



# Kent Academic Repository

Aston, J.C. and Saines, P.J. (2017) *Transition-Metal Dependent Cation Disorder in the Chiral Cubic AB(HCO<sub>2</sub>)<sub>3</sub> Metal-Organic Frameworks (A = Li or Na, B = Mn or Co)*. *Zeitschrift für Anorganische und Allgemeine Chemie*, 643 (4). pp. 287-293. ISSN 0044-2313.

## Downloaded from

<https://kar.kent.ac.uk/59778/> The University of Kent's Academic Repository KAR

## The version of record is available from

<https://doi.org/10.1002/zaac.201600350>

## This document version

Author's Accepted Manuscript

## DOI for this version

## Licence for this version

UNSPECIFIED

## Additional information

## Versions of research works

### Versions of Record

If this version is the version of record, it is the same as the published version available on the publisher's web site. Cite as the published version.

### Author Accepted Manuscripts

If this document is identified as the Author Accepted Manuscript it is the version after peer review but before type setting, copy editing or publisher branding. Cite as Surname, Initial. (Year) 'Title of article'. To be published in *Title of Journal*, Volume and issue numbers [peer-reviewed accepted version]. Available at: DOI or URL (Accessed: date).

## Enquiries

If you have questions about this document contact [ResearchSupport@kent.ac.uk](mailto:ResearchSupport@kent.ac.uk). Please include the URL of the record in KAR. If you believe that your, or a third party's rights have been compromised through this document please see our [Take Down policy](https://www.kent.ac.uk/guides/kar-the-kent-academic-repository#policies) (available from <https://www.kent.ac.uk/guides/kar-the-kent-academic-repository#policies>).

# Transition-Metal Dependent Cation Disorder in the Chiral Cubic $AB(\text{HCO}_2)_3$ Metal-Organic Frameworks (A = Li or Na, B = Mn or Co)

James C. Aston,<sup>[a]</sup> and Paul J. Saines<sup>\*[a]</sup>

We dedicate this, the first work from our group at the University of Kent, to Professor Anthony Cheetham on the occasion of his 70<sup>th</sup> birthday.

**Abstract:** This study examines the crystal structures of the  $AB(\text{HCO}_2)_3$  (where A = Li or Na and B = Mn or Co) metal-organic frameworks, which we find to adopt a chiral cubic  $P2_13$  structure. This shows that the Li containing formates are isostructural with their Na analogues, extending the phase stability of this chiral architecture. The Mn containing compounds have a magnetic sublattice similar to  $\beta$ -Mn, long of interest due to its highly frustrated antiferromagnetic coupling. In contrast the Co formates appear to have partially disordered alkali and transition metal cations, which prevents the formation of a clean  $\beta$ -Mn-like magnetic sublattice. We have also re-examined the magnetic properties of  $\text{NaMn}(\text{HCO}_2)_3$  finding it to be a simple paramagnet down to 2 K with only weak antiferromagnetic coupling.

## Introduction

Dense metal-organic frameworks (MOFs), have recently attracted great attention for their ability to exhibit functional magnetic and electronic properties more commonly associated with metal oxides.<sup>[1]</sup> The unusual architectures frameworks adopt to accommodate the shape of even small non-spherical ligands, however, can modify these properties in unusual ways.<sup>[1d, 1g, 1i, 2]</sup> This gives rise to unique routes to functional properties such as relaxor ferroelectrics,<sup>[3]</sup> multiferroics<sup>[1c, 1d]</sup> and guest-dependent magnetism<sup>[2a]</sup>. Amongst the most promising frameworks with such functionalities are the  $AB(\text{HCO}_2)_3$  frameworks, in which A is a monovalent alkali metal, ammonium or a protonated alkylamine and B is typically a first row transition metal.<sup>[1c, 1d]</sup> This family of frameworks is known to exhibit five different structure types with three dimensional covalent connectivity, all of which feature octahedral B-site cations linked in a corner-sharing fashion through the formate ligands, with the A-site typically sitting in channels found in these structures.<sup>[4]</sup>

While several of the  $AB(\text{HCO}_2)_3$  structure types are modifications of the well-known perovskite structures two unique chiral structures are formed only by this family.<sup>[4]</sup> Of these the chiral cubic structure forms when A = Na, the smallest A-site cation incorporated into the formate frameworks thus far.<sup>[5]</sup> This structure is best described as featuring an edge-sharing network of alkali and transition metal cations with octahedral coordination,

