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Ligand Close Packing and the Geometry of the Fluorides of the Nonmetals of Periods 3, 4, and 5

E. A. Robinson[†] and R. J. Gillespie*

Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada

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This paper discusses the geometry of the fluorides of the nonmetals of periods 3, 4, and 5 in terms of the ligand close packing (LCP) model according to which molecular geometry is determined primarily by ligand–ligand repulsions (Pauli closed shell repulsions) rather than by the bonding and lone pair Pauli repulsions of the VSEPR model. The LCP model becomes the dominant factor in determing geometry when the ligands are sufficiently crowded that they may be regarded as essentially incompressible. Ligand close packing is a modification of the VSEPR model in which ligand–ligand repulsion (Pauli closed shell repulsion) is given more emphasis than bonding and nonbonding electron pair Pauli repulsion. The nonmetals of period 3 are large enough to form octahedral six coordinated molecules in which the ligands are close packed. The larger nonmetals of period 4 also have a maximum coordination number of six and an octahedral geometry although the ligands are not close packed. Ligand radii derived from the interligand distances in the molecules of period 3 depend only on the charge of the fluorine ligands and are consistent with the previously derived radii obtained from the fluorides of the close packed tetrahedral molecules of the period 2 elements. Although the ligands in the molecules of the period 4 nonmetals are not close packed, these elements are not large enough to form molecules with a higher coordination number. However, the larger period 5 nonmetals may have coordination numbers of seven and eight. The seven coordinated molecules have a pentagonal bipyramidal geometry in which the equatorial ligands are close packed. The eight coordinated molecules have a square antiprism geometry, which is not a close packed geometry although the fluorine interligand distances are only a little larger than expected for close packing. The difference between the axial and equatorial bond lengths in the trigonal bipyramidal pentafluorides and the pentagonal bipyramidal pentafluorides can be understood on the basis of ligand close packing. Ligand packing prevents the lone pair in AF_6E molecules from fully entering the valence shell and thereby exerting its full stereochemical effect so that these molecules have a C_{3v} distorted octahedral geometry rather than a geometry based on pentagonal bipyramidal seven coordination.

Introduction

The purpose of this paper is to provide a rationale for the geometry of the fluorides of the nonmetals of periods 3 and beyond which have coordination numbers up to six for periods 3 and 4 and up to eight for period 5. It is an extension of previously reported studies on molecules of the nonmetals of period 2 in which we showed that some quantitative aspects of the trigonal and tetrahedral molecules of these elements could be accounted for by means of the ligand close packing (LCP) model.[1−4] This model is based on the observation that the AX_3, AX_4, AX_3E, and AX_2E_2 molecules of the period 2 elements have an almost constant X···X distance for two given ligands X (= F, Cl, O) bonded to a given central atom A (= B, C, N, and O). This constant interligand distance is independent of the coordination number and of the number of lone pairs E showing that the ligands may be regarded as close packed around the central atom as was first suggested by Bartell for some carbon compounds.[5,6] Each ligand can be assigned an essentially constant ligand radius equal to one-half the interligand

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* To whom correspondence should be addressed. E-mail: gillespi@mcmaster.ca.

[†] Present address: 35 Beach Road West, Portishead, Bristol BS 20 7HX, U.K.

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X⋯X distance that depends only on the nature of the central atom A. The sum of their ligand radii can be used to predict the interligand distance for two different ligands X and Y with good accuracy. In the LCP model, emphasis is placed on ligand−ligand repulsions (Pauli closed shell repulsions) rather than on the Pauli repulsions between bonding and nonbonding electron pairs as in the VSEPR model. Ligand−ligand repulsions dominate when the ligands are packed so closely that they become essentially incompressible. Lone pairs play the same role in the LCP model as in the VSEPR model, although they cannot be assigned a constant radius because they spread out to the maximum possible extent around the central core pushing the ligands together until their mutual repulsion prevents them coming closer together, which for incompressible ligands is when the interligand distance equals the sum of the respective ligand radii. It is convenient therefore to use the term coordination number to include both ligands and lone pairs so that AX_6 and AX_5E molecules are, for example, both referred to as six coordinate. The advantage of the LCP model, in those cases where it is applicable, is that it is more quantitative than the VSEPR model, in that interligand distances can be predicted from the ligand radii, and hence bond angles can be predicted when bond lengths are known.

For the molecules of the period 2 elements, decreasing the coordination number from 4 to 3, while keeping the ligands close packed, necessarily decreases the length of a given bond. For example, the length of the BF bond in BF_3 (130.7 pm) is shorter than that in BF_4^- (138.2 pm) by just the amount needed to keep the ligands close packed. No electronic explanation of this decrease in bond length, such as back-donation from fluorine leading to double bond character in the BF bond in BF_3, is needed.

We have restricted this study to fluorides because they are the commonest of the higher coordination number molecules of the nonmetals so that many fewer data are available for molecules with other ligands. Moreover, fluorine is expected to be less compressible than the other halogens, and very probably than any other ligand, so it is most likely that the geometry of fluorides will be primarily determined by the LCP model.

In this paper, we show that the octahedral six coordinate fluorides of period 3 have close packed ligands and that the equatorial ligands of the seven coordinate pentagonal bipyramidal fluorides of the period 5 elements are also close packed. We also show that the LCP model provides a rationale for why the maximum coordination number for the elements of period 2 is four, whereas it is six for periods 4 and 5 and eight for period 5.

Six Coordinate Fluorides of Period 3

Whereas the maximum coordination number (including lone pairs) of the period 2 elements is four, the larger period 3 elements may have coordination numbers up to six. Close packing of six ligands around a central atom gives the observed octahedral geometry. The interligand distances in AF_6, AF_5Y, and AF_5E molecules of Si, P, S, and Cl are given in Table 1. The F⋯F distances are almost constant, for a given central atom as expected for close packing. The ligand radii of F, r(F) = $^1/_2$(F⋯F), bonded to Si, P, S, and Cl, respectively, are given in the table. These ligand radii decrease across period 3 from 119 pm for fluorine bonded to Si to 110 pm for fluorine bonded to Cl as expected from the increasing electronegativity of A and the consequent decrease in the negative charge on the ligand. These radii agree well with radii deduced for the period 2 fluorides taking into account the differences in the fluorine atomic charge as shown in Figure 1 which shows a plot of the ligand radius

