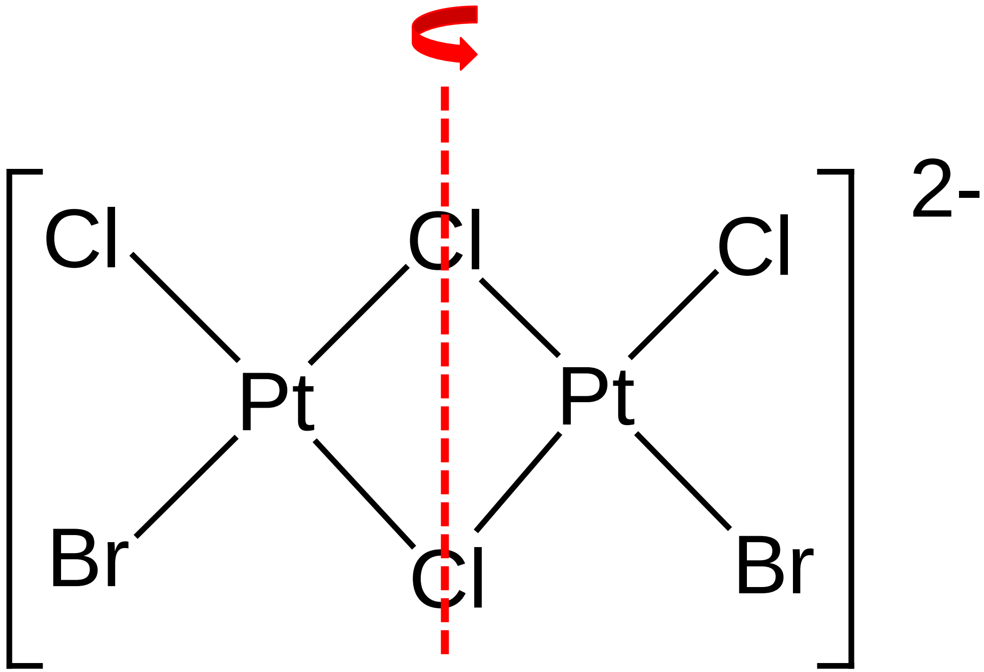
Examples of point group assignment



Examples of point group assignment

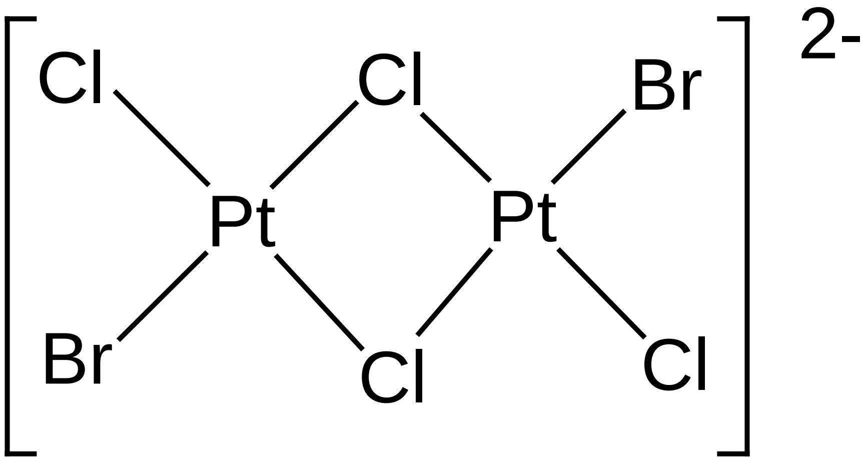


Examples of point group assignment

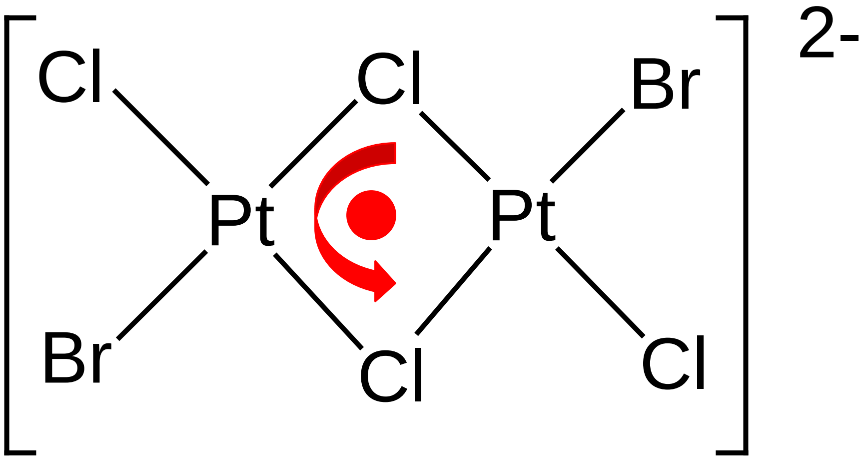


C_{2v}

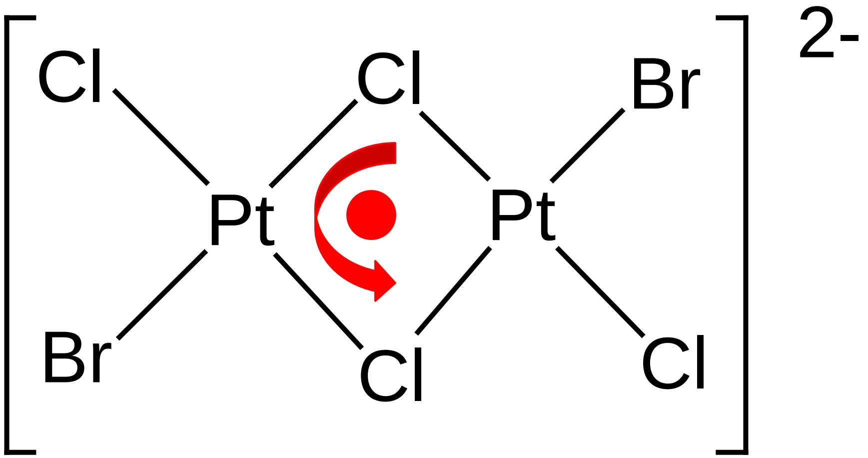
Examples of point group assignment



Examples of point group assignment

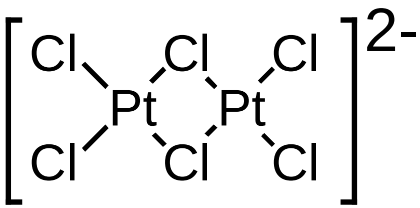


Examples of point group assignment

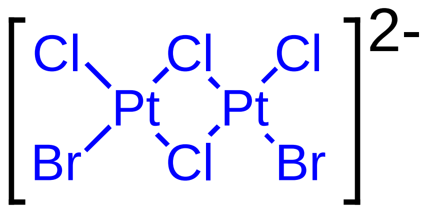


C_{2h}

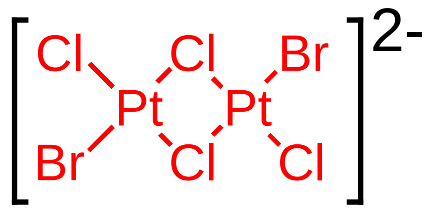
What are the point groups for the following Pt(II) ions?



A



B



C

A contains three C_2 axes, *i.e.*, [C_k?] is yes with k=2. It contains a plane of symmetry so [σ?] is yes. The three C_2 axes are perpendicular, *i.e*, there is a C_2 axis and two perpendicular C_2's which means that [$\perp C_2$?] is yes. There is a plane of symmetry perpendicular to the C_2 so [σ_h?] is yes and we arrive at the D_{2h} point group.

B contains only one C_2 axis, no $\perp C_2$'s, no σh, but it does have two σ_v's and is therefore a C_{2v} ion.

C contains a single C_2 axis and a horizontal plane (the plane of the ion) and therefore has C_{2h} symmetry.