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Supramolecular Structures of Cadmium(II) Coordination Polymers: A New Class of Ligands Formed by Linking Tripodal Tris(pyrazolyl)methane Units

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The new ligands $C_6H_4[CH_2OCH_2C(pz)_3]_2$ (pz = pyrazolyl ring), **1** (*ortho*), **2** (*meta*), and **3** (*para*), that can potentially bond two or more metal centers were obtained in a single step from the reaction of the appropriate dibromoxylene, 2 equiv of tris-2,2,2-(1-pyrazolyl)ethanol, and excess NaH. Although the arrangement of the tris(pyrazolyl)methane units in the solid-state structures of **1** and **3** are similar, the orientation of these groups with respect to the phenyl ring are different, with **1** showing a twisted structure and **3** a stepped structure. The reaction of $[Cd_2(THF)_5][BF_4]_4$ with the appropriate ligand yields each of the three coordination polymers of the formula $\{C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}(BF_4)_2\}_n$, **4** (*ortho*), **5** (*meta*), and **6** (*para*). In the solid-state structures of all three each tris(pyrazolyl)methane unit is tridentate, with each ligand bonded to two different cadmium(II) atoms, forming a coordination polymer containing 6-coordinate, pseudooctahedral cadmium(II) centers. Polymers **4** and **5** form wavelike chains whereas **6** is arranged in a stepped structure similar to the free ligand. The different connecting patterns of each ligand lead to very different supramolecular structures, structures organized by the BF_4^- groups through weak C−H···F hydrogen bonds. Crystallographic information: **1** is monoclinic, $P2(1)/n$, $a = 16.3157(13)$ Å, $b = 8.5880(6)$ Å, $c = 21.9227(17)$ Å, $\alpha = \gamma = 90°$, $\beta = 100.134(2)$ °, $Z = 4$; **3** is monoclinic, $P2(1)/n$, $a = 9.1965(9)$ Å, $b = 12.9185(12)$ Å, $c = 12.7306(12)$ Å, $\alpha = \gamma = 90°$, $\beta = 104.099(2)$ °, $Z = 2$; **4** is triclinic, $P\bar{1}$, $a = 10.7877(19)$ Å, $b = 12.582(2)$ Å, $c = 15.409(3)$ Å, $\alpha =103.860(4)°$, $\beta = 94.123(4)°$, $\gamma = 92.573(4)°$, $Z = 2$; **6** is monoclinic, $C2/c$, $a = 23.023(3)$ Å, $b = 12.2588(14)$ Å, $c = 18.119(2)$ Å, $\alpha = \gamma = 90°$, $\beta = 121.281(2)°$, $Z = 4$.

Introduction

Investigations into the architecture of supramolecular metal complexes formed by self-assembly processes have been ongoing since the early 1990s.[1] Complexes that defined unusual network topologies have attracted special interest because of their ability to include different chemical species and/or catalyze specific chemical transformations. A number of infinite 1-D, 2-D, and 3-D coordination polymers possessing specific geometries capable of accommodating anions and guest molecules have been developed.[2] The key features that determine the results of the assembly process are the ligand design, flexibility of the linker groups joining the coordination sites, and the stereochemical preferences of the coordinating metal ion.[3] In many cases, the stereochemical outcome of the metal-ion assembly process can be controlled by matching the stereochemical preference of the metal ion with the preferred binding sites in the ligand.[1,2]

We have been exploring the chemistry of metal complexes of tris(pyrazolyl)methane ligands (Chart 1),[4] a tripodal neutral ligand set isoelectronic to the more heavily studied tris(pyrazolyl)borate ligands.[5] The apparent reason that these ligands have not been studied extensively is that their preparations have been more difficult, and "second generation" tris(pyrazolyl)methanes have only recently been synthesized.[6] We have recently reported substantial improvements in the preparations of these ligands and developed chemistry whereby the central methine carbon atom can be fuctionalized with groups other than a hydrogen atom.[6c]

These tripodal pyrazolyl ligands force a facial bonding on a metal center. Using our recent ligand developments, we have

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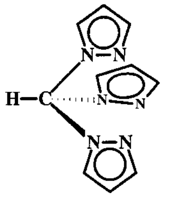
Chart 1



tris(1-pyrazolyl)methane

decided to exploit the potential use of these C_3-symmetric tripodal ligands in supramolecular chemistry. The use of other tripodal ligands for this type of chemistry has not been explored until recently.[7−16] Benzimidazole ligands were used in self-assembly of mono-, bi-, tri-, and tetranuclear complexes[17] and xylene-bridged 1,4,7-triazacyclononane ligands form mono- and binuclear species.[18] Recently dendrimers based on 1,4,7-triazacyclononane ligands have been reported.[19] Some interesting nontripodal pyrazolyl-based ligands have also been used in formation of metallamacrocycles and tubular coordination networks.[20]

We intend to explore the area of supramolecular coordination polymers using new ligands based on linking tris(pyrazolyl)methane groups through the central methine carbon atom. We have prepared ligands of this type that have either rigid or flexible linkers.[21] To date, most coordination polymers have been prepared with rigid ligands,[22] but we were particularly interested in flexible linkers because of the likelihood of preparing coordination polymers that are soluble in organic solvents.[23] Toward this end, we report here the preparation of the *ortho*, *meta*, and *para* isomers of the new ligands $C_6H_4[CH_2OCH_2C(pz)_3]_2$ (pz = pyrazolyl ring), two of which have been characterized in solid state by single-crystal X-ray diffraction. Also reported are the reactions of these ligands with cadmium(II) to form coordination polymers that have three very different supramolecular structures. Polynuclear complexes of d^{10} metals such as cadmium(II) have been shown to form unusual supramolecular structures[24−29] and exhibit photoluminescent properties.[30,31] Our new ligands, formed by linking two tripodal, tris(pyrazolyl)methane units, lead to the formation of coordination polymers with unique architectures.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. The ^1H NMR spectra were recorded on a Varian AM300 spectrometer using a broad-band probe. Proton chemical shifts are reported in ppm vs internal Me_4Si. Mass spectral data were recorded on a MicroMass QTOF spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. The compounds $[Cd_2(THF)_5][BF_4]_4$[6d] and $HOCH_2C(pz)_3$[6c] were prepared according to published methods.

