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# THE ROLE OF NONBONDED INTRAMOLECULAR INTERACTIONS ON MOLECULAR GEOMETRY AND ISOMERISM IN OCTAHEDRAL TITANIUM (IV) COMPLEXES

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A stereochemical model based upon the nonbonded interactions of donor atoms in the coordination sphere of a central atom is used to calculate the bond angles in octahedral titanium (IV) complexes of known structure. The model provides a set of criteria for estimating the conditions under which nonbonded intramolecular interactions are a factor in determining molecular geometry; a set of steric criteria for predicting which isomers of a complex should form preferentially is also presented. These criteria are used to account for the observed isomers of octahedral titanium (IV) complexes in which nonbonded intramolecular interactions are deemed significant.

## INTRODUCTION

Several studies have been made on octahedral titanium (IV) complexes, and it has been found that usually only one or two of several possible isomeric configurations for these molecules exist.<sup>1-9</sup> This preferential isomer formation has been discussed in terms of  $\pi$ -bonding, symmetry, statistical distributions, and steric effects.<sup>1-3</sup> The  $\pi$ -bonding argument has been applied the most widely to these structures; however, it will be shown here that for those complexes in which the nonbonded intramolecular interactions of the donor atoms around the central titanium atom are considered significant, the observed molecular geometry and isomerism are consistent with criteria given by a nonbonded interaction model.

## DISCUSSION AND RESULTS

### *Deviations from Regular Octahedral Geometry*

A stereochemical model for analyzing molecular geometry in terms of the nonbonded interactions of donor atoms around a central atom has been previously applied to the molecular complexes of tin.<sup>10</sup> This model, which may be applied generally to a central atom, assigns to each donor atom a conic region of space in the coordination sphere of the central atom. That region is described by a steric angle,  $\theta$ , which is defined by the relationship,  $\theta = 2 \arcsin \frac{A}{B}$ , where,

$A$  = van der Waals radius of the donor atom.

$B$  = sum of the covalent radii of the donor and central atoms. (Experimental bond lengths may be substituted, if known).

The molecular model for a particular isomer is then constructed by evenly distributing the steric angles around the central atom such that the distance (or overlap) between adjacent conic surfaces is equalized. The model may be used to estimate the bond angles around a central atom, investigate trends in central atom-donor bond lengths for a series of similar molecules, and provide a means of comparing steric interactions in different isomeric configurations.

Inherent in this approach is the neglect of secondary bonding and electronic effects of the central atoms and ligands.<sup>11</sup> Thus, this approach requires that applications of the model be limited to those cases in which the sum of the nonbonded repulsive interactions around a central atom are greater in magnitude than the sum of the energetic contributions due to molecular electronic effects other than those attributable to the formation of simple covalent bonds. There does exist, in terms of the nonbonded interaction model presented here, a convenient criterion for estimating whether such nonbonded interactions are likely to be dominant in a given octahedral complex. Let the octahedral distribution of ligand donor atoms be examined in terms of the three planar cross-sections

through the molecule which contain four donor atoms and the central atom. Then, if the sum of the four steric angles (derived from covalent radii) in such a plane is less than  $360^\circ$ , this implies that the van der Waals surfaces of adjacent donor atoms in that plane will not overlap to any appreciable extent in the molecule. *If the sum of the steric angles in each of the three planes is less than  $360^\circ$ , then nonbonded interactions are not likely to play a governing role in determining molecular geometry and isomerism.*

It will first be shown that nonbonded interactions around an octahedrally coordinated titanium atom can directly affect molecular geometry. This will be accomplished by applying the stereochemical model mentioned above to two octahedral complexes of titanium (IV) for which the detailed molecular structure is known, namely, the binuclear species,<sup>12</sup>  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ , and dichlorobis-(8-hydroxyquinolato)titanium (IV),<sup>13</sup>  $\text{TiCl}_2 \cdot 2\text{oxin}$ . Figure 1

