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## Key indicators

 Single-crystal X-ray study  
 $T = 140\text{ K}$   
 Mean  $\sigma(\text{N}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.021  
 $wR$  factor = 0.032  
 Data-to-parameter ratio = 17.8

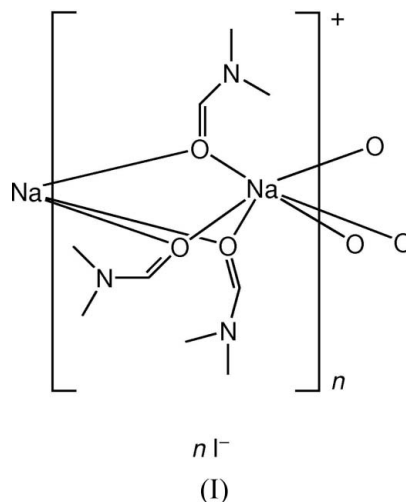
 For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

 Redetermination of *catena*-poly[[sodium(I)-  
 tri- $\mu$ -dimethylformamide- $\kappa^6\text{O}:O$ ] iodide]  
 at 140 K

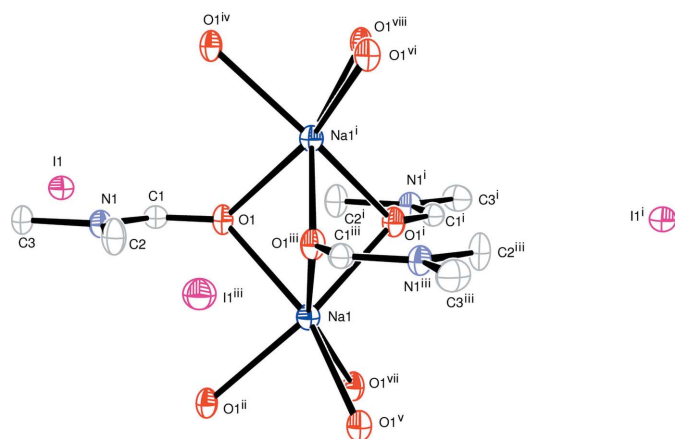
 The structure of the title compound,  $\{[\text{Na}(\text{C}_3\text{H}_7\text{NO})_3]\text{I}\}_n$ , has been redetermined at 140 (2) K. The  $\text{Na}^+$  cations lie on sites of 32 point symmetry and are linked into one-dimensional chains *via* bridging DMF molecules lying on mirror planes. The coordination geometry of  $\text{Na}^+$  is intermediate between octahedral and trigonal prismatic. The  $\text{I}^-$  anions lie on sites of  $\bar{6}$  point symmetry between the chains.

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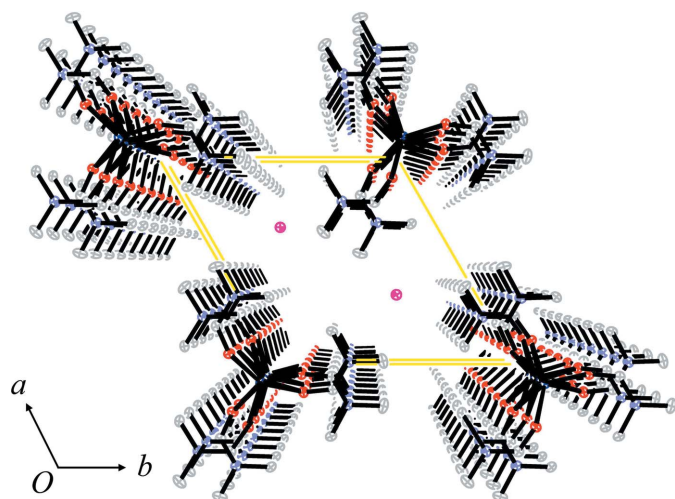
## Comment

 The structure of the title compound, (I), has been determined previously at room temperature (Gobillon *et al.*, 1962; Batsanov & Struchkov, 1994). In the first case, all atoms were refined using only isotropic displacement parameters. The second determination gave unsatisfactory  $R$  values ( $R = 0.140$ ). Compound (I) has been obtained as a by-product of a Heck reaction involving an aryl iodide in DMF, using  $\text{Na}_2\text{CO}_3$  as base. We have taken this opportunity to redetermine the structure of (I) at 140 (2) K, leading to significantly improved precision.