Note! Cadmium compounds and their wastes are extremely toxic and must be handled carefully!

o-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (1). α,α′-Dibromo-*o*-xylene, *o*-$(BrCH_2)_2$-C_6H_4 (2.64 g, 10 mmol) and tris-2,2,2-(1-pyrazoyl)ethanol, $HOCH_2C(pz)_3$ (4.88 g, 20 mmol) were dissolved in dry THF (125 mL). This

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Table 1. Crystal Data and Structure Refinement for *o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (**1**), *p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (**3**), {*o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (**4**), and {*p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (**6**)

	1	**3**	**4**	**6**
empirical formula	$C_{30}H_{30}N_{12}O_2$	$C_{30}H_{30}N_{12}O_2$	$C_{34}H_{36}B_2CdF_8N_{14}O_2$	$C_{36}H_{39}B_2CdF_8N_{15}O_2$
formula weight, g mol^{-1}	590.66	590.66	958.79	999.84
temperature, K	293(2)	293(2)	200(2)	210(2)
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*-1	*C*2/*c*
a, Å	16.3157(13)	9.1965(9)	10.7877(19)	23.023(3)
b, Å	8.5880(6)	12.9185(12)	12.582(2)	12.2588(14)
c, Å	21.9227(17)	12.7306(12)	15.409(3)	18.119(2)
α, deg	90	90	103.860(4)	90
β, deg	100.134(2)	104.099(2)	94.123(4)	121.281(2)
γ, deg	90	90	92.573(4)	90
volume, Å^3	3023.9(4)	1466.9(2)	2021.1(6)	4370.3(9)
Z	4	2	2	4
ρ(calcd), mg m^{-3}	1.297	1.337	1.575	1.520
abs coeff, mm^{-1}	0.088	0.091	0.629	0.586
F(000)	1240	620	968	2024
cryst size, mm^3	0.56 × 0.38 × 0.31	0.20 × 0.56 × 0.60	0.18 × 0.14 × 0.06	0.52 × 0.26 × 0.20
final *R* indices[a]	R1 = 0.0433,	R1 = 0.0486,	R1 = 0.0614,	R1 = 0.0273,
$[I > 2\sigma(I)]$	wR2 = 0.1020	wR2 = 0.1413	wR2 = 0.1259	wR2 = 0.0737

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2] \}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where *P* is $[2F_c^2 + \max(F_o^2, 0)]/3$.

solution was added dropwise to a suspension of NaH (1.5 g) in dry THF (300 mL) under an inert atmosphere. The mixture was stirred under reflux for 24 h and then allowed to cool at room temperature. To this solution enough water (150 mL) was added dropwise to consume the excess NaH and dissolve the resulting NaBr and NaOH. The THF−water mixture was extracted with ethyl ether (4 × 100 mL), and the combined organic extracts were washed with 100 mL saturated $NaHCO_3$ solution, with 100 mL saturated NaCl solution, and finally with 100 mL water. The organic layer was dried over anhydrous Na_2SO_4 and filtered and the solvent removed under vacuum, to afford the desired compound as a white-yellow powder (5.38 g, 9.1 mmol, 91%); mp 128−129 °C. Crystals suitable for the X-ray analysis were grown by layering a methylene dichloride solution of the ligand with hexanes. ^1H NMR ($CDCl_3$) δ: 7.65, 7.38 (d, m, *J* = 1.6 Hz, 6H, 3,5-H pz), 7.18 (m, 2H, C_6H_4), 6.32 (d of d, 3H, J_{HH} = 2.5, 4-H pz), 5.07 (s, 2H, O*CH*$_2$Ph), 4.44 (s, 2H, O*CH*$_2$C(pz)$_3$). Anal. Calcd for $C_{30}H_{30}N_{12}O_2$: C, 60.96; H, 5.08; N, 28.45. Found: C, 61.06; H, 4.98, N, 28.70.

***m*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (2).** The ligand was synthesized as above for **1** using α,α′-dibromo-*m*-xylene, *m*-$(BrCH_2)_2C_6H_4$. The removal of the solvent under vacuum afforded a white oil. All attempts to crystallize this oil failed (4.97 g, 8.4 mol, 84%). This oil was used in the synthesis of metal complexes as a THF solution (1.32 g of ligand in 100 mL of THF). ^1H NMR: ($CDCl_3$) δ: 7.65, 7.42 (br, m, 6H, 3,5-H pz), 7.10 (m, 2H, C_6H_4), 6.33 (m, 3H, 4-H pz), 5.11 (s, 2H, O*CH*$_2$Ph), 4.48 (s, 2H, O*CH*$_2$C(pz)$_3$). Accurate ES$^+$/MS calcd for M + H, $[C_{30}H_{30}N_{12}O_2 + H]^+$, 591.2693, found, 591.2692.

***p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (3).** The ligand was synthesized as above for **1** using α,α′-dibromo-*p*-xylene, *p*-$(BrCH_2)_2C_6H_4$. The solvent was removed under vacuum affording the desired compound as a white-yellow powder (5.56 g, 9.4 mmol, 94%,); mp 145−146 °C. Crystals suitable for the X-ray analysis were grown by layering a methylene dichloride solution of the ligand with hexanes. ^1H NMR (CD_3CN) δ: 7.65, 7.42 (d, m, *J* = 1.7 Hz, 6H, 3,5-H pz), 7.12 (m, 2H, C_6H_4), 6.11 (d of d, *J* = 2.5 Hz, 3H, 4-H pz), 5.11 (s, 2H, O*CH*$_2$Ph), 4.48 (s, 2H, O*CH*$_2$C(pz)$_3$). Anal. Calcd for $C_{30}H_{30}N_{12}O_2$: C, 60.96; H, 5.08; N, 28.45. Found: C, 60.87; H, 5.05, N, 28.76.

