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Crystal and Molecular Structure of 2-Biphenylyltellurium Tribromide, $C_{12}H_9TeBr_3$

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The structure of 2-biphenylyltellurium tribromide, $C_{12}H_9TeBr_3$, has been determined by means of single crystal data collected on an automated diffractometer with monochromatized Mo Kα radiation. The orange crystals are triclinic, space group $P\bar{1}$ with a = 8.668 (1) Å, b = 11.451 (2) Å, c = 7.640 (1) Å, α = 98.83 (1)°, β = 90.37 (1)°, γ = 109.98 (1)°, and V = 702.8 (2) Å^3. The density of 2.459 (1) g cm^{-3} calculated on the basis of two molecules per unit cell agrees with the flotation value of 2.46 (1) g cm^{-3}. The structure was solved by means of Patterson and Fourier summations and refined by full-matrix least-squares methods to a conventional R index of 6.2% based on 2495 independent observed reflections. The configuration about tellurium is trigonal bipyramidal. Two bromine atoms are in the axial positions with Te–Br distances of 2.647 (1) and 2.675 (1) Å and a Br–Te–Br bond angle of 178.46 (4)°. The third bromine atom, a carbon atom, and a pair of electrons occupy the equatorial positions with Te–Br = 2.490 (1) Å, Te–C = 2.136 (8) Å, and a Br–Te–C bond angle of 97.1 (3)°. The angles at tellurium between axial and equatorial atoms are all within 1.1° of the ideal 90° value. The least-squares plane of the six-membered ring bonded to tellurium makes an angle of 21.5 (2)° with the equatorial Br–Te–C plane and an angle of 47.2 (4)° with the least-squares plane of the second six-membered ring. Weak intermolecular Te···Br bonds with a separation of 3.713 (1) Å join pairs of molecules into dimers across centers of symmetry. A very short observed intramolecular Te···C(12) separation of 2.945 (9) Å is probably related to the ease with which the tribromide is converted to dibenzotellurophene dibromide.

Introduction

A structural study of 2-biphenylyltellurium triiodide has recently been reported.[1] The molecular structure of that substance was found to be essentially trigonal bipyramidal with two iodine atoms in axial positions and with the third iodine atom plus a carbon atom and a pair of electrons in the equatorial positions. However, the axial Te–I distances were observed to be 2.833 (1) and 3.099 (1) Å rather than the ~2.94 Å value usually observed.[2,3] Interestingly, the iodine atom involved in the longer Te–I bond also makes a strong intermolecular bond with another iodine atom at 3.239 (1) Å. Studies of several organotellurium diodides[2,3] have shown that these substances all involve structurally significant intermolecular bonding of the Te···I and/or the I···I type. In contrast, studies of organotellurium dibromides indicate that intermolecular bonding plays a much less important role in these substances. In diphenyltellurium dibromide,[4] there are no intermolecular Te···Br or Br···Br interactions of appreciable strength, but weak Te···Br and Te···S interactions at 3.591 and 3.588 Å, respectively, were observed in 1-thia-4-telluracyclohexane 4,4-dibromide.[5]

The study of 2-biphenylyltellurium tribromide reported here was undertaken with the thought that it might show the molecular structure of an organotellurium trihalide which is influenced to a lesser degree by the effects of intermolecular bonding than is the triiodide and thus give a truer representation of the structure of the free trihalide molecule. Efforts toward this objective proved to be highly successful.

Experimental Section

Preparation. The tribromide was prepared from 2-biphenylyltellurium trichloride[6] by essentially the same procedure used for the triiodide.[1] To 5.0 ml of a chloroform solution containing 0.46 mmol of bis(2-biphenylyl)ditelluride, 3.5 ml of a carbon tetrachloride solution containing 1.38 mmol of Br_2 were added dropwise with stirring. The ditelluride solution was initially red-brown in color. During the addition of bromine the color darkened to a deep brown but lightened abruptly to a pale yellow when the stoichiometric point of the tribromide was reached. The yellow solution was allowed to stand overnight, during which time a crop of deep orange colored crystals formed. The compound melts at 180–181 °C with decomposition (loss of HBr) to give dibenzotellurophene dibromide in a manner similar to the behavior of the trichloride.[6] The intermediate color during the addition of Br_2 is presumed to be due to formation of 2-biphenylyltellurium monobromide, a compound recently characterized by Schulz and Klar.[7]

