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Abstract

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ON THE QUESTION OF THE RELATIVE STABILITY OF ISOMERS IN MOLECULES $MX_{k-2}Y_2$

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For many compounds with square or octahedral configuration of composition $MX_{k-2}Y_2$, cis- and trans-isomers exist. On the other hand, molecules with structures of the type $TeCl_4$ and PCl_5, for example $(C_6H_5)_2SeHal_2$ or PF_3Cl_2, are known only in the form of one stable isomer, although in such molecules the existence of geometrical isomers is in principle possible (1,2). From the thermodynamic point of view, the presence or absence of geometrical isomers is determined by the difference in the free energies of the reactions of their formation. Since the differences in entropy changes upon formation of isomers are small, the relative yield of isomers is determined mainly by the thermal effects of the corresponding reactions. The strengths of the bonds being formed may serve as a measure of these quantities. This makes it possible to use the method of maximum overlap (3,4) to clarify the question of the existence of isomers of molecules $MX_{k-2}Y_2$ of different structures.

In this method, the stability of different molecular configurations is determined by the total overlap of the valence electrons of the central atom with the valence orbitals of the ligands. The calculation was carried out under the assumption that the central atom is bound to each ligand only by σ-bonds and that the ligands do not interact with one another. The overlap integrals were assumed proportional to the projections of the angular parts of the valence orbitals of the central atom onto the directions of the σ-bonds M—X and M—Y. In the model calculation it was assumed that the overlap integrals for M—Y bonds are twice as large as the overlap integrals for M—X bonds. A larger difference in the overlap integrals is unlikely, as is seen from the following examples.

Atom M	Ligand	Distance M—X, Å	Overlap integral
P	F	1.59	$\langle 2p\sigma,\ 3p\sigma\rangle = 0.24$
P	Cl	2.05	$\langle 3p\sigma,\ 3p\sigma\rangle = 0.35$
Se	C	1.95	$\langle 2p\sigma,\ 4p\sigma\rangle = 0.31$
Se	Br	2.55	$\langle 4p\sigma,\ 4p\sigma\rangle = 0.25$
Se	Cl	2.30	$\langle 3p\sigma,\ 4p\sigma\rangle = 0.23$

Atom M	Ligand	Distance M—X, Å	Overlap integral
Se	I	2.45	$\langle 4p\sigma,\ 5p\sigma\rangle = 0.24$

The relative stability of the isomers was estimated by comparing the sum of the square roots of the characteristic roots of the matrix products $(R'R)$ for each isomer considered (^{3,5}) (R is the overlap matrix, R' is the transposed matrix).

Molecules $MX_{k-2}Y_2$ with the following configurations were considered.

1. **Square.** In square hybridization, the s-, p_x-, p_y-, d_{z^2}-, and $d_{x^2-y^2}$-orbitals of the central atom may participate. If the directions of the σ-bonds are taken as the coordinate axes x and y, then the overlap matrices R for the cis- and trans-isomers will have the following form:

$$\begin{array}{r|cccc} S & 2 & 2 & 1 & 1 \\ p_x & 2\sqrt{3} & -2\sqrt{3} & 0 & 0 \\ R = p_y & 0 & 0 & \sqrt{3} & -\sqrt{3} \\ d_{z^2} & -\sqrt{5} & -\sqrt{5} & -\frac{\sqrt{5}}{2} & -\frac{\sqrt{5}}{2} \\ d_{x^2-y^2} & \sqrt{15} & \sqrt{15} & -\frac{\sqrt{15}}{2} & -\frac{\sqrt{15}}{2} \end{array}$$

trans-isomer

$$\times \begin{array}{r|cccc} S & 2 & 1 & 2 & 1 \\ p_x & 2\sqrt{3} & -\sqrt{3} & 0 & 0 \\ p_y & 0 & 0 & 2\sqrt{3} & -\sqrt{3} \\ d_{z^2} & -\sqrt{5} & -\frac{\sqrt{5}}{2} & -\sqrt{5} & -\frac{\sqrt{5}}{2} \\ d_{x^2-y^2} & \sqrt{15} & \frac{\sqrt{15}}{2} & -\sqrt{15} & -\frac{\sqrt{15}}{2} \end{array} \quad -$$

cis-isomer

The matrix products $(R'R)$ have the following characteristic roots:

trans-isomer	cis-isomer
$x_1 = 48.974$	$x_1 = 55.110$
$x_2 = 24.000$	$x_2 = 20.47$
$x_3 = 11.026$	$x_3 = 7.740$
$x_4 = 6.000$	$x_4 = 6.68$
$\sum \sqrt{x_i} = 17.67$	$\sum \sqrt{x_i} = 17.77$

$\sum \sqrt{x_i}$ for both isomers are almost identical; therefore the cis- and trans-isomers of the molecules MX_2Y_2 must have approximately the same stability, which agrees with the existence of both isomers.

