Chem. Educator **2002,** *7,* 261–264

The Three-Center, Four-Electron Bond in Hexacoordinated AB6-Type Main Group Molecules: An Alternative Model of Bonding without d-Orbital Participation in the Central Atom

Xiaoping Sun

Department of Natural Science and Mathematics, University of Charleston, 2300 MacCorkle Avenue S. E., Charleston, West Virginia 25304, xsun@ucwv.edu

Received June 3, 2002. Accepted August 16, 2002.

Abstract: The hexacoordinated AB_6-type main group molecules have long been thought to have sp^3d^2 hybridization on the central atom, accounting for their molecular geometry (octahedral). However, the s-p-d hybridization does not explain how an energetically unfavorable np → nd excitation in an atom of nonmetallic elements, such as sulfur and phosphorus, can be achieved. In this article, the author has re-examined bonding in SF_6 and PF_6^- (O_h symmetry) and proposed that the linear F–S–F and F–P–F bonds in both species are formed via the overlap of the 3p orbital on the central atom with terminal ligand orbitals, resulting in a three-center, four-electron bond. This alternative model, which does not involve d orbitals in bonding, is supported by a partial charge analysis using Allen's electronegativity approach. SF_6 or PF_6^- can be characterized by several ionic resonance structures containing a postulated SF_4^{2+} or PF_4^+ cation (octet on sulfur or phosphorus). The three-center, four-electron bond model can also be used to study bonding in hexacoordinated AB_5E (e.g., halogen pentafluorides) and AB_4E_2 (e.g., xenon tetrafluoride) explaining well the molecular geometry. The author believes that all the results will be useful in updating chemistry texts.

Introduction

The hexacoordinated AB_6-type main group molecules belong to an important class of compounds that are covered in general and inorganic chemistry textbooks [1]. This type of molecule possesses six electron pairs in the central atom. According to the valence-shell electron-pair repulsion (VSEPR) model they are predicted to have an octahedral structure (O_h symmetry), consistent with experimental observations. In order for the central atom to be coordinated by six ligands, the predominant common understanding is that two d orbitals are required to participate in bonding. As a result, two electrons in the s and p subshells are promoted to higher-level d orbitals forming six sp^3d^2 hybrid orbitals in the central atom. An intrinsic problem for sp^3d^2 hybridization is that it would involve the energetically unfavorable $s^2p^nd^0 \rightarrow s^1p^{n-1}d^2$ [n = 3(P), 4(S), or 5(Cl, Br. I)] excitation, which requires a large promotion energy. In addition, d orbitals in nonmetals are heavily shielded by the more penetrating s and p electrons and extremely diffuse. As a result, they have poor overlap with the orbitals of neighboring atoms. These two factors disfavor the utilization of d orbitals. For the related AB_5E-type molecules (E represents a lone pair of electrons), which possess a square pyramidal structure (C_{4v} symmetry), the sp^3d^2 hybridization does not explain the difference in bond distances in the basal and axial positions.

In a recent article [2], this author presented an alternative model that does not involve d orbitals in bonding in the pentacoordinated AB_5-type molecules such as phosphorus pentahalides PX_5 (X = F, Cl), which have five electron pairs in the central atom. Instead, three sp^2 hybrid orbitals (each contains a single electron) are formed on the central atom overlapping with ligand orbitals in the equatorial positions and the longer axial bonds are formed via the overlap of the unhybridized p orbital (containing two electrons) on the central atom and the two terminal ligand orbitals, resulting in a three-center, four-electron bond.

In this paper, the author uses simple molecular orbital theory and the recently redefined electronegativity [3–5] to analyze bonding in the hexacoordinated SF_6 and PF_6^- and related XF_5 (X = Cl, Br, or I) and XeF_4, which contain one and two lone pairs, respectively, in the central atom. This approach supports a new model for bonding in hexacoordinated AB_6, AB_5E, and AB_4E_2 types of main group molecules that only involves participation of s and p orbitals on the central atom.

Rigorous valence bond and molecular orbital calculations have been conducted on sulfur fluorides, including SF_2, SF_4, and SF_6, by different workers [6]. They all showed that formation of the S–F bonds in SF_6 is facilitated little by the use of 3d orbitals but rather through charge transfer from sulfur to fluorine. The qualitative model proposed by this author in the present article avoids the full-blown molecular orbital treatment and is more readily understood by undergraduate students. Together with the previous article [2], a more complete picture on bonding in hypervalent main group molecules is presented to our readers.

