stant is larger in II than in I (8.85 *vs.* 3.93 G). Assuming a ring-puckering coordinate of the type described for 2,5-dihydrofuran[24] (*i.e.*, the five-membered ring of II bends about the P_1-P_3 diagonal, and no stretching of the P–C, C=C, and P–P bonds and no deformations of the P–P–P or C=C–P angles occur), two conformations of II can be described (Figure 4), one with the 2-trifluoromethyl group inclined toward the C=C bond and the other with the 2-trifluoromethyl group inclined away from the olefinic bond. In the former conformation the 1 and 3 trifluoromethyl groups are very close to the π electrons of the C=C bond. A time-averaged ring-puckering vibration in II may thus lead to a smaller distance between the C-P-CF_3 fluorine atoms and the olefinic bond than in I. In the latter the C_4-P_1-P_2 and C_3-P_2-P_1 bond angles are necessarily ~80–85°; hence the C_4-P_1-C_1 and C_3-P_2-C_2 bond angles are ~115°, thus increasing the distance between the fluorine atoms and the double bond.[25]

Conclusion

This study indicates that the unpaired electron of the anion radicals of $(CF_3C)_2(PCF_3)_2$ and $(CF_3C)_2(PCF_3)_3$ occupies a molecular orbital primarily localized on the two ethylenic carbon atoms and that the spin density on the ethylenic carbon atoms is essentially the same in the two anion radicals. If 3d orbitals of phosphorus were important in the molecular orbital occupied by the unpaired electron, one would expect a larger delocalization of unpaired spin density to the phosphorus atoms. The fact that $(PCH_3)_5$, $(PCF_3)_4$, and $(CF_3C)_2S_2$ cannot be reduced to anion radicals suggests also that d orbitals must not greatly stabilize the lowest antibonding MO for these molecules. The relatively easy reduction to anion radicals of the permethylcyclopolysilanes[2] thus appears exceptional among compounds of second-row elements.

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Registry No. I, 42423-23-4; II, 42423-24-5; III, 42561-79-5.

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[25] (25) The following bond distances in angstroms were assumed in constructing models I and II: P–P, 2.22; C–P, 1.88; C–F, 1.33; C=C, 1.34; C–C, 1.50.

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Chalcogen Chemistry. IX.[1] Synthesis of Alkylammonium Dihalocyanoselenate(II) and Trihaloselenate(II) Salts

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Alkylammonium selenocyanates react with sulfuryl chloride or bromine to yield respectively dichloro- and dibromocyanoselenate(II) salts, R_4NSeX_2CN (R = *n*-C_3H_7, X = Cl, Br; R = CH_3, X = Cl). Conductivity and molecular weight data demonstrate the presence of discrete SeX_2CN anions in solution. Solid-state and solution infrared and Raman spectra indicate the SeX_2CN anions are T shaped with halogens occupying the trans positions in the T. Tetraethylammonium trichloro- and tribromoselenate(II) were prepared *via* the reaction of tetraethylammonium selenocyanate with 2 mol of SO_2Cl_2 and Br_2, respectively. Far-infrared and Raman spectroscopic data are consistent with the presence of planar $[Se_2X_6]^{2-}$ anions of D_{2h} symmetry in the solid state (I_2Cl_6 structure). However, conductivity studies indicate the trihaloselenate(II) salts behave as 1:1 electrolytes in nitromethane. Raman spectra strongly support the presence of discrete T-shaped $[SeX_3]^-$ in solution.

There exists a growing awareness of the biological importance of selenium as a trace element and as a cancer inhibitor.[3,4] In general it appears that it is the chemistry of the lower valences of selenium which is involved in its useful biological function.[4] In continuing our investigation of this area we report herein the preparation of some new selenium species derived from selenocyanate.

