

## COMMUNICATION

Tilting and twisting in a novel perovzalate,  $\text{K}_3\text{NaMn}(\text{C}_2\text{O}_4)_3$ <sup>†</sup>Xiaolong He,<sup>a,d,‡</sup> Xinyuan Zhang,<sup>c,‡</sup> Bifa Ji<sup>a,c</sup>, Wenjiao Yao,<sup>a\*</sup> Philip Lightfoot,<sup>b\*</sup> Yongbing Tang<sup>a,d,e,f\*</sup>

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

**In the title compound, the oxalate ligand simultaneously bridges both Mn-centred and Na-centred octahedra to produce a unique ‘doubly-interpenetrated’ perovskite-like lattice with an unconventional octahedral tilt system. In turn, the coordination requirements of the oxalate ligand lead to a rare ‘twisted’ conformation.**

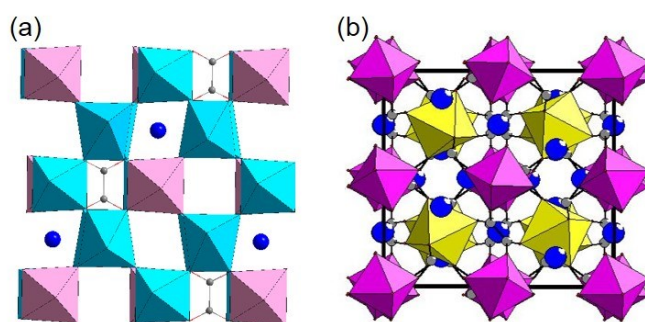
The field of ‘molecular’ and ‘hybrid’ perovskites has blossomed in recent years. Specifically, whilst retaining the basic  $\text{ABX}_3$  stoichiometry of traditional inorganic perovskites and 3D connectivity of linked  $\text{BX}_6$  octahedra, a diverse range of substitutions have been shown to be possible at the A, B and X sites.<sup>1–3</sup> For example, polyatomic anions such as formate, cyanide, thiocyanate and hypophosphite have been shown to act as the X linker, allowing larger molecular (generally organic) cations to occupy the A-site. In addition to the obvious compositional variations that this allows, a particular feature of these new classes of perovskite is their enhanced structural flexibility and diversity. Thus, ‘tilting’ of the octahedral  $\text{BX}_6$  units, a well-established feature of traditional inorganic perovskites, is now more flexible, since the X ligands here are extended ‘linkers’ rather than simply single-atom ‘pivots’. In a 2D sheet of rigid octahedral units linked by a single atom, rotation of one octahedral unit necessitates correlated anti-rotation of all adjoining octahedra within the layer.<sup>4</sup> This is no longer a strict requirement for rigid multi-atom linkers, and so-

called ‘forbidden’ or ‘unconventional’ tilt systems have recently been recognised and classified.<sup>5–7</sup> We shall refer to these as unconventional tilts.

A new family of perovskite-related compounds, ‘perovzalates’ with compositions  $\text{ALi}_3\text{M}(\text{C}_2\text{O}_4)_3$  [ $\text{A}^{\text{I}} = \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{M}^{\text{II}} = \text{Fe}, \text{Co}, \text{Ni}$ ], has recently been identified.<sup>8–10</sup> These are unusual in having the oxalate ligand acting effectively as a single-atom bridge between neighbouring octahedral centres, despite its multi-atom nature, to produce a genuine analogue of traditional oxide perovskites, with an infinitely-connected  $[\text{BO}_3]$  framework (Fig. 1a).

In this paper we introduce a new variant on the perovzalate theme, but here the oxalate ligand acts solely as a multi-atom linker between adjacent octahedral centres. Despite the similarities in stoichiometry to the original perovzalate family, this is therefore a distinct structure type. There are also similarities, but important and unique differences, to the hybrid perovskites based on molecular linkers such as formate, hypophosphite etc.

$\text{K}_3\text{NaMn}(\text{C}_2\text{O}_4)_3$  (**1**) was prepared during our exploratory searches for new oxalate-based materials as prospective cathodes for alkali-metal batteries.<sup>11–16</sup> The crystal structure was



**Fig. 1** (a) Structure of  $\text{KLi}_3\text{M}(\text{C}_2\text{O}_4)_3$ ;  $\text{LiO}_6$  octahedra in blue,  $\text{MO}_6$  octahedra in rose – note there are direct B-O-B links (b) Unit cell of **1**, showing  $\text{MnO}_6$  octahedra in pink,  $\text{NaO}_6$  octahedra in yellow and K atoms as blue spheres. Here, the inter-octahedral links are B-O-C-C-O-B.