The understanding of bonding in this class of molecules is essential in undergraduate chemical education.

Bonding in the AB_6-type Molecules

In most general and inorganic textbooks sulfur hexafluoride SF_6 and phosphorus hexafluoride PF_6^- anion are often chosen as representatives of the hexacoordinated AB_6-type main group molecules when discussing their bonding and structure. The understanding of the nature of bonding in SF_6 has been said to

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)05598-8, Published on Web 9/13/2002, 10.1007/s00897020598a, 750261xs.pdf

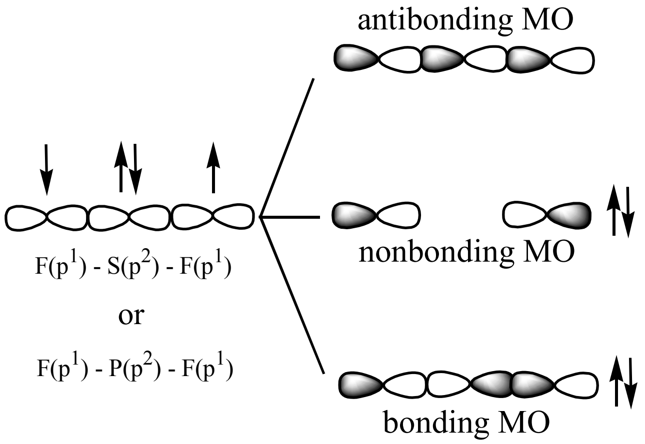

Figure 1. The three-center, four-electron σ bond formed in the octahedral SF_6 or PF_6^- in each of the *x*, *y*, and *z* orientations via the $F(p^1)$–$S(3p_x^2$, $3p_y^2$, or $3p_z^2)$–$F(p^1)$ or $F(p^1)$–$S(3p_x^2$, $3p_y^2$, or $3p_z^2)$–$F(p^1)$ orbital overlap. For each of the hexacoordinated molecules, the linear combination of the three p orbitals in each of *x*, *y*, and *z* orientations gives three molecular orbitals (bonding, nonbonding, and antibonding MOs). The bonding and nonbonding MOs are occupied and the antibonding MO unoccupied.

be an exceedingly difficult problem [1e]. Recently, this author has proposed [2] that in phosphorus pentahalides, PX_5 (X = F, Cl), a three-center, four-electron bond is formed in the axial positions via the overlap of the unhybridized p orbital on the central atom and the two axial ligand orbitals. This approach can be extended to the study of bonding in SF_6 and PF_6^-.

Unlike the pentacoordinated AB_5-type molecules (D_{3h} symmetry), in the hexacoordinated AB_6-type molecules such as SF_6 and PF_6^- (O_h symmetry), the six fluorine ligands approach to the central sulfur or phosphorus atom along the *x*, *y*, and *z* axes forming an octahedral structure. Thus, the ligand p orbitals have effective overlap with all the orthogonal sulfur or phosphorus 3p ($3p_x$, $3p_y$, $3p_z$) orbitals in six orientations (±*x*, ±y, ±*z*). Because all the S–F or P–F bond distances in SF_6 or PF_6^- are equal, this would require a filled 3p subshell in the central atom (achieved readily by s-p transition). Thus, the six S–F bonds in SF_6 result from the overlap of $F(p^1)$–$S(3p_x^2)$–$F(p^1)$, $F(p^1)$–$S(3p_y^2)$–$F(p^1)$, and $F(p^1)$–$S(3p_z^2)$–$F(p^1)$, and the six P–F bonds in PF_6^- are formed by the overlap of $F(p^1)$–$P(3p_x^2)$–$F(p^1)$, $F(p^1)$–$P(3p_y^2)$–$F(p^1)$, and $F(p^1)$–$P(3p_z^2)$– (p^1) forming three equivalent linear three-center, four-electron bonds in each of the molecules (Figure 1) along the *x*, *y*, and *z* axes, respectively. Apparently, all the S–F or P–F bonds formed in this manner should be equivalent resulting in an O_h symmetry for the molecule.

