

Preparation and Structure of $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ containing $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$, the First Tellurium–Nitrogen–Halogen Cation

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The reaction of TeCl_4 and $\text{N}(\text{SiMe}_3)_3$, followed by the addition of AsF_5 gives $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$, shown by its X-ray crystal structure to contain $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ $\{[(\text{Cl}_3\text{Te})\text{N}(\text{Te}(\text{Cl})\text{N}(\text{TeCl}_3)\text{Te}(\text{Cl}))]^{2+}\}$, the first tellurium–nitrogen–halogen cation.

A very extensive and important chemistry of sulfur(IV)–nitrogen–halogen compounds has been developed since Demarçay characterised $(\text{NSCl})_3$ and $[\text{S}_3\text{N}_2\text{Cl}]\text{Cl}$ in 1880.¹ Very recently a few analogous selenium–nitrogen–halogen compounds have been synthesized, e.g. $\text{Se}_3\text{N}_2\text{Cl}_2$,² Se_2NCl_3 ,^{3,4} ClSeNSeCl^{+4} and $\text{Cl}_2\text{SeNSeCl}_2$.⁵ Ternary tellurium–nitrogen–halogen species are unknown, except F_5TeNCl_2 ⁶ and the explosive azides Cl_3TeN_3 and $\text{Cl}_2\text{Te}(\text{N}_3)_2$.⁷ We report the preparation and X-ray crystal structure of the first ternary tellurium–nitrogen–halogen salt $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ containing the lattice-stabilised† $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$, a potential precursor to simple tellurium–nitrogen compounds. The salt contains $[(\text{Cl}_3\text{Te})\text{N}(\text{Te}(\text{Cl})\text{N}(\text{TeCl}_3)\text{Te}(\text{Cl}))]^{2+}$, which may be regarded as the dimer of $[\text{Cl}_3\text{Te}-\text{N}=\text{TeCl}]^+$, cf. the π -bonded monomeric $[\text{Cl}_2\text{SeNSeCl}_2]^{+5}$ and $[\text{F}_2\text{SNSF}_2]^{+8}$ reflecting the situation for related $\text{R}^1\text{N}=\text{E}=\text{NR}^2$ compounds ($\text{E} = \text{S}, \text{Se}$ monomer and $\text{R}^1, 2 = \text{Bu}^t, \text{SiMe}_3$; $\text{E} = \text{Te}$, dimer and $\text{R}^1 = \text{Bu}^t$ and $\text{R}^2 = \text{PPh}_2\text{NSiMe}_3$).^{9,10a} that appear to be stabilised by bulky groups. The preparation and characterisation of $[(\text{Bu}^t\text{N})\text{TeN}(\text{Bu}^t)\text{Te}(\text{NBu}^t)\text{N}(\text{Bu}^t)]$, $[(\text{Bu}^t\text{NH})\text{Te}^+\text{N}(\text{Bu}^t)\text{Te}(\text{NBu}^t)\text{N}(\text{Bu}^t)]\text{Cl}$ and

$[(\text{Bu}^t\text{N})\text{TeN}(\text{Bu}^t)\text{TeN}(\text{Bu}^t)\text{Te}]$ containing Te_2N_2 and Te_3N_3 rings have been very recently reported.^{10b}

The white thermally stable‡ and moisture-sensitive compound $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ was prepared in a two-step synthesis from TeCl_4 , $\text{N}(\text{SiMe}_3)_3$ and AsF_5 . A solution of $\text{N}(\text{SiMe}_3)_3$ (1.285 g, 5.5 mmol) in dried CH_2Cl_2 (30 ml) was added dropwise to a stirred suspension of TeCl_4 (2.964 g, 11 mmol) in dried CH_2Cl_2 (20 ml) under a nitrogen atmosphere over 30 min. A white precipitate under a pale yellow solution was refluxed for 1 h at 40 °C giving 1.673 g of a yellow powder§ that was placed on the glass frit of an extraction vessel and then continuously washed with CH_2Cl_2 for 3 h to remove soluble impurities. Addition of SO_2 (4.22 g) and AsF_5 (0.391 g, 2.24 mmol) onto the product (0.388 g) gave a yellow solution over a white precipitate. The solution was filtered after stirring at room temperature for 12 h and the volatiles removed under a dynamic vacuum giving a beige oil that solidified to a fluffy white solid (0.4 g) when heated to 30 °C for 30 s under vacuum. Recrystallisation from $\text{SO}_2\text{ClF}-\text{SO}_2$ (molar ratio, 1:9) led to colourless crystals of $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$. The compound did not lose SO_2 on evacuation under a dynamic vacuum for 2 h and is stable at 18 °C for at least 8 days under a nitrogen atmosphere.

