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Preparation and Crystal Structures of Ditellurium Octaselenium Bis(hexafluoroarsenate)–Sulfur Dioxide, $Te_2Se_8(AsF_6)_2 \cdot SO_2$, and "Tetratellurium Hexaselenium" Bis(hexafluoroarsenate), $Te_{3.7}Se_{6.3}(AsF_6)_2$

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The compound $Te_2Se_8(AsF_6)_2 \cdot SO_2$ has been prepared by the reaction of elemental tellurium with octaselenium bis(hexafluoroarsenate), $Se_8^{2+}(AsF_6^-)_2$, in liquid SO_2. The crystal structure has been determined by direct methods from three-dimensional x-ray counter measurements. Crystals are monoclinic with a = 7.337 (2) Å, b = 8.545 (3) Å, c = 36.030 (2) Å, and β = 91.52 (5)°. The structure, which has been refined in space group $P2_1/c$ to a final agreement index, R_2, of 0.094 for 1409 independent reflections, is made up of discrete $Te_2Se_8^{2+}$ and AsF_6^- ions and an SO_2 molecule. The $Te_2Se_8^{2+}$ cation may be regarded as a bicyclic cluster formed by a six-membered ring fused with an eight-membered ring, with the two Te atoms in the three-coordinate positions. The compound $Te_{3.7}Se_{6.3}(AsF_6)_2$ has been prepared by a reaction of a 1:1 Se–Te "alloy" with AsF_5 in liquid SO_2. The crystal structure has been determined by direct methods from three-dimensional x-ray counter measurements. Crystals are orthorhombic with a = 14.840 (6) Å, b = 10.828 (5) Å, and c = 13.345 (5) Å. The structure has been refined in space group *Pbcn* to a final agreement index, R_2, of 0.128 for 2477 independent reflections. It is composed of discrete AsF_6^- ions and of "$Te_{3.7}Se_{6.3}^{2+}$" ions with some positional and occupational disorder. The cation is a bicyclic cluster with a structure similar to that of $Te_2Se_8^{2+}$.

Introduction

It has been shown recently that sulfur can be oxidized by a number of oxidizing agents such as sulfuric acid, oleum, AsF_5, and SbF_5 to form the homonuclear polyatomic cations S_{16}^{2+}, S_8^{2+}, and S_4^{2+}.[1] It has also been shown that the reactions of elemental selenium and of elemental tellurium with the same oxidizing agents lead to the formation of the cations Se_8^{2+}, Se_4^{2+}, and Te_4^{2+}, respectively, as well as other cations that have been less well characterized.[1] The cations S_8^{2+} and Se_8^{2+} have been shown to have very similar nonplanar cyclic structures with an exo–endo conformation and a rather long and weak cross-ring bond.[2,3] The tetraatomic cations S_4^{2+}, Se_4^{2+}, and Te_4^{2+} all have the same square-planar structure.[4-6]

We have extended this investigation to interchalcogen compounds and we now report the preparation and crystal structures of the compounds $Te_2Se_8^{2+}(AsF_6^-)_2 \cdot SO_2$ and $Te_{3.7}Se_{6.3}^{2+}(AsF_6^-)_2$. These compounds both contain interchalcogen cations with similar bicyclic structures not previously encountered among the homonuclear cations of sulfur, selenium, and tellurium.

Experimental Work

(a) Preparation of $Te_2Se_8(AsF_6)_2 \cdot SO_2$. In a typical experiment, anhydrous SO_2 (40 ml) was distilled at −78 °C onto a mixture of powdered Te (0.002 mol, 0.255 g) and $Se_8(AsF_6)_2$ (0.001 mol, 1.009 g) which was prepared from the reaction of Se and AsF_5 as described previously.[7,8] The mixture was allowed to warm up to room temperature and stirred. The dark green color of the Se_8^{2+} species was found to diminish rapidly as the reaction proceeded. After stirring of the mixture for 12 h a light brown solution with a dark brown solid was obtained. The solution was filtered at −20 °C and allowed to stand at room temperature. Dark brown crystals were formed after 1 day. More product could be obtained by extracting the solid part of the original product with SO_2. As the solubility of the product in SO_2 is rather limited, a number of extractions were required in order to obtain a good yield of product. The dark brown crystalline material was quite stable at room temperature but was readily decomposed by the moisture of the atmosphere to give a mixture of the elements and other products. The crystals were handled in a drybox or in sealed tubes. Anal. Calcd for $Te_2Se_8As_2F_{12}SO_2$: Te, 19.20; Se, 47.54; As, 11.28; F, 17.15. Found: Te, 19.31; Se, 48.03; As, 12.24; F, 17.14.

(b) Preparation of $Te_{3.7}Se_{6.3}(AsF_6)_2$. Equimolar amounts of finely powdered selenium and tellurium were placed in a Pyrex glass tube. The contents of the tube were pumped to dryness for 24 h on a vacuum line and the tube was sealed. The materials were thoroughly mixed by shaking the tube which was then placed in a furnace and heated to 530 °C and maintained in the molten state for 12 h. On cooling a metallic looking material was produced which was pulverized in a porcelain mortar.

In a typical experiment AsF_5 (3 mol) was condensed onto 1 mol of Se–Te "alloy" and 40 ml of SO_2 at −196 °C. On warming to room temperature the color of the solution became red and the color intensified as stirring was continued. After 24 h of stirring a very dark red, almost black, solution was obtained. This solution was filtered and allowed to stand at room temperature for several days. A large quantity of black crystals of a variety of shapes and sizes was obtained but the most prominent crystal forms present were (312), (010), (100).

