Contribution from the Departments of Chemistry, University of South Carolina, Columbia, South Carolina 29208, and The University of Texas, Austin, Texas 78712

^{113}Cd Shielding Tensors of the Cadmium Complex of Texaphyrin, a Novel Expanded Porphyrin, and Its Pyridine and Benzimidazole Adducts

Michael A. Kennedy,[†] Jonathan L. Sessler,*[,‡] Toshiaki Murai,[‡] and Paul D. Ellis*[,†]

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The cadmium complex of an expanded five-coordinate porphyrin known as "texaphyrin" (Sessler et al. *J. Am. Chem. Soc.* **1988**, *110*, 5586) and its complexes with pyridine and benzimidazole have been investigated by solution- and solid-state ^{113}Cd NMR spectroscopy. In chloroform solution at 25 °C, the spectrum of unligated, five-coordinate Cd-texaphyrin is observed as a single resonance at 163 ppm. Similarly, a deuterated pyridine solution at 25 °C of cadmium texaphyrin produces a single resonance at 160 ppm. At −40 °C in deuterated pyridine, three resonances, corresponding to a mixture of free Cd-texaphyrin (150 ppm) and six-coordinate (140 ppm) and seven-coordinate (210 ppm) pyridine complexes, are observed in slow exchange. The benzimidazole complex of Cd-texaphyrin in chloroform was observed as a single resonance at 158 ppm. From solid-state MAS results, a single tensor was observed for the five-coordinate complex with a corresponding isotropic chemical shift of 194 ppm. The MAS spectrum of the sample collected after preparation of the pyridine complex of Cd-texaphyrin revealed two tensors presumed to be due to a mixture of six- and seven-coordinate species. Based upon the isotropic chemical shifts and the symmetry of the tensors the six-coordinate species was assigned to the isotropic shift of 188 ppm and the seven-coordinate species as assigned to the isotropic shift of 221 ppm. The MAS spectrum of the benzimidazole complex of Cd-texaphyrin consisted of a single tensor, assumed to represent the six-coordinate species, with an isotropic chemical shift of 188 ppm. The principle shielding tensor elements were determined for each complex and are discussed in terms of reported crystal studies of Cd-texaphyrin and in comparison to cadmium complexes with other porphyrin and similar macrocycle ligands.

Introduction

Sessler et al.[1,2] have recently reported the synthesis of a novel pentadentate aromatic porphyrin-like ligand, "texaphyrin" (**1**), which could find use in a variety of applications,[3,4] including photodynamic therapy,[5,6] heavy-metal chelation therapy,[3,4] radioimmunodiagnostics,[3,4] and magnetic resonance imaging.[7] The use of texaphyrin-based systems in these applications, however, will necessarily require both a detailed knowledge of the metal-binding properties of the texaphyrin ligand itself and a thorough understanding of the coordination chemistry of the resulting complexes (i.e. with regards to additional apical ligand binding). To date, the most thorough analyses in the texaphyrin series have been carried out by using the cadmium(II) derivatives.[1-6] Here, both solution ^{1}H NMR and solid-state X-ray structural methods have been used to probe the binding of pyridine and benzimidazole to the initially five-coordinate complex **2**.[2] Unfortunately, these studies have provided only limited insight into the actual changes in the electronic environment about cadmium that occur upon apical ligand binding. Such information, however, would be informative. We have, therefore reinvestigated this same cadmium complex (**2**) and its pyridine and benzimidazole adducts (**3**–**5**) using ^{113}Cd NMR both in solution and in the solid state. We have found that ^{113}Cd NMR provides a particularly convenient probe of the cadmium environment in these novel five-, six-, and seven-coordinate systems. **1**–**5** are depicted in Figure 1.

