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Cyanoscorpionates: Synthesis and Crystallographic Characterization of One-Dimensional Cu(I) Coordination Polymers

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A new cyanoscorpionate ligand, hydrotris(3-*t*-butyl-4-cyanopyrazolyl)borate ($\text{Tp}^{t\text{-Bu,4CN}}$) is reported. Both $\text{Tp}^{t\text{-Bu,4CN}}$ and hydrotris(4-cyano-3-phenylpyrazolyl)borate ($\text{Tp}^{\text{Ph,4CN}}$) form one-dimensional coordination polymers with Cu(I). The polymeric chains align to form channels which, in the case of $\text{Tp}^{t\text{-Bu,4CN}}$, can encapsulate solvent molecules, as evidenced by the characterization of one such polymer with encapsulated acetonitrile molecules.

Introduction

Polypyrazolylborates, also known as "scorpionates", have found a wide range of applications in inorganic and organometallic chemistry since they were first synthesized by Trofimenko in 1966.[1] All three basic forms of scorpionates, dihydrobispyrazolylborates (Bp), hydrotrispyrazolylborates (Tp), and tetrakispyrazolylborates (pzTp) carry a single negative charge and can act as bidentate or (except for Bp) face-capping tridentate ligands by coordinating a metal via the pyrazole nitrogen atoms not bound to the boron. The utility of these ligands stems from the relative ease with which one can synthesize pyrazole rings with a wide variety of substituents on the carbon atoms of the ring.[2] The pyrazole ring can be substituted in the 3, 4, and 5 positions, allowing for nine substitutable positions on the Tp ligand and imparting a tremendous versatility.

The rich chemistry of scorpionates has relied upon these substituted second generation ligands which provide altered steric and electronic properties and thereby change the electronic characteristics and coordination geometries of the metal atoms. The overwhelming majority of scorpionate ligands feature substitution on the pyrazole rings by relatively electronically innocent alkyl or aryl groups. Even with these ligands, substantial effects on the electronic properties of the coordinated metal ion are realized simply as a function of the steric requirements of the substituents, especially that in the 3-position.[3] The most notable employments of electronically active substituents are the trifluoromethyl-substituted scorpionates utilized most widely by Dias[4] and the cyano-substituted scorpionates reported by us[5] and Trofimenko.[6] The electron-withdrawing CF_3 substituent has been shown to reduce the electron density on the coordinated metal and significantly alter its reactivity. The CN substituent, aside from being electron-withdrawing, is also capable of coordinating to metal centers. The cyanoscorpionates, therefore, have the potential to be used in the synthesis of coordination polymers in which metal ions are coordinated to both the pyrazole and the cyano N atoms. The ligand reported by Trofimenko, Bp^{4CN}, has no pyrazole substituents aside from the CN group in the 4-position and spontaneously forms intractable polymers when exposed to a metal ion.[6] With an additional phenyl group in the 3-position, the $\text{Bp}^{\text{Ph,4CN}}$ ligand

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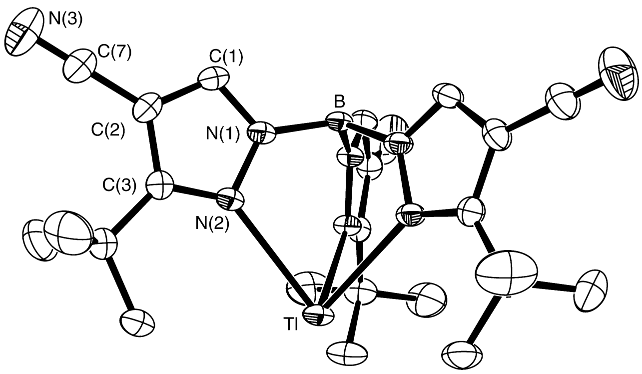

Figure 1. ORTEP drawing of TlTp$^{t\text{-Bu,4CN}}$ shown at the 50% probability level. H atoms have been omitted for clarity.

that we reported can lead to the isolation of homoleptic monomeric metal complexes, whose structures do not differ significantly from their noncyano analogues.[5a] We have also reported the incorporation of these complexes in coordination polymers with $Rh_2(CF_3COO)_4$.[7]

We have recently reported the synthesis of the cyano-substituted trispyrazolylborate, Tp^{Ph,4CN}, and the Fe, Co, and Mn complexes thereof,[5b] as well as the synthesis and metal complexes of the related cyanopyrazole with a *tert*-butyl group in the 3-position.[8] We report herein the synthesis of the cyanotrispyrazolylborate ligand with this new pyrazole, Tp$^{t\text{-Bu,4CN}}$, as well as the first crystallographically characterized coordination polymers employing this class of ligands.

