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A view on systematic truncation of tetrahedral ligands for coordination polymers†

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Bis-, tris- and tetrakis(carboxyphenyl)adamantanes were probed for the synthesis of coordination polymers of d-metals, with a successful outcome for Mn, Co, and Cd. Formation of **sql**, **hcb** and **dia** frameworks based on small clusters demonstrates the dominant role of the ligand shape in defining the outcome of crystallization.

Introduction

The systematic work of Wells¹ regarding holistic interpretation of the known massive set of inorganic crystal structures, including a topological viewpoint, facilitated the emergence of the area of coordination polymers (CP) based on the seminal ideas of Robson in the late 1980s.² Those ideas, along with the then dynamically developing supramolecular chemistry,³ emphasized the self-assembly approach on the nano-scale from pre-conceived ('pre-designed') building blocks (BBs). The area significantly transformed since then, and, powered by a more formal topological background,⁴ gave rise to the field of porous coordination polymers (PCP/MOFs), with their numerous, but still almost⁵ exclusive, potential uses.⁶

From the beginning there were discussions regarding the usage and meaning of the term 'design' of a structure with regard to coordination polymers, which implies an encoding of the structure on the level of the BB and realization *via* self-assembly.⁷ Coupled with the debatable question of whether crystal structures are predictable at all,⁸ the question "What

is 'design'?" is especially complex. For us, 'design' is primarily a process of experimentally driven heuristic search, which includes a sequence of: (a) a proposal of BB conformant with topological prerequisites, taking into account the given dominant interactions, followed by (b) analysis of the outcome either in terms of topology and fine local interactions. The process repeats in subsequent cycles, dealing with an improved concept.

Needless to say, the more efficient a pattern-based (*i.e.* common-sense, non-computational) analysis, the simpler the BB is. In this context, regular tetrahedral BBs,⁹ compatible with a number of networks, including the fundamental **dia** and **flu** nets, are still lagging behind, compared to the simpler linear and trigonal BBs. This is most probably due to higher costs of experimental efforts. It is interesting to note that one of the first papers, later recognized as paradigmatic in the area of design, was the report on the crystal structure of the tetrahedral 1,3,5,7-tetracarboxyadamantane exemplifying an H-bonded **dia** network by Ermer.¹⁰ Surely, since then there have been a number of interesting reports featuring CPs based on tetrahedral BBs carrying different functional groups (see ref. 11 and 12 and the references therein), with efforts arguably crowned at least in the area of PCPs by the relatively recently reported Zr-PCP based on tetrakis-(4-carboxybiphen-4'-yl)methane with an experimental surface area of 3411 m² g⁻¹.¹³ Still, there is room for further development, with ideas not so typical for building blocks of lower connectivity. In this contribution, we are probing the potentially productive idea regarding the possibility of 'truncation' of a regular tetrahedral ligand.

Removing one or two 'arms' of a tetrahedral BB and the comparison of the outcomes of crystallization together with the complete prototype are a powerful heuristic approach. Beyond the 'design' point, there is a very clear incentive in a more practical aspect: creation of pre-programmed defects¹⁴ for PCPs/MOFs based on tetrahedral building blocks, in which the 'truncated' arms could also, potentially, bear a functional entity. There is not much in the literature in this

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context for coordination polymers, however recently we employed this approach in the context of porous organic polymers.¹⁵

In this contribution, we probed a row of carboxylate ligands aiming initially at large cluster-based metal carboxylate compounds with 3d metals, particularly with manganese. While the initial goal still applies, an interesting reconnaissance in the field of ‘truncated’ tetrahedral ligands was successfully made. The analysis of the observed structural trends in coordination polymers forms the subject of this contribution.

Results and discussion

The carboxylic acid ligands 1-, 3-, 5-, 7-bridgehead functionalized oligo-(4-carboxyphenyl)adamantanes (where ‘oligo’ = 1,3-di-, 1,3,5-tri-, and 1,3,5,7-tetra-; the ligands are designated H_2L^2 , H_3L^3 , and H_4L^4 , respectively) were prepared by a sequence of reactions including phenylation, iodination, cyanodeiodination and subsequent hydrolysis to carboxylic acid (Fig. 1). The phenylation by the Newman procedure¹⁶ allows control over the number of substituents ($n = 1-4$) by variation of the reaction time, thus allowing the synthesis of all the derivatives following one generalized procedure. This is a local synthetic advantage compared to geometrically similar oligophenylmethanes, which cannot be obtained in such a generalized way.

