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Versatility of pyridine-2-methanol as a chelating ligand toward a manganese ion: synthesis and X-ray structural analysis on some manganese-pyridine-2-methanol derivatives

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Abstract

A systematic synthesis and X-ray structural analysis have been made for several manganese derivatives with pyridine-2-methanol as a chelating ligand; neutral Mn(C₅NH₄-2-CH₂OH)₂(C₆F₅CO₂)₂(1), trans-[Mn(C₅H₄N-2-CH₂-OH)₂{C₆F₄-1,4-(CO₂)₂]_{∞}(2), cis- $[Mn(C_5H_4N-2-CH_2-OH)_2\{C_6F_4-1,3-(CO_2)_2\}]_{\infty} (3), \ \{Mn(C_5H_4N-2-CH_2-OH)_2(4,4'-bipyridine)(CIO_4)\}_{\infty} (4), \ and \ Mn(C_5H_4N-2-CH_2-OH)_2(4,4'-bipyridine)(CIO_4)\}_{\infty} (4), \ and \ Mn(C_5H_4N-2-CH_2-OH)_2(4,4'-bipyridine)(CIO_4))_{\infty} (4), \ and \ Mn(C_$ CH_2 -OH)₃(ClO₄)₂(4,4-azopiridine) (pyridine-2-methanol) (5) are our results. 1 and 5 are monomers, while 2–4 are polymers. An oxidation state of the manganese ion in 1, 2, 3, and 5 is 2^+ , while that of 4 is suggested to be 3^+ . The magnetic data of 4 down to 2 K are measured. The length of the linker ligand has been suggested to afford a crucial effect on the dimensionality of the product. © 2003 Elsevier B.V. All rights reserved.

Keywords: Pyridine-2-methanol; Coordination polymers; X-ray analyses; Anti-ferromagnetic interactions

1. Introduction

Pyridine derivatives with an ortho-substituent $(C_5H_4N-X, Chart 1; X = CH_3, NH_2, CO_2H, OR, OH,$ CHO, SH and so on) are ubiquitous and yet very versatile ligands. Thus plethora of metal derivatives with them have been reported [1]. Pyridine derivatives with two ortho-substituents ($C_5H_3N-Y_2$, Chart 2) have recently been revived as an important supporting ligands of multiple metal-metal bonds and/or linear metal-metal bonded arrays which are composed by more than three metal atoms [2-11]. We have suspected in the course of our attempt to construct new supra structures based on manganese ions why pyridine-2methanol has not yet been well explored as a potential supporting ligand of such an array and/or as a simple dangling or chelating ligand to the best of our knowledge [12-14]. Therefore, we added pyridine-2-methanol at first as a simple monodentate pyridine ligand to-

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gether with pentafluorobenzoic acid to the solution which contains manganese(II) perchlorate ion in order to examine a substituent effect of the CH₂-OH group on the monomer structure and/or the supra structure of the resulting manganese complex. Single crystal X-ray structure analysis for the product has shown that the pyridine-2-methanol functions as a chelating ligand and





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the neutral $Mn(C_5NH_4-2-CH_2OH)_2(C_6F_5CO_2)_2$ monomer complex is formed in contrast to the findings by Hendrickson et al. [12–14]; they have obtained Mn_4 clusters instead by reacting this ligand with MnX_2 . The present paper reports on our systematic synthesis and single crystal X-ray analyses of pyridine-2-methanol derivatives with manganese ions which are entailed by other ligands.

2. Experimental

2.1. Materials and general procedures

Syntheses and manipulations were generally made under an open air unless otherwise described. Pyridine-2-methanol was purchased from Tokyo Kasei Kogyo Co., Ltd. Colorless liquid is requisite to the synthesis; results are not reproducible if colored pyridine-2-methanol is used. 4,4'-azopyridine was synthesized by literature method [15]. Other chemicals and solvents were purchased from Wako Pure Chemical Ind., Ltd. or Aldrich. *Caution! Organic perchlorate salts are potentially explosive. All perchlorates salts should be handled with care.*

