CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200903129

Effect of Bulkiness on Reversible Substitution Reaction at Mn^{II} Center with Concomitant Movement of the Lattice DMF: Observation through Single-Crystal to Single-Crystal Fashion

Madhab C. Das and Parimal K. Bharadwaj*[a]

Abstract: The porous coordination polymer ($\{[Mn(L)H_2O](H_2O)_{1.5}(dmf)\}_n$, **1**) (DMF = *N*,*N*-dimethylformamide) exhibits variety of substitution reactions along with movement of lattice DMF molecule depending upon bulkiness of the external guest molecules. If pyridine or 4-picoline is used as a guest, both lattice and coordinated solvent molecules are simultaneously substituted (complexes **6** and **7**, respectively). If a bulky guest like aniline is used, a partial substitution at the metal centers and full substitution at the channels takes place (complex **8**). If the guest is 2-picoline (by varying the position of bulky methyl group with respect to donor N atom), one Mn^{II} center is substituted by 2-picoline, whereas the remaining center is substituted by a DMF molecule that migrates from the channel to the metal center (complex **9**). Here, the lattice solvent molecules are substituted by 2-picoline molecules. For the case of other bulky guests like benzonitrile or 2,6-lutidine, both the metal centers are substituted by two DMF molecules, again migrating from the channel, and the lattice solvent molecules are substituted by these guest molecules (complex **10** and **11**, respectively). A preferential substitution of pyridine over benzonitrile (complex **12**) at the metal centers is observed only when the molar ratio of PhCN:Py is 95:5 or less. For the case of an aliphatic dimethylaminoacetonitrile guest, the metal centers remain unsubstituted (complex **13**); rather substitutions of the lattice solvents by the guest molecules take place. All these phenomena are observed through single crystal to single crystal (SC–SC) phenomena.

Keywords: crystal engineering · metal–organic frameworks · substitution reactions · supramolecular chemistry

Introduction

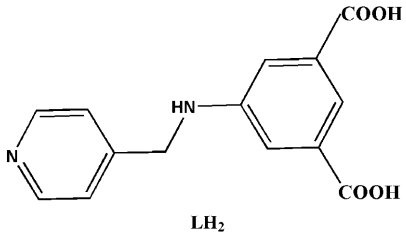
In recent times, there has been a growing interest in flexible and dynamic frameworks in the area of porous coordination polymers (PCPs) for their structural[1] and functional[2] responses to guest sorption and reactivity between network and guest species.[3,4] If the crystallinity is maintained upon guest removal/inclusion, then it becomes possible to locate the guests,[5–7] their orientation in the voids, and so on. Many applications, such as catalysis and storage, do not require single-crystal to single-crystal (SC–SC) transformation, but preservation of single crystallinity would be crucial if a crystal were to be integrated into a device, such as a substrate-triggered sensor,[7d] and can be used further to direct multiple small molecules cooperatively in chemical reactions. Rare are reactions within the coordination spheres of transition metals in solids;[8] they are often accompanied by tragic breakdown of the crystal, thus preventing the detection of the products. Reports of retention of single-crystallinity upon exchange of lattice solvent molecules are available in literature,[6,7] but substitution at the metal center by an *external* guest molecule is barely observed either in discrete systems[9] or in PCPs.[10] Herein, we have focused on SC–SC transformation through simultaneous metal–ligand bond breaking/new bond formation along with either movement of a lattice solvent molecule from channel to the metal center or exchange of lattice solvent molecules by external guests within PCPs affording various substituted products. Organic and coordination polymers in solids are known[5] for new bond formation by photo-induced cross-linking reactions. The bond breaking and new bond formation by reversible bipy/MeOH (bipy = 4,4′-bipyridyl) substitution in the lattice of a Co^{II} complex[11] has very recently been reported by Rosseinsky et al. It is, therefore, of considerable

[a] M. C. Das, Prof. Dr. P. K. Bharadwaj
Department of Chemistry
Indian Institute of Technology
Kanpur, 208016 (India)
E-mail: pkb@iitk.ac.in

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903129.

importance to study the processes that direct cooperative fluidity in dynamic crystals with a view to gaining better insight into the enthralling phenomenon of single-crystal transformations.

Previously we had demonstrated the synthesis of a PCP (complex **1**) based upon manganese carboxylate dimeric units linked through flexible reduced Schiff base ligand (LH_2, Scheme 1) and its remarkable ability to substitute the



LH_2

Scheme 1. Ligand LH_2.

coordinated aqua ligand, as well as the replacement of the lattice solvent molecules ($DMF+H_2O$) ($DMF=N,N$-dimethylformamide) by external cyano guest molecules.[10] The process is completely reversible and monitored through SC–SC fashion. Here, we extended our study a step further, wherein **1** undergoes either partial or complete substitution reactions of the aqua ligand depending upon bulkiness either by varying the position of the methyl group with respect to the donor N atom or by varying the length of the aromatic/aliphatic guest molecules with concerted movement of the lattice DMF molecule from the channel to the Mn^{II} center. The present study involves a new class of substitution reactions within PCPs that involves the concerted and spatially controlled introduction of different guest molecules at the reactive Mn^{II} sites with the retention of long-range order by cooperative motions to permit molecular transport through a porous solid.

