*Inorg. Chem.* **2005**, *44*, 5761–5769

Inorganic Chemistry

Article

# Novel Binding of Beryllium to Dicarboxyimidazole-Based Model Compounds and Polymers

**Paul G. Plieger,*,†,§ Deborah S. Ehler,† Brandy L. Duran,† Tammy P. Taylor,† Kevin D. John,*,†
Timothy S. Keizer,† T. Mark McCleskey,† Anthony K. Burrell,† Jeffrey W. Kampf,‡ Thomas Haase,‡
Paul G. Rasmussen,‡ and Jennifer Karr‡**

*Chemistry Division, MS J582, Los Alamos National Laboratory, Los Alamos, NM 87545,
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, and
Department of Chemistry, Massey University, Private Bag 11 222,
Palmerston North, New Zealand*

Received May 2, 2005

The ligand 4,5-dicarboxyimidazole ($H_2DCI$) and its methyl derivative 1-methyl-4,5-dicarboxyimidazole ($H_2MDCI$) have been shown to bind to Be(II) forming a zwitterionic species that has been structurally characterized. A new dicarboxyimidazole-based polymer has been prepared and its Be-binding properties have been studied using NMR ($^1H$ and $^9Be$) and fluorescence spectroscopy; it represents a rare example of beryllium binding to a polymer. Models of the mononuclear and polymeric Be(II)-binding sites have been studied using density functional theory (DFT), and the $^9Be$ NMR chemical shifts of these model materials have been calculated for the purpose of direct comparison to experimentally observed values. Differences in the binding modes of the mononuclear and polymeric species are discussed.

## Introduction

Beryllium is a particularly important metal for a number of applications that are vital to the aerospace, automotive, and electronics industries, in part because of its intrinsic heat and corrosion resistance. Despite its widespread use, beryllium, in comparison to its neighbors in the periodic table, is a poorly understood element. It is toxic both as a carcinogen and as the agent that initiates chronic beryllium disease (CBD), an incurable sometimes-fatal lung disease. Our groups have been engaged in beryllium studies focused on the fundamental understanding of the nature of selective binding sites[1] for Be(II) and the development of applications to detect the presence of Be(II) in the environment.[2] In the course of our studies, we have developed theoretical modeling methods to predict Be(II) speciation in complex solution environments.[3] We continue to pursue the design of selective ligands for beryllium with the challenging goals of developing potential chelation agents for CBD treatment and methods to separate and sequester beryllium from contaminated sites. As public concern related to Be(II) exposure mounts, as in Tallevast, Florida where residents and former employees of the Loral American Beryllium Co. want to know if their exposure to beryllium dust during the processing of the exotic metal put them at risk, the need for viable Be(II) remediation methods becomes quite apparent.

We report herein on the binding of beryllium to a water-soluble polymer and the monomer unit with a beryllium-binding pocket based on dicarboxyimidazole. This investigation was triggered by the observation that, in the crystal structure of 1-methyl-4,5-dicarboxyimidazole, the molecule is a zwitterion with one acidic proton located between the vicinal carboxy groups and the other on the 3-nitrogen of the imidazole (Figure 1).[4] The vicinal groups on a five-membered ring open to a slightly larger bite than those on a six-membered ring and offer a unique site for the chelation of metal ions with an O−O atom distance of 2.43 Å. Divalent beryllium, with its extremely small ionic radius and high

---

* To whom correspondence should be addressed. E-mail: kjohn@lanl.gov (K.D.J.); p.g.plieger@massey.ac.nz (P.G.P).
† Los Alamos National Laboratory.
‡ University of Michigan.
§ Massey University.

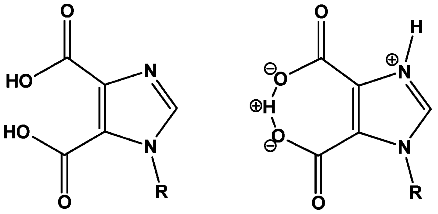
(1) Keizer, T. S.; Sauer, N. N.; McCleskey, T. M. *J. Am. Chem. Soc.* **2004**, *126*, 9484. (b) Keizer, T. S.; Sauer, N. N.; McCleskey, T. M. *J. Inorg. Biochem.* **2005**, *99* (5), 1174. (c) Keizer, T. S.; Scott, B. L.; Sauer, N. N.; McCleskey, T. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2403.

(2) McCleskey, T. M.; Ehler, D. S.; John, K. D.; Burrell, A. K.; Collis, G. E.; Minogue, E. M.; Warner, B. P. US Patent Application 10-812,444, Filed March 2004.

(3) Plieger, P. G.; Keizer, T. S.; John, K. D.; McCleskey, T. M.; Burrell, A. K.; Martin, R. L. *J. Am. Chem. Soc.* **2004**, *126*, 14651.

(4) Harmon, K. M.; Gill, S. H.; Rasmussen, P. G.; Hardgrove, G. L. *J. Mol. Struct.* **1999**, *478*, 145.

10.1021/ic050680c CCC: $30.25



**1a**, R = Me
**1b**, R = H

**Figure 1.** 4,5-Dicarboxyimidazole ligand (left) and its zwitterionic form (right).

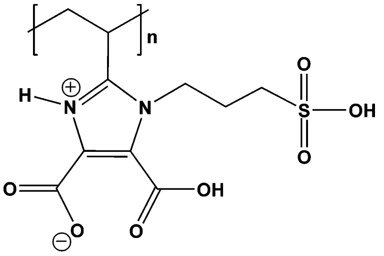


**Figure 2.** Sulfonated polymer used as tested for a beryllium-sequestering agent in this report.

charge-to-size ratio, was a candidate for chelation in this site, as the selective binding of beryllium is generally difficult because of its small size and high affinity for water. The 2.43 Å distance between the oxygen atoms is nearly ideal for supporting the Be(II) atom in a tetrahedral geometry with the typical 1.6 Å Be−O bonds and an approximate 2.55 Å O−O distance. This site is similar to maleic acid, which has been shown to bind Be,[5] but the imidazole ring offers a significant advantage in that it can be readily functionalized and incorporated directly into a polymer backbone. As described below, a model compound that chelated Be(II) and corroborated these concepts was readily prepared; therefore, we began to devise a polymeric analogue to the model compound (Figure 2).

Polymer binding of metals is well established in water treatment and many other processes that require the purification and sequestering of metal ions and has been the subject of many symposia and reviews.[6] In general, polymers offer the advantage of multiple binding sites and are readily filterable. However, polymers present the potential disadvantage of being difficult to disperse or solubilize in the medium under investigation. One of the key aspects of polymer assisted environmental remediation is the ability to process large volumes of material while producing only a small volume of waste. Beryllium is recognized as a significant industrial contaminant, and as such, issues with remediation are becoming more urgent. Unfortunately, reports of the binding of Be(II) to polymers are rare.[7] We describe below our efforts to design and test a new water-soluble polymer particularly suitable for beryllium binding with the long-term goal of producing a system capable of field use for environmental remediation at beryllium-contaminated sites.

