Layered Inorganic-Organic Frameworks based on the 2,2-Dimethylsuccinate ligand; Structural Diversity and its Effect on Nanosheet Exfoliation and Magnetic Properties

Supporting Information

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Experimental

Synthetic Method

Colourless sheet crystals of CoDMS1, Co(C₆H₈O₄)(H₂O), suitable for structure determination were made from a mixture of 2.5 mmol CoCl₂·6H₂O, 3.7 mmol 2,2-dimethylsuccinic acid and 6.2 mmol KOH in 9 ml deionized water. This mixture was placed in a 23 mL Teflon lined Parr autoclave and heated at 100 °C for 3 days, after which the resulting product was filtered off and washed with water. Increasing the reaction temperature to 150 °C and using half the quantity of the three reagents initially used resulted in the formation of purple blade crystals from which the structure of CoDMS2, Co₃(C₆H₈O₄)₂(OH)₂, was determined. A purer sample of this phase was subsequently made at 180 °C using the same concentrations and this was used for bulk analysis.

Heating a mixture of 2.5 mmol ZnCl₂, 3.7 mmol 2,2-dimethylsuccinic acid and 6.2 mmol KOH in 9 ml deionized water at 150 °C for three days, in a Teflon lined autoclave, lead to the formation of a pure phase of colourless block single crystals of ZnDMS, $Zn_7(C_6H_8O_4)_6(OH)_2$, suitable for structural determination. Single crystals of Li₂(C₆H₈O₄), LiDMS were synthesized by dissolving 0.5 mmol 2,2-dimethylsuccinic acid and 1.0 mmol lithium hydroxide monohydrate in minimal deionised water in a 8 ml borosilicate glass vial. Addition of 5 mL of ethanol resulted in a cloudy suspension, which became clear within minutes, and subsequent heating at 70 °C overnight yielded colourless rods, suitable for single crystal X-ray diffraction. A purer sample was synthesized for further analysis by combining a solution of 1.0 mmol 2,2-dimethylsuccinic acid in 5 ml ethanol with a solution of 2.0 mmol lithium acetate dihydrate in 5 ml ethanol and heating this subsequent mixture in an autoclave at 180 °C for 3 days, after which the resulting product was filtered and washed with ethanol. All phases synthesized in this work were dried at 60 °C for at least one hour after filtration.

Structural Determination

Single crystal X-ray diffraction data of all compounds were obtained using an Oxford Diffraction Gemini Ultra diffractometer using MoK_{α} radiation. This instrument was equipped with an Eos CCD detector and the crystals were mounted on a cryoloop. Data for all compounds were collected at temperatures close to 120 K. Absorption corrections were carried out using analytical methods implemented in Crysalis Pro for all compounds except LiDMS where empirical methods were employed.¹ The structures were solved by Patterson synthesis using DIRDIF 2008² except LiDMS where direct methods as implemented in SHELX-97³ were used. All subsequent refinements were carried out against $|F|^2$ using SHELX-97³ via the Win-GX interface (see Table S1 for summary of crystal data).⁴ The displacement parameters of all non-hydrogen atoms were refined anisotropically. Due to both twinning and the fragile sheet-like nature of LiDMS, substantial smearing of diffraction peaks could not be avoided leading to relatively low quality data. As a result it was necessary to constrain all lithium atoms, oxygen atoms, methyl carbons and other carbon atoms into different group and constrain these to have the same APD to achieve a stable refinement. The positions of the hydrogen atoms attached to the dicarboxylate ligands were geometrically constrained using the AFIX commands in SHELX-97. The hydroxy and aquo hydrogen atoms were readily located from the Fourier difference map and were restrained to have a bond distance of 0.85 Å to the oxygen atoms to which they are attached. The displacement parameters of the hydrogen atoms on the backbone of the ligand were constrained to be 1.2 times the size of the carbon to which they were attached, while those bonded to a methyl carbon or oxygen were fixed to be 1.5 times the atom to which they are bonded.

