1,2,4,5-Benzenetetracarboxylic Acid and 4,4′-Bipyridine as Ligands in Designing Low-Dimensional Coordination Polymers

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The combined use of 1,2,4,5-benzenetetracarboxylic acid (H_4bta) and 4,4′-bipyridine (bpy) as ligands with Mn^{II} and Co^{II} ions afforded two polymeric compounds with the formulae [Mn(Hbta)(Hbpy)(H_2O)$_2$] (**1**) and [H_2bpy][Co(bta)(bpy)(H_2O)$_2$] (**2**). **1** and **2** were prepared under hydrothermal conditions (145 °C, 3 h) and characterized by elemental analysis, IR spectroscopy, TG-DTA analysis and single-crystal X-ray diffraction methods. **1** exhibits a novel double chain structure growing along the *b* axis where the manganese atoms are linked by tris-monodentate $Hbta^{3-}$ ligands. The values of the manganese···manganese intrachain separations are 7.627(2) Å [Mn(1)···Mn(1c); c = –x + 1/2, y – 1/2, –z] and 9.274(4) Å [Mn(1)···Mn(1d); *d* = x, y + 1, –z]. Adjacent double chains in **1** are further linked through hydrogen bonds between the NH fragment of the $Hbpy^+$ cation and one of the carboxylate groups of the $Hbta^{3-}$ anion along the *a* axis, resulting in a sheetlike structure. **2** exhibits a rectangular grid arrangement of cobalt atoms bridged by bis-monodentate bta^{4-} and bpy ligands in the *bc* plane, the cobalt···cobalt separations across them being 6.228(2) and 10.074 (2) Å, respectively. The metal atoms in **1** and **2** are six-coordinate with two water molecules in *trans* positions (**1** and **2**), three (**1**)/two (**2**) carboxylate oxygen atoms and one (**1**)/two (**2**) pyridyl nitrogen atoms forming a distorted octahedral environment. The varying nature of the divalent metal ions [Mn **1** and Co **2**] along with the differing degrees of protonation of the tetracaboxylate [$Hbta^{3-}$ **1** and bta^{4-} **2**] and bipyridyl [$Hbpy^+$ **1** and bpy and H_2bpy^{2+} **2**] species account for the structural differences between **1** and **2**.

Introduction

The crystal engineering of supramolecular architectures or metal-organic coordination polymers is a growing field and it has attracted much attention in the past decades.[1–4] With the recent development of self-assembly supramolecular chemistry, it is possible to rationally design and synthesize supramolecular architectures or metal-organic coordination polymers based on covalent or supramolecular contacts (such as forces resulting from intermolecular non-bonded, non-covalent electrostatic forces (due to static and oscillating fixed charge interactions) and dispersion forces (due to induced transient charge interactions).[5–7] However, the assembly of molecular materials from organic ligands and metal ion building blocks to generate new supramolecular architectures is still a challenge.[8–10] Two main methods can be envisaged in order to construct open supramolecular architectures on the basis of the different interactions between the building blocks: one takes advantage of the covalent bonds and the other focuses on the supramolecular contacts.[11] The use of covalent bonds to link metal ions and organic molecules such as polycarboxylic acids or 4,4′-bipyridine (bpy), has resulted in a large number of porous frameworks with different dimensionalities and topologies.[12–15]

It is worth noting that the coordination ability of aromatic polycarboxylic acids towards transition metal complexes has received considerable attention due to the variety of the bridging modes of the carboxylate group with regards to the formation of extended frameworks.[16,17] The goal in the search for organic porous frameworks is not simply to mimic inorganic materials by using different

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building blocks. Some of the properties of organic compounds, such as low stability and low Lewis acidity, are inherently different. In this sense, 1,2,4,5-benzenetetracarboxylic acid (hereafter noted H_4bta) possesses several interesting characteristics: (a) it has four carboxylic groups whose deprotonation (partial or total) and subsequent coordination to the metal ions affords interesting structures with tunable dimensionality; (b) it can act not only as a hydrogen bond acceptor but also as a hydrogen bond donor, depending upon the degree of deprotonation; (c) due to steric hindrance, some of the carboxylic groups may not lie in the plane of the phenyl ring upon complexation to the metal ions, and thus, they can connect metal ions in different directions. Hence, H_4bta is a good choice for the construction of polymeric structures, as proved by the large number of metal-organic structures obtained from the Cambridge Structural Database (CSD).[18] The versatility of the deprotonated forms of H_4bta as ligands is illustrated by Scheme 1.

