

Solvent Control in the Synthesis of 3,6-Bis(pyridin-3-yl)-1,2,4,5-tetrazine-Bridged Cadmium(II) and Zinc(II) Coordination Polymers

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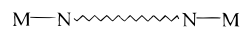
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The reaction of cadmium(II) and zinc(II) salts with 3,6-bis(pyridin-3-yl)-1,2,4,5-tetrazine (3,3'-pytz) affords coordination polymers, the structures of which are controlled by the choice of alcoholic solvent. Reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 3,3'-pytz in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ yields the 1:1 ligand/metal complex $\{[\text{Cd}(\mu\text{-}3,3'\text{-pytz})(\text{NO}_3)_2(\text{MeOH})_2]\}_\infty$, **1** [triclinic space group $P\bar{1}$; $a = 9.011(2)$ Å, $b = 9.338(4)$ Å, $c = 11.941(2)$ Å, $\alpha = 74.51(3)^\circ$, $\beta = 86.94(4)^\circ$, $\gamma = 86.50(5)^\circ$; $Z = 2$]. Replacement of MeOH with EtOH or $i\text{PrOH}$ in the above reaction affords respectively the 3:2 ligand/metal complexes $\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{EtOH})\}_\infty$, **2** [triclinic, space group $P\bar{1}$; $a = 9.060(4)$ Å, $b = 9.848(3)$ Å, $c = 13.208(4)$ Å, $\alpha = 86.76(3)^\circ$, $\beta = 79.04(3)^\circ$, $\gamma = 88.14(2)^\circ$; $Z = 2$] and $\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{CH}_2\text{Cl}_2)\}_\infty$, **3** [triclinic space group $P\bar{1}$; $a = 8.981(16)$ Å, $b = 9.93(2)$ Å, $c = 13.19(2)$ Å, $\alpha = 94.18(15)^\circ$, $\beta = 102.35(13)^\circ$, $\gamma = 88.12(15)^\circ$; $Z = 2$]. Complex **1** exhibits a zigzag chain polymer motif, whereas complexes **2** and **3** show noninterpenetrated ladder structures. Reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3,3'-pytz in MeOH or $\text{EtOH}/\text{CH}_2\text{Cl}_2$ solution affords a 3:2 ligand/metal complex $\{[\text{Zn}_2(3,3'\text{-pytz})_2(\text{NO}_3)_4(\text{ROH})_2(\mu\text{-}3,3'\text{-pytz})]\}_\infty$, **4** [$\text{R} = \text{Me}$; triclinic, space group $P\bar{1}$; $a = 7.5346(12)$ Å, $b = 10.7279(13)$ Å, $c = 15.219(2)$ Å, $\alpha = 85.364(11)^\circ$, $\beta = 80.627(12)^\circ$, $\gamma = 69.343(12)^\circ$; $Z = 2$] and **5** [$\text{R} = \text{Et}$; triclinic, space group $P\bar{1}$; $a = 7.590(3)$ Å, $b = 10.561(2)$ Å, $c = 15.951(5)$ Å, $\alpha = 87.56(2)^\circ$, $\beta = 83.49(4)^\circ$, $\gamma = 71.12(2)^\circ$; $Z = 2$]. The reaction in $i\text{PrOH}/\text{CH}_2\text{Cl}_2$ results in a 3:2 ligand/metal complex $\{[\text{Zn}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{CH}_2\text{Cl}_2)_2\}_\infty$, **6** [triclinic, space group $P\bar{1}$; $a = 9.1110(18)$ Å, $b = 12.474(3)$ Å, $c = 13.171(3)$ Å, $\alpha = 117.79(3)^\circ$, $\beta = 102.39(3)^\circ$, $\gamma = 101.13(3)^\circ$; $Z = 2$]. The isostructural complexes **4** and **5** both exhibit a unique hydrogen-bonding motif in coordination polymer chemistry which gives rise to an alternating single- and double-bridged species, whereas **6** exists as a noninterpenetrated ladder complex.

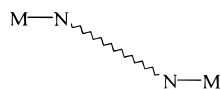
Introduction

The formation of inorganic coordination polymers using bridging bidentate ligands with late transition metals has recently received much attention.¹ Using a "building block" methodology, combination of linear 4,4'-bipyridyl-based ligands (Chart 1) and metal ions has produced a wide variety of solid-state architectures.^{1,2} Adamantoid,^{3–6} grid,^{2,7–11} "brickwall",¹² ladder,^{12–16} honeycomb,¹⁷ and "helical staircase"¹⁸ motifs have

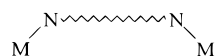
Chart 1. Possible Bridge Architectures with 4,4'- and 3,3'-N Donor Systems



(a) Linear formed by 4,4'-N donor ligand bridges



(b) *Transoid* formed by 3,3'-N donor ligands giving an "off axis rod" bridge



(c) *Cisoid* bridge formed by 3,3'-N donor ligands

been produced using ligands such as 4,4'-bipyridine (4,4'-bipy),^{3,5,7–11,14,17} 1,2-*trans*-bis(pyridin-4-yl)ethene (bpe),⁴ 2,7-diazapyrene (dap),⁶ 3,6-bis(pyridin-4-yl)-1,2,4,5-tetrazine (4,4'-

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pytz),¹⁸ and 1,4-bis(pyridin-4-yl)butadiene (pybut).¹³ For these reported complexes, the choice and role of metal ion, ligand functionality, anion, and solvent is crucial to the type of architecture observed.

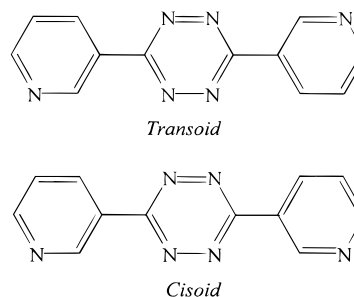
The effect of ligand functionality is illustrated by the control of the degree of interpenetration within Cu(I) adamantoid systems,^{3,4,6} the volume of each adamantoid unit and hence the degree of interpenetration being dependent upon the length and steric interactions of the bridging ligand. Thus, increasing the length of the bridging ligand increases the degree of interpenetration. In the complex $\{[\text{Cu}(\text{dap})_2]\text{PF}_6\}_\infty$,⁶ 3-fold interpenetration is observed and the Cu...Cu distance along the edge of the adamantane unit is 10.91 Å. The complex $\{[\text{Cu}(4,4'\text{-bipy})_2]\text{BF}_4\}_\infty$ has a longer Cu...Cu separation of 11.16 Å and therefore exhibits a greater 4-fold interpenetration of symmetry-related adamantoid lattices.³ When the adamantoid Cu...Cu separation is further increased to 13.55 Å in the complex $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_\infty$,⁴ the degree of interpenetration increases to 5-fold.

Anion control has been reported for the coordination polymers of Ag(I) with 4,4'-pytz,¹⁸ where the observed structures are dependent upon weak Ag(I)...nitrate interactions. The NO₃⁻ anion possesses 3-fold symmetry, and the complex $\{[\text{Ag}(4,4'\text{-pytz})\text{NO}_3]\}_\infty$ forms chains with interactions between Ag(I) and NO₃⁻ ions to give a templated helical staircase motif with 6-fold symmetry. In contrast, in the presence of the anions BF₄⁻ and PF₆⁻ the complexes $\{[\text{Ag}(4,4'\text{-pytz})(\text{MeCN})\text{X}]\}_\infty$ (X = BF₄⁻, PF₆⁻) exist as pairs of chains, each Ag(I) interacting weakly with each anion.

