Layered inorganic–organic frameworks based on the 2,2-dimethylsuccinate ligand: structural diversity and its effect on nanosheet exfoliation and magnetic properties†

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The structures of four new 2,2-dimethylsuccinate frameworks suitable for exfoliation into nanosheets using ultrasonication are reported. These hybrid compounds contain either monovalent (Li+) or divalent (Co2+ and Zn2+) cations, and they all feature hydrophobically capped covalently bonded layers that only interact with each other via weak van der Waals forces. Critically this shows that the use of this dicarboxylate ligand generally yields two dimensional compounds suitable for simple and affordable nanosheet exfoliation. This extends the range of frameworks that can be exfoliated and highlights the 2,2-dimethylsuccinate ligand as an excellent versatile platform for the production of nanosheets. The topologies of the layers in each framework were found to vary significantly and this appears to have a significant effect on the relative size of the nanosheets produced; increased space between methyl groups and more extensive inorganic connectivity appears to favour the formation of thin nanosheets with larger lateral dimensions. Additionally the magnetic properties of two of these frameworks were examined, and it was found that both exhibit strong low dimensional antiferromagnetic coupling despite their well-separated layers preventing three dimensional magnetic order.

1. Introduction

Inorganic–organic frameworks have become the focus of extensive research efforts due to the fascinating range of structures and properties that these versatile materials can exhibit.1,2 The structures of these hybrid compounds are significantly influenced by their metal cation and organic ligand building blocks, as well as by other factors such as synthesis temperature, leading to the adoption of architectures that are either porous or dense. Porous frameworks, often referred to as metal–organic frameworks (MOFs), are of interest for their catalytic, gas storage and separation properties, while denser frameworks exhibit properties more commonly associated with metal oxides and other purely inorganic materials, such as magnetic order or multiferroicity.1,3

Most of the work on hybrid frameworks has focused on the synthesis of single crystals and polycrystalline powders with large micron-sized grains. Recently, however, significant attention has been drawn to the possibility of making nano-sized particles of such frameworks to enable the preparation of thin films for technological applications.4 This has usually involved exploring the different “bottom-up” routes by which these materials can be synthesised, and subsequently exploration of how the properties of these materials differ from those of bulk frameworks. Recent work has shown, however, that bulk structures featuring covalently bonded layers with only weak interlayer interactions can be exfoliated into framework nanosheets by simple ultrasonication of the as-made bulk samples.5,6 This “top-down” approach provides a cost effective and readily available route for synthesising nanosheets that are typically 10 to 100 nm thick but have lateral dimensions of up to 10 μm. It is likely to be particularly useful and straightforward in the case of dense frameworks, since their stability is generally not affected by any solvent that may be present in structural cavities, as is found for porous frameworks. The preparation of these nanosheets, however, requires a framework with a suitable layered structure in the bulk phase. It is therefore important to show that a range of such layered materials can be made in a reliable manner to enable nanosheets containing different cations and featuring different layer topologies to be created, thereby increasing the functionality of these novel materials. A better understanding of the effects of layer topologies on nanosheet exfoliation will also enable the quality of the nanosheets obtained to be optimised.

†Electronic supplementary information (ESI) available: Details of synthetic conditions, structural determination, including bond distances and CIFs, and infrared spectroscopy measurements alongside plots of powder diffraction, thermogravimetric and magnetic data are available as supplementary information. CCDC 865494–865497. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30648d

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Amongst the dense frameworks, those containing linear dicarboxylates have attracted a sizable amount of interest and have been found to have significant variations in their structures depending on the precise nature of the cation, ligand and synthetic conditions used.\textsuperscript{7–10} One such framework, MnDMS (DMS = 2,2-dimethylsuccinate), Mn(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})(H\textsubscript{2}O),\textsuperscript{5} has already been demonstrated to form a structure highly suitable for nanosheet exfoliation, and the present work explores the possibility of preparing similar frameworks utilising the same DMS ligand by combining it with other monovalent and divalent cations, namely Li\textsuperscript{+}, Co\textsuperscript{2+} and Zn\textsuperscript{2+}. This study reveals that similar two dimensional frameworks with weakly interacting layers suitable for exfoliation can be produced using this approach, and that each compound produced adopts a unique layered topology showing that frameworks incorporating the DMS ligand are a versatile general platform for the creation of framework nanosheets. The exfoliated nanosheets of several of these compounds are characterised and the magnetic properties of two of the compounds are described.

