

Novel sheet-like manganese(II) networks. Synthesis and structure of $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]$ and $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2] \cdot \text{bpe}$ [bpe = *trans*-1,2-bis(4-pyridyl)ethene]

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Two new manganese(II) compounds of formula $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]$ **1** and $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2] \cdot \text{bpe}$ **2** [bpe = *trans*-1,2-bis(4-pyridyl)ethene] have been synthesized and characterized by single-crystal X-ray diffraction. The structures of compounds **1** and **2** consist of neutral chains containing manganese(II) ions bridged by mutually *trans* bpe molecules, the substantial difference being the bpe crystallization molecules which are in **2** and not in **1**. In both compounds the six-co-ordination of Mn^{2+} is achieved by means of two *trans* NCS^- ions and methanol molecules. In **1** adjacent chains are connected through weak hydrogen bonds in such a way to form a two-dimensional structure, in which rectangular holes are present. The $\text{Mn} \cdots \text{Mn}$ distance through the bpe bridge is 14.06(1) Å whereas that through the thiocyanate–methanol bridge is 6.73(1) or 7.54(1) Å. In **2** adjacent chains are linked through hydrogen bonds involving two nitrogen atoms of the solvate bpe molecule and two hydroxo groups from two methanol molecules in order to form layers. In each of these, four Mn^{2+} ions occupy the corners of a rectangle, which is constituted by four metal ions, four bpe and four methanol molecules. The $\text{Mn} \cdots \text{Mn}$ distances through co-ordinated and hydrogen-bonded bpe are 13.93(1) and 17.10(1) Å. Adjacent sheets are shifted in such a way that metal ions of the first approximately correspond to the center of the hole of the second one and *vice versa*.

A considerable research effort has been devoted to the building of supramolecular structures by organic and inorganic chemists in recent years.^{1–4} Covalent and hydrogen bonds are the most widely used tools to generate a great variety of one-, two- and three-dimensional either non-interpenetrating open networks with variable cavities or channels of desired size, or well entangled structures through interpenetration.^{5–8} Amongst the synthetic strategies to achieve these polymeric compounds in the context of co-ordination chemistry, one of the most fruitful choices consists in taking advantage of neutral organic rod-like rigid groups such as pyrazine (pyz) or 4,4'-bipyridine (4,4'-bipy) which can act as bridging ligands towards transition metal ions.⁹ So, the predictable assembly of metal complexes through pyz and 4,4'-bipy has produced a great variety of two- and three-dimensional metal containing networks,^{10–24} which are non-oxide open-framework materials with a very specific pore size and zeolitic type properties and interesting host–guest chemistry.

In recent works with the related N,N'-bidentate spacer *trans*-1,2-bis(4-pyridyl)ethene (bpe), an adamantoid network with Cu^{125} and a two-dimensional interpenetrated framework with Fe^{126} were reported exhibiting the same 1 : 2 metal to bpe molar ratio. The large cavities defined by the bridging bpe cause interpenetration leading to three- (Cu^1) and two-dimensional (Fe^{II}) structures with the metal ion exhibiting tetrahedral and octahedral stereochemistries, respectively. Furthermore, it has also been shown that the anion identity dictates the polymer framework topology.^{27,28} From the bpe ligand and CuSO_4 salt, a virtual three-dimensional structure was obtained which is made up of interpenetrating cationic grids of $[\text{Cu}(\text{bpe})_2]^{2+}$ linked by linear $[\text{Cu}(\text{bpe})(\text{H}_2\text{O})_2(\text{SO}_4)_2]^{2-}$ anionic chains filling cavities between the same grids. A second compound constituted of

bpe-bridged copper(II) chains of formula $[\text{Cu}(\text{bpe})(\text{H}_2\text{O})]^{2+}$ which are connected through sulfate anions to form a three-dimensional structure has been synthesized.²⁸ It is, therefore, evident that the framework topology depends not only on the counter ion but also on the bpe to metal molar ratio. In the present paper we report the preparation and crystal structures of two novel sheet-like polymers obtained by reaction of manganese(II) thiocyanate and bpe in methanol.

