

Crystal Structures of Tetrakis(thiourea)tellurium(II) Salts. Orientations of Ligands

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The crystal structures of monoclinic forms of the salts $[\text{Te}(\text{tu})_4]\text{Cl}_2$ (**1**) and $[\text{Te}(\text{tu})_4](\text{HF}_2)_2$ (**2**) (tu = thiourea) have been determined by X-ray methods. The structures of $[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**3**) and $[\text{Te}(\text{tu})_4](\text{ClO}_4)_2$ (**4**), determined earlier, have been refined and the structures of $[\text{Te}(\text{trtu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**5**) and $[\text{Te}(\text{trtu})_4](\text{ClO}_4)_2$ (**6**) (trtu = trimethylenethiourea) have been determined. They were refined to R 0.023 (**1**), 0.024 (**2**), 0.029 (**3**), 0.031 (**4**), 0.035 (**5**) and 0.041 (**6**) for 2249, 3395, 3555, 5732, 2841 and 3939 observed reflections, respectively. In salt **1** the cation has two-fold axis symmetry, in **2**, **3**, **5** and **6** it is centrosymmetric, and in **4** it is asymmetric.

The orientations of tu and trtu ligands in square-planar tellurium(II) complexes are discussed. The TeSC/SCN₂ dihedral angle (the thiourea twist angle) varies from 0.4 to 88.7°, and the Te–S–C bond angle from 93.5(1) to 107.8(1)°; the smaller bond angles occur for large twist angles. The S–C bond lengths, 1.715(3)–1.753(2) Å, correlate with Te–S bond lengths and twist angles. In the TeS₄ groups of the centrosymmetric $[\text{Te}(\text{tu})_4]^{2+}$ and $[\text{Te}(\text{trtu})_4]^{2+}$ ions, the Te–S bonds are 2.667(1)–2.701(1) Å; the longer bonds tend to be associated with large twist angles.

The crystal structures of the salts $[\text{Te}(\text{tu})_4]\text{Cl}_2$ and $[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (tu = thiourea) were reported some time ago.¹ In both salts the tellurium atoms lie in crystallographic symmetry centres, and the TeS₄ groups are exactly planar. The anhydrous salt crystallized from solutions of the dihydrate in hot methanol containing tu² as yellow triclinic plates, space group $P\bar{1}$ with $Z = 1$. In some samples, crystals of a different habit and a deeper yellow colour were observed. A crystal was picked out and subjected to X-ray analysis, and was a monoclinic form of $[\text{Te}(\text{tu})_4]\text{Cl}_2$, space group $C2/c$ with $Z = 4$, with the tellurium atoms located not in symmetry centres but on two-fold axes, so that the linear S–Te–S systems were asymmetric.

The salt $[\text{Te}(\text{tu})_4](\text{HF}_2)_2$ ³ also occurs in two forms, one triclinic, probable space group $P\bar{1}$ with $Z = 1$, the other monoclinic, probable space group $I2/c$ with $Z = 4$. For the latter, weak hkl reflections for l odd indicated that the tellurium atoms lie in symmetry centres,³ but tellurium atoms on two-fold axes with y close to zero could

give the same intensity distribution. A structure analysis was carried out: the $[\text{Te}(\text{tu})_4]^{2+}$ ion was centrosymmetric.

We report here the crystal structures of monoclinic $[\text{Te}(\text{tu})_4]\text{Cl}_2$ (**1**) and $[\text{Te}(\text{tu})_4](\text{HF}_2)_2$ (**2**), and refinements of the structures^{1,4} of $[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**3**) and $[\text{Te}(\text{tu})_4](\text{ClO}_4)_2$ (**4**). We also report the structures of $[\text{Te}(\text{trtu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**5**) and $[\text{Te}(\text{trtu})_4](\text{ClO}_4)_2$ (**6**) (trtu = trimethylenethiourea). For salts **5** and **6**, unit cell and space group data indicated that the tellurium atoms lie in symmetry centres,⁵ and the results confirm the centrosymmetry. The perchlorate **4** is then the only $[\text{TeL}_4]^{2+}$ salt of known structure^{1,4,6–9} in which the cation possesses no symmetry in the crystal.

Experimental

The crystal of complex **1** was picked out from among a majority of triclinic crystals, as noted above. The other salts were prepared as described.^{2,3,5}

Table 1. Crystallographic data.