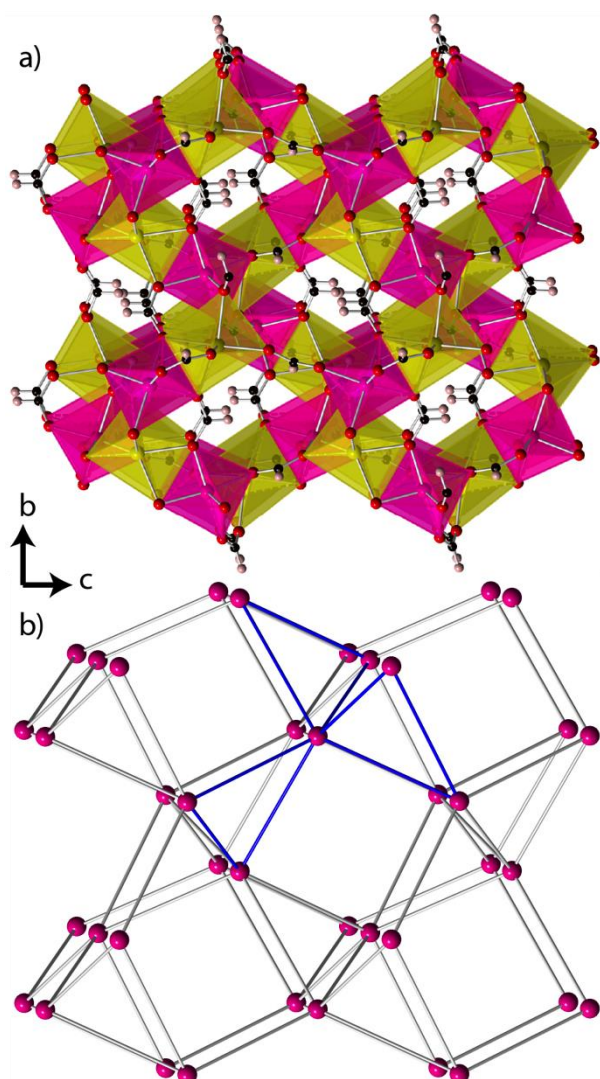
with each polyhedra connected to three others. This creates intersecting channels running along each crystallographic axis, which are occupied by the formate ligands (see Figure 1a). Two compounds with this structure type having been reported thus far,  $\text{NaMn}(\text{HCO}_2)_3$ <sup>[5a]</sup> and  $\text{NaCo}(\text{HCO}_2)_3$ <sup>[5b]</sup>. In the case of the Mn framework, which adopts  $P2_13$  symmetry, the A- and B-site cations are reported to order, as might be expected from the significant difference in their ionic radii. Examining the magnetic sublattice of the framework each Mn is at the centre of a windmill of equilateral triangles (see Figure 1b), with each triangle perpendicular to one of the  $\langle 111 \rangle$ -directions of the crystal structure. This is highly reminiscent of  $\beta$ -Mn, an elemental quantum spin liquid, whose magnetically active cations are reported to be arranged on a similar sublattice.<sup>[6]</sup>  $\beta$ -Mn has long been of interest for its surprisingly complex and unexplained magnetic phenomena, which includes large antiferromagnetic spin fluctuations<sup>[6a, 6b]</sup> and non-Fermi liquid behaviour<sup>[7]</sup>. Its highly unusual windmill magnetic topology, however, is very rare and cases with magnetic cations on this sublattice are almost exclusively limited to  $\beta$ -Mn and its various doped alloys.<sup>[8]</sup> The  $\text{NaMn}(\text{HCO}_2)_3$ <sup>[5a]</sup> framework is therefore interesting in that it achieves the same magnetic topology in a coordination framework, where naively, the structure formed might be expected to be more likely to be robust to significant changes in the B-site cation; this is typically found for the other architectures adopted by  $AB(\text{HCO}_2)_3$  frameworks.<sup>[4]</sup> This could allow  $\beta$ -Mn analogues to be formed with a wider range of paramagnetic cations with strongly frustrated magnetic coupling.

In contrast to  $\text{NaMn}(\text{HCO}_2)_3$  the previous report of  $\text{NaCo}(\text{HCO}_2)_3$ <sup>[5b]</sup> has it adopting  $I2_13$  symmetry, in which the Na and Co cations are completely disordered. This is a surprising result since that there is a larger size difference between Na and Co cations than in the  $\text{NaMn}(\text{HCO}_2)_3$  analogue (c.f. 1.02 Å for  $\text{Na}^+$  to 0.745 Å for  $\text{Co}^{2+}$  and 0.83 Å for  $\text{Mn}^{2+}$ )<sup>[9]</sup>, and  $d^7$   $\text{Co}^{2+}$  is likely to desire a more regular geometry than  $\text{Na}^+$  or  $d^6$   $\text{Mn}^{2+}$ . If the Co and Na cations are truly disordered this would prevent the magnetic cations in  $\text{NaCo}(\text{HCO}_2)_3$  from adopting the desired  $\beta$ -Mn-like magnetic topology. Given the potential interest in the precise arrangement of the magnetic cations in these frameworks we have reinvestigated the crystal structure of these Na compounds. We have also synthesised two new chiral cubic structures containing Li, showing that this structure can be stabilised with even smaller A-cations. We find that all four structures adopt a primitive  $P2_13$  cubic structure but that extensive disorder of the A- and B-site cations appears to occur in the Co compounds, preventing the formation of the clean, desired,  $\beta$ -Mn topology. In  $\text{LiCo}(\text{HCO}_2)_3$  the cations remain at least partially disordered, although the apparent extent of this decreases despite their more similar ionic radii. In contrast to the Co phases there is no

[a] Mr James C. Aston and Dr Paul J. Saines  
School of Physical Sciences  
University of Kent  
Ingram Building, Canterbury, CT2 7NH  
United Kingdom  
E-mail: P.Saines@kent.ac.uk

Supporting information for this article is given via a link at the end of the document.

indication of disorder in  $\text{NaMn}(\text{HCO}_2)_3$  or  $\text{LiMn}(\text{HCO}_2)_3$ , confirming the formation of two frameworks with  $\beta$ -Mn-like magnetic sublattices.



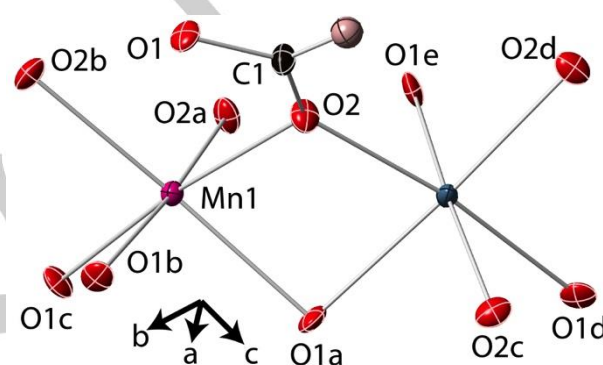
**Figure 1:** a) The structure of  $\text{NaMn}(\text{HCO}_2)_3$  with Na and Mn octahedra shown in gold and pink, respectively, and C, O and H atoms shown in black, red and pink. b) The Mn magnetic sublattice in  $\text{NaMn}(\text{HCO}_2)_3$ ; one unit in the windmill topology, which is reminiscent of  $\beta$ -Mn, is highlighted in blue.

