

A three-dimensional Al^{III}/Na^I metal-organic framework resulting from dimethylformamide hydrolysis

Agnieszka Plutecka and Urszula Rychlewska*

Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland
Correspondence e-mail: urszular@amu.edu.pl

Received 15 September 2008

Accepted 2 January 2009

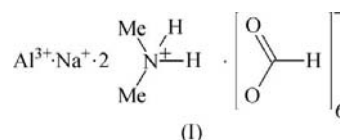
Online 10 January 2009

The three-dimensional metal-organic framework poly[bis(dimethylammonium) [hexa- μ_2 -formato- $\kappa^{12}O:O'$ -aluminium(III)-sodium(I)]], $\{(C_6H_8N)_2[AlNa(HCOO)_6]\}_n$, was obtained serendipitously and has been characterized by X-ray diffraction. The product has arisen as a result of a hydrolysis reaction of dimethylformamide (DMF) and contains dimethylammonium (DMA) cations included in structural voids formed by a three-dimensional $[AlNa(HCOO)_6]^-$ network. This study provides evidence that, in the presence of traces of aluminium, DMF stored in a glass bottle can be hydrolysed to formate and dimethylamine with simultaneous extraction of Na⁺ cations from the glass. It also demonstrates that care must be taken regarding the metal and water content when DMF is not freshly distilled, since the hydrolysis of amide can occur.

Comment

The crystal structure of the title compound, (I), contains a decomposition product of dimethylformamide (DMF) and constitutes the first example of a highly symmetrical three-dimensional network built solely of heterometallic $M-(\mu_2\text{-formato-}O:O')-M'$ units. Compound (I) displays $R\bar{3}$ symmetry, with Na^I and Al^{III} cations occupying special position sites $3a$ and $3b$, respectively, a formate anion in a general position ($18f$), and two dimethylammonium (DMA) cations disordered around the threefold axis. The disorder model for each cation comprises both dimethylammonium C atoms lying on a threefold axis (Wyckoff notation $6c$) and the NH₂ group in a general position ($18f$) statistically distributed around this axis. DMF hydrolysis leading to formic acid and DMA has been reported previously (Sletten & Jensen, 1973; Liu *et al.*, 2003; Wang *et al.*, 2004, 2006; Burrows *et al.*, 2005; Clausen *et al.*, 2005; Chen *et al.*, 2006; Hawxwell & Brammer, 2006). In the resulting crystal structures, formic acid often serves as an anionic ligand in the construction of metal-organic frameworks and DMA acts as a counter-cation to balance the charge.

The structure of (I) contains DMA cations included in voids in the three-dimensional $[AlNa(HCOO)_6]^-$ network. It is inferred that the source of Al^{III} cations is the aluminium foil and of Na^I cations is the glass container. Reports on the ability of formate solutions to extract Na^I cations have appeared in the literature previously (Alcock *et al.*, 2006, and references therein).



Each Al^{III} and Na^I cation is surrounded by six formate anions in an octahedral arrangement (Fig. 1). The *trans*-O–M–O angles are all 180°, while the *cis*-O–M–O angles can be divided into two groups: those related by a threefold axis (smaller than 90° in the case of Al^{III} and larger than 90° in the case of Na^I), and their supplementary angles (Table 1). For these *cis*-O–M–O angles, the maximum deviation in the bond angles from perfect octahedral geometry is 0.71° around Al^{III} and 0.84° around Na^I. There is one unique Al–O and one Na–O bond length (Table 1). Hence, the coordination polyhedron around each metal ion can be described as a trigonally distorted ($MO_3O'_3$) octahedron. Each formate anion connects two metal atoms in the *anti-anti* coordination mode, which results in infinite Al^{III}–O–C–O–Na^I chains forming a three-dimensional anionic network, similar to the reported homometallic coordination networks with formate as the only bridging ligand (Wang *et al.*, 2004, 2006).