Table 1. Bond Lengths, Bond Angles, and F⋯F Interligand Distances in Some Period 3 Six Coordinate Fluorides[a]

molecule	A−F$_{ax}$ (pm)	A−F$_{eq}$ (pm)	∠F$_{ax}$AF$_{eq}$ (deg)	∠F$_{eq}$AF$_{eq}$ (deg)	F⋯F (pm)	ref[b]
Silicon						
SiF_6^{2-}	168.4		90	90	238, 238	1
SiF_4(dipy)	165.7	163.1	93.1	97.4	239, (245)[c]	2
$SiF_5NH_3^-NH_4^+$	168.0	167.8	90.4	90.1	238, 237	3
$SiF_4(NH_3)_2$ (trans)		167.1		90.0		3
					av = 238 r(F) = 119	
Phosphorus						
PF_6^-	158.0		90	90	224, 224	4
PF_5py	158.2	158.9	91.8	88.4	228, 222	5
$PF_5H^-NMe_4^+$	159.4	159.5	88.8	90.0	223, 226	6
$PF_5.NH_3$	158.2	159.5	91.5	89.6	228, 225	7
					av = 224 r(F) = 112	
Sulfur						
SF_6	156.2	156.2(4)	90	90	221 221	8
SF_5Cl	158.8 (9)	156.3(3)	89.3	90.0	222, 221	9
SF_5Br	159.7(3)	159.7(3)	88.8	90.0	223, 226	10
SF_5OCl	156.0 (2)	156.0(2)	89.6	90.0	221, 221	11
SF_5OCN	155.4 (2)	155.4(2)	90.4	90.0	221, 221	12
SF_5NCO	156.7 (2)	156.7(2)	89.0	90.0	220, 222	13
SF_5CF_3	157.0 (2)	156.0(7)	89.5	90.0	220, 221	14
$SF_5C{\equiv}CH$	157.0(2)	156.0(7)	88.9	90.0	221, 221	15
					av = 221 r(F) = 111	
Chlorine						
ClF_5	157.1	166.9	86.0	89.7	221, (235)[d]	16
ClF_6^+	155.0	155.0	90	90	219, 219	17
					av = 220 r(F) = 110	

[a] All structures included in this table have bond lengths accurate to 1 pm or better and angles accurate to 1° or better. [b] Reference numbers in this table refer to the following references: (1) Average value of 10 undistorted or only very slightly distorted (<1°) structures with equal bond lengths accurate to 0.1 pm (International Crystal Structure Database numbers 23908, 41095, 41538, 59237, 60882, 65778, 72136, 72686, 73722, 75127). (2) Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402. (3) Plitzko, C.; Meyer, G. *Z. Anorg. Chem.* **1996**, *622*, 1646. (4) Average value of six undistorted or only very slightly distorted (<1°) structures with equal bond lengths accurate to 0.1 pm (International Crystal Structure Database numbers 74830, 90615, 90616, 90617, 90618, 203170). (5) Sheldrick, W. *J. Chem. Soc., Dalton. Trans.* **1974**, 1402. (6) Minkwitz, R.; Schneider, S.; Kornath, A. *Inorg. Chem.* **1998**, *37*, 4662. (7) Storzer, W.; Schomburg, D.; Roschenthaler, G.-V.; Schmutzler, R. *Chem. Ber.* **1983**, *116*, 367. (8) Kelly, H. M.; Fink, M. J. *J. Chem. Phys.* **1982**, *77*, 1813. (9) Marsden, C. J.; Bartell, L. S. *Inorg. Chem.* **1976**, *15*, 3004. (10) Neuvar, E. W.; Jache, A. W. *J. Chem. Phys.* **1963**, *39*, 596. (11) Kornath, A.; Hartfield, N.; Oberhammer, H. *Inorg. Chem.* **1997**, *36*, 5156. (12) Zylka, P.; Mack, H.-G.; Schmuck, A.; Seppelt, K.; Oberhammer, H. *Inorg. Chem.* **1991**, *30*, 59. (13) Oberhammer, H.; Seppelt, K.; Mews, R. *J. Mol. Struct.* **1983**, *101*, 325. (14) Marsden, C. J.; Christen, D.; Oberhammer, H. *J. Mol. Struct.* **1984**, *131*, 299. (15) Császár, A. G.; Hedberg, K.; Terjeson, R. J.; Gard, G. L. *Inorg. Chem.* **1987**, *26*, 955. (16) Altman, A. B.; Miakshin, I. N.; Sukhoverlov, V. F.; Romanov, G. V.; Spiridonov, V. P. *Dokl. Akad. Nauk SSSR.* **1978**, *241*, 360. (17) Christe, K. O.; Lehmann, J. F.; Schrobilgen, G. J. *Inorg. Chem.*, in press. [c] The NSiN angle is only 80.0° so the two fluorine atoms in this plane are not close packed and the F⋯F distance is accordingly larger than 238 pm. [d] The lone pair increases the length of the adjacent bonds in the base of the square pyramid so these ligands are not close packed with each other but only with the axial ligand.

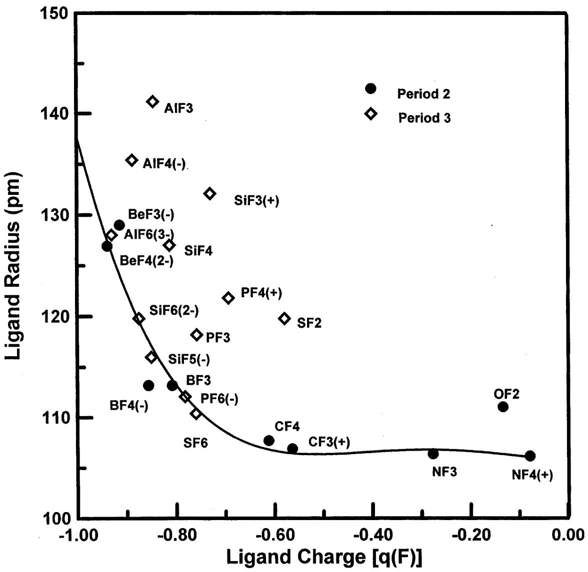

Figure 1. Plot of ligand charge against ligand radius for fluorides of the elements of groups 2 and 3.

of F against its charge. We see that the points for both the period 2 AF_4 molecules and the period 3 AF_6 molecules lie on the same smooth curve confirming that the fluorine ligands in the period 3 AX_6 molecules are indeed close packed as they are in the period 2 AX_4 molecules. The points for the period 3 AF_4 molecules, however, lie above this curve showing that in these molecules the fluorine ligands are not close packed as we discuss in a following section. Figure 1 also shows that as the charge of the fluorine ligand decreases its size decreases and becomes essentially constant for a charge of -0.6 or less.