Table I. Atomic Coordinates for $Te_2Se_8(AsF_6)_2 \cdot SO_2$[a]

Atom	x	y	z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
Te(11)	3074 (6)	1718 (5)	4278 (1)	49 (3)	46 (3)	33 (2)	−4 (2)	1 (2)	2 (2)
Te(12)	1502 (5)	4669 (5)	3133 (1)	44 (3)	40 (2)	41 (2)	2 (2)	2 (2)	5 (2)
Se(21)	−149 (8)	2702 (7)	4029 (1)	34 (3)	34 (3)	34 (3)	6 (3)	1 (3)	3 (3)
Se(22)	4249 (8)	2830 (7)	3299 (2)	40 (4)	43 (4)	39 (3)	6 (3)	−1 (3)	5 (3)
Se(31)	5016 (7)	3757 (7)	3904 (1)	33 (3)	51 (4)	28 (3)	−7 (3)	−3 (2)	3 (3)
Se(32)	538 (9)	5218 (7)	3805 (2)	68 (5)	30 (3)	45 (3)	10 (3)	2 (3)	−3 (3)
Se(41)	3416 (8)	−622 (7)	3833 (2)	50 (4)	39 (4)	47 (4)	6 (3)	−2 (3)	1 (3)
Se(42)	−876 (8)	2501 (8)	2969 (2)	39 (4)	62 (4)	48 (4)	0 (3)	−4 (3)	5 (3)
Se(51)	596 (8)	−858 (7)	3533 (2)	49 (4)	36 (4)	43 (3)	−10 (3)	−2 (3)	−2 (3)
Se(52)	1021 (8)	324 (7)	2937 (1)	43 (4)	47 (4)	36 (3)	−7 (3)	−2 (3)	−9 (3)
As(1)	3946 (8)	2432 (7)	2077 (1)	39 (3)	38 (4)	36 (3)	0 (3)	2 (3)	5 (3)
As(2)	2207 (9)	3724 (8)	463 (1)	44 (4)	65 (5)	50 (4)	0 (4)	4 (3)	−17 (3)
F(1)	4344 (74)	656 (69)	2280 (14)	119 (17)					
F(2)	3483 (65)	4153 (60)	1863 (12)	103 (15)					
F(3)	3131 (59)	3074 (54)	2485 (11)	89 (15)					
F(4)	4849 (54)	1797 (48)	1682 (9)	72 (11)					
F(5)	1821 (72)	1721 (64)	1962 (13)	116 (16)					
F(6)	5981 (77)	3217 (70)	2174 (14)	124 (18)					
F(7)	172 (86)	4508 (78)	548 (15)	148 (21)					
F(8)	4299 (83)	3019 (74)	378 (15)	138 (19)					
F(9)	1365 (89)	2722 (80)	116 (16)	146 (22)					
F(10)	3038 (91)	4956 (81)	775 (16)	146 (23)					
F(11)	2068 (145)	2376 (125)	762 (25)	297 (40)					
F(12)	2484 (137)	5252 (123)	146 (24)	266 (37)					
S	2607 (35)	6499 (31)	4923 (7)	100 (7)					
O(1)	3797 (89)	6258 (78)	5259 (17)	117 (21)					
O(2)	2396 (78)	5213 (70)	4673 (14)	99 (18)					

[a] Positional coordinates $\times 10^4$; thermal parameters $\times 10^3$. The latter appear in the expression $\exp(-2\pi^2(h^2a^{*2}U(11) + \ldots + 2hka^*b^*U(12) + \ldots))$. Standard errors in the last figures quoted are given in parentheses.

The material was quite similar in properties to $Te_2Se_8(AsF_6)_2 \cdot SO_2$ and was equally sensitive to moisture. Unfortunately, it did not prove possible to obtain a satisfactory analysis for this compound.

Crystal Data

(a) $(Te_2Se_8)(AsF_6)_2 \cdot SO_2$ is monoclinic with a = 7.337 (2) Å, b = 8.545 (3) Å, c = 36.030 (2) Å, β = 91.52 (5)°, V = 2258.4 Å^3, Z = 4, d_{measd} = 3.88 g/cm^3, d_{calcd} = 3.90 g/cm^3, fw 1327.70, $F(000)$ = 2328, λ(Mo Kα) 0.71069 Å, and μ(Mo Kα) = 198 cm^{-1}. The unit cell parameters were obtained from a least-squares refinement of 15 reflections in the region 15° < 2θ < 25°. Weissenberg and precession photographs indicated that reflections were absent for $h0l$ when $l = 2n + 1$ and for $0k0$ when $k = 2n + 1$, characteristic of the space group $P2_1/c$ [No. 14].[9] The density of the material was measured by the density bottle method using a Fluorolube oil.

