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^{113}Cd Shielding Tensors of Cadmium Compounds. 6. Single-Crystal NMR Study of the $CdCl_2$·18-crown-6 Complex

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The ^{113}Cd chemical shielding tensor and its orientation in the molecular frame have been determined for $CdCl_2$·18-crown-6 via a solid-state single-crystal NMR experiment. The shielding tensor elements are found to be σ_{33} = −700 ppm, $\sigma_2 2$ = 385 ppm, and σ_{11} = 414 ppm. The anisotropy and asymmetry parameters are determined to be $\Delta\sigma$ = −1100 ppm and η = 0.04, respectively. The unique shielding tensor element, σ_{zz}, lies 2.4° from the 3-fold rotation axis of the crown ligand and was also found to be the most shielded tensor element σ_{33}. The structural feature that determines the orientation of σ_{33} is found to be the anomalously long Cd–O bond lengths, i.e. 2.75 Å. The unusually large magnitude of the most shielded tensor element is analyzed in terms of the special geometry and corresponding shielding trend established for a series of cadmium complexes with similar porphyrin and crown ligands.

Introduction

Crown ether complexes of cadmium are of interest as models for more complicated biological systems, e.g. ion transport through membranes. Also, there have been recent reports of unexpected ^{113}Cd isotropic chemical shifts and magnitudes of ^{113}Cd shielding tensor elements in novel cadmium complexes with rigid macrocycle ligands, e.g. an expanded porphyrin[2] and a nitrogen analogue of 18-crown-6.[3] Together, these interests have provided impetus for a solid-state single-crystal ^{113}Cd NMR investigation of the cadmium complex of 18-crown-6.

The number of nitrogen atoms involved in coordination with cadmium increases from 4 to 6 in the following series of complexes with rigid macrocycle ligands: (i) cadmium tetraphenylporphyrin (Cd–TPP),[4] (ii) a cadmium complex of a novel expanded porphyrin called texaphyrin,[2] and (iii) a cadmium complex of an unsaturated nitrogen analogue of 18-crown-6.[3] Throughout this series, the unique tensor element, determined by the shielding effect of the all-nitrogen plane, shifts from 626 ppm in cadmium tetraphenylporphyrin[4] to 329 ppm in the expanded porphyrin[2] to −138 ppm in the unsaturated nitrogen analogue of the 18-crown-6 ligand.[3] The increased shielding magnitude of the unique tensor element correlates with the increased average Cd–N bond length in these complexes.

The cadmium complex of 18-crown-6 extends this series of compounds by changing the identity of the coordinating atom from nitrogen to oxygen. We have, therefore, proceeded in determining the chemical shielding tensor and its orientation for this complex.

Experimental Section

Crystals of $CdCl_2$·18-crown-6 were prepared as described by Paige and Richardson.[5] The crystals are rhombohedral (a = 7.712 (3) Å, α = 95.57 (2)°, Z = 1) and the crystal structure has been solved under the space group $R3$.

NMR data were collected as previously described.[6] The angular dependence of the shielding tensor is depicted in Figure 1. An acquisition time of 102.4 ms preceded by a 3.45-ms cross-polarization contact time was used in each case. Extraction of the elements of the chemical shielding tensor from ^{113}Cd shift data has been previously described.[7] The results of the present study are summarized in Table I. Crystallographic determination of the orientation of the unit cell reference frame relative to the cube frame was achieved in part by previously described methods.[8] Because of the rhomobohedral nature of the $CdCl_2$·18-crown-6 crystal, it is not possible to identify an axis as being the *a*, *b*, or *c* natural crystal axis if the Weissenberg technique is used alone to locate the unit cell axes. Therefore, it was necessary to identify the 100, 010, and 001 faces of the crystal via measurements on a CAD-4 diffractometer. The scheme previously outlined for obtaining the Euler rotation angles in triclinic crystal cells[9] consists of locating the natural *b* and *c* axes of the crystal via Weissenberg measurements combined with geometrical calculations according to the convention described by Rollett.[10]