The influence of solvent in the formation of coordination polymers is less well understood and *systematic* studies are rare. However, it is clear that the ability of the solvent to act as ligand can dramatically affect the extended structure of the network. This is illustrated by the products of the reaction of ZnSiF₆ with 4,4'-bipy which show a marked dependence upon the presence of water, a coordinating solvent.^{7,8} If the reaction is carried out in water, then the complex formed $\{[\text{Zn}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]\text{SiF}_6\}_\infty$ ⁷ exhibits an interpenetrated square grid structure. However in anhydrous DMF, the complex $\{[\text{Zn}(4,4'\text{-bipy})_2\text{SiF}_6 \cdot x\text{DMF}]\}_\infty$ is formed which exhibits noninterpenetrated square $[\text{Zn}(4,4'\text{-bipy})_2]_\infty$ grids cross-linked by bridging, weakly coordinated SiF₆²⁻ ions.⁸ Similarly the reaction of Co(SCN)₂ with 4,4'-bipy¹⁰ yields products whose structure is dependent on the presence of water. $[\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_2(4,4'\text{-bipy}) \cdot 4,4'\text{-bipy}]_\infty$ can be isolated in the presence of water in which the complex forms $[\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_2(4,4'\text{-bipy})]_\infty$ chains with each Co(II) center coordinated by two 4,4'-bipy ligands, two NCS⁻ ligands, and two water molecules. These chains are then linked by hydrogen-bonded 4,4'-bipy groups. In the absence of water, the reaction between Co(SCN)₂ and 4,4'-bipy affords a square grid structure, $[\text{Co}(\text{NCS})_2(4,4'\text{-bipy})_2]_\infty$, in which each Co(II) center is coordinated by four bridging 4,4'-bipy ligands and two NCS⁻ ligands.

Direct coordination to metal centres is not the only role of solvent, and indeed extremely subtle templating effects have also been observed. This is illustrated by the three modifications of $\{[\text{Co}_2(\text{NO}_3)_4(\mu\text{-}1,2\text{-bis}(\text{pyridin-4-yl})\text{ethane})_3]\}_\infty$,¹⁵ the principal structural difference lying in the conformations of the ligands. The complexes crystallized from MeOH/CHCl₃, MeOH/MeCN, and MeOH/MeCN containing ferrocene, show three anti bridges, two gauche and one anti bridges, and one gauche and two anti bridges, respectively. The change in ligand conformations in

Chart 2. Alternative Conformations of 3,3'-pytz



turn gives rise to different extended structures of these coordination polymers.

In contrast to the well-developed linear 4,4'-N-donor bridges listed above, 3,3'-N-donor ligands such as 3,3'-bipyridine (3,3'-bipy),¹⁹ 3,3'-dicyanodiphenylacetylene (dcpa),²⁰ and 3,6-bis(imidazol-1-yl)pyridazine (bimpydz)²¹ are still relatively unusual. These ligands are of particular interest owing to their potential to generate cisoid and transoid isomers and hence, in the latter case, to act as "off-axis rods"²⁰ (Chart 1). This is the case for the adamantoid complexes $\{[\text{Cu}(3,3'\text{-bipy})_2]\text{X}\}_\infty$ (X = BF₄⁻, PF₆⁻) where only transoid isomers of the ligand are observed.¹⁹ Cisoid and transoid isomers have been reported for dcpa complexes of Ag(I);²⁰ the cisoid isomer is formed in $\{[\text{Ag}(\text{dcpa})_2]\text{XF}_6\}_\infty$ (X = P, As, Sb) with the transoid isomer being observed in $\{[\text{Ag}(\text{dcpa})\text{CF}_3\text{SO}_3]\text{C}_6\text{H}_6\}_\infty$, $\{[\text{Ag}_2(\text{dcpa})(\text{CF}_3\text{SO}_3)_2]\}_\infty$, and $\{[\text{Ag}(\text{dcpa})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}\}_\infty$. The ligand bimpydz displays both cisoid and transoid isomers in binuclear Cu(II) systems.²¹ The complex $\{[\text{Cu}(\text{dien})_2(\mu\text{-bimpydz})][\text{NO}_3]_4$ (dien = diethylenetriamine) displays a Cu...Cu separation of 13.28 Å with transoid-oriented imidazoles, while the complex $\{[\text{Cu}(\text{dien})_2(\mu\text{-bimpydz})][\text{NO}_2][\text{BF}_4]_3 \cdot 0.5\text{MeCN}\}$ has a Cu...Cu separation of 12.88 Å with cisoid-oriented imidazoles. We report herein the use of 3,6-bis(pyridin-3-yl)-1,2,4,5-tetrazine (3,3'-pytz) as a building block ligand (Chart 2).

To develop further our understanding of supramolecular architecture construction, we have studied the roles of solvent as well as metal cation in complex formation with 3,3'-pytz bridging ligands. We thus report the crystallization, from a homologous series of alcohols, and structural characterization, by single crystal X-ray diffraction methods, of a series of three seven-coordinate Cd(II) complexes and a series of three six-coordinate Zn(II) complexes. In each case, the ligand (3,3'-pytz) and the anion (NO₃⁻) are kept constant. The only parameters which are varied are the metal ion [Cd(II) or Zn(II)] and the crystallization medium (MeOH/CH₂Cl₂, EtOH/CH₂Cl₂, or *i*PrOH/CH₂Cl₂).

Results and Discussion

Cadmium(II) Complexes of 3,3'-pytz. A bulk sample of the 1:1 ligand/metal complex $\{[\text{Cd}(\mu\text{-}3,3'\text{-pytz})(\text{NO}_3)_2(\text{MeOH})_2]\}_\infty$ (**1**) can be isolated using 1:1, 3:2, or 2:1 ligand/metal reaction stoichiometries in a CH₂Cl₂/MeOH solution. X-ray powder diffraction studies confirmed the formation of a single crystalline product which was initially identified by infrared spectroscopy and elemental analysis. Subsequently, single crystals of **1** were

