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Supramolecular Isomerism in Coordination Polymers of Isophthalato-Bridged Mn^{II} Complexes Using 4,4′-Dipyridyl *N*,*N*′-Dioxide

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A one-pot reaction of three components [Mn^{II}, isophthalate dianion (isop) and 4,4′-dipyridyl *N*,*N*′-dioxide (dpyo)] in water/methanol (1:1) causes self-assembly resulting in two 3D supramolecular isomers of the same stoichiometry, $\{[Mn(isop)(H_2O)_2]\cdot(dpyo)\cdot(H_2O)\}_n$ (colorless) (**1**) and $\{[Mn(isop)(H_2O)(dpyo)_{0.5}]\cdot(dpyo)_{0.5}\cdot(H_2O)_2\}_n$ (pink) (**2**). Both isomers crystallize in the same crystal system (triclinic) and space group ($P\bar{1}$). The structural determination of **1** reveals an isophthalato-bridged 1D coordination polymer, $\{[Mn(isop)(H_2O)_2]_n$, having 16- and 8-membered rings where isophthalate acts simultaneously as chelating and bridging ligand connected to three metal centers. In isomer **2** the 1D chains transform to a 2D arrangement through bridging dpyo that replaces a water molecule at metal axial position. Both the crystal structures result in a 3D supramolecular network achieved through H-bonding among the 1D (in **1**) or 2D (in **2**) coordination polymers with lattice water and dpyo molecules and also by means of π-π interactions in **1**. Low-temperature magnetic measurement indicates antiferromagnetic interaction in both the isomers and the best fits are given by the exchange parameters $J = -0.56 \pm 0.02\,cm^{-1}$, $g = 2.01 \pm 0.01$ and $R = 3.1 \times 10^{-5}$ for **1** and $J = -1.06 \pm 0.03\,cm^{-1}$, $g = 2.01 \pm 0.01$ and $R = 2.8 \times 10^{-5}$ for **2**.

Introduction

The study of supramolecular isomerism, i.e. the existence of polymorphism in molecular crystals for a given set of components, is of particular importance in the field of crystal engineering because the resulting structure plays an important role in determining the properties of the crystalline solid.[1] Moreover the investigation in this field is addressed not only to produce novel materials of potential applications, but also to develop fundamental understanding of facts influencing the crystal growth. Supramolecular isomers include structural isomers[2] and stereoisomers, in the former the atom connectivity is different whereas in the latter this is nonvariant amongst the isomers. The latter includes diastereomers[3] (*cis*/*trans* and conformational isomer) and enantiomers.[4] Literature survey reveals a number of coordination polymers reported as supramolecular isomers, but a substantial amount of them, based on the coexistence of different guest molecules,[1–5] are basically pseudo-polymorphs rather than true isomers. In order to explore the supramolecular isomerism phenomenon, different experimental approaches have been undertaken varying e.g. temperature,[6] solvent,[7] conformational freedom of the ligand,[2a] etc. However, factors responsible to get a particular polymorph under controlled and reproducible conditions are difficult to ascertain.

The aromatic polycarboxylate building blocks[8] with special conformations, such as benzene-1,3-dicarboxylic acid (isophthalic acid, H_2isop) with a 120° angle between two carboxylic groups, present versatile coordination modes,[9a] can yield predetermined networks,[9b–9d] and can function as mediator for transmitting the exchange interaction between paramagnetic metal centers.[9a,10] The coordination polymers recently reported by our group,[11] $\{[Mn(isop)(bpp)_2]\cdot 0.5H_2O\}_n$ (bpp, 1,3-bis(4-pyridyl)propane; isop, isophthalate dianion), and by Liu et al.,[9a] $[Mn(isop)(Him)_2]_n$, $\{[Mn(isop)(dpe)]\cdot 0.5dpe\cdot H_2O\}_n$ and $[Mn_2(isop)_2(bpy)_2]_n$ (Him, imidazole; bpy, 2,2′-bipyridine; dpe, (*E*)-1,2-bis(4-pyridyl)ethene), show the same Mn-isop connectivity. But their dimensionality varies on the selection of coligands. Presently we have chosen 4,4′-dipyridyl *N*,*N*′-dioxide (dpyo)[12] as coligand since i. it is a long spacer that allows the construction of microporous materials with large cavities or channels, ii. it possesses different hapticity in coordination (*cis* and *trans* μ-4,4′; μ-4,4; $μ_3$-4,4,4′ and $μ_4$-4,4,4′,4′) that may lead to novel topological architectures, iii. it has a strong capability to form hydrogen bonds that

