Inorganica Chimica Acta, 51 (1981) 217–223
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A Study of Square-Planar Tellurium(II) Complexes with Thiourea Type Ligands

P. W. C. BARNARD, J. D. DONALDSON, R. M. A. GRIMSEY
Department of Chemistry, Chelsea College, University of London, Manresa Road, London SW3 6LX, U.K.

G. DENNES
Université de Rennes, Laboratoire de Chimie Minérale D., Campus de Beaulieu, Avenue du Général Leclerc, 35031 Rennes Cédex, France

U. RUSSO
Istituto Chimica Generale e Inorganica, Università di Padova, Via Loredan 4, 35100 Padua, Italy

and S. CALOGERO*
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti, 35100 Padua, Italy

Received February 12, 1981

Four planar tellurium(II) complexes with thiourea type ligands have been characterized. Crystal structures for two of the complexes are reported. $Te(tu)_4(ClO_4)_2$, *[tu = thiourea] is triclinic, space group* $P\bar{1}$, a = *15.35,* b = *11.97,* c = *6.01* Å, $\alpha = 90.1$, $\beta = 91.0$, $\gamma = 108.0°$ *and* Z = *2;* $Te(dmtu)_4Cl_2$, *[dmtu = 1,3-dimethylthiourea] is monoclinic, space group* $P2_1/n$, a = *13.70,* b = *9.05,* c = *10.91* Å, $\beta = 101.6°$ *and* Z = *2. In both the complexes the tellurium is bonded to four sulphur atoms in a planar arrangement which is considerably distorted in the perchlorate but nearly regular in the chloride. In order to explain the structural and* ^{125}*Te Mössbauer spectroscopy results, a bonding model involving lone-pairs with s- and p-character is proposed.*

Introduction

Thiourea and some of its derivatives are known to form complexes with tellurium(II) [1]. Particularly interesting are the square-planar complexes TeL_4X_2 [2, 3] and TeL_2X_2, the latter of which also show *cis–trans* isomerism [3, 4]. Considerable attention has been paid to both types of complexes in attempts to correlate structural and ^{125}Te Mössbauer data [5–8]. According to Foss, [9] only the tellurium 5p electrons are involved in bonding while the 5s electrons are in a non-bonding orbital. The bond angles of close to 90°, the weak Te–S bonds [10] and the nearly regular square-planar TeS_4 arrangements in the TeL_4X_2 complexes are said by Foss to be related to the presence of two perpendicular three-centre molecular orbitals, each with two bonding electrons, and of a P_z orbital with two non-bonding electrons. This bonding model is, as a first approximation, consistent with the Mössbauer data in that the imbalance in the 5p orbital population would cause the large electric field gradients (efg) that give rise to the large quadrupole coupling constants observed in the spectra while the non-bonding pair of 5s tellurium electrons would account for the relatively high isomer shift values. Some of the complexes, however, have S–Te–S angles significantly different from 90° or have anomalous Mössbauer data that cannot be explained in terms of the use of only Te p-electrons and use of 5s and/or 5d orbitals has had to be invoked [8]. For the regular square-planar complexes of Te(II), however, the Foss model is not entirely satisfactory in that it requires the presence of two very different non-bonding electron-pairs namely a spherically symmetrical 5s-pair and a directional 5p-pair. Such an electron distribution would be unusual in terms of the chemistry of main-group elements in their lower-oxidation states. We now provide additional information on the bonding and structure of Te(II) complexes and suggest a more satisfactory description of the electron distribution around the tellurium atoms. The complexes proposed and discussed in this work are TeL_4X_2 (L = thiourea (tu) with X = ClO_4; L = dimethylthiourea (dmtu) with X = Cl; L = dicyclohexylthiourea (dchtu) with X = F and L = diphenylthiourea (dphtu) with X = Br.

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*Author to whom correspondence should be addressed.

TABLE I. Analytical Data.

Complex	Colour	M.P.[a] θ_c °C	Analysis (%)[b]				$\Delta\nu$(CS)	$\Delta\nu$(CN)
			C	H	N	X		
1. $Te(tu)_4(ClO_4)_2$	yellow	–	(4.9)(5.0)	(1.7)(1.7)	(11.6)(11.7)	– (14.8)	–	–
2. $Te(dmtu)_4Cl_2$	yellow	140	23.2(23.4)	5.2(5.2)	18.2(18.2)	11.8(11.5)	–9	+28
3. $Te(dchtu)_4F_2$	green	146	57.2(55.4)	8.6(8.6)	10.1(9.9)	–	–17	+26
4. $Te(dphtu)_4Br_2$	yellow-orange	146	54.0(52.0)	4.2(4.0)	9.6(9.3)	13.9(13.3)	–	–

[a] Melting points were determined under vacuum and are uncorrected. [b] Calculated values are given in parentheses.