Five Coordinate Fluorides of Period 3

The geometry of five coordinated molecules cannot be fully predicted by the VSEPR theory. The repelling points-on-a-sphere model (POS) predicts either the trigonal bipyramidal or the square pyramidal geometry for five points depending on the value of the exponent n in the expression for the potential energy which is the sum of the terms $V_{ij} = K/r_{ij}^n$ where K is a constant and r_{ij} is the distance between the points i and j. For large values of n, that is, for the nearly incompressible ligands of the LCP model, the trigonal bipyramid is predicted.[7-9] But the bond lengths are not all the same as is assumed in the points-on-a-sphere model because the axial bonds are invariably found to be longer than the equatorial bonds. However, if a trigonal bipyramidal molecule is considered in terms of the packing of the ligands when these ligands are all at the same distance from the core, the axial ligands are in contact with the equatorial ligands with a ligand−ligand distance of $2^{1/2}a = 1.41a$ where a is the bond length but the equatorial ligands are not in contact with each other with a ligand−ligand distance of $2 \sin 60° = 1.73a$. Thus, because of the smaller repulsion exerted by their equatorial neighbors the equatorial ligands are expected to be attracted closer to the core decreasing the length of the three equatorial bonds while only slightly increasing the length of the two axial bonds until equilibrium is reached, thereby further stabilizing the trigonal bipyramidal geometry. In this geometry, the $X_{eq}\cdots X_{ax}$ distance is expected to be twice the ligand radius of X, $2r(X)$, and the $X_{eq}\cdots X_{eq}$ distance is expected to be larger than $2r(X)$. Thus, the LCP model provides a rationale for the trigonal bipyramidal geometry of five coordinated molecules of the nonmetals in which the axial bonds are longer than the equatorial bonds. The alternative square pyramidal geometry has only been found for a very few main group molecules, in the solid state (none of which are fluorides), and for some transition metal molecules. Intermolecular interactions in the solid state are very probably responsible for the few exceptions among molecules of the main group elements while the geometry of transition metal molecules is affected by the distortion of the core from a spherical shape.[10,11]

Although the bonding in most trigonal bipyramidal molecules, and in particular the fluorides of the main group elements, is very polar and therefore primarily electrostatic in origin, it is frequently discussed in terms of covalent bonds formed by $sp^3d_{z^2}$ hybrid orbitals or in terms of an axial three-center four-electron "semi-ionic" bond, and three covalent trigonal sp^2 bonds. The bonding has also been described in terms of molecular orbitals based only on the s and p orbitals of the central atom and the ligand orbitals. These orbital descriptions of the bonding are sometimes said to explain the trigonal bipyramidal geometry. However, they are all based on the known geometry so that they are not explanations of the geometry.[4] In contrast, the LCP model gives a simple rationalization for the trigonal bipyramidal geometry including the difference in the equatorial and axial bond lengths, which otherwise can only be determined by experiment or by ab initio calculations.

Geometrical parameters for AF_5, AF_4Y, AF_3Y_2, and AF_4E molecules of silicon, phosphorus, and sulfur are given in Table 2. We see that the $A-F_{eq}$ bond lengths are uniformly shorter than the $A-F_{ax}$ bond lengths while the latter are usually similar to the AF bond lengths in the corresponding six coordinated molecules. The ligand radii for fluorine bonded to silicon, phosphorus, and sulfur of 116, 111, and 108 pm obtained from the average $F_{eq}\cdots F_{ax}$ distances are close to, but slightly shorter than, the radii obtained from the six coordinate molecules consistent with the close packing of the axial ligands with the equatorial ligands. That the ligand radii are slightly smaller than in the six coordinate molecules suggests that because the equatorial bonds are shorter and therefore stronger than in the six coordinate molecules the ligands are slightly more strongly compressed and are not strictly incompressible as appears to be the case for the four coordinate molecules of period 2 which have still shorter and stronger bonds. In other words, the conclusion that ligands have a fixed ligand radius, that is the basis

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Table 2. Bond Lengths, Bond Angles and F···F Interligand Distances in Some Five Coordinate Fluorides of Period 3

molecule	$A-F_{ax}$ (pm)	$A-F_{eq}$ (pm)	$\angle F_{ax}AF_{eq}$ (deg)	$F_{ax}\cdots F_{eq}$ (pm)	ref[a]
			Silicon		
$SiF_5^-BzlNMe_3^+$	166	162.2	90.2	232	1
$SiF_4Ph^-NPr_4^+$	169.1	162.6	87.3	229	2
$SiF_4Mes^-K^+$[b]	171.7	156.2	89.3	233	3
$SiF_4C_6H_2{}^tBu_3{}^-K^+$[b]	167.7	162.1	89.5	233	3
$SiF_3{}^-Xyl_2{}^-K^+$[b]	171.4	165.2	87.9	234	4
$SiF_3(Ph){}^tBu^-K^+$[b]	170	163.9	86.1	228	4
$SiF_3(Ph)Me^-N({}^nBu)_4{}^+$	169.5	162.1	87.9	230	5
$SiF_3Ph_2{}^-NMe_4{}^+$	170.5	166.2	86.2	230	1
$SiF_3(o\text{-}Tol)_2{}^-K^+$[b]	170.1	164	87.2	230	4
SiF_3(phenanthroline)	162.1	159	93.7	234	6
$SiF_4NH_2{}^-NH_4{}^+$	167.8	167.8	90	237	7
			av = 231 pm r(F) = 116 pm		
			Phosphorus		
PF_5(g)	157.7	153.4	90	220	8
PF_5(s)	158.5	152.2	90	220	9
PF_4Cl	158.1	153.5	90.3	221	10
PF_3Cl_2	159.3	153.8	90	221	10
PF_3Cl_2	159.3	154.6	89.3	221	11
PF_4Me	161.2	154.3	89.1	221	12
PF_4(2-methylpyrrole)	160.1	153.9	88.1	218	13
PF_3Me_2	164.3	155.3	89.9	226	8
$PF_3(NH_2)_2$	161.9	156	89.5	224	14
			av = 221 pm r(F) = 111 pm		
			Sulfur		
SF_4	164.6	154.5	87.9	222	15
F_3SCH_3	168.1	157.5	87.6	226	16
F_3SCF_3	167.9	159.6	84.1	219	16
F_3SCN	165.7	155.2	86.9	221	17
$F_4S{=}O$	158.4	152.8	85.8	213	18
$F_4S{=}CH_2$ ED	159.5	157.5	86.6	217	19
XR	159.3	156.1	86.8	217	20
$F_4S{=}C(CF_3)Me$	159.0	157.0	86.8	217	21
$F_4S{=}NF$	161.5	156.4	89.1	219	22
	153.5	156.4	87.2	214	
$F_4S{=}NH$[c]	161.1	155.0	85.8	215	22
	156.9	155.0	85.9	213	
$F_4S{=}NMe$	164.3	156.7	85.9	219	23
	154.6	156.7	85.9	212	
			av = 216 pm r(F) = 108 pm		