<sup>a</sup> Functional Thin Films Research Center, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China. E-mail: wj.yao@siaat.ac.cn; tangyb@siaat.ac.cn

<sup>b</sup> School of Chemistry and EaStChem, University of St Andrews, St Andrews, Fife, KY16 9ST, UK. E-mail: pl@st-andrews.ac.uk

<sup>c</sup> Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystals, Tianjin University of Technology, Tianjin 300384, China.

<sup>d</sup> Nano Science and Technology Institute, University of Science and Technology of China, Suzhou 215123, China.

<sup>e</sup> Shenzhen College of Advanced Technology, University of Chinese Academy of Sciences, Shenzhen 518055, China.

<sup>f</sup> Key Laboratory of Advanced Materials Processing & Mold, Ministry of Education, Zhengzhou University, Zhengzhou 450002, China

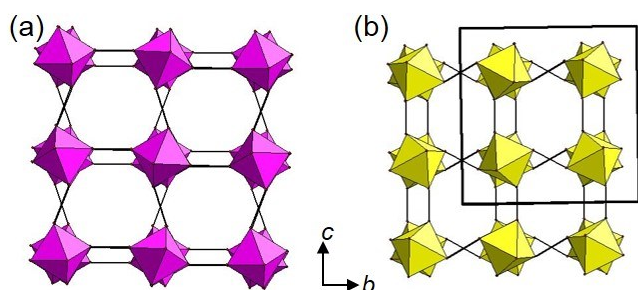
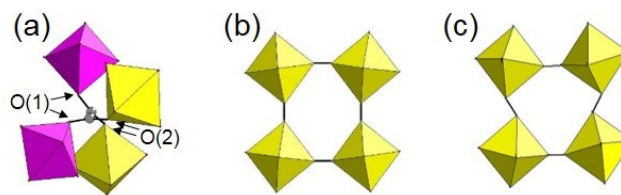
<sup>†</sup> Electronic Supplementary Information (ESI) available: Synthesis, single crystal X-ray diffraction, crystallographic data (CIF). CCDC 1953145 (**1**)

<sup>‡</sup> These authors contributed equally to this work.

**Table 1** Crystallographic data for **1**

Formula	$K_3NaMn(C_2O_4)_3$
CSD number	1953145
Temperature (K)	293
Mr (g/mol)	1837.16
Crystal system	cubic
Space group	$Ia\bar{3}$ (No. 206)
Unit cell parameters	$a = b = c = 13.4567(3) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
$V (\text{\AA}^3)$	2436.78(16)
Z	2
$F(000)$	1800
$\rho_{\text{calc}} (\text{g/cm}^3)$	2.504
$\theta$ range ( $^\circ$ )	3.71–30.75
Index ranges	$-14 \leq h \leq 18, -19 \leq k \leq 19, -12 \leq l \leq 19$
No. of reflections	8690
No. of refined parameters	619
R (all data)	0.0215/0.0576
Final R [ $I > 2\sigma(I)$ ]	0.0208/0.0573
Goodness-of-fit on $F^2$	1.232

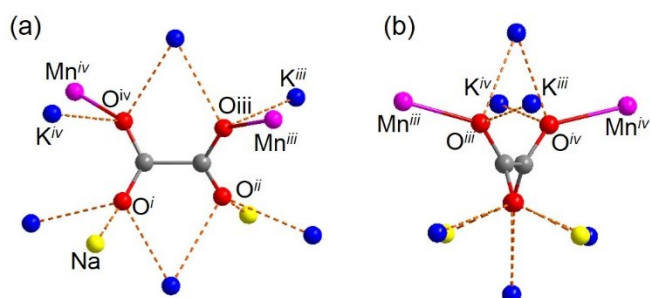
determined by single crystal X-ray diffraction (Table 1). Further synthetic and crystallographic details are given in ESI†. Compound **1** crystallises in the cubic space group  $Ia\bar{3}$  (No. 206). The crystal structure is shown in Fig. 1b. The unit cell is doubled along each cell edge relative to the aristotype cubic  $ABX_3$  perovskite, thus having eight times the unit cell volume. The structure is composed of Mn-centred octahedra with only slight distortions from ideality. On first inspection, these may be regarded as the perovskite-like B-sites, which are bridged to neighbouring  $MnO_6$  octahedra via oxalate ligands through *cis*-O-C-C-O pathways (*cis*-bi-monodentate coordination mode)<sup>17</sup> to form the  $[BX_3]$  framework. Closer inspection reveals how the alkali metals are accommodated into this expanded perovskite-like framework. The true beauty of the structure is revealed when one realises that the  $Na^+$  cation effectively occupies the position that would normally be regarded at the perovskite A-site (in the body-centre of each of the eight minicubes in the supercell), but

