Cadmium-113 NMR Spectroscopy. Long Bond Interactions and Chemical Shielding in the Cadmium Complex of an Unsaturated Nitrogen Analogue of 18-Crown-6

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Abstract: The liquid and solid state ^{113}Cd NMR spectra of a Cd^{2+} adduct of an unsaturated analogue of the 18-crown-6 have been determined. In the complex, the coordination sphere around the Cd^{2+} ion is six nitrogens, from the macrocycle, and two axial oxygen ligands. The resulting ^{113}Cd chemical shift in either phase is −75.0 ppm with respect to 0.1 M $Cd(ClO_4)_2$ solution. This result is considered surprising since this is a chemical shift value expected for a Cd^{2+} ion coordinated exclusively to oxygen atoms and not six nitrogen atoms and two oxygen atoms! The ^{113}Cd shielding tensor elements were determined to be $\sigma_{11} = -31.89$, $\sigma_{22} = -57.82$, and $\sigma_{33} = -138.27$ with a value for the asymmetry parameter, η, of 0.42. These data in combination with previously reported X-ray data suggest that the Cd^{2+} bonding to nitrogen is mainly electrostatic as compared to the expected coordinate covalent bonding that is characteristic of other cadmium–nitrogen complexes. The implications of these results are discussed.

Continuing effort over the past few years to investigate the structural determinants of ^{113}Cd NMR chemical shifts[1-3] has led to the study of a number of systems including cadmium-substituted porphyrins,[4] single crystals of cadmium complexes,[5-7] and cadmium-substituted metalloproteins.[8,9] In this regard, solid-state ^{113}Cd NMR spectroscopy has been an essential tool in circumventing problems associated with chemical exchange and solvent effects in solution studies of cadmium complexes. In such solution studies, the relationship between the isotropic cadmium chemical shift and structural parameters of the molecules of interest, such as metal ion site symmetry, ligand type, bond distance from the metal ion to ligand, and coordination number and geometry, may be obscured because of the simultaneous influence of dynamic processes in these systems.

The success of the solid-state NMR approach has been dependent upon the availability of suitable model systems of reasonably well-defined structure such that the cadmium chemical shift tensor data could be correlated with structural parameters characteristic of the molecules of interest in the absence of any confounding influence of molecular motion and chemical exchange. Furthermore, it is well accepted that the solid state NMR technique is capable of providing information not directly available from solution methods.[10-12] Presently, we report cadmium NMR data (both solution and solid state) on the cadmium complex of a fully unsaturated nitrogen analogue of 18-crown-6 (**1**), whose synthesis and properties have been reported previously.[13-15]
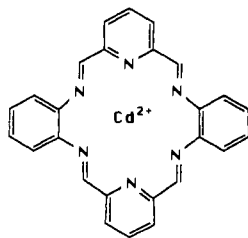
The ligand in complex **1** and related torands are effective hosts for various metal cations, although the detailed complexation properties are not obviously predictable by comparison with crown ethers, cryptands, and spherands.[16] For example, the ligand in **1** and a related torand[14,17,18] form surprisingly stable complexes

with alkali metal and alkaline earth ions. This contradicts the observations of weak complexes with saturated nitrogen analogues of crown ethers, which are often regarded as a consequence of the soft character of nitrogen relative to oxygen ligands. Moreover, these planar, open-faced macrocycles contradict the general principle that encapsulation of the metal by the polydentate ligand is required to produce very stable complexes. Apparently, there are unusual features to the metal binding characteristics of **1**. The ability of Cd^{2+} to mimic alkaline earth cations, specifically Ca^{2+}, and the sensitivity of ^{113}Cd shielding tensors to subtle changes in metal–ligand bonding make ^{113}Cd NMR an attractive structural probe for this system. Further, the unusual coordination environment produced by this macrocycle enables a unique test of

