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Substituted Selenourea–Tellurium Tetrahalide Adducts: Precursors to Selenium–Tellurium Alloys

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ABSTRACT

N,N-Dimethylselenourea (DMSeU) yields, with TeX_4 (X = Cl or Br), a variety of compounds having bonds from selenium to tellurium. Excluding molecules of solvation these compounds display the following stoichiometries: $[(DMSeU)_4Te]X_2$, $(DMSeU)_3(TeX_4)_2$, and $(DMSeU)_2Te_2X_6$. Tetramethylselenourea (TMSeU) gives, with $TeBr_4$, crystals of $(TMSeU)_2TeBr_4$. Both the carbon–selenium and tellurium–halogen bonds undergo hydrolysis under mild conditions to yield precipitates that are alloys of selenium and tellurium. Thus, this group of compounds affords a new approach to the synthesis of selenium–tellurium alloys. Some of the properties of these compounds, as well as the crystal structure of $[(DMSeU)_4Te]Cl_2$, are described in this article.

INTRODUCTION

The importance of Se–Te crystalline alloys in the fabrication of electrophotographic devices is well recognized. This subject was discussed at the Fifth International Symposium on the Chemistry of Selenium and Tellurium [1]. These alloys are generally prepared by heating, for extended periods, mixtures of the elements corresponding to the desired stoichiometries to temperatures about 20°C below that of the solidus [2]. Badesha, Fekete, and Tarnawskyj [3] described the preparation of crystalline Se–Te alloy powders by the reduction or coreduction of Se(IV) and/or Te(IV) compounds from their organic solutions by hydrazine. They reported on the control of average crystallite size using this method. Details of the chemical procedures are described elsewhere [4, 5].

Complexes of selenium and tellurium with sulfur- and selenium-containing ligands have been described in two extensive reviews by Husebye [6, 7]. Because both ureas and Te–halogen bonds are susceptible to hydrolysis, we reasoned that complexes between selenoureas and tellurium halides might hydrolyze while maintaining the integrity of the Te–Se bonds. In such a manner, it might be possible, through the hydrolysis of such compounds, to produce Se–Te alloys of controlled stoichiometries. Here we report on the preparation of compounds of this type. These compounds do hydrolyze to form Se–Te alloys, and the properties of these alloys will be described in a subsequent publication.

EXPERIMENTAL

Preparation and Characterization of the Compounds

$[TMSeU]_2TeBr_4$. *N,N,N′,N′*-tetramethylselenourea was prepared as described in the literature [8]. A solution containing 0.90 g (2 mmol) of $TeBr_4$ in the minimum volume of anhydrous ethanol required for dissolution was added, dropwise, to a solution of TMSeU (0.35 g, 2 mmol) also in anhydrous ethanol under an atmosphere of dinitrogen. The reaction mixture, stirred for 1 h, yielded an orange-yellow precipitate. This was collected by filtration under nitrogen, washed with anhydrous

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ethanol, and dried under reduced pressure over $CaSO_4$. The mp was 118–120° (dec). The yield of dry product was 91%. Anal. Calcd.: C, 14.90; H, 2.98; Br, 39.70. Found: C, 14.16; H, 2.83; Br, 41.04.

$[(DMSeU)_4Te]Cl_2$ and $[(DMSeU)_4Te]Br_2$. A solution of $TeCl_4$ (1 mmol) in the minimum quantity of anhydrous ethanol required for dissolution, was added dropwise, under nitrogen, to an excess (6 mmol) of DMSeU also dissolved in the minimum volume of ethanol. A precipitate formed that was collected, washed with cold, dry ethanol, and stored at reduced pressure over $CaSO_4$. $[(DMSeU)_4Te]Cl_2$, orange, mp 184° (dec). Anal. Calcd.: C, 17.95; Cl, 8.85. Found: C, 17.81; Cl, 9.18; yield 70%. A similar experiment with 9 mmol of DMSeU and 1.5 mmol of $TeBr_4$, produced $[(DMSeU)_4Te]Br_2$, yellow-brown, mp 172° (dec). Anal. Calcd.: C, 16.16; H, 3.59; Br, 17.98. Found: C, 16.86; H, 3.75; Br, 20.85; yield 75%.

