erization of $Co(CN)_5NCS^{3-}$ to $Co(CN)_5SCN^{3-}$. Unfortunately, the value of Q is not known, and consequently it is not possible on the basis of the comparison between adjacent and remote attacks of $Co(CN)_5{}^{3-}$ on $Co(NH_3)_5SCN^{2+}$ to ascertain the electron-mediating ability of sulfur attached to cobalt(III). Another comparison involves the reaction of $Co(NH_3)_5SCN^{2+}$ *via* adjacent attack with the reaction of $Co(NH_3)_5NCS^{2+}$ *via* remote attack. On the basis of the simplest thermodynamic argument,[4] we would expect the former reaction to be faster than the latter reaction by a factor of $\sim 6 \times 10^2$.[21] Additional considerations based on steric hindrance for adjacent attack[3] can be invoked to reduce this factor to a value of $\sim 10^2$. The observed factor has a value of 4×10^3 for Cr^{2+} and lies in the range 10^2-2×10^3 for $Co(CN)_5{}^{3-}$. If the lower limit obtained, we would conclude that the high reactivity for attack at S in the $Co(NH_3)_5SCN^{2+}$-Cr^{2+} reaction is absent in the corresponding reaction of $Co(CN)_5{}^{3-}$. Alternatively, if the upper limit were applicable, then the remarkable ability of S bound to Co(III) for mediating the transfer of an electron would be operative. Unfortunately, only a range of rate constants could be established for the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction, and the question of the electron-mediating ability of sulfur bound to cobalt(III) cannot be answered. However, it is noteworthy that the ratio of reactivities for Cr^{2+} attack on S in $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ is remarkably close to the upper limit for the corresponding ratio in the $Co(CN)_5{}^{3-}$ reactions, and this might be taken to indicate that the actual rate constant for the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction is near the upper limit indicated by the measurements. The agreement between these values may, however, be fortuitous. It must be recognized that the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction is extremely fast and may, in fact, be controlled by the rate of ligand addition to $Co(CN)_5{}^{3-}$. Under these circumstances, the Co(II) center cannot exhibit any kinetic discrimination toward various redox reagents and it becomes impossible to ascertain the relative mediating ability of various ligands for electron transfer.

Registry No. $Co(NH_3)_5SCN^{2+}$, 15005-69-3; $Co(CN)_5{}^{3-}$, 14971-18-7; $Co(NH_3)_5NCS^{2+}$, 14970-18-4.

[21] This value is $(3 \times 10^5)^{1/2}$, where 3×10^5 is the equilibrium constant for S to N linkage isomerization.[4]

Contribution from the Laboratory of Inorganic Chemistry, University of Thessaloniki, Thessaloniki, Greece

Tris(dialkyldiselenocarbamates) of Arsenic, Antimony, and Bismuth

G. E. Manoussakis,* C. A. Tsipis, and A. G. Christophides

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In previous papers we have reported the synthesis and spectroscopic study of some arsenic, antimony, and bismuth tris(dithiocarbamate) (tdtc) complexes.[1,2] The interpretation of the spectroscopic results of all those complexes indicated a distorted octahedral stereochemistry.

This work was undertaken to prepare and study the following octahedral complexes containing arsenic, antimony, and bismuth as central atoms and several diselenocarbamates as bidentate ligands: tris(diethyldiselenocarbamato)arsine, $As[SeC(Se)N(C_2H_5)_2]_3$, -stibine, $Sb[SeC(Se)N(C_2H_5)_2]_3$, and -bismuthine, $Bi[SeC(Se)N(C_2H_5)_2]_3$; tris(diisobutyldiselenocarbamato)arsine, $As[SeC(Se)N(C_4H_9)_2]_3$, -stibine, $Sb[SeC(Se)N(C_4H_9)_2]_3$, and -bismuthine, $Bi[SeC(Se)N(C_4H_9)_2]_3$; tris(dibenzyldiselenocarbamato)arsine, $As[SeC(Se)N(CH_2C_6H_5)_2]_3$, -stibine, $Sb[SeC(Se)N(CH_2C_6H_5)_2]_3$, and -bismuthine, $Bi[SeC(Se)N(CH_2C_6H_5)_2]_3$.