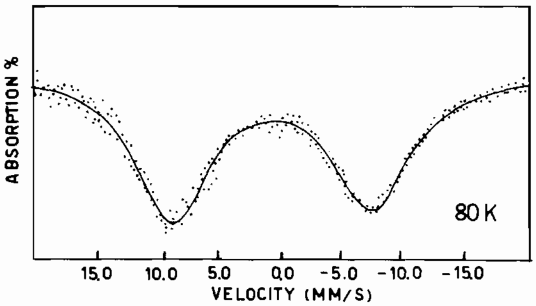

Fig. 1. Mössbauer spectrum of $Te(tu)_4(ClO_4)_2$. (1 cm = 1.2% absorption.

Experimental

The reagents were obtained from commercial sources and used without further purification and all of the complexes were prepared by similar methods [1]. The complexes were precipitated immediately when alcoholic solutions of the ligands (6 mmol dissolved in the minimum volume of alcohol) were added to warm solutions of TeO_2 (1 mmol in the minimum volume of the appropriate acid).

The products obtained were recrystallized until constant analysis values were obtained. The infrared spectra of the complexes were obtained on a Perkin Elmer 580 instrument using KBr pellets. Elemental analyses and melting points for the complexes are reported in Table I together with the IR shifts $\Delta\nu$(CS) and $\Delta\nu$(CN) from the free ligand frequencies ν(CS) and ν(CN).

The ^{125}Te Mössbauer spectrum of Fig. 1 was recorded on a conventional constant acceleration spectrometer. The source, ^{125}I/Cu, has been kept together with the sample at 80 K. The data points were fitted by an iterative least-squares program to Lorentzian lineshapes.

X-ray diffraction single crystal intensity data were obtained from two of the complexes for structural determination, giving the following crystal and intensity data.

Tetra(thiourea) Tellurium(II) perchlorate

$Te(tu)_4(ClO_4)_2 \cdot C_4H_{16}N_8O_8S_4Cl_2Te$, $M = 630.9$, triclinic, $a = 15.35(2)$, $b = 11.97(1)$, $c = 6.01(1)$ Å, $\alpha = 90.1(9)$, $\beta = 91.0(9)$, $\gamma = 108.0(9)°$, $U = 1050.0$ Å^3, $D_m = 2.03$ (by flotation), $D_c = 2.00$ g cm^{-3} for $Z = 2$, $F(000) = 620$, from statistics based on intensities the space group is $P\bar{1}$.

These data agree with previous partial parameters reported [11, 12]. A small well-shaped crystal, approximate length 0.35 mm, was selected and set up the *c* axis using a Nonius procession camera. A rotation photograph and zero, first and second layer Weissenberg photographs were obtained using Mo-Kα radiation. Intensity data were collected on a four-circle diffractometer and measurements were made in the θ–2θ scan mode; reflections for $2\theta_{max} = 64°$ were measured and those with $I < 2.58\sigma(I)$ were repeated. The intensities of five reflections were monitored every 100 reflections. 3025 reflections were collected and Lorentz and polarization corrections were applied.

*Tetrakis(dimethylthiourea) Tellurium(II) chloride**

$Te(dmtu)_4Cl_2 \cdot C_{12}H_{32}N_8S_4Cl_2Te$, $M = 615.2$, monoclinic, $a = 13.700(3)$, $b = 9.052(5)$, $c = 10.912(4)$ Å, $\beta = 101.6(7)°$, $U = 1325.58$ Å^3, $D_m = 1.52$ (by flotation), $D_c = 1.54$ g cm^{-3} for $Z = 2$, $F(000) = 620$, space group $P2_1/n$, crystal dimensions 0.35 × 0.20 × 0.70 mm. Intensity data were collected using a Philips PW 1100 four-circle diffractometer in the range $4 < 2\theta < 50°$, with Mo-Kα radiation. Using the criterion $I > 3\sigma(I)$, 1927 of the 2332 recorded intensities were independent and observable. Lorentz and polarization corrections were applied.