Our research group is engaged in the design of extended arrays of metal ions with mixed ligands, and recently, we obtained a supramolecular loop-chain network of pillared layers via 4,4′-bipyridine.[19] Our first attempts, using H_4bta and bpy as ligands towards first row transition metal ions, afforded the new coordination polymers [Mn(Hbta)(Hbpy)(H_2O)$_2$] (**1**) and H_2bpy[Co(bta)(bpy)(H_2O)$_2$] (**2**) (see Scheme 2). To the best of our knowledge,[18] compound **1** exhibits an unprecedented connection mode for the H_4bta ligand (see Scheme 1). The preparation, structural characterization, spectroscopic and thermal investigations of complexes **1** and **2** are presented here.

Results and Discussion

Description of the Structures

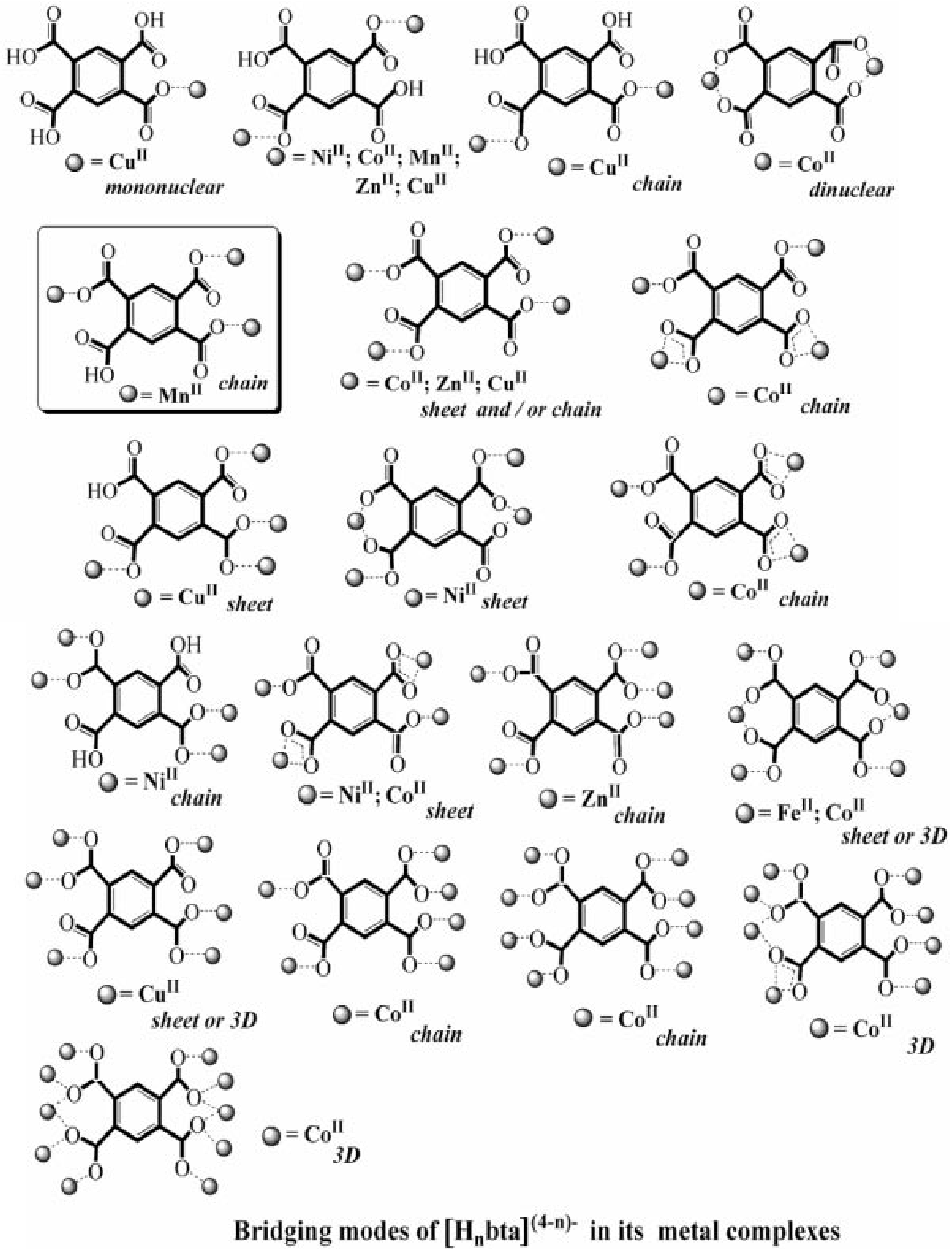
[Mn(Hbta)(Hbpy)(H$_2$O)$_2$]$_n$ (1)