Dithiocarbamate complexes of transition and nontransition metals have been extensively studied by many authors. However, the study of diselenocarbamate complexes has been almost limited to those of the transition metals.[3-10] As far as we know nothing is known about the diselenocarbamate complexes of the elements of group Va.

The donor properties and the spectroscopic behavior of the prepared diselenocarbamate compounds are compared to those of analogous sulfur compounds. The $-NR_2$ groups in diselenocarbamates have been selected according to their electron-donating capacity.

Experimental Section

Preparation. The dialkyldiselenocarbamate complexes studied were prepared according to the following general method. In a three-necked flask equipped with a reflux condenser, a mechanical stirrer, and a droping funnel, metal trichloride, MCl_3 (M = As, Sb, or Bi), in a quantity of approximately 10 mmol was mixed with carbon diselenide (≃30 mmol). Carbon tetrachloride (≃150 ml) was used as the solvent. To this mixture a solution of dialkylamine (≃60 mmol) in 50 ml of carbon tetrachloride was added dropwise over a period of 30 min. The mixtures were continuously stirred for 30 min at room temperature and afterward heated for 2 hr at 60-70°. After being cooled, the mixtures were filtered. The precipitates were washed with warm carbon tetrachloride and identified as amine hydrochlorides. The identification was done by comparison of their properties with those of authentic samples. The filtrates were concentrated under vacuum to a small volume (50 ml) and, after the addition of methanol or petroleum ether, tris(dialkyldiselenocarbamates) were obtained. The compounds were then recrystallized from a mixture of chloroform and methanol or from acetone. The recrystallized compounds were quite stable in air and were soluble in carbon tetrachloride, chloroform, acetone, benzene, and dichloromethane. All were practically insoluble in methanol, ethanol, petroleum ether, and water. Analytical data of the prepared compounds are shown in Table I. Carbon diselenide was prepared according to Ives, *et al.*[11]

Measurements. The infrared spectra, for Nujol mulls, chloroform solutions, and KBr disks, were obtained on a Beckman-IR 5A spectrophotometer. Proton nmr spectra were recorded on a Varian A-60A (60 Mc/sec) instrument in deuteriochloroform solutions and benzene solutions, using TMS as an internal standard. The uv-vis spectra were recorded on a Beckman DB-GT spectrophotometer with freshly prepared $CHCl_3$ solutions. The color of these solutions (concentration $\simeq 10^{-5}$ M) in ordinary daylight when freshly prepared was yellow. The yellow color of the solutions progressively decolorized

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Table I. Analytical Data for the Tris(dialkyldiselenocarbamate) Complexes of Arsenic, Antimony, and Bismuth

Compd	Color	Yield, %	Mp, °C	% Se		% C		% N		% H		% metal		Mol wt	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$As[SeC(Se)N(C_2H_5)_2]_3$	Yellow	80	205 dec	59.16	58.99	22.48	22.08	5.24	5.19	3.75	3.62	9.37	9.62	800.8	798
$Sb[SeC(Se)N(C_2H_5)_2]_3$	Yellow	82	163-165	55.90	55.80	21.24	21.02	4.96	4.83	3.54	3.60	14.36	14.21	847.5	845
$Bi[SeC(Se)N(C_2H_5)_2]_3$	Reddish	85	227 dec	50.68	50.54	19.26	19.23	4.49	4.49	3.21	3.15	22.36	22.38	934.8	936
$As[SeC(Se)N(C_4H_9)_2]_3$	Orange	65	157-159	48.90	48.57	33.44	33.26	4.34	4.48	5.57	5.62	7.74	8.01	968.8	971
$Sb[SeC(Se)N(C_4H_9)_2]_3$	Orange	63	123-124	46.65	46.50	31.90	31.48	4.14	4.15	5.32	5.20	11.99	11.88	1015.5	1020
$Bi[SeC(Se)N(C_4H_9)_2]_3$	Reddish	68	133-135	42.96	42.90	29.38	29.21	3.81	3.78	4.90	4.80	18.95	18.98	1102.8	1099
$As[SeC(Se)N(CH_2C_6H_5)_2]_3$	Yellow	78	192-194	40.40	40.35	46.04	46.08	3.58	3.62	3.58	3.57	6.40	6.36	1172.8	1175
$Sb[SeC(Se)N(CH_2C_6H_5)_2]_3$	Orange	73	157-159	38.85	38.80	44.28	44.32	3.44	3.50	3.44	3.44	9.98	9.95	1219.5	1215
$Bi[SeC(Se)N(CH_2C_6H_5)_2]_3$	Reddish	75	152-154	36.25	36.18	41.32	41.75	3.21	2.98	3.21	3.29	15.99	16.01	1306.8	1299

