Structural Information from NMR Studies of Paramagnetic Solids; ^{23}Na MAS Spectra of Sodium Lanthanide Salts of Ethylenediaminetetraacetic Acid

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Comparison of experimental and calculated ^{23}Na NMR spectra of complexes containing lanthanide cations indicates that paramagnetic effects in MAS NMR can yield quantitative structural information.

Solid state NMR spectroscopy has become an important technique for the study of a wide range of chemical systems.[1] Although much information can be obtained from these studies, widely applicable methods for the direct determination of structural parameters such as internuclear distances have proved elusive. One approach of potential value is to exploit the large anisotropic interactions that exist between nuclei and centres of unpaired electron density in paramagnetic solids. In this paper we discuss experiments that suggest that in the case of lanthanide-containing solids this approach can be of considerable value.

When electron relaxation is fast, as for the tripositive lanthanide ions other than Gd^{3+}, coupling to the individual electronic M_J states is not observed and the anisotropy results from dipolar coupling to the time averaged moments on the paramagnetic centres. If $\bar{\mu}_e$ is the average magnetic moment on a given paramagnetic centre and D_{en} is the dipolar coupling tensor than we have eqn. (1).

$$\mathcal{H}_n = \bar{\mu}_e D_{en} \mu_n = \gamma_n \bar{\mu}_e D_{en} I_n \qquad (1)$$

For a single nucleus interacting with one paramagnetic centre,[2] the shift tensor σ is given by eqn. (2) where $\hat{r}$ is the

$$\sigma = \frac{-(1 - 3\hat{r}.\hat{r})}{4\pi r^3}\chi \qquad (2)$$

vector joining the observed nucleus to a given paramagnetic centre, and χ is the magnetic susceptibility tensor. Analysis of the shift tensors obtained from spectra either of single crystals or powders should then enable investigation of magnetic or structural properties of the solid.

There have been several studies of shift anisotropy in paramagnetic solids, obtained either from the orientation dependence of the chemical shift in a single crystal,[3] or from analysis of powder lineshapes.[4,5] For many chemical applications, however, single crystals are not available, and magic angle spinning (MAS) is required to separate overlapping resonances in spectra from powders. In MAS experiments, the shift anisotropy is manifested in the spinning sideband envelope; indeed MAS NMR spectra are often characterised by large spinning sideband manifolds. While such spectra have now been obtained from a range of paramagnetic materials[6–10] there have been few attempts at analysis and interpretation of the spatial information contained in the sideband manifolds.[11] In part this is because factors other than the dipolar coupling often contribute to the observed spinning sideband manifold. For example, we have previously obtained ^{89}Y and ^{119}Sn MAS NMR spectra from the lanthanide stannates $Ln_2Sn_2O_7$,[12–14] but the high bulk magnetic susceptibilities of these materials and probable contributions to the anisotropy from the contact shift make their analysis difficult. In the present work we have chosen to study an ionic molecular crystal where such effects should be much reduced.

The $\frac{1}{2}$ to $-\frac{1}{2}$ transition is clearly visible in the ^{23}Na MAS NMR spectra from the diamagnetic compound NaY (edta)·8H$_2$O (edta = ethylenediaminetetraacetic acid) [Fig. 1(*a*)] and shows only a small chemical shift anisotropy. In contrast, resonances from the isomorphous paramagnetic compound, NaNd(edta)·8H$_2$O [Fig. 1(*b*)], are found to exhibit a very large shift anisotropy, with a broad envelope of well resolved spinning sidebands extending over about 500 ppm. Similar broad spinning sideband manifolds are obtained in the ^{23}Na spectra of the salts NaLn (edta)·8H$_2$O where Ln = Pr or Eu.

In order to interpret these spinning sideband manifolds, the contribution to the shift anisotropy resulting from dipolar coupling to the paramagnetic centres was calculated using