Results and Discussion

$CdCl_2$·18-crown-6. (18-Crown-6)cadmium dichloride crystallizes in the rhombohedral space $R3$. Paige and Richardson[5] have solved the crystal structure with cadmium at the origin. The cadmium coordination environment is shown in Figure 2 with the Cd atom at the origin of a 3-fold rotation axis of the crown ligand. The potential 6-fold rotation axis is reduced to a 3-fold axis due to the ruffled nature of the crown ligand. The cadmium ion is coordinated to six oxygen atoms in a plane from the crown ligand and axially coordinated to two chlorine atoms. The structural data, summarized in Table II, indicate that the Cd–Cl and Cd–O bond lengths are 2.3645 (5) and 2.752 (1) Å, respectively.

The point group symmetry operators are expected to generate a single chemically and magnetically distinct tensor for $CdCl_2$·18-crown-6. The 18-crown-6 complex with $CdBr_2$ is isostructural with $CdCl_2$·18-crown-6.[11] Therefore, although a single-crystal experiment has not been performed for this complex, the orientation of the ^{113}Cd chemical shielding tensor and corresponding interpretation should also be valid for $CdBr_2$·18-crown-6. Experimentally, a single resonance is observed for $CdCl_2$·18-crown-6 in each rotation plot and the behavior of this resonance as a function of rotation angle is depicted in Figure 1. The orientation of the ^{113}Cd shielding tensor is shown in Figure 2, and the tensor elements and corresponding direction cosines are given in Table I. Details of the structure and shielding tensor orientation data are provided in Table II. From the data in Table I, the isotropic chemical shift of $CdCl_2$·18-crown-6 can be calculated to be 33.0 ppm. The anisotropy, $\Delta\sigma$ = −1100 ppm, is the largest determined so far for any cadmium compound and nearly spans the known ^{113}Cd chemical shift range. The magnitude of the anisotropy combined with the nearly axial symmetry (η = 0.04) reflect the special geometry generated in the halogen derivatives of these Cd–crown complexes. Given the inherent symmetry of this molecule, it is not unexpected that the unique tensor element,

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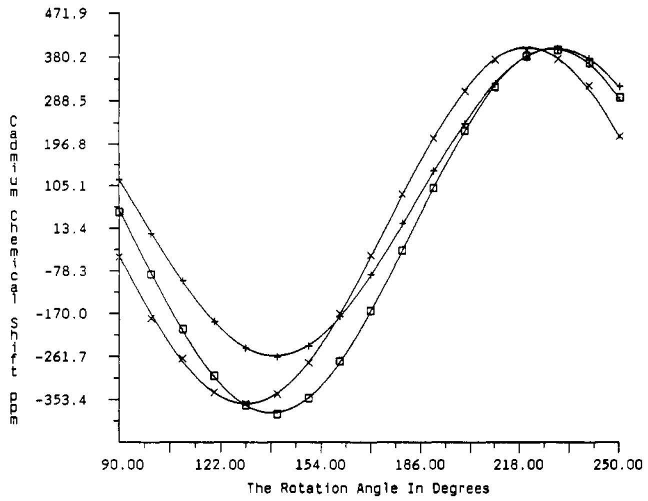

Figure 1. ^{113}Cd chemical shift of CdCl$_2$·18-crown-6 as a function of the rotation angle about the y axis of the laboratory reference frame. The symbols, +, □, and ×, indicate experimental points for rotations most nearly about the natural c, b, and a unit cell axes, respectively. In each case, the line drawn through the points represents the calculated angular dependence of the chemical shift based on the best fit of the experimental data with the known functional dependence.

