Table II. Values of the Pseudo-First-Order Anation Rate Constant, k_{an}, at Various Cl^- Ion Concentrations (1.0 *M* Ionic Strength; 45.0°; $NaClO_4$ and NaCl Variable)

$[Cl^-]$, *M*	$10^5 k_{an}$, sec^{-1}		
	Ref 3[a]	This work[b]	Ref 4
0.1	0.34	0.38	0.35
0.2	0.80	0.65	0.70
0.3	1.09	0.85	1.06
0.4	1.31	1.11	1.41
0.5	1.45	1.32	1.76
0.6	1.56	1.56	2.11
0.7		1.70	
0.8		1.90	
0.9		1.85	

[a] 0.001 *M* $HClO_4$. [b] 0.100 *M* $HClO_4$.

tion through the $MOH_2{}^{3+},Cl^-$ ion pair[4] and, by the principle of microscopic reversibility, the apparent first-order aquation rate constant for MCl^{2+} through the $MOH_2{}^{3+},ClO_4{}^-$ ion pair must be greater than the first-order aquation rate constant for the direct aquation of MCl^{2+}.

The values obtained for k_{an} fit the equation for the I_d mechanism with the ion pair $MOH_2{}^{3+},Cl^-$ as intermediate; thus

$$\frac{1}{k_{an}} = \frac{1}{k} + \frac{1}{kQ_o}\frac{1}{[Cl^-]} \qquad (7)$$

where *k* is the rate constant for the interchange of Cl^- for H_2O in reaction 1. The value obtained for *k* from the inverse of the intercept was $(3.48 \pm 0.35) \times 10^{-5}$ sec^{-1}. The value of the ratio of the intercept-to-slope was 1.21 ± 0.13 M^{-1}, in good agreement with the value obtained from equilibrium measurements.

The values of k_{an} obtained by us are listed in Table II where they can be compared with the values of k_{an} obtained by Langford and Muir[3] and with the values of k_{an} calculated by Burnett.[4] The values of k_{an} obtained by Langford and Muir at Cl^- concentrations from 0.1 to 0.4 *M* are larger than those obtained by us because Langford and Muir found *decreasing* values of k_{aq} with *decreasing* Cl^- concentration whereas we found k_{aq} to be independent of Cl^- concentration. Consequently, for a given value of $(k_{aq} + k_{an})$ in eq 5 at 1 *M* ionic strength, the value of k_{aq} from ref 2 is smaller and the value of k_{an} is larger than our values for k_{aq} and k_{an}, respectively. Furthermore, because the k_{an} values in ref 3 at the lower Cl^- concentrations were too large, the plot of k_{an} *vs.* Cl^- concentration must show a larger "bend-over" effect as the Cl^- concentration reaches the region where k_{aq} becomes constant than is the case for our k_{an} values; at Cl^- concentrations above 0.6 *M* k_{an} as predicted by the results of Langford and Muir[3] will not increase as much as observed by us.

The values of k_{an} given by Burnett[4] for 0.5 and 0.6 *M* Cl^- distinctly show the effect of the squared term for the Cl^- concentration in the expression for k_{an} and the calculated values of k_{an} are greater than the values of Langford and Muir being fit by Burnett. The relative importance of this squared term increases approximately twofold as the Cl^- concentration increases from 0.5 to 0.9 *M*. Since the expected increase was not found and k_{an} became essentially constant at 0.8–0.9 *M* Cl^-, it was concluded that the values obtained for k_{an} did not support the postulate that reaction 2 made an important contribution to the anation process in the media used.

Registry No. Chloropentaamminecobalt(III) perchlorate, 15156-18-0.