For the preparation of single crystals suitable for X-ray study, a solution of 0.98 mmol of $TeCl_4$ in 3 mL of anhydrous ethanol was placed in a small vial that was carefully placed in a larger vial containing a solution of 2.98 mmol of DMSeU in 7 mL of anhydrous ethanol. Anhydrous ethanol was then added carefully until the solution of the outer vial made contact with the solution of the inner vial. The larger vial was then sealed and placed in a refrigerator. Orange-red crystals were formed and harvested after two days. The sample was filtered, and the crystals were washed with anhydrous ethanol and dried in vacuo over anhydrous $CaSO_4$. The specimen used for the single crystal study was then selected.

$[DMSeU]_3[TeX_4]_2$, X = Cl or Br. Under an atmosphere of dry dinitrogen, a solution of $TeCl_4$ (13.35 g, 50 mmol) dissolved in the minimum volume of dried, redistilled acetonitrile was added dropwise to a solution of *N,N*-dimethylselenourea [9] (7.54 g, 50 mmol) also dissolved in the minimum volume of acetonitrile. A yellow precipitate began to form almost immediately, and the reaction mixture was stirred for 1 h. The yellow precipitate was removed by filtration under dry dinitrogen, washed with anhydrous diethyl ether, and dried to constant weight at reduced pressure over $CaSO_4$. The yellow powder melted at 159–160° (dec). Anal. Calcd.: C, 10.89; H, 2.42; Cl, 28.63; Te, 25.72. Found: C, 10.88; H, 2.29; Cl, 28.13; Te, 26.49; yield, based on DMSeU, 56%.

The tetrabromide was prepared in a similar manner except for the substitution of $TeCl_4$ by $TeBr_4$ and the use of carefully dried, redistilled ethanol as the solvent. The product is orange-yellow in color and melts at 183–184°C (dec). Anal. Calcd.; C, 8.02; H, 1.78; Br, 47.44; Se, 17.58; Te, 18.94. Found: C, 7.84; H, 1.62; Br, 47.82; Se, 17.45; Te, 18.62; yield, based on DMSeU, 99%. We were never successful in growing crystals of either of these two compounds that were of suitable quality for single crystal X-ray structure determination.

$2[DMSeU]_2Te_2Br_6 \cdot 3CH_3CN \cdot CH_3OH$. A solution made up of 0.5 g of $[DMSeU]_3[TeBr_4]_2$ in 40–50 mL of dry methanol was taken to reflux and filtered. The filtrate, on cooling, yielded a few orange crystals of the title compound. The presence of CH_3CN in the crystals was attributed to small amounts of that material present in the sample of $[DMSeU]_3[TeBr_4]_2$. The yields of these orange crystals were minimal, but the structure was established by single crystal X-ray structure determination.

Synthesis of $[Me_2NC(NH_2)—Se—Se—C(NH_2)NMe_2]^{+2}X_2^{-2}$. A solution containing *p*-ethoxyphenyltellurium trichloride (3.55 g, 10 mmol) in CH_3CN was added dropwise to a solution of DMSeU (3.01 g, 20 mmol) in CH_3CN under an atmosphere of dinitrogen. The reaction mixture was stirred for 1 h. A pale yellow precipitate separated, which was removed by filtration under dinitrogen, washed with CH_3CN, and dried under reduced pressure over $CaSO_4$. α,α'-Diselenobis(*N,N*-dimethylformamidinium) dichloride: mp 204°C (dec). Anal. Calcd.: C, 19.26; H, 4.29; N, 15.02; Cl, 19.04. Found: C, 19.03; H, 4.63; N, 14.30; Cl, 19.03; yield 56%.

Substitution of $TeBr_4$ for $TeCl_4$ in the procedure just described gave the dibromide that, as determined by single crystal X-ray diffraction studies, corresponded to the proposed formulation.

Attempts to Utilize Phosphine Tellurides as Coordinating Agents. A solution of tris-*n*-butylphosphine telluride [10] in acetonitrile was refluxed with a solution of $SeCl_4$ in the same solvent. A grey-black precipitate began to form and continued to separate over the 1.5 h of reflux. The alloy formed was found to be tellurium-rich: 86.97% Te, 13.17% Se.

Photoelectron Spectroscopy

XPS analyses were carried out at the Surface Science Facility of Texas A&M University. The selenourea–TX_4 samples were placed onto double-sided cellophane tape mounted on 12-mm diameter stainless steel stubs for X-ray photoelectron spectroscopy (XPS) analysis. Due to the sensitivity of the organometallics to the atmosphere, a nitrogen-filled glove box attached to the spectrometer was used to mount and load samples into the spectrometer.