Results and Discussion

Syntheses of Pyrazoles and Scorpionates. We have reported earlier the syntheses of 3-R-4-cyanopyrazole (R = Ph, *t*-Bu) by a modification of Tupper and Bray's method[9] for 4-cyano-3-phenylpyrazole (Hpz^{Ph,4CN}). We have also reported the synthesis of KTp^{Ph,4CN}.[5b] An analogous method was used to synthesize the sodium or potassium salts of Tp$^{t\text{-Bu,4CN}}$ by the combination of 4 equiv of 3-*t*-butyl-4-cyanopyrazole with sodium or potassium borohydride and heating above the melting point of the pyrazole. ESI mass spectrometry shows predominantly the trispyrazolylborate anion with small amounts of the bispyrazolylborate and tetrakispyrazolylborate anions. Higher mass peaks are observed, as in mass spectra of other scorpionates, which are consistent with adducts involving two scorpionate anions and a sodium ion. Infrared spectra of the potassium salt shows characteristic peaks at 2460 cm^{-1} and 2231 cm^{-1} for the B–H and $C\equiv N$ stretches, respectively.

X-ray quality crystals of the thallium salt, TlTp$^{t\text{-Bu,4CN}}$, were grown by layering a methanolic solution of the sodium salt on top of a solution of $TlNO_3$ in CH_3OH/H_2O. An Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawing[10] of TlTp$^{t\text{-Bu,4CN}}$ is shown in Figure 1, with pertinent X-ray data collection and structure solution parameters in Table 1 and selected bond distances and angles in Table 2.

TlTp$^{t\text{-Bu,4CN}}$crystallizes in the rhombohedral space group $R3m$, with both the Tl and B atoms situated on positions with $3m$ symmetry, such that each pyrazole ring is coplanar with a crystallographic mirror plane that also contains the central C atom and one methyl group of the *t*-butyl substituent. As with TlTp^{Ph,4CN},[5b] and other Tl trispyrazolylborate complexes, the Tl ion is coordinated by the three available N atoms of the Tp ligand.

Unlike the structure of TlTp^{Ph,4CN}, which showed a relatively short interaction between Tl and the cyano N atoms of three neighboring molecules, there are no such interactions evident in the structure of TlTp$^{t\text{-Bu,4CN}}$. This is consistent with the increased steric demands of the *t*-butyl substituent reducing the accessibility of the coordinated metal with respect to the somewhat less bulky phenyl substituent.[11] Although the cyano N atoms from neighboring Tp ligands are still situated between the pyrazole rings, the distance between the Tl and these N atoms is increased from 3.211 Å in TlTp^{Ph,4CN} to 3.854 Å in TlTp$^{t\text{-Bu,4CN}}$.

The structure of TlTp$^{t\text{-Bu,4CN}}$ is very similar to those reported for Tl salts of other Tp ligands,[5b,12] with a pyramidal coordination geometry around the Tl atom. As noted for TlTp^{Ph,4CN}, the Tl–N bonds in TlTp$^{t\text{-Bu,4CN}}$ (2.712 Å) are significantly longer than those in the Tl salt of the analogous noncyano ligand, TlTp$^{t\text{-Bu}}$ (2.583 Å).[12d] A similar relationship is present between the structures of TlTp^{Me2}[12e] and its fluorinated analog TlTp$^{(CF3)2}$,[12f] but such a relationship appears not to be present in transition metal complexes of Bp^{Ph,4CN},[5a] Bp$^{(CF3)2}$,[12f] or Tp^{Ph,4CN*}[5b] for which the M–N bond lengths are essentially unchanged from the related noncyano or nonfluorinated ligands. The Tl–N bond lengths appear to correlate with the electron withdrawing nature of the ligands, possibly mediated by the directionality of the Tl(I) lone pair.

Copper Complexes. Trispyrazolylborate complexes with a 2:1 ligand-to-metal ratio, so-called "sandwich" compounds, were among the first compounds isolated with the parent Tp ligand.[1] Ligands with substituents in the 3-position enabled more facile isolation of "half-sandwich" complexes with a 1:1 ligand-to-metal ratio.[11] The *t*-butyl group has been dubbed a "tetrahedral enforcer" because of the inability of Tp ligands with this 3-position substituent to support formation of sandwich compounds; the phenyl substituent has been shown to be of intermediate steric bulk, with the ability to stabilize both the sandwich and half-sandwich complexes.[3b]

Reaction of K or Tl salts of Tp^{Ph,4CN} and Tp$^{t\text{-Bu,4CN}}$ with $Cu(ClO_4)_2$ or $Cu(OTf)_2$ in air produces, in all cases, both a green Cu(II) product and a yellow Cu(I) product. These can

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Table 1. X-ray Crystal and Refinement Data

