Single-Crystal, Solid-State, and Solution ^{113}Cd and ^{77}Se NMR and X-ray Single-Crystal Study of a $[Cd(SeR)_2(N\text{-donor})_2]$ Complex

Raju Subramanian,[†,‡] Nandakumar Govindaswamy,[§] Rodolfo A. Santos,[†,||] Stephen A. Koch,*[,§] and Gerard S. Harbison*[,†]

Department of Chemistry, State University of New York at Stony Brook, New York 11794-3400, and Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304

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$[Cd(Se\text{-}2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)_2(bpy)]$ (**1**) has been characterized by X-ray crystallography and studied by solution and solid-state ^{113}Cd and ^{77}Se NMR to serve as an analog for biologically occurring $[M(S\text{-}Cys)_2(His)_2]$ centers. The unit cell parameters for **1** are as follows: $a = 21.99(2)$ Å, $b = 21.43(4)$ Å, $c = 16.72(3)$ Å, $V = 7881.3(4)$ Å^3, $Z = 8$, orthorhombic space group, *Pccn*. Two chemically inequivalent cadmiums and seleniums are found per unit cell. The principal values of the cadmium chemical shift tensors are ($\delta_{11} = 752$ ppm, $\delta_{22} = 570$ ppm, $\delta_{33} = 93$ ppm) and ($\delta_{11}= 733$ ppm, $\delta_{22} = 547$ ppm, $\delta_{33} = 100$ ppm) with respect to 0.1 M aq. $Cd(ClO_4)_2$. Those for selenium are ($\delta_{11} = -950$ ppm, $\delta_{22} = -1040$ ppm, $\delta_{33} = -1599$ ppm) and ($\delta_{11} = -933$ ppm, $\delta_{22} = -1069$ ppm, $\delta_{33} = -1586$ ppm) with respect to solid $(NH_4)_2SeO_4$. The orientation of the cadmium chemical shift tensor is similar to that of the previously published sulfur analog.

Introduction

Cadmium is often used as a substitute for zinc in NMR studies of the coordination environments of the active site in the zinc metalloproteins.[1,2] Zinc has a NMR accessible isotope (^{67}Zn) which is quadrupolar ($I = ^5/_2$), has a low natural abundance (4.11%)[3] and a poor receptivity (0.6 relative to ^{13}C)[4] and is otherwise a spectroscopically silent metal. The isotopes of cadmium (^{113}Cd and ^{111}Cd) are spin $^1/_2$ and are particularly good candidates for nuclear magnetic resonance (NMR) spectroscopy.[1,2] Cadmium has a large chemical shift range (∼1100 ppm) and the orientation and magnitude of cadmium chemical shift tensors are sensitive to the metal coordination sphere.[1,2]

Zinc centers in metalloproteins are frequently coordinated through the sulfur-containing cysteine and histidines.[5] ^{33}S, the magnetically active isotope of sulfur, is a quadrupolar nucleus ($I = ^3/_2$) with very low natural abundance (0.76%)[3] and poor receptivity of 0.02 relative to ^{13}C.[4] These factors make sulfur virtually inaccessible by NMR. Selenium may be substituted for sulfur without altering the sulfur coordination drastically. Moreover, selenocysteine occurs naturally in several proteins, and ^{77}Se, $I = ^1/_2$, 7.58% natural abundance,[3] and a receptivity (2.98 relative to ^{13}C)[4] gives an NMR signal with an adequate signal-to-noise ratio in a reasonable amount of time. Analogous to the study of the zinc sites by cadmium, selenium-substituted sulfur coordination can be directly probed by NMR.[6]