2. Octahedron. The matrix R for the trans-isomer has the form:

$$R = \begin{array}{c|cccccc}
s & 2 & 2 & 1 & 1 & 1 & 1 \\
p_x & 0 & 0 & \sqrt{3} & -\sqrt{3} & 0 & 0 \\
p_y & 0 & 0 & 0 & 0 & \sqrt{3} & -\sqrt{3} \\
p_z & 2\sqrt{3} & -2\sqrt{3} & 0 & 0 & 0 & 0 \\
d_{z^2} & 2\sqrt{5} & 2\sqrt{5} & -\dfrac{\sqrt{5}}{2} & -\dfrac{\sqrt{5}}{2} & -\dfrac{\sqrt{5}}{2} & -\dfrac{\sqrt{5}}{2} \\
d_{x^2-y^2} & 0 & 0 & \dfrac{\sqrt{15}}{2} & \dfrac{\sqrt{15}}{2} & -\dfrac{\sqrt{15}}{2} & -\dfrac{\sqrt{15}}{2}
\end{array}$$

The matrix for the cis-isomer is obtained by dividing the 1st column by two and multiplying the second column by two.

The matrix products $(R'R)$ have the following characteristic roots:

trans-isomer	cis-isomer
$x_1 = 49.77$	$x_1 = 44.39$
$x_2 = 24.00$	$x_2 = 32.38$
$x_3 = 15.00$	$x_3 = 11.12$
$x_4 = 7.23$	$x_4 = 8.11$
$x_5 = 6.00$	$x_5 = 6.00$
$x_6 = 6.00$	$x_6 = 6.00$
$\sum \sqrt{x_i} = 23.41$	$\sum \sqrt{x_i} = 23.39$

For octahedral molecules MX_4Y_2, both isomers also prove to be approximately equally stable.

3. Distorted tetrahedron (symmetry C_{2v}). Molecules of the type $TeCl_4$ have the structure shown in Fig. 1. For molecules MX_2Y_2 of this type there can be only three geometrical isomers: 1) the Y atoms are in positions 1,2, and the X atoms in positions 3,4. 2) the X atoms are in positions 1,2, and the Y atoms in positions 3,4. 3) the X atoms are in positions 2,4, and the Y atoms in positions 1,3.

The overlap matrix R for isomer I has the form:

$$R(I) = \begin{array}{c}
s \\ p_z \\ p_x \\ p_y \\ d_{z^2} \\ d_{x^2-y^2}
\end{array}
\begin{pmatrix}
2 & 2 & 1 & 1 \\
2\sqrt{3} & -2\sqrt{3} & 0 & 0 \\
0 & 0 & \sqrt{3} & 0 \\
0 & 0 & 0 & \sqrt{3} \\
2\sqrt{5} & 2\sqrt{5} & -\frac{1}{2}\sqrt{5} & -\frac{1}{2}\sqrt{5} \\
0 & 0 & -\frac{1}{2}\sqrt{15} & -\frac{1}{2}\sqrt{15}
\end{pmatrix}.$$

The overlap matrix for isomer II is obtained by dividing the 1st and 2nd columns by two and multiplying the 3rd and 4th columns by two, while the matrix R for isomer III is found by multiplying the 3rd column by two and dividing the 2nd column in half.

The characteristic roots of the matrices $(R'R)$ for the three isomers are as follows:

	Isomer I	Isomer II	Isomer III
x_1	48.87	42.19	55.11
x_2	10.50	31.06	20.47
x_3	6.63	17.93	7.74
x_4	24.00	7.82	6.68
$\Sigma\sqrt{x_i}$	17.71	19.07	17.10

Comparison of $\Sigma\sqrt{x_i}$ shows that isomer II should be appreciably more stable than the others. Structural data on the constitution of molecules $SeAr_2X_2$ (^{2}), where Ar—C_6H_5 or $CH_3C_6H_5$, and X = Cl or Br, confirm the calculation presented. In these molecules the aryl radicals occupy positions 2,4, and the halogens 1,2, since the overlap integrals for the σ-bond Se—C are larger than for Se—X (see above). Isomers for mixed halides of Te(IV) and Se(IV) likewise have not been described (^{1}).