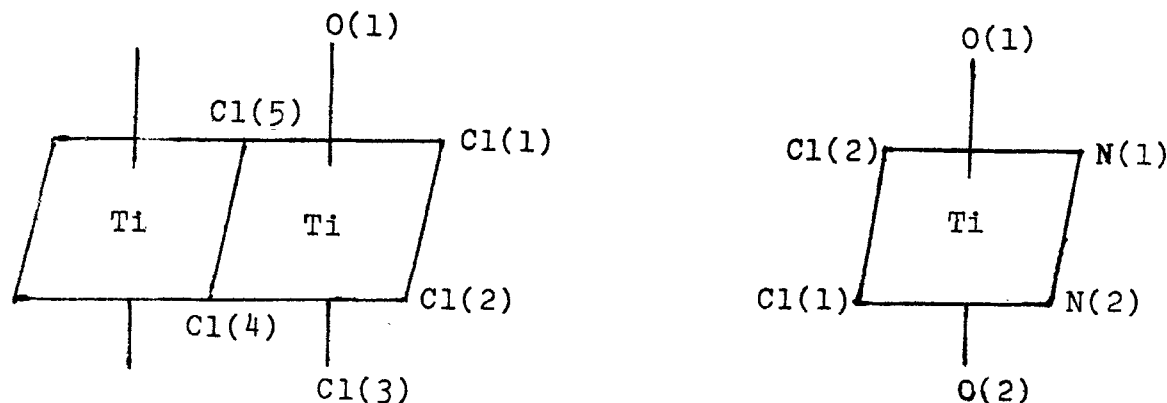


FIGURE 1 Structure and Labeling Schemes for  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$  and  $\text{TiCl}_2 \cdot 2\text{oxin}$ .

shows the molecular geometry and labeling schemes for the  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$  and  $\text{TiCl}_2 \cdot 2\text{oxin}$  molecules. The Ti—Cl, Ti—Cl(bridging), and Ti—O bond lengths in  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ , and the Ti—Cl, Ti—N, and Ti—O bond lengths in  $\text{TiCl}_2 \cdot 2\text{oxin}$  have each been averaged, and used to calculate steric angles. The steric angles obtained from these bond lengths were used to calculate the bond angles around the central titanium atoms in the two complexes. The averaged bond lengths and steric angles used in these calculations are listed in Table I.

The construction of the model assumes that a molecule is stereochemically nonrigid, and that the optimum orientation of the donor atoms depends

TABLE I.

Averaged bond lengths and steric angles used in the calculation of bond angles in  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$  and  $\text{TiCl}_2 \cdot 2\text{oxin}$ .

Compound	Averaged bond length (Å)	Steric angle <sup>o</sup>	
$(\text{TiCl}_4 \cdot \text{POCl}_3)_2^*$	Ti—Cl	2.22	108 <sup>o</sup>
	Ti—Cl (bridging)	2.49	93 <sup>o</sup>
	Ti—O	2.10	84 <sup>o</sup>
$\text{TiCl}_2 \cdot 2\text{oxin}^b$	Ti—Cl	2.283	106 <sup>o</sup>
	Ti—O	1.888	96 <sup>o</sup>
	Ti—N	2.20	86 <sup>o</sup>

\* Reference 12. <sup>b</sup> Reference 13. <sup>o</sup> There is no difference in the magnitude of solid steric angles and the steric angles used in planar representations. The van der Waals radii used in the calculations are taken from L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 260.

only upon the nonbonded interactions in the coordination sphere of the central atom. These conditions do not completely hold for the two complexes under consideration, since the positions of some donor atoms in the coordination sphere are interrelated by the external influences of chelation or bridging. Therefore, the criterion of stereochemical nonrigidity does not apply to these externally linked donor atoms. This complicating feature has been circumvented by keeping the experimentally determined bond angle between the linked donor atoms as an invariable parameter in the calculations. The evenly-spaced distribution of the steric angles around an octahedrally coordi-

nated central atom may be facilitated by considering the three dimensional representation as a composite based upon the distribution of steric angles in the three planar cross-sections which contain four donor atoms and the central atom. This separation of the problem into planar sections is applied to the determination of molecular geometry, and also the analysis of the effects of nonbonded interactions on isomerism presented here. It can be seen from a comparison of the calculated and observed bond angles in Table II that the molecular geometry of

mined structure that is known to the author. While it cannot be concluded that nonbonded interactions are necessarily dominant in this case, the predicted molecular geometry<sup>16</sup> and isomeric configuration are still found to be in accord with experiment.

