Chemistry 529
Problem Set #2 – Magnetic Resonance Methods

1. Construct a proper energy level diagram for a spin system where a single I_1 = ½ nucleus is coupling with three identical $I_{2,2',2''}$ = ½ nuclei where $\sigma_1 > \sigma_2$ and $J_{12} < 0$. Carefully label the diagram showing all allowed transitions for each set of nuclei. Derive the energy expressions for the resultant levels as well as for the allowed transitions. Also draw a qualitative NMR spectrum for this situation. [*Assume there is no scalar coupling between identical nuclei*]

2. What is the biggest contribution to "chemical shift" in the following cases. Explain.

   a) The ^{1}H NMR of a six-coordinate low-spin ferrous complex.

   b) The ^{1}H NMR of a six-coordinate low-spin ferric complex.

   c) The EPR of a six-coordinate low-spin ferrous complex.

   d) The EPR of a six-coordinate low-spin ferric complex.

3. There are two major ways for two magnetic moments to interact with each other. What are these and how do they manifest themselves in solution-phase 1D NMR?

4. What differences would you expect for the *g* factors of Co^{2+} in O_h vs. T_d coordination environments and in the ability to obtain a spectrum at room temperature?

5. Generate a *practical* problem set question (with a solution!!!!) on NMR spectroscopy. An example of such a question is shown below:

   The following figure shows the ^{1}H NMR spectrum of the SMe_2 signal of the following Pt dimer complete with ^{195}Pt satellites. Account for the coupling pattern that is observed.

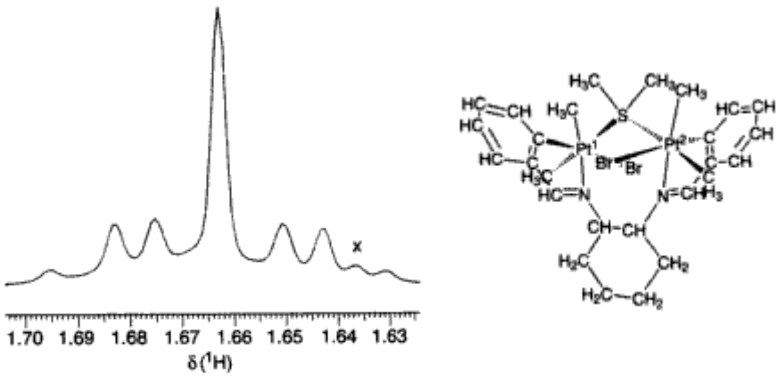

Figure 9.53 The 300 MHz ^{1}H NMR spectrum of the SMe_2 group of $[Pt_2(C_6H_4CH{=}N\text{-}1\text{-}C_6H_{10}\text{-}2\text{-}N{=}CHC_6H_4)Me_4Br_2(\mu\text{-}SMe_2)]$ in $CDCl_3$. x marks an impurity. (Reproduced with permission from Puddephatt *et al.* (1998) *Organometallics*, **17**, 32, copyright (1998) American Chemical Society.)

6. Generate a *practical* problem set question (with a solution!!!!) on EPR spectroscopy.