	1	2	3	4	5	6
Complex Formula	$[\text{Te}(\text{tu})_4]\text{Cl}_b$ $\text{C}_4\text{H}_{16}\text{Cl}_2\text{N}_8\text{S}_4\text{Te}$	$[\text{Te}(\text{tu})_4](\text{HF}_2)_2$ $\text{C}_4\text{H}_{16}\text{F}_4\text{N}_8\text{S}_4\text{Te}$	$[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ $\text{C}_4\text{H}_{20}\text{Cl}_2\text{N}_8\text{O}_2\text{S}_4\text{Te}$	$[\text{Te}(\text{tu})_4](\text{ClO}_4)_2$ $\text{C}_4\text{H}_{16}\text{Cl}_2\text{N}_8\text{O}_8\text{S}_4\text{Te}$	$[\text{Te}(\text{tru})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ $\text{C}_{16}\text{H}_{96}\text{Cl}_2\text{N}_8\text{O}_2\text{S}_4\text{Te}$	$[\text{Te}(\text{tru})_4](\text{ClO}_4)_2$ $\text{C}_{16}\text{H}_{92}\text{Cl}_2\text{N}_8\text{O}_8\text{S}_4\text{Te}$
<i>M</i>	502.99	510.09	539.02	630.98	699.28	791.24
System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>C</i> 2/c (No. 15)	<i>I</i> 2/a (No. 15)	<i>P</i> 2 ₁ /c (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 2 ₁ /c (No. 14)	<i>P</i> 1 (No. 2)
<i>a</i> /Å	17.247(1)	10.145(1)	6.001(1)	15.332(1)	9.296(1)	9.379(1)
<i>b</i> /Å	11.528(1)	7.885(1)	16.411(2)	11.949(1)	16.750(2)	9.778(1)
<i>c</i> /Å	8.880(2)	22.292(3)	9.912(1)	6.006(1)	9.700(1)	9.981(2)
α /°	92.61(1)	90.78(1)	98.16(1)	89.59(1)	117.89(1)	90.60(1)
β /°				90.96(1)		106.95(1)
γ /°				107.86(1)		118.29(1)
<i>V</i> /Å ³	1763.7(7)	1783.0(7)	966.2(4)	1047.1(4)	1494.3(6)	758.9(4)
<i>Z</i>	4	4	2	2	2	1
<i>D</i> _x /g cm ⁻³	1.894	1.900	1.853	2.001	1.554	1.731
<i>F</i> (000)	984	1000	532	620	706	398
μ (MoK α)/cm ⁻¹	25.00	22.24	22.97	21.11	15.07	15.11
Crystal volume/mm ³	0.0055	0.0148	0.0080	0.0054	0.0015	0.0160
Transmission factors	0.621–0.811	0.534–0.750	0.675–0.713	0.730–0.799	0.847–0.902	0.692–0.737
Scan rate/°min ⁻¹	6.71–1.01	6.71–1.12	6.71–1.06	6.71–1.55	6.71–1.01	6.71–1.06
θ _{max} /°	30	36	36	32	30	30
Unique reflections	2573	4206	4550	7215	4343	4408
Reflections <i>I</i> > 2 σ	2249	3395	3555	5732	2841	3939
No. of variables	120	134	138	308	152	179
Extinction coefficient,						
<i>g</i> × 10 ⁷	4.11	5.33	5.83	5.83	7.50	14.93
<i>R</i>	0.023	0.024	0.029	0.031	0.035	0.041
<i>R</i> _w	0.027	0.028	0.034	0.032	0.036	0.050
<i>S</i>	1.215	1.254	1.317	1.235	1.161	2.097
Max. $\Delta(\rho)$ /e Å ⁻³	0.70	0.53	0.66	0.77	0.38	1.20

Table 2. Fractional atomic coordinates for $[\text{Te}(\text{tu})_4]^{2+}$ salts with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
$[\text{Te}(\text{tu})_4]\text{Cl}_2$				
Te	0	0.16902(2)	$\frac{1}{4}$	1.646(3)
Cl	0.13935(4)	0.32370(5)	0.54652(6)	2.55(1)
S(1)	0.09404(4)	0.33864(5)	0.14678(6)	2.41(1)
S(2)	0.08308(3)	0.00323(5)	0.13272(7)	2.30(1)
N(1)	0.07626(15)	0.23780(18)	-0.12299(23)	3.47(5)
N(2)	0.08910(17)	0.43268(18)	-0.12304(24)	3.89(5)
N(3)	0.22056(14)	-0.07927(21)	0.20381(30)	4.05(5)
N(4)	0.19715(13)	0.09608(20)	0.30820(30)	3.82(5)
C(1)	0.08535(15)	0.33529(19)	-0.04763(25)	2.30(4)
C(2)	0.17445(13)	0.00908(21)	0.22368(27)	2.42(4)
$[\text{Te}(\text{tu})_4](\text{HF}_2)_2$				
Te	0	0	0	2.149(2)
S(1)	-0.11181(4)	0.17487(6)	0.08839(2)	2.853(7)
S(2)	0.10652(4)	0.28662(6)	-0.04421(2)	2.765(7)
F(1)	0.16589(12)	0.39252(16)	0.27821(5)	4.01(2)
F(2)	0.23384(14)	0.55793(22)	0.20248(7)	6.12(3)
N(1)	-0.02335(16)	0.28000(24)	0.19284(7)	3.53(3)
N(2)	0.12689(15)	0.13318(24)	0.13937(7)	3.60(3)
N(3)	-0.11232(16)	0.44489(23)	-0.07866(8)	3.51(3)
N(4)	-0.02253(18)	0.27335(24)	-0.14840(7)	3.88(3)
C(1)	0.00723(16)	0.19543(22)	0.14406(7)	2.52(3)
C(2)	-0.01930(16)	0.33933(21)	-0.09466(7)	2.46(3)
$[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$				
Te	0	0	0	1.866(3)
Cl	-0.51096(9)	0.32391(3)	0.26912(6)	2.506(9)
S(1)	0.12503(9)	0.15674(4)	0.03334(6)	2.729(9)
S(2)	0.10915(10)	-0.02419(4)	0.26872(6)	2.419(9)
O	-0.5301(4)	0.15305(12)	0.44426(19)	3.63(4)
N(1)	-0.28950(29)	0.17374(12)	0.09927(19)	2.41(3)
N(2)	-0.0275(3)	0.26545(13)	0.19028(23)	3.15(4)
N(3)	-0.0309(4)	0.09983(13)	0.40346(20)	2.96(4)
N(4)	-0.3067(4)	0.01187(13)	0.31524(25)	3.18(4)
C(1)	-0.0800(3)	0.20115(12)	0.11439(20)	1.92(3)
C(2)	-0.0954(4)	0.03346(13)	0.33249(20)	2.15(3)
$[\text{Te}(\text{tu})_4](\text{ClO}_4)_2$				
Te	0.24031(1)	0.06504(1)	0.35145(3)	2.238(3)
Cl(1)	-0.44031(5)	-0.70142(5)	0.88959(11)	2.95(1)
Cl(2)	0.15049(5)	0.51102(6)	0.62851(12)	3.17(1)
S(1)	0.29729(5)	0.24234(6)	0.63496(12)	3.05(1)
S(2)	0.39295(4)	0.02000(6)	0.39128(11)	2.72(1)
S(3)	0.17660(5)	-0.11525(7)	0.05944(12)	3.46(2)
S(4)	0.06698(4)	0.10392(6)	0.30550(10)	2.66(1)
O(1)	-0.51548(16)	-0.78830(20)	0.9917(4)	4.59(5)
O(2)	-0.35805(15)	-0.73421(20)	0.9199(4)	4.90(6)
O(3)	-0.42989(19)	-0.58932(19)	0.9841(4)	5.30(6)
O(4)	-0.45727(16)	-0.69604(21)	0.6547(4)	4.62(6)
O(5)	0.19629(19)	0.56528(23)	0.4345(4)	5.78(7)
O(6)	0.07613(16)	0.55642(19)	0.6783(4)	4.96(6)
O(7)	0.11311(18)	0.38700(18)	0.5945(4)	4.89(6)
O(8)	0.21185(19)	0.53082(28)	0.8145(5)	6.53(8)
N(1)	0.37738(20)	0.46645(22)	0.5689(5)	4.38(6)

