Supporting Information

X-ray diffraction

Room temperature powder X-ray diffraction (PXRD) data were initially collected in a Siemens D-5000 diffractometer using CuKα radiation (λ=1.5418 Å).

Further low temperature powder X-ray diffraction experiments were carried out in a Siemens D-500 using a stirling machine and CuKα radiation. The data were collected every 5 K from 275 to 255 K and every 30 or 25 K from 230 K down to 100 K.

The obtained PXRD patterns were analyzed by Le Bail refinement using the Rietica,[1] where the peak shapes were described by a pseudo-Voigt function and the background was modeled with an 6-term polynomial. Additionally, the PXRD patterns obtained at room temperature and 100 K were analyzed by Le Bail refinement using the GSAS and EXPGUI software,[2,3] where the peak shapes were described by a pseudo-Voigt function (CW profile function 3) and the background was modeled with an 4-term polynomial.

It should be indicated that the PXRD patterns of both phase I and II displayed marked preferential orientations: at the (12-5) and (012) diffraction peaks in the case of phase I, and along the families {h00} and {hkl} with h=k=l in the case of phase II.

Single-crystal X-ray diffraction data were collected between 295K and 100 K in a Bruker-Nonius x8 ApexII X-ray diffractometer equipped with a CCD detector and using monochromatic MoKα1 radiation (λ=0.71073 Å). For that experiment a suitable crystal of $[(CH_3)_2NH_2][Mg(HCOO)_3]$ was chosen and mounted on a glass fibber using instant glue. For the low temperature experiments, the crystal was cooled at a rate of 10K/min using a cold stream of nitrogen from a Kyroflex cryostream cooler. The data integration and reduction was performed using the Apex2 V.1.0-27 (Bruker Nonius, 2005) suite software. The intensity collected was corrected for Lorentz and polarization effects and for absorption by semiempirical methods on the basis of symmetry-equivalent data using SADABS (2004) of the suite software. The structures were solved by the direct method, and were refined by least squares method, on SHELXL-97 program[4]. To solve the structure, anisotropic thermal factors were employed for the non-H atoms. The hydrogen atoms of the formate ions were found in the Fourier map and their coordinates and isotropic thermal factors were refined. Meanwhile, the H-atoms of the DMA could not be found or added, presumably due to the disordered arrangement of this cation.

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[1] C.J. Howard, H. Hunter, B.A. Rietica, *A Computer Program for Rietveld Analysis of X-ray and Neutron Podwer Diffraction Patterns*, Australian Nuclear Science and Technology Organization Lucas Heights Research Laboratories.

[2] A.C. Larson, R.B. von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratories, Report LAUR 86-748, 1990.

[3] B.H. Toby, EXPGUI, a graphical user interface for GSAS, *J. Appl. Crystallogr.*, **2001**, 34, 210

[4] Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Analysis; University of Göttingen: Göttingen, Germany, 1997

Calorimetric properties

Differential scanning calorimetric (DSC) analyses were carried out in a TA Instruments MDSC Q-2000, with a liquid nitrogen cooling system, by heating/cooling the sample $[(CH_3)_2NH_2][Mg(HCOO)_3]$ at different rates (2.5–15 K/min) from 170 K up to 300 K under nitrogen atmosphere.

Raman spectroscopy

Powder Raman spectra were measured both at 300 K and at 100 K with a Renishaw inVia Raman microscope equipped with a CCD camera. Spectra were recorded over the wavenumber range of 50-3200 cm^{-1} using the linearly polarized 784 nm line of diode laser (with power of 150 mW), focused to a 65 µm spot through a 50x microscope objective onto the sample surface. A microcryostat from Linkam scientific instruments was used for the low temperature studies.

Elemental chemical analyses

Elemental chemical analyses for C, N and H were carried out using a FLASHEA1112 (ThermoFinnigan) Analyzer.

Element	Calculated	Obtained
N	6.8 %	6.6 %
C	29.3 %	29.1 %
H	5.4 %	5.2 %

Dielectric characterization

The complex dielectric permittivity of cold-press pelletized samples was measured as a function of frequency and temperature with a parallel-plate capacitor coupled to a Solartron 1260A Impedance/Gain-Phase Analyzer, capable of measuring in the frequency range 10 µHz to 32 MHz using an amplitude of 2 V. The capacitor was mounted in a Janis SVT200T cryostat refrigerated with liquid nitrogen, and with a Lakeshore 332 incorporated to control the temperature from 100 K up to 350 K. The data were collected upon heating the sample at an approximate rate of 0.8 K/min. The impedance analysis software SMART (Solartron Analytical) was used for data acquisition and processing.

For these studies pellets with an area of approximately 300 mm^2 and thickness of approximately 0.6 mm were used and Gold was sputtered on their surfaces to ensure a good electrical contact with the electrodes.

Impedance complex plane plots were analyzed using the LEVM program, a particular program for complex nonlinear least squares fitting. [5]

[5] J. Ross Macdonald, *LEVM version 8.0 Complex Nonlinear Squares Fitting Program*, 2003.