2.2. Synthesis of trans- $Mn(C_5H_4N-2-CH_2-OH)$ $(C_6F_5CO_2)_2$ (1)

76 mg (0.7 mmol) of 2-pyridinemethanol and 148 mg (0.7 mmol) of pentafluolobenzoic acid was dissolved in 10 ml of absolute ethanol. To this was added solid $Mn(ClO_4)_2 \cdot 6H_2O$ (507 mg, 1.4 mmol) with a small portion at one time and the mixture was stirred at room temperature for 5 h. The resulting colorless solution was filtered and the filtrate was left standing at room temperature for a week to afford colorless single crystals. Yield 75% based on the manganese salt. *Anal.* Calc. for $C_{26}H_{14}F_{10}MnN_2O_6$: C, 44.91; H, 2.03; N, 4.03. Found: C, 44.88; H, 2.01; N, 4.05%.

2.3. Synthesis of trans- $[Mn(C_5H_4N-2-CH_2-OH)_2 \{C_6F_4-1,4-(CO_2)_2\}]_{\infty}$ (2)

76 mg (0.7 mmol) of 2-pyridinemethanol and 83 mg (0.35mmol) of tetrafluorophthalic acid were dissolved in 10 ml of absolute ethanol. To this was added solid $Mn(ClO_4)_2 \cdot 6H_2O$ (127 mg, 0.35 mmol) with a small portion at one time and the mixture was stirred at room temperature for 5 h. The resulting colorless mixture was left standing in a refrigerator for a week to afford colorless crystals. Yield 88%. *Anal.* Calc. for C₂₀H₁₄-F₄MnN₂O₆: C, 47.16; H, 2.77; N, 5.50. Found: C, 47.11; H, 2.88; N, 5.56%.

2.4. Synthesis of cis- $[Mn(C_5H_4N-2-CH_2-OH)_2 \{C_6F_4-1, 3-(CO_2)_2\}]_{\infty}$ (3)

Similar synthetic procedure as **2** was employed. From 127 mg of $Mn(ClO_4)_2 \cdot 6H_2O$, colorless crystals **3** were obtained in 51% yield. *Anal.* Calc. for $C_{20}H_{14}F_4$ MnN₂O₆: C, 47.16; H, 2.77; N, 5.50. Found: C, 47.17; H, 2.89; N, 5.54%.

2.5. Synthesis of $[cis-\{Mn(C_5H_4N-2-CH_2-OH)_2(4,4'-bipyridine)(ClO_4)\}_{\infty}$ (4)

To an absolute ethanol solution (10 ml) which contained 76 mg (0.7 mmol) of 2-pyridinemethanol and 55 mg (0.35 mmol) of 4,4'-bipyridine, solid $Mn(ClO_4)_2 \cdot 6H_2O$ (127 mg, 0.35 mmol) was added by portions at one time with stirring and the stirring was continued for 5 h at room temperature. Then a dark purple solution was extracted with a large quantity of water. After filtration, the solvent was evaporated by standing at room temperature for several days to afford purple crystals in 41% yield. *Anal.* Calc. for C₂₂H₂₂ClMnN₄O₆: C, 49.96; H, 4.19; N, 10.60. Found: C, 49.56; H, 3.85; N, 10.69%.

2.6. Synthesis of mer-trans- $[Mn(C_5H_4N-2-CH_2-OH)_3]$ -(ClO_4)₂·(4,4-azopiridine)·(pyridine-2-methanol) (5)

129 mg (0.7 mmol) of azopyridine and 76 mg of 2pyridinemethanol (0.7 mmol) were dissolved in 10 ml of absolute ethanol. Solid $Mn(ClO_4)_2 \cdot 6H_2O$ (760 mg, 2.1 mmol) was added to this solution by portions at one time and the mixture was stirred at ambient temperature for 5 h. The resulting orange solution was filtered and the filtrate was left in a refrigerator for a month to afford orange crystals. Yield 37% based on the manganese salt. *Anal.* Calc. for C₃₄H₃₅Cl₂MnN₈O₁₂: C, 46.85; H, 3.93; N, 12.84. Found: C, 46.22; H, 4.11; N, 12.75%.