The structure of **1** is made up of neutral double zigzag chains of formula [Mn(Hbta)(Hbpy)(H_2O)$_2$] which run parallel to the *b* axis (Figure 1, a) with $Hbta^{3-}$ acting as a tris-monodentate bridging ligand. The resulting ribbon-like motifs are further linked via N−H···O hydrogen bonds involving the protonated pyridyl nitrogen of bpy [N(1)] and one of the carboxylate oxygen atoms [O(2b); b = $-x - 1/2, y - 1/2, z$] of the $Hbta^{3-}$ ligand (see Table 1) affording a sheet-like structure in the *ab* plane (Figure 1, b). The Mn(1) atom has a slightly distorted octahedral environment (MnO_5N) with two *trans* water molecules filling the axial positions (see Figure 2) The $Mn-O_{(carboxylate)}$ and $Mn-N_{(Hbpy^+)}$ bond lengths are in agreement with previous data of carboxylate- and bpy-containing manganese(II) complexes.[20] The $Hbta^{3-}$ anion is not planar since the dihedral angles between the COO groups and the aromatic ring of $Hbta^{3-}$ are 57.9(2) Å [O(1)−C(7)−O(2)], 64.5(2) Å [O(3)−C(8)−O(4)], 5.0(3) Å [O(5)−C(9)−O(6)] and 8.9(2) Å [O(7)−C(10)−O(8)]. The deprotonated carboxylate groups of each $Hbta^{3-}$ [O(1)−C(7)−O(2), O(3)−C(8)−O(4) and O(7)−C(10)−O(8)] are coordinated to three manganese atoms [Mn(1), Mn(1c) and Mn(1d) through O(7), O(1) and O(4), respectively; symmetry code: c = $-x + 1/2, y - 1/2, z$; d = $x, y + 1, -z$]. The values of the Mn···Mn separation through the $Hbta^{3-}$ ligand are 7.627(2) [Mn(1)···Mn(1c)] and 9.274(4) Å [Mn(1)···Mn(1d)]. The protonated carboxylic group remains uncoordinated but contributes to the stabilization of the structure through an extensive network of hydrogen bonds together with the water molecules and the free carboxylate oxygen atoms (see Table 1).

The pyridyl rings of the monoprotonated $Hbpy^+$ species are planar but the ligand as a whole is far from being planar [dihedral angle between the two pyridyl rings is 12.32(14)°]. $Hbpy^+$ acts as a terminal monodentate ligand being coordinated to the manganese atom through the nonprotonated N(2) pyridyl atom. The $Hbpy^+$ ligands are alternatively located right and left of each double chain (Figure 1, a) in such a way that the $Hbpy^+$ groups from two adjacent double chains are stacked along the *b* axis (Figure 1, b). The separation between the mean pyridyl planes of adjacent $Hbpy^+$ groups is 3.969(9) Å, a value that supports the occurrence of very weak π-π stacking interactions. Finally, weaker $C-H_{(Hbpy^+)}\cdots O_{(Hbta^{3-})}$ supramolecular interactions, the values of the C···O separations being less or equal than 3.22 Å (the sum of the van der Waals radii of the interacting atoms), are also observed.[18]

[H$_2$bpy]·[Co(bta)(bpy)(H$_2$O)$_2$]·(2)

The structure of this complex consists of a two-dimensional rectangular grid of *trans*-diaquacobalt(II) ions growing in the *ab* plane with bta^{4-} and bpy ligands acting as bis-monodentate bridges within each layer (Figure 3, a). These layers are connected to each other through hydrogen bonds between the protonated pyridyl nitrogen atoms of H_2bpy^{2+} [N(3)] and one of the uncoordinated carboxylate oxygen atoms [O(3)] (Figure 3, b and Table 1) to afford a three-dimensional network. In contrast to **1**, fully deprotonated bta^{4-} and both neutral bpy and diprotonated H_2bpy^{2+} are present in **2**. As in **1**, each Co^{II} ion has a somewhat distorted octahedral arrangement with two trans water molecules in the axial positions (Figure 4). The $Co-O_{(bta)}$ [2.077(2) Å] and $Co-N_{bpy}$ [2.169(3) Å] bond lengths are also in agreement with those reported for carboxylate- and bpy-containing cobalt(II) complexes.[21,22] The bta^{4-} ligand is not planar; the dihedral angles between the carboxylate groups and the mean plane of the phenyl ring are 56.75(10)° [C(1)−C(4)−O(1)−O(2)] and 33.94(9)° [C(5)−C(2)−O(3)−O(4)]. Each bta^{4-} group acts as a *trans* bis-monodentate ligand bridging two symmetry related Co^{II} ions thus affording a uniform chain of cobalt atoms along the (101) direction, the cobalt···cobalt separation across bridging H_2bta being 11.248(3) Å. These chains are cross-linked by bridging bis-monodentate bpy ligands along the *b* axis leading to a two dimensional quasi-square grid of cobalt atoms. The cobalt···cobalt separation through the