The chemical shift can be a represented by a second-rank tensor and has isotropic and anisotropic components. Although the magnitude of the chemical shift tensor (CST) is sensitive to the nuclear surroundings, it is the anisotropic components of the CST which are orientation dependent and can be related to a local molecular structure. This information is obtained to the maximum possible extent by a single-crystal NMR study of the nucleus under question. The magnitude and orientation of cadmium CSTs are sensitive to a variety of parameters, which include the type of ligands, coordination number, geometric distortions, and ligand charge. Some of the trends are quite unambiguous. For example, when the cadmium is surrounded by thiolate ligands, the cadmium chemical shifts are shifted downfield from the same species with nitro- and oxo-ligands (in that order).[1] However the dependence on other parameters is not well understood. The main purpose of undertaking such single crystal studies rests on one question: since the chemical shift parameters are sensitive to the surroundings, if only partial information about the CST is known, can local structure around the metal ion be inferred correctly?

In this paper, we present a combined ^{113}Cd and ^{77}Se NMR and X-ray crystallography single-crystal study of $[Cd(Se\text{-}2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)_2(bpy)]$.[7] This study complements our previous study of the thiolate analog[8] and is to the best of our knowledge the first single-crystal NMR study of an organoselenium metal complex.

Experimental Section

Synthesis of $[Cd(Se\text{-}2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)_2(bpy)]$ (1). $Li(Se\text{-}2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)$ (0.578 g, 2 mmol) was generated by the addition 2.1 mL of

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[†] University of Nebraska.

[‡] Present address: Beckman Institute for Advanced Science and Technology, 405, N. Mathews Avenue, Urbana, IL 61801.

[§] State University of New York, Stony Brook.

[||] Present address: Department of Chemistry, Cornell University, Ithaca, NY.

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(4) Receptivity (relative to ^{13}C) = $[\gamma_x^3/\gamma_c^3][N_xI_x(I_x + 1)/N_cI_c(I_c + 1)]$; where γ is the gyromagnetic ratio; N, the natural isotope abundance; and I, the spin quantum number.

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(7) Abbreviations: Se-2,4,6-i-$Pr_3C_6H_2$, 2,4,6-triisopropylbenzenethiolate; bpy, 2,2′-bipyridine; THF, tetrahydrofuran.

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Table 1. X-ray Crystallographic Parameters for **1**

empirical formula	$CdSe_2N_2C_{40}H_{54}$
fw	833.2
a, Å	21.99(2)
b, Å	21.43(4)
c, Å	16.72(3)
V, Å^3	7881(4)
Z	8
space group	*Pccn* (No. 56)
temperature	ambient
radiation	Mo Kα ($\lambda = 0.710\,78$)
linear abs coeff, cm^{-1}	24.08
scan mode	$\theta/2\theta$
2θ range deg	0−50
no. of obsns ($I > 3\sigma(I)$)	2219
no. of variables	425
R	0.038
R_w	0.040

$LiHBEt_3$ (obtained from Aldrich Chemicals) to a solution of 0.564 g of (2,4,6-i-Pr_3-C_6H_2-Se)$_2$[9] in 10 mL of THF. The THF was removed and the lithium selenolate was redissolved in 20 mL of methanol. $CdCl_2$ (0.183 g, 1.0 mmol) was added under N_2. A bright yellow solution resulted upon the addition of 2,2′-bipyridine (0.218 g, 1.4 mmol). Subsequent stirring and cooling of the solution to −20 °C gave 0.382 g (45% yield) of the bright yellow product. ^1H NMR ($CDCl_3$): 0.98 (d, 24 H, o-CH_3), 1.17 (d, 12H, p-CH_3), 2.73 (m, 2H, p-CH), 3.90 (m, 4H, m-CH), 6.65 (s, 4H, m-H), 7.19−7.97 (m, 8H, bpy) ppm.