## Results and Discussion

### Crystal Structures

All four compounds reported in this study were found to adopt a chiral cubic structure in  $P2_13$  (see Table 1 for crystallographic details), with a  $3^3 \cdot 5^6$  topology, as previously reported for  $\text{NaMn}(\text{HCO}_2)_3$ .<sup>[5a]</sup> They have the same asymmetric unit featuring a complete formate ligand and two cation sites (see Figure 2). The cations are in distorted octahedral geometries, each bonding to two crystallographically distinct oxygen anions. The extent to which the alkali and transition metals ordered on these sites,

however, varied very significantly between the four compounds. For  $\text{NaCo}(\text{HCO}_2)_3$  the presence of any cation order is in contrast with the previous report of Zhao *et al.*,<sup>[5b]</sup> who report this framework as adopting  $I2_13$  symmetry with complete disorder of the Na and Co cations. Reconstructed  $hkl$  images, however, reveal reflections of the type  $h+k+l = \text{odd}$ , which, although weak, are clearly present indicating the structure cannot be  $I$ -centred (see Figure 3 and Figure S1). Fascinatingly there are also additional weak reflections that may suggest the presence of a complex modulated structure with three different  $q$ -vectors, which ultimately refined to (0.345,0,0), (0,0.343,0) and (0,0,0.342). This is, to the best of our knowledge, the first report of a MOF featuring a modulated crystal structure, although there has been a previous report of a modulated magnetic structures in a Mn(succinate) framework<sup>[10]</sup>.



**Figure 2:** The asymmetric unit of  $\text{LiMn}(\text{HCO}_2)_3$  with thermal ellipsoids shown at 50% probability. Li is shown as dark blue and all other colours are as in Fig. 1. All non-hydrogen atoms are identified, with additional atoms shown to complete the coordination sphere of the Li and Mn atoms cations labelled alphabetically.

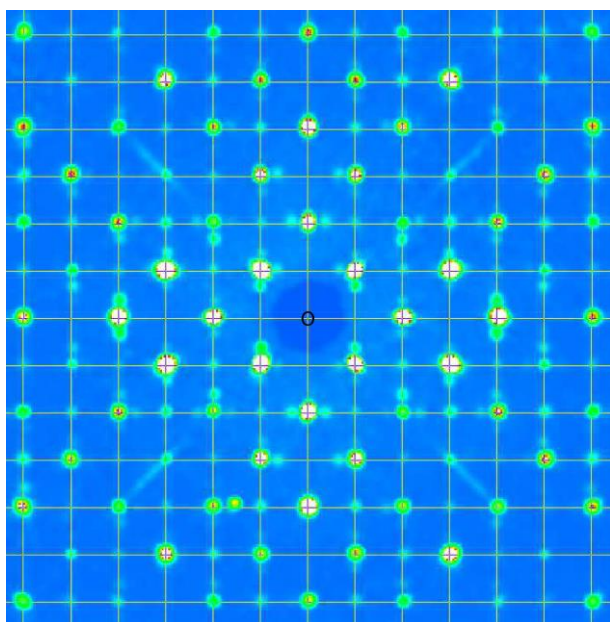
**Table 1:** Crystallographic data for the structures determined in this work by single crystal X-ray diffraction.

Compound	$\text{LiMn}(\text{HCO}_2)_3$	$\text{NaMn}(\text{HCO}_2)_3$	$\text{LiCo}(\text{HCO}_2)_3$	$\text{NaCo}(\text{HCO}_2)_3$
Formula	$\text{LiMnC}_3\text{H}_3\text{O}_6$	$\text{NaMnC}_3\text{H}_3\text{O}_6$	$\text{LiCoC}_3\text{H}_3\text{O}_6$	$\text{NaCoC}_3\text{H}_3\text{O}_6$
Formula Weight	196.93	212.98	200.92	216.97
T (K)	150(1)	150(1)	150(1)	120(1)
$\lambda$ (Å)	1.54184	0.71073	0.71073	0.71073
Crystal System	Cubic	Cubic	Cubic	Cubic
Space Group	$P2_13$	$P2_13$	$P2_13$	$P2_13$
a (Å)	8.75973(19)	9.14555(18)	8.5997(3)	8.96946(16)
V (Å <sup>3</sup> )	672.16(4)	764.94(3)	635.99(6)	721.60(4)
Z	4	4	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.946	1.849	2.098	1.997
$\mu$ (cm <sup>-1</sup> )	15.890	1.755	2.669	2.415
Refl.	643/365	2778/648	669/441	12199/673
meas./unique				
Rint	0.0314	0.0342	0.0347	0.0377
Parameters refined	34	34	35	35
$R_1$ , $wR_2^a$ (all)	0.0308, 0.0777	0.0231, 0.0452	0.0434, 0.1041	0.0365, 0.0702
$R_1$ , $wR_2^a$ (obs)	0.0303, 0.0767	0.0208, 0.0443	0.0421, 0.1027	0.0325, 0.0688
Goodness of Fit	1.165	1.077	1.130	1.173
Flack parameter	0.016(12)	-0.039(15)	-0.03(5)	0.004(19)

$$^a w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ and } P = (\max(F_o^2, 0) + 2F_c^2)/3; R_1 = \sum||F_o| - |F_c|| / \sum|F_o| \text{ and } wR_2 = \sqrt{[(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}$$

Attempts to solve the structure of  $\text{NaCo}(\text{HCO}_2)_3$  in an approximate commensurate superstructure with  $a \approx 27$  Å, unfortunately, were unsuccessful, likely because the modulated reflections are very

weak. We therefore refined the basic crystal structure as adopting  $P2_13$  symmetry, to establish the extent of cation ordering in this compound. This led to excellent fits to the data, which were optimised when partial order of the Co and Na cations is allowed for (*c.f.*  $R1$ ,  $wR2$  and goodness of fit values of 3.65 %, 7.02 % and 1.17 for a partially ordered model to 4.36 %, 7.36 % and 1.24 for a completely disordered model, which would be equivalent to  $I2_13$  symmetry). The B-site occupancy refined as 56.6(3) % Co with the remainder constrained to be occupied by Na and the A-site constrained to have opposite occupancies. The occupancy from a second crystal, which was collected at 150 K, was very similar, refining as 58.6(3) % and retained clear indications of the reflections indicative of a modulated crystal structure. Since the displacement parameters refined to sensible values it is most likely that the modulation in this structure is related to a more complex variation in the cation occupancy. There is also some evidence of diffuse scattering in the  $\langle 110 \rangle$ -directions of Figure 3, consistent with the presence of some disorder of the cations in this structure. Determining the precise cause of these weak, complex modulations is, however, beyond the scope of this work, whose focus was to establish whether this family of frameworks could be used to achieve clean  $\beta$ -Mn-like magnetic sublattices containing different cations.



