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The Crystal Structure, Solid and Solution ^{113}Cd NMR of Bis(α,α'-Dipyridyl)Cadmium(II) Nitrate Hemihydrate and its Relationship to Cd Containing Proteins

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In the last few years ^{113}Cd NMR has shown considerable promise as a probe of metal ion environments in a wide variety of compounds ranging from organometallics to metalloenzymes and metalloproteins [1–28]. With its demonstrated chemical shift range of ~900 ppm, it appears to have the sensitivity required to develop structure-chemical shift correlations that may be useful for a number of different types of studies. The correlation of Cd metal ion environment from solid state X-ray crystallography with solution ^{113}Cd NMR appears particularly attractive for the determination of the metal ion site geometry in metalloenzymes and metal containing phospholipids whose crystal structures are unknown or which are difficult to crystallize. The recent developments in solid state magic angle spinning ^{113}Cd NMR [25–28] make such correlations even more attractive. As part of a program of the determination of crystal structures, solution and solid state ^{113}Cd NMR, we prepared bis(α,α'-dipyridyl)Cd(II) nitrate, determined its crystal structure and measured the ^{113}Cd NMR in solution and in the solid state as well as solution ^{113}Cd NMR of a series of derivatives of this parent compound. We wish to report here the structure of the parent compound and its magic angle spinning solid state ^{113}Cd NMR, its aqueous and DMF ^{113}Cd NMR and to discuss the implication of these results to the utilization of ^{113}Cd NMR in biological systems.

Experimental

To prepare bis(α,α'-dipyridyl)Cd(II) nitrate hemihydrate 1.56 g (0.01 mol) α,α'-dipyridyl (Fisher) dissolved in 100 ml of water and added to a 100 ml solution containing 1.54 g (0.005 mol) Cd(NO$_3$)$_2$·4H$_2$O (Baker and Adamson). The resulting solution was warmed gently (~80 °C) for ½ hour and allowed to evaporate at room temperature. Diffraction quality crystals appeared after several days. The material for ^{113}Cd NMR studies was filtered and separated from the mother liquid and stored in closed vials until used.

TABLE I. Summary of Distances and Angles.

Cd(1)–N	2.34(1)–2.39(1) Å
Cd(2)–N	2.33(1)–2.43(1) Å
Cd(1)–O(1)	2.246(9) Å
Cd(1)–O(12)	2.43(1) Å
Cd(2)–O	2.41(1), 2.435(9) Å
N–Cd–N(chelate)	69.5(4)–71.2(4)°
N–Cd–N(non-chelate)	87.2(4)–100.9(4)°
O(12)–Cd(1)–O(1)	100.0(3)°
O(13)–Cd(2)–O(14)	87.9(3)°

The diffraction data crystals were sealed in thin walled glass capillaries and mounted on an Enraf-Nonius CAD-4 diffractometer for which the PDP-8A was interfaced to a PDP-11-40 [29].

The crystals were found to be orthorhombic: Pcab, D_x = 1.73 g/cm^3, D_m = 1.93 g/cm^3, a = 14.372(1), b = 35.134(2), c = 17.174(4) Å, Z = 16. With a μ = 10.6 cm^{-1} the maximum and minimum transmission factors were found to be 0.887–0.430 for the 3636 reflections used to solve and refine the structure. Final refinement by full-matrix least squares ended at R = 0.066 with anisotropic temperature factors [30]. The atomic positional and thermal parameters are available*. A brief summary of interatomic distances and angles are in Table I. An ORTEP [31] drawing of the structure is shown in Fig. 1.

The ^{113}Cd NMR solution spectra was measured on a highly modified Varian XL-100-15 described elsewhere [3, 32]. The ^{113}Cd resonances observed were with natural abundance Cd in solutions with variable concentration ranging from 56 m*M* to 125 m*M* in DMF/methanol(D) and found to vary slightly (4 ppm) with concentration.

