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Crystal and Molecular Structure of 2-Biphenylyltellurium Triiodide, $C_{12}H_9TeI_3$

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The structure of 2-biphenylyltellurium triiodide, $C_{12}H_9TeI_3$, has been determined by use of data collected on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.323$ (2) Å, $b = 9.647$ (1) Å, $c = 17.091$ (2) Å, $\beta = 92.20$ (1)°, and $V = 1536.0$ (4) Å^3. The density of 2.860 (1) g cm^{-3} calculated on the basis of four molecules per unit cell agrees with the flotation value of 2.86 (1) g cm^{-3}. The structure was solved by use of Patterson and Fourier summations and refined by use of full-matrix least-squares methods to a conventional R index of 4.6% based on 1750 independent observed reflections. The configuration about tellurium is essentially trigonal bipyramidal with two iodine atoms in axial positions and the third iodine plus a carbon atom and a pair of electrons in the equatorial positions. The axial Te–I distances are 2.833 (1) and 3.099 (1) Å with the I–Te–I angle 176.54 (4)°. The equatorial distances are Te–I = 2.769 (1) Å and Te–C = 2.15 (1) Å with a bond angle I–Te–C of 100.4 (3)°. The angles at tellurium between axial and equatorial atoms are all within 5° of the ideal 90° value. The plane of the six-membered ring bonded to tellurium makes a dihedral angle of 7.6 (4)° with the equatorial I–Te–C plane and 58.2 (5)° with the plane of the second six-membered ring. Two systems of intermolecular I···I bonds with distances of 3.239 and 3.772 Å link the molecules into chains along the 2_1 screw axes with cross-links parallel to the lattice-row line [101].

Introduction

Structural studies on a series of organotellurium diiodides have been previously reported.[1,2] The molecular structures of these compounds may be described as trigonal bipyramidal with two carbon atoms and an electron pair in the equatorial positions and two iodine atoms in the axial positions. However, the coordination about tellurium is usually expanded to octahedral by formation of intermolecular Te···I bonds. The result is an arrangement in which tellurium forms three distinctly different types of bonds: two normal, single, covalent bonds to carbon atoms, two bonds of order $^1/_2$ with the axial iodine atoms, and two secondary bonds to iodine atoms in neighboring molecules. The distances observed are 2.10–2.15 Å for Te–C, 2.89–2.95 Å for axial Te–I, and 3.69–3.81 Å for the intermolecular Te···I bonds. For comparison, the sum of the single-bond radii for tellurium and iodine is 2.70 Å and the sum of the van der Waals radii is 4.35 Å.

The present study of 2-biphenylyltellurium triiodide was undertaken as an initial investigation of the molecular structures and intermolecular bonding arrangements in the organotellurium triiodides.

Experimental Section

Preparation. The synthesis of 2-biphenylyltellurium triiodide has been reported by Schulz and Klar.[3] However, since a quantity of 2-biphenylyltellurium trichloride was on hand from its use in the synthesis of dibenzotellurophene,[4] this served as the starting material in the present synthesis of the triiodide. The trichloride was reduced to bis(2-biphenylyl)ditelluride by the procedure used to reduce dibenzotellurophene dichloride to dibenzotellurophene.[4] The resulting chloroform solution of the ditelluride was dried over $MgSO_4$ and filtered. A solution containing 3.3 mmol of I_2 in 35 ml of carbon tetrachloride was added dropwise, with stirring, to 11 ml of the dried chloroform solution containing 1.1 mmol of the ditelluride. During the addition, a crop of fine, dark red crystals of the triiodide formed and was filtered out. On standing overnight, an additional crop of crystals formed in the filtrate. These were small, well-formed, black polyhedra and were ideally suited in size and shape for the x-ray study. Both crops of crystals showed the same melting point of 163–165 °C dec, in excellent agreement with the value reported by Schulz and Klar.

Crystallographic Data. A preliminary examination of two crystals by means of precession photographs showed them to have monoclinic symmetry. The specimen selected for data collection was a nearly spherical polyhedron with maximum and minimum dimensions of 0.27 and 0.25 mm, respectively. The crystal was mounted on a Syntex $P\bar{1}$ autodiffractometer 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 the 2θ range from 36 to 46° to obtain the lattice parameters given with other crystallographic data in Table I.