X-ray Crystallography. A single crystal of **1** measuring 0.4 × 0.2 × 0.2 mm was grown by slowly cooling a hot (60 °C) acetonitrile solution to room temperature. Unit cell determinations and data collection were performed on a CAD4 diffractometer using standard procedures previously described.[8] The unit cell parameters and the systematic absences indicated the orthorhombic space group *Pccn* (No. 56). Parameters connected with crystallographic data acquisition are listed in Table 1. The crystal structure of **1** was solved with TEXRAY structure solution software package (Molecular Structure Corporation). The position of both the cadmiums was determined from an origin removed Patterson map and the other non-hydrogen atoms located and refined by using difference Fourier maps. Both decay and absorption corrections were applied and after calculation of the hydrogen atom positions and a full anisotropic refinement of the structure, a final R (R_w) value of 0.038 (0.040) was obtained.

NMR. Solution NMR samples were prepared by dissolving **1** in chloroform and filtering into a 10 mm tube. ^{77}Se and ^{113}Cd NMR were recorded on a Bruker AC-250 spectrometer operating at 47.7 and 55.4 MHz, respectively. 0.1 M aq. $Cd(ClO_4)_2$ and 1 M $(PhSe)_2$ in $CDCl_3$ were used to calibrate the spectrometer. A pulse width of 12.5 μs and 725 transients with a 2 s recycle delay were used for ^{113}Cd NMR. ^{77}Se NMR spectra were recorded with a pulse width of 30 μs and 1650 transients were collected using a 3 s recycle delay. All cadmium chemical shifts are reported with respect to 0.1 M aq. $Cd(ClO_4)_2$ and the ^{77}Se chemical shifts are referenced to solid $(NH_4)_2SeO_4$.

All solid state spectra were run on a home-built spectrometer operating at 7.1 T (corresponding to a ^{1}H frequency of 301.4 MHz). The crystal used for the ^{113}Cd and ^{77}Se single-crystal study had a volume ∼40 mm^3 and weighed 23 mg. The crystal was mounted in a glass support cell and placed on the goniometer head of a double resonance probe. Due to the high symmetry of the *Pccn* space group, only two mutually orthogonal plots are required for both ^{77}Se and ^{113}Cd single-crystal NMR analyses. Rotation plots were constructed from individual Cd and Se spectra obtained after 14.4° stepwise increments. Typically 512 transients were collected for each spectrum. The ^{77}Se and ^{113}Cd spectrum were acquired sequentially at the same goniometer position for each orientation of the crystal, in order to minimize systematic errors arising from inaccuracies in mounting the crystal. Peak positions were obtained by three-point fits to the maxima of the resonance lines and shielding tensors were obtained by standard methods.[8,10] CP/MAS spectra at various spinning speeds were obtained and the chemical shift tensor parameters extracted by applying a Herzfeld−Berger analysis.[11,12]

The ^{113}Cd NMR measurements were performed at the corresponding Larmor frequency of 66.88 MHz. The spectrometer was calibrated with $Cd(NO_3)_2 \cdot 4H_2O$, which also served to adjust the magic angle. The $\pi/2$ pulse was 3.5 μs, with Hartmann−Hahn contact times of 6 ms for the crystal work and 2 ms for the CP/MAS experiments, respectively, and a 4 s repetition time. CP/MAS spectra were acquired at several spinning speeds between 3.3 and 4.8 kHz. 2800 transients were averaged per spectrum, taking 512 points during signal acquisition.

For selenium NMR, the spectrometer frequency was set to 57.48 MHz and the instrument calibrated with solid $(NH_4)_2SeO_4$. Contact times of 3 and 2 ms were used for the single crystal and CP/MAS experiments, respectively, with the other acquisition parameters being the same as for ^{113}Cd. All shifts are given with respect to the isotropic shift frequency of $(NH_4)_2SeO_4$, which has a reported chemical shift of 1040.2 ppm with respect to dimethylselenium.[13]