Solution and Refinement of the Structures

The crystal structures of $Te(tu)_4(ClO_4)_2$ and $Te(dmtu)_4Cl_2$ were solved by difference electron-density syntheses following successful location of the Te atoms from three-dimensional Patterson syntheses. Full-matrix least-squares refinements on

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*A preliminary communication has been reported in ref. 13]

TABLE II. Final Atomic Co-ordinates ($\times 10^4$) and Anisotropic Temperature Factors[a] ($\times 10^3$) for $Te(tu)_4(ClO_4)_2$ with Estimated Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	2402	651	3515(1)	31.5(2)	28.0(3)	37.2(6)	4.0(2)	2.6(2)	6.0(2)
S1	2973(2)	2424(3)	6344(5)	41.7(7)	35.5(12)	44.0(20)	−0.3(10)	8.4(10)	3.4(10)
S2	3931(2)	200(3)	3916(5)	38.1(7)	45.5(13)	40.8(20)	5.2(10)	6.7(9)	11.4(10)
S3	1766(2)	−1150(3)	591(5)	46.6(8)	44.2(14)	47.3(21)	−4.8(11)	10.6(11)	0.5(11)
S4	670(2)	1038(3)	3052(5)	37.4(7)	41.7(13)	35.9(20)	3.4(9)	2.7(9)	11.1(10)
C1	−4401(2)	−7013(3)	8900(5)	40.6(7)	30.7(11)	48.1(20)	−0.1(9)	1.7(10)	8.0(9)
Cl2	1502(2)	5111(3)	6284(5)	43.3(7)	33.9(12)	48.4(21)	0.3(9)	−0.5(10)	5.5(10)
Cl	3594(8)	3625(11)	4815(20)	40(3)	41(5)	52(6)	−48(4)	1(3)	6(4)
C2	3661(7)	−737(10)	6235(18)	94(3)	39(5)	43(5)	−4(4)	5(4)	12(4)
C3	1105(8)	−2305(11)	2197(20)	40(3)	31(5)	52(6)	−5(4)	2(4)	6(4)
C4	1020(8)	1998(10)	861(19)	36(3)	40(6)	37(6)	4(5)	2(4)	13(5)
N1	3766(8)	4654(10)	5726(14)	56(3)	34(6)	58(6)	−7(5)	0(5)	9(5)
N2	3895(8)	3542(11)	2770(20)	58(3)	48(6)	48(6)	0(5)	22(5)	−4(5)
N3	3860(7)	−271(11)	8230(17)	44(2)	58(6)	33(5)	−5(4)	1(4)	6(4)
N4	3273(7)	−1880(9)	5958(17)	48(3)	29(5)	74(7)	−4(5)	3(5)	7(4)
N5	905(7)	−2176(10)	4256(18)	50(3)	42(6)	46(6)	6(4)	14(5)	7(5)
N6	765(8)	−3352(11)	1219(20)	61(3)	42(6)	73(8)	−13(5)	5(6)	3(5)
N7	1456(7)	3123(10)	1248(18)	51(3)	41(6)	44(6)	0(4)	−10(5)	6(5)
N8	843(7)	1616(9)	−1231(17)	47(3)	56(6)	31(5)	1(4)	−1(4)	11(5)
O1	−5156(7)	−7885(9)	9922(16)	61(3)	50(5)	64(6)	4(4)	16(5)	5(4)
O2	−3582(7)	−7339(7)	9195(17)	64(3)	67(6)	66(6)	8(5)	−6(5)	24(5)
O3	−4294(7)	−5893(9)	9863(17)	68(3)	40(5)	75(6)	−12(4)	10(5)	15(5)
O4	−4572(7)	−6960(9)	6563(16)	62(3)	64(5)	42(5)	5(4)	−3(4)	11(5)
O5	1969(7)	5646(10)	4359(18)	71(3)	62(6)	53(6)	18(5)	27(5)	11(5)
O6	757(7)	5553(4)	6758(17)	65(3)	48(5)	74(6)	5(5)	6(5)	27(5)
O7	1138(7)	3868(9)	5934(16)	62(3)	32(5)	75(6)	0(4)	4(5)	9(4)
O8	2120(8)	5306(11)	8127(20)	81(3)	118(9)	57(6)	−13(6)	−24(5)	12(6)
H1	3377(100)	4721(92)	6761(144)	53(35)					
H2	3550(103)	4960(170)	7014(123)	76(25)					
H3	3642(86)	3822(113)	2428(200)	27(35)					
H4	4614(142)	5274(108)	1352(152)	163(76)					
H5	4147(64)	441(84)	8476(154)	35(25)					
H6	3919(69)	−843(90)	9160(272)	0(63)					
H7	3247(82)	−1966(111)	4460(200)	62(38)					
H8	3225(67)	−2165(88)	7232(164)	31(27)					
H9	734(139)	−1983(167)	4386(320)	134(87)					
H10	2097(111)	−1408(151)	1020(274)	46(38)					
H11	1054(75)	−3447(96)	346(182)	38(30)					
H12	1127(131)	−3586(127)	1977(235)	63(40)					
H13	1092(128)	3309(160)	1774(294)	104(64)					
H14	1751(165)	3370(205)	627(379)	178(91)					
H15	593(82)	810(113)	−1580(202)	62(38)					
H16	1041(100)	2208(135)	−2407(241)	97(50)					