In the structure of (I), one can distinguish corrugated (001) anionic layers containing both metal atoms connected by the formate bridges (Fig. 1). These anionic layers are separated by

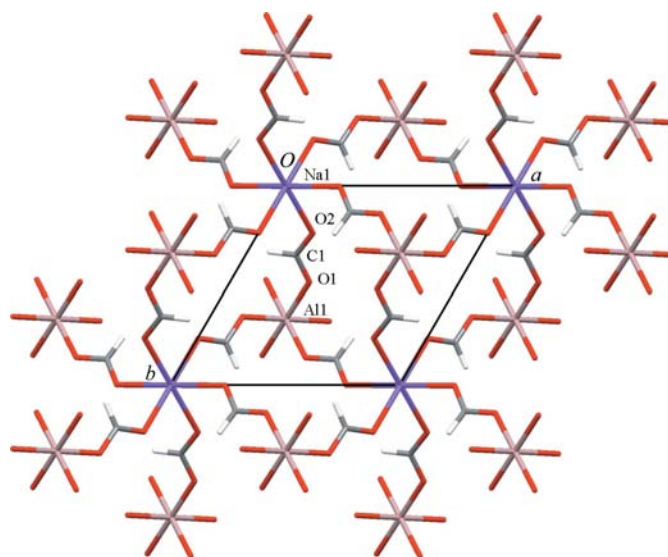
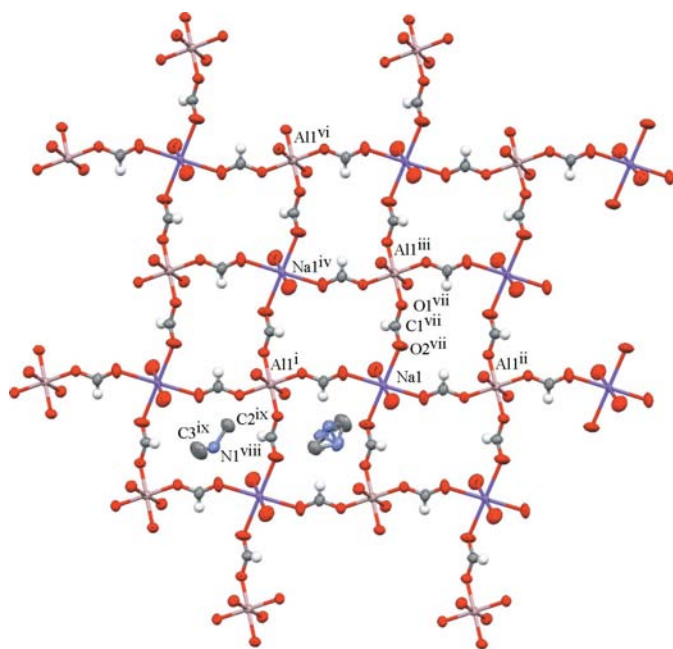


Figure 1
The three-dimensional coordination polymer, (I), and the bridging function of the carboxylate group.


Figure 2

The framework structure of (I), showing the DMA cations located in channels. In one of the channels one of the three different positions of the DMA cation is shown, and in the second channel the disorder of the DMA cation is shown. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $\frac{2}{3} - x + y, \frac{1}{3} - x, \frac{1}{3} + z$; (ii) $\frac{5}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$; (iii) $1 + x, y, z$; (iv) $\frac{2}{3} + x, \frac{1}{3} + y, \frac{1}{3} + z$; (vi) $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$].

the cationic $[\text{NH}_2(\text{CH}_3)_2]^+$ layers. Viewed approximately along the $[10\bar{2}]$ direction, a cubic network formed by heterometallic centres with interpenetrating channels occupied by DMA cations is observed (Fig. 2). The cross-section of the channels, measured between the mid-points of the Al^{III} and Na^{I} centres, has dimensions of $6.11 \times 6.11 \text{ \AA}$. A search of the Cambridge Structural Database (Version 5.29 of November 2007; Allen, 2002) reveals that such a highly symmetric three-dimensional arrangement of heterometallic centres bridged solely by the formate units, each utilizing its two O atoms to join to only two metals, has not been observed previously. This type of high-symmetry arrangement has so far appeared only in homometallic formates. The heterometallic formates reported in the literature display lower crystal symmetry and contain some of the formate anions linked to more than two metal ions or doubly linked to the same metal centre (Alcock *et al.*, 2006).

The electrostatic interactions between the anionic framework and the cations are augmented by hydrogen bonding. The H atoms of the DMA cation are involved in the formation of hydrogen bonds with both O atoms of the formate anions. Hydrogen-bond parameters are presented in Table 2.