Results and Discussion

Synthesis and Solid-State Structure. The solid-state structure of **1** was determined by X-ray crystallography. There are two distinct molecules in the unit cell, both of which have crystallographic C_2 symmetry. As a result, the asymmetric unit contains two half molecules. In the unit cell there are total of eight molecules, four each of molecule 1 and molecule 2. The C_2 axes, which pass through the Cd and bisect the Se−Cd−Se and N−Cd−N angles, are perpendicular to the *ab* face of the orthorhombic crystals. The metrical parameters for both molecules are listed in Table 2. Structural diagrams are shown in Figure 1. The two molecules are almost superimposable with only slight changes in the orientation of the selenolate ligands. The structure of **1** is also similar to that of the thiolate analog [Cd(S-2,4,6-i-Pr_3-C_6H_2)$_2$(bpy)] (**2**) which was studied earlier (Table 2).[8] In spite of the structural similarity of the molecules, **1** and **2** are not isomorphous.

The Cd−Se$_{(\text{average})}$ (2.553(4) Å) bond distance is longer than the Cd−S$_{(\text{average})}$ distance of (2.43(1) Å) reported for **2**, and the Cd−N$_{(\text{average})}$ (2.332(9) Å) bond distance in **1** is almost identical to the Cd−N$_{(\text{average})}$ distance of 2.336(2) Å in the sulfur analog. The Cd−Se distance in the [$CdSe_2N_2$] units of **1** is considerably shorter than the Cd−Se distances in the [Cd(SeR)$_4$] units in $[Cd(SePh)_4]^{2-}$ (2.648 Å)[14] and in $[Cd_4(SePh)_{10}]^{2-}$ (2.590 Å)[15] similar trends in bond distance were observed in the Cd−S and Zn−S analogs.[8,16] The Cd−Se−C$_{(\text{average})}$ bond angle for **1** and Cd−S−C$_{(\text{average})}$ bond angle are **2** is 92.8 and 99.5°, respectively.

Cadmium-113 NMR. Due to the unique symmetry properties of **1**, a remarkable advantage may be obtained in the NMR orientation analysis. Upon a 180° rotation of the crystal about any axis perpendicular to the magnetic field, each one of the three orthogonal crystal axes must pass once through a plane perpendicular to the field. At these three angles the pairs of resonances related by the particular symmetry axis which lies in this plane will be degenerate. For selenium, in a general position, there are three such “cross-over” points; however, for

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Table 2. Selected Bond Angles (deg) and Distances (Å) in **1** and Its Sulfur Analog

Cd1−Se(1), Cd2−Se(2)	2.549(4), 2.557(2)	Cd−S	2.417(2), 2.436(2)
Cd1−N(1), Cd2−N(2)	2.338(9), 2.325(9)	Cd−N	2.334(6), 2.337(6)
Cd1−Se(1)−C(11), Cd2−Se(2)−C(11)	92.2(3), 93.5(3)	Cd−S−C	98.2(2), 100.9(2)
Se(1)−Cd1−Se(1′), Se(2)−Cd2−Se(2′)	126.5(1), 124.3(1)	S−Cd−S	125.99(7)
Se(1)−Cd1−N(1), Se(2)−Cd(2)−N(2)	114.3(2), 112.9(2)	S−Cd−N(1)	116.7(2), 104.5(2)
Se(1)−Cd1−N(1′), Se(2)−Cd2−N(2′)	108.4(2), 111.5(2)	S(1)−Cd−N(2)	111.7(2), 114.0(2)
N(1)−Cd1−N(1), N(2)−Cd2−N(2)	71.7(4), 71.4(4)	N(1)−Cd−N(1)	70.4(2)

