Manipulating and quantifying spin states in solution as a function of pressure and temperature†

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Monitoring the spin states of species in solution is a crucial aspect of understanding magnetic properties as well as spin-labile sensing, supramolecular, catalytic and biochemical processes. Herein, we describe the first quantitative variable-pressure and variable-temperature method of determining spin states in solution, demonstrate that it is accurate, and identify a simultaneous $T$ and $P$ sensor system.

Determining the spin state of a system is fundamental to understanding its magnetic properties and chemical reactivity. The study of molecular magnetic phenomena relies upon the measurement of spin states under different conditions. Understanding reactivity and catalytic processes is greatly aided by being able to determine the spin states of various reactants, intermediates and products. Measurements of spin states in the solution phase are of particular importance, especially for the study of biologically relevant processes, including photosynthesis and solution phase are of particular importance, especially for the study of biologically relevant processes, including photosynthesis and supramolecular, catalytic and biochemical processes. Herein, we describe the first quantitative variable-pressure and variable-temperature method of determining spin states in solution, demonstrate that it is accurate, and identify a simultaneous $T$ and $P$ sensor system.

The application of hydrostatic pressure to spin-labile compounds typically favours the low spin (LS) state due to the smaller molecular volume compared to the high spin (HS) state. While this has been observed in pressure-induced solution spin crossover (SCO), by the Gouy method, and UV-vis and $^1$H NMR spectroscopies, these have all been qualitative measures of spin states. Herein, we establish a method for the accurate quantitative measurement of spin states in solution at variable pressures and temperatures, by extension of the ambient pressure Evans $^1$H NMR ‘tube-in-tube’ method to enable the use of a ‘single-tube’ that can be pressurised to 240 MPa. In addition to quantitative spin-state information, the $^1$H NMR spectra themselves can also yield useful chemical and 3D structural information about the subject complex. Thus, this method adds spin-state capabilities to high-pressure NMR techniques such as those already applied to host–guest, catalytic, and biomacromolecular systems.

In order to develop this method of quantifying solution spin states under pressure, three of our recently reported solution-phase (thermally-induced) SCO-active dinuclear iron(II) complexes of 4-substituted-3,5-bis[[2-(pyridylmethyl)-sulfanyl]methyl]-1,2,4-triazole (PSRT) ligands, where $R = \text{Ph, } \text{MePh or } \text{iBu}$, i.e. $[\text{Fe}_2 \text{(PSPhT)}_2 \text{(BF}_4)_4$, $[\text{Fe}_2 \text{(PSMePhT)}_2 \text{(BF}_4)_4$, and $[\text{Fe}_2 \text{(PSiBuT)}_2 \text{(BF}_4)_4$ (Fig. 1), were investigated by high-pressure $^1$H NMR spectroscopy. Spectra were recorded in CD$_2$CN solution at 30 MPa intervals between 0.1 MPa (atmospheric pressure) and 240 MPa, and at 5 different temperatures in the range of 278–313 K.

In each spectrum (Fig. 2 and Fig. S1–S3, ESI†), very broad and highly downfield shifted (up to ~100 ppm) proton signals typical of a paramagnetic substance are observed, indicating population of the HS state. As pressure is increased, these downfield signals shift upfield or towards a “normal” position expected for a diamagnetic material, indicating that a pressure-induced SCO towards the LS state occurs. At 240 MPa, the

![Fig. 1](image-url) PSRT ligand with the three $R$ groups used in this study (left), and the structure of the $[\text{Fe}_2 \text{(PSRT)}_2]^{4+}$ cations (right).
proton signals are still relatively far downfield, indicating that a significant population of the HS state remains, consistent with the SCO being incomplete within the pressure range studied. Proton signals that were shifted upfield by the paramagnetism (to ~5 ppm) concomitantly move downfield towards their diamagnetic values as pressure is increased.

