Crystal Structures of μ-Bromo-bis[bromobis(ethylenethiourea)tellurium(II)] Bromide Hexabromotellurate (IV) and *catena*-μ-Bromo-bis(trimethylenethiourea)tellurium(II) Hexabromotellurate(IV)

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The compound $Te_7(etu)_{12}Br_{16}$ (*1*) (etu = ethylenethiourea) forms rhombohedral crystals, space group $R\bar{3}c$ (No. 167) with $Z = 2$; $a = 16.902(1)$ Å and $\alpha = 92.60$ (1)°. The compound $Te_3(trtu)_4Br_8$ (*2*) (trtu = trimethylenethiourea) forms monoclinic crystals, space group $P2_1/c$ (No. 14) with $Z = 2$; $a = 9.496(2)$, $b = 27.279(4)$ and $c = 8.070(2)$ Å, and $\beta = 110.87(2)°$. The structures were determined by X-ray methods and refined to R 0.051 (*1*) and 0.046 (*2*) for 1467 and 2953 observed reflections, respectively. Compound *1* is $\{[Te_2(etu)_4Br_3]^+\}_3Br^-[TeBr_6]^{2-}$ and *2* is *catena*-$\{[Te(trtu)_2Br]^+\}_{2n}\{[TeBr_6]^{2-}\}_n$. The cations contain distorted square-planar *cis*-TeS_2Br_2 coordination groups, where one of the Br atoms in *1* bridges two Te atoms, while both Br atoms in *2* are bridging. Bond lengths in the *cis*-TeS_2Br_2 groups are: Te–S = 2.468(2)–2.491(4), Te–Br = 2.966(2)–3.099(1) Å; angle S–Te–Br = 174.7(1)–178.0(1)°. The $[TeBr_6]^{2-}$ ion in *1* is disordered; in *2*, the ion is centrosymmetric with Te–Br distances of 2.701(1), 2.723(1) and 2.679(1) Å.

In the course of work on ethylenethiourea (etu) complexes of divalent tellurium, a compound with apparent composition $Te_7(etu)_{12}Br_{16}$ (*1*) was obtained.[1] If the formula were correct, one of the seven tellurium atoms must be tetravalent. We have prepared a trimethylenethiourea (trtu) analogue, $Te_3(trtu)_4Br_8$ (*2*), in which one of the three tellurium atoms is tetravalent, and we report here the crystal structures of compounds *1* and *2*.

Experimental

The preparation of $Te_7(etu)_{12}Br_{16}$ (*1*) has been described.[1] The unit cell was first reported[1] to be *C*-centered monoclinic, but has now been found to be rhombohedral. According to Himes and Mighell,[2] "– many rhombohedral crystals have been incorrectly reported in centered monoclinic or in

triclinic space groups". The reddish-brown crystals are hexagonal prisms $\{10\bar{1}\}$, often tapering but in some cases terminated by well-developed rhombohedral faces $\{110\}$.

Compound 2 was prepared by dissolving TeO_2 (0.80 g, 5 mmol) in warm HBr (ca. 50 % w/w, 25 cm³) and adding first hot water (125 cm³), followed by a hot solution of trtu (1.74 g, 15 mmol) in water (25 cm³) with agitation. The mixture was filtered while hot and the filtrate was allowed to cool. Crystallization from hot solution was initiated by scratching of the beaker walls or, in later preparations, by seeding. The crystals were washed on the filter with methanol containing a little HBr and then with diethyl ether; yield ca. 2.0 g. Anal. $C_{16}H_{32}Br_8N_8S_4Te_3$: C, H, N, S. The crystals are dark red, flat, monoclinic prisms extended along the *c* axis, with $\{100\}$ dominant.

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Table 1. Crystallographic data.

No.	1	2
Compound	$Te_7(etu)_{12}Br_{16}$	$Te_3(trtu)_4Br_8$
Formula	$C_{36}H_{72}Br_{16}N_{24}S_{12}Te_7$	$C_{16}H_{32}Br_8N_8S_4Te_3$
M	3397.65	1486.82
System	Rhombohedral	Monoclinic
Space group	$R\bar{3}c$ (No. 167)	$P2_1/c$ (No. 14)
a/Å	16.902(1)	9.496(2)
b/Å		27.279(4)
c/Å		8.070(2)
α/°	92.60(1)	
β/°		110.87(2)
V/Å^3	4812.9(1.2)	1953.5(1.4)
Z	2	2
D_x/g cm^{-3}	2.344	2.528
D_m/g cm^{-3}	2.34	2.54
F(000)	3144	1368
μ(MoKα)/cm^{-1}	95.01	112.09
Crystal volume/mm^3	0.0023	0.0034
Transmission factors	0.392–0.472	0.066–0.786
Scan rate/° min^{-1}	5.03–0.75	6.71–1.01
θ_{max}/°	25	28
Unique reflections	3042	4718
Reflections $I > 2\sigma$	1467	2953
No. of variables	154	178
R	0.051	0.046
R_w	0.049	0.048
S	1.371	1.598
Max. $\Delta(\varrho)$/e Å^{-3}	3.00	1.92

