78891-56-2; $NiLCl_2$, 78891-55-1; $NiLBr_2$, 78891-54-0; $NiL(NCS)_2$, 78891-59-5; $CuL(ClO_4)_2$, 78891-53-9; $CuLBr_2$, 78891-52-8; 1,4-bis(2-formylphenyl)-1,4-dioxabutane, 52118-10-2; ethane-1,2-diamine, 107-15-3.

**Supplementary Material Available:** Listings of analytical data for the complexes (Table S1) and structure factors (Table S2) for the nickel complex (12 pages). Ordering information is given on any current masthead page.

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# Preparation and Crystal Structures of the Hexafluoroarsenate and Hexafluoroantimonate Salts of the Dimeric Thiodiselenazyl Cation $Se_4S_2N_4^{2+}$

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The reactions of $S_4N_4$ with $Se_4(AsF_6)_2$, $Se_4(Sb_2F_{11})_2$, and $Se_8(AsF_6)_2$ in $SO_2$ have been found to give the first well-characterized examples of a sulfur–selenium–nitrogen cationic ring in the compounds $(Se_4S_2N_4)(AsF_6)_2$ and $(Se_4S_2N_4)(SbF_6)_2$. Blue-green crystals of both compounds are isomorphous and crystallize in the monoclinic space group $P2_1/n$. The cell dimensions of the hexafluoroarsenate salt determined at −30 °C are $a$ = 10.358 (3) Å, $b$ = 16.002 (5) Å, $c$ = 9.748 (4) Å, and $\beta$ = 98.16 (3)°; those of the hexafluoroantimonate salt, determined at 22 °C, are $a$ = 10.619 (1) Å, $b$ = 16.523 (2) Å, $c$ = 9.873 (2) Å, and $\beta$ = 97.70 (1)°. In both salts, the bis(thiodiselenazyl) cation, $Se_4S_2N_4^{2+}$, is very similar to the bis(thiodithiazyl) cation in that it consists of two thiodiselenazyl rings linked by long Se···Se interactions of 3.12–3.18 Å between the diselenide bonds in each ring. The cation also has some significant interactions with the hexafluoroarsenate and hexafluoroantimonate anions. These cation–cation and anion–cation interactions are discussed and compared to similar interactions in the sulfur–nitrogen cations and other selenium compounds.

## Introduction

The synthesis of the monomeric and dimeric forms of the thiodithiazyl cation, $S_3N_2^+$ and $S_6N_4^{2+}$, by the oxidation of $S_4N_4$ with $Te_6^{4+}$ and $S_8^{2+}$, respectively, has been reported recently.[1] These novel oxidations raised the question as to whether the analogous reactions of $S_4N_4$ with the selenium cations $Se_4^{2+}$ and $Se_8^{2+}$ would also give a sulfur–nitrogen cation or alternatively a mixed sulfur–selenium–nitrogen cation, no example of which had been well characterized. The first report of a compound possibly containing a S–Se–N cation was made by Garcia-Fernandez,[2] who obtained a compound, which was reported to analyze as $SeS_2N_2Cl_5$, from the reaction of selenium dichloride and $S_4N_4$ in thionyl chloride. However, Bannister and co-workers[3] were unable to reproduce these results, and they suggested that the compound was probably $Se_2S_4N_4Cl_2$ for which some possible structures were postulated. Recently Street and co-workers[4] have reported the preparation of compounds formulated as $(S_2Se_4N_4^{2+})(Cl^-)_2$ and $(S_2Se_4N_4^{2+})(Br^-)_2$ from the reactions of bis[bis(trimethylsilyl)amino]sulfane and the appropriate selenium tetrahalide in methylene chloride. On the basis of infrared and mass spectroscopic data and the absence of an ESR signal from the solid compounds the structures of these new cations were proposed to be analogous to that of the $S_6N_4^{2+}$ cation as determined by Bannister et al.[5] However, because of the insolubility of the compounds, no crystals could be obtained for a definite X-ray crystallographic confirmation of the proposed structures.

In this paper, we show that oxidation of $S_4N_4$ using either of the cations $Se_4^{2+}$ and $Se_8^{2+}$ gives the sulfur–selenium–nitrogen dimeric cation $Se_4S_2N_4^{2+}$. The structure of this ion has been determined by an X-ray crystallographic study of its hexafluoroarsenate and hexafluoroantimonate salts.

## Experimental Section

Reaction vessels, the recording of IR spectra, and the preparation of $S_4N_4$ were the same as described previously.[1] Salts of $Se_4^{2+}$ and $Se_8^{2+}$ were prepared with use of established methods[6a] but with the following modifications.

**Preparations of $Se_8(AsF_6)_2$.** In a typical experiment 10.1 g (16 mmol of $Se_8$) of selenium powder (Alfa Inorganics) was used with the stoichiometric amount of $AsF_5$. The product was extracted near the freezing point of sulfur dioxide because of its increased solubility at low temperatures. The yield was 14.5 g (90% based on $Se_8$) of semicrystalline $Se_8(AsF_6)_2$.

**Preparation of $Se_4(AsF_6)_2$ and $Se_4(Sb_2F_{11})_2$.** In typical experiments 3.0 g (38 mmol) of powdered selenium was used with 57 mmol of $AsF_5$ and 70 mmol of $SbF_5$. In the latter case approximately twice as much solvent (100 mL) was used to avoid formation of the $SbF_5{\cdot}SO_2$ adduct.[6b] The products were used without further purification.

**Reaction of $S_4N_4$ with $Se_8(AsF_6)_2$ in $SO_2$.** $S_4N_4$ (0.152 g, 0.83 mmol) and $Se_8(AsF_6)_2$ (0.833 g, 0.83 mmol) were transferred to separate sides of a double-bulb reaction vessel. The vessel was then evacuated, and sulfur dioxide (ca. 15 mL) condensed at −196 °C onto the solid reactants. Both sides of the apparatus were flame sealed. The mixture was allowed to warm slowly to room temperature and stirred for 24 h. A dark green solution was obtained initially, which slowly changed to a reddish-brown solution containing a black precipitate, which was identified as a Se/S mixture by XRF and powder diffraction data. After filtration at room temperature and very slow removal of the solvent, blue-green crystals, identified by crystallographic examination as $Se_4S_2N_4(AsF_6)_2$, were obtained (0.25 g, 0.31 mmol; 37% yield based on $S_4N_4$). In some preparations an unidentified orange-red powder was also obtained. On exposure to air the blue-green crystals quickly decompose to a brown solid, which further decomposes to an orange material. Infrared spectrum of $Se_4S_2N_4(AsF_6)_2$: 1304 (w), 1260 (vw), 1223 (w), 1165 (m), 1153 (m), 1091

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(sh), 1008 (sh), 990 (s), 972 (sh), 948 (vs), 892 (sh), 805 (sh), 720 (vs), 678 (s, sh), 655 (s), 617 (s), 591 (sh), 565 (s), 532 (s), 485 (vw, sh), 473 (vw, sh), 445 (s), 382 (vs), 342 (s), 275 (m), 241 (w) $\mathrm{cm^{-1}}$.