The $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ salt¶ contains $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ (see Fig. 1), disordered AsF_6^- and SO_2 consistent with the FT-Raman (Fig. 2) and IR spectra (given in caption of Fig. 2). The X-ray powder photograph is consistent with the single-crystal data confirming that the bulk material is $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ (data deposited with supplementary material). The centrosym-

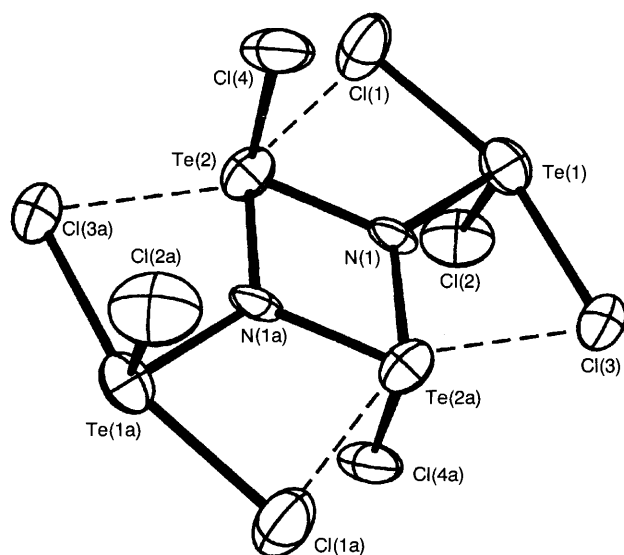


Fig. 1 Structure of the $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ cation showing intracationic contacts (a indicates symmetry equivalent atoms at 1.0 $-x, -y, -z$). Bond distances (Å) and angles (°): $\text{Cl}(1)-\text{Te}(1)$ 2.51(2), $\text{Cl}(2)-\text{Te}(1)$ 2.27(2), $\text{Cl}(3)-\text{Te}(1)$ 2.50(2), $\text{Te}(1)-\text{N}(1)$ 2.05(4), $\text{Te}(2)-\text{N}(1)$ 2.04(4), $\text{Te}(2)-\text{N}(1a)$ 1.98(4), $\text{Te}(2)-\text{Cl}(4)$ 2.30(2), $\text{Cl}(1)-\text{Te}(1)-\text{Cl}(3)$ 158.9(5), $\text{Cl}(2)-\text{Te}(1)-\text{Cl}(3)$ 91.8(6), $\text{Cl}(1)-\text{Te}(1)-\text{Cl}(2)$ 88.7(6), $\text{Cl}(4)-\text{Te}(2)-\text{N}(1)$ 95(1), $\text{Te}(1)-\text{N}(1)-\text{Te}(2)$ 124(1), $\text{Te}(2)-\text{N}(1)-\text{Te}(2a)$ 108(2), $\text{Te}(1)-\text{N}(1)-\text{Te}(2a)$ 127(2), $\text{Cl}(1)-\text{Te}(1)-\text{N}(1)$ 80(1), $\text{Cl}(3)-\text{Te}(1)-\text{N}(1)$ 79(1), $\text{Te}(2)-\text{N}(1)-\text{Te}(2)-\text{N}(1)$ 0.0. The transannular $\text{Te}\cdots\text{Te}$ separation is 3.252(2) Å. Shortest intracationic contacts (< 3.81 Å): $\text{Te}(2)\cdots\text{Cl}(1)$ 2.881(12), $\text{Te}(2a)\cdots\text{Cl}(3)$ 2.905(10). Shortest intercation–anion and intercation– SO_2 contacts (< 3.6 Å): $\text{Te}(1)\cdots\text{F}(1)$ 2.65(5), $\text{Te}(1)\cdots\text{F}(3)$ 3.16(5), $\text{Te}(1)\cdots\text{F}(7)$ 3.41(9), $\text{Te}(1)\cdots\text{F}(8)$, 3.18(8), $\text{Te}(1)\cdots\text{F}(10)$ 3.22(9), $\text{Te}(1)\cdots\text{F}(11)$ 3.46(6), $\text{Te}(2)\cdots\text{F}(5)$ 3.00(6), $\text{Te}(2)\cdots\text{F}(9)$ 3.12(8), $\text{Te}(1)\cdots\text{O}(2)$ 3.24(6), $\text{Te}(2)\cdots\text{O}(1)$ 2.88(4).