	TlTp$^{t\text{-Bu},4CN}$	$\{Tp^{Ph,4CN}Cu\}_n$	$\{Tp^{t\text{-Bu},4CN}Cu\}_n$	$\{[Tp^{t\text{-Bu},4CN}Cu][MeCN]\}_n$
formula	$C_{24}H_{31}N_9BTl$	$C_{30}H_{19}N_9BCu$	$C_{24}H_{31}N_9BCu$	$C_{24}H_{31}N_9BCu \cdot C_2H_3N$
fw	660.76	579.90	519.93	560.98
temp, K	153	150	150	150
crystal system	trigonal	monoclinic	monoclinic	monoclinic
space group	*R*3*m*	*P*2$_1$/*n*	*C*2/*c*	*C*2/*c*
a, Å	16.8644(10)	9. 5640(6)	26.8861(10)	27.0860(13)
b, Å	16.8644(10)	24.3600(14)	14.6844(5)	14.6756(8)
c, Å	8.1583(10)	11.4620(7)	17.1846(6)	17.0389(9)
α, deg	90	90	90	90
β, deg	90	92.564(3)	117.672(2)	117.585(2)
γ, deg	120	90	90	90
V, Å^3	2009.4(3)	2667.7(3)	6008.6(4)	6003.1(5)
Z	3	4	8	8
color, habit	colorless, prism	yellow, prism	yellow, prism	yellow, prism
dimen., mm	0.63 × 0.18 × 0.16	0.55 × 0.28 × 0.21	0.32 × 0.12 × 0.12	0.37 × 0.14 × 0.12
D_{calc}, g cm^{-3}	1.638	1.444	1.150	1.241
μ, mm^{-1}	6.057	0.858	0.753	0.760
unique refs (R_{int})	1215 (0.070)	5221 (0.029)	3480 (0.054)	5872 (0.0679)
obs refs, $I > 2\sigma(I)$	1197	4551	2825	4471
parameters	71	365	325	353
R, R_w	0.025, 0.050	0.0321, 0.0841	0.0338, 0.0833	0.0395, 0.0844
gof	1.064	1.029	1.062	1.038
T_{max}, T_{min}	0.4225, 0.1525	0.8404, 0.6498	0.9150, 0.7945	0.9143, 0.7652
ρ_{min}, ρ_{max}, e Å^{-3}	−2.335, 0.844	−0.343, 0.461	−0.202, 0.319	−0.357, 0.389

Table 2. Bond Lengths (Å) and Angles (deg.) for TlTp$^{t\text{-Bu},4CN}$

Tl−N	2.714(4)
B−N	1.544(5)
C≡N	1.150(9)
C−C≡N	179.7(8)
N−Tl−N	76.31(12)
N−B−N	112.2 (3)

be separated relatively easily because of the insolubility in methanol of the Cu(I) species. The Cu(II) products show IR peaks characteristic of ClO_4^- or OTf^- and analyze satisfactorily for complexes of the form $Tp^{R,4CN}CuX$ ($X = ClO_4$ or OTf), although we have been unable to obtain X-ray quality crystals of these products. Isolation of the Cu(I) product was surprising, although the tetrahedral geometry imposed by the Tp ligand might promote the reduction. The reductant has not been identified, although the B−H moiety is a potential candidate. The Cu(I) products can also be synthesized directly using Cu(I) starting materials under an inert atmosphere. Crystallographic analysis identified the Cu(I) products as polymeric species. ORTEP drawings of the asymmetric units for the structures are shown in Figure 2, with pertinent data collection and structure solution parameters in Table 1 and selected bond distances and angles in Table 3.

$\{Tp^{Ph,4CN}Cu\}_n$ and $\{Tp^{t\text{-Bu},4CN}Cu\}_n$ crystallize on general positions in the monoclinic space groups *P*2$_1$/*n* and *C*2/*c*, respectively. The pseudotetrahedral coordination environment of the Cu(I) ion includes the three pyrazole N atoms of a $Tp^{R,4CN}$ ligand and is completed by a cyano N atom of another $Tp^{R,4CN}$ ligand. The bond to the cyano N atom is about 0.2 Å shorter than those to the pyrazole N atoms. A one-dimensional polymer is thus formed, as shown in Figure 3, in which only one cyano group from a given ligand is coordinated to a neighboring Cu. Surprisingly, only one CN stretch is observed in the IR spectrum, even though there are both coordinated and uncoordinated CN groups in the structure. As indicated above, Trofimenko reported the synthesis of an intractable material, presumably polymeric, upon treatment of Bp^{4CN} with metal ions,[6] and we have earlier reported an apparent polymeric material synthesized by treating $Bp^{Ph,4CN}{}_2Cu$ with $Rh_2(CF_3COO)_4$.[8] The $\{Tp^{R,4CN}Cu\}_n$ species, however, represent the first isolated and crystallographically characterized examples of cyanoscorpionate coordination polymers. The polymers display a zigzag motif, with approximately 90° corners defined by the angle between the coordinated CN group and its symmetry-related partner within the asymmetric unit. Cu−N bond distances are well within the range found for other Cu(I)−Tp complexes.[13]

