

Written Qualifying Examination – Inorganic Chemistry II

January 22, 2007

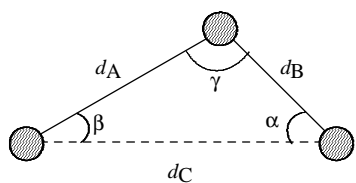
Questions related to E. A. Robinson, G. L. Heard, R. J. Gillespie,
J. Mol. Struct. **1999**, 485-486, 305-319

The referenced paper is one of the seminal works in the development of Ligand Close Packed (LCP) theory. The following ligand radii (pm) are taken from Table 5 of the paper and may be useful to you in answering the questions in this examination.

Central atom			
Ligand	Be	B	C
C		137	126
O	134	120	113
F	128	113	108
Cl	168	151	144
	Si	P	S
O	132	127	124
F	127	118	114
Cl	164	156	154

In addition you may find it useful to recall the Law of Cosines for both the general case of an obtuse triangle and the specific case of an isosceles triangle.

General case (obtuse triangle):



$$d_C = \sqrt{d_A^2 + d_B^2 - 2d_A d_B \cos \gamma}$$

$$\gamma = \arccos \left(\frac{d_A^2 + d_B^2 - d_C^2}{2d_A d_B} \right)$$

If $d_A = d_B$ (isosceles triangle):

$$d_C = \sqrt{2d_A^2(1 - \cos \gamma)} = 2d_A \sin(\gamma/2)$$

$$\gamma = \arccos \left(1 - \frac{d_C^2}{2d_A^2} \right) = 2 \arcsin \left(\frac{d_C}{2d_A} \right)$$

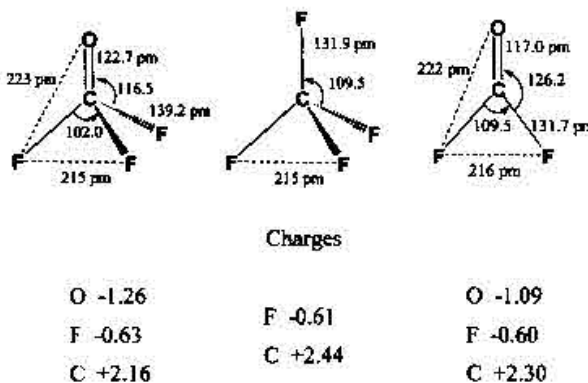
Answer **five (5)** of the following six questions. Be sure to indicate clearly the question you are answering in each case. If you answer all six questions, only the first five will be graded. Each of your answers should consist of one or two paragraphs (more if needed) composed of complete sentences in standard English.

1. Consider the following data for A–F distances (pm) given in the paper.

BeF_3^-	149	BeF_4^{2-}	155.4
BF_3	130.7	BF_4^-	138.2
CF_3^+	124.4	CF_4	131.9

As these data show, bond length increases with coordination number (CN) for a given central atom with a specific ligand (here, fluorine). How have the shorter lengths of the CN3 species been rationalized in the past? How does LCP theory predict this trend? Give sample calculations to show that these data are consistent with the concept of constant ligand radii.

2. The authors cite the previous work of Bartell, who first recognized that the geometry of substituted ethenes, aldehydes, ketones, and methanes could be explained on the basis of the close-packing of the ligands, from which values of interatomic nonbonded radii were determined. As Robinson *et al.* point out, Bartell radii are not generally applicable but apply only to ligands bonded to carbon. Why is this the case? What are the trends in a ligand atom's nonbonded radius as a function of the central atom to which it is bonded? What is the underlying reason for this trend? What part do the charges on the ligand and central atom play in this trend?
3. Figure 3 from the paper is shown below.



In COF_3^- and COF_2 , the C–O distances are shorter than the C–F distances, and the C–F distance in COF_3^- is longer than in CF_4 . Also, the F–C–F angles are $<109.5^\circ$. How do Robinson *et al.* explain these distances and angles? What reason do they cite for the C–O distances being shorter than the C–F distances in COF_3^- and COF_2 ? Is C really pentavalent in COF_3^- ?

4. The following data appear in Table 15 in the paper.

	N-X (pm)	XNX (°)	X··X (pm)
NH ₃	101.5	107.2	164
NF ₃	136.5	102.3	212.4
NCl ₃	175	106.8	280
N(CH ₃) ₃	145.8	110.9	240
N(SiH ₃) ₃	173.4	120	300

As predicted by VSEPR theory, NH₃, NF₃, and NCl₃ are trigonal pyramidal molecules (C_{3v}) with XNX bond angles $<109.5^\circ$. But VSEPR theory alone does not well explain the specific bond angles. In terms of LCP theory explain why the bond angle in NF₃ is less than that in NCl₃, and why the bond angle in NH₃ is the greatest of the three.

5. Use the data shown in problem 4 for this question. As noted in problem 4, VSEPR theory predicts a trigonal pyramidal structure for AX₃E molecules. Typically, as shown with the first three listed compounds, the bond angle is $<109.5^\circ$. But as the data show, the bond angle in N(CH₃)₃ is greater than the tetrahedral angle, and in N(SiH₃)₃ it is so great that the molecule is actually planar (D_{3h}). Why does VSEPR theory fail in these cases, and what factors given by the authors can explain the observed geometries?
6. By VSEPR theory, AX₆E molecules are predicted to have either a monocapped octahedral geometry (C_{3v}) or more likely a pentagonal pyramidal geometry (C_{5v}), with the lone pair acting as a pseudo-ligand E²⁻. While SeF₆²⁻ is monocapped octahedral (C_{3v}), SeCl₆²⁻ is neither of the predicted VSEPR geometries, being truly octahedral (O_h). How do the authors explain the geometries of both SeF₆²⁻ and SeCl₆²⁻? Why is SeF₆²⁻ monocapped octahedral rather than the usually preferred pentagonal pyramidal geometry?

Green Chemistry Question:

How might LCP considerations be useful to designing more environmentally benign synthetic strategies, such as molecular self-assembly? Illustrate your answer with one or more specific examples from either your course work in Green Chemistry or your research activities.