Experimental

Materials

Manganese(II) perchlorate hexahydrate, potassium thiocyanate and *trans*-1,2-bis(4-pyridyl)ethene were obtained from commercial sources and used as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Università degli Studi della Calabria (Italy).

Preparations

$[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]$ 1 and $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2] \cdot \text{bpe}$ 2. Single crystals of compound **1** (pale yellow parallelepipeds) were obtained, together with **2** (yellow parallelepipeds), by slow diffusion using an H-tube glass vessel. The starting solutions were methanolic solutions of $\text{Mn}(\text{NCS})_2$ (0.1 mmol) in one arm and bpe (0.1 mmol) in the other one. Compound **2** can also be obtained by itself in a good yield by reaction, in a beaker, of $\text{Mn}(\text{NCS})_2$ with an excess of bpe. (Found: C, 45.67; H, 4.20; N, 6.88. Calc. for $\text{C}_{16}\text{H}_{18}\text{MnN}_4\text{O}_2\text{S}_2$ **1**: C, 46.04; H, 4.35; N, 6.71. Found: C, 55.87; H, 4.59; N, 14.09. Calc. for $\text{C}_{28}\text{H}_{28}\text{MnN}_6\text{O}_2\text{S}_2$ **2**: C, 56.09; H, 4.71; N, 14.01%.)

IR spectra

IR Spectra were recorded on a Nicolet Impact 410 spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. The C–N stretching vibration of the thiocyanate group appears as a strong doublet at 2110 and 2090 cm^{-1} for compound **1** and as a single and strong peak at 2077 cm^{-1} for **2**. These features are consistent with the occurrence of thiocyanate–N co-ordination in **2** and bridging $\text{M–N–C–S}\cdots\text{CH}_3\text{OH}$ in **1**.²⁹ A strong absorption at 1610 cm^{-1} for **1** and a sharp strong doublet at 1610 and 1590 cm^{-1} for **2** (tentatively assigned to C–N stretching vibration of bpe) are consistent with the presence of co-ordinated (**1** and **2**) and unco-ordinated (**2**) bpe. The C–N stretching vibration of free bpe appears at 1590 cm^{-1} .

Crystallography

Crystals of dimensions 0.40 \times 0.35 \times 0.26, 0.35 \times 0.32 \times 0.28, 0.34 \times 0.30 \times 0.24 (**1**), 0.40 \times 0.30 \times 0.22 (**2**) were mounted on a Siemens R3m/V automatic diffractometer and used for data collection. In order to avoid the loss of solvent from both complexes **1** and **2**, single crystals were sealed in a Lindemann tube and then used for intensity data collection. Unfortunately the crystals of **1** decomposed during the data collection, which could only be completed using three different samples. Diffraction data were collected at room temperature by using graphite monochromated Mo–K α radiation ($\lambda = 0.71073 \text{ \AA}$) with the ω – 2θ scan method. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the range 2θ 15–30°. Information concerning crystallographic data collection and structure refinements is summarized in Table 1. Examination of two standard reflections, monitored after every 50, showed no sign of crystal deterioration for compound **2**. Lorentz-polarization corrections were applied to the intensity data. Of the 7714 (**1**), 3360 (**2**) measured reflections in the 2θ range 3–50° with index ranges $0 \leq h \leq 12$, $0 \leq k \leq 16$ and $-16 \leq l \leq 16$ (**1**) and $0 \leq h \leq 8$, $0 \leq k \leq 20$ and $-14 \leq l \leq 14$ (**2**), 3479 (**1**) and 2742 (**2**) were unique. From these, 954 (**1**), 1498 (**2**) were observed [$I > 3\sigma(I)$] and used for the refinement of the structures.

