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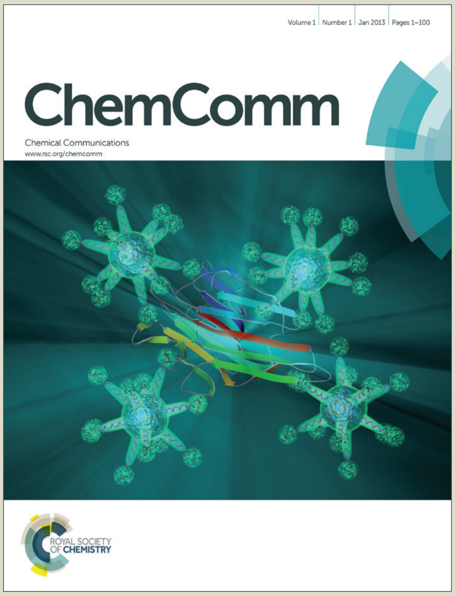

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ARTICLE TYPE

Probing post-synthetic metallation in metal-organic frameworks: Insights from X-ray crystallography

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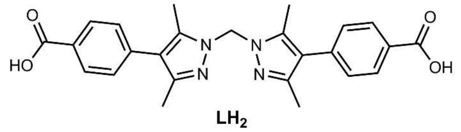
For post-synthetic metallation (PSMet) of a metal-organic framework (MOF, [Mn$_3$(L$_2$)(L′)] = 1) we show a solvent dependency for the form of the metallated product. PSMet of 1 with MnCl$_2$ in ethanol leads to a single metal entity per coordinating site while acetonitrile yields a remarkably complex multiply metallated product; thus, determining the extent of metallation requires an intimate understanding of the chemistry occurring in the MOF pores.

Post-synthetic metallation (PSMet) is widely used to enhance the properties of metal-organic frameworks (MOFs) for possible application to onboard gas storage, molecular separations, sensing, and heterogeneous catalysis.[1] Accordingly, numerous strategies have been explored towards incorporating non-coordinated metal chelating sites into the framework architecture of MOFs. For example, hard-soft acid-base (HSAB) theory, which in this context involves judicious choice of a metal ion in combination with a linker containing both hard and soft donors, has been commonly utilised.[2] Such a strategy provides a MOF with non-coordinated metal binding groups available for metallation as only one of the donor types is utilised in framework synthesis. Alternatively, protected secondary binding sites can be incorporated within the framework for subsequent post-synthetic deprotection and metal binding,[3] or metallation can occur by introduction of organometallic entities[4] directly onto the organic links of a framework.

An ultimate goal of PSMet is to realise analogous control of the reactivity at the metallated site to that observed in small molecule coordination chemistry. An important step towards achieving this goal is the precise structural characterisation of the post-synthetically included metal species. This is crucial as such knowledge has yielded fundamental insight into the reactivity of equivalent discrete metal-ligand compounds. However, this has proved challenging in MOF systems as PSMet reactions rarely proceed in a single-crystal to single-crystal (SC-SC) manner, thus limiting the potential for Single-Crystal X-ray Diffraction (SCXRD) analysis of the metallated framework and subsequent in-depth understanding of the metallation chemistry. Furthermore, SCXRD analysis is especially important when the inserted metal atom is presumed to be present in an unusual coordination environment.[5] In such cases an inability to clearly elucidate the exact nature of the post-synthetically introduced species can complicate simple measurements used to understand and quantify the extent of metallation.

