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THE CRYSTAL STRUCTURE OF TRIPHENYLSELENONIUM ISOTHIOCYANATE

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SUMMARY

Three dimensional X-ray crystal structure analysis shows that triphenylselenonium isothiocyanate consists of discrete ion pairs in the solid state with each pair having an Se-N contact (3.197(4)Å) and Se-C(NCS) contact (3.260(5)Å) significantly shorter than the respective van der Waals distance. These short distances are accompanied by acute Se-N-C (83.0(3)°) and Se-C-N (76.8(3)°) angles, and suggest a weak interaction between the triphenylselenonium cation and the π-electron system of isothiocyanate anion. $Ph_3Se(NCS)$ is neither isomorphous nor isostructural with $Ph_3Te(NCS)$. Refinement of the structure, based on 3126 reflections collected by automatic diffractometry, converged to a conventional R factor of 5.5% and a weighted R factor of 5.2%. Crystal data for $Ph_3Se(NCS)$ are as follows: $a = 12.417(4)$Å, $b = 11.556(5)$Å, $c = 12.633(3)$Å, $\beta = 113.17(2)°$, $V = 1666$Å^3 (23 ± 2°C) and $Z = 4$; space group $P2_1/c$.

INTRODUCTION

Among the many selenium compounds of the form R_3SeX, those involving ordinary pseudohalide ions have not been reported.[1,2] Recently, we synthesized and characterized the Ph_3Se^+ salts of N_3^-, NCS^-, $NCSe^-$ and NCO^- to compare them with the corresponding Ph_3TeX compounds.[3,4] As part of our effort to structurally characterize these Group (VI) onium salts we have determined the structure of $Ph_3Se(NCS)$.

EXPERIMENTAL

$Ph_3Se(NCS)$ was synthesized by ion exchange techniques using NCS^- saturated Dowex 1-X8 resin (20-50 mesh) and an aqueous solution of $Ph_3SeC\ell$ (1g/50 ml H_2O).[3] High quality crystals were obtained by recrystallization from methylene chloride and ethyl acetate.

$Ph_3Se(NCS)$ crystallizes in the monoclinic system, space group $P2_1/c$, with unit cell dimensions $a = 12.417(4)$Å, $b = 11.556(5)$Å, $c = 12.633(3)$Å, $\beta = 113.17(2)°$ and $V = 1666\text{Å}^3$ (23 ± 2°C). The floatation measured density ($CC\ell_4$ and cyclohexane) of 1.46(2) g/cm^3 agrees with the calculated value of 1.47 g/cm^3 for four formula units per unit cell.

A complete set of independent intensity data was collected by the θ-2θ scan technique on a Syntex $P2_1$ automatic diffractometer using graphite monochromatized Mo-Kα radiation and a crystal measuring 0.25 x 0.25 x 0.40 mm. Intensities and standard deviations of intensities were calculated according to the formulas $I = S\ (c - RB)$ and $\sigma(I) = S(c + R^2B)^{1/2}$ respectively, where S is the scan rate, c is the total integrated peak count, R is the ratio of scan time to background counting time and B is the total background count. Coincidence corrections were made as described in the $P2_1$ operations manual. The intensities of 4338 independent reflections were measured for $2\theta \leq 60°$; solution and refinement of the structure were based on the 3126 reflections having $F > 2\sigma(F)$. The intensities were corrected for an average drift in intensity of 2.2% as measured from three standard reflections (112), (102) and (224) checked every 100 reflections, and for Lorentz and polarization effects, but not for absorption. The calculated linear absorption coefficient (MoKα), μ, is 25.4 cm^{-1}.

The structure was solved by Patterson and Fourier techniques and was refined by least-squares methods. The scattering factors were taken from Cromer and Waber[5]; those for Se and S were corrected for the real and imaginary components of anomalous dispersion using the values of Cromer and Liberman.[6] The function minimized in the least-squares refinement was $\Sigma w(|F_{obs}|-|F_{calc}|)^2$ where $w = 0.46|F|/\sigma^2(F)$. Anisotropic thermal parameters were used for all of the non-hydrogen atoms. The refinement converged to a final R factor $(\Sigma||F_{obs}|-|F_{calc}||/\Sigma|F_{obs}|)$ of 5.5% and a weighted R factor $\Sigma w(|F_{obs}|-|F_{calc}|)^2/\Sigma w|F_{obs}|^2)$ of 5.2%. The goodness of fit, $[\Sigma w(F_{obs}-F_{calc})^2/(\text{no. of reflections - no. of variables})]^{1/2}$, equals 1.02. All hydrogen atoms were located and their positions refined in the final four cycles of refinement. They were assigned a temperature factor one unit greater than that of the attached carbon atom. No atom moved more than 0.3σ in the final cycle of refinement.