The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. All non-hydrogen atoms, except carbon of bpe and nitrogen thiocyanate atoms in **1** (in order not to decrease too much the data-to-parameters ratio), were refined anisotropically. All hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Full-matrix least-squares refinements were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$. Models reached convergence with R and R' listed in Table 1. The residual maxima and minima in the final Fourier-difference maps were 0.68 and -0.43 for **1** and 0.46 and -1.25 e \AA^{-3} for **2**. Solutions and refinements were performed with the SHELXTL PLUS system.³⁰ The final geometrical calculations were carried out with the PARST program.³¹ The graphical manipulations were performed using the XP utility of the SHELXTL PLUS system. Main interatomic bond distances and angles are listed in Tables 2 (**1**), 3 (**2**).

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See <http://www.rsc.org/suppdata/dt/1999/1813/> for crystallographic files in .cif format.

Results and discussion

The structure of compound **1** consists of neutral chains of manganese(II) ions bridged by mutually *trans* bpe molecules. The six-co-ordination of Mn^{2+} is achieved by means of two *trans* N-linked isothiocyanate ions and methanol molecules (Fig. 1, top). Neighbouring chains are connected through weak hydrogen bondings involving the sulfur atoms of NCS^- and the oxygen atoms of methanol (Fig. 1, bottom). The resulting two-

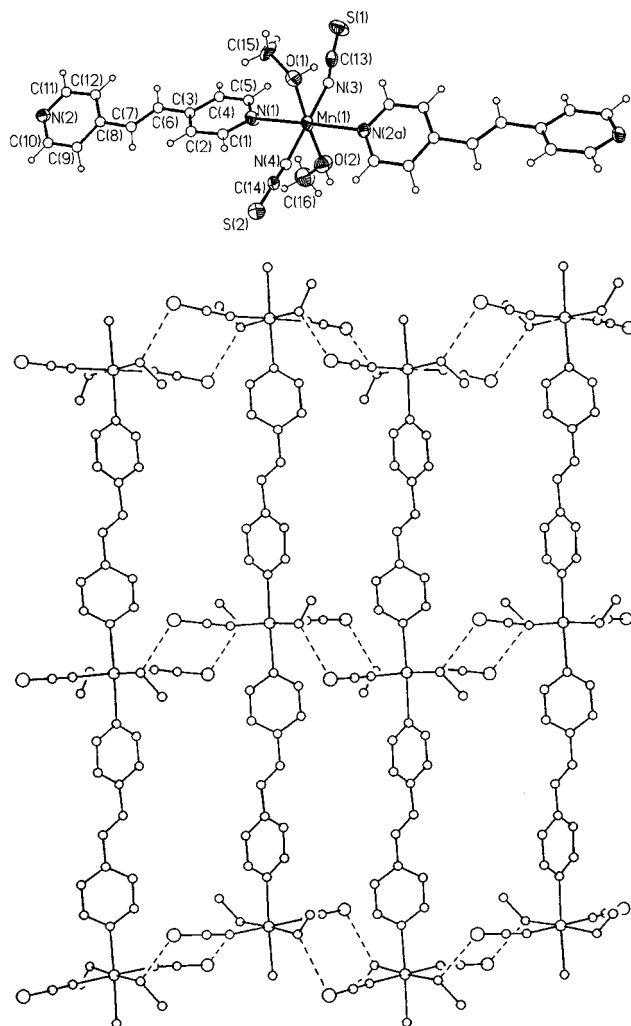


Fig. 1 Perspective view of the crystallographically independent $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]$ unit of compound **1** (top) and its polymerization through bridging bpe in a chain and between adjacent chains (bottom).