Recently we reported a Mn(II) framework that overcomes these challenges.[6] The material, [Mn$_3$(**L**$_2$)(**L′**)] (**1**, where **L** and **L'** are identical molecules, yet **L'** possesses a vacant di-pyrazolylmethane coordinating site), was prepared from MnCl$_2$·4H$_2$O and bis(4-(4-carboxyphenyl)-1*H*-3,5-dimethylpyrazolyl)methane (Chart 1, **LH$_2$**) that contains both carboxylate and pyrazole donors. **1** has a non-interpenetrated 3D structure which possesses vacant di-pyrazole donors, suitable for binding a wide variety of 1st and 2nd row transitions metals in a SC-SC manner.[╥] **1** also possesses notable structural flexibility which can aid in guest uptake and minimise guest disorder.[7] **1** is therefore an ideal material to study PSMet chemistry and subsequent metal-centred reactions. In this present work we explore the role of solvent in the MOF synthesis and PSMet process and how, along with the HSAB strategy, it contributes to generating free di-pyrazole donors within **1**. We were able to characterise reaction products yielded from post-synthetic reactions of **1** with MnCl$_2$ by SCXRD and, aided by EDX analysis, show that metallation is limited to particular solvents. In addition we demonstrate that the choice of solvent also determines the co-ligand and anion composition of the post-synthetically inserted metal atom. Accordingly, this work provides some important salutatory lessons for the application of PSMet to other MOF systems.



LH$_2$

Chart 1

We had originally rationalised that the presence of non-coordinated di-pyrazole moieties in **1** (two nitrogen donors from a di-pyrazole moiety of **L**) was the result of the donor requirements of the Mn$_3$ node; three ligands provide six nitrogen and twelve oxygen donors. However, given that Mn(II) is a borderline hard/soft acid we were intrigued that the as-synthesised structure of **1** was not metallated despite using an excess of MnCl$_2$ during MOF synthesis (1.7 equiv of MnCl$_2$·4H$_2$O per ligand compared with a 1:1 stoichiometry in

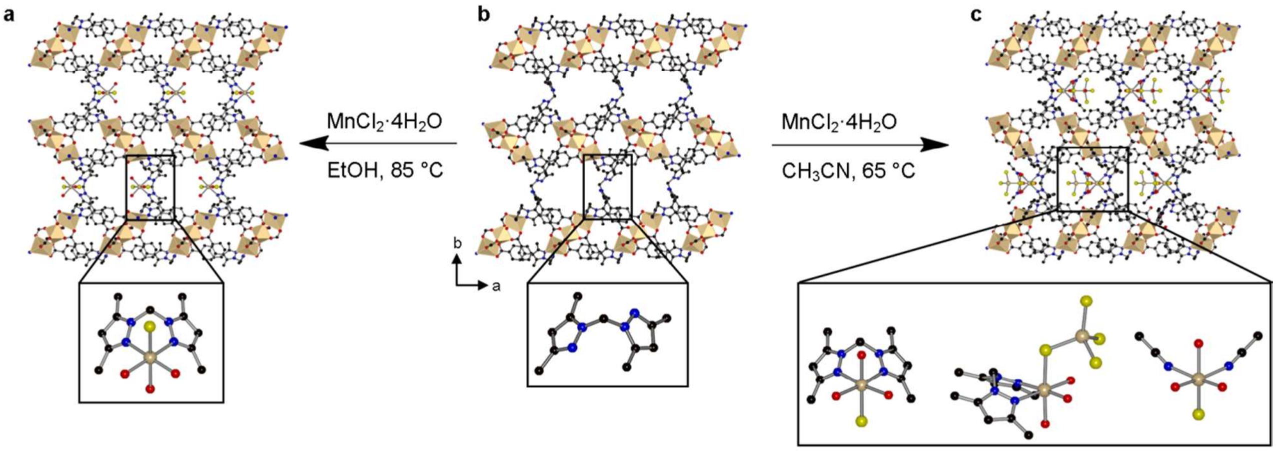


Figure 1. A scheme showing the PSMet of **1** with $MnCl_2$ under different conditions and their corresponding crystal structures; a) **1**·$[MnCl(H_2O)_3]Cl$·*x*EtOH (**1**·[Mn]·*x*EtOH), b) **1**, c) **1**·$[MnCl(H_2O)_3]Cl[Mn(H_2O)_3\text{-}\mu_2Cl\text{-}MnCl_3]·[MnCl(CH_3CN)_2(H_2O)_3]Cl·$*x*$CH_3CN$ (**1**·[Mn]·*x*CH_3CN). The di-pyrazole moiety is shown in the inset for each form.