Crystallographic Data. The tribromide crystals were well formed, but even the smallest ones had dimensions in the range from ~0.5 to ~1 mm. Because of the high absorption (μ = 112 cm^{-1} for Mo Kα radiation), a number of the smaller crystals were washed with chloroform in a sintered glass crucible to give specimens better suited for the x-ray study. A preliminary investigation of several of these by means of precession photographs showed them to have triclinic symmetry. The specimen used for the intensity measurements was roughly ellipsoidal with dimensions of 0.25 to 0.35 mm with the longest axis normal to the form {010}. The crystal was mounted with c^* approximately along the ϕ axis of a Syntex $P\bar{1}$ diffractometer equipped with a scintillation counter and a graphite monochromator. The automatic centering, indexing, and least-squares routines of the instrument were applied to 15 selected reflections in a 2θ range from 40 to 44° to obtain a set of lattice parameters. Based on λ(Mo Kα) 0.71073 Å, the results at 28 °C are a = 8.668 (1) Å, b = 11.451 (2) Å, c = 7.640 (1) Å, α = 98.83 (1)°, β = 90.37 (1)°, γ = 109.98 (1)°, and V = 702.8 (2) Å^3. The density calculated on the basis of two molecules per unit cell is 2.459 (1) g cm^{-3} while that measured by flotation in a mixture of methylene bromide and ethylene bromide is 2.46 (1) g cm^{-3}. The space group was therefore assumed to be $P\bar{1}$.

The intensity data were collected with Mo Kα radiation, a scan rate of 2.4° min^{-1}, and a scan range from 1.25° below the Kα1 peak to 1.25° above the Kα2 peak. Background counts were taken for one-half the scan time at each end of the scan range. The intensities of three standard reflections (220), (1$\bar{3}\bar{2}$), and (4$\bar{1}$2) were recorded after every 97 intensity measurements. The standards showed only random variations in a range consistent with the respective values of $\sigma(I)$. In all, 3335 reflections were measured, including 105 periodic checks of the standards. The remaining 3230 unique reflections represent all of those accessible within the range 3.5° < 2θ < 55° for Mo Kα radiation. Among these, 735 reflections for which $I \leq 3\sigma(I)$ were considered as unobserved and were omitted from the refinement. The data were corrected for Lorentz and polarization effects and processed as previously described,[2] with a value of 0.04 for p. Absorption corrections were made on the basis of 20 bounding faces approximately describing the ellipsoid previously mentioned. The resulting transmission factors ranged from 0.233 to 0.337.

Determination and Refinement of the Structure. For reasons of economy, only the 1579 observed reflections in the 2θ range from 3.5 to 45° were used in the earlier stages of the structure determination and refinement. Trial positions for the tellurium and bromine atoms were obtained from a three-dimensional Patterson summation. The carbon atoms were located by means of a difference Fourier and their positional and isotropic thermal parameters were refined with the positional and anisotropic thermal parameters of the tellurium and bromine atoms. This refinement converged to a conventional R index of 8.6% and a weighted index, R_w, of 11.2%.[8] A second difference Fourier showed maxima in the range of 0.6 ± 0.2 e Å^{-3} at positions close to those calculated for the nine hydrogen atoms on the basis of sp^2 C atoms and C–H distances of 0.95 Å. In the subsequent refinement, the hydrogen atoms were included in the structure factor

Table I. Atomic Positional Parameters in $C_{12}H_9TeBr_3$[a]