**Fig. 2** The two interpenetrating perovskite-like (*pcu*) sublattices (a) Mn-oxalate (b) Na-oxalate. The oxalate linkers are drawn in simplified form as rigid rods.**Fig. 3** (a) The oxalate environment in *cis*-bi-monodentate mode viewed almost along the C-C bond, showing the twisted conformation. Schematic representations of (b) conventional and (c) unconventional tilts.

it is not in the normal 12-coordinate environment. Instead, it occupies an octahedral site, directly comparable to that of Mn! By plotting the Mn-oxalate and Na-oxalate sublattices and representing the O-C-C-O bridges as direct links between adjacent octahedra (Fig. 2(a,b)) this stark similarity can be easily seen. The coordination mode of oxalate is the same in both sublattices, involving O(1) linkage to Mn and corresponding O(2) linkage to Na (Fig. 3a).

The coordination requirements enforced on the oxalate ligand itself, being common to both sublattices, lead to an unusual ‘twisted’ conformation of this ligand, discussed later.

The whole framework can be regarded as consisting of two topologically-equivalent, interpenetrated perovskite-like networks (*pcu* nets)<sup>18</sup>, with the oxalate ligand common to both. The  $K^+$  ions are placed on all the ‘faces’ of each of the minicubes, but they are displaced from the face-centres to allow suitable coordination to oxalate (eight-coordinate K), leading to the overall 3:1 K/Na composition. An additional key feature of the structure is the tilting of  $MnO_6$  and  $NaO_6$  octahedra, seen in Figs. 1 and 2. Again, each of these polyhedra behaves in the same way in this respect: adjacent octahedra of each type are tilted in anti-phase relative to each other looking along each of the three cubic axes (e.g., the *a*-axis in Fig. 2). This might be expected to lead to a Glazer-like<sup>4</sup> tilt system  $a^-a^-a^-$  for each set of octahedra, but the true situation is more complicated. For example, looking horizontally in Fig. 2a (along the *b*-axis) the tilt system is ‘conventional’, whereas looking vertically the tilt system is ‘unconventional’, with all octahedra tilting in the same sense. Simplified schematic plots of the distinction between the two types of tilt are shown in Fig. 3. Boström and co-workers<sup>6,7</sup> have identified and classified the various tilt modes available in these flexibly-hinged systems; in addition to the two well-known types of conventional tilt (in-phase and out-of-phase) there are four generic types of unconventional tilt (two distinct options for both in-phase and out-of-phase). The unconventional mode in **1** can be described, in the language of symmetry-mode analysis,<sup>19</sup> with the label  $M_5^+$ . Boström<sup>7</sup> suggests that this type of tilt is very rare, but it has been seen in much lower-symmetry variants, such as hypophosphites and formates containing organic cations at the perovskite A-site. However, **1** is a unique example of the highest possible symmetry for this type of structural distortion in a case with two distinct octahedral sites. On the contrary, the in-phase unconventional tilt type is somewhat more common, and its highest symmetry variant (space group  $Pa\bar{3}$ ) has been seen, for



**Fig. 4** Environment of the oxalate group in **1** (a) Front view, (b) side view.

example, in the 3D hybrid perovskite [PPN]Cd[Ag(CN)<sub>2</sub>]<sub>3</sub>·3EtOH<sup>20</sup> and in (CN<sub>3</sub>H<sub>6</sub>)<sub>3</sub>VF<sub>6</sub>, where the octahedra are isolated but effectively ‘linked’ by hydrogen bonds<sup>21</sup>. None of the previous examples exhibit the feature of dual interpenetration described here. As suggested above, the strict coordination requirements of the oxalate group in **1**, needing to simultaneously satisfy the unconventional tilting of both types of octahedra, in addition to the bonding around K<sup>+</sup>, put considerable strain on this anion, resulting in a non-planar conformation with O–C–C–O torsion angles of about 50.5 and 52.4°.