## Experimental Section

1-Methyl-4,5-dicarboxyimidazole ($H_2$MDCI) **1a** was prepared as previously reported,[4] and 4,5-dicarboxyimidazole ($H_2$DCI) **1b** was obtained from Aldrich and used as received. Beryllium carbonate was purchased from Mallinckrodt and Baker and used without further purification (Note: this material is no longer commercially available). *Caution! Beryllium salts are extremely toxic and should be handled with appropriate care.* All manipulations of the beryllium solid were handled in a Plas-Labs 818 Series HEPA-filtered (0.4 micron prefilter) reversed-pressure glovebox. All work with the beryllium solution was performed in a dedicated chemical fume hood.

**Synthesis of $[(H_2O)_2Be(HMDCI)][HMDCI]\cdot H_2O$ (2a).** $BeCO_3$ (0.070 g, 1 mmol) was added to $H_2$MDCI (0.340 g, 2 mmol) suspended in water (30 mL). Upon addition, both solids dissolved, and a small quantity of gas was seen to evolve. The solution reaction mixture was left to sit for approximately 1 week during which crystals of **2a** were formed. The crystals were filtered, washed with warm water, and dried to yield **2a** as a white powder. Anal. Calcd for **2a**: C, 32.96; H, 4.61; N, 12.81. Found: C, 32.80; H, 4.03; N, 12.61.

For the stoichiometric determination of **2a** in solution with a 2:1 ligand-to-metal ratio, 85 mg (0.50 mmol) of $H_2$MDCI (**1a**) was dissolved in 3.75 mL of $H_2O$ and 1.25 mL of $D_2O$, and 0.25 mL of 1 M $BeSO_4$ (0.25 mmol) was added. The pH was adjusted with KOH to pH 8 (**2a** was soluble below pH 9). $^9$Be NMR (3:1 $H_2O$/$D_2O$, pH 8.0): $\delta$ 2.17 ($\omega_{1/2} = 10$ Hz). $^1$H NMR (3:1 $H_2O$/$D_2O$, pH 8.0): $\delta$ 7.42 (1H, s, CH), 7.62 (1H, s, CH), 3.62 (3H, s, Me), 3.76 (3H, s, Me). For the stoichiometric determination of **2a** in solution with a 1:1 ligand-to-metal ratio, 85 mg (0.50 mmol) of $H_2$MDCI (**1a**) was dissolved in 3.75 mL of $H_2O$ and 1.25 mL of $D_2O$, and 0.50 mL of 1 M $BeSO_4$ (0.50 mmol) was added. The pH was adjusted with KOH to pH 8 ($Be(OH)_2$ precipitate was present above pH 5.8). The solution was filtered and the resulting $^9$Be and $^1$H NMR data recorded from the solution were identical to those of **2a** in a 2:1 ligand-to-metal ratio.

For the stoichiometric determination of **2b** in solution with a 2:1 ligand-to-metal ratio, 78 mg (0.50 mmol) of $H_2$DCI was dissolved in 3.75 mL of $H_2O$ and 1.25 mL of $D_2O$, and 0.25 mL of 1 M $BeSO_4$ (0.25 mmol) was added. The pH was adjusted with KOH to pH 8 (**2b** was soluble below pH 10). $^9$Be NMR (3:1 $H_2O$/$D_2O$, pH 8.0): $\delta$ 2.05 ($\omega_{1/2} = 11$ Hz). $^1$H NMR (3:1 $H_2O$/$D_2O$, pH 8.0): $\delta$ 7.58 (1H, s, CH), 7.67 (1H, s, CH). For the stoichiometric determination of **2b** in solution with a 1:1 ligand-to-metal ratio, 78 mg (0.50 mmol) of $H_2$DCI was dissolved in 3.75 mL of $H_2O$ and 1.25 mL of $D_2O$, and 0.50 mL of 1 M $BeSO_4$ (0.50 mmol) was added. The pH was adjusted with KOH to pH 8 ($Be(OH)_2$ precipitate was present above pH 5.8). The solution was filtered

---

(5) Alderighi, L.; Gans, P.; Midollini, S.; Vacca, A. In *Advances in Inorganic Chemistry: Main Group Chemistry*; Sykes, A. G., Cowley, A. H., Eds.; Academic Press: New York, 2000; Vol. 50, pp 109−172.

(6) Rivas, B. L.; Pooley, S. A.; Luna, M.; Geckeler, K. E. *J. App. Pol. Sci.* **2001**, *82*, 22. (b) Gohdes, J. W.; Duran, B. L.; Clark, N. C.; Robison, T. W.; Smith, B. F.; Sauer, N. N. *Sep. Sci. Technol.* **2001**, *36*, 2647. (c) Smith, B. F.; Robison, T. W.; Jarvinen, G. D. Water-Soluble Metal-Binding Polymers with Ultrafiltration: A Technology for the Removal, Concentration, and Recovery of Metal Ions from Aqueous Streams. In *Metal Ion Separations and Preconcentration: Progress and Opportunities*; Bond, A. H., Dietz, M. L., Rogers, R. D., Eds.; ACS Symposium Series 716; American Chemical Society: Washington, DC, 1999; p 294.

(7) Taylor, T. P.; Le, Q. T. H.; Ehler, D. S.; Sauer, N. N. *Sep. Sci. Technol.* **2003**, *38*, 1141. (b) Wei, X.-Q.; Lu, Z.-Y.; Zou, P.; Xie, M.-G. *Synth. Met.* **2003**, *137*, 1149. (c) Ganjali, M. R.; Rahimi-Nasrabadi, M.; Maddah, B.; Moghimi, A.; Faal-Rastegar, M.; Borhany, S.; Namazian, M. *Talanta* **2004**, *63*, 899.

and the resulting $^9$Be and $^1$H NMR data recorded from the solution were identical to those of **2b** in a 2:1 ligand-to-metal ratio.

**Synthesis of Poly[1-(4,5-dicarboxyimidazolyl))ethane] Grafted at 25% 3-Propane Sulfonic Acid (4).** The starting material polyvinazene was prepared by standard radical methodology using AIBN, and the method is described elsewhere.[8] Small amounts (typically 1% or less) of the divinylbenzene cross-linking reagent were added to the polymerization medium.

**Sulfonation of Polyvinazene.** LiH (0.029 g, 3.65 mmol) was added to a nitrogen-purged solution of polyvinazene (1.50 g, 10.4 mmol, based on the monomer) in acetonitrile (50 mL), and the solution was refluxed for 1 h. 1,3-Propanesultone (0.32 g, 2.6 mmol) was added, and the reaction mixture was stirred for 48 h. The polymer was filtered, washed with acetonitrile, and then dried under vacuum. The sulfonated polymer (**3**) was isolated as the $Li^+$ salt but could be conveniently protonated by the repeated addition of 20% sulfuric acid until the product was determined to be free of $Li^+$ using the flame test. $^1$H NMR ($D_2O$): $\delta$ 3.58 (2H, t, $CH_2$-$CH_2C\mathit{H_2}SO_3H$), 2.85 (2H, t, $C\mathit{H_2}CH_2CH_2SO_3H$), 2.10 (2H, q, $CH_2C\mathit{H_2}CH_2SO_3H$). The proton signals associated with the polymer backbone were too broad to be observed. IR (cm$^{-1}$): $\nu$ 2238, 1211, 1044. Microanalysis for sulfur showed that 24% sulfonation of the repeat groups was achieved.