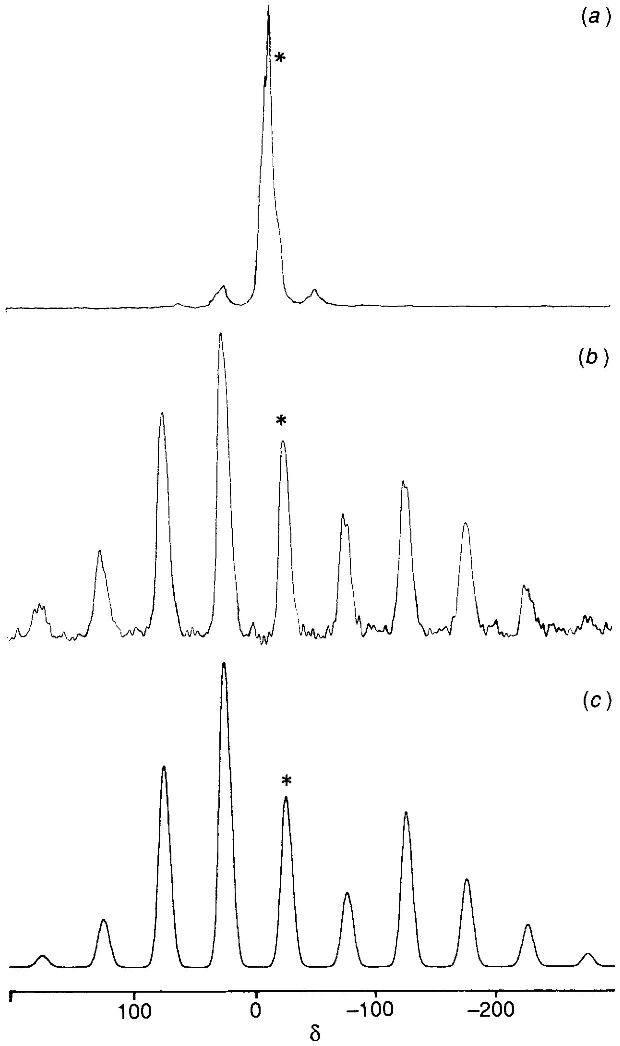

Fig. 1. Experimental 105 MHz ^{23}Na MAS NMR spectra of (*a*) NaY(edta)·8H$_2$O and (*b*) NaNd(edta)·8H$_2$O. (*c*) The ^{23}Na spectrum of NaNd(edta)·8H$_2$O simulated using the procedure described in the text. Experimental spectra were acquired using a Bruker MSL400 spectrometer. Chemical shifts are referenced externally to solid NaCl, MAS was carried out at 5.25 kHz in ZrO$_2$ rotors. Short (1 μs) pulses were used to ensure uniform excitation over the large spectral width. The experimental spectra shown here were processed without linebroadening, and the baselines were corrected manually. Isotropic resonances are indicated by a star; the remaining peaks are spinning sidebands. Least-squares fitting of the experimental spinning sideband intensities to those predicted using the theory of Maricq and Waugh[17,18] gave values for $\Delta(= \sigma_{11} - \sigma_{iso})$ of −222 ppm and $\eta[= (\sigma_{22} - \sigma_{33})/\Delta]$ of 0.56. The values of the corresponding parameters for the simulated spectra are −219 ppm and 0.34.

eqn. (2). The susceptibility was estimated on the basis of an isotropic free ion model. The atomic coordinates of the isomorphous compound NaSm(edta)$\cdot$8H_2O, determined by neutron diffraction,[15] were used in the calculations for NaNd(edta)$\cdot$8H_2O, after appropriate scaling for the slightly larger unit cell dimensions of the Nd^{3+} salt.[16] The overall tensor was calculated by summing the tensors for interactions of an individual ^{23}Na nucleus with all the paramagnetic centres within a given distance; it proved necessary to sum to 100 Å for convergence. The simulated spectrum [Fig. 1(*c*)] was then generated from the calculated tensor using the theory of Maricq and Waugh,[17,18] and applying 800 Hz of Gaussian linebroadening to the free-induction decay (FID) prior to Fourier transformation. Comparison of Fig. 1(*b*) and (*c*) shows that the agreement with experiment is good.

The close similarity of the simulated and experimental ^{23}Na MAS NMR spectra of NaNd(edta)$\cdot$8H_2O shows that the paramagnetic dipolar contribution to the shift anisotropy is, as hoped, dominant for this compound. This can in part be attributed to the small dipolar coupling of the ^{23}Na nucleus to other nuclei, including protons, in this compound. Furthermore, the compound has high symmetry, crystallising in the space group *Fdd*2, and a low density of paramagnetic ions; thus susceptibility broadening will also be small. This susceptibility broadening may, however, be responsible for the small discrepancy in the asymmetry parameter between the experimental and calculated spectra. Furthermore, the observed central $\frac{1}{2}$ to $-\frac{1}{2}$ transition for the $I = \frac{3}{2}$ ^{23}Na nucleus is affected by quadrupolar effects to second order. These effects are responsible for the lineshape of the central resonance in Fig. 1(*a*) but are minimised by working at a relatively high field (9.4 T); we have also obtained spectra at a lower field (4.7 T) and these show much broader isotropic peaks, with the sidebands not being properly resolved at equivalent spinning speeds.

For systems where the paramagnetic dipolar contribution is dominant, the observed shift anisotropy provides an accurate probe of molecular structure and magnetic properties. Measurement of the shift anisotropy in a compound of known structure enables the susceptibility to be calculated. Alternatively, if the susceptibility is known, or can be estimated, it should be possible to obtain structural information. We have demonstrated in this work that for a carefully chosen lanthanide complex such analysis is indeed possible. Because of the need to sum over many sites in the crystal, however, the approach is most valuable to test the validity of proposed models rather than to determine *a priori* structures. In the case of a dilute solid solution of paramagnetic ions in a diamagnetic host, strong dipolar coupling of a nucleus to more than one paramagnet is unlikely, and under these conditions obtaining accurate distance information, without a prior knowledge of the structure might become possible.

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