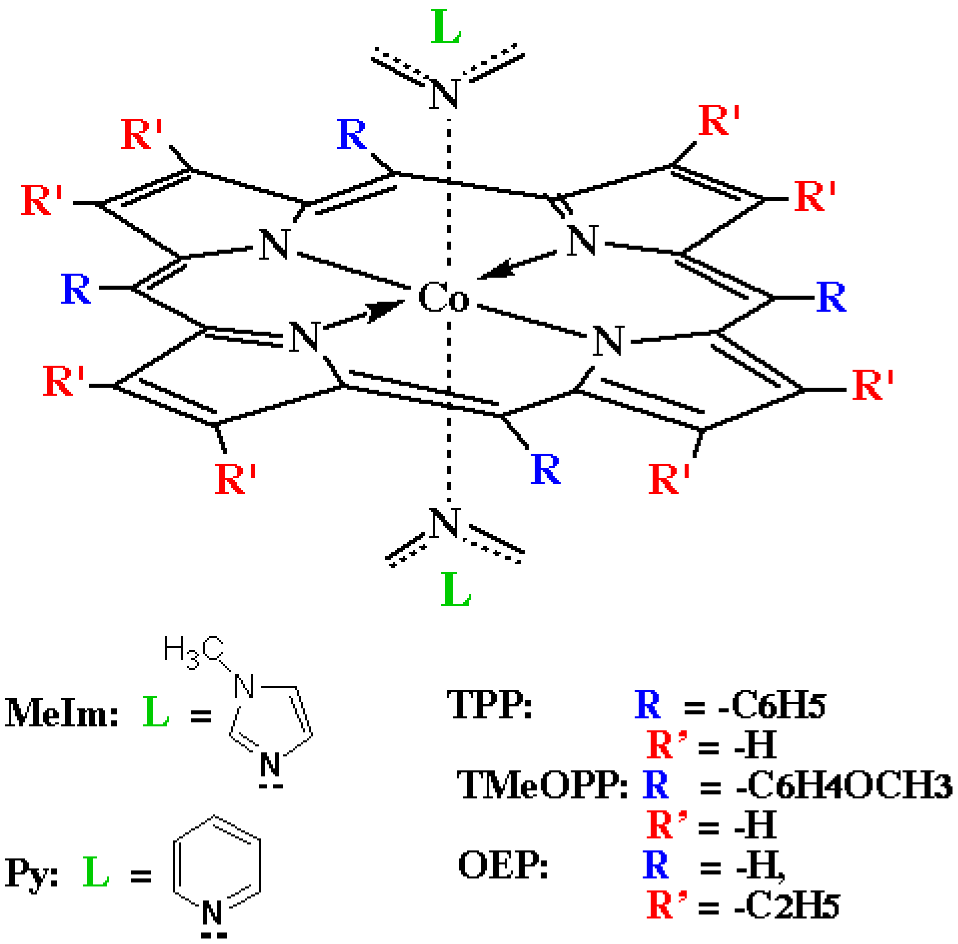
Solid State ^{59}Co NMR Studies of Hexacoordinated Porphyrins

Introduction

Solid state ^{59}Co magic-angle-spinning (MAS) NMR spectra were recorded on hexacoordinated Co(Por)L2 complexes, where Por = tetraphenylporphyrin, tetramethoxyphenylporphyrin, octaethylporphyrin, and L = imidazole, methylimidazole, pyridine:



These complexes constitute structural analogues of hemins and vitamin B12, derivatives that play fundamental biological functions. Understanding their electronic properties is thus a topic of intense investigation where ^{59}Co MAS NMR can play an important role.

Solid-State ^{59}Co NMR

Solid state NMR spectra in these kind of systems described by a Hamiltonian of the type

$$\mathcal{H}_{total} = \mathcal{H}_q^{(1)} + \mathcal{H}_{cs}^{(1)} + \mathcal{H}_q^{(2)}$$

$\mathcal{H}_q^{(1)}$: quadrupolar contribution to the first order
$\mathcal{H}_{cs}^{(1)}$: chemical shift contribution to the first order
$\mathcal{H}_q^{(2)}$: quadrupolar contribution to the second order

Since 1st-order effects make satellite transitions unobservable we concentrate on the central -1/2 -> +1/2 one. Upon sample spinning the NMR spectrum of this transition breaks up into a series of sharp lines (sidebands) arising from quadrupolar and shielding anisotropies, and broadened only by second order quadrupolar effects. The centerband of the resulting spectrum is centered at the sum of isotropic chemical and quadrupolar shifts:

$$\delta_{centerband} = \delta_{cs}^{iso} + \frac{(e^2qQ/h)^2}{\nu_0^2}\,\delta_q^{iso}$$

ν_0: Larmor frequency

and its frequency can be determined by changing the speed of sample rotation. Moreover, if these measurements are repeated at different magnetic fields strengths, the values of all chemical and quadrupolar parameters can be determined.