To quantitatively analyse the spin states at each pressure, we turned to the Evans method which under standard conditions (ambient pressure) uses a tube-in-tube experiment. The inner tube contains pure deuterated solvent and the outer tube contains the paramagnetic material in the same solvent. The frequency shift of the solvent signal, \(\Delta f\), in the outer tube compared to the pure solvent (to which the NMR spectrum is locked), is dependent on the magnetic susceptibility of the paramagnetic material, and hence \(\chi_M T\) can be calculated from \(\Delta f\) (Hz), the concentration \(m\) (g cm\(^{-3}\)), and the spectrometer frequency \(f\) (Hz) using the Evans method (eqn (1)) to obtain the mass susceptibility \(\chi_g\) (cm\(^3\) g\(^{-1}\)).\(^{10,15}\)

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\chi_g = 3\Delta f / (4\pi mf)
\]  

However, an inner tube is not feasible with our high-pressure cell and zirconia NMR tube, or for that matter with most high-pressure NMR setups, which typically involve specialised thick-walled glass or sapphire pressurisable tubes, or modified probes made from beryllium-copper or titanium alloys.\(^\text{10,16}\) In the absence of a reference frequency for the solvent CD\(_2\)HCN signal, our approach was to instead remove the lock on the CD\(_2\)HCN signal such that it would shift with varying pressure. The frequency shift at each pressure relative to atmospheric pressure is defined as \(\Delta f'\) (Fig. 3). This quantity could then be added to the known frequency shift from that in pure CD\(_2\)CN at atmospheric pressure, \(\Delta f^0\) (determined from our previous variable temperature Evans method data on these complexes),\(^\text{17}\) to obtain \(\Delta f\) and hence \(\chi_g\) from eqn (1), and therefore \(\chi_M T\) at each pressure.

For each Fe(II) solution, as the pressure increased the CD\(_2\)HCN signal shifted upfield (Fig. 3), resulting in increasingly negative values of \(\Delta f'(\text{Fe})\) (Fig. 3, red), which is consistent with the SCO towards the LS state. However, with the lock signal off, the CD\(_2\)HCN peak will gradually drift upfield with time in the absence of any pressure/temperature changes or change in magnetic susceptibility of the sample. This is due to the magnetic field strength of the NMR slowly, and reliably, decreasing with time after tuning. The magnitude of this effect is small in comparison to the signal shift upon pressure changes, but nonetheless time corrections were applied to \(\Delta f'(\text{Fe})\) values to minimise error (see the ESI† for details).

A correction must also be made for the CD\(_2\)HCN signal frequency shift with increasing pressure for a diamagnetic solution, so that the magnitude of the shift in the Fe(II) solution due to the SCO can be ascertained. For this purpose, the Zn(II) analogues of each complex, \([\text{Zn}_2(\text{PSRT})_2]_2(\text{BF}_4)_4\), were synthesised (see the ESI†). Typically in paramagnetic NMR studies, a free ligand is used as a diamagnetic reference; however, as this is the first high-pressure NMR magnetic susceptibility study, in order to check for any unforeseen chaotrope/kosmotrope effects with...
varying pressure, the Zn(II) complexes, which are of the same size, shape and charge as the Fe(II) complexes and so were considered to be superior to the free ligands, were also tested. Conveniently, this test demonstrates that the free ligand is in fact a perfectly acceptable diamagnetic reference, as it responds in the same way as the Zn(II) complexes do (Fig. S4, ESI†). Conveniently, this test demonstrates that the free ligand is in fact a perfectly acceptable diamagnetic reference, as it responds in the same way as the Zn(II) complexes do (Fig. S4, ESI†).

**Fig. 4** $\chi_M T$ vs. pressure vs. temperature for CD$_2$CN solutions of (left) [Fe$_2$(PSPhT)$_2$](BF$_4$)$_4$ (centre) [Fe$_2$(PS$i$BuT)$_2$](BF$_4$)$_4$ and (right) [Fe$_2$(PS$i$BuT)$_2$](BF$_4$)$_4$. The colour coding shows the wide and varied magnetic responses across the three complexes as a function of temperature and pressure.