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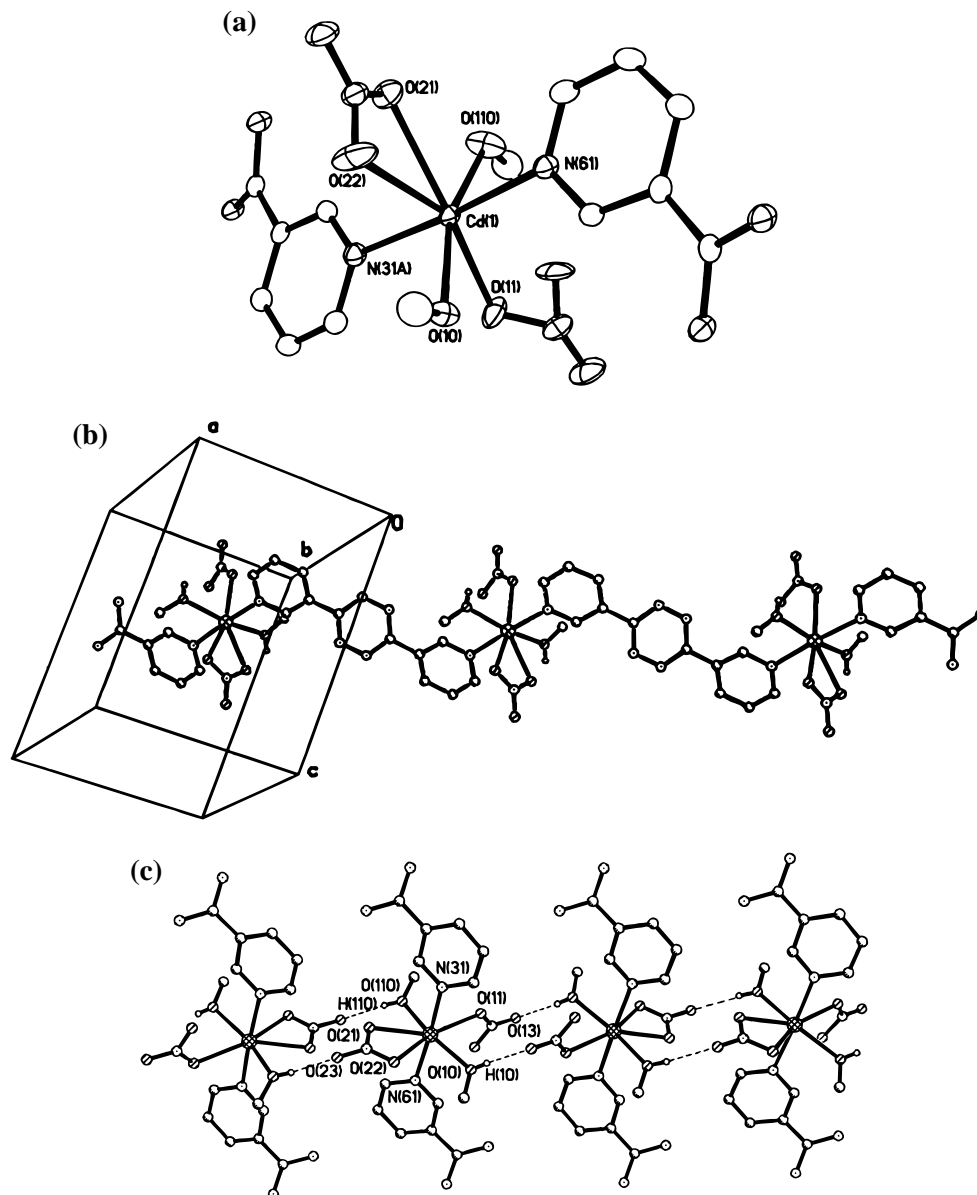


Figure 1. Cadmium coordination geometry (a) (displacement ellipsoids drawn at 50% probability), zigzag chain construction (b), and interchain hydrogen-bonding interactions (c) of $\{[\text{Cd}(\mu\text{-}3,3'\text{-pytz})(\text{NO}_3)_2(\text{MeOH})_2]\}_\infty$ (**1**).

prepared at the interface of layered solutions of 3,3'-pytz in CH_2Cl_2 and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in MeOH. X-ray powder diffraction on the bulk sample showed it to be identical to the single crystal used for structure determination. Similar procedures were employed for the production of single crystal and bulk specimens of the 3:2 ligand/metal complex $\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{EtOH})\}_\infty$ (**2**), the only difference being the replacement of MeOH by EtOH. A crystalline sample of the 3:2 ligand/metal complex $\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{CH}_2\text{Cl}_2)\}_\infty$ (**3**) was prepared at the interface of layered $^i\text{PrOH}$ and CH_2Cl_2 solutions using a 2:1 ligand/metal ratio only. The chain structure of **1** and the ladder structures of **2** and **3** are shown in Figures 1 and 2, and selected interatomic distances and angles are quoted in Table 1.

The structures of all three complexes are based on seven-coordinate (distorted pentagonal bipyramidal) cadmium(II). In $\{[\text{Cd}(\mu\text{-}3,3'\text{-pytz})(\text{NO}_3)_2(\text{MeOH})_2]\}_\infty$ (**1**) the Cd(II) ions are bridged by transoid 3,3'-pytz ligands [$\text{Cd}-\text{N} = 2.289(1), 2.303(1) \text{ \AA}$] to give a 1:1 ligand/metal infinite polymeric zigzag chain [$\text{Cd}\cdots\text{Cd} = 13.367(1) \text{ \AA}$; Figure 1]. The coordination sphere at Cd(II) is completed by one asymmetrically bidentate

nitrate [$\text{Cd}-\text{O} = 2.465(1), 2.618(1) \text{ \AA}$], one monodentate nitrate [$\text{Cd}-\text{O} = 2.371(2) \text{ \AA}$], and two methanol molecules [$\text{Cd}-\text{O} = 2.347(1), 2.381(1) \text{ \AA}$], which are involved in short hydrogen-bonding interactions to nitrate anions in adjacent chains (Table 3).

In $\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{EtOH})\}_\infty$ (**2**), each Cd(II) ion is coordinated by three transoid 3,3'-pytz ligands [$\text{Cd}-\text{N} = 2.306(3)-2.352(3) \text{ \AA}$] which bridge to adjacent Cd centers to give a 3:2 ligand/metal infinite ladder [$\text{Cd}\cdots\text{Cd} = 13.163(2), 13.129(2) \text{ \AA}$; Figure 2]. Two asymmetrically bidentate nitrates [$\text{Cd}-\text{O} = 2.394(3), 2.498(3), 2.364(3), 2.456(3) \text{ \AA}$] fill the remaining four coordination sites. The cavities formed between the "rungs" of the ladder are filled by EtOH molecules.

$\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{CH}_2\text{Cl}_2)\}_\infty$ (**3**) has a very similar structure to that of **2** (Figure 2), the only difference being the replacement of the solvent EtOH by CH_2Cl_2 molecules. Thus each seven-coordinate Cd(II) ion is ligated by three pyridyl nitrogen donors [$\text{Cd}-\text{N} = 2.305(7)-2.348(7) \text{ \AA}$] and two asymmetrically bidentate nitrates [$\text{Cd}-\text{O} = 2.362(6), 2.438(7), 2.389(6), 2.507(7) \text{ \AA}$] to give a ladder motif [$\text{Cd}\cdots\text{Cd} = 13.169(4), 13.104(4) \text{ \AA}$] within which the CH_2Cl_2 molecules are located.