Results and Discussion

The compound $\{[Mn(L)(H_2O)](H_2O)_{1.5}(dmf)\}_n$, (**1**) is prepared by the solvothermal technique using the ligand LH_2 with $Mn(NO_3)_2{\cdot}4H_2O$ in aqueous DMF.[10] The crystalline product once formed is insoluble in most of the organic solvents making it possible to study the substitution reactions. Complex **1** (hereafter, mother crystal) crystallizes in the monoclinic space group *C*2/*c* and the asymmetric unit contains one Mn^{II}, one $(L)^{2-}$ and two types of lattice solvent molecules (one bound water molecule, 1.5 free water and one free DMF molecule). Two carboxylates from two ligand moieties link two metal ions forming dimeric $[Mn_2(CO_2)_2]$ units (Figure 1) having wave like arrangements along the crystallographic *c* axis. A detailed crystallographic description of this complex has been given in our previous paper.[10] Substitution of the metal bound aqua ligand in complex **1** can be achieved by dipping a crystal at RT in the appropriate reagent used as solvent. To explore reversibility of these substitutions, the transformed crystal (complexes **6–13**) is dipped in DMF at RT with the cover of the vial open to the air. In each case, the crystal reabsorbs lost DMF and water molecules to regain the original formula ($\{[Mn(L)(H_2O)](H_2O)_{1.5}(dmf)\}_n$) of mother crystal of complex **1** as was observed earlier.[10] Also, in each and every case, the detail crystallographic investigation shows that the original structure including the H-bonding network is restored and the channel constitutes about 45% of the total crystal volume almost identical as that of complex **1**. Also, these first generation compounds are inter-exchangeable among themselves, as can be found previously.[10]

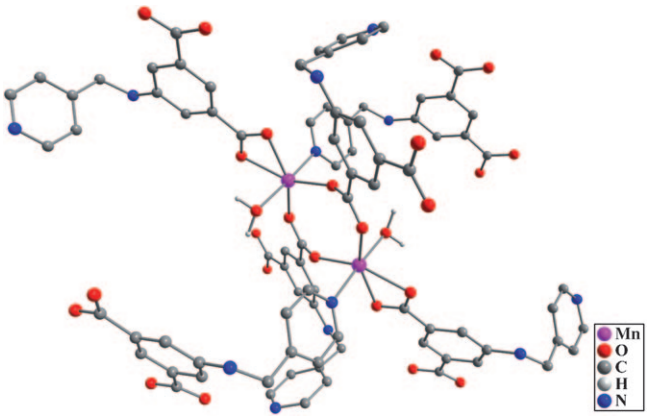


Figure 1. The dimeric $[Mn_2(CO_2)_2]$ unit.

The crystals of complex **1** show a remarkable ability to substitute the coordinated aqua as well as lattice solvent molecules for pyridine in a SC–SC manner. The channel of **1** constitutes 45.2% of the total crystal volume, which is high enough to accommodate guests of different sizes. To probe SC–SC transformations with different guests containing different substituents, a mother crystal of suitable size is chosen that is used throughout at room temperature (RT). When the mother crystal is immersed in pyridine (Py) for 4 h, it forms the crystal of complex **6**, $\{[Mn(L)(Py)](Py)_{0.5}\}_n$, (Figure 2). The X-ray structural determination reveals that the crystal system remains the same, but the space group is changes from *C*2/*c* to *I*2/*a*. The metal-bound aqua ligand and lattice solvent molecules (H_2O+DMF) are completely removed by Py molecules. The TGA of complex **6** indicates 26.5% weight loss at 210°C corresponding to 1.5 Py molecules and no decomposition is observed up to 370°C (see Figure S1 in the Supporting Information). Within the channels, the bound Py molecules, each from two alternative walls, are π stacked in opposite faces (centroid-to-centroid distance 4.213 Å) and have weak C–H···π interactions with benzene π moiety (C17–H17···centroid of C1–C6 3.589 Å) of the ligand unit. Similar C–H···π contacts are also observed for the unbound ones (C21-H21···centroid of C1–C6 4.003 Å). Additionally, one aromatic H atom of the coordinated Py molecule makes a contact with the π moiety of an uncoordinated pyridine molecule (C18-H18···centroid of lat-

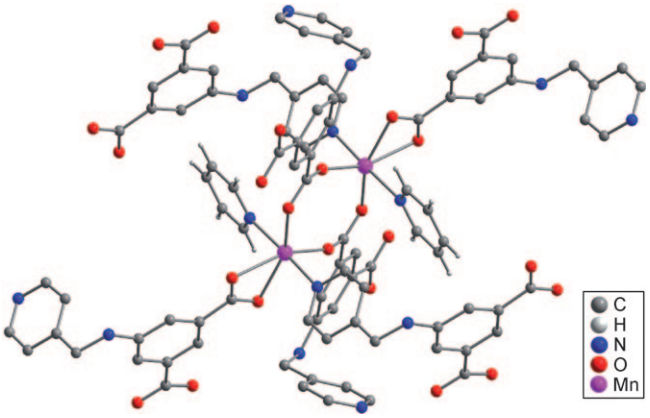


Figure 2. Py-substituted crystal of complex **6**.