The final positional and thermal parameters for the atoms are given in Tables I and II.*

RESULTS AND DISCUSSION

The structure of $Ph_3Se(NCS)$ is illustrated in Figure 1 and consists of discrete Ph_3Se^+ and NCS^- ion pairs separated from other ion pairs by van der Waals distances. A stereoscopic view of the packing within the unit cell is given in Figure 2, and interatomic angles are given in Table III.

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*The table of structure factors has been deposited as NAPS Document 03017 (21 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $6.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

Table I. Positional and Thermal Parameters of the Non Hydrogen Atoms[a,b,c]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Se	2178(.4)	2633(.3)	297(.4)	75(.3)	50(.2)	60(.3)	1(.3)	30(.2)	-4(.3)
N	1752(4)	5330(4)	542(4)	112(5)	86(9)	106(4)	11(4)	41(4)	18(3)
C	2490(5)	5215(4)	1417(5)	108(6)	54(3)	112(5)	-13(4)	71(5)	-8(3)
S	3565(2)	5011(2)	2652(2)	115(2)	217(2)	90(1)	-29(2)	38(1)	-2(2)
C(11)	2379(4)	997(3)	654(3)	80(4)	53(3)	52(3)	-4(3)	19(3)	5(2)
C(12)	1603(5)	550(4)	1062(4)	99(5)	81(4)	86(4)	-10(4)	36(4)	12(3)
C(13)	1674(6)	-622(5)	1326(5)	152(8)	96(5)	99(5)	-37(5)	50(5)	17(4)
C(14)	2500(6)	-1288(5)	1175(4)	172(8)	59(4)	77(4)	-19(5)	15(5)	10(3)
C(15)	3270(6)	-828(4)	760(5)	135(7)	63(4)	104(5)	17(4)	34(5)	-3(4)
C(16)	3205(5)	333(4)	476(4)	106(5)	63(4)	90(4)	2(4)	43(4)	0(3)
C(21)	3556(4)	2994(3)	48(3)	70(4)	52(3)	58(3)	-4(3)	20(3)	-14(2)
C(22)	3486(5)	3472(4)	-987(4)	90(5)	87(4)	68(4)	-13(4)	22(4)	5(3)
C(23)	4495(5)	3769(5)	-1110(5)	116(6)	84(4)	87(4)	-19(4)	50(4)	-4(4)
C(24)	5552(5)	8610(4)	-252(5)	101(6)	76(4)	123(6)	-17(4)	67(5)	-17(4)
C(25)	5625(5)	3142(5)	770(5)	79(5)	110(5)	111(6)	-3(4)	29(4)	0(4)
C(26)	4622(5)	2855(4)	930(4)	86(4)	93(5)	79(4)	-11(4)	28(4)	8(3)
C(31)	1019(4)	2529(3)	-1256(3)	69(4)	48(3)	66(3)	-5(3)	26(3)	0(2)
C(32)	1086(4)	1698(4)	-2015(4)	75(4)	59(3)	76(4)	9(3)	26(3)	-4(3)
C(33)	205(5)	1630(4)	-3090(4)	98(5)	68(4)	69(4)	-6(4)	35(4)	-11(3)
C(34)	-731(4)	2378(4)	-3402(4)	83(4)	76(4)	75(4)	2(4)	16(3)	8(3)
C(35)	-779(5)	3206(4)	-2645(4)	80(5)	78(4)	93(4)	19(4)	21(4)	11(3)
C(36)	103(4)	3295(4)	-1554(4)	84(5)	62(3)	79(4)	13(3)	29(4)	-1(3)

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[a] All values x 10^4.

[b] Values in parentheses above and in Table II are estimated standard deviations in the last digits as derived from the inverse matrix of the final least-squares refinement cycle.

Table II

Positional and Thermal Parameters of the Hydrogen Atoms[a]

Atom	x	y	z	B,Å^2
H(12)	101(4)	100(4)	104(4)	5.6
H(13)	116(5)	-83(5)	160(5)	6.9
H(14)	256(5)	-200(5)	143(5)	6.8
H(15)	385(5)	-124(5)	68(4)	6.4
H(16)	375(4)	64(4)	23(4)	5.4
H(22)	285(4)	359(4)	-141(4)	5.4
H(23)	447(4)	419(4)	-176(4)	5.8
H(24)	621(5)	378(5)	-32(4)	5.9
H(25)	625(5)	297(5)	126(5)	6.3
H(26)	470(4)	254(4)	162(4)	5.5
H(32)	175(4)	126(4)	-180(4)	4.7
H(33)	25(4)	112(4)	-360(4)	5.0
H(34)	-133(4)	234(4)	-412(4)	5.3
H(35)	-144(5)	366(4)	-281(4)	5.6
H(36)	8(4)	383(4)	-97(4)	4.9

a) The positional parameters have been multipled by 10^3. Hydrogen atoms were assigned a temperature factor one unit greater than that of the last refined isotropic temperature factor of the attached carbon atom.

