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Synthesis and structural characterization of five new coordination polymer chain structures using a new, Z-shaped ligand, 2,2′-bis-(4-pyridylethynyl)tolane

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Using the new ligand, 2,2′-bis-(4-pyridylethynyl)tolane we have synthesized five new coordination polymers: $HgBr_2$[2,2′-bis-(4-pyridylethynyl)tolane] (**1**), HgI_2[2,2′-bis-(4-pyridylethynyl)tolane] (**2**), Ni(acetylacetonate)$_2$[2,2′-bis-(4-pyridylethynyl)tolane] (**3**), Zn(acetylacetonate)$_2$[2,2′-bis-(4-pyridylethynyl)tolane] (**4**), and Cu(hexafluoro acetylacetonate)$_2$[2,2′-bis-(4-pyridylethynyl)tolane]·$CHCl_3$ (**5**). 2,2′-Bis-(4-pyridyl ethynyl)tolane is a rigid ligand with a Z-shape that promotes the formation of zig-zag chains. Compounds **1**–**5** were characterized by single crystal X-ray diffraction; and compounds **1**–**3** were additionally characterized by IR, elemental analysis, and thermogravimetric analysis. Compound **1** crystallizes in the monoclinic space group *C*2/*c* with $a = 29.761(3)$ Å, $b = 5.0531(5)$ Å, $c = 16.7823(15)$ Å, $\beta = 104.090(2)^\circ$, $V = 2447.9(4)$ Å^3, $Z = 4$. Each mercury is bound to two tolane ligands and two bromine anions, resulting in a tetrahedral coordination environment. Compound **2** crystallizes in the monoclinic space group *P*2/*c*, with $a = 20.3061(17)$ Å, $b = 5.6303(5)$ Å, $c = 24.5459(19)$ Å, $\beta = 110.338(2)^\circ$, $V = 2631.4(4)$ Å^3, $Z = 4$. Here also, each mercury is bound to two tolane ligands and two iodine anions in a tetrahedral coordination environment. The ligand orientation differs in compounds **1** and **2** being *trans* oriented in **1** and *cis* oriented in **2**. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.5947(14)$ Å, $b = 6.3082(6)$ Å, $c = 18.3939(18)$ Å, $\beta = 112.112(2)^\circ$, $V = 1568.9(3)$ Å^3, $Z = 2$. Each nickel is bound to two tolane ligands and two bidentate AcAc anions, resulting in an octahedral coordination environment. Compound **4**, which is isostructural with **3**, also crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.6990(9)$ Å, $b = 6.2724(4)$ Å, $c = 18.6433(11)$ Å, $\beta = 112.8610(10)^\circ$, $V = 1583.86(17)$ Å^3, $Z = 2$. Compound **5** crystallizes in the triclinic space group P-1 with $a = 6.5487(4)$ Å, $b = 11.6471(7)$ Å, $c = 14.3225(9)$ Å, $\alpha = 70.1360(10)^\circ$, $\beta = 89.3990(10)^\circ$, $\gamma = 88.7680(10)^\circ$, $V = 1027.18(11)$ Å^3, $Z = 1$.

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Each copper in **5** is bound to two tolane ligands and two bidentate hfAcAc anions, resulting in an octahedral coordination environment identical to that found in **3** and **4**.

KEY WORDS: *N*,*N*′-Bipyridyl ligands; coordination polymers; Z-shaped ligand; tolane.

Introduction

There has been an intense interest in the preparation and structural characterization of new organic/inorganic coordination polymers. The field is driven by the search for functional solid materials that may be useful as new porous frameworks,[1,2] as new grid structures for chiral separations,[3–14] or as new optical materials for sensing and LED applications,[12] among other potential uses. The key to achieving the synthesis of such structures is the organic ligands that one uses in their preparation. The most versatile ligands to date have been the *N*-R-*N*′-bipyridine-type ligands since they readily bind to many different metals, and the challenge has been to develop new ligand geometries to realize new structural motifs. Typical synthetic strategies have included varying the position of the nitrogen donor atom in the pyridine ring, as well as modifying the connecting R-group. We have been investigating the use of diverse *N*-R-*N*′-type ligands and have employed both strategies. In this paper, we report on the synthesis of the *N*-R-*N*′-bidentate ligand 2,2′-bis-(4-pyridylethynyl)tolane, which is also called the Z-ligand because of its zig-zag shape. Furthermore, we describe the utility of this ligand in assembling five new organic/inorganic coordination polymers.