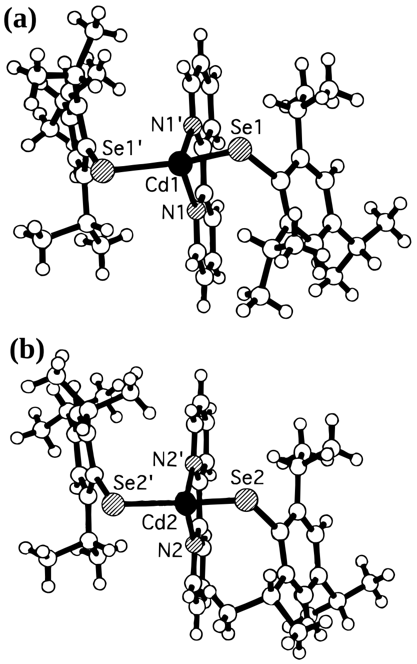

Figure 1. Structure of [Cd(Se-2,4,6-*i*-Pr$_3$-C$_6$H$_2$)$_2$(bpy)] (**1**), showing the two crystallographically distinct molecules in the unit cell.

cadmium, which is in a special position that makes the molecules related by the *a* and *b* axes degenerate, there is only a single cross over, corresponding to the crystallographic *c* axis. This allows assignment of the *c* crossover in the cadmium rotation plots which corresponds to approximately 110° in rotation plot B in Figure 3. An ambiguity nevertheless would still remain in the assignment of the *a* and *b* axes, which had to be resolved by assigning the faces using X-ray diffraction. However, with this exception, the tensor orientation can be obtained entirely from a single rotation plot and without any extrinsic information about the crystal orientation.

For a general orientation of the single crystal, four resonances are expected in the cadmium spectra. These correspond to the two crystallographically unique cadmiums and the magnetically inequivalent (but chemically identical) cadmiums in the unit cell which are related by the *c* glide operation. The cadmiums related by the inversion symmetry operations are magnetically equivalent. Figure 2 shows the ^{113}Cd spectrum for the rotation angle 190.8° in rotation plot A, and rotation plots constructed from the individual spectra are shown in Figure 3. The principal values of the chemical shift tensor derived for the two different cadmiums in the unit cell are given in Table 3. The orientation of the two tensors relative to a molecular frame has also been derived for the chemical shift tensors and the direction cosines relating the two systems are listed in Table 4. There is obviously a four-fold ambiguity in this assignment; however, the excellent agreement between principal axis frame and local molecular frame for one of these four possibilities makes this alternative the only likely one. Figure 4 depicts the Cd1 chemical shift tensor in a local molecular frame. The molecular reference frame is defined as follows: the *x* axis is normal to the plane defined by the Se1−Cd1−Se1′ angle, the *y* axis is the bisector of the N1−Cd1−N1′ and Se1−Cd−Se1′ angles (which by symmetry is identical with the crystallographic *c* axis), and the *z* axis is orthogonal to *x* and *y* (forming a right-handed basis) and lies along the Se1−Se1′ vector. The least shielded element ($\delta_{11} = 752$ ppm) is 2.4° off the *x* axis; the most shielded element ($\delta_{33} = 93$ ppm) is within 0.03° of the *z* axis and the δ_{22} (=570 ppm) is 2.4° off the *y* axis. The orientation of the chemical shift tensor of Cd2 is nearly identical to that of Cd1, with the δ_{11} and δ_{22} elements 2.1° from *x* and *y*, respectively, and the δ_{33} element virtually parallel to *z*.

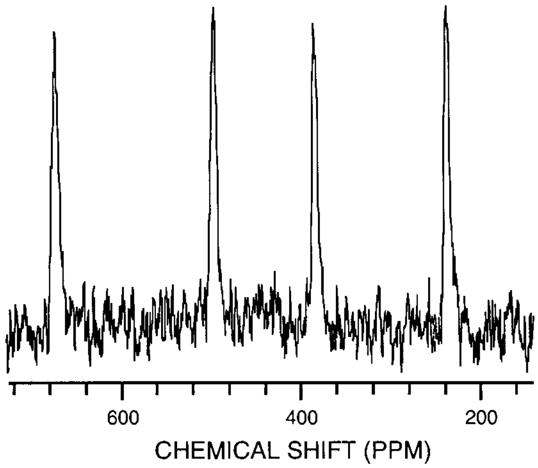

Figure 2. ^{113}Cd NMR spectrum of a single crystal of **1**.

