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Synthetic and Structural Studies of a Linear Bis-Catechol Amide, *N,N'*-Bis(2,3-dihydroxybenzoyl)-1,7-diazaheptane (5-LICAM), and Its Complexes with Ni^{2+} and Co^{2+}: Utilization of a Polymer-Supported, Sulfonated Analog, 5-LICAMS, as a Biomimetic Ligand for Divalent Metal Ion Removal from Aqueous Solution

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The synthesis and structural characterization of the linear bis(catechol) amide ligand, *N,N'*-bis(2,3-dihydroxybenzoyl)-1,7-diazaheptane (5-LICAM, **1**), was studied along with several metal complexes, namely, Ni^{2+} and Co^{2+}. We were able to obtain a single-crystal X-ray analysis of a derivative of **1**, the hemimethoxy ligand, 5-LICAM(OCH$_3$)$_2$, **2**, where partial demethylation of the fully methylated derivative of **1** was serendipitously obtained in the presence of a deficiency of BBr$_3$. The X-ray structure showed why we retained the methoxy group, during the partial demethylation reaction, in each catechol amide ring by the fact that a selective intramolecular hydrogen bond occurs between the one demethylated OH group in each catechol ring and the amide carbonyl in the adjacent position (C=O- - -HO, 1.67 Å). Reaction of **1** with a Ni^{2+} salt provided the first structurally characterized square planar, linear bis-catechol amide, dianionic metal complex, with cesium as the counterion, Cs$_2$[5-LICAM-Ni]·3DMF, **3**, (Ni−O, 1.87 Å, O−Ni−O, 87.9−92.5°). It is also interesting to note that one of the cesium atoms was cis-bonded to the catechol oxygens in each ring (O2- - -Cs1, O6−Cs1 = 3.23 Å, 3.03 Å) and to the carbonyl oxygen of one of the three DMF solvent molecules (Cs1−O=C, 3.13 Å), while the other cesium atom was bonded to all three carbonyl oxygens of the DMF molecules in the structure (Cs2−O7, O8 = 3.13, 3.12 Å). A Co^{2+} analogue of **3**, Cs$_2$[5-LICAM-Co]·DMF, **4**, provided a similar structure as ascertained by FT-IR, FAB/MS, and elemental analysis. In order to test the utilization of **1** in removing Ni^{2+} from aqueous solution for environmental inorganic applications, we synthesized the polymer pendant ligand version, **PS-5-LICAM**, bonded to modified 6% macroporous divinylbenzene−polystyrene beads (0.55 mmol/g), with an important modification of a sulfonate group on the catechol ring, **PS-5-LICAMS**, to impart hydrophilicity to the ligand site. Indeed, we found that the **PS-5-LICAMS** ligand removed 0.35 mmol of Ni/g of polymer beads from aqueous solution at pH 2.5, but unfortunately, was not selective to Ni^{2+} in competition with other divalent metal ions. An in depth discussion of the X-ray structure of ligand **2** and that of the Ni complex, **3**, will be presented.

Environmental aspects related to designing organic ligands to selectively complex metal ions from aqueous solution represents a new direction for inorganic chemistry. One focus being used by a number of research groups involves designing organic ligands that are biomimics of known biological systems and that selectively complex various metal ions. It is important to note that this approach has been directed more towards clinical rather then environmental applications.[2] Thus, the biomimetic approach has provided an array of organic ligands that fulfill the requirements of high selectivity to certain metal ions, especially for Fe^{3+} ion.[3]

In the course of carrying out an extensive environmental inorganic chemistry program that utilizes biomimetic, among many other ligands attached to modified divinylbenzene−polystyrene polymer beads, for selective metal ion removal and recovery from aqueous solutions, we decided to study one of the several linear catechol amide ligands we synthesized for the above-mentioned application; however, the initial focus was with the homogeneous version; i.e., a linear catechol amide ligand that is soluble in organic solvents. This approach might allow us to determine unequivocal structures and help identify plausible bonding modes on the polymers, which is a difficult and not always unequivocal task, utilizing primarily FT-IR and CP-MAS NMR techniques as well as elemental analysis.

Raymond and co-workers have primarily been responsible for developing the field of linear catechol amide chemistry as biomimics of siderophores, low molecular weight ligands that selectively transport Fe^{3+} ion into bacteria and fungi.[3,4] Apparently, one frustrating aspect of this biomimetic chemistry has been the general lack of X-ray crystal structures for the corresponding metal complexes. Among the extensive list of linear catechol amide ligands that Raymond and his co-workers[3,4] have synthesized, the linear bis(catechol) amide series[4c] was critical for us to develop as polymer pendant ligands for possible selectivity toward divalent metal ions; these are represented by such examples as Cu^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}, and Ni^{2+}.[5]

A perusal of the literature showed that the linear bis(catechol) amide series, 2-, 4-, 6-LICAM had been prepared by Weitl and

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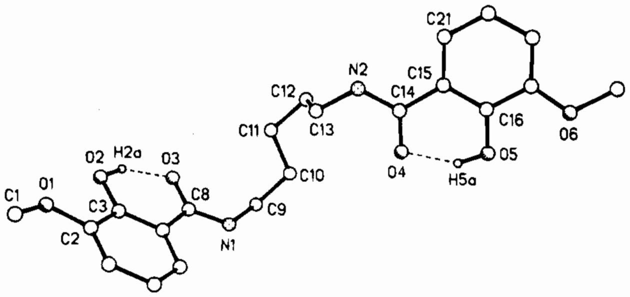


Figure 1. X-ray structure of **2** with the atom labeling scheme.