Solid state ^{113}Cd NMR spectra were obtained from *ca.* 0.5 g samples of natural abundance ^{113}Cd nuclide on a modified Bruker WP-200 spectrometer at 44.42 MHz (4.7 T) using cross polarization (CP) and magic-angle-spinning (MAS) techniques. The contact time

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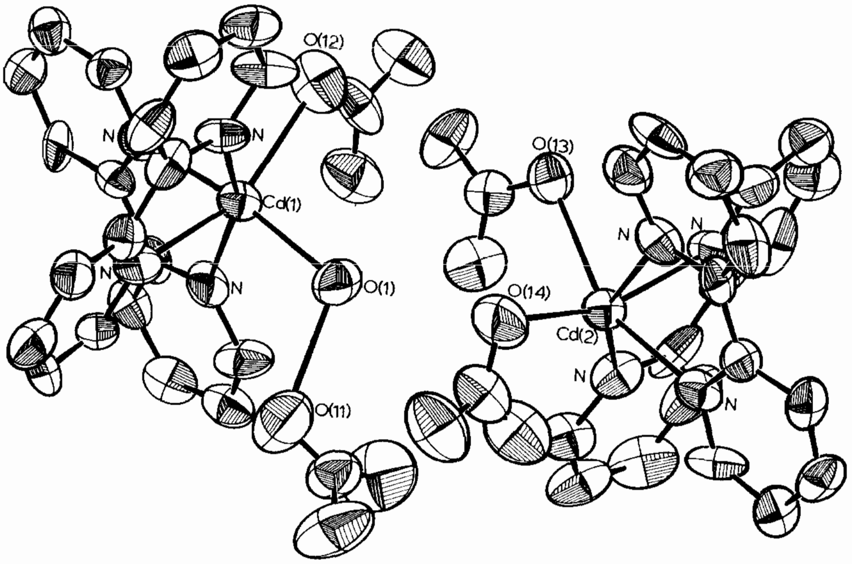

Fig. 1. An ORTEP [31] drawing of the two independent molecules in bis(2,2'-dipyridyl) Cd(II) nitrate hemihydrate. The thermal ellipsoids are drawn at the 50% probability level.

was 4 msec, the ^{1}H-90° spin-locking time was 5 msec, and the recycle time was 4 sec. Rotor speeds of approximately 4 KHz were employed. A solid solution of 0.1 *M* $Cd(ClO_4)_2$ was used as an external standard.

The crystal structure may be described as made up of two crystallographically and chemically distinct six-coordinate distorted octahedral Cd^{2+} species separated by ordinary non-bonding interatomic distances. The coordination polyhedron of Cd(2) (see Fig. 1) is made up of four nitrogens from α,α'-dipyridyl groups and 2 oxygen atoms of nitrate groups is a *cis* arrangement whereas Cd(1) has a similar arrangement, but one of the oxygen atoms is from water O(1) with a fairly short hydrogen bonded distance from O(1) to O(11) of 2.61(1) Å (see Table I). In addition, the Cd(1)–O(1) distance of 2.246(9) is considerably shorter than the 2.42 ± 0.02 Å average of the other three Cd–O distances (see also angles in Table I). By themselves these are perhaps not surprising. However, the solid state magic angle spinning ^{113}Cd NMR clearly show two resonances of equal intensity at +122 and +51 ppm, a separation of 71 ppm! These are deshielded relative to the 0.1 *M* $Cd(ClO_4)_2$ solution reference. In DMF/methanol-(D) solution, only one signal is observed at +66 ppm while a single resonance was observed at +172 in aqueous solution. Based on the solution data as well as the width of the resonances at half-height, Cd(1) is assigned to +122 ppm signal (width 283 Hz) while the +66 ppm signal (width 263 Hz) is due to Cd(2). This is consistent with previous assignments based on anisotropy of the cadmium [26].

The important point to be made is that in macromolecules in which Cd atoms are substituted for other metals and where such a difference in resonances of two ^{113}Cd atoms is observed, the current interpretation would be that there are two quite different Cd sites probably with significantly different coordination polyhedron. It is clear from the above that these sites may be very similar. Such results are particularly important to solid state ^{113}Cd NMR studies of macromolecules where the protein has lost/gained water molecules in the sample preparation process for ^{113}Cd NMR studies. It is to be noted that recently [27] a difference of 10 ppm was observed for Cd in two essentially identical octahedral environments.

Since Cd(2) has 2 additional oxygens of nitrates at 2.62(1), 2.69(1) Å and Cd(1) has 1 additional oxygen of nitrate at 2.67(1) Å, one might be tempted to explain the ^{113}Cd NMR based upon higher coordination number than six. However, evidence at this time tends to indicate that higher coordination for Cd tends to push the ^{113}Cd resonance to more shielded values or negative relative to the 0.1 *M* $Cd(ClO_4)_2$ water solution standard [32].

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