In the context of structural research, H_2L^2 has not yet been reported; H_3L^3 was reported only in the context of organic adducts, namely, two component H-bonded Borromean networks,^{17,18} while the single mention of H_4L^4 is associated with an early PCP of Zn, namely MOF-31.¹⁹

The initial experimental focus of our work was on mixed manganese carboxylates, with particular emphasis on formates as co-ligands, taking the porous manganese formate as the prototype,²⁰ and the mixed carboxylate $[Mn_3(HCOO)_4(ADC)]$ ($H_2ADC = 1,2$ -dicarboxyadamantane)²¹ as an example of the feasibility of such a strategy. The weaker and more labile coordination bonds of manganese than that of metals like cobalt, copper or zinc (Irving–Williams series) were also incentives to increase the chances for crystallization. Based on our experience, the higher lability manifests itself in the better solubility of manganese carboxylates in DMF and similar amide solvents, potentially allowing added

possibilities for modification, including the use of the co-ligand strategy aiming at less soluble large coordination-bonded cluster-based compounds.

The screening of crystalline CP formation with 3d metals was immediately successful in the case of $Mn(II)$ with H_2L^2 and H_4L^4 , as well as in the cases of $Co(II)$ and $Zn(II)$ (ref. 19) and H_4L^4 under the standard low temperature solvothermal method in DMF. However, no results were obtained in the case of H_3L^3 . Only when the screening scope was extended to include selected 4d metals, $Cd(II)$ yielded, as an exception, a crystalline product (Fig. 2 and Fig. S3†).‡ §

The compound $[Mn(DMF)(L^2)]$ (1), a 2D coordination polymer, is based on pentacoordinate Mn^{2+} ions combined pairwise in paddle-wheel units incorporating four carboxylate groups of the ligands (Fig. 2, S4†). The Mn–Mn distance in the unit is 3.13 Å, and the pair of free axial positions of the metal ions is occupied by DMF molecules. Paddle-wheel motifs, frequent for carboxylates, are observed for the mixed ligand complexes of the smaller analog of H_2L^2 ,²² the H_2ADC , but the layered $[Mn(ADC)]$ features infinite chain-clusters.²¹ The paddle-wheel units in 1 are joined by the angular ligands to form a layered structure, with layers having a topology of a ‘square’ or **sql** net. The latter is typical for linear ligands, but in the current case of $(L^2)^{2-}$, it is somewhat unexpected in view of the significant length of the ligand, which ensures a 16.2 Å separation of the paddle-wheel units. The corrugated layer is thick, app. ~18 Å vdW, while the protrusions, conditioned by the angularity of the ligand, are alternating, *i.e.* changing the direction at each paddle-wheel unit. The layers are stacked in a way that the bulge of one layer fills the dents in the others thus forming a particularly dense packing, which would be impossible in the case of planar layers.

The compound $[Cd(DMF)_{0.5}(H_2O)_{0.5}(L^3)] \cdot (NH_2Me_2) \cdot 0.5DMF \cdot 1.5H_2O$ (2) is a 2D coordination polymer built from ‘isolated’, mononuclear Cd^{2+} coordination-bonded units. The $\{CdO_7\}$ coordination environment (Fig. 2, S5†) includes the oxygen atoms of three carboxylate groups and one of the solvent molecules. The geometry of the coordination polyhedron is quite irregular; thus, the planes of the carboxylate groups are sequentially turned in relation to each other by 55.6, 86.9, and 79.5°. The coordinated solvent molecule slightly deflects the three groups from the otherwise planar arrangement, with the distance between the plane defined by carbon atoms