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Compound	CoDMS1	CoDMS2	ZnDMS	LiDMS	
Formula	$CoC_6H_{10}O_4$	$Co_3C_{12}H_{18}O_{10}$	$Zn_7C_{36}H_{50}O_{26}$	$Li_2C_6H_8O_4$	-
Formula Weight	221.08	499.06	1356.35	158.0	
T (K)	120(2)	121(2)	121(2)	120(2)	
Crystal System	Orthorhombic	Triclinic	Triclinic	Triclinic	
Space Group	<i>Cmca</i> (64)	<i>P</i> 1 (2)	<i>P</i> 1 (2)	<i>P</i> 1 (2)	
<i>a</i> (Å)	21.9175(12)	5.7864(2)	10.5108(8)	6.2511(6)	
<i>b</i> (Å)	10.2819(3)	12.1514(6)	11.5667(10)	9.8961(11)	
<i>c</i> (Å)	7.0879(3)	12.1524(7)	11.9714(10)	12.225(2)	
α (°)	90	73.604(5)	99.347(7)	101.862(13)	
β (°)	90	81.487(4)	114.566(8)	102.726(13)	
γ (°)	90	84.066(3)	106.545(7)	90.012(8)	
V (Å ³)	1597.28(12)	808.98(7)	1201.26(17)	721.11(16)	
Z	8	2	1	4	
$\rho_{calc} (g \text{ cm}^{-3})$	1.839	2.049	1.875	1.455	
μ (cm ⁻¹)	2.128	3.092	3.521	0.116	
Refl.	13031/1064	7261/3706	10975/5512	3459/2384	
Meas./Unique	$[R_{int} = 0.0563]$	$[R_{int} = 0.0289]$	$[R_{int} = 0.0268]$	[Merged data]	
Parameters Refined	Parameters 69 Refined		322	104	
$R1$, $wR2^{a}$ (all)	0.0564, 0.1295	0.0637, 0.1432	0.0361, 0.0576	0.1200, 0.2695	
$R1$, $wR2^{a}$ (obs)	0.0479, 0.1254	0.0533, 0.1370	0.0267, 0.0537	0.0910, 0.2523	
χ^2	1.160	1.146	1.027	1.009	
^a $w = 1/\left[\sigma^2 \left(F_o^2\right) + \left(a\right)\right]$	$(P)^2 + bP$ and	$P = \left(\max\left(F_o^2, 0\right) + 2F_c^2\right)$	$\left(\frac{1}{2}\right)/3; R1 = \sum \left\ F_{c}\right\ $	$ - F_c /\sum F_o $	and
$wR2 = \sqrt{\left\{\sum \left[w\left(F_o^2 - F_c^2\right)^2\right]\right\}}$	$\left[\frac{2}{2}\right] / \sum w \left(F_o^2\right)^2$				

Table S1 Crystallographic Data for structures determined by single crystal X-ray diffraction.

Col	DMS1	Co2-O14	2.163(4)	Zn2-O24	1.946(2)	Li1-08	2.004(11)
Co1-O2	2×2.025(2)	Co3-O1H	1.954(4)	Zn2-O1H	1.973(2)	Li2-02	1.887(12)
Co1-O1	2×2.066(2)	Co3-O13	1.972(4)	Zn2-O2	2.000(2)	Li2-07	1.969(12)
Co1-O1W	2.148(3)	Co3-O3	1.973(4)	Zn3-O1H	2×2.057(2)	Li2-O2	1.971(12)
Co1-O1W	2.274(3)	Co3-O2H	2.018(4)	Zn3-O23	2×2.072(2)	Li2-O3	1.988(11)
Col	DMS2	Co4-O2H	2× 2.066(4)	Zn3-O12	2×2.149(2)	Li3-O1	1.955(12)
Co1-O4	2×2.068(4)	Co4-O12	2× 2.073(4)	Zn4-O22	1.905(2)	Li3-07	1.989(11)
Co1-O1	2×2.090(4)	Co4-O14	2× 2.218(4)	Zn4-O21	1.929(2)	Li3-08	1.994(12)
Co1-O1H	2×2.094(4)	ZnDMS		Zn4-O4	1.974(2)	Li3-O6	2.017(10)
Co2-O2	2.028(4)	Zn1-O11	1.930(2)	Zn4-O13	1.978(2)	Li4-06	1.916(12)
Co2-O11	2.046(4)	Zn1-O1	1.944(2)	Li	DMS	Li4-O3	1.973(13)
Co2-O1H	2.084(4)	Zn1-O3	1.971(2)	Li1-04	1.898(12)	Li4-O4	1.985(11)
Co2-O2H	2.132(4)	Zn1-O1H	1.982(2)	Li1-05	1.950(12)	Li4-O1	2.089(10)
Co2-O3	2.139(4)	Zn2-O14	1.931(2)	Li1-O5	1.991(11)		

Table S2 Selected coordination bond distances (Å).

Infrared Spectroscopy

Infra-red spectra were collected between 4000 cm⁻¹ and 500 cm⁻¹ on a Bruker Tensor-27 ATR spectrometer. The spectrum of compound CoDMS2 has absorption bands at: v_{max}/cm^{-1} : 3587 and 3552 (OH), 2977, 2950, 2916 and 2870 (C-CH₃) 1620, 1585 and 1542 (v_{as} CO₂⁻); 1477 and1423 (v_s CO₂⁻) 1369, 1311, 1261 and 1218 (CH₂, CH₃ and C-O); 1161, 1134 and 1018

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(v_{as} C-C) and 991, 960, 945, 921, 891, 833, 787, 748, 720, 683, 648, 614 and 579 (metaloxygen bonding and C-H).⁵ The spectrum of compound ZnDMS has bands at: v_{max}/cm^{-1} : 3540 (OH, broad); 2997, 2970, 2927 and 2870 (C-CH₃); 1620, 1585 and 1542 (v_{as} CO₂⁻); 1477 and1423 (v_s CO₂⁻) 1369, 1311, 1261 and 1218 (CH₂, CH₃ and C-O); 1161, 1134 and 1018 (v_{as} C-C) and 991, 960, 945, 921, 891, 833, 787, 748, 720, 683, 648, 614 and 579 (metal-oxygen bonding and C-H). The spectrum of compound LiDMS has absorption bands at: v_{max}/cm^{-1} : 2970, 2904 and 2870 (C-CH₃); 1628, 1582 and 1562 (v_{as} CO₂⁻); 1470 and 1420 (v_s CO₂⁻); 1377, 1362, 1296, 1258 and 1211 (CH₂, CH₃ and C-O); 1173, 1134 and 1018 (v_{as} C-C); 988, 949, 922, 903, 841, 802, 741, 652 and 567 (metal-oxygen bonding and C-H).