{*o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (4). A solution of *o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (0.15 g, 0.25 mmol) in acetone (15 mL) was cannula filtered into a solution containing $[Cd_2(THF)_5][BF_4]_4$ (0.24 g, 0.25 mmol) in acetone (15 mL). Upon stirring for 1 h a white precipitate formed. The solution was filtered to leave a white solid (0.18 g, 82%); mp = 185−187 °C. Crystals suitable for the X-ray analysis were grown by vapor diffusion of ether into an acetonitrile solution of the polymer. ^1H NMR (CD_3CN) δ: 7.79, 7.60 (s, 6H, 3,5-H pz), 7.27 (m, 2H, C_6H_4), 6.49 (br, 3H, 4-H pz), 4.92 (s, 2H, O*CH*$_2$Ph), 4.43 (s, 2H, O*CH*$_2$C(pz)$_3$). Accurate ES$^+$/MS calcd for $\{[C_{30}H_{30}N_{12}O_2Cd][BF_4]\}^+$, 791.1690, found, 791.1711.

{*m*-$C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (5). This complex was prepared as above for **4** using *m*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (0.15 g, 0.25 mmol) and $[Cd_2(THF)_5][BF_4]_2$ (0.24 g, 0.25 mmol) to yield a white solid (0.17 g, 81%); mp = 179−184 °C. Crystals suitable for the X-ray analysis were grown by vapor diffusion of ether into an acetonitrile solution of the polymer. ^1H NMR (CD_3CN) δ: 7.69 (br, 6H, 3,5-H, pz), 7.22 (m, 2H, C_6H_4) 6.41 (br, 3H, 4-H pz), 5.04 (s, 2H, O*CH*$_2$Ph), 4.61 (s, 2H, O*CH*$_2$C(pz)$_3$). Accurate ES$^+$/MS calcd for $\{[C_{30}H_{30}N_{12}O_2Cd][BF_4]\}^+$, 791.1690, found, 791.1698.

{*p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (6). This complex was prepared as above for **4** using *p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (0.15 g, 0.25 mmol) and $[Cd_2(THF)_5][BF_4]_4$ (0.24 g, 0.25 mmol) to yield a white solid (0.15 g, 71%); mp = 146−154 °C. Crystals suitable for the X-ray analysis were grown by vapor diffusion of ether into an acetonitrile solution of the polymer. ^1H NMR (CD_3CN) δ: 7.71 (br, 6H, 3,5-H pz), 7.22 (m, 2H, C_6H_4) 6.42 (br, 3H, 4-H pz), 5.04 (s, 2H, O*CH*$_2$Ph), 4.61 (s, 2H, O*CH*$_2$C(pz)$_3$). Accurate ES$^+$/MS calcd for $\{[C_{30}H_{30}N_{12}O_2Cd][BF_4]\}^+$, 791.1690, found, 791.1694.

X-ray Structure Determinations for 1, 3, 4, 5, and 6. Crystal, data collection, and refinement parameters for **1**, **3**, **4**, and **6** are collected in Table 1. Colorless crystals of **1** and **3** were epoxied onto the end of a thin glass fiber. X-ray intensity data were measured at 293 K. Colorless crystals of **4**, **5**, and **6** were coated in inert oil on the end of a thin glass fiber and quickly transferred to the cold stream. X-ray intensity data were measured at 200 K for **4**, 173 K for **5**, and 210 K for **6**. X-ray intensity data were collected on a Bruker SMART APEX CCD-based diffractometer system using Mo Kα radiation (λ = 0.71073 Å). Crystal quality and unit cell parameters were initially determined based on reflections harvested from a set of three scans measured in orthogonal wedges of reciprocal space. Subsequently, a hemisphere of data was collected with a scan width of 0.3° in ω and an exposure time of 10 s per frame. The first 50 frames were recollected at the end of data set to monitor crystal decay. The raw data frames were integrated with the SAINT+ program using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied by SAINT. Analysis of the data showed negligible crystal decay during data collections.

Systematic absences in the data for **1** and **3** were consistent with the space group *P*2(1)/*n*. The compounds possess no crystallographically imposed symmetry, as all atoms are on general positions. No correction for absorption was applied to either solution. Compound **4** crystallizes in the triclinic space group $P\bar{1}$. The unit cell contains two crystallographically inequivalent cadmium atoms per asymmetric unit, both of which are located on inversion centers. The ligand, BF_4^- counterions and two acetonitrile molecules of crystallization are located on general positions. All non-hydrogen atoms were refined with anisotropic displacement parameters except for one acetonitrile molecule, which

Table 2. Selected Bond Distances (Å) and Angles (deg) for o-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (**1**) and p-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (**3**)

	selected bond distances (Å)	
	1	**3**
C(1)−N(12)	1.447(2)	1.465(2)
C(1)−N(22)	1.449(2)	1.457(2)
C(1)−N(32)	1.450(2)	1.4553(19)
C(2)−N(42)	1.450(2)	
C(2)−N(52)	1.458(2)	
C(2)−N(62)	1.458(2)	
N(11)−N(12)	1.348(2)	1.350(2)
N(21)−N(22)	1.346(2)	1.350(2)
N(31)−N(32)	1.349(2)	1.346(2)
N(41)−N(42)	1.352(2)	
N(51)−N(52)	1.351(2)	
N(61)−N(62)	1.343(2)	

	selected bond angles (deg)	
	1	**3**
N(12)−C(1)−N(22)	108.43(15)	107.98(13)
N(12)−C(1)−N(32)	108.00(14)	108.86(13)
N(22)−C(1)−N(32)	108.85(13)	108.26(13)
N(42)−C(2)−N(52)	109.33(16)	
N(42)−C(2)−N(62)	107.81(15)	
N(52)−C(2)−N(62)	109.12(15)	