#### Isomerism

The magnitude of the nonbonded interactions in the coordination sphere of the central atom varies with the geometric arrangement of the donor atoms. Therefore, the geometric isomers

TABLE II  
Comparison of calculated and observed bond angles in  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$  and  $\text{TiCl}_2 \cdot 2 \text{oxin}$

Bond angle <sup>o</sup>	$(\text{TiCl}_4 \cdot \text{POCl}_3)_2^a$ Calculated	Observed <sup>d</sup>	Bond angle <sup>o</sup>	$\text{TiCl}_2 \cdot 2 \text{oxin}^b$ Calculated	Observed
Cl(1)—Ti—Cl(2)	99°	98.2°	Cl(1)—Ti—Cl(2)	100°	97°
Cl(2)—Ti—Cl(3)	100°	96.8°	Cl(1)—Ti—N(2)	90°	91°
Cl(2)—Ti—Cl(4)	92°	91.0°	Cl(1)—Ti—O(1)	98°	100°
Cl(3)—Ti—Cl(4)	92°	92.0°	O(1)—Ti—N(2)	88°	— <sup>e</sup>
Cl(2)—Ti—O(1)	88°	87.8°	N(1)—Ti—N(2)	80°	— <sup>e</sup>
Cl(4)—Ti—O(1)	80°	82.6°			

<sup>a</sup> Reference 12. <sup>b</sup> Reference 13. <sup>c</sup> Labeling is consistent with Figure 1. <sup>d</sup> Bond angles that are equivalent by assuming  $c_2$  symmetry for the arrangement of donor atoms have been averaged. <sup>e</sup> No values for these bond angles were given in the communication.

these two titanium complexes may be reproduced in detail by a nonbonded interaction model. That nonbonded interactions exert strong influences on these molecular geometries is consistent with the sums of the steric angles, the nonbonded interatomic distances in the coordination sphere, which are slightly less than the sum of the van der Waals radii of adjacent donor atoms, and also, the fact that the  $3d^0$  electronic configuration of titanium (IV) imparts no special geometric requirements on the arrangement of ligands around the central atom.

Recently the detailed structures of the edge-bridged  $\text{Ti}_2\text{Cl}_{10}^{2-}$  and face-bridged  $\text{TiCl}_9^{2-}$  ions have been determined.<sup>14</sup> By estimating the different steric requirements for bridging and terminal chlorine atoms in these ions, it is found that the distortions in the coordination sphere of the central titanium atoms determined by the non-bonded interaction model are also in agreement with the observed deviations from the regular, octahedral geometry.

Finally, for the sake of thoroughness, it is of some interest to mention  $[\text{TiCl}(\text{acac})_2]_2\text{O}$ ,<sup>15</sup> the only other octahedral titanium complex of deter-

of a particular complex may differ in the extent of their total nonbonded repulsive interactions. When the intramolecular nonbonded distances between adjacent atoms are less than the sums of van der Waals radii, as is generally found for the titanium (IV) complexes under discussion, the nonbonded interactions lie in the exponentially repulsive region of the interatomic potential and are very sensitive to small positional changes. Consequently, small differences in the overlap of steric angles will correspond to large differences in the magnitude of the nonbonded repulsive interactions between atoms. In such cases where a steric model is applicable, the isomer which forms preferentially should be the one which minimizes the nonbonded interactions. This minimization criterion may be conveniently evaluated for an octahedral complex by summing the values of the four steric angles in the three mutually perpendicular planar cross-sections of the coordination sphere that contain four donor atoms and the central atom. Since the magnitude of the nonbonded repulsive interactions increases rapidly with the sum of the steric angles, selecting one isomer preferentially

over another will, for the most part, depend only upon a comparison of the planes with the largest sums of steric angles. *The isomer that is the least likely to exist will contain the plane which has the largest sum of steric angles.* If two competing isomers have the same values for their largest sums, then their next largest sums of steric angles may be compared to determine which isomer is preferred sterically.

