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Tetrapyridinium di-μ-oxo-bis[trifluorotellurate(IV)] bis[pentafluorotellurate(IV)]

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Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.006 Å
R factor = 0.029
wR factor = 0.064
Data-to-parameter ratio = 17.2

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

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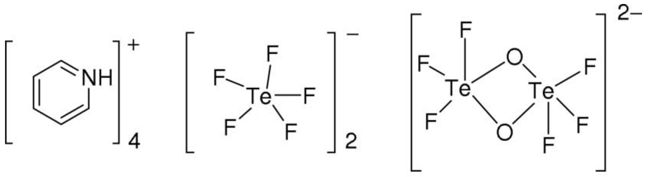
The title compound, $2C_5H_6N^+ \cdot TeF_5^- \cdot 0.5Te_2F_6O_2^{2-}$, contains two anions, $[TeF_5]^-$ and $[Te_2O_2F_6]^{2-}$. The $[Te_2O_2F_6]^{2-}$ anions are involved in H$\cdots$F/O bonding with the pyridinium cations. Crystallographically imposed inversion leads to molecular C_s symmetry for the $[Te_2O_2F_6]^{2-}$ anions. Extended chains of inversion-related pyridinium cations are built up by π–π interactions.

Comment

During our recent investigations (Klapötke *et al.*, 2003) on binary covalent tellurium azides, a stabilization of the tetra-azide $Te(N_3)_4$ as a pyridine adduct was desirable. Adducts of TeF_4 with Lewis bases L have been reported (L = Me_3N, dioxane, bipyridine and tetramethylethylenediamine), but apart from elemental analysis, no analytical information has been obtained (Greenwood *et al.*, 1966). In order to confirm the suggested formulae $[LTeF_3][TeF_5]$ for these adducts, further analytical information on the ionic compounds was necessary. An initial X-ray structure determination of the colorless crystal, obtained by reaction of excess pyridine (py) with neat TeF_4 at room temperature was believed to be $py_2[Te_2F_8][pyH]_2[TeF_5]$ (Klapötke *et al.*, 2003). For several reasons, this turned out to be rather unlikely.



(I)

First, this would imply a connection pattern different from that in crystalline TeF_4 (Edwards & Hewaidy, 1968; Kniep *et al.*, 1984). While the latter features polymeric chains (F—TeF_3—F—TeF_3—), with the apical F atoms connected in the so-called Te_2F_8 dimer, the two TeF_4 units would be associated through both basal and apical F atoms. This dimeric arrangement has only once been mentioned in the literature in the course of a theoretical treatment (Martynyuk *et al.*, 1999). Quantum chemical calculations then showed a poor agreement with the structure determination: both at DFT (density functional theory) and MP2 levels the separation distance of the two TeF_4 moieties is much larger than in the crystal.

Second, closer inspection of the crystal structure reveals that, on all N atoms of the pyridine rings, H atoms can be located, resulting in pyridinium cations. The charge problem resulting from this fact is easily resolved when the bridging F atoms (F4) are replaced by O atoms. Both displacement

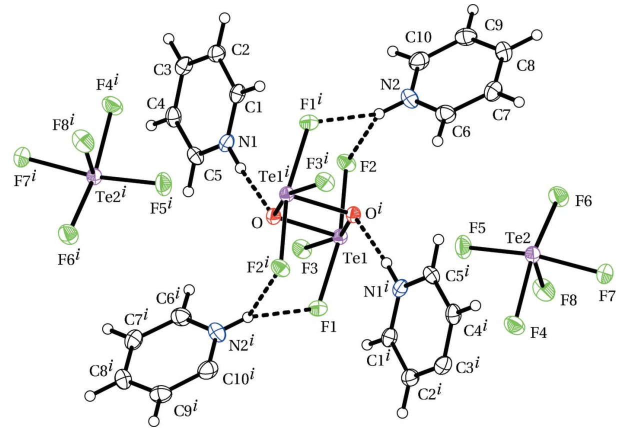


Figure 1
The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashed lines indicate hydrogen bonds.

parameters and *R* values refine favorably. Furthermore, quantum chemical investigations match to a much higher degree compared to Te_2F_8.

Hence, it has to be concluded that the crystal structure, in fact, contains the $[Te_2O_2F_6]^{2-}$ anion (Fig. 1), changing the composition to $[pyH]_4[TeF_5]_2[Te_2O_2F_6]$. The $[Te_2O_2F_6]^{2-}$ anion has also been found in the potassium salt $K_2[Te_2O_2F_6]$, reported as $KTeOF_3$ (Kessler & Jansen, 2001). The formation of the crystals described here can be explained by slow partial hydrolysis of two molecules of $[TeF_5]^-$ to form $[Te_2O_2F_6]^{2-}$ after extended periods.