XPS analysis was carried out on a KRATOS XSAM800 Surface Analysis System. Mg K-α X rays (1253.6 eV) without monochromatization were utilized to generate the spectra. Analysis chamber pressures ranged from 5×10^{-8} to 10^{-7} Torr during the experiments. The spectrometer was controlled by a DEC RT-11-based DS300 computer system,

and a program was used to determine the centroid positions of the gaussian peaks fitted within the experimental peaks. Shifts due to charging were corrected with reference to the energies of the adventitious carbon 1s peak at 285.0 eV and of Au $4f_{\frac{7}{2}}$ peak at 84.0 eV.

Valence states of Se and Te were determined from the magnitudes of binding energy shifts of 55.5 eV for the Se 3d peak, 573.1 eV for the Te $3d_{\frac{5}{2}}$ peak, and 583.5 eV for the Te $3d_{\frac{3}{2}}$ peak.

SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION

A red-orange plate (0.05 mm × 0.12 mm × 0.018 mm) of $C_{12}H_{32}Cl_2N_8Se_4Te$, RMM 802.8, was mounted on a glass fiber with vacuum grease at room temperature and cooled to 193 K in an N_2 cold stream. Preliminary examination and data collection were performed on a Siemens R3m/V X-ray diffractometer with MoKα radiation (λ = 0.71073 Å) using an oriented graphite monochromator. The unit cell is monoclinic, $P2_1/n$, with cell dimensions a = 9.443(2) Å, b = 9.373(2) Å, c = 15.273(4) Å, β = 100.12(2)° obtained from least-squares fitting of setting angles for 12 reflections: V = 1330.8(5) Å^3, D_x = 2.003 gcm^{-3}, μ = 6.26 mm^{-1}, Z = 2, $F(000)$ = 764. Intensity data were collected using seven-step Wyckoff scans for 4.0° ≤ 2θ ≤ 50°, −11 ≤ h ≤ 11, −11 ≤ k ≤ 0, − 18 ≤ l ≤ 0, with a scan range of 1.20° plus Kα separation and variable scan rates of 3.0 to 14.65° min^{-1}. Three check reflections, collected every 97 reflections, showed no significant trends in their intensities. Backgrounds were measured at the beginning and end of each scan for one-half of the total scan time. Lorentz and polarization corrections were applied to 2331 reflections. A semi-empirical absorption correction was applied: thin-plate, face (001), T_{max} = 1.000, T_{min} = 0.621. 1594 reflections with $I \geq 3\sigma_I$, R_{int} = 0.03, were used in further calculations, with σ_I obtained from counting statistics. The structure was solved by direct methods, followed by full-matrix least-squares anisotropic refinement of all non-hydrogen atoms: number of parameters = 124, quantity minimized = $\Sigma w(F_o - F_c)^2$, $w^{-1} = (\sigma_F)^2 + gF^2$. For the final refinements, δ/σ = 0.0014, gof = 0.96, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ = 0.062, $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{\frac{1}{2}}$ = 0.065, largest peak in difference Fourier map = 1.12 e/Å^3 and deepest hole = −0.95 e/Å^3, hydrogen atoms having been placed in idealized positions, C—H = 0.96 Å, with isotropic thermal parameters fixed at U = 0.08 Å^2. All calculations were performed with SHELXTL PLUS [11].

RESULTS AND DISCUSSION

Structures of the Compounds

Four types of selenourea–TeX_4 adducts are reported, and the type of compound obtained depends upon the nature of the substituents on selenourea, the relative concentration of the reagents, and the nature of the solvents used.