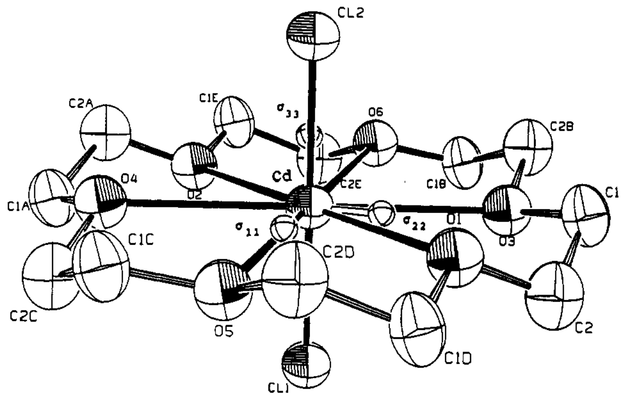

Figure 2. Ortep diagram, showing the orientation of the ^{113}Cd shielding tensor in the molecular frame of CdCl$_2$·18-crown-6. Tensor elements are designated by isotropic spheres with principal axes only. Directly bonded atoms are designated by anisotropic thermal ellipsoids with principal axes with quadrant shading. Nonbonded atoms are designated by anisotropic thermal ellipsoids without quadrant shading.

Table I. Direction Cosines Relating the Principal Elements of the ^{113}Cd Shielding Tensor to the Molecular Reference Frame in CdCl$_2$·18-crown-6.

tensor[a] elements,	ppm[b]	direction cosines			angles, deg		
		a'	b'	c'	a'	b'	c'
σ_{11}	414	−0.7049	0.6933	0.1495	134	46	81
σ_{22}	385	−0.2517	−0.4416	0.8611	104	116	31
σ_{33}	−700	0.6630	0.5694	0.4859	48	55	61

[a] The convention used for labeling the shielding tensor elements is according to that of Haeberlen, which ascribes $\sigma_{33} = \sigma_{zz}$ = the unique tensor element: Haeberlen, U. *High Resolution NMR in Solids*; Advances in Magnetic Resonance, supplement; Academic Press: New York, 1976. [b] The ^{113}Cd chemical shifts are reported with positive values to higher frequency/lower shielding relative to solid Cd(ClO$_4$)$_2$·6H$_2$O.

Table II. Structural Data for CdCl$_2$·18-crown-6: Interatomic Distances and Angles for the Primary Coordination Sphere and Details of the Ligand Geometry

	Interatomic Distances, Å		
Cd–Cl	2.364	Cd–O	2.752
	Interatomic Angles, deg		
Cl–Cd–O(1)	93.1	C(1)–O(1)–C(2)	112.5
O(1)–Cd–O(3)	60.3	O(1)–C(1)–C(2)	108.4
Cd–O(1)–C(1)	114.4	C(1)–C(2)–O(1)	108.1
Cd–O(1)–C(2)	117.0		
	Tensor[a] Element–Ligand Angles, deg		
σ_{11}–Cd–Cl(1)	91.4	σ_{11}–Cd–O(3)	117.6
σ_{11}–Cd–Cl(2)	88.5	σ_{11}–Cd–O(4)	62.3
σ_{11}–Cd–O(1)	57.6	σ_{11}–Cd–O(5)	5.1
σ_{11}–Cd–O(2)	122.3	σ_{11}–Cd–O(6)	174.8
σ_{22}–Cd–Cl(1)	91.9	σ_{22}–Cd–O(3)	28.0
σ_{22}–Cd–Cl(2)	88.1	σ_{22}–Cd–O(4)	151.9
σ_{22}–Cd–O(1)	32.4	σ_{22}–Cd–O(5)	92.5
σ_{22}–Cd–O(2)	147.6	σ_{22}–Cd–O(6)	87.4
σ_{33}–Cd–Cl(1)	177.5	σ_{33}–Cd–O(3)	94.1
σ_{33}–Cd–Cl(2)	2.4	σ_{33}–Cd–O(4)	85.8
σ_{33}–Cd–O(1)	89.3	σ_{33}–Cd–O(5)	94.4
σ_{33}–Cd–O(2)	90.7	σ_{33}–Cd–O(6)	85.5

[a] See footnote *a* of Table I.

