Chemistry 5021/8021 **Computational Chemistry** 3/4 Credits

Spring Semester 2004

Key

1. Mixing $AgCN_2$ and $Ni(CO)_4$ in chloroform under a CO atmosphere, you isolate a solid precipitate that microanalysis and mass spectroscopy indicate to be $NiC_4N_2O_2$. A ^{13}C NMR spectrum of the precipitate in chloroform with $Ni(CO)_4$ added as an internal standard shows a strong peak 6.6 ppm upfield from $Ni(CO)_4$ and a much smaller peak 8.4 ppm upfield from $Ni(CO)_4$. There is also a very strong peak 84 ppm upfield from $Ni(CO)_4$. An IR spectrum of the precipitate in a KBr pellet shows a strong absorption at 2154 cm^{-1} and very weak absorptions/shoulders at 2143, 2170, and 2188 cm^{-1}.

   After three recrystallizations from diisopropyl ether, your solid is composed of beautifully twinned light orange crystals. NMR and IR spectra of the recrystallized solid show only the strong peaks noted above, and none of the weak ones.

   An ultraviolet spectrum of the recrystallized solid in freon (who knew it would be soluble?) shows absorptions at 310 and 333 nm.

   Here are the questions:

   a. What is the structure of the molecules in the recrystallized solid? In a narrative fashion, describe in some detail how you came to your conclusion. Note that achieving 100% confidence can be very much more expensive than 99% confidence. It is perfectly OK to be satisfied with 99%.

$Ni(CO)_4$ is a well known compound that would appear to have some relevance to the subject compounds. Thus, as a starting point, I benchmarked levels of theory based on their ability to compute known properties of nickel tetracarbonyl. A quick search of the web turned up that the molecule is tetrahedral (T_d symmetry!) with NiC bond lengths of 1.838 Å and CO bond lengths of 1.142 Å and a CO stretching frequency of 2058 cm^{-1}. I tested HF/6-31G(d), HCTH/6-31G(d), and B98/6-31G(d). The final method gave bond lengths of 1.809 and 1.146 for NiC and CO, respectively, and I decided that this was good enough (using a much bigger basis set might have improved things, but I decided that that would cost too much). The CO stretching frequency for $Ni(CO)_4$ was

computed at the B98 level to be 2145 cm^{-1}, which is 4% too high—about what is expected since B98 is a hybrid model including HF exchange, and that causes frequencies to be a bit too high. So, I'll scale other frequencies computed at this level by 95.9%. (Note, incidentally, that there is no 6-31G(d) basis set for Ni, but G03 by convention uses a so-called McClean-Chandler basis for the first-row transition metals when 6-31G(d) is listed in the keyword line. Note also that there is no guarantee that we should expect our nickel systems to have singlet ground states, but it is a trivial matter to check that these states are indeed the lowest in energy—most of you probably just defaulted to choosing a singlet state and gave it no further thought.)

As for the unknown solid, an obvious choice is that the product of the initial reaction is $Ni(CO)_2(CN)_2$. Ni^{II} compounds are usually square planar, so there should be only two stereochemical possibilities, one where the carbonyl groups are trans to one another (D_{2h} symmetry) and one where they are cis (C_{2v} symmetry). I optimized the geometries for each at the B98/6-31G(d) level and computed IR frequencies and ^{13}C isotropic NMR shieldings (I also computed NMR shieldings for $Ni(CO)_4$ since that molecule was used as the internal standard for the spectral measurements). Note that NMR chemical shifts are reported as deshieldings usually, so a higher shielding means an upfield shift and a lower shielding means a downfield shift. In any case, here are the data:

Property	*Trans (D_{2h}) isomer*	*Cis (C_{2v}) isomer*
H_0 (E_h)	*-1920.245 87*	*-1920.237 89*
High intensity IR peaks scaled by 0.959 (cm^{-1})	*2154*	*2143, 2170, 2188*
^{13}C NMR shieldings relative to $Ni(CO)_4$ (ppm)	*6.6, 84.0*	*8.4, 84.1*

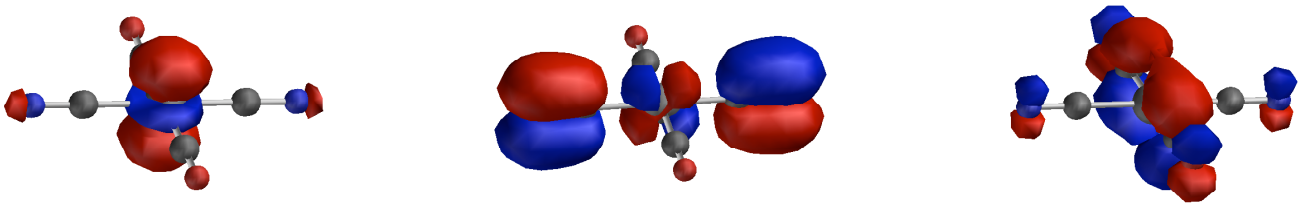
My, my, what remarkably close agreement with experiment… Evidently my solid is a mixture predominantly composed of the trans isomer (which, comfortingly, is the one that's lower in energy, albeit by too much probably to assume that the product mixture is produced from a thermodynamic equilibrium). Recrystallization removes the cis isomer from the crude precipitate.

b. To what electronic transitions do the two peaks in the UV spectrum correspond (show pictures of the orbitals)? Based on the nature of these transitions, how might you expect the geometries of the first and second excited states to differ

from the ground state (don't do an excited-state geometry optimization, just infer from the orbitals).

A survey of the first 6 excited singlet states using TDDFT (B98/6-31G(d)) finds that only the second and sixth have non-zero oscillator strengths, and fascinatingly enough the predicted absorptions are at 333 and 310 nm. The absorption at 333 nm is predicted to be completely dominated by a HOMO→LUMO transition (orbital 41→42) while the absorption at 310 nm is predicted to be dominated by a 39→42 transition. Pictures of these 3 orbitals are:

39	41 (HOMO)	42 (LUMO)



So, orbital 39 is a fairly pure d_{z^2} orbital on Ni, orbital 41 is an antisymmetric combination of CN π bonds with a weak antibonding interaction with Ni, and orbital 42 is a symmetric combination of CO π antibonds with no significant Ni contribution (only a Ni p_z orbital would have the right phase behavior to participate in this orbital, and no such orbital is nearby in energy). Thus, we would call the 333 absorption a ligand→ligand transition that moves charge from the CN fragments to the CO fragments. Looking at the orbital phases, depopulating the CN bonding orbitals will lengthen the CN bonds in the excited states and population the CO antibonding orbitals will lengthen the CO bonds. The two carbon atoms of the CO ligands will be drawn closer to the central Ni atom to maximize the bonding π overlap between them and the two carbon atoms of the CN fragments will also be drawn closer to Ni since the depopulated HOMO was antibonding between Ni and C. As for the 39→42 transition, this would be called a metal-to-ligand charge transfer (MLCT) band. The excited state geometry should see the CN fragments largely unaffected (there is no significant contribution of CN orbitals to either the depopulated or populated orbitals in the excited state). Again, however, we expect the CO fragments to draw closer to Ni and to lengthen the CO bond.*

2. Here continues a problem that will carry over to the final exam. We add to the data at:

`pollux.chem.umn.edu/8021/C4H6N2O2-PES/`

Full credit for sensible data.