dimensional structure contains almost rectangular holes, in which the $\text{Mn}\cdots\text{Mn}$ distance through the bpe bridge is 14.06(1) \AA whereas the one through the thiocyanate–methanol bridge is 6.73(1) or 7.54(1) \AA . The structure of compound **2** is made up of similar manganese(II) chains, the bridging units being two *trans* co-ordinated bpe ligands and bpe molecules of crystallization. Two *trans* isothiocyanato–N groups and two methanol molecules fill the remaining four sites around the metal atom (Fig. 2). A substantial difference with respect to **1** concerns the connection between adjacent chains which are linked through hydrogen bonds involving two nitrogen atoms of the solvate bpe molecule and two hydroxo groups from two methanol molecules of the neighbouring chains. Corrugated layers, made up of parallel chains spaced by hydrogen-bonded bpe molecules, are formed. In each layer four Mn^{2+} ions occupy the corners of a rectangle, each rectangle being constituted by four metal ions, four bpe and four methanol molecules. The $\text{Mn}\cdots\text{Mn}$ distances through co-ordinated and hydrogen-bonded bpe are 13.93(1) and 17.10(1) \AA . Within a rectangle, the lines corresponding to N atoms of opposite bpe are parallel to each other, but they do not lie on the same plane (Fig. 3). Adjacent sheets are shifted in such a way that metal ions of the first approximately correspond to the centre of the hole of the second one and *vice versa*. Thiocyanate groups penetrate in the rectangular ring of the neighbouring layer.

Each metal ion in complexes **1** and **2** is in a distorted octahedral environment. The Mn–N bond distances of bpe [average 2.31(1) \AA] in **1** are longer than the Mn–N from NCS^-

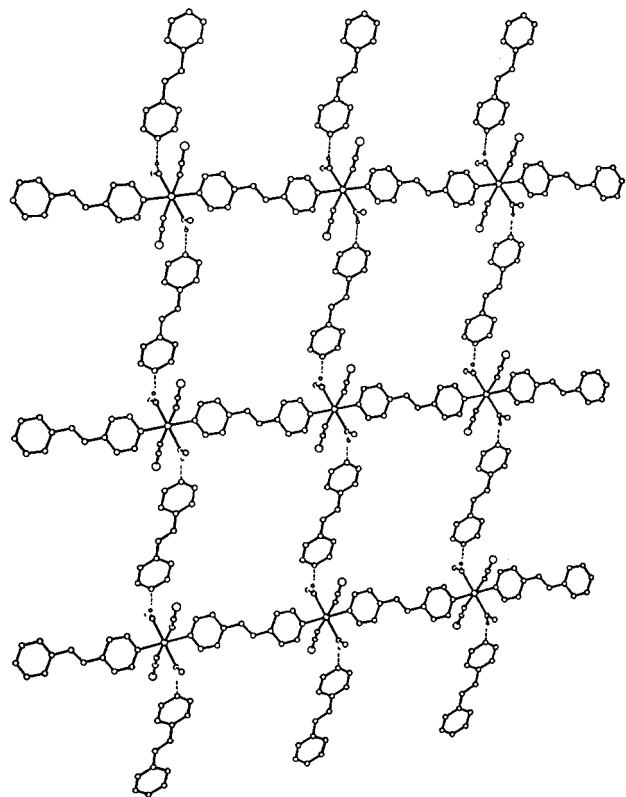
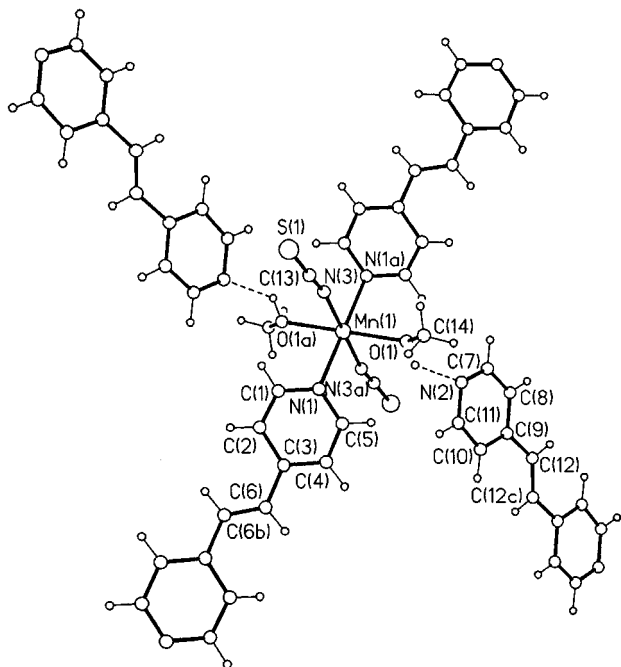


Fig. 2 Perspective view of the $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]\cdot\text{bpe}$ molecule of compound **2** (top) and its polymerization through hydrogen-bonded bpe (bottom).

