Inorganic NMR

Suggested reading:

- *NMR Spectroscopy in Inorganic Chemistry*, Iggo
- *Nuclear Magnetic Resonance*, Hore
- *NMR and Chemistry*, Akitt & Mann

Questions:

(i) Discuss the importance of timescale in NMR measurements. In what sense can the technique be used to explore dynamical processes, including fluxionality? Augment your answer with discussion of relevant examples, which may include the following compounds (and any others you wish to discuss): SF₄, XeF₆, Al₂Me₂, Co₄(CO)₁₂, Fe(Cp)₂(CO)₂, [Fe(Cp)(CO)]₂.

(ii) An important research paper describing an NMR study of diborane, B₂H₂ is available online at

http://dx.doi.org/10.1063/1.1669822

Using this paper, and to the best of your ability, rationalise the ¹H and ¹¹B NMR reported in Figures 1 and 2, respectively.

(iii) Account for the ¹¹⁹Sn NMR solution spectrum of the compound [Pt(PPh₃)₂(SnCl₃)H] given below.

![119Sn NMR spectrum](image)

[The spins and abundances of the only important nuclei are: ¹H: I = 1/2, 100%; ³¹P: I = 1/2, 100%; ¹¹⁹Sn: I = 1/2, 8.6%; ¹⁹⁵Pt: I = 1/2, 33.8%]
(iv) The $^{31}\text{P}$ and $^{195}\text{Pt}$ NMR spectra of a solution of Pt$_x$(PMe$_3$)$_y$ at 25 °C are shown below (coupling due to protons has been removed by broad band irradiation). Interpret the spectra, determine the values of $x$ and $y$ and hence establish the geometry of the molecule.

(v) Describe the low temperature $^{19}\text{F}$ NMR spectrum likely to be shown by each of the following.

\[
\text{XeF}_5^- \quad \text{PF}_3 \quad \text{ClF}_3
\]

$^{19}\text{F} : I = \frac{1}{2} (100\%); \quad ^{31}\text{P} : I = \frac{1}{2} (100\%); \quad ^{129}\text{Xe} : I = \frac{1}{2} (26.4\%)$

(vi) Predict and sketch the appearance of the $^{31}\text{P}$ NMR spectrum of both fac-Rh(PPh$_3$)$_3$Cl$_3$ and mer-Rh(PPh$_3$)$_3$Cl$_3$. [Consider only the following nuclear spins and abundances where relevant: $^{31}\text{P} I = 1/2 (100\%); \quad ^{103}\text{Rh} : I = 1/2 (100\%).$ You may ignore coupling to $^1\text{H}$.]
Past paper questions:

(2014) — this part was worth 5 marks.

(d) Describe the $^1$H NMR spectra for each of the following, using the data provided.

$$\begin{array}{cccc}
\text{[}^{14}\text{NH}_4\text{]}^+ & \text{SiH}_4 & \text{PH}_3 & \text{CH}_2\text{D}_2 \\
\end{array}$$

[Nuclear spins: $^2$H (i.e. D), $I = 1$; $^{14}$N, $I = 1$; $^{29}$Si, $I = \frac{3}{2}$; natural abundance 5%; $^{31}$P, $I = \frac{1}{2}$; natural abundance 100%; coupling to $^{13}$C can be ignored]

(2007) — this part was worth 20/3 marks.

(e) Describe the low temperature solution $^{19}$F NMR spectrum likely to be shown by each of the following:

$$\begin{array}{cccc}
\text{PF}_5 & \text{ClF}_3 & [^{11}\text{BF}_4]^+ & \text{^{71}GeF}_4 \\
\end{array}$$

[Consider only the following nuclear spins and abundances where relevant: $^{19}$F: $I = \frac{1}{2}$ (100%); $^{31}$P: $I = \frac{1}{2}$ (100%); $^{11}$B: $I = \frac{3}{2}$; $^{71}$Ge: $I = \frac{9}{2}$]
5. **Non-metal chemistry**

The Scheme shown below summarises some aspects of the chemistry of xenon.

\[ \text{Xe} + 3 \]

\[ \text{SbF}_3 \]

\[ \text{F}_2 \]

\[ \text{in liquid HF} \]

\[ \text{AuF}_3 \]

\[ \text{excess KI (aq)} \]

\[ \text{SiO}_2 \]

\[ \text{NaNO}_3 \]

\[ \text{NaF} \]

\[ \text{Xe} + \text{KF} + \text{I}_2 \]

\[ \text{SiF}_4 + 7 \]

\[ 8 + 9 \]

Identify the compounds 1 – 9, draw their structures, and explain the observations given below. *Note* that the Scheme does not necessarily imply anything about the stoichiometry of the reactions. A detailed assignment of the vibrational spectral data is not required.

**Compound 1** has a single stretching fundamental in its IR spectrum. It reacts with H\(_2\)(g) to generate 3 moles of gas per mole of 1. \[2\]

Continued over...
Compound 2 is an orange solid, the $^{129}$Xe NMR spectrum of which is a doublet, and which contains 31.5% Sb by weight. [2]

Compound 3 is a rather unreactive, insoluble gas. [2]

Compound 4 is a diamagnetic 1:1 electrolyte. Its $^{19}$F NMR spectrum shows fluorine in three chemically inequivalent environments in the ratio 1:2:6. The first two environments show a mutual $^{19}$F-$^{19}$F J-coupling and both show satellites due to coupling to $^{129}$Xe. The third environment gives rise to a singlet. [3]

Compound 5 has two stretching fundamentals in its Raman spectrum and one in its IR spectrum which does not coincide with either of the Raman-active fundamentals. Compound 5 reacts with excess KI (aq) to generate I$_2$, which requires 4 moles of S$_2$O$_5^-$ per mole of 5 to decolourise it. [3]

Compound 6 is a monomer in the gas phase, but predominantly a tetramer in solution and the solid state. [2]

Compound 7 is a dangerously explosive solid which contains no fluorine, and which has two IR-active fundamentals. [2]

Compounds 8 and 9 are produced in stoichiometrically equal amounts, together with NaF, when 6 reacts with NaNO$_3$ in a 1:1 ratio. The $^{129}$Xe NMR spectrum of 8 is a binomial quintet. The $^{19}$F NMR spectrum of a mixture of compounds 8 and 9 shows two peaks in the intensity ratio 4:1; only the former has satellites from coupling to $^{129}$Xe. The IR spectrum of 9 shows three stretching fundamentals. [4]

[NMR nuclei: $^{19}$F, I = $1/2$ (100%); $^{129}$Xe, I = $1/2$ (26.5%); $^{195}$Pt, I = $1/2$ (34%)]

[Atomic Masses: F, 19.0; Sb, 121.8; Xe, 131.3]