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A new 2-carboxylate-substituted 4,4′-bipyridine ligand: coordination chemistry of 4,4′-bipyridine-2-carboxylic acid and its synthetic intermediate 2-methyl-4,4′-bipyridine

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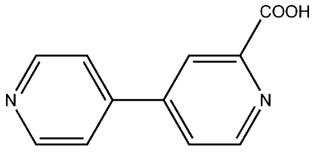
The first monocarboxylate-substituted 4,4′-bipyridine ligand, 4,4′-bipyridine-2-carboxylic acid (4-(pyridin-4-yl)pyridine-2-carboxylic acid (PPCAH)), has been successfully synthesized from 4,4′-bipyridine. Reactions with transition metals zinc and manganese were used to establish the coordination characteristics of the product, 4,4′-bipyridine-2-carboxylic acid, and of the synthetic intermediate, 2-methyl-4,4′-bipyridine, by single-crystal X-ray diffraction. The ligand PPCAH is useful for the formation of metal-containing building blocks that can be used in the assembly of mixed-metal framework materials. The synthesis and structure of one such mixed-metal coordination polymer, $Cu(PPCA)_2HgI_2$, is also presented.

Introduction

Due to rapid advances in the past several years, the field of supramolecular chemistry has progressed to the point where specified supramolecular structures can often be obtained *via* the assembly of judiciously selected building blocks under controlled reaction conditions.[1] One aspect, in particular, that has greatly affected the field of supramolecular chemistry is ligand design and synthesis, which continues to play an important role in the formation of new supramolecular complexes with desired structures and concomitant properties.[2]

Pyridyl ligands that contain carboxylate groups, such as pyrazinecarboxylate or pyridinecarboxylate, exhibit the coordination characteristics of both the pyridyl donor and the carboxylate group; and this dual functionality imparts these ligands with special networking abilities. Consequently, they have received increased attention by research groups for use in the synthesis of new mono- and bi-metallic inorganic–organic materials.[3] In particular one group of pyridyl based ligands, the pyrazinecarboxylates, has proven to be extremely versatile for the construction of new framework materials due to their ability to engage in several different coordination modes.[4] In fact, our recent studies on copper–mercury and copper–cadmium pyrazinecarboxylate systems, which have resulted in the formation of several intriguing mixed-metal frameworks,[5] demonstrate that 2-pyrazinecarboxylic acid and 2-methylpyrazine-5-carboxylic acid are excellent ligands for use in the assembly of extended mixed-metal structures. The first step involves the formation of a metal-containing building block by coordinating two ligands to one copper center, followed by the reaction of this copper-containing building block with a second metal cation. This strategy has resulted in numerous, new mixed-metal framework structures. In all these cases, however, the size of cavities in the resulting framework is limited by the length of the pyrazinecarboxylate ligand. Thus, to enable the assembly of larger networks, we decided to synthesize a new, longer ligand with coordination characteristics similar to those of the pyrazinecarboxylate ligand.

Although substituted bipyridyl ligands have been studied for many years due to their utility in the formation of supramolecular structures,[6] only a few examples of the synthesis of monomethyl-substituted 4,4′-bipyridine are recorded in the literature,[7] and no monocarboxylate-substituted 4,4′-bipyridine has been reported to date. Consequently, the coordination chemistry of the monomethyl-substituted 4,4′-bipyridine and the monocarboxylate-substituted 4,4′-bipyridine has yet to be investigated. As part of our continuing investigation of mixed-metal coordination compounds based on pyrazinecarboxylate ligands, we present herein the synthesis and coordination characteristics of the new 2-carboxylate-substituted 4,4′-bipyridyl ligand, 4,4′-bipyridine-2-carboxylic acid (PPCAH) (Scheme 1). The single-crystal structures of five complexes: $[Mn(2\text{-}Me\text{-}4,4'\text{-}bipy)(NO_3)_2(H_2O)_2]$ (**1**), $[Mn(2\text{-}Me\text{-}4,4'\text{-}bipy)_2(CH_3CN)_2(H_2O)_2](ClO_4)_2$ (**2**), $[Mn(PPCA)_2(H_2O)_2]\cdot 2H_2O$ (**3**), $[Zn(PPCA)_2(H_2O)_2]\cdot 2H_2O$ (**4**) and $Cu(PPCA)_2HgI_2$ (**5**) show that the ligand PPCA, and its synthetic intermediate 2-methyl-4,4′-bipyridine (2-Me-4,4′-bipy), are promising supramolecular reagents for the construction of hydrogen-bonded inorganic–organic hybrid materials. Furthermore, we demonstrate that PPCA has coordination characteristics similar to the pyrazinecarboxylate ligand, and that it is a useful ligand for the formation of



Scheme 1

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metal-containing building blocks that can be used in the assembly of mixed-metal framework materials.

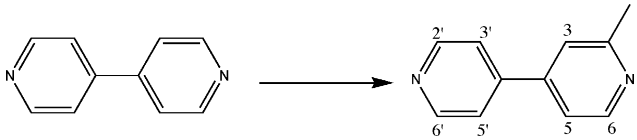
Experimental

All starting materials and solvents were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were collected at room temperature on a Varian Mercury/VX 300 spectrometer with chemical shifts reported in δ relative to $CDCl_3$ or DMSO-d_6. Melting point determinations were made on samples in sealed glass capillaries using an Electrothermal 9100 apparatus. X-Ray powder diffraction (XRD) patterns were acquired on a Rigaku D/Max-2200 powder X-ray diffractometer with graphite-monochromatized Cu-Kα radiation ($\lambda = 0.15148$ nm).

CAUTION! *Perchlorate salts are potentially explosive and should only be used in small quantities and handled with the necessary precautions.*

Synthesis

2-Methyl-4,4′-bipyridine. The method used to synthesize 2-methyl-4,4′-bipyridine is similar to that (Scheme 2) reported in the literature.[7a] 4,4′-Bipyridine (31.24 g, 0.2 mmol) was dissolved in a solution of 98% sulfuric acid (11 mL) in distilled water (140 mL) . Subsequently, acetic acid (60 g, 1.0 mol) and a solution of silver nitrate (3.40 g, 0.02 mmol) in water (20 mL) were added to the bipyridine solution. The resultant mixture was heated to 110 °C and maintained at that temperature for 30 min, at which point ammonium persulfate (45.64 g, 0.2 mol) was added portion-wise as a solid. Once the vigorous evolution of carbon dioxide had ceased, the solution was heated at reflux for an additional 30 min, allowed to cool, and made alkaline to a pH value of about 8. The reaction products were then extracted with ether and identified by TLC. The combined extracts were dried over $CaCl_2$ and evaporated *in vacuo*, to yield a solid yellow mixture (27.19 g). The yellow mixture was introduced as a solution in chloroform onto a column of alumina packed in hexanes. Elution with hexane–acetone (5 : 1) gave four bands. The third band was identified as 2-methyl-4,4′-bipyridine, H^1 NMR (δ, $CDCl_3$) 2.64 (s, CH_3), 7.32–7.51 (m, H3,3′,5,5′ aromatic protons), 8.59–8.72 (m, H2′, 6,6′ aromatic protons); mp 92–93 °C.



