# Geometry Indices

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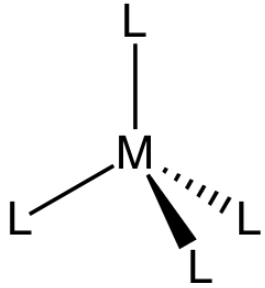
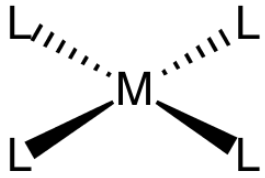
# Geometries of Transition Metal Complexes

- Transition metals centers exhibit a wide variety of coordination numbers and their complexes adopt a wide range of geometries.
- The most common coordination numbers of transition metal centers are 4, 5, and 6.
  - Transition metal centers with 6 ligands most commonly adopt an octahedral geometry.
  - Four- and five-coordinate metal centers exhibit limiting geometries, but also adopt distortions of these structures quite readily.
- Geometry indices have been developed so that four- and five-coordinate geometries can be quantitatively described.

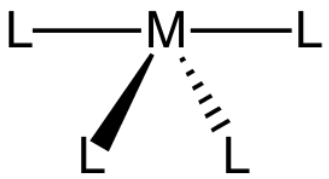
# Four-coordinate Geometries

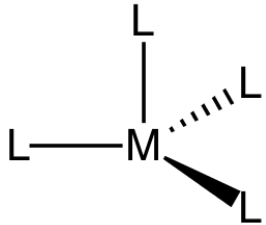
- For four-coordinate metal complexes, tetrahedral and square planar geometries are commonly observed.



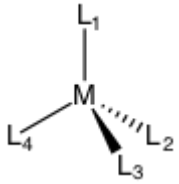



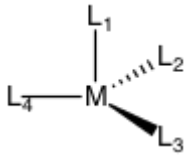

- As metals transition between these two geometries, there are several structures that can be considered distortions of these geometries - see-saw (or compressed tetrahedron, left) and triangular pyramid (right).



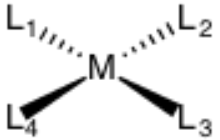



# Bond Angles in Different Geometries








| | Tetrahedral | Trigonal pyramid | Seesaw | Square planar |
|---|---|---|---|---|
| $L_1$-M-$L_2$ | 109.5° | 90° | 90° | 90° |
| $L_2$-M-$L_3$ | 109.5° | 120° | 120° | 90° |
| $L_3$-M-$L_4$ | 109.5° | 120° | 90° | 90° |
| $L_1$-M-$L_4$ | 109.5° | 90° | 180° | 90° |
| $L_1$-M-$L_3$ | 109.5° | 90° | 90° | 180° |
| $L_2$-M-$L_4$ | 109.5° | 120° | 90° | 180° |

# Geometry Index ($\tau_4$)

Houser and co-workers developed a geometry index that can be used to quantitatively describe the geometry adopted by four-coordinate complexes.

In a four-coordinate complex, there are 6 angles formed by the four M-L bonds. The two largest angles, α and β, are used to determine the $\tau_4$ value.

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141}$$

$\tau_4$ (tetrahedron) = 1
$\tau_4$ (square planar) = 0

Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.

# Geometry Index ($\tau_4'$)

Okuniewski and co-workers developed a geometry index that can be used to quantitatively describe the geometry adopted by four-coordinate complexes. This geometry index was created to allow for the easier differentiation between four-coordinate structures.

In a four-coordinate complex, there are 6 angles formed by the four M-L bonds. The two largest angles, α and β (where β > α), are used to determine the $\tau_4'$ value.

$$\tau_4' = \frac{\beta - \alpha}{250.5} + \frac{180 - \beta}{70.5}$$

$\tau_4'$ (tetrahedron) = 1
$\tau_4'$ (square planar) = 0

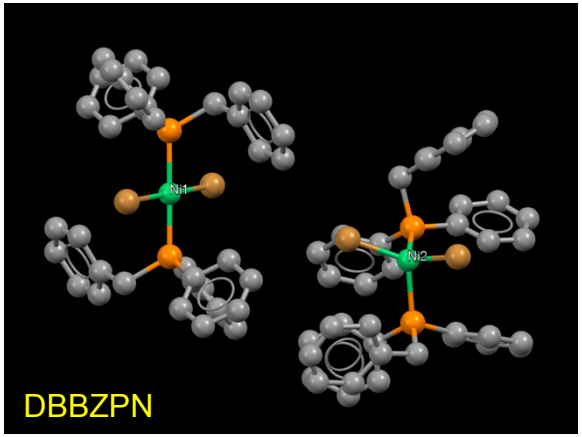
Okuniewski, A.; Rosiak, D.; Chojnacki, J.; Becker, B. *Polyhedron* **2015**, *90* (C), 47–57.