Figure 4 shows views down the direction of the chains, which run parallel to the *b*-axis in $\{Tp^{Ph,4CN}Cu\}_n$ and parallel to the *ac* diagonal in $\{Tp^{t\text{-Bu},4CN}Cu\}_n$. These drawings highlight the well-defined channel formed by two adjacent chains. The conformation of the channels is slightly different in the phenyl and *t*-butyl systems, with adjacent chains in $\{Tp^{Ph,4CN}Cu\}_n$ (Figure 4a) being somewhat less offset with respect to each other than in $\{Tp^{t\text{-Bu},4CN}Cu\}_n$ (Figure 4b). The phenyl substituents occupy a significant amount of space in this channel, but the channel in the *t*-butyl derivative is much more open, with a closest distance of 4.211 Å between methyl carbon atoms across the channel.

During an attempt to synthesize a mixed-metal block coordination polymer involving $Tp^{t\text{-Bu},4CN}$, we isolated crystals of $\{[Tp^{t\text{-Bu},4CN}Cu][MeCN]\}_n$ in which acetonitrile molecules have been trapped in the channels. Data collection and structure solution parameters in Table 1 show these crystals to be essentially isostructural with the unsolvated polymer—the metrical parameters of the polymer in this structure are also very similar to those in the unsolvated polymer (see Supporting Information). Figure 4c shows a

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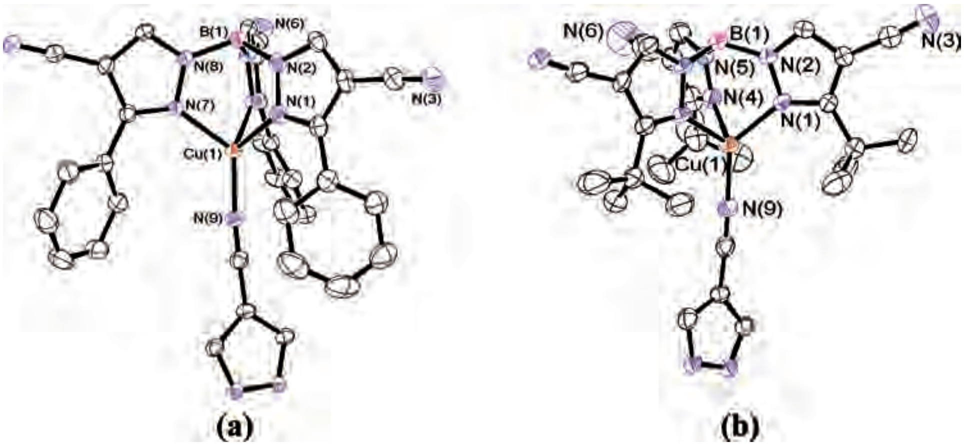

Figure 2. ORTEP drawings of one asymmetric unit of (a) $\{\mathrm{Tp}^{\mathrm{Ph,4CN}}\mathrm{Cu}\}_n$ and (b) $\{\mathrm{Tp}^{t\text{-}\mathrm{Bu,4CN}}\mathrm{Cu}\}_n$ showing 50% ellipsoids. An extra cyanopyrazole moiety has been included to complete the Cu coordination. H atoms have been omitted for clarity.

Table 3. Bond Lengths (Å) and Angles (deg.) for $\{\mathrm{Tp}^{\mathrm{R,4CN}}\mathrm{Cu}\}_n$[a]

length	R = Ph	R = *t*-Bu	Angle	R = Ph	R = *t*-Bu
Cu—N(1)	2.0641(16)	2.043(2)	N(1)—Cu—N(4)	90.87(6)	90.34(10)
Cu—N(4)	2.1107(16)	2.151(3)	N(1)—Cu—N(7)	86.29(6)	92.27(10)
Cu—N(7)	2.0884(15)	2.155(3)	N(1)—Cu—N(9)′	121.04(7)	131.39(11)
Cu—N(9)	1.8767(16)	1.882(3)	N(4)—Cu—N(7)	95.39(6)	94.06(10)
B—N(2)	1.550(3)	1.531(4)	N(4)—Cu—N(9)′	126.17(7)	120.51(11)
B—N(5)	1.545(3)	1.532(5)	N(7)—Cu—N(9)′	125.96(7)	118.97(11)
B—N(8)	1.553(3)	1.529(5)	Cu—N(9)′—C(d)	169.66(17)	175.0(3)
C(4)—N(3)	1.141(3)	1.149(4)	N(2)—B—N(5)	109.28(15)	111.3(3)
C(b)—N(6)	1.141(3)	1.143(5)	N(2)—B—N(8)	109.92(16)	110.2(3)
C(d)—N(9)	1.141(3)	1.149(4)	N(5)—B—N(8)	107.84(15)	107.8(3)
Cu···Cu′	8.589	8.733	C(2)—C(4)—N(3)	177.2(2)	176.0(4)
			C(a)—C(b)—N(6)	178.3(3)	177.1(6)
			C(c)—C(d)—N(9)	178.0(2)	174.1(3)

