thermodynamic stabilities of the related oxygen adducts. Recently, we have investigated the thermodynamics of oxygenation of the series of Co(m-Xbensacen)·py complexes in low-temperature toluene solutions.[30] Our preliminary results show that the stability order here again is unusual, i.e., Br > Cl > CH$_3$ ≥ CH$_3$O > H. At present, we are unable to explain these trends. Clearly, π interactions appear to be very small. Thus, solvent effects may be of prime importance. Recent studies have documented the importance of solvent effects on redox reactions of various porphyrins.[31,32] In our case, solvents used were different for each type of study so no direct comparisons can be made. Other factors to be considered include steric effects related to the large sulfur atoms and/or kinetic stability differences related to σ and π interactions and their effect on the rate of the "on" and "off" oxygenation reactions.

Acknowledgment. S.C.C. gratefully acknowledges financial support for these investigations from the National Institutes of Health, Grant HL 15640, from the Heart, Lung and Blood Institute.

Registry No. I (X = H, Y = S)·py, 68843-00-5; I (X = p-CH$_3$, Y = S)·py, 68842-96-6; I (X = p-CH$_3$O, Y = S)·py, 68842-97-7; I (X = p-Br, Y = S)·py, 68842-98-8; I (X = p-Cl, Y = S)·py, 68842-99-9; I (X = H, Y = O)·py, 50723-30-3; I (X = p-CH$_3$, Y = O)·py, 68842-94-4; I (X = p-CH$_3$O, Y = O)·py, 68924-08-3; I (X = p-Br, Y = O)·py, 68842-95-5; I (X = p-Cl, Y = O)·py, 68850-90-8; I (X = H, Y = S)·py·O$_2$, 68851-23-0; I (X = p-CH$_3$, Y = S)·py·O$_2$, 68851-19-4; I (X = p-CH$_3$O, Y = S)·py·O$_2$, 68851-20-7; I (X = p-Br, Y = S)·py·O$_2$, 68851-21-8; I (X = p-Cl, Y = S)·py·O$_2$, 68851-22-9; I (X = H, Y = O)·py·O$_2$, 36466-13-4; I (X = p-CH$_3$, Y = O)·py·O$_2$, 68851-15-0; I (X = p-CH$_3$O, Y = O)·py·O$_2$, 68851-16-1; I (X = p-Br, Y = O)·py·O$_2$, 68851-17-2; I (X = p-Cl, Y = O)·py·O$_2$, 68851-18-3; I (X = m-CH$_3$, Y = S)·py, 85422-52-2; I (X = m-CH$_3$O, Y = S)·py, 85422-53-3; I (X = m-Br, Y = S)·py, 85422-54-4; I (X = m-Cl, Y = S)·py, 85422-55-5; I (X = m-CH$_3$, Y = O)·py, 85422-56-6; I (X = m-CH$_3$O, Y = O)·py, 85422-57-7; I (X = m-Br, Y = O)·py, 85422-58-8; I (X = Cl, Y = O)·py, 85422-59-9; I (X = m-CH$_3$, Y = S)·py·O$_2$, 85422-60-2; I (X = m-CH$_3$O, Y = S)·py·O$_2$, 85422-61-3; I (X = m-Br, Y = S)·py·O$_2$, 85422-62-4; I (X = m-Cl, Y = S)·py·O$_2$, 85442-21-3; I (X = m-CH$_3$, Y = O)·py·O$_2$, 85422-63-5; I (X = m-CH$_3$O, Y = O)·py·O$_2$, 85422-64-6; I (X = m-Br, Y = O)·py·O$_2$, 85422-65-7; I (X = m-Cl, Y = O)·py·O$_2$, 85422-66-8.

Supplementary Material Available: Listings of measured and calculated EPR parameters for all complexes (4 pages). Ordering information is given on any current masthead page.