[a] Reference numbers in this table refer to the following references: (1) Schomburg, D.; Krebs, R. *Inorg. Chem.* **1984**, *23*, 1378. (2) Schomburg, D. *J. Organomet. Chem.* **1981**, *221*, 137. (3) Johnson, S. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1989**, *28*, 3182. (4) Johnson, S. E.; Payne, J. S.; Day, R. O.; Holmes, J. M.; Holmes, R. R. *Inorg. Chem.* **1989**, *28*, 3190. (5) Harland, J. J.; Payne, J. S.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 760. (6) Krebs, G.; Hensen, K.; Fuess, H. *Chem. Ber.* **1983**, *116*, 3125. (7) Plitzko, C.; Meyer, C. *Z. Anorg. Chem.* **1996**, *622*, 1946. (8) Hansen, K. W.; Bartell, L. S. *Inorg. Chem.* **1965**, *4*, 1777. (9) Mootz, D.; Wiebecke, M. *Z. Anorg Chem.* **1987**, *548*, 39. (10) Macho, C.; Minkwitz, R.; Rohmann, J.; Steger, B.; Wölfel, V.; Oberhammer, H. *Inorg. Chem.* **1986**, *25*, 2828. (11) French, R. J.; Hedberg, K.; Shreeve, J. M.; Gupta, K. D. *Inorg. Chem.* **1985**, *24*, 2774. (12) Oberhammer, H.; Grobe, J.; Le Van, D. *Inorg. Chem.* **1982**, *21*, 275. (13) Hewson, M. J.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Chem. Commun.* **1973**, 190. (14) Marsden, C. J.; Hedberg, K.; Shreeve, J. M.; Gupta, K. D. *Inorg. Chem.* **1984**, *23*, 3659. (15) Tolles, M. W.; Gwinn, W. D. *J. Chem. Phys.* **1962**, *36*, 1119. (16) Downs, A. J.; McGrady, G. S.; Bamfield, E. A.; Rankin, D. W. H.; Robertson, H. G.; Boggs, J. E.; Dobbs, K. D. *Inorg. Chem.* **1989**, *28*, 3286. (17) Mack, H.-G.; Oberhammer, H.; Jacobs, J.; Kronberg, M.; Willner, H. *Inorg. Chem.* **1996**, *35*, 806. (18) Hedberg, L.; Hedberg, K. *J. Phys. Chem.* **1982**, *86*, 598. (19) Bock, H.; Boggs, J. E.; Kleeman, G.; Lentz, D.; Oberhammer, H.; Peters, E. M.; Seppelt, K.; Simon, A.; Solonki, B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 944. (20) Buschmann, J.; Koritsanszky, T.; Kuschel, R.; Luger, P.; Seppelt, K. *J. Am. Chem. Soc.* **1991**, *113*, 233. (21) Günther, H,; Oberhammer, H.; Mews, R.; Stahl, I. *Inorg. Chem.* **1982**, *21*, 1872. (22) DesMarteau, D. D.; Eysel, H. H.; Oberhammer, H.; Günther, H. *Inorg. Chem.* **1982**, *21*, 1607. [b] [K-18 crown-6]$^+$. [c] Calculated structure.

of the LCP mode, is not quite so valid for period 3 molecules. Nevertheless, the model, if only semiquantitative, is still very useful for understanding molecular geometry.

In AF_4Y, AF_3Y_2, AF_4E, and AF_3E_2 molecules, the fluorine ligands are always found in the more crowded axial positions. In terms of the LCP model, fluorine adopts this preferred position because it is smaller than other ligands. In terms of the VSEPR model, fluorine ligands always adopt the axial positions because bonding pair domains decrease in size with increasing electronegativity of the ligand and fluorine is the most electronegative ligand. In short, the smaller ligands or the smaller bonding pair domains preferentially occupy the less crowded axial sites.

Table 3. Bond Lengths and Interligand Distances in AX_6 and AX_4 Molecules

	A−X (pm)	X···X (pm)	−q(X)	ref[a]
$SiF_6{}^{2-}$	168	238	0.91	*b*
SiF_4	156	254	0.81	1
$PF_6{}^-$	158	224	0.85	*b*
$PF_4{}^+$	146	238	0.78	2

[a] Reference numbers in this table refer to the following references: (1) Beagley, B.; Brown, D. P.; Freeman. J. M. *J. Mol. Struct.* **1973**, *18*, 337. (2) Casteel, W. J.; Kolb, P.; LeBlond, N.; Mercier, H. P. A.; Dorman, H. B.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2000**, *39*, 1813. [b] From Table 1.

Four Coordinate Fluorides of Period 3

Bond lengths, bond angles, and interligand distances for SiF_4, and $PF_4{}^+$, are compared with those of the corresponding six coordinated molecules in Table 3. In each case, the bond lengths are shorter in the four coordinated molecules than in the six coordinated molecules, but they are not short enough to reduce the interligand distance to the close packed value obtained from the six coordinate molecules. We conclude that in the AF_4 molecules the ligands are not close packed as we have already seen in Figure 1, although the tetrahedral geometry is nevertheless determined by ligand−ligand and bond−bond repulsions. Because the A atom in a period 3 molecule is larger and the bonds therefore longer than those in the corresponding period 2 molecule, they are weaker, and the attractive forces between A and X are not strong enough to bring the four X ligands in a period 3 AX_4 molecule into "contact". The reduction in bond length from the AF_6 molecules to the AF_4 molecules is, however, analogous to that for the period 2 AX_4 and AX_3 molecules. The reduction in the bond length from $SiF_6{}^{2-}$ to SiF_4 has sometimes been "explained" by invoking double bond resonance structures for SiF_4[12] much as they have also been invoked to explain the decrease in bond length from $BF_4{}^-$ to BF_3. However, there is no other evidence for this supposed double bond character which is more reasonably explained on the basis that four ligands can pack more closely than six.