X-Ray structure analyses. Data for unit cell dimensions and intensities were recorded on a CAD4 diffractometer using graphite-monochromated MoKα radiation (λ = 0.71069 Å). Intensities were recorded by ω scan, and the scan width was $1.00+0.35$ tanθ, plus 25 % on each side for background. The intensities were corrected for Lorentz and polarization effects, decay, and absorption. Maximum decay corrections, based on the intensities of three reference reflections measured every 2 h of exposure time, were 1.052 for *1* and 1.035 for *2*. Reflections with $I > 2\sigma(I)$ were regarded as observed and were used in the calculations. These were carried out using the Enraf-Nonius SDP programs. Atomic scattering factors, with anomalous dispersion terms included, were from Ref. 3. Refinement was full matrix least-squares, the sum minimized being $\Sigma w\Delta^2(F)$, with $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$, and $\sigma^2(I) = \sigma^2(I)_{count} + (0.02I)^2$.

Crystal data are given in Table 1. The structures were solved by direct (MULTAN) and Fourier difference methods. The intensity distributions were centric, indicating that the space group of *1* was $R\bar{3}c$ and not $R3c$; this was confirmed by the structure refinement. The Te atom of the $[TeBr_6]^{2-}$ ion of *1* was first placed in a twofold position of 32 symmetry and the Br atoms in general twelve-fold positions. However, large thermal parameters for these atoms indicated that the ion was disordered. Half-ions were therefore placed on each side of the 32 symmetry centre, with Te on the three-fold axis.

Anisotropic thermal parameters were used for all atoms except hydrogen and the disordered Te atom. Hydrogen atoms were placed geometrically with bond lengths N–H = 0.87 and C–H = 0.95 Å, and were held fixed with a common fixed value for B_{iso}.

The parameter shifts in the last cycle of re-

finement were less than one percent of the associated e.s.d.'s. The highest peak, viz. 3.0 e Å^{-3}, in the final difference Fourier map for compound *1* lay within the disordered [TeBr$_6$]$^{2-}$ ion. Atomic coordinates for non-hydrogen atoms are given in

Table 2. Thermal parameters, complete bond lengths and angles, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Table 2. Fractional atomic coordinates with e.s.d.'s in parentheses.

Atom	x	y	z	B_{eq}/Å^2
(a) Te$_7$(etu)$_{12}$Br$_{16}$ (*1*)				
Te(1)	0.87143(6)	0.34071(6)	0.09744(6)	3.33(2)
Te(2)[a]	0.23753(16)	0.23753[b]	0.23753[b]	6.5(1)[c]
Br(1)	0.84852(9)	0.51073(9)	0.13646(10)	4.48(4)
Br(2)	$\frac{3}{4}$	0.28692(10)	0.21308[d]	6.80(5)
Br(3)[a]	0.3317(4)	0.3614(3)	0.1941(3)	10.6(2)
Br(4)[a]	0.3986(3)	0.3417(3)	0.2212(3)	9.9(1)
Br(5)	0	0	0	4.59(2)
S(1)	0.97005(23)	0.38930(25)	0.00472(24)	4.3(1)
S(2)	0.90300(25)	0.20167(23)	0.06052(25)	4.5(2)
N(1)	0.9467(7)	0.4542(7)	−0.1347(7)	4.3(3)
N(2)	0.8370(7)	0.4267(8)	−0.0787(7)	4.7(3)
N(3)	0.7677(7)	0.2066(7)	−0.0361(8)	4.8(3)
N(4)	0.8284(7)	0.0976(7)	−0.0414(6)	4.0(3)
C(1)	0.9142(8)	0.4242(8)	−0.0711(8)	3.3(3)
C(2)	0.8284(9)	0.1681(8)	−0.0066(9)	3.9(4)
C(3)	0.8896(9)	0.4853(9)	−0.1879(8)	4.7(4)
C(4)	0.8110(9)	0.4601(10)	−0.1539(9)	5.5(4)
C(5)	0.7187(9)	0.1586(10)	−0.0927(10)	5.4(5)
C(6)	0.7621(9)	0.0823(9)	−0.0994(10)	5.2(4)
(b) Te$_3$(trtu)$_4$Br$_8$ (*2*)				
Te(1)	0.55579(8)	0.30715(2)	0.38145(8)	2.90(1)
Te(2)	0	0	0	2.47(2)
Br(1)	0.71585(14)	0.27920(4)	0.12556(14)	4.16(3)
Br(2)	0.21347(13)	−0.07026(4)	0.06599(15)	3.90(3)
Br(3)	0.12038(13)	0.04586(4)	−0.21844(14)	4.38(3)
Br(4)	0.17422(14)	0.05454(4)	0.27183(15)	4.37(3)
S(1)	0.4228(3)	0.37140(9)	0.1676(3)	3.48(6)
S(2)	0.4176(3)	0.32726(10)	0.5811(3)	3.91(6)
N(1)	0.1346(10)	0.3494(3)	0.0034(12)	5.0(2)
N(2)	0.2983(9)	0.3011(3)	−0.0676(11)	4.1(2)
N(3)	0.6355(10)	0.3742(3)	0.8311(11)	3.9(2)
N(4)	0.4681(9)	0.4221(3)	0.6202(10)	3.2(2)
C(1)	0.2712(11)	0.3369(3)	0.0238(12)	3.1(2)
C(2)	0.5179(11)	0.3796(3)	0.6863(11)	3.0(2)
C(3)	0.0035(4)	0.3295(5)	−0.1438(20)	6.7(4)
C(4)	0.0518(13)	0.3064(4)	−0.2820(16)	5.2(3)
C(5)	0.1771(14)	0.2736(4)	−0.1996(14)	4.5(3)
C(6)	0.7186(15)	0.4172(4)	0.9280(15)	5.1(3)
C(7)	0.6169(14)	0.4595(4)	0.9013(15)	5.3(3)
C(8)	0.5342(12)	0.4686(4)	0.7070(15)	4.4(3)