2. Experimental

All compounds reported in this work were synthesised hydrothermally using commercially available starting materials, which were used without further purification. The sample of bulk MnDMS, Mn(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})(H\textsubscript{2}O), used for magnetic property measurements, was made using the method recently reported; this involved heating a mixture of 2.5 mmol MnCl\textsubscript{2}·6H\textsubscript{2}O, 3.7 mmol 2,2-dimethylsuccinic acid and 6.2 mmol KOH in 9 mL water at 140 °C for 3 days in a 23 mL Teflon-lined Parr autoclave.\textsuperscript{5} Using a similar approach and substituting CoCl\textsubscript{2}·6H\textsubscript{2}O, ZnCl\textsubscript{2}, LiOH or Li(CH\textsubscript{3}COO)·2H\textsubscript{2}O for MnCl\textsubscript{2}·6H\textsubscript{2}O, we discovered that it was possible to produce four new compounds, namely CoDMS1 [Co(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})(H\textsubscript{2}O)], CoDMS2 [Co\textsubscript{2}(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})(OH\textsubscript{2})\textsubscript{2}], ZnDMS, [Zn\textsubscript{2}(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})\textsubscript{6}(OH\textsubscript{2})\textsubscript{2}] and LiDMS [Li\textsubscript{2}(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})\textsubscript{2}]. Concentrations and synthesis temperature were optimised for each compound to obtain higher quality crystals and/or purer phases, as described in the ESL.\textsuperscript{†} Details of the structure determinations, including crystallographic data and selected bond distances, are given in Tables S1 and S2.

Powder X-ray diffraction (PXRD) patterns of all samples made in this study were collected over the range of 5–60° (2θ) by a position sensitive linear detector on a Bruker D8 Advance diffractometer using Cu Ka radiation. Results from this indicated that ZnDMS could be obtained in a pure form at 150 °C (see Fig. S1† for the Le Bail fit). CoDMS1 and CoDMS2 were found to prefer to form at lower and higher temperatures, respectively. Samples of CoDMS2 were always found to be contaminated by CoDMS1, although this contamination could be reduced to a very small amount in reactions carried out above 150 °C (see Fig. S2†). In contrast, CoDMS1 formed preferentially over CoDMS2 at temperatures below 125 °C, although it was inevitably contaminated by a significant amount of either CoDMS2 or, at temperatures below 100 °C, an unidentified phase (see Fig. S3†). Several small peaks in the cleanest diffraction pattern of LiDMS, made at 180 °C, could not be unambiguously assigned, suggesting the possible presence of impurity phases (see Fig. S4†). Microanalysis results indicated that samples of most phases could be obtained in high purity. CoDMS2 was found to have 28.84% C and 3.55% H (28.88% C and 3.64% H expected), ZnDMS had 31.84% C and 3.64% H (31.88% C and 3.72% H expected) and LiDMS gave 45.47% C and 4.98% H (45.61% C and 5.10% H expected). By contrast, microanalysis results showed that all samples of CoDMS1 contained significant amounts of impurities. Therefore only limited characterisation of CoDMS1 is presented.