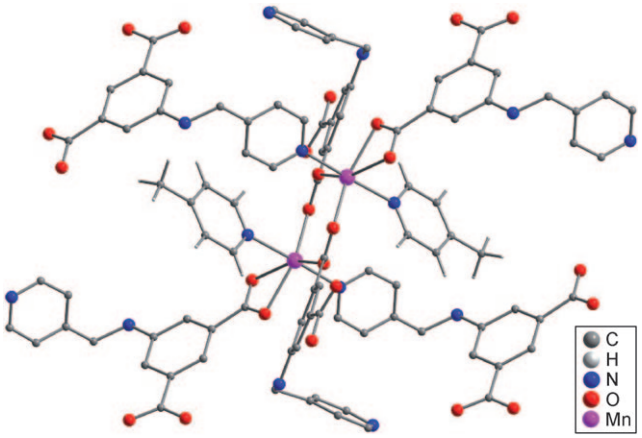


Figure 4. 4-Picoline-substituted crystal of complex **7**.

tice Py 3.721 Å). A 3D packing diagram is depicted in Figure 3, which shows that the non-coordinated Py molecules are almost perpendicular in direction with respect to the coordinated Py molecules within the channels (dihedral angle between the mean planes constituted by these two types of Py molecules is 83.43°). The coordinated Py molecule is also perpendicular (85.79°) to that of the basal plane of the octahedron around Mn^{II} center formed by the four carboxylate O atoms (O1–O4) whereas, the dihedral angle between the basal plane and the non-coordinated Py is 66.62°.

When the mother crystal is kept in 4-picoline for 10 h, it affords complex **7**, $\{[Mn(L)(4\text{-Pic})](4\text{-Pic})_{0.5}\}_n$, (Figure 4). Unlike the previous case, however, the space group remains the same as that of the mother crystal (*C*2/*c*). The coordinated aqua ligand is substituted by one 4-picoline molecule, whereas the lattice DMF and water molecules are also replaced by another half of 4-pic molecule. The coordinated 4-picoline is involved in C-H···π interactions from the terminal methyl C–H moieties to the benzene π clouds of alternative walls (C20–H20C···centroid of C1–C6 3.424 Å) and within themselves (C20–H20B···centroid of coordinated 4-Pic 3.399 Å). The 4-picoline present in the lattice is situated in the center of the channel and is engaged in two symmetric C–H···π interactions with benzene π clouds from both sides of the wall (C22–H22···centroid of C1–C6 3.953 Å). Also, the coordinated picoline is almost perpendicular to the uncoordinated one with a dihedral angle of 81.36° (see Figure S2 in the Supporting Information). A 30.02% weight loss during TG analysis indicates removal of all the 4-picoline molecules at 310 °C and the complex is stable up to 360 °C (see Figure S1 in the Supporting Information).

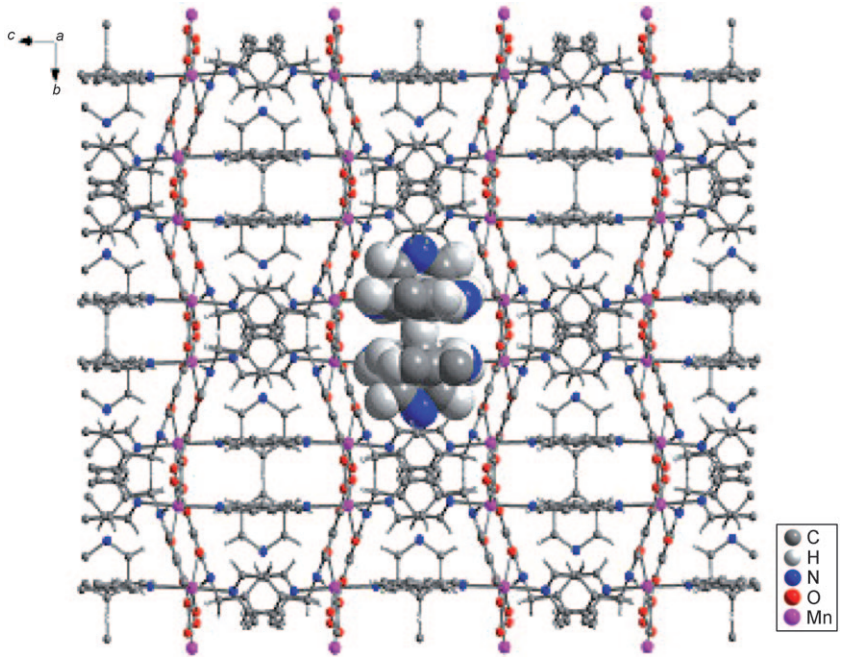


Figure 3. A 3D packing diagram of Py-substituted crystal of complex **6**. One of the cavities is shown in space-filling model.

Next to investigate the substitution phenomenon by a guest containing weak donor N atom, such as aniline, the mother crystal of complex **1** is immersed in aniline for 18 h. The crystallographic determination at 100 K shows the space group is changed from *C*2/*c* to $P2_1/n$ in complex **8**, $\{[Mn(L)(aniline)][Mn(L)(H_2O)](aniline)_2\}_n$. There are two crystallographically independent Mn^{II} ions, two $(L)^{2-}$, three aniline molecules and a water molecule in the asymmetric unit. One Mn^{II} center is coordinated to one aniline N atom, whereas the other one remains coordinated to a water molecule (Figure 5). All other free water and DMF

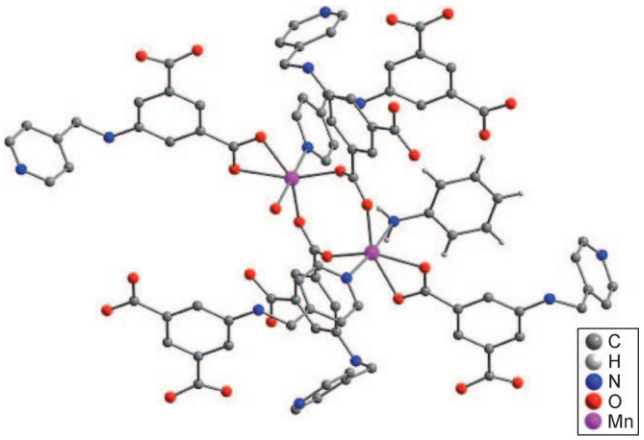


Figure 5. Partially substituted $[Mn_2(CO_2)_2]$ unit by aniline guest.