Over the last decade, ^{113}Cd NMR has been used extensively as a structural probe for both metalloproteins and simple synthetic systems. For instance, in 1983 Jakobsen et al.[8] reported a detailed study of the cadmium complex of tetraphenylporphyrin and its pyridine adduct, which were considered as model compounds for cadmium-substituted hemeproteins. From that work, it was concluded that the relatively small chemical shifts accompanying changes in the ligand environment could arise from large changes in the individual shielding tensor elements. More recently, Kennedy and Ellis[9] reported a ^{113}Cd NMR study of Cd-protoporphyrin IX, its ester, and pyridine adducts and Cd-myoglobin. Again, the cadmium shielding tensors were shown to be very sensitive to structure and identity of the coordinating ligands, specifically the identity and geometry of the axial ligand present on the naturally occuring protoporphyrin. Thus, at present, ^{113}Cd NMR appears well established as a means of probing structural changes about the cadmium in complexes derived from the basic square-planar environments of natural and synthetic tetrapyrrolic ligand systems (e.g. square pyramidal and octahedral). Unfortunately, considerably less is known about the utility of ^{113}Cd NMR as a structural tool for probing ligation changes associated with other basic planar coordination environments (e.g. those derived for rigid pentadentate and hexadentate macrocycle ligands). For instance, only very recently have Marchetti et al.[10] reported the results of the ^{113}Cd study of a cadmium complex of a nitrogen analogue of 18-crown-6. In this study, the cadmium shielding tensor was found to be sensitive to the coordination environment (i.e. unusually long Cd-N bond lengths (2.50–2.79 Å)) enforced by the rigid hexadentate macrocycle ligand. Unfortunately, to date, no comparable ^{113}Cd NMR studies have been carried out with cadmium complexes derived from formally analogous pentadentate macrocycle ligands. Such studies, however, would be of interest as they would contribute further to the growing body of ^{113}Cd shielding tensor data for putative biological model systems derived from similar rigid macrocycle ligands. The pentadentate texaphyrin framework, being both rigid and aromatic, was considered to be an especially advantageous system with which to carry out such studies.

Experimental Section

The five-coordinate cadmium complex of **1** (complex **2**) was prepared as either the nitrate or chloride complexes[11] as described by Sessler et al.[2] using 95.3% isotopically pure ^{113}Cd (U.S. Services, Inc.) in the form of $Cd(NO_3)_2$ or $CdCl_2$. The pyridine complexes were prepared by evaporating an ~40% pyridine solution of complex **2** dissolved in chloroform. This was done by bubbling a stream of nitrogen gas through the solution at room temperature. The benzimidazole complex (**5**) was prepared by evaporating a dilute solution of complex **2** in methanol in the presence of an ~10 mol excess of benzimidazole using the same

[†] University of South Carolina.
[‡] The University of Texas.

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(11) In the case of the nitrate the resulting material has been shown to be rigorously five-coordinate, but in the case of the chloride some coordinative participation of the counteranion has been implicated.[2]

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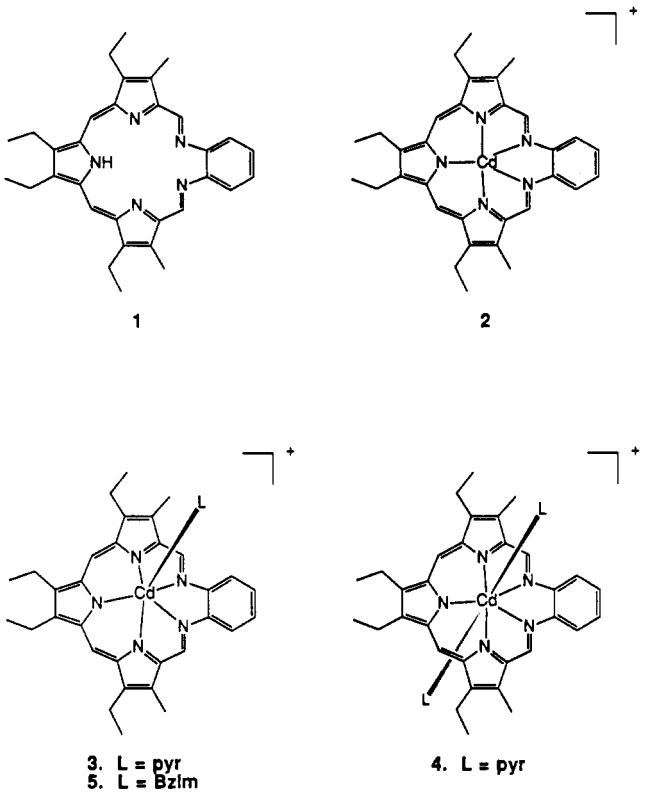

Figure 1. Schematic representations of the free base "texaphyrin" (**1**) and representative five-, six-, and seven-coordinate cationic cadmium(II) complexes (**2–5**) derived from this "expanded porphyrin". In all cases, chloride serves as the counter ion.

bubbling method used to prepare the pyridine complex.

All ^{113}Cd NMR experiments were performed on a Varian XL 300 NMR spectrometer operating at 66.547 MHz. Solution experiments were performed by using a Varian 10-mm broad-band (30–120 MHz) NMR probe. Chemical shifts were referenced relative to 0.1 M cadmium perchlorate in water at 20 °C. Solid-state NMR experiments were performed with a Doty MAS probe (Doty Scientific Inc.). Typically, 3.5–7.0 mg of sample was used and an adequate signal to noise ratio was obtained after 5–10 h of total acquisition time. Data acquisition for CP/MAS experiments employed a standard Hartmann–Hahn spin-locked cross-polarization pulse sequence.[12,13] Best estimates of the chemical shielding anisotropy ($\Delta\sigma$) and the asymmetry (η) were extracted from the spinning sideband patterns for each complex by analysis using a Simplex algorithm in conjunction with a MAS spectral simulation program.[14–16]