TABLE 1 Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(dmseu)_4TeCl_2$

	x	*y*	*z*	*U(eq)*[a]
Te	5000	5000	0	23(1)
Cl	548(3)	473(3)	1419(2)	31(1)
Se(1)	4889(1)	2128(1)	561(1)	29(1)
C(1)	3556(13)	1447(13)	−434(10)	29(4)
N(1)	2298(10)	968(12)	−263(8)	31(4)
N(2)	3821(11)	1487(12)	−1245(8)	32(4)
C(2)	2703(18)	1064(20)	−2002(11)	54(6)
C(3)	5231(16)	1786(18)	−1476(12)	48(6)
Se(2)	7984(1)	4836(2)	563(1)	28(1)
C(4)	8445(11)	3758(12)	−399(8)	19(3)
N(3)	8925(11)	2418(12)	−195(8)	34(3)
N(4)	8310(10)	4221(11)	−1218(8)	30(4)
C(5)	8697(14)	3358(14)	−1920(9)	33(4)
C(6)	7917(14)	5737(14)	−1453(10)	33(4)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Tetrabromobis(*N*, *N*, *N'*, *N'*-tetramethylselenourea)tellurium(IV) is inferred to have a structure like that of the thiourea analogue [12]. The four halogen atoms and the tellurium atoms are assumed to be coplanar, and the selenourea ligands are expected to occupy the two remaining axial positions. However, the crystal structure of this compound was not determined.

The crystal structure of $[DMSeU]_4TeCl_2$ has been determined as described above (see Tables 1, 2 and 3). Its structure is similar to that of tetrakis(selenourea)tellurium(II) dichloride [13]. Since Te is on a center of symmetry in the unit cell of $(DMSeU)_4TeCl_2$, the five-atom unit ($TeSe_4$) is planar. However, it deviates significantly from D_{4h} symmetry since Te–Se(1) = 2.802 (1)Å, Te–Se(2) = 2.832 (1)Å, and Se(1)–Te–Se(2) = 86.8 (1)°. The nearly planar $SeCN_2$ portions of the substituted selenourea are twisted from the $TeSe_4$ plane, as may be seen in Figure 1. There are no close contacts between the Cl^- ions and Te or Se, but there are short Cl···H distances, ranging from 2.40 to 2.55 Å, between Cl^- and the H-atoms of the NH_2 groups. In the event

TABLE 2 Bond Lengths (Å) for $(dmseu)_4TeCl_2$

Te–Se(1)	2.832(1)	Te–Se(2)	2.802(1)
Te–Se(1A)	2.832(1)	Te–Se(2A)	2.802(1)
Se(1)–C(1)	1.905(13)	C(1)–N(1)	1.339(17)
C(1)–N(2)	1.307(20)	N(2)–C(2)	1.477(19)
N(2)–C(3)	1.463(20)	Se(2)–C(4)	1.895(12)
C(4)–N(3)	1.353(16)	C(4)–N(4)	1.309(17)
N(4)–C(5)	1.440(19)	N(4)–C(6)	1.496(17)

TABLE 3 Bond Angles (°) for $(dmseu)_4TeCl_2$

Se(1)–Te–Se(2)	86.8(1)	Se(1)–Te–Se(1A)	180.0(1)
Se(2)–Te–Se(1A)	93.2(1)	Se(1)–Te–Se(2A)	93.2(1)
Se(2)–Te–Se(2A)	180.0(1)	Se(1A)–Te–Se(2A)	86.8(1)
Te–Se(1)–C(1)	97.6(4)	Se(1)–C(1)–N(1)	116.2(11)
Se(1)–C(1)–N(2)	122.5(9)	N(1)–C(1)–N(2)	121.3(11)
C(1)–N(2)–C(2)	120.3(12)	C(1)–N(2)–C(3)	124.6(11)
C(2)–N(2)–C(3)	114.7(13)	Te–Se(2)–C(4)	98.5(3)
Se(2)–C(4)–N(3)	115.5(9)	Se(2)–C(4)–N(4)	124.5(9)
N(3)–C(4)–N(4)	120.0(11)	C(4)–N(4)–C(5)	122.0(11)
C(4)–N(4)–C(6)	121.5(11)	C(5)–N(4)–C(6)	116.1(11)

that hydrolysis occurs at the Te–C bonds, the $TeSe_4$ unit might be preserved for the formation of the Te–Se alloys. It should be noted that the formation of this compound is accompanied by a reduction in the oxidation number of tellurium from +4 to +2.

The adducts $(DMSeU)_3(TeX_4)_2$ are the ones about which our knowledge is most limited. We never succeeded in growing single crystals of these materials. In fact, most of the other compounds reported were discovered as a result of attempts to grow single crystals of this material.