[a] C(a), C(b), C(c), and C(d) represent C(12), C(14), C(22), and C(24), respectively in R=Ph structure and C(10), C(12), C(18), and C(20), respectively in R=t-Bu structure.

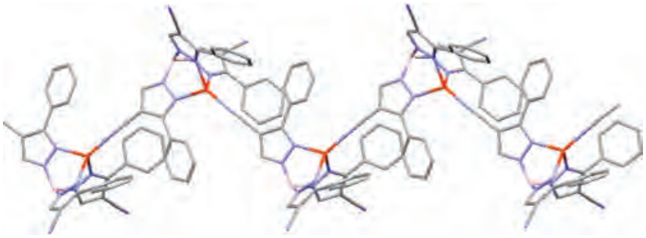

Figure 3. Mercury[14] drawing showing five units of the extended structure of $\{\mathrm{Tp}^{\mathrm{Ph,4CN}}\mathrm{Cu}\}_n$. Atom colors: Cu (orange), N (blue), B (pink), C (gray).

space-filling view down one channel of this structure. In this view, two methyl carbon atoms at the front have been deleted to give a clear view of the acetonitrile molecule. Figure 5 shows a view from the top of the channel (direction indicated by arrow in Figure 4c), in which the acetonitrile molecules and the methyl groups that protrude into the channel are shown in space-filling format. From this view, it can be seen that the *t*-butyl methyl groups form pockets along the channel in which the acetonitrile molecules are situated. A similar structure has also been characterized with encapsulated methanol molecules (CIF and figures are included as Supporting Information).

Conclusions

The cyanoscorpionate ligands continue to display interesting structural constructs. In concert with reported data for the analogous noncyano ligands $\mathrm{Tp}^{\mathrm{Ph}}$ and $\mathrm{Tp}^{t\text{-}\mathrm{Bu}}$, the *t*-butyl-substituted ligand, $\mathrm{Tp}^{t\text{-}\mathrm{Bu,4CN}}$ allows less access to the coordinated metal than does the phenyl-substituted ligand, $\mathrm{Tp}^{\mathrm{Ph,4CN}}$, hence the absence of close contacts between the Tl atom and the cyano N atoms from adjacent Tp ligands in the structure of $\mathrm{TlTp}^{t\text{-}\mathrm{Bu,4CN}}$. Isolation of a Cu(I) product in which the metal is bound not only by the pyrazole N atoms of one Tp ligand but also by the cyano N atom of an adjacent Tp ligand reaffirms and provides the first concrete evidence for the ability of this class of ligands to be used in the synthesis of coordination polymers through secondary coordination of the cyano group. With the inherent 3-fold symmetry of the Tp ligand, this property establishes the $\mathrm{Tp}^{\mathrm{R,4CN}}$ ligands as potential synthons for the rational design of coordination oligomers and polymers with defined architectures. Such polymers have promise in terms of electronic/magnetic materials and catalytic surfaces. Encapsulation of acetonitrile molecules within the polymeric architecture of $\{\mathrm{Tp}^{t\text{-}\mathrm{Bu,4CN}}\mathrm{Cu}\}_n$ suggests the possibility that two- or three-dimensional polymeric species involving the cyanoscorpionate ligands might be useful as hosts for small molecules in catalytic systems.

Experimental Section

General Information. Unless otherwise stated, all solvents and reagents were used as received from Aldrich, Acros, or Fisher Scientific without further purification. $\mathrm{KTp}^{\mathrm{Ph,4CN}}$[5b] and 3-*tert*-butyl-4-cyanopyrazole[9] were synthesized as previously described. IR spectra were recorded on a Nicolet Avatar 360 FTIR. Electrospray mass spectra were obtained on a Finnigan LCQ DECA spectrometer. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, AZ. When dry methanol is specified, it was prepared by distillation from sodium methoxide.