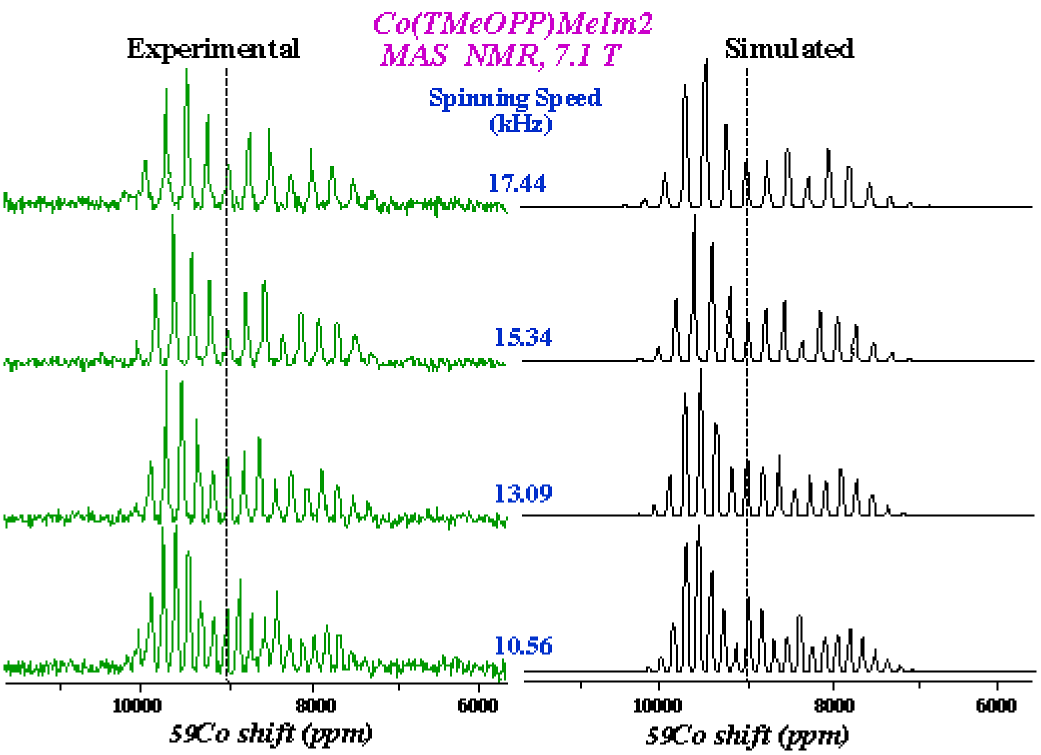
Experimental

All Co(Por)L2 complexes were prepared according to published methods and positively identified by means of elemental analysis and 1H NMR. ^{59}Co MAS NMR spectra of these compounds were acquired at two different magnetic fields (4.7 & 7.1 Tesla) with variable spinning speeds in the 10-18 kHz range. The center band frequencies in the spectra were accurately identified in this manner and quadrupolar parameters extracted from the variable field data. Finally, the lineshapes of the different MAS spectra were simulated in order to extract the ^{59}Co CSA NMR parameters. Instrumental dead times were taken into account in these simulations by delaying the initial digitization points; second order quadrupolar effects were also taken into account with their tensors assumed colinear and with identical asymmetries as the chemical shifts.

