

Bis(tetraethylammonium) tetraiodo- zincate at 150 and 301 K

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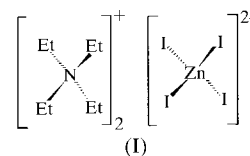
Data validation number: IUC0000058

The refinements described here for $(\text{NEt}_4)[\text{ZnI}_4]$ completely confirm the results previously obtained for the isostructural tetrabromocadmate at room temperature [Geselle & Fuess (1994). *Acta Cryst.* **C50**, 1582–1585]. Here again, isolated MX_4 ($M = \text{Zn}$ and $X = \text{I}$) tetrahedra are accompanied by two cations in a 'swastika' conformation and a third in a virtually planar *trans* conformation. One of the former cations is particularly disordered.

Comment

A search of the Cambridge Structural Database (Allen & Kennard, 1993) by means of the CSSR component of the Chemical Database Service at Daresbury (Fletcher *et al.*, 1996) strongly suggested that the present iodozincate was isostructural with the corresponding bromocadmate described by Geselle & Fuess (1994) (hereafter referenced as G&F). Indeed, adoption of the atomic coordinates as given by G&F led to a completely successful refinement of the iodozincate structure for data both at 301 and 150 K. In what follows, the data sets and the structural results derived from them are designated accordingly as 301 and 150 K.

G&F have already provided a detailed and virtually complete description of the isostructural room-temperature form of bis(tetraethylammonium) tetrabromocadmate. Their general description applies equally to the tetraiodozincate structures, (I), described here. The same atom-labelling scheme has been used for both zincate structures and differs very little, if at all, from that used by G&F. Thus, once more, rather regular and essentially isolated MX_4 tetrahedra (now $M = \text{Zn}$ and $X = \text{I}$) are present in the structure. These are accompanied by three tetraethylammonium cations centred on N1, N2 and N3, and, for convenience, designated by number as 1, 2 and 3, respectively.



Adopting the nomenclature of G&F, the conformation of cations 1 and 2 may be described as swastika-like. This is particularly apparent when they are viewed down the fourfold axis. It is, however, to some extent misleading because this projection disguises the considerable height of the ions. Whereas cation 1 is comparatively ordered, cation 2 is not and appears as a superimposed pair of mirror plane related and half-occupied species with N2, C4 and C6 in common. This disorder has implications for the placement of H atoms in this cation as explained below. This disorder is, as expected, greater in the room-temperature (301 K) structure than in that at 150 K. Its effect is observable in the shortening of the N—C and C—C bonds of cation 2 compared with the other cations. Cation 3, described by G&F as interstitial in nature and *trans* in conformation, is much flatter. In effect, the methylene groups [C7, C9, C11 and C11ⁱ; symmetry code: (i) $y + \frac{1}{2}, x - \frac{1}{2}, z$] are ordered on either side of the virtually planar arrangement of N3, C8, C10, C12 and C12ⁱ.

For all of the structures mentioned here, the distribution of the ionic species may be represented as follows. The anions and the 'interstitial' (G&F) cations 3 lie on either side of layers containing cations 1 and 2. A simple, if perhaps rather far-fetched, analogy might be the structures of the tetragonal oxides of divalent tin and lead (Wells, 1962). While the MX_4 anions and cations 1 and 2 correspond to M and O , respectively, of the tetragonal oxides, cation 3 takes the place of the stereochemically active lone pair of the divalent metal atoms. Thus the MX_4 anions have five nearest-neighbour cations in the form of a square (tetragonal) pyramid with cations 1 and 2 in the base and cation 3 at the apex. Conversely, whereas cations 1 and 2 have four nearest neighbour anions in a tetrahedral arrangement, cation 3 has only one.

Experimental

The title compound was isolated from reactions of bis(tetraethylammonium) $\text{Zn}(\text{DMIT})_2$, where DMIT is the dianion of 1,3-dithiole-2-thione-4,5-dithiol, and a source of iodide [SbI_3 (150 K) or AsI_3 (301 K)] and recrystallized from ethanol on each occasion.