Thermogravimetric analysis (TGA) of the bulk frameworks was performed in air on a TA instruments Q500 using a heating rate of 10 °C min\textsuperscript{−1}. The temperature and field dependence of the dc magnetization was measured with a Quantum Design MPMS 5XL SQUID magnetometer. Powder samples were gently-ground, contained in gel caps, and held in a straw with a uniform diamagnetic background. Experimental details of the infra-red spectroscopy are described in the ESL.\textsuperscript{†}

3. Results and discussion

3.1 Structure of CoDMS1, Co(C\textsubscript{6}H\textsubscript{8}O\textsubscript{4})(H\textsubscript{2}O)

The architecture and composition of CoDMS1 is quite similar to MnDMS and features approximately 10 Å thick covalently bound layers that only interact with each other via weak van der Waals forces (see Fig. 1a). The dimethyl groups of the ligand protrude out into the interlayer space, providing the layers with hydrophobic caps. The covalently bonded layers contain corner-sharing chains of CoO\textsubscript{6} octahedra, which are crosslinked by the backbone of the dicarboxylate ligands (see Fig. 1b). This provides the structure with the same overall connectivity as the analogous Mn phase, I\textsuperscript{0}O\textsuperscript{1}, according to the terminology of Cheetham et al.\textsuperscript{1} The asymmetric unit of CoDMS1, however, is smaller than that of MnDMS and has only one Co cation, half a DMS ligand and the oxygen atom and one hydrogen of a water molecule, with the Co cation and the aqueous oxygen atom occupying special positions (see Fig. 2). The presence of only half a carboxylate ligand in the structure reflects disorder of the

![Fig. 1](image-url)
methyl groups on the ligand between the two possible middle carbons atoms of the backbone, which is not found in MnDMS. A random arrangement of methyl groups in neighbouring ligands would result in several very short contacts between methyl hydrogens, at distances less than the sum of two van der Waals hydrogen radii, 2.40 Å. In particular, distances of 1.78 Å between H4C atoms on adjacent ligands along the chain direction and 1.75 Å between H4B atoms on neighbouring ligands from adjacent layers would be physically unreasonable. There must, therefore, be some short-range ordering of the location of the methyl groups, both between and within the layers, in order to prevent an arrangement featuring these short H–H interactions.

Co cations in CoDMS1 have a bond valence of 2.04, consistent with Co²⁺, and their octahedral coordination is more regular than that found in MnDMS (see Table S2† for bond distances). They are coordinated to four oxygen atoms from different carboxylate ligands and two water molecules located in the trans-positions. The corner-sharing connectivity between octahedra within a chain occurs via the oxygen atoms from the water molecules, rather than via a carboxylate oxygen atom as found in MnDMS. Consequently, all carboxylate oxygen atoms are bonded to only one cation and the DMS ligands can be described as having (1111) connectivity. The hydrogen atoms on the water molecule are hydrogen bonded to one of the distinct carboxylate oxygen atoms, O1 at a distance of 2.10(4) Å (the \(O_{\text{acceptor}} - O_{\text{donor}}\) distance is 2.805(3) Å).

3.2 Structure of CoDMS2, \(\text{Co}_2(\text{C}_6\text{H}_8\text{O}_4)_2(\text{OH})_2\)

CoDMS2 also features covalently bonded layers with similar thickness and interlayer interactions to those found in CoDMS1 and MnDMS (see Fig. 3a). The composition and topology of its layers are, however, significantly different (see Fig. 3b). The asymmetric unit of CoDMS2 features four Co cations, two of which are on special positions, two DMS ligands and two hydroxide groups (see Fig. 4). Three of the four Co cations adopt octahedral coordination with bond valencies between 1.92 and 2.08, and the fourth is tetrahedral with a bond valence of 1.84 (see Table S2† for bond distances). The most dominant feature of the covalently bonded layers are rings of eight CoO₆ polyhedra, consisting of six octahedra and two tetrahedra, the latter located on opposite sides of the rings (see Fig. 3b). The rings are stacked along the \(a\)-axis and are connected along the \(b\)-axis via hydroxide ligands located on the trans-corners of the octahedrally coordinated Co1 cations, the only cation not included in the rings; these also bond to a Co2 and a Co3 cation from the inorganic rings. The \(\text{Co}_2\text{O}_6\) octahedra share an edge with a \(\text{Co}_4\text{O}_6\) octahedra and an edge and a corner with two \(\text{Co}_2\text{O}_4\) tetrahedra, leading to \(\text{I}_2\text{O}_0\) connectivity overall.