(b) $(Te_{3.7}Se_{6.3})^{2+}(AsF_6^-)_2$ is orthorhombic with a = 14.840 (6) Å, b = 10.828 (5) Å, c = 13.345 (5) Å, V = 2144.4 Å^3, Z = 4, d_{measd} = 4.16 g/cm^3, d_{calcd} = 4.16 g/cm^3, fw 1347.6, $F(000)$ = 2338.6, λ(Mo Kα) 0.71069 Å, and μ(Mo Kα) = 175 cm^{-1}. Weissenberg and precession photographs indicated that reflections were absent for $0kl$ when $k = 2n + 1$, for $h0l$ when $l = 2n + 1$, and for $hk0$ when $h + k = 2n + 1$, characteristic of the space group $Pbcn$ [No. 60].[9] Since there are eight general positions in this space group, the cations must possess either a center of symmetry or a twofold axis or they must be disordered. The density of the compound was measured by the density bottle method. The experimental value, 4.16 g cm^{-3}, corresponds to the density expected from a crystal of composition $(Te_{3.7}Se_{6.3})(AsF_6)_2$ rather than $Te_4Se_6(AsF_6)_2$ (d_{calcd} = 4.21 g/cm^3) or $Te_3Se_7(AsF)_2$ (d_{calcd} = 4.06 g/cm^3). However, only one density measurement was made and its accuracy is uncertain.

X-Ray Intensity Measurements

(a) $Te_2Se_8(AsF_6)_2 \cdot SO_2$. The crystal which was an irregular block of approximate dimensions 0.30 × 0.18 × 0.10 mm was sealed in a quartz capillary and mounted on a Syntex $P\bar{1}$ diffractometer with its 0.30-mm edge, which was perpendicular to the (100) face, almost coincident with the ϕ axis of the diffractometer. Intensities were measured with graphite-monochromated Mo Kα radiation, using a θ–2θ scan, with a scan rate varying from 2.0 to 24.0°/min in 2θ, so that the weaker reflections were examined more slowly to minimize counting errors. Stationary-background counts, with a time equal to half the scan time for each reflection, were made at each end of the scan range. The scan width varied from 2° at low 2θ to 2.5° for high-angle reflections. One standard reflection was regularly checked to monitor the stability of the crystal and its alignment, but no significant variation was observed. A total of 1732 independent reflections within a unique quadrant with 2θ < 42° were measured, resulting in 1409 reflections with intensities greater than 3 times their standard error, based on counting statistics. Lorentz, polarization, and absorption corrections were applied to the observed intensities.

(b) $(Te_{3.7}Se_{6.4})(AsF_6)_2$. Intensities were measured in a manner similar to that described above. A total of 2477 independent reflections, within a unique octant with 2θ < 55° were measured, resulting in 967 reflections with intensities greater than 3 times their standard error. Lorentz, polarization, and absorption corrections were applied to the observed intensities treating the crystal, which had dimensions of 0.14 × 0.15 × 0.34 mm, as a cylinder.

Structure Determinations

(a) $(Te_2Se_8)(AsF_6)_2 \cdot SO_2$. The structure factors were put on an absolute scale by calculating accurately the statistical distribution of the E values for all the intensities. The resulting reflection statistics were of the type usually found in hypercentric crystal structures. The averaged computed values were $|E|_{av}$ = 0.798, $|E|_{av}^2$ = 1.000, $|E^2 - 1|_{av}$ = 0.968, $|E^2 - 1|_{av}^2$ = 2.000, and $|E^2 - 1|_{av}^3$ = 8.000. A total of 127 reflections had E values above 1.6. The most consistent set of signs for 108 of these was determined using the direct methods programs SINGEN and PHASE from the X-Ray 71 system.[10] An E map was computed using the calculated phases. The map revealed the positions of 12 independent heavy atoms and showed that 10 of these atoms formed a bicyclic cluster. Two atoms of the cluster were taken to be Te since the peaks on the E map corresponding to these atoms were larger than all of the remaining atoms of the cluster. The latter were assumed to be Se and the two remaining heavy atoms were assumed to be As. The scattering factors for the neutral heavy atoms were all corrected for anomalous dispersion using values for the real and imaginary parts given in ref 11. Full-matrix least-squares refinement of positional and isotropic temperature parameters gave a conventional agreement index, R_1 of 0.26. Subsequent electron density difference syntheses revealed the positions of all of the light atoms. Anisotropic temperature factors were introduced for the heavy atoms leading to a final agreement index, $R_2 = [\sum w(|F_o|^2 - |F_c|^2)/\sum wF_o^2]^{1/2}$, of 0.0935 where $w = 1/\sigma^2$, being the standard error obtained from counting statistics. The final parameters are given in Table I. The largest shift Δ/σ in the final cycle was 0.2. The final R value was 0.098. A final difference Fourier showed no significant peaks.

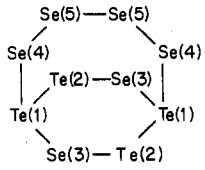
(b) $Te_{3.7}Se_{6.3}(AsF_6)_2$. The structure factors were put on an absolute scale by calculating accurately the statistical distribution of the E values for all of the intensities. The resulting reflection

Table II. Atomic Coordinates for $Te_{3.7}Se_{6.3}(AsF_6)_2$[a]