Table 2. (contd)

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
N(2)	0.38928(20)	0.35404(23)	0.2815(5)	4.61(6)
N(3)	0.38583(16)	-0.02794(21)	0.8207(4)	3.28(5)
N(4)	0.32788(18)	-0.18591(20)	0.5965(4)	3.68(5)
N(5)	0.09100(18)	-0.21682(21)	0.4249(4)	3.74(6)
N(6)	0.07631(21)	-0.33252(22)	0.1250(5)	4.50(7)
N(7)	0.14541(20)	0.31158(22)	0.1227(5)	4.24(6)
N(8)	0.08488(17)	0.16282(21)	-0.1206(4)	3.37(5)
C(1)	0.35894(17)	0.36218(22)	0.4803(5)	2.78(5)
C(2)	0.36588(15)	-0.07346(21)	0.6233(4)	2.36(4)
C(3)	0.11091(17)	-0.22915(22)	0.2175(5)	2.78(5)
C(4)	0.10144(16)	0.20034(22)	0.0848(4)	2.54(5)

Table 3. Fractional atomic coordinates for $[\text{Te}(\text{trtu})_4]^{2+}$ salts with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
$[\text{Te}(\text{trtu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$				
Te	0	0	0	2.720(5)
Cl	0.44441(13)	-0.23554(6)	0.44733(11)	4.63(2)
S(1)	0.11358(13)	0.08847(5)	0.24549(11)	4.39(3)
S(2)	0.23335(11)	0.05153(6)	-0.06147(11)	4.62(2)
O	0.34938(29)	-0.15446(13)	0.13693(28)	4.13(6)
N(1)	-0.0150(3)	0.18839(16)	0.0256(3)	3.84(8)
N(2)	0.2277(3)	0.21602(16)	0.2338(3)	3.79(7)
N(3)	0.4552(3)	-0.01332(15)	0.1957(3)	3.80(7)
N(4)	0.5041(4)	0.10325(16)	0.1629(4)	3.38(8)
C(1)	0.1074(4)	0.17044(18)	0.1602(4)	3.30(8)
C(2)	0.4113(4)	0.04645(19)	0.1139(4)	3.60(7)
C(3)	-0.0191(5)	0.25566(23)	-0.0508(5)	4.8(1)
C(4)	0.0579(5)	0.31255(21)	0.0708(5)	4.7(1)
C(5)	0.2287(5)	0.28944(21)	0.1840(5)	4.5(1)
C(6)	0.6025(5)	-0.02007(23)	0.3437(5)	4.7(1)
C(7)	0.6552(6)	0.05089(28)	0.4186(5)	6.2(1)
C(8)	0.6596(5)	0.10398(24)	0.3053(5)	5.5(1)
$[\text{Te}(\text{trtu})_4](\text{ClO}_4)_2$				
Te	0	0	0	3.041(6)
Cl	0.23900(13)	-0.19729(10)	0.35198(9)	4.93(2)
S(1)	0.17948(10)	0.01909(10)	-0.16985(9)	4.02(2)
S(2)	0.22768(12)	0.30459(10)	0.12234(9)	4.26(2)
O(1)	0.3209(4)	-0.0684(3)	0.28879(29)	6.40(9)
O(2)	0.1190(5)	-0.3348(5)	0.2529(4)	8.4(1)
O(3)	0.1805(6)	-0.1542(6)	0.4430(5)	18.5(2)
O(4)	0.3543(8)	-0.2315(6)	0.4390(6)	19.4(2)
N(1)	0.2408(3)	-0.1878(3)	-0.02578(29)	4.38(6)
N(2)	0.3344(3)	-0.1314(3)	-0.21312(30)	4.90(7)
N(3)	0.2643(4)	0.2037(3)	0.3706(3)	4.43(7)
N(4)	0.1946(4)	0.3970(3)	0.3527(3)	5.34(8)
C(1)	0.2559(4)	-0.1113(4)	-0.1314(3)	3.30(6)
C(2)	0.2292(4)	0.2992(3)	0.2958(4)	3.59(7)
C(3)	0.2970(5)	-0.3035(4)	0.0048(4)	5.51(9)
C(4)	0.3149(5)	-0.3632(4)	-0.1247(5)	5.6(1)
C(5)	0.4115(4)	-0.2316(4)	-0.1909(4)	4.99(9)
C(6)	0.2573(6)	0.1925(5)	0.5152(4)	6.3(1)
C(7)	0.2888(8)	0.3426(7)	0.5834(5)	9.2(2)
C(8)	0.1934(7)	0.4079(5)	0.4964(5)	8.4(1)

Table 4. Distances (Å) and angles (°) in monoclinic $[\text{Te}(\text{tu})_4]\text{Cl}_2$ with e.s.d.'s in parentheses. Primed atoms related to unprimed ones over molecular two-fold axis.