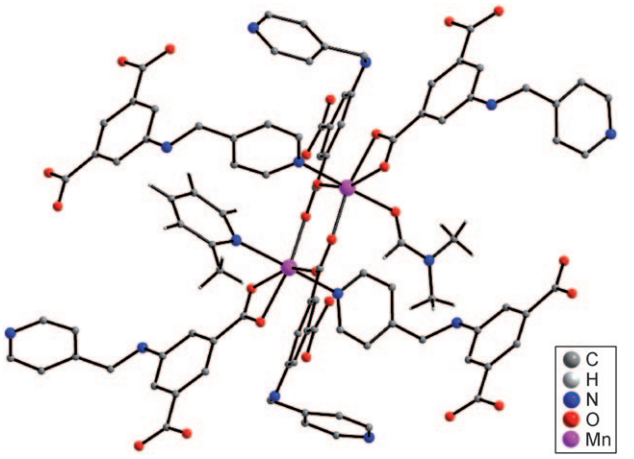


Figure 6. Fully substituted $[Mn_2(CO_2)_2]$ unit by a 2-picoline guest and the migrated lattice DMF molecule.

molecules are exchanged by two aniline molecules per formula unit. Complete substitution remains unsuccessful even after keeping the crystal dipped in aniline as long as three months. The coordinated aniline molecule makes a dihedral angle of 31.04° with the basal plane of the octahedron of Mn1 center. The π···π stacking interactions among the coordinated aniline molecules form two alternative walls, laying in opposite faces with respect to each other (center-to-center distance 4.544 Å), other non-covalent C/N–H···O/π interactions (C42-H42···centroid of C1–16 3.783 Å; C30–H30···centroid of C1–16 3.425 Å; N5–H5B···O3 3.285(9) Å/135.42(5)°) among the non-coordinated ones and the host framework sustains the porous framework structure. Within the channel, the non-coordinated ones are in different orientations with respect to the coordinated one (see Figure S3 in the Supporting Information). The mean planes of non-coordinated ones make dihedral angles of 47.24° and 83.70° with the plane of the coordinated one and an angle of 42.02° within themselves. TGA of complex **8** indicates that it loses all the solvent molecules up to 300 °C, with a mass loss of approximately 31.5 % (calculated loss of 31.4 %) and no further loss up to 360 °C (see Figure S1 in the Supporting Information).

When the mother crystal is immersed in 2-picoline for 6 h, complex **9**, $\{[Mn(L)(2\text{-}Pic)][Mn(L)(dmf)](2\text{-}Pic)\}_n$ is formed. Here, the space group is changed from $C2/c$ to $P2_1/n$, as in the case of aniline. To our surprise, the bound aqua ligand to one metal center is substituted by a 2-Picoline molecule and the remaining centre is coordinated through the N atom of one DMF molecule (Figure 6). Thus the unbound lattice DMF molecule migrates 5.672 Å, all the way from the channel to one of the metal centers of the dimeric $[Mn_2(CO_2)_2]$ unit to substitute the coordinated aqua ligand. Rosseinsky et al. have revealed[11] that Co(bipy) chains (bipy = 4,4′-bipyridyl) in a synthetic material of $[Co_2(bipy)_3(SO_4)_2(H_2O)_2]$-(bipy)($CH_3OH$) undergo a reversible bimolecular substitution reaction upon heating to 368 K. The incoming guest species displaces metal-bound water upon heating to produce a chain that has bipy and CH_3OH bound to alternate metal centers along the chain. The extra framework bipy and MeOH molecules must move by 2.8 Å and 4.41 Å, respectively, to bind to one of the two nearest metal centers. For the sake of comparison, here the lattice DMF molecule is moves by 5.672 Å to coordinate to the Mn^{II} center. The coordinated 2-picoline molecules approaching face-to-face from the two alternative walls are π stacked with a centroid-to-centroid distance of 4.085 Å. The non-coordinated 2-picoline molecule makes a H-bonding contact with a carboxylate O atom (C43–H43C···O1 3.339(5) Å/166.96°), two C–H···π interactions with phenyl moieties (C39–H39···centroid of C1–C6 3.574 Å, C41–H41···centroid of C15–C20 3.877 Å) and a C–H···N interaction with the coordinated one (C30–H30···N7 3.504(4) Å/142.90°). On the other hand, the migrated DMF molecule is in interaction with the benzene π cloud (C36–H36 A···centroid of C1–C6 3.465 Å). The non-coordinated 2-picoline makes an angle of 69.89° with the coordinated one. Figure S4 in the Supporting Information represents the 3D packing diagrams of complex **9**. TGA indicates that it loses all the solvent molecules up to 295 °C, with a mass loss of approximately 28.4 % (calculated loss of 28.5 %) and no further loss up to 340 °C (see Figure S1 in the Supporting Information).