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Inner-Orbital Binding-Energy Shifts of Antimony and Bismuth Compounds

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Two previous reports[1,2] have described inner-orbital binding-energy shifts for related compounds based on members of the group Va and IVa family of elements. In our first study[1] analogous nitrogen, phosphorus, and arsenic chemical environments were compared both experimentally and theoretically, with the aid of atomic SCF calculations, to determine the relative chemical shifts. The other investigation[2] compared identical compounds of carbon, silicon, germanium, tin, and lead. In each case the chemical shift effects for these compounds were observed to decrease with increasing atomic size, and although part of this effect could be attributed to the increasing atomic radii, the additional decreases were thought to arise from a charge equalization through π bonding. The present work in X-ray photoelectron spectroscopy completes the comparison of the group Va compounds by extending the investigations to include antimony and bismuth compounds. Atomic SCF calculations are presented for the entire series of group Va elements and the experimental data for antimony and bismuth are compared with the previously reported nitrogen, phosphorus, and arsenic measurements.

Experimental Section

Two independent X-ray photoelectron spectrometers of the electrostatic-analyzer type[3] manufactured by Varian were used to collect the binding-energy data reported herein. The description, operation, sample preparation techniques, and reproducibility of the Varian IEE-15 spectrometer have previously been discussed.[1,2,4,5] The corrected binding-energy measurements were referenced to the thin layer of adsorbed hydrocarbon contaminant assuming a value[6] of 285.0 eV for the resulting C "1s" line. The high reproducibility of the Varian spectrometer yielded a standard deviation of *ca.* ±0.3 eV for the binding-energy data obtained from those compounds upon which several replicate measurements were taken. The antimony and bismuth compounds used in this study were commercially available samples of high purity.

Atomic SCF calculations[7] were completed for nitrogen, phosphorus, arsenic, antimony, and bismuth as neutral atoms (with outer electron configuration s^2p^3), 1+ ions (s^2p^2), and 2+ ions (s^2p^1) in the lowest Hund's-rule energy states. The results of these calculations agreed, where such comparisons were possible, with near-limit[8] Hartree–Fock calculations.

Results and Discussion

The Sb "$3d_{3/2}$," "$3d_{5/2}$," and "4d" binding energies are reported in Table I for a series of 15 antimony compounds. The relative area ratio of the Sb "$3d_{3/2}$"-"$3d_{5/2}$" doublet

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Table I. Experimental Binding Energies of Various Antimony Compounds

	Measured binding energy, eV						
		Sb					
	Direct	Direct			Corrected[a]		
Compound	C “1s”	“$3d_{3/2}$”	“$3d_{5/2}$”	“4d”	“$3d_{3/2}$”	“$3d_{5/2}$”	“4d”
$KSbF_6$	286.7	543.8	534.2	39.6	542.1	532.5	37.9
$SbCl_5[(C_6H_5)_3PO]$[b]	285.2	541.7	532.6	37.0	541.5	532.4	36.8
$(C_6H_5)_4PSbCl_6$[c]	285.2	541.2	532.1	36.3	541.0	531.9	36.3
SbF_3	286.0	542.2	532.9	37.4	541.2	531.9	36.4
$K_2H_2Sb_2O_7 \cdot 4H_2O$	285.5	541.8	531.7	36.0	541.3	531.2	35.5
Sb_2O_5	286.9	542.2	532.9	37.8	540.2	531.0	35.9
$Sb(OCOCH_3)_3$	286.6	541.5	532.0	36.6	539.9	530.4	35.0
Sb_2O_3	287.2	541.6	532.3	37.3	539.4	530.1	35.1
SbI_3	286.6	541.5	532.2	37.2	539.9	530.6	35.6
$Sb(SC_{12}H_{25})_3$	285.7	540.1	530.7		539.4	530.0	
$NaSbO_3$	287.4	541.6	532.5	37.0	539.2	530.1	34.6
Sb_2S_3	286.8	540.8	531.5	36.1	539.0	529.7	34.3
Sb_2S_5	287.5	541.2	531.9	36.4	538.7	529.4	33.9
AlSb	286.4	539.3	530.2	34.9	537.9	528.8	33.5
Sb	284.3	537.1	527.8	31.6	537.8	528.5	32.3