[2.24(2) Å]. This trend is also observed in **2**, where the Mn–N value of bpe is 2.30(1) Å whereas the corresponding one of NCS^- is shorter [2.17(1) Å]. The lengthening of Mn–N_{NCS} distance value in **1** with respect to **2** is probably due to the hydrogen bond formation in which the thiocyanate groups are involved. The Mn–O distances values are shorter in **2** than in **1** [2.194(5) and 2.27(2) Å respectively]. The best equatorial plane in complex **1** is defined by the N(4), O(1), N(3), O(2) atoms [the largest deviation from the mean plane is 0.02(1) Å for N(4) and the manganese atom is 0.037(3) Å out of this plane] whereas all the octahedral manganese(II) planes are perfectly planar in **2** and the metal atom lies in these planes. The pyridyl rings

Table 1 Summary of crystal data^a for $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]$ **1** and $[\text{Mn}(\text{bpe})(\text{NCS})_2(\text{CH}_3\text{OH})_2]\cdot\text{bpe}$ **2**

	1	2
Formula	$\text{C}_{16}\text{H}_{18}\text{MnN}_4\text{O}_2\text{S}_2$	$\text{C}_{28}\text{H}_{28}\text{MnN}_6\text{O}_2\text{S}_2$
<i>M</i>	417.4	599.6
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$, no. 14	$P2_1/c$, no. 14
<i>a</i> /Å	10.382(4)	7.356(4)
<i>b</i> /Å	13.482(7)	17.096(6)
<i>c</i> /Å	14.038(4)	12.310(5)
β /°	91.71(3)	93.66(4)
<i>U</i> /Å ³	1964(1)	1545(1)
<i>Z</i>	4	2
<i>D_c</i> /kg m ⁻³	1.412	1.289
<i>F</i> (000)	860	622
μ (Mo–K α)/cm ⁻¹	9.01	5.96
<i>R</i>	0.086	0.070
<i>R'</i>	0.088	0.077

^a Details in common: *T* = 25 °C, *I* > 3 σ (*I*).

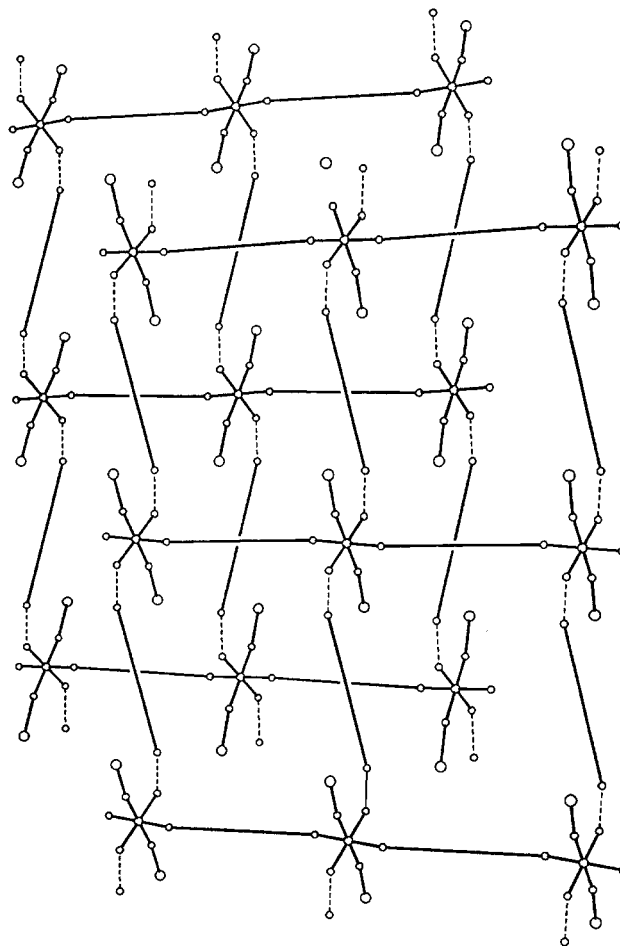


Fig. 3 A schematic drawing showing two corrugated adjacent sheets of compound **2**.

are planar, as expected, with deviations, from the mean plane, not greater than 0.03(2) Å for C(9) (**1**) and 0.018(6) Å for C(3) (**2**) atoms. The dihedral angle between the pyridyl rings is 31.7(7)° in **1** and 0.0° (for symmetry) in **2**.

