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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 phenomena¹ relies upon the measurement of spin states under different conditions. Understanding reactivity² and catalytic processes³ 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 photosynthesis⁴ and iron-containing enzyme activity,⁵ noting that life persists at pressures in excess of 100 MPa (~1000 atmospheres). However, there is no established method of quantifying spin states in solution as a function of both pressure and temperature.

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.⁶ While this has been observed in pressure-induced solution spin crossover (SCO), by the Gouy method,⁷ and UV-vis⁸ and ¹H NMR⁹ 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 ¹H NMR 'tube-in-tube' method¹⁰ to enable the use of a 'single-tube' that can be pressurised to 240 MPa. In addition to quantitative spin-state information, the ¹H NMR spectra themselves can also yield useful chemical and 3D structural information about the subject complex.¹¹ Thus, this method adds spin-state capabilities to high-pressure NMR techniques such as those already applied to host-guest,¹² catalytic,¹³ and biomacromolecular systems.¹⁴

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}-4*H*-1,2,4-triazole (**PSRT**) ligands, where **R** = Ph, ^{Me}Ph or ⁱBu, *i.e.* [Fe₂(**PSPhT**)₂](BF₄)₄, [Fe₂(**PS^{Me}PhT**)₂](BF₄)₄, and [Fe₂(**PSⁱBuT**)₂](BF₄)₄ (Fig. 1), were investigated by high-pressure ¹H NMR spectroscopy. Spectra were recorded in CD₃CN 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

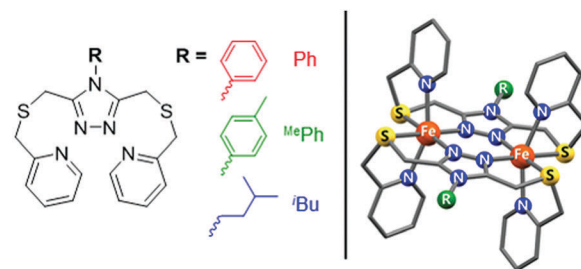


Fig. 1 **PSRT** ligand with the three **R** groups used in this study (left), and the structure of the [Fe₂(**PSRT**)₂]⁴⁺ cations (right).

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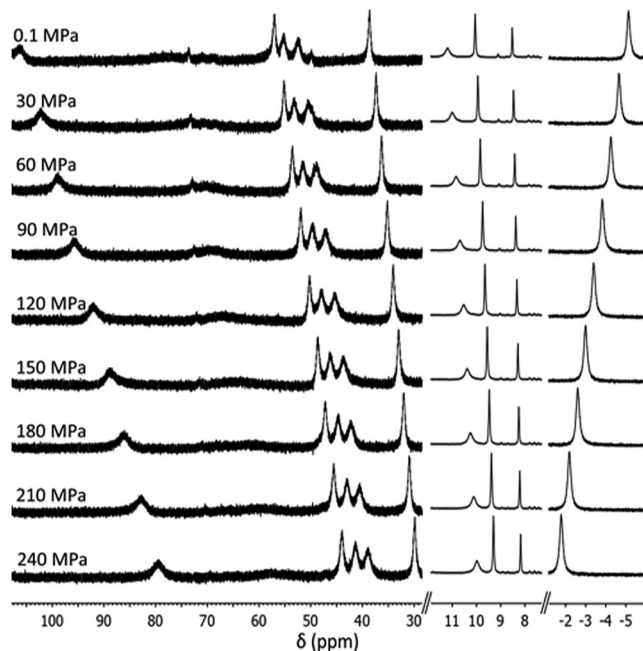


Fig. 2 Stacked ^1H NMR spectra of $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$ in CD_3CN solution showing a qualitative SCO at room temperature (293 K) from 0.1 MPa (top) to 240 MPa (bottom). Note that the spectra have been truncated to highlight the downfield shifted signals of some methylene and pyridyl protons (left) and phenyl protons (centre), and the upfield shifted pyridyl proton signal (right). For the full spectra, see Fig. S1, ESI†

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, Δf , 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 Δf (Hz), the concentration m (g cm^{-3}), and the spectrometer frequency f (Hz) using the Evans method (eqn (1)) to obtain the mass susceptibility χ_g ($\text{cm}^3 \text{g}^{-1}$).^{10,15}

$$\chi_g = 3\Delta f / (4\pi m f) \quad (1)$$

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.^{13b,16} In the absence of a reference frequency for the solvent CD_2HCN signal, our approach was to instead remove the lock on the CD_2HCN signal such that it would shift with varying pressure.