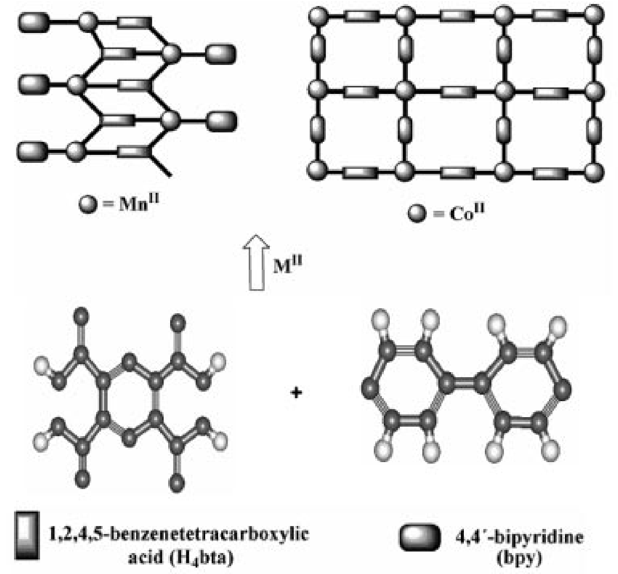


Scheme 1

bpy bridge is 11.476(2) Å. The pyridyl rings of bpy are practically planar within experimental error, but the ligand as a whole deviates significantly from planarity [the dihedral angle between the mean planes of the two pyridyl rings is 19.29(1)°]. Centrosymmetric H_2bpy^{2+} cations are placed between the layers and they link these layers into a three-dimensional network through hydrogen bonds of the type $N-H\cdots O_{carboxylate}$, the shortest cobalt···cobalt interplanar separation being 8.977(3) Å. Additional hydrogen bonds involving coordinated water molecules and one carboxylate oxygen atom [2.728(4) Å for $O(1w)\cdots O(4c)$ (c = $-x$, $-y + 1$, $-z + 1$) contribute to the stabilization of this 3D network.

Infrared Spectra and TG-DTA Analysis

The infrared spectra of the two complexes are quite similar, with a broad band centered at ca. 3395−3370 which is due to the O−H stretching vibration of water molecules involved in extensive hydrogen bonding interactions.[23] Furthermore, they exhibit the $\nu_{as(OCO)}$ and $\nu_{s(OCO)}$ vibrations of the carboxylate groups which occur at 1690 and 1490 cm^{-1} for **1** and at 1680 and 1480 cm^{-1} for **2**, respectively. $\Delta\nu[\nu_{as(COO)} - \nu_{s(COO)}]$ is ca. 200 cm^{-1} for both complexes, a value which suggests the occurrence of monodentate coordination of the carboxylate groups.[24] This is also in agreement with the crystal structure (vide supra). Less



Scheme 2

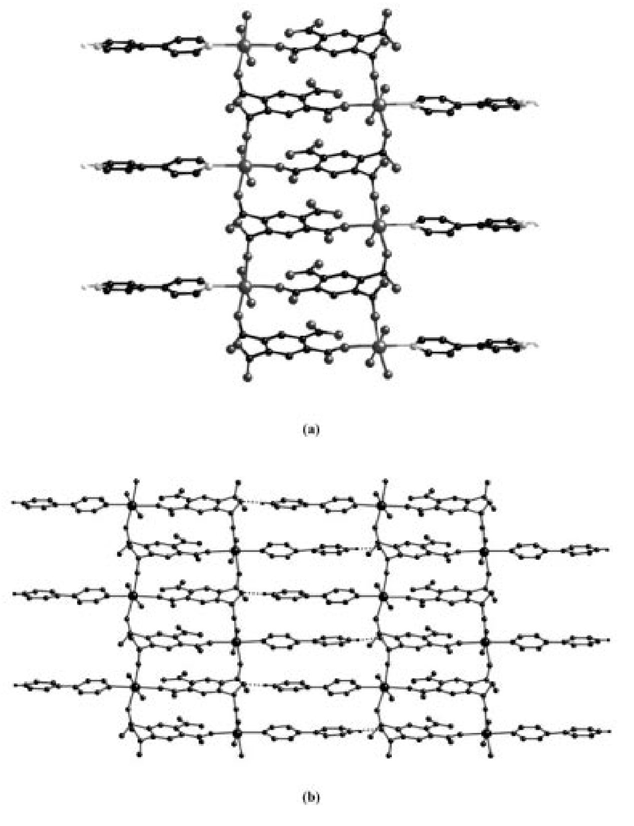


Figure 1. X-ray structure of $[Mn(Hbta)(Hbpy)(H_2O)_2]_n$ (**1**); (a) view along the *c*-axis illustrating the double-chain and (b) view of the layer structure formed through the N−H···O hydrogen bonds of adjacent double chains

significant absorptions occur at 3050 (stretching vibrations of aromatic C−H groups), 820−700 (out-of-plane C−H bending of phenyl and pyridyl rings) and 557 cm^{-1} ($\nu_{(M-N)}$ vibration).[25,26]

