

Polymeric tris(μ_2 -acetone- κ^2 O:O)-sodium polyiodide at 120 K

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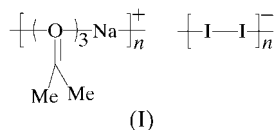
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In the title compound, $[\text{Na}(\text{C}_3\text{H}_6\text{O})_3]_n(\text{I}_2)_n$, all non-H atoms are in special positions of the space group $P6_3/mcm$, with the Na atom in $2b$, the I atom in $4c$, the carbonyl O atom and the C atom attached to it both in $6g$, and the methyl C atom in $12k$. The H atoms of the rotationally disordered methyl groups are in $24l$ general positions but with occupancies of 0.5, because they occur in two sets related by a crystallographic mirror plane. Infinite chains are created by face-sharing octahedral Na-coordination polyhedra, with Na—O and Na...Na distances of 2.439 (5) and 3.2237 (4) Å, respectively. I atoms form infinite linear chains, in which the I-atom separation is 3.2237 (4) Å.

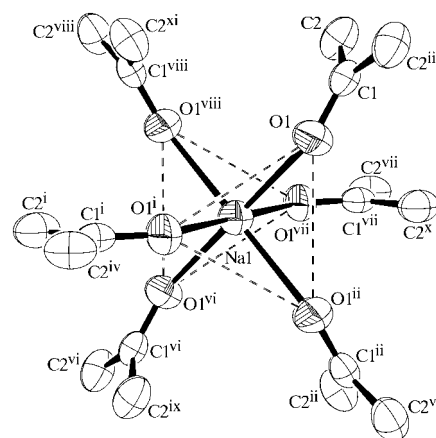
Comment

The preliminary information as to the nature of the title compound, (I), was no more than that it probably contained sodium and iodine (from the circumstances under which it was obtained) and the solvate acetone [because after ready decomposition on exposure to the atmosphere, (I) could be reconstituted by recrystallization from that solvent]. A search based purely on cell dimensions, using the CSEAR component of the Crystal Structure Search and Retrieval system (CSSR) of the EPSRC's Chemical Database Service (CDS) at Daresbury, England (Fletcher *et al.*, 1996), suggested close similarity to the structure of *catena*-[tris(μ_2 -dimethylformamide-*O,O*)]sodium iodide, (II) [CSD (Allen, 2002) refcodes

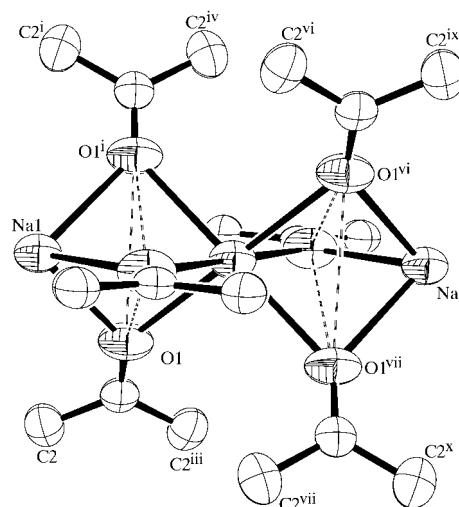


NAIDMF (Gobillon *et al.*, 1962) and NAIDMF01 (Batsanov & Struchkov, 1994)]. The assumption of the presence of Na and I atoms in (I) and the same hexagonal space group ($P6_3/m$) as (II) led to the successful solution and refinement of the structure of (I), which is reported here.

The coordination of the Na atom in (I) is shown in Fig. 1, along with the labelling scheme (with the exception of atom I1, which is not present in this figure). The coordination of the Na atom is determined by the $3m$ site symmetry and is octahedral in nature, with six identical Na—O distances [2.439 (5) Å] and all of the *trans* O—Na—O angles exactly 180°. The octahedron is elongated by 16% in the *c* direction, as estimated by the increase relative to the ideal value of the perpendicular distance of Na from the shared faces of the coordination polyhedron, and as shown by the presence of two distinct values for the *cis* O—Na—O angles [81.08 (17) and 98.82 (17)°] and the lengths of the O—O octahedron edges [3.170 (13) Å on the shared faces of the octahedron and 3.707 (4) Å otherwise; Table 1]. The face sharing of the Na-coordination polyhedra, brought about by the μ_2 -bridging function of the carbonyl O atoms, results in the formation of


Figure 1

The coordination of Na in (I). Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. Dashed lines indicate the O—O edges of the shared faces of the coordination octahedron. [Symmetry codes: (i) $-y, x - y, z$; (ii) $-x + y, -x, z$; (iii) $x, y, \frac{1}{2} - z$; (iv) $-y, x - y, \frac{1}{2} - z$; (v) $-x + y, -x, \frac{1}{2} - z$; (vi) $-y, -x, z - \frac{1}{2}$; (vii) $x, x - y, z - \frac{1}{2}$; (viii) $-x + y, y, z - \frac{1}{2}$; (ix) $-y, -x, -z$; (x) $x, x - y, -z$; (xi) $-x + y, y, -z$.]


