Framework Ordering in Solid Cadmium Cyanides from Cadmium-113 NMR Spectroscopy†

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On the basis of solid state ^{113}Cd NMR spectra an ordering scheme is proposed for the cyanide units in the framework host lattice of $Cd(CN)_2{\cdot}2/3H_2O{\cdot}Bu^tOH$ which differs from that derived from X-ray diffraction data and which dictates a different choice of space group.

Recent work has shown that lattice structures based on cadmium cyanide are quite diverse, giving rise to several new classes of host–guest materials where rigid CN rods connect the metal centres.[1–3] At the same time these studies have again brought to light an old problem, that of distinguishing cyanide carbon from nitrogen by X-ray diffraction.[4] This is exemplified by the recently reported structures of cadmium cyanide itself,[3] and also that of $Cd(CN)_2{\cdot}2/3H_2O{\cdot}Bu^tOH$.[2] In the latter case, the Bu^tOH guest resides in the linear channels of an infinite honeycomb structure composed of CdCNCd rods. Two-thirds of the Cd atoms are tetrahedrally coordinated by CN, the remaining Cd atoms being octahedrally coordinated by four CN groups and two water oxygens.

The diffraction data were consistent with the space groups *Ammm*, A222, *Am*2*m*, *A*2*mm* and *Amm*2, and a number of these were eliminated on the basis of unsatisfactory R and R_w values upon refinement. The final space group chosen, *Amm*2, gave the best R and R_w values along with reasonable values for all bond distances. This choice of space group requires an ordering scheme as outlined in Fig. 1*a* with the octahedral Cd centre coordinated by two N and two C atoms as well as the two water oxygens. C and N atoms were assigned assuming that Cd–C linkages were shorter than those formed by Cd and N. This then produces ordered tetrahedral metal centres of CdC_4 and CdN_4.

Previous work has shown that ^{113}Cd NMR spectroscopy is an excellent technique to probe short range interactions in solids[5,6] and the presence of protons in the lattice in this case

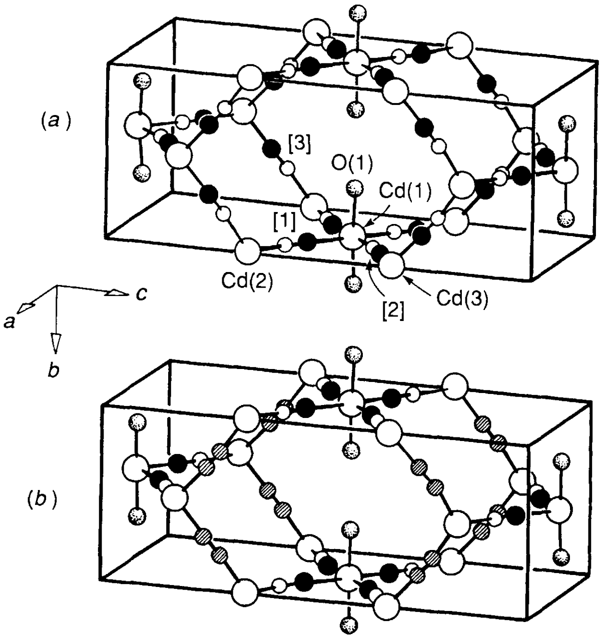

Fig. 1 The orthorhombic unit cell of $Cd(CN)_2{\cdot}2/3H_2O{\cdot}Bu^tOH$, showing only the host lattice framework: (*a*) ordering scheme proposed from diffraction data. CN groups [1], [2], [3] are distinct; (*b*) ordering scheme from ^{113}Cd NMR spectroscopy. CN groups [1], [2] identical, Cd (2), (3) identical. Solid circles are N atoms, cross hatched circles are either C or N atoms.