Table 1. Hydrogen bonds in **1** and **2**

D−H···A	D···A	H···A	<D−H···A
1[a][b][c]			
N(1)−H(1)···O(2b)	2.683(4)	1.834(2)	168.9(2)
O(1W)−H(12W)···O(3)	2.725(4)	1.834(2)	171.7(4)
O(1W)−H(11W)···O(3e)	2.831(4)	1.814(5)	167.4(5)
O(2W)−H(21W)···O(2a)	2.720(4)	1.848(6)	174.8(7)
O(2W)−H(22W)···O(8c)	2.708(4)	1.990(5)	165.6(5)
2[a][b][c]			
N(3)−H(3)···O(3ai)	2.596(4)	1.742(2)	171.3(2)
O(1W)−H(11W)···O(2bi)	2.649(3)	1.807(6)	154.7(5)
O(1W)−H(21W)···O(4ci)	2.728(3)	1.879(5)	168.8(5)

[a] Values of the interatomic distances and angles in Å and degrees, respectively. [b] D = donor and A = acceptor. [c] Symmetry code: a = *x*, *y* − 1, *z*; b =−*x* − 1/2, *y* − 1/2, *z*; c = −*x* + 1/2, *y* − 1/2, *z*; e = −*x*, *y* − 1/2, −*z* + 1/2; ai = −*x* + 1/2, *y* − 1/2, *z*; bi = −*x*, *y*,−*z* + 1/2; ci = −*x*, −*y* + 1, −*z* + 1.

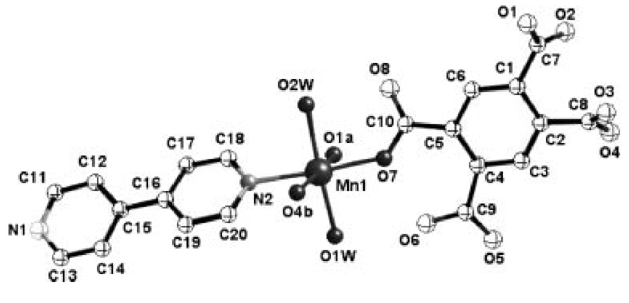


Figure 2. Coordination sphere of the manganese atom in $[Mn(Hbta)(Hbpy)(H_2O)_2]_n$ (**1**)

The $[Mn(Hbta)(Hbpy)(H_2O)_2]$ and H_2bpy $[Co(bta)(bpy)(H_2O)_2]$compounds show a similar thermal behavior. Two steps are observed in the TG-DTG/DTA curves of **1** and **2** (Figure S1, supplementary material): the first one, no thermal decomposition of the compounds occurs, confirming that the networks remain stable below ca. 174 °C; the second one, three overlapped weight loss peaks are observed $\{[T_{\text{strong peak}}]_{\text{DTG}}$ ca. 230 °C; $[T_{\text{little peak}}]_{\text{DTG}}$ ca. 374 °C and $[T_{\text{little peak}}]_{\text{DTG}}$ ca. 455 °C$\}$. This last process is followed by two strong endothermic peaks $\{[T_{\text{strong peaks}}]_{\text{DTA}}$ ca. 190 and 233 °C for **1** and ca. 140 and 228 °C, for **2**$\}$ whose weight loss corresponds to the release of H_2O, H_4bta and bpy groups, in agreement with another similar complex $[H_2bpy][H_3bta]_2$, recently reported.[19]

Conclusion

Two polymeric complexes with chains or rectangular grids, $[Mn(Hbta)(Hbpy)(H_2O)_2]_n$ (**1**) and $[H_2bpy][Co(bta)(bpy)(H_2O)_2]$ (**2**), respectively, were constructed from 1,2,4,5-benzenetetracarboxylic acid (H_4bta) in the presence of an auxiliary ligand (4,4′-bipyridine) under hydrothermal conditions. The auxiliary ligand, play an important role in the synthesis of the complexes by engaging in coordination or acting as a template. The coordination modes of the H_4bta ligands in the two complexes are different, to the