Figure 2

Part of a chain of face-sharing Na-coordination polyhedra in (I). The representation, including the symmetry codes where given, is the same as for Fig. 1, but only selected atoms are labelled.

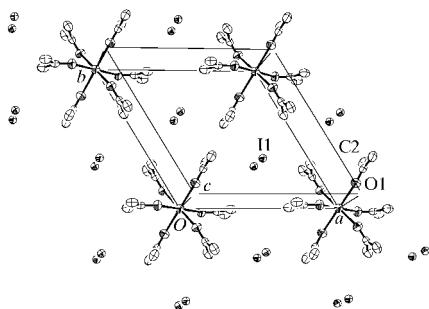


Figure 3
The unit cell of (I), viewed approximately along *c*. The representation is the same as for Fig. 2, except that symmetry codes are not given.

infinite chains, as shown in Fig. 2, propagated in the *c* direction, with Na atoms at $0,0,0$ and $0,0,\frac{1}{2}$.

The acetone solvate molecule is not well determined but is clearly recognizable in terms of its bond lengths and angles (Table 1). The molecule, except for the methyl H atoms, lies on a crystallographic mirror plane parallel to *c*. The methyl groups are rotationally disordered between two mirror-plane-related arrangements, and the occupancies of the H atoms are therefore 0.5, while the sites of the C atoms attached to the H atoms are fully occupied.

The I atoms, of which there are four in the unit cell, occur in two infinite linear rows ($\frac{2}{3}, \frac{1}{3}, z$ and $\frac{1}{3}, \frac{2}{3}, z$), also propagated in the *c* direction, with I at $z = \frac{1}{4}$ and $\frac{3}{4}$ in both cases. The I—I separation, which is identical to the Na—Na separation, is $c/2$ or 3.2237 (4) Å. The relative dispositions of the rows of Na polyhedra and the linear I_n chains is shown in Fig. 3.

The unit cell contains two Na and four I atoms, each species being in a symmetry-related set, and from charge-balance considerations each I atom must, on average, carry a charge of $-\frac{1}{2}$. This situation could be achieved in many ways, of which perhaps the most likely are as follows: neutral I atoms and I^- anions may simply alternate along the length of the rows; alternatively, there could be a mixture of I^- and I_n^- ions, with, for *n* odd and greater than 1, mono- and polyiodide species in the ratio $n-2:1$; finally, taking into account the fact that the I atoms are related by symmetry and that the I—I separation in the chains, while greater than twice the normal covalent radius of I (2.80 Å), is much less than twice the van der Waals radius [3.96 Å; values for radii taken from *PLATON* (Spek, 2003)] allows the possibility of weak I—I bonds or at least charge transfer along the multiply negatively charged polyiodide chains.

The structure of (I) and the published structure of (II) differ more than first anticipated, although a general similarity can be observed in figures of the form of Fig. 3, shown here for (I). The structures differ as follows [properties for (I) *versus* (II)]: space group, $P6_3/mcm$ *versus* $P6_2c$; Na coordination, octahedral *versus* trigonal prism; the nature and orientation of the planar solvate molecules, acetone oriented parallel to *c* *versus* DMF perpendicular to *c*; the I—I separation, $c/2$ *versus* cell translation in the direction of *c*; and hence the nature of the I chains, infinite polyiodide *versus* independent I^- anions. There is some evidence to suggest that the difference in the type of iodide anion present in the two structures may be more

apparent than real. In reporting the unit cell, space group and *R* factor (0.1390) corresponding to the CSD entry NAIDMF01 (Batsanov & Struchkov, 1994), the *CSSR* comments that the 'I atoms (are) disordered over two sites'. This statement suggests that I is present in the structure of (II) in a greater amount than originally thought and may exist in an infinite polyiodide form similar to that described here for (I). Indeed, in the early stages of the refinement of (I) based on the structure of (II), *R* values very similar to and actually slightly better than those achieved for (II) by Batsanov & Struchkov (1994) were obtained for the isolated I^- model in space group $P\bar{6}2c$. Upon introducing a second I atom, $c/2$ from that in the original model, to account for the residual electron density of $\sim 27 e \text{ \AA}^{-3}$, the refinement was much improved. The introduction of additional I atoms into the Batsanov & Struchkov (1994) structure need not bring about a change in space group, which would in any case be difficult if the nature of the Na coordination and orientation of the dimethylformamide solvate molecules in (II) were to remain unchanged.