Table I. Crystallographic Data for $C_{12}H_9TeI_3$

Cell dimensions at 28 °C (λ(Mo Kα) 0.710 73 Å): $a = 9.323$ (2) Å,[a] $b = 9.647$ (1) Å, $c = 17.091$ (2) Å, $\beta = 92.20$ (1)°, $V = 1536.0$ (4) (Å)^3

Density: obsd, by flotation, 2.86 (1) g cm^{-3}; calcd, for $Z = 4$, 2.860 (1) g cm^{-3}

Systematic absences: $0k0$ with $k = 2n + 1$; $h0l$ with $h + l = 2n + 1$

Space group: $P2_1/n$, an alternate setting of $P2_1/c$, No. 14

Equivalent positions: A = x, y, z; B = $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; C = $1 - x, 1 - y, 1 - z$; D = $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$

Crystal dimensions: approximately spherical with maximum diameter 0.27 mm and minimum diameter 0.25 mm

Absorption: $\mu = 80.6$ cm^{-1}, T(min) = 0.23, T(max) = 0.25

[a] Estimated standard deviations in the least significant digits are given in parentheses in this table and in following tables.

The intensity data were collected with Mo Kα radiation, a scan rate of 2° min^{-1}, and a scan range from 1.00° below the Kα_1 peak to 1.00° above the Kα_2 peak. Background counts were taken for half the scan time at each end of the scan range. The intensities of three standard reflections (600), (060), and (0,0,12) were recorded after every 97 intensity measurements. These showed only random statistical variations which were consistent with the $\sigma(I)$ values involved. Reflection data were collected in the range $2° < 2\theta < 46°$ yielding a total of 2298 measurements exclusive of standards but including 146 space group absences and 402 reflections for which $I < 3\sigma(I)$. The latter were considered unobserved and were omitted from the refinement. The number of unique, observed reflections remaining was 1750. The data were corrected for Lorentz and polarization effects and processed as previously described,[1] with a value of 0.04 for p. Because of the size and shape of the crystal, no corrections for absorption were considered necessary. The calculated maximum and minimum transmission factors given in Table I indicate that absorption effects could have caused errors of no more than ±2% in $|F_o|$ values.

Determination and Refinement of the Structure. Trial positions for the tellurium and iodine atoms were obtained from a three-dimensional Patterson summation. The solution of the remainder of the structure was straightforward. The carbon atoms were located by means of a difference Fourier and the positional and thermal parameters (anisotropic for I and Te and isotropic for C) were refined to a conventional R index of 5.3% and a weighted index, R_w, of 6.4%.[5] At this point the nine hydrogen atoms were added to the structure factor calculations but their parameters were not refined. The positions were calculated on the basis of sp^2 C atoms with C–H distances of

Table II. Atomic Positional Parameters in $C_{12}H_9TeI_3$[a]

Atom	x	y	z
I(1)	0.162 58 (9)	0.177 96 (10)	0.008 19 (5)
I(2)	0.177 64 (9)	0.486 51 (9)	0.160 59 (5)
I(3)	0.449 33 (10)	0.295 86 (10)	0.316 72 (5)
Te	0.300 03 (8)	0.225 18 (8)	0.156 53 (5)
C(1)	0.503 9 (13)	0.273 9 (13)	0.108 4 (7)
C(2)	0.533 9 (14)	0.408 1 (13)	0.087 0 (7)
C(3)	0.670 9 (15)	0.437 2 (16)	0.063 9 (9)
C(4)	0.773 9 (14)	0.333 7 (15)	0.060 2 (8)
C(5)	0.741 1 (13)	0.202 4 (14)	0.083 0 (8)
C(6)	0.607 6 (12)	0.168 1 (13)	0.109 9 (7)
C(7)	0.579 0 (13)	0.023 1 (13)	0.137 1 (8)
C(8)	0.662 9 (14)	−0.035 0 (15)	0.196 8 (8)
C(9)	0.644 5 (16)	−0.170 5 (15)	0.221 3 (8)
C(10)	0.536 7 (16)	−0.247 3 (15)	0.186 8 (9)
C(11)	0.450 7 (14)	−0.191 9 (14)	0.126 0 (9)
C(12)	0.470 0 (13)	−0.057 1 (13)	0.099 4 (8)

[a] The idealized (calculated) positional parameters of the hydrogen atoms are given in Table IV which is available as part of the supplementary material.