Results and Discussion

Solution-State Results. A study of the dynamic equilibria for complexes **2–5** in chloroform solution has been carried out by Sessler et al.[2] using ^{1}H NMR to track the changes in chemical shift of the mesolike imine protons associated with the addition of pyridine and benzimidazole to the initially five-coordinate complex **2**. In this study, it was found that in chloroform the binding constant for the formation of **5** from **2** ($k \simeq 2 \times 10^4$ M^{-1}) was roughly 10^3 greater than for the formation of the corresponding seven-coordinate benzimidazole complex from **5**. On the other hand, the formation constant for **3** (from **2**) was determined to be roughly a factor 10^2 smaller than that for the formation of the seven-coordinate complex **4** from the six-coordinate species **3** ($K \simeq 3 \times 10^2$ M^{-1}). Thus, as was anticipated on the basis of solid-state X-ray structural studies, concentration regimes may be chosen in solution where the six- and seven-coordinate complexes **5** and **4** dominate in the case of benzimidazole and pyridine, respectively. The considerably greater overall binding affinity of the better π-base, benzimidazole, however, means that even at low ligand to complex ratios, nearly complete conversion to the six-coordinate complex (**5**) will have occurred, whereas the pyridine an initially 5×10^{-3} M solution of **2** will only be ca. 35% converted to **4** after the addition of a full 10 equiv. In practical terms, these results suggest that it should be possible to obtain relatively "pure" solutions of **5** but that, under normally accessible concentration regimes, mixtures of **2**, **3**, and **4** will always pertain, even if the latter species is present in greatest concentration.

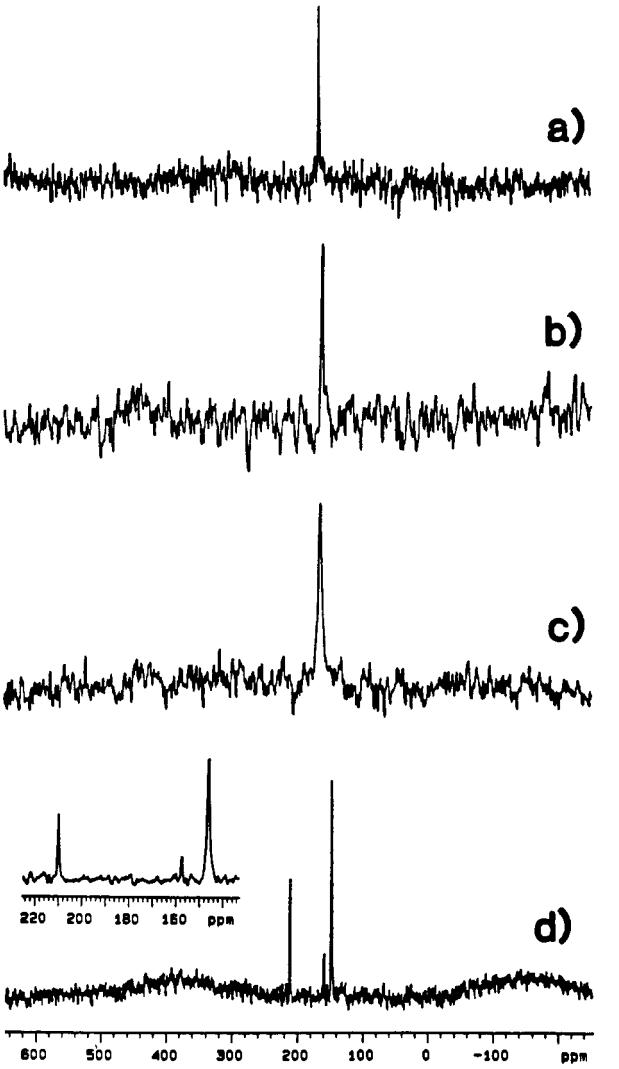

Figure 2. Solution-state spectra: of (a) a 0.57 mM solution of **2** in $CHCl_3$ at 25 °C (number of transients = 268 073); (b) a 0.25 mM solution of **5** in $CHCl_3$ in the presence of a 18.7/1 mole ratio of benzimidazole at 25 °C (number of transients = 718 201); (c) a 1.55 mM solution of **2** in pyridine-d_5 at 25 °C, (number of transients = 277 305); (d) a 1.55 M solution of **2** in pyridine-d_5 at −40 °C (number of transients = 53 134). All spectra were collected at 66.547 MHz and are proton coupled. A 30° Ernst angle pulse of 12 μs was used for 100W rf power at the observe frequency.