The selenium atom in Ph$_3$Se(NCS) is covalently bonded to three carbon atoms and has a nitrogen contact (3.197(4)Å) significantly shorter than the sum of the respective van der Waals radii of 3.45Å.[7] Similarly, the Se-C(NCS) distance is short at 3.260(5)Å, suggesting a weak bonding between the ions. Such contacts, at distances greater than the usual covalent bond distance but shorter than the sum of the van der Waals radii, have been found in the other triphenylselenonium[8] and triphenyltelluronium[9,10] salts studied to date. This type of interaction, called secondary bonding, has been reviewed by Alcock and is common to many Se(IV) and Te(IV) compounds with halogen or oxygen as ligands.[11] Reports of secondary bonding of Se(IV) to nitrogen or sulfur, however, are not

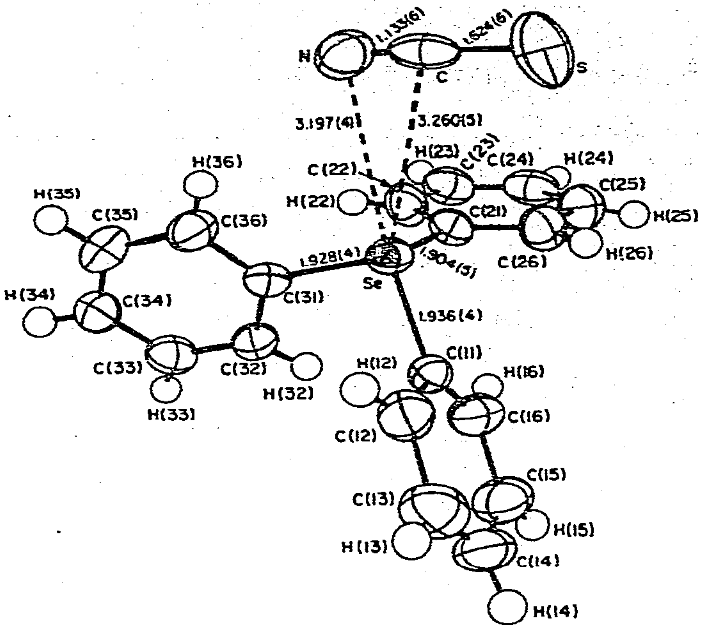

Figure 1. Atom labelling scheme and selected interatomic distances in $Ph_3Se(NCS)$

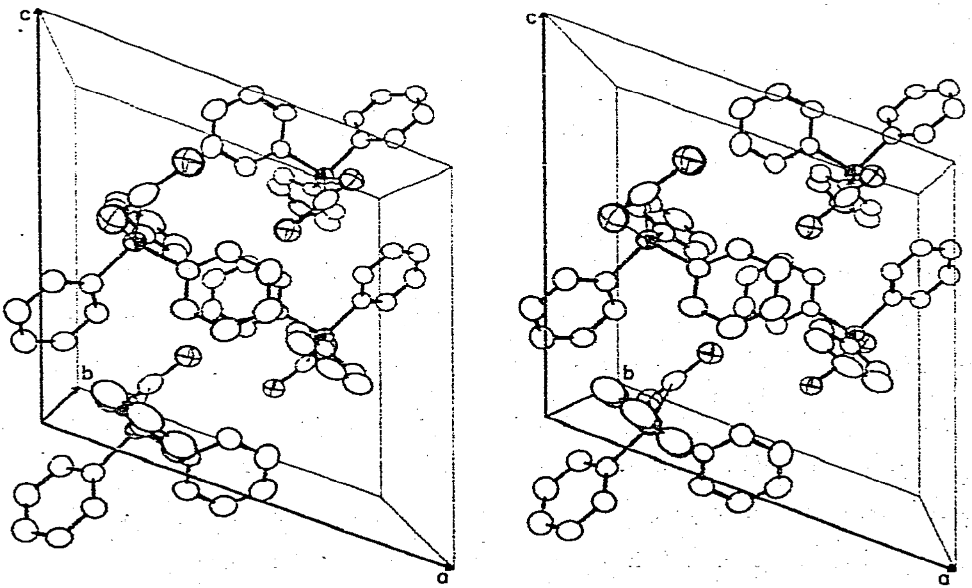

Figure 2. Stereoscopic view of the unit cell of $Ph_3Se(NCS)$

Table III

Interatomic Distances (Å) and Angles (Deg)[a]