Bond lengths					
Te–S(1)	2.726(1)			C(1)–N(1)	1.314(3)
Te–S(2)	2.632(1)			C(1)–N(2)	1.310(3)
S(1)–C(1)	1.726(2)			C(2)–N(3)	1.309(3)
S(2)–C(2)	1.739(2)			C(2)–N(4)	1.302(3)
Bond angles					
S(1)–Te–S(1')	88.32(3)			S(1)–C(1)–N(1)	122.1(2)
S(1)–Te–S(2)	92.58(2)			S(1)–C(1)–N(2)	119.2(2)
S(1)–Te–S(2')	175.60(2)			N(1)–C(1)–N(2)	118.7(2)
S(2)–Te–S(2')	86.86(2)			S(2)–C(2)–N(3)	116.8(2)
Te–S(1)–C(1)	107.11(7)			S(2)–C(2)–N(4)	122.7(2)
Te–S(2)–C(2)	106.63(8)			N(3)–C(2)–N(4)	120.6(2)
Angles between planes²					
(1)–(2)	6.3	(2)–(4)	68.0	(4)–(6)	12.7
(1)–(3)	69.5	(3)–(5)	35.1	(5)–(6)	67.7

^aPlane (1): TeS(1)S(1'); plane (2): TeS(2)S(2'); plane (3): TeS(1)C(1); plane (4): TeS(2)C(2); plane (5): S(1)C(1)N(1)N(2); plane (6): S(2)C(2)N(3)N(4).

Table 5. Distances (Å) and angles (°) in the centrosymmetric $[\text{Te}(\text{tu})_4]^{2+}$ and $[\text{Te}(\text{trtu})_4]^{2+}$ ions with e.s.d.'s in parentheses.

	$[\text{Te}(\text{tu})_4](\text{HF}_2)_2$	$[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	$[\text{Te}(\text{trtu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	$[\text{Te}(\text{trtu})_4](\text{ClO}_4)_2$
Bond lengths				
Te–S(1)	2.670(1)	2.687(1)	2.680(1)	2.667(1)
Te–S(2)	2.697(1)	2.681(1)	2.684(1)	2.701(1)
S(1)–C(1)	1.728(1)	1.724(2)	1.733(3)	1.733(2)
S(2)–C(2)	1.740(2)	1.738(2)	1.734(4)	1.729(3)
C(1)–N(1)	1.316(2)	1.324(2)	1.313(4)	1.302(3)
C(1)–N(2)	1.315(2)	1.308(2)	1.320(4)	1.315(3)
C(2)–N(3)	1.311(2)	1.324(3)	1.323(4)	1.303(3)
C(2)–N(4)	1.306(2)	1.304(3)	1.312(4)	1.316(3)
Bond angles				
S(1)–Te–S(2)	90.76(1)	89.71(2)	87.20(4)	89.82(2)
Te–S(1)–C(1)	106.19(5)	104.88(6)	102.33(11)	107.81(8)
Te–S(2)–C(2)	98.18(5)	101.25(6)	105.18(12)	100.93(8)
S(1)–C(1)–N(1)	118.1(1)	122.2(1)	121.4(3)	123.3(2)
S(1)–C(1)–N(2)	123.0(1)	118.7(2)	119.1(3)	117.6(2)
N(1)–C(1)–N(2)	118.9(2)	119.1(2)	119.5(3)	119.1(2)
S(2)–C(2)–N(3)	120.0(1)	118.2(2)	121.3(3)	122.4(2)
S(2)–C(2)–N(4)	120.4(1)	121.9(2)	118.4(3)	117.7(2)
N(3)–C(2)–N(4)	119.5(2)	119.9(2)	120.3(3)	119.9(2)
Angles between planes^a				
(1)–(2)	84.1	71.3	54.6	63.1
(1)–(3)	92.1	68.1	49.7	34.5
(2)–(4)	0.4	27.3	39.9	6.7
(3)–(5)	85.2	68.7	50.3	55.6
(4)–(5)	15.1	7.8	6.1	20.6

^aPlane (1): TeS(1)S(2); plane (2): TeS(1)C(1); plane (3): TeS(2)C(2); plane (4): S(1)C(1)N(1)N(2); plane (5): S(2)C(2)N(3)N(4).

Structure analyses. X-ray measurements were made on a CAD4 diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å). Unit cell dimensions were determined from the diffractometer angles for 23–25 automatically centred reflections. The ω -scan mode was used for intensities. The scan width was $1.00 + 0.35 \tan \theta$, plus 25% on each side for background. The intensities were corrected for Lorentz and polarization effects, decay (max. 6.5%, for complex 6) and absorption. 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, and refinements were by full-matrix least-squares, the sum minimized being $\Sigma w\Delta^2(F)$ with $w^{-1} = \sigma^2(F) =$

$\sigma^2(I)/4LpI$, where $\sigma^2(I) = \sigma^2(I)_{\text{count}} + (0.02I)^2$. Atomic scattering factors, including anomalous dispersion terms, were taken from Ref. 10. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogens were placed geometrically, at N–H 0.87 and C–H 0.95 Å, except the HF₂[−] hydrogen of complex 2 and the H₂O hydrogens of 3 and 5, which were placed midway between the F atoms and found from Fourier difference maps, respectively. For the hydrogens of complexes 1–4, positions and individual B_{iso} 's were then refined along with the other variables, whereas the hydrogens of 5 and 6 were kept fixed (H₂O hydrogens of 5 after a few cycles of refinement) with a common fixed B_{iso} for each structure.