Scheme 2

4,4′-Bipyridine-2-carboxylic acid (PPCAH). 2-Methyl-4,4′-bipyridine (0.85 g, 5 mmol) was dissolved in 50 mL distilled water. Potassium permanganate (2.37 g, 15 mmol) was added while stirring, and the resulting mixture was heated at reflux for 12 h (Scheme 3). A brown precipitate (MnO_2) was isolated by filtration, and the filtrate was extracted with ether to remove unreacted 2-methyl-4,4′-bipyridine starting material. Addition of concentrated hydrochloric acid precipitated a white powder, which was recrystallized from water. Yield: 23.9%. H^1 NMR (δ) (DMSO-d_6) 8.89 (dd, H2, H6, H6′), 8.44 (d, H3′, H5′), 8.14 (dd, H5); mp 218–219 °C.

Complex 1: [Mn(2-Me-4,4′-bipy)$(NO_3)_2(H_2O)_2$]. $Mn(NO_3)_2\cdot 6H_2O$ (0.05 mmol) dissolved in CH_3CN (3 mL) was layered onto a solution of 2-methyl-4,4′-bipyridine (0.05 mmol) in CH_2Cl_2 (2 mL) to give colorless plate crystals (58% yield) suitable for X-ray analysis.

Complex 2: [Mn(2-Me-4,4′-bipy)$_2(CH_3CN)_2(H_2O)_2](ClO_4)_2$. $Mn(ClO_4)_2\cdot 6H_2O$ (0.05 mmol) dissolved in CH_3CN (3 mL) was layered onto a solution of 2-methyl-4,4′-bipyridine (0.05 mmol) in CH_2Cl_2 (2 mL) to give colorless plate crystals (53% yield) suitable for X-ray analysis.

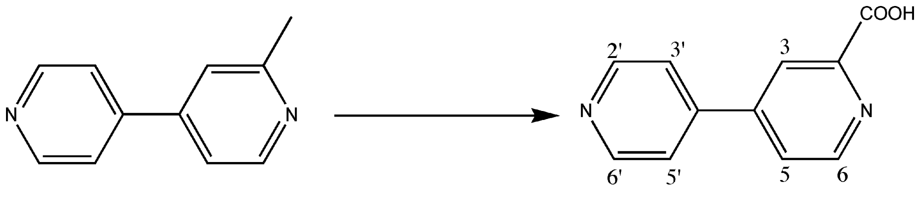
Complex 3: [Mn(PPCA)$_2(H_2O)_2]\cdot 2H_2O$. Na_2CO_3 (0.025 mmol) was added to 4,4′-bipyridine-2-carboxylic acid (PPCAH) (0.05 mmol) in H_2O (3 mL). Once the solution became clear, $Mn(NO_3)_2\cdot 6H_2O$ (0.1 mmol) in CH_3CN (3 mL) was layered onto it. Two days later, yellow prismatic crystals (42% yield) suitable for X-ray analysis were harvested.

Complex 4: [Zn(PPCA)$_2(H_2O)_2]\cdot 2H_2O$. Na_2CO_3 (0.025 mmol) was added to 4,4′-bipyridine-2-carboxylic acid (PPCAH) (0.05 mmol) in H_2O (3 mL). Once the solution became clear, $Zn(BF_4)_2\cdot 6H_2O$ (0.1 mmol) in CH_3CN (3 mL) was layered onto it. Two days later, colorless plate crystals (46% yield) suitable for X-ray analysis were harvested.

Complex 5: [Cu(PPCA)$_2HgI_2$]. PPCAH (0.5 mmol), HgI_2 (0.5 mmol), and $Cu(NO_3)_2\cdot 3H_2O$ (0.5 mmol) were placed in a 23 mL Teflon-lined autoclave with 10 mL water. The autoclave was subsequently sealed and heated to 160 °C at 1 °C min^{-1} and held at that temperature for 72 h. At the end of this period, the autoclave was cooled to 80 °C at 0.1 °C min^{-1} and held at that temperature for 12 h before cooling to room temperature at the same rate. Rectangular turquoise crystals (32% yield) suitable for X-ray analysis were harvested.

X-Ray crystallography

X-Ray intensity data for **1–5** were measured at 150 K on a Bruker SMART APEX CCD-based diffractometer (Mo-Kα radiation,



Scheme 3

$\lambda = 0.71073$ Å).[8] For **1**, initial unit cell indexing was ambiguous. The data are metrically consistent with an unusual *C*-centered orthorhombic unit cell with $a = 19.331$ Å, $b = 43.975$ Å, $c = 7.245$ Å. After raw data frame integration and Lp corrections (SAINT+),[8] examination of the intensity data with XPREP[9] showed $R_{\text{int}} = 0.079$ for this cell. However the pattern of systematic absences in the intensity data agreed with no space group. Processing the data according to a primitive monoclinic cell (reported below) with half the volume gave $R_{\text{int}} = 0.053$ and absences corresponding to $P2_1/c$. A reasonable solution was obtained in $P2_1/c$ but resulted in high (>20%) *R*-factors and several unacceptable displacement parameters. An excellent refinement was obtained in $P2_1/c$ by treating the crystal as being twinned by pseudo-merohedry, *i.e.*, the primitive monoclinic crystal is twinned to emulate the *C*-centered orthorhombic cell. The twin law applied is $\{1\,0\,1/0\,\bar{1}\,0/0\,0\,\bar{1}\}$, derived analogously to a previously reported example of this form of twinning.[10] The major twin fraction refined to 0.553(1). The crystal system and space group choice were further verified by ADDSYM/PLATON.[11] For **1–5**, the raw data frame integration and Lp corrections were performed with SAINT+.[8] For all complexes, analysis of the data showed negligible crystal decay during collection and no absorption correction was applied for **1–4**, while an absorption correction using SADABS[8] was used for **5**; direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to carbon were placed in geometrically idealized positions and included as riding atoms. All water hydrogens were located in difference maps and refined with a common isotropic displacement parameter with the O–H distances restrained to be approximately equal. Crystal data are summarized in Table 1, selected bond lengths and angles are given in Table 2 and all hydrogen bonds involved are tabulated in Table 3.