**Figure 3:** A  $0kl$  reciprocal lattice image reconstructed from a full sphere of single crystal X-ray diffraction data with the origin of the image marked with an O. Inspection reveals weak reflections of the type  $h+k+l = \text{odd}$ , which breaks the I-centring conditions confirming the adoption of a primitive cell. Weak satellite peaks are evident near the most intense reflections, suggestive of a modulated structure.

The crystal structure determined for  $\text{LiCo}(\text{HCO}_2)_3$  showed that cation order in these materials are not complete, with 86.5(6) % of the A- and B-sites occupied by Li and Co, respectively; significant improvements were noted when using this model compared to that in which complete order is assumed (*c.f.*  $R1$ ,  $wR2$  and goodness of fit values of 4.21 %, 10.41 % and 1.13 to 7.57 %, 19.6 % and 1.19). Unlike  $\text{NaCo}(\text{HCO}_2)_3$  there was,

however, no indication of any satellite or other reflections that could not be accounted for in the  $P2_13$  structure. It is surprising that the cation order in  $\text{LiCo}(\text{HCO}_2)_3$  is apparently more complete than in  $\text{NaCo}(\text{HCO}_2)_3$ , given the smaller difference in ionic radii between Li and Co in the former (*c.f.* 0.76 Å for  $\text{Li}^+$  and 1.02 Å for  $\text{Na}^+$  to 0.745 Å for  $\text{Co}^{2+}$ ), although this may be partially a result of our study neglecting the structural modulations of  $\text{NaCo}(\text{HCO}_2)_3$ . Examination of the Mn frameworks, in contrast indicated that the order of the alkali and Mn cations in  $\text{NaMn}(\text{HCO}_2)_3$  and  $\text{LiMn}(\text{HCO}_2)_3$  is complete with no significant improvement in the fit achieved by allowing this to disorder. It is also important to note that, although the sample of  $\text{NaMn}(\text{HCO}_2)_3$  examined in this work was made under ambient conditions, the previous report of Paredes-García *et al.*,<sup>[5a]</sup> in which the same material was made under similar solvothermal conditions to those used for the other compounds in this work, did not indicate the presence of any cation disorder.

The confirmation of occupational disorder of the A- and B-site cations in the Co frameworks examined in this study is the first example of such disorder in the  $\text{AB}(\text{HCO}_2)_3$  frameworks.<sup>[4]</sup> This is likely made possible by the much smaller size of the alkali metals on the A-sites in these materials. The bond requirements of the alkali and transition metals, however, still remain significantly different, which can be probed by examining the bond valencies and distortions to coordination environments of these cations. The transition metal cations in  $\text{LiMn}(\text{HCO}_2)_3$ ,  $\text{NaMn}(\text{HCO}_2)_3$  and  $\text{LiCo}(\text{HCO}_2)_3$  have bond valencies of 2.08, 2.03 and 2.10, while the alkali cations in these materials have values of 1.00, 1.35 and 1.10, respectively (see Table 2 for bond distances and Table S1 for bond angles).<sup>[11]</sup> Extensively disordered  $\text{NaCo}(\text{HCO}_2)_3$ , however, has a much lower bond valency of 1.56 for Co on the B-site, which is a reflection that the environment calculated here is an average of close to a 50:50 mixture of Na and Co on the B-site in this structure. This is also reflected by the unphysically high bond valency of 2.09 for Na in this compound. Correspondingly the bond valencies of the A-site in this framework are calculated as 1.43 and 1.92 for Co and Na, respectively. This emphasises that despite the apparent disorder in  $\text{NaCo}(\text{HCO}_2)_3$  the local environment of these cations are likely to significantly deviate from those suggested by the local structure, which may also contribute to the structural modulation. The relative degree of distortions of the octahedra in these four frameworks can also be quantified as:

$$\Delta d = \frac{1}{n} \sum_n \left[ \frac{d_n - \langle d \rangle}{\langle d \rangle} \right]^2$$

where  $d_n$  is the bond distance for each M-O pair and  $\langle d \rangle$  is the average M-O bond.<sup>[12]</sup> For the ordered Mn containing frameworks the  $\Delta d$  for the Mn cations is much lower than for the alkali cations (*c.f.*  $6.36 \times 10^{-6}$  for Mn to  $6.29 \times 10^{-3}$  for Li in  $\text{LiMn}(\text{HCO}_2)_3$  and  $2.41 \times 10^{-6}$  for Mn to  $3.99 \times 10^{-5}$  for Na in  $\text{NaMn}(\text{HCO}_2)_3$ ). For  $\text{LiCo}(\text{HCO}_2)_3$  the  $\Delta d$  of the Co cations,  $9.11 \times 10^{-7}$ , is significantly lower than for  $\text{LiMn}(\text{HCO}_2)_3$ , as would be expected to maximise the ligand field stabilisation energy of the Co  $d^7$  cations. In contrast the  $\Delta d$  of the Co cations for the extensively disordered  $\text{NaCo}(\text{HCO}_2)_3$  is  $1.36 \times 10^{-4}$ , much higher than for any of the other transition metal sites. This is unlikely to reflect the local environment around each Co cation, which would be expected to

be much more regular octahedra. The  $\Delta d$  of the alkali cations in  $\text{LiCo}(\text{HCO}_2)_3$  and  $\text{NaCo}(\text{HCO}_2)_3$  are  $1.79 \times 10^{-4}$  and  $8.09 \times 10^{-5}$ .