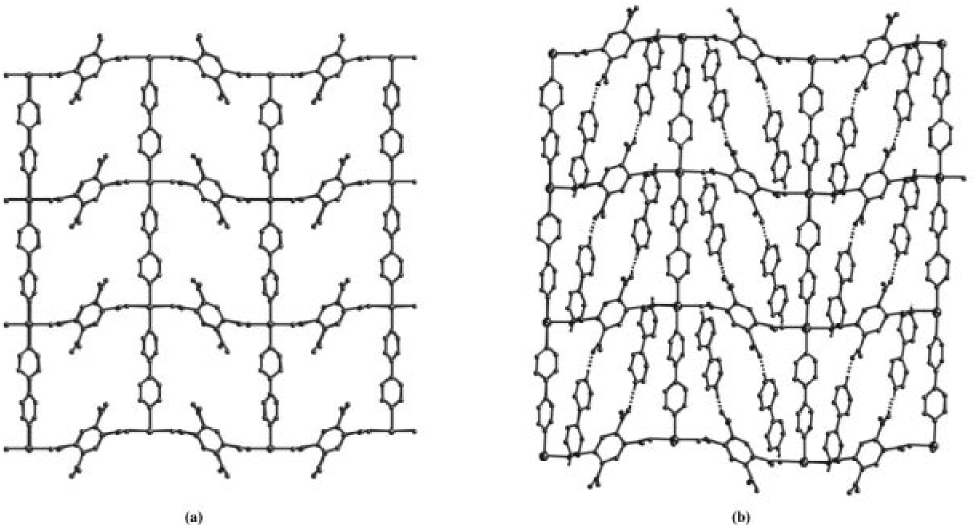


Figure 3. (a) Projection on the *ab*-plane of the two-dimensional layered architecture showing the quasi-square grids; (b) addition of the connecting $H_2bpy^{2\pm}$ illustrating the modus of growth of the 3D structure

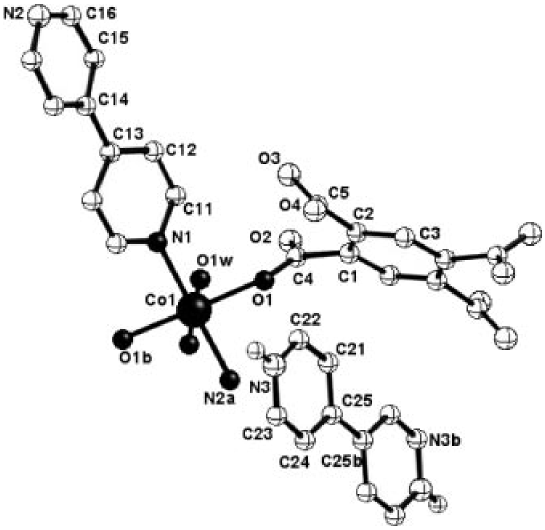


Figure 4. A perspective view of the locally expanded unit for **2**

best of our knowledge, where **1** exhibits an unprecedented connection mode. In both compounds, the introduction of mixed ligands provides the probability of generating multiple binding forces, such as coordination bonds, hydrogen bonding and other supramolecular interactions.

Experimental Section

General Remarks: Elemental analyses (C, N N) were carried out with an EA 1108 CHNS-0 automatic analyzer. FT-IR spectra were performed with a ThermoNicolet Avatar 360 FT-IR spectrometer on samples prepared as KBr pellets. Thermal analyses (TG-DTA) were done on a PerkinElmer Diamond TG-DTA system (SEGAI Service of the University of La Laguna) under a nitrogen atmosphere (flow rate: 80 $cm^3 min^{-1}$) in the temperature range 290−550 °C. The samples [3.542 **1** and 1.351 mg **2**] were heated in an aluminium crucible (45 μL) at a rate of 10 °C min^{-1}. The TG curves were analyzed by mass loss as a function of temperature. The number of decomposition steps was identified by using the derivative thermogravimetric curve (DTG). The DTA curves were analyzed as differential thermal analysis [ΔT(μV)].

[Mn(Hbta)(Hbpy)(H_2O)$_2$]$_n$ (1) and [H_2bpy]·[Co(bta)(bpy)(H_2O)$_2$] (2): The reagents and solvents were purchased from commercial sources (Aldrich) and used as received. These compounds were prepared similarly to [H_2bpy][H_3bta]$_2$.[19] Thus, for compound **1**, a sample of manganese acetate tetrahydrate (0.35 mmol) was dissolved in 5 mL of deionized water. 1,2,4,5-benzenetetracarboxylic acid H_4bta (0.39 mmol) was suspended in 5 mL of H_2O/NaOH (0.75 mmol) whilst stirring at ambient temperature for 10 min. A water solution of 4,4′-bipyridine bpy (0.75 mmol) was added dropwise to a 1,2,4,5-benzenetetracarboxylic acid solution. After that the clear solution, was mixed with the previously prepared manganese acetate whilst stirring. The mixture was then transferred to a

