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Bis(trimethylammonium) tetrachloromercurate(II) at 343 K

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Key indicators

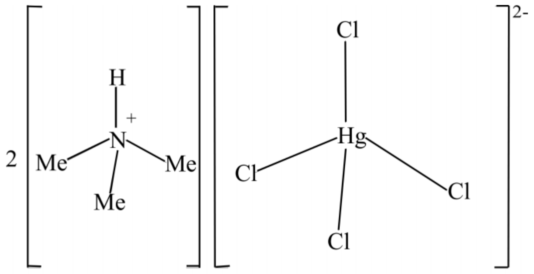
Single-crystal synchrotron study
T = 343 K
Mean σ(N–C) = 0.028 Å
H-atom completeness 11%
R factor = 0.051
wR factor = 0.079
Data-to-parameter ratio = 15.5

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

In order to investigate a possible phase transition at 324 K in the title compound, $(NHMe_3)_2[HgCl_4]$, the crystal structures at 295 and 343 K have been determined, using restrictions of the non-crystallographic site symmetry of the trimethylammonium (TrMA) ions. The hydrogen-bond network, namely N—H···Cl, undergoes a considerable change, by a 38° rotation of one of the TrMA cations about the N—H bond axis. This transition is shown to be a non-symmetry-breaking structural transition, which corresponds to a gradual loss of the orientational order of the TrMA cations.

Comment

Crystals of alkylammonium tetrachlorometallates with the general formula $A_2[MX_4]$, where M is a divalent metal ion and X is a halogen, have been widely investigated, owing to their interesting physical properties related to different phase transitions. The nature of the complicated phase transitions in these mixed organic–inorganic salts can be related either to temperature annealing of the crystal structure with intrinsic disorder of alkylammonium and $[MX_4]^{2-}$ groups (Stucky *et al.*, 1967; Williams *et al.*, 1992*a*; Mahoui *et al.*, 1996*a*,*b*; Mahmoudkhani & Langer, 1999) or to a reorientation of the organic cation, thereby changing the hydrogen-bond network (Williams *et al.*, 1992*b*). Compared with their tetramethylammonium analogs, the trimethylammonium tetrachlorometallates have been less studied, although the possibility for a variety of interionic bond networks is high. Structural studies of the pure trimethylammonium salts $(NHMe_3)_2[MCl_4]$ appear to be limited to the room temperature phase (Ben Salah *et al.*, 1983; Williams *et al.*, 1992*b*).



(I)

The crystal structure of the title compound, (I), at room temperature was studied by Ben Salah *et al.* (1983), where discrete trimethylammonium (TrMA) cations and $[HgCl_4]$ dianions are found with two simple hydrogen bonds from the N—H groups of the two independent TrMA cations to a single

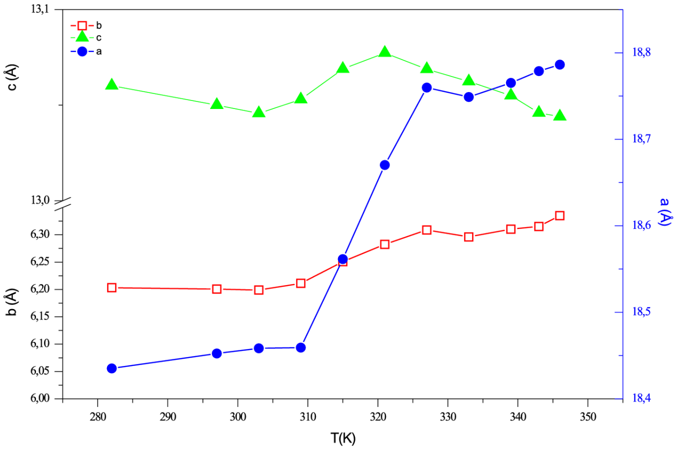


Figure 1
The temperature dependence of the unit-cell parameters of (I).