Compound 4 (compound numbers refer to those listed in Table 4) contains a four-coordinate tellurium(II) atom to which are coordinated two selenium atoms. The third and fourth coordination positions on the divalent tellurium are bridged, by bromine atoms, to two of the coordination positions of a hexabromotellurate(IV) ion. Since this complex bears two tellurium atoms, each in a different formal oxidation state, it has been used as a standard in the XPS work. Details on the structure of this compound will be published subsequently.

Infrared spectroscopy did not reveal any obvious differences among the various compounds, that allowed drawing any meaningful conclusions about their structures. XPS gave some suggestive, but not conclusive, information about the oxidation states of selenium and tellurium in these compounds. The results of the XPS measurements are summarized in Table 4.

Inasmuch as the structure of compound 4 is known and displays shifts of 1.3 ± 0.2 eV [Te(II)]

TABLE 4 Binding Energies of Selenium and Tellurium and Shifts in the Binding Energies of Selenium and Tellurium in Some of Their Compounds. All values are listed in electron volts.

Compound	*Binding Energy of Se 3d*	*Shift in Binding Energy (relative to the free element)*
1. Se	55.50	—
2. $(DMSeU)_3(TeBr_4)_2$	55.80	0.30
3. $(DMSeU)_3(TeCl_4)_2$	55.55	0.05
4. $(DMSeU)_2Te_2Br_6$	55.70	0.20
	Binding Energy of Te $3d_{\frac{5}{2}}$	
5. Te	573.1	—
6. $TeBr_4$	576.7	3.6
7. $TeCl_4$	576.9	3.8
8. $(C_6H_5)_2Te_2$	573.5	0.4
2. $(DMSeU)_3(TeBr_4)_2$	573.35,[b] 575.10,[a] 576.55[b]	0.25,[b] 2.0,[a] 3.35[b]
3. $(DMSeU)_3(TeCl_4)_2$	573.75,[b] 576.15[a]	0.65,[b] 2.05[a]
4. $(DMSeU)_2Te_2Br_6$	574.20,[b] 576.35[a]	1.10,[b] 3.25[a]
	574.60,[b] 576.30[a]	1.50,[b] 3.20[a]
	Binding Energy of Te $3d_{\frac{3}{2}}$	
5. Te	583.5, 584.1[b]	—
2. $(DMSeU)_3(TeBr_4)_2$	583.65,[b] 585.45,[a] 587.2[b]	0.15,[b] 1.95,[a] 3.7[b]
3. $(DMSeU)_3(TeCl_4)_2$	584.1,[b] 586.50	0.6,[b] 3.0[a]
4. $(DMSeU)_2Te_2Br_6$	585.45,[d] 586.65[d]	1.95,[b] 3.15[a]

[a]Major peak.
[b]Minor peak(s).
[c]Observations on separate runs.
[d]Observations on separate runs, but curves not resolved.