CCDC references numbers 267236–267239 and 601017.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606280f

Results and discussion

Synthesis

The synthesis of the intermediate, 2-methyl-4,4′-bipyridine, was similar to the method reported in the literature.[7a] 4,4′-Bipyridine was mixed with sulfuric acid, silver nitrate and ammonium persulfate in an aqueous solution. The resulting yellow solid, a mixture of 2,2′,6-trimethyl-4,4′-bipyridine, 2,2′-dimethyl-4,4′-bipyridine, 2-methyl-4,4′-bipyridine and 4,4′-bipyridine, was separated using an alumina column before oxidation. It was found that oxidation of the entire mixture made it difficult to isolate the desired product, PPCAH, but that the product PPCAH can be isolated if a mixture consisting of only 2-methyl-4,4′-bipyridine and 4,4′-bipyridine (the fourth band off the column) is oxidized.

Structures

The two crystallographically independent molecules of complex **1**, $[Mn(2\text{-Me-}4,4'\text{-bipy})(NO_3)_2(H_2O)_2]$, are shown in Fig. 1. The 2-Me-4,4′-bipy ligand is coordinated in a monodentate fashion

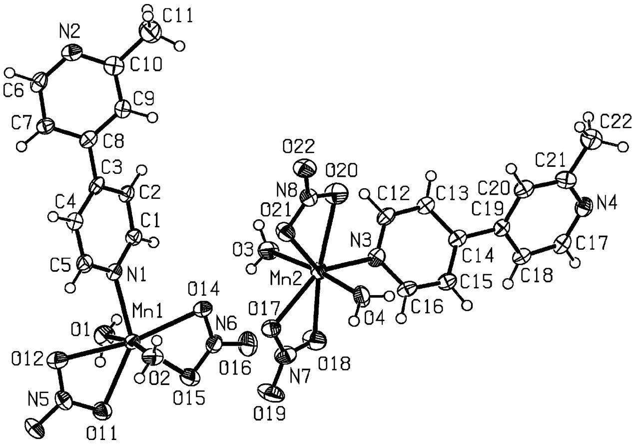


Fig. 1 Thermal ellipsoid plot of the two crystallographically independent molecules in complex **1** with atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1 Crystallographic data for **1–5**

Empirical	**1**	**2**	**3**	**4**	**5**
Formula	$C_{11}H_{14}MnN_4O_8$	$C_{26}H_{30}Cl_2MnN_6O_{10}$	$C_{22}H_{22}MnN_4O_8$	$C_{22}H_{22}N_4O_8Zn$	$C_{22}H_{14}CuHgI_2N_4O_4$
M_r	385.20	712.40	525.38	535.81	916.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	24.007(3)	11.1520(8)	19.3775(10)	19.4456(12)	30.3812(18)
b/Å	7.2451(9)	13.1262(9)	7.6358(4)	7.6438(4)	5.0478(3)
c/Å	19.331(2)	11.6168(8)	15.1202(7)	14.8027(9)	16.3401(9)
β/°	113.671(2)	112.855(1)	93.305(1)	93.582(1)	108.268(1)
V/Å^3	3079.5(7)	1567.00(19)	2233.50(19)	2195.9(2)	2379.6(2)
Space group	$P2_1/c$	$P2_1/n$	$I2/a$	$I2/a$	$C2/c$
Z	8	2	4	4	4
D_c/g cm^{-1}	1.662	1.510	1.562	1.621	2.558
2θ Range/°	1.9–50.3	4.3–52.8	4.2–52.7	4.2–52.7	2.8–52.7
μ(Mo-Kα)/mm^{-1}	0.908	0.656	0.649	1.178	9.970
Refl. meas.	29733	16385	11586	8881	12484
Indep. refl.	5505	3214	2292	2263	2444
No. param. refined	461	215	182	182	156
$R1$ [$I > 2\sigma(I)$, all data]	0.0452, 0.0500	0.0384, 0.0421	0.0344, 0.0391	0.0277, 0.0302	0.0310, 0.0353
$wR2$ [$I > 2\sigma(I)$, all data]	0.0958, 0.0980	0.1008, 0.1032	0.0833, 0.0860	0.0742, 0.0753	0.0782, 0.0806
GOF	1.125	1.053	1.045	1.077	1.083
$\Delta\rho_{\text{max/min}}$/e$^-$ Å^{-3}	+0.51/−0.31	+0.58/−0.48	+0.32/−0.20	+0.46/−0.28	+1.95/−1.01