Experimental

Materials and methods

The chemicals for all syntheses were purchased from commercial sources and were used as received. ^{1}H and ^{13}C NMR spectra of the ligand were recorded in $CDCl_3$ on a Varian Mercury/VX 300 spectrometer operating at 300 MHz (proton) or 75 MHz (carbon). Infrared spectra were recorded on a Nicolet 5DXBO FT-IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) measurements were carried out using a TA Instruments SDT 2960 simultaneous DTA-TGA. Compounds **1**–**3** were heated under flowing helium from 30 to 1000°C at a heating rate of 20°C min^{-1}. Elemental analyses were carried out by Desert Analytics Laboratory.

Synthesis of the 2,2′-bis-(4-pyridylethynyl) tolane ligand

A 200 mL Schlenk flask was charged with 2-bromo-iodobenzene (23.0 g, 81.5 mmol) which was dissolved in piperidine. $Pd(PPh_3)_2Cl_2$ (0.1 g, 0.1 mmol) and CuI (0.5 g, 2.5 mmol) were then added, the flask was evacuated, and then charged with acetylene. The flask was then placed on a mechanical shaker overnight. The product was extracted with hexanes and washed with ammonium hydroxide and water. The crude product was then filtered over silica (hexanes) and recrystallized from ethanol resulting in 2,2′-dibromotolane (8.4 g, 61%) as white crystals. ^{1}H NMR ($CDCl_3$) = 7.63–7.61 (m, 2H), 7.60–7.59 (m, 2H), 7.29 (dt, $J = 7.7$, 1.4 Hz, 2H), 7.19 (dt, $J = 8.2$, 1.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) = 133.6, 132.5, 129.7, 127.0, 125.5, 125.1, 92.2.

A 100 mL Schlenk flask was charged with 2,2′-dibromotolane (3.00 g, 8.9 mmol) which was dissolved in 10 mL THF/NEt_3 (50/50). TMS acetylene (3.94 g, 40.1 mmol) was then added to the flask, which was flushed with N_2. $Pd(PPh_3)_2Cl_2$ (0.1 g, 0.1 mmol), CuI (0.1 g, 0.5 mmol) and PPh_3 (0.13 g, 0.5 mmol) were added and the reaction was stirred at 70°C overnight. The product was extracted with methylene chloride and washed with ammonium hydroxide and water. Following column chromatography (hexanes), 2,2′-bis-(trimethylsilylethynyl) tolane (1.63 g, 49%) was isolated as a yellowish solid. ^{1}H NMR ($CDCl_3$) = 7.33–7.29 (m, 2H). 7.28–7.26 (m, 2H), 7.10–7.00 (m, 4H), 0.02 (s, 18H); ^{13}C NMR ($CDCl_3$) = 132.2, 131.9, 128.1, 128.0, 126.1, 125.6, 103.4, 98.7, 92.1, 0.0.

A 100 mL Schlenk flask was charged with 2,2′-bis-(trimethylsilylethynyl)tolane (1.63 g, 4.4 mmol) and dissolved in 10 mL THF/NEt_3 (50/50) and approximately 10 mL of a 10% KOH/EtOH solution. 4-bromopyridine (3.42 g, 4.4 mmol) was added to the solution, and the flask was flushed with N_2 gas. $Pd(PPh_3)_2Cl_2$ (0.1 g, 0.14 mmol), CuI (0.04 g, 0.21 mmol), and PPh_3 (0.1 g, 0.03 mmol) were added followed by an N_2 purge and stirring at 70°C for 2 days. The product was extracted with methylene chloride and washed with NH_4OH and H_2O. Flash chromatography using CH_2Cl_2 as eluent and slowly increasing the polarity with methanol (>2%) resulted in 2,2′-bis-(4-pyridylethynyl)tolane (1.02 g, 61%) as a grayish-white solid. ^{1}H NMR ($CDCl_3$) = 8.47 (bs, 4H), 7.60–7.56 (m, 4H), 7.38–7.35 (m, 4H), 7.25 (d, $J = 5.5$ Hz, 4H); ^{13}C NMR ($CDCl_3$) = 149.6, 132.3, 132.1, 131.1, 129.0, 128.5, 126.0, 125.5, 124.5, 92.5, 92.1, 90.8. Melting point: 189–191°C. Anal. Calcd. for $C_{28}H_{16}N_2$—C, 88.40; H, 4.24; N, 7.36. Found: C, 86.42; H, 4.85; N, 7.16.