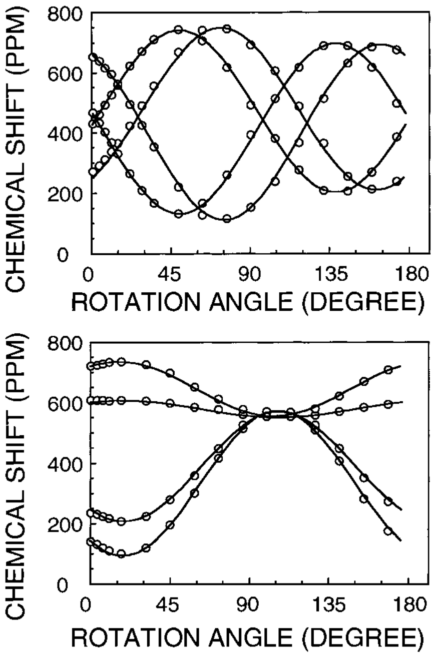

Figure 3. Two orthogonal rotation plots of the four ^{113}Cd NMR resonance frequencies against rotation angle.

The ^{113}Cd CP/MAS spectrum consists of two sets of side-bands consistent with the crystal structure. The isotropic shifts

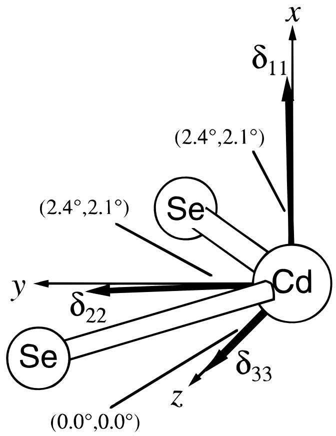

Figure 4. Orientation of the principal axes of the cadmium chemical shift tensor in **1** with respect to a molecular frame. The two values given beside each angle are for Cd1 and Cd2, respectively.

Table 3. Principal Values and Solution Chemical Shifts of the Cd and Se Tensors in **1**[a]

	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	δ_{soln}	$\Delta\sigma$	η
Cd(1)	752	570	93	472		−568	0.48
Cd(2)	733	547	100	460	411.0	−540	0.51
Se(1)	−950	−1040	−1599	−1195		−600	0.22
Se(2)	−933	−1069	−1585	−1196	−1231.2	−584	0.35

[a] The cadmium and selenium chemical shifts are referenced with respect to 0.1 M aq. $Cd(ClO_4)_2$ and solid $(NH_4)_2SeO_4$, respectively. The errors in chemical shifts for Cd and Se in the solid state are ±1 ppm.

Table 4. Cadmium Chemical Shift Tensor Direction Cosines in **1**, Compared with Those of a Selected Molecular Frame Defined in the Text

principal values	shift tensor direction cosines				reference frame direction cosines		
	a	*b*	*c*		*a*	*b*	*c*
cadmium 1							
δ_{11}	0.9796	0.1993	−0.0224	*x*	0.9862	0.1654	0
δ_{22}	−0.0204	−0.0118	−0.9997	*y*	0	0	−1
δ_{33}	0.1995	−0.9798	0.0075	*z*	0.1654	−0.9862	0
cadmium 2							
δ_{11}	0.2474	0.9687	0.0153	*x*	0.2110	0.9775	0
δ_{22}	−0.0006	0.0160	−0.9998	*y*	0	0	−1
δ_{33}	0.9688	−0.2474	−0.0045	*z*	0.9775	−0.2110	0