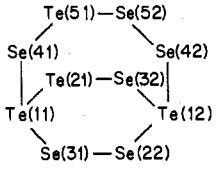
Atom	*x*	*y*	*z*	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Te(1)	3320 (2)	−1056 (3)	2298 (2)	26 (1)	57 (2)	43 (1)	−2 (2)	5 (2)	3 (2)
Te(21)[b]	−4268 (23)	−2362 (36)	1303 (23)	37 (7)	61 (13)	43 (11)	7 (7)	6 (8)	−10 (8)
Se(22)[b]	4380 (34)	−2197 (50)	3612 (35)	18 (17)	41 (18)	51 (17)	2 (14)	9 (12)	23 (13)
Se(3)	4620 (3)	−624 (5)	1033 (4)	33 (2)	65 (3)	37 (2)	2 (2)	9 (2)	4 (2)
Se(4)	3331 (3)	1129 (5)	3166 (3)	36 (2)	55 (3)	38 (2)	5 (2)	5 (2)	0 (2)
Se(52)[b]	−4258 (9)	2366 (10)	2951 (7)	34 (*)	60 (*)	39 (*)	0 (*)	0 (*)	0 (*)
Te(51)[b]	4251 (12)	2447 (14)	2018 (11)	34 (*)	57 (*)	43 (*)	0 (*)	0 (*)	0 (*)
As	1681 (3)	859 (5)	174 (4)	34 (2)	51 (3)	46 (3)	6 (2)	5 (2)	4 (2)
F(1)	675 (20)	1455 (39)	−182 (29)	37 (15)	137 (35)	102 (26)	18 (20)	−5 (19)	−23 (27)
F(2)	1408 (25)	976 (52)	1392 (27)	69 (25)	263 (57)	58 (22)	40 (33)	11 (19)	−26 (31)
F(3)	1365 (26)	−538 (40)	219 (37)	79 (26)	88 (33)	165 (41)	42 (25)	−4 (29)	33 (35)
F(4)	2048 (22)	2344 (35)	244 (35)	49 (19)	87 (25)	175 (39)	31 (20)	21 (24)	−13 (28)
F(5)	2730 (24)	331 (36)	512 (22)	100 (28)	127 (31)	47 (18)	74 (24)	−17 (18)	33 (19)
F(6)	1965 (25)	802 (48)	−1027 (27)	85 (27)	290 (52)	75 (24)	127 (33)	52 (22)	84 (31)

[a] Parameters are present as in Table I. [b] Occupation numbers: Te(21), 0.5(*); Se(22), 0.5(*); Te(51), 0.33(2); Se(52), 0.61(3). Parameters with standard errors given as (*) were not refined in the final round.

statistics were of the type usually found in hypercentric crystal structures. The averaged computed values are $|E|_{av} = 0.724$, $|E|_{av}^2 = 1.000$, $|E^2 - 1|_{av} = 1.097$, $|E^2 - 1|_{av}^2 = 2.898$, and $|E^2 - 1|_{av}^3 = 16.794$. Such a distribution confirms the centrosymmetric space group. A total of 385 reflections had *E* values above 1.4. The most consistent set of signs for 370 of these reflections was determined using the direct-method programs SINGEN and PHASE from the X-Ray 71 system.[10] Using the calculated phases, an *E* map was computed and this showed the positions of the six heavy atoms in the asymmetric unit. For all of these atoms the scattering factors of tellurium[11] were initially used. A full-matrix least-squares refinement of positional and isotropic temperature parameters gave a conventional agreement index R_1 of 0.23. The resulting temperature factor discrepancies and a difference synthesis indicated the probable selenium atoms in cation



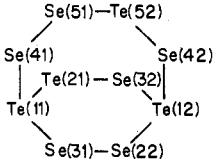
I



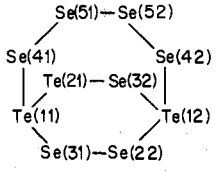
II

I (atoms 3, 4, and 5) and the octahedral array of fluorine atoms around the single arsenic atom. The cation appeared at this stage as a bicyclic ring with C_2 point group symmetry lying around the twofold axis. Refinement of positional and anisotropic temperature factors for all reflections converged at $R = 0.136$.

At this stage, the temperature factor of atom 2 of the cation (assumed to be Te) was unduly large while that of atom 5 (assumed to be Se) was particularly small. This suggested that sites 2 and 5 contained both Te and Se atoms and that the cation had one of the structures II or III. In this case the crystal either must be disordered,



III



IV

preserving the average twofold crystallographic symmetry axis of the cation, or must belong to a space group ($Pbc2_1$ or $P2_1cn$) in which the twofold axis is lost. Neither of the two noncentrosymmetric space groups should give rise to the observed systematic absences, but if the deviation from the higher symmetry were small, it is possible that the additional reflections would be too weak to observe. At this stage the structure was refined independently in all three space groups on the assumption that the cation had the configuration II.[12] In the *Pbcn* refinement the cation was assumed to be disordered by including Te(51), Se(52), Te(21), and Se(22) each with half-weight and allowing all their parameters to refine independently. Anisotropic temperature factors were used for all atoms. In the two noncentrosymmetric refinements only the heavy atoms were refined anisotropically. In all three cases the refinement ended with R_2 between 0.12 and 0.13 and an examination showed that the imaginary component of the structure factors in the two noncentrosymmetric refinements was not making a large enough contribution to $|F|$ to make a significant difference to the agreement index. We are therefore unable to say which space group is correct and for simplicity we continue the discussion only in terms of the disordered centrosymmetric structure. The temperature factors in the *Pbcn* refinement indicated that Se(52) might be more abundant than Te(51) and this was confirmed by an additional refinement of the occupation numbers with temperature factors set to values typical of those found for other Se and Te atoms. The result indicated a cation composition of $Te_{3.7}Se_{6.3}$ corresponding to a 2:1 mixture of cations II (or III) and IV. This composition is in good agreement with that deduced from the measured density, but this agreement may be fortuitous.