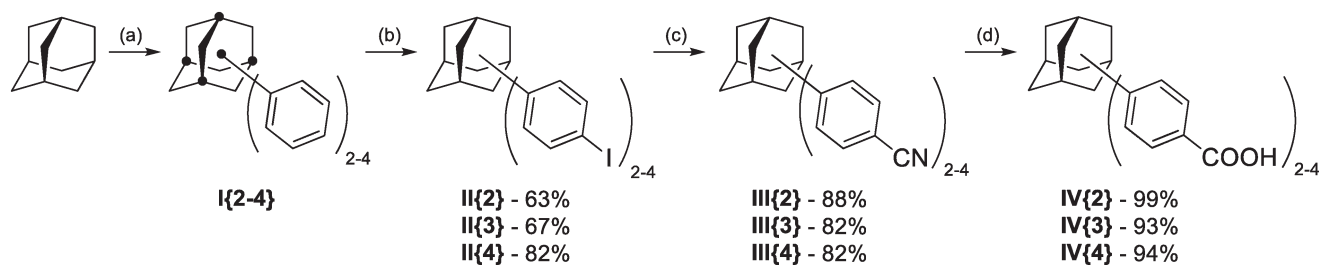


Fig. 1 Reagents and conditions: (a) PhH (excess), tBuBr, AlCl₃, reflux, 5–60 min; Friedel–Crafts arylation, time dependent product ratio; (b) procedure 1 (II{2}) and II{3}): I₂, HIO₃, AcOH, H₂SO₄, H₂O, reflux, 4 h; procedure 2 (II{4}): PIFA, CHCl₃, r.t.–50 °C, 5 h; (c) CuCN, DMF, reflux, 4 h; Rosenmund–von Braun reaction (d) step 1: KOH, H₂O, 160 °C, 6 h; step 2: HCl, conc.