Oxalate has two ideal conformers: planar, point group  $D_{2h}$  and twisted,  $D_{2d}$ , conformation. The barrier to rotation around the long C–C single bond between the two carboxy groups is quite weak, in fact comparable to that in ethane.<sup>22</sup> The  $D_{2d}$  conformer is reported to be dominant in diluted solutions, whereas in crystalline chemistry, ‘crystal-packing’ forces: electrostatic effects, hydrogen bonding,  $\pi$ – $\pi$  stacking, and steric hindrance effects encourage the existence of the  $D_{2h}$  conformation.<sup>23</sup> Such is the case for most of the known oxalate complexes with alkali, alkaline earth, and/or transition metal ions as charge-balancing cations. The oxalate group in Cs<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>24</sup> is noteworthy for adopting a ‘staggered’ conformation with an O–C–C–O torsion angle  $\sim 81^\circ$ . Considering the title compound, the environment of each O atom of the oxalate group is illustrated in Fig. 4. Attractions to O<sup>*i*</sup> and O<sup>*ii*</sup> are similar to each other, whereas those to O<sup>*iii*</sup> and O<sup>*iv*</sup> are quite different, as reflected by respective values of corresponding bond valence (Mn–O bond length 2.216 Å corresponds to a bond valence of 0.367, K–O bond length 2.936 Å corresponds to a bond valence of 0.114, Na–O bond length 2.382 Å corresponds to a bond valence of 0.209).<sup>25</sup> Accordingly, O<sup>*iii*</sup> and O<sup>*iv*</sup> displace towards left and right, respectively. The displacements of O<sup>*iii*</sup> and O<sup>*iv*</sup> from the plane result in the deformation of the oxalate group from a planar motif and the final torsion angles of 50.5 and 52.4°.

In summary, we have isolated a unique new variant on the perovskite structure. K<sub>3</sub>NaMn(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> exhibits several new structural features, *viz.* unconventional octahedral tilting, interpenetration of two topologically identical perovskite-like frameworks and an unusual, twisted conformation of the oxalate ligand. In contrast to most of the previously known perovskites with multi-atom X linkers, a molecular species is not required at the A-site. Moreover, the oxalate ligand can now be added to the

list of molecular anions which can support the formation of ‘molecular’ perovskites. Moreover, all previous examples of molecular perovskites have employed only bidentate linkers; hence, additional degrees of freedom and structural opportunities should be possible by the use of the tetradentate oxalate ligand. It would be of interest to explore other possible combinations of cations, perhaps including small molecular species, to extend the chemistry of this new family. It is also of note that a higher-symmetry version of this structure type, space group  $Ia\bar{3}d$ , is also feasible. This requires the two distinct octahedral cation sites to become equivalent, leading to a *bcs* net,<sup>18</sup> which may be possible either by disorder of the monovalent/divalent cations at the Na and Mn sites, which has been reported in related systems with formate linkers,<sup>26</sup> or by deliberate design of a composition containing exclusively monovalent or divalent cations at the octahedral sites, with consequent charge balance being required at the K-sites, or by some other mechanism. Analysis of compound **1** in two space groups based on single crystal and powder XRD confirmss unambiguously the  $Ia\bar{3}$  structure rather than  $Ia\bar{3}d$  (ESI†). Comparisons of the *pcu* and *bcs* nets are provided in Figure S4, ESI†. The potential for new physical properties in related systems, perhaps aimed towards ferroic or multiferroic behaviour,<sup>6</sup> should also be considered.

We acknowledge support from National Natural Science Foundation of China (22005329, 51822210, 51972329), Newton International Fellowships Alumni 2018/2019 (AL\180020, AL\191011), Key Area Research and Development Program of Guangdong Province (2019B090914003), Shenzhen Science and Technology Planning Project (Nos. JCYJ20190807172001755, JCYJ20180507182512042), and Science and Technology Planning Project of Guangdong Province (2019A1515110975, 2019A1515011902).

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- (a) E. Sletten and L. H. Jensen, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1973, **29**, 1752–1756; (b) Z. Wang, B. Zhang, T. Otsuka, K. Inoue, H. Kobayashi and M. Kurmoo, *Dalton Trans.*, 2004, 2209–2216.
- Y. Wu, S. Shaker, F. Brivio, R. Murugavel, P. D. Bristowe and A. K. Cheetham, *J. Am. Chem. Soc.*, 2017, **139**, 16999–17002.
- (a) G. Thiele and D. Messer, *Z. Anorg. Allg. Chem.*, 1980, **464**, 255–267; (b) M. J. Cliffe, E. N. Keyzer, M. T. Dunstan, S. Ahmad, M. F. L. De Volder, F. Deschler, A. J. Morris and C. P. Grey, *Chem. Sci.*, 2019, **10**, 793–801.
- A. M. Glazer, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **28**, 3384–3392.
- (a) S. G. Duyker, J. A. Hill, C. J. Howard, A. L. Goodwin, *J. Amer. Chem. Soc.*, 2016, **138**, 11121–11123; (b) C. J. Howard, R. L. Withers, K. S. Knight, Z. Zhang, *J. Phys.: Condens. Matter*, 2008, **20**, 135202.
- H. L. B. Boström, M. S. Senn and A. L. Goodwin, *Nat. Commun.*, 2018, **9**, 2380.
- H. L. B. Boström, *CrystEngComm.*, 2020, **22**, 961–968.