Supplementary Figures



Fig. S1 X-ray diffraction pattern of a sample of ZnDMS indicating its purity, fitted using the Le Bail method as implemented in the program Rietica.⁶ The crosses, and upper and lower continuous lines are the experimental, calculated and difference profiles, respectively. The vertical markers indicate the allowed Bragg reflections and the inset shows the weaker reflections in more detail. The final R_p , R_{wp} and χ^2 values are 7.7 %, 14.4 % and 12.4 and the cell parameters were determined to be a = 10.5544(14) Å, b = 11.5823(9) Å, c = 12.0053(13) Å, $\alpha = 99.591(8)^\circ$, $\beta = 114.382(10)^\circ$ and $\gamma = 106.484(9)^\circ$.



Fig. S2 X-ray diffraction pattern of a sample of CoDMS2 indicating its purity, fitted using the Le Bail method as implemented in the program Rietica.⁶ The format is the same as in Fig. S1 and the arrows indicate the reflection revealing the presence of a small amount of phase CoDMS1. The final R_p , R_{wp} and χ^2 values are 10.4 %, 20.1 % and 27.1 and the cell parameters were determined to be a = 5.803(4) Å, b = 12.150(4) Å, c = 12.168(8) Å, $\alpha = 73.66(6)^\circ$, $\beta = 81.49(5)^\circ$ and $\gamma = 84.05(6)^\circ$.



Fig. S3 X-ray diffraction pattern of a sample of CoDMS1, synthesised at 75 °C, indicating its purity, fitted using the Le Bail method as implemented in the program Rietica.⁶ The format is the same as in Fig. S1 and the arrows indicate the reflection revealing the presence of an unknown impurity. The final R_p , R_{wp} and χ^2 values are 4.6 %, 8.8 % and 11.8 and the cell parameters were determined to be a = 22.131(10) Å, b = 10.381(8) Å and c = 7.061(9) Å.



Fig. S4 X-ray diffraction pattern of a sample of LiDMS indicating its purity, fitted using the Le Bail method as implemented in the program Rietica.⁶ The format is the same as in Fig. S1. The final R_p , R_{wp} and χ^2 values are 6.3 %, 9.4 % and 18.7 and the cell parameters were determined to be a = 6.2271(4) Å, b = 10.0146(7) Å, c = 12.3622(6) Å, $\alpha = 102.262(7)^\circ$, $\beta = 102.470(7)^\circ$ and $\gamma = 90.217(7)^\circ$.



Fig. S5 X-ray diffraction pattern of a sample obtained from nanosheets created from ZnDMS indicating its purity, fitted using the Le Bail method as implemented in the program Rietica.⁶ The format is the same as in S1. The final R_p , R_{wp} and χ^2 values are 8.2 %, 13.4 % and 25.4 and the cell parameters were determined to be a = 10.5499(14) Å, b = 11.5854(11) Å, c = 12.0048(16) Å, $\alpha = 99.595(10)^\circ$, $\beta = 114.395(11)^\circ$ and $\gamma = 106.465(9)^\circ$.



Fig. S6 X-ray diffraction pattern of a sample obtained from nanosheets created from LiDMS indicating its purity, fitted using the Le Bail method as implemented in the program Rietica.⁶ The format is the same as in S1. A comparison with Fig. S4 clearly indicates a significant increase in preferred orientation in the directions in which the nanosheet layers stack. The final R_p , R_{wp} and χ^2 values are 6.2 %, 11.3 % and 28.0 and the cell parameters were determined to be a = 6.2159(4) Å, b = 10.0124(4) Å, c = 12.3362(6) Å, $\alpha = 102.349(6)^\circ$, $\beta = 102.282(5)^\circ$ and $\gamma = 90.189(4)^\circ$.



Fig. S7 Weight, expressed as a percentage of initial weight, versus temperature for CoDMS1 determined using TGA. The inset shows the rate of change in weight with temperature.



Fig. S8 Weight, expressed as a percentage of intial weight, versus temperature for CoDMS2 determined using TGA. The inset shows the rate of change in weight with temperature.



Fig. S9 Weight, expressed as a percentage of initial weight, versus temperature for ZnDMS determined using TGA. The inset shows the rate of change in weight with temperature.



Fig. S10 Weight, expressed as a percentage of initial weight, versus temperature for LiDMS determined using TGA. The inset shows the rate of change in weight with temperature.



Fig. S11 Plot of χ ' and phase angle versus temperature for CoDMS2 measured from AC magnetic susceptibility measurements.



Fig. S12 Isothermal magnetisation of MnDMS measured at 1.9 K.



Fig. S13 Isothermal magnetisation of compound CoDMS2 measured at 15 K.

References

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