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assist in building supramolecular assemblies and iv. its high melting point may provide the possibility of generating materials with higher thermal stability, an important precondition in the conversion of microporous frameworks from laboratory curiosities to practical materials. In the present contribution we report on the synthesis, the crystal structure determination, magnetic behavior and thermal study of two supramolecular isomers, $\{[\mathrm{Mn(isop)(H_2O)_2}]\cdot(\mathrm{dpyo})\cdot(\mathrm{H_2O})\}_n$ (colorless) (**1**) and $\{[\mathrm{Mn(isop)(H_2O)(dpyo)_{0.5}}]\cdot(\mathrm{dpyo})_{0.5}\cdot(\mathrm{H_2O})_2\}_n$ (pink) (**2**) obtained simultaneously from one pot reaction of three components [$\mathrm{Mn^{II}}$, isophthalate dianion (isop) and 4,4′-dipyridyl *N*,*N*′-dioxide (dpyo)] on refluxing in water/methanol (1:1).

Results and Discussion

Description of Structures

Isomer 1

The X-ray structure analysis reveals that **1** consists of one-dimensional $[\mathrm{Mn(isop)(H_2O)_2}]_n$ polymeric chains (Figure S1), uncoordinated dpyo ligands, and lattice water molecules. The ribbon chain (Figure 1) is similar to that reported by us $\{[\mathrm{Mn(isop)(bpp)_2}]\cdot 0.5\mathrm{H_2O}\}_n$, having *trans*-located monocoordinated 1,3-bis(4-pyridyl)propane ligands,[11] and to the analogous $[\mathrm{Mn(isop)(Him)_2}]_n$, and $\{[\mathrm{Mn(isop)(dpe)}]\cdot 0.5\mathrm{dpe}\cdot\mathrm{H_2O}\}_n$.[9a] The infinite polymer comprises of 8- and 16-membered rings built up by almost coplanar manganese(II) and isop atoms (the metal ion being slightly displaced by 0.110(1) Å towards the axial aquo O(2w)). The eight-membered ring is formed by two symmetry related bridging carboxylate groups consisting of two manganese(II) ions at a distance of 4.097(1) Å. Thus the isop dianion acts simultaneously as a chelating and bridging ligand connecting three metal ions (μ_3 coordination mode). The distorted octahedral coordination geometry about $\mathrm{Mn^{II}}$ is achieved through a chelating carboxylate group, two carboxylate oxygens from symmetry related isop, and two water molecules located at the axial positions. The $\mathrm{Mn{-}OH_2}$ coordination bond lengths are 2.197(2) and 2.205(2) Å, while the Mn–O(isop) distances vary in a wide range, being somewhat longer the distances of the chelating carboxylate (2.382(1), 2.219(1) Å vs. 2.082(1), 2.128(1) Å, Table 1).

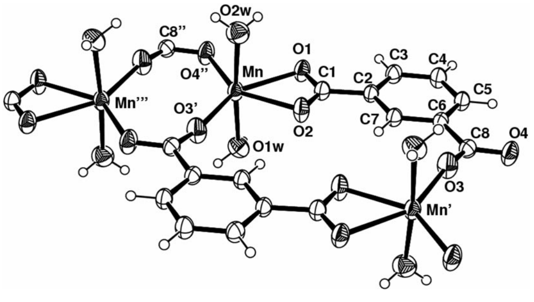

Figure 1. ORTEP view showing a detail of the coordination chain of isomer **1**.