Atoms	Angle	Atoms	Distance
N-C-S	177.9(5)	C(11)-C(12)	1.361(7)
C(11)-Se-C(21)	102.2(2)	C(12)-C(13)	1.388(8)
C(11)-Se-C(31)	98.8(2)	C(13)-C(14)	1.355(9)
C(21)-Se-C(31)	101.8(2)	C(14)-C(15)	1.366(9)
C(11)-Se-N	160.1(1)	C(15)-C(16)	1.383(7)
C(21)-Se-N	89.8(1)	C(16)-C(11)	1.369(6)
C(31)-Se-N	94.2(1)	C(21)-C(22)	1.390(6)
Se-N-C	83.0(3)	C(22)-C(23)	1.365(7)
Se-C-S	101.3(2)	C(23)-C(24)	1.346(8)
Se-C-N	76.8(3)	C(24)-C(25)	1.370(8)
C(12)-C(11)-C(16)	122.5(4)	C(25)-C(26)	1.379(8)
C(11)-C(12)-C(13)	118.3(5)	C(26)-C(21)	1.364(6)
C(14)-C(13)-C(12)	120.0(6)	C(31)-C(32)	1.383(6)
C(13)-C(14)-C(15)	121.0(5)	C(32)-C(33)	1.371(6)
C(14)-C(15)-C(16)	119.9(6)	C(33)-C(34)	1.376(7)
C(11)-C(16)-C(15)	118.2(5)	C(34)-C(35)	1.371(7)
C(26)-C(21)-C(22)	119.8(5)	C(35)-C(36)	1.387(7)
C(21)-C(22)-C(23)	119.1(5)	C(36)-C(31)	1.372(6)
C(22)-C(23)-C(24)	121.5(5)		
C(23)-C(24)-C(25)	119.7(5)		
C(24)-C(25)-C(26)	120.3(5)		
C(21)-C(26)-C(25)	119.6(5)		
C(32)-C(31)-C(36)	121.8(4)		
C(31)-C(32)-C(33)	119.0(4)		
C(32)-C(33)-C(34)	120.2(4)		
C(33)-C(34)-C(35)	120.2(4)		
C(34)-C(35)-C(36)	120.7(5)		
C(31)-C(36)-C(35)	118.1(4)		

a) The atom labeling scheme and additional distances are given in Figure 1.

common although some intermolecular Se(II)-N contacts have been reported. In Se(SCN)$_2$ for example, an Se-N contact was found to be 2.98Å.[12] Most of the X-A···Y secondary interactions are approximately linear,with deviations of up to 15° from linearity being common.[11] In the present structure the C(11)-Se···N angle is 160.1(1)°.

The short Se-N and Se-C distances, which are accompanied by acute Se-N-C and Se-C-N angles of 83.0(3)° and 76.8(3)°, respectively, suggest that the weak bonding interaction of the NCS group with selenium is localized at the NC portion of the group. We therefore designate $Ph_3Se(NCS)$ as an isothiocyanate. Presumably the interaction involves the π-electron system of the group, possibly in a donor capacity to the selenium atomic orbitals. Such an interaction is consistent with the observed C-N stretching frequency for $Ph_3Se(NCS)$ being 10 cm^{-1} below that reported for KNCS (vide infra).

The present study and that of $Ph_3SeC\ell\cdot 2H_2O$[8] establish the conformation of the triphenylselenonium ion. The cation is of the AX_3E type and has the expected trigonal pyramidal shape with the selenium atom in $Ph_3Se(NCS)$ 0.87Å out of the trigonal plane (plane 2, Table IV).† Ph_3Se^+, however, possesses only a pseudo-3-fold axis due to the conformation adopted by the phenyl rings. The Se-C distances are within the range observed for selenium-aromatic carbon distances (1.92-1.95Å)[13] and have a mean value of 1.923(8)Å, identical to that in $Ph_3SeC\ell\cdot 2H_2O$ (1.93(1)Å). Similarly, the mean values of the C-Se-C angles are identical at 100.9(3)° and 100(1)°, respectively. These angles, which are slightly larger than the corresponding angles in the geometrically similar Ph_3Te^+ ion,[9,10] reflect the tendency of lighter members of Group (VI) to have larger valence angles.[8]