**Reaction of $S_4N_4$ with $Se_8(AsF_6)_2$ in Methylene Chloride.** The same weights of reactants were used as described above. Methylene chloride (ca. 20 mL) was condensed at −196 °C onto the solid reactants and allowed to warm to room temperature. The bright yellow solution quickly turned to an orange-brown solution containing a black precipitate. The reaction mixture was then shaken for 12 h, and the solution turned crimson red. No further changes occurred on shaking for a further 60 h. After filtration and removal of solvent (ca. 1 week) both orange-yellow and light red crystals were obtained. The orange-yellow crystals were identified as unreacted $S_4N_4$ by comparison of a single-crystal Raman spectrum with that of an authentic sample. Crystallographic examination of the light red crystals identified them as the $S_4N_4$ adduct of arsenic pentafluoride, $S_4N_4{\cdot}AsF_5$.[7]

**Reaction of $S_4N_4$ with $Se_4(AsF_6)_2$.** $S_4N_4$ (0.250 g, 1.36 mmol) and $Se_4(AsF_6)_2$ (940 mg, 1.36 mmol) were transferred to one side of the reaction vessel. Sulfur dioxide (ca. 15 mL) was condensed onto the solid reactants at −196 °C, and both sides of the ampule were flame sealed. Upon warm-up to room temperature, a yellow solution was first obtained, which became deep red as it reacted with undissolved $S_4N_4$. At room temperature a dark green solution containing a brown solid was obtained, which after stirring for 90 min became reddish brown. The solution was filtered, and slow removal of the solvent (ca. 1 week) produced crystals of similar morphology and color to those isolated from the reaction of $S_4N_4$ with $Se_8^{2+}$ described above. Indeed, the final series of color changes noted for the $Se_4^{2+}$ reaction indicated that the reaction is essentially the same as with $Se_8^{2+}$ except that it is faster, which is consistent with the stronger oxidizing power of $Se_4^{2+}$. Crystallographic examination confirmed that the major crystalline product from this reaction was identical with that produced in the $Se_8^{2+}$ reaction, namely $(Se_4S_2N_4)(AsF_6)_2$.

**Reaction of $S_4N_4$ with $Se_4(Sb_2F_{11})_2$.** $S_4N_4$ (462 mg, 2.5 mmol) and $Se_4(Sb_2F_{11})_2$ (2.80 mg, 2.3 mmol) were transferred to the reaction vessel. Sulfur dioxide (ca. 20 mL) was then added to the evacuated vessel at −196 °C, and both sides were flame sealed. The reaction proceeded in a similar manner to that described above. Dark blue-green crystals, which were obtained after removal of the solvent, were identified as $Se_4S_2N_4(SbF_6)_2$ by crystallographic examination. Infrared spectrum of $Se_4S_2N_4(SbF_6)_2$: 1304 (w), 1260 (w), 1223 (w), 1155 (m, br), 1091 (vw), 1010 (s, sh), 995 (s), 972 (s), 949 (vs), 892 (sh), 847 (sh), 811 (sh), 721 (vs), 678 (s, sh), 655 (s, br), 637 (s, sh), 618 (s, sh), 565 (vs, br), 532 (vs, br), 447 (s), 389 (sh), 371 (s), 359 (s), 319 (sh), 272 (vs) $\mathrm{cm^{-1}}$.

**X-ray Crystallography.** Crystals of $(Se_4S_2N_4)(AsF_6)_2$ are dark blue-green prisms and plates. The crystal used in the final data collection was obtained by cleaving one of the larger crystals in the products from the $S_4N_4/Se_4^{2+}$ reaction into smaller fragments and shaping one of these crystals until it was approximately a sphere of radius 0.09 mm. Preliminary precession photographs indicated that the crystal was monoclinic, and the crystal data were obtained on a Syntex P2$_1$ diffractometer using graphite monochromatized Mo K$\bar{\alpha}$ radiation ($\lambda$ = 0.71069 Å).

With the identification of the compound as $(Se_4S_2N_4)(AsF_6)_2$ containing the selenium analogue of the bis(thiodithiazyl) cation, $S_6N_4^{2+}$, a preliminary study of the original crystal at lower temperatures using a Syntex LT1 attachment to the diffractometer was initiated. It was hoped that these studies would give further information on the inter-ring bonding interactions that would be useful in the interpretation of the ESR and variable-temperature magnetic susceptibility measurements of salts of the $S_6N_4^{2+}$ and $Se_4S_2N_4^{2+}$ cations.[8]

Similarly, blue-green crystals of $(Se_4S_2N_4)(SbF_6)_2$ were isolated from the reaction of $S_4N_4$ with $Se_4(Sb_2F_{11})_2$, and precession photographs indicated that they were isomorphous with the hexafluoroarsenate salt. Because of our interest in the anion–cation interactions in these salts a data set was collected on a crystal, which approximated to a sphere of radius 0.13 mm.

**Crystal Data.** At room temperature (22 °C), $(Se_4S_2N_4)(AsF_6)_2$ is monoclinic, space group $P2_1/n$, with $a$ = 10.373 (3) Å, $b$ = 16.089 (4) Å, $c$ = 9.799 (3) Å, $\beta$ = 98.095 (25)°, $V$ = 1619.1 (8) Å$^3$, $D_{\text{calcd}}$ = 3.36 g cm$^{-3}$ for $Z$ = 4 ($Se_4S_2N_4^{2+}$ dimers), fw = 813.8, and $F(000)$ = 1480; Mo K$\bar{\alpha}$ radiation ($\lambda$ = 0.71069 Å); $\mu$(Mo K$\bar{\alpha}$) = 144.8 cm$^{-1}$.

At room temperature (22 °C), the isomorphous hexafluoroantimonate salt $(Se_4S_2N_4)(SbF_6)_2$ is monoclinic, space group $P2_1/n$, with $a$ = 10.619 (1) Å, $b$ = 16.523 (2) Å, $c$ = 9.873 (2) Å, $\beta$ = 97.70 (1)°, $V$ = 1716.6 (4) Å$^3$, $D_{\text{calcd}}$ = 3.51 g cm$^{-3}$ for $Z$ = 4 ($Se_4S_2N_4^{2+}$ dimers), fw = 907.5, and $F(000)$ = 1624; Mo K$\bar{\alpha}$ radiation ($\lambda$ = 0.71069 Å); $\mu$(Mo K$\bar{\alpha}$) = 126.6 cm$^{-1}$.

At −30 °C, $(Se_4S_2N_4)(AsF_6)_2$ is monoclinic with $a$ = 10.358 (3), $b$ = 16.002 (5), $c$ = 9.748 (4) Å, $\beta$ = 98.16 (3)°, $V$ = 1599.4 (9) Å$^3$, and space group $P2_1/n$.

At approximately −75 °C, $(Se_4S_2N_4)(AsF_6)_2$ is monoclinic with $a$ = 10.347 (2) Å, $b$ = 15.970 (4) Å, $c$ = 9.725 (3) Å, $\beta$ = 98.14 (2)°, $V$ = 1590.8 (7) Å$^3$, and space group $P2_1/n$. However, at this temperature there is substantial broadening of the reflection profiles as shown by $2\theta/\omega$ scans on the diffractometer. Below this temperature some of the reflection profiles measured were definitely split into two components with significant losses in intensities. Overall the symmetry appeared to be triclinic with some twinning. This process was reversed on warming the crystal, and data sets were collected on the hexafluoroarsenate salt at both −30 °C and room temperature. At each of the temperatures above −95 °C, unit cell dimensions were obtained from least-squares refinements of $2\theta$, $\omega$, and $\chi$ for the same 15 high-angle reflections.

Intensity data on the two salts were collected in the $\theta$–$2\theta$ mode with use of the data collection options specified in Table I. For all three data sets, Lorentz, polarization, and spherical absorption corrections were applied to all reflections. Subsequent averaging of equivalent data and exclusion of systemically absent and zero intensity data resulted in the final numbers of nonzero data shown in Table I.