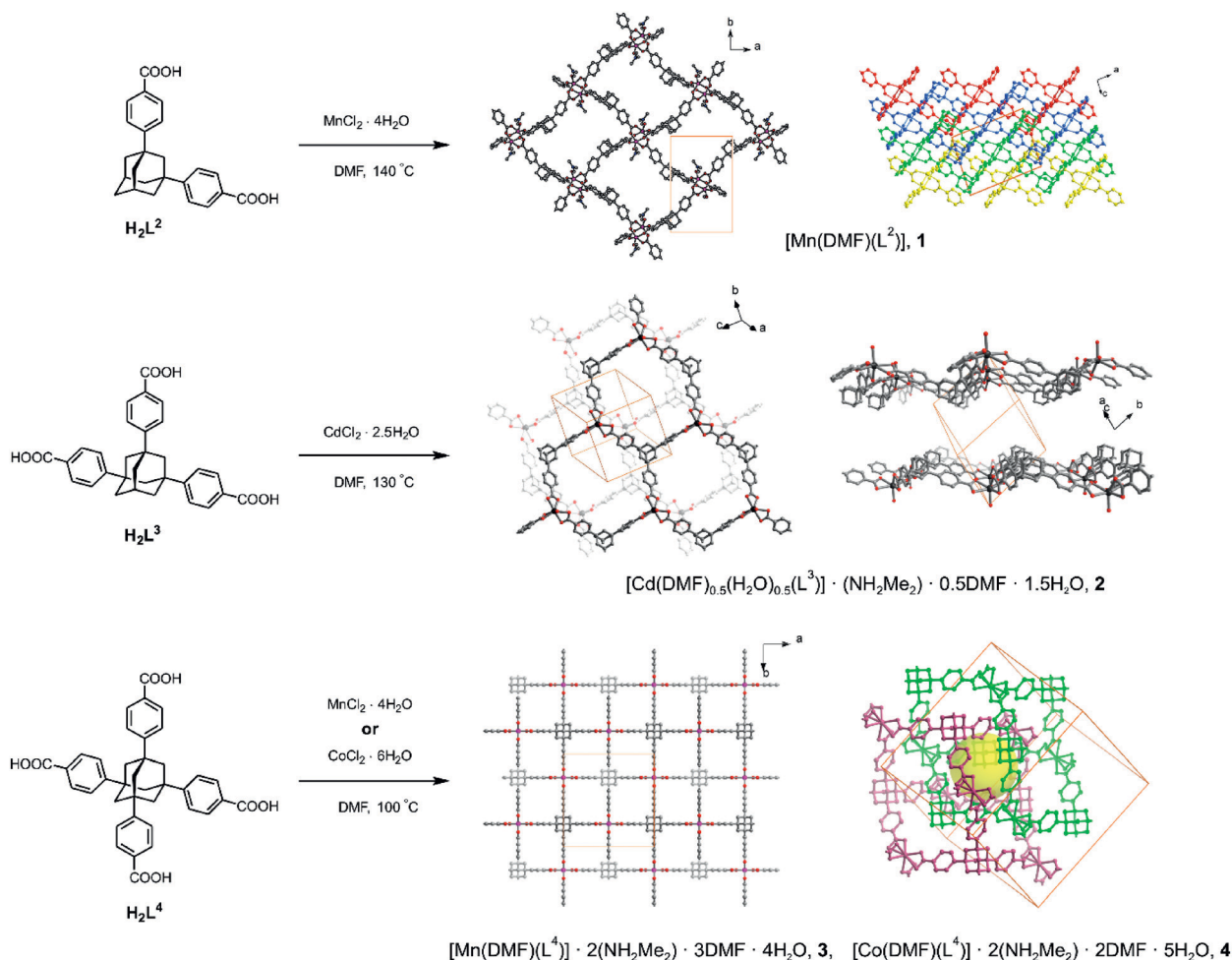


Fig. 2 Synthesis and structures of the newly obtained coordination polymers.

of the latter and cadmium of 0.636 \AA . The two trigonal-pyramidal nodes, the coordination-bonded unit and the ligand itself, when combined together gives rise to a 2D layered structure with a hexagonal or **hcb** net topology. The puckered layers are loosely packed with an interlayer vdW distance of $5\text{--}12 \text{ \AA}$, and the interlayer space is filled both by the protruding coordinated and non-coordinated solvent molecules. The vdW pore opening dimensions limited by the meshes of the hexagonal net are at a remarkable $11 \times 13 \text{ \AA}$ (as estimated from the space filling model). However, upon regular structural collapse of the layered structure along the $\langle 1,1,1 \rangle$ direction, the presumed dense stack of the layers would possess pores with dimensions as low as $4 \times 4 \text{ \AA}$ vdW.

Despite the formally simple structures of the compounds, there are some peculiarities worth noting. The immediate success of the crystallization efforts in the case of Cd could, probably, be associated with the geometric flexibility of the d^{10} closed shell ion and the higher coordination number, allowing the coordination of the 'deplanarizing' solvent molecule; these factors harmonize the geometric requirements for the trigonal-pyramidal BBs. The conditions of electro-neutrality demand that either one of the three carboxyl groups of H_3L^3 should remain protonated or there is an addi-

tional counteranion present in the structure. The relatively low variation of the Cd–O distances rather suggests complete deprotonation of all the carboxyl groups. Full deprotonation is also indirectly supported by the large separation between the layers (Fig. 2) together with the block crystal morphology, which points out the significant strength of interactions in the direction perpendicular to the layers. H-bonds are too weak to sustain such near-isotropy, and Coulombic interactions with the cations in the interlayer space should be held responsible²³ (effective interlayer interactions between layers conveyed by H-bonding are possible only for small separations below 4 \AA (ref. 24)).

The moderate quality of the diffraction data and hence the low residual electron density observed in the interlayer space did not allow unambiguous determination of all the species there, even if a DMF moiety was localized with a high reliability. Yet the indirect structural evidence demands the presence of a cation, and the only realistic possibility is the cation $[Me_2NH_2]^+$, which is a typical constituent of CPs obtained from DMF due to hydrolysis of the solvent at elevated temperatures.²⁵ Fragments, corresponding to the dimethylammonium, indeed could be found in the structure (see also the ESI†).



Finally, the structural data for **2** suggests that in the assumed $P\bar{1}$ symmetry, the coordinated solvent molecule could be represented as a 0.5/0.5 site shared by DMF and water molecules. Alternatively, when the structure is refined in the $P1$ symmetry, the predominant localization of solvent molecules could be better differentiated, but such a small difference is not enough for lowering the ascribed overall symmetry.

Published results on CPs with ligands of that particular trigonal-pyramidal type as H_3L^3 are scarce. A single report discussed a series of complexes of Mn, Zn and Cd based on tris-(4-carboxyphenyl)methane, which consisted of coordination bonded clusters of at least three metal atoms or a contiguous 1D cluster chain as in the complex of manganese.²⁶

The compound $[Mn(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 3DMF \cdot 4H_2O$ (**3**) is a 3D coordination polymer based on an isolated Mn^{2+} metal center, which could be classified as hexacoordinated. However, the geometry of the actual $\{MnO_8\}$ environment is complex, consisting of three distinct groups of 4–2–2 atoms, with bond/contact distances of 2.09–2.29, 2.42 and 2.73 Å, respectively. The 1:1 ratio of the effectively tetrahedral coordination bonded unit and the tetrahedral ligand leads to the formation of a 3D framework with a topology of a diamond or *dia* net. The overall structure consists of two loosely packed interpenetrated frameworks, leaving 59% of the solvent accessible space, which is filled by guest solvent molecules. The pore ‘bottle-necks’ could be described as having vdW dimensions being not smaller than 5×5 Å (estimation along the *z*-axis). Unfortunately, the refinement of the diffraction data did not give practically any information about the actual contents of the voids. While the structure of the framework itself does not contradict the existence of the ligand in just the doubly deprotonated form, the method of preparation and the TGA data, suggesting the presence of dimethylammonium cations in analogy to the case of **2** (see also the ESI†), provide evidence in favour of full deprotonation of the ligand.