The possible geometric arrangements of donor atoms around the octahedrally coordinated titanium atoms in  $\text{TiCl}_2 \cdot 2\text{oxin}$  and  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$  are shown in Figures 2 and 3, respectively.<sup>17</sup> Applying the observed bond lengths in these complexes to the calculation of steric angles (see Table I for the individual values), the degree of steric crowding in the three planar cross-sections of each isomer is estimated by the sums of the steric angles listed in Table III.

The sums of the steric angles in the three planar sections for each isomer are listed in the order of decreasing magnitude. It is found that for  $\text{TiCl}_2 \cdot 2\text{oxin}$ , the largest-sum plane of isomer I has a value which is less than the values for the largest-sum planes of the other isomers; hence, it is predicted that isomer I would form preferentially. This prediction agrees with experiment. Although only one isomer of  $\text{TiCl}_2 \cdot 2\text{oxin}$  has been observed to date, it may be noted that the unobserved isomers may still be ranked comparatively, according to the extent of their nonbonded interactions in the coordination sphere. Under the constraints of two *cis*-bridging chlorine atoms, there exist only two geometric arrangements for the donor atoms around titanium in  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ . A comparison of the data in Table II shows that the predicted isomer, VI, is also the experimentally observed isomer.

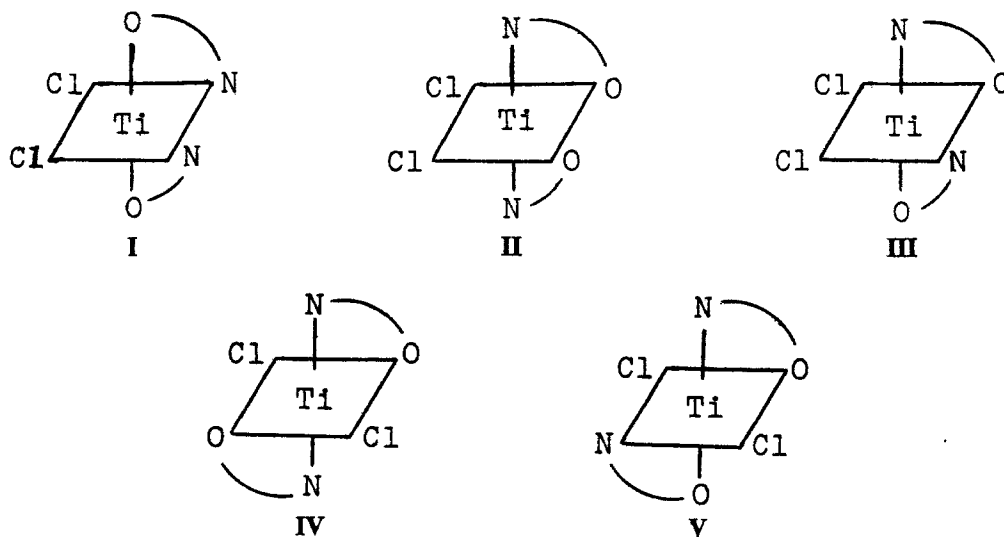


FIGURE 2 Possible octahedral isomers for  $\text{TiCl}_2 \cdot 2\text{oxin}$ .

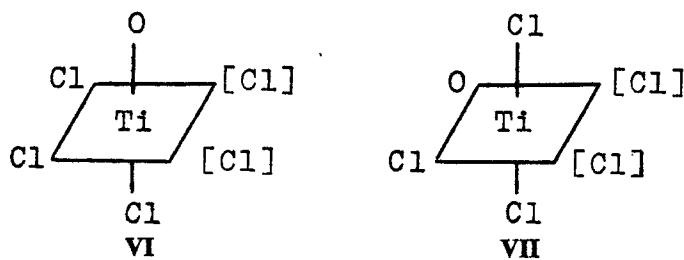


FIGURE 3 Possible isomeric configurations for the octahedral environment around one of the titanium atoms in  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ . The *cis* bridging chlorides are indicated by brackets.

TABLE III

Analysis of preferred isomers for  $\text{TiCl}_2 \cdot 2\text{oxin}$  and  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ , based on the sums of steric angles in planar sections through the central titanium atom.