**Hydrolysis to Prepare 4.** Concentrated HCl (5 mL) was added to a nitrogen-purged solution of **3** (1.0 g, 3.7 mmol, based on the monomer) in water (20 mL) resulting in the formation of a white precipitate. The mixture was heated to reflux during which time the precipitate dissolved. The mixture was refluxed for several weeks, with periodic sampling to test for nitrile absorption in the IR. When the reaction was observed to be complete, the remaining solvent was removed in vacuo, and the product, **4**, was dried. IR (cm$^{-1}$): $\nu$ 2243w, 1732, 1207, 1041.

**Beryllium Binding to 4.** In a 20 mL vial, 16 mg of **4** (0.076 mmol) was dissolved in 1.5 mL of $H_2O$ and 0.50 mL of $D_2O$, and 75.2 $\mu$L of 1 M $BeSO_4$ (0.075 mmol) was added. The pH was adjusted with NaOH to pH 5.0 and 7.0, for two aliquots. Both solutions were soluble with no precipitation present. $^9$Be NMR: (pH 5.0) $\delta$ 0.65 ($\omega_{1/2} = 40$ Hz); (pH 7.0) $\delta$ 0.70 ($\omega_{1/2} = 105$ Hz).

**Physical Measurements.** $^9$Be NMR spectra were recorded on a Bruker Avance 400 at 56.22 MHz and referenced to an external standard of $Be(H_2O)_4{}^{2+}$ (as the sulfate salt). All of the NMR samples containing beryllium were contained within Teflon sleeves in addition to the standard glass NMR tube. Chemical shifts are reported relative to $SiMe_4$ for the $^1$H NMR and $Be(H_2O)_4{}^{2+}$ for the $^9$Be NMR and are reported in parts per million. Fluorescence measurements were recorded at pH 7 for 100 $\mu$M of $H_2MDCI$ (**1a**), $H_2DCI$ (**1b**), and **4** in the presence of 50, 100, 200, and 400 $\mu$M concentrations of beryllium sulfate, using a Photon Technology International fluorimeter (Lawrenceville, NJ) with an 814 photomultiplier detection system, a 75 W xenon lamp, and Felix32 software. Elemental analyses were determined with a Perkin-Elmer CHN 2400 instrument. FT-IR spectra were obtained with a Perkin-Elmer Spectrum BX FT-IR system.

**Crystallography of $[(H_2O)_2Be(HMDCI)][HMDCI]\cdot H_2O$ (2a).** Colorless prisms of **2a** were crystallized from water at room temperature. A crystal with dimensions of 0.44 × 0.42 × 0.28 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 158(2) K; the detector was placed at a distance of 4.916 cm from the crystal. A total of 2382 frames were collected with a scan width of 0.3° in $\omega$ and $\varphi$ with an exposure time of 20 s/frame. The frames were integrated using the Bruker SAINT[9] software package with a narrow frame algorithm. The integration of the data yielded a total of 15826 reflections to a maximum $2\theta$ value of 52.8° of which 3466 were independent and 2839 were greater that $2\sigma(I)$. The final cell constants were based on the *xyz* centroids of 7525 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS[10] but not corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10)[11] software package using space group $P2_1/n$ with $Z = 4$ for the formula $C_{12}H_{16}N_8BeO_{11}$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms located on a difference Fourier map and allowed to refine isotropically. The full-matrix least-squares refinement based on $F^2$ converged at R1 = 0.02889 and wR2 = 0.0358 for $I > 2\sigma(I)$ and R1 = 0.0762 and wR2 = 0.0796 for all data. Additional details are presented in Tables 1 and 2 and are given in the Supporting Information as a CIF file.

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for **2a**

| | |
|---|---|
| Be(1)−O(1) | 1.5993(18) |
| Be(1)−O(3) | 1.5993(18) |
| Be(1)−O(5) | 1.6163(18) |
| Be(1)−O(6) | 1.6433(19) |
| O(1)−Be(1)−O(3) | 115.42(11) |
| O(1)−Be(1)−O(5) | 106.61(10) |
| O(3)−Be(1)−O(5) | 108.60(11) |
| O(1)−Be(1)−O(6) | 108.58(11) |
| O(3)−Be(1)−O(6) | 109.61(10) |
| O(5)−Be(1)−O(6) | 107.73(10) |

**Table 2.** Hydrogen Bonding Bond Lengths (Å) and Angles (deg) for **2a**[a]

| | (D−H) | (H⋯A) | (D⋯A) (Å) | (deg) |
|---|---|---|---|---|
| N(1)−H(1A)⋯N(3) | 0.964(19) | 1.847(19) | 2.8064(16) | 172.8(16) |
| O(11)−H(11B)⋯O(10) | 0.87(2) | 1.84(2) | 2.7064(15) | 172(2) |
| O(6)−H(6E)⋯O(4) | 0.86(2 | 1.83(2) | 2.6659(14) | 163.3(19) |
| O(11)−H(11A)⋯O(2) | 0.95(2) | 1.78(2) | 2.7271(15) | 174.1(19) |
| O(5)−H(5C)⋯O(8) | 0.91(2 | 1.83(2) | 2.7282(14) | 171.5(17) |
| O(7)−H(7)⋯O(9) | 1.09(2) | 1.34(2) | 2.4324(14) | 179.0(19) |
| O(5)−H(5B)⋯O(11) | 0.89(2) | 1.68(2) | 2.5687(15) | 175.0(19) |
| O(6)−H(6D)⋯O(9) | 0.86(2) | 1.83(2) | 2.6608(14) | 161.0(19) |

[a] Symmetry operations: (A) $-0.5 - x$, $0.5 + y$, $0.5 - z$; (B) $-1 - x$, $1 - y$, $1 - z$; (C) $-x$, $-y$, $1 - z$; (D) $-0.5 - x$, $-0.5 + y$, $0.5 - z$.

## Computational

Computational calculations were performed using the program GAUSSIAN03 for Windows,[12] running on a Dell OPTIPLEX GX270 personal computer equipped with an Intel Pentium 4 3.2GHz processor and 2.0 GB of RAM. We found that Becke's three-parameter hybrid exchange correlation functional[13] containing the nonlocal gradient correction of Lee, Yang, and Parr (B3LYP),[14] in conjunction with the 6-31(d) basis set, gave a satisfactory geometry for the most part. All optimized structures were confirmed as minima by calculation of the vibration frequencies. NMR shieldings for beryllium were evaluated at the minima using B3LYP with 6-311+G(2d,p) as the basis set and the GIAO (gauge-including

---

(8) Johnson, D. M, Ph.D. Thesis, University of Michigan, Ann Arbor, MI, **2000**.