Atom	*x*	*y*	*z*
Te	0.568 64 (7)[b]	0.717 48 (5)	0.172 03 (8)
Br(1)	0.461 29 (15)	0.817 33 (12)	0.460 37 (16)
Br(2)	0.681 31 (14)	0.622 81 (10)	−0.121 22 (15)
Br(3)	0.433 98 (16)	0.820 16 (12)	−0.014 29 (18)
C(1)	0.798 9 (11)	0.868 7 (8)	0.225 5 (12)
C(2)	0.813 0 (13)	0.988 0 (9)	0.203 2 (16)
C(3)	0.967 8 (15)	1.082 8 (9)	0.225 7 (16)
C(4)	1.104 6 (15)	1.052 7 (11)	0.268 8 (16)
C(5)	1.088 8 (13)	0.932 3 (11)	0.293 6 (15)
C(6)	0.932 0 (11)	0.835 8 (9)	0.271 0 (12)
C(7)	0.908 6 (12)	0.706 8 (9)	0.300 6 (12)
C(8)	1.005 7 (13)	0.642 0 (12)	0.221 7 (15)
C(9)	0.973 4 (17)	0.516 7 (13)	0.236 1 (17)
C(10)	0.842 8 (16)	0.454 3 (11)	0.333 5 (16)
C(11)	0.748 9 (15)	0.518 8 (10)	0.413 6 (14)
C(12)	0.782 6 (12)	0.644 4 (9)	0.401 1 (12)

[a] The idealized (calculated) positional parameters of the hydrogen atoms are given in Table III which is available as part of the supplementary material. [b] The numbers given in parentheses here and in succeeding tables are the estimated standard deviations in the least significant digits.

Table II. Atomic Thermal Parameters in $C_{12}H_9TeBr_3$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te	75 (1)	43 (1)	135 (1)	4 (1)	2 (1)	13 (1)
Br(1)	140 (2)	102 (1)	197 (3)	44 (1)	38 (2)	5 (1)
Br(2)	138 (2)	72 (1)	162 (2)	6 (1)	25 (2)	−3 (1)
Br(3)	140 (2)	102 (1)	239 (3)	32 (1)	−49 (2)	47 (1)
C(1)	87 (13)	45 (7)	122 (16)	−13 (8)	−9 (9)	10 (9)
C(2)	119 (17)	49 (8)	243 (25)	3 (9)	−15 (16)	24 (11)
C(3)	157 (20)	49 (9)	214 (25)	−30 (10)	−4 (18)	13 (12)
C(4)	132 (19)	88 (11)	186 (23)	−33 (12)	−5 (17)	18 (13)
C(5)	101 (16)	97 (11)	151 (20)	1 (11)	−8 (15)	8 (12)
C(6)	68 (12)	72 (9)	122 (16)	2 (9)	−7 (11)	14 (10)
C(7)	99 (14)	72 (9)	115 (16)	25 (9)	−41 (12)	−1 (10)
C(8)	111 (17)	107 (12)	185 (22)	39 (12)	−5 (16)	15 (13)
C(9)	192 (24)	123 (14)	216 (26)	99 (16)	−48 (21)	−23 (16)
C(10)	198 (24)	80 (11)	177 (23)	44 (13)	−25 (19)	23 (12)
C(11)	168 (20)	81 (11)	156 (21)	28 (12)	−14 (16)	28 (12)
C(12)	108 (15)	78 (9)	106 (16)	28 (9)	−6 (13)	10 (10)

[a] All parameters have been multiplied by 10^4. The anisotropic temperature factor expression is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The hydrogen atoms were assigned the fixed isotropic thermal parameters listed in Table III, which is available as part of the supplementary material.

Table VI. Bond Distances and Angles in the 2-Biphenylyltellurium Tribromide Molecule

(a) Distances, Å

Te–Br(1)	2.647 (1)	C(6)–C(1)	1.388 (13)
Te–Br(2)	2.675 (1)	C(7)–C(8)	1.385 (15)
Te–Br(3)	2.490 (1)	C(8)–C(9)	1.387 (18)
Te–C(1)	2.136 (8)	C(9)–C(10)	1.403 (19)
C(1)–C(2)	1.366 (13)	C(10)–C(11)	1.364 (17)
C(2)–C(3)	1.398 (14)	C(11)–C(12)	1.384 (15)
C(3)–C(4)	1.393 (18)	C(12)–C(7)	1.393 (14)
C(4)–C(5)	1.381 (16)	C(6)–C(7)	1.474 (14)
C(5)–C(6)	1.418 (13)		