Raymond,[4c] while the 5-LICAM analogue, **1**, in that series, had not been prepared. Therefore, we decided to study the metal complexes of **1** in organic solvents, while concomitant studies were being performed with the sulfonated version, **PS-5-LICAMS**, attached to a modified 6% crosslinked macroporous divinylbenzene-polystyrene bead for removal of divalent metal ions from aqueous environmental solutions. In this paper, we report on the *first X-ray crystallographic analyses of both a linear bis(catechol) amide ligand, 5-LICAM(OCH$_3$)$_2$, 2, and a metal complex of 1, a square planar, linear bis(catechol) amide, dianionic Ni^{2+} complex, 3.* The structurally similar Co^{2+} complex was also synthesized and characterized by spectroscopic techniques. The counterion used for **3** was a Cs$^+$ cation and a dramatic Cs$^+$ coordination was observed on all oxygen atoms, including the solvent, DMF. We will also demonstrate that the similar polymer pendant ligand version, that was sulfonated to impart hydrophilicity to the ligand site, **PS-5-LICAMS**, can indeed remove Ni^{2+} ions and other divalent metal ions from aqueous acidic solutions.

Results and Discussion

Synthesis of the 5-LICAM Ligand, 1. The 5-LICAM ligand, **1**, was prepared according to the previously reported method by Fish and Tannous, with some modifications.[6] During our investigations of the purification of **1** by various recrystallization methods, we serendipitously found that a product resulting from an incomplete demethylation reaction gave large, cube-shaped, single crystals (up to 0.6 cm). The FT-IR spectrum of this compound showed a very strong and broad band at 1245 cm^{-1}, characteristic of the aryl alkyl ether C−O−C stretching vibration. The FAB$^+$ mass spectral data (m/z = 403 for the [M + H]$^+$, 100%) indicated that this compound was a partially demethylated (two of four methoxy groups) derivative, 5-LICAM(OCH$_3$)$_2$, **2**.

Description of the Crystal Structure of 2. We were curious about the distribution of the methyl groups in compound **2** and decided to conduct an X-ray crystallographic study. Interestingly, the X-ray structure of **2** (Figure 1, Tables 1 and 2), shows that the two methyl groups are each located in the positions *meta* to the two carbonyl groups, while the *ortho* −OH groups form hydrogen bonds with this carbonyl. In the structure, the two catechol amide rings are bridged by the zigzag −(CH$_2$)$_5$− chain, and arrange themselves in a *trans* fashion as shown in Figure 1. Two hydrogens on the *ortho* OH groups each form hydrogen bonds with the amide carbonyl groups providing the following data: H(2a)−O(2) = 0.92 Å, C=O(3)···H(2a) = 1.68 Å, H(5a)−O(5) = 0.92 Å, and C=O(4)···H(5a) = 1.66 Å, respectively. The asymmetric unit of **2** consists of one formula, $C_{21}H_{26}N_2O_6$, and this molecule does not contain any crystallographically imposed symmetry features. Overall, **2** appears to be normal in terms of the other bond lengths and bond angles.

Table 1. Data for Crystal Structure Analysis of 5-LICAM(OMe)$_2$, **2**, and Cs$_2$[Ni(5-LICAM)]·3DMF, **3**[a]

compound	2	3
formula	$C_{21}H_{26}N_2O_6$	$C_{28}H_{39}N_5O_9NiCs_2$
a, Å	8.324(2)	18.266(4)
b, Å	10.376(2)	13.234(3)
c, Å	12.697(3)	15.982(3)
α, deg	80.61(2)	90.00
β, deg	75.28(2)	115.37(2)
γ, deg	69.72(2)	90.00
Z; V, Å^3	2; 991.6(3)	4; 3491(1)
space group	$P\bar{1}$ (No. 2)	Cc (No. 9)
D_{calc}, g/cm^3	1.35	1.74
μ(Cu Kα), mm^{-1}	0.822	17.292
cryst size, mm	0.26 × 0.36 × 0.58	0.08 × 0.13 × 0.15
$2\theta_{max}$, deg	115.0	114.0
temp, K	130	130
no. of data collcd	2714	2689
no. of data used ($F_o > 4\sigma(F_o)$)	2488	2282
min, max abs cor	0.74, 0.89	0.13, 0.34
no. of variables	262	193
final R/R_w, %	4.9/10.3	6.8/7.1

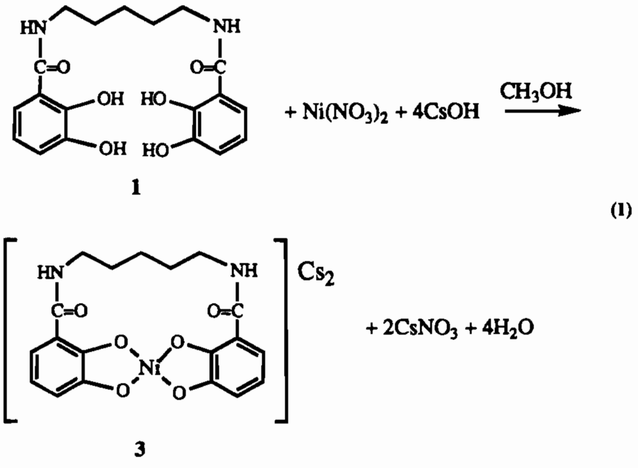
[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = \Sigma(|F_o| - |F_c|)\sqrt{w}/|F_o|\sqrt{w}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 5-LICAM(OCH$_3$)$_2$, **2**

