

INORGANIC CHEMISTRY CUMULATIVE EXAM

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Lone pair effects in inorganic chemistry

by Donald Wink

The presence of a classical lone pair is a familiar part of inorganic chemistry, because this is the basis of Lewis acid-base theory. Lone pairs are also important in the structural chemistry of inorganic complexes.

All explanations should be in prose and should take one or two paragraphs.

1. Lone pairs and Lewis acid-base theory (25 points)

(a-15 points) Explain the role of lone pairs in Lewis acid-base theory. Provide three different examples of how this theory explains the interactions of inorganic molecules.

(b-10 points) The nature of the atom with the lone pair can affect the strength of the Lewis acid-base interactions. One way of describing this is through Hard-Soft Acid Base theory. Explain how HSAB expands the original Lewis acid-base theory. Provide at least two examples of how this is seen actual chemical reactions.

2. Lone pairs and inorganic stereochemistry (30 points)

(a-10 points) Lone pairs are often thought to occupy space because they cause molecules like ammonia, phosphine, etc. to adopt a pyramidal molecular structure. However, there are some molecules, such as tris(trimethylsilyl)amine that are planar, not pyramidal. Explain why this molecule may have a stereochemically inactive lone pair.

(b-20 points) The directionality of stereochemically active lone pairs means they are often modeled as hybrids of *s* and *p* orbitals. However, Mudring and Rieger (*Inorganic Chemistry*, 2005, 44, 6240) have recently shown that Tl^+ salts can exhibit lone pair behavior. Specifically, while K^+ and Rb^+ salts of 18-crown-6 show simple symmetric hexagonal coordination of the oxygens around the potassium and rubidium ions, identical Tl^+ salts show that the thallium ion is displaced well above the plane of the six oxygen atoms. Explain how an ion, like Tl^+ , can have such pyramidalization of its coordination sphere (hint: consider the likely electron configuration of the ions involved).

3. The strange case of Pb(II) (45 points)

(a-5 points). What is the expected electron configuration of Pb(II) ion?

(b-20 points). For some metal atoms a lone pair may or may not be stereochemically active, depending on the ligand sphere. This is a reason, for example, why the coordination geometry of lead(II) ion is so varied and unpredictable. Darensbourg and her coworkers (*Inorganic Chemistry*, **2004**, *43*, 5798-5800) have pointed out how this can frustrate efforts to design reliable lead sequestering agents, and also allow lead to interfere in many binding sites for other atoms in biology.

A recent example of this occurs with ligands such as L^1 at right. Explain why L^1 and related ligands are expected to be very good ligands for a host of M(II) ions. You can use Pt^{2+} as an example. Predict the structure of PtL^1 .

When L^1 is bound to Pb(II) the resulting complex has a dimer, $Pb_2(L^1)_2$. The lead atoms are connected to the two sulfurs and only interact weakly, if at all, with the nitrogens. The dimer is held together by a bridge to one of the sulfur atoms. As a result, the coordination geometry of the lead is, to a first approximation, a trigonal pyramid of S atoms with the lead at the apex. Explain how a Pb(II) atom can have a geometry that is reminiscent of ammonia.

(c-20 points) In contrast to the S_2N_2 systems discussed in question 3b, Fleischer and Shollmeyer (*Inorganic Chemistry*, **2004**, *43*, 5529-5536) have examined simple complexes of Pb(II) with $H_2NCH_2CH_2S^-$, L^2 . They have isolated complexes of this ligand, including a $Pb(L^2)_2$ complex. The complex has a trigonal bipyramidal geometry around Pb with C_2 symmetry and 2 axial N atoms and 2 equatorial S atoms. Draw the structure of $Pb(L^2)_2$. Explain whether this complex has a stereochemically active lone pair on Pb.