Table 1. Selected bond lengths (Å) and angles (°) for isomers **1** and **2**.[a]

	1, X = O(2w)	**2**, X = O(10)
Mn–O(1)	2.382(1)	2.325(2)
Mn–O(2)	2.219(1)	2.242(2)
Mn–O(3′)	2.082(1)	2.089(2)
Mn–O(4′′)	2.128(1)	2.098(2)
Mn–O(1w)	2.205(2)	2.195(2)
Mn–X	2.197(2)	2.280(2)
Mn–Mn′′′	4.097(1)	4.300(1)
Mn–Mn′	7.376(1)	7.168(2)
O(1)–Mn–O(2)	56.71(5)	57.57(6)
O(1)–Mn–O(3′)	152.30(5)	156.44(7)
O(1)–Mn–O(4′′)	86.04(5)	88.05(7)
O(1)–Mn–O(1w)	85.54(6)	93.84(8)
O(1)–Mn–X	91.43(6)	86.08(7)
O(2)–Mn–O(3′)	96.55(6)	100.09(7)
O(2)–Mn–O(4′′)	142.51(5)	145.47(7)
O(2)–Mn–O(1w)	89.38(6)	85.56(7)
O(2)–Mn–X	86.15(7)	88.02(6)
O(3′)–Mn–O(4′′)	120.94(6)	114.43(7)
O(3′)–Mn–O(1w)	87.22(6)	91.44(9)
O(3′)–Mn–X	93.96(7)	85.73(8)
O(4′′)–Mn–O(1w)	92.04(6)	94.40(8)
O(4′′)–Mn–X	91.09(6)	93.17(8)
O(1w)–Mn–X	175.49(6)	172.42(7)
C(1)–O(1)–Mn	87.71(9)	88.04(14)
C(1)–O(2)–Mn	94.89(10)	92.00(12)
C(8)–O(3)–Mn′	166.55(15)	172.6(2)
C(8′′)–O(4′′)–Mn	118.02(11)	121.83(16)

[a] Symmetry operations: **1**: (′) –*x* + 1, –*y* + 1, –*z* + 1, (′′) *x* – 1, *y* – 1, *z*; (′′′) –*x*, –*y*, –*z* + 1; **2**: (′) –*x*, –*y* + 2, –*z* + 1; (′′) *x*, *y* – 1, *z*; (′′′) –*x*, –*y* + 1, –*z* + 1.

Adjacent polymers are arranged in a stair-like fashion in such a way that aromatic isop rings undergo π-π stacking interactions (centroid-to-centroid distance of facing rings is 3.509(2) Å). The crystal packing illustrated by two perspective views in Figure 2 shows uncoordinated dpyo molecules inserted in between the chains. A view, down [110] direction, shows coordinated water molecules O(1w) and O(2w) connected to the dpyo oxygens through hydrogen bonds (Table S1), leading to a three-dimensional structure. The dpyo rings are not coplanar but slightly tilted (dihedral angle of 21.8(1)°), and in addition to H-bonds, each dpyo interacts with a symmetry related molecule through π-π interactions (distance between the centroids of 3.731(2) Å with a slippage of 1.471 Å). Finally the X-ray structural analysis evidences lattice water molecules in the unit cell, weakly interacting with symmetry related O(2) of carboxyl groups.

Isomer 2

The structural determination of **2** reveals it comprises of coordination polymers structurally very similar to those found in **1**, but connected by bridging dpyo ligands which replace a coordinated water molecule forming a 2D arrangement (Figures 3 and 4, top). The distance between metals through the dpyo bridge is 12.529 Å. The bond lengths and angles in the coordination environment show a trend similar to that observed in isomer **1** (Table 1). The main difference is detected in the Mn–O(dpyo) axial distance of **2**, that is ca. 0.1 Å longer than the correspondent

