Structure and Ordering in Metal Cyanide Lattices: the Use of Doubly Labelled Cyanide (^{13}C–^{15}N) to Simplify the ^{13}C MAS NMR Spectrum†

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The relatively simple procedure of incorporating doubly labelled ^{13}C–^{15}N into metal cyanide lattices gives a significant simplification of the MAS NMR spectrum, yielding readily interpretable structural information, and the first example of ^{13}C–$^{63,65}Cu$ *J* coupling constants in the solid state, for $NMe_4Cu(I)Zn(CN)_4$.

The difficulty in distinguishing C from N by X-ray diffraction has proved to be a serious problem in the study of metal cyanide lattices.[1–3] Recent ^{113}Cd NMR studies[4,5] of several cadmium cyanides have shown that ordered lattice space groups chosen on the basis of the refinement of X-ray data were incorrect.

Metal cyanides form an extremely extensive and versatile group of compounds, many with potential as lattice framework hosts. There are few which have a suitable spin 1/2 metal nucleus at the lattice vertices which may serve as NMR probes to check for local order, such as ^{113}Cd in the cadmium cyanides. Hoskins *et al.*[1] recently reported a mixed copper–zinc cyanide, $NMe_4Cu(I)Zn(CN)_4$, and proposed Cu–C–N–Zn ordering, although neither the C and N nor the Cu and Zn atoms could be distinguished explicitly. An initial attempt to use ^{13}C solid-state NMR spectroscopy as an independent method for examining the cyanide ordering resulted in a relatively weak cyanide ^{13}C signal [Fig. 1(*a*)] which was not easily interpretable. Recognizing that the spectral complexity has its origin in the coupling of ^{13}C to the quadrupolar ^{14}N nucleus, and perhaps also to $^{63,65}Cu$, we decided to incorporate doubly labelled ^{13}C–^{15}N cyanide into $NMe_4Cu(I)Zn(CN)_4$ at the 25% level. The resulting magic angle spinning ^{13}C NMR spectrum [Fig. 1(*b*, *c*)] of the enriched sample shows considerable fine structure which yields significant new information by inspection. The spinning sideband manifold consists of quartets which can be assigned to ^{13}C–$^{63,65}Cu$ *J* coupling, the first example of its kind. Close inspection of an individual quartet shows partially resolved fine structure on the outer lines, indicative of the slightly different coupling constants between ^{13}C and ^{63}Cu or ^{65}Cu; $^{1}J(^{13}C, ^{63}Cu) = 324$ and $^{1}J(^{13}C, ^{65}Cu) = 347$ Hz. This observation immediately confirms the Cu–C–N–Zn ordering scheme proposed in the structural study.[1]

The ^{13}C NMR spectrum obtained for the same enriched material under static conditions also shows interesting fine structure which results from dipolar couplings to $^{63,65}Cu$ and ^{15}N, in addition to the *J* coupling and the ^{13}C chemical shift anisotropy, thus confirming the Cu–C–N–Zn ordering scheme. The ^{13}C static NMR spectrum can be calculated assuming Cu–C–N to be an A–M–X spin system and summing powder pattern contributions from the (mCu,nN), $m = -3/2$ to $+3/2$, $n = -1/2$ to $+1/2$, spin states.[6,7] The calculations are simplified considerably by the colinearity of the two dipolar and the chemical shifts tensors. The ^{15}N NMR spectra obtained under static and spinning conditions offer an