The thiocyanate ligands have the expected linear geometry, with N–C–S angles of 170(3) and 177(1)° for S(1) and S(2) in compound **1** and 178.2(7)° in **2**. The C–N–Mn angles are 161(2) and 173(2)° for S(1) and S(2) in **1** and 169.4(6)° in **2**. Two weak hydrogen bonds, which are responsible for the two-dimensional structure, are formed between adjacent chains through NCS^- and co-ordinated methanol molecules in **1** (see end of Table 2).

Table 2 Selected interatomic distances (Å) and angles (°) for compound **1** with estimated standard deviations (e.s.d.s) in parentheses^a

Mn(1)–N(1)	2.33(1)	Mn(1)–N(3)	2.23(2)
Mn(1)–N(4)	2.20(2)	Mn(1)–O(1)	2.28(2)
Mn(1)–O(2)	2.26(2)	Mn(1)–N(2a)	2.30(1)
N(1)–Mn(1)–N(3)	90.2(5)	N(1)–Mn(1)–N(4)	90.4(5)
N(3)–Mn(1)–N(4)	178.7(7)	N(1)–Mn(1)–O(1)	91.9(5)
N(3)–Mn(1)–O(1)	89.9(7)	N(4)–Mn(1)–O(1)	89.0(6)
N(1)–Mn(1)–O(2)	90.7(5)	N(3)–Mn(1)–O(2)	87.9(7)
N(4)–Mn(1)–O(2)	93.3(6)	O(1)–Mn(1)–O(2)	176.6(4)
N(1)–Mn(1)–N(2a)	177.8(5)	N(3)–Mn(1)–N(2a)	90.2(5)
N(4)–Mn(1)–N(2a)	89.1(5)	O(1)–Mn(1)–N(2a)	90.3(5)
O(2)–Mn(1)–N(2a)	87.1(5)		
Hydrogen bonds ^b			
A	D	H	A...D
S(1)	O(1)	H(1o)	3.16(1)
S(2)	O(2)	H(2o)	3.17(1)

^a Symmetry code: a $-x, -y, -z$. ^b A = Acceptor, D = donor.

Table 3 Selected interatomic distances (Å) and angles (°) for compound **2** with e.s.d.s in parentheses^a

Mn(1)–O(1)	2.194(5)	Mn(1)–N(3)	2.170(6)
Mn(1)–N(1)	2.298(5)		
O(1)–Mn(1)–N(3)	93.1(2)	O(1)–Mn(1)–N(1)	90.7(2)
N(3)–Mn(1)–N(1)	88.9(2)	N(3)–Mn(1)–O(1a)	86.9(2)
N(1)–Mn(1)–O(1a)	89.3(2)	N(1)–Mn(1)–N(3a)	91.1(2)
Hydrogen bonds ^b			
A	D	H	A...D
N(2)	O(1)	H(1o)	2.68(1)
			132(1)

^a Symmetry code: a $-x, -y, -z$. ^b A = Acceptor, D = donor.

Analogously, the two-dimensional structure of **2** is obtained by means of hydrogen bonds which involve the nitrogen atoms of solvate bpe ligands and the oxygen atoms of co-ordinated methanol molecules (see end of Table 3).