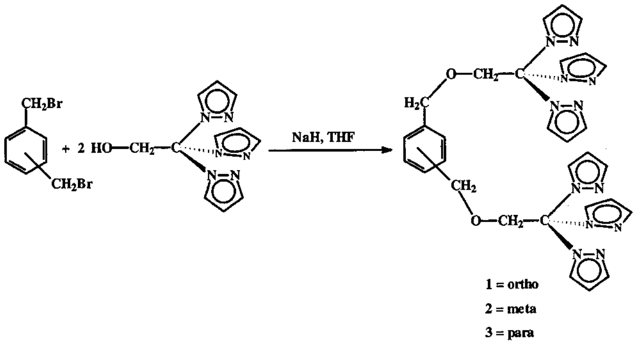
was refined with isotropic displacement parameters due to unstable thermal motion. All lattice parameters are based on the least-squares refinement of all data with $I > 5(\sigma)I$. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with the program SADABS. Systematic absences in the intensity data for **5** were uniquely consistent with the noncentrosymmetric space group $P\bar{4}2_1c$. E-statistics also indicated a noncentrosymmetric space group. A chemically reasonable apparent solution was obtained readily in this space group by a combination of direct methods and difference Fourier syntheses, which identified a cadmium atom bound octahedrally into an infinite one-dimensional chain by two crystallographically equivalent m-$C_{30}H_{30}N_{12}O_2$ ligands, the BF_4^- counterions, and two solvent molecules (Et_2O and CH_3CN). At this point, however, problems in the refinement of the initial model were encountered. A very large electron density peak of 4.5 $e^-/Å^3$ (ca 4.5 times larger than the next-highest peak) was observed in the Fourier difference map, located ca. 1 Å from the Cd center, as well as some slight irregularities in pyrazolyl ring geometry in the vicinity of this peak. After the application of a number of different absorption corrections (face-indexed, SADABS, none) failed to alleviate the situation, several different space groups and/or twinning models were attempted. Although chemically reasonable solutions could be found in numerous lower symmetry space groups, including many that allow for the possibility of twinning by merohedry or for pseudo-tetragonal orthorhombic twinning (i.e. $P4_2/m$, $P4_2$, $P\bar{4}$, $Ccc2$, $P2_12_12$, etc.), the same large residual electron density peak was observed at the same position even after application of the various twin laws. In addition, large correlations, unstable refinements, and high R-factors resulted. Also, the same phenomenon was duplicated in multiple crystals from different reactions. The origin of the large electron density peak remains unclear, and though the overall structural features are reliable, subtler geometric details are obviously less accurate. Compound **6** crystallizes in the monoclinic space group $C2/c$. The cadmium atom and the centroid of the ligand phenyl ring are both located on inversion centers. The BF_4^- counterions and two acetonitrile molecules of crystallization are located on general positions. Another acetonitrile is located on a 2-fold rotation axis. The structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares against F^2, using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters; the hydrogen atoms could be located by Fourier difference synthesis, but were placed in idealized positions and refined with isotropic displacement parameters, using a riding model. All computations were made using SHELXTL NT 5.10 and SADABS software (G. Sheldrick, Bruker AXS, Madison, WI).

Results and Discussion

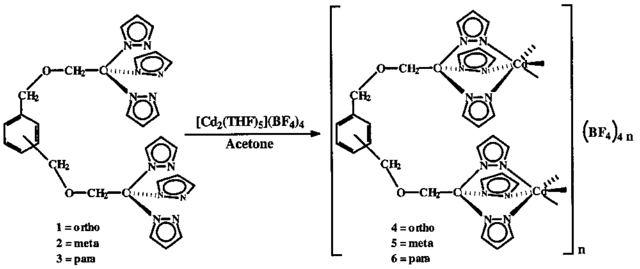
Ligand Design. The ligands $C_6H_4[CH_2OCH_2C(pz)_3]_2$ (pz = pyrazolyl ring), **1** (*ortho*), **2** (*meta*), and **3** (*para*) (see Scheme 1) have special features: *a:* the rigid architecture of facial bonding is encoded in each tris(pyrazolyl)methane group; *b:* the different positions of the ether sidearms on the arene ring (1,2-, 1,3-, and 1,4-) induce different orientations of the binding groups, but the length of the connecting chains introduces flexibility into each; *c*: molecular mechanics calculations show the overall length and structure of the xylene-based bridge prevent simultaneous coordination of both sides of one metal center for the *meta* and *para* cases, but do not rule out such coordination for the *ortho* ligand. Therefore, for any given metal ion type bonding to these three ligands, made from linked, tridentate tris(pyrazolyl)methane units, a specific but different orientation is expected, leading to coordination polymers with different supramolecular structures.

Syntheses of Ligands. Starting from $HOCH_2Cpz_3$, prepared in high yield as reported previously,[6c] all three ligands were obtained in a single step (Scheme 1). The appropriate dibromoxylene and 2 equiv of tris-2,2,2-(1-pyrazolyl)ethanol were dissolved in THF, and this solution was added to a suspension of excess NaH in THF. High yields of the desired products in pure form were obtained without the need for chromatography or recrystallization. The *meta* derivative **2** is an oil that could not be crystallized. In a reaction in which the tris-2,2,2-(1-pyrazolyl)ethanol was mixed with NaH, followed by reaction with dibromoxylenes, the desired ligands were difficult to isolate in pure form.

Scheme 1



Scheme 2



Syntheses of Complexes. The reaction of $[Cd_2(THF)_5][BF_4]_4$ with the appropriate ligand yields each of the three coordination polymers of the formula $\{C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$, **4** (*ortho*), **5** (*meta*), and **6** (*para*) (Scheme 2).