2.7. Single crystal X-ray analysis on 1-5

Suitable crystals of these five compounds were obtained from recrystallization processes described above. The selected crystals were glued to the top of a fine glass rod. Accurate cell dimensions were determined by leastsquare refinements of 20–25 reflections on a MAC MXC3 diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The reflection data were collected at r.t. Complete crystal data are collated in Table 1. The structures were solved by the direct method, SIR97 for 1, 2, 4, and 5 and SIR92 in a CRYSTAN-GM program package for 3. The structures were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms using SHELXS97 on F^2 except 3, to which aforementioned CRYSTAN-GM program package was applied

Table 1	
Crystal	data

Compound	1	2	3	4	5
Empirical formula	$C_{26}H_{14}F_{10}MnN_2O_6$	$C_{16}H_{14}F_4MnN_2O_4$	$C_{16}H_{14}F_4MnN_2O_4$	C22H22ClMnN4O6	$C_{34}H_{35}Cl_2MnN_8O_{12}$
Formula weight	695.3	509.3	509.3	528.8	873.5
Crystal system	monoclinic	monoclinic	monoclinic	tetragonal	triclinic
Space group	$P2_1/a$	$P2_1/n$	$P2_1/n$	P4/ncc	$P\bar{1}$
a (Å)	16.720(4)	17.25(1)	15.688(6)	24.775(9)	11.519(4)
b (Å)	6.015(1)	9.526(6)	9.066(3)	24.775(9)	18.678(6)
<i>c</i> (Å)	13.390(3)	5.933(4)	14.996(4)	15.024(7)	19.381(6)
α (°)					81.91(3)
β (°)	104.71(2)	94.89(5)	111.62(3)		74.82(3)
γ (°)					74.70(3)
Ζ	2	2	4	16	4
D_{calc} (g cm ⁻³)	1.76	1.73	1.70	1.80	1.50
Crystal dimensions	$0.5 \times 0.5 \times 0.3$	0.4 imes 0.2 imes 0.2	$0.50 \times 0.40 \times 0.30$	0.2 imes 0.1 imes 0.1	0.6 imes 0.4 imes 0.4
(mm ³)					
V (Å ³)	1302.4(6)	971.7(4)	1983(1)	9221(7)	3870(4)
μ (Mo K α) (cm ⁻¹)	5.37	8.03	7.82	7.83	5.73
Scan type	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
Scan range	$1.70 + 0.35 \tan \theta$	$1.10 + 0.35 \tan \theta$	$1.15 + 0.35 \tan \theta$	$1.25 + 0.3535 \tan \theta$	$1.25 + 0.35 \tan \theta$
Scan speed (deg min ⁻¹)	6.0	6.0	6.0	6.0	6.0
$2\theta_{\max}$ (°)	50.0	55.0	55.0	45.0	45.0
Temperature (K)	298	298	298	298	298
Unique reflections	2290	2239	4573	3020	10113
Reflections with					
$ F_{\rm o} > 3\sigma(F_{\rm o})$	1821	926	1777	1091	4511
Number of parameters	222	152	304	253	1028
Refined					
R	0.054	0.087	0.091	0.12	0.09
$R_{ m w}$	0.158	0.232	0.089	0.24	0.23

Mo K α radiation ($\lambda = 0.71073$ Å); $R = \sum ||F_0|| - |F_c|| / |F_0|$; $R_w = [\sum (|F_0| - F_c|)^2 / \sum w(F_0)^2]^{1/2}$ where $w = 1/\sigma^2(F)$.

on *F*. The positions of H atoms were assigned with common isotropic displacement factors and were refined by use of geometrical restraints in the final refinement cycle. The final *R* and R_w values are also listed in Table 1. Tables for atomic coordinates, thermal parameters, and bond lengths and angles are available as supplementary material. Selected bond lengths and angles are given in Table 2.

2.8. Spectroscopies and magnetic measurements

IR spectra were measured by use of a JASCO Herschel 460+ for KBr samples. Magnetic data were measured by use of a SQUID magnetometer (a Quantum Design MPMS-5P) between 2 and 300 K. The fit and the analysis of the data were made by use of the computer software Kaleida-Graph 3.52.