Because the central atom A does not have its maximum coordination number in AX_4 and AX_5 molecules and the ligands are not all close packed, there is space for another ligand so that these molecules are good Lewis acids. Thus, they readily form AX_4Y molecules such as $SiF_5{}^-$ and $PhSiF_4{}^-$ and AX_4Y_2 and AX_5Y molecules such as $SiF_4(py)_2$, $PF_6{}^-$, and PF_5py in the same way that period 2 AX_3 molecules such as BF_3 and BCl_3 readily form AX_3Y molecules such as $BF_3{\cdot}NH_3$ and $BF_4{}^-$.

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Table 4. Bond Lengths for AF_6 Molecules of Periods 4 and 5

molecule	A−X (pm)	F···F (pm)	ref[a]
GeF_6^{2-}	179.4	254	1
AsF_6^-	171.3	242	2
SeF_6	168.4	238	3
BrF_6^+	155	219	4
SnF_6^{2-}	195.9	277	5
SbF_6^-	191.7	271	6
TeF_6	182.4	258	7
	181.5	257	8
IF_6^+	178	252	4

[a] Reference numbers in this table refer to the following references: (1) Averduk, F.; Hoppe, R. *J. Fluorine Chem.* **1990**, *47*, 481. (2) Loss, S.; Roehr, C. *Z. Naturforsch.* **1998**, *B53*, 75. (3) Bartell, L. S.; Jin, A. *J. Mol. Spectrosc.* **1984**, *118*, 47. (4) Lehmann, J. F.; Schrobilgen, G. J. *Inorg. Chem.*, in press. (5) Benne, G.; Hoppe, R. *J. Fluorine Chem.* **1990**, *48*, 219. (6) Preus, H.; Lenhoff, D.; Minkwitz, R. *Acta Crystallogr.* **1992**, *C48*, 1648. (7) Seip, H. M.; Stølevik, R. *Acta Chem. Scand.* **1966**, *20*, 1535. (8) Gundersen, G.; Hedberg, K.; Strand, T. G. *J. Chem. Phys.* **1978**, *68*, 3548.

Although the AX_4 fluorides have interligand distances that exceed the sum of the interligand radii and they cannot therefore be regarded as truly close packed, it has been noted previously by Hargittai[13] that some four coordinate molecules, in particular SO_2X_2 molecules, have a very constant O···O distance of 248 pm suggesting that the oxygen ligands are close packed. However, the F···F distance in SO_2F_2 (228 pm), for example, is appreciably longer than in SF_6 (221 pm) which is not consistent with the close packing of the fluorine ligands in SO_2F_2. Because the SO bonds are quite short and the O···O distance is almost constant, it is quite possible that the O···O distance represents twice the interligand radius of oxygen even though all four ligands are not close packed. However, the constant O···O distance could simply be a consequence of the almost constant OSO bond angle of close to 122° and an almost constant SO bond length of close to 142 pm.

Fluorides of the Elements of Period 4 and Beyond

AF_6 and AF_5 Molecules. Bond lengths for the octahedral AF_6 halides of periods 4 and 5 are given in Table 4. These bond lengths increase from period 3 to 5 with increasing size of the central atom, and the interligand distances increase correspondingly. Given that the ligands in period 3 molecules are close packed, those in period 4 and 5 molecules cannot be close packed. Ligand−ligand and/or bond−bond repulsions, nevertheless, play an important role in determining the octahedral geometry. Although the ligands in period 4 molecules are not close packed because of the larger size of the atoms of the period 4 elements, these atoms are not large enough to allow more than six ligands to be packed around them. However, the atoms of period 5 elements are large enough to have as many as seven and even eight small ligands such as F and O.

Table 5. Seven Coordinate Fluorides of Period 5[a]

molecule	bond length (pm) axial	bond length (pm) equatorial	$\angle F_{eq}AF_{eq}$ (deg)	$\angle F_{ax}AF_{eq}$ (deg)	$F_{eq}\cdots F_{eq}$	ref[b]
$TeF_7^-\ Me_4N^+$	179	186	72	90(3)	219	1
$TeF_6OMe^-\ Me_4N^+$	182.2	191.5	72	90	225	1
$TeF_5(OMe)_2^-Me_4N^+$						1
trans MeO isomer		192.2	72.0		226	
cis MeO isomer		194(2)	72.0		228	
IF_7 neutron diff	178.6	185.8	72.0	90.0	218	2, 3
electron diff	178.1	185.7	72.0	90.0	218	
$IOF_6^-NMe_4^+$	182.3	188	72	90	221	4, 5

[a] In each case, the quoted bond lengths are averages. For the purposes of calculating the interligand distances, the molecules were assumed to have a regular pentagonal bipyramidal geometry. In the case of the neutron diffraction structure for IF_7, the deviations from a regular pentagonal bipyramid are very small. [b] Reference numbers in this table refer to the following references: (1) Mahjoub, A. R.; Drews, T.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1036. (2) Adams, W. J.; Bradford-Thompson, H.; Bartell, L. S. *J. Chem. Phys.* **1970**, *53*, 440. (3) Marx, R.; Mahjoub, A. R.; Seppelt, K.; Iberson, R. M. *J. Chem. Phys.* **1994**, *101*, 585. (4) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P. A.; Sanders, J. C. P.; Schrobilgen, G. J.; Wilson, W. W. ACS Symposium Series 555; Thrasher, J. S., Strauss, H., Eds.; American Chemical Society: Washington, DC, 1994. (5) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 3351.

