Written Qualifying Examination – Inorganic Chemistry I

June 16, 2009

Questions related to S. Noury, B. Silvi, and R. J. Gillespie, *Inorg. Chem.*, **2002**, *41*, 2164.

Questions Related to the Assigned Paper (10.0 points)

1. (2.0 points) The title of this paper is "Chemical Bonding in Hypervalent Molecules: Is the Octet Rule Relevant?". What is the definition of *hypervalent* in terms of the original Lewis concept of the octet rule? How was the bonding in hypervalent molecules once described on the basis of hybrid orbitals? What evidence (prior to this paper) makes it inappropriate to describe hypervalent bonding in terms of such hybrid orbitals? What is meant by the term *modified octet rule*, and how does this model circumvent the problems of the hybrid orbital approach to bonding in hypervalent molecules? On the basis of the modified octet rule, are bonds in hypervalent molecules expected to be different from those in nonhypervalent molecules? By way of illustrating your answer, show how one might describe the bonding in a molecule such as PF_5 on the basis of the modified octet rule and compare it to the model for PF_3.

2. (2.0 points) The paper examines the bonding in a variety of molecules with central atoms in groups 15-17 using *ELF* topological analysis. That is *ELF*? Define the *ELF* terms *core basin*, *monosynaptic basin*, *disynaptic basin*, and *valence shell population*. Describe why *ELF* is particularly well suited to address the two central questions of this paper:

(i) How many electrons does the valence shell of the central atom in a hypervalent molecule contain?

(ii) How should the bonding in a hypervalent molecule be described, and is it different from that in a similar nonhypervalent molecule?

3. (2.0 points) Refer to Table 1 from the paper, reproduced below.

Table 1. Properties of the AX Bonds in Reference Molecules: Disynaptic Basin Population $V(A, X)$, Ligand Monosynaptic Basin Population $V(X)$, Monosynaptic Basin Population $V(A)$, Valence Shell Population $N_v(A)$, Effective Valence Population $N_{eff}(A)$

	$V(A, X)$	$V(X)$	$V(A)$	$N_v(A)$	$N_{eff}(A)$
NF_3	0.84	6.83	2.56	5.08	
NCl_3	1.23	6.50	2.56	6.26	
HNO	1.99	5.16	2.55	6.62	
PF_3	0.84	6.97	2.12	4.64	
PCl_3	1.28	6.59	2.13	5.96	
PMe_3	1.90		2.16	7.86	
HPO	2.02	5.46	2.28	6.35	
PH_2Me (H)	1.97		2.11	7.88	
(Me)	1.83				
AsF_3	7.81		2.35	25.77	5.16
$AsCl_3$	0.99	6.90	2.35	5.32	
$AsMe_3$	1.85		2.48	8.03	
AsH_2Me (H)	2.01		2.35	8.13	
(Me)	1.76				
HAsO	7.47		2.54	12.1	6.21
SF_2	0.60	7.03	2.24	5.68	
SCl_2	0.97	6.62	2.32	6.58	
SeF_2	0.15	7.51	2.34	4.97	
$SeCl_2$	0.90	6.75	2.39	6.58	
ClF	0.49	6.20	6.39	6.88	
BrF	0.15	6.54	6.63	6.78	
BrCl	0.84	6.64	6.68	7.52	

For the nonhypervalent molecules of P and As shown in Table 1, what trends in disynaptic basin populations are evident with different ligands? What trends in valence shell populations are evident? Why do these trends occur? The monosynaptic basin populations are greater than 2, and those of As molecules (2.35, except for $AsMe_3$) are larger than those of P molecules (~2.13). Explain. Looking at these data overall, do the nonhypervalent group 15 molecules obey the classical or modified octet rule?

4. (2 points) Refer to Table 2 from the paper, shown below.

Table 2. Properties of the AX Bonds in Group 15 Hypervalent Molecules: Disynaptic Basin Population $V(A, X)$, Ligand Monosynaptic Basin Population $V(X)$, Valence Shell Population $N_v(A)$, Effective Valence Population $N_{eff}(A)$

		$V(A, X)$	$V(X)$	$N_v(A)$	$N_{eff}(A)$
NF_5	F_{ap}[a]	0.79	7.20	4.61	
	F_{eq}	1.01	6.75		
PF_5	F_{ap}	1.03	6.82	5.33	
	F_{eq}	1.09	6.78		
PCl_5	Cl_{ap}	1.33	6.56	7.13	
	Cl_{eq}	1.49	6.43		
PMe_5	Me_{ap}	1.86		9.42	
	Me_{eq}	1.90			
PF_3O	F	1.06	6.80	5.13	
	O	1.95	5.88		
PCl_3O	Cl	1.51	6.43	6.33	
	O	1.80	5.93		
PFO_2	F	1.03	6.83	4.51	
	O	1.74	6.13		
$PClO_2$	Cl	1.62	6.36	5.22	
	O	1.80	6.04		
PH_3CH_2	H	2.01		8.52	
	C	2.49	1.20		
PF_3CH_2	F	1.02	6.82	7.07	
	C	4.01			
PMe_3CH_2	Me	1.94		8.41	
	CH_2	2.59	1.21		
AsF_5	F_{ap}	7.88		39.45	5.03
	F_{eq}	7.90			
$AsCl_5$	Cl_{ap}	1.16	6.76	6.10	
	Cl_{eq}	1.26	6.72		
$AsMe_5$	Me_{ap}	1.90		9.68	
	Me_{eq}	1.96			
AsF_3O	F	7.88		31.61	5.07
	O	7.98			
$AsCl_3O$	Cl	1.27	6.71	11.71	5.82
	O	7.89			
$AsFO_2$	F	7.84		23.76	5.12
	O	7.96			
$AsClO_2$	Cl	0.83	7.10	16.73	4.95
	O	7.95			

[a] The abbreviations ap and eq refer to apical and equatorial positions of the substituent.

Describe the trends in disynaptic basin populations in these hypervalent molecules (Table 2), and compare them to the trends among comparable nonhypervalent molecules (cf. Table 1). Is the bonding in hypervalent molecules different from that in nonhypervalent molecules? What trends in valence shell populations (or where necessary, effective valence populations) are evident with various ligands and central atoms (N, P, As)? Why do these trends occur? Are these data consistent with the modified octet rule model of bonding in hypervalent molecules? Explain.

5. (2 points) In addition to the molecules listed in Table 2, the authors studied hypervalent molecules from group 16 and group 17. In molecules for which the group 16 element valence shell population can be obtained, the values range from 2.18 for SeF_6 through 7.26 for SCl_6 to 11.0 $SeMe_6$ to 11.1 for $TeMe_6$. In the few molecules with group 17 central atoms for which valence shell populations can be obtained, the value is considerably less than 8. How do the trends in these molecules compare with those apparent in the group 15 hypervalent molecules? Explain any similarities or differences. Considering all the data in this paper, is the modified octet rule an appropriate description of the bonding in hypervalent molecules? Explain in detail.

Green Chemistry Question (2.0 points) Explain how electron density calculations in general and *ELF* analysis in particular might be applied to the practice of Green Chemistry. In answering this question, you should demonstrate your understanding of the general concepts of Green Chemistry, as well as your understanding of electron density topological analysis.