Topotactic Lithium Exchange in Manganese(III) Arsenate Hydrate: a Switchable Jahn–Teller Distorted Framework

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The topotactic lithium exchange reaction of $MnAsO_4 \cdot H_2O$ with $LiNO_3$ at 200 °C to give $LiMnAsO_4(OH)$ is accompanied by a drastic change in the framework geometry, resulting from an unusual switch in the Jahn–Teller distortion of the $Mn^{III}O_6$ octahedra from having four short Mn–O(As) and two long $Mn–OH_2$ bonds to having two short and two long Mn–O(As) bonds plus two intermediate Mn–OH bonds in the lithium derivative, suggesting that frameworks containing Jahn–Teller ions might have potential as flexible host materials.

Reactions involving the exchange or insertion of alkali metal cations into the channels or between the layers of suitable precursor structures are of interest both in the search for new battery materials,[1] ionic exchangers[2] and conductors,[3] and for the structural and electronic changes induced in the host material. As part of this effort, the exchange of acidic protons with metal cations in solid oxo-salts has been extensively studied.[4] We have recently reported the synthesis, characterisation, and structure of a new compound, manganese(III) arsenate hydrate $MnAsO_4 \cdot H_2O$,[5] and in this communication we describe the topotactic lithium exchange reaction of this material and the large structural changes undergone by the framework.

Polycrystalline, dark-green $MnAsO_4 \cdot H_2O$ was prepared as previously described.[5] An intimate mixture of solid $LiNO_3$ and $MnAsO_4 \cdot H_2O$ in a 4 : 1 molar ratio was heated at 200 °C for 3 weeks in air, and the product was then washed with dilute nitric acid and water and dried at 60 °C. Chemical analysis of

the yellow residue showed it to be $LiMnAsO_4(OH)$.† The X-ray diffraction (XRD) profile of this novel compound was recorded on a Siemens D501 powder diffractometer between 15 and 130° 2θ in 0.04° steps, counting for 15 s per point, using graphite-monochromated Cu-Kα radiation.

The complex XRD pattern of $LiMnAsO_4(OH)$ was auto-indexed[6] on a primitive triclinic unit cell‡ that can be transformed to a C-centred triclinic cell with parameters $a =$

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† Mn, As and H_2O were analysed as described elsewhere[5] and the lithium content was determined by atomic emission spectro-photometry. Observed [and calculated for $LiMnAsO_4(OH)$] results: Li : As ratio = 0.96 [1.0], Mn oxidation state = +3.1 [+3.0] and H_2O content = 7.9% [7.3%].

‡ The conventional, primitive triclinic unit cell for $LiMnAsO_4(OH)$ has parameters $a = 5.271(1)$, $b = 5.593(4)$, $c = 7.243(3)$ Å, $\alpha = 110.08(3)$, $\beta = 75.57(4)$ and $\gamma = 78.41(3)°$.

(a)

(b)
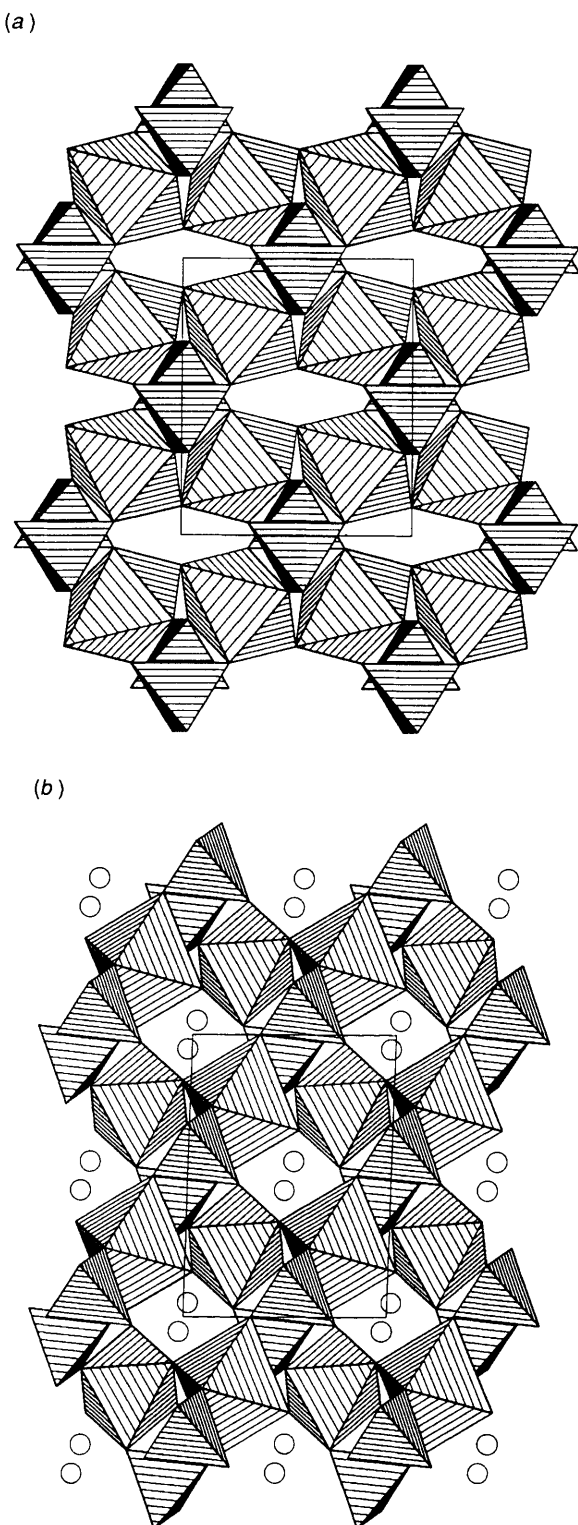
Fig. 1 Polyhedral (001) views (b-axis vertical) of (a) MnAsO$_4$·H$_2$O, and (b) LiMnAsO$_4$(OH) with lithiums shown as open circles. Hydrogen atoms are not included.