 The  $\text{Na}^+$  cation in (I) is coordinated by six DMF molecules lying on mirror planes (Fig. 1). The bond distances (Table 1) and coplanar nature of O1, C1 and N1 suggests a degree of double-bond character between C1 and N1 in addition to that between C1 and O1. This suggests the presence of a partial positive charge on N1 and a partial negative charge on O1, as suggested by Gobillon *et al.* (1962), which may lead to enhanced electrostatic interaction between the DMF molecules and the  $\text{Na}^+$  cation.

 The geometry at Na1 is intermediate between octahedral and trigonal prismatic; when viewed along the  $c$  axis (Fig. 2),


**Figure 1**

Part of the polymeric structure of (I), viewed approximately perpendicular to the  $c$  axis, showing displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (i)  $-x + y, -x, \frac{1}{2} - z$ ; (ii)  $y, x, -\frac{1}{2} + z$ ; (iii)  $-y, x - y, z$ ; (iv)  $y, x, \frac{1}{2} + z$ ; (v)  $-x, -x + y, -\frac{1}{2} + z$ ; (vi)  $-x, -x + y, \frac{1}{2} + z$ ; (vii)  $x - y, -y, -z$ ; (viii)  $x - y, -y, 1 - z$ .]


**Figure 2**

Perspective view of (I) along the  $c$  axis. H atoms have been omitted.

the angle between O atoms in successive layers is  $29.0^\circ$ . The bridging DMF molecules generate one-dimensional chains along  $c$ . The positions of the DMF molecules alternate along the  $c$  axis, leading to an ABAB pattern of DMF sites.

Gobillon *et al.* (1962) have described the structure of (I) as containing C—H...I hydrogen bonds, involving C1 and C3. The C...I distances determined in the current study [C1...I1 = 4.261 (3) and C3...I1 4.349 (4) Å] are outside the normal range for such an interaction, based on the van der Waals radii of the elements involved (Pauling, 1960). The interaction of the cationic polymer with the anions is, therefore, best described as largely electrostatic.

## Experimental

Crystals of (I) were obtained by crystallization from a hexane–chloroform (1:1) mixture of the solid residues from a Heck reaction. A mixture of 1-butyl-3-methylimidazolium hexafluorophosphate (0.188 ml, 1.0 mmol), Pd(OAc)<sub>2</sub> (112 mg, 0.50 mmol) and triphenyl-

phosphane (256 mg, 1.0 mmol) was suspended in dry tetrahydrofuran (15 ml) and stirred overnight under nitrogen. The resulting brown suspension was evaporated *in vacuo* and washed with CH<sub>2</sub>Cl<sub>2</sub>. The dried residue was then used as a catalyst for a Mizoroki–Heck reaction, according to the following typical procedure. Iodobenzene (1.0 mmol), sodium acetate (1.5 mmol), and *tert*-butyl acrylate (1.4 mmol) were placed in a Schlenk tube under N<sub>2</sub>, and the reagents were suspended in dimethylformamide (DMF, 3 ml), before injection of the catalyst (0.05 mmol) in DMF (3 ml). The reaction mixture was stirred for 8 h at 353 K, before cooling and extraction of the organic components with several portions of hexane. Extraction of the residue with chloroform followed by layering with hexane yielded crystals of (I).

## Crystal data

[Na(C<sub>3</sub>H<sub>7</sub>NO)<sub>3</sub>]I  
 $M_r = 369.18$   
 Hexagonal,  $P\bar{6}2c$   
 $a = 11.8038$  (14) Å  
 $c = 6.3881$  (7) Å  
 $V = 770.81$  (15) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.11$  mm<sup>-1</sup>  
 $T = 140$  (2) K  
 $0.25 \times 0.04 \times 0.01$  mm

## Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer  
 Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2006)  
 $T_{\min} = 0.621, T_{\max} = 0.979$   
 10001 measured reflections  
 657 independent reflections  
 607 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.032$   
 $S = 1.01$   
 657 reflections  
 37 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.41$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 281 Friedel pairs  
 Flack parameter: 0.00 (3)

**Table 1**

Selected geometric parameters (Å, °).