The Cd complex of texaphyrin (**2**) and its adducts **3–5** were reexamined in solution in order to confirm the above conclusions and to determine if each species could be resolved by ^{113}Cd NMR. The results of these experiments are shown in Figure 2. Figure 2a shows the spectrum of **2** in chloroform. A single resonance corresponding to an isotropic chemical shift of 163 ppm relative to 0.1 M cadmium perchlorate in water is observed. Figure 2b shows a spectrum of **2** in chloroform in the presence of a 18.7/1 molar ratio of benzimidazole to starting complex. From the equilibrium data,[2] it is expected that the resonance at 158 ppm is representative of **5** in solution. Finally, parts c and d of Figure 2 show the spectra of **2** in deuterated pyridine at +25 and −40

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Table I. Summary of ^{113}Cd Shielding Tensor Data for a Series of Cadmium Complexes with Rigid Nitrogen Chelating Macrocycle Ligands

cadmium complex	coord no., atom: ring	coord no., atom: axial ligand	^{113}Cd shielding tensor elements	shielding anisotropy, asym ($\Delta\sigma$, η)	ref
Cd–tetraphenylporphyrin	4, N	0	σ_{11} = 285, σ_{22} = 285, σ_{33} = 626, $\bar{\sigma}$ = 399	$\Delta\sigma$ = 341, η = 0.00	8
Cd–tetraphenylporphyrin pyridyl adduct	4, N	1, N	σ_{11} = 397, σ_{22} = 397, σ_{33} = 502, $\bar{\sigma}$ = 399	$\Delta\sigma$ = 105, η = 0.00	8
Cd–protoporphyrin IX dimethyl ester	4, N	0	σ_{11} = 336, σ_{22} = 338, σ_{33} = 770, $\bar{\sigma}$ = 480	$\Delta\sigma$ = 432, η = 0.01	9
Cd–protoporphyrin IX dimethyl ester	4, N	1, N	σ_{11} = 407, σ_{22} = 442, σ_{33} = 588, $\bar{\sigma}$ = 480	$\Delta\sigma$ = 163, η = 0.32	9
expanded porphyrin "texaphyrin"	5, N	0	σ_{11} = 111, σ_{22} = 146, σ_{33} = 325, $\bar{\sigma}$ = 194	$\Delta\sigma$ = 197, η = 0.26	this work
expanded porphyrin "texaphyrin" pyridyl adduct	5, N	1, N	σ_{11} = 83, σ_{22} = 172, σ_{33} = 310, $\bar{\sigma}$ = 188	$\Delta\sigma$ = 183, η = 0.73	this work
expanded porphyrin "texaphyrin" pyridyl adduct	5, N	2, N	σ_{11} = 175, σ_{22} = 176, σ_{33} = 310, $\bar{\sigma}$ = 221	$\Delta\sigma$ = 134, η = 0.01	this work
expanded porphyrin "texaphyrin" benzimidazole adduct	5, N	1, N	σ_{11} = 93, σ_{22} = 153, σ_{33} = 319, $\bar{\sigma}$ = 188	$\Delta\sigma$ = 196, η = 0.46	this work
nitrogen analogue of 18-crown-6	6, N	2, O	σ_{11} = −32, σ_{22} = −57, σ_{33} = −138, $\bar{\sigma}$ = −760	$\Delta\sigma$ = −93.5, η = 0.42	10

°C, respectively. In Figure 2c, a single resonance is observed at 160 ppm. This resonance is inferred to represent an averaged chemical shift due to the rapid equilibriation among complexes **2**–**4**. At −40 °C, however, the exchange rate in solution is apparently sufficiently low such that resonances for all three species expected in solution are observed. Under these conditions, the small peak at 158 ppm is assigned to the free complex **2**, since this chemical shift corresponds to that observed for **2** in chloroform (shown in Figure 2a), and it is expected that the unligated five-coordinate complex **2** would be the minor component in pyridine solution. From the ^{113}Cd NMR spectrum run in the presence of benzimidazole (δ = 158 ppm; cf. Figure 2c), the resonance at 148 ppm is assigned to **3**. Also, from the equilibria data,[2] it is expected that the six-coordinate complex would be one of the dominant species under the conditions of the experiment. The resonance at 210 ppm is assigned to the seven-coordinate complex **4**. This conclusion is based on solid-state results discussed below and on reports of solution- and solid-state chemical shifts that have been reported for octahedral nitrogen complexes in the range 185–400 ppm.[17] Therefore, by lowering the temperature to −40 °C and by making comparisons to similar systems, it is possible to assign the chemical shifts to all three species undergoing exchange. Unfortunately, the analogous low-temperature experiment for benzimidazole in chloroform could not be successfully performed due to the low solubility of both the unligated Cd–texaphyrin and benzimidazole in chloroform.