Experimental Section

The compounds containing selenium–bromine bonds are fairly stable to the atmosphere, whereas those containing selenium–chlorine bonds are rapidly hydrolyzed. As a precautionary measure and due to the toxicity of most selenium compounds, all preparations and handling operations were carried out in polyethylene glove bags filled with dry dinitrogen. Infrared, Raman, and proton nuclear magnetic resonance spectra and molecular weight and conductivity data were obtained as previously reported.[1,5]

Chemicals. Solvents were purified as previously noted.[5] Potassium selenocyanate was prepared by the literature method,[6] except that the melt was slowly poured directly into acetone from which it crystallized. Tetraalkylammonium halides were obtained from Eastman; *n*-propylammonium and *n*-butylammonium salts were used exclusively so that the "*n*" designation is not used further below.

Tetraalkylammonium Selenocyanates. Tetramethylammonium selenocyanate was prepared by stirring tetramethylammonium bromide (4.66 g, 30.2 mmol) and potassium selenocyanate (4.36 g, 30.2 mmol) in 50 ml of acetonitrile for 1 hr. Filtration followed by reduction of volume to 20 ml gave a 69% yield of tetramethylammonium selenocyanate. Recrystallization was done in CH_3CN-CCl_4; dec pt 266–268°, lit.[7] 267–268°. *Anal.* Calcd for $C_5H_{12}N_2Se$: C, 33.53; H, 6.75; N, 15.64. Found: C, 33.48; H, 6.70; N, 15.65.

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[2] (2) University of Georgia Graduate School Postdoctoral Fellow, 1970–1971.

[3] (3) G. N. Schrauzer and W. J. Rhead, *Experientia*, 27, 1069 (1971).

[4] (4) See the series of papers on "Biological Aspects of Organic Selenium and Tellurium Compounds" in *Ann. N. Y. Acad. Sci.*, 192, 167 (1972).

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Other tetraalkylammonium selenocyanates were prepared similarly. Tetraethylammonium selenocyanate, dec pt 184°, was recrystallized from 1:1 $CHCl_3$–CCl_4. *Anal.* Calcd for $C_9H_{20}N_2Se$: C, 45.95; H, 8.57; N, 11.91. Found: C, 45.85; H, 8.57; N, 11.92. Tetrapropylammonium selenocyanate, mp 147.5–149.5°, was recrystallized from 1:1 $CHCl_3$–CCl_4. *Anal.* Calcd for $C_{13}H_{28}N_2Se$: C, 53.60; H, 9.68; N, 9.62. Found: C, 53.67; H, 9.73; N, 9.70. Tetrabutylammonium selenocyanate decomposed at 135–140°.

Tetraalkylammonium Dihalocyanoselenates. Tetramethylammonium dichlorocyanoselenate(II) was prepared in 53% yield by treating a filtered solution of $(CH_3)_4NSeCN$ (2.29 g, 12.8 mmol) in 50 ml of CH_3CN with SO_2Cl_2 (1.72 g, 12.8 mmol) in 20 ml of CH_3CN. The solution turned red upon addition of the first portion of SO_2Cl_2 and then yellow upon addition of the last portion. After a stirring period of 0.5 hr, a precipitate formed. The product was filtered and recrystallized from CH_3CN. The yellow needles start to decompose at 196°; decomposition is complete at 210–215°. *Anal.* Calcd for $C_5Cl_2H_{12}N_2Se$: C, 24.02; H, 4.34; N, 11.20; Cl, 28.36. Found: C, 23.94; H, 4.74; N, 11.18; Cl, 28.30.

Tetrapropylammonium Dichlorocyanoselenate(II). This compound was prepared by slow addition of SO_2Cl_2 (1.64 g, 12.2 mmol) in 15 ml of $CHCl_3$ to a filtered solution of tetrapropylammonium selenocyanate (3.54 g, 12.2 mmol) in 35 ml of $CHCl_3$. The solution turned deep reddish brown at first and then bright yellow with the addition of the last portions of SO_2Cl_2. The yellow precipitate formed at –20° was filtered and recrystallized from $CHCl_3$, yield 82%, mp 120.5–124.5°. *Anal.* Calcd for $C_{13}Cl_2H_{28}N_2Se$: C, 43.10; H, 7.79; N, 7.74; Cl, 19.60. Found: C, 43.12; H, 7.67; N, 7.68; Cl, 19.50.