(b) Bond Angles, deg

Br(1)–Te–Br(2)	178.46 (4)	C(1)–C(6)–C(7)	120.8 (8)
Br(1)–Te–Br(3)	90.13 (5)	C(5)–C(6)–C(7)	122.0 (9)
Br(2)–Te–Br(3)	89.06 (5)	C(6)–C(7)–C(8)	120.9 (10)
Br(1)–Te–C(1)	88.9 (3)	C(6)–C(7)–C(12)	120.8 (9)
Br(2)–Te–C(1)	89.9 (3)	C(12)–C(7)–C(8)	118.2 (10)
Br(3)–Te–C(1)	97.1 (3)	C(7)–C(8)–C(9)	120.7 (11)
Te–C(1)–C(2)	120.8 (7)	C(8)–C(9)–C(10)	120.2 (11)
Te–C(1)–C(6)	115.8 (6)	C(9)–C(10)–C(11)	119.0 (11)
C(6)–C(1)–C(2)	123.2 (9)	C(10)–C(11)–C(12)	120.8 (11)
C(1)–C(2)–C(3)	119.4 (10)	C(11)–C(12)–C(7)	121.0 (10)
C(2)–C(3)–C(4)	118.9 (10)	C(3)···C(6)–C(7)	177.6 (8)[a]
C(3)–C(4)–C(5)	121.2 (10)	C(6)–C(7)···C(10)	175.1 (7)[a]
C(4)–C(5)–C(6)	120.1 (10)	C(4)···C(1)–Te	174.9 (5)[a]
C(5)–C(6)–C(1)	117.2 (9)	C(1)–Te···C(12)	71.4 (3)[b]

[a] Nonbonded angle given to show distortion from ideal, 180° value. [b] A nonbonded angle to be compared with C(1)–Te–C(12) bond angle of 81.7 (2)° in dibenzotellurophene.

Table VII. Comparison of Bond Distances (Å) and Bond Angles (deg) about Tellurium in $C_{12}H_9TeBr_3$ and $(C_6H_5)_2TeBr_2$

	$C_{12}H_9TeBr_3$	$(C_6H_5)_2TeBr_2$[a]
Te–Br(ax)[b]	2.647 (1)	2.682 (3)
	2.675 (1)	
Te–C(eq)	2.136 (8)	2.14 (3)
Br(ax)–Te–Br(ax)	178.46 (4)	178.0 (2)
C(eq)–Te–Br(eq)	97.1 (3)	
C(eq)–Te–C(eq)		96.3 (1.2)
Br(ax)–Te–C(eq)	88.9 (3)	90.5 (6)
	89.9 (3)	90.8 (6)

[a] The $(C_6H_5)_2TeBr_2$ molecule has symmetry 2, thus reducing the number of independent distances and angles. (See ref 4.) [b] Axial and equatorial atoms are designated by (ax) and (eq).

calculations with positional parameters fixed at the calculated values and with assigned isotropic thermal parameters 0.5 Å^2 greater than the *B* values on the adjacent carbon atoms. The next stage of least-squares refinement (henceforth based on the full data set of 2495 observed reflections) converged at $R = 7.1\%$ and $R_w = 9.0\%$. A comparison of $|F_o|$ and $|F_c|$ values of the strongest low-order reflections at this point indicated that the effects of secondary extinction were significant. The intensities of all reflections were therefore processed by SECEXT.[9] Further least-squares refinement resulted in final convergence at $R = 6.2\%$ and $R_w = 7.6\%$. In the final least-squares cycle, the largest shift in a positional or thermal parameter for Te or Br was 0.01 σ and for C, 0.02 σ. The final "goodness of fit" defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ was 2.68. In this expression N_o = 2495, the number of observed reflections, and N_v = 145, the number of variable parameters. A final difference Fourier showed no maxima above 0.7 e Å^{-3} except in the vicinity of the tellurium and bromine atoms where several maxima up to 2.6 e Å^{-3} were noted.

The final positional and thermal parameters of the nonhydrogen atoms are listed in Tables I and II. A listing of the calculated positional parameters and the assigned isotropic thermal parameters for the hydrogen atoms is given in Table III.[10] The root-mean-square amplitudes of vibration of the nonhydrogen atoms along the three principal axes of the vibrational ellipsoids, together with the corresponding *B* values, are given in Table IV.[10] A set of structure factors was calculated on the basis of the tabulated parameters and is available as Table V.[10] The atomic scattering factors were those given in Table 2.2A of ref 11 and the real and imaginary components of anomalous dispersion from Table 2.3.1 of ref 11 were applied to the scattering factors for tellurium and bromine. An analysis of the values of $||F_o| - |F_c||/\sigma(F_o)$ for the 735 unobserved reflections showed 74% to be less than 1, 20.5% in the range from 1 to 2, 4.1% in the range from 2 to 3, and 1.1% in the range from 3 to 4. Three reflections had values greater than 4 with a maximum value of 4.5.