*Synthesis of HgBr$_2$[2,2′-bis-(4-pyridylethynyl)tolane] (**1**)*

$HgBr_2$ (0.005 mmol) was dissolved in 1 mL of methanol and then layered on top of a 1 mL solution of the ligand (0.01 mmol) in dichloromethane with a layer of neat methanol separating them. Yellow plates suitable for X-ray diffraction were isolated in 64% yield. IR (KBr pellet, cm^{-1}) – 697(m), [759(s), 822(s) (C—C bends)], 1007(s), 1064(m), [1214(s) (C—H bend)], 1316(w), 1421(s), [1442(m), 1475(m), 1500(m) (C—H bends)], 1533(m), [1604(s) (C═C stretch)], 1920(w), [2222(m) (C≡C stretch)], [3057(w) (C—H stretch)]. Anal. Calcd. for **1** – C, 45.40; H, 2.18; N, 3.78%. Found: C, 45.50; H, 2.26; N, 3.79%.

*Synthesis of HgI$_2$[2,2′-bis-(4-pyridylethynyl)tolane] (**2**)*

HgI_2 (0.01 mmol) was dissolved in 1 mL of ethanol and then layered on top of a 1 mL solution of the ligand (0.02 mmol) in dichloromethane with a layer of neat ethanol separating them. Yellow needles suitable for X-ray diffraction were isolated in 90% yield. IR (KBr pellet, cm^{-1}) – [753(m), 823(m) (C—C bends)], 948(w), 1006(m), 1055(w), 1093(w), [1209(m) (C—H bend)], 1417(w), [1446(w), 1475(w), 1500(w) (C—H bend)], [1602(s) (C═C stretch)], [2225(w) (C≡C stretch)], 2331(w), 2361(w), [3013(w), 3067(w) (C—H stretch)]. Anal. Calcd. for **2** – C, 40.29; H, 1.93; N, 3.36%. Found: C, 38.50; H, 1.76; N, 3.08%.

*Synthesis of Ni(acetylacetonate)$_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**3**)*

Ni(acetylacetonate)$_2$ (0.005 mmol) was dissolved in 1 mL of methanol and then layered on top of a 1 mL solution of the ligand (0.01 mmol) in dichloromethane with a layer of neat methanol separating them. Yellow plates suitable for X-ray diffraction were isolated in 61% yield. IR (KBr pellet, cm^{-1}) – 653(m), 697(w), [763(s), 829(s) (C—C bends)], 928(m), 1013(s), 1055(w), 1089(m), [1206(s) (C—H bend)], 1258(m), 1309(m), [1363(m), 1400(s), 1460(s), 1483(s), 1514(s) (acetylacetonate vibrations)], [1597(s) (C—C stretch)], 1930(w), 1959(w), [2220(w) (C≡C stretch)], [2448(w) (nickel acetylacetonate)], 2917(w), 2958(w), [3068(w) (C—H stretch)]. Anal. Calcd. for **3** – C, 71.61; H, 4.74; N, 4.40%. Found: C, 70.74; H, 4.65; N, 4.84%.

*Synthesis of Zn(acetylacetonate)$_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**4**)*

Zn(acetylacetonate)$_2$ (0.005 mmol) was dissolved in 1 mL of ethanol and then layered on top of a 1 mL solution of the ligand (0.01 mmol) in dichloromethane with a layer of neat methanol separating them. Yellow plates suitable for X-ray diffraction were isolated in 30% yield. Infrared and microanalytical data were not obtained for **4** due to the low product yield.

Synthesis of Cu(hexafluoroacetylacetonate)$_2$(2,2′-bis-(4-pyridylethynyl)tolane)·CHCl$_3$ (5)

Cu(hexafluoroacetylacetonate)$_2$ (0.01 mmol) was dissolved in 1 mL of methanol and then layered on top of a 1 mL solution of the ligand (0.02 mmol) in chloroform with a layer of neat methanol separating them. Green plates suitable for X-ray diffraction were isolated in 74% yield. Infrared and microanalytical data for **5** were not obtained.

Single-crystal structure determinations

Suitable single crystals of **1**–**5** were selected and attached in air to thin glass fibers. Intensity measurements were made using a Bruker SMART APEX platform diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[15] The structures were solved and refined by a combination of direct methods and difference Fourier syntheses, using SHELXTL.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in the calculated positions and refined using a riding model. Crystal data, data collection parameters, and refinement statistics for **1**–**5** are compiled in Table 1. Relevant interatomic distances and bond angles for **1**–**5** are collected in Table 2.

Results and discussion

HgBr$_2$[2,2′-bis-(4-pyridylethynyl)tolane] (1)

The one-dimensional coordination polymer **1** crystallized from the reaction between the bidentate Z-ligand and HgBr$_2$, which were slowly diffused together. The mercury cations in **1** are located on two-fold rotation axes and are connected to symmetry related pairs of Z-ligands and bromine atoms, giving rise to a distorted tetrahedral coordination environment around the mercury atom (Fig. 1). All of the mercury bond distances are normal with Hg—N at 2.418(3) Å and Hg—Br at 2.4894(4) Å. The N—Hg—N angle is compressed from the ideal tetrahedral angle to 100.19(14)° while the bromines are pushed apart to a 152.13(2)° angle.