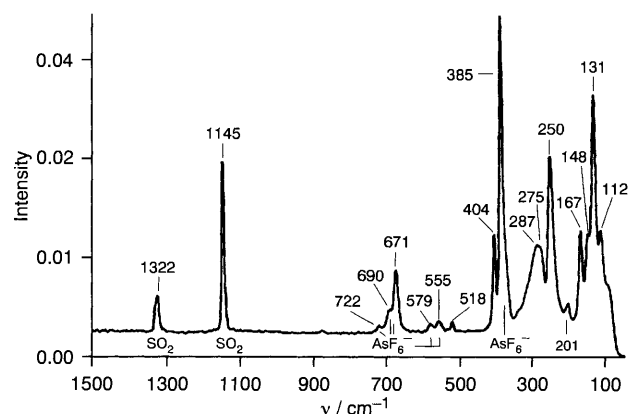
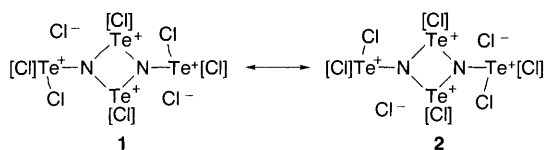


Fig. 2 FT-Raman spectrum of $\text{Te}_4\text{N}_2\text{Cl}_8(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ [measured on a FT-IR spectrometer Bruker IFS66 equipped with a FT-Raman accessory Bruker FRA106 using a Nd-YAG laser; the data were collected in the back-scattering mode (180° excitation; resolution, 4 cm^{-1} ; laser power: 81 mW; number of scans, 300; room temp.)]. Peaks attributable to SO_2 and AsF_6^- are assigned in the spectrum. Peaks attributable to the cation $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ are at 518 and 395 [$\nu(\text{TeN})$], 333, 324 287 and 250 [$\nu(\text{TeCl})$ in the plane], 404 cm^{-1} [$\nu(\text{TeCl})$ perpendicular to the plane]. The IR spectrum (Nujol mull between CsI plates) shows bands attributable to SO_2 (1320m, 1145m cm^{-1}) and AsF_6^- (738m, 695m, 608sh, 390s cm^{-1}) and the bands for the $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ are found at 518m [$\nu(\text{TeN})$], 400s [$\nu(\text{TeCl})$ perpendicular to the plane], 378m, 368m, 328m, 314m, 294m, 280m [$\nu(\text{TeCl})$ in the plane], 270m, 255 m, 245m, 235m cm^{-1} .



metric $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ cation contains a planar four-membered Te_2N_2 ring with Te–N bond lengths of 2.04(9) and 1.98(4) Å similar to that expected (2.04 Å)^{10c} for a $\text{Te}^{\text{IV}}\text{–N}$ bond and similar to distances in other related Te_2N_2 rings.¹⁰ The two exocyclic Te–N bond distances [2.05(4) Å] are not significantly different from those in the Te_2N_2 ring, *i.e.* each tellurium atom is joined to three nitrogen atoms by single bonds. The ten tellurium, nitrogen, Cl(1) and Cl(3) atoms are roughly coplanar (within 0.34 Å from the least-square plane). The tellurium–chlorine bond lengths [Te(1)–Cl(2) 2.27(2), Te(2)–Cl(4) 2.20(2) Å, perpendicular to the plane] are similar to those in $\text{TeCl}_3\text{AsF}_6$ [av. 2.264(2) Å],¹¹ *i.e.* are of bond order one. The longer tellurium–chlorine distances [Te(1)–Cl(1) 2.51(2), Te(1)–Cl(3) 2.50(2) Å] within the plane correspond to a bond order of about 0.5 implying that the bonding within the cation may be described approximately by valence bond structures **1** and **2** and related resonance structures. Consistently, there are four intracationic tellurium–chlorine contacts [$2 \times \text{Te}(2)\cdots\text{Cl}(1)$ 2.881(12), $2 \times \text{Te}(2)\cdots\text{Cl}(3)$ 2.905(10) Å] that are considerably less than the sum of the corresponding isotropic van der Waals radii (3.81 Å)¹² and are responsible for the axial portions of the $\text{N}_{\text{eq}}\text{Te}(1)\text{Cl}(2)_{\text{ax}}\text{Cl}(1)_{\text{ex}}\text{Cl}(3)_{\text{ax}}\text{E}$ (E = lone pair of electrons) moieties lying in the plane of the Te_2N_2 ring and the essentially coplanar geometry of the $\text{Te}_4\text{N}_2\text{Cl}_4$ fragment of the $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ cation.