Table 6. Distances (Å) and angles (°) in the asymmetric cation of [Te(tu)₄](ClO₄)₂ with e.s.d.'s in parentheses.

Bond lengths					
Te–S(1)	2.649(1)		C(1)–N(1)	1.305(4)	
Te–S(2)	2.564(1)		C(1)–N(2)	1.304(4)	
Te–S(3)	2.716(1)		C(2)–N(3)	1.300(3)	
Te–S(4)	2.843(1)		C(2)–N(4)	1.300(3)	
S(1)–C(1)	1.728(2)		C(3)–N(5)	1.308(3)	
S(2)–C(2)	1.753(2)		C(3)–N(6)	1.309(3)	
S(3)–C(3)	1.715(3)		C(4)–N(7)	1.313(3)	
S(4)–C(4)	1.730(2)		C(4)–N(8)	1.310(3)	
Bond angles					
S(1)–Te–S(2)	91.16(2)		S(1)–C(1)–N(2)	123.6(2)	
S(1)–Te–S(3)	178.14(2)		N(1)–C(1)–N(2)	118.2(3)	
S(1)–Te–S(4)	90.94(2)		S(2)–C(2)–N(3)	118.5(2)	
S(2)–Te–S(3)	90.70(2)		S(2)–C(2)–N(4)	120.2(2)	
S(2)–Te–S(4)	177.42(2)		N(3)–C(2)–N(4)	121.2(3)	
S(3)–Te–S(4)	87.20(2)		S(3)–C(3)–N(5)	123.0(2)	
Te–S(1)–C(1)	106.11(9)		S(3)–C(3)–N(6)	118.8(2)	
Te–S(2)–C(2)	98.13(7)		N(5)–C(3)–N(6)	118.1(3)	
Te–S(3)–C(3)	104.50(9)		S(4)–C(4)–N(7)	120.0(2)	
Te–S(4)–C(4)	93.47(8)		S(4)–C(4)–N(8)	120.4(2)	
S(1)–C(1)–N(1)	118.2(2)		N(7)–C(4)–N(8)	119.6(3)	
Angles between planes^a					
(1)–(2)	83.7	(2)–(6)	15.5	(6)–(7)	25.4
(1)–(3)	92.8	(3)–(7)	88.7	(7)–(8)	20.0
(1)–(4)	80.9	(4)–(8)	6.5	(8)–(9)	17.8
(1)–(5)	90.0	(5)–(9)	84.1	(6)–(9)	24.6
Distances from least-squares plane (1)					
Te	0.014(1)	S(2)	−0.022(1)	S(4)	−0.020(1)
S(1)	0.014(1)	S(3)	0.014(1)		

^aPlane (1): TeS(1)S(2)S(3)S(4); plane (2): TeS(1)C(1); plane (3): TeS(2)C(2); plane (4): TeS(3)C(3); plane (5): TeS(4)C(4); plane (6): S(1)C(1)N(1)N(2); plane (7): S(2)C(2)N(3)N(4); plane (8): S(3)C(3)N(5)N(6); plane (9): S(4)C(4)N(7)N(8).

Crystal data are given in Table 1. The structures of complexes **1**, **2**, **5** and **6** were solved by Patterson and Fourier difference methods. The refinements of the structures of complexes **3** and **4** started with the previously determined coordinates.^{1,4} An extinction coefficient, g , in $F_{\text{corr}} = F_o(1 + gI_o)^{-1}$, was included and refined for all structures except **4**. The shift/error ratios in the last refinement cycles were less than 0.01. Atomic coordinates for non-hydrogen atoms are listed in Tables 2 and 3. Thermal parameters, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Results and discussion

Dimensional data for the cations are given in Tables 4–6, and their structures are shown in Fig. 1. The TeS_4 coordination groups are planar or nearly so. In complex **1** the tellurium atoms lie on two-fold axes and the TeS_4 groups are slightly tetrahedrally distorted; the angle between the $\text{TeS}(1)\text{S}(1')$ and $\text{TeS}(2)\text{S}(2')$ planes, intersecting in the two-fold axis, is 6.3° . In complexes **2**, **3**, **5** and **6** the tellurium atoms lie in symmetry centres and the TeS_4 groups are exactly planar. In complex **4** no molecular symmetry element is present and the largest distance of an atom from the TeS_4 least-squares plane is $0.022(1) \text{ \AA}$.