Table 2. Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{20}H_{16}MnO_{10}N_2$	$C_{30}H_{24}CoO_{10}N_4$
Molecular mass	499.29	659.47
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	*C*2/*c*
a/Å	20.694(4)	15.255(3)
b/Å	7.627(2)	11.476(2)
c/Å	24.512(5)	15.972(3)
β/°		90.89(3)
V/Å^3	3868.8(15)	2795.8(9)
Z	4	4
$D_{calcd.}$/g cm^{-3}	1.714	1.538
μ/mm^{-1}	0.749	0.682
Independent reflections	5558	3993
Observed reflections [$I > 2\sigma(I)$]	3353	2642
Refined parameters	319	219
*R*1 (*F*2)[a]	0.0744	0.0654
*wR*2 (*F*2)[b]	0.1024	0.1047
S	1.118	1.095

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2]/\Sigma w|F_o|^2]^{1/2}$.

Table 3. Selected bond lengths (Å) and angles (°) for **1**; symmetry code: a = x, y − 1, z; b = −x + 1/2, y − 1/2, z

Mn(1)−O(1)	2.179(2)	Mn(1)−O(1w)	2.126(3)
Mn(1)−O(4a)	2.149(2)	Mn(1)−O(2w)	2.183(3)
Mn(1)−O(7b)	2.206(2)	Mn(1)−N(21)	2.276(3)
O(1)−Mn(1)−O(1W)	90.8(1)	O(4a)−Mn(1)−O(7b)	95.8(1)
O(1)−Mn(1)−O(2W)	85.5(1)	N(2)−Mn(1)−O(4a)	84.5(1)
O(1)−Mn(1)−N(2)	89.5(1)	N(2)−Mn(1)−O(7b)	177.1(1)
O(1)−Mn(1)−O(4a)	173.2(1)	O(1W)−Mn(1)−O(4a)	86.3(1)
O(1)−Mn(1)−O(7b)	90.2(1)	O(1W)−Mn(1)−O(7b)	90.0(1)
O(1W)−Mn(1)−O(2W)	175.3(1)	O(2W)−Mn(1)−O(4a)	95.9(1)
O(1W)−Mn(1)−N(2)	92.9(1)	O(2W)−Mn(1)−O(7b)	85.7(1)
O(2W)−Mn(1)−N(2)	91.4(1)		

Table 4. Selected bond lengths (Å) and angles (°) for **2**; symmetry code: a = −x, y, −z; b = −x, y − 1, z

Co(1)−O(1)	2.077(2)	Co(1)−N(1)	2.169(3)
Co(1)−O(1W)	2.114(2)		
O(1)−Co(1)−O(1a)	179.2(1)	O(1a)−Co(1)−O(1W)	89.5(1)
O(1)−Co(1)−O(1W)	90.5(1)	O(1W)−Co(1)−O(1Wa)	176.5(1)
O(1)−Co(1)−O(1Wa)	89.5(1)	O(1W)−Co(1)−N(1)	91.8(1)
O(1)−Co(1)−N(1)	89.6(1)	O(1W)−Co(1)−N(2b)	88.2(1)
O(1)−Co(1)−N(2b)	90.4(1)		

reaction vessel placed inside a preheated oven at 145° for 3 h. The compound **2**, was prepared similarly to the manganese compound from $Co(NO_3)_2 \cdot 6H_2O$ (0.36 mmol). After several days, crystals of **1** and **2** were manually harvested under the microscope and analyzed using single-crystal X-ray diffraction (see Table 2). (**1**) $C_{20}H_{16}MnN_2O_{10}$ (499.3): calcd. C 48.11, H 3.23, N 5.61; found C 48.21, H 3.45, N 5.76. (**2**) $C_{30}H_{24}CoN_4O_{10}$ (659.5): calcd. C 54.64, H 3.67, N 8.50; found C 53.82, H 3.58, N 8.05.