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Zintl Anions from the Extraction of Zintl Phases with Non-Amine Solvents: Isolation of $(Me_4N)_4Sn_9$, $[K(HMPA)_2]_4Sn_9$, and K_4SnTe_4 and Structural Characterization of $(Bu_4N)_2M_x$ ($M = Te$, $x = 5$; $M = Se$, $x = 6$; $M = S$, $x = 6$)

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Received July 16, 1982

Polyatomic main-group anions like Sn_9^{4-}, Te_5^{2-}, Se_6^{2-}, S_6^{2-}, and $SnTe_4^{4-}$ have been isolated without the use of cryptate ligands. The polychalcogenides $(Bu_4N)_2M_x$ (where M = Te, x = 5; M = Se, x = 6; M = S, x = 6; Bu = n-C$_4$H$_9$) are obtained by the aqueous extraction of binary alkali-metal/main-group alloys in the presence of Bu$_4$NBr. These polychalcogenides are isomorphous and have been structurally characterized by X-ray crystallography. The nonastannide(4−) anion has been isolated both as the tetrakis(tetramethylammonium) compound, $[(CH_3)_4N]_4Sn_9$, and as the HMPA (hexamethylphosphoric triamide) solvate, $[K(HMPA)_2]_4Sn_9$. Both compounds are somewhat thermally unstable at 25 °C. The compound K_4SnTe_4 has been isolated by the aqueous extraction of ternary K/Sn/Te alloys.

Although the existence of solution-phase polyatomic main-group anions has been known for over 50 years,[1] they have received very little attention relative to other major classes of clusters (e.g., borane and transition-metal polyhedra). Recently there has been renewed interest in the homo- and heteroatomic main-group polyanions (Zintl anions) derived from the Zintl phases,[2] which are alloys composed of an alkali or alkaline-earth metal and one or more main-group elements. Numerous examples of polyanions devoid of intercluster metal–metal interactions such as Sn_9^{4-},[3] $Tl_2Te_2^{2-}$,[4] Sb_7^{3-},[5] and Bi_4^{2-}[6] have been isolated by Corbett and co-workers through the use of cryptate ligands in amine solvents.[7] Schäfer and co-workers have prepared (by high-temperature methods) and characterized a large number of Zintl phases that contain substantial intercluster interaction. Recent examples include the two structurally different forms of $(Si_2As_4{}^{6-})_n$ in $Ca_3Si_2As_4$[8] and $Sr_3Si_2As_4$[8] and the $(AlAs_3{}^{6-})_n$ anion[9] in Ca_3AlAs_3.[10] We would like to report the convenient preparation and characterization of several novel main-group anions, without the use of cryptates or amine solvents. examples include the structurally characterized isomorphous series of polychalcogenides $(Bu_4N)_2M_x$ (M = Te, x = 5; M = Se, x = 6; M = S, x = 6), noncryptated nonastannide(4−) anions such as $(Me_4N)_4Sn_9$ and $[K(HMPA)_2]_4Sn_9$, and anhydrous Zintl phases such as K_4SnTe_4.

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(1) For a discussion of selected early works in the field of main-group polyanions, see: Jolly, W., Ed. "Metal-Ammonia Solutions"; Bowden, Hutchinson and Ross: Stroudsburg, PA, 1972.

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(7) Encasement of K$^+$ with the cryptate is believed to hinder electron transfer to K$^+$ from the anionic cluster, thereby preventing reversion to the alloy phase.

(8) Eisenmann, B.; Schäfer, H. *Z. Anor. Allg. Chem.* **1982**, *484*, 142–152.