Compound (I) at 150 K

Crystal data

$(\text{C}_8\text{H}_{20}\text{N})_2[\text{ZnI}_4]$
 $M_r = 833.47$
Tetragonal, $P\bar{4}2_1m$
 $a = 13.6929$ (5) Å
 $c = 14.8094$ (6) Å
 $V = 2776.70$ (18) Å³
 $Z = 4$
 $D_x = 1.994$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 10650
reflections
 $\theta = 2.03$ – 26.35°
 $\mu = 5.334$ mm⁻¹
 $T = 150$ (2) K
Plate, colourless
 $0.25 \times 0.10 \times 0.05$ mm

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
 φ - ω scans
 Absorption correction: empirical (SORTAV; Blessing, 1997)
 $T_{\min} = 0.536$, $T_{\max} = 0.766$
 10 650 measured reflections

2989 independent reflections
 2277 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$
 $\theta_{\max} = 26.35^\circ$
 $h = -14 \rightarrow 17$
 $k = -17 \rightarrow 13$
 $l = -14 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.122$
 $S = 1.035$
 2989 reflections
 134 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.64 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.18 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = -0.12 (7)

Compound (I) at 301 K**Crystal data**

$(\text{C}_8\text{H}_{20}\text{N})_2[\text{ZnI}_4]$
 $M_r = 833.47$
 Tetragonal, $P4_2/m$
 $a = 13.8199$ (6) \AA
 $c = 14.8975$ (7) \AA
 $V = 2845.3$ (2) \AA^3
 $Z = 4$
 $D_x = 1.946 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 4735 reflections
 $\theta = 2.49$ – 21.71°
 $\mu = 5.206 \text{ mm}^{-1}$
 $T = 301$ (2) K
 Block, colourless
 $0.30 \times 0.28 \times 0.17 \text{ mm}$

Data collection

Bruker SMART 1000 CCD diffractometer
 φ - ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)
 $T_{\min} = 0.196$, $T_{\max} = 0.413$
 17 580 measured reflections

2678 independent reflections
 1825 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.081$
 $\theta_{\max} = 25.02^\circ$
 $h = -16 \rightarrow 16$
 $k = -16 \rightarrow 13$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.135$
 $S = 0.993$
 2678 reflections
 134 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983)
 Flack parameter = 0.29 (9)

Refinements based on the coordinates of G&F proceeded smoothly and rapidly to the final conclusions presented here. The only difficulties encountered were in the placement and refinement of certain H atoms as described below. Twin refinement was found to be appropriate in the case of 301 K but not for 150 K. There were 1302 Friedel pairs in the 150 K data set and 1167 in the 301 K data set. Electron densities of magnitude greater than $1 \text{ e } \text{\AA}^{-3}$ were observed in the final difference maps as maxima at 0.32 (150 K) and 1.38 \AA (301 K) from Zn1 and in 150 K as a minimum 1.32 \AA from I3. In general, H atoms were placed in geometrical positions and refined with a riding model. The disorder of cation 2 required the liberal application of *SHELXL97 FREE* instructions to accomplish this. For cation 3, while most of the H atoms were positioned by the normal geometrical processes, C8 and C10, methyl C with site symmetry m , were treated specially. For these, the H atoms were forced to satisfy the m site symmetry of the C atoms to which they were attached, which may or may not actually be the case, in the following manner.

The H atoms were placed with the *AFIX 33* instruction thus preventing rotational refinement of the methyl groups. In addition, for each methyl group, manual intervention was used in order to enforce the relationship $y = x - \frac{1}{2}$ for one H of the group and that the other two H had identical z coordinates. *AFIX 33* was also used for the C6 methyl group of cation 2 of the 301 K structure because refinement of the rotational parameter proved to be extremely unstable. The occupancies of 0.5 presented along with the fractional atomic coordinates in the supplementary (CIF) data associated with this report are entirely appropriate in the case of the atoms C3, H3A–B, H4A–C, C5, H5A–B and H6A–C because they arise from the disorder of cation 2. This is not, however, the case for the H atom pairs H7A/B, H8B/C, H9A/B and H10B/C. Here, the individual atoms of each pair are related by the operation of a crystallographic mirror plane. Each such pair could then be represented equally well by one atom of the pair but with full occupancy. The pairwise half-occupied representation which has in fact been retained in the supplementary data might be regarded as an artefact arising from the mode of operation of the *SHELXL97 AFIX* instruction.

For compound (I) at 150 K, 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: starting parameters from G&F; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

For compound (I) at 301 K, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: starting parameters from G&F; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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