C1—O1	1.238 (3)	C3—N1	1.457 (4)
C1—N1	1.316 (4)	Na1—O1	2.3954 (15)
C2—N1	1.460 (5)		
O1—Na1—O1 <sup>i</sup>	80.40 (5)	O1—Na1—O1 <sup>ii</sup>	87.62 (7)

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

H atoms were included in calculated positions and refined using a riding model, with C—H = 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for H1, and C—H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl groups. The methyl groups were allowed to rotate about their local threefold axes.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2003), *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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**References**

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## supporting information

*Acta Cryst.* (2007). E63, m787–m789 [https://doi.org/10.1107/S1600536807007052]

## Redetermination of *catena*-poly[[sodium(I)-tri- $\mu$ -dimethylformamide- $\kappa^6$ O:O] iodide] at 140 K

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*catena*-poly[[sodium(I)-tri- $\mu$ -dimethylformamide- $\kappa^6$ O:O] iodide]

### Crystal data

[Na(C<sub>3</sub>H<sub>7</sub>NO)<sub>3</sub>]I

$M_r = 369.18$

Hexagonal,  $P\bar{6}2c$

Hall symbol: P -6c -2c

$a = 11.8038$  (14) Å

$c = 6.3881$  (7) Å

$V = 770.81$  (15) Å<sup>3</sup>

$Z = 2$

$F(000) = 368$

$D_x = 1.591$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4526 reflections

$\theta = 3.8$ – $27.5^\circ$

$\mu = 2.11$  mm<sup>-1</sup>

$T = 140$  K

Needle, colourless

$0.25 \times 0.04 \times 0.01$  mm

### Data collection

Oxford Diffraction Xcalibur3 CCD  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Thin-slice  $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(ABSPACK; Oxford Diffraction, 2006)

$T_{\min} = 0.621$ ,  $T_{\max} = 0.979$

10001 measured reflections

657 independent reflections

607 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\max} = 27.6^\circ$ ,  $\theta_{\min} = 3.8^\circ$

$h = -15 \rightarrow 15$

$k = -15 \rightarrow 15$

$l = -8 \rightarrow 8$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.032$

$S = 1.01$

657 reflections

37 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0162P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.41$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

Absolute structure: Flack (1983), 281 Friedel  
pairs

Absolute structure parameter: 0.00 (3)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2666 (3)	0.2349 (3)	0.2500	0.0182 (6)	
H1	0.3494	0.2396	0.2500	0.022*	
C2	0.1453 (3)	0.3513 (4)	0.2500	0.0249 (9)	
H2A	0.0717	0.2648	0.2152	0.037*	0.50
H2B	0.1515	0.4151	0.1458	0.037*	0.50
H2C	0.1315	0.3775	0.3890	0.037*	0.50
C3	0.3875 (3)	0.4718 (3)	0.2500	0.0261 (8)	
H3A	0.3957	0.5170	0.3826	0.039*	0.50
H3B	0.3864	0.5254	0.1337	0.039*	0.50
H3C	0.4620	0.4575	0.2336	0.039*	0.50
I1	0.6667	0.3333	0.2500	0.02405 (9)	
N1	0.2663 (3)	0.3463 (3)	0.2500	0.0197 (6)	
Na1	0.0000	0.0000	0.0000	0.0191 (3)	
O1	0.1683 (2)	0.12459 (19)	0.2500	0.0206 (5)	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0183 (16)	0.0198 (16)	0.0173 (15)	0.0100 (14)	0.000	0.000
C2	0.021 (2)	0.0151 (17)	0.0412 (19)	0.0106 (15)	0.000	0.000
C3	0.0259 (18)	0.0160 (16)	0.0264 (18)	0.0029 (15)	0.000	0.000
I1	0.02509 (11)	0.02509 (11)	0.02196 (14)	0.01255 (6)	0.000	0.000
N1	0.0200 (16)	0.0160 (15)	0.0238 (14)	0.0095 (14)	0.000	0.000
Na1	0.0177 (5)	0.0177 (5)	0.0219 (8)	0.0088 (2)	0.000	0.000
O1	0.0156 (11)	0.0141 (10)	0.0298 (12)	0.0057 (9)	0.000	0.000