8. W. J. Yao, Y. Y. Guo and P. Lightfoot, *Dalton Trans.*, 2017, **46**, 13349.
9. R. Clulow, A. J. Bradford, S. L. Lee and P. Lightfoot, *Dalton Trans.*, 2019, **48**, 14461.
10. H. Y. He, W. J. Yao, S. Tunmee, X. L. Zhou, B. F. Ji, N. Z. Wu, T. Y. Song, P. Kidkhunthod and Y. B. Tang, *J. Mater. Chem. A.*, 2020, **8**, 9128–9136.
11. W. J. Yao, A. R. Armstrong, X. L. Zhou, M. T. Sougrati, P. Kidkhunthod, S. Tunmee, C. H. Sun, S. Sattayaporn, P. Lightfoot, B. F. Ji, C. L. Jiang, N. Z. Wu, Y. B. Tang & H. M. Cheng, *Nat. Commun.*, 2019, **10**, 3483.
12. T. Y. Song, W. J. Yao, P. Kidkhunthod, Y. P. Zheng, N. Z. Wu, X. L. Zhou, S. Tunmee, S. Sattayaporn, and Y. B. Tang, *Angew. Chem. Int. Ed.*, 2020, **59**, 740–745.
13. Y. Q. Lan, W. J. Yao, X. L. He, T. Y. Song & Y. B. Tang, *Angew. Chem. Int. Ed.*, 2020, **59**, 9255–9262.
14. B. F. Ji, W. J. Yao, Y. P. Zheng, P. Kidkhunthod, X. L. Zhou, S. Tunmee, S. Sattayaporn, H. M. Cheng, H. Y. He & Y. B. Tang, *Nat. Commun.*, 2020, **11**, 1225.
15. J. H. Cai, Y. Q. Lan, H. Y. He, X. Y. Zhang, A. R. Armstrong, W. J. Yao, P. Lightfoot & Y. B. Tang, *Inorg. Chem.*, 2020, **59**, 16936–16943.
16. W. K. Wang, B. F. Ji, W. J. Yao, X. Y. Zhang, Y. P. Zheng, X. L. Zhou, P. Kidkhunthod, H. Y. He & Y. B. Tang, *Sci. China Mater.*, 2020, 10.1007/s40843-020-1512-0.
17. H. Liu, W. Gu, G. Xu, Y. Feng, Y. Kou, L. Feng, S. Yan, D. Liao, P. Cheng, *Inorg. Chem. Commun.*, 2007, **10**, 1099–1101.
18. O. Delgado-Friedrichs, M. D. Foster, M. O’Keeffe, D. M. Proserpio, M. M. J. Treacy, O. M. Yaghi, *J. Solid State Chem.*, 2005, **178**, 2533–2554.
19. B. J. Campbell, H. T. Stokes, D. E. Tanner and D. M. Hatch, *J. Appl. Crystallogr.*, 2006, **39**, 607–614.
20. J. A. Hill, A. L. Thompson and A. L. Goodwin, *J. Am. Chem. Soc.*, 2016, **138**, 5886–5896.
21. C. Black and P. Lightfoot, *Acta Crystallogr., Sect. C: Struct. Crystallogr. Cryst. Chem.*, 2017, **73**, 244–246.
22. P. A. W. Dean, *J. Chem. Educ.*, 2012, **89**, 417–418.
23. (a) M. J. S. Dewar and Y. J. Zheng, *J. Mol. Struct. Theochem.*, 1990, **209**, 157–162. (b) G. Marinescu, M. Andruh, F. Lloret, M. Julve, *Coord Chem Rev.*, 2011, **255**, 161–185.
24. R. E. Dinnebier, S. Vensky, M. Panthöfer, M. Jansen, *Inorg. Chem.*, 2003, **42**, 1499–1507.
25. N. E. Brese and M. O’Keeffe, *Acta Crystallogr, Sect B: Struct Sci.*, 1991, **47**, 192–197.
26. J. C. Aston, P. J. Saines, *Z. Anorg. Allg. Chem.*, 2017, **643**, 287–293