**Structure Solutions.** The structure of the hexafluoroarsenate salt was assumed, on the basis of volume considerations and by analogy with the $S_4N_4/S_8^{2+}$ system, to contain a mixed sulfur–selenium analogue to the $S_3N_2^+$ ($S_6N_4^{2+}$) cation. Normalized structure factors were therefore calculated with the assumption that the unit cell contained 16 $(Se_2SN_2)(AsF_6)$ molecules, and the solution was attempted with use of the direct-methods routines in the program SHELX.[9] The best $E$ map obtained was not immediately interpretable since, although many of the highest peaks in the map were within reasonable bonding distances, several additional peaks were spurious and formed bonds that were much too short. However, with the aid of a Patterson map, six heavy-atom positions (initially assumed to be selenium) were found, which gave reasonable $R$ factors on least-squares refinement. Subsequent Fourier maps gave the positions of all the lighter atoms and enabled the selenium and arsenic positions to be correctly assigned. For the two data sets collected on the hexafluoroarsenate salt, block-diagonal least-squares refinements (two blocks) with all atoms having anisotropic temperature factors converged to the final agreement indices in Table I. Similarly for the room-temperature data set collected on the isomorphous hexafluoroantimonate salt, the final coordinates from the above refinements were used with the scattering curve for antimony replacing that for arsenic. Block-diagonal least-squares refinement of this model with all atoms having anisotropic temperature factors converged to the final agreement indices in Table I. For each refinement comparisons of the average $w(\Delta F^2)$ as a function of $\sin\theta$ and $F_o$ showed no systematic trends, which confirms the suitability of the weighting schemes used.

For all refinements, neutral-atom scattering factors in the analytical form were taken from ref 11. All calculations were performed on a CDC 6400 computer using a series of programs in the XRAY 76 system,[12] the program SHELX,[9] and some local programs. The final atomic positional parameters from the refinements of both salts are given in Table II, and the corresponding parameters of the $AsF_6^-$ salt at room temperature along with the temperature factors for all three refinements have been deposited as supplementary material (Tables A and B).[13] Interatomic distances and angles calculated with use of the coordinates in Table II are included in Table III and IV.

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**Table I.** Details of Data Collections and Structure Refinements

| | $(Se_4S_2N_4)(AsF_6)_2$ | | $(Se_4S_2N_4)(SbF_6)_2$ |
|---|---|---|---|
| | room temp (22 °C) | low temp (−30 °C) | room temp (22 °C) |
| reflctns used in unit cell determn (no. of reflctns/2$\theta$ range) | 15/(28 < 2$\theta$ < 32°) | | |
| radiation | Mo K$\bar{\alpha}$ (graphite monochromated) ($\lambda$ = 0.710 69 Å) | | |
| max 2$\theta$ scan type, deg | 50, $\theta$–2$\theta$ | 50, $\theta$–2$\theta$ | 55, $\theta$–2$\theta$ |
| scan speeds, deg $min^{-1}$ (dependent on intensity of a 2-s prescan) | 3.5[a] | 3.5[a] | 2.5–29.3 |
| scan range | ($K\alpha_1$ − 1.0°)–($K\alpha_2$ + 1.0°) | ($K\alpha_1$ − 1.0°)–($K\alpha_2$ + 1.0°) | ($K\alpha_1$ − 0.8°)–($K\alpha_2$ + 0.8°) |
| bkgd measmts | stationary counter–stationary crystal equal to one-fourth scan time at each end of the scan | | |
| std reflctns (no./interval) | 2/48[b] | 2/68[b] | 3/67[b] |
| quadrants collected | ($h,k,\pm l$) | | |
| no. of data collected (including std) | 3284[c] | 3212[d] | 4501[e] |
| abs cor | spherical, $\mu r$ = 1.3 | spherical, $\mu r$ = 1.3 | spherical, $\mu r$ = 1.65 |
| no. of indep data[f] | 2506[g] | 2580[h] | 3583[i] |
| no. of data $F > 6.0\sigma(F)$ | 1504 | 1666 | 2517 |
| no. of data $F > 2.0\sigma(F)$ | 2129 | 2248 | 3287 |
| $R_1$ } 6$\sigma$ data[10] | 0.049 | 0.045 | 0.057 |
| $R_2$ | 0.052 | 0.050 | 0.066 |
| $R_1$ } 2$\sigma$ data[10] | 0.079 | 0.069 | 0.073 |
| $R_2$ | 0.072 | 0.066 | 0.079 |
| max shift/error, final cycle | 0.18 | 0.15 | 0.16 |
| wts | $2(\sigma(F))^2 + 0.0012F^2$ | $w = xy$[j] | $w = xy$[k] |
| final diff Fourier | | | |
| max peak, e $Å^{-3}$ | +1.20 | +1.04 | +3.50 } near Sb |
| min trough, e $Å^{-3}$ | −1.20 | −1.12 | −3.50 |

[a] Intense reflections were collected at 29.3° $min^{-1}$. [b] No decline in the intensities of the standards was observed during data collection. [c] In addition 254 equivalent data in the quadrants ($-h,k,\pm l$) were collected. [d] In addition all 1020 equivalent data in the quadrants ($-h,k,\pm l$) with $2\theta \leqslant 35°$ were collected. [e] In addition 211 equivalent data with negative $h$ and $k$ indices were collected. [f] Systematically absent reflections and reflections with $F_o$ = 0.0 excluded. [g] $R_{merge}$ = 0.0246 for 335 equivalent reflections. [h] $R_{merge}$ = 0.0312 for 496 equivalent reflections. [i] $R_{merge}$ = 0.0320 for 368 equivalent reflections. [j] $x = F/55$ if $F < 55$, or $x = 90/F$ if $F > 90$, otherwise $x = 1.0$; $y = (\sin\theta)/0.26$ if $\sin\theta < 0.26$, or $y = 0.295/\sin\theta$ if $\sin\theta > 0.295$, otherwise $y = 1.0$. [k] $x = F/33$ if $F < 33$, or $x = 45/F$ if $F > 45$, otherwise $x = 1.0$; $y = (\sin\theta)/0.28$ if $\sin\theta < 0.28$, or $y = 0.36/\sin\theta > 0.36$, otherwise $y = 1.0$.

**Table II.** Final Atomic Positional ($\times 10^4$) Parameters with Standard Deviations in Parentheses[a]

| atom | $x$ | $y$ | $z$ | atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Se(1) | 371 (1) | 1917 (1) | 3751 (2) | F(11) | 3152 (11) | 1730 (10) | 4072 (10) |
| | 330 (1) | 1929 (1) | 3733 (1) | | 3081 (13) | 1683 (12) | 4202 (13) |
| Se(2) | −344 (1) | 2013 (1) | 1349 (1) | F(12) | 2384 (7) | 2178 (5) | 1781 (10) |
| | −369 (1) | 2031 (1) | 1358 (1) | | 2290 (8) | 2159 (6) | 1780 (12) |
| Se(3) | 304 (1) | 3912 (1) | 1433 (1) | F(13) | 4143 (13) | 1394 (12) | 977 (10) |
| | 346 (1) | 3880 (1) | 1461 (1) | | 4215 (16) | 1344 (16) | 889 (14) |
| Se(4) | 1039 (1) | 3843 (1) | 3819 (1) | F(14) | 4900 (9) | 929 (5) | 3322 (9) |
| | 1051 (1) | 3792 (1) | 3823 (1) | | 4966 (10) | 858 (7) | 3383 (11) |
| S(1) | −2412 (3) | 1878 (2) | 3027 (4) | F(15) | 2621 (10) | 731 (6) | 2294 (14) |
| | −2386 (3) | 1923 (2) | 3049 (4) | | 2589 (13) | 627 (6) | 2259 (16) |
| S(2) | 3089 (3) | 3986 (2) | 2131 (4) | F(16) | 4637 (10) | 2383 (7) | 2767 (20) |
| | 3061 (3) | 3927 (2) | 2141 (4) | | 4653 (13) | 2403 (8) | 2869 (26) |
| N(1) | −1209 (11) | 1836 (7) | 4169 (11) | F(21) | −1720 (8) | 3687 (5) | 2860 (8) |
| | −1217 (12) | 1874 (8) | 4173 (12) | | −1686 (9) | 3702 (6) | 2838 (10) |
| N(2) | −1999 (11) | 1960 (7) | 1545 (11) | F(22) | −2416 (10) | 4829 (6) | 1333 (11) |
| | −2002 (11) | 2002 (7) | 1592 (11) | | −2466 (13) | 4900 (8) | 1205 (14) |
| N(3) | 1889 (11) | 3990 (7) | 1005 (11) | F(23) | −4331 (9) | 5076 (6) | 2463 (12) |
| | 1902 (12) | 3946 (7) | 1012 (12) | | −4480 (13) | 5120 (9) | 2484 (18) |
| N(4) | 2697 (11) | 3914 (7) | 3635 (11) | F(24) | −3623 (10) | 3910 (7) | 4017 (9) |
| | 2676 (12) | 3849 (8) | 3601 (12) | | −3675 (12) | 3854 (9) | 4109 (11) |
| M(1)[b] | 3662 (1) | 1541 (1) | 2511 (1) | F(25) | −3903 (9) | 3692 (6) | 1563 (9) |
| | 3660 (1) | 1494 (1) | 2513 (1) | | −3972 (10) | 3654 (7) | 1476 (10) |
| M(2)[b] | −3046 (1) | 4386 (1) | 2674 (1) | F(26) | −2146 (10) | 5052 (6) | 3792 (12) |
| | −3095 (1) | 4406 (1) | 2672 (1) | | −2142 (13) | 5132 (8) | 3828 (15) |