The compounds are insoluble in acetone and precipitate from the reaction. They are soluble in acetonitrile and dimethylformamide and are air stable. ^1H NMR spectra run in acetonitrile-d_3 are clearly different from the free ligand in this solvent

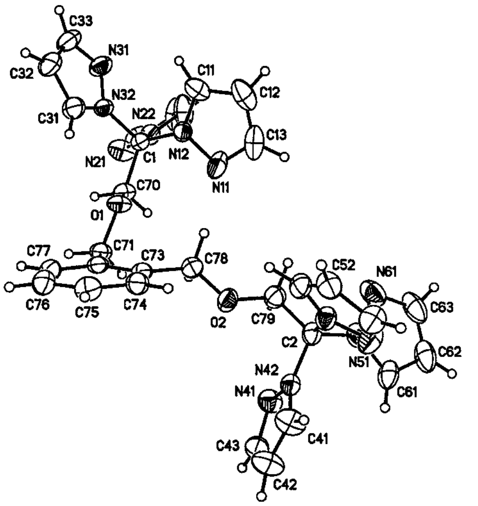


Figure 1. ORTEP diagram of *o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (50% ellipsoids).

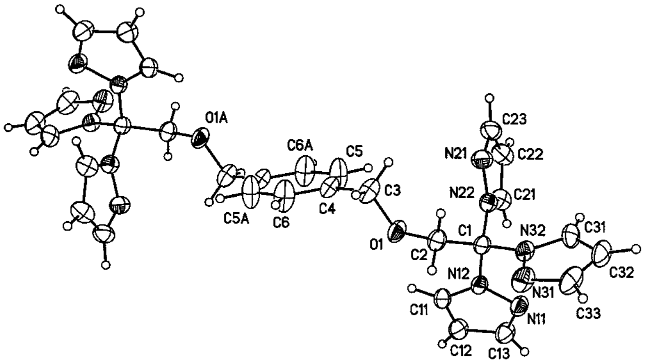


Figure 2. ORTEP diagram of *p*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$ (50% ellipsoids).

showing that the acetonitrile does not displace the tris(pyrazolyl)methane ligand when the polymer dissolves. High-resolution electrospray mass spectroscopy shows in each case a monocationic cluster for the repeating unit of the polymer, $\{C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)\}^+$.

Solid-State Structures. The molecular structures of ligands **1** and **3**, together with the crystallographic numbering schemes are presented in Figures 1 and 2 and selected bond distances and angles are given in Table 2. The ligand structures consist of discrete molecules without significant intermolecular associations. The orientation of the three pyrazolyl rings is a propeller arrangement with only one of the donor nitrogen atoms oriented toward the potential bonding "pocket" of the ligand. However, the orientation of the sidearms in the two structures is different. In the case of **1** the two ether linkages and tris(pyrazolyl)methane units are twisted away from each other with one above and one slightly below the plane of the central phenyl ring. In contrast, **3** adopts a stepped structure with the two ether linkages and tris(pyrazolyl)methane units oriented above and below the plane of the central phenyl ring. All interatomic parameters for the two structures are similar, as expected, making the orientation of the arms the only important difference in the two ligands.

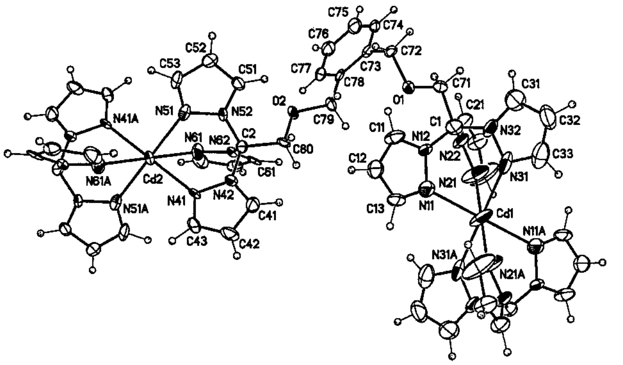


Figure 3. ORTEP diagram of $\{o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n^{n2+}$ showing one ligand linking the two independent cadmium(II) octahedra (50% ellipsoids).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $\{o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (**4**) and $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (**6**)

	bond distances (Å)	
	4	**6**
Cd(1)−N(11)	2.239(8)	2.2783(16)
Cd(1)−N(21)	2.317(10)	2.2820(17)
Cd(1)−N(31)	2.318(11)	2.3271(16)
Cd(2)−N(41)	2.281(8)	
Cd(2)−N(51)	2.263(9)	
Cd(2)−N(61)	2.353(9)	
	selected bond angles (deg)	
	4	**6**
N(11)−Cd(1)−N(21)	78.3(3)	79.52(6)
N(11)−Cd(1)−N(31)	79.6(3)	78.86(6)
N(21)−Cd(1)−N(31)	77.4(4)	77.20(6)
N(41)−Cd(2)−N(51)	79.8(3)	
N(41)−Cd(2)−N(61)	78.4(3)	
N(51)−Cd(2)−N(61)	77.1(3)	
N(11)−Cd(1)−N(11)A	180	180
N(11)−Cd(1)−N(21)A	101.7(3)	100.48(6)
N(11)−Cd(1)−N(31)A	100.4(3)	101.14(6)
N(21)−Cd(1)−N(21)A	180.0(3)	180.0
N(21)−Cd(1)−N(31)A	102.6(4)	102.80(6)
N(31)−Cd(1)−N(31)A	180	180
N(41)−Cd(2)−N(41)B	180	
N(41) −Cd(2)−N(51)B	100.2(3)	
N(41)−Cd(2)−N(61)B	101.6(3)	
N(51)−Cd(2)−N(51)B	180	
N(51)−Cd(2)−N(61))B	102.9(3)	
N(61)−Cd(2)−N(61))B	180	

$\{$***o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2$**$\}_n$ **(4).** A labeled ORTEP diagram of one ligand linking the two independent cadmium(II) in the polymer chain is shown in Figure 3, and selected bond distances and angles are given in Table 3. Both cadmium(II) atoms are located on inversion centers. Each tris(pyrazolyl)methane unit is tridentate, with each ligand bonded to two different cadmium(II) atoms, forming a coordination polymer containing 6-coordinate, pseudooctahedral cadmium(II) centers. The average Cd−N bond distance for Cd(1) is 2.29 Å and for Cd(2) is 2.30 Å with a range in each case of slightly less than 0.1 Å. The chelating pyrazolyl rings restrict the intraligand bond angles to an average of 78.4° for both cadmium centers with a range of 2.2° and 2.7°, respectively. As observed with the free ligand, the two ether linkages and tris(pyrazolyl)methane units are twisted away from each other with one slightly above and one below (as pictured) the plane of the central phenyl ring.