Solid-State Results. Cd–Texaphyrin. Figure 3a shows the CP/MAS spectrum of complex **2**. This spectrum is independent of the counterion employed in the preparation of **2**, i.e. $Cd(NO_3)_2$ or $CdCl_2$. From this spectrum, the isotropic chemical shift is 194.32 ppm. The best estimates of the shielding parameters (summarized in Table I) were extracted from the analysis of the sideband intensities. The simulated MAS spectrum shown in Figure 3b was calculated from the best-fit parameters and demonstrates a good fit compared to the experimental spectrum. From the determination of the crystal structures of complexes **4** and **5**, the Cd–N bond distances are known to be between 2.24 and 2.52 Å. These bond lengths are roughly 10% longer than typical Cd–N bond lengths in tetrapyrrolic porphyrin-type ligands such as tetraphenylporphyrin.[8] The longer Cd–N bond lengths in Cd–texaphyrin result in the shielding of the isotropic chemical shift from 399 ppm in Cd–tetraphenylporphyrin (Cd–TPP) to 194 ppm in Cd–texaphyrin. Concomitant with the shielding of the isotropic chemical shift is the shielding of all the principle elements of the shielding tensor as indicated in Table I. The unique tensor element, σ_{33}, which samples the bonding within the plane of the macrocycle ligand, is shielded by 300 ppm compared to that of Cd–TPP. The large shielding of the unique element is consistent with the chemical shift expected due to the longer Cd–N bond lengths and due to an increase in the electron density around the cadmium nucleus associated with increasing the coordination number from 4 to 5. The σ_{11} and σ_{22} elements are expected to be oriented in the plane of the ligand, sampling the bonding

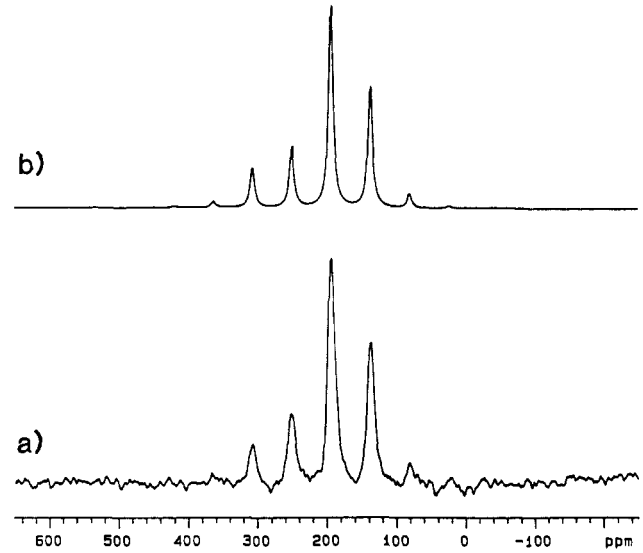

Figure 3. (a) Cross-polarization MAS spectrum of **2** (contact time, 2 ms; recycle delay, 2 s; number of repetitions, 16 271; spinning rate, 3756 Hz). (b) Simulated MAS spectrum of **2** using best estimate of tensor parameters determined as discussed in text (isotropic chemical shift, 194 ppm; asymmetry, 0.26; anisotropy, 197 ppm).

interaction perpendicular to the plane of the expanded porphyrin. The chemical shift to greater shielding by 140–175 ppm of the σ_{11} and σ_{22} elements compared to those for Cd–TPP is expected since, in the absence of axial ligands, there is no axial ligation for the NO_3^- complex and very weak axial ligation in the case of Cl^{2-}. In either case, any plane orthogonal to the plane of the ligand will sample only the bonds between the cadmium ion and the chelating ligand, which in the case of the expanded porphyrin involves long bonds relative to Cd–TPP. The reduced anisotropy from 341 ppm for Cd–TPP to 194 ppm for **2** is also consistent with an increase in the electron density around the cadmium nucleus due to increased coordination number and longer bonds.

Pyridine Adducts. Figure 4a shows a MAS spectrum of mixture of **3** and **4** collected by drying a solution of **2** in a mixture of 40% pyridine in chloroform. Two shielding tensors are evident and are presumed to indicate a mixture of **3** and **4**. The isotropic chemical shift for each tensor was determined by acquiring spectra at several spinning rates. The best estimate of the tensor elements for each tensor is summarized in Table I. The tensor corresponding to an isotropic chemical shift of 221 ppm is assigned to **4** on the basis of the reported chemical shift of octahedral nitrogen complexes with cadmium occurring at 185–400 ppm[12] and on the basis of the axial symmetry of the tensor, which reflects the pseudoaxial symmetry of **4**. The simulated MAS spectrum for this tensor is shown in Figure 4c and is in good agreement with the experimentally observed sideband pattern in Figure 4a. Accordingly, complex **4** is expected to exhibit a smaller anisotropy than the corresponding complex **3** due to a higher coordination symmetry. Experimentally it was determined that $\Delta\sigma$ = 134 ppm for **4** compared to $\Delta\sigma$ = 183 for **3**. The tensor with an isotropic