Tetrapropylammonium Dibromocyanoselenate(II). To a solution of tetrapropylammonium selenocyanate (2.16 g, 7.45 mmol) in 30 ml of $CHCl_3$ was added bromine (1.19 g, 7.45 mmol) in 15 ml of $CHCl_3$. The solution turned red and an orange-yellow precipitate formed. The precipitate was filtered and recrystallized from CH_2Cl_2, mp 130.5–132.0, 89% yield. *Anal.* Calcd for $Br_2C_{13}H_{28}N_2Se$: C, 34.61; H, 6.26; N, 6.21; Br, 35.42. Found: C, 34.79; H, 6.26; N, 6.23; Br, 35.40.

The reaction of tetrabutylammonium selenocyanate with bromine led to an oil; the reaction of KSeCN with Br_2 in acetonitrile gave a precipitate of KBr. These and other results indicate the stability and crystallinity of dihalocyanoselenate(II) salts are dependent on the nature of the cation and the preparative medium.

Tetraethylammonium Trihaloselenates. Tetraethylammonium trichloroselenate(II) was prepared by treating a solution of tetraethylammonium selenocyanate (5.19 g, 22.1 mmol) in 50 ml of $CHCl_3$ with SO_2Cl_2 (5.96 g, 44.1 mmol) in 15 ml of $CHCl_3$ with constant stirring. The solution was red at first and then yellow; finally a yellow solid precipitated. Filtration and recrystallization (2:1 CH_2Cl_2-CH_3CN) gave $(C_2H_5)_4NSeCl_3$ in 23% yield, dec pt 243–244°. *Anal.* Calcd for $C_8H_{20}Cl_3NSe$: C, 30.45; H, 6.39; N, 4.44; Cl, 33.70. Found: C, 30.59; H, 6.39; N, 4.40; Cl, 33.61.

Tetraethylammonium tribromoselenate(II) was prepared by treating tetraethylammonium selenocyanate (2.71 g, 11.5 mmol) in 50 ml of $CHCl_3$ with bromine (3.69 g, 23.0 mmol) in 15 ml of $CHCl_3$. A red-orange precipitate formed and the solution was placed at –20°. The mixture was filtered and the solid washed with two 100-ml portions of CH_2Cl_2. Recrystallization from CH_2Cl_2-CH_3CN gave red-orange $[(C_2H_5)_4N]SeBr_3$, dec pt 136–138°, in 32% yield. *Anal.* Calcd for $Br_3C_8H_{20}NSe$: C, 21.40; H, 4.49; N, 3.12; Br, 53.40. Found: C, 21.47; H, 4.76; N, 3.04; Br, 53.15.

Results and Discussion

Dihalocyanoselenate(II) Salts. The preparation of dichloro- and dibromocyanoselenate(II) salts may be effected by the reaction of an appropriate halogenating agent with a tetraalkylammonium selenocyanate (eq 1 and 2). Conductivity

$$R_4NSeCN + SO_2Cl_2 \rightarrow R_4NSeCl_2CN + SO_2 \quad (R = C_3H_7, CH_3) \qquad (1)$$

$$(C_3H_7)_4NSeCN + Br_2 \rightarrow (C_3H_7)_4NSeBr_2CN \qquad (2)$$

and molecular weight data for the compounds prepared may be found in Table I. These data suggest the compounds behave as 1:1 electrolytes and that the SeX_2CN^- ion is undissociated in solution.