[a] Anisotropic temperature factors are in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl)]$ and for the hydrogen atoms $U_{11} = U$, in this and in the following Table.

F were computed. The scattering factors of ref. 14 were used and both the real and imaginary components of anomalous dispersions were included. The atoms were refined anisotropically. The hydrogen atoms were located from difference – Fourier maps and then included in the last refinement cycle. The final conventional R values were 0.032 for $Te(tu)_4(ClO_4)_2$ and 0.025 for $Te(dmtu)_4Cl_2$. The final atomic co-ordinates are listed in Tables II and III. Bond distances and angles for the two complexes are listed in Table IV. The tellurium(II) co-ordination spheres in both the complexes are shown in Fig. 2. Observed and calculated structure factors may be obtained from the authors on request. All computations were performed using the SHELX system of programs [15].

TABLE III. Final Atomic Co-ordinates and Anisotropic Temperature Factor ($\times 10^4$) for Te(dmtu)$_4$Cl$_2$ with Estimated Standard Deviations in Parentheses.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	0000	0000	0000	283(2)	314(2)	250(2)	−30(2)	64(1)	−21(2)
S1	−75(1)	−464(2)	2414(1)	687(9)	568(9)	311(6)	89(6)	185(6)	281(7)
S2	−215(1)	2893(1)	368(1)	504(7)	319(6)	411(7)	−37(5)	−13(5)	8(6)
C1	3134(1)	976(1)	146(1)	444(6)	495(7)	332(6)	−20(5)	64(5)	447(6)
N1	−670(3)	1743(5)	3690(4)	347(21)	452(25)	332(21)	−24(19)	64(17)	−12(19)
N2	−1827(3)	901(5)	2035(4)	382(23)	474(27)	367(25)	−118(21)	37(19)	−28(20)
N3	654(3)	4483(5)	2314(4)	415(25)	409(24)	410(24)	−89(19)	80(20)	−29(19)
N4	1681(3)	2882(5)	1592(4)	449(26)	534(25)	566(26)	−287(22)	143(21)	−91(20)
C1	−922(3)	836(5)	2732(4)	411(25)	330(25)	300(23)	20(19)	154(20)	2(20)
C2	789(4)	3457(5)	1501(4)	434(27)	311(24)	377(25)	−12(21)	128(21)	−73(21)
C5	321(5)	1886(8)	4471(6)	502(33)	613(37)	384(30)	52(28)	−52(26)	−55(30)
C6	−2546(5)	2046(9)	2133(8)	363(31)	682(45)	652(51)	−166(38)	−16(34)	59(30)
C7	−286(4)	5195(7)	2379(6)	529(31)	449(35)	537(32)	−110(29)	178(25)	80(27)
C8	2555(5)	3297(12)	2521(12)	363(33)	1020(65)	1011(91)	−470(66)	120(41)	−80(38)
H51	896(55)	1848(86)	3990(69)	110(26)					
H52	595(56)	1079(91)	4970(75)	141(27)					
H53	389(82)	2601(132)	4625(108)	143(53)					
H61	−2301(49)	3043(79)	1934(60)	79(22)					
H62	−2714(55)	1952(86)	2950(76)	100(28)					
H63	−3042(53)	1980(78)	1499(66)	81(23)					
H71	−917(57)	4505(90)	2163(72)	122(28)					
H72	−703(58)	5585(91)	1439(77)	126(28)					
H73	−285(61)	5820(99)	2822(80)	120(33)					
H81	3107(56)	2847(87)	2176(68)	121(26)					
H82	2675(60)	4474(94)	2364(79)	155(31)					
H83	2429(67)	3070(107)	3407(89)	120(42)					
HN1	−1143(42)	2245(65)	3928(53)	59(18)					
HN2	−1965(44)	340(69)	1495(54)	38(21)					
HN3	1118(39)	4748(63)	2825(49)	37(17)					
HN4	1765(29)	2295(47)	1046(38)	45(10)					