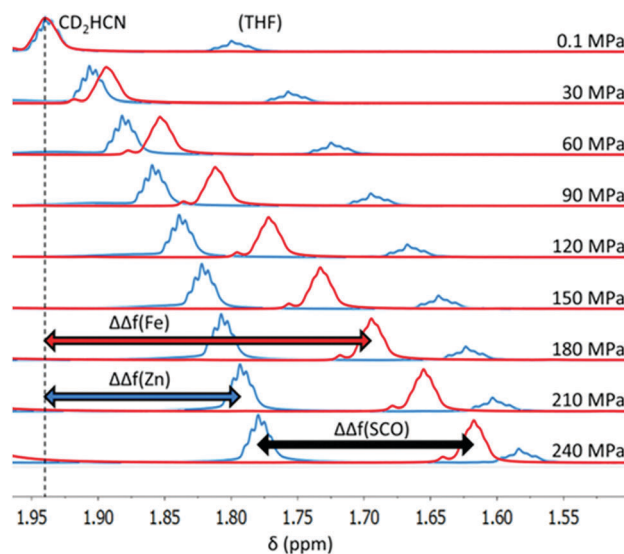


Fig. 3 Frequency shift of the CD_2HCN signal for $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$ (red spectra) and the diamagnetic analogue $[\text{Zn}_2(\text{PS}'\text{BuT})_2](\text{BF}_4)_4$ (blue spectra) from 0.1 MPa to 240 MPa at 293 K. The magnitude of the shifts, $\Delta\Delta f(\text{Fe})$ and $\Delta\Delta f(\text{Zn})$, for the Fe(II) and Zn(II) solutions respectively, are indicated, as well as their difference, $\Delta\Delta f(\text{SCO})$, which is due to a decrease in magnetic susceptibility in the Fe(II) solution. Note: to aid visualisation, both $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$ spectra (red) and $[\text{Zn}_2(\text{PS}'\text{BuT})_2](\text{BF}_4)_4$ spectra (blue) are manually referenced such that the CD_2HCN signal is at 1.94 ppm at 0.1 MPa, because $\Delta\Delta f(\text{Fe})$, $\Delta\Delta f(\text{Zn})$, and $\Delta\Delta f(\text{SCO})$ are defined as relative to atmospheric pressure.

The frequency shift at each pressure relative to atmospheric pressure is defined as $\Delta\Delta f$ (Fig. 3). This quantity could then be added to the known frequency shift from that in pure CD_3CN at atmospheric pressure, Δf^0 (determined from our previous variable temperature Evans method data on these complexes),¹⁷ to obtain Δf and hence χ_g from eqn (1), and therefore $\chi_M T$ at each pressure.

For each Fe(II) solution, as the pressure increased the CD_2HCN signal shifted upfield (Fig. 3), resulting in increasingly negative values of $\Delta\Delta f(\text{Fe})$ (Fig. 3, red), which is consistent with the SCO towards the LS state. However, with the lock signal off, the CD_2HCN 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 $\Delta\Delta f(\text{Fe})$ values to minimise error (see the ESI† for details).

A correction must also be made for the CD_2HCN 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, $[\text{Zn}_2(\text{PSRT})_2](\text{BF}_4)_4$, 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

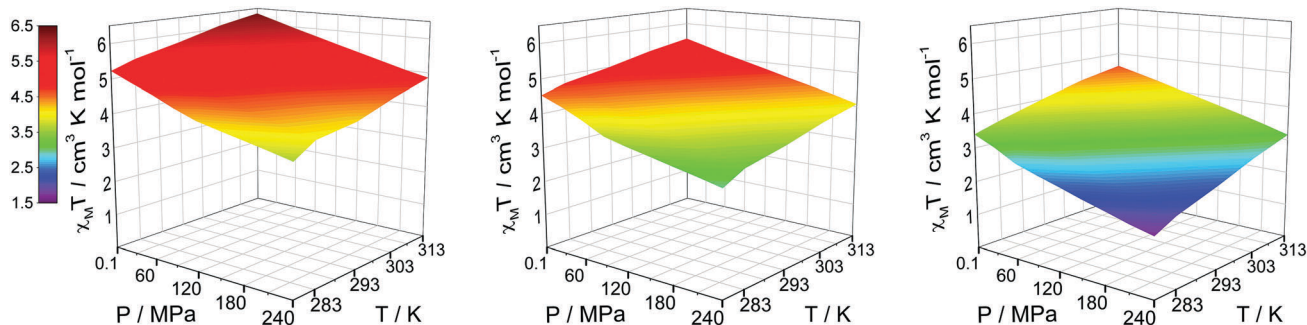


Fig. 4 $\chi_M T$ vs. pressure vs. temperature for CD_3CN solutions of (left) $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$, (centre) $[\text{Fe}_2(\text{PS}^{\text{Me}}\text{PhT})_2](\text{BF}_4)_4$, and (right) $[\text{Fe}_2(\text{PS}^{\text{Bu}}\text{T})_2](\text{BF}_4)_4$. The colour coding shows the wide and varied magnetic responses across the three complexes as a function of temperature and pressure.