(9) *Saint Plus*, version 6.02; Bruker Analytical X-ray Inc.: Madison, WI, 1999.

(10) Sheldrick, G. M. *SADABS*. Bruker Analystical X-ray Inc.: Madison, WI, 1997.

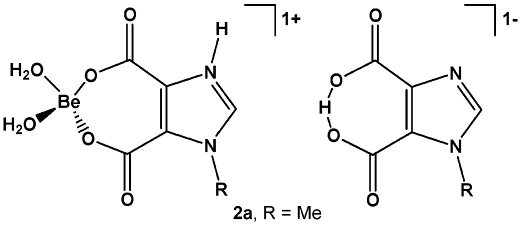
(11) Sheldrick, G. M. *SHELXTL*, version 5.10; Bruker Analytical X-ray Inc.: Madison, WI, 1997.

atomic orbital) NMR method[15] as implemented by Cheeseman et al.[16] in the Gaussian03 package. The $Be(H_2O)_4^{2+}$ complex is the standard reference for $^9$Be NMR spectroscopy and is defined as 0.00 ppm. Structure determination for this complex (B3LYP/6-31-(d)) followed by calculation of the magnetic shielding (B3LYP/6-311G+(2d,p) gave a value of 108.96 ppm. The calculated chemical shift in this study is reported relative to $Be(H_2O)_4^{2+}$, using the expression $\delta_{\text{complex}} = \sigma_{\text{reference}} - \sigma_{\text{complex}}$.

## Results and Discussion

The binding of a metal by a polymer brings up the difficult issue of determining the nature of the metal binding site. Many of the approaches to studying the binding of metals to polymers involve the application of NMR and optical spectroscopic techniques.[17] A common theme in these studies is the direct analysis of mononuclear model systems to provide more complete details on the nature of the metal binding site as the complex/heterogeneous nature of the polymer complicates binding-site determination. We have therefore studied the mononuclear species, $[(H_2O)_2Be(HL)][HL]\cdot H_2O$ [HL = HMDCI$^-$ (**2a**) or HDCI$^-$ (**2b**)], as they represent the two distinct Be(II)-binding sites presented by the polymer (**4**).

**Synthesis and Characterization of the Mononuclear Species.** The preparation of **2a** and **b** was achieved by the mixing of 1 equiv of beryllium carbonate (or sulfate) with 2 equiv of $H_2$MDCI (**1a**) or $H_2$DCI (**1b**) to produce $[(H_2O)_2Be(HL)]^+$ [HL = HMDCI$^-$ (**2a**) or HDCI$^-$ (**2b**)]. The 1:2 ratio is needed to generate the cationic Be(II) complex and the anionic counterpart (Figure 3).



**2a**, R = Me
**2b**, R = H

**Figure 3.** $[(H_2O)_2Be(HL)][HL]\cdot H_2O$; HL = HMDCI$^-$ (**2a**) or HDCI$^-$ (**2b**).

**X-ray Crystal Structure of 2a.** Single crystals suitable for X-ray diffraction measurements were obtained by the slow evaporation of an aqueous solution of beryllium carbonate with $H_2$MDCI (1:2 ratio) at room temperature. The molecular structure of **2a** is shown in Figures 4 and 5. Selected bond lengths and angles are listed in Tables 1 and 2. The asymmetric unit consists of a cationic beryllium complex $[(H_2O)_2Be(HMDCI)]^+$ and an anionic equivalent of HMDCI$^-$ in addition to one water molecule of crystallization held in the crystal lattice by hydrogen bonding (Figure 5). The cationic Be(II) complex contains one beryllium atom coordinated to two acid oxygen atoms from the ligand with two coordinated water molecules making up the tetrahedral geometry of the metal atom. There is a proton on the imino-N1 on the imidazole resulting in a +1 charge overall on this beryllium-complexed ligand (Figure 4a). The second HMDCI$^-$ molecule acts as a counterion with one proton held between the oxygen atoms of the acid functionalities. The imino-N3 atom is deprotonated resulting in an overall negative charge on this molecule (Figure 4b). Extensive hydrogen bonding is present between the coordinated water molecules, all four carbonyl oxygens, and the free nitrogens on both of the HMDCI$^-$ molecules; the water molecule of solvation and one of the carboxylate oxygen atoms are on the uncomplexed HMDCI$^-$ equivalent (Figure 5). The hydrogen bonds vary in strength as indicated by the varying donor−acceptor bond lengths (2.432−2.806 Å), with the shortest bond existing between the carboxylic oxygens of the anionic form of the ligand [O(7)−H(7)···O(9)] as expected from the close proximity of these electronegative atoms. This proton is shared almost equally between these electronegative atoms [D−H = 1.09(2) Å and H···A = 1.34-(2) Å]. The longest hydrogen bond is between the protonated nitrogen on the cationic Be(II) complex and the free nitrogen of the uncomplexed HMDCI$^-$ molecule, a consequence of the weaker basicity of these nitrogen atoms.

The most striking feature about this crystal structure is the binding motif employed by beryllium. A search of Cambridge Stucture Database[18] revealed eight metal coordination structures of this basic ligand. Seven of these employed the ligand bound in a N/O chelating fashion (Figure 6a),[19] with the eighth example bound by one carboxylic oxygen atom (Figure 6b).[20] None of the reported structures bound any metal atom in a chelating fashion utilizing both carboxylic oxygens, like the one in the current

---

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(16) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(17) DeRosa, M. C.; Mosher, P. J.; Yap, G. P. A.; Focsaneanu, K.-S.; Crutchley, R. J.; Evans, C. E. B. *Inorg. Chem.* **2003**, *42*, 4864. (b) Chen, C.-Y.; Chen, C.-Y. *J. App. Polym. Sci.* **2002**, *86*, 1986.

(18) *CSD*, version 5.25, July 2004 update; Cambridge Crystallographic Data Centre: Cambridge, U.K., 2004; www.ccdc.cam.ac.uk.

(19) Bayon, J. C.; Net, G.; Rasmussen, P. G.; Kolowich, J. B. *J. Chem. Soc., Dalton Trans.* **1987**, 3003 (b) Rajendiran, T. M.; Kirk, M. L.; Setyawati, I. A.; Caudle, M. T.; Kampf, J. W.; Pecoraro, V. L. *Chem. Commun.* **2003**, 824. (c) Sengupta, P.; Dinda, R.; Ghosh, S.; Sheldrick, W. S. *Polyhedron* **2001**, *20*, 3349. (d) Caudle, M. T.; Kampf, J. W.; Kirk, M. L.; Rasmussen, P. G.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1997**, *119*, 9297. (e) Smith, T. S., II; Root, C. A.; Kampf, J. W.; Rasmussen, P. G.; Pecoraro, V. L. *J. Am. Chem. Soc.* **2000**, *122*, 767. (f) Net, G.; Bayon, J. C.; Butler, W. M.; Rasmussen, P. G. *Chem. Commun.* **1989**, 1022.