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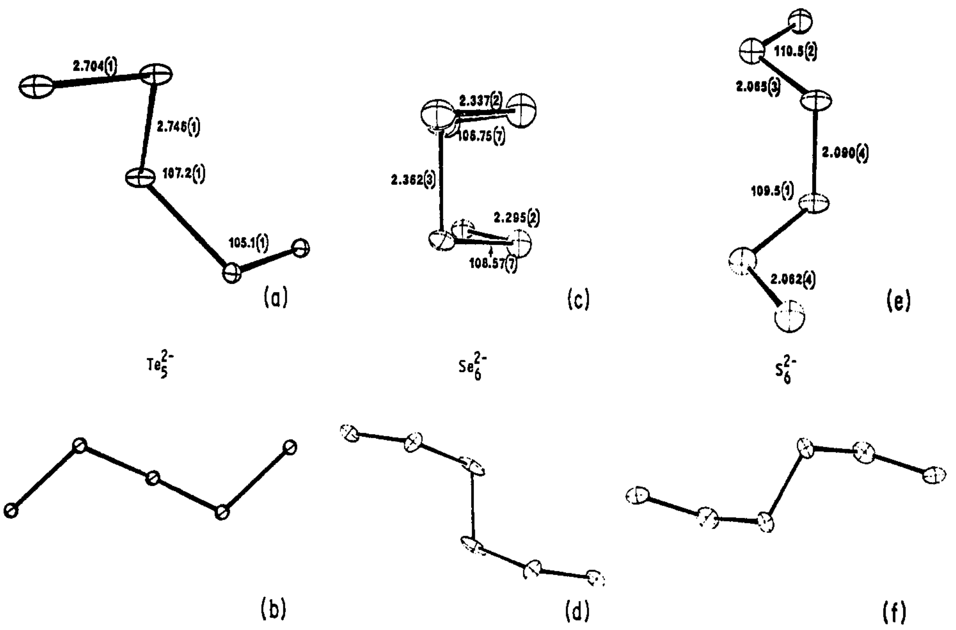

Figure 1. Structures of the polychalcogenides Te_5^{2-}, Se_6^{2-}, and S_6^{2-}. The bottom row contains views parallel to the crystallographic twofold axis.

Table I. Selected Physical Properties of the Polychalcogenides

		Te_5^{2-}	Se_6^{2-}	S_6^{2-}
bond lengths, Å		Te(1)-Te(2) = 2.746 (1)	Se(1)-Se(1′) = 2.362 (3)	S(1)-S(1′) = 2.090 (4)
		Te(2)-Te(3) = 2.704 (1)	Se(1)-Se(2) = 2.337 (2)	S(1)-S(2) = 2.065 (3)
			Se(2)-Se(3) = 2.295 (2)	S(2)-S(3) = 2.062 (4)
bond angles, deg		Te(2)-Te(1)-Te(2′) = 107.2 (1)	Se(1)-Se(1′)-Se(2) = 106.75 (7)	S(1)-S(1′)-S(2) = 109.5 (1)
		Te(1)-Te(2)-Te(3) = 105.1 (1)	Se(1)-Se(2)-Se(3) = 108.57 (7)	S(1)-S(2)-S(3) = 110.5 (2)
visible abs,[a] (nm)	25 °C	375 (vbr), 530	385 (sh), 440, 625 (br)	605
	−90 °C	375 (sh), 530[b]	385 (sh), 440, 615 (br)[b]	340, 462
Raman,[c] cm^{-1}	solid	195, 170	285, 255 (sh), 240	440, 395
	soln	195, 170	405, 285, 235	538

[a] In acetone solution. Abbreviations: br = broad, sh = shoulder, v = very. [b] The absorption bands are sharper at −90 °C than at 25 °C. [c] Excitation at 514 nm.

Results

When the Zintl phase K_2T_3[11] is treated with concentrated aqueous Bu_4NBr, a black solid precipitates from a bright purple solution. Filtration, drying, and recrystallization from acetone at −40 °C gives good yields of large, metallic black crystals of composition $(Bu_4N)_2Te_5$. Since K_2Te_3 is completely soluble in water, the formation of $(Bu_4N)_2Te_5$ must be accompanied by the formation of lower tellurides, Te_x^{2-} ($x < 3$).