Experimental

Crystals of (I) were obtained accidentally while storing DMF in a glass bottle with an aluminium-covered cork.

Crystal data

$(\text{C}_2\text{H}_8\text{N})_2[\text{AlNa}(\text{HCO}_2)_6]$
 $M_r = 412.27$
 Trigonal, $R\bar{3}$
 $a = 8.2510 (10) \text{ \AA}$
 $c = 22.949 (3) \text{ \AA}$
 $V = 1353.0 (3) \text{ \AA}^3$

$Z = 3$
 Cu $K\alpha$ radiation
 $\mu = 1.83 \text{ mm}^{-1}$
 $T = 296.0 (5) \text{ K}$
 $0.20 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Kuma KM-4 κ -geometry diffractometer
 Absorption correction: multi-scan (XEMP; Siemens, 1989)
 $T_{\text{min}} = 0.635, T_{\text{max}} = 0.833$
 1164 measured reflections

553 independent reflections
 443 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 2 standard reflections every 50 reflections
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.104$
 $S = 1.07$
 553 reflections
 47 parameters

3 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Al1—O1	1.8999 (14)	C1—O1	1.262 (3)
Na1—O2	2.4082 (18)	C1—O2	1.215 (3)
O1—Al1—O1 ⁱ	90.71 (7)	C1—O1—Al1	130.15 (16)
O1—Al1—O1 ⁱⁱ	89.29 (7)	O2—C1—O1	126.0 (3)
O2—Na1—O2 ⁱⁱⁱ	90.84 (7)	C1—O2—Na1	126.08 (18)
O2—Na1—O2 ^{iv}	89.16 (7)	C3—N1—C2	121.7 (5)
Al1—O1—C1—O2	177.75 (19)	O1—C1—O2—Na1	−171.65 (18)

Symmetry codes: (i) $-x + y, -x + 1, z$; (ii) $x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$; (iii) $x - y, x, -z$; (iv) $-x + y, -x, z$.

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1N \cdots O2	0.90	2.00	2.876 (7)	165
N1—H2N \cdots O2 ^v	0.90	2.30	3.059 (7)	142
N1—H2N \cdots O1 ^v	0.90	2.30	3.118 (6)	151

Symmetry code: (v) $-y + 1, x - y, z$.

All H atoms were placed in idealized positions and refined as riding on their carrier atoms, with methyl $\text{C—H} = 0.96 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, formate $\text{C—H} = 0.96 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and ammonium $\text{N—H} = 0.90 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. Geometric restraints were applied to the N—C bonds and $\text{C}\cdots\text{C}$ intramolecular contacts within the DMA cation.

Data collection: *KM-4 Software* (Kuma, 1997); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software* and *XEMP* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3021). Services for accessing these data are described at the back of the journal.

References

- Alcock, N. W., Wilson, M. P. & Rodger, P. M. (2006). *Acta Cryst.* **E62**, m388–m390.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Burrows, A. D., Cassar, K., Friend, R. M., Mahon, M. F., Rigby, S. P. & Warren, J. E. (2005). *CrystEngComm*, **7**, 548–550.
- Chen, J., Ohba, M. & Kitagawa, S. (2006). *Chem. Lett.* **35**, 526–527.
- Clausen, H. F., Poulsen, R. D., Bond, A. D., Chevallier, M.-A. S. & Iversen, B. B. (2005). *J. Solid State Chem.* **178**, 3342–3351.
- Hawxwell, S. M. & Brammer, L. (2006). *CrystEngComm*, **8**, 473–476.
- Kuma (1997). *KM-4 Software*. Kuma Diffraction, Wroclaw, Poland.
- Liu, S., Wang, Ch., Zhai, H. & Li, D. (2003). *J. Mol. Struct.* **654**, 215–221.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Siemens (1989). *XEMP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sletten, E. & Jensen, L. H. (1973). *Acta Cryst.* **B29**, 1752–1756.
- Wang, X.-Y., Gan, L., Zhang, S.-W. & Gao, S. (2004). *Inorg. Chem.* **43**, 4615–4625.
- Wang, Y., Cao, R., Bi, W., Li, X., Yuan, D. & Sun, D. (2006). *Microporous Mesoporous Mater.* **91**, 215–220.