Under conditions similar to those used in the synthesis of **3**, a compound of cobalt, $[Co(DMF)(L^4)] \cdot 2(NH_2Me_2) \cdot 2DMF \cdot 5H_2O$ (**4**) was obtained and its isostructurality to **3** was proven by powder X-ray diffraction. Concerning the structures of **3** and **4**, it is quite curious that while Yaghi and co-workers had performed a broad screening of tetrahedral ligands,¹⁹ including 1,3,5,7-adamantanetetracarboxylic acid (H_4ATC), tetrakis-(4-carboxyphenyl)methane (H_4MTB), and H_4L^4 , they did report the same structural type only in the case of the smallest representative and only for a compound of cadmium, $Cd(ATC)[Cd(H_2O)_6](H_2O)_5$, or MOF-32. Unlike in **3**, where there is significant structural evidence against the presence of large counteranions in the structure, the cadmium complex features it. The presence of $[Cd(H_2O)_6]^{2+}$ is seemingly conditioned by the method of preparation, involving an aqueous alkaline solution. Unfortunately, not much is known about the permanent porosity of those early complexes.

All the isolated compounds were phase-pure, as was witnessed from the PXRD patterns (Fig. S7–S9†). The solvent content of the compounds **2–4** was established by a combina-

tion of TGA, elemental analysis and, indirectly, single crystal XRD data (see the ESI† for the explanation of the slight difference of composition ascribed for the isostructural compounds **3** and **4**).

Compounds **3** and **4** are structurally possible PCP/MOF class materials, *i.e.* possessing permanent porosity typically associated with 3D framework structures. Together with **2**, they were subjected to direct degassing at 200 °C under vacuum, *i.e.* without preliminary solvent exchange. N_2 gas sorption experiments demonstrated that all degassed compounds possessed significant, if not high, surface areas. Even for the degassed **2'**, a BET surface area of $196 \text{ m}^2 \text{ g}^{-1}$ was observed (Fig. S18†), despite layered CP structures, which typically do not possess permanent porosity. However, partial structural collapse has most probably occurred due to appreciable non-closed hysteresis (see the ESI†), indicating narrow pores, much smaller (<5 Å) than that expected for an idealized structure of this type.

For the degassed materials derived from 3D framework materials, the surface areas are appreciably larger. Thus for **3'**, the BET surface area is $289 \text{ m}^2 \text{ g}^{-1}$, while for **4'**, it reaches $423 \text{ m}^2 \text{ g}^{-1}$ (Fig. 3). In both cases, the observed adsorption isotherm, which is of type II, is practically degenerated to a linear dependence, evidencing broad distribution of pore sizes, non-characteristic for crystalline microporous solids, but rather to amorphous ones, with a significant contribution of mesoporosity. Compound **4'** demonstrated a higher surface area, despite being derived from an isostructural material, probably due to the higher stability of the coordination bonds of Co^{2+} than that of Mn^{2+} . The surface area simulated by a spherical probe for a hypothetical framework identical to the one found in **3**, but with all the guest molecules removed including the counteranions, reaches $3295 \text{ m}^2 \text{ g}^{-1}$ (simple Monte Carlo integration with a nitrogen-sized spherical probe, 3.68 Å).²⁷ While the real framework should have a somewhat lower surface area, it is clear that the demonstrated porosity is only a small fraction of the theoretically possible.

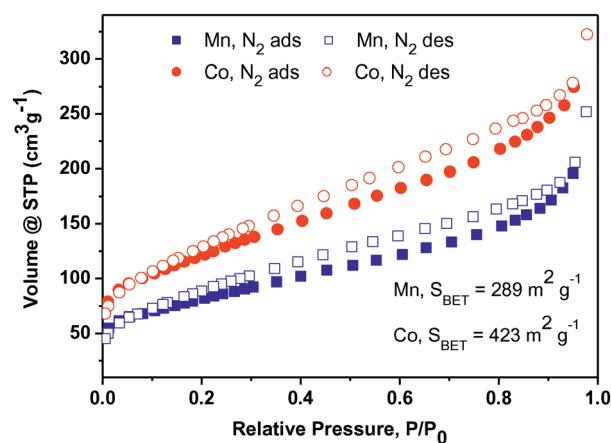


Fig. 3 N_2 adsorption isotherms for compounds **3** and **4**.