σ_{zz}, is nearly aligned with the 3-fold rotation axis, i.e. declined with an angle of 2.4°. The unique element, σ_{zz}, is also the most shielded element. In these complexes, the plane of oxygen atoms contributes more shielding to the Cd nucleus than any plane containing axial halogen atoms. This is primarily due to the anomalously long Cd–O bond lengths in these Cd·18-crown-6 complexes.[11] The significance of the geometries of Cd complexes with crown ligands will be discussed in further detail below. The perpendicular shielding tensor elements, σ_{xx} and σ_{yy}, have similar magnitude and sign and, therefore, are expected to have similar orthogonal environments. Both tensor elements are found to lie less than 2° from the best least-squares plane defined by the Cd atom and the six oxygen atoms of the macrocycle ligand, and both are nearly perpendicular to the Cl–Cd–Cl line. Hence, the shielding magnitude of σ_{xx} and σ_{yy} is likely dominated by the electronic perturbation of the Cd nucleus by the two axial halogen atoms with bonds perpendicular to the Cd–O plane.

The magnitude of the σ_{33} element in CdCl$_2$·18-crown-6 is the most shielded ^{113}Cd tensor element reported by ~350 ppm.[8] However, this result is not surprising if one considers the recent observations of Sessler et al.[2] and Marchetti et al.[3] (see Table III). Sessler et al. report the ^{113}Cd shielding tensor elements for an expanded porphyrin in which the Cd atom is coordinated to (and lies in the plane with) five nitrogen atoms of an unsaturated porphyrin ligand. The isotropic chemical shift of the texaphyrin occurs at 191 ppm, which is shielded by 200–300 ppm compared to normal four-coordinate porphyrins. The unique tensor element, σ_{zz} = 329 ppm, is shielded by ~300 ppm compared to Cd–TPP.[4] The shielding of the Cd nucleus correlates with the lengthening of the average Cd–N bond length from 2.1 Å in Cd–TPP to 2.39 Å in the texaphyrin complex.[2]

Marchetti et al.[3] recently determined the ^{113}Cd shielding tensor elements in a Cd complex of the nitrogen analogue of 18-crown-6, in which the Cd ion sits asymmetrically in the nitrogen plane pocket of the ligand. This six-nitrogen, two-oxygen coordination complex has an isotropic ^{113}Cd chemical shift of −75 ppm (σ_{33} = −138 ppm, σ_{22} = −57.82 ppm, and σ_{11} = −31.89 ppm). The abnormally long Cd–N bonds (2.50–2.79 Å) constrained by the rigidity of the macrocycle yield a complex that, according to its isotropic chemical shift, feigns to be an all-oxygen coordination complex. The unexpected chemical shift was postulated to be due to the primarily electrostatic rather than covalent Cd–ligand interaction correlated with the long bond interactions. From the well-defined structure of the crown ligand, the unique tensor element should be perpendicular to the best plane of the macrocycle ligand; therefore, the orientation of the most shielded element was determined by the plane containing the six nitrogen atoms. However, it has been established that, in monodentate ligands with normal bond lengths (2.1–2.2 Å), coordination of cadmium to nitrogen causes deshielding compared to oxygen. From this example, it is clear that bond length can dominate ligand identity in cases of special geometry. Comparison of the ^{113}Cd shielding tensor for the expanded porphyrin Cd complex with that for the unsaturated nitrogen analogue of 18-crown-6 reveals that the

Table III. Summary of ^{113}Cd Shielding Tensor Data for a Series of Cadmium Complexes with Rigid Polydentate Ring Type Ligands

ligand	ring coordn no., atom type	Cd–ligand bond lengths, Å	^{113}Cd shielding[a] tensor elements, ppm[b]
tetraphenylporphyrin	4, N	2.14	$\sigma_{11} = 285$ $\sigma_{22} = 285$ $\sigma_{33} = 626$
expanded "texaphyrin" porphyrin	5, N	2.25–2.53	$\sigma_{11} = 120$ $\sigma_{22} = 123$ $\sigma_{33} = 329$
nitrogen analogue of 18-crown-6	6, N	2.50–2.79	$\sigma_{11} = -32$ $\sigma_{22} = -57$ $\sigma_{33} = -138$
18-crown-6	6, O	2.75	$\sigma_{11} = 414$ $\sigma_{22} = 384$ $\sigma_{33} = -700$

[a] See footnote *a* of Table I. [b] The ^{113}Cd chemical shifts are recorded with positive values occurring to high frequency/lower shielding relative to solid $Cd(ClO_4)_2 \cdot 6H_2O$.

shielding of the unique element is correlated with a lengthening of the average Cd–N bond length from 2.39 to ~2.65 Å. The $CdCl_2 \cdot$18-crown-6 complex exhibits an unique tensor element ($\sigma_{33} = -700$ ppm) that represents a shielding by 559 ppm relative to the unique tensor element for the Cd complex of the nitrogen analogue of 18-crown-6. An increase in the average Cd–N bond length, from 2.65 to 2.752 Å, is simultaneously observed (Table III). The shielding of 559 ppm correlates with changing the ligand's coordinating atom identity from nitrogen to oxygen.