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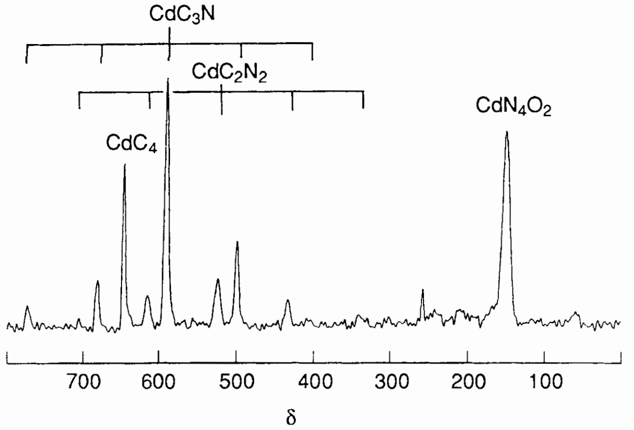

Fig. 2 ^{113}Cd CP-MAS NMR spectrum of $Cd(CN)_2{\cdot}2/3H_2O{\cdot}Bu^tOH$. Spectra were recorded at 39.93 MHz on a Bruker CXP-180 NMR spectrometer equipped with a Doty Scientific probe. Cross-polarization contacts were 5 ms, delay times 4 s. The peak at ~260 is due to a trace impurity (possibly a hydrated Cd salt) not present in all samples prepared.

allows for the use of cross-polarization techniques.[7] The spectrum obtained for $Cd(CN)_2{\cdot}2/3H_2O{\cdot}Bu^tOH$ is shown in Fig. 2.

Spectral lines for octahedrally coordinated Cd usually occur well to low frequency of tetrahedral Cd lines,[6] and hence the single line at 148.9 ppm can be assigned to an ordered, octahedrally coordinated Cd atom. After accounting for the spinning side band manifolds, three distinct tetrahedral Cd lines can be identified, instead of the two expected from the ordering scheme predicted by the *Amm*2 space group symmetry. Comparison with previous work[6] shows that the lines can be assigned as follows: 645.3 ppm, CdC_4; 589.4 ppm, CdC_3N; 523.2 ppm, CdC_2N_2. The intensity ratios are close to the 1 : 2 : 1 ratio expected for a random orientation of two of the four cyanides coordinating each of the tetrahedral Cd centres. Hence the ^{113}Cd NMR spectrum suggests that the cyanides are only partially ordered. The weighting towards C_4 ordering for the tetrahedral carbons requires that the octahedral Cd is coordinated by 4 N atoms (see Fig. 1*b*).

In light of this new information the choice of space group for $Cd(CN)_2{\cdot}2/3H_2O{\cdot}Bu^tOH$[2] should be re-examined. In fact, space groups *Amm*2 and *Am*2*m*, derived from the X-ray refinement, are not allowed by the ordering scheme obtained from the NMR data, and the correct space group must be one of *Ammm*, *A*2*mm* or *A*222. By repeating the refinement in one of these space groups and assuming the ordering scheme obtained from the NMR results, it is possible that improved R and R_w values may result.

Some other features that reinforce the marked difference between the space-average symmetry obtained from crystallography and the actual local symmetry can be obtained by examining some spectral details. For instance, the only true tetrahedral, or near-tetrahedral site is CdC_4, and for this Cd atom, spinning side bands are not observable for the spinning speed used, indicating quite a small chemical shift anisotropy. However, for CdC_3N and CdC_2N_2 the large number of spinning side bands indicate a very strong chemical shift anisotropy and hence much lower local symmetry consistent with 3- or 2-fold rotation axes or a mirror plane. In addition, the increased width of the resonance lines on going from CdC_4 to CdC_2N_2 reflects the increased influence of the quadrupolar ^{14}N nucleus.

This work indicates a powerful role for ^{113}Cd NMR spectroscopy in arriving at correct structural information in the many possible cadmium cyanide structures, and in the monitoring of crystal engineering procedures implemented to modify the ordering in these cyanide lattices.

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References

1 T. Kitazawa, S. Nishikiori, R. Kuroda and T. Iwamoto, *Chem. Lett.*, 1988, 459, 1988, 1729; M. Imamura, T. Kitazawa and T. Iwamoto, Abstract, VI Int. Symp. on Molecular Recognition and Inclusion, Berlin, Sept. 1990; T. Kitazawa, M. Imamura, H. Yuge and T. Iwamoto, Abstract, VI Int. Symp. on Molecular Recognition and Inclusion, Berlin, Sept. 1990.
2 B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 60.
3 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
4 D. T. Cromer and A. C. Larson, *Acta Crystallogr., Sect. B*, 1973, **29**, 251.
5 *Multinuclear NMR*, ed. J. Mason, Plenum Press, New York, 1987, p. 576.
6 S. Nishikiori, C. I. Ratcliffe and J. A. Ripmeester, *Can. J. Chem.*, 1990, **68**, 2270.
7 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.*, 1974, **56**, 1776.