Table III. Atomic Thermal Parameters in $C_{12}H_9TeI_3$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	83 (1)	102 (1)	27 (1)	7 (1)	−12 (1)	−14 (1)
I(2)	72 (1)	76 (1)	22 (1)	5 (1)	2 (1)	−4 (1)
I(3)	99 (1)	112 (1)	24 (1)	−38 (1)	−9 (1)	2 (1)
Te	60 (1)	59 (1)	21 (1)	−5 (1)	2 (1)	2 (1)
C(1)	63 (15)	82 (16)	19 (5)	3 (13)	5 (7)	−7 (7)
C(2)	93 (18)	64 (16)	24 (5)	−6 (13)	8 (8)	7 (7)
C(3)	104 (21)	91 (19)	38 (6)	−43 (16)	7 (9)	3 (9)
C(4)	63 (16)	104 (20)	37 (6)	−22 (15)	2 (8)	−8 (9)
C(5)	63 (17)	86 (18)	33 (6)	2 (14)	−9 (8)	−4 (8)
C(6)	61 (15)	77 (16)	18 (5)	1 (13)	−1 (7)	3 (7)
C(7)	60 (16)	74 (16)	30 (5)	18 (13)	8 (7)	−5 (7)
C(8)	77 (18)	95 (19)	34 (6)	−6 (15)	−9 (8)	−4 (9)
C(9)	122 (21)	103 (20)	28 (6)	26 (17)	−6 (9)	4 (9)
C(10)	109 (20)	73 (16)	38 (7)	−3 (15)	15 (10)	10 (8)
C(11)	80 (18)	73 (17)	46 (7)	−12 (14)	0 (9)	−5 (9)
C(12)	54 (15)	68 (16)	33 (5)	−5 (13)	1 (7)	3 (8)

[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 IV, which is available as part of the supplementary material.

0.95 Å. The B value on each H atom was set 0.5 Å^2 higher than the value on the adjacent carbon atom. After refinement had again converged with anisotropic thermal parameters on all atoms except hydrogen, the intensities of all reflections were corrected for the effects of secondary extinction by use of SECEXT.[6] Further least-squares refinement then resulted in final convergence with $R = 4.6\%$ and $R_w = 5.3\%$. In the final least-squares cycle, the largest shift was 0.01σ in a positional parameter and 0.02σ in a thermal parameter. The "goodness of fit", defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, was 1.99. In this expression, $N_o = 1750$, the number of observed reflections used in the refinement, and $N_v = 145$, the number of variable parameters. A final difference Fourier showed no maxima above 0.5 e Å^{-3} except in the vicinity of the tellurium and iodine atoms where several maxima in the range 1.0–1.8 e Å^{-3} were observed.

The final atomic positional and thermal parameters are given in Tables II and III. Table IV[7] lists the calculated positional parameters and the assigned isotropic thermal parameters for the hydrogen atoms. The root-mean-square amplitudes of vibration along the three principal axes of the vibrational ellipsoids, together with the corresponding B values, are given in Table V.[7] A set of structure factors was calculated on the basis of the tabulated parameters and is available as Table VI.[7] The atomic scattering factors were those given in Table 2.2A of ref 8 and the real and imaginary components of anomalous dispersion from Table 2.3.1 of ref 8 were applied to the scattering factors for tellurium and iodine. An analysis of the values of $||F_o| - |F_c||/\sigma(F_o)$ for the 402 unobserved reflections showed 74% to be less than 1, 16% in the range from 1 to 2, 6.9% in the range from 2 to 3, and 2.0% in the range from 3 to 4. Four reflections had values greater than 4 with a maximum value of 5.3.

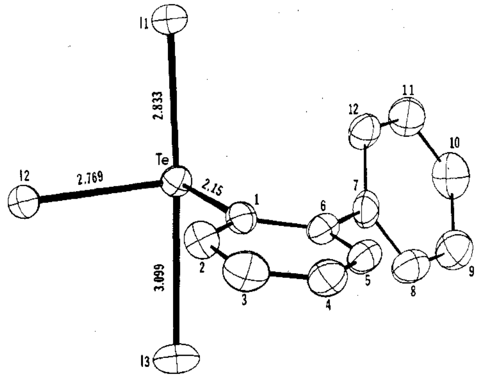

Figure 1. ORTEP plot of the 2-biphenylyltellurium triiodide molecule showing thermal ellipsoids at the 50% probability level. Carbon atoms are indicated by the numbers 1–12 and hydrogen atoms are omitted.