Table I. Molecular Weight[a] and Conductivity[b] Data for SeX_2CN^- and SeX_3^- Salts

Compd	(Formula wt)/2	Obsd mol wt	Slope $\Lambda_0 - \Lambda_e$[c] *vs.* $\sqrt{c}$	Λ_e at 10^{-3} *M*
$(CH_3)_4NSeCl_2CN$			219	104.4
$(C_3H_7)_4NSeCl_2CN$	181.1	215, 225	214	92
$(C_3H_7)_4NSeBr_2CN$	225.6	242, 240, 211	233	91.6
$(C_3H_7)_4NSeCN$			200	96.8
$(C_2H_5)_4NSeCl_3$			218	81.0
$(C_2H_5)_4NSeBr_3$			225	108

[a] In nitrobenzene. [b] In nitromethane. [c] Λ_0 and Λ_e are the equivalent conductances (cm^2 $equiv^{-1}$ ohm^{-1}) at infinite dilution and at concentration *c*, respectfully.

Infrared and Raman spectral data for $(C_3H_7)_4NSeCl_2CN$ and $(C_3H_7)_4NSeBr_2CN$ may be found in Table II. The vibrational spectrum of $(CH_3)_4NSeCl_2CN$ was virtually identical with that for the tetrapropylammonium salt and is not presented.

Solid-State Infrared and Raman Spectra. In order to assign vibrational modes it must first be established that discrete SeX_2CN^- species exist both in the solid state and in solution. This appears likely in the solid state considering the structure of the triselenocyanate ion.[8] The latter may be thought of as a T-shaped (AX_3E_2[9]) molecule with $SeCN^-$ groups occupying trans positions of the T and CN^- the remaining position. $SeBr_2CN^-$ and $SeCl_2CN^-$ are isoelectronic and therefore presumably isostructural with the $[Se(SeCN)_2CN]^-$ ion.

The vibrational spectroscopic data provide strong support for this view. Considering the CN^- group as a unit, six normal modes (3 A_1, 2 B_1, B_2) are expected for a T-shaped tetraatomic molecule of C_{2v} symmetry. Five of these six modes are clearly seen for both $SeBr_2CN^-$ and $SeCl_2CN^-$ (Table II); $\nu_6(B_2)$ a low-frequency out-of-plane bending mode was not found. The selenium–halogen modes lie close in frequency to those previously observed for linear X-Se^{II}-X systems.[5,10] The CN frequency for the two anions is shifted to higher energy by *ca.* 75 cm^{-1} relative to $SeCN^-$,[11] while the Se–C frequency is decreased by *ca.* 42 cm^{-1}. These shifts are in accord with those expected when coordination of $SeCN^-$ occurs *via* Se. It is interesting that both Se coordination in more familiar selenocyanate complexes and oxidative addition by halogenating agents cause similar shifts in C–N and Se–C modes.

Raman spectral data for solid $K(SeCN)_3 \cdot {}^1/_2H_2O$ were obtained in order to compare the spectrum of the triselenocyanate ion (of known structure[8]) with that of $SeBr_2CN^-$. For solid $K(SeCN)_3 \cdot {}^1/_2H_2O$ peaks were observed at 106 (mw) (Se–Se–Se bend), 134 (s) (Se–Se–Se sym str), and 188 (w) (Se–Se–Se asym str) cm^{-1}. These frequencies are in reasonably close agreement with those observed for $SeBr_2CN^-$, thus supporting similar structures for the two species.

Solution Infrared and Raman Spectra. Limited solubility prevented observation of most of the weak absorptions seen in the solid-state spectra. However, one prominent feature in the Raman spectrum of the dihalocyanoselenate(II) ions was the strong, polarized symmetric X–Se–X stretch (ν_2, A_1); other modes were of weak or very weak intensity. Only the strong asymmetric X–Se–X stretch was observed in the solution infrared spectra of the two anions. Finally, it may be seen in Table II that there is very close agreement between those frequencies observed in solution and in the solid state.