Table 5. Selenium Chemical Shift Tensor Direction Cosines in **1**, Compared with Those of a Selected Molecular Frame Defined in the Text

principal values	shift tensor direction cosines				reference frame direction cosines		
	a	*b*	*c*		*a*	*b*	*c*
selenium 1							
δ_{11}	0.8159	0.0397	0.5767	*x*	0.8881	−0.0818	0.4523
δ_{22}	0.3216	−0.7977	−0.5101	*y*	0.1477	−0.8810	−0.4494
δ_{33}	−0.4803	−0.6017	0.6381	*z*	−0.4353	−0.4659	0.7703
selenium 2							
δ_{11}	−0.1684	0.7135	−0.6801	*x*	−0.0637	0.8805	−0.4696
δ_{22}	0.7819	−0.3233	−0.5328	*y*	0.8643	−0.1866	−0.4671
δ_{33}	0.6001	0.6215	0.5034	*z*	−0.4989	0.4356	0.7492

for the two distinct cadmiums are similar and agrees well with the single-crystal study results. Despite the high resolution of the spectrum, *J* couplings to either ^{77}Se or ^{14}N are not seen. Solution ^{113}Cd NMR gives a single peak at 411 ppm.

The ^{113}Cd chemical shift value is 20 ppm upfield of the sulfur analogue. Among the chalcogens, sulfur is known to be the most deshielding and the upfield shift for **1** with respect to the sulfur analogue is expected.[1] The ^{113}Cd isotropic value observed in the solid state is downfield, as compared to the solution NMR value, indicative of the presence of solvent effects.

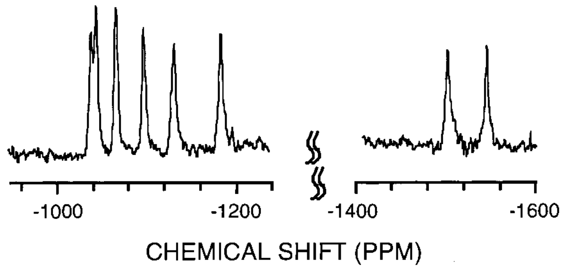

Figure 5. ^{77}Se NMR spectrum of a single crystal of **1**.

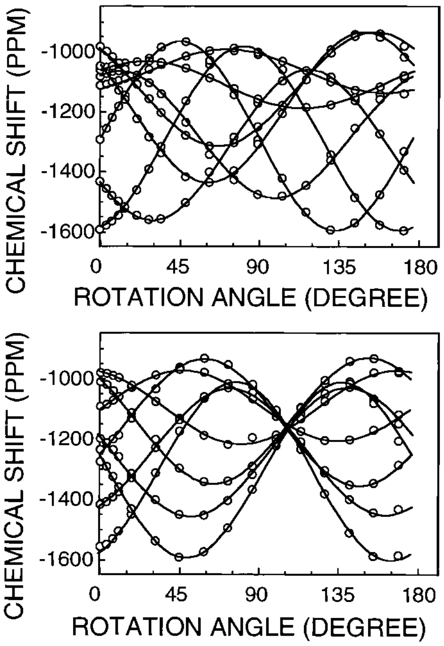

Figure 6. Two orthogonal rotation plots of the ^{77}Se NMR resonance frequencies against rotation angle.

Compared to the sulfur analog, the δ_{11} and δ_{22} tensor elements in **1** are shifted upfield by approximately 60 ppm and may be rationalized by the heavy-atom effect,[17] which is thought to arise from relativistic spin−orbit coupling effects. However, the isotropic chemical shift in **1** is upfield by only 20 ppm due to a compensatory downfield shift in the δ_{33} element.

The features of the tensor orientation of **1** parallel that of the sulfur analog.[8] The orientation of the tensor agrees well with the empirical rules proposed by Ellis.[1,18] The most deshielded axis is almost perpendicular to the plane containing cadmium and the deshielding pair of seleniums.

Selenium-77 NMR. The selenium analog offers an additional advantage in that selenium is a spin $^1/_2$ nucleus and the environment around selenium can be probed using NMR. The NMR results are therefore applicable to the metal−thiolate centers implicated in various biological systems.