1). To further examine this we first explored the synthesis of **1** with a ten-fold excess of $MnCl_2·4H_2O$ under standard conditions (DMF/H_2O, 100 °C). PXRD confirmed the phase purity of **1** and EDX analysis revealed only trace quantities (background levels[‡]) of chloride present in the sample.

To further investigate the observation that no measurable quantity of Mn(II) can be incorporated into the available di-pyrazole site during synthesis, PSMet of **1** with $MnCl_2·4H_2O$ in DMF was performed at 65, 100, and 120 °C for 16 h using 10-fold excess of Mn(II) (Table 1). EDX analysis again revealed only trace quantities of chloride for all of these reactions, irrespective of the reaction temperature. We also explored PSMet of **1** in a 2:1 DMF/H_2O solvent mixture. Again, EDX analysis also revealed only trace amounts of chloride. Similarly, no metallation was observed in DMSO. Given our previous results indicated that metallation of **1** is facile, we proceeded to investigate metallation in other common laboratory solvents. Notably, PSMet in methanol and ethanol gave 62 and 70% metallation of **1** with Mn (10-fold excess) respectively, based on a 2:1 ratio of Mn(II) to Cl indicating complete metallation (three Mn atoms from the Mn_3 node, in addition to one $MnCl_2$ complex bound to the di-pyrazole donors). Increasing the reaction temperature from 65 to 85 °C afforded improved metallation in EtOH (Table 1), and thus these crystals were analysed by SCXRD.

Table 1. Outcomes of PSMet experiments for **1** showing reaction conditions and the extent of metallation as determined by EDX.

Entry[a]	**solvent**	**Temp (°C)**	**Average Mn:Cl ratio**[b]	**% Metallation**[c]
1	DMF	65	1:0.043	9.2 ± 5.0
2	DMF	100	1:0.044	8.9 ± 4.8
3	DMF	120	1:0.046	9.3 ± 5.5
4	DMF/H_2O	100	1:0.038	7.6 ± 2.2
5	DMSO	65	1:0.020	4.0 ± 3.8
6	MeOH	65	1:0.350	70.0 ± 4.6
7	MeOH	85	1:0.320	64.1 ± 6.8
8	EtOH	65	1:0.309	61.8 ± 2.2
9	EtOH	85	1:0.488	97.6 ± 3.5
10	CH_3CN	25	1:0.038	7.6 ± 1.1
11	CH_3CN	65	1:0.695	140 ± 5.9

[a] Conditions: 3 mL of solvent, 25 mg of **1** (0.017 mmol), 10 equiv. of $MnCl_2·4H_2O$, heated for 24 h.

[b] Quantitative metallation corresponds to a Mn:Cl ratio of 4:2; a metal loading of 1 × $MnCl_2$ is addition to the three Mn atoms from the framework Mn_3 node. The amount of Mn is normalised to 1.

[c] EDX results are calculated as an average of at least three areas of a sample (3 mm^2 of crystalline sample) and presented with their standard deviations.

X-ray analysis of **1**·$[MnCl(H_2O)_3]Cl$·*x*EtOH (**1**·[Mn]·*x*EtOH) revealed the anticipated octahedral Mn(II) complex bound to the di-pyrazole donors of **L′**. In addition to the two pyrazole nitrogen donors from **L′**, this well defined metal centre (lying on a mirror plane) is coordinated by three water ligands (Mn-O: 2.291(14), 2.233(6) Å) and a chloride ligand (Mn-Cl: 2.512(5) Å) (Figure 1a). A non-coordinated chloride counter-ion was found in the difference map, located ~6.2 Å from the post-synthetically introduced Mn(II) atom. The donor set of the Mn(II) atom is common in coordination compounds synthesised from $MnCl_2$, particularly in salen and Schiff-base derivatives.[8] As expected, the di-pyrazole donors of **1** provide a chelating site for the metal centre, and in doing so, switch from an *anti* to a *syn* conformation found in the nonmetallated, as-synthesised framework (Figure 1b). The occupancy of the post-synthetically introduced Mn(II) centre was further assessed by refining the occupancy of the Mn and found to be approximately 80%, similar to what we have previously observed for Co(II), Rh(I)[6] and other metals.[9]