(20) Huang, D.; Zhang, X.; Zhu, H.; Chen, C.; Liu, Q. *Acta Crystallogr., Sect. E* **2001**, 57, m441

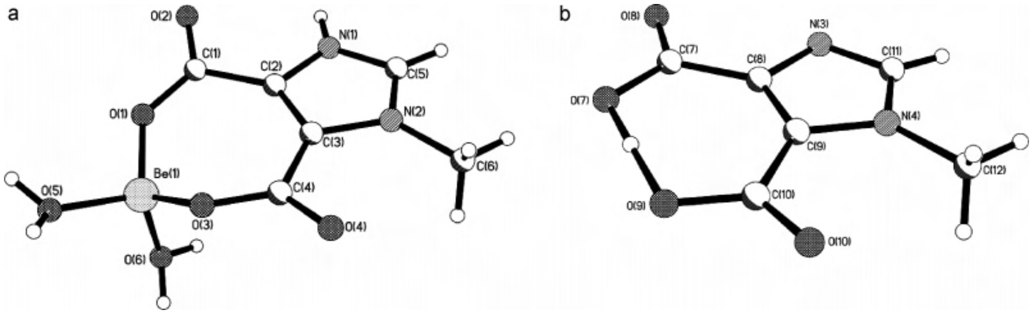


**Figure 4.** Perspective view of the molecular structure of the cation (left) and anion (right) of **2a** (solvent molecules have been removed for clarity).

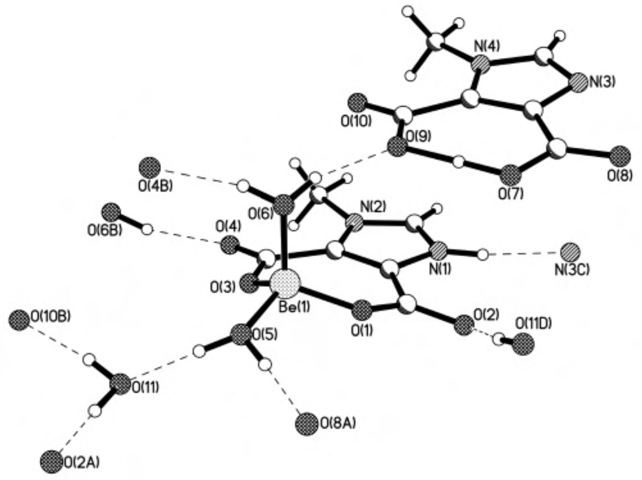


**Figure 5.** Molecular structure of **2a** showing the hydrogen bonding network. Symmetry operations: (A) $-0.5 - x, 0.5 + y, 0.5 - z$; (B) $-1 - x, 1 - y, 1 - z$; (C) $-x, -y, 1 - z$; (D) $-0.5 - x, -0.5 + y, 0.5 - z$.

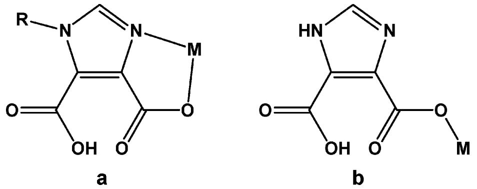


**Figure 6.** The previously reported crystallographic binding modes for ligands derived from $H_2$MDCI/ $H_2$DCI.

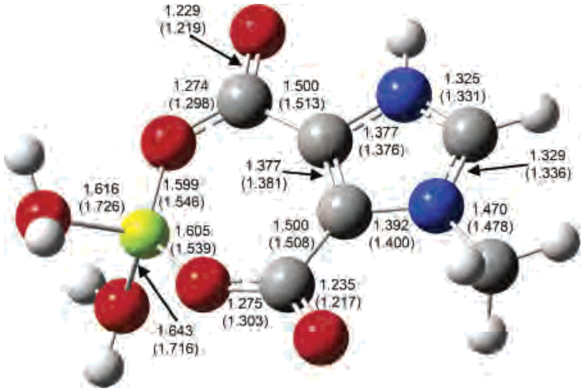


**Figure 7.** Comparison of bond lengths of the optimized structure of the cation of **2a** with those determined from the X-ray analysis (calculated values in brackets).

example. In this regard beryllium is acting more like a proton than a larger metal cation.

**NMR Spectroscopic Measurements on Mononuclear 1a and b.** The $^9$Be and $^1$H NMR spectra were recorded for varying ratios of $H_2$MDCI and $H_2$DCI (Be(II) at pH 8). From the table it can be seen that adding the ligand to Be(II) in a 2:1 ratio results in a fully soluble species with 2 proton signals at the C(2) position. The 1:1 ratio of ligand-to-beryllium resulted in the formation of a precipitate ($Be(OH)_2$) and was filtered off. The NMR analysis of the remaining dissolved solution revealed virtually identical results to that of the totally soluble 2:1 ligand-to-beryllium species. The free ligand, $H_2$MDCI, in $CHCl_3$ has a signal for C(2) at 7.79 ppm.[21] In the solvent conditions employed in the current study (3:1 $H_2O/D_2O$), this value is shifted slightly downfield to 7.57 ppm. The proton NMR results for **2a** and **b** provide evidence that the structural features seen in the X-ray analysis are also present in solution. The $^9$Be NMR chemical shift values of 2.17 and 2.05 ppm for **2a** and **b**, respectively, are typical of a $BeL(H_2O)_2$ complex for which L is a bidentate bis-carboxylate with a chelate ring size greater than 5 atoms.[3]

**$^9$Be NMR Chemical Shift Prediction for 2a and 2b Using DFT Methods.** We have recently shown that theoretical methods can be useful in predicting solution structure and aid in the interpretation of the solution NMR.[3] To help with the interpretation of the current solution NMR results, the cationic Be(II) complex of **2a** was optimized and the $^9$Be NMR chemical shift was calculated. The optimized geometry of the cation at the B3LYP/6-31(d) level of theory is a good match with that determined by the X-ray structural analysis (Figure 7). Average bond length discrepancies are 0.075 Å for the coordination sphere of beryllium and 0.011 Å for the remaining bond lengths of the ligand. The largest errors result from the Be$-H_2O$ bond lengths. This has been observed previously.[3,22]

A $^9$Be NMR chemical shift value of 2.00 ppm for **2a** was calculated for the optimized structure at the B3LYP/6-311g+(2d,p) level of theory and compares favorably with that of the experimentally observed value of 2.17 ppm for **2a**. The close agreement between the experimental and theoretical beryllium chemical shifts is further evidence that the cationic species observed in the X-ray structure is retained in solution.