Table 2 Interatomic distances (Å) and bond angles (°) with esds () for **1–5**

Complex **1**							
Mn(1)–O(2)	2.134(3)	Mn(1)–O(15)	2.308(3)	Mn(2)–O(4)	2.130(3)	Mn(2)–O(18)	2.316(3)
Mn(1)–O(1)	2.162(3)	Mn(1)–O(14)	2.409(3)	Mn(2)–O(3)	2.149(3)	Mn(2)–O(17)	2.346(3)
Mn(1)–N(1)	2.221(3)	Mn(1)–O(12)	2.421(3)	Mn(2)–N(3)	2.238(3)	Mn(2)–O(20)	2.470(4)
Mn(1)–O(11)	2.272(3)			Mn(2)–O(21)	2.274(3)		
O(2)–Mn(1)–O(1)	170.58(12)	O(1)–Mn(1)–O(14)	94.03(12)	O(4)–Mn(2)–O(3)	171.95(13)	O(3)–Mn(2)–O(17)	88.23(12)
O(2)–Mn(1)–N(1)	93.52(12)	N(1)–Mn(1)–O(14)	83.42(12)	O(4)–Mn(2)–N(3)	92.23(12)	N(3)–Mn(2)–O(17)	141.01(12)
O(1)–Mn(1)–N(1)	91.82(13)	O(11)–Mn(1)–O(14)	136.43(10)	O(3)–Mn(2)–N(3)	95.16(13)	O(21)–Mn(2)–O(17)	84.31(10)
O(2)–Mn(1)–O(11)	84.94(11)	O(15)–Mn(1)–O(14)	54.00(10)	O(4)–Mn(2)–O(21)	85.68(12)	O(18)–Mn(2)–O(17)	55.08(10)
O(1)–Mn(1)–O(11)	85.98(12)	O(2)–Mn(1)–O(12)	86.30(11)	O(3)–Mn(2)–O(21)	91.42(12)	O(4)–Mn(2)–O(20)	90.91(13)
N(1)–Mn(1)–O(11)	140.15(12)	O(1)–Mn(1)–O(12)	86.37(12)	N(3)–Mn(2)–O(21)	134.24(12)	O(3)–Mn(2)–O(20)	93.44(12)
O(2)–Mn(1)–O(15)	97.63(11)	N(1)–Mn(1)–O(12)	85.67(11)	O(4)–Mn(2)–O(18)	91.30(13)	N(3)–Mn(2)–O(20)	80.61(12)
O(1)–Mn(1)–O(15)	83.73(12)	O(11)–Mn(1)–O(12)	54.49(10)	O(3)–Mn(2)–O(18)	85.99(12)	O(21)–Mn(2)–O(20)	53.78(10)
N(1)–Mn(1)–O(15)	136.51(13)	O(15)–Mn(1)–O(12)	136.76(11)	N(3)–Mn(2)–O(18)	86.35(12)	O(18)–Mn(2)–O(20)	166.84(11)
O(11)–Mn(1)–O(15)	82.84(11)	O(14)–Mn(1)–O(12)	169.08(10)	O(21)–Mn(2)–O(18)	139.35(11)	O(17)–Mn(2)–O(20)	138.07(10)
O(2)–Mn(1)–O(14)	94.29(12)			O(4)–Mn(2)–O(17)	84.01(12)		
Complex **2**							
Mn(1)–O(1)#1	2.1430(15)	Mn(1)–N(3)#1	2.2498(19)	Mn(1)–N(1)	2.2714(16)	Mn(1)–N(1)#1	2.2714(15)
Mn(1)–O(1)	2.1430(16)	Mn(1)–N(3)	2.2498(19)				
O(1)#1–Mn(1)–O(1)	180.0	O(1)–Mn(1)–N(3)	89.14(7)	N(3)#1–Mn(1)–N(1)	87.98(6)	N(3)#1–Mn(1)–N(1)#1	92.02(6)
O(1)#1–Mn(1)–N(3)#1	89.14(7)	N(3)#1–Mn(1)–N(3)	180.0	N(3)–Mn(1)–N(1)	92.02(6)	N(3)–Mn(1)–N(1)#1	87.98(6)
O(1)–Mn(1)–N(3)#1	90.86(7)	O(1)#1–Mn(1)–N(1)	88.60(6)	O(1)#1–Mn(1)–N(1)#1	91.40(6)	N(1)–Mn(1)–N(1)#1	180.0
O(1)#1–Mn(1)–N(3)	90.86(7)	O(1)–Mn(1)–N(1)	91.40(6)	O(1)–Mn(1)–N(1)#1	88.60(6)		
Complex **3**							
Mn(1)–O(1)	2.1654(12)	Mn(1)–O(3)	2.1684(14)	Mn(1)–N(1)#1	2.2520(14)	Mn(1)–N(1)	2.2520(14)
Mn(1)–O(1)#1	2.1655(12)	Mn(1)–O(3)#1	2.1684(14)				
O(1)–Mn(1)–O(1)#1	97.05(7)	O(1)#1–Mn(1)–O(3)#1	85.96(5)	O(3)–Mn(1)–N(1)#1	93.31(5)	O(3)–Mn(1)–N(1)	92.47(5)
O(1)–Mn(1)–O(3)	85.96(5)	O(3)–Mn(1)–O(3)#1	93.90(8)	O(3)#1–Mn(1)–N(1)#1	92.46(5)	O(3)#1–Mn(1)–N(1)	93.31(5)
O(1)#1–Mn(1)–O(3)	167.06(5)	O(1)–Mn(1)–N(1)#1	100.46(5)	O(1)–Mn(1)–N(1)	73.78(5)	N(1)#1–Mn(1)–N(1)	171.53(7)
O(1)–Mn(1)–O(3)#1	167.07(5)	O(1)#1–Mn(1)–N(1)#1	73.78(5)	O(1)#1–Mn(1)–N(1)	100.46(5)		
Complex **4**							
Zn(1)–O(1)	2.1086(11)	Zn(1)–O(3)#1	2.1099(12)	Zn(1)–N(1)#1	2.1155(14)	Zn(1)–N(1)	2.1155(14)
Zn(1)–O(1)#1	2.1086(11)	Zn(1)–O(3)	2.1099(12)				
O(1)–Zn(1)–O(1)#1	95.96(6)	O(1)#1–Zn(1)–O(3)	170.40(4)	O(3)#1–Zn(1)–N(1)#1	91.81(5)	O(3)#1–Zn(1)–N(1)	92.95(5)
O(1)–Zn(1)–O(3)#1	170.40(4)	O(3)#1–Zn(1)–O(3)	92.21(7)	O(3)–Zn(1)–N(1)#1	92.95(5)	O(3)–Zn(1)–N(1)	91.81(5)
O(1)#1–Zn(1)–O(3)#1	86.69(5)	O(1)–Zn(1)–N(1)#1	97.77(5)	O(1)–Zn(1)–N(1)	77.56(5)	N(1)#1–Zn(1)–N(1)	173.13(7)
O(1)–Zn(1)–O(3)	86.69(5)	O(1)#1–Zn(1)–N(1)#1	77.56(5)	O(1)#1–Zn(1)–N(1)	97.77(5)		
Complex **5**							
Hg(1)–N(2)	2.411(5)	Hg(1)–I(1)#1	2.6545(5)	Cu(1)–O(1)	1.933(4)	Cu(1)–N(1)#2	1.972(5)
Hg(1)–N(2)#1	2.411(5)	Hg(1)–I(1)	2.6545(5)	Cu(1)–O(1)#2	1.933(4)	Cu(1)–N(1)	1.972(5)
N(2)–Hg(1)–N(2)#1	106.1(3)	N(2)–Hg(1)–I(1)	101.34(13)	O(1)–Cu(1)–O(1)#2	180.0	O(1)–Cu(1)–N(1)	84.57(19)
N(2)–Hg(1)–I(1)#1	99.64(12)	N(2)#1–Hg(1)–I(1)	99.64(12)	O(1)–Cu(1)–N(1)#2	95.43(19)	O(1)#2–Cu(1)–N(1)	95.43(19)
N(2)#1–Hg(1)–I(1)#1	101.33(13)	I(1)#1–Hg(1)–I(1)	144.78(3)	O(1)#2–Cu(1)–N(1)#2	84.57(19)	N(1)#2–Cu(1)–N(1)	179.998(1)