6.871, b = 8.421, c = 7.243 Å, α = 94.21, β = 118.14, and γ = 86.50°, similar to those of monoclinic MnAsO$_4$·H$_2$O (a = 7.031, b = 7.825, c = 7.466 Å, α = 90, β = 112.14, γ = 90°). This suggested that the exchange of lithium for hydrogen is topotactic, so we attempted to fit the X-ray profile of LiMnAsO$_4$(OH) by the Rietveld method[7] with the GSAS program,[8] using the coordinates of MnAsO$_4$·H$_2$O[5] as a starting model but lowering the space group symmetry from

(a)

(b)
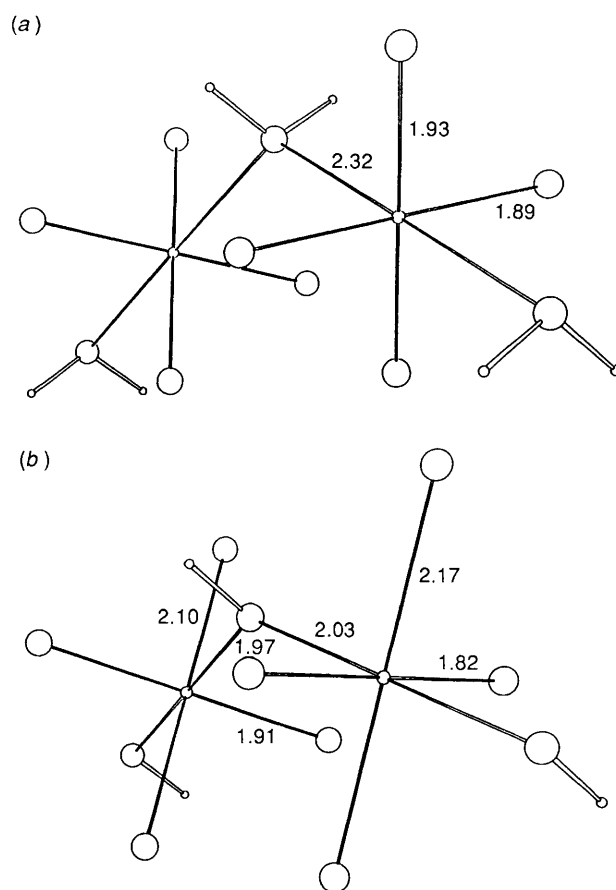
Fig. 2 The linking of Jahn–Teller distorted MnO$_6$ octahedra through (a) water molecules in MnAsO$_4$·H$_2$O, and (b) hydroxy groups in LiMnAsO$_4$(OH), with Mn–O distances in Å labelled. The hydrogen atom in the latter structure was not located but has been shown for clarity.

monoclinic $C2/c$ to triclinic $C\bar{1}$. Refinement of the MnAsO$_5$ framework proved successful, and a bond valence calculation[9] for these atoms showed an anomalously low valence sum for O(2b), enabling us to locate Li in the small channels close to this atom. Finally Li and all of the framework atoms were refined independently giving a good fit to the profile.§ It was not possible to locate the remaining H atom, but the bond valence calculations showed that it is attached to O(3), as are those in MnAsO$_4$·H$_2$O,[5] confirming that the lithium derivative is correctly formulated as an arsenate hydroxide rather than as a hydrogenarsenate oxide. A neutron study will be performed to locate the hydrogen atom precisely.

Polyhedral representations of the MnAsO$_4$·H$_2$O and LiMnAsO$_4$(OH) structures are shown in Fig. 1. MnO$_6$ octahedra linked through *trans*-vertices by H$_2$O or OH$^-$ groups form infinite zigzag chains in the [101] direction that are interconnected by AsO$_4$ tetrahedra, resulting in a three-dimensional framework. Small channels run parallel to the c-axis into which the hydrogen atoms project and in which the lithium ions are located.