Complex	Isomer <sup>a</sup>	Sums of steric angles	Predicted isomer	Observed isomer
$\text{TiCl}_2 \cdot 2\text{oxin}$	I	384°, 384°, 384°	I <sup>d</sup>	I <sup>b</sup>
	II	404°, 374°, 374°		
	III	394°, 384°, 374°		
	IV	404°, 384°, 364°		
	V	394°, 394°, 364°		
$(\text{TiCl}_4 \cdot \text{POCl}_3)_2$	VI	402°, 393°, 393°	VI	VI <sup>c</sup>
	VII	417°, 393°, 378°		

<sup>a</sup> Isomer numbers are consistent with Figures 2 and 3. <sup>b</sup> Reference 13. <sup>c</sup> Reference 12. <sup>d</sup> Sums of steric angles for each isomer are listed in the order of descending magnitude. Thus, a comparison of the sums of the steric angles in the first column is used to predict which isomer forms preferentially.

The octahedral species,  $\text{TiCl}_4\text{Br}_2^{2-}$ ,  $\text{TiCl}_4\text{I}_2^{2-}$ , and  $\text{TiCl}_2\text{Br}_4^{2-}$  have been prepared and reported to have the *cis*-configuration.<sup>7</sup> It has been noted elsewhere<sup>10</sup> that for complexes of the type  $\text{MA}_4\text{B}_2$ , the steric argument leads to a preference for the *cis*-configuration, regardless of whether *A* or *B* is the larger donor atom.<sup>19</sup> Thus, the predictions of a nonbonded interaction model agree with the observed *cis* geometries of the mixed halogen complexes,  $\text{TiCl}_4\text{Br}_2^{2-}$ ,  $\text{TiCl}_4\text{I}_2^{2-}$ , and  $\text{TiCl}_2\text{Br}_4^{2-}$ . Also, several octahedral titanium (IV) complexes of the type  $\text{TiF}_4 \cdot 2\text{L}$ , or  $\text{TiF}_4 \cdot \text{LL}'$  have been synthesized and characterized.<sup>2,3</sup> It has been found that these complexes exist predominantly in the *cis*-configuration, except for those cases where two bulky ligands have steric requirements beyond the donor atoms that necessitate the *trans*-configuration.<sup>2</sup> This preference for the *cis*-configuration is consistent with the nonbonded interaction approach, however, the presence of four small fluorine atoms in the coordination sphere of these tetrafluoride complexes leads to sums of steric angles in the molecular planar cross-sections that are less than 360°. Thus, nonbonded interactions in these complexes do not necessarily govern molecular geometry or isomerism.

The recent experimental study by Borden and Hammer<sup>1</sup> on the formation of octahedral titanium (IV) complexes in the  $\text{TiCl}_4$ - $\text{TiF}_4$ -tetrahydrofuran (THF) system provides excellent data upon which to further test the steric criterion of isomer

formation. This study confirmed the presence of various isomers of  $\text{TiF}_4 \cdot 2\text{THF}$ ,  $\text{TiClF}_3 \cdot 2\text{THF}$ ,  $\text{TiCl}_2\text{F}_2 \cdot 2\text{THF}$ , and  $\text{TiCl}_3\text{F} \cdot 2\text{THF}$ . The possible isomers of each of these complexes are shown in Figures 4 through 7, respectively. Since the detailed molecular geometries of these complexes are not known, the steric angles used to represent the chlorine, fluorine, and oxygen (THF) donor atoms are derived from bond lengths obtained by summing the covalent radii of donor and central atoms. The covalent radii and steric angles used in the analysis of these complexes are listed in Table IV. The sums of the

TABLE IV

Values of steric angles obtained from bond lengths derived from covalent radii used in the analysis of  $\text{TiF}_x\text{Cl}_{4-x} \cdot 2\text{THF}$  complexes.

Steric angle	Covalent radii <sup>a</sup>	van der Waals radii <sup>b</sup>
	Ti 1.34 Å	
Ti—Cl 103°	Cl .99 Å	Cl 1.8 Å
Ti—F 83°	F .72 Å	F 1.35 Å
Ti—O 86°	O .73 Å	O 1.4 Å

<sup>a</sup> R. T. Sanderson, "Inorganic Chemistry," Reinhold Publishing Corp., New York, N.Y., 1967, p. 74.