[a] The first line in each entry gives the final coordinates for the low-temperature refinement of the structure $(Se_4S_2N_4)(AsF_6)_2$; the second corresponds to the final parameters for the room-temperature refinement of the structure of $(Se_4S_2N_4)(SbF_6)_2$. [b] M = As, Sb.

Tabulations of the observed and calculated structure factors for both structures have been included in the supplementary material (Tables C–E).

## Discussion of Crystal Structures

The structure determinations show that the crystals obtained from the reactions of $S_4N_4$ with the cations $Se_4^{2+}$ and $Se_8^{2+}$ are the same and contain a selenium analogue of the dimeric thiodithiazyl cation, that is, $Se_4S_2N_4^{2+}$, as hexafluoroarsenate or hexafluoroantimonate salts. The $Se_4S_2N_4^{2+}$ cation is formulated as the dimeric ion on the basis of rather short contacts between the selenium atoms in two adjacent thiodiselenazyl rings (Figure 1). In contrast to the $S_6N_4^{2+}$ cation[1] the $Se_4S_2N_4^{2+}$ cation in the present compounds has slightly asymmetric interactions between the two thiodiselenazyl rings and does not have crystallographic inversion symmetry.

The diselenide bonds in the two rings of the $Se_4S_2N_4^{2+}$ cation do not show the appreciable lengthening over accepted single-bond lengths (e.g., 2.335 Å in $Se_8$[13]) that have been observed for the disulfide bonds in the analogous $S_6N_4^{2+}$ and

Table III. Bond Distances (Å) in the Compounds $(Se_4S_2N_4)(MF_6)_2$ (M = As, Sb)[a]

| | M = As | M = Sb | | M = As | M = Sb |
|---|---|---|---|---|---|
| Se(1)-Se(2) | 2.358 (2) | 2.369 (2) | S(1)-N(1) | 1.550 (11) | 1.553 (12) |
| Se(3)-Se(4) | 2.345 (2) | 2.356 (2) | S(1)-N(2) | 1.570 (12) | 1.551 (13) |
| Se(1)-N(1) | 1.746 (12) | 1.756 (13) | S(2)-N(3) | 1.537 (11) | 1.546 (12) |
| Se(2)-N(2) | 1.753 (12) | 1.781 (12) | S(2)-N(4) | 1.580 (12) | 1.556 (13) |
| Se(3)-N(3) | 1.755 (12) | 1.770 (13) | Se(1)···Se(4) | 3.159 (2) | 3.171 (2) |
| Se(4)-N(4) | 1.756 (12) | 1.771 (13) | Se(2)···Se(3) | 3.111 (2) | 3.147 (2) |

| | M = As | M = Sb |
|---|---|---|
| M(1)-F(11) | 1.708 (11) [1.761] | 1.880 (14) [1.941] |
| -F(12) | 1.742 (8) [1.758] | 1.889 (9) [1.910] |
| -F(13) | 1.658 (12) [1.734] | 1.798 (16) [1.905] |
| -F(14) | 1.715 (9) [1.731] | 1.857 (11) [1.883] |
| -F(15) | 1.680 (10) [1.721] | 1.826 (12) [1.871] |
| -F(16) | 1.681 (11) [1.760] | 1.841 (13) [1.931] |
| M(2)-F(21) | 1.761 (8) [1.768] | 1.885 (9) [1.899] |
| -F(22) | 1.697 (11) [1.726] | 1.863 (14) [1.903] |
| -F(23) | 1.719 (9) [1.748] | 1.875 (14) [1.928] |
| -F(24) | 1.695 (10) [1.724] | 1.858 (13) [1.895] |
| -F(25) | 1.709 (9) [1.727] | 1.874 (11) [1.896] |
| -F(26) | 1.704 (10) [1.737] | 1.859 (13) [1.903] |

[a] Values in brackets are thermally corrected (riding model) bond lengths in the $MF_6^-$ anions.

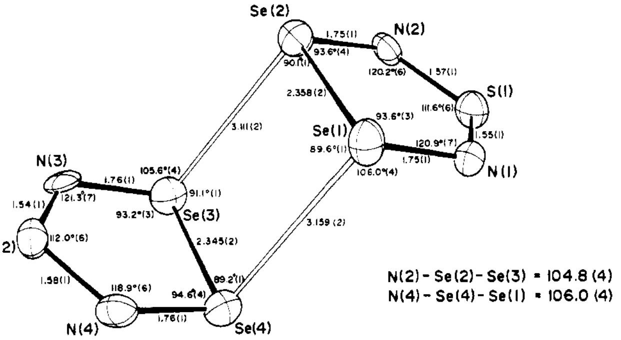

**Figure 1.** ORTEP view of the dimeric cation in the compound $(Se_4S_2N_4)(AsF_6)_2$ at −30 °C showing some principal bond lengths (Å) and bond angles (deg).

$S_3N_2^{+\cdot}$ cations.[1] The lengths of the diselenide bonds are generally comparable to the Se–Se bond lengths in other compounds containing diselenide bonds or chains of selenium atoms,[14] although, in compounds containing several directly bonded selenium atoms, interactions between adjacent bonds result in a significant alternation in these bond lengths. However, in the majority of these compounds there are significant intermolecular (ionic) contacts, and their influence on the Se–Se bond lengths is at present not well understood.

