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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

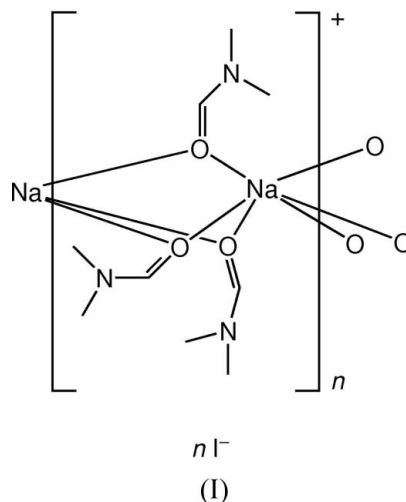
 For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

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

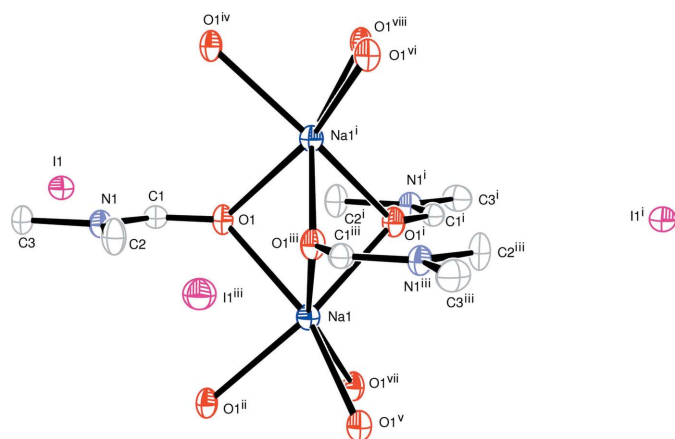
 The structure of the title compound, $\{[\text{Na}(\text{C}_3\text{H}_7\text{NO})_3]\text{I}\}_n$, has been redetermined at 140 (2) K. The Na^+ cations lie on sites of 32 point symmetry and are linked into one-dimensional chains *via* bridging DMF molecules lying on mirror planes. The coordination geometry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

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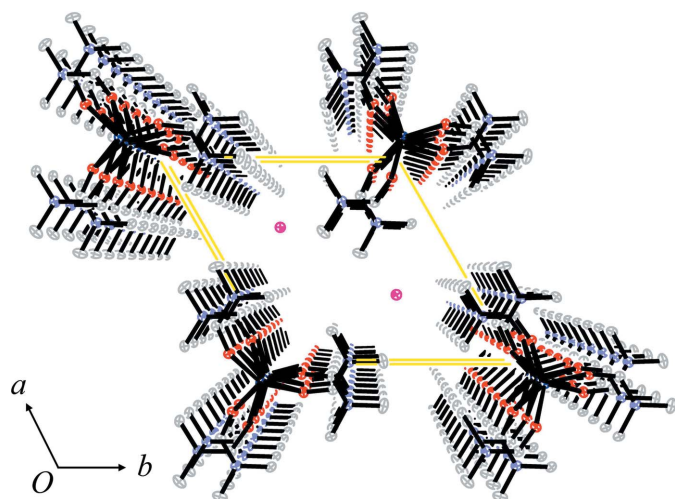
Comment

 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 Na_2CO_3 as base. We have taken this opportunity to redetermine the structure of (I) at 140 (2) K, leading to significantly improved precision.

 The 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 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° . 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 $C-H \cdots I$ hydrogen bonds, involving C1 and C3. The $C \cdots I$ distances determined in the current study [$C1 \cdots I1 = 4.261(3)$ and $C3 \cdots I1 = 4.349(4)$ 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), $Pd(OAc)_2$ (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_2Cl_2 . 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_2 , 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

$[Na(C_3H_7NO)_3]I$
 $M_r = 369.18$
 Hexagonal, $P6_3/c$
 $a = 11.8038(14)$ Å
 $c = 6.3881(7)$ Å
 $V = 770.81(15)$ Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 2.11$ mm⁻¹
 $T = 140(2)$ 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 $I > 2\sigma(I)$
 $R_{int} = 0.054$

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⁻³
 $\Delta\rho_{min} = -0.35$ e Å⁻³
 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 ⁱ	80.40 (5)	O1–Na1–O1 ⁱⁱ	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 $U_{iso}(H) = 1.2U_{eq}(C)$ for H1, and $C-H = 0.98$ Å and $U_{iso}(H) = 1.5U_{eq}(C)$ 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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