**Table 2:** Selected bond distances (Å) in the  $\text{AB}(\text{HCO}_2)_3$  frameworks. A- and B-sites refers to those with majority alkali and transition metal cation occupancies, respectively. There are three symmetry equivalent bonds for each table entry.

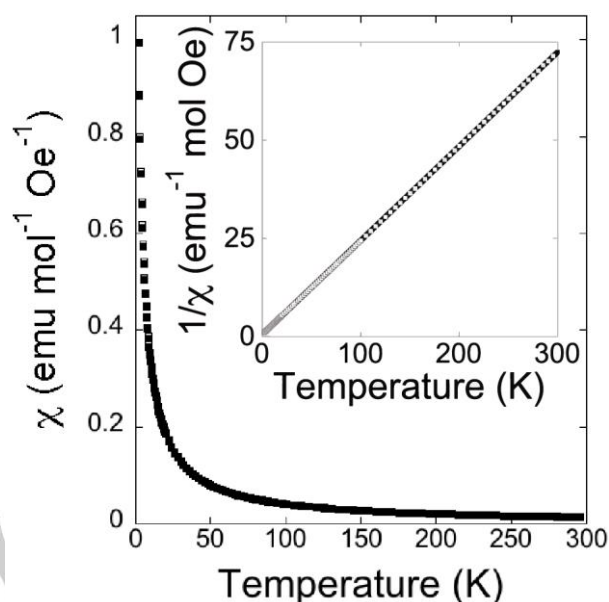
Bond	$\text{LiMn}(\text{HCO}_2)_3$	$\text{NaMn}(\text{HCO}_2)_3$	$\text{LiCo}(\text{HCO}_2)_3$	$\text{NaCo}(\text{HCO}_2)_3$
A-O1	2.186(7)	2.3664(16)	2.067(6)	2.243(3)
A-O2	2.079(6)	2.3367(15)	2.123(5)	2.203(3)
B-O1	2.176(3)	2.1875(15)	2.094(4)	2.165(3)
B-O2	2.187(3)	2.1943(15)	2.098(4)	2.216(3)

This work shows that the  $P2_13$  chiral cubic structure can be stabilised for the smaller Li A-site cations as well as for the Na containing frameworks. The relative cation size over which this architecture can be stabilised can be quantified using the tolerance factor for hybrid frameworks, recently derived by Kieslich *et al.*<sup>[13]</sup>,  $\alpha = (r_{A,eff} + r_{X,eff})/\sqrt{2}(r_B + 0.5h_{X,eff})$ , where  $r$  refers to the effective molecular or ionic radius of the A-site, B-site and X(anionic)-site while  $h_{X,eff}$  refers to the height of the anions in the direction between B-site cations. Calculating these values for the four frameworks examined in this study give tolerance factors of 0.56, 0.57, 0.59 and 0.60 for  $\text{LiMn}(\text{HCO}_2)_3$ ,  $\text{LiCo}(\text{HCO}_2)_3$ ,  $\text{NaMn}(\text{HCO}_2)_3$  and  $\text{NaCo}(\text{HCO}_2)_3$ , respectively<sup>1</sup>; 0.56 is the smallest tolerance factor for a  $\text{AB}(\text{HCO}_2)_3$  framework reported to date. Comparison with the behaviour of the remainder of the  $\text{AB}(\text{HCO}_2)_3$  frameworks,<sup>[4]</sup> suggests that this cubic phase is likely adopted by any other  $\text{AB}(\text{HCO}_2)_3$  frameworks that form with a tolerance factor in this range. Frameworks with tolerance factors significantly higher than 0.60 most likely give rise to the polar  $Pna2_1$  structure adopted by  $\text{NH}_4\text{Cd}(\text{HCO}_2)_3$ ,<sup>[14]</sup> which has a tolerance factor of 0.63; this has been referred to as the so-called Perovskite III structure, because of its resemblance to a perovskite phase with every second channel in the structure doubly occupied by the A-site cations. It is distinguished from the Perovskite II structure, that is formed over the 0.64–0.69 range, by its ligands binding in a completely *syn-anti* fashion,<sup>[15]</sup> as is found for the chiral cubic structure, suggesting this ligand binding motif is preferred for those structures with tolerance factors below 0.63.

### Magnetic Properties of $\text{NaMn}(\text{HCO}_2)_3$

As a bulk sample of  $\text{NaMn}(\text{HCO}_2)_3$  was made in close to pure form during this study we have re-examined the magnetic properties of this material. Previous studies by Paredes-García *et al.*<sup>[5a]</sup> have indicated significant divergence of field-cooled (FC) and zero-field cooled (ZFC) magnetic susceptibilities in fields below 1 kOe near 40 K, with maxima observed in susceptibilities at 22 and 34 K. On this basis they suggested  $\text{NaMn}(\text{HCO}_2)_3$  is likely a canted antiferromagnet, which would imply it had impressive magnetic ordering temperatures compared to related Mn formate frameworks, which typically order near 10 K.<sup>[4, 5c, 16]</sup> In contrast the work of Eikeland *et al.*<sup>[5c]</sup> suggests that  $\text{NaMn}(\text{HCO}_2)_3$  obeys Curie-Weiss law down to 2 K, indicating it remains paramagnetic even at very low temperatures, consistent with their Curie-Weiss constant of  $-0.91(6)$  K, which suggests that only very weak antiferromagnetic coupling is present. They, however, reported

that  $\text{NaMn}(\text{HCO}_2)_3$  has an unusually low effective magnetic moment of  $5.44 \mu_B$ .