AX_7 Molecules. Complete structure determinations have been made for the following seven coordinated molecules: TeF_7^-, TeF_6OMe^-, $TeF_5(OMe)_2^-$, IF_7, and IOF_6^- (Table 5). They all have a distorted pentagonal bipyramidal structure in which there is some displacement, or puckering, of the equatorial ligands out of the pentagonal plane. Although the structures of three, four, five, and six coordinated molecules may be predicted by the VSEPR model or by ligand−ligand repulsion, a similar prediction cannot be made for seven coordinate molecules. The simple repelling points-on-a-sphere model predicts three structures depending on the repulsion force law considered, a monocapped octahedron, a monocapped trigonal prism, and a pentagonal bipyramid.[7,14] Moreover, as the vertices of a seven vertex polyhedron cannot all be equivalent, there is no requirement that all the bonds be of the same length as in three, four, and six coordinated molecules which means that the points-on-a-sphere model is not necessarily an appropriate model. Nevertheless, all AX_7 molecules of the nonmetals have an approximately pentagonal bipyramidal geometry with shorter axial than equatorial bonds so this is clearly the favored structure for these molecules. Transition metal fluorides in contrast have been found to have all three of the mentioned structures. This is presumably a consequence of their nonspherical cores.[10,11]

The known nonmetal pentagonal bipyramid molecules (Table 5) are in most cases distorted by small displacements of the equatorial ligands out of the pentagonal plane so that these bonds have slightly different lengths and the FAF angles differ slightly from the ideal angle of 72°. IF_7 is the most well studied of these molecules. In the solid state, the low temperature ordered phase IF_7(III)[15] has an almost perfect pentagonal bipyramidal structure with an axial bond length of 179.5 pm, an average equatorial bond length of 184.9 pm with two of the equatorial bonds being distorted by 2.7° from the equatorial plane, and $F_{eq}\cdots F_{eq}$ distances of 216 and 218 pm.[15] The molecule is distorted in the vapor phase having a puckered pentagonal ring of equatorial fluorine ligands with

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(13) Hargittai, I. *The Structure of Volatile Sulphur Compounds*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985.

(14) Thompson, H. B.; Bartell, L. S. *Inorg. Chem.* **1968**, *7*, 488.

(15) Marx, R.; Mahjoub, A. R.; Seppelt, K.; Ibberson, R. M. *J. Chem. Phys.* **1994**, *101,* 585.

an average equatorial bond length of 186 pm and an axial bond length of 179 pm giving an average $F_{eq}\cdots F_{eq}$ distance of 218 pm.[16] The ab initio calculated structure of IF_7 has D_{5h} symmetry.[16,17] The reason for the distortion found in the experimental vapor phase structure is still somewhat controversial,[15] but the puckering is consistent with the close packing of the equatorial ligands which implies strong ligand−ligand repulsions as has been previously pointed out by Christe et al.[17] It should be noted that the undistorted D_{5h} structure determined by crystallography cannot be regarded as definitive because any dynamic puckering, which perhaps is unlikely at the low temperature used for the study, would not be observed and because crystal forces could well freeze out any dynamic distortions.

The TeF_7^- ion has a pentagonal bipyramidal structure with a similarly puckered pentagonal equatorial ring of five fluorine atoms. From the average bond lengths and assuming an undistorted pentagonal bipyramidal structure, a $F_{eq}\cdots F_{eq}$ distance of 220 pm was calculated. Thus, the ligand radii of fluorine bonded to iodine and to tellurium are 109 and 110 pm, respectively. These values are in the range of those found for fluorine bonded to the period 2 and 3 nonmetals although they are somewhat larger than expected from the calculated fluorine charges of 0.59 for IF_7 and 0.70 for TeF_7^-, as can be seen by comparing the values for the radii and ligand charges with those for the period 2 and 3 molecules plotted in Figure 1. Because the bonds in the period 5 molecules are considerably longer than in the corresponding period 2 and 3 molecules, the bonding forces are correspondingly weaker, and it seems reasonable to assume that they are not strong enough to compress the ligands to their essentially incompressible limit as they attract the ligands toward the central core. Thus, the assumption of a constant ligand radius which works well for period 2 and 3 molecules is only an approximation for the fluorides of period 5 elements. It appears that seven coordination just becomes possible for Te and I and for the small ligands F, O, and OMe, giving pentagonal bipyramidal molecules in which the ligands are tightly packed in the equatorial plane. It is not clear why the pentagonal bipyramid with five tightly packed ligands is the favored structure for the seven coordinated period 5 molecules. Christe et al.[17] have proposed a bonding scheme for IF_7 based on that first proposed for XeF_5^{-}[18] in which they describe the axial bonds as being formed from sp hybrids and the equatorial bonds as resulting from five six-center delocalized orbitals. Although this bonding scheme is consistent with the known geometry, it cannot be regarded as an *explanation* of the geometry. The ab initio calculated electron density shows the presence of two axial bond paths and five equatorial bond paths, in other words, five localized equatorial bonds.[19]

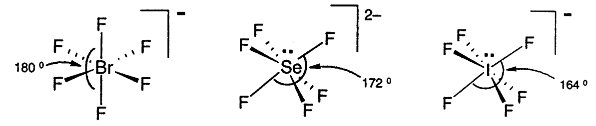

Figure 2. Structures of BrF_6^-, SeF_6^{2-}, and IF_6^-.

In these pentagonal bipyramidal molecules, the equatorial ligands are closely packed while the axial ligands are not, so the equatorial bonds are longer than the axial bonds. In contrast, in trigonal bipyramidal molecules, the axial bonds are longer than the equatorial bonds, because the equatorial ligands are not close packed. If the axial ligands were at the same distance from the central core as the equatorial ligands in IF_7, the $F_{ax}\cdots F_{eq}$ distance would be 277 pm which is much larger than the distance between the closely packed equatorial ligands. The repulsive forces between the axial and the equatorial ligands are therefore weaker than between the equatorial ligands so that the axial ligands are attracted closer to the core and when equilibrium is reached the axial bonds are shorter than the equatorial bonds.

The slightly larger and less electronegative O and OMe ligands occupy the less crowded axial positions in the pentagonal bipyramidal molecules. It has been pointed out by Christe et al.[20] that the rapid exchange of axial and equatorial ligands that is found in IF_7 in the gas phase and for TeF_7^- in solution is inhibited by the preference of these less electronegative ligands to remain in the axial positions so that these molecules are rigid rather than fluxional.