<sup>b</sup> L. Pauling, "Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, 1960, p.260.

steric angles in the three planar sections for each isomer are listed in Table V, along with the structural assignments of both the nonbonded interaction model and the fluorine-19 magnetic resonance spectra. It is assumed in the discussion that only the donor atom of tetrahydrofuran produces nonbonded interactions that affect molecular geometry.

The isomer predicted for  $\text{TiF}_4 \cdot 2\text{THF}$  is the *cis*-configuration, VIII, which is in agreement with the unambiguous F-19 nmr assignment.<sup>1</sup> An examination of the steric angle sums in Table V, however, indicates that nonbonded interactions do not necessarily represent the dominant factor in determining the molecular geometry and preferred isomers of  $\text{TiF}_4 \cdot 2\text{THF}$ . The isomer predicted for  $\text{TiClF}_3 \cdot 2\text{THF}$  according to the steric criterion is XI, which is not in agreement with the nmr structure assignment, X. It must be noted, however, that the first order fluorine-19 magnetic resonance spectra of all three  $\text{TiClF}_3 \cdot 2\text{THF}$  isomers are identical, and that the structural assignment from the fluorine-19

nmr data required, in turn, a difficult assignment for the  $\pi$ -bonding order of the three different ligands. On the other hand, although the structural assignment on steric grounds is clear, the argument for this complex shall not be pursued vigorously, since the sum of the steric angles in any one plane

of a particular isomer of  $\text{TiClF}_3 \cdot 2\text{THF}$  is slightly less than  $360^\circ$ , which indicates that the total non-bonded repulsive interactions may not be large.

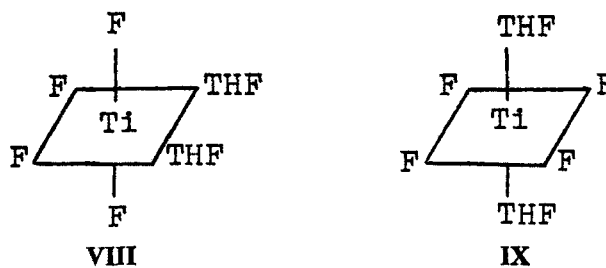
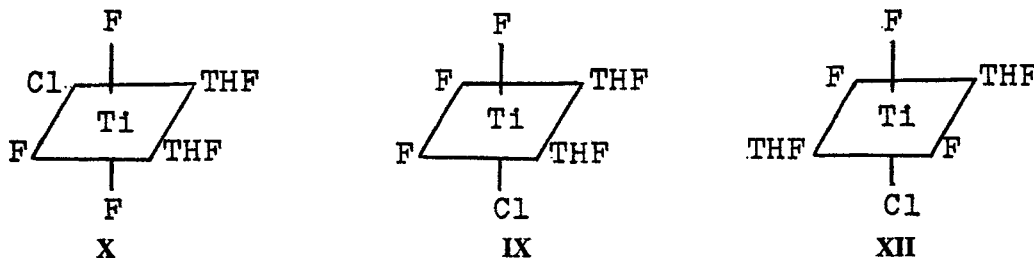
The analysis of the preferred isomers of  $\text{TiCl}_2\text{F}_2 \cdot 2\text{THF}$  provides particularly strong evidence for the validity of the nonbonded interaction