**Fluorescence Measurements on 1a and b.** Fluorescence measurements were recorded at pH 7 for 100 $\mu$M of $H_2$-MDCI (**1a**) and $H_2$DCI (**1b**) in the presence of 50, 100, 200,

---

(21) O'Connell, J. F.; Parquette, J.; Yelle, W. E.; Wang, W.; Rapoport, H. *Synthesis* **1988**, 767.

(22) Dr. Richard L. Martin, Private communication (June 2004).

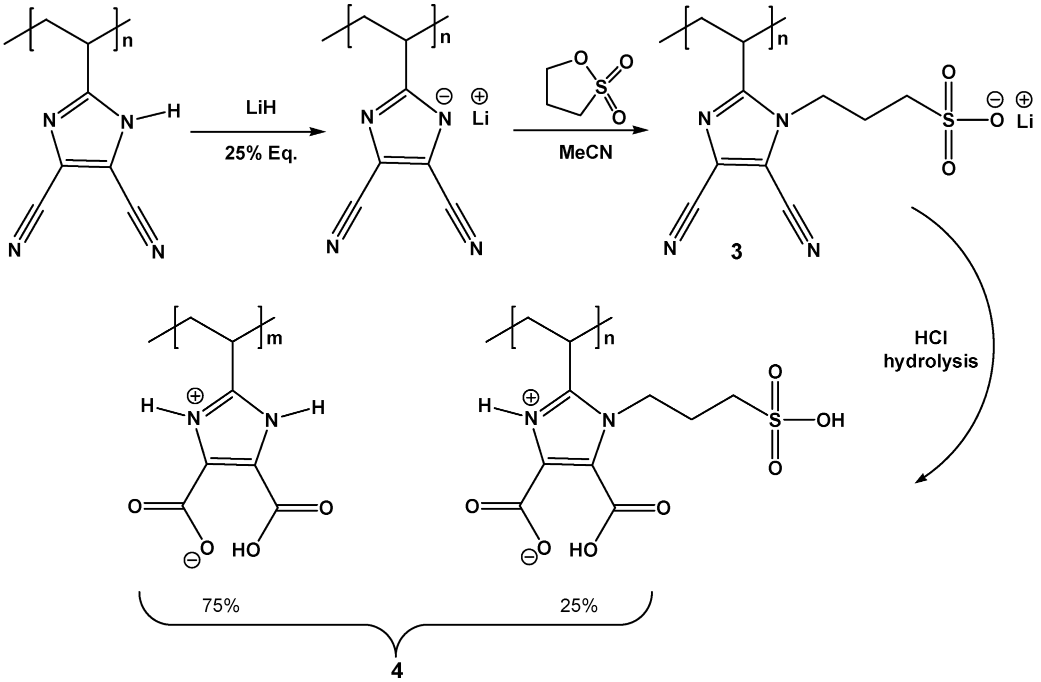


**Figure 8.** Synthetic scheme for poly[1-(4,5-dicarboxyimidazolyl))ethane] grafted at 25% 3-propane sulfonic acid.

and 400 $\mu$M concentrations of beryllium sulfate. At pH 7, beryllium sulfate solutions are highly insoluble ($K_{sp} = 10^{-20}$)[5] with $Be(OH)_x$ species readily precipitating. For the above fluorescence measurements, at no time was a precipitate observed indicating that the beryllium was bound to and hence solubilized by the ligand. Ligand **1a** had an inherent fluorescence at 400 nm which is extremely weak and did not alter significantly in the presence of increasing concentrations of beryllium. Ligand **1b** did not display any fluorescence response, which could be attributed to the fact that the additional N-bound proton creates a proton-quenching pathway. Protons in the C(2) position of imidazole derivatives are well known to display weak fluorescence,[23] whereas substituents at the 2-position appear to remove a proton-quenching mechanism.[24]

**Synthesis and Characterization of Polymer-Bound Species.** As our model ligand was prepared by the hydrolysis of the corresponding dicyano imidazole, it was natural to take the same approach to preparing the analogous polymer. We have previously reported the first polymers of 2-vinyl-4,5-dicyanoimidazole, or vinazene,[25] and potential applications of these polyvinazene materials are described in the patents.[26] The hydrolysis of the polyvinazene follows the same path as that of the model compound, except that prolonged boiling in acid or base is necessary to fully convert the polymer nitrile groups to carboxylates, and in most cases, a small residual peak attributed to nitrile can be observed in the infrared spectra. The conversion of the functional groups on polymers is well-known to offer resistance to going to completion,[27] but this should not have a marked influence on the overall binding characteristics of the polymer. A significant advantage of this polymer is the unusually high density of functionality per repeat group, and it has extensive possibilities for intra- and interchain hydrogen bonding. The analogous molecular species, 4,5-dicarboxyimidazole, is extremely insoluble in water, although it is readily dissolved in base. This was of concern to us with respect to the polymer because it was desirable to bind beryllium in a near-neutral solution and the polymer did not dissolve until a pH of ~10. To enhance the polymer water solubility, we introduced a further modification. The parent polymer, polyvinazene, can be alkylated with electrophiles, such as propane sultones, to produce the propane sulfonic acid. This graft reaction can be carried out to varying degrees, and we have found that if one-quarter of the repeat units are grafted, the polymer solubility in water is greatly enhanced. Figure 8 illustrates the synthesis for the propane sulfonic acid example. The successful partial sulfonation of the polymer prompted us to study both model ligands, **1a** and **b**.

**NMR Measurements on the Sulfonated Polymer.** $^9$Be NMR data was recorded for the 25% sulfonated dicarboxyimidazole polymer at pH 7 in the presence of 10 mM Be-

---

(23) Brookman, J.; Chacon, J. N.; Sinclair R. S. *Photochem. Photobiol. Sci.* **2002**, *1*, 327.

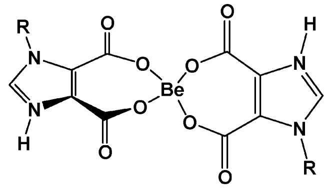
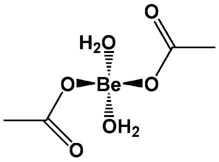
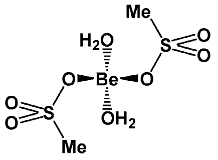
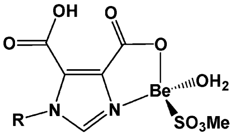
(24) Causey, C. P.; Allen, W. E. *J. Org. Chem.* **2002**, *67*, 5963. (b) Henary, M. M.; Fahrni, C. J. *J. Phys. Chem. A* **2002**, *106*, 5210. (c) Matsumiya, H.; Hoshino, H.; Yotsuyanagi, T. *Analyst* **2001**, *126*, 2082. (d) Li, Y.; Liu, Y.; Bu, W.; Lu, D.; Wu, Y.; Wang, Y. *Chem. Mater.* **2000**, *12*, 2672.

(25) Johnson, D. M.; Rasmussen, P. G. *Macromolecules* **2000**, *33*, 8597.