The average lengths of the four Se–N bonds in the $Se_4S_2N_4^{2+}$ cations at 1.75 (1) Å for the $AsF_6^-$ salt and 1.77 (1) Å for the $SbF_6^-$ salt are comparable to the Se–N distance of 1.77 (1) Å observed in the anion $[N_3Se_3O_6^{3-}]$[15] and distances of 1.77–1.80 (3) Å in $Se_4N_4$.[16] The bonds are, however, significantly shorter than the sum of the covalent radii of 1.87 Å[17] but nonetheless longer than the quoted selenium–nitrogen

Table IV. Bond Angles (Deg) in the Compounds $(Se_4S_2N_4)(MF_6)_2$ (M = As, Sb)

| | M = As | M = Sb |
|---|---|---|
| N(1)-Se(1)-Se(2) | 93.6 (3) | 94.0 (4) |
| N(2)-Se(2)-Se(1) | 93.6 (4) | 92.9 (4) |
| N(1)-S(1)-N(2) | 111.6 (6) | 112.5 (7) |
| S(1)-N(1)-Se(1) | 120.9 (7) | 120.3 (7) |
| S(1)-N(2)-Se(2) | 120.2 (6) | 120.3 (7) |
| N(3)-Se(3)-Se(4) | 93.2 (3) | 93.9 (4) |
| N(4)-Se(4)-Se(3) | 94.6 (4) | 93.5 (4) |
| N(3)-S(2)-N(4) | 112.0 (6) | 112.7 (7) |
| S(2)-N(3)-Se(3) | 121.3 (7) | 119.9 (7) |
| S(2)-N(4)-Se(4) | 118.9 (6) | 120.0 (7) |
| F(11)-M(1)-F(12) | 86.9 (5) | 85.3 (6) |
| -F(13) | 177.8 (8) | 178.6 (11) |
| -F(14) | 89.8 (5) | 89.8 (6) |
| -F(15) | 88.5 (7) | 88.8 (8) |
| -F(16) | 88.9 (8) | 86.7 (9) |
| F(12)-M(1)-F(13) | 91.3 (6) | 93.8 (7) |
| -F(14) | 176.7 (5) | 175.0 (5) |
| -F(15) | 87.9 (4) | 88.3 (5) |
| -F(16) | 89.8 (5) | 89.5 (5) |
| F(13)-M(1)-F(14) | 92.0 (6) | 91.1 (7) |
| -F(15) | 92.7 (7) | 92.3 (9) |
| -F(16) | 89.8 (9) | 92.2 (11) |
| F(14)-M(1)-F(15) | 92.4 (5) | 91.8 (5) |
| -F(16) | 89.7 (5) | 90.0 (6) |
| F(15)-M(1)-F(16) | 176.6 (6) | 175.1 (8) |
| F(21)-M(2)-F(22) | 88.0 (4) | 88.5 (5) |
| -F(23) | 178.8 (5) | 178.8 (6) |
| -F(24) | 89.5 (5) | 88.4 (5) |
| -F(25) | 88.8 (4) | 88.1 (4) |
| -F(26) | 89.0 (4) | 89.1 (5) |
| F(22)-M(2)-F(23) | 90.9 (5) | 90.3 (7) |
| -F(24) | 177.4 (5) | 176.5 (6) |
| -F(25) | 90.3 (5) | 90.0 (5) |
| -F(26) | 89.8 (5) | 88.4 (6) |
| F(23)-M(2)-F(24) | 91.7 (5) | 92.8 (7) |
| -F(25) | 91.1 (5) | 92.1 (6) |
| -F(26) | 91.1 (5) | 90.6 (6) |
| F(24)-M(2)-F(25) | 89.4 (5) | 88.2 (5) |
| -F(26) | 90.4 (5) | 93.2 (6) |
| F(25)-M(2)-F(26) | 177.9 (5) | 176.8 (6) |
| Se(2)-Se(1)-Se(4) | 89.64 (6) | 90.08 (6) |
| N(1)-Se(1)-Se(4) | 106.0 (4) | 105.9 (4) |
| Se(1)-Se(2)-Se(3) | 90.11 (6) | 89.68 (6) |
| N(2)-Se(2)-Se(3) | 104.8 (4) | 104.9 (4) |
| Se(4)-Se(3)-Se(2) | 91.08 (6) | 90.89 (6) |
| N(3)-Se(3)-Se(2) | 105.6 (4) | 106.3 (4) |
| Se(3)-Se(4)-Se(1) | 89.16 (6) | 89.35 (6) |
| N(4)-Se(4)-Se(1) | 106.0 (4) | 106.4 (4) |

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double-bond length of 1.64 Å[18] and the Se–N bond of 1.67 (5) Å observed in the compound $\alpha$-$Ag_3NSeO_3$.[19] Some other reported Se–N bond lengths are 1.807 (5) and 1.814 (4) Å in the compound 3,4-diphenyl-1,2,5-selenadiazole,[20] 1.832 (6)–1.845 (3) Å in the compounds $R_2Se_x$ ($R = NC_5H_{10}$, $x = 4$; $R = NC_4H_8O$, $x = 2$, 3, and 4),[14e] 1.805 (3) Å in the phenyl selenoimine $C_{14}H_{13}NOSe$,[21a] 1.83 (4) Å in 3,4-benzo-1,2,5-selenadiazole[18] and 2.19 (2) and 2.20 (2) Å in the 1:2 adduct of $SeOCl_2$ with pyridine.[18] From these values it is apparent that the Se–N bonds in the thiodiselenazyl rings have considerable double-bond character although due to the lack of comparable data on similar ring systems it is not possible to estimate the bond order.

The average S–N bond length in the two thiodiselenazyl rings of the $Se_4S_2N_4^{2+}$ cation is 1.56 (1) Å for the $AsF_6^-$ salt and 1.55 (1) Å for the $SbF_6^-$ salt, and the average N–S–N and S–N–Se angles are respectively 111.8 (6)° and 120.3 (7)° for the $AsF_6^-$ salt and 112.7 (7)° and 120.1 (7)° for the $SbF_6^-$ salt. These S–N distances are comparable to the S–N bond lengths to S(3) in the thiodithiazyl rings of the $S_3N_2^+$ and $S_6N_4^{2+}$ cations,[1] and the S–N–Se angles in the present selenium cations are the same (120°) as the S–N–S angles in the sulfur analogues. However, the average N–Se–Se angles in the thiodiselenazyl rings of 93.8 (4)° for the $AsF_6^-$ salt and 93.6 (4)° for the $SbF_6^-$ salt are slightly smaller than the N–S–S angles (96–97°) in the thiodithiazyl rings. Overall the most significant differences between the thiodithiazyl and thiodiselenazyl rings are the lengthening of the disulfide bond compared to the diselenide bond in $Se_4S_2N_4^{2+}$ and possibly a shortening of the Se–N bonds adjacent to the diselenide bond over the corresponding S–N bonds in the thiodithiazyl cations.

The bonding in the $Se_4S_2N_4^{2+}$ cation may be discussed with use of either the MO or valence-bond schemes described previously for $S_6N_4^{2+}$.[1] Valence structures in which the positive charge is on selenium or structures in which the $\pi$-electron density is concentrated more in the Se–Se and Se–N bonds would presumably be more favored than in the sulfur analogues.

One of the most important findings in the present study is the close similarity in the structures of the bis(thiodithiazyl) and bis(thiodiselenazyl) cations, which lends weight to the argument that the inter-ring interactions must be considered as significant, although weak, bonding interactions. In the cation of the $AsF_6^-$ salt the weak Se···Se bonds between the two rings have lengths of 3.121 (3) and 3.180 (3) Å at room temperature, or 0.88 and 0.82 Å, respectively, less than twice the van der Waals radius for selenium (4.0 Å[17]). At –30 °C the asymmetry in the interactions between the rings is slightly reduced and the Se···Se bonds have lengths of 3.121 (2) and 3.162 (2) Å. The Se–Se bond lengths in each ring of the dimer do not change in length between 22 and –30 °C although it is noteworthy that the significant difference between the Se–Se bond lengths in each ring of the dimer exists at both temperatures (e.g., 2.345 (2) and 2.360 (2) Å at –30 °C). The asymmetry in the weak interactions between the diselenide bonds in the dimers can also be seen in the Se–Se–Se angles between the two rings, which are slightly distorted from the ideal 90° angles.

In the hexafluoroantimonate salt the inter-ring Se···Se distances are again different, 3.147 (2) and 3.171 (2) Å, and the lengths of the two diselenide bonds in the thiodiselenazyl rings are 2.356 (2) and 2.369 (2) Å. It is notable that the inter-ring contacts are significantly longer by ca. 0.01–0.02 Å than those in the hexafluoroarsenate salt.