[a]Disordered, occupancy 0.5. [b]$x = y = z$. [c]B_{iso}. [d]$z = \frac{1}{2} - y$.

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Results and discussion

Compound *1*, Te$_7$(etu)$_{12}$Br$_{16}$, consists of din-uclear, mono-Br-bridged [Te$_2$(etu)$_4$Br$_3$]$^+$ cations and Br$^-$ and [TeBr$_6$]$^{2-}$ anions in the ratio 3:1:1. The bridging Br atom lies on a two-fold sym-metry axis. Compound *2*, Te$_3$(trtu)$_4$Br$_8$, consists of infinite chains of cationic, Br-bridged [Te (trtu)$_2$Br]$^+$ units and [TeBr$_6$]$^{2-}$ anions in a ratio of 2:1; consecutive cationic units are symmetry re-lated through the glide plane *c*, the translation of which is *c*/2 = 4.035 Å.

The cationic species. Both are based on divalent tellurium and contain distorted, square-planar *cis*-TeS$_2$Br$_2$ coordination groups. One of the Br atoms in *1*, and both Br atoms in *2* are bridging. Bond lengths and angles are listed in Table 3, and views are shown in Figs. 1 and 2. In *1*, terminal Te–Br(1) is slightly shorter than bridging Te–Br(2). Similar *cis*-TeS$_2$Br$_2$ groups with etu or trtu as thio ligands occur in two crystalline forms of dinuclear, di–Br-bridged [Te$_2$(etu)$_4$Br$_2$]Br$_2$,[4] and in mononuclear *cis*-Te(trtu)$_2$Br$_2$.[5] Bond lengths in the former are: Te–S = 2.481(2)–2.495 (3), Te–Br = 3.015(1)–3.079(1) Å, and in the lat-ter: Te–S = 2.499(5), Te–Br = 2.994(2) Å. The cation of *1* is the first example of a dinuclear tell-urium(II) complex with only one bridge. Infinite helices of Br-bridged, trapezoid-planar TeS$_2$Br$_2$ groups occur in Te(S$_2$COEt)$_2$Br.[6]

The TeS$_2$Br$_2$ groups are almost, but not ex-actly, planar (see TeS$_2$/TeBr$_2$ plane angles, Table 3). The largest deviation of an atom from the TeS$_2$Br$_2$ least-squares plane is 0.029(4) Å for S(2) in *1* and 0.056(1) Å for Te(1) in *2*.

In *1*, the bond angle at the bridging Br(2) atom is 93.99(4)° and the non-bonded distance across the two-fold axis [Te(1)···Te(1')] is 4.440(2) Å. The Br(1)···Te(1') distance is 4.110(2) Å and cor-responds to a Br(1)Te(1)Br(2)Te(1') torsion an-gle of 45.9°. In compound *2*, the bond angle at the bridging Br atoms is larger, 111.64(4)°, and the non-bonded distance across the glide plane (Te(1)···Te(1')) is 5.099(1) Å; the non-bonded Te (1)···Br distances are 5.696(1) and 7.189(1) Å and the corresponding torsion angles are 80.6 and 161.2°.