[a] Measurements referenced to hydrocarbon-contaminant C “1s” line, assuming a value of 285.0 eV. [b] The phosphorus “2p” binding energy was measured and found to have a value of 134.0 ± 0.2 eV. [c] The phosphorus “2p” binding energy in this compound was 133.2 ± 0.4 eV.

was found to be slightly smaller (1:2) than the expected 2:3 ratio. The greater-than-expected intensity of the Sb “$3d_{5/2}$” line can be explained by a slight contribution of the oxygen “1s” line which appears[9] at *ca.* 531-533 eV depending on whether the oxygen is in a bridging or terminal position. The relative-area ratio of the Sb “$3d_{3/2}$”-“$3d_{5/2}$” peaks did not significantly change when the compound under study contained oxygen, such as $K_2H_2Sb_2O_7$, or when the oxygen resulted from residual spectrometer contamination which presumably was the case in $KSbF_6$. It would not be expected that the relative *position* of the Sb “$3d_{5/2}$” line would be affected significantly by the small oxygen background. Supporting this contention is the intense signal obtained from “d” electrons in general and the fact that the Sb “$3d_{3/2}$”-“$3d_{5/2}$”-“4d” energy level separations remained quite constant at 9.3 ± 0.3 and 495.3 ± 0.4 eV, respectively. The P “2p” binding energy 134.0 ± 0.2 eV in $SbCl_5[(C_6H_5)_3PO]$ agreed with previous work[9] on $(C_6H_5)_3PO$; however, the phosphorus “2p” binding energy 133.2 ± 0.4 eV of $(C_6H_5)_4PSbCl_6$ was higher (*ca.* 1-2 eV) than that of previously studied[10,11] quaternary phosphonium compounds.

Table II contains the Bi “$4f_{5/2}$” and “$4f_{7/2}$” binding-energy measurements from 11 bismuth-containing compounds. The relative peak areas of the Bi “$4f_{5/2}$”-“$4f_{7/2}$” lines were in the expected 3:4 ratio, and these two peaks had a constant energy spacing of 5.3 ± 0.1 eV over the entire range of compounds. The experimental data in Tables I and II show the expected general increase in binding energy with increasing substituent electronegativity.

Table II. Experimental Binding Energies of Various Bismuth Compounds

	Measured binding energy, eV				
		Bi			
	Direct	Direct		Corrected[a]	
Compound	C “1s”	“$4f_{5/2}$”	“$4f_{7/2}$”	“$4f_{5/2}$”	“$4f_{7/2}$”
BiF_3	286.8	168.0	162.8	166.2	161.0
$Bi(SO_4)_3 \cdot H_2O$	285.8	167.4	162.2	166.6	161.4
BiOCl	287.6	167.9	162.7	165.3	160.1
$Bi_2Ti_2O_7$	287.3	167.6	162.2	165.3	159.9
$(BiO)_2Cr_2O_7$	286.5	166.5	161.3	165.0	159.8
BiI_3	286.6	166.4	161.1	164.8	159.5
Bi_2O_3	287.3	167.2	161.8	164.9	159.5
$Bi_2O_4 \cdot 2H_2O$	288.0	167.6	162.4	164.6	159.4
$NaBiO_3$	287.7	167.2	162.0	164.5	159.3
Bi_2S_3	285.9	165.3	160.0	164.4	159.1
Bi	284.3	161.6	156.4	162.4	157.1

[a] Measurements referenced to hydrocarbon-contaminant C “1s” line, assuming a value of 285.0 eV.