The structure of $(Bu_4N)_2Te_5$ at 125 K[12] consists of isolated tetrabutylammonium cations and the novel pentatelluride(2−) anion (Figure 1a). The Te_5^{2-} anion resides on a crystallographic twofold axis (Figure 1b) with the axis passing through the central Te atom. Distances in this and the other chalcogenides are reported in Table I. The Te_5^{2-} anion closely resembles a small section of the infinite spiral chain of Te atoms present in elemental tellurium, with the average Te–Te distance in Te_5^{2-} (2.725 (1) Å) shorter than the corresponding distance in the element[13] (2.835 (2) Å) and comparable to the Te–Te distances in $(cryptK)_2Te_3{\cdot}en$ (2.692 (5) and 2.720 (4) Å) reported by Cisar and Corbett[14] or in $MgTe_2$ (2.70 (1) Å).[15]

Visible absorption and Raman data for Te_5^{2-} are presented in Table I. With the structural characterization of Te_5^{2-}, the structures of all pentachalcogenides, M_5^{2-} (M = Te, Se, S), are now known.

Treatment of the homogeneous phase disodium hexaselenide, Na_2Se_6,[16] prepared from the reaction of Na_2Se and Se, with aqueous solutions of Bu_4NBr results in a dark black-green precipitate. Recrystallization from acetone gives high yields of well-formed black crystals (appearing green when powdered and diluted into KBr). The structure[17] shows the compound to consist of isolated tetrabutylammonium cations and the novel hexaselenide(2−) anion (Figure 1c). The Se_6^{2-} anion is bisected by a crystallographic twofold axis at

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(11) Klemm, W.; Sodomann, H.; Langmesser, P. *Z. Anorg. Allg. Chem.* **1939**, *241*, 281.

(12) All structures discussed in this paper were solved with the UCLA Crystallographic Computing Package of C. E. Strouse. All data was collected in the θ–2θ scanning mode. Crystal data for $(Bu_4N)_2Te_5$ at 125 K: $C_{32}H_{72}N_2Te_5$, M_r = 1122; monoclinic; space group $C2/c$; a = 26.308 (9), b 12.633 (6), c = 19.938 (6) Å; β = 138.38 (2)°; Z = 4; Mo Kα radiation, λ = 0.71059 Å; Syntex $P2_1$ diffractometer; μ = 33 cm^{-1}. An absorption correction was applied to the 1931 observed reflections with $F_o^2 > 3\sigma$ (F_o^2 criteria); the structure (non-H atoms) was solved by a combination of direct methods and difference Fourier syntheses. All H atom positions were located or calculated to yield a final R = 0.027 and R_w = 0.032 with all non-H atoms refined anisotropically and H atoms refined isotropically.

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(17) Crystal data for $(Bu_4N)_2Se_6$ at 125 K: $C_{32}H_{72}N_2Se_6$, M_r = 958; monoclinic; space group $C2/c$; a = 22.358 (9), b = 13.895 (5), c = 20.680 (10); β = 137.95 (3)°; Z = 4; Mo Kα radiation, λ = 0.71069 Å; Syntex $P2_1$ diffractometer. A total of 1512 out of 2493 reflections were considered observed with $F_o^2 > 5\sigma(F_o^2)$; solution and refinement as for $(Bu_4N)_2Te_5$ gives R = 0.042 and R_w = 0.048. Hydrogen atom positions were not refined.

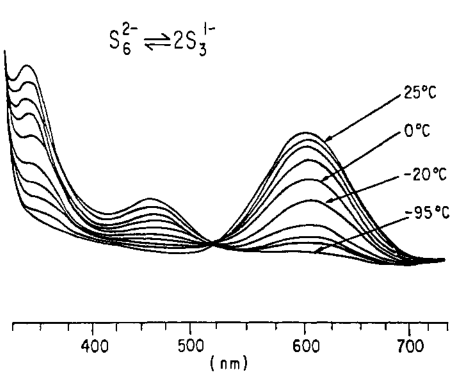

Figure 2. Visible absorption spectrum showing the $S_6^{2-} \rightleftharpoons 2S_3^-$ equilibrium in acetone as a function of temperature.