Table VII. Bond Distances and Angles in the 2-Biphenylyltellurium Triiodide Molecule

(a) Distances, Å

Te–I(1)	2.833 (1)	C(6)–C(1)	1.405 (17)
Te–I(2)	2.769 (1)	C(7)–C(8)	1.381 (19)
Te–I(3)	3.099 (1)	C(8)–C(9)	1.386 (20)
Te–C(1)	2.152 (12)	C(9)–C(10)	1.364 (21)
C(1)–C(2)	1.377 (18)	C(10)–C(11)	1.394 (21)
C(2)–C(3)	1.380 (18)	C(11)–C(12)	1.392 (19)
C(3)–C(4)	1.389 (20)	C(12)–C(7)	1.413 (18)
C(4)–C(5)	1.364 (19)	C(6)–C(7)	1.502 (18)
C(5)–C(6)	1.384 (17)		

(b) Bond Angles, Deg

I(1)–Te–I(3)	176.54 (4)	C(1)–C(6)–C(7)	123.5 (1.1)
I(1)–Te–I(2)	89.78 (4)	C(5)–C(6)–C(7)	119.9 (1.1)
I(2)–Te–I(3)	87.08 (3)	C(6)–C(7)–C(8)	120.3 (1.2)
I(1)–Te–C(1)	94.0 (3)	C(6)–C(7)–C(12)	120.1 (1.1)
I(2)–Te–C(1)	100.4 (3)	C(8)–C(7)–C(12)	119.5 (1.2)
I(3)–Te–C(1)	85.2 (3)	C(7)–C(8)–C(9)	122.2 (1.3)
Te–C(1)–C(2)	119.9 (9)	C(8)–C(9)–C(10)	118.7 (1.4)
Te–C(1)–C(6)	116.8 (9)	C(9)–C(10)–C(11)	120.5 (1.3)
C(2)–C(1)–C(6)	122.8 (1.1)	C(10)–C(11)–C(12)	121.6 (1.3)
C(1)–C(2)–C(3)	117.8 (1.2)	C(11)–C(12)–C(7)	117.5 (1.2)
C(2)–C(3)–C(4)	121.1 (1.3)	C(3)· · ·C(6)–C(7)	177.5 (9)[a]
C(3)–C(4)–C(5)	119.5 (1.2)	C(6)–C(7)· · ·C(10)	177.9 (9)[a]
C(4)–C(5)–C(6)	122.1 (1.2)	C(4)· · ·C(1)–Te	175.0 (7)[a]
C(5)–C(6)–C(1)	116.6 (1.2)		

[a] Nonbonded angle given to show distortion from ideal 180° value.

Table VIII. Intermolecular Bonding: Distances and Angles about Iodine Atoms in $C_{12}H_9TeI_3$[a]

(a) Distances, Å

I(1)–Te	2.833 (1)	I(1)· · ·I(3)	3.772 (1)
I(2)–Te	2.769 (1)	I(2)· · ·I(3)	3.239 (1)
I(3)–Te	3.099 (1)	I(3)· · ·I(2)	3.239 (1)
		I(3)· · ·I(1)	3.772 (1)

(b) Angles, Deg

Te–I(1)· · ·I(3)	166.12 (4)	Te–I(2)· · ·I(3)	174.01 (4)
Te–I(3)· · ·I(1)	170.09 (4)	Te–I(3)· · ·I(2)	75.48 (4)
		I(1)· · ·I(3)· · ·I(2)	98.09 (4)

[a] Intermolecular bonds are indicated here and in Figure 2 by means of dotted lines.

Description and Discussion of the Structure

The 2-biphenylyltellurium triiodide molecule and a view of the crystal structure down the b axis are shown in Figures 1 and 2, respectively. Individual bond distances and angles within the molecule are listed in Table VII and the main features of the coordination and bonding about the iodine atoms are presented in Table VIII.