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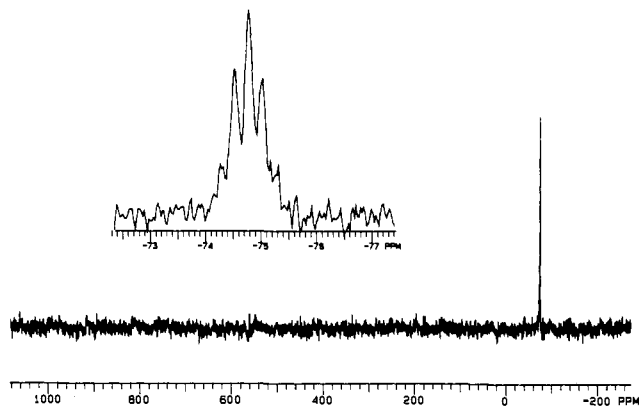† University of South Carolina.
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Figure 1. Solution NMR spectrum of complex 1 (20 mg in 2 g of Me$_2$SO-d_5) at 22 °C: number of repetitions, 40 545; recycle delay, 0.42 s. Insert: Expanded plot of peak observed without decoupling.

^{113}Cd NMR shielding principles.

We have found that the solution cadmium NMR isotropic chemical shift is unusually shielded (−75.0 ppm). This has also been confirmed using the solid-state CP/MAS technique. These and additional data suggest that complex **1** in solution consists of a strongly bound (nonexchanging) cadmium ion, but one which is weakly coordinated electronically; the latter characteristic is reflected in the chemical shielding tensor properties of cadmium in this complex in both the solution and the solid state. What is meant by this term "weakly coordinated electronically" is that the bonding in this system is more ionic rather than the usual donor–acceptor relation between a ligand and a metal such as cadmium. This type of bonding leads to a type of atomic identity crisis in that the Cd^{2+} can no longer recognize the identity of nitrogen as a ligand atom. These results are discussed in terms of previous data and correlations regarding cadmium chemical shielding tensor–structure correlations, and also in terms of the binding properties of the 18-crown-6 analogue.

Experimental Section

All ^{113}Cd solution NMR experiments were carried out at 22 °C in either Me$_2$SO-d_6 or pyridine-d_5 on a Varian XL-400 spectrometer operating at 88.734 MHz using a Varian NMR probe. Chemical shifts were referenced relative to 0.1 M cadmium perchlorate in water at 22 °C. Proton NMR spectra were obtained using a Nicolet NT-300 spectrometer operating at 300 MHz for samples dissolved in Me$_2$SO-d_6. Chemical shifts are reported as δ values referenced to residual Me$_2$SO-d_5 (δ = 2.490).

Cadmium perchlorate complex **1**[19] was prepared by the method of Drew et al.[13] as follows. A mixture of 213 mg (0.18 mmol) of the barium perchlorate complex of the same macrocyclic ligand,[20] 386 mg (0.92 mmol) of Cd(ClO$_4$)$_2$·6H$_2$O, and 150 mL of anhydrous methanol was stirred under reflux for 2 days, then concentrated to 40 mL using a rotary evaporator. The product, which crystallized upon standing at 2–3 °C overnight, was collected as dark red prisms by vacuum filtration and dried in vacuo (226 mg, 85%) dec >350 °C; ^{1}H NMR (w) 9.27 (s, d, J = 20 Hz, N=CH, 4 H), 8.50 (t, J = 7.7 Hz, py-H4, 2 H), 8.26 (d, J = 7.7 Hz, py-H3,5, 4 H), 7.76 (m, phenyl H3,6, 4 H), 7.64 (m, phenyl-H4,5, 4 H); IR (KBr) 3090 (w), 1630 (m), 1590 (m), 1490 (m), 1455 (m), 1385 (w), 1280 (w), 1100 (s, br), 825 (m), 780 (w), 760 (m), 745 (m), 630 (m).