TABLE IV. Bond Distances (Å) and Angles (°), with Standard Deviations in Parentheses, for Te(tu)$_4$(ClO$_4$)$_2$ and Te(dmtu)$_4$Cl$_2$.

Distances	Te(tu)$_4^{2+}$	Te(dmtu)$_4^{2+}$	Angles	Te(tu)$_4^{2+}$	Te(dmtu)$_4^{2+}$
Te–S1	2.638(3)	2.690(1)	S1–Te–S2	91.2(1)	88.8(0)
Te–S2	2.573(4)	2.674(1)	S2–Te–S3	90.7(2)	–
Te–S3	2.707(3)	–	S3–Te–S4	87.3(1)	–
Te–S4	2.845(4)	–	S4–Te–S1	90.9(1)	–
S1–C1	1.733(9)	1.736(4)	S1–Te–S3	178.2(1)	–
S2–C2	1.762(9)	1.731(4)	S2–Te–S4	177.4(1)	–
S3–C3	1.707(9)	–	Te–S1–C1	106.4(4)	104.4(1)
S4–C4	1.744(9)	–	Te–S2–C2	98.3(4)	107.5(1)
C1–N1	1.328(17)	1.320(5)	Te–S3–C3	104.3(4)	–
C1–N2	1.335(17)	1.318(5)	Te–S4–C4	93.3(4)	–
C2–N3	1.313(17)	1.322(5)	S1–C1–N1	117.8(9)	120.1(3)
C2–N4	1.440(17)	1.314(5)	S1–C1–N2	123.6(9)	120.3(3)
C3–N5	1.301(17)	–	S2–C2–N3	118.3(8)	119.2(3)
C3–N6	1.332(17)	–	S2–C2–N4	115.9(8)	122.0(3)
C4–N7	1.324(17)	–	S3–C3–N5	123.0(9)	–
C4–N8	1.332(17)	–	S3–C3–N6	117.6(9)	–
C5–N1	–	1.456(6)	S4–C4–N7	120.3(8)	–
C6–N2	–	1.449(6)	S4–C4–N8	120.3(8)	–
C7–N3	–	1.454(6)	N1–C1–N2	118.5(8)	119.6(4)

(continued on facing page)

TABLE IV. *(continued)*

Distances	$Te(tu)_4^{2+}$	$Te(dmtu)_4^{2+}$	Angles	$Te(tu)_4^{2+}$	$Te(dmtu)_4^{2+}$
C8–N4	–	1.454(7)	N3–C2–N4	115.4(8)	118.7(4)
			N5–C3–N6	119.3(8)	–
			N7–C4–N8	119.4(9)	–
			C1–N1–C5	–	125.7(4)
			C1–N2–C6	–	124.4(4)
			C2–N3–C7	–	126.1(4)
			C2–N4–C8	–	125.0(4)
			Perchlorate moiety		
C11–O1	1.444(9)		O1–C11–O2	109.3(6)	
C11–O2	1.435(12)		O1–C11–O3	109.6(5)	
C11–O3	1.421(11)		O1–C11–O4	110.1(5)	
C11–O4	1.429(10)		O2–C11–O3	110.2(6)	
C12–O5	1.417(10)		O2–C11–O4	108.8(6)	
C12–O6	1.433(12)		O3–C11–O4	108.9(6)	
C12–O7	1.433(10)		O5–C12–O6	110.0(7)	
C12–O8	1.417(12)		O5–C12–O7	109.5(6)	
			O5–C12–O8	109.9(6)	
			O6–C12–O7	108.3(6)	
			O6–C12–O8	110.2(7)	
			O7–C12–O8	107.8(7)	