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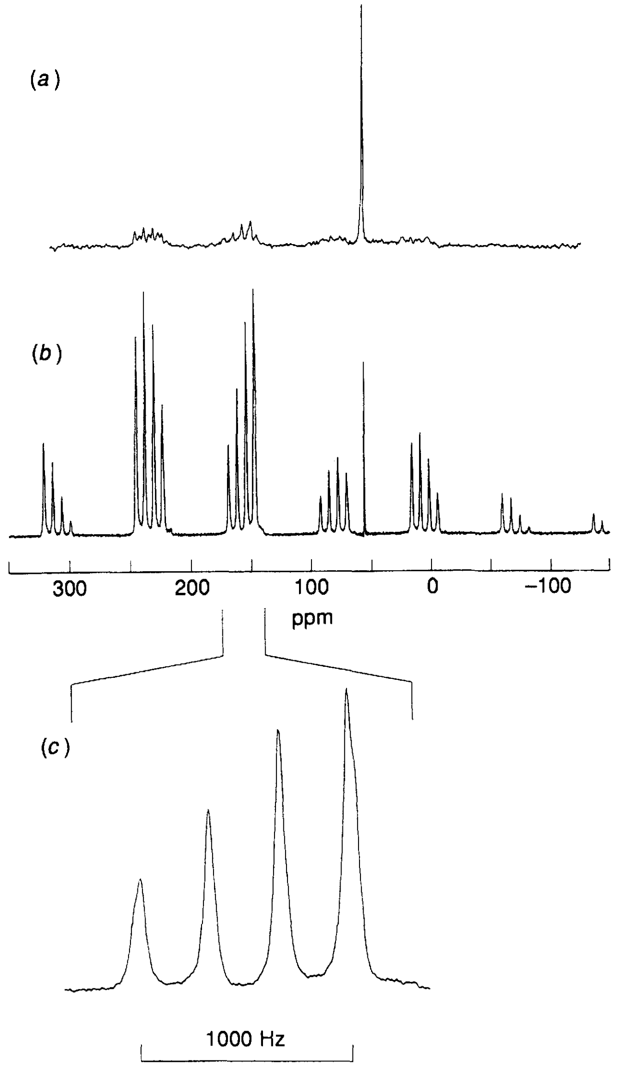

Fig. 1 ^{13}C CPMAS NMR spectra of $NMe_4Cu(I)Zn(CN)_4$: (*a*) sample with natural isotopic distribution; (*b*) sample enriched to 25% ^{13}C–^{15}N cyanide; (*c*) detail of centreband quartet. The line at about 55 ppm is due to the NMe_4^+ carbons.

Table 1 NMR results for doubly labelled $NMe_4Cu(I)Zn(CN)_4$

	Chemical shift anisotropy (ppm)						
Nucleus	$\delta_\perp$	$\delta_\parallel$	δ_{iso}	R(C,N)/ Hz	J(C,N)/ Hz	R(Cu,C)/ Hz	J(Cu,C)/ Hz
^{15}N	324	−105	181	−1788	−18		
^{13}C	275	−78	157	−1788	−18	1004^a	324^a
						1075	347

^{a} ^{63}Cu values top, ^{65}Cu values bottom.

independent means of evaluating the ^{13}C–^{15}N dipolar coupling and the ^{13}C–^{15}N J coupling, 18 Hz, as well as the ^{15}N chemical shift tensor. A calculated ^{13}C powder pattern is shown in Fig. 2, and inspection shows it to be an excellent match for the experimental ^{13}C NMR spectrum. The principal components of the ^{13}C and ^{15}N chemical shift tensors, the dipolar and J couplings, are listed in Table 1.

The dipolar coupling constants R can be converted into internuclear distances r_{am} according to eqn. (1), yielding

$$R = (\mu_0/4\pi)\,\hbar/2\pi)\gamma_a\gamma_m < r_{am}{}^{-3}> \qquad (1)$$

values of 1.999 and 1.197 Å for Cu–C and C–N. These are considerably longer than the X-ray diffraction values of 1.877 and 1.081 Å respectively. It is important to remember that X-ray diffraction and NMR do not measure exactly the same