Of more concern is the fact that the refinement ended with $R_2 = 0.12$ when with diffractometer measurements we had expected to obtain an agreement index better than 0.09. A final difference Fourier revealed that the discrepancy was associated with tails on all of the heavy atoms at a distance of 0.5 Å along the *y* direction, too far away to be accounted for by anisotropic thermal motion or positional disorder of the atoms. Such a feature suggests a systematic error in the intensity measurements but an examination of the discrepancies in the structure factors failed to indicate any systematic effects. Both absorption and extinction corrections had been applied and an independent set of intensity measurements from another crystal led to essentially the same results. This data set was, however, less complete and it was not used in the refinement reported here. In the final refinement the atomic scattering factors were corrected for anomalous dispersion using the real and imaginary parts given in ref 11. All reflections were given unit weight except that where $I < 3\sigma$ and $|F_c| < |F_o|$ zero weight was used. The resulting values of $|F_o| - |F_c|$ showed no systematic variation with $|F_o|$. Programs of the X-Ray 71 system[10] and the locally written program CUDLS were used to give $R_2 = 0.128$ for the *Pbcn* refinement. The final R_1 value was 0.129. The largest shift Δ/σ in the final cycle was 0.5. The final parameters are given in Table II and the observed and calculated structure factors for both structures are available.[13]

Discussion

The cations of these two crystals are isostructural but have different compositions. The $Te_2Se_8^{2+}$ ion is the best characterized. It consists of a bicyclic ring which is very close to possessing a twofold axis, the standard deviations between equivalent bonds and angles being 0.03 Å and 3.0°, respectively (Figure 1). It can be thought of as a six-membered ring linked across the middle by a chain of four Se atoms with the two Te atoms in the three-coordinate positions. Alternatively, it can be thought of as two fused eight-membered rings with the endo–exo conformation found in Se_8^{2+} (Figure 2; cf. the isostructural ion in Figure 3). As the two three-coordinate positions must carry a formal positive charge, it is not surprising that they are occupied by the more electropositive Te atoms. The Se–Se bond lengths vary between 2.32 and 2.40 Å with a mean of 2.36 Å, close to the Se–Se bond lengths of 2.34 Å in the Se_8 molecule[14] and 2.37 Å in hexagonal selenium.[14] The central bond in the four-atom Se chain is longer

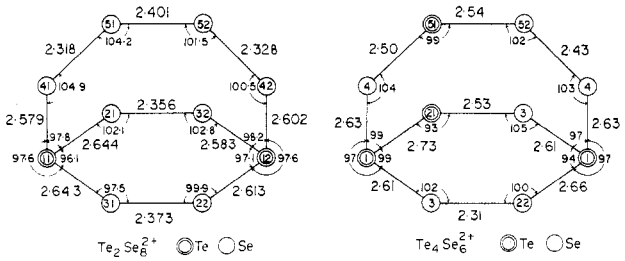


Figure 1. Dimensions in $Te_2Se_8^{2+}$ (left) and $Te_4Se_6^{2+}$ (right). Se atoms are shown by single circles; Te atoms by double circles. Standard errors for $Te_2Se_8^{2+}$ are 0.008 Å and 0.2°; for $Te_4Se_6^{2+}$ they are about 0.01 Å and 1°, but because of the disorder the bond lengths involving atoms on the 2 and 5 sites are much less certain (see Table III).

than the two outer ones, an effect that has also been observed in chains of four or more sulfur atoms.[14] The Te–Se distances vary from 2.58 to 2.64 Å with a mean of 2.61 Å close to the mean (2.58 Å) of the Se–Se and Te–Te distances found in the elements.[15]

The cation in the second compound is less well characterized because of the partial substitution of Te for Se(2) and Se(5). The occupation numbers for the 2 and 5 sites obtained from the crystal structure analysis and the measured density are consistent with a structure which contains a random distribution of $Te_3Se_7^{2+}$ and $Te_4Se_6^{2+}$ cations in the proportion of 1:2. The two structures thus provide evidence for a series of isostructural cations $Te_xSe_{10-x}^{2+}$ with x = 2, 3, and 4. The positions of the Te and Se atoms on the disordered sites have been refined separately but it is not possible to use these to obtain an unambiguous measure of the bond lengths in the separate ions. The best set of bond lengths we can calculate (Figure 1, right), are similar to those in $Te_2Se_8^{2+}$ except that the Te–Se distances show a wider range, the shorter bonds (average 2.53 Å) being associated with the two-coordinate Te atoms and the longer ones (average 2.63 Å) being associated with the three-coordinated Te atoms.

In the Appendix we describe a procedure for predicting the bond lengths in the $Te_xSe_{10-x}^{2+}$ ions using four fitted parameters. The procedure is based on the bond-valence principle that the sum of the individual bond strengths (valences) around each atom must equal the valence of the atom. The alternation of bond lengths is seen to be a natural consequence of the three-coordination at the 1 position of the ion. In $Te_2Se_8^{2+}$ the predicted lengths (Table III) agree with those observed to within 0.02 Å, the level at which the cation can be said to possess C_2 symmetry. Although the discrepancy between the predictions and observations is larger for the other two ions, the difference can be completely accounted for by the uncertainty in the bond lengths derived from the disordered structure. In particular, the position of Se(52) is the average of the Se(52) positions in the two ions (II and IV) and the bond lengths associated with it will be particularly uncertain.