All Co cations are bonded to two hydroxide ligands, which are located in a trans-fashion in the case of the octahedrally coordinated Co, and the remainder of their coordination spheres are made up of two or four oxygen atoms from different carboxylate ligands, for tetrahedral and octahedral Co, respectively. Both distinct carboxylate ligands have one oxygen atom that bonds to two Co cations, with all others bonded to one cation each, giving these ligands (1112) connectivity.
3.3 Structure of ZnDMS, Zn$_2$\((\text{C}_8\text{H}_8\text{O}_4)\)$_6$\((\text{OH})_2$

ZnDMS also features covalently bonded, 1 nm thick hydrophobically capped layers, but their architecture is significantly different from the other DMS phases. Notably, the dimethyl groups of adjacent layers appear to be more intertwined than in the other phases described in this work (see Fig. 5a). Similarly to CoDMS2, the layers also feature cations in both tetrahedral and octahedral environments, but in this case they are interconnected into an I$_{0}$O$_{2}$ structure. The asymmetric unit of ZnDMS contains four Zn atoms, three DMS ligands and one hydroxide group (see Fig. 6). The only octahedrally coordinated Zn cation, Zn$_3$, occupies a special position and is bonded to hydroxide groups in trans-positions that also each connect to Zn1 and a Zn2 cation to make a Zn$_2$O$_{18}$ cluster. The other distinct Zn cation is bound to a cluster via an organic carboxylate bridge. Two such tetrahedra are bonded into a dimer, via two carboxylate bridges, resulting in a structure where clusters and dimers alternate along the a-axis (see Fig. 5b). Connectivity along the second dimension of the layer only occurs via the backbone of the ligand.

The four distinct Zn cations in ZnDMS all have bond valencies of between 1.99 and 2.11, consistent with that expected for divalent cations (see Table S2 for bond distances). The octahedrally coordinated Zn cations are bound to four oxygen atoms from different carboxylate groups and two hydroxide groups, while the two distinct tetrahedral Zn cations in the Zn$_2$O$_{18}$ cluster are both bound to three oxygen atoms from different carboxylate groups and one hydroxide group; the Zn cations in the tetrahedral dimers are bonded to four carboxylate ligands. All oxygen atoms on the carboxylate ligands bond to only one cation, leading to the ligands featuring (1111) connectivity.

Fig. 4 The asymmetric unit of CoDMS2 with 60% probability ellipsoids. The hydrogen atoms labels are omitted for the sake of clarity. Additional non-hydrogen atoms, indicating the coordination sphere of all cations in CoDMS2, are labelled alphabetically. The colours are as in Fig. 3.

Fig. 5 The structure of compound ZnDMS featuring (a) the arrangement of two layers and the hydrophobic region between them and (b) the structure of a single layer highlighting the Zn cluster and dimer elements contained within. The Zn atoms and ZnO$_x$ polyhedra are dark blue and all other colours are the same as in Fig. 1.

Fig. 6 The asymmetric unit of ZnDMS with 60% probability ellipsoids. The labels on the hydrogen atoms are omitted for the sake of clarity. Additional non-hydrogen atoms, included to illustrate the coordination sphere of all cations in the structure, and the locations of the five Zn cations in the cluster, are labelled alphabetically. The colours are the same as in Fig. 5.
The network. The Li atoms and LiO₄ tetrahedra are green and all other colours are as in Fig. 1.

