

Magic-angle Sample-spinning N.M.R. Spectroscopy of an Antiferromagnetically Coupled Copper Formate Dimer

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The first solid-state carbon-13 magic-angle sample-spinning n.m.r. spectra of an antiferromagnetically-coupled species, $[\text{Cu}(\text{HCO}_2)_2(\text{C}_5\text{H}_5\text{N})]_2$ are reported, the results indicating that essentially diamagnetic behaviour can be observed at -180°C , while increasing temperature results in a shifted and progressively broadened resonance, owing to spin unpairing.

While solution-state n.m.r. spectroscopy has long been used to study paramagnetic systems,¹ it is only recently that high-resolution solid-state n.m.r. studies of paramagnetic solids have been reported.²⁻⁴ It has been shown that a combination of magic-angle sample-spinning (m.a.s.s.) and high-power proton decoupling, together with variable-temperature operation, can be used to probe both structure and spin dynamics in paramagnetic solids. In this communication we report the first high-resolution solid-state n.m.r. spectra of a paramagnetic solid exhibiting antiferromagnetic behaviour. In contrast to the characteristic Curie law temperature dependence of the magnetic susceptibility of paramagnets, antiferromagnets exhibit magnetic susceptibilities that *decrease* with decreasing temperature, below the Néel temperature. In the case of the copper(II) alkanoates, antiferromagnetic coupling arises as a result of an intramolecular exchange interaction between covalently bonded pairs of copper atoms, resulting in a singlet ground state with a low-lying triplet state.^{5,6} In $[\text{Cu}(\text{HCO}_2)_2(\text{C}_5\text{H}_5\text{N})]_2$ (**1**), the singlet-triplet separation is large enough ($2J \sim 600 \text{ cm}^{-1}$) that diamagnetic behaviour is observed below -160°C , while the magnetic moment rises to nearly $1 \mu_{\text{B}}$ at room temperature.⁷

A sample of (**1**), selectively ^{13}C enriched ($\sim 10\%$) in the formate ligands, was prepared basically as described by Martin and Waterman,⁷ but using ^{13}C formic acid (MSD Isotopes, Rahway, NJ). Spectra were obtained on a homebuilt spectrometer⁸ at a carbon frequency of 90.5 MHz, using a Doty probe (Doty Scientific, Columbia, SC). Figure 1(a) shows the ^{13}C m.a.s.s. n.m.r. spectrum of (**1**) at -181°C . The dominant feature in this spectrum is the resonance from the enriched formate carbons, with an isotropic chemical shift of 163 p.p.m. from tetramethylsilane, and intense spinning sidebands arising from the large chemical shift anisotropy of the formate species. The weaker peaks between the formate carbon sidebands are due to the unlabelled pyridine carbons, which we have verified by examining an unenriched sample of (**1**), for which these resonances are the dominant spectral features. From the relative intensities of the spinning side-

bands,⁹ the principal components of the chemical shift tensor for the formate carbons are found to be $\delta_{11} = 216 (\pm 10)$, $\delta_{22} = 177 (\pm 10)$, $\delta_{33} = 97 (\pm 10)$ p.p.m. These values are similar to those found for calcium formate at room temperature:¹⁰ $\delta_{11} = 234$, $\delta_{22} = 189$, $\delta_{33} = 104$ p.p.m. Thus, the spectrum of Figure 1(a) is consistent with a rigid, diamagnetic formate species.

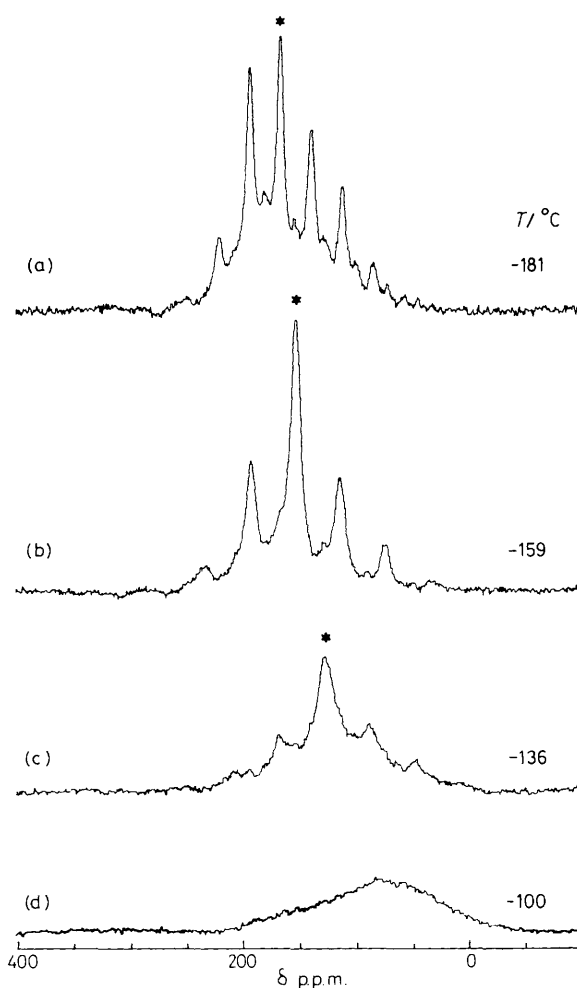
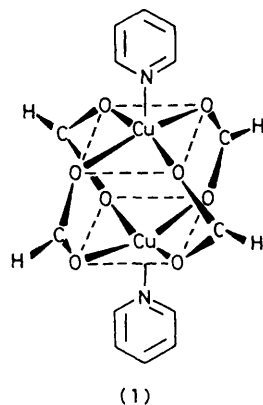