3. Results and discussion

3.1. Molecular and crystal structures

The whole scheme of the synthesis is summarized in Scheme 1. The molecular structure analysis on 1 (Fig. 1) has clearly revealed for the first time that the pyridine-2methanol can function as a chelating ligand for a single manganese ion [16,17].¹ Fig. 1 also shows that two C₆F₅CO₂⁻ anions coordinate to one Mn(II) ion as a monodentate terminal ligand. Thus, a mononuclear trans geometry is formed for this combination of ligands. The IR spectrum of 1 exhibits a lower-energy shifted broad band due to the OH stretching (from 3260 to 3170 cm^{-1}). Similar lower energy shifts were observed for 2, 3, and 5. The Fourier synthesis at the final stage of the leastsquares refinement for X-ray analysis has successfully located the position of the H atom of the OH group in pyridine-2-methanol. The finding indicates that pyridine-2-methanol functions as a neutral ligand. The oxidation state of the manganese ion is thus estimated to be 2^+ . The molecular and crystal structure analyses on 2 (Figs. 2 and 3) have shown that the tetrafluoroterephthalate ligand bridges two manganese ions with a *trans* geometry via one terminal oxygen in each carboxylate group to afford one-dimensional infinite chains (Fig. 3). The formal oxidation state of the manganese ion is estimated to be 2^+ . When 2, 4, 5, 6-tetrafluoro-isophthalate is employed instead, a cis-isomer 3 is obtained (Fig. 4). The crystal packing diagram (Fig. 5) shows that 3 forms a quasi-onedimensional infinite chain in almost the ac-plane; one O atom in each CO_2^{-} group coordinates to a Mn ion as a

¹ Some chelating examples on similar 2, 6-substituted pyridine dimethanol ligand were reported previously for Mo and Re.

Table 2	
Selected bond-lengths (Å) and angles (°)	

Compound	1	2	3	4	5 mol · 1	$mol \cdot 2$
Mn–N(py)	2.242(3)	2.233(1)	2.281(8)	2.109(2)	2.207(2)	2.181(2)
			2.284(9)	2.168(2)	2.230(2)	2.197(2)
					2.228(1)	2.231(1)
Mn–O(py)	2.59(3)	2.200(1)	2.198(7)	1.888(2)	2.227(1)	2.2432(9)
			2.219(6)	1.782(2)	2.183(1)	2.185(1)
					2.1809(9)	2.198(1)
Mn–O(CO ₂)	2.152(3)	2.1293(9)	2.095(7)			
			2.151(6)			
Mn–N(bipy)				2.188(2)		
$O(pv)-Mn-O(CO_2)$	90.2(1)	91.63(2)	84.3(3)			
	89.8(1)	88.37(2)	87.2(2)			
			90.2(2)			
			175.9(2)			
O(py)–Mn–N(py)	89.0(1)	73.32(1)	72.0(3)		80.0(9)	
	91.0(1)	106.68(1)	72.1(3)		95.6(9)	
			159.6(3)		90.1(9)	
			90.0(2)		94.2(9)	
N(py)–Mn–O(CO ₂)	74.0(1)	85.24(2)				
	106.0(1)	94.76(2)				
N(py)–Mn–N(py)		180.00				
O(py)–Mn–O(py)	180.00(2)	180.00	93.2(2)		175.5(9)	
$O(CO_2)$ - Mn - $O(CO_2)$	180.00(2)	180.00	91.0(2)			
N(py)–Mn–N(bipy)					89.4(9)	
					93.9(8)	
					87.1(8)	
					91.8(9)	
O(py)–Mn–N(bipy)					98.6(9)	
					93.4(9)	
					80.0(9)	
					88.1(8)	
N(bipy)–Mn–N(bipy)					167.9(9)	



Scheme 1.

monodentate ligand. Fig. 6 shows the molecular structure of **4**, which has a similar *cis*-geometry to that of **3**. Two 4,4-bipyridine ligands coordinate to one manganese ion in a *cis*-disposition. An infinite Z-shaped chain thus constructed is shown in Fig. 7. This one-dimensionalzigzag chain is quite similar to that of $[Mn(hfac)_2(4,4'-bipy)]_n$ which was recently reported by Liao et al. [18]. However, two pyridyl rings are somewhat twisted in contrast to that of the hfac derivative. One perchlorate ion is situated in a close proximity to one manganese ion. As is described below, the metric parameters on Mn–O distances of 4 are quite short compared with those of 1–3, and 5, suggesting that the pyridine-2-methanol functions as an anion in 4. These suggest that the manganese ion is



Fig. 1. The ORTEP drawing of trans-Mn(C₅H₄N-2-CH₂-OH) (C₆F₅CO₂)₂ (1).