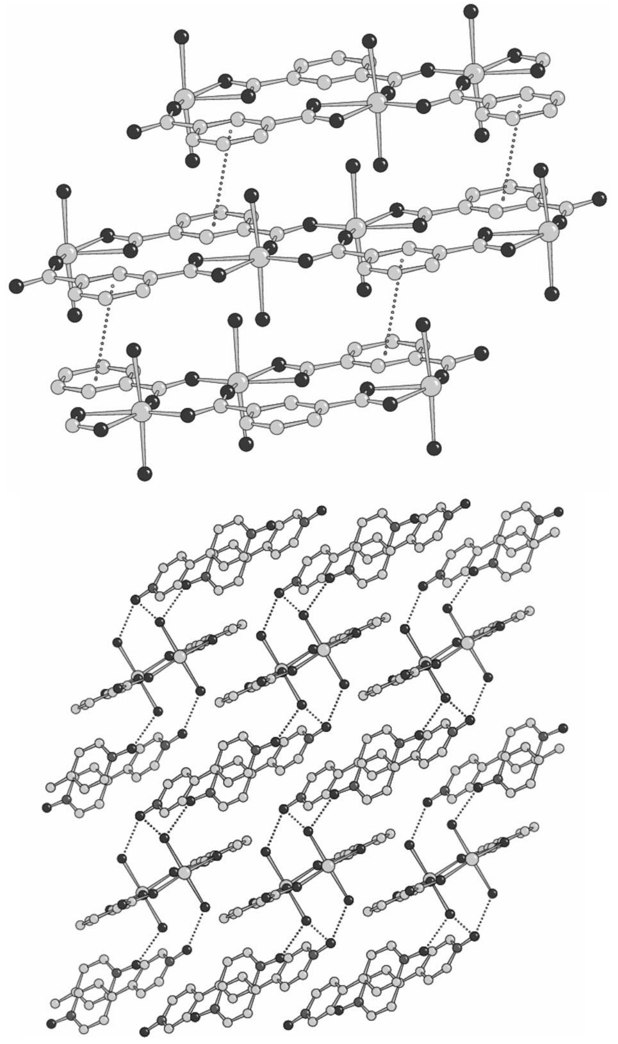

Figure 2. Crystal packing of isomer **1** showing π-π interactions between phenyl rings of adjacent polymers (top); a view down the direction of polymer propagation showing H-bonds (dotted lines) occurring among water molecules and dpyo oxygens (bottom) [lattice water molecules not shown for clarity].

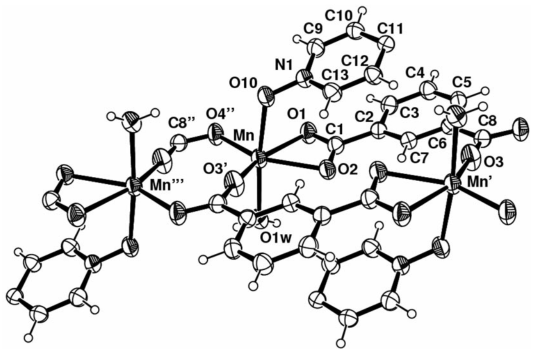

Figure 3. ORTEP view showing a detail of the Mn(isop) chain in isomer **2**.