O(1)−C(1)	1.425(4)	O(6)−C(18)	1.438(3)
O(1)−C(2)	1.373(2)	O(6)−C(17)	1.358(2)
O(2)−C(3)	1.354(3)	O(5)−C(16)	1.350(2)
O(4)−C(14)	1.255(2)	O(3)−C(8)	1.260(3)
N(1)−C(8)	1.331(2)	N(2)−C(14)	1.338(2)
N(1)−C(9)	1.465(3)	N(2)−C(13)	1.447(3)
O(3)···H(2A)	1.68	O(4)···H(5A)	1.66
C(1)−O(1)−C(2)	117.5(2)	C(18)−O(6)−C(17)	116.5(1)
O(1)−C(2)−C(3)	114.0(2)	O(6)−C(17)−C(16)	114.4(2)
O(2)−C(3)−C(2)	117.1(2)	O(5)−C(16)−C(17)	117.8(2)
O(3)−C(8)−C(4)	120.3(2)	O(4)−C(14)−C(15)	120.4(2)
C(8)−N(1)−C(9)	123.1(2)	C(14)−N(2)−C(13)	121.5(2)

Thus, in the partial demethylation reaction, the selective intramolecular hydrogen bond between the one demethylated OH group in each catechol ring, and the amide carbonyl in the adjacent position, provides a rationale for the formation of **2**. Furthermore, the subsequently modified demethylation procedure, where a large excess of BBr$_3$ was used, did indeed afford pure **1** and was confirmed by FT-IR, FAB$^+$ mass spectrometry, and elemental analysis (see the Experimental Section).

Synthesis of the Nickel-5-LICAM Complex, 3. The synthesis the square-planar Ni^{2+} complex of **1** is readily accomplished by allowing Ni(NO$_3$)$_2$ to react with **1** in the presence of CsOH in methanol to provide complex **3** (eq 1).



(1)

Like many transition metal catecholate complexes, the product,

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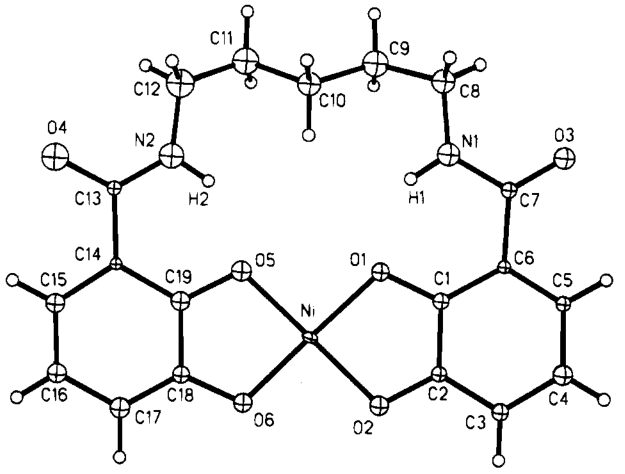

Figure 2. Thermal ellipsoid plot of the $[Ni(5\text{-}LICAM)]^{2-}$ anion of **3** with the atom labeling scheme.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Cs_2[Ni(5\text{-}LICAM)]\cdot 3DMF$, **3**[a]

Ni−O(1)	1.88(2)	Ni−O(2)	1.90(2)
Ni−O(5)	1.85(1)	Ni−O(6)	1.84(2)
Ni−O(mean)	1.87(1)		
O(1)−C(1)	1.32(2)	O(2)−C(2)	1.33(3)
O(5)−C(19)	1.33(3)	O(6)−C(18)	1.33(2)
O−C(mean)	1.33(1)		
C(7)−O(3)	1.25(3)	C(13)−O(4)	1.27(3)
N(1)−C(7)	1.38(3)	N(2)−C(13)	1.28(3)
N(1)−C(8)	1.41(3)	N(2)−C(12)	1.41(3)
O(1)···H(1)	1.91(1)	O(5)···H(2)	1.91(1)
O(1)−Ni−O(2)	87.9(6)	O(5)−Ni−O(6)	88.5(6)
O(1)−Ni−O(5)	92.5(7)	O(2)−Ni−O(6)	91.2(7)
O(1)−Ni−O(6)	177.2(7)	O(2)−Ni−O(5)	178.8(8)
Ni−O(1)−C(1)	111(1)	Ni−O(2)−C(2)	108(1)
Ni−O(5)−C(19)	110(1)	Ni−O(6)−C(18)	111(1)
C(7)−N(1)−C(8)	124(2)	C(13)−N(2)−C(12)	126(2)
O(3)−C(7)−N(1)	120(2)	O(4)−C(13)−N(2)	122(2)

[a] The estimated standard deviations in the mean bond distances and the mean bond angles are calculated by the equation $s_l = \{S_n(l_n - l)^2/n(n - 1)\}^{1/2}$, where l_n is the distance (angle) of the *n*th bond, *l* the mean distance (angle), and *n* the number of bonds.

thus obtained, was air-sensitive and showed a strong tendency to form solvates. The DMF-solvated crystals, $Cs_2[Ni(5\text{-}LICAM)]\cdot 3DMF$, **3**, can be obtained after recrystallization in a DMF/diethyl ether mixture of solvents.

