

## High Resolution $^{13}\text{C}$ MAS NMR Spectra of Paramagnetic Lanthanide Complexes

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A substantial improvement in the resolution of  $^{13}\text{C}$  MAS NMR spectra of paramagnetic lanthanide acetates results from replacement of the protons by deuterons; this is attributed to the removal, in the deuterated sample, of residual broadening due to incomplete proton decoupling.

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There are still few examples of high-resolution spectra from paramagnetic solids,<sup>1–5</sup> the relatively broad lines often associated with these spectra having limited their use in applications to chemical problems. Line broadening in MAS spectra can result from both the large anisotropic bulk

magnetic susceptibilities<sup>6,7</sup> of the paramagnetic samples and their short spin–spin relaxation times. The latter contribution, whilst observed to be a relatively large contribution to the line widths of  $^1\text{H}$  spectra of copper(II) compounds,<sup>5</sup> has been shown to be negligible for compounds of the majority of

lanthanide ions, owing to their short electron relaxation times.<sup>8</sup>

<sup>13</sup>C CP MAS spectra from La, Pr, Nd, Sm, and Eu acetates have already been reported<sup>1,2</sup> and show a large dispersion of chemical shifts. However, we have observed that the <sup>13</sup>C CP MAS spectra of a variety of paramagnetic complexes often show poor resolution,<sup>9</sup> in contrast with the <sup>119</sup>Sn and <sup>89</sup>Y spectra of lanthanide mixed metal oxides.<sup>4</sup> Furthermore, the broadening in these <sup>13</sup>C CP MAS spectra is more pronounced for protonated compared with non-protonated carbons.<sup>9</sup> This paper, however, describes experiments which show that the replacement of the protons by deuterons results in a substantial improvement in resolution. This suggests that residual dipolar coupling to protons is responsible in spectra of protonated samples for a substantial degree of broadening, in addition to that caused by the mechanisms discussed above, and opens up novel approaches to the study of paramagnetic compounds using solid state NMR.

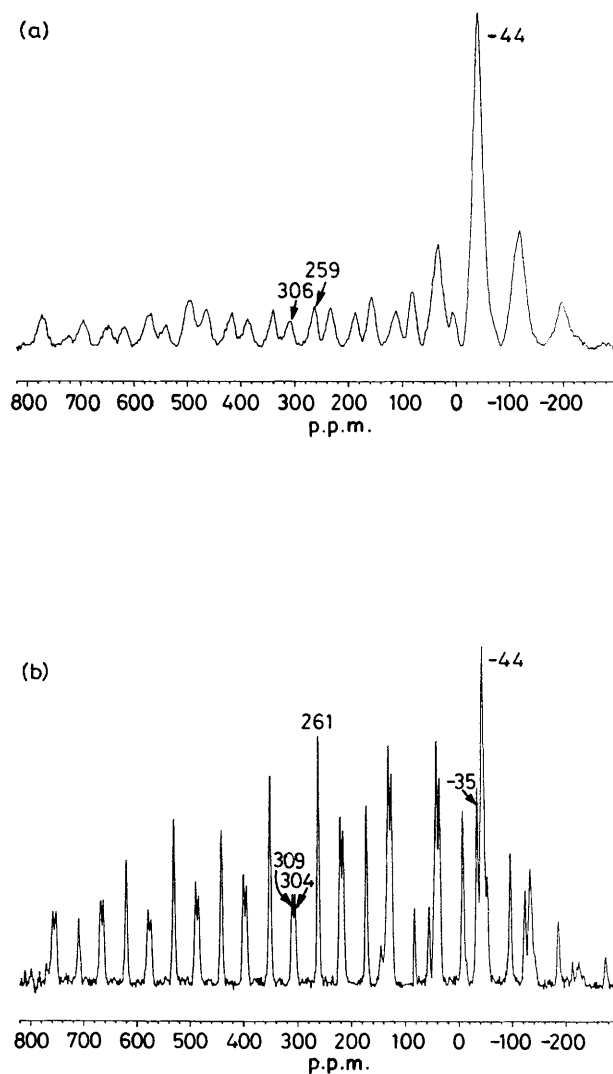
Figure 1(a) shows the <sup>13</sup>C CP MAS spectrum of Eu(MeCO<sub>2</sub>)<sub>3</sub>·4H<sub>2</sub>O.† Only three resonances are present, the remaining peaks are spinning sidebands. The methyl group resonances are contained in the broad peak at -44 p.p.m. and the resonances from the carboxyl carbons are observed at 306 and 259 p.p.m. The greater spinning sideband manifold associated with the carboxyl carbons is consistent with their closer proximity to the europium ion. Of the three crystallographically distinct acetate groups in the structure, two are chelated to a single europium ion while the third also acts as a bridge to a second europium ion.<sup>11</sup> That only three resonances can be resolved is consistent with <sup>13</sup>C CP MAS spectra of the trihydrate reported previously<sup>2</sup> where resonances at 321.1, 274.4, and -30.8 p.p.m. were observed. The trihydrate structure has a similar co-ordination around the europium ion to that of the tetrahydrate, but contains one fewer water molecule in the lattice. The resonances at 321.1 and 274.4 p.p.m. were assigned, on the basis of their intensity and chemical shift anisotropy, to the chelating, and the chelating plus bridging carbons, respectively.