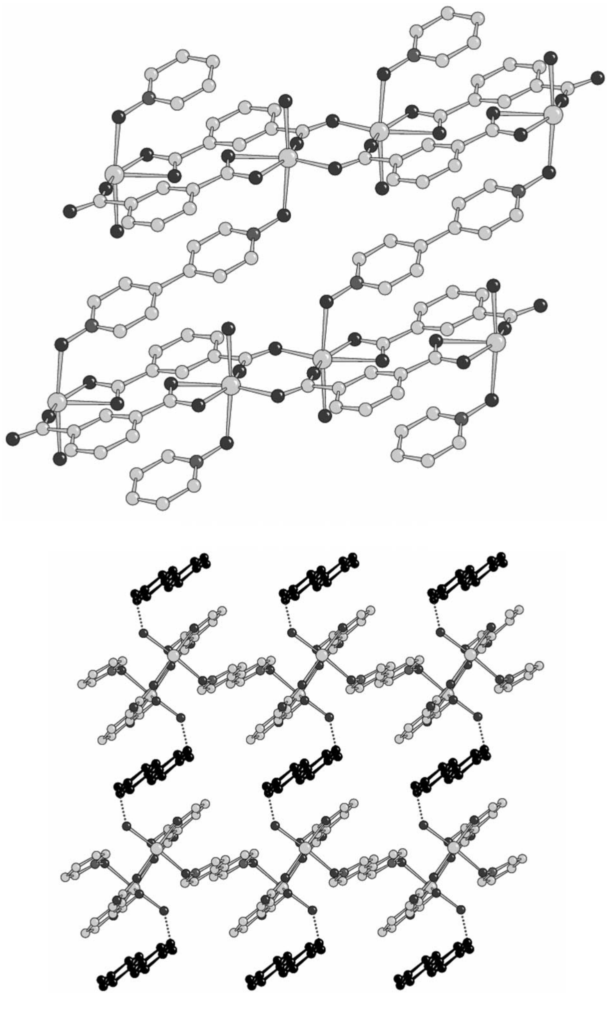

Figure 4. Crystal packing of isomer **2**. Top: 2D layered structure. Bottom: view down the polymer propagation direction showing H-bonds connecting the 2D structure with lattice dpyo molecules (black color). Lattice water molecules not shown for clarity.

Mn–O(2w) measured in **1**. It is worth of note that the Mn–Mn separations embracing the eight-membered and 16-membered rings, of 4.300(1) and 7.168(2) Å, respectively, are significantly different with respect to the correspondent values of 4.097(1) and 7.376(1) Å found in isomer **1**. These separations seem to be modulated by ligands occupying the *trans*-axial positions of the Mn^{II} ions and by the crystal packing. In fact in the topologically similar 1D polymers $\{[Mn(isop)(bpp)_2]\cdot 0.5H_2O\}_n$[11] and $[Mn(isop)(Him)_2]_n$,[9a] the correspondent intermetallic distances are 4.397, 7.276 Å, and 4.480(2), 7.098(2) Å, respectively, while in the infinite 2D double-layer of $\{[Mn(isop)(dpe)]\cdot 0.5dpe\cdot H_2O\}_n$[9a] these are 4.028, 7.591 Å.

The layers of **2** are connected through a H-bonding scheme occurring between the aquo ligand O(1w) and uncoordinated dpyo molecules (Figure 4, bottom). Finally, two lattice water molecules contribute to strengthen and construct the 3D network. The coordinated and lattice dpyo molecules, being located on symmetry centers, present coplanar rings.

Although both isomers form under similar conditions (same batch) it is reasonable to conclude that the free energy difference between the two crystalline forms is small.[13] In addition, we would like to underline that the two major themes used in inorganic crystal engineering strategies (coordination polymer and the use of hydrogen-bonding), are often viewed as quite distinct. In the present work these features appear to be highly interdependent.

Magnetic Properties

From the magnetic point of view, complexes **1** and **2** can be considered as dinuclear ones, in which two Mn^{II} ions are linked by two carboxylate bridges in *syn-anti* fashion since coupling through isop in **1** and through isop/dpyo in **2** are almost negligible. The temperature dependence (300 K to 2 K) as $\chi_M T$ (χ_M being the magnetic susceptibility for two Mn^{II} ions) for complexes **1** and **2** are shown in Figures 5 and 6, respectively. For both the isomers $\chi_M T$ value is ca. 9.0 $cm^3 mol^{-1} K$ at 300 K (a value which is as expected for two quasi-isolated Mn^{II} ions) and it is practically constant till 100 K. On further lowering the temperature the $\chi_M T$ decrease is pronounced reaching a value of 2.3 and 1.2 $cm^3 mol^{-1} K$ for isomers **1** and **2**, respectively, at 2 K. The shape of these curves are characteristic of the occurrence of weak antiferromagnetic interactions between the Mn^{II} centers.

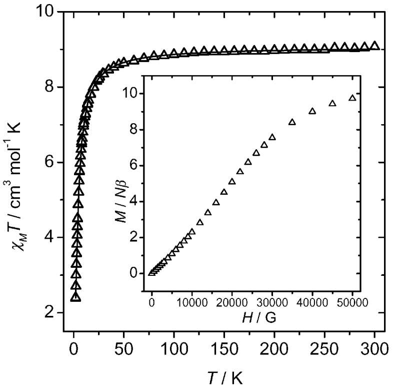

Figure 5. Plot of $\chi_M T$ vs. T for isomer **1** (solid line represents the best-fit calculation. Inset: plot of the reduced magnetization at 2 K).