The proton signals observed in the $^1$H NMR spectrum of the Zn(II) analogues, at the same concentration in CD$_2$CN as the corresponding Fe(II) complexes, were recorded to determine the frequency shift of CD$_2$HCN relative to atmospheric pressure for the diamagnetic Zn(II) solutions, defined as $\Delta f$(Zn) (Fig. 3, blue). This enabled point-by-point corrections, for $\Delta f$(Zn) at each pressure and temperature investigated, to be made to the Fe(II) spectra. The resulting $\Delta f$(SCO) = $\Delta f$(Fe) – $\Delta f$(Zn) values are the frequency shifts of CD$_2$HCN relative to atmospheric pressure due only to a change in magnetic susceptibility of the Fe(II) solution (Fig. 3).

From the known $\chi_M T$ at atmospheric pressure,\textsuperscript{17} eqn (1) can be used to calculate the $\Delta f$ for the particular temperature and concentration of the Fe(II) solution, which we label $\Delta f^{\text{w}}$, the frequency shift of CD$_2$HCN at atmospheric pressure relative to that of an internal reference standard of pure CD$_3$CN, if it was present in the high pressure cell. $\Delta f$(SCO) is then the change in this frequency shift, arising from the change in spin state only, as pressure is applied. Hence, the frequency shift of CD$_2$HCN at each pressure relative to pure CD$_3$CN at that pressure is obtained simply by $\Delta f = \Delta f^{\text{w}} + \Delta f$(SCO). Finally, $\chi_M$ at each pressure can then be calculated from these $\Delta f$ values using eqn (1), considering the changes in the density of acetonitrile (and hence concentration of the complex), to give a quantitative description of the spin state at any pressure/temperature.

**Fig. 5** $\Delta$py-H5 vs. $\chi_M$ for [Fe$_2$(PSPhT)$_2$](BF$_4$)$_4$ in CD$_2$CN at variable pressure/temperature. Hollow data points represent the spectra recorded at 278 K in one solution, with the linear fit shown as the dashed line. Solid data points recorded on another solution at 283–313 K, with a solid line for the linear fit. For the $\chi_M$ values calculated for [Fe$_2$(PSPhT)$_2$](BF$_4$)$_4$, the maximum error between data points for the same solution is 2.8–2.9%, and the maximum error between data points for different solutions is 7.4%. See the ESI† for more details.
of the Evans method from a tube-in-tube method to a single tube method that can be applied to the study of pressure and temperature effects.

It is possible to calculate the fraction HS, \( \gamma_{\text{HS}} \), directly from proton chemical shifts\(^{11\text{c}} \) instead of using the Evans method. However, these methods require a fully HS baseline to be reached\(^{11\text{b}} \) and/or a very wide (200 K) temperature range.\(^{11\text{c}} \) Although our method requires careful application of corrections, it produces quantitative \( \gamma_{\text{M/T}} \) values (but not \( \gamma_{\text{HS}} \)) and can operate in narrow ranges of magnetic susceptibility and temperature.

We have described a robust method for determining the spin states quantitatively in high-pressure solutions. In the test case of the \([\text{Fe}_2(\text{PSRT})_3]\text{[BF}_4\text{]}_2\) complexes, an SCO was observed, and the spin state is tuned by both pressure and temperature in solution, raising the possibility of solution-based simultaneous pressure/temperature sensing. Unlike a thermally induced SCO, which is limited by the freezing/boiling points of the solvent, the pressure is limited only by instrumention and so has the potential to access a much wider range of spin states in solution. Although applied here only to simple Fe(n) SCO compounds, this robust method could extend to study the effects of pressure on spin-labile (bio)catalysts, sensors or host–guest chemical processes.

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Conflicts of interest

There are no conflicts to declare.

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