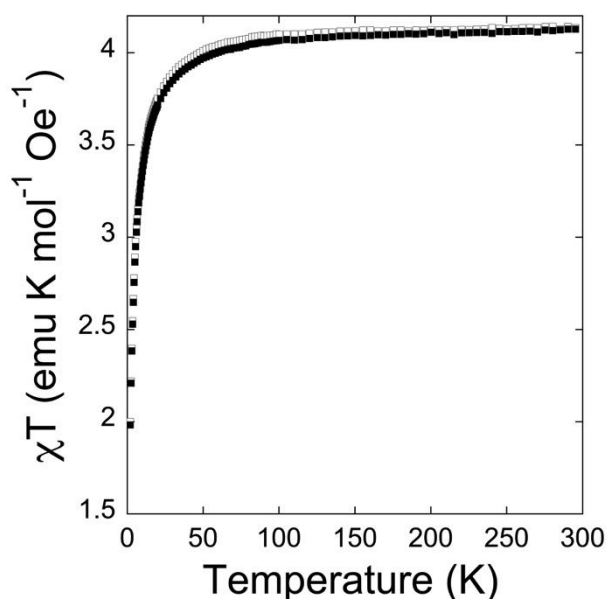
**Figure 4:** Plot of variable temperature magnetic susceptibility of  $\text{NaMn}(\text{HCO}_2)_3$  for 100 Oe FC (filled symbols) and ZFC (hollow symbols) measurements. The insert shows a Curie-Weiss fit to the inverse ZFC susceptibility.

Our re-examination of the magnetic properties of  $\text{NaMn}(\text{HCO}_2)_3$  via 100 Oe field cooled (FC) and zero-field cooled (ZFC) susceptibility measurements suggest that this compound is indeed paramagnetic down to 2 K (the lowest temperature examined), with no divergence noted between FC and ZFC measurements and Curie-Weiss paramagnetic behaviour maintained to 2 K (see Figure 4). The Curie-Weiss temperature obtained from fits to our data is  $-2.1$  K, broadly consistent with that suggested by Eikeland *et al.*<sup>[5c]</sup>, but we find that the effective magnetic moment derived from this fit is  $5.78 \mu_B$ , quite close to the spin only value of  $5.92 \mu_B$  for  $\text{Mn}^{2+}$ , which is typically observed for  $\text{Mn}^{2+}$ . We also note that  $\chi T$  shows only a gradual decrease from  $4.14 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$  at 300 K to around  $3.97 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$  at 50 K (see Figure 5).  $\chi_{\text{M}}T$  then decreases rapidly, but smoothly below that consistent with increasingly significant antiferromagnetic coupling at low temperatures but with no indication of any phase transitions. This is in contrast to the behaviour reported by Paredes-García *et al.*<sup>[5a]</sup>, which shows clear indications of abrupt changes and divergence in  $\chi_{\text{M}}T$  below 50 K. On this basis we would suggest that the indications of canted antiferromagnetic behaviour in this material measured by Paredes-García *et al.*<sup>[5a]</sup> are likely caused by a ferromagnetic impurity. The unusually low effective magnetic moment measured by Eikeland *et al.*<sup>[5c]</sup> may similarly arise from the presence of a small amount of an impurity or be caused by an increase in the Mn oxidation of their sample from  $\text{Mn}^{2+}$  to  $\text{Mn}^{2.5+}$ . The later would

<sup>1</sup> Note that for consistency with previously reported tolerance factor calculations for this family of compounds we have used the ionic radii of the high spin state

six-coordinate transition metals and eight coordinate ionic radii for the alkali metals.

be highly unusual as mixed valence frameworks are particularly rare.



**Figure 5:** Plot of  $\chi T$  versus temperature for of  $\text{NaMn}(\text{HCO}_2)_3$  from 100 Oe FC and ZFC measurements. The format is the same as Figure 4.

Unfortunately the potential for forming well ordered magnetic  $\beta$ -Mn-like sublattices in the  $\text{AB}(\text{HCO}_2)_3$  chiral cubic frameworks, which initially appeared the most interesting aspect of this structure, are restricted to only Mn. That the Co analogues exhibit extensive cation disorder and Ni frameworks of this type do not form, at least during our study, indicates this family of Li and Na compounds are unlikely to be successful routes to forming  $\beta$ -Mn magnetic sublattices with cations other than Mn. Why well ordered sublattices of this type only form when Mn cations occupy the B-site is unclear since it is unlikely that the magnetic interactions that play a critical role in stabilising  $\beta$ -Mn itself are significant enough to play an equivalent role in the framework analogues.<sup>[17]</sup> Furthermore this study also confirms that while the magnetic coupling in  $\text{NaMn}(\text{HCO}_2)_3$  is antiferromagnetic it is relatively weak. This would require it to be cooled to below 0.2 K to confirm if it is magnetically frustrated, which is experimentally challenging to achieve.

## Conclusions

We have examined the structures of the  $\text{AB}(\text{HCO}_2)_3$  (A = Li or Na and B = Mn or Co) frameworks, shining new light on the structures of the Na compounds and determining the crystal structures of the Li analogues for the first time. We find that all four structures adopt  $P2_13$  chiral cubic structures with a  $3^3 \cdot 5^6$  topology, expanding this architecture to frameworks with lower tolerance factors. The Mn compounds both feature a fully ordered  $\beta$ -Mn-like magnetic sublattice but extensive disorder of the alkali and transition metal cations in the Co-containing samples prevent these materials

from being a route to expanding these highly frustrating topologies to other cations. This disorder may be responsible for the observed incommensurate modulations in the crystal structure of  $\text{NaCo}(\text{HCO}_2)_3$ , which is extremely rare in metal-organic frameworks. Our re-examination of the magnetic properties of  $\text{NaMn}(\text{HCO}_2)_3$  indicates it features only weak antiferromagnetic coupling.