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Table II. Infrared and Raman Spectral Data (cm^{-1})

A. $(C_3H_7)_4NSeCNCl_2$

	Raman			
Ir[a]	Solid Ar, 5145 Å	CH_3CN soln Kr, 5682 Å	CH_3NO_2 soln Kr, 5682 Å	Assignment and approx description
2145 w	2153 w	2154 w, p	2155 w, p	C–N str
514 ms	515 w	512 w, p	519 w, p	$\nu_1(A_1)$ Se–C str
474 w				
	396 vw		394 w	
375 m	372 vw		370 w	$\nu_5(B_1)$ Se–C in-plane bend
	337 vw			
315 mw	315 w			
	301 vw	301 sh, w	301 sh, w	
271 s	268 s	267 vs, p ($\rho = 0.36$)	267 vs, p ($\rho = 0.36$)	$\nu_2(A_1)$ sym Cl–Se–Cl str
230 vs[b]	230 vw			$\nu_4(B_1)$ antisym Cl–Se–Cl str
	198 w			
142 m	140 m			$\nu_3(A_1)$ Cl–Se–Cl def
115 w				
	105 w			
	59 w			
47 w				

B. $(C_3H_7)_4NSeBr_2CN$

	Raman			
Ir[a]	Solid Kr, 6471 Å	CH_3CN soln Kr, 5682 Å	CH_3NO_2 soln Kr, 5682 Å	Assignment and approx description
2147 w	2145 wm	2150 vw, p ($\rho = 0.1$)	2149 w, p ($\rho = 0.09$)	C–N str
518 m	519 w		521 vw (p?)	$\nu_1(A_1)$ Se–C str
475 w				
372 w	378 w		375 vw	$\nu_5(B_1)$ Se–C in-plane bend
	334 w			
		330 vw	300 vw	
	313 w			
255 sh, w	252 vw			
	222 vvw			
190 vs[c]	180 s	185 sh, w	185 sh, w	$\nu_1(B_1)$ antisym Br–Se–Br str
158 m	151 s	152 s, p ($\rho = 0.24$)	154 s, p ($\rho = 0.25$)	$\nu_2(A_1)$ sym Br–Se–Br str
	134 vw			
110 mw	111 vw			$\nu_3(A_1)$ Br–Se–Br def
	94 w			
44 w	48 m			

[a] Nujol mull. [b] In $CHCl_3$ solution: 225 (s) cm^{-1}. [c] In $CHCl_3$ solution: 190 (s) cm^{-1}.

Table III. Infrared and Raman Spectra of Solid $(C_2H_5)_4NSeCl_3$ and $(C_2H_5)_4NSeBr_3$ (cm^{-1})

$(C_2H_5)_4NSeCl_3$				$(C_2H_5)_4NSeBr_3$			
Ir[a]	Assignment and approx description	Raman	Assignment and approx description (D_{2h})	Ir[a]	Assignment and approx description	Raman	Assignment and approx description (D_{2h})
				352 w			
		388 vw		212 s, br	$\nu_{16}(B_{3u})$ terminal $SeBr_2$ sym str $\nu_{12}(B_{2u})$ terminal $SeBr_2$ antisym str		
		284.5 s	$\nu_1(A_{1g})$ terminal $SeCl_2$ sym str				
270	$\nu_{16}(B_{3u})$ terminal $SeCl_2$ sym str					171 s	$\nu_1(A_{1g})$ terminal $SeCl_2$ sym str
251 s, br	$\nu_{12}(B_{2u})$ terminal $SeCl_2$ -antisym str			160 sh, w	$\nu_{17}(B_{3u})$ ring str		
		242 s	$\nu_6(B_{1g})$ terminal $SeCl_2$ antisym str				
						152 s	$\nu_6(B_{1g})$ terminal $SeBr_2$ antisym str
	$\nu_{17}(B_{3u})$ ring str					133 w	
235		148 s	$\nu_{11}(B_{2g})$ terminal $SeCl_2$ wag			123 s	$\nu_2(A_{1g})$ ring breathing
						119 w	
137 mw	$\nu_{13}(B_{2u})$ ring str					116 w	
						104 w	
						91 s	$\nu_{15}(B_{2g})$ twist
81 ms	$\nu_{18}(B_{3u})$ terminal $SeCl_2$ scissors or lattice mode?					78 m	$\nu_8(B_{1g})$ terminal $SeBr_2$ rock
				80 s	$\nu_{13}(B_{2u})$ ring str	60 w	
						49 m	$\nu_4(A_{1g})$ ring def

[a] Nujol mull.