Figure 1. Variable-temperature 90.5 MHz (8.45 Tesla) ^{13}C solid-state n.m.r. spectra of $[\text{Cu}(\text{H}^{13}\text{CO}_2)_2(\text{C}_5\text{H}_5\text{N})]_2$ obtained using m.a.s.s. and dipolar decoupling. (a) Spectrum obtained at -181°C , 252 scans, m.a.s.s. at 2.5 kHz (* indicates the isotropic chemical shift). (b) Spectrum obtained at -159°C , 252 scans, m.a.s.s. at 3.5 kHz. (c) Spectrum obtained at -136°C , 380 scans, m.a.s.s. at 3.5 kHz. (d) Spectrum obtained at -100°C , 620 scans, m.a.s.s. at 3.2 kHz. A recycle time of 2 s was used at all temperatures. Exponential multiplication corresponding to a 50 Hz line broadening was used for each spectrum to improve the signal-to-noise ratio.

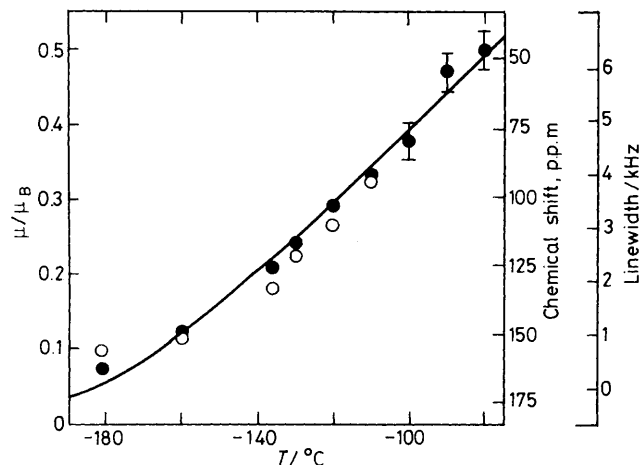


Figure 2. Isotropic chemical shift (●) and linewidth (full width at half height, ○) data superimposed on a plot of magnetic moment vs. temperature for $[\text{Cu}(\text{HCO}_2)_2(\text{C}_5\text{H}_5\text{N})]_2$ (calculated using the results of ref. 7).

When the temperature is raised above -181°C , however, the resonance shifts upfield and broadens rapidly, as shown in Figure 1(b–d). By -100°C the linewidth of the individual sidebands exceeds the spinning speed, so that the resonance is no longer broken up into spinning sidebands by magic-angle rotation, and thus becomes difficult to observe.

As shown in Figure 2, the changes in both the isotropic chemical shift and the individual component linewidth of the formate resonance are closely correlated with the increasing magnetic moment of (1) upon increasing temperature. The temperature-dependent chemical shift is a well known effect, arising from both Fermi contact and dipolar interactions between the unpaired electron density and the nuclear magnetic moments, shifts of the order of 50–100 p.p.m. having been observed previously for paramagnetic lanthanide^{3,4} and uranium compounds² in the solid state. However, the dramatic temperature-dependent line broadening seen in Figure 1 has not been observed previously in paramagnetic solids. It is generally believed that electron spin paramagnetism can broaden n.m.r. signals in the solid state either

by decreasing the spin–spin relaxation time (resulting in broader individual spinning sideband linewidths) or by anisotropic magnetic susceptibility effects (resulting in a broader overall linewidth).⁴ The line broadening observed for (1) is apparently due primarily to the former effect, since the total width of the resonance does not change significantly with temperature.

The results presented above demonstrate that it is a straightforward matter to obtain high-resolution n.m.r. spectra of antiferromagnetic solids at low temperatures. The ability to vary the magnetic properties in this particular system from completely diamagnetic to paramagnetic behaviour should provide new insight into paramagnetic broadening mechanisms in solid-state n.m.r. One important area where such an understanding is of some interest concerns oxygen-binding proteins such as hemerythrin, where antiferromagnetic coupling between iron centres is thought to occur.¹¹

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