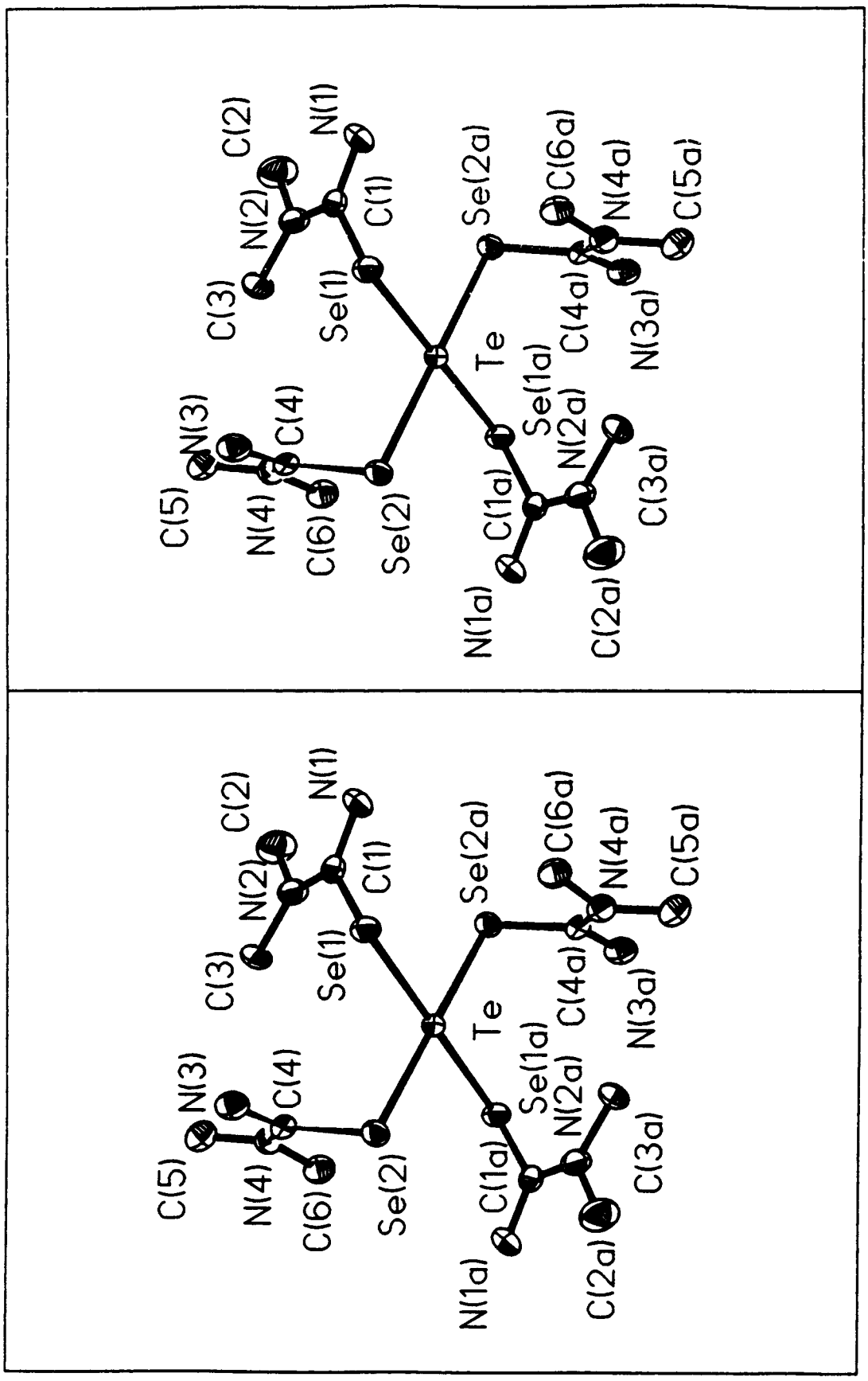

FIGURE 1 Stereographic views of $(DMSeU)_4Te$ unit with H-atoms omitted. (Thermal ellipsoids at 0.50 probability.)

and 3.23 ± 0.3 eV [Te(IV)] relative to Te(O), the several shifts in the XPS spectra of compounds 2 and 3 indicate the presence of tellurium atoms having different oxidation states. The shifts observed for compounds 6, 7, and 8 serve as comparisons with which to compare the magnitudes of the shifts with those observed for known compounds of tellurium in which the element has known formal oxidation states. Comparison of the selenium shifts shows that in all of the compounds in which the selenium is coordinated to tellurium, the selenium atom acts as a donor atom that increases the binding energy of the 3d electron. However, for both compounds having the stoichiometry $(DMSeU)_3(TeX_4)_2$, compounds 2 and 3, only a single peak for the binding energy of the Se 3d electron was observed, and this peak was completely symmetrical. Hence, we concluded that, in compounds 2 and 3, tellurium is present as Te(II) and Te(IV), and selenium atoms are bonded in such a similar manner that they cannot be distinguished by XPS. In the absence of a crystal structure determination, the structure of this compound remains unresolved.

^{77}Se and ^{125}Te NMR chemical shifts were measured in DMSO-d_6 for the compounds $(DMSeU)_3(TeX_4)_2$. These measurements were complicated by the formation of Se–Te precipitates during the time of the measurements. In each case a single ^{77}Se NMR resonance was observed: at δ 1212 (X = Cl) and at δ 1205 (X = Br) (relative to Me_2Se). This is consistent with the proposed similarity of the environment of the selenium atoms in these compounds as indicated by the XPS data. In the case of X = Cl, two ^{125}Te resonances of about equal intensity were measured at δ 1510 and δ 1616 (relative to Me_2Te). This, again, corroborates the XPS data. However, for X = Br, only a single ^{125}Te resonance at δ 1861 was observed.

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SUPPLEMENTARY MATERIAL AVAILABLE

Supplementary X-ray diffraction data have been deposited with the Cambridge Crystallographic Data Centre.

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