Despite the large shifts induced by the europium ions, the resolution is, however, disappointing and little improvement could be obtained on varying the decoupling offset. Figure 1(b) shows the spectrum of the deuteriated compound,‡ collected using single  $\pi/2$  <sup>13</sup>C pulses. A comparison of spectra 1(a) and (b) reveals a dramatic increase in resolution for the deuteriated sample associated with a substantial reduction in the linewidths of individual resonances; the linewidth of the resonance at  $\delta$  259 for example decreases from 730 to 210 Hz. There is sufficient resolution that the resonance at 306 p.p.m. in (a) can now be seen to consist of two resonances. Similarly, two methyl resonances can also be resolved. The short *T*<sub>1</sub> relaxation times of the <sup>13</sup>C nuclei, due to the europium ions, enabled the use of short recycle delays; spectra with reasonable signal to noise ratios could therefore be collected in a few hours, although CP methods could not be employed.

The effect of deuteration was also investigated in studies of the Pr, Nd, and Sm acetates; dramatic decreases in linewidth were observed again. Hence, a major source of broadening in

the protonated acetates appears to result from incomplete proton decoupling. This mechanism may, at least for paramagnetic compounds where the anisotropic part of the magnetic susceptibility is relatively small, be dominant. The relative residual linewidths of the deuteriated samples were found to be in the order Sm < Eu  $\leq$  Nd < Pr acetate. This is consistent with predictions of the relative magnitudes of the anisotropy in the magnetic susceptibility of these samples.<sup>12</sup>

The results presented here show that it is possible to obtain high resolution <sup>13</sup>C spectra of paramagnetic solids. Specific deuteration, coupled with the exploitation of relaxation effects of a paramagnetic ion,<sup>3</sup> should offer opportunities for the selective observation of resonances in more complex systems and for the use of lanthanide ions as structural probes in molecular solids.



**Figure 1.** The <sup>13</sup>C CP MAS NMR spectrum of Eu(MeCO<sub>2</sub>)<sub>3</sub>·4H<sub>2</sub>O collected on a Bruker CXP200 spectrometer operating at 50.32 MHz for <sup>13</sup>C, using a spinning speed of 3.9 kHz. The isotropic resonances, identified by varying the spinning speed, are labelled with their chemical shift. (b) The <sup>13</sup>C MAS NMR spectrum of Eu(CD<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>·4D<sub>2</sub>O collected using a recycle time of 0.75 s and a spinning speed of 4.5 kHz. The resonance at -44 p.p.m. overlaps with one of the spinning sidebands from the peak at 309 p.p.m. at this spinning speed.

† The europium acetates were prepared by boiling a mixture of MeCO<sub>2</sub>H (or CD<sub>3</sub>CO<sub>2</sub>D) and H<sub>2</sub>O or D<sub>2</sub>O (approximately 1 : 1) with excess Eu<sub>2</sub>O<sub>3</sub>, decanting the solution, and leaving to crystallise. They were then recrystallised from H<sub>2</sub>O or D<sub>2</sub>O. The ground up crystals were then characterised using X-ray powder diffraction and the powder patterns of both samples were compared to patterns simulated using LAZY PULVERIX<sup>10</sup> using the known crystal structures of the tri- and tetra-hydrates.<sup>2,11</sup> Both acetates were found to have crystallised with the tetrahydrate structure.

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