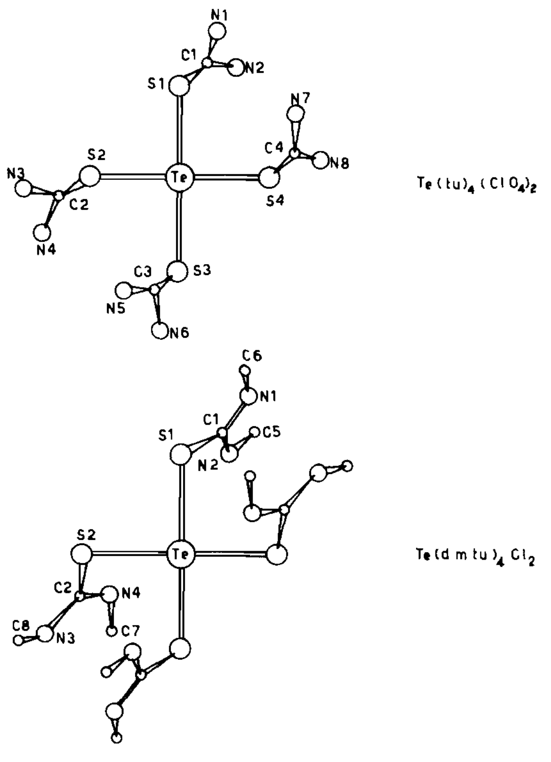

Fig. 2. The co-ordination sphere of the tellurium(II) in $Te(tu)_4(ClO_4)_2$ and $Te(dmtu)_4Cl_2$.

Results and Discussion

The infrared spectra of the four compounds listed in Table I are consistent with the presence of Te–S bonding in the complexes in that the C–N frequency shows a positive shift from the free ligand values while the C–S stretching has a negative shift because of the weakening of the C = S double bonds on Te–S bond formation.

The crystal structures determined in this work confirm the presence of planar TeL_4 moieties with four Te–S bonds in two of the TeL_4X_2 complexes.

Crystal Structure of $Te(tu)_4(ClO_4)_2$

The structure consists of $Te(tu)_4^{2+}$ moieties and ClO_4^- ions with the Te in a distorted square planar site surrounded by S atoms at distances of 2.57, 2.64, 2.71 and 2.85 Å. The large differences in the Te–S bond distances are unusual but the average length of 2.691 Å although considerably larger than the sum of the covalent single-bond radii (2.41) is similar to the distances found in other $Te(tu)_4^{2+}$ complexes [16] and the Te–S bond lengths in $Te(dmtu)_4Cl_2$ also described here. The S–Te–S bond angles are in the range 87.3 to 91.2 and average 90° within experimental error.

The C–N bond lengths are in the range 1.30–1.44 Å with an average value, 1.34 Å, close to the ones previously reported [2] The perchlorate ions show

TABLE V' Mössbauer Parameters for Tellurium(II) Complexes with Thiourea Type Ligands at 80 K.

Complex	δ mm s^{-1} [a]	Δ mm s^{-1}
$Te(tu)_4(ClO_4)_2$ [b]	1.00 ± 0.05	16.50 ± 0.20
$Te(tu)_4Cl_2$ [c]	0.91 ± 0.06	15.62 ± 0.06
$Te(tu)_4Cl_2 \cdot 2H_2O$ [c]	0.93 ± 0.06	15.62 ± 0.06
$Te(etu)_4Cl_2$ [c]	0.93 ± 0.12	16.00 ± 0.21
$Te(tu)_4Br_2$ [c]	1.00 ± 0.06	15.65 ± 0.06
$Te(tu)_4(SCN)_2$ [c]	0.86 ± 0.07	16.11 ± 0.07
$Te(tu)_4(NO_3)_2$ [c]	0.87 ± 0.10	15.19 ± 0.18

[a] With respect to $^{125}I/Cu$ source. [b] Present work. [c] From Ref. 5, (etu = ethylenethiourea).

no significant distortion from the regular tetrahedral angle and the bond lengths are close to the expected value, 1.44 Å (Table IV). Evidence is found for hydrogen bonds between the perchlorate oxygens and the tu groups present in $Te(tu)_4(ClO_4)_2$: N5–H···O7 (3.16), N6–H···O6 (3.19), N2–H···O3 (3.20), N6–H···O7 (3.30), N2–H···O4 (3.43) and N1–H···O4 (3.70 Å).