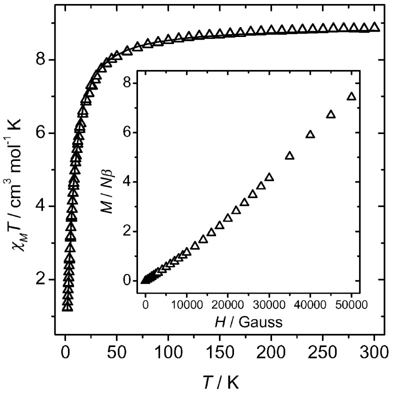

Figure 6. Plot of $\chi_M T$ vs. T for isomer **2** (solid line represents the best-fit calculation. Inset: plot of the reduced magnetization at 2 K).

Taking into account the pseudo-dinuclear nature[11] of **1** and **2**, the susceptibility data were fitted by Kahn's[14] formula based on the exchange Hamiltonian $H = -JS_iS_j$. The best fits are given by the exchange parameters $J = -0.56 \pm 0.02\ cm^{-1}$, $g = 2.01 \pm 0.01$ and $R = 3.1 \times 10^{-5}$ for **1** and $J = -1.06 \pm 0.03\ cm^{-1}$, $g = 2.01 \pm 0.01$ and $R = 2.8 \times 10^{-5}$ for **2**. The J values are comparable with those reported for similar Mn^{II} systems. The plot of the reduced magnetization ($M/N\beta$) vs. H achieves the value of ca 10 $N\beta$ (corresponding to two Mn^{2+} ions) for **1** (Figure 5), and 8 $N\beta$ (less than for two uncoupled Mn^{2+} ions) for **2** (Figure 6); but these do not follow the Brillouin function, undoubtedly as a result of the small antiferromagnetic coupling between the manganese centers.

Since the plot of the reduced magnetization is extremely sensitive for small changes in the J values, this feature indicates that AF coupling in **2** must be higher. Indeed, the fit calculations show that, being very small, J value is almost double in **2** (–0.5 and –1.0 cm^{-1} in **1** and **2**, respectively). In the isomer **1**, one of the Mn–O bridging distances (Mn–O(4′′) = 2.128(2) Å) is slightly longer than the values measured in **2** (Mn–O(3′) = 2.089(2) and Mn–O(4′′) = 2.098(2) Å). This variation could be an empirical explanation of the different J values.

Thermal Analyses

Isomer **1** starts dehydration (Figure S2, Supporting Information) at ca. 80 °C and the deaquation process completes at ca. 150 °C, yielding a pink species (indicating the coordination of dpyo), which slowly loses mass on further hearting. Whereas **2** starts dehydration (Figure S3) at ca. 40 °C and becomes deaquated at ca. 90 °C which also loses mass upon further heating. After deaquation the color of the isomers is identical and their thermal profiles are close comparable. The very slow decomposition within the long range of temperature (150–325 °C for **1** and 90–360 °C for **2**) hints the attainment of hexa coordination by Mn^{II} even after deaquation. This may occur if the ligand isop either acts as pentadentate or most likely dpyo acts as bridging ligand.

Conclusions

Two unique supramolecular isomers of Mn^{II}, using dpyo and isop as building blocks, **1** (colorless) and **2** (pink), have been synthesized from the same reaction mixture under refluxing solvent condition, and their ratio varies with the duration of heating at reflux temperature. Initially the isomer **1** predominates and finally **2** is the major one, but both the components are still present after four hours, indicating that there is only a minor energy difference between the crystalline forms. On the other hand, isomer **1** is obtained as single product through hydrothermal technique only. Thus the dpyo species play a key role in modifying the topology of the $[Mn(isop)(H_2O)_2]_n$ chain in **1** by replacing a coordinated water molecule and forming a 2D arrangement

(**2**). The dpyo molecule confirms a strong capability either to form hydrogen bonds in **1** or to behave as coordinating ligand in **2**. Such a one-pot synthesis illustrates a rare example of exchanged-ligand dependent topological supramolecular isomerism.