Table 3 Hydrogen bonds for complexes **1–4** [distances (*d*) in Å and angles (∠) in °]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(*DHA*)
Complex **1**				
O(1)–H(1A)···O(17)#1	0.83(2)	2.11(3)	2.929(5)	167(6)
O(1)–H(1B)···O(20)#2	0.83(2)	2.26(4)	3.000(5)	147(5)
O(2)–H(2A)···N(2)#3	0.83(2)	1.93(3)	2.718(4)	159(6)
O(2)–H(2B)···O(22)#4	0.83(2)	2.11(2)	2.930(4)	170(5)
O(3)–H(3A)···O(13)#5	0.83(2)	2.02(3)	2.795(5)	155(5)
O(3)–H(3B)···O(14)	0.83(2)	2.05(2)	2.877(5)	173(6)
O(4)–H(4A)···N(4)#6	0.83(2)	1.88(3)	2.689(5)	164(6)
O(4)–H(4B)···O(16)#7	0.84(2)	2.25(3)	3.044(5)	159(5)
Complex **2**				
O(1)–H(1A)···O(11)	0.79(2)	2.02(2)	2.814(2)	176(3)
O(1)–H(1B)···N(2)#2	0.81(2)	1.92(2)	2.729(2)	175(3)
Complex **3**				
O(3)–H(3A)···O(4)	0.809(14)	1.866(16)	2.6560(19)	165(3)
O(3)–H(3B)···O(2)#2	0.796(13)	1.956(14)	2.7490(18)	174(2)
O(4)–H(4A)···O(1)#3	0.808(14)	1.960(14)	2.7665(18)	176(2)
O(4)–H(4B)···N(2)#4	0.805(14)	2.041(17)	2.780(2)	152(3)
Complex **4**				
O(3)–H(3A)···O(4)	0.799(8)	1.884(11)	2.6562(17)	162(3)
O(3)–H(3B)···O(2)#2	0.792(8)	1.971(9)	2.7564(17)	171(2)
O(4)–H(4A)···O(1)#3	0.781(8)	2.004(9)	2.7753(17)	169(2)
O(4)–H(4B)···N(2)#4	0.789(8)	2.031(12)	2.777(2)	158(2)

Symmetry codes: complex **1**: (#1) $x, y - 1, z$; (#2) $x, -y + 1/2, z - 1/2$; (#3) $-x + 1, y + 1/2, -z + 3/2$; (#4) $x, -y + 3/2, z - 1/2$; (#5) $x, -y + 1/2, z + 1/2$; (#6) $-x, y + 1/2, -z + 3/2$; (#7) $x, y + 1, z$; complex **2**: (#1) $-x, -y, -z + 1$; (#2) $x - 1, y, z - 1$; complex **3**: (#1) $-x + 1/2, y, -z + 1$; (#2) $-x + 1/2, -y + 1/2, -z + 1/2$; (#3) $x, y + 1, z$; (#4) $x - 1/2, y + 1/2, z + 1/2$; complex **4**: (#1) $-x + 1/2, y, -z + 1$; (#2) $-x + 1/2, -y + 1/2, -z + 1/2$; (#3) $x, y + 1, z$; (#4) $x - 1/2, y + 1/2, z + 1/2$; complex **5**: (#1) $-x, y, -z + 1/2$; (#2) $-x + 1/2, -y - 1/2, -z$.

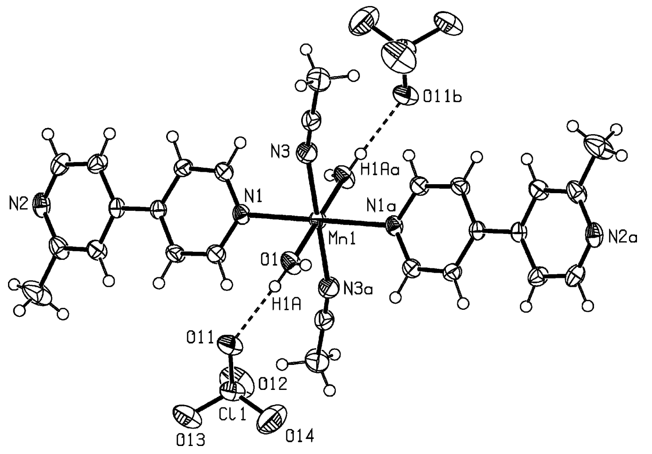


Fig. 2 Thermal ellipsoid plot of complex **2** with atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are shown in dotted black lines. The suffix "a" (lower case) refers to symmetry equivalent atoms (symmetry code $-x, -y, 1 - z$).

to each of the Mn(II) atoms, leaving one pyridyl coordination site open. In this respect, this complex is quite different from many related complexes consisting of $M(NO_3)_2$ and 4,4′-bipyridine ligands, where the bipyridine ligand is typically coordinated to a metal center on both ends, thus affording extended structures.[12] In the case of the 2-Me-4,4′-bipy ligand, however, the open coordination site is sterically protected by the adjacent methyl group which, apparently, blocks further coordination, and thus prevents the formation of an extended coordination polymer structure.[12] In complex **1**, two nitrate anions and two water molecules complete the coordination environment around each manganese atom.

When the anion was changed to ClO_4^-, complex **2** was obtained. As shown in Fig. 2, **2** is a mononuclear complex of composition $[Mn(2\text{-}Me\text{-}4,4'\text{-}bipy)_2(CH_3CN)_2(H_2O)_2](ClO_4)_2$, in which the manganese atom resides on a crystallographic center of symmetry and is surrounded by two oxygen atoms from water molecules, two nitrogen atoms from acetonitrile molecules and two nitrogen atoms from two different 2-Me-4,4′-bipy ligands, forming a pseudo-octahedral coordination environment. The uncoordinated perchlorate anions are connected to the two coordinated water molecules *via* O–H···O hydrogen bonds. Here also, the 2-Me-4,4′-bipy ligand is coordinated to Mn *via* only one pyridine nitrogen to form a ML_2 mononuclear complex, which is comparable to some known monodentate 4,4′-bipyridine based complexes, such as $[Cu(4,4\text{-}bipy)_2(H_2PO_4)_2(H_2O)_2]$,[13] and $[Mn(4,4\text{-}bipy)_2(H_2O)_4][ClO_4]_2$.[14] Again, however, the N2 pyridyl nitrogen is sterically protected by the adjacent methyl group, which prevents the formation of an extended coordination polymer structure.

Complexes **3** and **4** are isomorphous. As shown in Fig. 3, two symmetric PPCA ligands are each chelated to the metal center *via* one nitrogen atom and one oxygen atom. The asymmetric unit contains half of the $M(C_{11}H_7N_2O_2)_2(H_2O)_2$ [M = Mn (**3**) or Zn (**4**)] complex located on a two-fold axis of rotation, and one independent uncoordinated water molecule. The $M(PPCA)_2$ unit in **3** or **4** with two uncoordinated terminal nitrogen atoms is similar to the $M(pyrazinecarboxylato)_2$ unit where, however, the terminal N···N separation in **3** or **4** is significantly longer than those found in metal containing building blocks based on pyrazinecarboxylate ligands.[5,15] In complex **3** or **4**, two water molecules complete the distorted octahedral coordination environment around the metal, while two uncoordinated water molecules are connected to the $Mn(PPCA)_2(H_2O)_2$ unit *via* O–H···O hydrogen bonds.