Solid-state ^{113}Cd NMR experiments were performed at 66.565 MHz on a Varian XL-300 spectrometer which had been modified for solids NMR use. Samples were packed into 7-mm o.d. ceramic rotors and spun in a Doty MAS probe (Doty Scientific, Inc.). Data acquisition for CP/MAS experiments included a standard Hartmann–Hahn spin-locked cross-polarization pulse sequence.[21,22] Resulting spinning side-band patterns were analyzed, and shielding tensor data were obtained using a Simplex algorithm along with a MAS spectral simulation program.[23-25]

(19) The composition of this complex is reported as [CdL(OH$_2$)-(ClO$_4$)]·MeOH,[6,13] where L = 4,5:15,16-dibenzo-3,6,14,23,24-hexaoxatricyclo[17.3.1.1^{8,12}]tetracose-1(23),4,8(24),9,11,15,19,21-octaene. Methanol was not detected in our spectroscopic examination of vacuum-dried complex.
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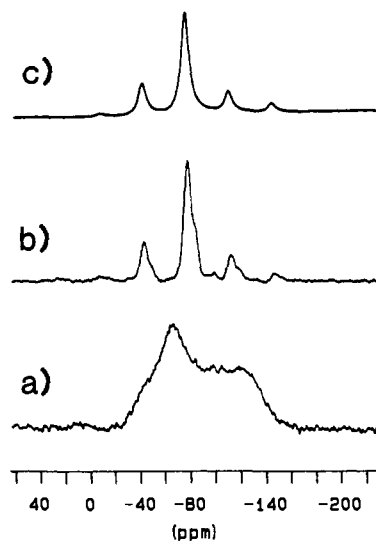

Figure 2. (a) Static powder CP spectrum of complex **1**: contact time, 2 ms; recycle delay, 6 s; number of repetitions, 4225. (b) CP/MAS spectrum of complex **1**: contact time, 2 ms; recycle delay, 2 s; number of repetitions, 19 713; spinning rate, 2.29 kHz. (c) Simulated MAS spectrum using optimized parameters.

The two-parameter optimization resulted in best estimates for the scaled anisotropy (delta, δ) and asymmetry parameter (eta, η) for the data set in question.

Results and Discussion

Presented in Figure 1 is the ^{113}Cd NMR spectrum of complex **1** in Me$_2$SO-d_6 at 22 °C. A single line (line width 50 Hz) is apparent at a chemical shift of −75.0 ppm relative to cadmium perchlorate. Also shown (Figure 1) is the multiplet structure of this resonance due to J coupling between cadmium and the imine methine protons (4 protons). The observed $^3J_{Cd-H}$ in Me$_2$SO-d_6 is 22 Hz. The multiplet collapsed with 5-W proton decoupling to a singlet (line width 9 Hz) at the same chemical shift. Similar spectra were obtained for complex **1** in pyridine-d_6 and resulted in a single line (line width 52 Hz) at a chemical shift of 3.78 ppm at 22 °C, but with no discernible multiplet structure. The analysis of **1** in pyridine was complicated by the formation of an insoluble precipitate upon standing overnight.

In order to determine whether the cadmium complex was in rapid or slow exchange, 2 equiv of solid cadmium perchlorate as added to the sample of **1** in Me$_2$SO-d_6 and the acquisition was repeated. The resulting spectrum (not shown) showed separate resonances at −25.6 ppm due to added perchlorate (compare with 23.5 ppm for 0.6 M cadmium perchlorate in Me$_2$SO) and at −74.6 ppm due to the complex.

Complex **1** (19.2 mg in 1.68 mL of Me$_2$SO) was titrated with pyridine-d_5, and the corresponding NMR spectrum was monitored at each point. The observed cadmium shift changed from −74.85 ppm (no addition) to 0.89 ppm (18.7 mmol of pyridine added). A plot of the inverse of the change in chemical shift versus reciprocal pyridine concentration was linear (r = 0.999) with an extrapolated chemical shift at infinite pyridine concentration of 8.3 ppm, in reasonable agreement with that observed for the complex in pyridine (3.78 ppm). The apparent dissociation constant for pyridine is 0.64 M.