Description and Discussion of the Structure

The structure of the 2-biphenylyltellurium tribromide molecule and the intermolecular packing arrangement are shown in Figure 1. Observed intramolecular bond distances and bond angles are listed in Table VI. The configuration about tellurium is probably best described as trigonal bipyramidal with Br(1) and Br(2) in the axial positions and with Br(3), C(1), and a pair of electrons in the equatorial plane. The distances and angles about tellurium in the tribromide have values very close to those observed in the earlier study of diphenyltellurium dibromide, as shown by the comparisons in Table VII. In neither molecule is the trigonal bipyramidal geometry distorted by the effects of intermolecular bonding or packing, a situation in contrast to that in the organotellurium iodide analogues.[1-3]

Data derived from least-squares planes calculations are given in Table VIII. Each six-membered ring is closely planar but atoms bonded to the rings show relatively large displacements from the least-squares planes. Evidence for angular distortion

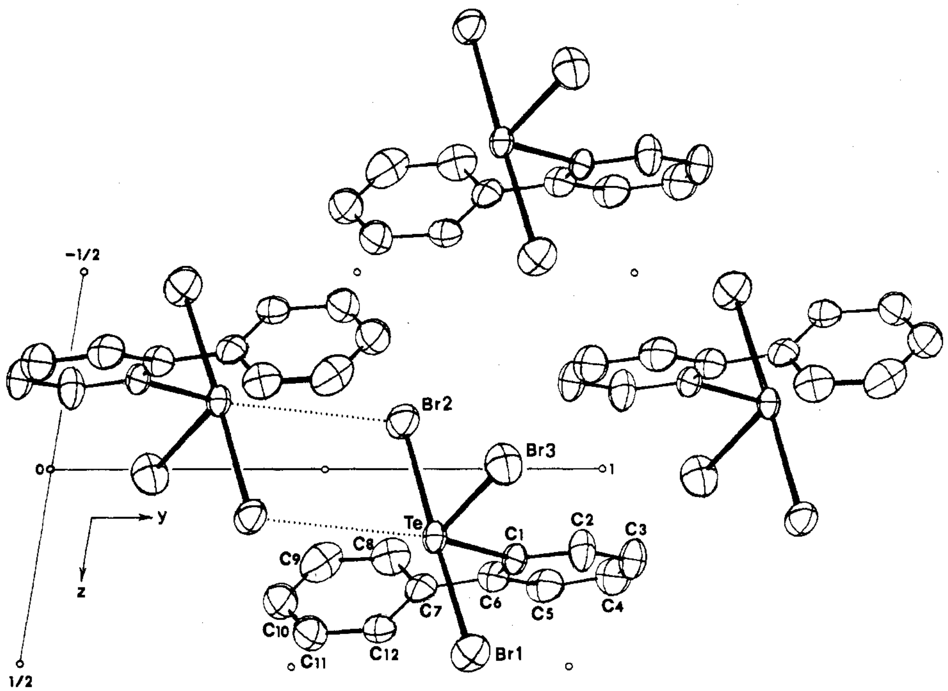

Figure 1. ORTEP plot showing the packing arrangement of 2-biphenylyltellurium tribromide molecules as viewed down the *a* axis of the unit cell. The thermal ellipsoids are shown at the 25% probability level, and the dotted lines indicate weak intermolecular Te···Br interactions.