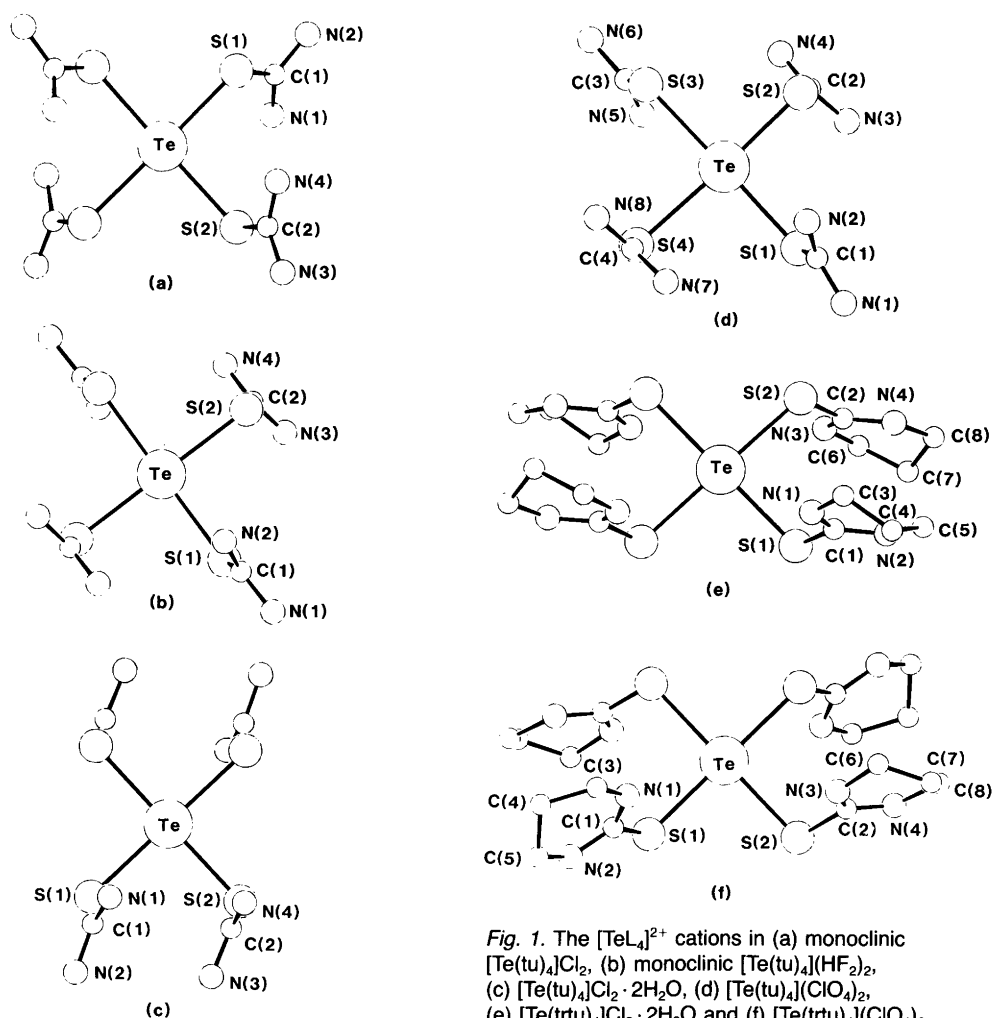


Fig. 1. The $[\text{TeL}_4]^{2+}$ cations in (a) monoclinic $[\text{Te}(\text{tu})_4]\text{Cl}_2$, (b) monoclinic $[\text{Te}(\text{tu})_4](\text{HF}_2)_2$, (c) $[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, (d) $[\text{Te}(\text{tu})_4](\text{ClO}_4)_2$, (e) $[\text{Te}(\text{trtu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and (f) $[\text{Te}(\text{trtu})_4](\text{ClO}_4)_2$.

Table 7. Distances (Å) and angles (°) for tu and trtu groups in square-planar tellurium(II) complexes.

No.	Complex	Te–S	S–C	Te–S–C	Tilt ^a	Twist ^b	Ref.
1	[Te(tu) ₄]Cl ₂	2.726(1)	1.726(2)	107.11(7)	69.5	35.1	This work
		2.632(1)	1.739(2)	106.63(8)	68.0	12.7	
2	[Te(tu) ₄](HF ₂) ₂	2.670(1)	1.728(1)	106.19(5)	84.1	0.4	This work
		2.697(1)	1.740(2)	98.18(5)	87.9	85.2	
3	[Te(tu) ₄]Cl ₂ ·2H ₂ O	2.687(1)	1.724(2)	104.88(6)	71.3	27.3	This work
		2.681(1)	1.738(2)	101.25(6)	68.1	68.7	
4	[Te(tu) ₄](ClO ₄) ₂	2.649(1)	1.728(2)	106.11(9)	83.7	15.5	This work
		2.564(1)	1.753(2)	98.13(7)	87.2	88.7	
		2.716(1)	1.715(3)	104.50(9)	80.9	6.5	
		2.843(1)	1.730(2)	93.47(8)	90.0	84.1	
7	<i>cis</i> -Te(tu) ₂ Cl ₂	2.457(1)	1.750(2)	106.01(7)	67.6	19.5	13
8	<i>cis</i> -Te(tu) ₂ Br ₂	2.476(1)	1.742(3)	105.85(9)	69.6	20.4	13
9	<i>cis</i> -Te(tu) ₂ I ₂	2.521(1)	1.738(3)	105.15(9)	71.2	24.0	13
10	<i>cis</i> -Te(tu) ₂ (SCN) ₂	2.458(1)	1.749(2)	105.62(9)	80.3	17.6	14
5	[Te(trtu) ₄]Cl ₂ ·2H ₂ O	2.680(1)	1.733(3)	102.33(11)	54.6	39.9	This work
		2.684(1)	1.734(4)	105.18(12)	49.7	50.3	
6	[Te(trtu) ₄](ClO ₄) ₂	2.667(1)	1.733(2)	107.81(8)	63.1	6.7	This work
		2.701(1)	1.729(3)	100.93(8)	34.5	55.6	
11	<i>cis</i> -Te(trtu) ₂ (SCN) ₂	2.530(1)	1.743(4)	104.71(14)	74.7	39.5	14
12	<i>cis</i> -Te(trtu) ₂ (SeCN) ₂	2.592(1)	1.734(4)	104.54(13)	73.7	39.5	14

^aTeS₂/TeSC dihedral angle; ^bTeSC/SCN₂ dihedral angle.