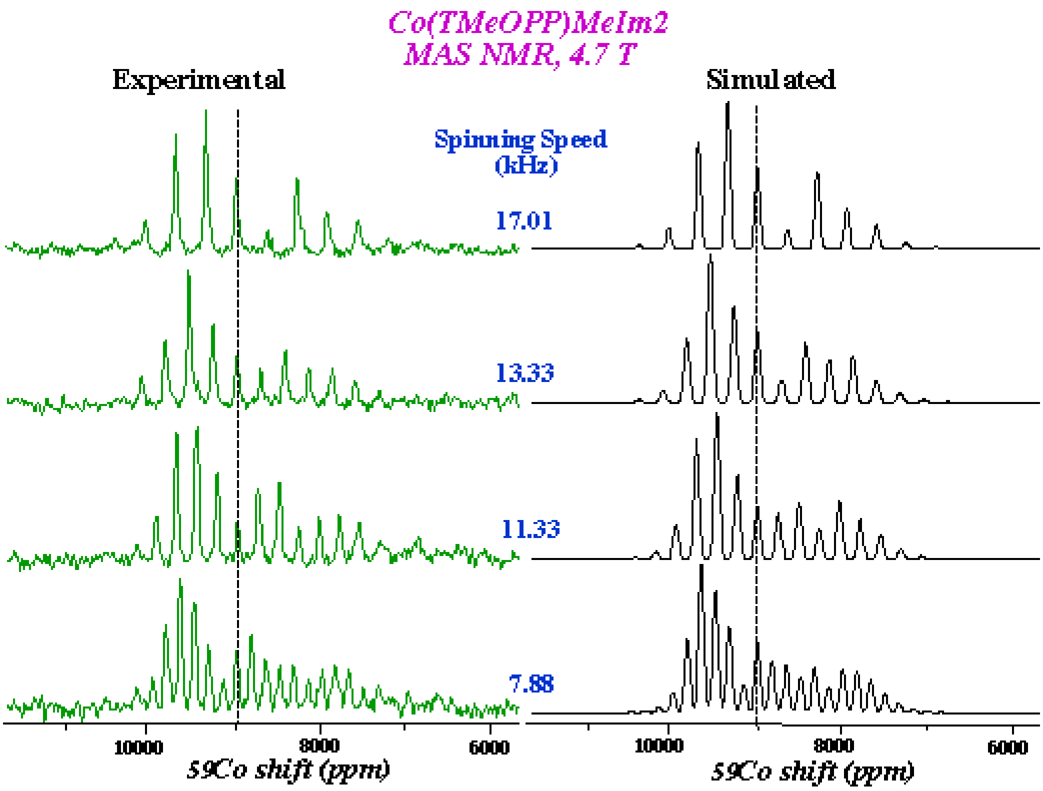
Summary of Results

Imidazole and N-methilimidazole complexes have similar spectroscopic properties. An example of the variable-speed data recorded on

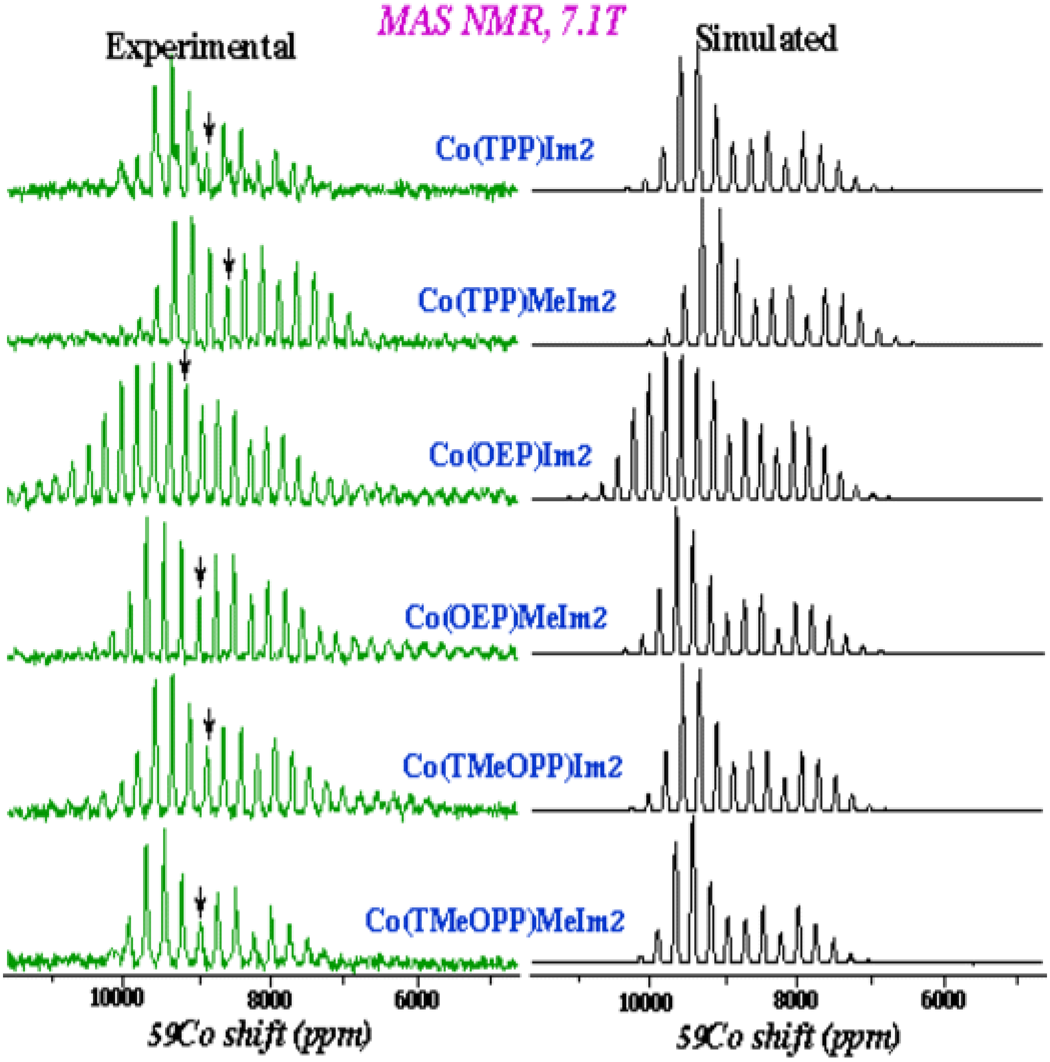
Co(TMeOPP)(MeIm)2 complex at 7.1 T
(dashed line = centerband position)