In both structures the angles at Se are larger (average 102°) than those at Te (average 97°) just as the bond angles in

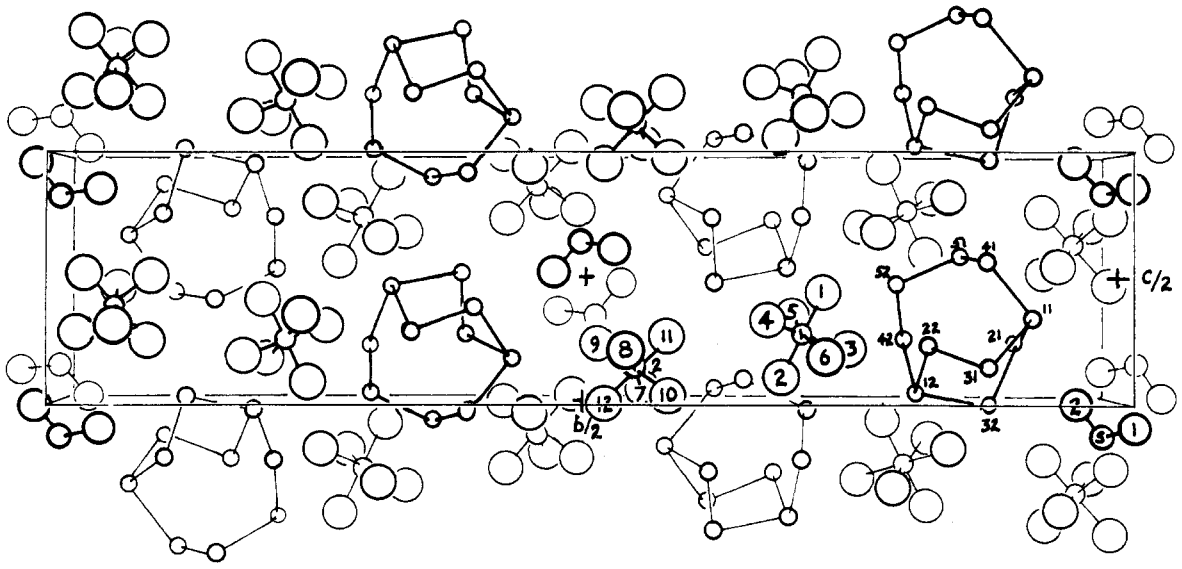


Figure 2. $Te_2Se_8(AsF_6)_2 \cdot SO_2$ viewed down the a axis. The long axis is c. Circles in increasing order of size represent Se and Te, As, S, and O. The origin is at the center of the cell.

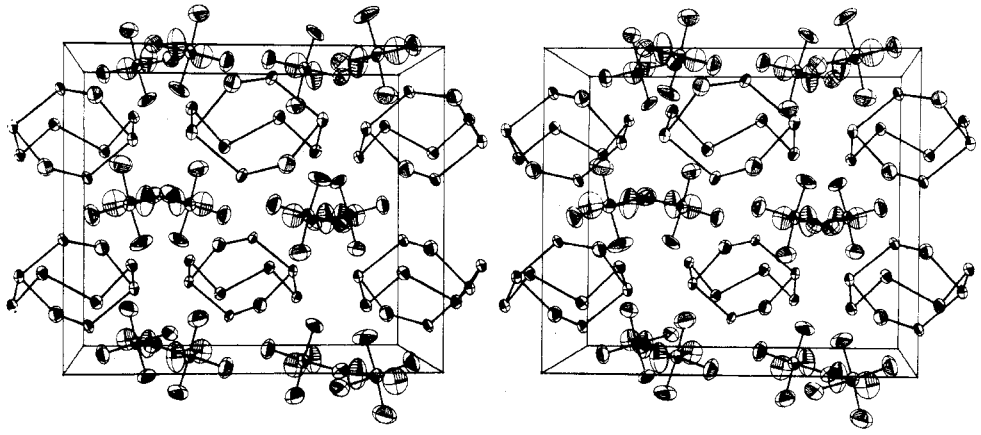


Figure 3. Stereoscopic view of $Te_{3.7}Se_{6.7}(AsF_6)_2$. The a axis is horizontal, b out of the page, and c vertical.

Table III. Predicted[a] and Observed Bond Lengths (Å) in $Te_xSe_{10-x}^{2+}$ Cations

		$Te_2Se_8^{2+}$ [c]			$Te_3Se_7^{2+}$ [d]			$Te_4Se_6^{2+}$ [e]		
Atom	Valence[a]	Bond	Calcd	Obsd	Bond	Calcd	Obsd	Bond	Calcd	Obsd
11-21				2.61 (1)	Te-Te	2.80	2.73 (3)	Te-Te	2.80	2.73 (3)
12-22				2.64 (1)	Te-Se	2.61	2.66 (5)	Te-Se	2.61	2.66 (5)
11-31	0.93	Te-Se	2.61	2.58 (1)	Te-Se	2.61	2.61 (1)	Te-Se	2.61	2.61 (1)
12-32				2.64 (1)						
11-41				2.60 (1)	Te-Se	2.61	2.63 (1)	Te-Se	2.61	2.63 (1)
12-42				2.58 (1)						
21-32				2.37 (1)	Te-Se	2.51	2.53 (4)	Te-Se	2.51	2.53 (4)
22-31	1.12	Se-Se	2.33	2.36 (1)	Se-Se	2.33	2.31 (5)	Se-Se	2.33	2.31 (5)
41-51				2.33 (1)	Se-Se	2.33	2.43[b]	Se-Te	2.51	2.50 (2)
42-52				2.32 (1)				Se-Se	2.33	2.43[b]
51-52	0.93	Se-Se	2.41	2.40 (1)	Se-Se	2.41	2.51[b]	Te-Se	2.61	2.54[b]

[a] See Appendix. [b] Standard error uncertain. [c] σ(obsd − calcd) = 0.02 Å. [d] σ = 0.06 Å. [e] σ = 0.05 Å.