The Z-ligands in **1** rest on inversion centers, such that the asymmetric unit contains one mercury atom, one bromine atom, and half of a Z-ligand. The overall structure consists of zig-zag chains of the 1-D coordination polymer running parallel to (101); and these chains stack in an offset fashion along the crystallographic *b*-axis (Fig. 2). Despite the possibility for aromatic stacking interactions, the closest ring–ring centroid distance is greater than 4.7 Å, with the nearest, perpendicular interchain distance being only about 3.5 Å. The ring centroids are, however, in the vicinity of the triple bond pi clouds of ligands in neighboring chains (centroid (N1—C5) – C6—C7 midpoint = 3.58 Å, centroid (C8—C13) – C6—C7 midpoint = 3.49 Å). Thermal analysis of **1** indicates that the coordination polymer chains are stable up to 123°C.

HgI$_2$[2,2′-bis-(4-pyridylethynyl)tolane] (2)

The one-dimensional coordination polymer **2** crystallizes from the reaction of HgI$_2$ and the Z-ligand upon slow diffusion of the two solutions together. The mercury cation is connected to two iodine atoms and two crystallographically distinct Z-ligands (Fig. 3), both of which lie on inversion centers. Both **1** and **2** possess mercury in a highly distorted tetrahedral coordination environment (compound **2** has a compressed N—Hg—N angle of 100.6(2)° and an expanded I—Hg—I angle of 146.01(2)°) and have normal mercury-ligand bond lengths (average Hg—N is 2.429 Å and average Hg—I is 2.661 Å in **2**). Both structures consist of zig-zag coordination polymer chains running

Table 1. Crystal Data and Structure Refinement Summary for **1–5**

	1	**2**	**3**	**4**	**5**
CCDC deposit no.	246679	246680	246681	246682	246683
Empirical formula	$C_{28}H_{16}Br_2HgN_2$	$C_{28}H_{16}HgI_2N_2$	$C_{38}H_{30}N_2NiO_4$	$C_{38}H_{30}N_2O_4Zn$	$C_{39}H_{30}Cl_3CuF_{12}N_2O_4$
Formula weight	740.84	834.82	637.35	644.01	977.45
Temperature (K)	200(2)	293(2)	173(2)	150.0(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$P2/c$	$P2_1/c$	$P2_1/c$	P-1
a (Å)	29.761(3)	20.3061(17)	14.5947(14)	14.6990(9)	6.5487(4)
b (Å)	5.0531(5)	5.6303(5)	6.3082(6)	6.2724(4)	11.6471(7)
c (Å)	16.7823(15)	24.5459(19)	18.3939(18)	18.6433(11)	14.3225(9)
α	90	90	90	90	70.1360(10)
β	104.090(2)	110.338(2)	112.112(2)	112.8610(10)	89.3990(10)
γ	90	90	90	90	88.7680(10)
Volume (Å^3)	2447.9(4)	2631.4(4)	1568.9(3)	1583.86(17)	1027.18(11)
Z	4	4	2	2	1
Density (calculated)	2.010	2.107	1.349	1.350	1.580
Absorption coefficient	9.571	8.213	0.662	0.819	0.824
$F(000)$	1392	1536	664	668	487
Crystal size (mm^3)	0.10 × 0.07 × 0.04	0.24 × 0.06 × 0.04	0.41 × 0.26 × 0.12	0.44 × 0.30 × 0.20	0.56 × 0.44 × 0.18
Reflections collected	7648	16689	9972	16118	9539
Independent reflections	2507 [R(int) = 0.0289]	5362 [R(int) = 0.0619]	3208 [R(int) = 0.0394]	3931 [R(int) = 0.0361]	4204 [R(int) = 0.0210]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	None	Semi-emperical from equivalents	Semi-emperical from equivalents
Data/restraints/parameters	2507/0/150	5362/0/298	3208/0/207	3931/0/207	4204/1/286
Goodness-of-fit on F^2	0.937	1.027	1.026	1.013	1.003
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0236$, $wR_2 = 0.0485$	$R_1 = 0.0403$, $wR_2 = 0.0840$	$R_1 = 0.0433$, $wR_2 = 0.1219$	$R_1 = 0.0329$, $wR_2 = 0.0796$	$R_1 = 0.0580$, $wR_2 = 0.1694$
R indices (all data)	$R_1 = 0.0266$,	$R_1 = 0.0626$,	$R_1 = 0.0531$,	$R_1 = 0.0388$,	$R_1 = 0.0635$,
R indices (all data)	$wR_2 = 0.0491$	$wR_2 = 0.0913$	$wR_2 = 0.1262$	$wR_2 = 0.0805$	$wR_2 = 0.1747$