Additional data were obtained for complex **1** in the solid state using the CP/MAS technique. Analysis of the MAS spectrum (Figure 2b) yielded an anisotropy of −93.41 ppm and an asymmetry parameter of 0.42. These optimized parameters correspond to tensor elements (σ_{11} = −31.89, σ_{22} = −57.82, σ_{33} = −138.27 ppm) and were used to compute the spectrum in Figure 2c.

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Furthermore, these parameters correspond to an isotropic shift of −76.0 ppm in the solid state. This close agreement with the isotropic shift of the complex in Me_2SO suggests that the complex has similar structures in solid and solution states, with a molecule of Me_2SO replacing the axial water ligand observed in the crystal structure. Typically as in bis(dioxane)cadmium-tetraphenylporphyrin,[26] the axial solvate ligands in complex 1 may cause little or no perturbation of the cadmium resonance. Here the in-plane ligands appear to be the weakest interaction. In the absence of any bulk solvent effect, the isotropic shifts in the solution and solid state would be the same. The deshielding observed upon titration with pyridine is expected, since pyridine is a stronger ligand relative to Me_2SO and would therefore be expected to perturb the cadmium coordination environment significantly in the direction of decreased shielding. This deshielding effect is considerably larger that those observed for pyridine coordination to Cd(tetraphenylporphyrin) (33 ppm)[4] or for replacement of Me_2SO by one tertiary nitrogen ligand in cadmium nitrate·Me_2SO solvates at (∼31 ppm).[27]

The highly shielded cadmium isotropic shift of complex 1 in Me_2SO is unexpected in view of the predominant paramagnetic contribution of ligands to cadmium chemical shifts in the order S > N > O. The observed −75.0-ppm isotropic shift is in the region characteristic of the divalent cadmium ion in an all-oxygen ligand environment. A ligand likely only furnishing oxygen atoms to Cd^{2+} is the cryptate reported by Mennitt et al.[28] The cryptate with its six oxygen donor atoms gives rise to chemical shift of −62 ppm. The shielded nature of this resonance probably reflects somewhat longer bonds expected for the cryptate relative to normal oxygen ligands to Cd^{2+}. In many cases observed to date, the imposition of even a single nitrogen into what would otherwise be a pure oxo-ligand coordination environment results in a significant deshielding effect on the cadmium resonance. In the case of Concanavalin A or the lectins from the pea or lentil,[8,9] for example, the cadmium resonance corresponding to the S1 site is deshielded by 167 ppm (Con A), 174 ppm (lentil), and 180 ppm (pea) relative to the cadmium resonance for the S2 site. In these protein systems, the metal ion at the S2 site is in a pure oxo-ligand environment, while there is in addition to oxygen-type ligands, a single nitrogen in the cadmium coordination sphere at the S1 site. By comparison with cadmium complexes having mixed nitrogen and oxygen coordination as in cadmium–ethylenediaminetetracetate[29] (EDTA), the cadmium nucleus generally experiences significant deshielding relative to the pure oxo-ligand complexes. The cadmium-EDTA resonance is pH dependent and occurs at chemical shifts of 85 ppm and greater. The cadmium complex of *meso*-tetraphenylporphyrin,[4] wherein the metal ion is in an all-nitrogen ligand environment, has an isotropic chemical shift of 399 ppm in the solid state. The chemical shifts of ^{113}Cd coordinated to three bidentate nitrogen ligands in Me_2SO solutions range from 278 to 403 ppm.[27]

In addition to ligand element type, some have argued that the coordination numbers of cadmium complexes influence the ^{113}Cd chemical shifts.[30,31] Although there are notable exceptions to this correlation, shielding roughly increases as the coordination number increases. An attempt has been made to explain this in terms of poorer electron pair orientation and accompanying weakening of metal–ligand bonding interactions.[31] Without regard to electron pair orientation, one would generally expect that increasing the coordination number would shield Cd by increasing metal–ligand distances. For example, the ionic radius of Cd^{2+} increases smoothly from 0.87 (pentacoordinate) to 1.10 (octa-

coordinate).[32] As bond distance increases, orbital overlap and covalent bond character decline, resulting in a smaller perturbation from the isolated ion electronic configuration. Hence, ligand type, coordination number, complex geometry, and ligand orientation all affect bond covalency.