Table II. Proton Chemical Shifts (τ) in Ppm[a]

Metal	Solvent	$-N(CH_2CH_3)_2$		$-N[CH_2CH(CH_3)_2]_2$			$-N(CH_2C_6H_5)_2$	
		$-CH_2-$	$-CH_3$	$-CH_2-$	$-CH<$	$-CH_3$	$-CH_2-$	$-C_6H_5$
Arsenic	$CDCl_3$	6.03 q	8.62 t	6.24 d	7.68 m	9.01 d	4.89 s	2.59 s
	C_6H_6	6.52 q	9.18 t	6.33 d	7.70 m	9.30 d	4.97 s	2.89 s[b]
Antimony	$CDCl_3$	6.04 q	8.62 t	6.27 d	7.63 m	9.01 d	4.90 s	2.58 s
	C_6H_6	6.54 q	9.15 t	6.35 d	7.66 m	9.28 d	4.96 s	2.89 s[b]
Bismuth	$CDCl_3$	6.07 q	8.59 t	6.30 d	7.56 m	9.01 d	4.92 s	2.61 s
	C_6H_6	6.60 q	9.13 t	6.37 d	7.57 m	9.27 d	4.95 s	2.86 s[b]

[a] Key: q, quartet; t, triplet; d, doublet; m, multiplet; s, singlet. [b] In C_6D_6.

as they aged. Molecular weights were determined in $CHCl_3$ solutions, using a Perkin-Elmer molecular weight apparatus, Model 115.

Results and Discussion

The prepared tris(diselenocarbamate) complexes (tdsc) are new compounds. The compounds were synthesized by the previously described method[1] for analogous tris(dithiocarbamate) complexes (tdtc). The method used consists of the direct mixing of metal chlorides, dialkylamines, and carbon diselenide instead of the usual method of preparation of diselenocarbamate complexes by reaction of sodium dialkyldiselenocarbamate and metal chloride.[3] The polymerization of carbon diselenide to dark resins always occurs quantitatively when carbon diselenide is added to a solution of a secondary amine and sodium hydroxide.[3,11,12] By using the method of preparation described in this paper, polymerization of carbon diselenide was not observed and resin formation was reduced to negligible proportions. High yields of the required diselenocarbamate complexes were obtained.

Infrared Spectra. The general appearance of the ir spectra of the studied tdsc complexes is similar to that of the spectra of the corresponding tdtc complexes. This is something that might be expected because the force fields of selenium compounds are not widely different from those of the sulfur compounds.[13-17]

The bands in the region 1410-1500 cm^{-1} fall between the stretching frequencies of single and double C-N bonds and can be therefore assigned to the partial double-bonding character of the C-N bond. The sets of bands around 1100-1200 and 800-950 cm^{-1} have been attributed to the vibrations of the system -C(Se)Se. These bands have slightly lower frequencies than those of the tdtc complexes. The observed slight shifting (30-100 cm^{-1}) is reasonably assigned to the mass difference of selenium and sulfur atoms.[18-20]