AX_6E and AX_5E_2 Molecules. Because AX_7 molecules of the nonmetals have a pentagonal bipyramidal geometry we might expect that AX_6E molecules would have five ligands in a pentagonal plane and a lone pair in an axial position opposite a single axial ligand X. This structure has, however, never been observed. Among the four known fluorides of this type, BrF_6^- has a regular octahedral geometry while SeF_6^{2-}, $IF_6^{\ -}$, and XeF_6 have a flattened octahedral shape with C_{3v} symmetry (Figure 2). This distortion is consistent with a lone pair occupying a position in the largest face of this distorted octahedron but not exhibiting the full stereochemical effect expected for a lone pair. In each case, the bonds surrounding the supposed position of the lone pair are longer than the opposing bonds (Table 6) which is also consistent with the presence of a lone pair in this position. The degree of distortion from octahedral geometry, as shown by the angle between opposing bonds, is 180° in undistorted BrF_6^-, 174° in SeF_6^{2-}, and 164° in $IF_6^{\ -}$ (Figure 2). It is sometimes said that the lone pair is inactive in BrF_6^- and only weakly active in the other three fluorides. Although six ligands are not close packed in the six coordinated fluorides of selenium and bromine in period 4, they do not form any AX_7 molecules, so it is not surprising that they cannot accommodate a lone pair in their valence shell. In BrF_6^-, it appears that the lone pair is not in the valence shell but remains surrounding the core which is therefore a Br^{4+} core with a spherical 4s pair of electrons in its outer shell

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(16) Christe, K. O.; Curtis, E. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1993**, *115,* 1520.

(17) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P. A.; Sanders, J. C. P.; Schrobilgen, G. J.; Wilson, W. W. In *Inorganic Fluorine Chemistry: Toward the 21st Century*; Thrasher, J. T.; Strauss, H., Eds.; ACS Symposium Series 555; American Chemical Society: Washington, DC, 1994; p 66.

(18) Christe, K. O.; Curtis, E. C.; Dixon, D. A.; Mercier, H. P.; Saunders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1991**, *113,* 3351.

(19) Lin, Z.; Bytheway, I. *Inorg. Chem.* **1996**, *35*, 594.

(20) Christe, K. O.; Dixon, D. A.; Sanders, J. C. P.; Schrobilgen, G. J. Scott, S. T.; Wilson, W. W. *Inorg. Chem.* **1995**, *34*, 1868.

Table 6. Structural Data for AX_6E Molecules and the Corresponding AX_5E and AX_4E_2 Molecules

molecule	long bond[a] (pm)	short bond[a] (pm)	opposed bond angle (deg)	bond length in AX_5E, AX_4E, and AX_5E_2 molecules (pm)	ref[b]
BrF_6^-	185	185	180	BrF_5 169.4 176.8	1
SeF_6^{2-}	202	184	172	SeF_4 168.2 177.1	2
IF_6^-	201	186	164	IF_5 181.4 187.3	3
XeF_6	191	186		XeF_5^+ 181.7 186.3	4

[a] Average values. In each case, there is some distortion from the ideal O_h or C_{3v} symmetry. [b] Reference numbers in this table refer to the following references: (1) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1972**, *28*, 3275. (2) Mahjoub, A. R.; Zhang, X.; Seppelt, K. *Chem. Eur. J.* **1995**, *1*, 261. (3) Mahjoub, A. R.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 321. (4) Gavin, R. M.; Bartell, L. S. *J. Chem. Phys.* **1968**, *48*, 2460, 2466.

rather than a Br^{6+} core. This supposition is consistent with the observation that the BrF bonds which have a length of 185.4 pm are much longer than the bonds in BrF_5 (equatorial 176.8 pm, axial 169.7 pm) where the lone pair occupies the valence shell (Table 6). The Se atom is larger than the Br atom, and it appears that in SeF_6^{2-} the lone pair is not entirely in the core but protrudes very slightly into the valence shell causing the observed small distortion from octahedral geometry. The larger period 5 atoms I and Xe form seven coordinated atoms so that in IF_6^- and XeF_6 so it might seem that their valence shells could accommodate a lone pair. However, in general, a lone pair takes up more space in a valence shell than a bonding pair, particularly a pair bonding a very electronegative fluorine ligand, so it is perhaps not surprising that even in these molecules there is not sufficient space for a full lone pair. Only some of the density of the lone pair protrudes into the valence shell, and the rest remains as an outer layer of the core. Thus, these molecules have an octahedral geometry somewhat distorted by this partial lone pair. The data in Table 6 show that in each of these molecules the AF bonds, particularly the bonds adjacent to the lone pair, are longer than those in the corresponding less crowded AX_5E and AX_4E molecules.

All AX_6E chlorides, bromides, and iodides of the elements of groups 14, 15, and 16, such as $SeCl_6^{2-}$, have octahedral structures with unusually long bonds.[21] Given the larger size of the Cl, Br, and I ligands compared to fluorine, the octahedral structures of these molecules with the "lone pair" forming the outer layer of a spherical core is not unexpected. All these molecules may be considered to be highly ionic with a close packed octahedral arrangement of very ionic ligands surrounding a spherical A^{4+} core with a pair of electrons in an s type orbital forming the outer layer, rather than an A^{6+} core. It is only in some of the fluorides that there is sufficient space in the valence shell for the "lone pair" to at least partially occupy the valence shell.

The XeF_5^- molecule is the only known example of an AX_5E_2 molecule.[18] It has a pentagonal planar structure with a bond length of 201 pm. If two lone pairs were to remain in the core giving an Xe^{4+} core, it would be expected to have a prolate ellipsoidal shape with the two lone pairs occupying what might be described as two 5s5p hybrids. This core shape would be expected to best accommodate five ligands if they were to lie in a pentagonal plane around its major axis giving the observed planar pentagonal geometry. This is the same geometry as predicted by the VSEPR model with two lone pairs in the less crowded axial positions of a pentagonal bipyramid. The molecule is best described as having two lone pairs both partially occupying the valence shell. The length of the bonds is increased by the presence of these partial lone pairs so that they are longer than all other known Xe−F bonds except those in XeF_8^{2-}.

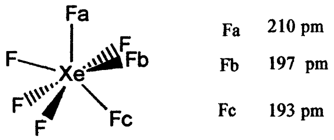

Figure 3. Structure of XeF_7^-.

AX_8 and AX_7E Molecules. IF_8^- and TeF_8^{2-} are the only known examples of AX_8 molecules of the nonmetals.[22,23] Both have the square antiprism structure predicted by the points-on-a-sphere model. IF_8^- has very nearly equal I−F bond lengths of 188−190 pm, FIF angles of 73.3° and 78.1°, and F···F distances in the range 225−238 pm. The smallest of these distances is slightly larger than the close packed distance of 218 pm in IF_7 which is consistent with the square antiprism not being a truly close packed arrangement.