4. Trigonal bipyramid. Molecules MX_3Y_2 having the structure of a trigonal bipyramid may have three isomers, as is seen from Fig. 2: 1) the Y atoms are in positions 1,2, and X in 3,4,5. 2) the Y atoms are in positions 1,3, X in 2,4,5. 3) Y in 3,4, and X in 1,2,5.

The matrix R for isomer I has the form:

$$R(I) = \begin{array}{c} s \\ p_x \\ p_y \\ p_z \\ d_{z^2} \\ d_{x^2-y^2} \\ d_{xy} \end{array} \begin{pmatrix} 2 & 2 & 1 & 1 & 1 \\ 0 & 0 & \sqrt{3} & -\sqrt{3}/2 & -\sqrt{3}/2 \\ 0 & 0 & 0 & 3/2 & -3/2 \\ 2\sqrt{3} & -2\sqrt{3} & 0 & 0 & 0 \\ 2\sqrt{5} & 2\sqrt{5} & -\frac{1}{2}\sqrt{5} & -\frac{1}{2}\sqrt{5} & -\frac{1}{2}\sqrt{5} \\ 0 & 0 & \frac{1}{2}\sqrt{15} & -\frac{1}{4}\sqrt{15} & -\frac{1}{4}\sqrt{15} \\ 0 & 0 & 0 & -\frac{3}{4}\sqrt{5} & -\frac{3}{4}\sqrt{5} \end{pmatrix}.$$

The matrix R for isomer II is found by dividing and multiplying by two the second and third columns, and the matrix for isomer III by dividing by two the 1st and 2nd columns and multiplying by two the 3rd and 4th. The characteristic roots of the products $(R'R)$ are as follows:

	Isomer I	Isomer II	Isomer III
x_1	49.27	44.79	41.27
x_2	24.00	31.22	39.55

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

	Isomer I	Isomer II	Isomer III
x_3	10.13	10.13	10.10
x_4	10.13	8.54	6.00
x_5	5.40	4.33	2.10
$\Sigma\sqrt{x_i}$	20.60	20.46	19.78

The most stable should be isomer I; isomer II is somewhat less stable than I, while isomer III proves to be the least stable.

The following mixed halides of phosphorus and antimony have been described (^{1}): PF_3Cl_2, PF_3Br_2, PF_3I_2, PCl_2Br_3, PCl_3Br_2, SbF_2Cl_3, and all of them are known only in the form of a single isomer. An X-ray structural study of PCl_2F_3 (^{2}) showed that the Cl atoms are arranged along the z axis, and the F atoms in the equatorial plane, i.e., isomer I is indeed the most stable. Data on the structures of other mixed halides are lacking; however, the absence of geometrical isomers in all such compounds speaks in favor of the calculation performed.

Fig. 1

5. Hexagonal bipyramid. Complex uranium compounds $UO_2X_4Y_2$ have the structure of a hexagonal bipyramid, with the ligands located at the vertices of a hexagon perpendicular to the O—U—O bond line. Such compounds should have three isomers—ortho, meta, and para—as do the corresponding benzene derivatives.

In the formation of six σ-bonds with ligands, the $s-$, p_z-, p_x-, p_y-, $d_{z^2-dx^2-y^2}-$, $d_{xy}-$, and $f_{x(x^2-y^2)}$-valence orbitals of uranium may participate. Taking account of the overlap of these orbitals with the valence orbitals of the ligands X and Y under the same assumptions as before (it is assumed that the M—Y bond is twice as strong as the M—X bond, and that the overlap integrals are proportional to the angular parts of the central-atom orbitals) led to the following results:

	Ortho isomer	Para isomer	Meta isomer
$\Sigma\sqrt{x_i}$	31.65	31.64	31.61

Thus, for molecules or ions $UO_2X_4Y_2$ all three isomers should be close in stability.

Fig. 2

Theoretical consideration of the relative stability of isomers of compounds of the type $MX_{k-2}Y_2$ by the method of maximum overlap leads to the conclusion that, for square, octahedral, and hexagonal arrangements of ligands, all geometrical isomers have approximately the same stability and can be realized synthetically. By contrast, compounds with configurations of a distorted tetrahedron (symmetry C_{2v}) and a trigonal bipyramid should have only one stable isomer, and not all those possible from the standpoint of molecular geometry, owing to significant differences in their relative stability.

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