the midpoint of the central (Se(1)–Se(1′)) bond (Figure 1d). As with Te_5^{2-}, there is a slight lengthening of the central Se–Se bond relative to the outer Se–Se bonds. All Se–Se distances in Se_6^{2-} are shorter than those in the trigonal form of Se (2.373 (5) Å[18]).[19] Although very long selenium chains exist in liquid Se, the Se_6^{2-} anion is believed to be the largest Se chain characterized in a solid and can be compared with the Se_3^{2-} anion in $BaSe_3$[20] (Se–Se = 2.40 (5) Å) and Se_5^{2-} in Rb_2Se_5[21] (Se–Se from 2.31 (2) to 2.37 (2) Å).

The reaction of the yellow-brown material of nominal composition Na_2S_3 (prepared from $Na_2S + 2S$) with aqueous solutions of Bu_4NBr rapidly produces a bright orange-red precipitate and a nearly colorless solution. Filtration, drying, and recrystallization from acetone gives high yields of dark red (at 25 °C) needles. The material is identified as $(Bu_4N)_2S_6$ on the basis of elemental analysis[22] and an X-ray structure determination. At 125 K the structure[23] consists of tetrabutylammonium cations and unbranched hexasulfide(2−) anions (Figure 1e). In contrast to the paucity of structural data on polytellurides and polyselenides, there are numerous examples of polysulfides. Since the admirable, but crude, solution of the structure of Cs_2S_6 in 1953,[24] polysulfides such as Rb_2S_5,[21] K_2S_5,[25] Tl_2S_5,[26] Na_2S_4,[27] and Cs_2S_5[28] have been structurally characterized.

When red crystals of $(Bu_4N)_2S_6$ are dissolved in acetone at room temperature, a brilliant blue solution is obtained. It has been shown previously that the blue S_3^- ion is present, among other species, in solutions of alkali polysulfides in polar solvents,[29] in solutions of sulfur in ammonia,[30] in sulfur containing molten salts,[31] and in minerals like ultramarine.[32] Thus, the blue solutions obtained from dissolution of $(Bu_4N)_2S_6$ consist mostly of S_3^- are evidenced by the single visible absorption at 605 nm. The dissociation $S_6^{2-} \rightleftharpoons 2S_3^-$ is also supported by Raman spectroscopy. In solutions of $(Bu_4N)_2S_6$ at room temperature, the Raman bands at 445 and 390 cm^{-1} observed in solid S_6^{2-} are very weak compared to the intense 538-cm^{-1} band characteristic of S_3^-.[30] The dissociation $S_6^2 \rightarrow 2S_3^-$ observed at 25 °C is reversed upon concentrating or cooling the solution (i.e., S_6^{2-} is deposited). The dimerization of two S_3^- to S_6^{2-}, as a function of temperature in acetone solution, can be observed by visible spectroscopy (Figure 2).

If an analogous homolytic bond cleavage is considered for the polyanions of the heavier group 6B elements, a greater extent of dissociation might be anticipated if the primary factor influencing dissociation was the bond strength of the element. In fact, on the basis of visible absorption and Raman spectroscopies, the extent of dissociation apparently decreases for the heavier elements with $S_6^{2-} \gg Se_6^{2-} > Te_5^{2-}$. Inspection of the data in Table I shows no dramatic change in the Raman spectra of Se_6^{2-} or Te_5^{2-} when the solid-state spectra are compared with the solution spectra,[33] in contrast to the case for the S_6^{2-} system. Also, no prominent changes in color or visible light absorpton are observed when dilute solutions of $(Bu_4N)_2Se_6$ or $(Bu_4N)_2Te_5$ are cooled from 25 to −80 °C (Table I). In contrast, major changes are observed in the S_6^{2-} system under these conditions (Table I). Thus, it seems reasonable to ascribe the relative degree of dissociation of these polychalcogenides to the preferential solvation of the smaller sulfur polyanions.