Compared to related complexes based on 4,4-bipyridine,[12–15] the introduction of the 2-carboxylate functional group enables the PPCA ligand to chelate to the metal center, enabling it to readily form ML_2 metal containing building block as has been observed for $M(pyrazinecarboxylate)_2$ complexes.[5]

Hydrogen bonding is one of the important supramolecular forces in biological macromolecules and coordination chemistry; and, as such, it has received increasing interests in recent years. In fact, hydrogen bonding has become a key concept in the emerging field of crystal engineering because of the combination of strength and directionality attributable to this class of interaction.[16] In complexes **1–4**, there exist a large number of hydrogen bonding donors and acceptors that further connect the complexes into networks of higher dimensionality. Specifically, in complex **1**, each coordinated H_2O molecule affords two hydrogen bonding donors (OH). Three oxygen atoms from the two NO_3^- anions act as hydrogen bonding acceptors, and the uncoordinated second pyridine nitrogen also acts as a hydrogen bonding acceptor (Fig. 4(a)). As shown in Fig. 4(b), the O–H···O hydrogen bonds connect the $Mn(2\text{-}Me\text{-}4,4'\text{-}bipy)(NO_3)_2(H_2O)_2$ units into 2D layers. These layers are further connected through the 2-Me-4,4′-bipy ligand *via* Mn–N coordination bonds and N···H–O

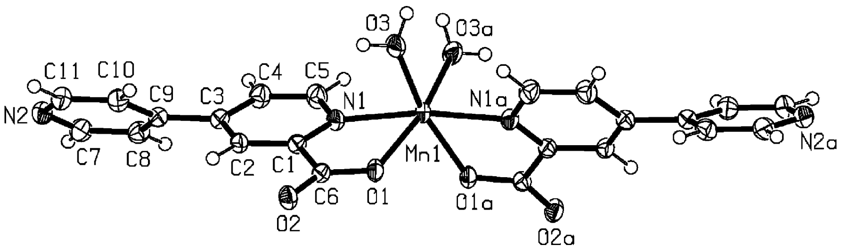


Fig. 3 Thermal ellipsoid plot of $[Mn(PPCA)_2(H_2O)_2]\cdot 2H_2O$ (**3**) with atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix “a” (lower case) refers to symmetry equivalent atoms (symmetry code $1/2 - x, y, 1 - z$).

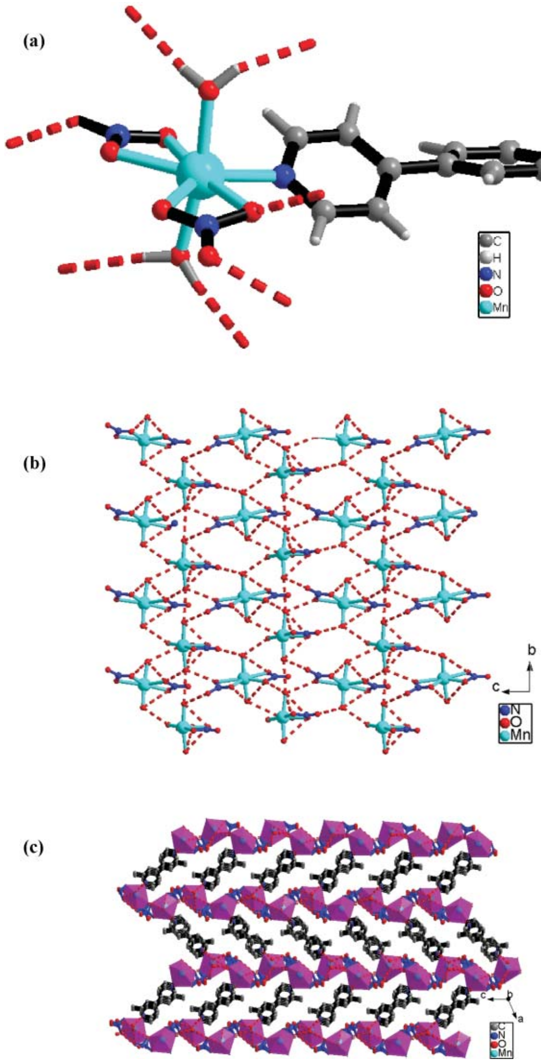


Fig. 4 (a) Hydrogen bonding donors and acceptors of one of the two independent molecules in **1**. Hydrogen bonds are indicated by dotted red lines. (b) 2D O–H···O hydrogen bonded inorganic layer; 2-methyl-4,4′-bipyridine and hydrogen atoms are omitted for clarity. (c) Hydrogen bonded 3D inorganic–organic network; Mn coordination spheres are represented as pink polyhedra.

hydrogen bonds, to form a hydrogen bonded 3D inorganic–organic network (Fig. 4(c)).

In complex **2**, the uncoordinated ClO_4^- anions are hydrogen bonded to the coordinated water molecules, which are also involved in hydrogen bonding interactions with the second pyridine nitrogen. Unlike in complex **1**, the hydrogen bonding in **2** does not increase the dimensionality of the structure beyond a 1-D chain (Fig. 5(a)). As shown in Fig. 5(b), each Mn(2-Me-4,4′-bipy)$_2$(CH_3CN)$_2$(H_2O)$_2$ unit is connected to two adjacent complexes *via* four O–H···N hydrogen bonds, forming Mn_2(2-Me-4,4′-bipy)$_2$(H_2O)$_2$ metallamacrocycles. Two adjacent metallamacrocycles share a manganese(II) ion, thus generating an infinite 1D chain (Fig. 5(b)).

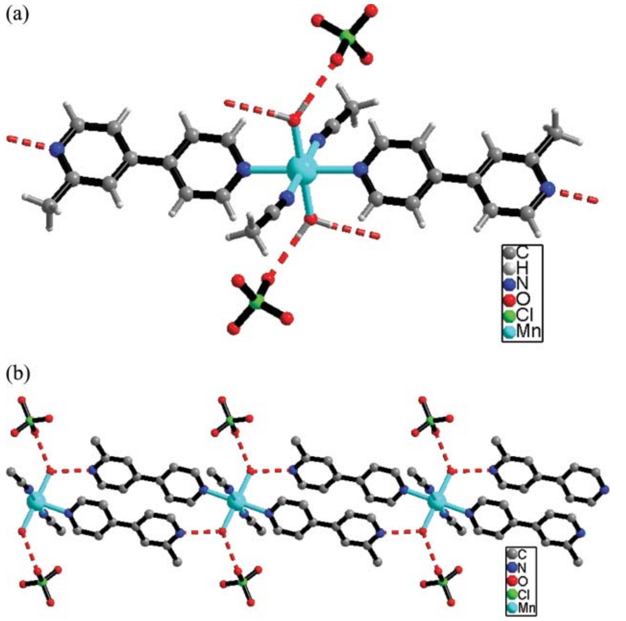


Fig. 5 (a) Hydrogen bonding donors and acceptors in **2**. (b) Hydrogen bonded 1D chain in **2**. Hydrogen bonds are indicated by dotted red lines.