Table IV. Interatomic Distances (Å) and Angles (deg) in $Te_2Se_8(AsF_6)_2SO_2$[a]

AsF_6^- Ions

		F(2)	F(3)	F(4)	F(5)	F(6)
As(1)-F(1)	1.71 (6)	177[b]	89	90	86	97
As(1)-F(2)	1.69 (5)		92	89	91	86
As(1)-F(3)	1.69 (4)			178	89	91
As(1)-F(4)	1.68 (4)				177	86
As(1)-F(5)	1.71 (5)					177
As(1)-F(6)	1.66 (6)					
Av As-F	1.69					

		F(8)	F(9)	F(10)	F(11)	F(12)
As(2)-F(7)	1.67 (6)	178	92	86	95	87
As(2)-F(8)	1.68 (6)		90	92	86	92
As(2)-F(9)	1.62 (6)			172	96	86
As(2)-F(10)	1.64 (6)				92	86
As(2)-F(11)	1.58 (10)					176
As(2)-F(12)	1.75 (10)					
Av As-F	1.66					

SO_2 Molecule

S-O(1)	1.49 (7)	O(1)-S-O(2)	117 (4)
S-O(2)	1.43 (6)		

Interionic Distances Less Than 3.5 Å

Te(11)-F(7)	3.12 (6)	Te(12)-F(3)	2.98 (4)
Te(11)-F(10)	3.24 (7)	Te(12)-F(5)	3.01 (5)
Te(11)-O(1)	3.29 (6)	Te(12)-F(4)	3.29 (4)
Te(11)-F(9)	3.33 (6)		
Te(11)-O(2)	3.35 (8)		
Se(21)-F(7)	3.13 (6)	Se(22)-F(3)	3.03 (4)
Se(21)-F(10)	3.25 (7)	Se(22)-F(1)	3.37 (6)
Se(31)-O(1)	3.12 (6)	Se(32)-O(2)	3.38 (5)
Se(31)-F(4)	3.35 (4)	Se(32)-F(11)	3.11 (10)
Se(41)-F(10)	2.97 (6)		
Se(41)-F(4)	3.17 (4)		
Se(51)-F(5)	3.23 (5)	Se(52)-F(6)	2.88 (6)
Se(51)-F(2)	3.27 (5)	Se(52)-F(3)	3.27 (4)
Se(51)-F(7)	3.39 (6)		
S-F(8)	2.85 (7)		
S-F(9)	3.10 (7)		
S-F(12)	2.89 (11)		
O(1)-F(8)	3.11 (9)	O(2)-F(9)	3.08 (9)
O(1)-F(12)	3.16 (12)		
O(1)-O(1)	3.38 (9)		

[a] Cation distances and angles are given in Table III and Figure 1. [b] 177° is the angle F(2)-As(1)-F(1), etc. Indicated standard error in angles is 3°.

elemental selenium (Se_8, 105.3°; hexagonal Se, 102.8°) are larger than those in elemental Te (101.8°).[15] However, such a reduction in angle is also expected from purely geometrical considerations when the larger Te atom is substituted for Se assuming all the other atoms remain in the same place.

The AsF_6^- ions in both crystals show large thermal motions but are otherwise regular with As–F averaging 1.66 and 1.69 Å (Tables IV and V). The atoms of the SO_2 molecule also have large temperature factors but the molecule is otherwise similar to that found in crystalline SO_2.[16] All of the interionic

Table V. Interatomic Distances and Angles in $Te_{3.7}Se_{6.3}(AsF_6)_2$[a]

AsF_6^- Distances and Angles[b]

		F(2)	F(3)	F(4)	F(5)	F(6)
As-F(1)	1.69	92[c]	96	86	178	88
As-F(2)	1.68		88	87	89	178
As-F(3)	1.58			174	87	94
As-F(4)	1.70				91	87
As-F(5)	1.72					89
As-F(6)	1.66					
Av As-F	1.66					

Interionic Distances

Te(1)-F(5)	2.95 (3)	Se(4)-F(4)	3.28 (4)
Te(1)-F(6)	3.02 (4)	Te(1)-F(4)	3.29 (4)
Se(3)-F(5)	3.07 (4)	Te(1)-F(2)	3.37 (5)
Se(4)-F(6)	3.10 (4)	Se(22)-F(3)	3.44 (7)
Te(21)-F(1)	3.15 (5)	Te(1)-F(2)	3.46 (5)
Te(21)-F(3)	3.19 (6)	Se(52)-F(3)	3.46 (5)
Se(22)-F(1)	3.20 (6)	Se(3)-F(4)	3.48 (4)
		Te(51)-F(1)	3.48 (4)

[a] Cation distances are given in Table III and Figure 1. [b] Indicated standard error in As-F is 0.04 Å and in F-As-F is 2°, but see text regarding positional disorder. [c] 92° is the angle F(2)-As-F(1), etc.

and intermolecular distances are greater than 2.85 Å and as expected the weak interionic bonding occurs from O or F to S, Se, or Te.

The packing in $Te_2Se_8(AsF_6)_2 \cdot SO_2$ is shown in Figure 2 and that in $Te_{3.7}Se_{6.3}(AsF_6)_2$ is shown in Figure 3.