When the mother crystal was allowed to sink in benzonitrile (PhCN) for a day, complex **10**, $[\{[Mn(L)(dmf)](PhCN)_{0.5}\}_n]$ is formed. X-ray study reveals that space group remains same as that of mother crystal ($C2/c$) and the PhCN molecule exchanges the lattice solvent molecules within the channel with subsequent movement of the lattice DMF molecule from the channel to the Mn^{II} center to substitute the aqua ligand (Figure 7). Although, at this stage we are unable to explain the difference in substitution reactions between aniline and benzonitrile, this likely owed to the longer size of PhCN molecule as a result of which they might not be coordinated to the metal centers to approach face-to-face direction from the alternate wave-like walls to avoid steric repulsion. The ligand substitution occurs exclusively at the Mn^{II} center for which the labile metal-bound aqua ligand is displaced by the DMF molecule driven by the

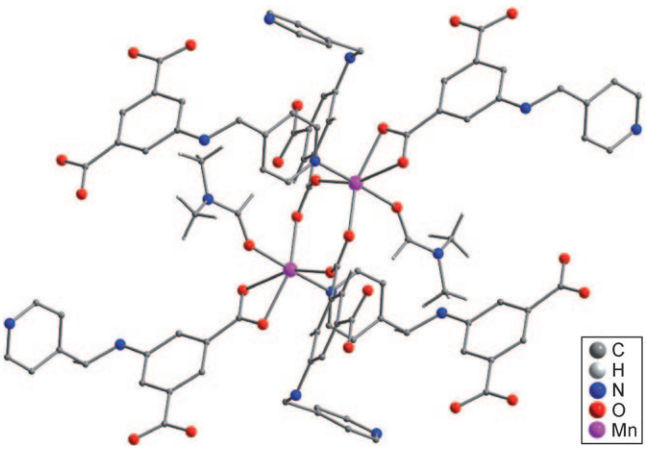


Figure 7. Fully substituted Mn^{II} centers of $[Mn_2(CO_2)_2]$ dimeric unit by migration of lattice DMF molecules in complex **10**.

cooperativity between the incoming guests and the structural rearrangement around the metal center. Here also, the extra-framework DMF molecule must move by 5.672 Å to bind the nearest Mn^{II} center, which makes possible to incorporate the guest PhCN molecule with concomitant elimination of the lattice, as well as coordinated aqua ligands from the crystal lattice. The PhCN molecule is precisely located by two non-classical C−H···O interactions with the carboxylate O atoms from each of the walls (C17–H17···O4 3.100(3)/111.86°, C18–H18···O1 3.437(4)/166.87°) and the migrated DMF molecule makes an interaction with the benzene π cloud (C24–H24A···centroid of C1−C6 3.629 Å) of the ligand unit. Figure S5 (Supporting Information) represents the packing diagram of this complex. Appearance of a new peak at $\tilde{\nu}=2229\ cm^{-1}$ in the IR spectra compared to that of the mother crystal is attributed to the C≡N stretching vibrations. The thermal analysis of complex **10** reveals a loss of all solvent molecules cleanly up to about 310 °C (27.6 % calculated, found 27.4 %) and afterwards, no weight loss occurs till about 360 °C (see Figure S1 in the Supporting Information).

To survey the possibility of substitution trend by putting two methyl groups adjacent to the donor N atom, 2,6-lutidine (2,6-lut) has been chosen and the mother crystal was allowed to react with 2,6-lutidine for 2 days. The complex **11**, $[\{[Mn(L)(dmf)](2,6\text{-lut})_{0.5}\}_n]$, obtained whose structure was similar to that of complex **10** (see Figure S6 in the Supporting Information). The crystal system and the space group remain the same as the mother crystal. The lattice DMF molecule displaces the coordinated aqua ligand covering the distance from the channel to the metal site with subsequent incorporation of half of the guest 2,6-lutidine molecule. The lutidine molecule is H-bonded with a carboxylate O atom (C15-H15B···O4 3.598(6)/159.17°) and the migrated DMF molecule (C20–H20B···N3 3.571(4)/169.75°). This DMF makes further contact with benzene π moiety (C20–H20A···centroid of C1−C6 3.552 Å) of the ligand. TG analysis reveals that the compound loses all solvent molecules up to 315 °C (calculated loss 32.4 %, found 32.6 %) and stable up to about 350 °C (see Figure S1 in the Supporting Information). A 3D packing diagram is depicted in Figure S7 in the Supporting Information.

In an attempt to understand the preferential substitution at Mn^{II} center, the mother crystal (complex **1)** was dipped into a mixture of Py and PhCN (molar ratio of PhCN:Py = 95:5 or less). We found that both the Mn^{II} centers of the dimeric unit are substituted by Py molecules (Figure 8) and

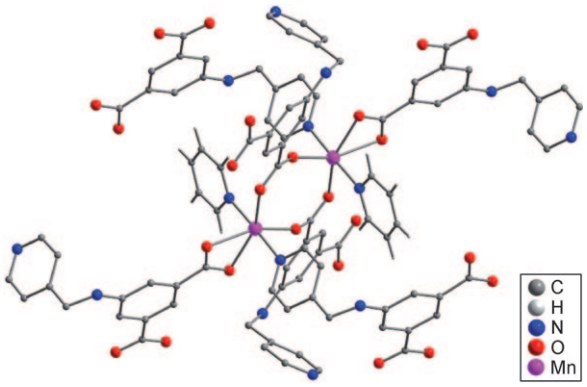


Figure 8. Py-substituted crystal of complex **12** when molar ratio of PhCN:Py = 95:5 or less.