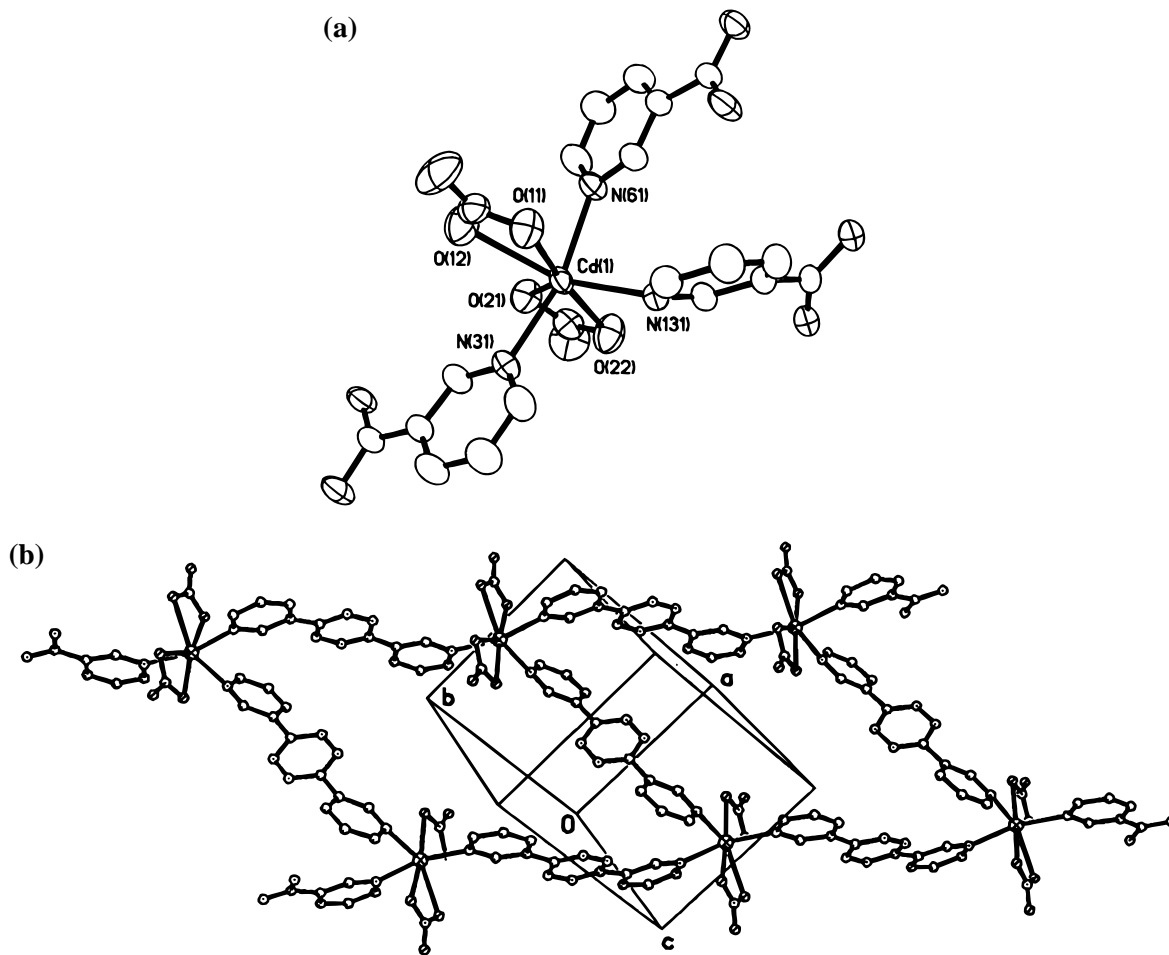


Figure 2. Cadmium coordination geometry (a) (displacement ellipsoids drawn at 50% probability) and ladder construction (b) of $\{[\text{Cd}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{EtOH})\}_\infty$ (**2**).

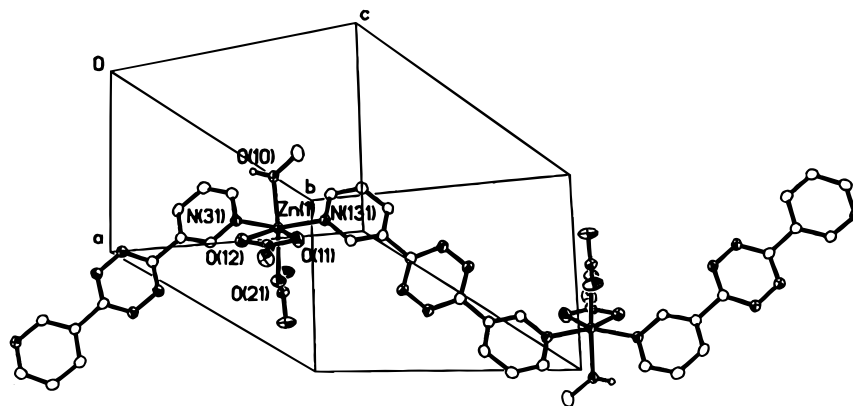


Figure 3. Molecular structure of the binuclear zinc unit in $\{[\text{Zn}_2(3,3'\text{-pytz})_2(\text{NO}_3)_4(\text{MeOH})_2(\mu\text{-}3,3'\text{-pytz})]\}_\infty$ (**4**) (displacement ellipsoids drawn at 50% probability).

Zinc(II) Complexes of 3,3'-pytz. The Zn(II) complexes, $\{[\text{Zn}_2(3,3'\text{-pytz})_2(\text{NO}_3)_4(\text{ROH})_2(\mu\text{-}3,3'\text{-pytz})]\}_\infty$ (**4**, R = Me; **5**, R = Et) and $\{[\text{Zn}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{CH}_2\text{Cl}_2)_2\}_\infty$ (**6**) were prepared in bulk and could be isolated using 1:1, 3:2 or 2:1 ligand/metal reaction stoichiometries in MeOH/ CH_2Cl_2 , EtOH/ CH_2Cl_2 , and $i\text{PrOH}/\text{CH}_2\text{Cl}_2$ solutions, respectively. Preliminary identification was carried out using infrared spectroscopy and elemental analysis. Single crystals of all three complexes were grown by layering an alcohol solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a CH_2Cl_2 solution of 3,3'-pytz. When diffusion was complete, single crystals of **5** and **6**, but not **4**, had formed. Single crystals of **4** were grown by Et_2O diffusion into the mother liquor

(Figures 3 and 4; Tables 2 and 3). The structures of **4**, **5**, and **6** are shown in Figures 3 and 4, and selected interatomic distances and angles are listed in Table 2.

The structures of all three complexes are based on six-coordinate (distorted octahedral) zinc(II). In the isostructural complexes **4** and **5** the Zn(II) ions are bridged by a single transoid-3,3'-pytz molecule [**4**, Zn–N = 2.055(2) Å; **5**, Zn–N = 2.074(4) Å] and terminally ligated by a single transoid-3,3'-pytz molecule [Zn–N = 2.079(2) Å (**4**), 2.082(4) Å (**5**)], one alcohol molecule [Zn–O = 2.107(2) Å (**4**), 2.128(4) Å (**5**)] and two nitrate anions, one monodentate [average Zn–O = 2.125(2) (**4**), 2.111(4) Å (**5**)] and one asymmetrically bidentate

Table 1. Selected Interatomic Distances (Å) and Angles (deg) in the Cd Coordination Spheres of {[Cd(μ -3,3'-pytz)(NO₃)₂(MeOH)₂]}_∞ (**1**), {[Cd₂(μ -3,3'-pytz)₃(NO₃)₄](EtOH)}_∞ (**2**), and {[Cd₂(μ -3,3'-pytz)₃(NO₃)₄](CH₂Cl₂)}_∞ (**3**)^a

	1	2	3		1	2	3
Cd-pyridyl N							
Cd(1)-N(31 ⁱ)	2.304(1)	2.306(3)	2.343(7)	N(31)-Cd(1)-N(61)	175.46(4)	166.95(11)	166.99(18)
Cd(1)-N(61)	2.290(1)	2.335(3)	2.305(7)	N(31)-Cd(1)-N(131)		100.80(11)	90.2(2)
Cd(1)-N(131)		2.351(3)	2.348(7)	N(131)-Cd(1)-N(61)		89.99(11)	100.2(2)
Cd-alcohol							
Cd(1)-O(10)	2.343(1)			N(31)-Cd(1)-O(10)	95.92(4)		
Cd(1)-O(110)	2.378(1)			N(61)-Cd(1)-O(10)	84.53(4)		
				N(31)-Cd(1)-O(110)	89.93(4)		
				N(61)-Cd(1)-O(110)	90.92(4)		
Cd-nitrate							
Cd(1)-O(11)	2.373(1)	2.394(3)	2.362(6)				
Cd(1)-O(12)		2.498(4)	2.438(7)				
Cd(1)-O(21)	2.466(1)	2.364(3)	2.389(6)				
Cd(1)-O(22)	2.619(1)	2.456(4)	2.507(7)				
Cd...Cd separation							
	13.367(1)	13.163(2)	13.169(4)				
		13.129(2)	13.104(4)				