From the close similarity in the structures of the $S_6N_4^{2+}$ and $Se_4S_2N_4^{2+}$ cations it appears that the interactions between the rings are very similar, and both can be regarded as three-electron bonds.[1] Although its structure has not been determined, the cation $[Se(C_2F_5)]_2^+$ is also presumed to dimerize via pairing of the single $\pi^*$ electrons in two moieties in a side-on or end-on configuration and a similar bonding description to that for the weak bonds in the present cation might apply.[22] Furthermore, in the comparison of the $Se_4S_2N_4^{2+}$ cation to its sulfur analogues it may be noted that the weak Se···Se interactions appear to be slightly stronger than the S···S interactions between the thiodithiazyl rings of the $S_6N_4^{2+}$ cation, which are only ca. 0.7 Å less than twice the van der Waals radius of sulfur (3.7 Å).[17] A similar trend is also observed in the transannular interactions in the $Se_8^{2+}$ and $S_8^{2+}$ cations[23,24] and can also be seen in $Se_4N_4$ and $S_4N_4$,[16,25] since the Se···Se and S···S distances in these two cages are 2.748 (9) and 2.595 (1) Å, respectively, or 1.25 and 1.11 Å less than the van der Waals contact distances.

Some other short Se···Se interactions of comparable length to those in the $Se_4S_2N_4^{2+}$ cation have been observed in compounds such as $KSe(SeCN)_3\cdot{}^1/_2H_2O$ where there are four Se–Se bonds somewhat longer than single bonds (2.395 (2)–2.419 (2) Å) and four secondary Se···Se "bonds" (3.089 (2)–3.255 (2) Å) trans to these primary bonds, which result in dimeric units. These dimeric units may also be linked together by some additional weaker contacts >3.3 Å.[14d] Even in the crystal structures of the various forms of elemental selenium there are several intermolecular contacts between rings or chains of selenium atoms, which are significantly less than van der Waals distances. Typically, however, these contacts are 3.4 Å or more in length and are significantly longer than the inter-ring distances in the present cation. Similarly in selenium bis(diethyldiselenophosphinate) and dimorpholinotriselane the shortest intermolecular contacts are 3.679 (4) and 3.404 (2) Å, respectively.[14e,18] It has been suggested elsewhere that the shortest intramolecular contacts in the cations $Se_{10}^{2+}$ (3.30–3.49 Å) and $Se_8^{2+}$ (≥2.84 Å) are weak bonds resulting from population of the antibonding orbitals of the corresponding bonds in the parent clusters from which these structures are derived.[26,27]

Several anion–cation interactions are shorter than the sum of the appropriate van der Waals radii (Se + F = 3.35 Å, S + F = 3.20 Å). They are given in Table V, and some related angles are included in the supplementary material (Table G).

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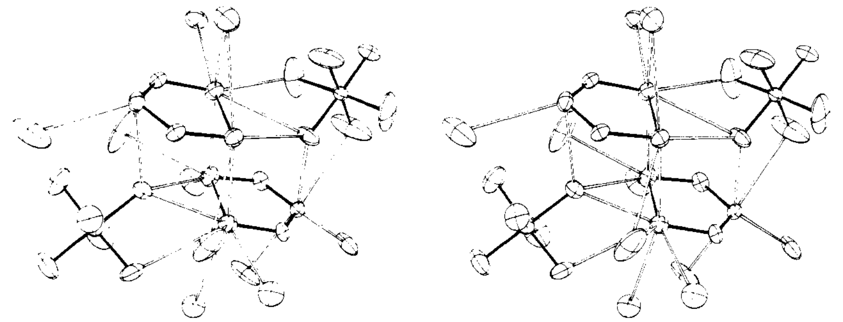

**Figure 2.** Stereoscopic view of the compound $(Se_4S_2N_4)(AsF_6)_2$ including all the anion–cation and cation–cation interactions (unfilled lines) less than the van der Waals distances.

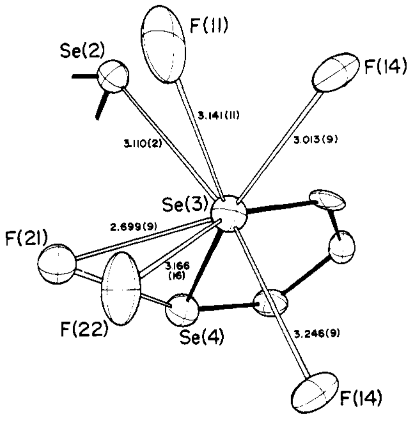

**Figure 3.** Environment of Se(3).

A view of the cation in the $AsF_6^-$ salt with these interactions included is shown in Figure 2. Although there are some slight variations of up to ±0.05 Å in the analogous Se···F and S···F contacts in the two salts, the geometries of the contacts remain essentially the same. However, in the hexafluoroantimonate salt, these contacts appear to be slightly longer and hence weaker than those in the hexafluoroarsenate salt. In the following discussion distances for the hexafluoroarsenate salt will be quoted. A feature of the anion–cation interactions is that the environments of the two hexafluoroarsenate and hexafluoroantimonate anions are completely different. As a consequence the dimeric $Se_4S_2N_4^{2+}$ cations are not centrosymmetric (unlike all examples of the $S_6N_4^{2+}$ cation) and the planes of the two thiodiselenazyl rings in each cation make a small but nonetheless significant angle with respect to each other (1.56° in the $AsF_6^-$ salt and 1.43° in the $SbF_6^-$ salt (supplementary material, Table F)).

In the $AsF_6^-$ salt at −30 °C the environment of anion 2 resembles that of the anions in $(S_6N_4)(AsF_6)_2$[1] with the fluorine atom F(21) asymmetrically bridging the diselenide bond Se(3)–Se(4) of ring 2 [Se(3)···F(2) = 2.699 (9) Å, Se(4)···F(21) = 2.889 (8) Å] and also forming a close sulfur-fluorine contact [2.991 (9) Å] with S(1) in ring 1. These Se···F and S···F contacts are 0.65, 0.46, and 0.21 Å less than van der Waals distances. Due to the asymmetry in the bridging interactions this anion is rotated slightly and a further contact Se(3)···F(22) of 3.166 (10) Å is now less than the sum of the van der Waals radii. An analogous contact to Se(4) involves another anion. The two fluorine atoms F(21) and F(22) are −0.15 and 1.62 Å out of the plane of ring 2.

The environment of the second $AsF_6^-$ anion in the structure can be obtained by exaggerating the rotation of anion 2 above until there are two fluorine atoms virtually in the plane of the thiodiselenazyl ring. Thus this anion can be considered to be almost bidentate with contact distances Se(1)···F(11), Se(1)···F(12), Se(2)···F(11), and Se(2)···F(12) of 2.868 (11), 3.057 (10), 3.228 (13), and 2.810 (8) Å, respectively. However, the fluorine atom F(11) is still significantly out of the plane of the thiodiselenazyl ring (by −0.38 Å) compared with F(12) (by 0.18 Å) and does not form a close contact with S(2). Nevertheless the atom F(12) is still able to interact with S(2) [S(2)···F(12) = 2.992 (9) Å], and further the rotation of the anion makes the contact S(2)···F(16) [3.042 (11) Å] also less than van der Waals distances. The lengths of these S···F contacts are marginally longer than the analogous contacts to the atom S(3) in the $S_6N_4^{2+}$ dimers. Other S···F contacts shorter than or close to the van der Waals limits are included in Table V.