In addition to the tetraalkylammonium polychalcogenides, we have been able to synthesize and isolate other types of main-group anions such as the highly reactive 22-electron *nido*-nonastannide(4−) anion (Sn_9^{4-}), without the use of cryptates. Treatment of a DMF solution of Me_4NBPh_4 with an alloy of nominal composition K_4Sn_9 instantly gives a red-brown precipitate, indentified as the highly insoluble[34] $(Me_4N)_4Sn_9$ by elemental analysis.[35] Tetrakis(tetramethylammonium) nonastannide is thermally unstable, decomposing slowly at 25 °C (or very rapidly at 90 °C) to give nearly quantitative yields of Me_3N and lower yields of various methylated stannanes, principally hexamethyldistannane, Me_6Sn_2.[36] However, we have found certain solvated K salts of Sn_9^{4-} to be more convenient and soluble sources of the nonastannide(4−) anion. When K_4Sn_9 is dissolved in 1:1 mixture of en and HMPA at 25 °C and then the en is slowly removed, nearly quantitative yields of large red-black crystals were obtained and identified as $[K(HMPA)_2]_4Sn_9$ by elemental analysis[37] and ^{119}Sn NMR.[38]

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(19) For a comparison to other Se–Se distances, see: Cordes, A. In "Selenium"; Zingaro, R., Cooper, W., Eds.; Van Nostrand-Reinhold: New York, 1974.

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(21) Böttcher, P. *Z. Kristallogr.* **1979**, *150*, 65–73.

(22) Anal (Galbraith Analytical Laboratories, Knoxville, TN). Calcd for $C_{32}H_{72}N_2S_6$: C, 56.77; H, 10.64; N, 4.14; S, 28.45. Found: C, 56.35; H, 10.46; N, 4.04; S, 28.91.

(23) Crystal data for $(Bu_4N)_2S_6$ at 125 K: $C_{32}H_{72}N_2S_6$, $M_r = 676$; monoclinic; space group $C2/c$; $a = 21.098$ (11), $b = 13.783$ (7), $c = 15.477$ (6) Å; $\beta = 115.30$ (4)°; $Z = 4$; Mo Kα radiation, $\lambda = 0.71069$ Å; Syntex P2$_1$ diffractometer. A total of 1512 out of 2493 reflections measured were considered observed with $F_o^2\ g\ 3\sigma(F_o^2)$; solution and refinement as for $(Bu_4N)_2Se_6$ gave $R = 0.048$ and $R_w = 0.060$. Since solid $(Bu_4N)_2S_6$ is bright orange at −196 °C and dark red at 25 °C, the structure was independently redetermined at 25 °C on a different crystal. However, the solution of the 25 °C data set showed the bonded and nonbonded distances in S_6^{2-} to be the same within 0.02 Å as in the 125 K structure.

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(30) Chivers, T.; Lan, C. *Inorg. Chem.* **1982**, *21*, 453.

(31) Gruen, D.; McBeth, R.; Zielen, A. *J. Am. Chem. Soc.* **1971**, *93*, 6691.

(32) Hofman, V.; Herzenstiel, E.; Schonemann, E.; Schwarz, K. *Z. Anorg. Allg. Chem.* **1969**, *367*, 119.

(33) Although the bands at 285 and 250 cm^{-1}, which appear at 290 and 245 cm^{-1} in solution, are still the dominant feature of the Raman spectrum of Se_6^{2-}, a new band appears at 405 cm^{-1}. This band is reasonably assigned to a lower polyselenide (Se_3^-) by analogy to the S_6^{2-} system.

(34) When larger tetraalkylammonium salts are employed, no precipitate is observed and the Sn_9^{4-} is decomposed to Sn.

(35) Anal (Galbraith Microanalytical Laboratories). Calcd for $C_{16}H_{48}N_4Sn_9$: C, 14.07; H, 3.52; N, 4.10; Sn, 78.30. Found: C, 13.87; H, 3.35; N, 3.92; Sn, 78.05.