Crystal Structure of Te(dmtu)₄ Cl₂

The structure consists of discrete $Te(dmtu)_4^{2+}$ and Cl^- ions. The tellurium atom is located at the centre of a nearly regular square-planar site with S1–Te–S2 = 88.8°. The Te–S bond lengths, 2.690 and 2.674 Å, are in the range of the previously reported values [16]. Following Elder's notation [17], the complex has a ++– – conformation with two *cis*-dmtu above and two below the TeS_4 plane, as in $Te(tu)_4Cl_2$, $Te(tu)_4Cl_2 \cdot 2H_2O$ [2] and $Te(tu)_4(ClO_4)_2$.

It is interesting to note that only one nitrogen in every dmtu is involved in hydrogen bonding and that four hydrogen bonds are formed between chloride ions and nitrogen atoms with lengths N–H···Cl of 3.17, 3.23, 3.24 and 3.27 Å.

¹²⁵Te Mössbauer Data

The Mössbauer data for $Te(tu)_4(ClO_4)_2$ are reported in Table V together with those of similar planar Te(II) complexes [5] for comparison purposes. Good agreement is observed between the data for $Te(tu)_4(ClO_4)_2$ and those for the other compounds listed in Table V in that they show large quadrupole splittings and relatively high shifts. The large Δ values are consistent with the square planar structures of the complexes because of the necessarily unequal population of Te p orbitals in the z-direction compared with the x- and y-directions.

Bonding Models

The three centre bond model involving two nonbonding electron pairs of 5s character and one of 5p character that has been used previously [9] to describe the bonding in planar or near-planar Te(II) complexes suffers from a number of disadvantages. The presence of the pure 5s and pure 5p non-bonding electron pairs required by the model is energetically unfavourable and inconsistent with most of the chemistry of the main group elements in their lower oxidation states. If a pure 5s non-bonding orbital were present in the $Te(tu)_4Cl_2$ complexes changes in the Mössbauer chemical isomers shift would be very small because they would be affected by changes in shielding due to changes in relatively weak p-interaction in the x- and y-directions. The variations in shifts observed (Table V) are, however, relatively large for Te compounds of similar type. The details of distortion of some of the complexes are also very difficult to explain in terms of partial use of Te 5s electrons while maintaining a pure p-type non-bonding orbital.

In the case of Te(II) the best way of ensuring the maintenance of a planar arrangement (regular or distorted) around the Te is to have two identical non-bonding electron pairs directed along the z-axis one above and one below the xy-plane. This can be achieved in Te(II) chemistry by s–p_z mixing to form two lone-pair orbitals one below and one above the xy plane. This model accounts for all of the structural and Mössbauer data for the planar of tellurium(II) complexes. There would be little or no s-character in the equatorial bonding orbitals, and hence the Te–S bonds would be long and weakly covalent. There would be no close approach of anions along the z-direction occupied by the lone pair orbitals. For instance, in $Te(tu)_4(ClO_4)_2$ the distance between the Te and the nearest perchlorate oxygen, along a line roughly equivalent to the z-direction, is 4.25 Å, while in $Te(dmtu)_4Cl_2$ the corresponding Te–Cl distance is 4.35 Å suggesting a strong electrostatic repulsion along the z-direction. The imbalance in the 5p orbital occupancy in the z direction compared with the xy directions would give rise to the large efg responsible for the large observed quadrupole splittings. Since the s-electron density would remain in what is essentially Te non-bonding orbitals, the s-density at the nucleus would be large and the shift high.

Because the requirement of the proposed model for the bonding in Te(II) complexes to the presence of two identical non bonding orbitals directed along th z-axis it can account for those complexes with low Mössbauer chemical isomer shifts and those complexes, like $Te(tu)_4ClO_4$, that are planar but not regular square planar. Any mixing of Te 5s electron density with p_x and p_y orbitals will, provided the two directional lone-pair orbitals remain identical, result in a lowering of the shift while still retaining planar geometry. Again differences can occur in the bond lengths to Te in the xy plane by allowing appropriate mixing of Te s, p or d orbitals character but the overall geometry will remain planar provided the lone-pair orbitals above and below the xy plane remain similar.

In conclusion we suggest the nature of the bonds in the planar complexes containing tellurium(II) bonded to sulphur atoms is best explained in terms of a model that requires orbital mixing to produce two nearly identical non-bonding orbitals directed along the +z and −z directions above and below the TeS_4 or TeS_2Cl_2 planes.

Acknowledgement

Partial support by NATO RG 157.80 grant is acknowledged. One of us R.M.G. is grateful to the SRC for a studentship.

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