Table 2. Bond Lengths and Angles for **1**–**5**

Bond	Distance (Å)	Bonds	Angles (°)
1			
Hg—N(1)	2.418(3)	N(1)—Hg—N(1)#1	100.19(14)
Hg—Br	2.4894(4)	N(1)—Hg—Br	99.04(7)
		N(1)#1—Hg—Br	98.74(7)
		Br—Hg—Br#1	152.13(2)
		C(1)—N(1)—Hg	121.7(2)
		C(5)—N(1)—Hg	121.2(3)
2			
Hg—N(1)	2.423(6)	N(1)—Hg—N(2)	100.6(2)
Hg—N(2)	2.435(6)	N(1)—Hg—I(2)	100.73(18)
Hg—I(1)	2.6745(7)	N(2)—Hg—I(2)	101.76(15)
Hg—I(2)	2.6475(7)	N(1)—Hg—I(1)	101.22(17)
		N(2)—Hg—I(1)	99.33(16)
		I(2)—Hg—I(1)	146.01(2)
		C(1)—N(1)—Hg	120.0(5)
		C(5)—N(1)—Hg	121.0(6)
		C(19)—N(2)—Hg	122.7(5)
		C(15)—N(2)—Hg	119.5(5)
3			
Ni—N(1)	2.1515(19)	O(2)—Ni—O(2)#1	180.00(11)
Ni—O(2)	2.0151(16)	O(2)—Ni—O(1)	90.87(6)
Ni—O(1)	2.0258(16)	O(2)#1—Ni—O(1)	89.13(6)
		O(1)—Ni—O(1)#1	180.00(16)
		N(1)#1—Ni—O(2)	90.21(7)
		O(2)#1—Ni—N(1)#1	89.79(7)
		O(1)—Ni—N(1)#1	88.75(7)
		O(1)#1—Ni—N(1)#1	91.25(7)
		N(1)#1—Ni—Ni(1)	180.00(9)
		C(5)—N(1)—Ni	122.69(16)
		C(1)—N(1)—Ni	120.29(16)
		C(15)—O(1)—Ni	125.07(16)
		C(17)—O(2)—Ni	126.11(16)
4			
Zn—N(1)	2.2361(12)	O(2)—Zn—O(2)#1	180.00(7)
Zn—O(2)	2.0428(10)	O(2)—Zn—O(1)	89.42(4)
Zn—O(1)	2.0720(11)	O(2)#1—Zn—O(1)	90.58(4)
		O(1)—Zn—O(1)#1	180.00(9)
		O(2)—Zn—N(1)#1	90.48(4)
		O(2)#1—Zn—N(1)#1	89.52(4)
		O(1)—Zn—N(1)#1	88.36(4)
		O(1)#1—Zn—N(1)#1	91.64(4)
		N(1)—Zn—N(1)#1	180.00(6)
		C(5)—N(1)—Zn	122.49(10)
		C(1)—N(1)—Zn	120.10(10)
		C(15)—O(1)—Zn	125.04(10)
		C(17)—O(2)—Zn	126.62(10)
5			
Cu—N(1)	2.051(2)	O(2)—Cu—O(2)#1	180.00(12)
Cu—O(2)	2.031(2)	O(2)—Cu—N(1)#1	90.13(9)
Cu—O(1)	2.242(2)	O(2)#1—Cu—N(1)	89.87(9)
		N(1)#1—Cu—N(1)	180.000(1)
		O(2)—Cu—O(1)	86.21(8)
		O(2)#1—Cu—O(1)	93.79(8)
		N(1)#1—Cu—O(1)	88.10(9)
		N(1)—Cu—O(1)	91.90(9)
		O(1)—Cu—O(1)#1	180.0
		C(5)—N(1)—Cu	122.6(2)
		C(1)—N(1)—Cu	120.4(2)
		C(21)—O(1)—Cu	122.9(2)
		C(23)—O(2)—Cu	127.7(2)

parallel to (101), and the chains in both compounds stack along the crystallographic *b*-axis (Fig. 4). However there is an unexpected difference between **1** and **2**, namely the *trans* versus *cis* orientation of the Z-ligands coordinated to the Hg center, and this difference is illustrated in Fig. 5. In the *trans* orientation, the central tolane units (Ph—C≡C—Ph) of the ligands are approximately parallel; whereas in the *cis* orientation, the central tolane groups of two ligands attached to the same metal point directionally opposite.

No aromatic stacking interactions are present in **2**, with the closest ring-ring centroid distance being greater than 4.4 Å. In contrast to **1**, no ring-alkyne pi cloud interactions can be identified for **2**. Thermal analysis indicates that the chains in **2** are stable to 187°C.