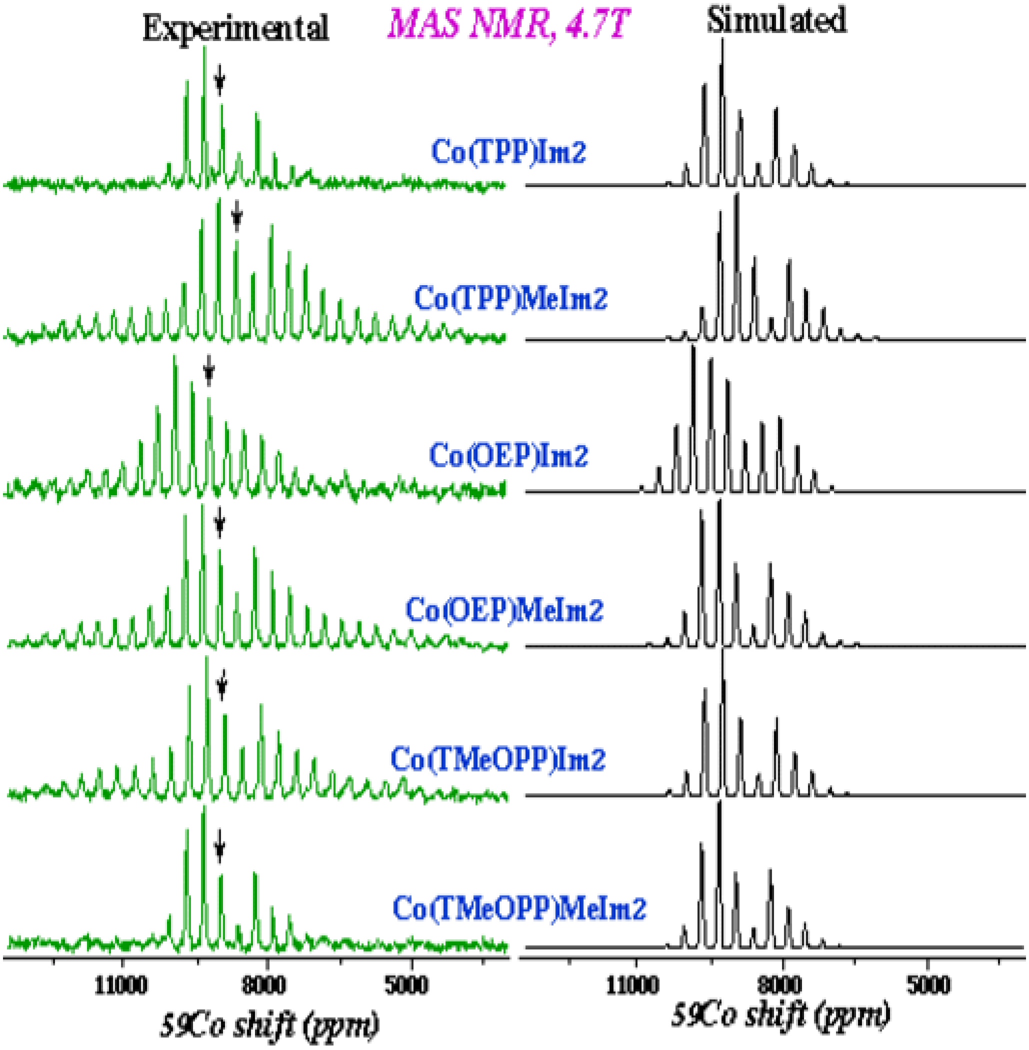
Co(TMeOPP)(MeIm)2 complex at 4.7 T



The various high-speed spectra at 7.1 T
(arrow = centerband position)

