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LETTERS

## Downfield displacement of the NMR signal of water in deuterated dimethylsulfoxide by the addition of deuterated trifluoroacetic acid

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### Abstract

Addition of  $d_1$ -trifluoroacetic acid to compounds in  $d_6$ -DMSO gives rise to a downfield displacement of the water signal in the  $^1\text{H}$  NMR spectrum. © 2000 Elsevier Science Ltd. All rights reserved.

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Deuterated dimethylsulfoxide ( $d_6$ -DMSO) is one of the most commonly used NMR solvents, in part due to its ability to dissolve compounds with poor solubility in other common NMR solvents. However, the hygroscopic nature of DMSO often leads to a substantial water signal at 3.35 ppm in the  $^1\text{H}$  NMR spectrum which can obscure C–H signals in this region of the spectrum, e.g. those which are adjacent to oxygen functions, such as ethers or alcohols.

We were interested in the stability of terpyridine platinum(II) complexes in solutions containing 10% trifluoroacetic acid. During NMR experiments with such complexes, we noted that the residual water peak was absent after the addition of deuterated trifluoroacetic acid ( $d_1$ -TFA) to the  $d_6$ -DMSO solutions and thus allowed signals to be assigned in this region of the spectrum. Fig. 1 shows the  $^1\text{H}$  NMR spectrum of [(3-hydroxypropylthiolato) (terpyridine)platinum(II)] hexafluorophosphate (5 mg in 1 mL of  $d_6$ -DMSO) prior to (top) and after (bottom) addition of 20  $\mu\text{L}$  of  $d_1$ -TFA. The methylene signal at 3.4 ppm, which is assigned to the  $\text{CH}_2\text{OH}$  group is obscured by the water signal at 3.35 ppm in the normal spectrum. However, after addition of  $d_1$ -TFA the signal is clearly visible with the correct integration.<sup>†</sup> The signal due to water (3.35 ppm), the alcohol (4.3 ppm) and TFA are in fast exchange, giving rise to one signal at 12.2 ppm.

In order to investigate this process we titrated  $d_1$ -TFA against a known concentration of water in a spiked  $d_6$ -DMSO solution, as illustrated in Fig. 2 (moles of TFA titrated against moles of water hydrogen atoms). Only one signal is observed for both the water and TFA protons because they are in fast exchange.

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<sup>†</sup> The  $\text{CH}_2\text{S-Pt}$  signal is coincident with the partially-deuterated DMSO signal.

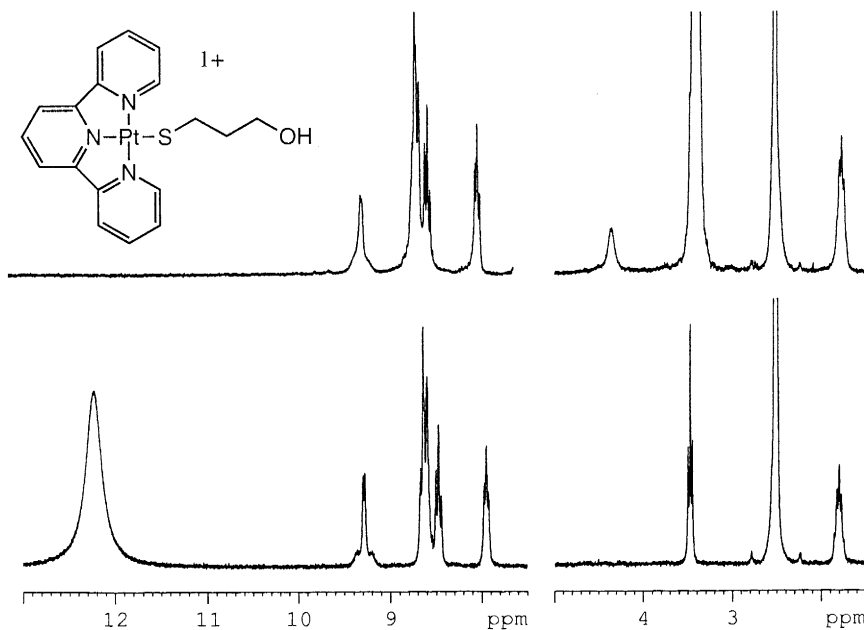


Fig. 1.  $^1\text{H}$  NMR spectra (250 MHz) of  $[(\text{HOCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{terpy})\text{Pt}(\text{II})](\text{PF}_6)$  in  $d_6$ -DMSO before (top) and after (bottom) addition of  $d_1$ -TFA

On addition of 1 equivalent of TFA (relative to water), this averaged signal occurs approximately midway (9.5 ppm) between the signals for free water in  $d_6$ -DMSO (3.35 ppm) and free TFA in  $d_6$ -DMSO (14.40 ppm).