Cl atom of the $[HgCl_4]^{2-}$ dianion. We performed differential scanning calorimetry (DSC) measurements between 100 and 400 K, which confirmed the existence of three phase transitions. This has prompted us to investigate the structure of (I) at elevated temperature and clarify the possible changes in crystal structure during the claimed phase transition at 324 K. The temperature dependence of the lattice parameters was studied in the range above room temperature (Fig. 1). The net behavior is an increase of the unit cell volume with increasing temperature. However, especially the *a* lattice parameter, in particular, exhibits anomalous behavior in the range 310–325 K; this coincides, within experimental error, with the anomalies observed in the DSC. Albeit weak evidence, these results suggest that there may be changes in the crystal structure at these temperatures.

Refinements of the structure at 343 K were performed, with the structure at room temperature reported by Ben Salah *et al.* (1983) as the starting model. However, the refinement was somewhat unstable, because the structure parameters of the C atoms were highly correlated with each other. In fact, the resulting N—C distance of 1.2 Å was much shorter than the original value. The application of a restraint on the N—C distances (1.5 Å) gave convergence at $R = 0.052$, with a large distortion of the trimethylammonium group. In the next refinement, we treated the TrMA ion as a rigid-body in order to suppress the parameter correlation. The rigid body was constructed from the structure of the TrMA ion with the C_3 symmetry of the room-temperature phase. The positional parameters of the H atoms bonded to N atoms were calculated and fixed during the refinement. Here, we adopted the axis through the N and H atoms as the threefold axis. Thus the monoclinic axis unique axis was taken as *c* for the rest of the refinement. One N—C distance is refined as the single independent parameter. [N(*i*) is the center of the group, H(*i*) is on the threefold axis, *i.e.* along (001) of a Cartesian coordinate system, C(*i*) is on the (*ac*) plane, φ, χ and ψ are the Eulerian angles defining the orientation of the group]. The positions and the orientations of these groups were refined. The relevant crystallographic data, including the atomic coordinates and the list of observed structure factors for the 295 K phase, have been included only in the deposited material.