In contrast to the previously reported crystal structure of $K_2[Te_2O_2F_6]$, in the present case, hydrogen bridging between $[pyH]^+$ cations and $[Te_2O_2F_6]^{2-}$ anions is found, with H$\cdots$O/F distances between 1.99 and 2.36 Å. In contrast to $[Te_2O_2F_6]^{2-}$, and $[TeF_5]^-$ anions in ammonium pentafluorotellurates (Mahjoub *et al.*, 1992), the $[TeF_5]^-$ anions participate in intermolecular interactions, with a Te2$\cdots$F8^{ii} distance of 3.151 (2) Å [symmetry code: (ii) $x, 1.5 - y, \frac{1}{2} + z$]. Additionally, pairs of inversion-related pyridinium cations show π–π interactions, forming extended chains in the crystal structure.

The structural parameters of the $[Te_2O_2F_6]^{2-}$ anion in the crystal structure are slightly different from those reported previously (Kessler O = 1.900 (2) *versus* 1.906 (3) Å, Te1—O^{i} = 2.119 (2) *versus* 2.048 (3) Å, Te—F = 1.964 (2)–2.007 (2) *versus* 1.990 (3)–2.061 (2) Å, Te$\cdots$Te^{i} = 3.1803 (4) *versus* 3.1076 (5) Å]. The square-pyramidal structure of the $[TeF_5]^-$ anion is in accordance with those found in ammonium pentafluorotellurates, with Te—F$_{\rm apical}$ = 1.859 (6)/1.867 (2) Å and Te—F$_{\rm basal}$ = 1.937 (6)–1.975 (3) Å (Mahjoub *et al.*, 1992).

Experimental

A suspension of TeF_4 (1.0 mmol) in dry pyridine (5 ml) was stirred for 12 h under argon. All volatile material was then pumped off *in vacuo*. Slow crystallization from CH_2Cl_2 yielded, after several months, $[pyH]_4[TeF_5]_2[Te_2O_2F_6]$ as colorless crystals, probably as a result of partial hydrolysis.

Crystal data

$2C_5H_6N^+\cdot TeF_5^-\cdot 0.5Te_2O_2F_6^{2-}$
M_r = 583.42
Monoclinic, $P2_1/c$
a = 10.1509 (2) Å
b = 20.0739 (3) Å
c = 7.9950 (1) Å
β = 105.8894 (8)°
V = 1566.88 (4) Å^3
Z = 4

D_x = 2.473 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 35743 reflections
θ = 3.1–27.5°
μ = 3.81 mm^{-1}
T = 200 (2) K
Block, colorless
0.30 × 0.20 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: numerical (*X-RED32* and *X-SHAPE*; Stoe & Cie, 1997)
$T_{\rm min}$ = 0.350, $T_{\rm max}$ = 0.690
36947 measured reflections

3586 independent reflections
2948 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.073
$\theta_{\rm max}$ = 27.5°
$h = -13 \rightarrow 13$
$k = -26 \rightarrow 26$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.064
S = 1.08
3586 reflections
208 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.4788P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 1.00 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.10 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Te1—O	1.900 (2)	Te2—F8	1.870 (2)
Te1—F3	1.964 (2)	Te2—F7	1.937 (2)
Te1—F2	1.998 (2)	Te2—F4	1.949 (2)
Te1—F1	2.007 (2)	Te2—F6	1.956 (2)
Te1—O^{i}	2.119 (2)	Te2—F5	1.969 (2)
Te1—Te1^{i}	3.1803 (4)		
O—Te1—F3	83.21 (10)	F7—Te2—F4	87.25 (10)
O—Te1—F2	85.08 (9)	F8—Te2—F6	80.77 (11)
F3—Te1—F2	86.18 (8)	F7—Te2—F6	86.94 (10)
O—Te1—F1	84.17 (9)	F4—Te2—F6	160.75 (11)
F3—Te1—F1	87.64 (9)	F8—Te2—F5	79.79 (11)
F2—Te1—F1	168.16 (8)	F7—Te2—F5	161.35 (12)
F8—Te2—F7	81.57 (11)	F4—Te2—F5	89.67 (10)
F8—Te2—F4	80.22 (11)	F6—Te2—F5	89.99 (10)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O	0.88	1.88	2.752 (3)	175
N2—H2$\cdots$F2	0.88	2.24	2.837 (4)	125
N2—H2$\cdots$F1^{i}	0.88	2.09	2.859 (4)	146

Symmetry code: (i) $-x+1, -y+1, -z+1$.

H atoms were placed in geometrically idealized positions (N—H = 0.88 Å and C—H 0.95 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N). The highest residual electron density is located 2.53 Å from Te1 and 1.51 Å from F3. The deepest hole is located 0.89 Å from atom Te1.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997);

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program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1996); software used to prepare material for publication: *SHELXL97*.

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