Upon exposure to air, $Cs_2[Ni(5\text{-}LICAM)]\cdot 3DMF$, **3**, turned from yellow to dark brown, and we noted that the crystal surface was full of water droplets. It should be stated that this air and moisture sensitivity probably accounts for the inaccurate elemental analysis we observed for **3**. Nevertheless, the FAB^+ mass spectrum of **3** showed both the $\{[Ni(5\text{-}LICAM)]+H\}^-$ anion at *m/z* = 429 (31%) and the cation-anion, $\{Cs^+ + [Ni(5\text{-}LICAM)]^{2-}\}$, at *m/z* = 561(18%). The FT-IR spectrum was also consistent with **3** and, more importantly, the structural identity of this complex was unequivocally determined by single crystal X-ray analysis.

Description of the Crystal Structure of 3. The structure of **3** is made up of two Cs^+ cations, three DMF solvent molecules, and $[Ni(5\text{-}LICAM)]^{2-}$ anions. Figure 2 shows a thermal ellipsoid drawing of **3**, while Table 3 provides the important bond lengths and angles. The Ni^{2+} center is bonded by four oxygen donor atoms from the two catechol amide rings, and features square-planar coordination. The four oxygen atoms around Ni^{2+}, i.e., O(1), O(2), O(5), and O(6), are within 0.03 Å of the least-squares plane. The Ni−O bond distances, averaging 1.87(1) Å, are comparable with the typical Ni−O bond distances found in other Ni^{2+} oxo complexes with square-planar coordination; for example, 1.84 Å in bis-(2-hydroxy-5-methylacetophenato)nickel(II)[7] and 1.84 Å in bis-(2,2,6,6,-tetramethylheptane-3,5-dionato)nickel(II).[8] Other structurally characterized Ni^{2+} complexes that contain catecholate or semiquinone ligands in their coordination spheres, include $Ni(phenSQ)_2(py)_2$ (phenSQ = 9,10-phenanthrenesemiquinone),[9] $[Ni(DTBSQ)_2]_4$ (DTBSQ = 3,5-di-*tert*-butylbenzosemiquinone),[9] and $[Ni(CTH)DTBSQ]PF_6$ (CTH = dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[10]

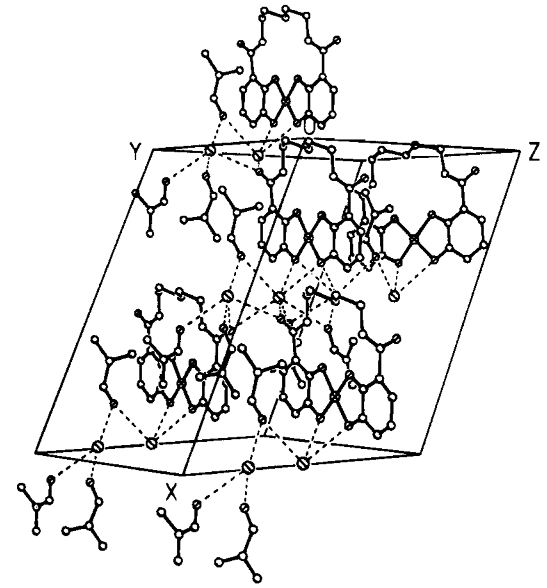

Figure 3. The packing diagram in the unit cell of **3** to show the Cs^+ polymeric structure.

In the metal complexes that contain quinoid molecules, ambiguity may arise with regards to the charge distribution between the metal center and the ligand; i.e., three possible forms including quinone, semiquinone, and catecholate for the same type of ligand can often complicate the assignment of the proper oxidation states at the metal center. Pierpont and Buchanan pointed out that the average C−O bond distances in the coordinated quinoid ligands are very sensitive to the charge of the ligand; i.e., C−O = 1.23(1) Å for quinones, C−O = 1.29(1) Å for semiquinones, and C−O = 1.35(1) Å for catecholates, respectively.[11] In the case of **3**, the average C−O distance was found to be 1.33(1) Å, and is, therefore, consistent with the catecholate form.[12]

Another conspicuous structural feature found in this Ni^{2+} complex is that, in comparison to the free ligand, **2**, the two amide carbonyl groups in the structure are rotated ~180° (see Figures 1 and 2). This allows the two amido hydrogen atoms to form H-bonds with the *ortho* oxygen atoms. The N−H and O···H distances found in these H-bonds are 0.88 Å (assumed) and 1.9(1) Å, respectively. Although situated in a general position, the molecule possesses pseudo-C_{2v} symmetry with the C_2 axis passing through Ni^{2+} and C(10). The Cs^+ atoms were