^a For **1**, symmetry operation i: $x - 1, y - 1, z$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) in the Zn(II) Coordination Spheres of {[Zn₂(3,3'-pytz)₂(NO₃)₄(ROH)₂(μ -3,3'-pytz)]}_∞ (**4**, R = Me; **5**, R = Et) and {[Zn₂(μ -3,3'-pytz)₃(NO₃)₄](CH₂Cl₂)}_∞ (**6**)

	4	5	6		4	5	6
Zn-pyridyl N							
Zn(1)-N(31)	2.080(2)	2.082(4)	2.182(4)	N(31)-Zn(1)-N(61)			172.33(16)
Zn(1)-N(61)			2.173(5)	N(31)-Zn(1)-N(131)	118.34(8)	119.47(18)	85.65(16)
Zn(1)-N(131)	2.055(2)	2.074(4)	2.134(4)	N(61)-Zn(1)-N(131)			101.28(16)
Zn-alcohol							
Zn(1)-O(10)	2.106(2)	2.128(4)		N(31)-Zn(1)-O(10)	86.67(7)	86.12(17)	
				N(131)-Zn(1)-O(10)	91.41(7)	89.09(17)	
Zn-nitrate							
Zn(1)-O(11)	2.150(2)	2.350(5)	2.276(4)				
Zn(1)-O(12)	2.300(2)	2.149(5)	2.231(4)				
Zn(1)-O(21)	2.125(2)	2.111(4)	2.099(4)				
Zn...Zn separation							
coordinated	13.006(1)	12.885(2)	13.261(2), 13.156(2)				
H-bonded	13.205(1)	13.189(2)					

Table 3. Selected Hydrogen-Bonding Interactions in the Complexes {[Cd(μ -3,3'-pytz)(NO₃)₂(MeOH)₂]}_∞ (**1**) and {[Zn₂(3,3'-pytz)₂(NO₃)₄(ROH)₂(μ -3,3'-pytz)]}_∞ (**4**, R = Me; **5**, R = Et)^a

	D-H...A	D-H/Å	H...A/Å	D...A/Å	\angle D-H...A/deg
1	O(10)-H...O(13 ⁱ)	0.69	2.11	2.767(2)	160
	O(110)-H...O(23 ⁱⁱⁱ)	0.77	2.10	2.866(1)	172
4	O(10)-H(10)...N(61 ⁱⁱⁱ)	0.83	1.88	2.698(3)	169
5	O(10)-H(1S1)...N(61 ^{iv})	0.97	1.78	2.745(6)	173.5

^a Symmetry codes: i, $1 - x, -y, -z$; ii, $-x, -y, 1 - z$; iii, $2 - x, -y, -z$; iv, $-x, 3 - y, -z$.

[Zn-O = 2.150(2), 2.300(2) (**4**), 2.149(5), 2.350(5) Å (**5**)] to generate centrosymmetric binuclear molecular units [Zn...Zn = 13.006(1) Å (**4**), 12.885(2) Å (**5**); Figure 3]. The binuclear units are linked by a hydrogen-bonding interaction between the alcohol and the uncoordinated 3,3'-pytz pyridyl nitrogen (Table 3) to form an unprecedented alternating coordinated single bridge and hydrogen-bonded double-bridge chain motif [Zn...Zn = 13.205(1) Å (**4**), 13.189(2) Å (**5**); Figure 4].

Unlike **4** and **5**, compound **6** does not contain coordinated alcohol. Instead, the Zn(II) center is ligated by three pyridyl nitrogen donors [Zn-N; 2.134(4)-2.182(5) Å], a bidentate nitrate [Zn-O; 2.231(4), 2.276(4) Å] and a monodentate nitrate [Zn-N; 2.099(4) Å]. Each of the three 3,3'-pytz ligands bridges to an adjacent Zn(II) center forming a ladder motif [Zn...Zn = 13.261(2), 13.156(2) Å; Figure 5]. As in the ladder structure of

3, the cavities between the rungs of the ladder are filled with CH₂Cl₂ solvent molecules.

Extended Structural Motifs. The zigzag chain structure of **1**, although structurally similar to those in {[Cu(NCMe)₂(μ -4,4'-bipy)](BF₄)}_∞ and related complexes,²³ has a different construction. It results from the bridging ligand conformation rather than the metal coordination geometry. The ladder motif exhibited by complexes **2**, **3**, and **6** is rare; a database search reveals only five other examples of such architectures; in {[Cd₂(μ -1,4-bis(pyrid-4-yl)methyl-benzene)₃(NO₃)₄]}_∞ (**7**),¹² {[Cu₂(MeCN)₂(μ -1,4-bis(pyrid-4-yl)butadiene)₃](PF₆)₂]}_∞ (**8**),¹³ {[Co₂(μ -4,4'-bipy)₃(NO₃)₄]}_∞ (**9**),¹⁴ {[Co₂(μ -1,2-bis(pyrid-4-yl)ethane)₃(NO₃)₄]}_∞ (**10**),¹⁵ and [Cd₂(μ -1,4-bis(pyrid-4-yl)methyl-benzene)₃(NO₃)₄]}_∞ (**11**),¹⁶ the spaces between the rungs of the ladders are filled either by interpenetration (**7** and **8**) or, as in the case of **2**, **3**, and **6**, by solvent molecules (**9** and **10**). In **9**, either MeCN or CHCl₃ is present within each void, while in **10**, which is crystallized from MeOH/CHCl₃ mixtures containing Co(II) nitrate and 1,2-bis(pyrid-4-yl)ethane, all the bridging ligands have the anti conformation and CHCl₃ occupies the cavities. In **11** the inclusion of a *p*-dibromobenzene molecule inhibits interpenetration.

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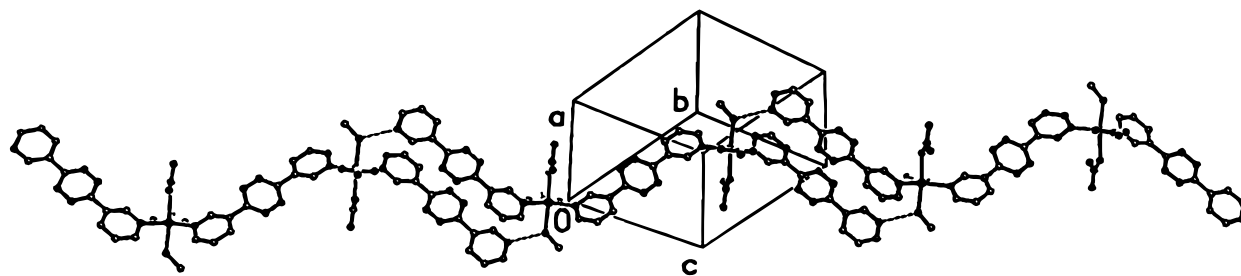


Figure 4. Chain construction of $\{[\text{Zn}_2(3,3'\text{-pytz})_2(\text{NO}_3)_4(\text{MeOH})_2(\mu\text{-}3,3'\text{-pytz})]\}_\infty$ (**4**) showing the hydrogen-bonding interactions between binuclear units.