the lattice solvent molecules are substituted by PhCN molecules to give rise to complex **12**, which has the molecular formula, $[\{[Mn(L)(Py)](PhCN)_{0.5}\}_n]$. If Py is present in less than 5 % in the mixture, the lattice DMF molecule migrates to coordinate to the Mn^{II} centers to form complex **10** in which the channels are occupied by guest PhCN molecules. A 3D packing diagram of complex **12** is depicted in Figure S8 in the Supporting Information and shows the Py substituted Mn^{II} centers and PhCN guests-filled channels. The coordinated pyridine moiety makes a very short C-H···π interaction with the PhCN moiety (C18–H18···centroid of PhCN moiety 3.138 Å). A weight loss of 30.7 % is observed in TGA that indicates the loss of all solvent molecules up to 290 °C (see Figure S1 in the Supporting Information).

Addition of the bulky nitrile guest molecule dimethylaminoacetonitrile (DMAN) to the mother crystal of complex **1** was also investigated. The X-ray structural determination shows that the space group is changed from *C*2/*c* to $P2_1/n$ and none of the Mn^{II} centers lose the aqua ligand. However, all the lattice solvent molecules are substituted by two DMAN molecules to form $[\{[Mn_2(L)_2(H_2O)_2](DMAN)_2\}_n]$, complex **13** (Figure 9). These lattice DMAN molecules are in C−H···O (C31–H31B···O7 3.258(7) Å/150.05°) and C−H···π (C34–34A···centroid of C1−C6 3.309 Å) interactions with the host framework. The thermal analysis (see Figure S1 in the Supporting Information) shows loss of all solvent molecules cleanly up to ≈270 °C (calculated loss 24.1 %, found 24.3 %) and afterwards, no weight loss occurs till ≈330 °C. A 3D packing diagram is shown in Figure S9 in the Supporting Information.

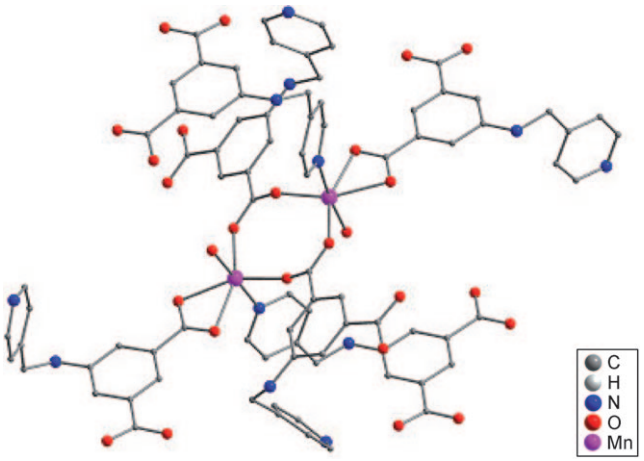


Figure 9. A fully unsubstituted $[Mn_2(CO_2)_2]$ dimeric unit of crystal of complex **13**. Only lattice solvent molecules are substituted by DMAN molecules (not shown in image).

Throughout the reactions, transparency of the single crystal is retained. Sometimes, there remains a possibility of dissolution of a crystal in a certain liquid followed by crystallization or re-nucleation at the surface and augmentation of a new phase. This possibility for mother crystal **1** is ruled out by analsis of the photographs taken of the mother crystal (Figure 10) and when it transforms to first generation com-

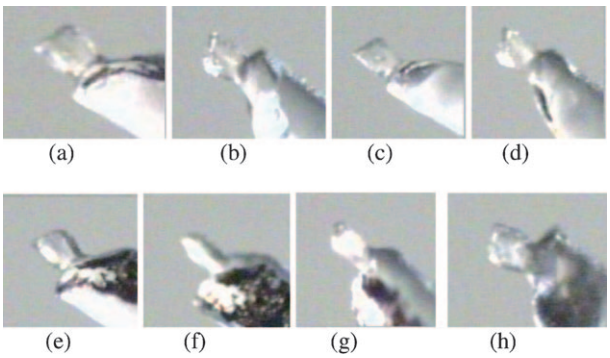


Figure 10. Photographs of the crystals of complex **6–13** (a–h, respectively).

pounds that show no change in size, morphology, color, and transparency. Also, insolubility in different guest solvents has been checked by using NMR spectroscopy measured with commercially available deuterated $[D_5]$pyridine, $[D_7]$2-picoline, $[D_7]$aniline, $[D_5]$benzonitrile solvents after immersion of the crystals of the original compound for 15 h, which show no peak corresponding to the framework complex **1**.