Fig. 7 The structure of compound LiDMS, indicating (a) the arrangement of two layers and the hydrophobic region between them and (b) the structure of a single layer highlighting the two-dimensional Li–O–Li network. The Li atoms and LiO₄ tetrahedra are green and all other colours are as in Fig. 1.

Fig. 8 The asymmetric unit of LiDMS with 60% probability spheres. The labels on the hydrogen atoms are omitted for the sake of clarity. Additional non-hydrogen atoms, included to illustrate the coordination sphere of all cations in the structure, are labelled alphabetically. The colours are the same as in Fig. 7.

3.4 Structure of LiDMS, Li₂(C₆H₈O₄)

The structure of LiDMS features the weakly interacting 10 Å thick layers typical of the other compounds in this work, although the methyl groups in adjacent layers appear to be slightly more separated than in the other compounds (see Fig. 7a). The layers consist of a 2-D network of corner-sharing LiO₄ tetrahedra bridged by carboxylate groups of the ligand molecules (see Fig. 7b), resulting in trigonal connectivity and an arrangement that appears more corrugated than in the other compounds in this work. The asymmetric unit of LiDMS consists of four lithium atoms and two dicarboxylate ligands (see Fig. 8). The lithium atoms have distorted tetrahedral coordination and have bond valencies between 0.98 and 1.08, consistent with that expected for Li⁺. Both Li1 and Li2 are coordinated by oxygen atoms from four different ligand molecules, while the oxygen atoms in the coordination spheres of Li3 and Li4 come from three different ligand molecules, leading to the formation of seven-membered rings involving the carbon skeleton of the ligand and respective lithium atoms. All oxygen anions bond to two different Li⁺ cations, giving the ligands (2222) connectivity.

3.5 Cation induced topological changes and their effect on nanosheet exfoliation

A comparison of the structure of MnDMS and the four structures published in this work confirms that the incorporation of the DMS ligand generally causes the framework to adopt an architecture with covalently bonded layers that weakly interact with each other. Such layered structures appear to provide an efficient way of accommodating the bulky neighbouring methyl groups on the ligand, suggesting that inclusion of this ligand in a framework will, at least in most cases, lead to the formation of hydrophobically capped layers suitable for exfoliation using ultrasonication in common organic solvents. The precise nature and composition of the layer is, however, dependent on the cation selected and, as discussed below, this has a significant effect on the exfoliation of nanosheets. The structure of compound CoDMS1 is the most similar to that of MnDMS. The preference of d⁷ Co to adopt a more regular octahedra than that adopted by d⁵ Mn is, however, thought to cause a change in the connectivity of the corner-sharing chains and a rearrangement of the dicarboxylate ligands leading to disorder of the methyl groups.

Increasing the temperature at which the reaction occurs leads to the formation of a more dense structure, CoDMS2, which has increased inorganic connectivity, and a composition change from Co(C₆H₄O₄)(H₂O) to Co₂(C₆H₈O₄)₂(OH)₂. These changes are thought to be driven by an increased tendency towards dehydration with increasing temperature, analogous to the effects observed amongst the Co succinate phases by Forster et al. In this case, the transition between the low and high temperature Co containing phases is accompanied by a third of the Co adopting tetrahedral coordination. Changing the cation to Zn or Li results in a further increase in the fraction of cations adopting tetrahedral coordination in the structure, which is probably due to the preference of these cations for adopting tetrahedral geometry. The extent of inorganic connectivity within the layers is, however, very different in these compounds, with ZnDMS adopting I⁰O² connectivity while LiDMS is I⁰O⁰. In LiDMS the lower cation charge leads to twice the number of metal sites being available per dicarboxylate ligand, and alongside the absence of any other ligands this leads to an increase in ligand–metal binding to (2222) connectivity, much higher than found in the other frameworks.