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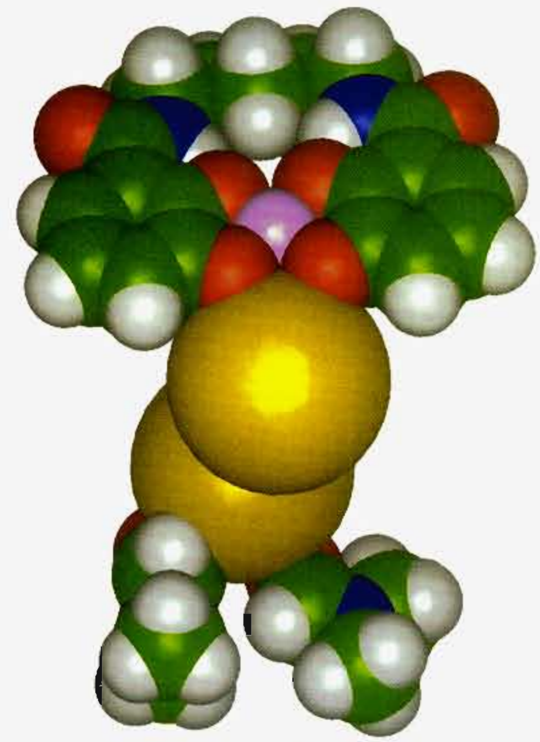
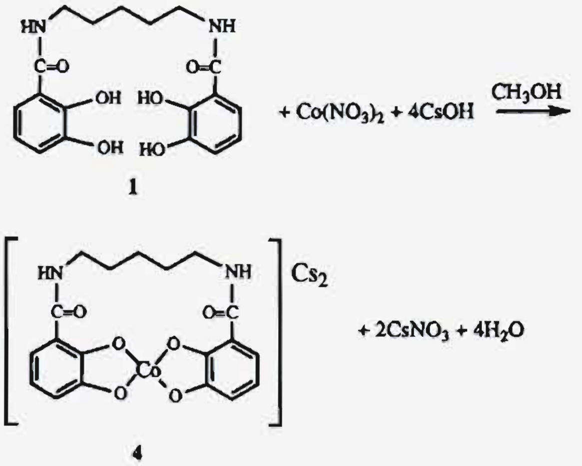


Figure 4. Molecular Graphics Space-Filling Model of **3**. atoms/color: H/white; N/blue; C/green; O/red; Ni/magenta; Cs/yellow.

found to interact with two *meta* oxygen atoms in the [Ni(5-LICAM)]$^{2-}$ anion, and with two amide carbonyl oxygen atoms in another. This cation–anion aggregate is then flanked by three DMF molecules, through their oxygen atoms, giving the whole complex a polymeric structure. However, it is difficult to fully describe the complex arrangement of the Cs$^+$ cations, [Ni(5-LICAM)]$^{2-}$ anions, and solvent DMF molecules in the structure, therefore, we show the unit cell packing diagram in Figure 3, and as well, a molecular graphics space-filling model, generated from the X-ray data, is also shown in Figure 4, both for clarity of structure **3**.

Structure of the Co^{2+}–5-LICAM Complex, 4. The corresponding Co^{2+} complex with **1**, complex **4**, was synthesized and provided similar spectroscopic data to that obtained for **3**. For example, the FT-IR was similar to **3**, while the FAB$^+$ mass spectrum shows the following ions at *m/z* (%) 562, [Cs(Co-5-LICAM)]$^-$ (70), and *m/z* (%) 430, [(Co-5-LICAM)+H]$^-$ (44). Thus, we depict complex **4** as a four-coordinate Co^{2+}-5-LICAM complex:



(2)

The Polymer Pendant Ligand, PS-5-LICAMS: Synthesis and Reactivity. A similar synthetic procedure was then extended to the polymer pendant ligand version, **PS-5-LICAM**, to ascertain whether divalent metal ions, such as Ni^{2+}, can be removed from aqueous acidic solution and thereby demonstrate that this preorganized, square-planar ligand has environmental applications.[5] Thus, we have successfully anchored **PS-5-LICAM** to modified 6% cross-linked macroporous, divinylbenzene-polystyrene beads. In order to provide a more hydrophilic environment, we used our previously found polymer pendant ligand sulfonation procedure[5] to increase the kinetics and metal binding capacities in aqueous solution, while also preventing the catechol ligand from being readily oxidized to the weaker binding *o*-quinone ligand. The synthesis for **PS-5-LICAMS** is summarized in eq 3.

The FT-IR spectrum of this polymer showed three medium-to-strong bands from 1640 to 1540 cm^{-1}, characteristic of C=O coupled with amido C–N stretching vibrations. In addition, a very strong and broad band at 1250 cm^{-1} attributable to the C–O stretching for the phenolic OH groups, while the S=O stretch for the sulfonic acid substitutents at 1229 and 1176 cm^{-1} were also observed for **PS-5-LICAMS**. The ligand concentration of the **PS-5-LICAMS** ligand on the polymer beads was estimated by elemental analysis to be ~0.55 mmol/g.

Indeed, we found that this polymer pendant ligand version, **PS-5-LICAMS**, could remove Ni^{2+} ions from aqueous solution at pH 2.5, but showed no selectivity to other divalent metal ions that also prefer four coordination.[5] For example, the **PS-5-LICAMS** metal ion removal concentrations (mmol/g) for divalent metal ions in competition with Cu^{2+} at pH 2.5 were as follows: Ni^{2+} (0.35)/Cu^{2+} (0.41); Zn^{2+} (0.37)/Cu^{2+} (0.42); and Mn^{2+} (0.38)/Cu^{2+} (0.35). This clearly showed divalent metal ion removal, but no selectivity for any particular metal ion. It is interesting to note, given the fact that the Cs$^+$ counterion in the X-ray of **3** was responsible for the polymeric structure (Figure 3), that an analog of **PS-5-LICAMS** ligand, **PS-2-LICAMS**, showed a reasonable distribution coefficient factor (30 min K_d, 1200, at pH = 3.0) for the removal of the radionuclide, ^{137}Cs$^+$, from aqueous acidic solution. Thus, the potential use of the **PS-2–6-LICAMS** series of ligands for removing the radioactive isotope, ^{137}Cs$^+$, and other radionuclides, from low level radioactive nuclear waste may be feasible.[13]