Table IV. Solution Raman Spectra of $(C_2H_5)_4NSeCl_3$ and $(C_2H_5)_4NSeBr_3$ (cm^{-1})

$(C_2H_5)_4NSeCl_3$[a]			$(C_2H_5)_4NSeBr_3$[b]	
CH_3NO_2 soln	CH_3CN soln	Assignment and approx description (C_{2v})	CH_3NO_2 soln	Assignment and approx description (C_{2v})
519 w				
412 w, p	412 mw, p	Cation		
383		Cation	264 vw, br	$\nu_1(A_1)$ unique Se-Br
338 w, p	342 m, p	$\nu_1(A_1)$ unique Se–Cl str	187 sh, w	$\nu_4(B_1)$ antisym Br-Se-Br str
254 mw, p	252 mw, p	$\nu_2(A_1)$ sym Cl-Se-Sl str	155 m, p	$\nu_2(A_1)$ sym Br-Se-Br str
228 w	231 w	$\nu_4(B_1)$ antisym Cl-Se-Cl str		

[a] Kr, 6471 Å. [b] Kr, 5682 Å.

Taken as a whole the Raman, infrared, conductivity, and molecular weight data indicate the existence of discreet SeX_2CN^- species in solution and in the solid state. However, limited association in the solid state (as for $SeBr_2(tmtu)$,[10] tmtu = tetramethylthiourea) or slight dissociation in solution cannot be ruled out completely.

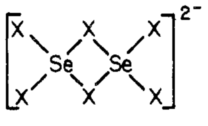
Trihaloselenium(II) Salts. Tetraethylammonium trichloro- and tribromoselenate(II) were prepared *via* the reaction of tetraethylammonium selenocyanate with 2 mol of halogenating agent (eq 3 and 4). The production of cyanogen

$$(C_2H_5)_4NSeCN + 2SO_2Cl_2 \rightarrow (C_2H_5)_4NSeCl_3 + ClCN + 2SO_2 \quad (3)$$

$$(C_2H_5)_4NSeCN + 2Br_2 \rightarrow (C_2H_5)_4NSeBr_3 + BrCN \quad (4)$$

halide and sulfur dioxide as indicated by eq 3 and 4 was assumed. Pure products were not obtained utilizing other alkylammonium selenocyanates.

Solid-State Structure. These new selenium(II) species are apparently halogen analogs of the known selenium triselenocyanate anion.[12] The structure of the latter in $KSe(SeCN)_3 \cdot {}^1/_2H_2O$ is known; the anion is dimeric in the solid state with the selenium atoms forming a planar array of D_{2h} symmetry.[13] A number of other species with similar structures are well known, *e.g.*, I_2Cl_6,[14] $[(etu)_2TeBr_2Te(etu)_2]^{2+}$ (etu = ethylenethiourea),[15] and $[Te_2(tu)_6]^{4+}$ (tu = thiourea).[16] It therefore appears reasonable to suggest the dimeric structure I for the trihaloselenate(II) anions in the solid state.



I (D_{2h})

The infrared and Raman spectral data listed in Table III are consistent with structure I for the trihaloselenate(II) anions. Thus the lack of matching infrared and Raman frequencies seen in Table III is expected for structure I where the mutual exclusion rule should apply due to the presence of a center of symmetry. This situation may be contrasted with data for the dihalocyanoselenate(II) salts where excellent agreement between the fundamental frequencies observed in the infrared and Raman spectra was found (Table I).