Compound **1** can be considered as the first generation product from the reaction of the precursor $[\text{Mn}(\text{NCS})_2(\text{CH}_3\text{OH})_4]$ with bpe by substituting two *trans* co-ordinated solvent molecules by two bridging bpe groups. It is noteworthy that **1** was obtained together with **2** from the same solution and that solely **2** is the final product when an excess of bpe is used. It is, therefore, reasonable to assume that complex **1** transforms into **2** as the amount of bpe in solution is increased. The structure of **2** shows that the substitution of co-ordinated methanol in **1** by bpe is stopped due to the trapping of bpe between two solvent molecules through hydrogen bonds. Sheet structures, containing both co-ordinated and hydrogen-bonded bridging N-donor ligands, are not very unusual. They were found in some 4,4'-bipyridine compounds: $[\text{Zn}(\text{H}_2\text{O})_4(\text{bipy})][\text{NO}_3]_2 \cdot \text{bipy}$ ¹⁶ (**3**), $[\text{Cu}(\text{H}_2\text{O})_2(\text{bipy})(\text{F}_3\text{B})_2] \cdot \text{bipy}$ ²⁴ (**4**), $[\text{Mn}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{bipy})_2] \cdot \text{bipy}$ ²² (**5**), $[\text{Co}(\text{NCS})_2(\text{H}_2\text{O})_2(\text{bipy})] \cdot \text{bipy}$ ¹⁸ (**6**). All these compounds are very similar to **2** both as regards the presence of layers and their relative spatial displacements, even if the metal ions [Zn^{2+} (**3**), Cu^{2+} (**4**), Co^{2+} (**6**) and ligand 4,4'-bipyridine instead of bpe] are different. In particular, close analogies were found between compounds **2** and **5** and **6**, which have the same counter ion (NCS^-) or the same metal (**5**). Interestingly, **6** forms together with another compound, of formula $[\text{Co}(\text{NCS})_2(\text{bipy})][\text{NO}_3]_2 \cdot 2(\text{CH}_3\text{CH}_2)_2\text{O}$,¹⁸ where all the 4,4'-bipy ligands are co-ordinated (two ligand molecules replace water molecules in the co-ordination sphere of Co^{2+}) and the sheets are not interpenetrated. Only the supramolecular assembly **5** was observed in the Mn^{2+} case, as proof of the different behaviour of the two ions.

We believe that the interest in compound **2** is not only

dependent on the formation of a supramolecular assembly containing co-ordinated and hydrogen-bonded bpe molecules, but mainly because of useful information in understanding the bpe ligand reactivity with divalent metal ions. In fact bpe is a ligand similar to 4,4'-bipy, but, due to its greater length, it can bridge metal ions at larger distances, allowing bigger holes in the rings constituted by four metal ions and four ligands. This is a condition of obtaining structures constituted by interpenetrating grids, such as observed in $[\text{Cu}(\text{bpe})_2][\text{Cu}(\text{bpe})(\text{H}_2\text{O})_2(\text{SO}_4)]^{28}$ and $[\text{Fe}(\text{NCS})_2(\text{bpe})_2]$.²⁶ In particular, in the latter complex, the concatenation among parallel sheet families involves $\text{Fe}(\text{NCS})_2$ groups of one located in the holes of the other and *vice versa*. For this reason, the rings, constituted by four Fe^{II} and four bpe molecules, which are squared without concatenation, become rhombic and the $\text{S} \cdots \text{S}$ lines of the $\text{Fe}(\text{NCS})_2$ groups are placed along the longer diagonal of the rhombuses. Looking at the structure of **2**, one can understand that the loss of co-ordinated solvent and subsequent bpe binding would lead to a neutral square grid network of formula $[\text{Mn}(\text{NCS})_2(\text{bpe})_2]$. This sheet formation does not automatically lead to the polycatenane, because in this case the interpenetration between them is also necessary. Nonetheless, it is an indispensable condition and therefore our compound can be considered a precursor of a polycatenane system. Most likely, the major metal affinity for the nitrogen atom in the case of Fe^{II} allows the development of the reaction towards the polycatenane, whereas, in the manganese(II) case, the greater metal affinity for the oxygen atom stops the reaction at the previous level of supramolecular entity (compound **2**). Further experimentation, aimed at investigating the production of similar frameworks with other bpe-containing first-row transition metal ions having large channels, guest inclusion or interpenetration, is in progress.

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