To a first approximation, the configuration about tellurium may be described as trigonal bipyramidal. In this repre-

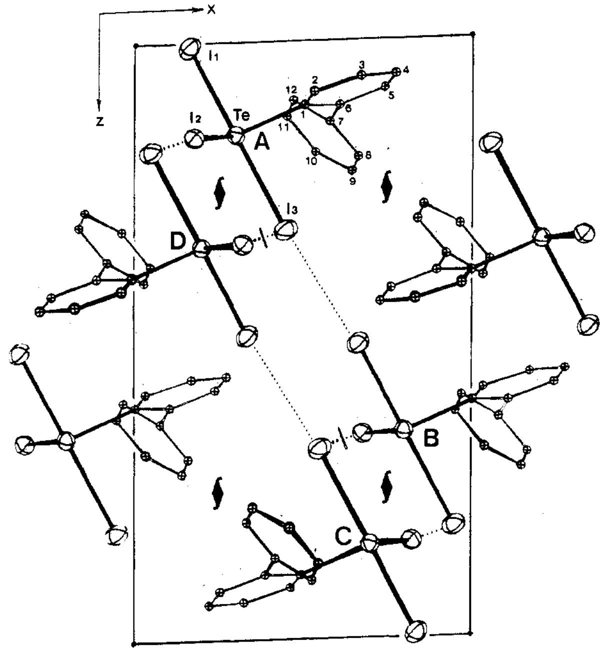

Figure 2. Packing arrangement of 2-biphenylyltellurium triiodide molecules as viewed down the *b* axis of the unit cell. Intermolecular bonds are indicated by means of dotted lines and the coordinates of the symmetry positions A, B, C, and D are given in Table I.

sentation, the axial positions are occupied by I(1) and I(3) while C(1), I(2), and a pair of electrons occupy the equatorial positions. Although the bond angles about tellurium given in Table VII are consistent with this description, the axial Te–I bond distances are significantly displaced from the usual values around 2.94 Å.[1,2] Thus the Te–I(1) distance of 2.833 (1) Å is some 0.11 Å shorter and the Te–I(3) distance of 3.099 (1) Å is ~0.16 Å longer than the expected value. These pronounced differences in the axial bond lengths suggest an alternate representation of the substance, namely, as an aryldiiodotelluronium salt, $[ArI_2Te^+]I^-$, in which I(3) becomes an iodide ion. However, in this case the observed Te–I(3) distance would appear to be considerably shorter than expected. While no clear-cut comparison appears to be available in known structures, some information is provided in the case of β-$(CH_3)_2TeI_2$ which is actually a telluronium salt consisting of $(CH_3)_3Te^+$ and $CH_3TeI_4^-$ ions.[9] In this compound, the tellurium atom in the $(CH_3)_3Te^+$ ion makes contacts with three iodine atoms, each in a different anion, at distances of 3.84, 3.97, and 4.00 Å, all of which are shorter than the sum of the van der Waals radii, 4.35 Å. While the $(CH_3)_3Te^+\cdots I$ distance would be expected to be shorter than ~3.8 Å if only one Te–I contact were involved, the Te–I(3) bond length of 3.099 Å in 2-biphenylyltellurium triiodide appears much too short for an interionic contact in a telluronium salt. The distances and angles about I(3) also provide some information for comparison of trigonal-bipyramidal and telluronium salt models. In Table VIII we note that I(3) has three neighbors: a Te atom at 3.099 Å, an I(3) atom at 3.239 Å in a neighboring molecule, and an I(1) atom at 3.772 Å in a third molecule. By use of the relationship between bond order and bond distance proposed by Pauling,[10] we find that the above bond distances correspond to bond orders of 0.27, 0.15, and 0.03, respectively, with a total bond order of only 0.45. Thus I(3) forms no really strong bonds with any other atoms. On the other hand, the three bond angles about I(3) are not far from the ideal values of 180 and 90° one expects for directed valences about an iodine atom. Considering all factors, the best representation of the triiodide appears to be trigonal bipyramidal about Te with significant tendencies toward a telluronium salt structure.