Figure 4 shows a view perpendicular to three adjacent chains of the polymer. Each chain shows an irregular wave-type arrangement with the intrachain Cd(1)···Cd(2) distance of 12.18 Å. The chains are arranged in sheets where the shortest interchain Cd···Cd distances are 10.79 Å between Cd(1)···Cd(1) and Cd(2)···Cd(2) located in adjacent chains. The shortest Cd(1)···Cd(2) interchain distance is 12.42 Å. Figure 5 shows a view parallel to the layers of chains shown in Figure 4. The

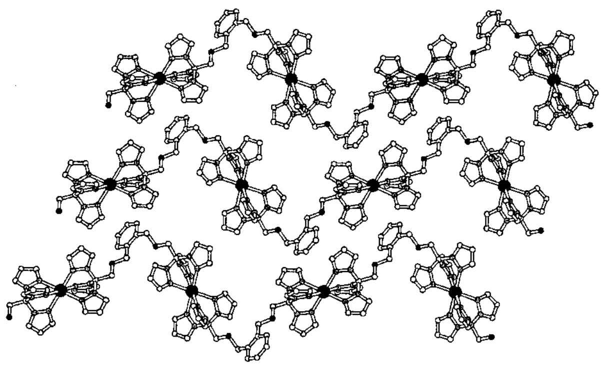


Figure 4. View perpendicular to the sheet formed from three adjacent chains of $\{o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n{}^{n2+}$.

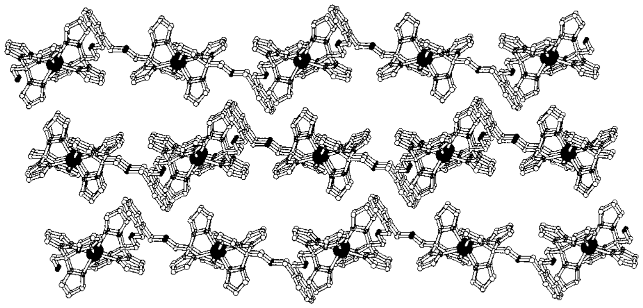


Figure 5. View parallel to the layers of chains shown in Figure 4 of $\{o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n{}^{n2+}$.

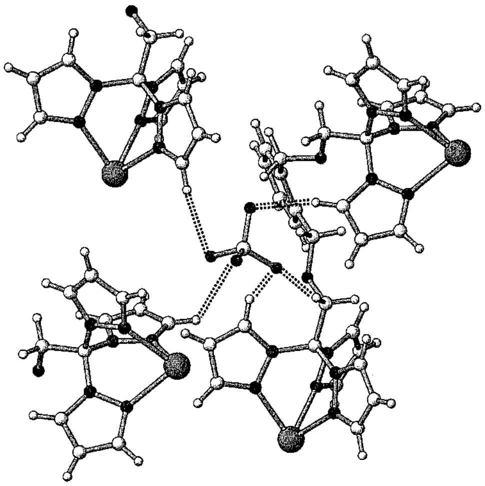


Figure 6. Weak C−H···F hydrogen bonds for $\{o\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n{}^{n2+}$.

layers alternate repeating arrangements with a close Cd(1)···Cd(2) interlayer distance of 9.79 Å.

The organization shown in Figures 4 and 5 is supported by weak C−H···F hydrogen bonds. One of the two BF_4^- counterions in the asymmetric unit makes five C−H···F hydrogen bonds, Figure 6. Three bonds (2.249, 2.285, and 2.405 Å with C−H···F angles of 164.82°, 154.31°, and 135.12°, respectively) are all made to one polymer chain. A fourth bond at 2.435 Å (168.70°) is directed at a polymeric strand within the same sheet and a fifth at 2.431 Å (130.51°) to a third polymeric strand that is located in an adjacent sheet. The average (C)-H···F bond distance of 2.36 Å is significantly shorter than the sum of the van der Waals radii for H and F atoms (2.54 Å),[32] and the bond angles are fairly close to linear, indicative of C−H···F weak hydrogen bonding behavior.[33] The other BF_4^- counterion from the asymmetric unit is involved in only one C−H···F hydrogen bond (2.430 Å distance with an angle of 175.06°).