(36) $(Me_4N)_4Sn_9$ is heated to 100 °C under vacuum, and the volatiles were fractionated into a series of cold traps. The Me_3N in the −196 °C trap and the Me_6Sn_2 in the −78 °C trap were identified by MS (Me_3N) and MS and ^{1}H NMR (Me_6Sn_2). In addition to Me_6Sn_2, several higher methylated stannanes were observed in the MS of the pyrolysis residue.

(37) Anal (Galbraith Microanalytical Laboratories). Calcd for $C_{48}H_{144}N_{24}O_8P_8K_4Sn_9$: C, 21.68; H, 5.42; N, 12.65; P, 9.33; K, 5.89: Sn, 40.22. Found: C, 21.41; H, 5.75; N, 12.25; P, 8.29; K, 5.75; Sn, 38.51.

(38) When dissolved in en, $[K(HMPA)_2]_4Sn_9$ displays a five-line spectrum in the ^{119}Sn NMR essentially identical with that previously reported for Na_4Sn_9 in en.[39]

(39) Rudolph, R.; Wilson, W.; Parker, F.; Taylor, R.; Young, D. *J. Am. Chem. Soc.* **1978**, *100*, 4629.

It is also possible to isolate unsolvated Zintl phases from the aqueous extraction of certain ternary alloys. Aqueous extraction of the ternary Zintl phase, obtained from the high-temperature reaction of KSn with Te, gives a bright red-orange solution. Filtration and evaporation to near dryness, followed by treatment with DMF or acetone, gives nearly quantitative yields of K_4SnTe_4. The tetrapotassium tetratellurastannate[40] was identified by elemental analysis[41] and ^{125}Te and ^{119}Sn NMR spectroscopies.[42] A solvate of Na_4SnTe_4 was previously isolated,[43] but no analytical data were reported.

In summary, the results presented here show that a very large number of novel materials can be obtained by extraction of various Zintl phases. The isolation of Zintl anions in large amounts, in high yields, and without the use of amine solvents and expensive cryptates should greatly facilitate the study of the chemistry of these polyanions.

Experimental Section

General Considerations. The preparation of the alloys and subsequent reactions are all performed under an argon atmosphere (<1 ppm O_2). The nonaqueous solvents are dried by standard techniques, and all solvents are degassed before use. Ethylenediamine is distilled from a red solution of K_4Sn_9. Raman spectra were obtained in sealed 5-mm Pyrex tubes with 514.5-nm excitation.

]K(HMPA)$_2$]$_4$Sn$_9$. An alloy of nominal composition K_4Sn_9 is prepared by fusion of the elements under Ar in quartz vessels. The alloy (1 g) is dissolved in 10 mL of a 1:1 (v:v) mixture of en/HMPA. Slow removal of the en under vacuum gives >90% yield of black-red crystals of $[K(HMPA)_2]_4Sn_9$, which were identified as described in the text. This material decomposes slowly at 25 °C and should be stored at −78 °C.

$[(CH_3)_4N]_4Sn_9$. The alloy K_4Sn_9 is added to excess $(CH_3)_4NB(C_6H_5)_4$[44] in DMF. The red-brown precipitate (identified as described in the text) is filtered and dried briefly under vacuum to give a quantitative yield of $[(CH_3)_4N]_4Sn_9$. This material should be stored at −78 °C.

Polychalcogenides $(Bu_4N)_2M_x$ ($M = Te$, $x = 5$; $M = Se$, $x = 6$; $M = S$, $x = 6$). The preparations of these materials are essentially identical. Typically, 1–3 g of the binary compounds K_2Te_3 (from K + Te), Na_2Se_6 (from Na_2Se + Se) and "Na_2S_3" (from Na_2S + S) are dissolved in 5–10 mL of water containing a twofold excess of Bu_4NBr (recrystallized twice from ethyl acetate). The reactions are stirred overnight at 25 °C and filtered. Drying under vacuum followed by slow cooling of concentrated acetone solutions to −40 °C gives high yields (ca. 60% for Te_5^{2-} and >90% for Se_6^{2-} and S_6^{2-}) of the polychalcogenides.