We also investigated acetonitrile (CH_3CN) as a solvent for PSMet of **1** with $MnCl_2·4H_2O$. EDX analysis of a reaction carried out in CH_3CN at 65 °C revealed 140% metallation (based on a 2:1 ratio of Mn to Cl indicating 100% metallation), which suggested the presence of an additional pore-bound manganese complex. Often the exact nature of the post-synthetically metallated species cannot be readily determined but, due to the facile SC-SC nature of metallations exhibited by **1**, crystals of this sample were suitable for SCXRD analysis. This allowed us to elucidate the exact molecular structure of this material and to understand the chemical form of the post-synthetically metallated compound completely, a process not readily achievable for other MOFs. In the crystal structure of **1**$·[MnCl(H_2O)_3]Cl[Mn(H_2O)_3\text{-}\mu_2Cl\text{-}MnCl_3]·[MnCl(CH_3CN)_2(H_2O)_3]Cl$ $x CH_3CN$ (**1**$·[Mn]·xCH_3CN$), **L′** is present as two crystallographically unique forms, each of which are metallated with a different Mn(II) species. One di-pyrazole unit chelates an octahedral Mn(II) atom coordinated by three water ligands and a chloride ligand (Mn-Cl: 2.454(3) Å) (Figure 1c), as observed for **1**$·[Mn]·x$EtOH. The di-pyrazole unit from the other crystallographically unique **L′** molecule coordinates a second octahedral Mn(II) atom with a different coordination environment. Two nitrogen atoms from **L′** and three water molecules contribute to the coordination sphere while the sixth donor (Mn-Cl: 2.643(2) Å) is a chloride atom from a $[MnCl_4]^{2-}$ counter ion (Figure 1c).

While $[MnCl_4]^{2-}$ counter-ions are common in coordination complexes of manganese(II),[10] only two structures exist in the CSD where this anion is directly bound to a manganese atom.[11] Furthermore, a CSD search of compounds with the same donor set ($[MnN_2O_3ClMnCl_3]$) revealed that this dimetallic coordination complex is unique. In addition to these two framework-bound Mn(II) cations and the Mn atom of the $[MnCl_4]^{2-}$ counter ion, a third Mn(II) complex is located in the pores of **1**, also on a mirror plane. This metal centre has a similar donor atom composition; two nitrogen donors (albeit provided by the acetonitrile solvent), three water ligands, and a chloride ligand. The crystallographic occupancy of the four Mn(II) atoms was refined and found to be essentially quantitative; the di-pyrazole-bound Mn(II) atoms (with the $[MnCl_4]^{2-}$ counter ion) were found to refine above 97.5%, while the pore-bound Mn complex refined at 88% occupancy. In addition, two chloride counter-ions were located in the difference map. Further structure refinement and modelling of the electron density revealed partially occupied chloride ions and a $MnCl_4^{2-}$ anion (SI). Interestingly, the three unique Mn(II) species are in close proximity along the *c* axis with intermolecular contacts between the O atoms of the water ligands and chloride ligands. Although the hydrogen atoms of the water ligands could not be located in the difference map, the O···Cl distances between Mn(II) complexes average 3.22 Å. This distance is in the expected range for a O-H···Cl-M (M = metal) hydrogen bonding interaction,[12] and may help to facilitate regular ordering of the metal species in the pores of **1**.