The thiourea ligands are attached differently in the two compounds. The C–S–Te–S–C sequence is *cis* in *1* and *trans* in *2* (see Figs. 1 and 2); in *1* the two etu groups lie on the same side of the

Table 3. Distances (Å) and angles (°) in the cationic tellurium(II) species, with e.s.d.'s in parentheses.[a]

	Te$_7$(etu)$_{12}$Br$_{16}$	Te$_3$(trtu)$_4$Br$_8$
(a) Bonds		
Te(1)–Br(1)	2.966(2)	3.065(1)
Te(1)–Br(2)	3.036(1)	
Te(1)–Br(1')		3.099(1)
Te(1)–S(1)	2.477(4)	2.468(2)
Te(1)–S(2)	2.491(4)	2.475(2)
S(1)–C(1)	1.701(13)	1.765(9)
S(2)–C(2)	1.717(14)	1.757(8)
(b) Bond angles		
Br(1)–Te(1)–Br(2)	92.60(5)	
Br(1)–Te(1)–Br(1')		89.46(2)
Br(1)–Te(1)–S(1)	85.47(9)	87.62(6)
Br(1)–Te(1)–S(2)	174.71(11)	177.53(6)
Br(2)–Te(1)–S(1)	178.06(10)	
Br(1')–Te(1)–S(1)		175.55(5)
Br(2)–Te(1)–S(2)	92.25(10)	
Br(1')–Te(1)–S(2)		90.48(6)
S(1)–Te(1)–S(2)	89.66(13)	92.29(8)
Te(1)–Br(2)–Te(1')	93.99(4)	
Te(1)–Br(1')–Te(1')		111.64(4)
Te(1)–S(1)–C(1)	104.1(5)	100.1(3)
Te(1)–S(2)–C(2)	105.0(5)	100.0(3)
(c) Angles between planes[b]		
(1)–(2)	2.1	4.3
(2)–(3)[c]	108.8	−92.4
(2)–(4)[c]	−99.9	−78.8
(3)–(5)	1.4	61.9
(4)–(6)	1.4	88.1

[a]Primed atoms over molecular two-fold axis in Te$_7$(etu)$_{12}$Br$_{16}$, and over glide plane *c* in Te$_3$(trtu)$_4$Br$_8$.
[b]Plane (1): Br(1)Te(1)Br(2) or Br(1)Te(1)Br(1'); plane (2): S(1)Te(1)S(2); plane (3): Te(1)S(1)C(1); plane (4): Te(1)S(2)C(2); plane (5): S(1)C(1)N(1)N(2); plane (6): S(2)C(2)N(3)N(4). The atoms defining least-squares planes (5) and (6) lie in the planes within error limits. [c]Te–S torsion angles.

TeS$_2$ plane and in *2* the two trtu groups lie on op-posite sides. The TeS$_2$/SCN$_2$ plane angles, i.e. the thiourea twist angles,[7] are different, being nearly 0° in *1* and closer to 90° in *2*.

Some short N–H···Br distances occur in the ca-tions, indicating hydrogen bonds. In *1*, distances across the two-fold axis are: N(2)···Br(1') 3.525 (12), H···Br(1') 2.76 Å, N(3)···Br(1') 3.395(10) and H···Br(1') 2.64 Å. In *2*, with Br(1″) at
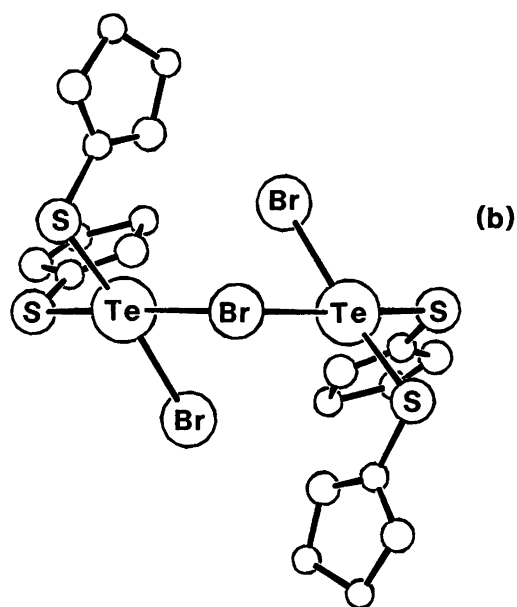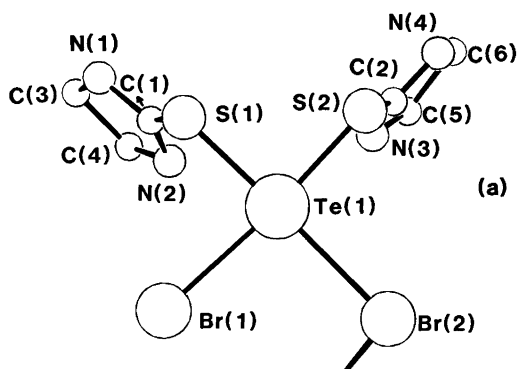
Fig. 1. Views of Te$_7$(etu)$_{12}$Br$_{16}$: (a) the cis-TeS$_2$Br$_2$ group; (b) the [Te$_2$(etu)$_4$Br$_3$]$^+$ cation as seen along the two-fold axis.