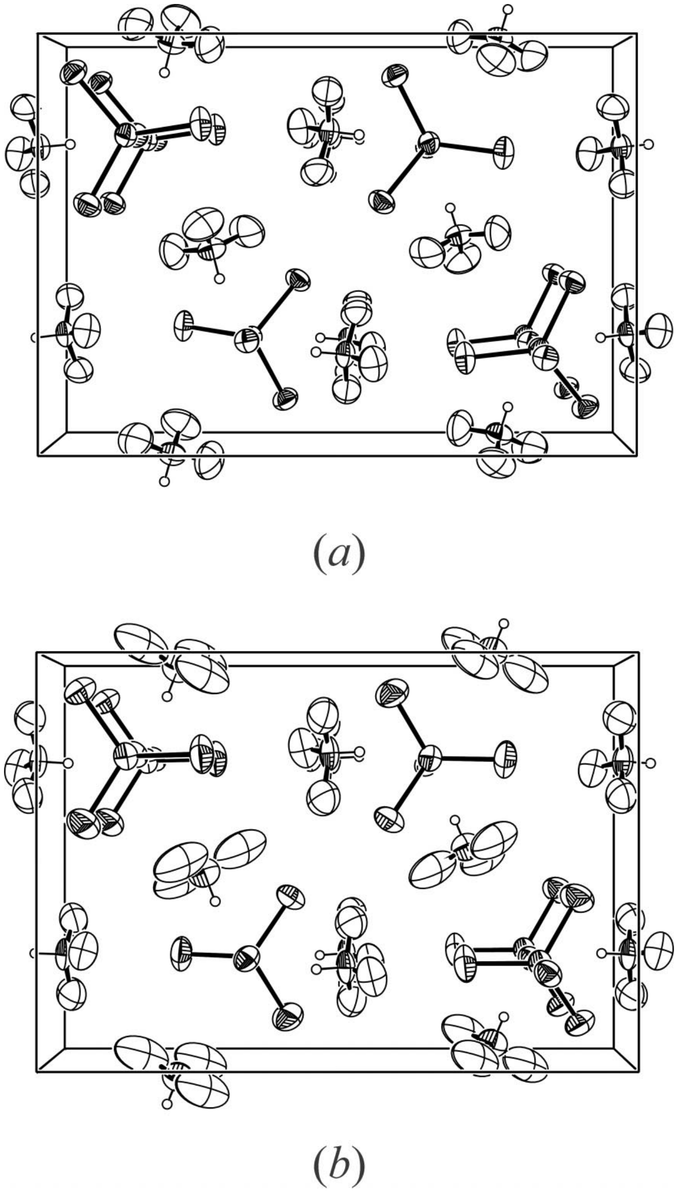


Figure 2
The crystal structure of (I): (*a*) at 295 K and (*b*) at 343 K. Displacement ellipsoids are shown at the 50% probability level.

The changes can be well described by increase in amplitude of the thermal motions of atoms. The tetrachloromercurate(II) ion is found to have a distorted tetrahedral geometry. However, the distortion is nearly temperature-independent. The Hg—Cl distances vary between 2.433 (9) and 2.568 (9) Å at 295 K, and between 2.414 (4) and 2.604 (4) Å at 343 K (Table 1). A slightly longer distance for Hg—Cl1 than those of the other Hg—Cl bonds is due to the effect of the hydrogen bonds. The crystal structures of (I) at 295 and 343 K is shown in Fig. 2. In each case, the asymmetric unit is one formula unit. The anisotropic displacement parameters of the Hg, Cl and N atoms show a quasi-isotropic behavior at 343 K, whereas the three C atoms have slightly elongated displacement ellipsoids, which can be explained by an oscillation about the local threefold axis containing the N and H atoms of the trimethylammonium ion. Tus it is evident that the disorder of the alkylammonium increases with temperature and it is to be expected that this should affect the orientation of the $HgCl_4$ tetrahedra through the hydrogen bond linking the two entities. As shown in Fig. 2, no major structural readjustment occurs, but each individual ion undergoes a rotational change; the most dramatic effect is associated with the TrMA2 ion, which rotates *ca.* 38° around the axis passing through atoms N2*a* and H2*a* [φ, χ and ψ are 137.58 (149), 23.21 (63) and −45,47(145)° at 295 K, and 120.94 (281), 25.22 (124) and −7.59 (336)° at 343 K]. Such a rotation of the organic cations was reported by Williams *et al.* (1992*b*) for dimethylammonium tetrachlorocobaltate at 235 K, where the phase transition is characterized by a rotation of one of the organic cations about the *b* axis. The apparent distances between the N and C atoms are shorter at 343 K than at 295 K, suggesting more orientational disorder at 343 K. Such behavior has been reported by Amami *et al.* (2002) for $(NMe_4)_2[HgCl_4]$. As a consequence, important changes are produced in the N—H···Cl contacts in the system. At room temperature, the atom Cl1 participates in two medium-strong hydrogen bonds (Gilli, 1995) of the N—H···Cl type, with N1*a*(1−*x*,1−*y*,1−*z*) and N2*a*(−1/2+*x*, 1/2−*y*, 1/2+*z*). The closest (N—)H···Cl contact for Cl2 and Cl3 with H1*a* on N1*a* (2.981 Å) is ~0.4 Å longer than the distance range for (N—)H···Cl hydrogen bonding suggested by Steiner (1998). Since this distance is so much longer than the corresponding values for the other Cl atoms (2.433–2.568 Å), it cannot be regarded as an N—H···Cl hydrogen bond. At 343 K, the N2*a*—H2*a*···Cl1 distance is strongly reduced (2.46 Å at 295 K and 2.26 Å at 343 K), giving rise to a very strong hydrogen bond (Table 2). The bonding from the second ammonium ion is perturbed much less; the H1*a*—Cl1 is retained, but slightly reduced. The different phases of (I) identified by X-ray diffraction show that the transition mechanisms are induced by the alkylammonium ion linked to a Cl atom by a hydrogen bond.