varying pressure, the $\text{Zn}(\text{II})$ complexes, which are of the same size, shape and charge as the $\text{Fe}(\text{II})$ 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 $\text{Zn}(\text{II})$ complexes do (Fig. S4, ESI†). ^1H NMR spectra of the $\text{Zn}(\text{II})$ analogues, at the same concentration in CD_3CN as the corresponding $\text{Fe}(\text{II})$ complexes, were recorded to determine the frequency shift of CD_2HCN relative to atmospheric pressure for the diamagnetic $\text{Zn}(\text{II})$ solutions, defined as $\Delta\Delta f(\text{Zn})$ (Fig. 3, blue). This enabled point-by-point corrections, for $\Delta\Delta f(\text{Zn})$ at each pressure and temperature investigated, to be made to the $\text{Fe}(\text{II})$ spectra. The resulting $\Delta\Delta f(\text{SCO}) = \Delta\Delta f(\text{Fe}) - \Delta\Delta f(\text{Zn})$ values are the frequency shifts of CD_2HCN relative to atmospheric pressure due only to a change in magnetic susceptibility of the $\text{Fe}(\text{II})$ solution (Fig. 3).

From the known $\chi_M T$ at atmospheric pressure,¹⁷ eqn (1) can be used to calculate the Δf for the particular temperature and concentration of the $\text{Fe}(\text{II})$ solution, which we label Δf^0 , the frequency shift of CD_2HCN at atmospheric pressure relative to that of an internal reference standard of pure CD_3CN , if it was present in the high pressure cell. $\Delta\Delta f(\text{SCO})$ 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_2HCN at each pressure relative to pure CD_3CN at that pressure is obtained simply by $\Delta f = \Delta f^0 + \Delta\Delta f(\text{SCO})$. Finally, χ_g at each pressure can then be calculated from these Δf 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.

Applying this method to CD_3CN solutions of $[\text{Fe}_2(\text{PSRT})_2](\text{BF}_4)_4$ reveals the solution SCO induced by both pressure and temperature for each of the three complexes (Fig. 4, Fig. S7–S12, and Tables S9–S11, ESI†). The SCO is gradual and incomplete within the pressure range available. The $[\text{Fe}_2(\text{PSRT})_2](\text{BF}_4)_4$ series of complexes are potential candidates for solution sensor applications, *i.e.* for simultaneous sensing of pressure and temperature in solution over, in particular, a wide range of pressure, based on their different magnetic susceptibility responses.¹⁸

The proton signals observed in the ^1H NMR spectrum (Fig. 2) are the population-weighted average signals of the HS and LS states, and therefore the extent to which the signals are

shifted from the fully LS spectrum reflects the magnetic susceptibility of the complex in solution. Assuming the ideal Curie behaviour, the chemical shift, δ , of a proton signal has a linear relationship with χ_M .^{11b} This allows for the correlation of the processed data, χ_M , as calculated by our adapted Evans method, with raw δ spectral data for pyridyl protons py-H4 and py-H5 (Fig. 5 and Fig. S14–S19, ESI†). Indeed good linear relationships are observed, indicating a high level of accuracy in the adapted high pressure Evans method of calculating χ_M or $\chi_M T$.

The most significant error here is in knowing the exact concentration of the solutions used, which is always the case for the standard Evans method and typically results in 5–10% error.¹⁹ The error associated with the extra corrections needed (time, Zn analogues) for our adapted method is smaller (3–5%) and contains the error in accurately reading the signal position, which is also present in the standard method. Therefore, no significantly large errors are introduced through our extension

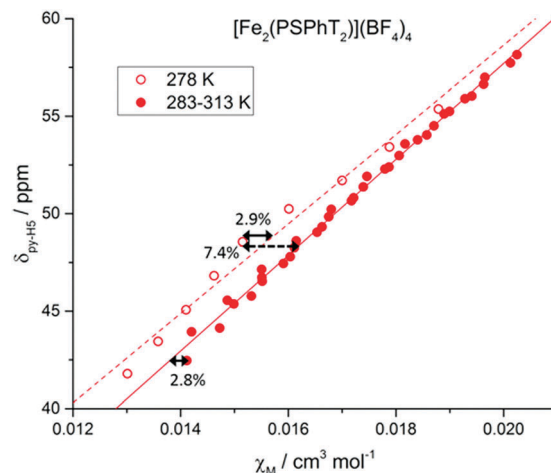


Fig. 5 $\delta(\text{py-H5})$ vs. χ_M for $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$ in CD_3CN at variable pressure/temperature. Hollow data points represent the spectra recorded at 278 K in one solution, with the linear fit shown as the dashed line. Solid data points recorded on another solution at 283–313 K, with a solid line for the linear fit. For the χ_M values calculated for $[\text{Fe}_2(\text{PSPht})_2](\text{BF}_4)_4$, 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, γ_{HS} , directly from proton chemical shifts^{11b,c} instead of using the Evans method. However, these methods require a fully HS baseline to be reached^{11b} and/or a very wide (200 K) temperature range.^{11c} Although our method requires careful application of corrections, it produces quantitative $\chi_{\text{M}}T$ values (but not γ_{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 $[\text{Fe}_2(\text{PSRT})_2](\text{BF}_4)_4$ 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 instrumentation and so has the potential to allow access to a much wider range of spin states in solution. Although applied here only to simple Fe(II) SCO compounds, this robust method could be extended 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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