There are eight magnetically inequivalent seleniums in the unit cell, and eight selenium resonances are expected for a general orientation of the crystal. Figure 5 shows the ^{77}Se spectrum which corresponds to a rotation angle of 21.8° in rotation plot A. The two orthogonal rotation plots are shown in Figure 6, and the derived chemical shift tensor parameters

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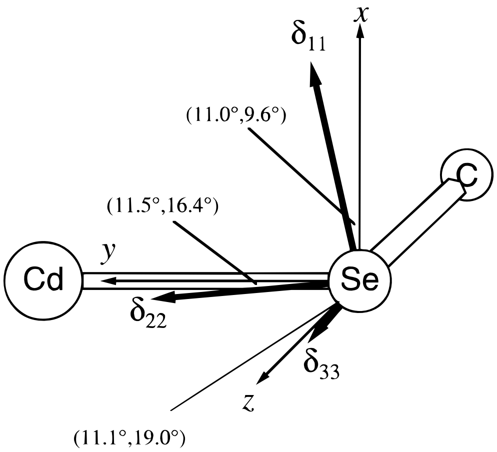

Figure 7. Orientation of the principal axes of the selenium chemical shift tensor in **1** with respect to a molecular frame. The two values given beside each angle are for Se1 and Se2, respectively.

are summarized in Table 3. The molecular frame of reference for ^{77}Se is defined as follows: *y* is along the Se−Cd bond vector (the carbon directly bonded to selenium); *z* is in the Cd−Se−C plane normal to the Cd−Se vector; and *x* is orthogonal to *z* and *y* so as to form a right-handed basis. Agreement between selenium principal axis and local molecular frames is not nearly so good; Figure 7 shows the assignment which gives the best correspondence between the two frames, for Se1. The shielding tensor of Se1′ and Se2′ are related to Se1 and Se2, respectively, by a C_2 rotation about Cd1 and Cd2 in the local molecular frame. The Cd−Se−C angle is 92.1°, and therefore the *z* axis of the local molecular frame is almost collinear with the Se−C axis.

The general features of the chemical shift tensor orientation for Se1 are as follows: the least shielded element ($\delta_{11} = -950$ ppm) is 11.0° off the *x* axis, the most shielded element ($\delta_{33} = -1599$ ppm) is 11.1° off the *z* axis, and the δ_{22} element ($=-1040$ ppm) is 11.5° off the *y* axis. The magnitude of the principal values and the tensor orientations of Se2 are similar to Se1.

The ^{77}Se chemical shift anisotropies of 584 and 604 ppm measured in the present work are comparable to the 531 ppm shielding anisotropy measured by Collins *et al.* in dimethylselenium[13] and considerably smaller than those typically observed for selenium in double-bonded systems. There has been no published single-crystal study of a comparable selenium compound, and so meaningful comparison of our tensor orientation with others is impossible.

The ^{77}Se CP/MAS spectra of a powdered sample of **1** was also obtained at several spinning speeds. The principal values of the shielding tensor obtained from a least-squares fit of the intensity of the sidebands were in excellent agreement to those obtained from the single-crystal experiment. Solution ^{77}Se NMR gives a single peak at −1231.2 ppm with respect to solid $(NH_4)_2SeO_4$.

Conclusion

[Cd(Se-2,4,6-*i*-Pr$_3$-C$_6$H$_2$)$_2$(bpy)] (**1**) has been characterized by X-ray crystallography and studied by solution, solid-state, and single-crystal ^{113}Cd and ^{77}Se NMR to serve as an analogue for biologically occurring [M(S-Cys)$_2$(His)$_2$] centers. The X-ray structure and the ^{113}Cd chemical shift parameters parallel that of the sulfur analogue. Though structure−chemical shift correlations are well documented for cadmium, such studies are yet to be done on selenium.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles for **1** are available (22 pages). Ordering information is given on any current masthead page.

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