X-ray Crystallographic Study: Diffraction experiments for **1** and **2** were carried out with Mo-K_α radiation using a Nonius KappaCCD diffractometer at 273(1) K. A summary of the crystallography data and structure refinement is given in Table 2. Both structures were solved by direct methods and refined with the full-matrix least-squares technique on F^2 using the SHELXS-97[27] and SHELXL-97[28] programs. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were placed in calculated positions and refined isotropically. The hydrogen atoms of the water molecules and those of the carboxylic groups were found in a difference Fourier map and refined isotropically for compound **1**. The final full-matrix least-squares refinement was performed minimizing the function $\Sigma w(|F_o|^2 - |F|^2)$ with $w = 1/[\sigma^2(F_o)^2 + mP^2 + nP]$ and $P = (F_o{}^2 + 2F_c{}^2)/3$ with $m = 0.0197$ **1** and 0.0183 **2** and $n = 7.3045$ **1** and 12.1543 **2**. The values of the discrepancy indices $R1$ ($wR2$) for all data were 0.1437 (0.1186) for **1** and 0.1204 (0.1224) for **2**, whereas those listed in Table 2 correspond to the data with $I > 2\sigma(I)$. The final Fourier difference map showed maximum and minimum height peaks of 0.512 and −0.394 eÅ^{-3} for (**1**) and 0.523 and −0.515 eÅ^{-3} for (**2**). The final geometrical calculations and the graphical manipulations were carried out with PARST95[29] and PLATON[30] programs, respectively. Selected bond lengths (Å) and angles (°) for **1** and **2** are listed in Table 3 and Table 4, respectively. CCDC-231515 (for **1**) and -231516 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] P. Lightfoot, A. Snedden, *J. Chem. Soc., Dalton Trans.* **1999**, 3549.

[2] Y. B. Dong, M. D. Smith, R. C. Layland, H.-C. zur Loye, *J. Chem. Soc., Dalton Trans.* **2000**, 775.

[3] K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward, M. J. Zaworotko, *Chem. Commun.* **1999**, 1327.

[4] H. Gudbjartson, K. Biradha, K. M. Poirier, M. J. Zaworotko, *J. Am. Chem. Soc.* **1999**, *117*, 2599.

[5] M. L. Tong, H. K. Lee, X. M. Chen, R. B. Huang, T. C. M. Mak, *J. Chem. Soc., Dalton Trans.* **1999**, 3657.

[6] L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc.* **1998**, *120*, 2676.

[7] C. H. Chang, K. C. Hwang, C. S. Liu, Y. Chi, A. J. Carty, L. Scoles, S. M. Peng, G. H. Lee, J. Reedijk, *Angew. Chem. Int. Ed.* **2001**, *40*, 4651.

[8] O. M. Yaghi, C. E. Davis, G. Li, H. L. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861.

[9] Y. Cui, H. L. Ngo, W. B. Lin, *Inorg. Chem.* **2002**, *41*, 1033.

[10] J. W. Ko, K. S. Min, M. P. Suh, *Inorg. Chem.* **2002**, *41*, 2151.

[11] V. G. Albano, M. C. Aragoni, M. Arca, C. Castellari, F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis, L. Loddo, G. Verani, *Chem. Commun.* **2002**, 1170.

[12] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.

[13] R. Cao, D. F. Sun, Y. C. Liang, M. C. Hong, K. Tatsumi, Q. Shi, *Inorg. Chem.* **2002**, *41*, 2087.

[14] P. M. Foster, A. K. Cheetham, *Angew. Chem. Int. Ed.* **2002**, *41*, 457.

[15] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O′Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[16] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148.

[17] S. M.-F. Lo, S. S.-Y. Chui, L.-Y. Shek, Z.-Y. Lin, X. X. Zhang, G.-H. Wen, I. D. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 6293.

[18] F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

[19] C. Ruiz-Pérez, P. A. Lorenzo-Luis, M. Hernández-Molina, M. M. Laz, P. Gili, M. Julve, *Crystal Growth & Design* **2004**, *4*, 57.

[20] Y. Rodríguez-Martín, M. Hernández-Molina, J. Sanchiz, C. Ruiz-Pérez, F. Lloret, M. Julve, *Dalton Trans.* **2003**, 2359.

[21] F. S. Delgado, J. Sanchiz, C. Ruiz-Pérez, F. Lloret, M. Julve, *Cryst. Eng. Commun.* **2003**, *5*, 280.

[22] E. I. Stiefel, G. F. Brown, *Inorg. Chem.* **1972**, *11*, 434.

[23] E. Berti, F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, E. Pitzalis, *Inorg. Chem. Commum.* **2002**, *5*, 1041.

[24] L. J. Zhang, J. Q. Xu, Z. Shi, W. Xu, T.-G. Wang, *Dalton Trans.* **2003**, 1148.

[25] G. B. Hix, K. D. M. Harris, *J. Mater. Chem.* **1998**, *8(3)*, 579.

[26] D. Cheng, M. A. Khan, R. P. Houser, *Inorg. Chim. Acta* **2003**, *351*, 2.

[27] G. M. Sheldrick, *SHELXS*, University of Göttingen, Germany, **1997**.

[28] G. M. Sheldrick, *SHELXL, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.

[29] M. Nardelli, *PARST95* (An update to *PARST)* a system of *FORTRAN* routines for calculating molecular structure parameters from the results of crystal structure analyses, *J. Appl. Cryst.* **1995**, *28*, 659.

[30] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, 34.

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