# Bond Angles in Different Geometries

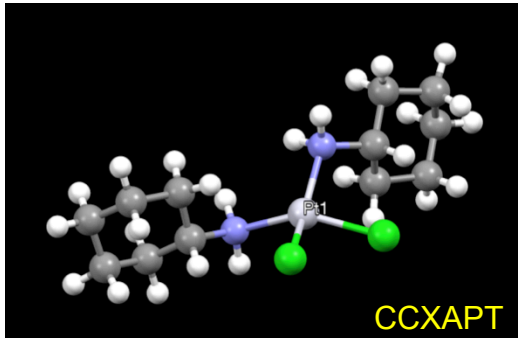
| | β (largest angle) | α (2nd largest angle) | $\tau_4$ | $\tau_4'$ |
|---|---|---|---|---|
| **Tetrahedral** | 109.5° | 109.5° | 1.00 | 1.00 |
| **Trigonal pyramidal** | 120° | 120° | 0.85 | 0.85 |
| **Seesaw** | 180° | 90° | 0.64 | 0.36 |
| **Seesaw** | 180° | 109.5° | 0.50 | 0.28 |
| **Seesaw** | 180° | 154.4° | 0.18 | 0.10 |
| **Seesaw** | 180° | 170° | 0.07 | 0.04 |
| **Square planar** | 180° | 180° | 0.00 | 0.00 |

# Calculation of $\tau_4$ and $\tau_4'$ - Examples

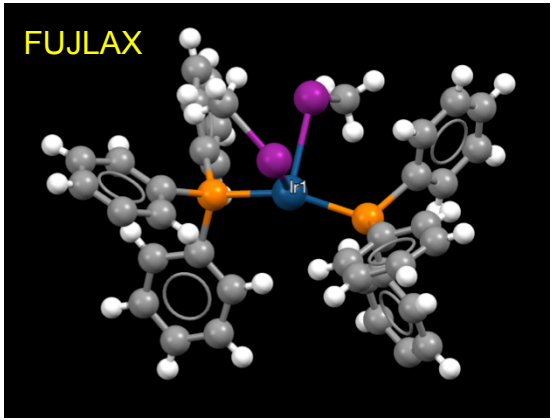
- The structures shown below can be found in the Teaching Subset of Mercury, which is freely available from the CCDC.
- The angles were measured in Mercury and the two largest angles are listed below each structure.




| Ni1 | Ni2 |
|---|---|
| β = 180.0° | β = 119.6° |
| α = 180.0° | α = 118.7° |
| $\tau_4$ = 0 | $\tau_4$ = 0.86 |
| $\tau_4'$ = 0 | $\tau_4'$ = 0.86 |