The binding of the cadmium to the macrocycle in the complex is clearly substantial in view of the fact that the cadmium does not exchange with $CdClO_4$ in Me_2SO. Based on the observation of resolved resonances and the fact that the ^{113}Cd line width of cadmium perchlorate did not change in the presence and absence of 1, we can estimate an upper limit for the exchange process to be 10 s^{-1}. Thus, although the cadmium does not appear to be ligated to any of the nitrogens in the usual sense of covalent interaction, the barrier to dissociation of cadmium from the complex is substantial.

The X-ray data reported previously[13] for 1 show approximately hexagonal bipyramidal geometry in which cadmium is coordinated to axial water and perchlorate oxygens and to the six nitrogen atoms, which lie roughly in the equatorial plane. It is notable that the Cd–N bond distances in 1 and in the isomorphous Pb^{2+} complex are long in comparison with those of a smaller nitrogen macrocycle, such as the cadmium complex of tetraphenylporphyrin.[26] Typical Cd–N bond distances have an average of 2.14 Å for the porphyrin complex,[26] and range from 2.370 to 2.482 Å in a typical hexacoordinate nitrogen macrocycle.[33] Complex 1 is isomorphous with the Pb^{2+} complex and has Cd–N bond distances ranging from 2.50 to 2.79 Å. In addition to the anomalously long bond distances in 1, the asymmetric position of the metal ion results in a site symmetry that does not conform to the symmetry of the macrocycle. The cadmium is closer to three of the nitrogens than to the other three, whereas the macrocycle has four imino nitrogens and two pyridyl nitrogens. That the size of the cadmium is less than optimal is reflected in the failure of the cadmium ion to serve as a template in the synthesis of 1.[13]

A lengthening of the Cd–L bond for N^- and S^- donor ligands is suggested to relate to the observed shifts to higher shielding in complexes with steric demands.[34] Indeed, Cd complexes of substituted pyridines and phenanthrolines with sterically hindered groups show significantly shielded (25–100 ppm) signals relative to unhindered analogues.[35] The present results are an extreme example of this effect. In fact, the magnitude of the effect of bond lengthening on the chemical shift is far greater than the dependency of base strength which measures electron donor ability of the ligand and chemical shift.[35]

Since the paramagnetic contributions to the shielding constant dominate for Cd complexes, the relationship between increased bond length and increased shielding implies substantially less covalency to the metal ligand bond. In the extreme, the metal is in an ionic form and there is no covalent bonding between the metal and the ligand atoms. Nonetheless, the metal ion is far from free and we have to address the nature of the bonding which operates between the ligand and metal ion at these long distances.

The ^{113}Cd resonance of a complex of six tertiary amine ligands would be expected to occur at about 186 ppm,[27] which is 261 ppm lower shielding than the observed resonance of complex 1. This remarkable effect may be attributed to the conformational requirements of this relatively rigid macrocycle. The cavity radius of this hexaaza[18]annulene is fixed at approximately 1.3 Å, which is about 0.2 Å too large for octacoordinate Cd^{2+}. This constraint ensures poor metal–ligand orbital overlap, low bond covalency, and shielding of the metal nucleus. As a result of the nonoptimal cavity size, the primary bonding interaction in 1 must then be considered a mixture of ionic and covalent bonding, the ionic portion being significantly larger than normal coordinate covalent Cd–N bonds. In a way, the macrocycle is acting as an electrostatic

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trap via attractive ion/dipole interactions. This is entirely consistent with other complexation properties of this macrocyclic ligand, which forms very stable complexes with sodium and potassium salts in Me_2SO.[17] Despite the fact that nitrogen ligands are generally considered to be relatively soft, this and other hexaaza[18]annulene derivatives form stronger alkali metal complexes than their oxygen analogues. Therefore, Cd^{2+} complexes of other sexipyridine-derived torands[18] would be expected to show similar chemical shifts. This explanation accounts for the chemical shift of the cadmium and the essential absence of nitrogen ligand effect on that shift. Moreover, the nitrogen–cadmium distance differentiation has analogy in tin complexes where the metal–ligand atom distances are determined by the ionic Coulombic terms rather than by formal bonding distances.[36]