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C1—O1	1.238 (3)	C3—H3A	0.980
C1—N1	1.316 (4)	C3—H3B	0.980
C1—H1	0.950	C3—H3C	0.980
C2—N1	1.460 (5)	Na1—O1	2.3954 (15)
C2—H2A	0.980	Na1—O1 <sup>i</sup>	2.3954 (15)
C2—H2B	0.980	Na1—O1 <sup>ii</sup>	2.3954 (15)
C2—H2C	0.980	Na1—Na1 <sup>iii</sup>	3.1941 (4)
C3—N1	1.457 (4)	O1—Na1 <sup>iii</sup>	2.3954 (15)

O1—C1—N1	125.5 (3)	O1—Na1—O1 <sup>i</sup>	117.02 (8)
O1—C1—H1	117.2	O1 <sup>iii</sup> —Na1—O1 <sup>i</sup>	87.62 (7)
N1—C1—H1	117.2	O1 <sup>v</sup> —Na1—O1 <sup>i</sup>	80.40 (5)
N1—C2—H2A	109.5	O1 <sup>iv</sup> —Na1—O1 <sup>ii</sup>	87.62 (7)
N1—C2—H2B	109.5	O1—Na1—O1 <sup>ii</sup>	80.40 (5)
H2A—C2—H2B	109.5	O1 <sup>iii</sup> —Na1—O1 <sup>ii</sup>	80.40 (5)
N1—C2—H2C	109.5	O1 <sup>v</sup> —Na1—O1 <sup>ii</sup>	117.02 (8)
H2A—C2—H2C	109.5	O1 <sup>i</sup> —Na1—O1 <sup>ii</sup>	157.01 (9)
H2B—C2—H2C	109.5	O1 <sup>iv</sup> —Na1—Na1 <sup>vi</sup>	48.19 (3)
N1—C3—H3A	109.5	O1—Na1—Na1 <sup>vi</sup>	131.81 (3)
N1—C3—H3B	109.5	O1 <sup>iii</sup> —Na1—Na1 <sup>vi</sup>	131.81 (3)
H3A—C3—H3B	109.5	O1 <sup>v</sup> —Na1—Na1 <sup>vi</sup>	48.19 (3)
N1—C3—H3C	109.5	O1 <sup>i</sup> —Na1—Na1 <sup>vi</sup>	48.19 (3)
H3A—C3—H3C	109.5	O1 <sup>ii</sup> —Na1—Na1 <sup>vi</sup>	131.81 (3)
H3B—C3—H3C	109.5	O1 <sup>iv</sup> —Na1—Na1 <sup>iii</sup>	131.81 (3)
C1—N1—C3	121.6 (3)	O1—Na1—Na1 <sup>iii</sup>	48.19 (3)
C1—N1—C2	122.2 (3)	O1 <sup>iii</sup> —Na1—Na1 <sup>iii</sup>	48.19 (3)
C3—N1—C2	116.2 (3)	O1 <sup>v</sup> —Na1—Na1 <sup>iii</sup>	131.81 (3)
O1 <sup>iv</sup> —Na1—O1	157.01 (9)	O1 <sup>i</sup> —Na1—Na1 <sup>iii</sup>	131.81 (3)
O1 <sup>iv</sup> —Na1—O1 <sup>iii</sup>	117.02 (8)	O1 <sup>ii</sup> —Na1—Na1 <sup>iii</sup>	48.19 (3)
O1—Na1—O1 <sup>iii</sup>	80.40 (5)	Na1 <sup>vi</sup> —Na1—Na1 <sup>iii</sup>	180.0
O1 <sup>iv</sup> —Na1—O1 <sup>v</sup>	80.40 (5)	C1—O1—Na1	134.40 (8)
O1—Na1—O1 <sup>v</sup>	87.62 (7)	C1—O1—Na1 <sup>iii</sup>	134.40 (8)
O1 <sup>iii</sup> —Na1—O1 <sup>v</sup>	157.01 (9)	Na1—O1—Na1 <sup>iii</sup>	83.62 (6)
O1 <sup>iv</sup> —Na1—O1 <sup>i</sup>	80.40 (5)		

Symmetry codes: (i)  $x-y, -y, -z$ ; (ii)  $-y, x-y, z$ ; (iii)  $-x+y, -x, -z+1/2$ ; (iv)  $-x, -x+y, z-1/2$ ; (v)  $y, x, z-1/2$ ; (vi)  $-x+y, -x, -z-1/2$ .