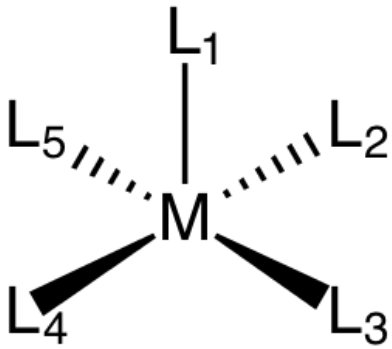



β = 150.6° α = 150.6°
$\tau_4$ = 0.42
$\tau_4'$ = 0.42

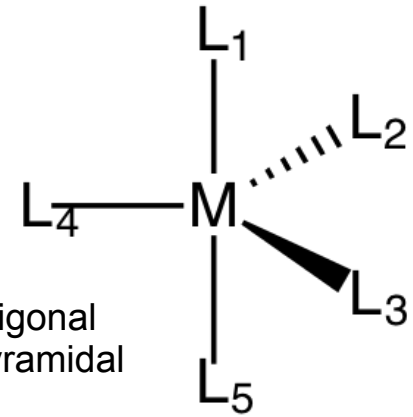



β = 156.6° α = 102.6°
$\tau_4$ = 0.71
$\tau_4'$ = 0.55

# Bond Angles in Different Geometries (CN = 5)




Square pyramidal




Trigonal bipyramidal

| | Square pyramidal | Trigonal bipyramidal |
|---|---|---|
| $L_1$-M-$L_2$ | 90° | 90° |
| $L_1$-M-$L_3$ | 90° | 90° |
| $L_1$-M-$L_4$ | 90° | 90° |
| $L_1$-M-$L_5$ | 90° | 180° |
| $L_2$-M-$L_3$ | 90° | 120° |
| $L_2$-M-$L_4$ | 180° | 120° |
| $L_2$-M-$L_5$ | 90° | 90° |
| $L_3$-M-$L_4$ | 90° | 120° |
| $L_3$-M-$L_5$ | 180° | 90° |
| $L_4$-M-$L_5$ | 90° | 90° |

# Geometry Index ($\tau_5$)

Addison, Reedijk, and co-workers developed a geometry index that can be used to quantitatively describe the geometry adopted by five-coordinate complexes.

In a five-coordinate complex, there are 10 angles formed by the five M-L bonds. The two largest angles, α and β (where β > α), are used to determine the $\tau_5$ value.

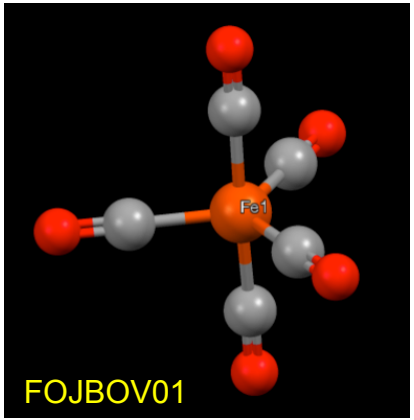
$$\tau_5 = \frac{\beta - \alpha}{60}$$

$\tau_5$ (trigonal bipyramidal) = 1
$\tau_5$ (square pyramidal) = 0

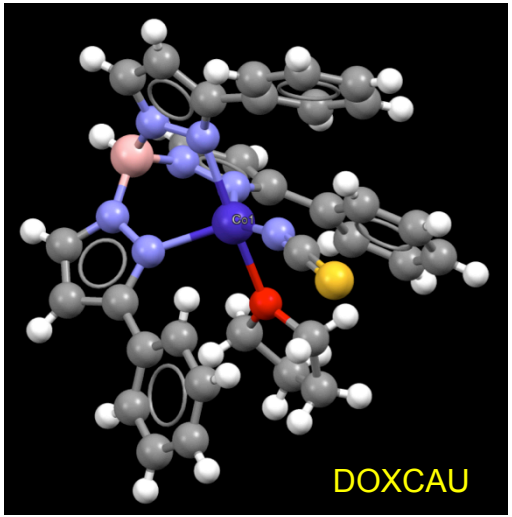
Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

# Calculation of $\tau_5$ - Examples

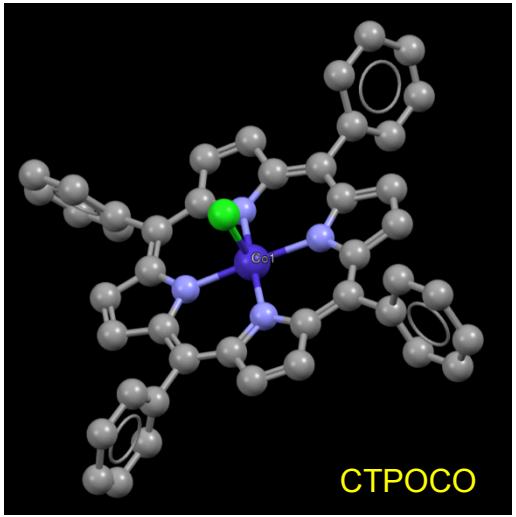
- The structures shown below can be found in the Teaching Subset of Mercury, which is freely available from the CCDC.
- The angles were measured in Mercury and the two largest angles are listed below each structure.




β = 176.4° α = 122.0°
$\tau_5$ = 0.91




β = 175.0° α = 145.0°
$\tau_5$ = 0.50




β = 176.8° α = 176.8°
$\tau_5$ = 0