Fig. 2. The ORTEP drawing of *trans*- $[Mn(C_5H_4N-2-CH_2-OH)_2 \{C_6F_4-1,4-(CO_2)_2\}]_{\infty}$ (2).



Fig. 3. Infinite Z-shaped chain structures of 2. The view almost along the a axis.

in the 3^+ oxidation state. The crystal packing diagram in Fig. 7 demonstrates also that the perchlorate ion is close to hydrogen atoms of 4,4-bipyridine ligands, indicating possible hydrogen bonds among the oxygen atoms in perchlorate ions and the hydrogens of 4,4-bipyridines; the perchlorate ion is located in the center of channels which are composed of the manganese ions and 4,4'-bpy. When *trans*-4,4'-azobipyridine, which has a bent skeleton but is expected to be functionally similar to 4,4'-bipyridine, is reacted with Mn(ClO₄)₂ · 4H₂O and 2-pyridinemethanol in absolute ethanol, no such polymer as **4** has yet been obtained. Instead, tris(2-pyridine methanol) manganese perchlorate **5** is obtained (Fig. 8). Two independent molecules are contained in the crystal,



Fig. 4. The ORTEP drawing of $\mathit{cis}\mbox{-}[Mn(C_5H_4N\mbox{-}2\mbox{-}CH_2\mbox{-}OH)_2\{C_6F_4\mbox{-}1,3\mbox{-}(CO_2)_2\}]_\infty$ (3).



Fig. 5. The crystal packing diagram of 3 showing a quasi one-dimensional infinite chain. The view almost along the b axis.

which indicates that the crystal is composed of a racemic mixture of two chiral isomers. The crystal contains each one free 2-pyridine methanol and 4,4'-azobipyridine molecules (Fig. 9) in addition to two perchlorate ions for each manganese ion;azo N₂ positions of one solvate 4,4'azobipyridine are disordered. Perhaps these two ligands are held by hydrogen bonds to perchlorate ions. The formal oxidation state of the manganese ion is presumed to be 2⁺. From the comparison of molecular structures for 1–4, it has been shown that the geometry of bis(2pyridinemethanol) manganese derivatives depends on the coexisting ligand together with the mutual positioning of two sets of N and O coordinating atoms in bis(2pyridinemethanol) ligands; two N atoms and two O atoms are located in *trans* positions for 1 and 2, while this



Fig. 6. The ORTEP drawing of $[cis-{Mn(C_5H_4N-2-CH_2-OH)_2(4,4'-bipyridine)(ClO_4)}_{\infty}(4)$.



Fig. 7. An infinite Z-shaped chain constructed from 4.



Fig. 8. The ORTEP drawing of mer-trans- $Mn(C_5H_4N-2-CH_2-OH)_3(ClO_4)_2(4,4-azopiridine)(pyridine-2-methanol)$ (5) for one molecule.



Fig. 9. The crystal packing diagram of 5, which indicates solvate molecules. The view is almost along the a axis.

trans preference is not kept in 3 and 4 which have *cis*geometries. However, the octahedral skeleton for 3 is severely distorted from the ideal one. For tris-chelated compound 5, *trans* dispositions are seen for each one set of N–N and O–O combinations and one set of N–O combination. Similar severe distortion from the ideal octahedral geometry as 3 is observed for 5. These distortions are reflected clearly on the bond-angle parameters as shown in Table 2. Details on these bonding parameters are discussed below.