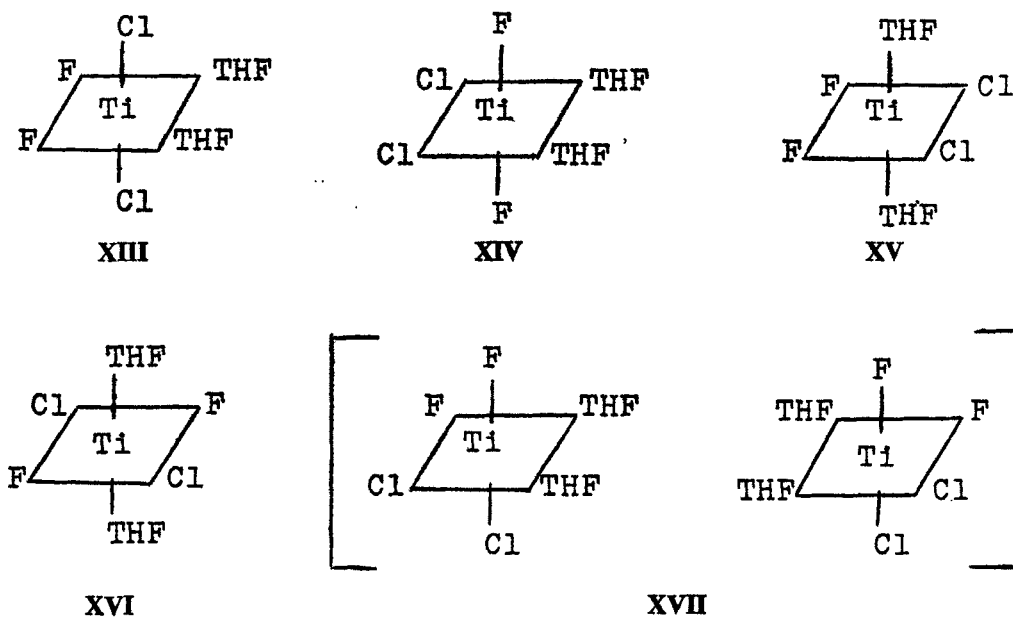
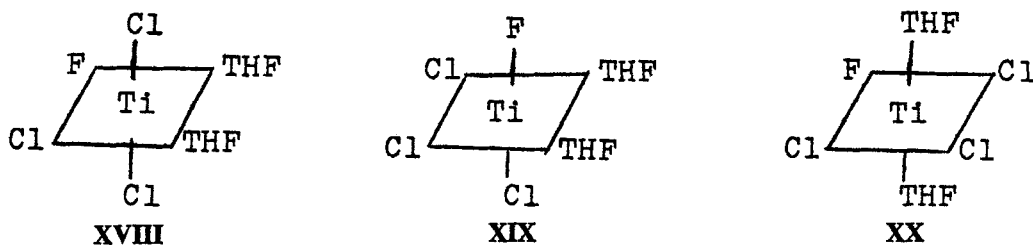
TABLE V

Analysis of preferred isomers for the octahedral  $\text{TiF}_x\text{Cl}_{4-x} \cdot 2\text{THF}$  complexes

Complex	Isomer	Sum of steric angles	Predicted isomer	F-19 nmr assignment*
$\text{TiF}_4 \cdot 2\text{THF}$	VIII	$338^\circ, 335^\circ, 335^\circ$	VIII	VIII
	IX	$338^\circ, 338^\circ, 332^\circ$		
$\text{TiClF}_3 \cdot 2\text{THF}$	X	$358^\circ, 355^\circ, 335^\circ$	XI	X
	XI	$355^\circ, 355^\circ, 338^\circ$		
	XII	$358^\circ, 352^\circ, 338^\circ$		
$\text{TiCl}_2\text{F}_2 \cdot 2\text{THF}$	XIII	$375^\circ, 375^\circ, 338^\circ$	XV (1) XVII(2)	(XIV, or XV, or XVI) and XVII
	XIV	$378^\circ, 355^\circ, 355^\circ$		
	XV	$372^\circ, 358^\circ, 358^\circ$		
	XVI	$378^\circ, 372^\circ, 338^\circ$		
	XVII	$375^\circ, 358^\circ, 355^\circ$		
$\text{TiCl}_3\text{F} \cdot 2\text{THF}$	XVIII	$395^\circ, 375^\circ, 358^\circ$	XIX	XIX or XX
	XIX	$378^\circ, 375^\circ, 375^\circ$		
	XX	$392^\circ, 378^\circ, 358^\circ$		

\* Reference 1.

FIGURE 4 Possible octahedral isomers for  $\text{TiF}_4 \cdot 2\text{THF}$ .FIGURE 5 Possible octahedral isomers of  $\text{TiClF}_3 \cdot 2\text{THF}$ .