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Footnotes

† Like some other dications, *e.g.* S_8^{2+} ,^{14a} $\text{S}_3\text{N}_2^{2+}$,^{14b} $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ is almost certainly not stable as a gas-phase species, and therefore it can be said to be *lattice-stabilised*. The dication is stabilised in the solid state by the lattice energy of the 1 : 2 salt and is estimated by the Kapustinskii equation¹³ with $r(\text{Te}_4\text{N}_2\text{Cl}_8^{2+}) = 390$ pm and $r(\text{AsF}_6^-) = 293$ pm as 1013 kJ mol⁻¹.

‡ Melts with decomposition at 175 °C but (as is the case for ' Te_2NCl_5 ', see footnote §) we cannot rule out decomposition prior to this temperature.

§ The yellow powder is extremely moisture sensitive, melts with decomposition at *ca.* 170 °C, and does not explode on grinding. Its IR spectrum is similar to that attributed to ' Te_2NCl_5 ' produced in a similar reaction reported in a recent thesis by Wollert,¹⁵ which came to our attention during the preparation of this manuscript. *Spectroscopic data of a typical product*: IR (KBr, range 4200–400 cm⁻¹) ν/cm^{-1} : 1405w (Si–C) (impurity), 1250w (Si–C) (impurity), 830m (NTeN), 755s (NTeN), 698m (NTeN), 684m (NTeN), 605w (NTeN), 565m (NTeN); the Te–Cl vibrations are expected below 400 cm⁻¹. Main fragments in the mass spectrum (70 eV, direct inlet method) are attributable to: Te^+ , TeCl^+ , TeNCl^+ , TeCl_2^+ , TeNCl_2^+ , TeCl_3^+ , Te_2^+ and Te_2Cl^+ . The yellow powder probably contains more than one major product.

¶ *Crystal data*: $\text{As}_2\text{Cl}_8\text{F}_{12}\text{N}_2\text{Te}_4 \cdot 2\text{SO}_2$, $M = 1327.98$, monoclinic, space group $P2_1/c$, $a = 8.758(9)$, $b = 11.529(8)$, $c = 14.37(1)$ Å, $\beta = 103.58(7)^\circ$, $U = 1411(2)$ Å³, $Z = 4$, $D_c = 3.126$ g cm⁻³, $\mu(\text{Mo–K}\alpha) = 74.22$ mm⁻¹,

$\lambda(\text{Mo–K}\alpha) = 0.71069$ Å, $F(000) = 1192$, crystal size 0.20 x 0.26 x 0.27 mm. Crystals were mounted in dried capillary tubes in a Vacuum Atmospheres Dri-Lab and flame sealed. Data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo–K α radiation at $18 \pm 1^\circ\text{C}$ using ω – 2θ scans ($2\theta_{\text{max}} = 46^\circ$). Of the 3063 reflections collected 2020 were unique ($R_{\text{int}} = 0.074$). The structure was determined by direct methods¹⁶ and the data were corrected for Lorentz and polarization effects. An empirical absorption correction using psi-scan was applied which resulted in absorption coefficients ranging from 0.675 to 1.0. Refinement by full-matrix least squares¹⁶ with all atoms assigned anisotropic thermal parameters resulted in the final residuals $R = 0.0680$, $R_w = 0.0870$ for 1080 observed reflections [$I \geq 2.5\sigma(I)$] and 209 parameters. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.¹⁷ Scattering factors were taken from ref. 18 and effects of anomalous dispersion were included in F_c ;¹⁹ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Ibers.²⁰

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