Solid-state ^{113}Cd CP/MAS experiments have been performed for the $CdX_2 \cdot$18-crown-6 (X = Cl, Br, I) complexes at various magnetic field strengths. From the CP/MAS experiments for $CdCl_2 \cdot$18-crown-6, the tensor parameters (e.g. anisotropy, isotropic chemical shift, and asymmetry) are in agreement with those determined from the present single-crystal NMR experiment. A detailed analysis of these experiments will be published elsewhere. However, the magnitude of the isotropic chemical shift for each complex is pertinent to this discussion. In the series of the X = Cl, Br, and I complexes with Cd·18-crown-6, the isotropic ^{113}Cd chemical shifts are 33, ca. −25, and ca. −172 ppm, respectively. This result is consistent with the "normal" halogen effect, i.e. a correlation of chemical shifts for light atoms with electronegativities of the substituent atoms; e.g., ^{13}C chemical shifts in halomethanes are ordered as $\delta_{CH_3I} < \delta_{CH_3Br} < \delta_{CH_3Cl} < \delta_{CH_3F}$.[12] In addition, Summers et al.[13] have reported similar high-frequency shifts for halogen anion coordination with cadmium complexes of 2-substituted benzimidazoles under conditions of slow exchange in solution. However, it is well-known[14] that for heavy atoms, i.e. atoms with atomic number ≥35 (Br), spin–orbit effects on chemical shifts become significant. Cheremisin and Schastnev[15] have presented a third-order perturbation treatment of the effects of spin-orbital (SO) interactions on ^{13}C NMR chemical shifts. Analogously, one would like to do a similar calculation for the SO effect of the halogen series on the ^{113}Cd chemical shift. However, in lieu of a complete theoretical treatment, we are at this time only able to report the order of the ^{113}Cd shielding determined for the series of halogen derivatives of Cd·18-crown-6.

Conclusion

The $CdCl_2$ complex of 18-crown-6 has been investigated via single-crystal ^{113}Cd NMR. The crown structure of the macrocycle provides a well-defined coordination environment for interpretation of the orientation of the shielding tensor elements. The isotropic chemical shift of +33 ppm relative to 0.1 M $Cd(ClO_4)_2$ is not unexpected for a six-oxygen, two-chlorine coordination system. Solid-state NMR reveals, however, that the magnitude of the most shielded tensor element is anomalously large with respect to currently reported data. The most shielded element, observed at −700 ppm, is ~350 ppm more shielded than any previously reported ^{113}Cd chemical shielding tensor element. For $CdCl_2 \cdot$18-crown-6, the experimentally determined orientation of the ^{113}Cd chemical shielding tensor reveals that the anomalous tensor element is indeed found perpendicular to the plane containing the six oxygen atoms. The remaining deshielded tensor elements have similar orthogonal environments as expected from the near-axial symmetry and are perpendicular to the plane containing the two chlorine atoms.

The important implication from solid-state ^{113}Cd NMR studies of the series of Cd porphyrins and Cd·18-crown-6 complexes discussed above is that long-bond interactions can dominate the shielding contribution normally associated with a given ligand identity. It is evident that extraordinarily long bond lengths, due to the constraint of rigid ligand structures such as porphyrins and crown molecules, can either reinforce or cancel the shielding contribution characteristic of a specific ligand identity, leading to heretofore unexpected magnitudes of ^{113}Cd shielding tensor elements.

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Registry No. $CdCl_2 \cdot$18-crown-6, 65079-34-7; ^{113}Cd, 14336-66-4; Cd, 7440-43-9; O_2, 7782-44-7.

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