The differences in the layered architecture between the four DMS frameworks provide a glimpse into the potential variation and functionality that could be introduced into analogous phases and, more significantly, has an effect on the exfoliation of the bulk material into nanosheets. This can be seen from the contrast in exfoliation behaviour between MnDMS, ZnDMS and LiDMS frameworks. ZnDMS and LiDMS were found to be readily exfoliated into nanosheets using similar methods to those previously employed for MnDMS. As was the case for MnDMS, ultrasonication of 0.15 mg mL⁻¹ mixtures of ZnDMS and LiDMS, in ethanol and acetonitrile respectively, for twenty minutes (Elmasonic S30 at 37 kHz, 80 W) resulted in milky colloidal suspensions. These suspensions exhibited the Tyndall effect,
could be exfoliated to single layers,\(^5\) even the relatively thin nanosheets of ZnDMS were typically still observed to exceed 10 layers. Interestingly, AFM characterisation of the exfoliated LiDMS indicated that it could generally be reduced to thinner nanosheets, whose thickness is less than 10 nm (or \(\sim 10\) elementary layers), while still retaining lateral dimensions of well over a \(\mu\)m. (see Fig. 11a). There is also evidence that unilamellar nanosheets have been produced at significantly larger lateral sizes than for either of the MnDMS\(^5\) or ZnDMS compounds examined here (see Fig. 11b).

The creation of nanosheets from frameworks featuring the DMS ligand, beyond the already described MnDMS, shows that the incorporation of the DMS ligand into a framework provides an excellent general platform for synthesising compounds suitable for exfoliation using ultrasonication. The typical lateral dimensions of the exfoliated nanosheets compared to thickness tends to decrease in the order LiDMS > MnDMS > ZnDMS.\(^5\) In light of this, we propose that two factors could principally be the cause of the above outcome. Firstly, examination of the crystal structures appears to indicate that the separation of the methyl groups in adjacent layers decreases in that same sequence and, therefore, the smaller relative lateral size of the nanosheets may be caused by increased difficulty in separating out methyl groups from adjacent layers. Secondly, the degree of inorganic connectivity decreases in the same sequence and, since previous nanoindentation studies have suggested that the mechanical stability of inorganic connectivity tends to be greater than that of organic connectivity, this may play a role in the cohesiveness of individual layers during ultrasonication.\(^5,13\) The DMS frameworks studied to date are unique amongst the linear dicarboxylates in forming structures that are exclusively suitable for nanosheet exfoliation.\(^5,10\) This is likely to be because of the presence of two methyl groups located close together in space, requiring such structures to form to accommodate the bulky nature of these substituents. Therefore exploration of frameworks incorporating other linear dicarboxylate ligands with bulky substituents, which lack the potential to form additional interactions e.g. hydrogen bonding or \(\pi-\pi\) stacking, is important in order to determine if they also produce such exfoliatable structures or feature alternative ways of accommodating their bulky functional groups.

### 3.6 Thermal analysis

TGA measurements of CoDMS1 indicates that it loses significant weight over two regions, between 130 \(^\circ\)C and 230 \(^\circ\)C where 7.8% of initial weight is lost, and then between 280 \(^\circ\)C and 340 \(^\circ\)C, leading to a final weight of 37.9% (see Fig. S7†). These two changes are probably caused by the loss of the coordinated water (expected weight change of 8.2%) and the decomposition of the remainder of the framework to make Co\(_2\)O\(_4\) (expected final weight of 36.3%), as confirmed by PXRD. CoDMS2 was found to have a much simpler decomposition pathway with significant weight loss only being recorded between 270 \(^\circ\)C and 350 \(^\circ\)C, after which 51.2% of initial weight remains (see Fig. S8†); this is broadly consistent with the decomposition of the framework to form Co\(_2\)O\(_4\) (expected final weight of 48.3%). As was the case for CoDMS1, the discrepancy between the...
expected and obtained weight loss can probably be attributed to the small amount of impurities present in both samples.