Conclusions

A new linear bis(catechol) amide, 5-LICAM, **1**, along with its partially methylated derivative 5-LICAM(OCH$_3$)$_2$, **2**, was prepared and characterized by elemental analysis, FT-IR and FAB/MS. The X-ray crystal structure of **2** was determined and shows intramolecular H-bonding between the *ortho* OH and C=O groups and, to our knowledge, is the first crystallographically characterized linear bis(catechol) amide ligand. The tetradentate ligand **1** can readily chelate divalent metal ions, such as Ni^{2+}, forming the square-planar complex [Ni(5-LICAM)]$^{2-}$, **3**, which was also structurally characterized by single crystal X-ray analysis. Although a number of M(cat)$_2$$^{2-}$ (M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc.; cat = catecholates) complexes were known as early as 1918,[14] and their chemical properties were the subject of several other studies,[15] complex **3** is the first structurally characterized example of a square-planar Ni^{2+} catecholate complex and, as well, in a linear bis-(catechol) amide ligand.

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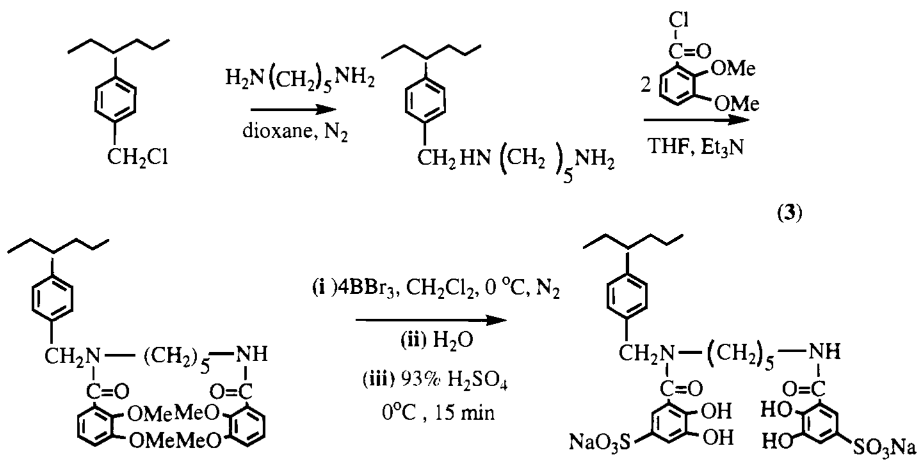

(3)

PS-5-LICAMS

All the spectroscopic and structural information we obtained from the present study contributes to our on-going studies on the polymer pendant ligand chemistry using polymer-supported, sulfonated catechol and linear bis-and tris(catechol) amide ligands, as shown with the example, the **PS-5-LICAMS** ligand, to selectively remove and recover metal ions from aqueous solution.[5] Clearly, the approach of structurally defining the homogeneous biomimetic ligands and their metal complexes provides invaluable information for extending these systems to their polymer pendant versions for future environmental applications.

Experimental Section

Purchased chemicals were used as obtained. Solvents were purified and degassed. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres double-stage glovebox.

Physical Measurements. ^{1}H NMR spectra were obtained on a 300 MHz Bruker Fourier transform spectrometer located in the Department of Chemistry, University of California, Berkeley. The UV/vis spectra were measured on a Hewlett Packard 8452A diode array spectrophotometer. The FT-IR spectra were determined as solids in a KBr matrix in the mid-IR region (400−4000 cm^{-1}) with the use of a computer controlled Nicolet Impact 400 FT-IR spectrometer. FAB/MS spectra were recorded with a MS-50 instrument and elemental analyses were carried out by the microanalytical laboratory, both located in the Department of Chemistry, University of California, Berkeley. The space-filling model for **3** was generated from the X-ray data using the Biosym Technologies software with the Insight II molecular modeling system. Melting points were measured on a capillary melting point apparatus and are uncorrected.

Preparation of *N,N'*-Bis(2-dihydroxy-3-methoxybenzoyl)-1,7-diazaheptane (5-LICAM(OCH$_3$)$_2$), 2. A sample of 2,3-dimethoxybenzoic acid (10.0 g, 54.9 mmol) was stirred with 20 mL (274 mmol) of thionyl chloride in a round-bottom flask equipped with a drying tube at room temperature for 2 h. After removal of the excess $SOCl_2$ by a rotary-evaporator, the white crystals that appeared upon cooling were dissolved in 30 mL of benzene (thrice), which was then rotary evaporated to give a benzene soluble acid chloride. To a solution containing this acid chloride in CH_2Cl_2 (80 mL) was added dropwise a solution containing 3.10 g (30.3 mmol) of 1,5-diaminopentane in CH_2Cl_2 (20 mL) followed by a dropwise addition of a solution containing 5.60 g (55.3 mmol) of triethylamine in CH_2Cl_2 (10 mL) under dry N_2. The reaction was stirred at room temperature for 12 h. After the solvent was removed by vacuum, a light yellow oil was obtained, which was dissolved in 100 ml $CHCl_3$ and washed with deionized H_2O, 5% NaOH, 5% HCl, and H_2O (twice). The final pale yellow solution was dried over anhydrous $MgSO_4$, filtered and stripped of solvent to give a yellow-orange cream.