Conformations of the [TeL₄]²⁺ ions. In complex 1 the –C(NH₂)₂ moieties of the ligands lie alternately above and below the TeS₄ plane; the ion is a +–+– conformer. This notation was introduced⁶ for the geometry of the [Te(etu)₄]²⁺ ions (etu = ethylenethiourea) in [Te(etu)₄]Cl·2H₂O; in the latter, the tellurium atoms also lie on two-fold axes. The ions in these salts, and in [Te(etu)₄]Br₂·2H₂O¹¹ if isomorphism with the dichloride dihydrate is confirmed, are the only +–+– conformers characterised to date. A centre of symmetry, as in four of the present salts as well as in triclinic [Te(tu)₄]Cl₂,¹ in [Te(etu)₄]Cl₂,⁹ [Te(dmtu)₄]Cl₂ (dmtu = *N,N'*-dimethylthiourea)⁴ and [Te(ptu)₄](ClO₄)₂·6H₂O (ptu = phenylenethiourea),⁸ imposes ++–– geometry: two adjacent ligand groups lie above the TeS₄ plane and two lie below. These conformers are numerous, and include examples with the geometry not symmetry-imposed: the [Te(etu)₄]²⁺ ion in [Te(etu)₄][TeCl₆], in which the tellurium atoms lie on two-fold axes,⁷ and the asymmetric [Te(tu)₄]²⁺

ion in the perchlorate. Unit cell and space group data indicate that in [Te(tu)₄]Br₂, [Te(tu)₄](SCN)₂, [Te(tu)₄](NO₃)₂,² [Te(tu)₄]F₂·2H₂O, triclinic [Te(tu)₄](HF₂)₂,³ [Te(etu)₄]Br₂ and [Te(etu)₄](ClO₄)₂,¹¹ the tellurium atoms lie in symmetry centres.

Thiourea twist angles and Te–S–C bond angles.

The orientations of the thiourea ligands relative to the TeS₄ plane, apart from positions above or below the plane, are defined by the Te–S–C bond angle and the TeS₂/TeSC and TeSC/SCN₂ dihedral angles.¹ With reference to metal-thiourea complexes, these dihedral angles have been termed tilt and twist angles, respectively,¹² and we have adopted these names. Data for tu and trtu ligands in tellurium(II) complexes, where accurately determined, are listed in Table 7. For 20 groups, the Te–S–C bond angles are 93.47(8)–107.81(8)°, and the tilt angles are 49.7–90.0°, except for one group in complex 6 where it is 34.5°. The twist angles vary more, from 0.4 to 88.7°.

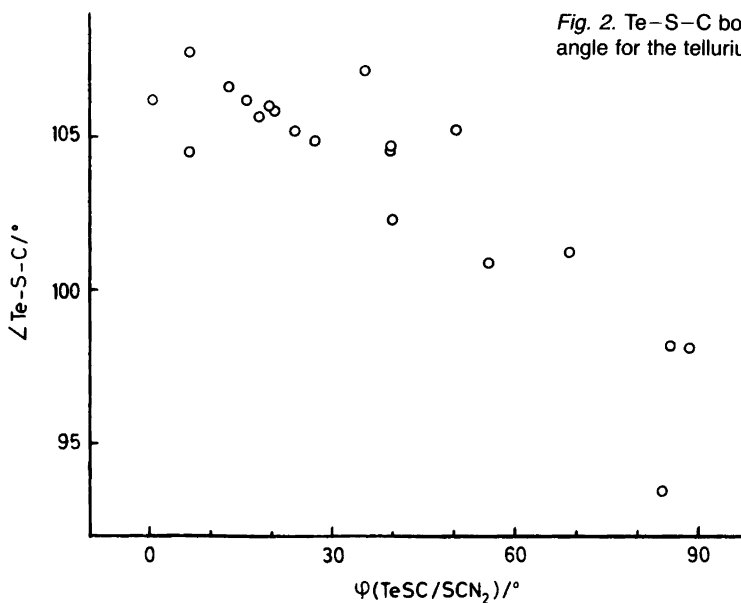


Fig. 2. Te-S-C bond angle versus thiourea twist angle for the tellurium(II) complexes of Table 7.

Bonding in metal-thiourea complexes has been discussed with regard to which sulfur orbitals participate in the central atom-to-sulfur bond. A small twist angle, ideally zero, indicates bonding through a sulfur lone-pair orbital, while a larger twist angle, ideally 90°, indicates bonding through the sulfur S-C π orbital.^{12,15,16} These are, according to photoelectron spectra, the highest filled orbitals of the thioureas.¹⁷ Bonding of the former type is characterized by a larger bond angle at sulfur,^{12,15,16} and bonding of the latter type might be expected to elongate the S-C bond,¹⁵ although significant correlations between bonding type and bond lengths have so far not been derived.

A plot of the Te-S-C bond angles versus the thiourea twist angles (Fig. 2) for the complexes of Table 7 shows that the smaller bond angles occur for large twist angles, although the scatter of points is rather large.

Thiourea S-C bond lengths. These depend on the Te-S bond lengths, as has been noted for tetramethylthiourea (tmtu).^{9,13} They also vary with the twist angle. Linear regression of $d(S-C)$ on $d(Te-S)$ gave $r = -0.73$ for the 20 data points, whereas regression on $d(Te-S)$ and the twist angle (φ) gave multiple $r = 0.90$. The derived regression eqn.

$$d(S-C) = 1.949 - 0.084 d(Te-S) + 2.0 \times 10^{-4} \varphi$$

fits the observed $d(S-C)$ with a Δ_{rms} of 0.004 Å. Thus, at constant twist angle an increase of $d(Te-S)$ by 0.4 Å decreases $d(S-C)$ by ca. 0.03 Å, and a change of twist angle from zero to 90° at constant $d(Te-S)$ increases $d(S-C)$ by ca. 0.02 Å.