neighbours are methylene groups, with the C atoms at distances of 3.77(2), 3.95(2) and 3.97(2) Å from Br(3), and 3.80(2) and 3.99(2) Å from Br(4). In [Me$_4$N]$_2$[TeBr$_6$], Me$\cdots$Br contact distances of 3.69 and 3.82 Å have been found.[8]

The Br$^-$ ion of *1* lies in a position of $\bar{3}$ symmetry, and is surrounded by six N(4)–H groups with N(4) at 3.460(10) Å and H at 2.62 Å.

In *2*, the [TeBr$_6$]$^{2-}$ ion is centrosymmetric. The bond lengths are: Te(2)–Br(2) 2.701(1), Te(2)–Br(3) 2.723(1) and Te(2)–Br(4) 2.679(1) Å, and the angles are: Br(2)–Te(2)–Br(3) 89.71(3), Br(2)–Te(2)–Br(4) 91.80(3) and Br(3)–Te(2)–Br(4) 89.76(3)°. The average bond length, 2.701 Å, is equal to that in [Me$_4$N]$_2$[TeBr$_6$], in which the ion has $\bar{3}$ symmetry.[8] The ion is surrounded by methylene groups, with three C atoms at distances of 3.916(10)–3.974(9) Å from Br(2), one at 3.872(9) Å from Br(3), and five at 3.692(10)–3.972(11) Å from Br(4). The H atoms of two N–H groups are at distances of 2.75 and 2.82 Å from Br(3), the N atoms being 3.564(6)
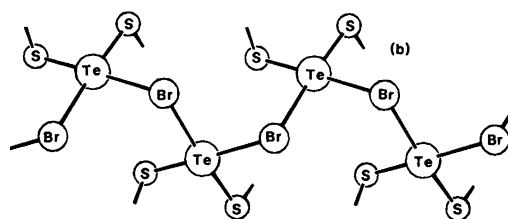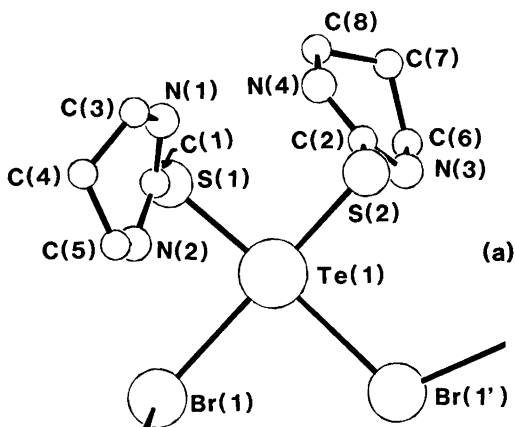
$x, y, \frac{1}{2}+z$, N(3)$\cdots$Br(1'') = 3.415(7) and H$\cdots$Br(1'') 2.64 Å.

The [TeBr$_6$]$^{2-}$ ions and the ionic environment. The [TeBr$_6$]$^{2-}$ ion is disordered in compound *1*. The Te atoms of two half-ions lie on a three-fold symmetry axis on either side of a 32 symmetry centre, 0.696(3) Å apart. The dimensions of the half-ions are: Te–Br 2.719(5) and 2.743(5) Å, and Br–Te–Br 87.0(1)–96.8(2) and 173.0(2)°. The nearest

Fig. 2. Views of Te$_3$(trtu)$_4$Br$_8$: (a) the cis-TeS$_2$Br$_2$ group; (b) the chain as seen normal to the glide plane.

and 3.666(7) Å distant, respectively. A rather short distance, 3.937(1) Å, is found between Br(2) and the Te atom of a TeS_2Br_2 group located at $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

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