Tentative frequency assignments in Table III were made by analogy with those for I_2Cl_6[17] assuming structure I. An

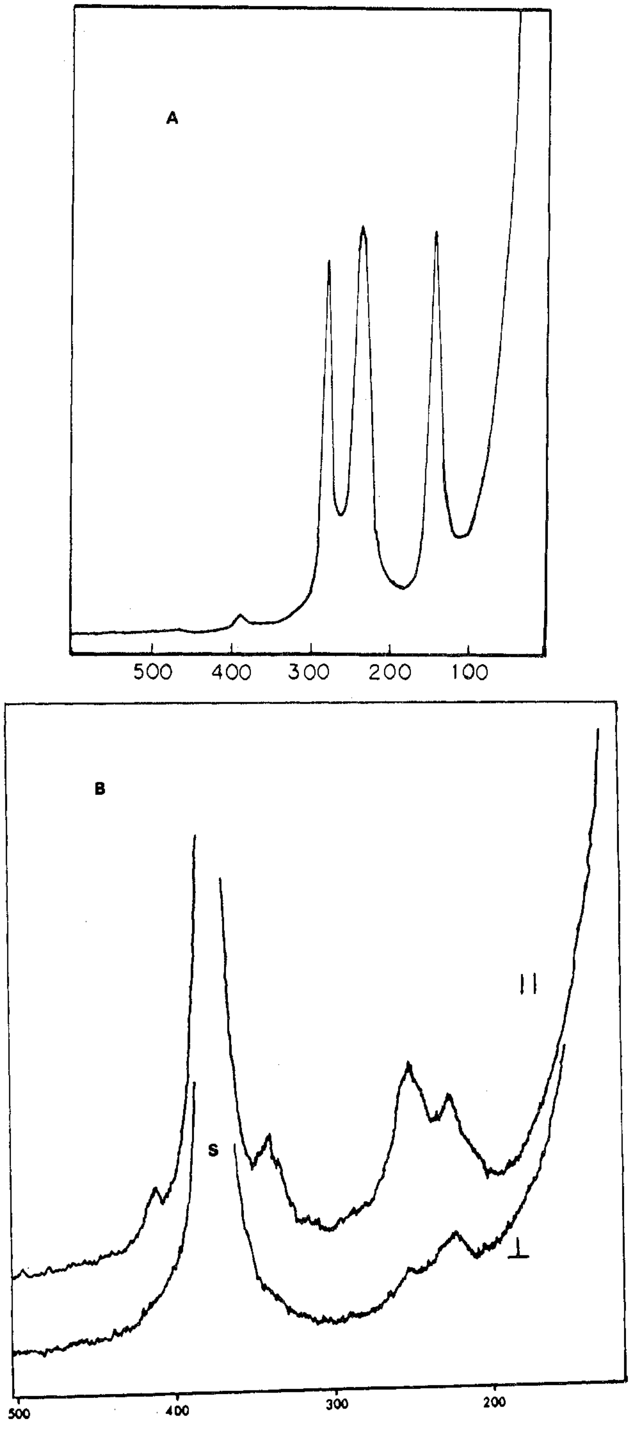


Figure 1. Laser Raman spectrum of $(C_2H_5)_4NSeCl_3$: A, solid state; B, solution, S = solvent absorption. Ordinates, cm^{-1}.

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interesting feature of the spectra is the "crossover" which occurs with respect to the highest frequency mode. In $Se_2Cl_6^{2-}$ the highest frequency absorption seen is a Raman-active mode, $\nu_1(A_{1g})$, while for $Se_2Br_6^{2-}$ infrared-active mode or modes lie at highest frequency. This sort of inversion has been observed previously in compounds containing linear X-M-X [M = Se, Te; X = Cl, Br] systems[10,18] and supports the existence of such groupings in the present case.