TGA indicates that the decomposition of ZnDMS occurs at a slightly higher temperature than for the Co phases (see Fig. S9†), between 300 °C and 440 °C, after which 42.9% of the initial sample weight remains. This is consistent with the formation of ZnO, as confirmed by PXRD (expected final weight of 42.0%). Decomposition of LiDMS begins at an even higher temperature, 400 °C (see Fig. S10†), which is similar to other recently reported Li-based frameworks, and results in approximately 47% weight loss with a further 5%, mass loss around 600 °C.14 The final mass recovered was 46%, corresponding to lithium carbonate (47% mass calculated) and con

3.7 Magnetic properties of MnDMS, Mn(C₆H₈O₄)(H₂O) and CoDMS2, Co₃(C₆H₈O₄)₂(OH)₂

Magnetic susceptibility measurements of MnDMS carried out in an applied field of 40 Oe field feature a broad peak centred around 8 K, consistent with low-dimensional antiferromagnetic order (see Fig. 12).15 This feature is identical in both field cooled (FC) and zero field cooled (ZFC) measurements and remains unchanged at higher applied fields. Well above the ordering temperature, the compound exhibits Curie–Weiss paramagnetism with a fit to 1/χ indicating a Θ (Curie–Weiss theta) of −12.1 K, consistent with predominantly antiferromagnetic interactions, and a magnetic moment, μeff, of 5.95 μB, very close to the spin-only moment expected for high spin Mn²⁺, i.e. 5.92 μB. χmT decreases from 4.23 cm³ mol⁻¹ K at 300 K to very close to zero at low temperature, with a rapid decrease below 30 K (see Fig. 12 insert), consistent with extensive, purely antiferromagnetic ordering within the layers despite the large distances between them preventing three dimensional magnetic ordering. The observed behaviour could be caused by antiferromagnetic ordering within the corner-sharing octahedral chains or by neighbouring chains coupling antiferromagnetically, but it is uncertain which occurs since the intrachain Mn–O–Mn bond angle is 116.48(8)°, in the range that could lead to either antiferromagnetic or ferromagnetic nearest neighbour coupling.16 Examination of the magnetic structures of this material using neutron diffraction could differentiate between these two possibilities, but the large amount of hydrogen in the ligand prevents such a study from being easily done in this case.17

A plot of C′(χ′(Θ))⁻¹ as a function of T/Θ (where C = the Curie constant and χ = the magnetic susceptibility) provides insight into the nature of the magnetic exchange interactions above the ordering temperature and can reveal the presence of any magnetic frustration (see Fig. 13).18 The plot shows positive deviation from Curie–Weiss behaviour for MnDMS, consistent with purely antiferromagnetic behaviour. This extends to temper-atures above Θ, suggesting the presence of weak antiferromagnetic interactions up to around 30 K. This is consistent with the behaviour of χmT, and the strong low dimensional magnetic order is confirmed by AC magnetic susceptibility measurements, which do not show any frequency dependence of χ′ or any significant features in the phase angle of the susceptibility (see Fig. S11†). Isothermal magnetisation measurements carried out at 1.9 K indicate that the magnetisation does not saturate. Indeed, an induced magnetisation of only 1.6 μB per mole is obtained under an applied field of 50 kOe, suggesting that purely antiferromagnetic magnetic ordering occurs even under a strong applied field (see Fig. S12†).