To a solution that contained the above-mentioned material in CH_2Cl_2 (80 mL) was added dropwise 10.0 g (40.0 mmol) of boron tribromide in CH_2Cl_2 (50 mL) at 0 °C, under N_2 and with stirring. A greenish flocculent precipitate formed immediately. After ~1 h of stirring, 100 mL of deionized H_2O was added slowly, and the mixture was stirred overnight. The product was collected by filtration, washed well with H_2O, and dried in air. The powder was dissolved in hot methanol, and H_2O was added to precipitate the product, 74% yield (8.2 g after dried *in vacuo*). X-ray quality single crystals were obtained from methanol solution by slow evaporation of the solvent: mp 157−161 °C; FT-IR (KBr) 3378 (s), 2936 (s), 2840−2815 (m), 1646 (s), 1593 (s), 1549 (s), 1488 (s), 1467 (s), 1450 (s), 1438 (m), 1385 (m), 1365 (m), 1303 (s), 1245 (vs, b), 1180 (w), 1119 (w), 1087 (m), 1031 (w), 923 (w), 903 (w), 835 (w), 829 (w), 734 (s) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6, ppm) 3.3−3.4 (complex m, 10H, CH$_2$), 3.8 (s, 6H, CH$_3$), 6.7−7.4 (complex m, 6H, ArH), 8.8 (m, 2H, NH), 11.7 (s, 2H, *o*-OH); FAB$^+$ mass spectrum *m/z* (%) 403 [M + H]$^+$ (100), 388 [M − CH$_3$ + H]$^+$ (10), 372 [M − 2CH$_3$]$^+$ (15), 253 [M$^+$ − C$_8$H$_7$O$_3$ + 2H]$^+$ (78). Anal. Calcd for $C_{21}H_{26}N_2O_6$: C, 62.36; H, 6.99; N, 6.92. Found: C, 62.44; H, 6.50; N, 6.95.

Preparation of *N,N'*-Bis(2,3-dihydroxybenzoyl)-1,7-diazaheptane (5-LICAM), 1. The precursor compound, S-LICAM(OCH$_3$)$_4$, was prepared in the same manner as described above. To a solution containing 30.2 g (120 mmol) of boron tribromide in CH_2Cl_2 (50 mL) was added dropwise a solution of 5-LICAM(OCH$_3$)$_4$ in CH_2Cl_2 (80 mL) at 0 °C, under N_2 and with stirring. The precipitate was stirred overnight. After 100 mL of deionized H_2O was added slowly, the mixture was stirred for 3 h more. The product was collected by filtration, washed well with H_2O, and dried in air. Recrystallization from methanol gave white fiber-like thin crystals of **1**, in 82% yield (8.4 g after being dried *in vacuo*): mp 172−174 °C; FT-IR (KBr) 3369 (vs), 2943 (m), 2866 (m), 1640 (s), 1584 (s, b), 1549 (s, b), 1491 (m), 1461 (s), 1385 (s, b), 1338 (s, b), 1259 (vs, vb), 1180 (m), 1084 (w), 841 (w), 794 (m), 742 (s) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 3.3−3.4 (complex m, 10H, CH$_2$), 6.7−7.3 (complex m, 6H, ArH), 8.8 (m, 2H, NH), 9.1 (s, 2H, *m*-OH), 12.9 (s, 2H, *o*-OH); FAB$^+$ mass spectrum *m/z* (%) 375 [M + H]$^+$ (100), 341 [M − 2OH + H]$^+$ (10), 327 [M − 3OH + 4H]$^+$ (21), 239 [M − C$_7$H$_5$O$_3$ + 2H]$^+$ (87), 221 [M − C$_7$H$_5$O$_3$ − OH + H]$^+$ (34), 207 [M − C$_7$H$_5$O$_3$ − 2OH + 3H]$^+$ (60). Anal. Calcd for $C_{19}H_{22}N_2O_6$: C, 60.96; H, 5.88; N, 7.49. Found: C, 60.61; H, 5.93; N, 7.38.

Preparation of Cs$_2$[Ni(5-LICAM)]·3DMF, 3. A degassed solution containing 0.270 g (1.6 mmol) of CsOH·H$_2$O in MeOH (10 mL) was added dropwise to a degassed solution consisting of 0.150 g (0.4 mmol) of **1** and 0.116 g (0.4 mmol) of Ni(NO$_3$)$_2$·6H$_2$O in MeOH (40 mL) under dry N_2 at room temperature. The solution turned from green to yellow, and a small amount of mustard-colored precipitate formed. After the solvent was removed by vacuum, the product was washed with 2 mL of MeOH and 2 mL of THF (twice). X-ray diffraction quality single crystals of **3** were obtained from DMF/diethyl ether (1:1 v/v) solution by a slow diffusion technique, ~45% yield (from crystals obtained upon recrystalization): FT-IR (KBr) 3418 (s, vb), 2939 (m), 2862 (m), 1610 (s), 1575 (vs), 1537 (s), 1464 (s), 1435 (s), 1388 (m), 1300 (w), 1254 (m), 1219 (vs), 1066 (m), 987 (w), 756 (m) cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 3.2−3.4 (complex m, 10H, CH$_2$), 6.0−6.7

(complex m, 6H, ArH), 8.0 (s, 2H, NH); FAB$^+$ mass spectrum *m/z* (%) 561 [Cs(Ni-5-LICAM)]$^{\cdot}$ (18), 429 [(Ni-5-LICAM)+H]$^-$ (31), 373 [(Ni-5-LICAM)-Ni+3H]$^-$ (30). Anal. Calcd for $C_{28}H_{39}N_5O_9NiCs_2$: C, 36.78; H, 4.93; N, 7.66. Found: C, 37.80; H, 3.71; N, 6.38.