## Experimental Section

All reagents used in this work were obtained commercially and used without further purification except methanol, which was dried over evacuated 3A molecular sieves.  $\text{NaMn}(\text{HCO}_2)_3$  was synthesised by a method similar to Eikeland et al.<sup>[5c]</sup> In a typical synthesis 10 mL of 0.6 M NaOH (Fisher Scientific, Laboratory Grade) and 1.4 M  $\text{H}_2\text{CO}_2$  (Acros Organics, 98 % purity) methanol solution were placed at the bottom of a tall glass vial with 10 mL of 0.2 M  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (Acros Organics, 99 %) methanol (Fisher Scientific, Analytical Grade) solution placed on top. This leads to the formation of colourless block crystals within a week, which were recovered by filtration and washed with methanol. This method was also attempted for Co and Ni containing phases but lead to the formation of the known  $\text{A}_2(\text{HCO}_2)_4(\text{H}_2\text{O})_4$  phases, instead.<sup>[18]</sup>

The other three samples synthesised during this study were made under mild solvothermal conditions via a modification of the method of Zhao et al.<sup>[5b]</sup> In this approach 1 mmol  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Sigma Aldrich, 97 %) or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Acros Organics, 99 %), 1 mmol NaOH or LiOH (Alfa Aesar, 98 %) and 1 mmol  $\text{H}_2\text{CO}_2$  were added to a 25 mL autoclavable glass jar containing 10 mL N,N-dimethylformamide (DMF, Fisher Scientific, Laboratory Grade) and heated to 140 °C at a rate of 10 °/minute. After heating at this temperature for 72 hours the jars were then cooled back to room temperature slowly over a period of 12 hours to encourage crystallisation, which yielded single crystals suitable for analysis by single crystal diffraction. It should be mentioned that for  $\text{NaCo}(\text{HCO}_2)_3$  the crystals used were obtained from a reaction in which the quantity of reagents and solvent used was tripled and carried out in a 100 mL autoclavable jar. Extensive attempts to synthesise Ni containing analogues of these phases using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 98 %) as a starting material were also unsuccessful.

Single crystal structure determinations were carried out using a dual source Rigaku Oxford Diffraction Supernova equipped with Mo  $K\alpha$  and Cu  $K\alpha$  micro-focus sources (0.8 kV, 50 mA), with multi-layered focusing optics and an Atlas S2 CCD detector. Samples were cooled using an Oxford Cryosystems cryostream with the samples held on MiTeGen micro loops. Data were integrated and absorption corrections performed using CrysAlisPro software suite version 171.38.41<sup>[19]</sup> using direct methods in SHELXS<sup>[20]</sup> or SHELXT<sup>[21]</sup> and least-squares refinements carried out using SHELXL-2014<sup>[22]</sup> via the Olex2 graphical user interface<sup>[23]</sup> (deposited in the CCDC as entries 1505569-1505572). The displacement parameters of non-hydrogen atoms were refined anisotropically and hydrogen atom positions located geometrically using the AFIX commands in SHELX-2014, with their displacement parameters constrained to 1.2 times that of the carbon on which they rode. Where cation disorder was found to occur cations sharing the same site were constrained to occupy the same position and equal displacement parameters, via the EXYZ and EADP commands in SHELX-2014. These disordered site were constrained to be fully occupied with equal amounts of both metals present, as required for charge balance in the absence of significant levels of defects.

Powder diffraction patterns to assess sample purity were collected using a Rigaku Miniflex utilising Cu K $\alpha$  radiation (40 kV, 15 mA) and a D/teX Ultra detector. Rietveld fits, carried out using the programme Rietica<sup>[24]</sup>, confirmed that NaMn(HCO<sub>2</sub>)<sub>3</sub> was made with only a small amount of Mn<sub>2</sub>(HCO<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>, with phase fractions of 96.4(5) % and 3.65(16) %, respectively (see Figure S2). Mn<sub>2</sub>(HCO<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub> only orders weakly antiferromagnetically below 3.7 K and we see no clear indication of this in our susceptibility data.<sup>[25]</sup> Unfortunately, and in contrast to the results reported by Zhao *et al.*<sup>[5b]</sup> for NaCo(HCO<sub>2</sub>)<sub>3</sub>, hydrothermal synthesis lead to samples with significant unidentifiable impurities for all three frameworks. Magnetic property measurements of NaMn(HCO<sub>2</sub>)<sub>3</sub> were carried out using a MPMS-7 Quantum Design magnetometer. The sample was held in a gelatin capsule mounted inside a pierced straw with a uniform diamagnetic background.