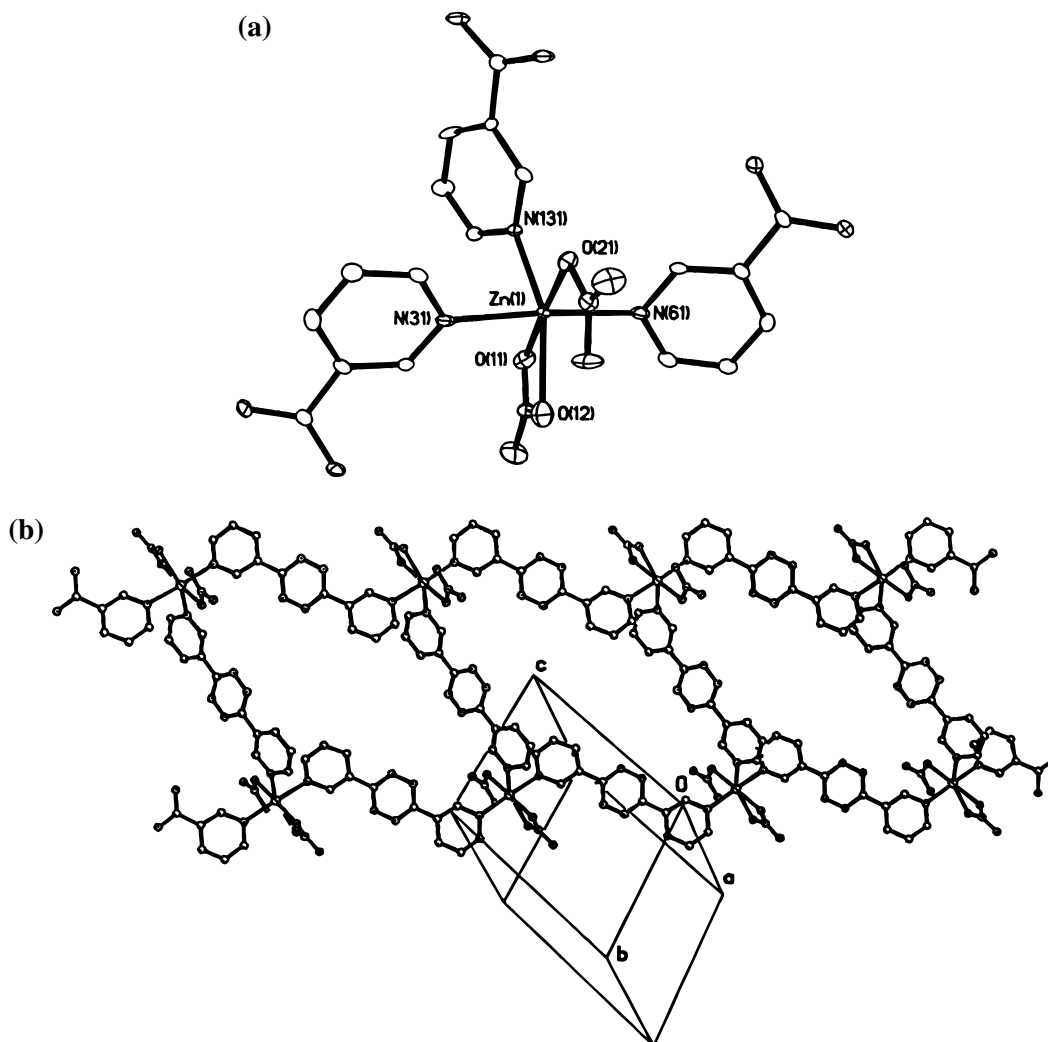


Figure 5. Zinc coordination geometry (a) (displacement ellipsoids drawn at 50% probability) and ladder construction (b) of $\{[\text{Zn}_2(\mu\text{-}3,3'\text{-pytz})_3(\text{NO}_3)_4](\text{CH}_2\text{Cl}_2)_2\}_\infty$ (**6**).

The chain architecture exhibited by **4** and **5** is also unusual. Binuclear Zn(II) units, held together by a single coordinated 3,3'-pytz bridge, are linked by pairs of 3,3'-pytz molecules, one pyridyl nitrogen of which is coordinated to the Zn(II) center, while the other is involved in an O—H \cdots N hydrogen-bonded contact to a coordinated alcohol molecule in an adjacent binuclear unit (Figure 4). Similar O—H \cdots N contacts are known in 4,4'-bipy coordination polymers cross-linked with hydrogen-bonded 4,4'-bipy moieties but in these complexes both N-donors of the 4,4'-bipy molecule hydrogen-bond to coordinated H₂O molecules.^{9–11} To the best of our knowledge, complexes **4** and **5** are the first to be linked by hydrogen-bonding interactions involving alcohols.

In all six structures, the 3,3'-pytz bridging ligand adopts the transoid isomeric form. Although 3,3'-bipyridine has only been reported in the transoid form,¹⁹ cisoid and transoid-arrangements have been observed previously for 3,3'-dicyanodiphenylacetylene (dcpa)²⁰ and 3,6-bis(imidazol-1-yl)pyridazine (bimpydz),²¹ and, as noted earlier, the form observed appears to be anion-dependent. Solvent dependence is observed in the formation of complexes with both anti and gauche isomers of the flexible ligand 1,2-bis(pyrid-4-yl)ethane. We have yet to see any occurrence of the cisoid isomer of 3,3'-pytz despite using a range of metal centers, anions, and solvents.²²

The metal—metal separations in the above complexes exhibit consistent trends. For all three ladders, **2**, **3**, and **6**, the M \cdots M

Table 4. Crystallographic Summary

	1	2	3	4	5	6
empirical formula	C ₁₄ H ₁₆ CdN ₈ O ₈	C ₁₉ H _{14.5} CdN ₁₁ O _{6.5}	C ₁₈ H ₁₃ CdN ₁₁ O ₆	C ₁₉ H ₁₆ N ₁₁ O ₇ Zn	C ₂₀ H ₁₈ N ₁₁ O ₇ Zn	C ₁₉ H ₁₄ Cl ₂ N ₁₁ O ₆ Zn
<i>M</i>	536.73	613.32	633.25	575.8	589.82	628.68
space group	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> /Å	9.011(2)	9.060(3)	8.981(16)	7.5346(12)	7.590(3)	9.1110(18)
<i>b</i> /Å	9.338(4)	9.848(3)	9.93(2)	10.7279(13)	10.561(2)	12.474(3)
<i>c</i> /Å	11.941(2)	13.208(4)	13.19(2)	15.219(2)	15.951(5)	13.171(3)
α/deg	74.51(3)	86.76(3)	94.12(15)	85.364(11)	87.56(2)	117.79(3)
β/deg	86.96(4)	79.04(3)	102.35(13)	80.627(12)	83.49(4)	102.39(3)
γ/deg	86.50(5)	88.14(2)	88.12(15)	69.343(12)	71.12(2)	101.13(3)
<i>V</i> /Å ³	965.8(4)	1154.8(6)	1146(4)	1135.3(2)	1202.0(6)	1216.7(4)
<i>Z</i>	2	2	2	2	2	2
<i>T</i> /°C	−123(2)	24(2)	−123(2)	−123(2)	24(2)	−123(2)
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ _{calc} mg m ^{−3}	1.85	1.764	1.835	1.684	1.630	1.716
μ/mm ^{−1}	1.19	1.010	1.133	1.17	1.089	1.291
<i>R</i>	0.0224	0.0315	0.0563	0.0392	0.0615	0.0452
<i>R</i> _w	0.0277	0.0802	0.1255	0.0589	0.1031	0.1164