Our 20 Oe field-cooled magnetic susceptibility measurements of CoDMS2 feature a broad maximum near 17 K and a further
increase in susceptibility below 6 K (see Fig. 14). Measurements carried out in higher applied fields, however, show that the increase in susceptibility detected at very low temperatures decreases significantly as the applied field is raised. This is consistent with the paramagnetic-like feature being caused by the presence of a magnetic impurity, most likely the small amount of CoDMS1 established as being present in this compound (see Fig. S2†). The broad maximum in susceptibility near 17 K does not change significantly with increasing applied magnetic field, suggesting that CoDMS features low dimensional antiferromagnetic order below this temperature. \( \chi_m T \) was found to decrease from 2.61 cm\(^3\) mol\(^{-1}\) at 300 K to almost zero at low temperatures, consistent with the compound having strongly antiferromagnetic behaviour within its magnetically isolated layers (see insert of Fig. 14). Above 20 K CoDMS2 is a Curie–Weiss paramagnet with a fit to \( 1/\chi \) measured in an applied field of 20 Oe yielding a \( \Theta \) of \(-73.4\) K, consistent with predominantly antiferromagnetic interactions, and a \( \mu_{\text{eff}} \) of \( 5.10 \mu_B \), close to the maximum value of \( 5.20 \mu_B \) expected.

A plot of scaled inverse susceptibility \( \text{versus} \) scaled temperature shows that CoDMS2 only deviates from Curie–Weiss behaviour at temperatures significantly below \( \Theta \) (see Fig. 13). This is possibly due to competing interactions between neighbouring Co cations in its CoO\(_x\) layers, as found in similar Co frameworks, with every Co bonded to at least three other neighbouring cations via oxygen bridges.\(^{8,19}\) The presence of frustration would also be consistent with the large disparity between \( \Theta \) and the magnetic ordering temperature. Deviation from Curie–Weiss behaviour occurs in a positive fashion, consistent with purely antiferromagnetic behaviour, until very low temperatures where the presence of the magnetic impurity obscures the behaviour of CoDMS2. Isothermal magnetisation measurements of CoDMS2, carried out at 15 K to minimise the influence of the paramagnetic impurity, indicate that induced magnetisation remains very low even under an applied field of 50 kOe, with a value of only \( 0.005 \mu_B \) being recorded (see Fig. S13†). This result is consistent with CoDMS2 featuring very strong antiferromagnetic order, despite its low dimensionality.

4. Conclusions

This study demonstrates that it is possible to prepare a number of hybrid frameworks featuring the 2,2-dimethylsuccinate ligand in combination with either monovalent or divalent cations; these compounds can be readily separated into nanosheets \( \text{via} \) ultrasound in simple organic solvents critically extending this beyond the initial MnDMS system. While these structures all feature hydrophobically capped layers, which only interact weakly \( \text{via} \) van der Waals forces, the topologies adopted by the layers vary significantly. Two Co frameworks were prepared with the low-temperature structure featuring corner-sharing chains of CoO\(_x\) octahedra, while the high-temperature phase has two-dimensional inorganic connectivity and a mixture of octahedral and tetrahedral Co\(^{2+}\). The Zn\(^{2+}\) and Li\(^+\) phases were found to feature predominantly tetrahedral coordination environments, as might be expected for these cations; whilst Zn\(^{2+}\) has cations arranged in a mixture of clusters and dimers without any extended inorganic connectivity, the Li\(^+\) compound has \( \text{IO}_6 \) connectivity. The variation in layer topology was shown to have a significant effect on the relative dimensions of the exfoliated nanosheets, suggesting that factors such as the extent of inorganic connectivity and separation of the neighbouring methyl groups could be fine-tuned to produce improved nanosheets. Despite this it appears that, in general, the use of a linear ligand with bulky substituents, which lack the potential to form stronger non-covalent interactions \( \text{e.g.} \) hydrogen bonding and \( \pi-\pi \)
stacking, provides a suitable platform for the synthesis of exfoliable frameworks. Additionally, the magnetic properties of MnDMS and CoDMS2 were examined and both compounds exhibit strong low dimensional antiferromagnetic behaviour, despite the well-separated nature of their layers preventing three-dimensional ordering. MnDMS was found to feature weak anti-ferromagnetic interactions above its $\theta$, while CoDMS2 only orders well below its $\theta$ due to the competing interaction pathways in this framework.

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