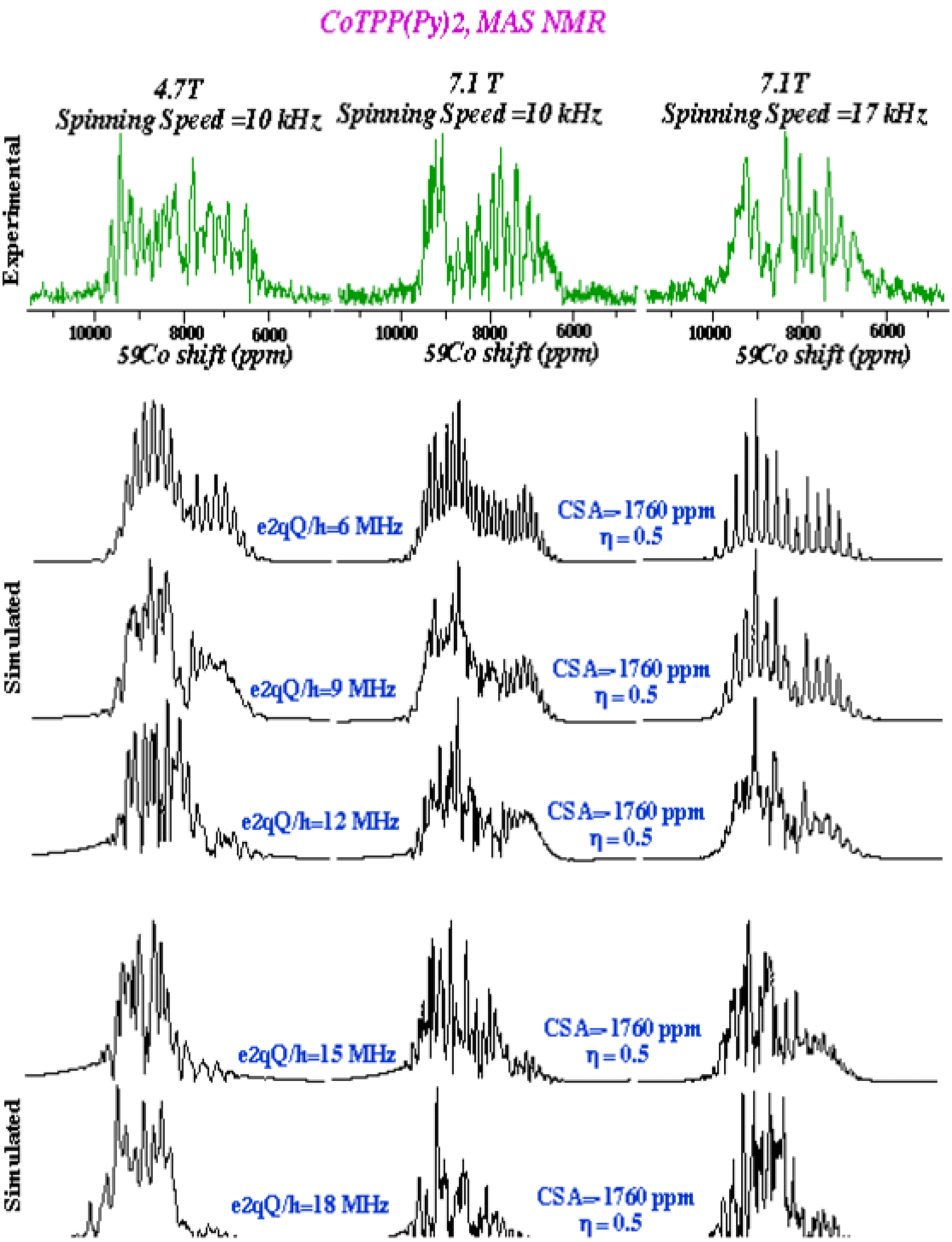


The various high-speed spectra at 4.7 T



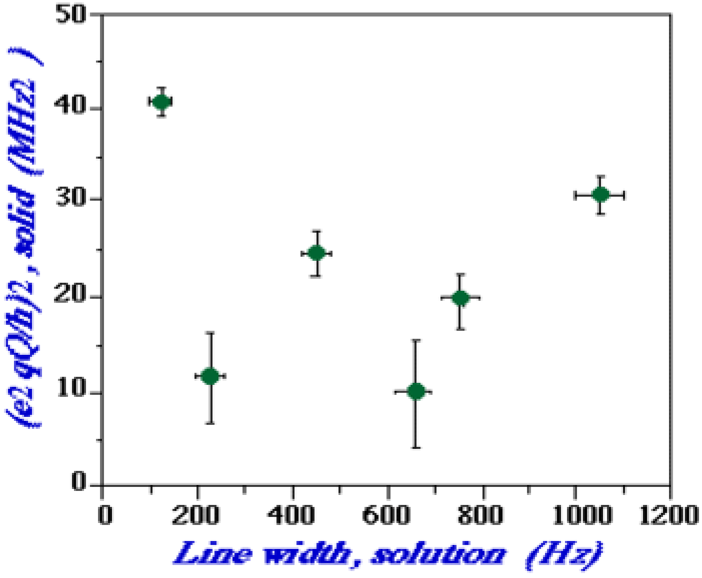
According to these data, the quadrupole coupling constants of all the cobalt sites are fairly small (3-5 MHz) but the CSA's are large, spanning in excess of 2,000 ppm.

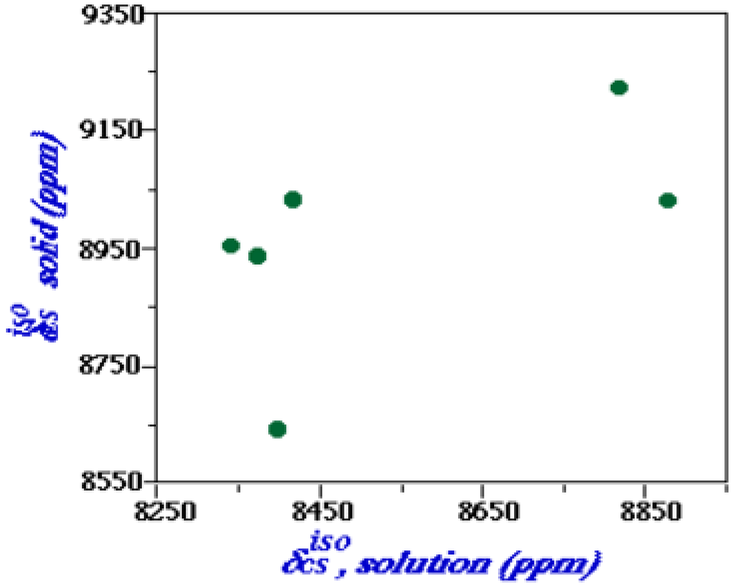
The situation is different for the pyridine complex: although the CSA is still ca. 2,000 ppm large, the coupling constant is much larger:



Discussion

The chemical shifts and quadrupolar coupling of Co(III) complexes are highly dependent on the environment surrounding the metal site. A combination of Ramsey's chemical shift formalism and the Townes- Dailey model for quadrupole couplings can be used to extract electronic informations from these parameters. This type of analysis was reported on hexacoordinated Co(III) complexes in solution state. However, serious discrepancies arise when comparing the CSA and quadrupolar information inferred from these solution studies with that measured in the solid:





Furthermore, although literature studies support a linear correlation between CSA and quadrupolar coupling constant values, these correlations fail when applied to the homologous porphyrin series. This suggests an unsuitability of simple qualitative techniques for understanding the electronic structure of Co(III) metalloporphyrins.