The cadmium shielding tensor of **1** is necessarily nonaxial since the metal ion site symmetry is lower than that of the macrocycle which at best could have a 2-fold rotation axis.[37,38] Based upon detailed studies involving single crystals of cadmium complexes coordinated exclusively by oxo ligands[5,6] and also mixed N–O and S–O complexes,[7] it has been found that the most shielded tensor element is oriented orthogonal to the longest Cd–ligand bond. From the X-ray structure of **1**, the longest Cd–ligand bonds occur within the pseudoplane containing the six nitrogen atoms. Hence the most shielded tensor element in **1** should be oriented most nearly orthogonal to the pseudoplane containing the metal ion and six nitrogens. The two remaining shielding tensor elements are found, experimentally, to have similar magnitudes, and, therefore, are expected to have similar orthogonal environments.[6] We,

therefore, assign the perpendicular tensor elements to lie in the pseudoplane of the ligand. This assignment is consistent with the [113]Cd powder pattern depicted in Figure 2a. The fact that all the tensor elements are more shielded than those of cadmium perchlorate confirm the necessarily weak in-plane and axial covalent interactions for this complex.

The unusual [113]Cd NMR spectral properties of this cadmium complex and the stability data have led to an unusual situation. The cadmium ion is weakly covalently ligated and yet strongly bound. We propose an interpretation based upon inefficient covalent Cd–N bonding, manifested by the long Cd–N bonds in **1**, that arises because of the nonoptimal size of the macrocycle cavity. This interpretation is derived from observations of the [113]Cd NMR spectra but it can be applied to other systems where such spectral data are not available. In this vein these data and conclusions offer an attractive rationale for the equally strong binding of Ca^{2+} ions in related torands. The data clearly contrast with the expectation that Ca^{2+} would not bind in such systems, in view of the absence of known covalent bonding between Ca^{2+} and N donors. Finally, this kind of bonding avoids the inconsistencies of models based on hard/soft acid base theory and may prove useful for finding other examples.

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Bimodal Inclusion of Nitroxide Radicals by β-Cyclodextrin in Water As Studied by Electron Spin Resonance and Electron Nuclear Double Resonance[1]

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Abstract: Bimodal inclusion of some nitroxide radicals in aqueous solutions of β-cyclodextrin has been detected by electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) spectroscopy. Inclusion complexes in which nitroxide radicals reside in the cavity of β-cyclodextrin in two different ways are observed. The assignments are based on differences in hyperfine splittings (hfs's). Three nitroxide radicals, diphenylmethyl *tert*-butyl nitroxide (**1**), α-methylbenzyl *tert*-butyl nitroxide (**2**), and α-(2,4,6-trimethoxyphenyl)benzyl *tert*-butyl nitroxide (**3**), have been used as spin probes. In each case, both the nitrogen and β-hydrogen hfs's change in magnitude upon inclusion. On the basis of the characteristic change of hfs upon inclusion, the direction of incorporation is assigned. The association constants, $\Delta H°$, and $\Delta S°$ are determined from the concentration and temperature dependences of the ESR intensity of each species. The nature of the interaction between β-cyclodextrin and the functional group in the probe is discussed.

Inclusion phenomena by various kinds of molecular receptors have attracted a great deal of attention as a step toward the understanding of the mechanism of molecular recognition.[2] Cyclodextrin (CD) is at the origin of the study of water-soluble molecular receptors since it has a relatively hydrophobic cavity

that can include various organic molecules.[3,4] In CD inclusion complexes the structure and the site of inclusion has been studied by using various spectroscopic techniques.[2] X-ray diffraction studies have shown a definitive structure for the CD inclusion complex. Although some indication of statistical disorder of small

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