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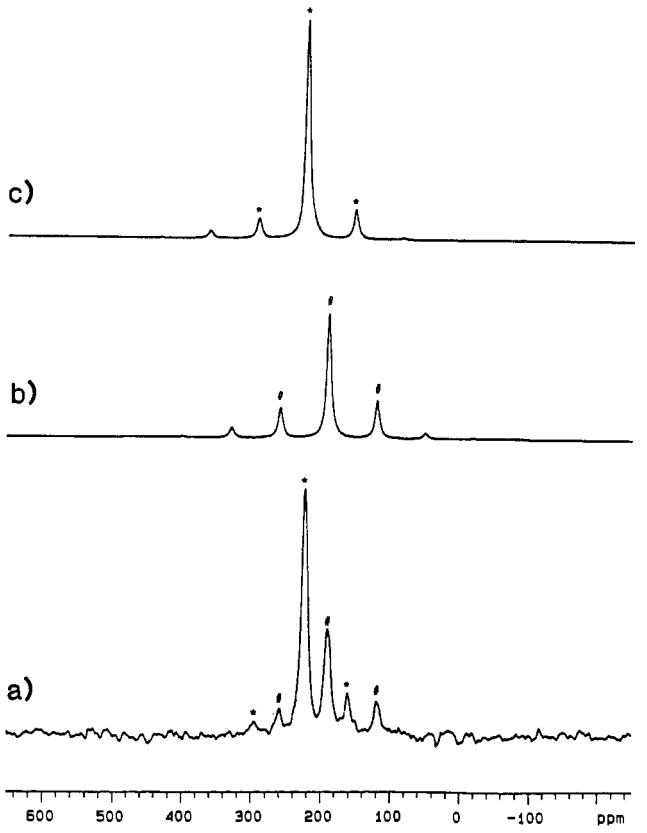

Figure 4. (a) Cross-polarization MAS spectrum of a mixture of **3** and **4** (contact time, 2 ms; recycle delay, 2 s; number of repetitions, 33 071; spinning rate, 4622 Hz). (b) Stimulated MAS spectrum of **3** using best estimate of tensor parameters determined as discussed in text (isotropic chemical shift, 188 ppm; asymmetry, 0.73; anisotropy, 183 ppm). (c) Simulated MAS spectrum of **4** using best estimate of tensor parameters determined as discussed in text (isotropic chemical shift, 221 ppm; asymmetry, 0.01; anisotropy, 134 ppm).

chemical shift of 188 ppm is assigned to complex **3**. The six-coordinate complex of Cd–texaphyrin with benzimidazole (**5**), for which six- rather than seven-coordinate binding has been shown to predominate in both solution and the solid state,[2] is also observed to have an isotropic chemical shift of 188 ppm. This supports the chemical shift assignment made for complex **3**. The asymmetry of 0.73 for the shielding tensor of **3** indicates a lower symmetry relative to **2** upon binding a single equivalent of pyridine. The pseudo-5-fold rotation axis perpendicular to the plane of the starting five-coordinate complex **2** is apparently reduced upon pyridine coordination. Such a reduction in local symmetry could occur if the geometry of the coordinated pyridine molecule is such that the pyridine ring is not normal to the plane of the macrocycle. The small shielding observed of the isotropic chemical shift upon binding a single pyridine ligand is not surprising in light of results reported by Jakobsen et al.[3] Specifically, the small change in the isotropic chemical shift of Cd–TPP (399 ppm) upon binding pyridine (432 ppm) was shown to result from nearly compensating large changes in the unique (−124 ppm) and perpendicular (+112 ppm) tensor elements. Likewise, Kennedy and Ellis[5] have reported a more striking example in which the isotropic chemical shift of Cd–PPIXDME (480 ppm) was reported to be identical with that of its pyridyl adduct, Cd–PPIXDME–py (480 ppm). However, when pyridine was bound, the unique element, σ_{33}, for Cd–PPIXDME (770 ppm) was shielded by 182 ppm whereas the in-plane elements for Cd–PPIXDME (336–338 ppm) were deshielded by 70–100 ppm. Clearly, one might expect a small change in the isotropic chemical shift for Cd–texaphyrin upon binding of either a single pyridine or benzimidazole. Depending on the magnitude of the compensating shifts of the unique and in-plane elements, either greater or lesser shielding might be expected.