As shown in Fig. 6, there are three types of hydrogen bonds present in complex **3**: one between adjacent Mn(PPCA)$_2$(H_2O)$_2$ complexes (O–H···O, labeled α) and two between Mn(PPCA)$_2$(H_2O)$_2$ units and uncoordinated H_2O molecules (O–H···O labeled β and O–H···N labeled γ). The α-type hydrogen bonds join the Mn(PPCA)$_2$(H_2O)$_2$ units in the *c* direction, where each coordinated water affords one hydrogen bond donor (OH) and where the uncoordinated oxygen atom from the PPCA ligand acts as hydrogen bond acceptor (Fig. 6(a)). The β-type interactions connect Mn(PPCA)$_2$(H_2O)$_2$ units *via* pairs of uncoordinated H_2O molecules in the *b* direction. Overall, the two oxygen atoms from the carboxylate groups act as hydrogen

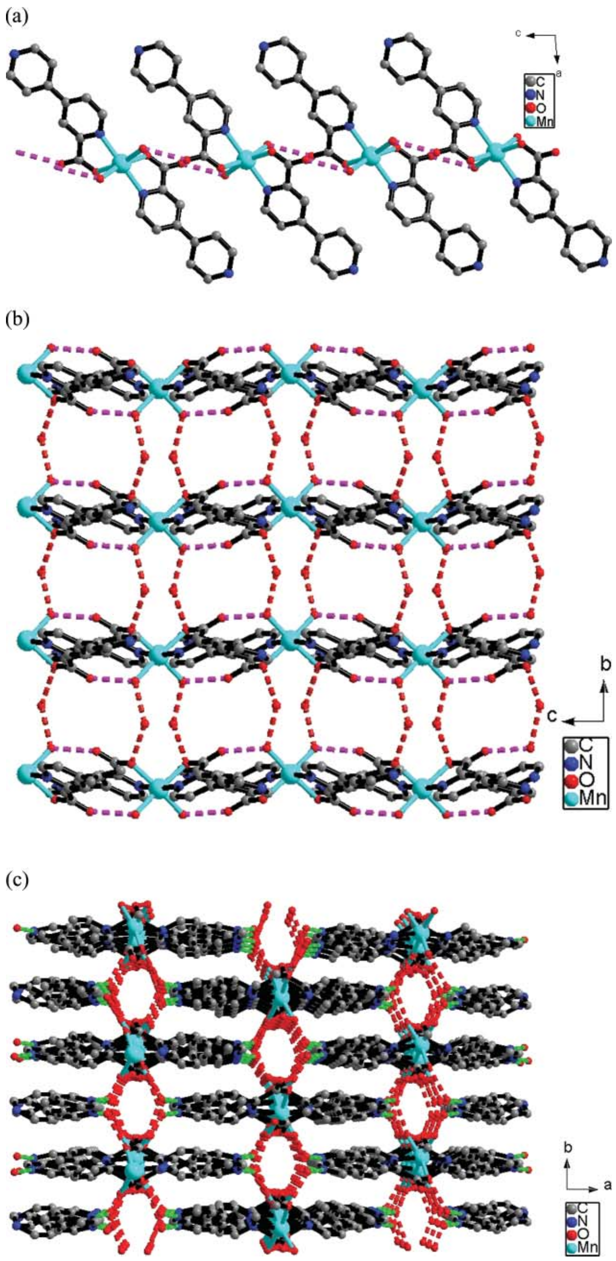


Fig. 6 (a) α-type O–H···O hydrogen bonded chain structure.)b) 2D layer bonded by α and β-type O–H···O hydrogen bonds. (c) 3D hydrogen bonded supramolecular structures in **3**. α-, β-type O–H···O hydrogen bonds and γ-type O–H···N hydrogen bond are indicated by purple, red and green dotted lines respectively.

bonding acceptors, the two coordinated H_2O molecules act as two hydrogen bonding donors, and the uncoordinated H_2O molecules act as two hydrogen bonding donors and two acceptors to form the 2D sheets (Fig. 6(b)). The 2D hydrogen bonded sheets formed by α- and β-type O–H···O hydrogen bonds are further linked into a 3D supramolecular network by γ-type O–H···N hydrogen bonds, where the uncoordinated pyridine nitrogen acts as the hydrogen bond acceptor (Fig. 6(c)), similar to the situation observed for complexes **1** and **2**.

When the PPCAH ligand is reacted with $Cu(NO_3)_2{\cdot}3H_2O$ and HgI_2, turquoise crystals of complex **5** are obtained. X-Ray crystallographic analysis reveals that **5** is a mixed-metal coordination polymer consisting of $Cu(PPCA)_2$ units linked by HgI_2 groups. The square planar Cu(II) lies on a crystallographic inversion center and is coordinated by two nitrogen atoms (Cu(1)–N(1) 1.972(5) Å) and two oxygen atoms (Cu(1)–O(1) 1.933(4) Å) from two inversion-related PPCA ligands (Fig. 7). The Hg(II) atom lies on a two-fold axis of rotation in a distorted tetrahedral HgI_2N_2 environment (Hg(1)–N(2) 2.411(5) Å, Hg(1)–I(1) 2.654(5) Å), and links the $Cu(PPCA)_2$ units into an infinite zigzag chain by coordinating to two nitrogen atoms from two C_2 axis-related $Cu(PPCA)_2$ building blocks (Fig. 8). These 1D zigzag chains run along the crystallographic [10-1] direction, and the Cu···O weak interactions [Cu(1)–O(2)* distance is 2.677(5) Å (symmetry codes * = x, $y - 1$, z and $1/2 - x$, $1/2 - y$, $-z$)] expand the coordination of Cu(II) into a 4 + 2 mode, thus linking these chains into 2D layers parallel to the crystallographic *ab* plane (Fig. 9). The $Cu(PPCA)_2$ building block, as it exists in complex **5**, is similar to the Cu(pyrazinecarboxylato)$_2$ building block,[15] further demonstrating that the PPCAH ligand is, as intended, an extended pyrazinecarboxylcyclic acid analog.

Bulk phase purity was established by powder X-ray diffraction for complexes **1**, **3** and **4**. As this requires grinding the samples, powder X-ray diffraction of complex **2**, which contains a perchlorate group, was not carried out in the interest of safety. The agreement between the calculated and measured diffraction patterns, shown in Fig. 10, supports phase purity of the complexes and rules out the possibility of a second phase.