Apart from the different environments of the $MF_6^-$ anions another slight difference in the geometries of the contacts to the $Se_4S_2N_4^{2+}$ and $S_6N_4^{2+}$ cations is in the number of additional Se···F contacts to each Se atom in the $Se_4S_2N_4^{2+}$ cation. With the exception of Se(3), each Se atom forms three Se···F contacts, which may be considered to be reasonably close to the extensions of the Se–Se, Se–N, and inter-ring Se–Se bonds

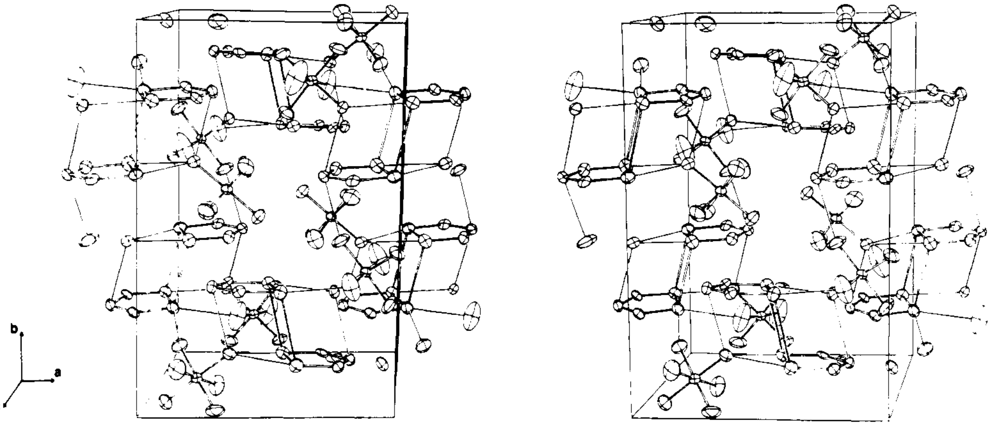

**Figure 4.** Stereoscopic view of the crystal packing of $(Se_4S_2N_4)(AsF_6)_2$ at −30 °C. Some of the shorter interionic contacts are indicated.

**Table V.** Geometry of the Anion–Cation and Cation–Cation Interactions: Contact Distances (Å)[a]

| | | | | | |
|---|---|---|---|---|---|
| Se(1)···Se(4) | 3.159 (2) | 3.171 (2) | Se(3)···S(2) | 2.871 (4) | 2.873 (4) |
| ···S(1) | 2.870 (4) | 2.872 (4) | ···F(21) | 2.699 (9) | 2.715 (10) |
| ···F(11) | 2.868 (11) | 2.924 (14) | ···F(22) | 3.166 (10) | 3.407 (14) |
| ···F(12) | 3.057 (10) | 3.045 (11) | ···F(14)$^{\mathrm{V}}$ | 3.246 (9) | 3.290 (11) |
| ···F(23)$^{\mathrm{I}}$ | 3.296 (10) | 3.303 (15) | ···F(11)$^{\mathrm{III}}$ | 3.141 (11) | 3.191 (14) |
| ···F(25)$^{\mathrm{II}}$ | 2.905 (9) | 2.876 (10) | ···F(14)$^{\mathrm{III}}$ | 3.013 (9) | 3.043 (11) |
| Se(2)···Se(3) | 3.111 (2) | 3.147 (2) | Se(4)···S(2) | 2.874 (4) | 2.884 (4) |
| ···S(1) | 2.881 (4) | 2.891 (4) | ···F(21) | 2.889 (8) | 2.942 (9) |
| ···F(12) | 2.810 (8) | 2.806 (9) | ···F(26)$^{\mathrm{VI}}$ | 3.018 (11) | 3.027 (13) |
| ···F(23)$^{\mathrm{I}}$ | 3.342 (10) | 3.370 (15) | ···F(13)$^{\mathrm{VII}}$ | 3.098 (13) | 3.014 (17) |
| ···F(24)$^{\mathrm{I}}$ | ··· | [3.374 (13)] | | | |
| ···F(11)$^{\mathrm{III}}$ | 3.228 (13) | 3.291 (16) | | | |
| S(1)···F(21) | 2.991 (9) | 3.046 (10) | S(2)···F(12) | 2.992 (9) | 3.041 (10) |
| ···F(14)$^{\mathrm{IV}}$ | 3.220 (10) | ··· | ···F(16) | 3.042 (11) | 3.064 (14) |
| ···F(16)$^{\mathrm{IV}}$ | 3.137 (11) | 3.226 (14) | ···F(23)$^{\mathrm{VIII}}$ | 3.170 (10) | 3.253 (14) |
| | | | ···F(25)$^{\mathrm{VIII}}$ | 3.275 (10) | ··· |
| | | | ···F(15)$^{\mathrm{V}}$ | 2.961 (10) | 2.971 (11) |

[a] Roman numerals as superscripts refer to atoms related to the position $x, y, z$ by the following transformations: (I) $-{}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$; (II) ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (III) $-{}^1/_2 + x, {}^1/_2 - y, -{}^1/_2 + z$; (IV) $-1 + x, y, z$; (V) ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; (VI) $-x, 1 - y, 1 - z$; (VII) $-{}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (VIII) $1 + x, y, z$. The first column in each entry refers to the low-temperature refinement of the structure of $(Se_4S_2N_4)(AsF_6)_2$, and the second column refers to the equivalent data from the room-temperature structure of $(Se_4S_2N_4)(SbF_6)_2$.

at each Se, although the deviation in the X–Se···F angles from 180° are more marked than the corresponding contacts in the sulfur cations. There are also two additional contacts to Se(3) from atoms F(11) and F(22). A view of the overall geometry of Se(3) is given in Figure 3 where it may be seen that the four longest contacts appear to surround a space in the coordination shell of the selenium, which can reasonably be attributed to a lone pair of electrons on Se. Furthermore this assumed lone-pair direction is approximately tetrahedrally related to the Se–Se and Se–N primary bonds and the 2c–3e inter-ring Se–Se bond. The deviations of many of the Se···F contacts at the other Se atoms in the cation from the projections of the bonds with which they are presumed to interact may then also be related to the presence of a lone pair on each of these other atoms. The view that these interactions are formed in the directions of three of the four remaining corners of a cube surrounding the selenium, which was proposed[1] for the interactions in the $S_6N_4^{2+}$ ion, is valid in the present case. However the larger size of Se and the increased stereoactivity of the lone pair on each Se (compared with S) with respect to the primary bonds means that the lone pair is closer to the nucleus and has a reduced stereoactivity with respect to the secondary bonds. This presumably allows two further interactions to Se(3) (from F(11) and F(22)) to become significant.

In general these interactions may thus be described as forming in directions that best avoid the bonding pairs and any lone pairs on the central atom and involve some charge transfer from the fluorine atoms into the $\sigma^*$ orbitals of the bonds approximately opposite. According to the classification proposed by Dunitz et al.[28] for weak interactions with sulfur (and which may also presumably be applied to selenium) interactions that are collinear with the Se–N and Se–Se bonds of the five-membered ring would be regarded as type I (nucleophilic) interactions in agreement with our own description. However the interaction that is roughly collinear with the long Se–Se bond and in addition the S···F(11) or S···F(21) interactions, which are approximately perpendicular to the plane of the $Se_2SN_2$ rings, would be regarded as type II or electrophilic interactions. This implies an interaction between filled Se $3p_\pi$ (or S $2p_\pi$) orbitals and a vacant orbital on fluorine. As this is a highly unlikely type of interaction it would appear that the Dunitz description of type II weak interactions is not applicable in the present case. Although the remaining one or two interactions on some of the Se atoms cannot be related directly to any of the $\sigma$ bonds in the cation, it is worth emphasizing that, as is the case in many other compounds of the nonmetals with lone pairs, the weak interactions tend to form in the general direction of an unshared electron pair on the Se atoms but nevertheless avoid the direction of maximum electron density.