K_4SnTe_4. The alloy KSn (prepared from the fusion of K + Sn) is melted with 1 equiv of Te under argon. After cooling, the material is crushed and the plug of Sn removed. The finely powdered ternary K/Sn/Te alloy is extracted with water (~5 mL of H_2O/g of alloy for 30 min), filtered, and evaporated until the solution is saturated. Treatment of the deep red-orange solution with DMF gives a bright orange-red solid. The solid is stirred with acetone, filtered, and dried briefly under vacuum to give >80% yield of analytically pure K_4SnTe_4 as a dark black-red powder.

Acknowledgment. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38. We are grateful to the groups of Drs. J. M. Williams and W. M. Butler for the use of the diffractometers and many helpful discussions. We thank Drs. J. P. Haushalter and R. P. Van Duyne for the Raman spectra, and Dr. J. Hunt for the use of the variable-temperature visible absorption spectrometer.

Registry No. $[K(HMPA)_2]_4Sn_9$, 85533-98-8; $[(CH_3)_4N]_4Sn_9$, 85533-92-2; $(Bu_4N)_2Te_5$, 85533-94-4; $(Bu_4N)_2Se_6$, 85533-95-5; $(Bu_4N)_2S_6$, 85533-96-6; K_4SnTe_4, 85533-99-9.

Supplementary Material Available: Listings of atomic positions and thermal parameters, observed and calculated structure factors, and distances and angles within the Bu_4N^+ cation (27 pages). Ordering information is given on any current masthead page.

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(40) A Raman and Mössbauer study of $SnTe_4^{4-}$ and its metal complexes will be published elsewhere.

(41) Anal (Schwarzkopf Microanalytical Laboratories, Woodside, NY). Calcd for K_4SnTe_4: K, 19.87; Sn, 15.16; Te, 64.97. Found: K, 19.56; Sn, 15.43; Te, 64.52.

(42) ^{119}Sn NMR: three peaks in the ratio 0.136:1.000:0.133; (calculated for Sn:Te (1:4) 0.140:1.000:0.140) with $J(^{125}\text{Te}-^{119}\text{Sn}) = 2860$ Hz. ^{125}Te NMR: five peaks in the ratio 0.054:0.047:1.000:0.047:0.054 (calculated 0.043:0.038:1.000:0.038:0.043) with $J(^{125}\text{Te}-^{117}\text{Sn}) = 2740$ Hz. These compare favorably with literature values for Na_4SnTe_4[43] in solution.

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(44) Prepared from $(CH_3)_4NBr$ and $NaB(C_6H_5)_4$ in water.

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Phosphazenes. 2. Synthesis of Ketone- and Enol-Substituted Cyclotriphosphazenes

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Received August 31, 1982

The reactions of the enolate anions of acetaldehyde, acetone, and acetophenone with hexachlorocyclotriphosphazene and methylpentachlorocyclotriphosphazene have been investigated. These reactions led exclusively to enol-substituted phosphazene compounds. Acetonyl-substituted phosphazene compounds were synthesized via the reaction of 2-methoxyallyl bromide with a metallophosphazene followed by hydrolysis. The 2-methoxyallyl-substituted phosphazene product was found to undergo a rapid migration of the double bond prior to the hydrolysis step. The mechanistic aspects of the various reactions are discussed as well as the factors that affect the migration of the allylic double bond.

Introduction

Studies of the chemistry of cyclic phosphazene compounds are important for a variety of reasons. Small-ring phosphazenes are ideal "models" for the reactions of high-polymeric phosphazenes,[2] while other interests lie in the use of cyclic compounds as mechanistic probes[3] or in studies related to the bonding within the phosphazene skeleton.[4]

In recent years, the reactions of phosphazenes with lithium,[5,6] Grignard[3,7] or organocopper reagents[8] have been investigated as a means of binding organic substituents directly

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