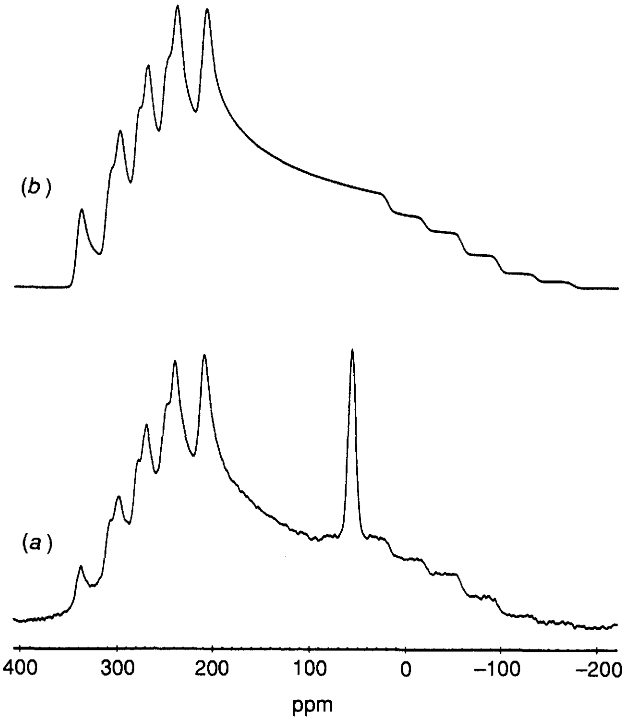

Fig. 2 (*a*) ^{13}C NMR powder spectrum of $NMe_4Cu(I)Zn(CN)_4$ enriched in doubly labelled cyanide; (*b*) spectrum calculated with parameters listed in Table 1. The line at about 55 ppm is due to the NMe_4^+ carbons.

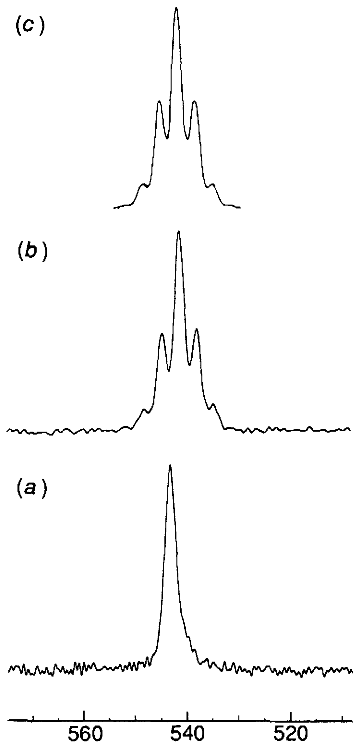

Fig. 3 ^{65}Cu MAS spectra of (*a*) $NMe_4Cu(I)Zn(CN)_4$; (*b*) as (*a*) but sample enriched in doubly labelled cyanide; (*c*) simulated spectrum assuming a statistical distribution of J couplings to 0, 1, 2 and 3 ^{13}C nuclei appropriate to a ^{13}C incorporation level of 25%.

quantity, and that both X-ray and NMR values will be modified considerably by the presence of motional averaging. In fact the unusual thermal ellipsoids of the C and N atoms obtained from the analysis of the X-ray diffraction results are indicative of some motion of the CN groups. Also, there is an unknown contribution from anisotropic J coupling, so that the effective dipolar coupling is $R_{\mathrm{eff}} = S(R - \Delta J/3)$ with $\Delta J = J_{\parallel} - J_{\perp}$ and S is an order parameter which depends on the motion. A more detailed analysis will depend on ^{13}C and ^{15}N static NMR spectra obtained at low temperatures so as to reduce the effect of motional averaging.

Finally, we present a ^{65}Cu NMR spectrum for both the unlabelled and doubly labelled samples of NMe_4-Cu(I)Zn$(CN)_4$ (Fig. 3). The NMR spectrum of the labelled material shows superimposed resonances of ^{65}Cu attached to 0, 1, 2 and 3 ^{13}C nuclei, with corresponding multiplets arising from the J coupling. The relative intensities of the multiplets follow a statistical distribution appropriate for 25% labelling. The relatively sharp ^{65}Cu spectrum, owing to the presence of Cu on exact tetrahedral lattice sites, makes the natural abundance material suitable as a chemical shift and cross-polarization standard for solid-state Cu NMR studies.

Incorporation of ^{13}C, ^{15}N doubly enriched cyanide has a tremendous potential for elucidating local order and structure in metal cyanides. The incorporation is usually relatively simple, and at enrichment levels of 10–25% the natural abundance ^{14}N-coupled ^{13}C NMR signals become essentially invisible.

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