

## Answer on Question #77893, Chemistry / Inorganic Chemistry

What is meant by stereochemically inactive/active s orbital? (with respect to octahedral geometry)

Answer

In the context of VSEPR theory, single pairs usually affect molecular geometry. For example,

c

e

N

H

3

takes a trigonal pyramidal structure due to the presence of a single pair on nitrogen; if there were no single pair, then this would be a trigonal plan, cf.

FROM

e

B

F

3

. These so-called stereochemically active single pairs, because they affect the stereochemistry in nitrogen.

In a few rare cases, single pairs do not affect molecular geometry, and they are called stereochemically inactive. The only example that I can think of, from my point of view, is in

c

e

[

X

e

F

8

]

2

-

, which must have 8 pairs of links and 1 single pair around xenon. Despite the presence of a single pair, the dianion takes a square anti-prismatic structure, without any obvious position in the space for a single pair. Looking at Inorganic Chemistry by Shriver and Atkins (6th ed.), There are a few more examples

c

e

[

S

e

F

6th

]

2

-

and

c

e

[

T

e

C

I

6th

]

2

-

, which are octahedral despite the presence of six pairs of bonds and one single pair around the central atom.

In VSEPR theory, these stereochemically inactive single pairs are rationalized by placing them in the s-orbital, which is non-directional. The electron pair in the s-orbit has a spherically symmetric electron density and, therefore, can not influence the shape of the molecule. However, this is not quite orbital which is stereochemically active, it is the electron, and therefore the most common term is "stereochemically (in) an active lone pair".

There is another context that should be mentioned, since it occurs frequently, and this refers to the compounds of tin (II) and lead (II). The electron configurations of these two ions terminate

n

m

a

t

h

r

m

s

2

, and this s-orbital single pair tends to generate some distortion in stereochemistry.

An excellent example is oxide. Solid

c

e

M

g

O

has a structure in which

c

e

M

g

2

+

octahedrally coordinated by six ions

c

e

O

2

-

(rock salt / halite structure), but

c

e

S

n

O

and

c

e

P

b

O

have unevenly distributed square pyramidal coordination

c  
e  
M  
2  
+  
four ions

c  
e  
O  
2  
-

. Traditionally, this is due to the presence of a stereochemically active single pair on Sn (II) or Pb (II).

However, this description can not be complete, because if the geometry is determined only by a single pair on the metal, then we can expect that PbS will have the same structure - and this is not so. In fact, PbS has the same structure as MgO, with regular octahedral coordination, so it is clear that the anion should play a role. The full explanation is beyond the scope of this answer, but one of the ways to rationalize it is to use the second-order Jahn-Teller distortion. The interested reader can refer to Chem. Soc. Rev. Chem. Soc. Rev. Chem. Soc. Rev. 2011, 40 (9), 4455-4463.

However, the "stereochemically active single pair" is a recurrent theme in the structural chemistry of Sn (II) and Pb (II) (sometimes also Tl (I) and Bi (III)). For example, Iviv beauty salons

c  
e  
S  
n  
C  
p  
2

and

c

e

p

b

C

p

2

take a curved structure, rather than a linear structure

c

e

M

g

C

p

2

(and more famous

c

e

F

e

C

p

2

). Again, VSEPR theory is not the best way to explain this; the correct explanation will include the MO theory.