Table IX. Results of Least-Squares Planes Calculations

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

Plane A		Plane B		Plane C	
C(1)	−0.020*	C(7)	0.006*	I(1)	0.000*
C(2)	−0.003*	C(8)	0.006*	I(2)	0.000*
C(3)	0.020*	C(9)	−0.014*	I(3)	0.000*
C(4)	−0.013*	C(10)	0.010*	Te	0.039
C(5)	−0.010*	C(11)	0.002*		
C(6)	0.026*	C(12)	−0.010*		
Te	0.153	C(6)	−0.039		
C(7)	0.081				
Rms dev[b]	0.017	Rms dev	0.009		

Interplanar angle: plane A–plane B = 58.2 (5)°

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

As in the organotellurium diiodides, intermolecular bonding plays an important role in 2-biphenylyltellurium triiodide. In the present case the secondary bonds are all of the I···I type and this may account for the black color and metallic luster of the crystals.[2] As shown by means of dotted lines in Figure 2, there are two sets of secondary or intermolecular bonds in the structure. One set links the molecules into chains along 2_1 screw axes by way of I(2) and I(3) atoms. These secondary bonds are unusually strong with a separation of only 3.239 Å, a value of 1.06 Å less than the van der Waals separation of 4.30 Å. The second set of secondary bonds is much weaker with an I(1)···I(3) separation of 3.772 Å. In this case linear chains are formed parallel to the lattice-row line [101]. The only other intermolecular contact shorter than the sum of van der Waals radii is between Te and I(2) atoms in neighboring molecules along the 2_1 screw axes. This distance is 3.881 Å but the angular relationships about the atoms involved are such that no directed valences appear to be indicated. All intermolecular distances involving carbon or hydrogen atoms are either close to or greater than the sums of the appropriate van der Waals radii.

Data derived from least-squares planes calculations are given in Table IX. While both six-membered rings are fairly planar, ring 1 (formed by atoms C(1) through C(6)) shows greater deviations from planarity. Also, the atoms bonded to this ring, Te and C(7), show rather large displacements of 0.153 and 0.08 Å, respectively, from the least-squares plane. Further evidence of distortion in this ring is found in the angles about atoms C(1) and C(6), which show significant displacements from the ideal 120° values. The angle between the least-squares planes of the two six-membered rings is 58.2 (4)° with C(12) making an unexpectedly short intramolecular contact of only 3.317 Å with tellurium. The packing distances previously observed between Te and an aromatic carbon atom are 3.83 Å or greater.[11] This short distance between tellurium and C(12) in the present structure has possible chemical significance. When 2-biphenylyltellurium or 2-biphenylylselenium halides are heated to the melting (decomposition) point, which is usually about 165 °C, hydrogen halide gas is eliminated and a dibenzotellurophene or dibenzoselenophene derivative is formed.[4] The five-membered heterocyclic ring is closed as the chalcogen atom displaces a proton from atom C(12). The position occupied by C(12) with respect to the coordination about tellurium is ~0.70 Å above the C(1)–Te–I(2) or equatorial plane as seen in Figure 1. The angle C(1)–Te···C(12) is 68.1°. It is of interest to compare this value with the C(1)–Te–C(12) bond angles of 81.7 and 81.8° observed in dibenzotellurophene[11] and dibenzotellurophene diiodide,[1] respectively.

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Supplementary Material Available: Table IV, the calculated (idealized) positions and assigned isotropic thermal parameters of the hydrogen atoms, Table V, the root-mean-square amplitudes of vibration, and Table VI, the observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

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(5) The computer programs used in the present work are listed in footnote 4 of ref 1. 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 $w = [1/\sigma(F_o)]^2$.
(6) 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 had the value 6.6×10^{-7} and the maximum correction in $|F|$ measured was 26%.
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Molecular Structure of Aquodipyridinecopper(II) Dithiodipropionate, $Cu(O_2CCH_2CH_2S-)_2 \cdot 2C_5H_5N \cdot H_2O$