With the assumption that chloride ions charge balance the structure, the composition obtained from the crystal structure of **1**$·[Mn]·xCH_3CN$ amounts to a Mn:Cl ratio of 5:4 rather than the 2:1 ratio used to calculate the extent of metallation. EDX analysis, therefore, indicates 88% metallation according to this ratio. We note however that the single crystal of **1**$·[Mn]·xCH_3CN$ analysed and reported herein was taken directly from the $CH_3CN/MnCl_2$ reaction solution, while the sample prepared for EDX was washed several times with methanol, thus likely removing a portion of the pore bound Mn complex.

Steric effects obviously play a role in allowing entry of the metallating species into the MOF but it is intriguing that the solvent has such a significant effect on the metallation of **1**. While the exact nature of the solvated Mn(II) species is difficult to ascertain, studies on the complexation of $MnCl_2$ species in DMF indicate that the stability constants to do not follow the Irving-Williams trend. Ishiguro and co-workers reported that the stability constants for the formation of MCl_n (M = metal, n = 1 – 4) are greatest for Mn(II) compared to other first row d^5-d^{10} transition metals.[13] Furthermore, the pore apertures of **1** span only 4.6 × 6 Å (considering the van der Waals radii), which may inhibit the diffusion of larger, species. In this case $Mn(DMF)_mCl_n$ complexes may not be able to diffuse effectively throughout the structure of **1** and, considering their enhanced stability in DMF, are inhibited from binding the di-pyrazole donors.

Due to the unusually high extent of metallation for **1**$·[MnCl_2]·xCH_3CN$, we further investigated the structural effects of CH_3CN on **1**. Therefore, crystals of **1**·DMF were solvent exchanged with CH_3CN to yield the form **1**$·CH_3CN$. X-ray analysis revealed a SC-SC transformation, involving a change in symmetry ($P2_1/m$ to $P\text{-}1$) and a switch of the di-pyrazole moiety from an *anti* to a *syn* conformation (SI). The predisposition of the di-pyrazole moiety in the structure of **1**$·CH_3CN$ may facilitate facile metallation of **1** in this solvent.

Conclusions

While a variety of factors (HSAB considerations, charge balance, framework design) affect the formation of free coordinating sites in **1**, we have shown that this is also aided by solvent choice; the synthesis solvent, DMF, cannot effectively facilitate metallation of the di-pyrazole moiety of **1** with $MnCl_2$. This also suggests that solvent choice may be able to govern the generation of metal-free coordination sites in other MOFs that would otherwise have coordinated donors. *In-situ* and PSMet experiments revealed that solvent choice is crucial for metallation of **1** (in this case with Mn(II)), particularly when considering the extent of metallation and the coordination environment of the species bound to the di-pyrazole sites. The facile SC-SC metallation of **1** allows X-ray crystallographic characterisation of metallation products which is vital for studying the potential properties of post-synthetically metallated MOFs. Furthermore, the peculiar bimetallic Mn(II) complex found in **1**$·[Mn]·xCH_3CN$ further highlights the importance of solvent choice and the ability to accurately characterise metallation products in MOF materials to understand their properties.

Notes and references

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† Electronic Supplementary Information (ESI) available: synthetic details, TGA and EDX data, PXRD, gas adsorption isotherms, details of SCXRD collections. See DOI: 10.1039/b000000x/

‡ **1** synthesised under standard conditions (1.7 equiv. of $MnCl_2 \cdot 4H_2O$) also showed trace quantities of chloride by EDX (supporting information), presumably due to impurities introduced during sample preparation. In addition, the structure of **1** does not show any electron density which could be attributed to a metallated species

╥ We previously reported that metallation of **1** occurs in a SC-SC manner. We are confident that this is the case in the present study as the morphology of the crystals of **1** remains consistent throughout the metallation processes (which would not be the case if dissolution and re-precipitation/crystallisation occurred), especially in solvents not typically used for the synthesis of the MOF.

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