*Ni(acetylacetonate)$_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**3**) and Zn(acetylacetonate)$_2$(2,2′-bis-(4-pyridylethynyl)tolane (**4**)*

Compound **3** crystallized out of solution through the slow diffusion of the reactants. Both the Ni center and the Z-ligand rest on inversion centers, and the asymmetric unit therefore contains one Ni center, one acetylacetonate, and half a Z-ligand (Fig. 6). This arrangement gives Ni a distorted [4 + 2] octahedral coordination environment with an Ni—N distance of 2.1515(19) Å and an average Ni—O distance of 2.02 Å. Because the Z-ligands are attached to the Ni center in a *trans* fashion, the zig-zag character of the 1-D chains is solely a product of the ligand geometry (Fig. 7). The chains stack along the *b*-axis while simultaneously forming layers perpendicular to the *c*-axis.

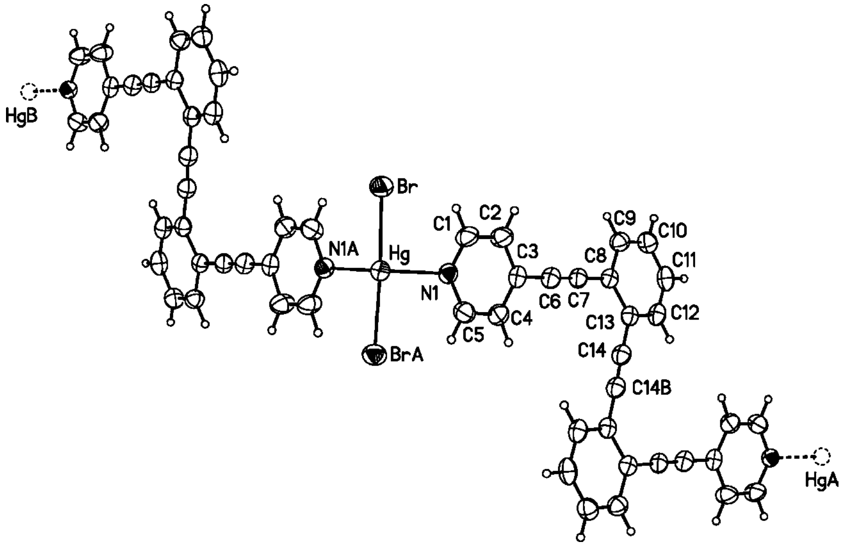

Fig. 1. Thermal ellipsoid plot of the Hg coordination environment in $HgBr_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**1**). Displacement ellipsoids drawn at the 50% probability level.

Thermal analysis shows a multi-step decomposition of **3** starting at 203°C.

Compound **4** was also characterized by single crystal X-ray diffraction and was determined to be isostructural to **3**. Compound **4**, likewise, contains Zn^{2+} in a [4 + 2] octahedral coordination environment with a Zn—N distance of 2.2361(12) Å and an average Zn—O distance of 2.06 Å. A thermal ellipsoid plot of the asymmetric unit of **4** is shown in Fig. 8. No significant aromatic interactions are present in either **3** or **4**.

*Cu(hexafluoroacetylacetonate)$_2$(2,2′-bis-(4-pyridylethynyl)tolane)·CHCl$_3$ (**5**)*

As with **3** and **4**, compound **5** crystallized out of solution through the slow diffusion of the

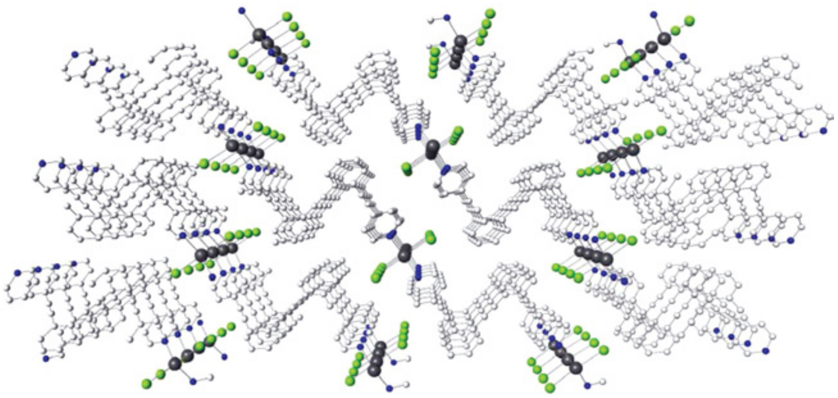

Fig. 2. The crystal packing of **1** viewed along the *b*-axis. Z-ligands are *trans* oriented about Hg^{2+}. Hg atoms shown as black spheres; Br, green; N, blue; C, white; H atoms not shown.