Conclusion

In summary, a variety of modes of substitution reactions at two Mn^{II} centers of a $[Mn_2(CO_2)_2]$ unit within a porous 3D PCP have been observed via SC–SC fashion. Both lattice and coordinated solvent molecules are simultaneously substituted either by pyridine or 4-picoline. When a bulky aromatic guest like aniline is used, a partial substitution at the metal centers and full substitution at the channels takes place. For the case of 2-picoline, one Mn^{II} center is substituted by 2-picoline whereas the rest one is substituted by a DMF molecule that is migrated from the channel to the metal center. Here the lattice solvent molecules are substituted by 2-picoline molecules. When bulkiness is more for the guests like benzonitrile and 2,6-lutidine, both the metal centers are substituted by two DMF molecules again migrated from the channel and the lattice solvent molecules are substituted by these guest molecules. For the case of dimethylaminoacetonitrile guest, an aliphatic bulky guest, no substitution is observed either of the metal centers rather substitution at the channels of the lattice solvents by this guest molecules takes place. Also, the preferential substitution of pyridine over benzonitrile at the metal centers is also observed up to a certain mixture of molar ratio of them.

Experimental Section

Materials: 5-Aminoisophthalic acid, 4-pyridinecarboxaldehyde were acquired from Aldrich and used as received. The metal salt and the guest solvent molecules were obtained from Fluka Chemicals and used without further purification. Solvents were purified prior to use following standard procedures.

Physical measurements: Spectroscopic data were collected as follows: IR (KBr disk, 400–4000 cm^{-1}) Perkin–Elmer Model 1320; thermogravimetric analysis (heating rate of 5 °C min^{-1} under a nitrogen atmosphere) Mettler Toledo Star System.

X-ray structural studies: Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography*. The data integration and reduction were processed with SAINT[12] software. An empirical absorption correction was applied to the collected reflections with SADABS[13] using XPREP.[14] The structure was solved by the direct method using SHELXTL[15] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97[16] program package. The non-hydrogen atoms were refined anisotropically (except as noted). H atoms of the water molecules of complex **8** and **13** could not found in difference Fourier map. All other H atoms were placed in calculated positions. Several DFIX commands were used to fix the bond distances of solvent molecules. For **11**, atom N3 of benzonitrile molecule sits on a special position with symmetry multiplicity of two and occupancy of each of the rest atoms is fixed to 0.5 because of the close proximity with its symmetry self. Data collection and structure solution parameters for compounds complex **6–9** are given in Table 1 and those of complex **10-13** are given in Table 2. CCDC-754622 (**6**), CCDC-754623 (**7**), CCDC-710375 (**8**), CCDC-754624 (**9**), CCDC-754625 (**10**), CCDC-754626 (**11**), CCDC-754627 (**12**), CCDC-754628 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of LH_2 and $\{[Mn(L)(H_2O)](H_2O)_{1.5}(dmf)\}_n$, (1). The ligand and the complex were synthesized following literature method reported by us.[10]

Table 1. Crystal data and structure refinement for complex **6–9**.

	6	**7**	**8**	**9**
empirical formula	$C_{43}H_{35}Mn_2N_7O_8$	$C_{46}H_{41}Mn_2N_7O_8$	$C_{46}H_{43}Mn_2N_7O_9$	$C_{43}H_{41}Mn_2N_7O_9$
formula weight	887.66	929.74	947.75	909.71
T [K]	100(1)	100(1)	100(1)	100(1)
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	0.71069	0.71069	0.71069	0.71069
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*I*2/*a*	*C*2/*c*	*P*21/*n*	*P*21/*n*
a [Å]	16.386(5)	19.143(6)	16.263(5)	16.403(5)
b [Å]	14.990(4)	14.876(5)	14.877(4)	15.202(4)
C [Å]	18.184(6)	16.423(5)	18.884(6)	17.988(6)
α [°]	90.00	90.00	90.00	90.00
β [°]	114.567(5)	111.779(4)	111.985(5)	111.833(5)
γ [°]	90.00	90.00	90.00	90.00
V [Å^3]	4062(2)	4343(2)	4237(2)	4164(2)
Z	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.451	1.422	1.486	1.451
μ [mm^{-1}]	0.685	0.644	0.663	0.671
F(000)	1824	1920	1960	1880
independent refl.	5014	5218	10480	7749
refl. used ($I>2\sigma(I)$)	2765	3587	5885	4048
R_{int}	0.0684	0.0653	0.0671	0.0742
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.010	1.027	1.056	1.019
R indices [$I>2\sigma(I)$]	$R_1=0.0654$, $wR_2=0.1488$	$R_1=0.0711$, $wR_2=0.1651$	$R_1=0.0672$, $wR_2=0.1573$	$R_1=0.0720$, $wR_2=0.1804$
R indices (all data)	$R_1=0.0835$, $wR_2=0.1941$	$R_1=0.1011$, $wR_2=0.2226$	$R_1=0.1051$, $wR_2=0.1889$	$R_1=0.1089$, $wR_2=0.2284$

Table 2. Crystal data and structure refinement complex **10–13**.