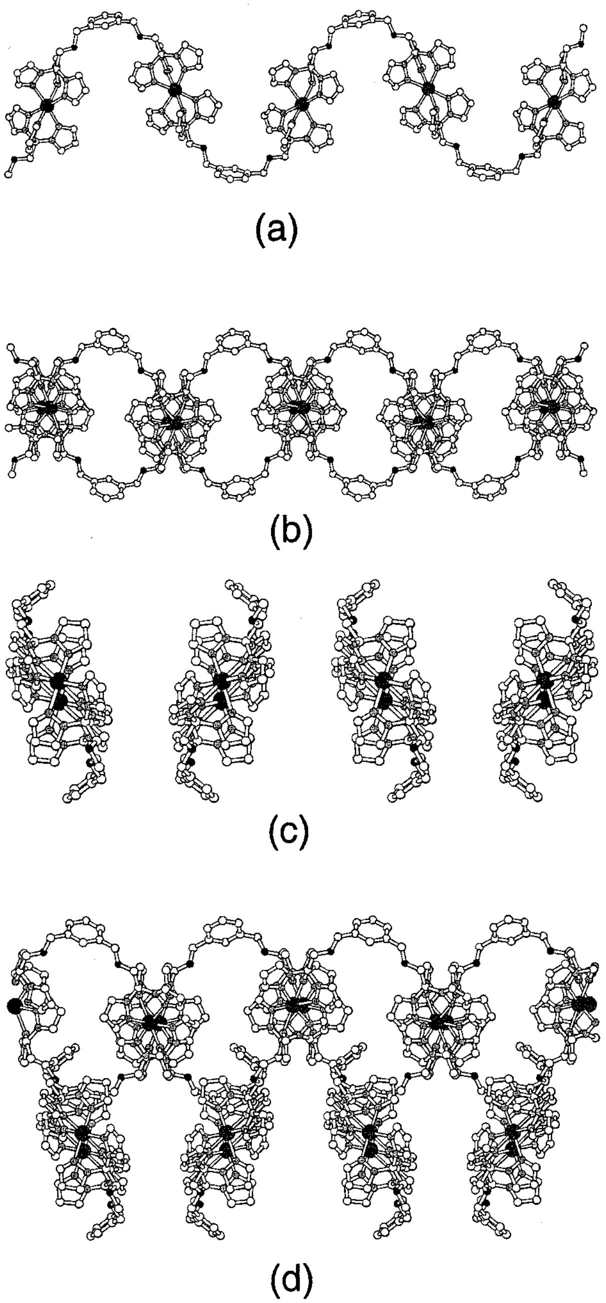


Figure 7. $\{m\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n{}^{n2+}$: (a) View perpendicular to one chain and (b) a similar view with the same orientation as (a) of multiple chains. (c) View along the chain direction for four of the chains. The arrangements in (b) and (c) are related by a 90° rotation, and as shown in (d) they are stacked vertically with respect to each other.

$\{m\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (5). Difficulties were encountered in the final solution of the structure of **5**, but the overall appearance of the polymer chains and supramolecular structure were clearly determined. Figure 7a shows a view perpendicular to the wavelike chain of the polymer. The

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(32) (a) Bondi, A *J. Phys. Chem.* **1964**, *68,* 441. (b) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100,* 7384.

(33) (a) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D.; *Organometallics* **1998**, *17,* 296. (b) Steiner, T.; Desiraju, G. R. *J. Chem. Soc., Chemm. Commun.* **1998**, 891. (c) Mann, K. L. V.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 3029. (d) Paul, R. L.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Reeves, Z. R.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2000**, 845.

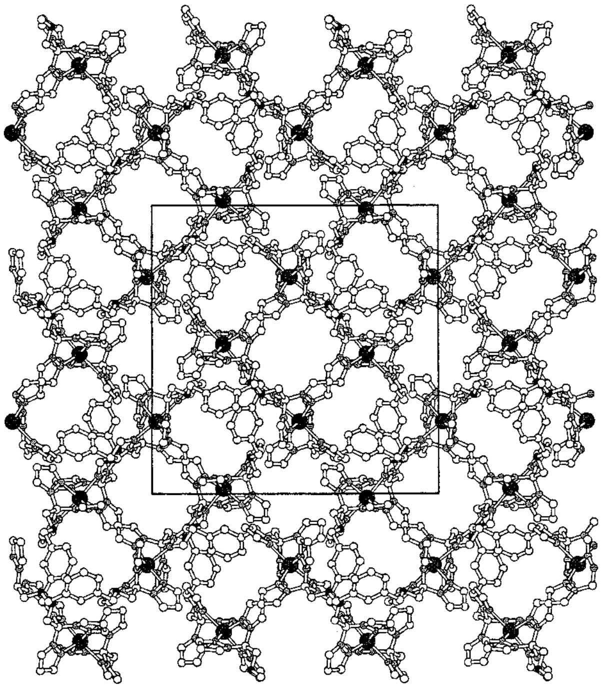

Figure 8. View down the tetragonal *c*-axis, an axis that is vertical to the views in Figure 7 of $\{m\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n^{n2+}$.

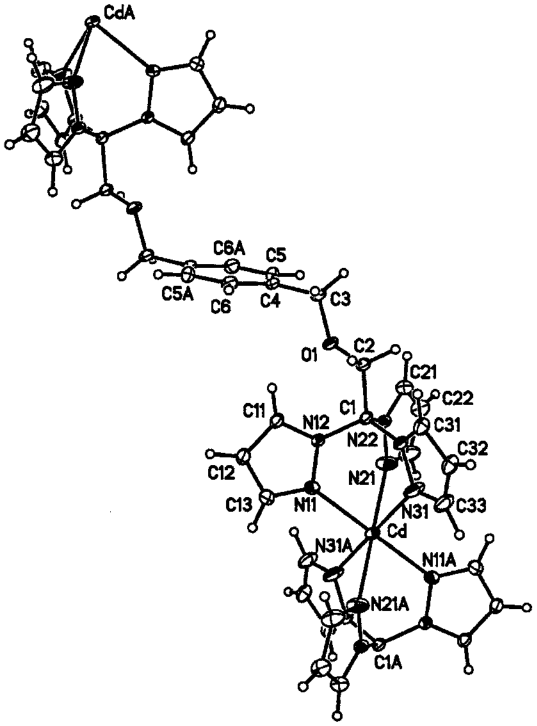

Figure 9. ORTEP diagram of $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n^{n2+}$ showing one ligand linking two equivalent cadmium(II) atoms (50% ellipsoids).