Table VIII. Results of Least-Squares Planes Calculations

Distances of Atoms from Least-Squares Planes, (Å)[a]

Plane A		Plane B		Plane C		Plane D	
C(1)	−0.004*	C(7)	−0.017*	Br(3)	0.000*	Br(1)	0.000*
C(2)	0.001*	C(8)	0.007*	Te	0.000*	Br(2)	0.000*
C(3)	0.006*	C(9)	0.003*	C(1)	0.000*	Br(3)	0.000*
C(4)	−0.009*	C(10)	−0.004*	C(4)	−0.243	Te	−0.031
C(5)	0.005*	C(11)	−0.005*	C(12)	0.035		
C(6)	0.001*	C(12)	0.016*				
Te	−0.173	C(6)	−0.148				
C(7)	0.051						
Rms dev[b]	0.051	Rms dev	0.010				

Interplanar Angles, deg
[plane A] − [plane B] = 47.2 (4)
[plane A] − [plane C] = 21.5 (2)

[a] Atoms used to define least-squares planes are indicated by asterisks. [b] The root-mean-square deviations (Å) of the asterisked atoms from their respective least-squares planes.

in the 2-biphenylyl moiety is also indicated by the angles C(3)···C(6)–C(7), C(6)–C(7)···C(10), and C(4)···C(1)–Te which show deviations of 2.4, 4.9, and 5.1°, respectively, from the ideal 180° value. Bond angles within the rings at the joining atoms, C(5)–C(6)–C(1) and C(8)–C(7)–C(12), also show significant deviations, in this case 2.8 and 1.8°, respectively, from their ideal 120° value. The angle between the least-squares planes of the two six-membered rings is 47.2 (4)° and C(12) makes a surprisingly short intramolecular contact of only 2.945 (9) Å with the tellurium atom. This is even shorter than the Te···C(12) separation of 3.317 Å observed in 2-biphenylyltellurium triiodide and $\sim$0.9 Å less than the shortest intermolecular Te···C distance of 3.830 Å observed in dibenzotellurophene.[12] A possible chemical significance of these short Te···C(12) separations has been discussed in terms of conversion of the 2-biphenylyltellurium trihalides to dibenzotellurophene dihalides when heated.[1,6] In this connection, it is interesting to note that C(12) is only 0.035 Å out of the equatorial Br(3)–Te–C(1) plane and that the angle C(1)–Te···C(12) is 71.4°, a value to be compared with the actual C(1)–Te–C(12) bond angle of 81.7° observed in dibenzotellurophene. The details of the interatomic relationships involved about tellurium in 2-biphenylyltellurium tribromide

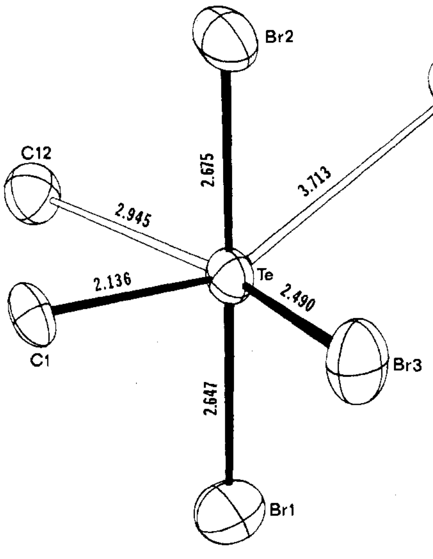

Figure 2. A view of the coordination about tellurium. The angles involved are given in Tables VIb and IXb. Ellipsoids are shown here at the 50% level.

Table IX. Selected Distances and Angles Involving Nonbonded Atoms[a]

(a) Distances, Å			
Te···C(12)	2.945 (9)	Te···Br(2′)	3.713 (1)
(b) Angles, deg			
Br(1)–Te···C(12)	89.0 (2)	Br(1)–Te···Br(2′)	103.37 (4)
Br(2)–Te···C(12)	91.6 (2)	Br(2)–Te···Br(2′)	78.13 (4)
Br(3)–Te···C(12)	168.6 (2)	Br(3)–Te···Br(2′)	108.85 (4)
C(1)–Te···C(12)	71.5 (3)	C(1)–Te···Br(2′)	151.0 (2)
Br(2′)–Te···C(12)	82.4 (3)	Te′–Br(2′)···Te	101.87 (4)

[a] Unprimed atoms are in the symmetry position, x, y, z; primed atoms are in $1-x, 1-y, -z$.

are shown in Figure 2. The conversion of the trihalide to the dibenzotellurophene dihalide may be visualized as involving the formation of a bond between Te and C(12) as the Te–Br(3) and C(12)–H(12) bonds are broken. The biphenylyl moiety becomes planar in the process, but the remainder of the molecule, including the two axial halogens, is essentially unchanged.