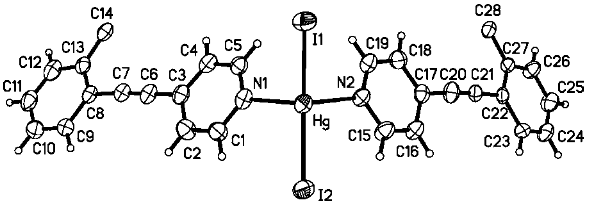

Fig. 3. The asymmetric unit of HgI_2(2,2′-bis-(4-pyridylethynyl)tolane) (**2**). Displacement ellipsoids are drawn at the 30% probability level.

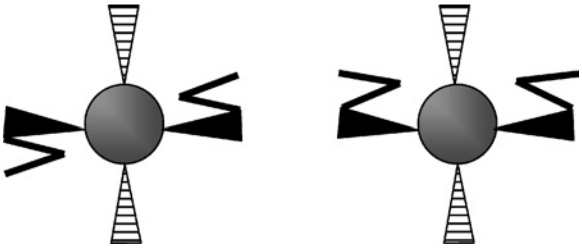

Fig. 5. *cis* and *trans* arrangements of two Z-ligands about an Hg^{2+} center.

reactants. Both the Cu center and the ligand rest on inversion centers with the asymmetric unit containing one Cu center, one $hfAcAc^-$, and half a Z-ligand (Fig. 9). Additionally, the asymmetric unit contains one chloroform solvate molecule, disordered over two orientations.

The ligand arrangement about Cu is a distorted [4 + 2] octahedral environment. An unusual characteristic of **5** is that the longest bond is a metal–oxygen bond (Cu—O(1) = 2.242(2) Å, Cu—N = 2.051(2) Å, and Cu—O(2) = 2.031(2) Å in **5**), whereas the metal–nitrogen bonds are the longest bonds in **3** and **4**. However, as in **3** and **4**, the polymer chain structure is propagated through the *trans* Cu—N bonds, and the zig-zag character of the chains is a result of the ligand geometry alone (Fig. 10). The polymeric chains stack along the crystallographic *a*-axis while simultaneously forming layers perpendicular to the *b*-axis. No significant aromatic interactions were observed for **5**.

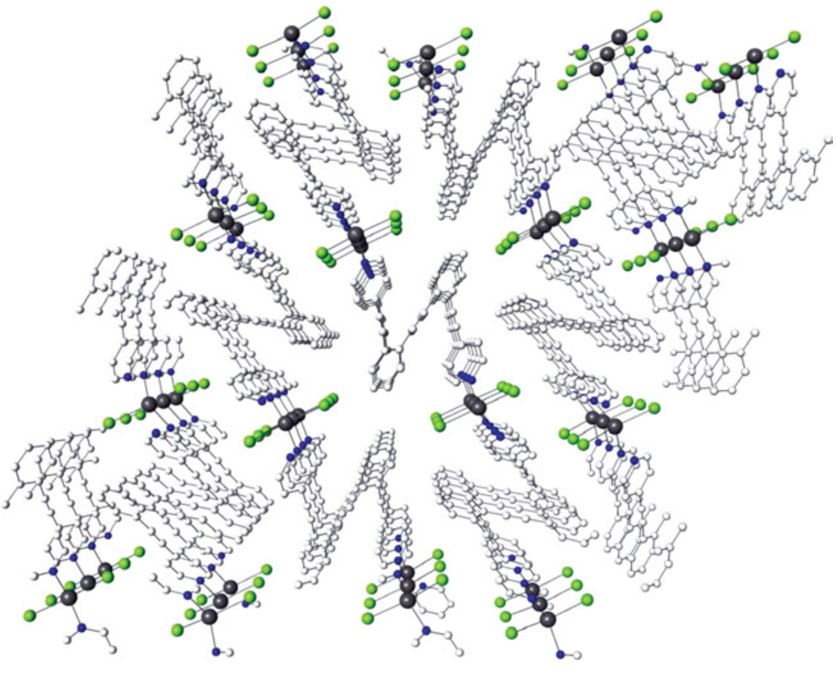

Fig. 4. Crystal packing in **2** viewed along [010] and highlighting the *cis* orientation of the Z-ligands around Hg^{2+}. Hg atoms shown as black spheres; I, green; N, blue; C, white; H atoms not shown.