(26) (a) Rasmussen, P. G.; Reybuck, S. E.; Jang, T.; Lawton, R. G. US Patent 5,712,408, 1998. (b) Rasmussen, P. G.; Reybuck, S. E.; Johnson, D. M.; Lawton, R. G. US Patent 6,096,899, 2000. (c) Rasmussen, P. G.; Reybuck, S. E.; Johnson, D. M.; Lawton, R. G. US Patent 6,274,724, 2001. (d) Rasmussen, P. G.; Reybuck, S. E.; Johnson, D. M.; Lawton, R. G. US Patent 6,384,068, 2002. (e) Rasmussen, P. G.; Reybuck, S. E.; Johnson, D. M.; Lawton, R. G. US Patent 6,482,954, 2002.

(27) Hussain, M. A.; Liebert, T.; Heinze, T. *Macromol. Rapid Commun.* **2004**, *25*, 916. (b) Scaffaro, R.; Carianni, G.; La Mantia, F. P.; Zerroukhi, A.; Mignard, N.; Granger, R.; Arsac, A.; Guillet, J. *J. Polym. Sci., Part A* **2000**, *38*, 1795. (c) Stephens, E. B.; Tour, J. M. *Macromolecules* **1993**, *26*, 2420.

**Table 3.** Model Mononuclear Complexes and Their Calculated $^{9}$Be Chemical Shift Values (B3LYP/6-311g+(2d,p)

| model complex | $^{9}$Be NMR chemical shift |
|---|---|
|  | 2.30 |
|  | 2.37 |
|  | 2.04 |
|  | 4.24 |

(II). The simple observation that all of the beryllium was soluble at this pH and at this concentration is strong evidence that the beryllium is bound to the polymer. A single peak was observed at 0.70 ppm ($\omega_{1/2} = 105$ Hz). The chemical shift and the line width of the polymer bound Be(II) does display a slight pH dependence going from 0.70 ppm at pH 7 to 0.65 ppm ($\omega_{1/2} = 40$ Hz) at pH 5.

The $^{9}$Be NMR chemical shift of the sulfonated polymer has shifted from that of the nonsulfonated mononuclear compound by almost −1.5 ppm, indicating that the binding environment is different from that of the small molecule species. A number of potential binding environments were modeled in an attempt to identify the polymer-binding site, and their resultant $^{9}$Be NMR chemical shifts were calculated.

**$^{9}$Be NMR Chemical Shift Prediction of Polymer-Bound Be(II) Using DFT Methods.** The $^{9}$Be chemical shift value is considerably different from that of the monomer in both sharpness ($\omega_{1/2}$ of polymer = 40−100 Hz vs mononuclear = 9−11 Hz) and position (polymer = 0.65−0.70 ppm vs mononuclear = 2.05−2.17 ppm). To help in the interpretation of this result, we investigated various model complexes and calculated their $^{9}$Be NMR chemical shifts. The results are presented in Table 3.

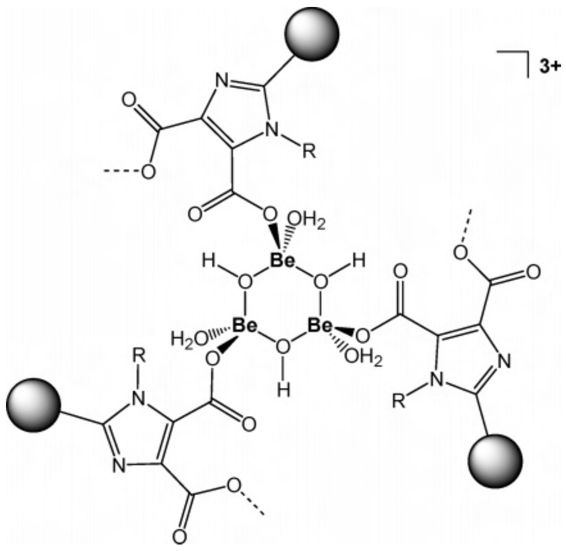


**Figure 9.** Model sites for mononuclear polymer-bound Be(II).

A variety of binding sites were modeled in an attempt to predict the $^{9}$Be NMR chemical shifts in the polymer-bound Be(II) environment. As a starting point, we can assume that the binding site is much different than that observed for **2a** and **b** because of chemical shift considerations (polymer = 0.65−0.70 ppm vs mononuclear = 2.05−2.17 ppm). A variety of mononuclear species were modeled applying a variety of potential binding motifs observed for dicarboxyimidazole-based ligand sets and for carboxyl and sulfonato-bound species, all of which the polymer could potentially adopt. Initially, a 2:1 ligand-to-Be species ratio was modeled as in Table 3 (entry 1); however, the calculated chemical shift of 2.3 ppm (Table 3) occurs at a lower field than that predicted for **2a** and **b** (i.e., further from the polymer experimental $^{9}$Be NMR chemical shift), and therefore, it is unlikely to be the correct binding motif. In addition, the N/O bound 1(HMDCI)/1(Be) species was modeled (Table 3; entry 4); however, the calculated value of 4.24 ppm (Table 3) suggests that this binding motif, again, does not represent the polymer binding site. Finally, models of sulfonato-bound and carboxyl-bound mononuclear species (Table 3) were modeled with neither showing $^{9}$Be NMR chemicals shifts (2.04 and 2.37 ppm) close to the experimentally observed Be(II)−polymer chemical shift of 0.6−0.7 ppm.

The larger line widths of the polymeric species (40−100 Hz) relative to that of the mononuclear complexes **2a** and **b** (ca. 10 Hz) suggest that the polymer-bound species is in a much more asymmetric environment. A line width of 100 Hz could be indicative of a low-coordinate species (i.e., trigonal), but this is extremely unlikely considering the aqueous environment. The broad signal, more than likely, suggests that multiple Be(II)-containing species are present at pH = 7, whereas at pH = 5, the line width of 40 Hz is more consistent with a single 4-coordinate complex.[3] $^{9}$Be NMR chemical shifts in the region of 0.5−1.0 ppm have been observed previously in a variety of polypeptide sequences where beryllium is bound by one or more carboxylate groups.[28] Furthermore, the polymer bound spe-

---

(28) Keizer, T. S.; McCleskey, T. M.; Meza-Romero, R.; Chou, Y. K.; Vandenbark, A. A.; Scott, B. L.; Burrows, G. G. *J. Biol. Chem.* submitted for publication.