$${}^a R = R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b R_w = \sqrt{\{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}}. \quad {}^c R_w = \sqrt{\{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}}.$$

distance along the side is slightly longer than that along the rung (Table 1), while the Cd(II) ions in the zigzag chain in **1** are significantly further apart than those in the ladders (Table 1). This can be related to the difference in the two ∠Cd–N–C angles for the coordinated pyridinyl groups, the maximum Cd···Cd separation corresponding to a minimum difference in these angles. Whereas for the zigzag chain in **1**, the ∠Cd–N–C angles differ by only 1.3 and 3.5° [120.1(1), 121.4(1)° for N(61); 119.1(1), 122.6(1)° for N(31)], for the ladders they differ by 4.4 and 10.6° [**2**: 119.0(2), 123.4(2)° for N(31); 116.0(2), 126.6(2)° for N(61)] and by 5.4 and 10.6° [**3**: 118.3(4), 123.7(4)° for N(61); 115.9(4), 126.5(4)° for N(31)]. The separation between the coordinated Zn(II) centers in **4** [13.006(1) Å] and **5** [12.885(2) Å] is shorter than that between the hydrogen-bonded Zn atoms [13.205(1) Å, **4**; 13.189(2) Å, **5**]. The Zn···Zn separations in the ladder, **6** (average 13.209 Å), are considerably longer than those between the coordinated Zn(II) centers in **4** and **5** due to the longer Zn–N bonds in **6** [2.134(4)–2.182(5) Å] compared to those in **4** [2.055(2), 2.079(2) Å] and **5** [2.074(4), 2.082(4) Å]. The difference in Zn–N bond lengths is attributed to ligand location: equatorial in **4** and **5** but axial in **6**.

Role of Solvent in the Construction of Molecular Architecture. From these results the choice of solvent is clearly critical in determining the molecular architecture of the resultant complex. In this study the coordinating ability of the alcoholic solvent is the underlying reason behind the differences in the extended structure of each series of coordination polymers. Of the three alcohols, MeOH is the most, and ⁱPrOH the least, effective ligand, a trend which mirrors that of the more extensively studied alkoxides.²⁴ Of the two metal cations, Zn(II) is the better Lewis acid.²⁵ Thus, whereas MeOH coordinates both metals, EtOH coordinates only Zn(II), and ⁱPrOH coordinates neither metal. Upon coordination of a solvent molecule one of the available coordination sites at the metal center is taken up thus restricting the possible number of bridging ligands that are used to generate the extended structure. This in turn has a profound effect upon the extended structures of the coordination polymers. For example, because of MeOH coordination in **1** there are only sufficient coordination sites for two trans located pyridinyl ligands in **1** whereas in **2** and **3**,

which exhibit no solvent coordination, there is room for three mer located pyridinyl ligands in **2** and **3**. The net effect is the construction of a simple zigzag chain in **1** and ladder motifs in **2** and **3**. A similar effect is observed for the Zn(II) series of compounds **4**–**6**. Therefore, it can be seen that the solvent is playing a controlling role over the network structure. This clearly has wider implications for research in coordination networks. In this case the coordination properties of the solvent are the most dominant feature but in other systems the “templating” role will also be important. The solvent used in the network preparation should not be thought of as “innocent” but rather as a potential participant in any coordination polymer formation.

Conclusions

The molecular architecture of both Cd(II) and Zn(II) nitrates bridged by 3,3'-pytz is profoundly influenced by the alcohol present in the crystallization medium. Simple zigzag chains (**1**), ladder structures (**2**, **3**, and **6**), and chains based on alternating single-coordinate/double hydrogen-bonded contacts (**4** and **5**) have been characterized. The coordinating ability of the alcohol is of particular significance; MeOH ligates both cations, EtOH ligates only Zn(II), and ⁱPrOH ligates neither cation. As the number of alcohol ligands decreases, the vacated coordination sites are occupied by extra bridging ligands forcing a change from chain (**1**, **4**, and **5**) to ladder (**2**, **3**, and **6**) motifs. The Lewis acidity of the metal cation also influences the hydrogen-bonding capability of the coordinated alcohol. Those coordinated to Zn(II) (MeOH in **4** and EtOH in **5**) but not that coordinated to Cd(II) (MeOH in **1**) form relatively short O–H···N hydrogen-bonds to uncoordinated pyridyl nitrogens forcing a change from a simple zigzag chain (**1**) to the complex alternating double- and single-bridged system.

Experimental Section

X-ray Data Collection, Solution and Refinement. Crystal data and summaries of the crystallographic analyses for **1**–**6** are given in Table 4. Diffraction data for **1**–**5** were collected on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems open flow cryostat²⁶ using ω–θ scans and graphite-monochromated Mo Kα radiation; those for **6** were collected at 150 K using an Enraf-Nonius FAST TV area detector situated at the window of a rotating molybdenum anode generator operating at 55 kV, 50 mA.²⁷ Absorption corrections were applied using either ψ-scans (**1**, **4**, and **5**) or numerically (**2** and **3**). All

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six structures were solved by direct methods using either SIR92²⁸ (1 and 4) or SHELXS-97²⁹ (2, 3, 5, and 6) and full-matrix least-squares refinement undertaken using either CRYSTALS³⁰ (1 and 4) or SHELXL-97³¹ (2, 3, 5, and 6). For 1 and 4, all hydrogen atoms were found and refined with isotropic displacement parameters and all non-hydrogen atoms were refined with anisotropic displacement parameters. For 2, 3, 5, and 6, all hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their parent atoms with the exception of the hydrogens on the disordered solvent molecules in 2 and 3 and the EtOH hydrogen involved in the hydrogen bonding in 5. All non-hydrogen atoms were refined with anisotropic displacement parameters except for those of the disordered solvent molecules in 2 and 3. Complexes 2 and 3 contained disordered EtOH and CH₂Cl₂ solvent, respectively. The EtOH molecule was disordered over two sites, related by a center of inversion located between the two carbon atoms thus giving 50% oxygen and 100% carbon occupancy. The CH₂Cl₂ solvate was disordered over two centrosymmetrically related sites with 50% occupancy. A high standard deviation in the unit cell parameters of complex 3 was accounted for by poor crystal quality and 11.3% crystal decay during data collection.

Synthesis. General Procedures. All reagents (Aldrich) were used as received. Elemental analyses (C, H, N) were carried out in the University of Nottingham. Mass spectra were obtained using a Vacuum Generators VG 70E micromass spectrometer. Infrared spectra were obtained as KBr pressed pellets using a Perkin-Elmer 1600 series FTIR spectrometer and ¹H NMR spectra on a Bruker DPX300 spectrometer.