The eqns. $d(S-C) = 2.147 - 0.159 d(Te-S)$ and $d(Se-C) = 2.281 - 0.142 d(Te-Se)$ were derived for tmtu and tetramethylselenourea (tmsu) ligands in tellurium(II) complexes.¹³ No account was taken of the twist angles, since their ranges were smaller, viz. 51.5–62.8° for the tmtu complexes and 50.0–65.4° for the tmsu complexes. The coefficients indicate that the dependence of $d(S-C)$ on $d(Te-S)$, or of $d(Se-C)$ on $d(Te-Se)$, is stronger for the tmtu and tmsu ligands than for the tu and trtu ligands.

Bond lengths in centrosymmetric TeS_4 groups. A survey of bond lengths in centrosymmetric $trans-TeL_2X_2$ and $[TeL_4]X_2$ complexes gave a mean value of 2.682(3) Å for 20 Te-S bonds.¹⁸ The thio ligands were tu, etu, trtu, tmtu and SCN, and the range was 2.651(6)–2.728(4) Å. In the centrosymmetric $[Te(tu)_4]^{2+}$ and $[Te(trtu)_4]^{2+}$ ions of complexes 2, 3, 5 and 6, the Te-S bond lengths are 2.667(1)–2.701(1) Å, mean 2.683(4) Å. The

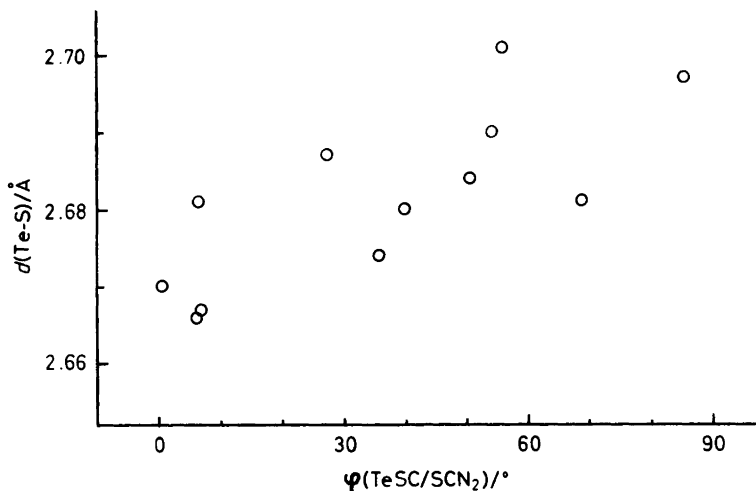


Fig. 3. Te-S bond length versus thiourea twist angle for the centrosymmetric TeS_4 groups of $[\text{Te}(\text{tu})_4](\text{HF}_2)_2$, $[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, $[\text{Te}(\text{trtu})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, $[\text{Te}(\text{trtu})_4](\text{ClO}_4)_2$, $[\text{Te}(\text{etu})_4]\text{Cl}_2$ ⁹ and $[\text{Te}(\text{dmu})_4]\text{Cl}_2$.⁴

twist angles are 0.4–85.2°. For the two independent bonds of each ion the average lengths are 2.684, 2.684, 2.682 and 2.684 Å; the average twist angles are 42.8, 48.0, 45.1 and 31.2°. The bond length versus twist angle data are plotted in Fig. 3. Also plotted are data for the centrosymmetric ions of $[\text{Te}(\text{etu})_4]\text{Cl}_2$ ⁹ [Te-S 2.681(1) and 2.666(1) Å, twist angles 6.3 and 5.8°] and $[\text{Te}(\text{dmu})_4]\text{Cl}_2$ ⁴ [Te-S 2.690(1) and 2.674(1) Å, twist angles 54.2 and 35.2°], but not data for $[\text{Te}(\text{ptu})_4](\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ⁸ or triclinic $[\text{Te}(\text{tu})_4]\text{Cl}_2$,¹ which are less accurate. The points scatter, but the Te-S bond lengths generally increase with increasing twist angle: for twist angles <45°, Te-S = 2.666(1)–2.687(1), mean 2.675(3) Å for seven points, whereas for twist angles >45°, Te-S = 2.681(1)–2.701(1), mean 2.691(4) Å for five points. Large twist angles, presumably signifying bonding through the thiourea S-C π orbital, tend to elongate not only the S-C bonds but also the Te-S bonds.

The anions. In the HF_2^- ion of complex 2, $\text{F}\cdots\text{F} = 2.249(2)$ Å, $\text{F}-\text{H} = 1.13(4)$ and $1.12(4)$ Å, and $\text{F}-\text{H}-\text{F} = 170(4)^\circ$. This may be compared with $\text{F}\cdots\text{F} = 2.264(3)$ Å in the linear, symmetric ion of NaHF_2 .¹⁹ In the two independent ClO_4^- ions of complex 4, $\text{Cl}-\text{O} = 1.417(2)$ – $1.441(2)$, mean 1.430(3) Å. In the ClO_4^- ion of complex 6, two of the oxygen atoms have large thermal parameters

and the Cl-O distances come out as 1.344(3)–1.399(2) Å.

The closest tellurium-anion approaches are $\text{Te}\cdots\text{Cl}^- = 3.913(1)$ Å in complex 1 and $\text{Te}\cdots\text{O}(1) = 3.835(3)$ Å in 6.

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