Solution Structure. Solution Raman spectral data for $(C_2H_5)_4NSeCl_3$ and $(C_2H_5)NSeBr_3$ may be found in Table IV while the solid-state and acetonitrile solution spectra of $(C_2H_5)_4NSeCl_3$ are reproduced in Figure 1. A comparison of the observed frequencies and relative intensities for the trihaloselenate(II) salts in solution *vs.* the solid state shows that substantial changes in the number of peaks observed and the absorption frequencies occur. In addition, conductivity data indicate that the trihaloselenate(II) salts behave as 1:1 electrolytes in nitromethane solution. The Raman spectra and conductivity data may be easily interpreted if it is assumed that the dimeric anion in the solid state dissociates in solution (eq 5). The SeX_3^- ion so produced is expected to

$$[Se_2X_6]^{2-}(s) \rightarrow 2[SeX_3]^-(solv) \qquad (5)$$

be a T-shaped molecule (C_{2v}) exhibiting six fundamental absorptions, 3 A_1, 2 B_1, and B_2. Of these, three high-frequency modes are expected, 2 A_1 and B_1.

Despite solubility problems, the observed spectrum for $(C_2H_5)_4NSeCl_3$ in nitromethane and acetonitrile (Figure 1) solution corresponds closely to that expected assuming the presence of $[SeCl_3]^-$(solv). Two polarized and one depolarized absorptions are seen in the Se-Cl stretching region and are reasonably assigned to the unique Se-Cl (ν_1, A_1), symmetric Cl-Se-Cl (ν_2, A_1), and antisymmetric Cl-Se-Cl (ν_4, B_1) stretching modes, respectively (Table IV). The remainder of the observed peaks are assigned to the tetraethylammonium ion.

Solubility problems were more severe for $(C_2H_5)_4NSeBr_3$ and spectral data could only be obtained in nitromethane solution. Nevertheless it is readily seen (Table IV) that a much simpler spectrum is observed in solution relative to the solid state and that the observed solution spectrum is readily interpreted in terms of a T-shaped C_{2v} structure.

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Registry No. $(CH_3)_4NSeCN$, 31386-68-2; $(C_2H_5)_4NSeCN$, 42531-78-2; $(C_3H_7)_4NSeCN$, 42531-79-3; $(C_4H_9)_4NSeCN$, 7677-15-8; $(CH_3)_4NSeCl_2CN$, 42531-60-2; $(C_3H_7)_4NSeCl_2CN$, 42531-61-3; $(C_3H_7)_4NSeBr_2CN$, 42531-62-4; $(C_2H_5)_4NSeCl_3$, 42531-63-5; $(C_2H_5)_4NSeBr_3$, 42531-64-6.

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Thermal Decomposition of the Higher Oxides of Cesium in the Temperature Range 320-500°[1]

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The thermal decomposition of solid cesium superoxide was investigated over the temperature range 320 to 440° and covered the composition range $Cs_2O_{2.06}$ to $Cs_2O_{3.96}$.[2] As a result of this work it is concluded that there is no solid solution formation, or sesquioxide formation, over the indicated composition range. The reaction path was experimentally determined to be: $2CsO_2(s) = Cs_2O_2(s) + O_2(g)$. The values for Δu°, ΔH°, ΔS°, and K_p were calculated at the mean temperature of 380°. Also, the thermal decomposition of cesium peroxide was studied between 320 and 500°, covering the composition range $Cs_2O_{1.15}$ to $Cs_2O_{1.94}$. The reaction path may be written as: $2Cs_2O_2(s) = 2Cs_2O(s) + O_2(g)$. The values of Δu°, ΔH°, ΔS°, and K_p were calculated at the mean temperature of 410°.

I. Introduction

During the thermal decomposition of alkali metal superoxides, oxygen is reversibly released with the formation of a lower oxide.[3-8] Some investigators have claimed that the alkali metal sesquioxide is formed as an intermediate.[9-11] However, recent thermal decomposition studies have shown the process to proceed without sesquioxide formation. The alkali metal superoxide decomposes first to the peroxide then to the monoxide.[5-8]

The thermal decomposition of cesium superoxide at elevated

(1) Based on work in partial fulfillment of the requirements of the Ph.D. degree of S. P. Berardinelli, Sr.

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