Experimental

Crystalline (I) was obtained in place of the desired product $I_3SnCH_2CH_2CO_2Me$ when a solution obtained by the addition of a saturated solution of NaI in acetone (100 ml) to a solution of HCl, $SnCl_2$ and $H_2C=CHCO_2Me$ (0.1 mol each) in diethyl ether (45 ml) was exposed to air overnight. Further exposure of the lustrous dark crystalline solid to air overnight resulted in the formation of a dark-grey powder, which recovered its crystalline form on recrystallization from acetone. The crystalline material was stable for weeks when stored in closed vessels with a little acetone.

Crystal data

$[Na(C_3H_6O)_3](I_2)$	Mo $K\alpha$ radiation
$M_r = 451.02$	Cell parameters from 14 507 reflections
Hexagonal, $P6_3/mcm$	$\theta = 2.9\text{--}27.5^\circ$
$a = 11.7086$ (13) Å	$\mu = 4.13 \text{ mm}^{-1}$
$c = 6.4475$ (8) Å	$T = 120$ (2) K
$V = 765.48$ (15) Å ³	Plate, brown
$Z = 2$	$0.50 \times 0.22 \times 0.04 \text{ mm}$
$D_x = 1.957 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD area-detector diffractometer	352 independent reflections
φ and ω scans	261 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	$R_{int} = 0.102$
$T_{min} = 0.150$, $T_{max} = 0.389$	$\theta_{max} = 27.5^\circ$
6540 measured reflections	$h = -14 \rightarrow 15$
	$k = -15 \rightarrow 14$
	$l = -8 \rightarrow 7$

Table 1

Selected geometric parameters (Å, °).

Na1—O1	2.439 (5)	O1—O1 ⁱⁱ	3.170 (13)
Na1—Na1 ⁱⁱⁱ	3.2237 (4)	O1—O1 ⁱⁱⁱ	3.707 (4)
O1—C1	1.210 (11)	I1—I1 ⁱⁱⁱⁱ	3.2237 (4)
C1—C2	1.461 (10)		
O1—Na1—O1 ^{xiv}	180	Na1—O1—Na1 ⁱⁱⁱ	82.7 (2)
O1—Na1—O1 ⁱⁱ	81.08 (17)	O1—C1—C2	120.7 (5)
C1—O1—Na1	138.63 (11)	C2 ⁱⁱⁱ —C1—C2	118.6 (10)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.133$
 $S = 1.09$
 352 reflections
 20 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 1.5007P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.94 \text{ e } \text{\AA}^{-3}$

Intensity data were collected for a full sphere of reflections on the basis of a C-centred orthorhombic cell, corresponding to the primitive hexagonal cell noted above, and were reindexed accordingly. The heavy-atom method, as implemented in *SHELXS86* (Sheldrick, 1985), provided initial positions for Na and I, assuming equal numbers of Na and I atoms and the space group *P62c*. Subsequent difference syntheses provided features identifiable as a representative acetone solvate molecule. As noted above, this model did refine but only to an *R* value in excess of 0.10, with a large ($\sim 27 \text{ e } \text{\AA}^{-3}$) residual electron density, and the refinement required the application of constraints to most of the coordinates of the non-H atoms of the acetone molecule. Refinement improved dramatically with the addition of a second I atom at the site of the residual electron density. At this point, the *PLATON* (Spek, 2003) ADDSYM test (for additional/missing crystallographic symmetry) was applied, leading to the adoption of the space group *P6₃/mcm*, in which the refinement was completed. In the final stages of refinement, the H atoms of the methyl groups of the acetone molecule were introduced in calculated positions (with C—H distances of 0.98 Å and, taking account of the rotational disorder of the methyl groups over two arrangements related by a crystallographic mirror plane, occupancies of 0.5) and were refined using a riding model with U_{iso} values equal to $1.5U_{\text{eq}}$ of the parent C atom. The refinement program (*SHELXL97*; Sheldrick, 1997) continually recommended correction for extinction. This correction was investigated but not retained in the final refinement because, although the correction did indeed improve the *R* values, it also promoted an erroneous residual electron density ($\sim 1.6 \text{ e } \text{\AA}^{-3}$)

midway between the Na atoms. In the absence of any form of chemical elemental analysis, several attempts were made to incorporate Sn atoms into the structure, but all of these proved unsuccessful.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1688). Services for accessing these data are described at the back of the journal.

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