3,6-Bis(pyridin-3-yl)-1,2,4,5-tetrazine (3,3'-pytz). 3,3'-pytz was prepared by a variation of the method described by Charonnat and Fabiani.³² 3-Cyanopyridine (20.00 g, 0.192 mol) and hydrazine hydrate (20.00 cm³, 20.58 g, 0.411 mol) were heated for 8 h. The resultant orange solid was dissolved in a mixture of glacial acetic acid (800 cm³) and water (1200 cm³), and after cooling to 0 °C, excess sodium nitrite (30.00 g, 0.435 mol) suspended in water (50 cm³) was added slowly. After 1 h, the pink product was collected and recrystallized from EtOH (yield: 7.589 g, 0.0321 mol, 17%). Found (calcd) for C₁₂H₈N₆: C, 60.85 (61.00); H, 3.25 (3.40); N, 35.50 (35.55). Electron impact mass spectrum: 236.1 [M⁺], 104.0 [C₆H₄N₂⁺]. IR (ν, cm⁻¹): 3453 w, 1581 s, 1488 w, 1393 s, 1269 w, 1192 w, 1127 m, 1111 m, 1058 w, 1016 m, 918 m, 822 m, 704 s, 600 s. ¹H NMR (300.13 MHz, CDCl₃, 298 K (ppm)): δ 9.87 (1H, s), 8.91 (2H, m), 7.60 (1H, m).

{[Cd(μ-3,3'-pytz)(NO₃)₂(MeOH)₂]}_∞, 1. A solution of Cd(NO₃)₂·4H₂O (0.050 g, 1.62 × 10⁻⁴ mol) in MeOH (10 cm³) was added to a solution of 3,3'-pytz in CH₂Cl₂ (10 cm³) (0.077 g, 3.26 × 10⁻⁴ mol). After vigorous mixing, a pink precipitate was obtained (yield: 0.077 g, 1.44 × 10⁻⁴ mol, 51%). Found (calcd) for C₁₄H₁₆Cd₁N₈O₈: C, 30.15 (31.35); H, 2.70 (3.00); N, 20.75 (20.90). IR (ν, cm⁻¹): 1596 m, 1437 m, 1384 s, 1190 m, 1112 m, 1061 w, 1028 m, 911 w, 833 w, 810 w, 692 m, 641 m, 600 m. Red crystals suitable for X-ray diffraction were grown by slow diffusion of layered MeOH and CH₂Cl₂ solutions over 3 days.

{[Cd(μ-3,3'-pytz)₃(NO₃)₄(EtOH)]}_∞, 2. A solution of Cd(NO₃)₂·4H₂O (0.051 g, 1.65 × 10⁻⁴ mol) in EtOH (10 cm³) was added to a solution of 3,3'-pytz (0.075 g, 3.17 × 10⁻⁴ mol) in CH₂Cl₂ (10 cm³). After vigorous mixing, a pink precipitate was obtained (yield: 0.103 g, 1.68 × 10⁻⁴ mol, 52%). Found (calcd) for C₃₇H₂₇Cd₂N₂₂O_{12.5}: C, 36.90 (36.90); H, 2.20 (2.25); N, 24.85 (25.60). IR (ν, cm⁻¹): 3362 w, 1603 m, 1456 m, 1393 s, 1293 m, 1273 m, 1192 m, 1121 m, 1062 w, 1046 m, 1030 m, 920 w, 312 w, 696 m, 641 w, 603 w. Deep pink crystals suitable for X-ray diffraction were grown by slow diffusion of layered EtOH and CH₂Cl₂ solutions over 3 days.

{[Cd(μ-3,3'-pytz)₃(NO₃)₄(CH₂Cl₂)]_∞, 3. A solution of Cd(NO₃)₂·4H₂O (0.033 g, 1.65 × 10⁻⁴ mol) in ⁱPrOH (10 cm³) was layered upon a solution of 3,3'-pytz (0.05 g, 2.12 × 10⁻⁴ mol) in CH₂Cl₂ (10 cm³). Crystals suitable for X-ray diffraction were obtained at the interface of the solutions (yield: 0.054 g, 8.82 × 10⁻⁵ mol, 42%). Found (calcd) for C₃₇H₂₆Cd₂N₂₂O₁₂Cl₂: C, 35.95 (35.10); H, 2.05 (2.05); N, 24.10 (24.35). IR (ν, cm⁻¹): 3444 w, 1603 m, 1456 m, 1385 s, 1291 m, 1192 m, 1119 m, 1045 m, 1029 m, 919 w, 817 w, 733 w, 696 m, 641 w, 603 w.

{[Zn₂(3,3'-pytz)₂(NO₃)₄(MeOH)₂(μ-3,3'-pytz)]_∞, 4. A solution of Zn(NO₃)₂·6H₂O (0.155 g, 5.21 × 10⁻⁴ mol) in MeOH (40 cm³) was added to a solution of 3,3'-pytz (0.254 g, 10.80 × 10⁻⁴ mol) in CH₂Cl₂ (40 cm³). After vigorous mixing, a red crystalline solid formed over the period of 10 min (yield: 0.186 g, 3.23 × 10⁻⁴ mol, 32%). Found (calcd) for C₃₈H₃₂N₂₂O₁₄Zn₂: C, 39.30 (39.65); H, 2.60 (2.80); N, 27.30 (26.75). IR (ν, cm⁻¹): 3446 w, 1654 w, 1608 w, 1384 s, 1262 w, 1194 w, 1119 w, 1052 w, 915 w, 696 w, 607 w. Red crystals suitable for X-ray diffraction were grown by diffusion of Et₂O vapor into the red solution formed after the initial diffusion of layered MeOH and CH₂Cl₂ solutions.

{[Zn₂(3,3'-pytz)₂(NO₃)₄(EtOH)₂(μ-3,3'-pytz)]_∞, 5. A solution of Zn(NO₃)₂·6H₂O (0.155 g, 5.21 × 10⁻⁴ mol) in EtOH (40 cm³) was added to a solution of 3,3'-pytz (0.25 g, 10.6 × 10⁻⁴ mol) in CH₂Cl₂ (40 cm³). After vigorous mixing, a red crystalline solid formed immediately (yield: 0.282 g, 4.78 × 10⁻⁴ mol, 46%). Found (calcd) for C₄₀H₃₆N₂₂O₁₄Zn₂: C, 40.20 (40.75); H, 2.85 (3.10); N, 26.30 (26.10). IR (ν, cm⁻¹): 3422 w, 1606 m, 1384 s, 1192 w, 1119 m, 1052 m, 918 w, 820 w, 695 m, 652 w, 600 w. Deep pink crystals suitable for X-ray diffraction were grown by diffusion of layered EtOH and CH₂Cl₂ solutions.

{[Zn₂(μ-3,3'-pytz)₃(NO₃)₄(CH₂Cl₂)₂]}_∞, 6. A solution of Zn(NO₃)₂·6H₂O (0.154 g, 5.18 × 10⁻⁴ mol) in ⁱPrOH (40 cm³) was added to a solution of 3,3'-pytz (0.252 g, 10.7 × 10⁻⁴ mol) in CH₂Cl₂ (40 cm³). After vigorous mixing, a red solid formed immediately (yield: 0.263 g, 4.49 × 10⁻⁴ mol, 44%). Red crystals suitable for X-ray diffraction were grown by diffusion of layered ⁱPrOH and CH₂Cl₂ solutions. Found (calcd) for C₃₇H₂₆Cl₂N₂₂O₁₂Zn₂: C, 39.55 (37.90); H, 2.50 (2.25); N, 25.80 (26.30). IR (ν, cm⁻¹): 3446 w, 1607 m, 1478 s, 1393 s, 1306 s, 1195 w, 1121 m, 1046 m, 920 m, 817 m, 732 m, 695 m, 644 w, 608 m.

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Supporting Information Available: Six X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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