The geometry around selenium in Ph_3Se^+ is distorted tetrahedral with a lone pair presumably occupying the fourth position. When secondary interactions are considered, $Ph_3Se(NCS)$ is four coordinate and $Ph_3SeC\ell\cdot 2H_2O$ is six coordinate,[8] despite the structural invariance of the cation. The N-Se-C(21,31), C-Se-C and N-Se-C(11) angles in $Ph_3Se(NCS)$ might also be taken to suggest that selenium is in a distorted octahedral environment with three primary bonds, one secondary bond and two vacant equatorial sites. Four coordinate $(CH_3)SeI$ may be similarly described.[11] Selenium in $Ph_3SeC\ell\cdot 2H_2O$ is also in a distorted octahedral environment (with an

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† Table IV, Least-Squares Planes in $Ph_3Se(NCS)$, has been deposited along with the Structure Factors Table. See preceding footnote.

axial C(31)-Se-O(1) angle of 158.9(3)°), but has three primary bonds, three secondary bonds and no vacant sites.[8] We note that in all three structures, the secondary coordination sites deviate from the _pseudo_-3-fold axis of the R_3Se^+ cation by about 30 to 50°. In $Ph_3Se(NCS)$ the Se-N, Se-C(NCS) and Se-S vectors make angles of 42, 33 and 36°, respectively, with the _pseudo_-3-fold axis of the cation.

The closest selenium contacts in $Ph_3Se(NCS)$, other than those noted above, are H(33) [x, $\bar{y}$-1/2, z+1/2] at 3.52(5)Å and C(33) [x, $\bar{y}$-1/2, z+1/2] at 3.847(5)Å. The closest Se-Se distance is 6.324(2)Å [x, $\bar{y}$-1/2, z+1/2].

In $Ph_3Se(NCS)$ and $(CH_3)_3SeI$,[14] secondary bonding does not lead to a coordination number higher than that expected from the stoichiometry of the compound as it does in the telluronium species $(CH_3)_3Te(CH_3TeI_4)$,[15] $Ph_3Te(NCS)$[9] and $Ph_3Te(NCO)$.[10] The tendency of selenium(IV) toward lower coordination numbers accompanies the increase in the C-Se-C angles noted above. On the basis of the above observations anhydrous $Ph_3SeC\ell$[16]* probably has a structure similar to that of $Ph_3Se(NCS)$ and $(CH_3)_3SeI$. Less Se···Cℓ interaction would be expected, however, due to the more electronegative Cℓ.

Bond distances and angles within the three crystallographically independent phenyl rings appear normal, and are listed in Table III. The mean values of the 18 independent phenyl C-C distances and the C-C-C angles are 1.37(3)Å and 120(2)°, respectively. The rings are planar with no carbon atom deviating more than 0.018(5)Å from the least-squares plane of its respective phenyl ring. Equations of the least-squares planes of the three phenyl rings are given in Table IV, planes 3 to 5. The 18 independent phenyl C-H distances have a mean value of 0.9(2)Å. Dihedral angles between the phenyl groups containing carbon atoms (11)-(21), (11)-(31) and (21)-(31) are 116.7°, 89.5° and 109.4°, respectively.

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* We have isolated a species of $Ph_3SeC\ell$ from $CH_2C\ell_2$ whose cell constants are identical to those reported in reference 16 for anhydrous $Ph_3SeC\ell$. A subsequent structure determination of the species, however, shows it to be $Ph_3SeC\ell \cdot H_2O$.[19]

The isothiocyanate group is essentially ionic with a C-N distance similar to that of the NCS ion in KNCS (1.149(14)Å), and a C-S distance significantly shorter than that in KNCS (1.689(13)Å)[17]. $Ph_3Se(NCS)$ is neither isomorphous nor isostructural with $Ph_3Te(NCS)$, which is bi-oligomeric in the solid state.[9,18] Although the NCS group is structurally similar to those in $Ph_3Te(NCS)$, it is non-bridging. The nearest nonhydrogen contact to the sulfur atom is C(15) [$1-x, y+1/2, \bar{z}-1/2$] at 3.769(7)Å while the nearest hydrogen contact is H(32) [$x, \bar{y}-1/2, z+1/2$] at 3.00(5)Å. The closest selenium atom is at 3.917(2)Å. Unlike $Ph_3Te(NCS)$, which shows three infrared C-N stretching vibrations around 2062 cm^{-1} due to three bridging crystallographically independent NCS groups, $Ph_3Se(NCS)$, as expected, shows a single stretching vibration at 2042 cm^{-1}.[3,4]

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