	10	**11**	**12**	**13**
empirical formula	$C_{41}H_{42}Mn_2N_7O_{10}$	$C_{41}H_{43}Mn_2N_7O_{10}$	$C_{45}H_{35}Mn_2N_7O_8$	$C_{36}H_{34}Mn_2N_8O_{10}$
formula weight	902.70	903.70	911.68	848.59
T [K]	100(1)	100(1)	100(1)	100(1)
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	0.71069	0.71069	0.71069	0.71069
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*P*21/*n*
a [Å]	18.688(6)	18.596(6)	17.950(7)	16.361(5)
b [Å]	15.052(4)	15.005(5)	15.228(5)	15.209(4)
C [Å]	16.259(5)	16.246(4)	16.336(6)	17.463(6)
α [°]	90.00	90.00	90.00	90.00
β [°]	113.104(3)	113.042(5)	114.960(4)	110.410(5)
γ [°]	90.00	90.00	90.00	90.00
V [Å^3]	4207(2)	4172(2)	4048(3)	4073(2)
Z	4	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.425	1.439	1.496	1.384
μ [mm^{-1}]	0.666	0.671	0.689	0.683
F(000)	1868	1872	1872	1744
independent refl.	4350	5121	5003	10165
refl. Used ($I>2\sigma(I)$)	2435	3180	3131	5844
R_{int}	0.0748	0.0600	0.0684	0.0756
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.029	1.140	1.023	1.046
R indices [$I>2\sigma(I)$]	$R_1=0.0739$, $wR_2=0.1696$	$R_1=0.0744$, $wR_2=0.1703$	$R_1=0.0744$, $wR_2=0.1720$	$R_1=0.0749$, $wR_2=0.1777$
R indices (all data)	$R_1=0.1044$, $wR_2=0.2268$	$R_1=0.1048$, $wR_2=0.2174$	$R_1=0.1040$, $wR_2=0.2226$	$R_1=0.1179$, $wR_2=0.2356$

Acknowledgements

We gratefully acknowledge the financial support received from the Council of Scientific and Industrial Research, New Delhi, India and SRF to M.C.D.

[1] a) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem.* **2003**, *115*, 444–447; *Angew. Chem. Int. Ed.* **2003**, *42*, 428–431; b) G. J. Halder, C. J. Kepert, *J. Am. Chem. Soc.* **2005**, *127*, 7891–7900; c) E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.* **2005**, *127*, 6374–6381; d) C.-L. Chen, A. M. Goforth, M. D. Smith, C.-Y. Su, H.-C. zur Loye, *Angew. Chem.* **2005**, *117*, 6831–6835; *Angew. Chem. Int. Ed.* **2005**, *44*, 6673–6677.

[2] a) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, N. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.* **2003**, *2*, 190–195; b) L. G. Beauvais, M. P. Shores, J. R. Long, *J. Am. Chem. Soc.* **2000**, *122*, 2763–2772.

[3] H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186–2187.

[4] K. Takaoka, M. Kawano, M. Tominaga, M. Fujita, *Angew. Chem.* **2005**, *117*, 2189–2192; *Angew. Chem. Int. Ed.* **2005**, *44*, 2151–2154.

[5] a) X. Gao, T. Friscic, L. R. MacGillivray, *Angew. Chem.* **2004**, *116*, 234–238; *Angew. Chem. Int. Ed.* **2004**, *43*, 232–236; b) Q. Chu, D. C. Swenson, L. R. MacGillivray, *Angew. Chem.* **2005**, *117*, 3635–3638; *Angew. Chem. Int. Ed.* **2005**, *44*, 3569–3572.

[6] a) M. P. Suh, Y. E. Cheon, E. Y. Lee, *Chem. Eur. J.* **2007**, *13*, 4208–4215; b) H.-L. Li, M. Eddaoudi, M. O'Keefe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279; c) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; d) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.* **2005**, *34*, 109–119, and references therein.

[7] a) K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem.* **2002**, *114*, 3545–3548; *Angew. Chem. Int. Ed.* **2002**, *41*, 3395–3398; b) C.-D. Wu, W. Lin, *Angew. Chem.* **2005**, *117*, 1994–1997; *Angew. Chem. Int. Ed.* **2005**, *44*, 1958–1961; c) K. Biradha, M. Fujita, *Angew. Chem.* **2002**, *114*, 3542–3545; *Angew. Chem. Int. Ed.* **2002**, *41*, 3392–3395; d) G. J. Halder, C. J. Keppert, *J. Am. Chem. Soc.* **2005**, *127*, 7891–7900; e) L. Dobrzańska, G. O. Lloyd, C. Esterhuysen, L. J. Barbour, *Angew. Chem.* **2006**, *118*, 5988–5991; *Angew. Chem. Int. Ed.* **2006**, *45*, 5856–5859.

[8] a) N. M. Alfaro, F. A. Cotton, L. M. Daniels, C. A. Murillo, *Inorg. Chem.* **1992**, *31*, 2718–2723; b) K. Hanson, N. Calin, D. Bugaris, M. Scancella, S. Sevov, *J. Am. Chem. Soc.* **2004**, *126*, 10502–10503.

[9] a) S. Supriya, S. K. Das, *J. Am. Chem. Soc.* **2007**, *129*, 3464–3465; b) S. M. Mobin, A. K. Srivastava, P. Mathur, G. K. Lahiri, *Inorg. Chem.* **2009**, *48*, 4652–4654.

[10] M. C. Das, P. K. Bharadwaj, *J. Am. Chem. Soc.* **2009**, *131*, 10942–10949.

[11] D. Bradshaw, J. E. Warren, M. J. Rosseinsky, *Science* **2007**, *315*, 977–980.

[12] SAINT+, 6.02ed., Bruker AXS, Madison, WI, **1999**.

[13] SADABS, Empirical Absorption Correction Program, G. M. Sheldrick, University of Göttingen, Göttingen, **1997**.

[14] XPREP, 5.1 ed., Siemens Industrial Automation Inc., Madison, WI, **1995**.

[15] SHELXTL Reference Manual: version 5.1, G. M. Sheldrick, Bruker AXS, Madison, WI, **1997**.

[16] SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen, Göttingen, Göttingen, **1997**.

Received: November 14, 2009
Published online: March 22, 2010