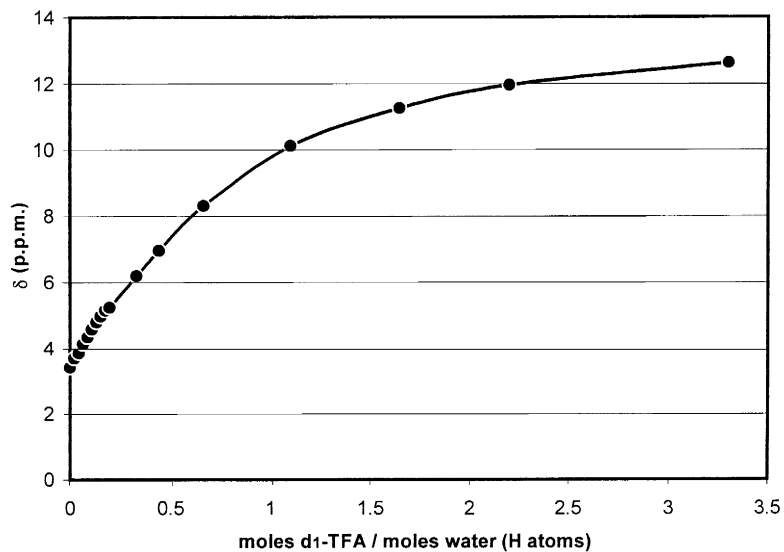


Fig. 2. Displacement of the water signal in  $d_6$ -DMSO upon titration with  $d_1$ -TFA

Fig. 2 thus serves as a guide to the amount of TFA which is needed in order to displace the water signal to an appropriate position in the spectrum. Addition of very small quantities is sufficient to displace the signal to around 5 ppm, a region which is normally free of other signals. Addition of more substantial quantities (usually greater than 10  $\mu\text{L}$ ) displaces the signal beyond the aromatic region to around 13 ppm.

The final concentration of  $d_1$ -TFA under these conditions is usually between 1 and 5%, depending on the water content of the  $d_6$ -DMSO and the hygroscopic nature of the molecule being studied.

It should also be noted that signals from other exchangeable protons will be displaced in a similar fashion, as seen in Fig. 1. It is therefore expedient to record the spectrum under normal conditions, add a small quantity of  $d_1$ -TFA (10–20  $\mu\text{L}$  in a standard 0.5 mL sample) and then re-record the spectrum. Fig. 3 illustrates such an experiment on a sample of inositol (1 mg in 0.5 mL of DMSO), which also has a signal which coincides with the water signal. The normal spectrum (top) shows the signals for the six hydroxyl groups (at 4.3–4.6 ppm) in addition to the methine signals (at 2.8–3.8 ppm). Addition of  $d_1$ -TFA (20  $\mu\text{L}$ ) displaces the water and hydroxyl signals, and also removes the coupling between the CH and OH groups giving the simplified spectrum shown at the bottom. The averaged signal for the exchangeable protons is observed as a broad singlet at 9.1 ppm.

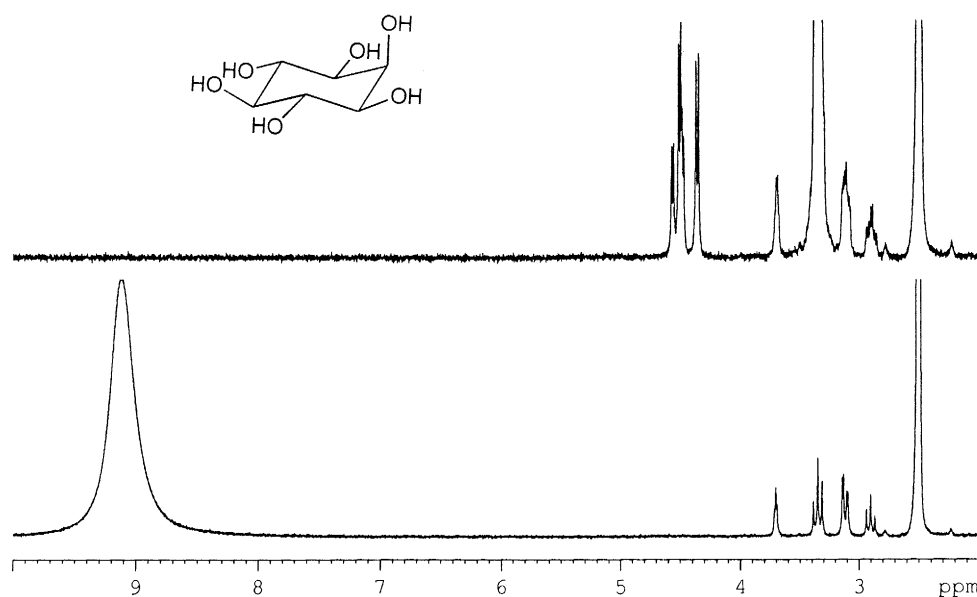


Fig. 3.  $^1\text{H}$  NMR spectra (250 MHz) of inositol in  $d_6$ -DMSO prior to (top) and after (bottom) addition of  $d_1$ -TFA

In conclusion, this straightforward technique should prove useful in the clarification of many  $^1\text{H}$  NMR spectra, provided that the species being studied are stable to dilute TFA solutions.

### Acknowledgements

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