Comparison of the bond distances in the two compounds (Table 1) reveals a surprising change in the Jahn–Teller distortion of the MnO$_6$ octahedra, as illustrated in Fig. 2. In

Table 1 Bond distances (Å) in $MnAsO_4 \cdot H_2O^5$ and $LiMnAsO_4(OH)$ with estimated standard deviations in parentheses[a]

$MnAsO_4 \cdot H_2O$		$LiMnAsO_4(OH)$			
Mn–O(1) × 2	1.891(5)	Mn(a)–O(1a) × 2	1.908(8)	Mn(b)–O(1b) × 2	1.821(9)
Mn–O(2) × 2	1.934(4)	Mn(a)–O(2b) × 2	2.104(9)	Mn(b)–O(2a) × 2	2.168(9)
Mn–O(3) × 2	2.320(4)	Mn(a)–O(3) × 2	1.966(11)	Mn(b)–O(3) × 2	2.026(10)
Mean Mn–O	2.048(4)	Mean Mn(a)–O	1.99(1)	Mean Mn(b)–O	2.00(1)
As–O(1)× 2	1.687(5)	As–O(1a)	1.630(8)		
		As–O(1b)	1.711(9)		
As–O(2) × 2	1.665(4)	As–O(2a)	1.607(10)		
		As–O(2b)	1.693(10)		
Mean As–O	1.676(5)	Mean As–O	1.66(1)		
		Li–O(1a)	2.49(4)	Li–O(1b)	2.33(3)
		Li–O(2b)	1.84(3)	Li–O(2b)	2.22(3)
		Li–O(3)	2.08(4)		
		Mean Li–O	2.19(3)		

[a] Sites in the former monoclinic structure that are split into two when the symmetry is lowered to triclinic in the latter are labelled (a) and (b).

$MnAsO_4 \cdot H_2O^5$ the distortion is of the well-known [4 + 2] type usually encountered for Mn^{3+} and other high spin $3d^4$ ions, with four short bonds (2 × 1.89, 2 × 1.93 Å) to arsenate oxygens and two long bonds to the shared water molecules (2.32 Å), similar to those in other Mn^{III} compounds such as $MnPO_4 \cdot H_2O$.[10] However, in both of the non-equivalent $Mn(a)O_6$ and $Mn(b)O_6$ octahedra in $LiMnAsO_4(OH)$, the two Mn–OH distances have shortened drastically to (a) 1.97 Å and (b) 2.03 Å, while the four Mn–O(As) distances have split into two short [(a) 1.91 Å and (b) 1.82 Å] and two long [(a) 2.10 Å and (b) 2.17 Å] pairs. The degree of distortion for Mn(b) is clearly greater than that for Mn(a), although the mean Mn–O distances for the two are almost equal. This [2 + 2 + 2] Jahn–Teller mode is uncommon but has been reported for MnF_3 in which the Mn–F distances are 2 × 1.79, 2 × 1.91 and 2 × 2.09 Å.[11] The change in the MnO_6 geometries decreases the Mn · · · Mn distance in the chains of octahedra from 4.05 Å in $MnAsO_4 \cdot H_2O$ to 3.63 Å in $LiMnAsO_4(OH)$, and distorts the AsO_4 tetrahedra resulting in two short and two long As–O bonds. Li^+ is in an irregular 5-coordinate environment in the channels [Fig. 1(b)] with contacts to four arsenate and one hydroxy oxygens.

The origin of these drastic changes in framework geometry may be ascribed to the loss of H^+ from the framework rather than to the insertion of Li^+ into the channels. In $MnAsO_4 \cdot H_2O$, each Mn^{3+} is surrounded by two *trans* H_2O groups, in which the oxygen carries a formal charge of 0, and four arsenate oxygens with formal charges of 3/4−, and so the most energetically favoured Jahn–Teller distortion is with four short bonds to the latter oxygens and two long ones to the former. However, when the water molecule loses a proton the oxygen becomes more negatively charged than the arsenate oxygens with a formal charge of 1−, so that a Jahn–Teller distortion with short Mn–OH bonds becomes more favourable. This is achieved, within the constraints imposed by the topology of the structure, by shortening the Mn–OH bonds, and putting antibonding electron density into one of the pairs of Mn–O(As) bonds. Presumbly a further deprotonation to

give Li_2MnAsO_4O would impose too severe a strain on this structure through further changes in Mn–O bond lengths, and so this product was not formed despite the excess of lithium present in the reaction mixture.

The ability of the $MnAsO_4(OH_n)^{(2-n)-}$ ($n = 1,2$) framework to switch between different Jahn–Teller distorted modes while retaining its topology is very unusual, if not unique. This result suggests that microporous materials containing Jahn–Teller ions might act as more flexible hosts for intercalation and catalytic reactions than those based on rigid polyhedra alone, through such geometric changes induced by the loss or gain of species bonded to the framework.

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