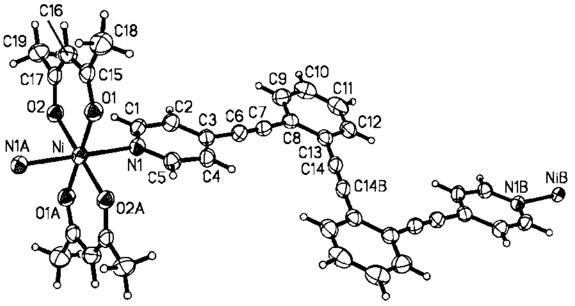

Fig. 6. Ellipsoid plot of Ni(AcAc)$_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**3**). Displacement ellipsoids are shown at the 50% probability level.

Conclusion

We have synthesized the new *N*-R-*N*′-bidentate ligand, 2,2′-bis-(4-pyridylethynyl) tolane, which has a Z-shape. We have successfully used this ligand in the preparation of five new coordination polymers that consist of zig-zag 1-D chains. The zig-zag 1-D chains form as a direct consequence of the ligand coordination environment around the metal center in combination with the inherent shape of the Z-ligand. While the highly conjugated nature of the ligand suggests the possibility of aromatic interactions in the compounds, none of the five display significant pi–pi interactions.

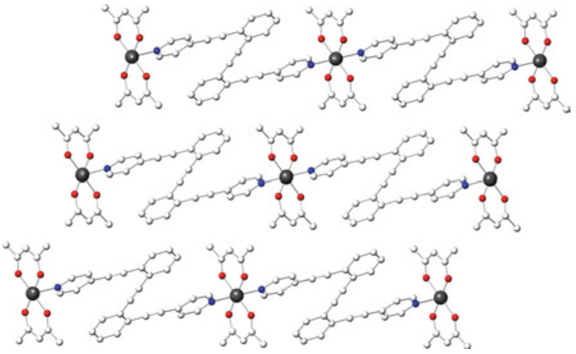

Fig. 7. Crystal packing of Ni(AcAc)$_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**3**) viewed along [010]. Ni atoms are shown as black spheres; O, red; N, blue; C, white; H atoms omitted.

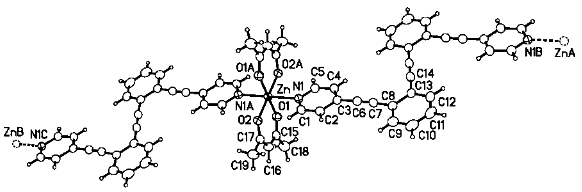

Fig. 8. Displacement ellipsoids drawn at the 50% probability level for Zn(AcAc)$_2$(2,2′-bis-(4-pyridylethynyl)tolane) (**4**).

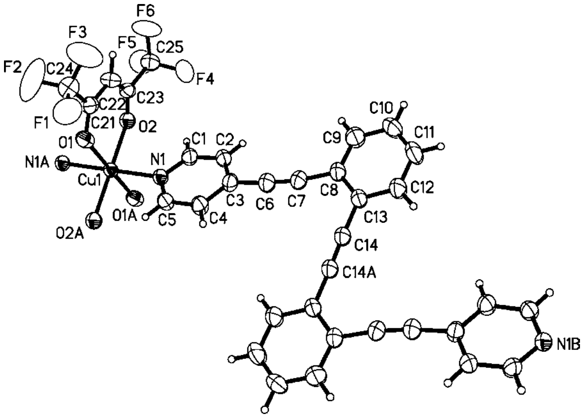

Fig. 9. The copper coordination environment (40% probability ellipsoids) in Cu(hfAcAc)$_2$(2,2′-bis-(4-pyridylethynyl)tolane (**5**). Inversion centers are located at the Cu center and the C14–C14A midpoint.

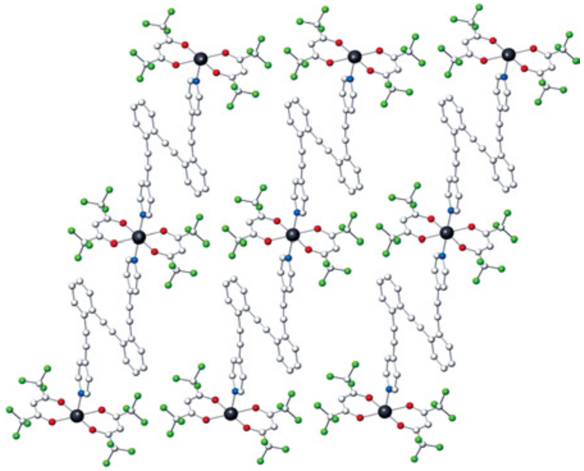

Fig. 10. Packing of **5** viewed along the crystallographic *a*-axis. Chloroform solvate molecules have been omitted for clarity. Cu atoms are shown as black spheres; F, green; O, red; N, blue; C, white; H atoms omitted.

Acknowledgments

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