Potassium Hydrotris(3-*tert*-butyl-4-cyanopyrazolyl)borate ($\mathbf{KTp}^{t\text{-}\mathbf{Bu,\ 4CN}}$). Potassium borohydride (0.064 g, 1.7 mmol) and 3-*tert*-butyl-4-cyanopyrazole (1.0 g, 6.7mmol) were combined in a round-bottom flask fitted with a reflux condenser and slowly heated to 210 °C for 1 h. The reaction mixture was allowed to cool, and the resulting powder was washed with CH_3CN and boiling toluene to yield $\mathrm{KTp}^{t\text{-}\mathrm{Bu,4CN}}$ as a pale yellow solid (0.59 g, 1.19 mmol, 70.0%). IR (KBr, cm^{-1}): 2460 (ν_{BH}, m) 2231(ν_{CN}, s). ESI-MS (THF, negative detection): m/z = 148.3$[\mathrm{pz}^{t\text{-}\mathrm{Bu,4CN}}]^-$, 456.4$[\mathrm{Tp}^{t\text{-}}$

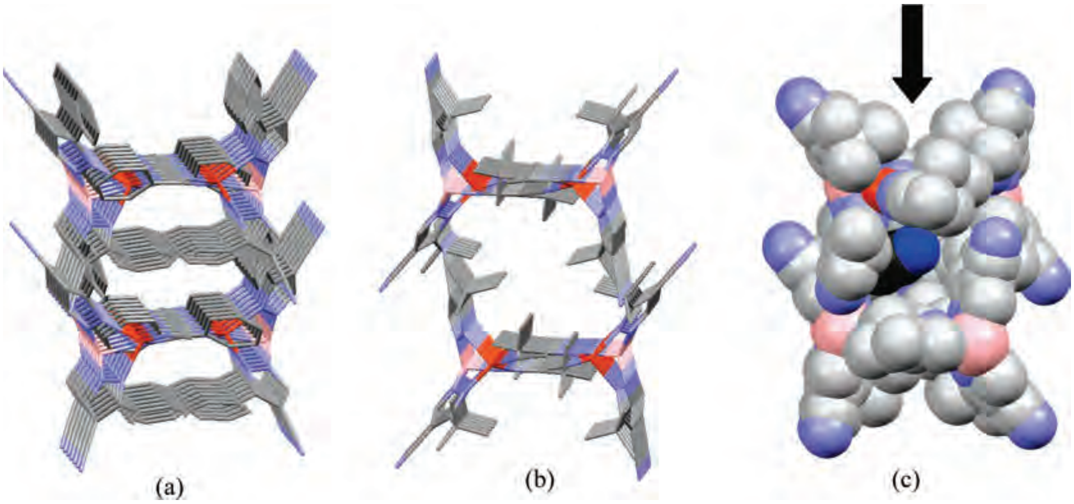

Figure 4. Mercury drawings directed down the channels of (a) $\{Tp^{Ph,4CN}Cu\}_n$ and (b) $\{Tp^{t\text{-}Bu,4CN}Cu\}_n$. Colors as in Figure 3. A Mercury space-filling plot of $\{[Tp^{t\text{-}Bu,4CN}Cu][MeCN]\}_n$ is shown in (c), with two methyl groups in the front removed to reveal the acetonitrile molecule (dark gray and dark blue). Arrow indicates the direction of view shown in Figure 5.

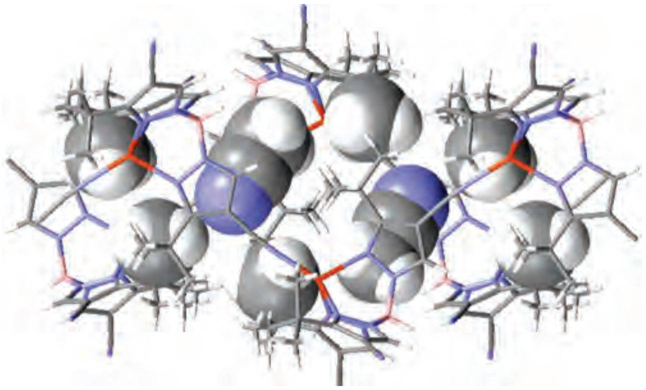

Figure 5. Mercury drawing of the top view of $\{[Tp^{t\text{-}Bu,4CN}Cu][MeCN]\}_n$ showing the acetonitrile molecules and the protruding methyl groups in space-filling format.

$Bu,4CN]^-$ (major peaks); 309.5$[Bp^{t\text{-}Bu,4CN}]^-$, 603.5$[pz^{t\text{-}Bu,4CN}Tp^{t\text{-}Bu,4CN}]^-$, 788.1$[NaBp^{t\text{-}Bu,4CN}Tp^{t\text{-}Bu,4CN}]^-$, 934.9$[NaTp_2{}^{t\text{-}Bu,4CN}]^-$ (minor peaks).