Electronic Spectra. The electronic spectral data for the tdsc complexes are shown in Figure 1, representatively. In the spectra of all compounds studied, there are three absorption bands in the regions 33.3-35.2 kK (band I), 31-32 kK (band II), and 23-24 kK (band III). Band I is a strong band ($\log \epsilon = 4.7-4.9$) and may be assigned to a $\pi \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ band in the corresponding tdtc compounds shifts toward higher frequencies. Band II is a shoulder ($\log \epsilon = 4.5-4.6$), is attributed to a second $\pi \rightarrow \pi^*$ transition, and also exhibits a blue shift on the corresponding tdtc compounds. This band was assigned by Jansen[21] to an $n \rightarrow \sigma^*$ transition on the basis of his experimental evidence, but later the same author,[22] on the basis of LCAO MO calculations of the transition energies, attributed this band to a $\pi \rightarrow \pi^*$ transition. Band III is a low-intensity band ($\log \epsilon = 3.5-4.1$). In the arsenic and antimony compounds, band III occurs as a shoulder. According to Shankaranarayana,[23] this low-intensity band arises from the moving of a nonbonding electron from a 4p orbital of the selenium atom in the C=Se group to an antibonding π molecular orbital.[24]

In all compounds studied, the basicity of the $-NR_2$ group seems to affect the position of bands I, II, and III (blue shifting).

In the spectra of the tdsc and tdtc compounds, the nature of the central atom (As, Sb, or Bi) does not alter greatly the position of the various bands. The sequence in the tdtc is normal for the blue shift (As > Sb > Bi). The shift becomes more pronounced as the electronegativity of the central atom increases. However, in the case of tdsc compounds, the sequence is abnormal with Bi > As > Sb. It is of course not easy to offer an explanation of this discrepancy, but it is resonable to assume that in the tdsc compounds the back-donation effect, $M(n\pi) \rightarrow L(d\pi)$, is more pronounced. This is in accordance with the suggestion of Jensen, *et al.*[25]

Also one explanation of the more pronounced back-donation

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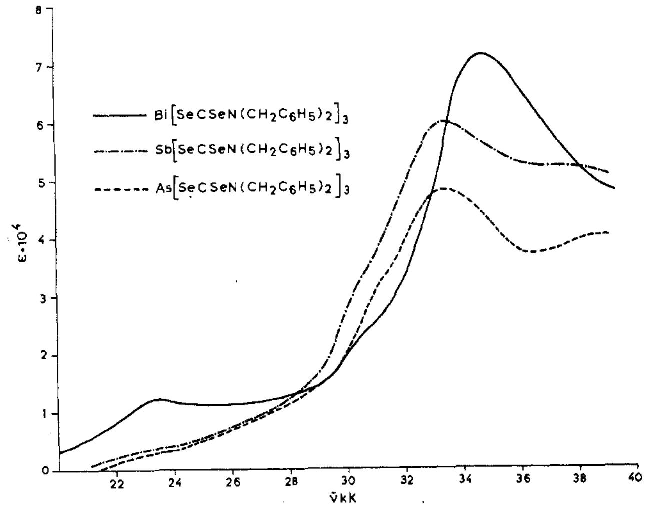

Figure 1. The absorption spectra of tris(dibenzyldiselenocarbamates) in chloroform.

of the bismuth compounds may be that the 6s lone pair electrons of the bismuth are more weakly bonded than the 5s and 4s lone pair electrons of the antimony and arsenic, respectively. Generally, the spectra of the prepared tdsc compounds, in both the visible and the ultraviolet regions, closely resemble those of the corresponding tdtc compounds except for a shift to lower frequencies. According to Cervone, *et al.*, this could be due to the smaller inter-electronic repulsions with selenium-containing ligands.[26]

Proton Nmr Spectra. The observed signals (Table II) in the pmr spectra appeared to be shifting to lower frequencies (smaller τ values) toward the signals of the corresponding protons of free amines. The shift differences are greater for those protons situated near the central atom and become smaller for those more distant. This is probably due to the deshielding effect which is less pronounced for the distant protons. The value of resonance frequencies is only slightly affected by the nature of the central metal atom and only a small shift to lower fields is observed as the electronegativity of the metal is decreased. But since the differences in the electronegativities of the central atoms are very small, it seems reasonable to accept the contribution of the back-donation effect as the cause of the observed shifting.

The proton signals of the studied tdsc compounds were observed to be shifted to lower magnetic fields relative to those of tdtc complexes. This difference could be correlated with the lower electron density around selenium atoms.