Still, the two compounds demonstrate significant stability against direct degassing under elevated temperatures, in accordance with the ascribed complete deprotonation of the ligand. Two-fold interpenetration contributes to the stability by better resisting complete collapse, without preservation of local order. Milder methods of activation, including solvent-exchange and supercritical CO₂ drying, might give much better results, but this possibility is going beyond the scope of the present contribution.

Conclusions

The screening of a regular series of tetrahedral and 'truncated' tetrahedral carboxylate ligands based on tetraphenyladamantanes regarding the formation of coordination polymers with d metals showed a strong tendency towards the formation of the simplest **sql**, **hcb** and **dia** types (at least as a result of screening of successful crystallization outcomes in a typical process employing DMF). The last two structures are surprisingly based on isolated metal centers, which is quite rare for polycarboxylate ligands of such a large size. The structure formation in these last two cases is dominantly ligand-controlled, with observed matching of geometry of the trigonal-pyramidal and tetrahedral ligands to the requirements for the hexagonal and diamondoid nets, respectively. The demonstrated **dia** structure is a prototype for robust cation conductive materials based on even larger tetrahedral ligands, the stability of which should also rely on low solubility of the large hydrophobic building blocks. This work does not state that alternative crystalline phases could not be obtained under comparable conditions (e.g. we expect a possible tetranuclear Fe(II) complex with (L⁴)⁴⁻ with a **flu**-net topology). It rather suggests that other approaches should be followed to obtain highly porous and stable compounds with these ligands, preferably *via* targeting larger clusters. The latter demands effective co-ligands in the case of 3d metals, or, alternatively, cations of higher charge with a more pronounced tendency towards coordination-bonded cluster formation, like Zr(IV).

Notes and references

‡ Compounds 1–4 were prepared by heating solutions of metal chlorides and the ligands in DMF at 100–140 °C. For example, 3 was obtained in a phase pure form as follows: a mixture of MnCl₂·4H₂O (20 mg, 0.1 mmol) and H₄L⁴ (31 mg, 0.05 mmol) was dissolved in 2 mL of *N,N*-dimethylformamide (DMF) and sealed in a 3 mL borosilicate glass tube. The tube was heated at 100 °C for 72 h, then cooled to ambient temperature at a rate of 6 °C h⁻¹. The formed crystals were separated, washed with a few small portions of DMF and dried in air for one day. The yield of the compound, which consists of near colourless crystals, was >52 mg (~50 %, ligand-based). See also the ESI†

§ Selected crystal data for 1–3: [Mn(DMF)(L³)] (1): FW = 502.47 g mol⁻¹, monoclinic, *P*2₁/c, *a* = 12.5159(10) Å, *b* = 19.1864(14) Å, *c* = 9.9596(8) Å, *V* = 2383.8(3) Å³, β = 94.649(3)°, *Z* = 4, *R*₁ = 0.0409; *wR*₂ = 0.1005. [Cd(DMF)_{0.5}(H₂O)_{0.5}(L³)]·(NH₂Me₂)·0.5DMF·1.5H₂O (2): FW = 761.63 g mol⁻¹, triclinic, *P*1̄, *a* = 11.0682(4) Å, *b* = 13.5036(5) Å, *c* = 14.6691(5) Å, *V* = 6014.9(14) Å³, α = 70.055(2)°, β = 79.314(2)°, γ = 87.896(2)°, *Z* = 2, *R*₁ = 0.0728; *wR*₂ = 0.2051. [Mn(DMF)(L⁴)]·2(NH₂Me₂)·3DMF·4H₂O (3): FW = 669.59 g mol⁻¹ (without solvent molecules),

orthorhombic, *I*4/*mma*, *a* = 17.335(3) Å, *b* = 17.748(2) Å, *c* = 19.551(3) Å, *V* = 6014.9(14) Å³, *Z* = 4, *R*₁ = 0.099; *wR*₂ = 0.305.

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