The only intermolecular contacts in 2-biphenylyltellurium tribromide appreciably shorter than the sum of van der Waals radii are between Te and Br(2) at 3.713 (1) Å. (The sum of the van der Waals radii for these atoms is 4.15 Å.) These weak Te···Br(2′) and Te′···Br(2) interactions join pairs of molecules into loose dimers across centers of symmetry as indicated by dotted lines in Figure 1.

If one includes C(12) and Br(2′), the coordination about tellurium may be considered roughly octahedral, as depicted in Figure 2. The angles involved at tellurium in this extended description of the coordination are listed in Table IX.

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Supplementary Material Available: Table III, the calculated positions and assigned isotropic thermal parameters of the hydrogen atoms; Table IV, the root-mean-square amplitudes of vibration; and Table V, the observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(8) The computer programs used in the present work are listed in footnote 4 of ref 2 above. The function $\sum w\|F_o| - |F_c\|^2$ was minimized in the least-squares refinement and the discrepancy indices were defined as $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_w = [\sum w\|F_o| - |F_c\|^2/\sum w|F_o|^2]^{1/2}$, where $w = [1/\sigma(F_o)]^2$.

(9) In the SECEXT program, secondary extinction corrections are computed by use of the expression $F_{cor} = F_o(1 + C\beta J_o)^{1/2}$ with symbols defined by W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963). In the present case C has the value 6.7×10^{-6} and the maximum increase in a value of $|F|_{meas}$ is 43%.

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Studies of the Ion *trans*-Dioxobis(ethylenediamine)osmium(VI). X-Ray Diffraction and Aqueous Oxygen-18 Exchange

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The crystal structure of the *trans*-dioxobis(ethylenediamine)osmium(VI) bis(hydrogen sulfate) salt, $[Os(en)_2O_2](HSO_4)_2$, has been determined by x-ray diffraction techniques. Crystals of the compound belong to the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 8.763$ (1) Å, $b = 14.697$ (3) Å, $c = 5.523$ (1) Å, and $\beta = 106.169$ (4)°. The density of 2.61 g/cm³, calculated on the basis of two formula units per unit cell, agrees with the flotation density of 2.57 g/cm³. Resolution of the structure was accomplished by Patterson and Fourier methods with refinement by full-matrix least-squares treatment leading to a conventional R factor of 5.84%. A total of 1205 independent reflections whose intensities were above background were used. Presence of an inversion center located on osmium dictates trans geometry for the $Os(en)_2O_2^{2+}$ ion. The osmium–oxygen distance is 1.74 ± 0.01 Å and the average osmium–nitrogen distance is 2.11 ± 0.01 Å. The intrachelate N–Os–N angle is 80.2 ± 0.5°. Strong hydrogen bonding between HSO_4^- ions in adjacent unit cells is observed (O---O = 2.56 (2) Å). Evidence is presented for weak hydrogen bonding involving HSO_4^- ions, osmyl oxygens, and amine moieties. The kinetics of exchange of oxygen atoms between the *trans*-dioxobis(ethylenediamine)osmium(VI) ion and solvent water has been investigated. Although decomposition of the complex precluded extensive measurements except at low temperature, the specific rate was found to increase with increasing pH in the range $1 \leq pH \leq 8.9$. At 0 °C and pH 4.3 the first-order specific rate of oxygen exchange is $2.9 \pm 0.1 \times 10^{-8}$ s⁻¹.

Introduction

Development of the aqueous chemistry of osmium has been limited by a scarcity of tractable starting materials.[1] Promising new routes to a variety of stable bis(ethylenediamine) osmium complexes are offered by the ion *trans*-dioxobis(ethylenediamine)osmium(VI) which is prepared in high yield from osmium tetroxide.[2,3] In this article we present an investigation of the ion employing x-ray diffraction techniques in the solid phase and oxygen-18-exchange measurements in aqueous solution.

Experimental Section

I. X-Ray Diffraction. Crystal Preparation. Crystals of $[Os(en)_2O_2]Cl_2$ were prepared as described previously[2,3] from osmium tetroxide (Englehard Industries, Inc.). Subsequently a 0.4-g sample of the salt was dissolved in ca. 20 ml of 0.5 M sulfuric acid and a column of cation-exchange resin (30 ml, Dowex 50X2-100) was