Phase pure samples of compounds **1** and **3** were subjected to thermogravimetric analysis. The TGA curve for compound **1** displayed four consecutive weight loss intervals. The first of these, occurring over the temperature range 100–150 °C, corresponds to the loss of coordinated water molecules (10.05%; theoretical, 9.35%). Decomposition of the sample at approximately 150 °C is indicated by an abrupt, large multiple step weight loss. Likewise for compound **3**, a 14.32% weight loss between room temperature

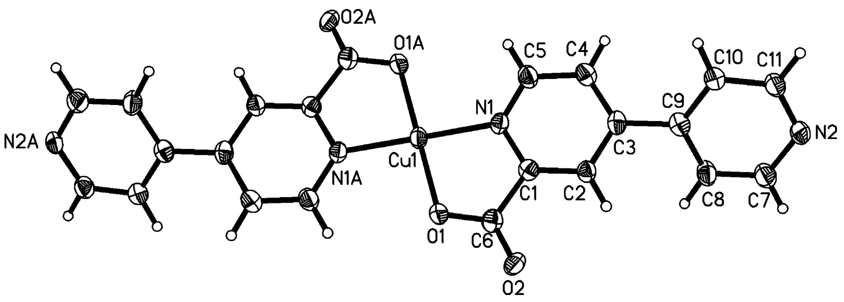


Fig. 7 Thermal ellipsoid plot of the $Cu(PPCA)_2$ unit in the polymeric chain of **5**. Displacement ellipsoids are drawn at the 50% probability level. The suffix "A" refers to symmetry equivalent atoms (symmetry code $1/2 - x$, $-1/2 - y$, $-z$).

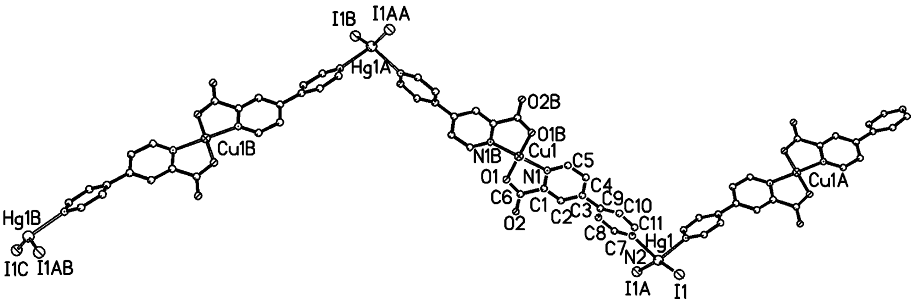


Fig. 8 View of the 1D zigzag chain of complex **5**.

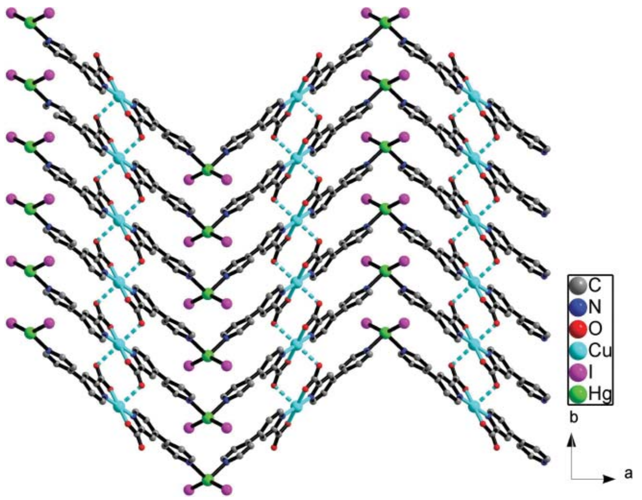


Fig. 9 The 2D layer parallel to the crystallographic *ab* plane, the Cu · · · O weak interactions are indicated by dotted cyan lines.

and 140 °C is consistent with the loss of water molecules from the compound (theoretical, 13.70%). However, compound **3** is much more thermally stable than compound **1**. Sample decomposition as indicated by a large, abrupt weight loss occurs for compound **3** at approximately 360 °C. TGA on compound **5** was not carried out due to problems with volatilizing mercury.

Conclusions

We have successfully synthesized the 2-carboxylate-substituted 4,4′-bipyridyl ligand, 4-(pyridin-4-yl)pyridine-2-carboxylic acid (PPCAH), and five complexes assembled from either PPCA or its synthetic intermediate, 2-methyl-4,4′-bipyridine. The ligand PPCAH, and its synthetic intermediate, 2-methyl-4,4′-bipyridine, are promising supramolecular reagents for the construction of hydrogen bonded inorganic–organic hybrid materials. Furthermore, we demonstrate that the PPCAH ligand is a good candidate for the formation of metal-containing building blocks and mixed-metal coordination polymers. As it is a longer ligand with coordination characteristics similar to those of the pyrazinecarboxylate ligand, we believe that PPCAH can be useful for the two-step assembly of mixed-metal framework materials with large cavities.

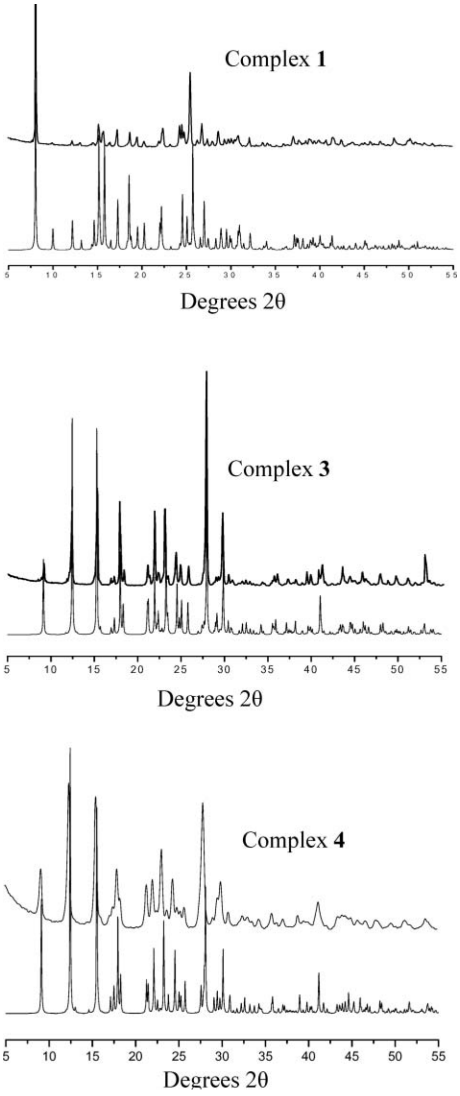


Fig. 10 Observed powder X-ray diffraction patterns (above) and simulated patterns (below) of complexes **1**, **3** and **4**.

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