Benzimidazole Adduct. Figure 5a shows the MAS spectrum of the benzimidazole complex of texaphyrin (**5**). The tensor is

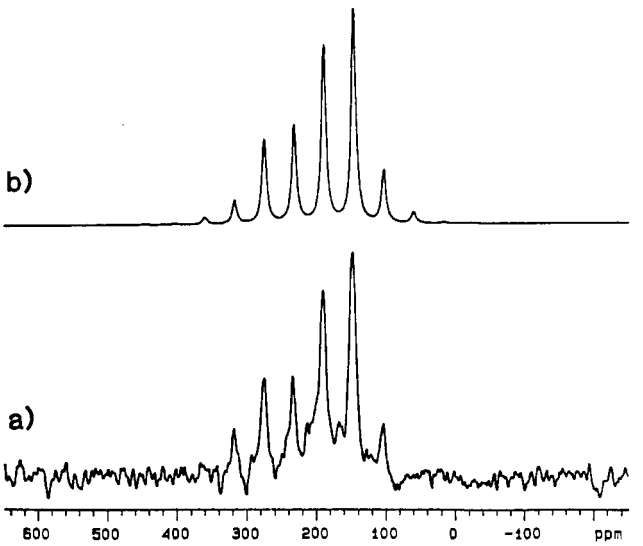

Figure 5. (a) Cross-polarization MAS spectrum of **5** (contact time, 2 ms; recycle delay, 2 s; number of repetitions, 15 186; spinning rate, 2857 Hz). (b) Stimulated MAS spectrum of **5** using best estimate of tensor parameters determined as discussed in text (isotropic chemical shift, 188 ppm; asymmetry, 0.46; anisotropy, 196 ppm).

presumed to correspond to the six-coordinate complex on the basis of results of early solution and solid-state X-ray studies.[2] The best estimates of the tensor parameters are summarized in Table I. The isotropic chemical shift is 188 ppm. As was observed in the case of the pyridine adduct **3** (vide supra), the symmetry of the shielding tensor for **5** has been reduced compared to that for **2** as indicted by an asymmetry of 0.46. In this particular case, the crystal structure of **5** indicates that the Cd–benzimidazole bond makes an angle of 86° with the plane of the ligand. Thus, to a first approximation, deviations from perpendicularity would not be expected to account for the reduced symmetry of the tensor. The value of the asymmetry parameter, in all probability, reflects the low symmetry of the appended ligand.

Comparison with Other Rigid Macrocycle Ligand–Cadmium Complexes. The magnitude of the unique element for complexes **2–5** (310 ppm to 325 ppm) is intermediate between that of the tetrapyrrole porphyrins Cd–TPP (502 ppm and 626 ppm) and Cd–protoporphyrin IX dimethylester (588 ppm and 770 ppm) and the cadmium complex of the nitrogen analogue of 18-crown-6[4] (−138 ppm). This series of ligands provides a well-defined geometry in which to interpret the ^{113}Cd shielding tensor data. Specifically, the unique tensor element, which samples the current densities due to bonding in the plane of the chelating macrocycle ligand, consistently reflects the length of the Cd–N bonds in the cadmium complexes with these porphyrin derivatives. The tetrapyrrole porphyrins, such as Cd–TPP and Cd–PPIXDME and their pyridine adducts have relatively short Cd–N bonds (~2.1 Å) compared to those in the five-coordinate expanded porphyrin (2.25–2.55 Å), whereas the average Cd–N bond length for the Cd complex with the nitrogen analogue of 18-crown-6 is ~2.7 Å. A clear correlation exists between with ligand structure and Cd–N bond length with the greatest shielding of the cadmium nucleus being observed for those complexes with the longest cadmium to nitrogen distances. This observation is similar to one of the conclusions reported by Munakata et al.[18] They reported that as the chelate ring size of cadmium chelate compounds decreases (from eight to five in a series of diamine complexes), the ^{113}Cd nucleus becomes more deshielded due to decrease of the chelate ring strain. Again, we conclude that increased chelate ring size, i.e. from four-coordinate tetrapyrrolic ligands to hexadentate macrocycles such as the nitrogen analogue of 18-crown-6, leads to increased shielding of the cadmium nucleus, however, due to increasingly poor electronic overlap of the π-system with the

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cadmium ion rather than an increase in ring strain in these rigid porphyrin-like chelate ligands.