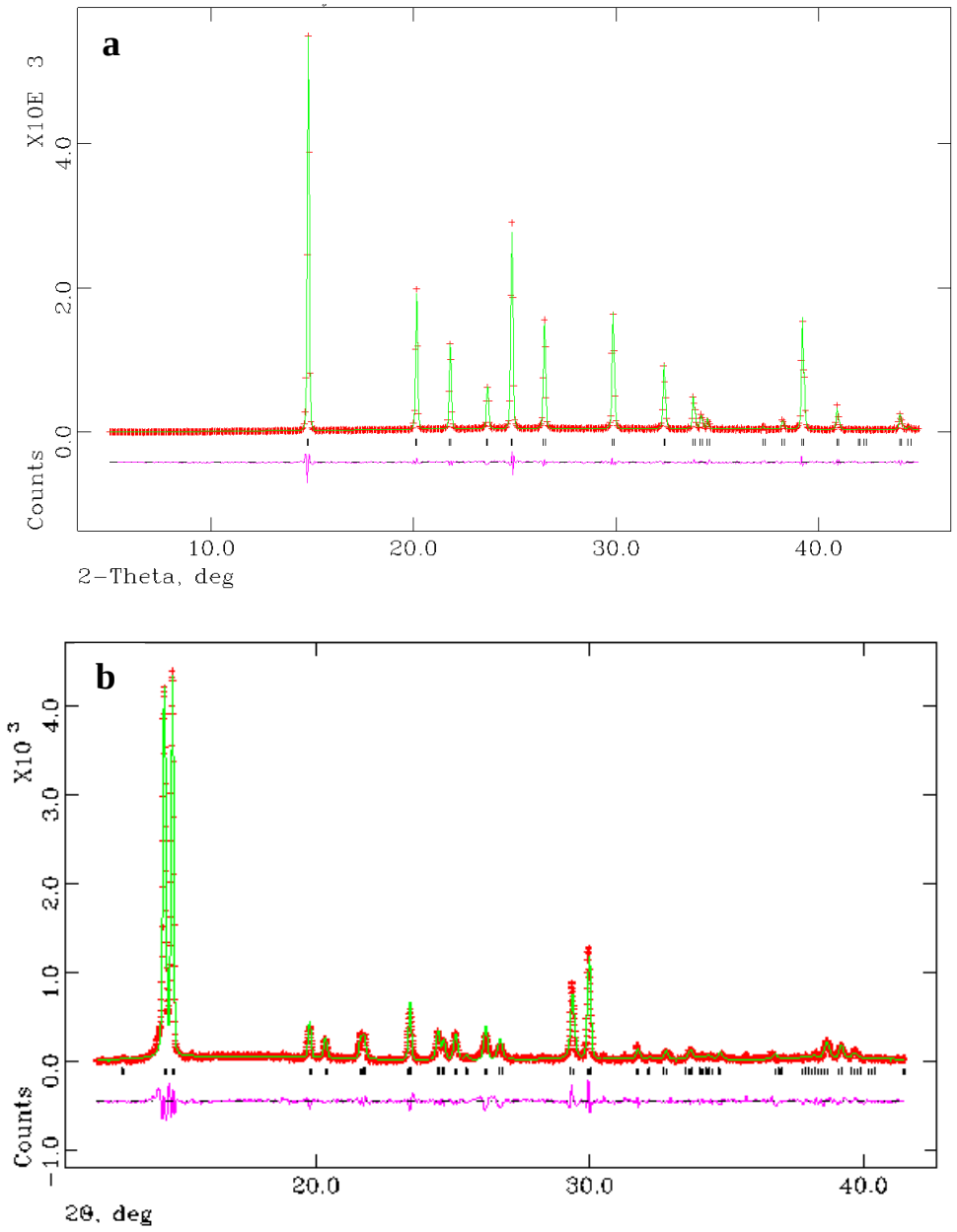

Figure S1. LeBail refinement of the (a) room temperature and (b) 100 K XRPD pattern. Key: observed data (+) and calculated profile (solid line); the difference plot is drawn below the profile. Tick marks indicate peak positions of the $[(CH_3)_2NH_2][Mg(HCOO)_3]$ phase.

Table SI. Data collection, cell and refinement parameters from the single-crystal X-ray diffraction study.

Chemical formula	$MgC_5H_{11}NO_6$
Formula Mass	205.46
Crystal system	Trigonal
a/Å	8.1421(2)
b/Å	8.1421(2)
c/Å	22.5820(12)
α/°	90.00
β/°	90.00
γ/°	120.00
Unit cell volume/Å^3	1296.48(8)
Temperature/K	293(2)
Space group	$R\bar{3}c$
No. of formula units per unit cell, *Z*	6
Radiation type	MoKα
Absorption coefficient, μ/mm^{-1}	0.204
No. of reflections measured	1989
No. of independent reflections	355
R_{int}	0.0455
Final R_1 values ($I > 2\sigma(I)$)	0.0383
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1080
Final R_1 values (all data)	0.0405
Final $wR(F^2)$ values (all data)	0.1101
Goodness of fit on F^2	1.226

Table SII. Selected bond lengths and bond angles from the single-crystal X-ray diffraction study at room temperature.