The present study reveals that the anomalies in DSC observed at 325 K are related to a reorientational disorder of one of the trimethylammonium cations about an axis passing through the N and H atoms. Finally, it is noticed that the phase transition at 325 K is a non-symmetry-breaking transition. Further information about the structural changes at the phase transitions is provided by the result of the maximum entropy method (MEM). Sections of the total electron-density, through the sites of TrMA1 and TrMA2 at 295 and 343 K, show a smoother density for the region around the N atoms at 343 K. This indicates a much larger range of positions for the C atoms.

Experimental

The title complex was obtained by mixing a solution of trimethylammonium chloride and mercury chloride in an acetone–ethanol solution, in the stoichiometric ratio 4:1. After a few weeks, colorless crystals of (I) were obtained by slow evaporation.

Crystal data

$(C_3H_{10}N)_2[HgCl_4]$
$M_r = 462.63$
Monoclinic, $P2_1/n$ (*c* axis unique)
$a = 18.741$ (2) Å
$b = 6.302$ (2) Å
$c = 13.069$ (3) Å
$\gamma = 91.68$ (1)°
$V = 1542.8$ (6) $Å^3$
$Z = 4$
$D_x = 1.991$ Mg m^{-3}
Synchrotron radiation
$\lambda = 0.5000$ nm
Cell parameters from 25 reflections
$\theta = 27.3–8.8°$
$\mu = 5.79$ mm^{-1}
$T = 343$ (2) K
Polyhedron, colorless
0.16 × 0.14 × 0.12 mm

Data collection

Huber four-circle Kappa diffractometer with Siemens SMART CCD area detector
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.474$, $T_{max} = 0.695$
6993 measured reflections
2174 independent reflections
1191 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 16.3°$
$h = -19 \rightarrow 20$
$k = -7 \rightarrow 7$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.079$
$S = 2.30$
1191 reflections
77 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0876P)^2 + 1.1621P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.90$ e $Å^{-3}$
$\Delta\rho_{min} = -0.96$ e $Å^{-3}$
Extinction correction: B–C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.24 (5)

Table 1
Selected geometric parameters (Å, °).

Hg—Cl1	2.604 (4)	Hg—Cl4	2.414 (4)
Hg—Cl2	2.442 (10)	N1*a*—C1*a*	1.50 (3)
Hg—Cl3	2.430 (7)	N2*a*—C4*a*	1.40 (3)
Cl1—Hg—Cl2	104.1 (3)	Cl2—Hg—Cl4	117.5 (4)
Cl1—Hg—Cl3	101.4 (2)	Cl3—Hg—Cl4	117.3 (4)
Cl1—Hg—Cl4	102.68 (15)	C1*a*—N1*a*—C1/2*a*	112.9 (16)
Cl2—Hg—Cl3	110.9 (3)	C4*a*—N2*a*—C4/1*a*	114.9 (18)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*a*—H1*a*···Cl1^{i}	0.97	2.48	3.272 (12)	138
N1*a*—H1*a*···Cl2^{ii}	0.97	3.09	3.699 (18)	124
N1*a*—H1*a*···Cl3^{ii}	0.97	3.12	3.656 (17)	117
N2*a*—H2*a*···Cl1^{iii}	1.00	2.26	3.13 (2)	147

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

Single-crystal X-ray diffraction experiments with synchrotron radiation were performed on beamline F1 of HASYLAB at DESY Hamburg, using a Huber four-circle Kappa diffractometer equipped with a Siemens SMART CCD area detector. A double-crystal Si(111) monochromator was used to selecte a wavelength of $\lambda = 0.500$ Å. No H atoms could be located from the Fourier map. The H atoms of the ammonium groups were calculated and fixed. However, the H atoms of the methyl groups were not included in the structure analysis.

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Data collection: *SMART* (Siemens, 1995); cell refinement: *MACH*3 in *CAD*-4 *UNIX Software* (Nonius, 1998); data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *JANA*2000 (Petricek & Dusek, 2000); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *JANA*2000.

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