One of the reviewers of this manuscript pointed out that the totally symmetric 3s orbital (a_{1g}) on sulfur of SF_6 (O_h symmetry) can also interact with the six $2p_z$ orbitals on the six fluorine ligands (LCAO, TASO of a_{1g} symmetry with a positive lobe pointing toward S). Qualitatively, this interaction should make the actual S–F bond order greater than would be expected (0.5) only from the three-center, four-electron bond; the Raman spectroscopic analysis indicates that the S–F bond order is close to one [7]. It may account for the special stability of the S–F (or P–F) bond in SF_6 or (PF_6^-). Although the energy of 3d orbitals in SF_6 is substantially lower than those in a free sulfur atom presumably due to the polarization in SF_6 exerted by the electronegative fluorines, the 3d orbitals in SF_6 (or PF_6^-) are still higher in energy than its 3p, and the fluorine orbitals are at lower energy levels than that of 3p in sulfur or phosphorus. Therefore, electron transfer from the 3p orbitals of sulfur to the lower-level ligand orbitals is expected to be energetically favorable; promotion of these same electrons to 3d orbitals is not. The three-center, four-electron bond model, which has effectively avoided the use of higher-energy d orbitals in bonding, can serve as an alternative qualitative approach to the study of bonding in hypervalent main group molecules.

The absence or unimportance of d-orbital participation in bonding in SF_6 or PF_6^- is further supported by examining the electric charge on the central sulfur or phosphorus atom using Allen's partial charge formula for AB_n-type compounds [3], eq 1, which accounts for the effect of the electronegativity (EN) difference in Allen's scale [3–5].

$$\delta_A = (\text{group no. of A}) - (\text{no. of nonbonding electrons on A}) - 2\,\Sigma[EN_A/(EN_A + EN_B)] \qquad (1)$$

The last term in eq 1 is twice the sum of the electronegativity weighting $[EN_A/(EN_A + EN_B)]$ function over all the A–B bonds. The electronegativity (EN) values in Allen's scale are defined quantitatively as the average ionization energies of all the s and p electrons in the valence shell, and they are experimentally determined and obtained from the National Institute of Science and Technology (NIST) energy level tables [3, 4, 8]. Thus, this redefined electronegativity has become a more quantitative concept than the traditional descriptive meaning of electronegativity, the ability of an atom to attract electrons. The application of this method in analysis of partial electric charge on various molecules has been well reviewed in a journal article [9] as well as in a recently published general chemistry textbook [1a]. It has also been successfully used by this author [2] in analysis of atomic charges in the pentacoordinated AB_5-type main group molecules. In SF_6 and PF_6^-, $EN_S = 2.589$, $EN_P = 2.253$, and $EN_F = 4.193$ (Allen's scale [3–5, 8]). Thus, the atomic charges on sulfur and phosphorus are calculated respectively by eq.1 as

$$\delta_S(SF_6) = 6 - 0 - 2 \times 6\,[2.589/(2.589 + 4.193)] = +1.45$$

$$\delta_P(PF_6^-) = 5 - 0 - 2 \times 6\,[2.253/(2.253 + 4.193)] = +0.81$$

The calculations indicate that in SF_6 and PF_6^- the central atom carries a substantial positive charge due to the partial electron transfer to the more electronegative fluorine valence shell. This could make the d-orbital participation in bonding unnecessary or unimportant, qualitatively consistent with high-level valence bond and molecular orbital calculations [6]. SF_6 and PF_6^- can be characterized by several prevalent resonance structures including three ionic structures as well as a pure covalent structure (Figure 2).

Each of the ionic structures contains an $F^- SF_4^{2+} F^-$ or $F^- PF_4^+ F^-$ in which the fluoride anions occupy two opposite terminal positions in order to minimize the electrostatic repulsion between the two anions. Within the postulated SF_4^{2+} and PF_4^+ cations, all the S–F and P–F bonds are purely covalent with the +2 and +1 electric charge localized on sulfur and phosphorus, respectively. Thus, the average charge on sulfur and phosphorus across all the structures are +1.5 and 0.75,

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)05598-8, Published on Web 9/13/2002, 10.1007/s00897020598a, 750261xs.pdf

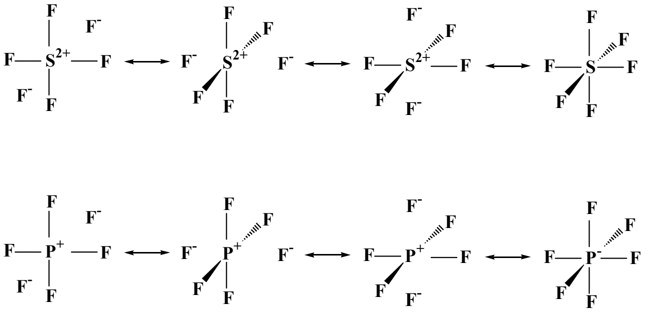

Figure 2. Resonance structures of the octahedral SF_6 and PF_6^-. In the postulated SF_4^{2+} and PF_4^+ the positive charge resides on sulfur and phosphorus, respectively. The two F^- anions in each of the ionic structures occupy two opposite axial positions in order to minimize the electrostatic repulsion between the anions. The sulfur and phosphorus atoms in all the postulated cations are octet, and they have no d-orbital participation in bonding.