Experimental Section

Materials: High purity manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and 4,4′-dipyridyl *N*,*N*′-dioxide were purchased from Aldrich Chemical Company. All other chemicals used were of analytical grade.

Physical Measurements: Elemental analyses (C, H and N) were performed using a Perkin–Elmer elemental analyzer. IR spectra (4000–600 cm^{-1}) were taken in KBr pellets using a Jasco FT-IR (model 300E). Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (30 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants. Thermal analysis was done on a Perkin–Elmer Pyris Diamond system.

Crystallographic Data Collection and Refinement: Crystal data and details of data collection and refinement for the complexes reported are summarized in Table 2. The data collections were carried out at 293(3) K using Mo-K_α radiation (λ = 0.71073 Å) on a Nonius DIP-1030H system, 30 frames with a ϕ rotation of 5–6° and exposure time of 20 min. Cell refinement, indexing and scaling of the data sets were performed using programs Denzo and Scalepack.[15] The contribution of hydrogen atoms at calculated positions was included in final cycles of refinement. The structures were solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[16] All the calculations were performed using the WinGX System, version 1.70.01.[17]

CCDC-653494 (for **1**) and -653495 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and details of the structure determination for isomers **1** and **2**.

	1	**2**
Empirical formula	$C_{18}H_{18}MnN_2O_9$	$C_{18}H_{18}MnN_2O_9$
M_r [$g mol^{-1}$]	461.28	461.28
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	8.821(3)	9.214(3)
b [Å]	9.989(3)	10.043(3)
c [Å]	12.418(3)	11.982(4)
α [°]	99.07(1)	69.30(2)
β [°]	98.80(2)	78.14(2)
γ [°]	115.24(2)	69.09(2)
V [Å^3]	947.2(5)	964.9(5)
Z	2	2
$D_{calcd.}$ [$g cm^{-3}$]	1.617	1.588
μ (Mo-K_α) [mm^{-1}]	0.754	0.740
$F(000)$	474	474
Reflections collected	11023	11251
Unique reflections	4850	4787
R_{int}	0.0312	0.0336
θ_{max} (°)	29.61	29.62
Observed reflections [$I > 2\sigma(I)$]	3786	3010
Parameters	291	289
Goodness-of-fit (F^2)	1.029	0.891
$R1$[a] [$I > 2\sigma(I)$]	0.0353	0.0441
wR_2[a]	0.0992	0.1119
Residuals [e Å^{-3}]	0.254, –0.240	0.565, –0.217

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

Synthesis

{[Mn(isop)(H_2O)$_2$]·(dpyo)·(H_2O)}$_n$ (1) and {[Mn(isop)(H_2O)(dpyo)$_{0.5}$]·(dpyo)$_{0.5}$·(H_2O)$_2$}$_n$ (2): A methanolic solution (10 mL) of dpyo (1 mmol, 0.188 g) was added dropwise to an aqueous solution (5 mL) of $MnCl_2 \cdot 4H_2O$ (1 mmol, 0.197 g) with constant stirring and to this mixture an aqueous solution (5 mL) of disodium isophthalate (1 mmol, 0.210 g) was added. The reaction mixture was refluxed for 15 min and filtered. The filtrate was kept in a $CaCl_2$ desiccator. After a few days, colorless (**1**) and pink (**2**) crystals suitable for X-ray analysis were obtained as mixture. They were easily separable by a tweezer. Yield 65% for **1**, 15% for **2**. $C_{18}H_{18}MnN_2O_9$ (461.28): calcd. C 46.82, H 3.90, N 6.07; found (for **1**) C 46.31, H 4.12, N 5.78; found (for **2**) C 46.34, H 4.10, N 5.81.

Yields given above refer to 15 min refluxing time (**1** is the major component), but with increasing time the ratio reverses. However, the minor does not disappear, even not after four hours of heating. The pure isomer **1** is obtained as single product by a hydrothermal technique (same ratio of the reactants in a Teflon™-lined steel vessel at 120 °C for 8 h; overnight cooling at 27 °C).

Supporting Information (see also the footnote on the first page of this article): Figure S1, thermogravimetric analysis curves, Table showing of hydrogen bonding parameters and IR spectral bands for isomers **1** and **2**.

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