FIGURE 6 Possible octahedral isomers for  $\text{TiCl}_2\text{F}_2 \cdot 2\text{THF}$ .FIGURE 7 Possible octahedral isomers for  $\text{TiCl}_3\text{F} \cdot 2\text{THF}$ .

approach to preferential isomer formation. It was ascertained from the resonance spectra that two isomers of  $\text{TiCl}_2\text{F}_2 \cdot 2\text{THF}$  form, XVII, and (XIV, XV, or XVI). The steric analysis predicts that XV is the preferred isomer, with XVII as the second most likely. This assignment is consistent with the F-19 nmr assignment; it also correlates significantly with the finding of Borden and Hammer that the observed isomer ratio (XIV, XV, or XVI): XVII is 9:2, which presumably indicates a predominance of the sterically favored isomer.

Finally, the nmr structural assignment for the existing isomer of  $\text{TiCl}_3\text{F} \cdot 2\text{THF}$  is either XIX or XX. A comparison of the sums of the steric angles for the three isomers of  $\text{TiCl}_3\text{F} \cdot 2\text{THF}$ , not only indicates that XIX is preferred, but that the assignment

should be unequivocal, since an examination of the steric angle sums in Table V indicates that bonded repulsive interactions in both XVIII and XX must be much greater than the repulsive interactions in XIX.

#### ACKNOWLEDGEMENT

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#### REFERENCES

1. R. S. Borden and R. N. Hammer, *Inorg. Chem.* **9**, 2004 (1970).
2. E. L. Muetterties, *J. Amer. Chem. Soc.* **82**, 1082 (1960).



3. D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.* **8**, 1116 (1969).
4. D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966).
5. D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.* **6**, 8 (1967).
6. D. S. Dyer and R. O. Ragsdale, *J. Phys. Chem.* **71**, 2309 (1967).
7. R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.* **7**, 1603 (1968).
8. R. C. Fay and R. N. Lowry, *Inorg. Chem.* **6**, 1512 (1967).
9. N. Serpone and R. C. Fay, *Inorg. Chem.* **6**, 1835 (1967).
10. R. F. Zahrobsky, *J. Amer. Chem. Soc.* **93**, 3313 (1971).
11. It has been pointed out<sup>10</sup> that this model is the counterpart of the Gillespie-Nyholm valence shell electron pair repulsion model in that both models disregard the factors upon which the other is based. This simple separation of molecular energies into two parts, non-bonded interactions and the electronic properties of the central atom and ligands, will be warranted if it can be demonstrated that distinguishable cases exist in which one of these factors dominates and governs molecular geometry. This nonbonded interaction model recognizes that ligand atoms are bonded to a central atom and utilizes parameters associated with simple covalent bonding. The model does exclude  $\pi$ -bonding effects, substituent and electronegativity effects, etc., which have been referred to as secondary bonding and electronic effects.
12. C.-I. Branden and I. Lindqvist, *Acta Chem. Scand.* **14** 726 (1960).
13. A. G. Swallow and B. F. Studd, *Chem. Commun.* 1197 (1967).
14. T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.* **10**, 122 (1971).
15. K. Watenpauh and C. N. Caughlan, *Inorg. Chem.* **6**, 963 (1967).
16. The criteria for determining preferred isomeric configurations are presented in the following section. It may be noted, however, that the two possible arrangements of ligands around a titanium atom in  $[\text{TiCl}(\text{acac})_2]_2\text{O}$  may be described as having either a *cis* or *trans* relationship between the chlorine atom and bridging oxygen atom. By taking into account the reduced spatial requirements in the coordination sphere between two oxygen donor atoms on a given acetylacetonate ligand, it may be shown that the *cis* configuration is preferred sterically.
17. Only those isomers which have bridging or chelating donor atoms in a *cis* relationship are considered as plausible.
18. The model relates to nonbonded interactions around one central atom. Thus, it does not make a prediction about the relative *cis* or *trans* disposition of the two  $\text{POCl}_3$  ligands, since they reside on different titanium atoms.
19. The relative values of the steric angle sums obtained in Table V for the *cis* and *trans* isomers of  $\text{TiF}_4 \cdot 2\text{THF}$  is typical of  $\text{MA}_4\text{B}_2$  complexes, where *B* represents a larger donor atom than *A*.