Thallium Hydrotris(3-*tert*-butyl-4-cyanopyrazolyl)borate, $TlTp^{t\text{-}Bu,4CN}$. To a solution of $KTp^{t\text{-}Bu,4CN}$ (1.08 g, 2.18 mmol) in 20 mL of methanol was added a solution of $TlNO_3$ (0.58 g, 2.18 mmol) in 20 mL of 50/50 methanol/water. The mixture was stirred for 1 h. Concentration of the solution on a rotary evaporator resulted in a yellow precipitate of $TlTp^{t\text{-}Bu,4CN}$, which was collected and washed with water to give 1.20 g (1.82 mmol, 83.4%) of light yellow powder. IR (KBr, cm^{-1}): 2452 (ν_{BH}, m) 2221(ν_{CN}, s). ESI-MS (CH_3OH, positive detection): $m/z = 458.2$ $[H_2Tp^{t\text{-}Bu,4CN}]^+$, 662.0 $[TlTp^{t\text{-}Bu,4CN}]H^+$. Elemental Analysis, Found (Calcd for $C_{30}H_{19}N_9BTl\cdot 5H_2O$): C, 37.74 (38.39); H, 4.26 (5.50); N, 17.68 (16.79). X-ray quality crystals were grown by layering a solution of $KTp^{t\text{-}Bu,4CN}$ in methanol on top of a solution of $TlNO_3$ in water/methanol. After allowing the solutions to diffuse together for a week, the top was removed and the solvent allowed to slowly evaporate, producing light yellow crystals.

Hydrotris(4-cyano-3-phenylpyrazolyl)boratocopper(II) Perchlorate, $Tp^{Ph,4CN}CuClO_4$, and Hydrotris(4-cyano-3-phenylpyrazolyl)boratocopper(I), $\{Tp^{Ph,\ 4CN}Cu\}_n$. To a solution of $KTp^{Ph,4CN}$ (0.5 g, 0.90 mmol) in 5 mL of methanol was added a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.33 g, 0.90 mmol) in 55 mL of 50/50 methanol/CH_2Cl_2. The mixture was stirred for half an hour, and $\{Tp^{Ph,4CN}Cu\}_n$ was filtered off as a yellow precipitate from a green solution of $Tp^{Ph,4CN}CuClO_4$. $\{Tp^{Ph,4CN}Cu\}_n$ was purified by washing thoroughly with methanol and water to give 0.198 g (0.34mmol, 37.78%) of yellow powder. IR (KBr, cm^{-1}): 2472 (ν_{BH}, m) 2226 (ν_{CN}, s). Elemental Analysis, Found (Calcd for $C_{30}H_{19}N_9BCu\cdot 4H_2O$): C, 55.74 (55.27); H, 3.25 (4.17); N, 17.23 (19.34).[15] X-ray quality crystals were grown by layering a solution of $KTp^{Ph,4CN}$ in methanol on top of a solution of $Cu(ClO_4)_2\cdot 6H_2O$ in CH_2Cl_2/methanol. The green $Tp^{Ph,4CN}CuClO_4$ solution was concentrated on a rotary evaporator resulting in precipitation of a green powder. Further purification was accomplished by washing with water, THF/methanol to remove unreacted starting materials. The final product is a green solid: 0.34 g (0.5 mmol, 55.56%). IR (KBr, cm^{-1}): 2486 (ν_{BH}, m), 2230 (ν_{CN}, s), 1080 (ν_{ClO_4}, s). Elemental Analysis, Found (Calcd for $C_{30}H_{19}N_9BCuClO_4\cdot THF$): C, 55.26 (54.34); H, 3.62 (4.47); N, 16.14 (16.78).

Hydrotris(3-*tert*-butyl-4-cyanopyrazolyl)boratocopper(II) Triflate, $Tp^{t\text{-}Bu,4CN}CuCF_3SO_3$, and Hydrotris(3-*tert*-butyl-4-cyanopyrazolyl)boratocopper(I), $\{Tp^{t\text{-}Bu,4CN}Cu\}_n$. $KTp^{t\text{-}Bu,4CN}$ (0.4 g, 0.80 mmol) was dissolved in 5 mL of methanol, and to this solution was added a 55 mL methanol/CH_2Cl_2 (50/50) solution of $Cu(CF_3SO_3)_2$ (0.292 g, 0.80 mmol). The mixture was stirred for half an hour. $\{Tp^{t\text{-}Bu,4CN}Cu\}_n$ was collected as a yellow precipitate by filtration and washed with methanol and water (0.151 g, 0.29 mmol, 36.3%). IR (KBr, cm^{-1}): 2466 (ν_{BH}, m), 2230 (ν_{CN}, s). Elemental Analysis, Found (Calcd for $C_{24}H_{31}N_9BCu\cdot H_2O$): C, 54.28 (53.59); H, 6.07 (6.18); N, 22.71 (23.43). X-ray quality crystals were grown by layering a solution of $KTp^{t\text{-}Bu,4CN}$ in methanol on top of a solution of $Cu(CF_3SO_3)_2$ in CH_2Cl_2/methanol. $Tp^{t\text{-}Bu,4CN}CuCF_3SO_3$ remained in the reaction solution and was condensed and washed by water and THF/methanol to yield a green solid (0.297 g, 0.44 mmol, 55.0%). IR (KBr, cm^{-1}): 2447 (ν_{BH}, m), 2229 (ν_{CN}, s), 1032 ($\nu_{CF_3SO_3}$, s), 639 ($\nu_{CF_3SO_3}$, m). Elemental Analysis, Found (Calc'd for $C_{24}H_{31}N_9BCu\ CF_3SO_3\cdot 2H_2O$): C, 42.57 (42.59); H, 4.63 (5.00); N, 18.25 (17.88).