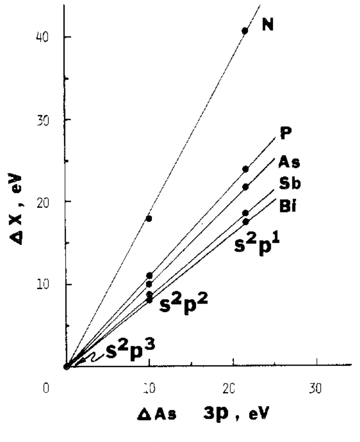

Figure 1. A comparison of the change in inner-orbital energies obtained from atomic SCF calculations of the ground-state atom (with outer electron configuration s^2p^3), the 1+ ion (s^2p^2), and the 2+ ion (s^2p^1) for each member of the group Va elements. The changes in the N 1s, P 2p, As 3p, Sb 3d, and Bi 4f orbital energies (ΔX) were compared with the change in the As 3p orbital energy yielding relative shift effects of 1.00, 0.59, 0.54, 0.46, and 0.43, respectively.

The theoretically determined chemical shifts for the group Va atoms and 1+ and 2+ ions are compared in Figure 1. Atomic SCF calculations were completed on nitrogen, phosphorus, arsenic, antimony, and bismuth for the following outer-electron configurations: s^2p^3 (^4S), s^2p^2 (^3P), and s^2p^1 (^2P). Parallel changes were observed in each of the inner-electron orbital-energy levels after removal of the outermost electrons. The free-atom shifts (ΔX) of the N 1s, P 2p, As 3p, Sb 3d, and Bi 4f electrons were compared with the As 3p shifts resulting in the following relative shifts: N, 1.00; P, 0.59; As, 0.54; Sb, 0.46; Bi, 0.43. The previously observed[2] trend of a smaller binding-energy range with increasing atomic size, from the classical charged-shell atomic

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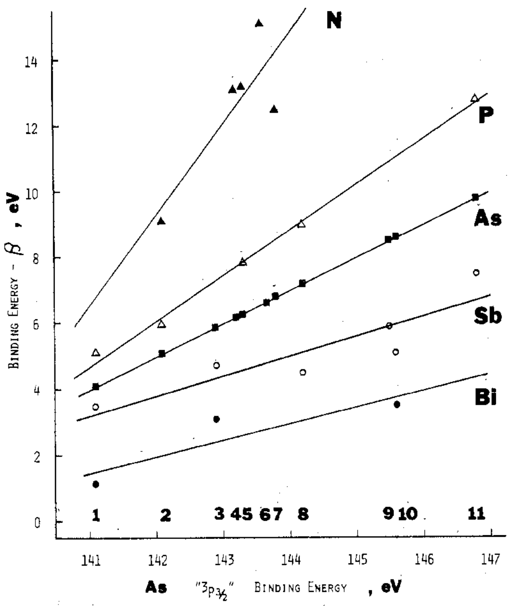

Figure 2. The nitrogen "1s" ($\beta = 389$), phosphorus "2p" ($\beta = 125$), arsenic "$3p_{3/2}$" ($\beta = 137$), antimony "$3d_{5/2}$" ($\beta = 525$), and bismuth "$4f_{7/2}$" ($\beta = 156$) corrected binding energies *vs.* the arsenic "$3p_{3/2}$" binding energies. The relative shifts for the compounds of group Va are as follows: N, 1.00; P, 0.50; As, 0.36; Sb, 0.21; Bi, 0.18. The numbers near the bottom of this figure indicate the position of the binding energies of those compounds having the same number, kind, and arrangement of substituent atoms in the following arsenic compounds: 1, As; 2, $(C_6H_5)_3As$; 3, As_2S_3; 4, As_4N_4; 5, $(C_6H_5)_3AsO$; 6, $NaAsO_2$; 7, $(C_6H_5)_4AsCl$; 8, As_2S_5; 9, As_2O_5; 10, As_2O_3; 11, $KAsF_6$.

model[12] (*i.e.*, $\Delta E \propto 1/r$), was found once again. However, the overall-shift ranges for the group Va elements were significantly lower than those found for the corresponding group IVa elements[2] with the same charge on the ions. It should be noted that the relative shifts with respect to nitrogen in this work are much larger than those previously reported.[1] The difference resulted from what would appear to be an unequal perturbation of the valence electrons upon forming an outer-electron configuration by using d orbitals[1] in a first-row atom such as nitrogen (two separable ranges are actually observed[1] for nitrogen, one with d's and one without d's).