3.2. Molecular parameters

From the molecular parameters listed in Table 2, following trends have been clarified. Mn-pyridine N bond distances are in the range 2.109-2.284 Å, which is close to normal Mn-pyridine N distances [16,17]. Mn-O (pyridine-methanol) distances are in the range 1.782-2.243 A, while Mn–O (carboxylate) distances are in the range 2.095–2.152 A. For 1–3, each carboxylate group acts as a monodentate ligand via one O atom. Thus Mn-O distances for these complexes are longer than those in which carboxylate groups act as a bidentate chelating ligand [18]. Mn-pyridine N and Mn-O (pyridine-methanol) distances are found very short for 4 (2.109 (2) and 2.168 (2) Å for Mn-N and 1.782 (2) and 1.888 (2) Å for Mn–O, respectively), compared with those of 1–3 and 5; the finding is best accounted for in terms of the anion formation of NC_5H_4 – CH_2O^- and the coordination to the manganese ion via O- as described above. The Mn–N (bipy) distance in 4 is 2.188(2) Å, which is close to those found for other Mn-4,4'-bipy complexes [19], but is significantly shorter than that of $[Mn(hfac)_2(4,4-bipy)]_n$ (2.257(5) Å) [15]. The crystal of **5** is composed from racemic mixtures as described above. Mn–N distances of molecule 1 (2.181–2.231 Å, average 2.203 Å) are slightly shorter than those of molecule 2 (2.207–2.230 Å, average 2.222 Å), while Mn–O distances of the former molecule (2.185–2.243 Å, average 2.221 Å) are only slightly longer than those of the latter molecule (2.181–2.227 Å, average 2.197 Å).

Distortions from ideal octahedral geometry for **3** and **5** are evaluated from the bond angles around the relevant manganese ion. O3–Mn–N2 angle is $159.6(3)^{\circ}$, O1–Mn–N1 is 156.0(3), N1–Mn–O3 is $72.0(3)^{\circ}$ for **3**. These angles are far from the ideal linear and right angles. Similar deviations are observed for **5**; N–Mn–N angles are 151.0(5), $109.1(4)^{\circ}$, and $97.7(5)^{\circ}$, O–Mn–O angles are $105.5(5)^{\circ}$, $161.6(4)^{\circ}$, $108.8(4)^{\circ}$, 156.0(4), $88.7(5)^{\circ}$, and $87.0(5)^{\circ}$, and N–Mn–O angles are in the range $72.6(5)^{\circ}$ – $105.6(5)^{\circ}$ and $157.0(5)^{\circ}$ – $157.9(5)^{\circ}$. Bond angles around respective manganese ions for **1**, **2**, and **4** are quite close to 180° and/or 90° (Table 2).

3.3. Magnetic data

Oxidation states estimated above are based on the assumption that 2-pyridinemethanol is a neutral ligand; the oxidation states of manganese ion for 4 was deduced from the Mn–O bond distances at first and later by magnetic susceptibility measurements. The precise magnetic behavior of 4 for the temperature range 10–300 K is shown in Fig. 10 in the forms of χ_m vs. *T* and $\chi_m^{-1}T$ vs. *T* plots. The $\chi_m T$ value at room temperature is 3.65 cm³ K/mol, which is slightly lower than that of the non-interacting spin-only value of 3.77 cm³ K/mol for



Fig. 10. Plots of molar susceptibility χ_m vs temperature for compound 4. The solid line represents a least-squares fit of the data to the theoretical equation by Hiller et al. [21].

Mn(III) (S = 2) and $g_{Mn} = 2.00$. This value decreases slowly 300 K until from 19 K and abruptly decreases to 2.98 cm³ K/mol below this temperature, which is typical for an anti-ferromagnetically interacting system. The magnetic data for 4 are in agreement with the assignment of the 3⁺ oxidation state to the manganese ion.

3.4. Polymer formation

Four kinds of bidentate ligands have been examined to investigate the influence of these ligands on the structure and/or dimensionality of coordination polymers in addition to pyridine-methanol. An interesting observation is that the positions of CO_2^- groups in $C_6F_4(CO_2)_2^{2-}$ do not afford dramatic change on the gross polymer structures of 2 and 3 in spite of having different geometries around the corner manganese ions for these complexes. The use of 4,4'-bipyridine as a linker affords significant change on the polymer structure 4 as was described in the molecular and crystal structure section. However, 4,4'-azopyridine, of which function is expected to be likely to that of 4,4'-bipyridine, is contained as only a solvate molecule in the crystal in addition to one 2-pyridinemethanol solvate molecule. Both molecules are held via hydrogen bonds with perchlorate ions in the crystal of 5. The lengths of these four bifunctional linkers are significantly different. In this context it is quite interest to refer to the paper by Cotton and his group [20] in which they have suggested that the length of the linker determines the type and the structure of the polymer formed and the dimensionality of the polymer is reduced from two to one if a longer linker is used. It is worthwhile to point out the relevance of their suggestion to our finding that 4,4-azopyridine, which is the longest linker employed in this study, does not afford polymer.

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