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The crystal and molecular structure of the title complex has been determined from single-crystal three-dimensional x-ray data collected by counter methods. Cu(DTDP)·2py·H_2O (DTDP = dithiodipropionate) crystallizes as light blue rectangular plates in space group $Pna2_1$ (C_{2v}^9, No. 33) with $Z = 4$; $a = 22.268$ (15), $b = 14.855$ (12), $c = 5.670$ (4) Å; $d_{calcd} = 1.583$, $d_{obsd} = 1.57$ (1) g/cm^3. Least-squares refinement of 1077 reflections having $F \geq 2\sigma$ gave a conventional R factor of 0.071. The structure contains no discrete molecules; it consists of crystallographically equivalent Cu(II) ions linked by the DTDP ligands to form infinite chains with alternating left- and right-handed disulfide chirality for adjacent DTDP ligands. A trans puckered arrangement of two pyridine nitrogen atoms and two carboxylate oxygen atoms forms the base of the approximately square-pyramidal CuN_2O_3 ligand set. Cu–N bond lengths (2.02 (1), 2.06 (1) Å) and Cu–O(carboxylate) bond lengths (1.95 (1), 1.95 (1) Å) are appropriate for equatorial ligation. The Cu(II) ion is displaced 0.21 Å from this CuN_2O_2 plane toward an apically bonded water molecule (Cu–O(H_2O) = 2.23 (1) Å). Bonding interactions between the Cu(II) ions and disulfide groups are not implied from the structural data. The title complex was crystallized from pyridine–water mixtures of a dark green precursor with the empirical formula Cu^{II}DTDP·$^1/_2H_2O$. Electronic spectral and magnetic ($\mu = 1.40$ (5) μ_B) studies of this latter complex indicated the presence of ($\sim CO_2)_4Cu_2$ dimeric units; however, further studies are required to establish whether the crystal contains discrete molecular dimers or is polymeric. Pseudoisotropic ESR spectra ($g = 2.08$) of the title complex are presented and discussed.

Introduction

The coordination geometry and molecular structure of copper(II)–L-cystinate complexes (cystinate = ($O_2CCH(NH_2)CH_2S-)_2$) remain a poorly charted area of copper(II)–amino acid chemistry. Both the variety and the poor solubility of the aqueous copper(II)-L-cystinate solution species have restricted the scope of solution studies. However, a combination of detailed solution equilibria studies and careful structural analyses led Hawkins and Perrin to conclude that a dimeric species, di-μ-cystinato-dicopper(II), was a major component of aqueous copper(II)–L-cystinate systems.[2] Studies of molecular models established that both amino acid fragments of L-cystine could not bind to the same Cu(II) ion, implying that the solution dimer was ligand-bridged. A subsequent crystallographic study of a bis-μ-(D-penicillamine disulfide)-dicopper(II) complex (the ligand is tetramethylcystine) supported this inference.[3] However, it is not yet known whether the difficultly soluble copper(II)–L-cystinate complexes are ligand-bridged dimers or ligand-bridged polymers. Moreover, details of the coordination structure such as cis/trans attachment of the amino acid fragments, the possible binding by disulfide, etc., remain unknown. These issues were addressed in part in a study of microcrystalline and needle modifications of Cu^{II}-L-cys·H_2O (cys = cystinate) which will be presented elsewhere.[4] Unfortunately, neither cystine complex could be obtained in a form suitable for a single-crystal x-ray diffraction study. Because of its structural relationship to cystine, complexes of ($^-O_2CCH_2CH_2S-)_2$ (dithiodipropionate or DTDP) may bear indirectly on the above structural questions. We report here the synthesis and molecular structure of Cu^{II}DTDP·2py·H_2O. The preparation of a pyridine-free precursor of composition Cu^{II}DTDP·$^1/_2H_2O$ is also reported.

Experimental Section

Preparation of $Cu(O_2CCH_2CH_2S-)_2 \cdot {}^1/_2H_2O$ (I). A solution containing 4.20 g of ($HO_2CCH_2CH_2S-)_2$ (0.02 mol) and 0.34 g of $NaHCO_3$ (0.04 mol) in 250 ml of distilled H_2O was heated to 60 °C to expel CO_2 and filtered through a 0.22-μm pore size membrane. Addition of a similarly filtered solution of 3.40 g (0.02 mol) of $CuCl_2 \cdot 2H_2O$ in 100 ml of distilled water to the ligand solution resulted in the precipitation of a dark green microcrystalline product. The product was collected by filtration, thoroughly washed with H_2O, acetone, and ether, and air-dried. The yield was quantitative. Anal. Calcd for $CuC_6H_8O_4S_2 \cdot {}^1/_2H_2O$: C, 25.67; H, 3.23. Found: C, 25.8; H, 3.1.

Preparation of $Cu(O_2CCH_2CH_2S-)_2 \cdot 2py \cdot H_2O$ (II). A deep blue stock solution was obtained by adding 6.0 g of I to a mixture of 100 ml of distilled water and 30 ml of pyridine (dissolution of I was not immediate) and diluting the resulting solution to 200 ml with additional