The experimentally measured binding energies for the N "1s", P "2p", As "$3p_{3/2}$", Sb "$3d_{5/2}$", and Bi "$4f_{7/2}$" electrons are plotted against the arsenic "$3p_{3/2}$" binding energies of compounds containing equivalent substituents on the group Va element (Figure 2). Unfortunately, only a small number of related nitrogen compounds[13] which were referenced only with respect to the residual C "1s" line[14] (some of these compounds were not identical with the corresponding arsenic compounds) were available for comparison purposes. However, the results certainly demonstrate general chemical shift effects similar to those observed for the group IVa compounds.[2] The nitrogen-containing compounds exhibit the largest shift effects of group Va and decreasing effects are seen with increasing atomic size. The relative shifts of the group Va compounds are as follows: N, 1.00; P, 0.50; As, 0.36; Sb, 0.21; and Bi, 0.18; they are quite similar to those reported for the group IVa compounds[2] as expected from a comparison of the atomic SCF calculations and the simple atomic radii ratios[2] of the two groups of elements. The considerably smaller experimental values of the relative shifts of As, Sb, and Bi as compared to their free-atom values may possibly be attributed to more $p_\pi \rightarrow d_\pi$ feedback in the compounds of these elements as compared to similar phosphorus compounds.

Registry No. $KSbF_6$, 16893-92-8; $SbCl_5[(C_6H_5)_3PO]$, 18828-04-1; $(C_6H_5)_4PSbCl_6$, 38188-09-9; SbF_3, 7783-56-4; $K_2H_2Sb_2O_7 \cdot 4H_2O$, 10090-54-7; Sb_2O_5, 1314-60-9; $Sb(OCOCH_3)_3$, 6923-52-0; Sb_2O_3, 1309-64-4; SbI_3, 7790-44-5; $Sb(SC_{12}H_{25})_3$, 6939-83-9; $NaSbO_3$, 15432-85-6; Sb_2S_3, 1345-04-6; Sb_2S_5, 1315-04-4; AlSb, 25152-52-7; Sb, 7440-36-0; BiF_3, 7787-61-3; $Bi(SO_4)_3 \cdot H_2O$, 38162-92-4; BiOCl, 7787-59-9; $Bi_2Ti_2O_7$, 12048-51-0; $(BiO)_2Cr_2O_7$, 37-235-828; BiI_3, 7787-64-6; Bi_2O_3, 1304-76-3; $Bi_2O_4 \cdot 2H_2O$, 12-233-293; $NaBiO_3$, 12232-99-4; Bi_2S_3, 1345-07-9; Bi, 7440-69-9.

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Stereochemistry of the Bis(amino)sulfides and -disulfides

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Although the stereochemistry of sulfur-nitrogen compounds has aroused much recent interest,[1-3] little is known of the conformation of species containing several S-N bonds or of the dynamics of the stereochemical processes occurring in such molecules. This note reports the results of a dynamic nmr investigation of several bis(amino)sulfides, $(R_2N)_2S_n$, where R = CH_3, C_2H_5, or *i*-C_3H_7 and $n = 1$ or 2. These compounds represent a series whose behavior should reflect properties of simple sulfur-nitrogen frameworks containing two S-N bonds. In addition the disulfides are of interest because there is no information presently available on the stereochemical relationships within an N-S-S-N unit even though the S-S moiety is of considerable chemical and biological interest.

Experimental Section

The compounds $(R_2N)_2S_n$ (R = CH_3, C_2H_5, C_3H_7; $n = 1, 2$) were prepared *via* the direct reaction of S_nCl_2 with the appropriate amine using a literature method.[4] Nmr spectra were recorded in CCl_2F_2 solutions on an HA-100 spectrometer equipped with variable-

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