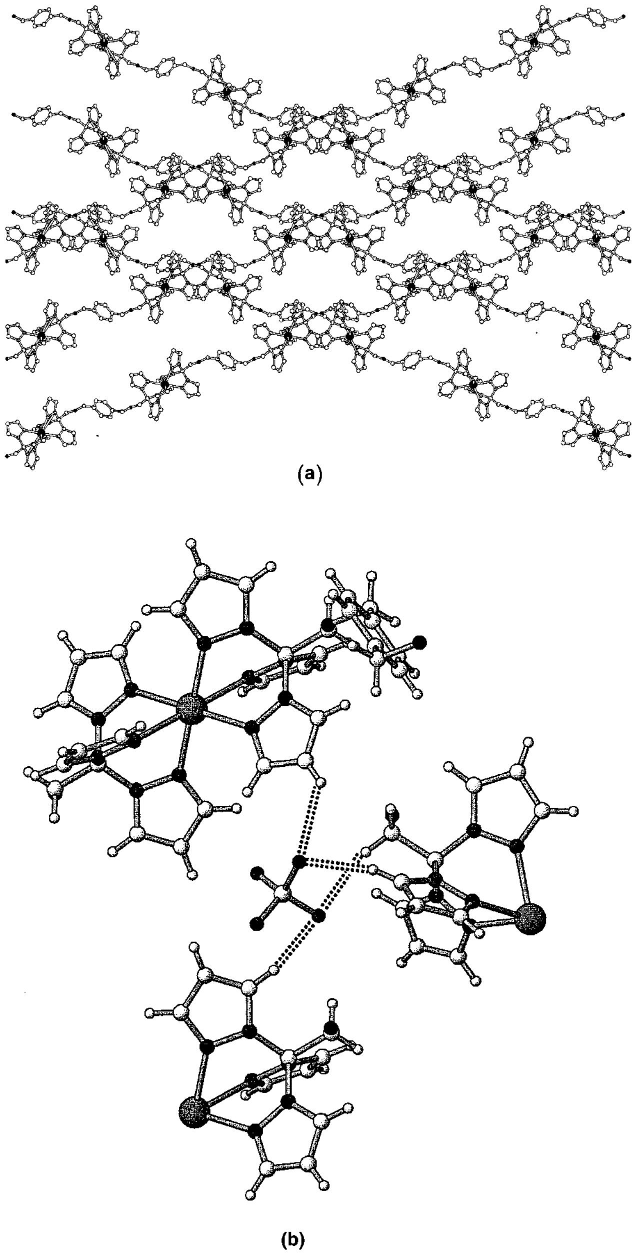

Figure 10. (a) Orientation of sheets and (b) weak C−H···F hydrogen bonds of $\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd\}_n^{n2+}$.

octahedral cadmium(II) units are both located on the same side of the linking phenyl group. As shown in Figure 7b, a view with the same orientation as 7a, the orientation of these chains within successive layers alternate forming cavities surrounded on two opposite sides by the phenyl groups and the other two sides by the octahedral cadmium(II) groups. Figure 7c shows a view along the chain direction for four of the chains emphasizing the face-to-face orientation of adjacent chains. As with the structure of **4**, each chain has an oval shape. The arrangements in 7b and 7c are related by a 90° rotation, and as shown in Figure 7d they are stacked vertically with respect to each other causing these two arrangements to alternate from either orientation. Finally, Figure 8 shows a view down the tetragonal *c*-axis, an axis that is vertical to the views in Figure 7. Two types of cavities are formed. The larger cavities are 7 by 6 Å^2 and the smaller cavities are 7 by 4 Å^2. The larger cavities are filled by the BF_4^- counterions that are presumably organizing the supramolecular structure through weak C−H···F hydrogen bonds.

$\{p\text{-}C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$ (6). An ORTEP diagram of one ligand linking two equivalent cadmium(II) atoms in the polymer chain is shown in Figure 9, and selected bond distances and angles are given in Table 3. The structure is centrosymmetric with inversion centers located in the center of each phenyl ring and at the unique cadmium(II) locations. Each tris(pyrazolyl)methane unit is tridentate, with each ligand bonded to two different cadmium(II) atoms, forming a coordination polymer containing 6-coordinate, pseudooctahedral cadmium(II) centers. The average Cd−N bond distance is 2.29 Å, the same as observed with **4**. The chelating pyrazolyl rings restrict the intraligand bond angles to 78.5°.

Figure 10a shows the polymers chains form a stepped structure, analogous to that seen for the free ligand, with one cadmium group above and one below the phenyl rings. The intrachain Cd···Cd distance is very long at 16.79 Å. The chains are arranged in sheets with the closest interchain Cd···Cd distance of 12.86 Å. In the supramolecular structure the sheets are angled at 42.6° with respect to each other. There are close intersheet Cd···Cd distances of 9.06 Å where the octahedral cadmium(II) groups nearly intersect. Figure 10b, with an orientation similar to that in 10a, shows that the BF_4^- groups through weak C−H···F hydrogen bonds organize this structure. Each BF_4^- group makes bonds of 2.371 and 2.506 Å, with the corresponding angles of 158.12° and 115.99°, to two strands within each sheet. It also makes two bonds to a strand in the next sheet of 2.371 and 2.265 Å, with the corresponding angles of 158.12° and 161.88°.

Conclusions

Three new ligands of the formula *ortho*-, *meta*-, and *para*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$, ligands that link together two tris(pyrazolyl)methane units, have been prepared based on a central phenyl ring and flexible ether linkages. The architecture of the new ligands is very different from other linking ligands used to prepare coordination polymers. The orientations of the two ether linkages and tris(pyrazolyl)methane units in the solid-state structures of the *ortho* and *para* ligands are very different. Reactions of these ligands with $[Cd_2(THF)_5][BF_4]_4$ yields each of the three coordination polymers of the formula $\{C_6H_4[CH_2OCH_2C(pz)_3]_2Cd(BF_4)_2\}_n$. The supramolecular structures of each of these coordination polymers, organized by the BF_4^- groups through weak C−H···F hydrogen bonds, are very different from each other demonstrating that these structures can be controlled by choice of ligand. Results of reactions of these ligands with other metal centers will be reported elsewhere.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **1**, **3**, **4**, and **6** are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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