**Keywords:** Cation Ordering • Magnetic Properties • Metal-organic framework • X-ray diffraction

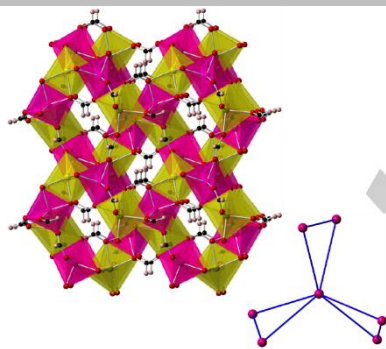
- [1] a) C. N. R. Rao, A. K. Cheetham, A. Thirumurugan, *J. Phys.: Condens. Matter* **2008**, *20*, 083202; b) M. Kurmoo, *Chem. Soc. Rev.* **2009**, *38*, 1353-1379; c) G. Rogez, N. Viart, M. Drillon, *Angew. Chem. Int. Ed.* **2010**, *49*, 1921-1923; d) Z. Wang, K. Hu, S. Gao, H. Kobayashi, *Adv. Mater.* **2010**, *22*, 1526-1533; e) G. Givaja, P. Amo-Ochoa, C. J. Gomez-Garcia, F. Zamora, *Chem. Soc. Rev.* **2012**, *41*, 115-147; f) P. J. Saines, M. Steinmann, J.-C. Tan, W. Li, P. T. Barton, A. K. Cheetham, *Inorg. Chem.* **2012**, *51*, 11198-11209; g) G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison, M. Evangelisti, *Adv. Mater.* **2013**, *25*, 4653-4656; h) F.-S. Ke, Y.-S. Wu, H. Deng, *J. Solid State Chem.* **2015**, *223*, 109-121; i) P. J. Saines, J. A. M. Paddison, P. M. M. Thygesen, M. G. Tucker, *Mater. Horiz.* **2015**, *2*, 528-535.
- [2] a) Z. Wang, B. Zhang, H. Fujiwara, H. Kobayashi, M. Kurmoo, *Chem. Commun.* **2004**, 416-417; b) M. Kurmoo, H. Kumagai, K. W. Chapman, C. J. Kepert, *Chem. Commun.* **2005**, 3012-3014.
- [3] a) G.-C. Xu, W. Zhang, X.-M. Ma, Y.-H. Chen, L. Zhang, H.-L. Cai, Z.-M. Wang, R.-G. Xiong, S. Gao, *J. Am. Chem. Soc.* **2011**, *133*, 14948-14951; b) B. Zhou, Y. Imai, A. Kobayashi, Z.-M. Wang, H. Kobayashi, *Angew. Chem. Int. Ed.* **2011**, *50*, 11441-11445.
- [4] S. M. Bovill, P. J. Saines, *CrystEngComm* **2015**, *17*, 8319-8326.
- [5] a) V. Paredes-García, A. Vega, M. A. Novak, M. G. F. Vaz, D. A. Souza, D. Venegas-Yazigi, E. Spodine, *Inorg. Chem.* **2009**, *48*, 4737-4742; b) J.-P. Zhao, S.-D. Han, R. Zhao, Q. Yang, Z. Chang, X.-H. Bu, *Inorg. Chem.* **2013**, *52*, 2862-2869; c) E. Eikeland, N. Lock, M. Filsø, M. Stingaciu, Y. Shen, J. Overgaard, B. B. Iversen, *Inorg. Chem.* **2014**, *53*, 10178-10188.
- [6] a) Y. Kohori, Y. Noguchi, T. Kohara, *J. Phys. Soc. Jpn.* **1993**, *62*, 447-450; b) H. Nakamura, K. Yoshimoto, M. Shiga, M. Nishi, K. Kakurai, *J. Phys.: Condens. Matter* **1997**, *9*, 4701; c) J. A. M. Paddison, J. R. Stewart, P. Manuel, P. Courtois, G. J. McIntyre, B. D. Rainford, A. L. Goodwin, *Phys. Rev. Lett.* **2013**, *110*, 267207.
- [7] J. R. Stewart, B. D. Rainford, R. S. Eccleston, R. Cywinski, *Phys. Rev. Lett.* **2002**, *89*, 186403.
- [8] M. Miyakawa, R. Y. Umetsu, M. Ohta, A. Fujita, K. Fukamichi, T. Hori, *Phys. Rev. B* **2005**, *72*, 054420.
- [9] R. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751-767.
- [10] P. J. Saines, J. R. Hester, A. K. Cheetham, *Phys. Rev. B* **2010**, *82*, 144435.
- [11] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192-197.
- [12] J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, M. T. Fernández-Díaz, *Inorg. Chem.* **2000**, *39*, 917-923.
- [13] G. Kieslich, S. Sun, A. K. Cheetham, *Chem. Sci.* **2014**, *5*, 4712-4715.
- [14] L. C. Gómez-Aguirre, B. Pato-Doldán, A. Stroppa, S. Yáñez-Vilar, L. Bayarjargal, B. Winkler, S. Castro-García, J. Mira, M. Sánchez-Andújar, M. A. Señaris-Rodríguez, *Inorg. Chem.* **2015**, *54*, 2109-2116.
- [15] Z. Duan, Z. Wang, S. Gao, *Dalton Trans.* **2011**, *40*, 4465-4473.
- [16] a) Z. Wang, B. Zhang, K. Inoue, H. Fujiwara, T. Otsuka, H. Kobayashi, M. Kurmoo, *Inorg. Chem.* **2007**, *46*, 437-445; b) B. Liu, R. Shang, K.-L. Hu, Z.-M. Wang, S. Gao, *Inorg. Chem.* **2012**, *51*, 13363-13372.
- [17] D. Hobbs, J. Hafner, *J. Phys.: Condens. Matter* **2001**, *13*, L681.
- [18] a) L.-P. Sun, S.-Y. Niu, J. Jin, G.-D. Yang, L. Ye, *Eur. J. Inorg. Chem.* **2006**, *2006*, 5130-5137; b) A. S. Kotovaya, S. G. Shova, E. I. Melnik, Y. A. Simonov, A. P. Gulya, E. Pahontu, *Russ. J. Coord. Chem.* **2013**, *39*, 23-32.
- [19] *CrysAlis PRO* version 171.38.41, Agilent Technologies, Yarnton, Oxfordshire, England, **2016**.
- [20] G. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.
- [21] G. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3-8.
- [22] G. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.
- [23] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
- [24] B. A. Hunter, C. J. Howard, Lucas Heights Laboratories, **1998**.
- [25] D. G. Kellerman, Y. A. Barykina, K. A. Zheleznikov, A. P. Tyutyunnik, V. N. Krasilnikov, *Phys. Status Solidi B* **2016**, In Press DOI: 10.1002/pssb.201600107.

**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

**FULL PAPER**

The  $AB(\text{HCO}_2)_3$  frameworks containing Li and Na adopt a chiral cubic structure with  $P2_13$  symmetry. The Mn compounds have a magnetic lattice very similar to highly frustrated  $\beta$ -Mn but this is not the case for the Co frameworks due to cation disorder

*James Aston, Paul J. Saines\****Page No. – Page No.****Title**

Layout 2:

**FULL PAPER**

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

*Author(s), Corresponding Author(s)\****Page No. – Page No.****Title**

Text for Table of Contents



ARTICLE

---

Additional Author information for the electronic version of the article.

Author: ORCID identifier  
Author: ORCID identifier  
Author: ORCID identifier

WILEY-VCH

---