A very interesting feature of the nmr spectra of the studied compounds is that the resonance of methyl protons is shifted to lower magnetic fields going from As to Bi, but methylene protons have shown an inverse magnetic behavior and are shifted to higher magnetic fields going from As to Bi. While there is no simple way of theoretically explaining this phenomenon, perhaps the inverse effect can be correlated with the diamagnetic anisotropy contribution to methylene and methyl protons from the π-electron system in the $\mathrm{C}\overset{\cdots}{-}\mathrm{Se}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bonds. In some cases the methyl protons are possibly located in the paramagnetic region of the π current while the methylene protons are in the diamagnetic region. The proton signals of the coordinated diselenocarbamato groups in benzene solutions were observed to occur at higher fields than those observed in chloroform solutions (Table II). The benzene-induced solvent shifts are probably due to a benzene-solute interaction at the electron-deficient nitrogen atom of diselenocarbamato groups.

We have concluded here that on replacing sulfur by selenium in the studied carbamate complexes, there is little difference in the ionic character between the Se–M and S–M bonds and the molecular structure does not change significantly.

Registry No. $As[SeC(Se)N(C_2H_5)_2]_3$, 41667-73-6; $Sb[SeC(Se)N(C_2H_5)_2]_3$, 41667-74-7; $Bi[SeC(Se)N(C_2H_5)_2]_3$, 25929-21-9; $As[SeC(Se)N(C_4H_9)_2]_3$, 41667-76-9; $Sb[SeC(Se)N(C_4H_9)_2]_3$, 41667-77-0; $Bi[SeC(Se)N(C_4H_9)_2]_3$, 41667-78-1; $As[SeC(Se)N(CH_2C_6H_5)_2]_3$, 41667-79-2; $Sb[SeC(Se)N(CH_2C_6H_5)_2]_3$, 41667-80-5; $Bi[SeC(Se)N(CH_2C_6H_5)_2]_3$, 41667-81-6.

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Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007

2-Bis(trifluoromethyl)phosphinopentaborane (9) and Its Nickel Tricarbonyl Complex

Anton B. Burg

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Recent repetitions of the synthesis of $1\text{-}(CF_3)_2PB_5H_8$ [1] led to the isolation of the isomer $2\text{-}(CF_3)_2PB_5H_8$. This isomer was not noticed before, presumably because of its unexpectedly high volatility and its irreversible conversion to the 1 isomer.

Synthesis. The initial experiment leading to the discovery of $2\text{-}(CF_3)_2PB_5H_8$ was performed as described before,[1] but the poor quality of the available butyllithium led to low yields (for example, 5% of the 2 isomer and 10% of the 1 isomer), and impurities, probably including $C_4H_9P(CF_3)_2$ and $C_4H_9OP(CF_3)_2$, could not be eliminated. For better results, ethyllithium was employed, with the special advantage that the formation of LiB_5H_8 could be monitored by isolating the coproduced ethane. One fairly successful experiment was based upon the reaction of a 10-mg piece of bright lithium (freshly cut under dry methane) with C_2H_5Br (2 mmol) in ether[2] during 12 hr at −45° in a tube attached to the high-vacuum line. The formation of ethylene did not exceed 2%, *vs.* 100% in a parallel experiment at 25°.

For other experiments, a newly delivered commercial sample of LiC_2H_5 in benzene was filtered from the black precipitate, crystallized from the dark-brown solution, and redissolved in dry benzene to make a 0.7 *M* stock solution. Measured portions of this were freed of benzene in the high-vacuum line and redissolved in ether at −78°.

The best yield came from an experiment using 1.075 mmol of LiC_2H_5 with 1.312 mmol of B_5H_9, yielding 1.075 mmol of C_2H_6 during 2 hr at −50°; then 1.033 mmol of $(CF_3)_2PCl$, mixed in at −125°, reacted during a warm-up to −78° (12 hr). The ether and excess B_5H_9 were distilled off *in vacuo* at −45° and the phosphinopentaboranes were delivered during slow warming, finally to 50°. They were separated by repeated fractional condensation at −20 to −30°. The yield of $2\text{-}(CF_3)_2PB_5H_8$ was 0.158 mmol; of $1\text{-}(CF_3)_2PB_5H_8$, 0.331 mmol; total, 0.484 mmol or 45%.

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