Jakobsen et al.[3] and Kennedy and Ellis[5] have shown that four-coordinate Cd-porphyrins, which bind a single axial pyridine ligand and experience a resulting displacement of the cadmium ion out of the plane of the ligand (or further displacement from the plane of the ligand), undergo a concomitant shift of all the tensor elements. However, if the axially coordinating ligand binds without perturbing the position of the Cd^{2+} in the plane, only a change in the nonunique elements should be observed. From the data in Table I, the unique tensor element, σ_{33}, is shielded for complexes **3**–**5**, 310, 310, and 319 ppm, respectively, relative to that for complex **2** (325 ppm). These observations are consistent with those for axial pyridine coordination to Cd-TPP and Cd-PPIXDME, although the roughly 100 ppm shielding that occurs for the four-coordinate porphyrin is attenuated to a 10–15 ppm effect for the cadmium complex of the "expanded" texaphyrin system. The apparent reduced sensitivity to axial pyridine ligation of the Cd complex of the expanded porphyrin as reflected in the ^{113}Cd shielding tensor prompts the suggestion that the bonding requirements of the Cd^{2+} ion have been unusually well satisfied by the texaphyrin ligand. From Table I, the σ_{33} tensor element varies over a small range from 310 to 325 ppm for all the complexes **2**–**5**. In complex **4**, the Cd^{2+} resides in the plane of the ligand. However, in complex **5**, the Cd^{2+} lies 0.338 Å out of the ligand plane. Apparently, the change in the electron distribution in **5** compensates for the pulling of the Cd^{2+} out of the plane. Upon binding of pyridine to Cd-tetraphenylporphyrin, Jakobsen et al.[3] observed the unique element to be shielded by 124 ppm (see Table I).

Conclusions

From this study of the cadmium complex of texaphyrin and its pyridyl and benzimidazole adducts, the following observations have been made. First, a clear correlation exists between Cd-N bond length associated with cadmium complexes with rigid nitrogen-chelating aromatic macrocycle ligands, namely increasing bond length leads to increased shielding. Similar observations by others[18] have been interpreted in terms of strain of the chelate ring. However, it is difficult to disentangle the influence of the varying hybridization and the possibility of increased electron density about the cadmium ion associated with increasing coordination number. Second, the sensitivity of the "in-plane" tensor elements to apical binding of π-base ligands is clearly reduced compared to those of naturally occuring tetrapyrrolic porphyrins. This phenomenon may be due to an electronic overlap of the cadmium ion with the texaphyrin ligand such that the electron density undergoes a redistribution in such a way that compensates for axial ligand binding. This change in sensitivity of "in-plane" tensor elements between tetrapyrrolic porphyrins and texaphyrin to axial ligands is of potential interest to those practitioners of qualitative MO theory.

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Contribution from the Department of Chemistry,
Youngstown State University, Youngstown, Ohio 44555

Chemical-Ionization and Electron-Ionization Mass Spectra of Dimethylglyoxime and Its Complexes with Nickel(II), Palladium(II), and Platinum(II)[1]

Steven M. Schildcrout* and Lisa M. Besozzi

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Positive-ion methane chemical-ionization (CI) mass spectra are reported for the title compounds. Also "self-CI" is reported for dimethylglyoxime at high sample pressures with no reagent gas. For the metal complexes, the respective protonated molecules dominate the CI spectra, and higher mass peaks are observed for adducts with reagent-gas ions and for protonated dimers, whose relative abundances increase with sample pressure. Charge transfer from reagent-gas ions is seen in each case, and a small but significant abundance of only one metal-containing fragment is seen for each metal complex. In contrast, free dimethylglyoxime has a methane CI spectrum dominated by fragments, although the above-mentioned ion types are formed also, and its self-CI spectrum shows more abundant protonated monomer and dimer. Comparisons are made with electron-ionization mass spectra, which show extensive fragmentation at 70 eV, where some previously unrecognized or misassigned fragments are now assigned on the basis of isotopic peak ratios in natural-abundance and deuterated samples. Thermal reactions appear to have affected some previously reported spectra. The CI spectral assignments are verified similarly.

Introduction

Although dimethylglyoxime (2,3-butanedione dioxime or H_2dmg) has long, been used as a chelating agent for Met(II), where Met = Ni, Pd, and Pt, there has been little study of the mass spectra and gaseous ion chemistry of it or its metal complexes.

There are reports of positive-ion electron-ionization (EI) mass spectra for H_2dmg[2] and its chelates (Figure 1) $Met(Hdmg)_2$.[2-6] Because of possible interference from thermal reactions or of incomplete data analysis, some of these studies of the complexes show disagreements in assignments and presence or absence of certain mass spectral peaks. In the most thorough of these and the only one to consider the Pt complex and the deuterated Ni-$(Ddmg)_2$, Westmore and Fung[5] suggested structures for the fragment ions, concluding that the molecular ions of the complexes are very stable and that metal-to-ligand π bonding in the fragments prevents a simple rationalization of the fragmentation pathways in terms of formal oxidation states accessible by the metal. The latter approach has been used successfully with other coordination compounds.[7] Positive-ion chemical-ionization (CI) mass spectra

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