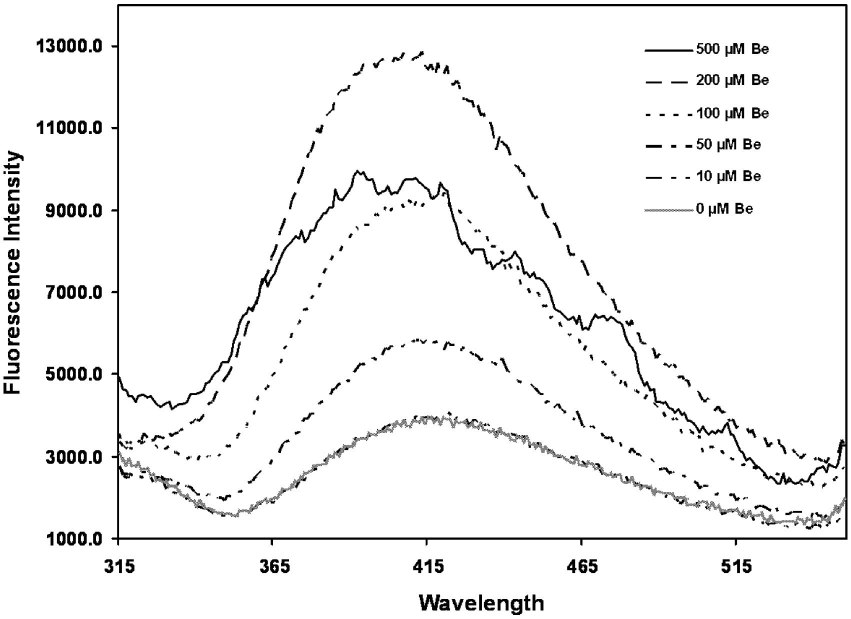


**Figure 10.** Potential polymer binding motif based on $Be_3(OH)_3(H_2O)_6^{3+}$.

cies may be polynuclear in nature as species such as $Be_3(OH)_3(H_2O)_6^{3+}$ and $Be_4O(OAc)_6$ have $^9$Be NMR chemicals shifts of 0.61 and 0.90 ppm, respectively.[3,29] One possible cluster binding site is shown in Figure 9. The structure shown in Figure 9 illustrates a highly symmetric species that experimentally should give a narrow $^9$Be NMR line width. Given that it possesses a geometry similar to $Be_3(OH)_3(H_2O)_6^{3+}$ ($^9$Be NMR $= 0.61$ ppm), it should also provide a chemical shift value in the desired range. Attempts to model this species using DFT methods met with limited success. The computed geometry and $^9$Be NMR chemical shift (2.58 ppm) of the trimetallic species shown in Figure 9 was a poor fit for the experimentally observed value. In an attempt to calibrate this result, the $^9$Be NMR chemical shift of $Be_3(OH)_3(H_2O)_6^{3+}$ was computed to be 1.02 ppm which is roughly 40% higher than the experimentally observed value of 0.61 ppm. Additional work is underway to elucidate what factors can be improved to better model multinuclear clusters in an attempt to better determine the nature of the polymer-binding site.

**Fluorescence Measurements on a Partially Propane-Sulfonated Polymer.** Fluorescence measurements were recorded at pH 7 for 100 $\mu$M dicarboxyimidazole sites in the polymer (**4**) in the presence of 10, 50, 100, 200, and 500 $\mu$M concentrations of beryllium sulfate (Figure 10). The polymer sample displays an inherent fluorescence at 425 nm which, unlike **1a**, increases in intensity with increasing Be(II) concentration. The fluorescence band maximum at approximately 425 nm is slightly red shifted relative to **1a** ($\lambda_{max} = 400$ nm) and can be attributed to the electronic perturbation caused by substitution at the C(2) position. This same C(2) perturbation may explain why the polymer displays a relatively strong inherent fluorescence response, whereas the mononuclear species (**2a** and **b**) do not. The increase in fluorescence response with increasing Be(II) concentration could be the result of the removal of a separate proton-quenching pathway (more than likely caused by the replacement of a carboxyl proton by beryllium). The formation of an exiplex may also be used to explain the change in polymer-based fluorescence. Formation of an exiplex could be favored because of the high density of imidazole units within the polymer, which may facilitate the necessary $\pi$ stacking. Addition of Be(II) salt would serve to “break-up” the exiplex structure providing the change in fluorescence intensity. We explored the potential of exiplex formation in highly concentrated solutions of the monomer (40 mM) and observed no change in the fluorescence intensity upon addition of Be(II) suggesting that this is not a plausible explanation.

The maximum fluorescence intensity of the Be-polymer species is observed at 200 $\mu$M Be concentration beyond which increasing the Be loading results in diminished fluorescence intensity presumably caused by the precipitation of the Be-bound polymer. Furthermore, the band blue shifts slightly by approximately 10−15 cm$^{-1}$ at high Be concentrations. The titration suggests that the Be(II) bound species is multinuclear (each monomer unit binding at least 2 equiv. of Be(II)) and not mononuclear as in **2a** and **b**. In addition, the fact that the polymer fluorescence intensity depends on the Be(II) concentration suggests that the carboxyl groups of the dicarboxyimidazole unit are directly involved in Be(II) binding. Binding to the pendant sulfonato group may still be possible, although binding to such a remote site would not be expected to result in the observed changes in dicarboxyimidazole-based fluorescence intensity.

## Conclusions

We have demonstrated that Be(II) binds to dicarboxyimidazole ligands to form a zwitterionic species $[(H_2O)_2Be(HMDCI)_2][HMDCI]\cdot H_2O$. The binding mode is unprec-

---

(29) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem. Commun.* **2000**, *3*, 350.

edented in that both carboxylic oxygens are bound to the Be(II) center. Solution NMR studies confirm the need for two ligand equivalents and suggests that the solution structure of the mononuclear species is the same as that observed in the solid state. Density functional theoretical methods have been employed to model mononuclear- and polymer-bound Be(II) species. DFT appears to model the $^9$Be NMR chemical shift of the mononuclear species to within 5% of the experimentally observed values. However, we have yet to accurately model the Be-polymer site. Chemical shift and line width analysis suggest that the polymer-bound species involves coordination to the carboxylates, is polynuclear in nature, or both. Furthermore, the fact that the fluorescence response of the polymer is directly linked to Be(II) concentration suggests that the carboxyl groups of the dicarboxyimidazole unit are directly involved in binding. We attribute the lack of $H_2$MDCI and $H_2$DCI fluorescence responses to a proton-quenching pathway that does not exist in the polymer.

Poly[1-(4,5-dicarboxyimidazolyl))ethane] grafted at 25% with 3-propane sulfonic acid appears to be a viable candidate for environmental remediation methods. On the basis of the fluorescence titration studies, each monomer unit appears to be able to bind at least 2 equiv of Be(II). The fact that the polymer exhibits a concentration-dependent fluorescence response provides the added benefit of the polymer being applied in Be(II) sensor technologies. Future work will focus on more detailed theoretical analyses of the polymer binding site, determination of polymer-Be(II) binding constants, and competition experiments with environmental interferents.

**Acknowledgment.** Support for this research was provided by the Los Alamos National Laboratory's Laboratory Directed Research and Development Office under an Exploratory Research grant. This research was performed at Los Alamos National Laboratory under contract with the University of California (Contract No. W-7405-ENG-36).

**Supporting Information Available:** Crystallographic data for **2a** in CIF format and NMR data ($^1$H and $^9$Be). This material is available free of charge via the Internet at http://pubs.acs.org.

IC050680C