Synthesis of $[Tp^{Ph,4CN}Cu]_n$ from Cu(I) Salt. In a nitrogen-filled glovebox, to a light brown solution of $[Cu(CF_3SO_3)]_2\cdot C_6H_6$ (0.0226 g, 0.0450 mmol) in 25 mL of dried, degassed methanol was added, dropwise, a solution of $KTp^{Ph,4CN}$ (0.050 g, 0.0901 mmol) in 25 mL of dried, degassed methanol. There was an immediate color change to a cloudy yellow green, and the solution was allowed to

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(15) We have had some difficulty obtaining good nitrogen analyses for the Cu polymers.

stir for 1 h. A light yellow precipitate was isolated by filtration, removed from the glovebox, and washed with methanol and water to give 0.0513 g (0.0851mmol, 98.3%) of [Tp^{Ph,4CN}Cu]$_n$.

Synthesis of [Tp$^{t\text{-}Bu,4CN}$Cu]$_n$ from Cu(I) Salt. Same as above, using 0.0253 g (0.0505 mmol) of [Cu(CF$_3$SO$_3$)]$_2$·C$_6$H$_6$ and 0.050 g (0.101 mmol) of KTp$^{t\text{-}Bu,4CN}$. Yield 0.0293 g (0.0564 mmol, 55.8%).

X-ray Crystallography. For {Tp^{Ph,4CN}Cu}$_n$, {Tp$^{t\text{-}Bu,4CN}$Cu}$_n$, and {[Tp$^{t\text{-}Bu,4CN}$][MeCN]}$_n$ crystals were affixed to a nylon cryoloop using oil (Paratone-n, Exxon) and mounted in the cold stream of a Bruker Kappa-Apex-II area-detector diffractometer. The temperature at the crystal was maintained at 150 K using a Cryostream 700EX low-temperature apparatus (Oxford Cryosystems). The unit cells were determined from the setting angles of the reflections collected in 36 frames of data. Data were measured using graphite monochromated Molybdenum Kα radiation ($\lambda = 0.71073$ Å) collimated to a 0.6 mm diameter and a CCD detector at a distance of 50 mm from the crystal with a combination of phi and omega scans. A scan width of 0.5 degrees and scan time of 10 s were employed. Data collection, reduction, structure solution, and refinement were performed using the Bruker Apex2 suite (v2.0−2).[16] All available reflections to $2\theta_{max} = 52°$ were harvested and corrected for Lorentz and polarization factors with Bruker SAINT (v6.45).[17] Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS 2004/1.[18] The structures were solved (direct methods) and refined (full-matrix least-squares against F^2) with the Bruker SHELXTL package (v6.14−1).[19] All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included at idealized positions; hydrogen atoms were not refined. Pertinent details are given in Table 1.

For TlTp$^{t\text{-}Bu,4CN}$, data were collected with a Bruker SMART-1000 CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation source. The data collected were processed to produce conventional intensity data by the program SAINT-NT (Bruker).[16] The intensity data were corrected for Lorentz and polarization effects and absorption corrections were applied using the SADABS[18] empirical method. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the WinGX suite of programs.[20] All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included at idealized positions, but were not refined. Pertinent details are given in Table 1.

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Supporting Information Available: X-ray crystallographic information for TlTp$^{t\text{-}Bu,4CN}$, {Tp^{Ph,4CN}Cu}$_n$, {Tp$^{t\text{-}Bu,4CN}$Cu}$_n$, {[Tp$^{t\text{-}Bu,4CN}$Cu][MeCN]}$_n$, in CIF format are available, as well as Mercury drawings of and CIF-format crystallographic data for {[Tp$^{t\text{-}Bu,4CN}$Cu][MeOH]}$_n$. This material is available free of charge via the Internet at http://pubs.acs.org.

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