Bond Lengths (Å)	
Mg octahedra	
Mg-O1	2.089(1)
Formate	
C1-O1	1.235(2)
DMA	
C2-N1	1.417(4)
Bond Angles (degrees)	
Formate	
O1-C1-O1	127.1(2)
DMA	
C2-N1-C2	117.3(5)

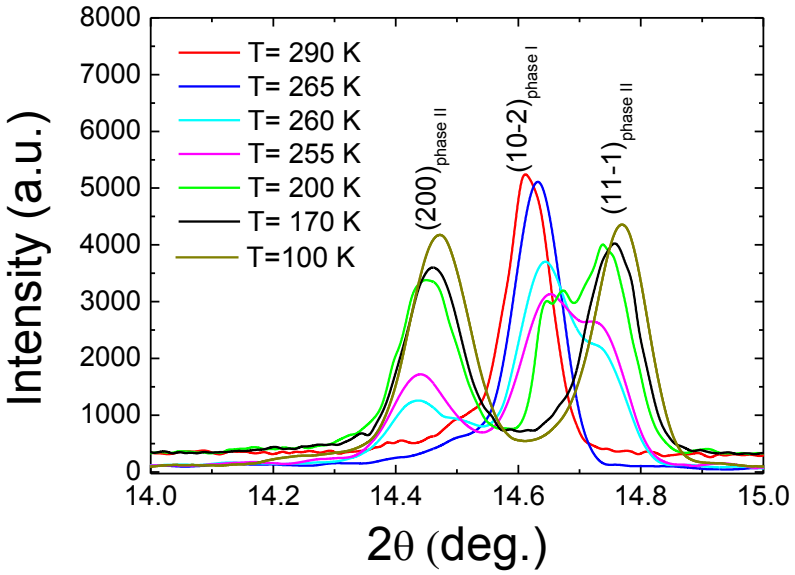

Figure S2. Details of the XRPD pattern obtained at different temperatures showing the structural evolution of the $[(CH_3)_2NH_2][Mg(HCOO)_3]$ compound as a function of temperature.

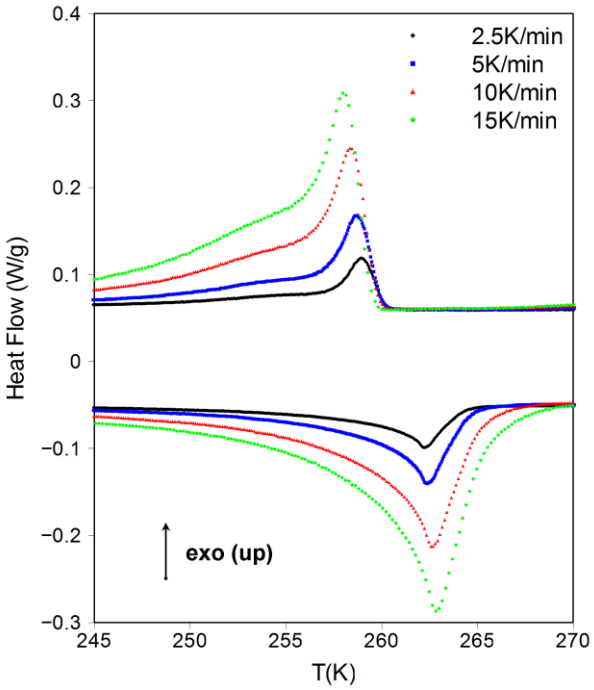

Figure S3. DSC results as a function of temperature obtained by heating and cooling $[(CH_3)_2NH_2][Mg(HCOO)_3]$ at different temperature rates (2.5-15 K/min).

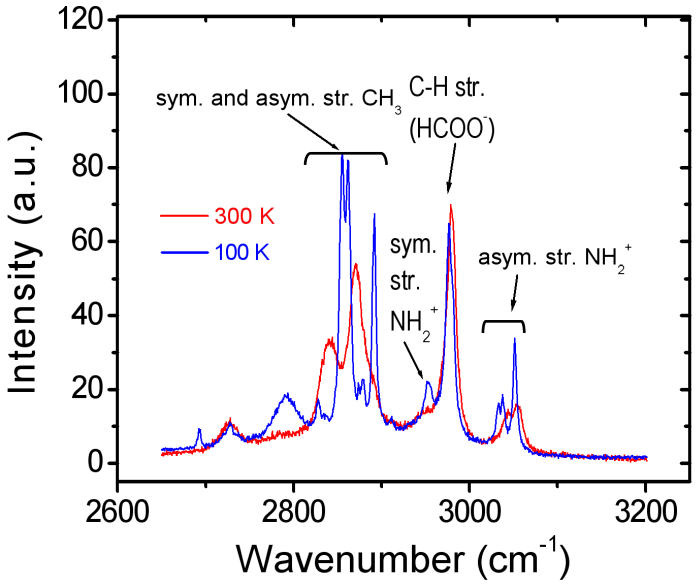

Figure S4. Detail of the Raman spectra results of $[(CH_3)_2NH_2][Mg(HCOO)_3]$, corresponding to the high wavenumber region at temperature of T=100K and 300 K.