Preparation of Cs_2[Co(5-LICAM)]·DMF, 4. Complex **4** was prepared in the similar manner as described above for complex **3** except that 0.116 g (0.4 mmol) of $Co(NO_3)_2 \cdot 6H_2O$ was used in the place of $Ni(NO_3)_2 \cdot 6H_2O$. The pink powder obtained by recrystallization from DMF/diethyl ether solution showed an almost identical FT-IR spectrum (KBr pellet) as that of **3**. FAB$^+$ mass spectrum: *m/z* (%) 562 [Cs-(Co-5-LICAM)]$^-$ (70), 430 [(Co-5-LICAM) + H]$^-$ (44). Anal. Calcd for $C_{22}H_{25}N_3O_7CoCs_2$: C, 33.39; H, 3.25; N, 5.47. Found: C, 32.89; H, 3.67; N, 5.11.

Preparation of PS-5-LICAM. To 5.0 g (1.78 mmol/g Cl, 8.9 mmol) of chloromethylated Amberlite-XE-298A beads, swelled in 80 mL of dioxane for 1 h, was added dropwise, under N_2, 2.9 g (28.0 mmol) of $H_2NCH_2(CH_2)_3CH_2NH_2$ in 20 mL of dioxane. After this mixture was stirred at room temperature for 10 h, the beads were washed with dioxane, H_2O/dioxane (1:1), H_2O, and MeOH and then dried under vacuum at 60 °C for 15 h. To these aminated Amberlite-XE-298A beads in 80 mL of THF was added dropwise 30 mL of a THF solution containing 1.8 g (9.0 mmol) of 2,3-dimethoxybenzoyl chloride followed by a dropwise addition of a 20 mL THF solution containing 1.2 g (12.0 mmol) of triethylamine. The reaction was kept at 50 °C with gentle agitation for 2 days. After the triethylamine hydrochloride precipitate was decanted from the solvent, the polymer was washed with dioxane/MeOH (1:1), MeOH, H_2O, and MeOH. The product beads were dried under vacuum at 60 °C for 10 h. This product was then swelled in 100 mL of CH_2Cl_2 for 30 min and to this was added dropwise at 0 °C, 4.0 g (16.0 mmol) of BBr_3 in 30 mL of CH_2Cl_2. After the reaction was stirred under N_2 at 0 °C for 14 h, the solvent was decanted, and 50 mL of deionized H_2O was slowly added. The polymer was then soaked in H_2O for 10 h and washed with MeOH and then dried under vacuum at 60 °C for 20 h. The **PS-5-LICAM** polymer beads, thus obtained, analyzed for 1.71% N (0.61 mmol/g of the **5-LICAM** ligand).

Sulfonation of PS-5-LICAM. Thus, 5.0 g of **PS-5-LICAM** beads were swelled in 50 mL of CH_2Cl_2 for 1 h, then filtered and air-dried for 2 h. The solvent treated polymer was added to 50 mL of cold 93% H_2SO_4 and kept at this temperature for 15 min to allow for diffusion of the acid into the polymer structure. After the reaction was allowed to warm up to room temperature during a 20 min time period, the polymer was filtered, and neutralized with a mixture of 200 g of ice containing 10 g of Na_2SO_4 and 1 g of NaOH. After thorough washing with deionized H_2O, the polymer beads were rinsed with MeOH and finally dried under vacuum at 60 °C for 14 h. The product thus obtained, **PS-5-LICAMS** polymer beads, showed 1.57% N (0.56 mmol/g of ligand or 1.12 mmol/g of catechol) and 3.18% S (0.99 mmol/g of sulfonic acid substituents). FT-IR data for **PS-5-LICAMS** (KBr, cm^{-1}): 1462 (C—C); 1640(C=O); 1271 (C—O); 1229 and 1177 (S=O).

X-ray Crystallographic Studies. The crystallographic data sets for **2** and **3** were collected on a Syntex P2$_1$ four-circle diffractometer using Cu Kα radiation using $\theta-2\theta$ scan techniques. The stability of the experimental setup and crystal integrity for each data collection was monitored by measuring two representative reflections for every 198 reflections. While no statistically significant change of intensities was detected for the standard reflections in **2**, a 2% linear decay in the intensities of two standard reflections in **3** was observed. Therefore, the observed intensities in **3** were corrected for this decay.

Both structures were solved with direct methods and refined with full-matrix least squares techniques.[16] The calculations were performed using the Siemens SHELXTL PLUS crystallographic software package. An empirical absorption correction based on the program XABS was applied to **3**.[17] Table 1 gives crystal data and details for structure analysis of the two compounds, **2** and **3**. Hydrogen atoms were added geometrically and refined using a riding model with isotropic temperature factors equal to 0.020 Å^2. The final coordinates and average temperature factors (U_{eq}) of the atoms in compounds **2** and **3** are given in the Supplementary Material. We note that the scattering for complex **3** was dominated by the heavy atoms, Ni and Cs, and to refine the carbon atoms with anisotropic thermal parameters is somewhat like refining H atoms with anisotropic thermal parameters when the remaining atoms are C, N, and O. Since the data was collected at low temperature, the thermal parameters are small, and consequently, thermal motion is less crucial to the structural model in comparison to a room temperature structure.

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Supplementary Material Available: Tables of atomic positional parameters and anisotropic thermal parameters for **2** and **3**, tables of bond distance and bond angles, and tables of atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å^2 $\times$ 10^3) and their esd's for **2** and for **3** (7 pages). See any current masthead page for ordering information.

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