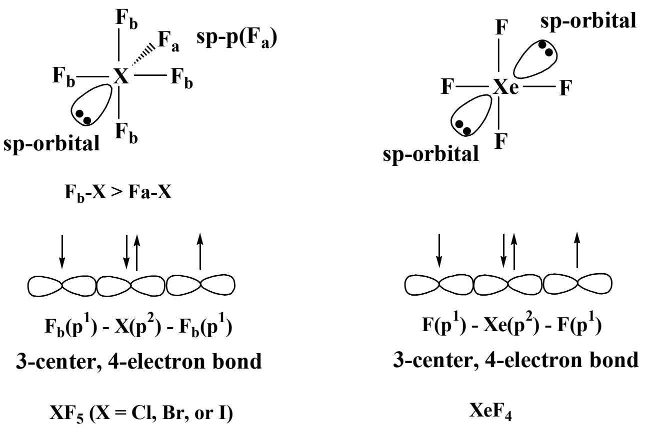

Figure 3. The structure of and bonding in XF_5 (X = Cl, Br, or I) and XeF_4. In each of the molecules, the central atom is sp-hybridized, resulting in two sp orbitals pointing toward the axial positions. The unhybridized, orthogonal p_x and p_y orbitals overlap with terminal fluorine p orbitals forming 3-center, 4-electron bonds: $F_b(p^1)$–X (p_x^2 or p_y^2)–$F_b(p^1)$ in XF_5 and $F(p^1)$–Xe (p_x^2 or p_y^2)–$F(p^1)$ in XeF_4.

respectively, consistent with the above calculations ($\delta_S = +1.45$ and $\delta_P = +0.81$).

The central sulfur and phosphorus atoms in SF_4^{2+} and PF_4^+ are octets in their valence shells, and they do not have a d component in bonding. The bonding in the pure covalent structures of SF_6 and PF_6– could involve d orbitals according to the sp^3d^2 hybridization model; however, the contribution of a pure covalent structure in each of the molecules is small (25%), indicating that the d component, if any, would be trivial (at least much smaller than that expected from the sp^3d^2 hybridization model).

The resonance structures in Figure 2 show that the net contribution of several F–S–F or F–P–F combinations leads to the average S–F or P–F bond order close to one (0.75). This is consistent with the above qualitative molecular orbital analysis, which takes into account a three-center, four-electron bond as well as the interaction of 3s orbital in the central atom with the ligand orbitals.

Gillespie [10] has described BF_3 and SiF_4 as ionic molecules consisting of a central cation-like atom (B^{3+} or Si^{4+}) surrounded by anion-like ligands (F^-). Recently, this author [2] described PF_5 and SF_4 using several ionic resonance structures containing the postulated PF_3^{2+} and SF_3^+ cations for PF_5 and SF_4, respectively. In this article, SF_6 and PF_6^- have been described to resonate among three ionic $F^-SF_4^{2+}F^-$ and $F^-PF_4^+F^-$ structures, respectively. In all the cases, the positive charge on the central atom of the molecule, created by a large difference in electronegativities between the central and terminal atoms, can be estimated reasonably by eq. 1 using Allen's quantitatively redefined, experimentally determined electronegativity. This method has been demonstrated to be a fairly practical, effective approach to the study of main group molecules, especially useful in general and inorganic chemistry courses.

Bonding in the AB_5E- and AB_4E_2-type Molecules

The three-center, four-electron bond model can also be used as an alternative approach to analysis of the hexacoordinated main group molecules that contain one or two lone pairs of electrons in the central atom, namely, the AB_5E or AB_4E_2 type molecules, where E represents a lone pair. The halogen pentafluoride XF_5 (X = Cl, Br, or I) belongs to the AB_5E type. Each of them possesses a square pyramidal structure (C_{4v} symmetry) [1f] with a lone pair in the central halogen atom. In all the XF_5 molecules the basal X–F_b bonds (all are equivalent) are about 0.1 Å longer than the axial X–F_a bond (Cl–F_b = 1.72 Å and Cl–F_a = 1.62 Å in ClF_5, Br–F_b = 1.77 Å and Br–F_a = 1.68 Å in BrF_5, and I–F_b = 1.87 Å and I–F_a = 1.84 Å in IF_5) [1f]. This shows that bonding in basal and axial positions must be different (Figure 3). Two sp hybrid orbitals could form on the central halogen atom pointing toward the axial positions. The shorter axial X–F_a bond is reasonably formed by the overlap of an sp orbital with the fluorine p orbital; the lone pair resides in another sp orbital in the opposite axial position. Two sets of the longer, linear basal F_b–X–F_b bonds are reasonably formed by the overlap of the unhybridized, orthogonal p_x and p_y orbitals, respectively, with the terminal fluorine p orbitals leading to a three-center, four-electron bond (Figure 3).