Acknowledgment. We wish to thank the National Research Council of Canada for research operating grants.

Appendix. Bonding in $Te_xSe_{10-x}^{2+}$ Ions

The existence of a correlation between bond length and the strength or valence of a bond has long been known.[17] Recently Baur[18] has shown that bond lengths in minerals can be predicted using Pauling's electrostatic valence principle. A similar result can be achieved by calculating bond lengths with the aid of a suitable bond valence–bond length correlation[17] using bond valences that have been chosen in such a way that their sum around each atom is equal to the atomic valence of that atom. However, the assignment of atomic valences (the number of valence electrons involved in bonding) to the Se and Te atoms in $Te_xSe_{10-x}^{2+}$ ions is not unambiguous. We have assumed that each of the atoms would have a valence of 2 in the neutral Te_xSe_{10-x} species. By analogy with the method used to derive the valences in $Te_2Se_2^{2+}$,[19] we have further assumed that the two electrons formally removed to form the cation are electrons from two different lone pairs. Their removal leaves two additional unpaired electrons which can contribute to the intraionic bonding. Changing Te_xSe_{10-x} to $Te_xSe_{10-x}^{2+}$ therefore introduces an additional four valences to be distributed among the ten atoms, two valences (ionic) being involved in interionic bonding and two (covalent) in intraionic bonding. We expect that the larger share of this

valence will be associated with the three-coordinate Te atoms and a smaller share with the two-coordinate atoms and we have arbitrarily assigned total valences of 3.0 and 2.25, respectively, to these atoms. If each atom contributes equally 0.2 valence unit (vu) to the interionic bonding, 2.80 and 2.05 vu, respectively, are left for the intraionic bonding. As can be seen from Table III, this leads to the intraionic bonds having valences of either 0.93 or 1.12 vu, and the alternation of bond strengths is seen to be a direct consequence of the three-coordination around Te(1).

The bond lengths (R) can be calculated from the bond valences (S) using the expression[16]

$$S = (R/R_0)^{-N}$$

where R_0 and N are fitted parameters for each pair of bonds. The parameters for Se–Se (R_0 = 2.38 Å, N = 5) and Te–Se (R_0 = 2.57 Å, N = 5) were chosen to fit the observed bond lengths; the values for Te–Te (R_0 = 2.76 Å, N = 5) were chosen so that any Te–Se bond had a length midway between the Se–Se and Te–Te bonds of the same strength. As a further check these parameters also predict that all the bonds in the isostructural series Se_4^{2+} (2.28 Å), $Se_2Te_2^{2+}$ (2.476 Å), and Te_4^{2+} (2.664 Å) have the expected strength of 1.25 vu.[18] The predicted bond valences and bond lengths for the three ions with x = 2, 3, and 4 are compared with the observed lengths in Table III.

Registry No. $Te_2Se_8(AsF_6)_2 \cdot SO_2$, 58249-22-2; $Te_{3.7}Se_{6.3}(AsF_6)_2$, 58249-23-3; Se–Te, 12067-42-4; $Se_8(AsF_6)_2$, 52374-78-4; Te, 13494-80-9; AsF_5, 7784-36-3.

Supplementary Material Available: Listings of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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A Highly Distorted Homoporphyrin Complex. Crystal and Molecular Structure of (10*H*-10-Hydroxyl-21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21-homoporphinato)nickel(II)

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The (10*H*-10-hydroxyl-21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21-homoporphinato)nickel(II) crystallizes in the space group $P2_1/c$; the unit cell has the dimensions a = 11.895 (5) Å, b = 29.229 (8) Å, c = 12.963 (5) Å, and β = 121.81 (6)° and contains four molecules. Intensity data were collected by θ–2θ scanning with Mo Kα radiation, and 4461 data were retained as observed and used for the solution and refinement of structure. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to conventional and weighted R values of 0.065 and 0.082, respectively. The nickel atom exhibits square-planar coordination; the four Ni–N bond lengths are equal to 1.879 ± 0.010 Å. The homoporphyrin skeleton is far from planar and highly distorted. The individual pyrrole groups within the macrocycle are markedly noncoplanar; each makes an angle of 39–45° with the four-nitrogen plane. There are also very large angles (88.0 and 81.5°) between the opposite pyrrole planes. The overall effect of the distortions of the skeleton is to generate a saddle-shaped surface.

Introduction

Homoporphyrins are synthetic porphyrin derivatives by insertion of an *extra* carbon atom between two pyrroles of the macrocycle. The first recently described metal complex with such an expanded macrocyclic ligand is the (21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21*H*-21-homoporphinato)nickel(II).[1] A severe distortion of the homoporphinato core was observed limiting the π delocalization within the macrocycle. According to spectroscopic studies (visible spectra, NMR),[2] the (10*H*-10-hydroxyl-21-ethoxycarbonyl-5,10,15,20-tetraphenyl-21-homoporphinato)nickel(II) appeared to be much more distorted than the former complex. For this reason, we have undertaken its structure determination.

Experimental Section

A sample of the title compound was kindly supplied by Dr. H. J. Callot. Crystals suitable for x-ray study were grown by slow evaporation of nitromethane–dichloromethane solutions. Preliminary precession photographs indicated the crystal symmetry to be monoclinic and the systematic absences were consistent with the unique space group $P2_1/c$. Precise lattice constants were obtained by least-squares