The single known example of an AX_7E molecule is XeF_7^- which has a monocapped octahedral structure rather like AX_6E molecules (Figure 2) with the seventh ligand forming a long bond (210 pm) opposite the presumed position of the lone pair of an AX_6E molecule (Figure 3).[24] In this molecule, the lone pair must again be very largely in the core but sufficiently stereochemically active to increase the length of the unique bond.

An AX_8E Molecule. XeF_8^{2-} is the only known example of an AX_8E molecule.[24] It has a square antiprism structure despite the presence of a lone pair. It is not surprising that this is therefore another example of a molecule with a sterically inactive "lone pair" because the eight approximately closely packed ligands leave no space for the lone pair in the valence shell which therefore remains in the core. As in the AX_6E molecules where the bonds are longer than in a related AX_6 molecule, in XeF_8^{2-}, the bonds, which have an average length of 202 pm, are longer than the bonds in XeF_6 which have an average length of 189 pm.

Some Chemical Consequences of Close Packing. Because the OH ligand is very similar in size to a fluorine ligand, it would be expected that there should be a similar large number of high coordination number hydroxides of the elements of period 3 and beyond. However, there are only a few such molecules. The theoretically possible hydroxides of P, S, and Cl and of As, Se, and Br, such as $P(OH)_5$ and $S(OH)_6$, are known only as their four coordinated oxo acids such as $PO(OH)_3$ and $SO_2(OH)_2$ derived by the elimination

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(21) For references to individual molecules see ref 11.

(22) Mahjoub, A. R.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 876.

(23) Mahjoub, A. R.; Ellern, A.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1125.

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of water from the theoretical hydroxides. Thus, it would appear that the hexahydroxides of the period 3 and 4 elements are unstable because the close packing of the OH ligands facilitates the elimination of water to give the much less crowded and more stable four coordinated molecules. In contrast, the period 5 six coordinated $Te(OH)_6$ and $IO(OH)_5$ are stable molecules because the hydroxide groups in these molecules are not close packed. We would not, however, expect the seven coordinated pentagonal bipyramidal $Te(OH)_7^-$ and $I(OH)_7$ to be stable molecules because, if they were to have the pentagonal bipyramidal IF_7 structure, five of the OH groups would be close packed and therefore expected to eliminate water to give the six coordinate $TeO(OH)_5{}^-$ ion.

It is interesting to note also that, although $S(CH_3)_6$ and $Se(CH_3)_6$ are not known, $Te(CH_3)_6$ is a stable molecule and that, although $P(CH_3)_5$ is not known, the four coordinated $H_2C{=}P(CH_3)_3$ is a stable molecule that can be imagined as being formed by the elimination of CH_4 from $P(CH_3)_5$.

$As(CH_3)_5$ is, however, a stable molecule. Presumably, the crowding of the ligands is not so severe in a trigonal bipyramidal molecule because only the axial ligands are truly close packed.

Computations

Wave functions were calculated using the Gaussian 94 package[25] at the B3LYP /6-311++G(2d,2p) level[26]. The analysis of the electron density distributions[27] to obtain the atomic charges was carried out using the AIMPAC suite of programs.[28] For IF_7 and TeF_7^-, larger basis sets were used. For iodine, the Huzinaga MIDI basis set[29] was decontracted and supplemented with a d-type polarization set. For tellurium, Huzinaga's (43333/4333/43) was decontracted and supplemented with w d-type polarization set[30] equivalent to give a (43333/4333/43D) basis set.

Summary and Conclusions

The packing of the ligands (and lone pairs) around a central atom is the most important factor in determining coordination numbers and an important factor in determining geometry. Thus, the limitation of the period 2 nonmetals to a coordination number of four is due to their small size while the larger nonmetals of periods 3 and 4 may have coordination numbers up to six and the still larger elements of period 5 may have coordination numbers of 7 and 8. We have shown that interligand distances in the six coordinated fluorides of the period 3 nonmetals are very nearly constant for a given central atom (Si, P, S, and Cl) indicating that the fluorine ligands are essentially close packed around the central atom as has been found previously for the three and four coordinated molecules of the period 2 nonmetals. A characteristic ligand radius for fluorine bonded to each of these elements can be obtained from the interligand distance. These radii depend only on the charge of the fluorine atom, and they are consistent with the radii deduced from the close packed fluorides of period 2.

Whereas all the period 2 nonmetal molecules appear to have close packed ligands, this is not the case for the molecules of the nonmetals of the subsequent periods where only the six coordinate molecules of the period 3 nonmetals and the equatorial ligands of the pentagonal bipyramidal molecules of period 5 may be regarded as close packed. Moreover, beyond period 3, it seems that because of the relative weakness of the bonds, the ligands are not attracted so strongly by the central atom and therefore not compressed to the same extent as for period 2 and 3 molecules so that the apparent ligand radius increases slightly as in IF_7 and TeF_7^-. Consequently, the concepts of ligand close packing and characteristic ligand radii are not as useful for the molecules of period 3 and beyond as they are for the molecules of period 2. Nevertheless, ligand−ligand and ligand−lone pair repulsion, or ligand−lone pair packing, provides a basis for understanding (1) the overall geometry of the fluorides (and probably most molecules) of periods 3−5, (2) the different bond lengths in trigonal bipyramidal and pentagonal bipyramidal molecules, (3) the puckering of the nominally planar pentagonal ring of the pentagonal bipyramidal molecules, (4) the octahedral and C_{3v} distorted octahedral geometry of AX_6E molecules in which the lone pair E is stereochemically inactive or only partially active, (5) the limitation of the period 2 nonmetals to a coordination number of four and of period 3 and 4 nonmetals to a coordination number of six, and (6) why molecules such as $S(OH)_6$ and $Se(OH)_6$ are unknown whereas $Te(OH)_6$ is a stable species.

That the nonmetal elements of period 2 are limited to a coordination number of four in their molecules has led in the past to an overemphasis on the octet rule and the unjustified opinion that the bonding in molecules with high coordination numbers that do not obey the octet rule is in some way exceptional. The bonding in molecules with coordination numbers of five and higher is polar and is essentially no different from that in related molecules with a coordination number of four or less. Consequently, as we have discussed elsewhere,[31,32] the term hypervalent that has been invented to describe these molecules is unnecessary, as it means little more than a molecule with a coordination number of greater than four.

Acknowledgment. We thank the Petroleum Research Fund of the American Chemical Society for financial support of this work. We thank Dr. Ting-hua Tang for calculating some of the atomic charges.

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