This alternative model explains well the molecular geometry. Especially, it explains why the axial X–F_a bond (bond order 1) is shorter than the four basal X–F_b bonds (bond order 0.5); the traditional sp^3d^2 hybridization model cannot account for the difference in bond distances. Xenon tetrafluoride XeF_4 is an example of AB_4E_2-type molecules possessing a square planar structure (D_{4h} symmetry) with two lone pairs in the central xenon atom (Figure 3). This molecule also fits the three-center, four-electron bond model, and the higher-energy d orbitals can be avoided in bonding. Similar to XF_5 (X = Cl, Br, or I), in XeF_4 two sp hybrid orbitals could reasonably form on Xe pointing toward the axial positions and holding a lone pair in each of them. The two sets of linear F–Xe–F bonds are formed as three-center, four-electron bonds (Figure 3), the same as formation of the basal F_b–X–F_b bonds in the above-discussed halogen pentafluorides XF_5.

Conclusion

The author has studied several hexacoordinated main group molecules using the three-center, four-electron bond model. It avoids effectively the use of higher-energy d orbitals in bonding and explains well the molecular geometry. Especially, it explains the difference in basal and axial bond distances in halogen pentafluoride, XF_5 (X = Cl, Br, or I; the AB_5E-type molecules); the s-p-d hybridization does not. The model proposed in this article can serve as a general alternative approach to the study of hypervalent main group molecules in undergraduate general and inorganic chemistry courses. The author believes that this approach would be useful in updating chemistry texts.

References and Notes

1. Examples of general and inorganic textbooks: (a) Spencer, J. N.; Bodner, G. M.; Rickard, L. H. *Chemistry: Structure and Dynamics;* Wiley & Sons: New York, 1999; (b) Brown, T. L.; LeMay, Jr., H. E.; Bursten, B. E. *Chemistry: The Central Science,* 8th ed.; Prentice-Hall: New York, 2000; (c) Kotz, J. C.; Treichel, Jr., P. *Chemistry and Chemical Reactivity,* 4th ed.; Saunders: Philadelphia, PA 1999; (d) Chang, R. *General Chemistry: The Essential Concepts,* 3rd ed.; McGraw-Hill: New York, 2002; (e) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity,* 4th ed.; Harper Collins: New York, 1993; (f) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements;* Pergamon Press: New York, 1984.
2. Sun, X. *Chem. Educator* [Online] **2002,** *7,* 11–14; DOI 10.1007/s00897010525a.
3. Allen, L. C. *J. Am. Chem. Soc.* **1989,** *111,* 9115–9116.
4. Allen, L. C. *J. Am. Chem. Soc.* **1989,** *111,* 9003–9014; Allen, L. C. *J. Am. Chem. Soc.* **1992,** *114,* 1511.
5. Sun, X. *Chem. Educator* [Online] **2000,** *5,* 54–57; DOI 10.1007/s00897990363a.
6. Hay, P. J. *J. Am. Chem. Soc.* **1977,** *99,* 1003–1012; Cioslowski, J; Mixon, S. T. *Inorg. Chem.* **1993,** *32,* 3209–3216; Harcourt, R. D. *Int. J. Quantum Chem.* **1996,** *60,* 553–566.
7. Fontal, B.; Spiro, T. G. *Spectrochimica Acta* **1977,** *33A,* 507–515.
8. Mann, J. B.; Meek, T. L.; Allen, L. C. *J. Am. Chem. Soc.* **2000,** *122,* 2780–2783.
9. Pfennig, B. W.; Frock, R. L. *J. Chem. Educ.* **1999,** *76,* 1018–1022.
10. Gillespie, R. J. *J. Chem. Educ.* **1998,** *75,* 923–925.

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)05598-8, Published on Web 9/13/2002, 10.1007/s00897020598a, 750261xs.pdf