In several other selenium compounds similar charge-transfer interactions to those observed here are also of some importance in determining the packing in these compounds.[21,23,26,29] Thus, in examples of the $Se_4^{2+}$ cation (and all other planar dipositive chalcogen cations) fluorine or oxygen atoms are found to bridge the edges of the square-planar cation or interact with the selenium atoms along the extensions of the diagonals of the square.[29] In these structures the Se···O interactions are of lengths 2.69–2.93 Å (bridging) and 3.11 and 3.17 Å (along the diagonals) in $Se_4(HS_2O_7)_2$ and the Se···F interactions are 2.66–3.20 Å in $Se_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$. In both cases it is presumed that the charge-transfer interactions involve transfer of electron density to the two lowest unoccupied molecular orbitals of the $Se_4^{2+}$ cation, which are both antibonding.[29] Similarly in $Se_8(AlCl_4)_2$ there are several Se···Cl interactions that are approximately collinear to the primary bonds or are approximately trans to the assumed positions of the lone pairs on each Se atom[23] (cf. discussion of contacts above), and in $Se_{10}^{2+}$, the Se···F contacts vary from 2.86 Å up to the van der Waals limit.[26]

Overall, the role of the contacts to the $Se_4S_2N_4^{2+}$ cation, as in $S_6N_4^{2+}$ appears to be to maintain and stabilize the charge distribution in the cation via predominantly nucleophilic contacts. The most significant effect of the anion–cation interactions to each ring appears to be in the difference between the Se–Se bond lengths in the two rings of the cation and the asymmetry in the weaker inter-ring bonds. As with the sulfur cations $S_3N_2^+$ and $S_6N_4^{2+}$ the effect of the cation–cation and anion–cation charge-transfer interactions on the bonding in the thiodiselenazyl rings is difficult to estimate quantitatively.[30] As a result of the charge transfer involving the anions in the $AsF_6^-$ structure there appears to be some lengthening of some of the As–F bonds. In particular, the fluorine atoms, F(11) and F(21), involved in the strongest

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(28) Rosenfield, R. E.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860.

(29) Cardinal, G.; Gillespie, R. J.; Sawyer, J. F.; Vekris, J. E. *J. Chem. Soc., Dalton Trans.*, in press.

(30) Note, however, a linear correlation between S–N and Se–N bond lengths with the adjacent S···N and Se···N contact distances in compounds with $SN_2$ and $SeN_2$ fragments has been commented upon by: Gieren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 5070.

Se···F and S···F interactions both form As–F bonds (As(1)–F(11) = 1.742 (8) Å, As(2)–F(21) = 1.761 (8) Å) that are somewhat longer than the other As–F bonds and also longer than the As–F bond of 1.719 (3) Å in potassium hexafluoroarsenate.[31] It is clear from Figure 2 that these weak anion–cation bonding interactions also have a significant effect on the thermal motion of the hexafluoroarsenate anions. For example, the librations in anion 1 are limited principally to rotations about the F(11)–As(1)–F(14) axis as is shown by the thermal ellipsoids for the "equatorial" fluorines, which are significantly elongated along axes in the equatorial plane and approximately tangential to the As–F bonds. This evidence is probably more conclusive than the bond-length differences, which are notably reduced on applying thermal corrections to the bond lengths since the riding correction for the "equatorial" fluorines is larger than that for the "axial" fluorines. The distortion in the octahedral geometry of the two hexafluoroarsenate anions due to the lengthening of these As–F bonds is slight (1–2° in some cases).

In the hexafluoroantimonate salt, the average Sb–F bond length is 1.86 (1) Å and no individual value(s) appears to be significantly longer than the remaining values. This is consistent with the slightly weaker Se···F and S···F interactions involving these anions. However, it may still be observed that those atoms that are involved in the shortest interionic interactions also have the smallest anisotropic thermal parameters (for example, atoms F(12), F(14), and F(21)). The observed average Sb–F bond length is slightly longer than that for $K^+SbF_6^-$ of 1.844 (7) Å.[32]

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**Registry No.** $Se_4S_2N_4(AsF_6)_2$, 79135-72-1; $Se_4S_2N_4(SbF_6)_2$, 79135-73-2; $S_4N_4$, 28950-34-7; $Se_8(AsF_6)_2$, 79152-63-9; $Se_4(AsF_6)_2$, 53513-64-7; $Se_4(Sb_2F_{11})_2$, 53513-63-6.

**Supplementary Material Available:** Tables A–G, giving final positional and anisotropic thermal parameters, structure factor amplitudes at room and low temperature, equations of least-squares planes, and geometry of the anion–cation interactions in compounds (59 pages). Ordering information is given on any current masthead page.

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# Chelating 2-(Diphenylphosphino)pyridine. Synthesis and Structure of Dichlorodicarbonyl(2-(diphenylphosphino)pyridine)ruthenium(II)

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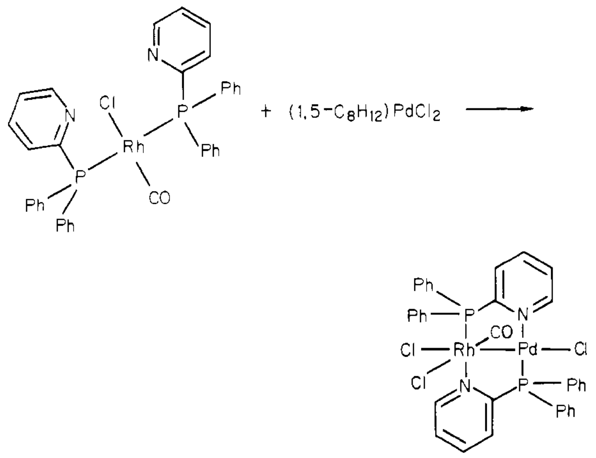
The white complex $Ru(Ph_2Ppy)(CO)_2Cl_2$ ($Ph_2Ppy$ = 2-(diphenylphosphino)pyridine) has been synthesized by the addition of chlorine to $[Ru(CO)_3Ph_2Ppy]_3$ and has been characterized by a single-crystal X-ray structural analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with $a$ = 8.375 (3) Å, $b$ = 15.034 (4) Å, and $c$ = 15.559 (3) Å at 140 K. The structure was refined by full-matrix least-squares methods to a final $R$ of 0.030 for the 1367 reflections that had $I > 3\sigma(I)$. The complex is six-coordinate with a four-membered chelate ring involving Ru–P and Ru–N bonding to the 2-(diphenylphosphino)pyridine ring. The following trans ligand pairs are present: PRuCl, NRuCO, and ClRuCO. The conversion of $Ru(Ph_2Ppy)(CO)_2Cl_2$ into $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ is described.

## Introduction

We have recently described the use of 2-(diphenylphosphino)pyridine ($Ph_2Ppy$) in the stepwise construction of binuclear transition-metal complexes.[1-4] Two coordination modes for this ligand have been encountered previously. In a number of complexes (e.g., $Rh(Ph_2Ppy)_2(CO)Cl$[1,2] and $Ru(CO)_3(Ph_2Ppy)_2$[4]) this ligand acts as a phosphorus-bound monodentate ligand. In these cases it closely resembles triphenylphosphine. The presence of the uncoordinated nitrogen however allows such complexes to bind a second metal ion. An example is shown in reaction 1.[1,2] In the product, 2-(diphenylphosphino)pyridine acts as a bridging ligand. Other coordination modes for $Ph_2Ppy$ that are readily anticipated include monodentate coordination through nitrogen and chelation of a single metal ion. In the latter case this ligand should structurally resemble ortho-metalated[5] triphenylphosphine.



(1)

One of the five products resulting from the reaction between $Ru(CO)_3(Ph_2Ppy)_2$ and $(1,5\text{-}C_8H_{12})PdCl_2$ is a white crystalline material with the composition $Ru(Ph_2Ppy)(CO)_2Cl_2$.[4] Here we report on an independent synthesis of this material, the first

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