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N,N-Dialkyldiselenocarbamate Complexes of Arsenic, Antimony and Bismuth

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Six new iodo bis(N,N-dialkyl diselenocarbamate) and three new tris(N,N-dialkyl diselenocarbamate) complexes of Arsenic, Antimony and Bismuth have been prepared and studied by i.r., n.m.r. and electronic spectra. The spectral data are discussed and compared to those of the corresponding dithiocarbamates.

Introduction

In the last few years a number of papers have been published on the reactions between halogens and dithiocarbamate complexes of the transition and non transition metals. The study, however, of the reaction of the halogens with diselenocarbamate complexes is limited to the metals nickel [1], gold [2] and iron [3]. In the case of nickel it has been pointed out that diseleno- or dithiocarbamate oxidation reactions take place to yield halogeno diseleno- or dithio-carbamate complexes in which the metal atom appears in an unusually high oxidation number. Also oxidation reactions take place in which the dithiocarbamate ligands are oxidized to thiuramdisulfides producing thiuramdisulfide complexes. The latter is also supported by Barnard and Woodbridge [4] who take the equimolar mixtures of bis(N,N-dialkyl selenocarbamoyl) mono- and tri-selenides by oxidation of the sodium salts of the analogous diselenocarbamate complexes with hydrogen peroxide, under a variety of conditions.

Another case is that where by reacting halogens with diselenocarbamate complexes, only substitution reactions take place, and the metal atom maintains its oxidation number as has been pointed out in our previous paper with the analogous complexes of As, Sb and Bi [5]. Continuing our work on the afore mentioned complexes, we prepared six new iodo bis(N,N-dialkyl diselenocarbamate) complexes of the general type $IM(Se_2CNR_2)_2$ where M = As, Sb, Bi and R = Et, i-Bu, R_2 = Me, Ph, and three new tris[N,N-(methyl)phenyldiselenocarbamate] complexes of the following type $M[Se_2CN(CH_3)C_6H_5]_3$ where M = As, Sb, Bi. The characterization and study of the prepared compounds were done by elemental analysis (Table I), molecular weight determination, and by i.r., n.m.r. and electronic spectroscopy.

Results and Discussion

Infrared Spectra

The most important frequencies of infrared absorption are shown in Table II. In the tris diselenocarbamate complexes a set of bands occur in the region of 1480–1490 cm^{-1} which lie between the stretching frequencies of C–N single and double bonds [6, 7]. In the iodo derivatives a blue shift is observed which is evidence of the increased double bond character of the C–N bond. Generally, such a result is to be expected in view of the –I inductive effect of the iodine atom. A similar shift has been observed for the bromo, iodo and tetrafluoroborate bis(dithiocarbamate) complexes relative to tris(dithiocarbamate) complexes [8–10]. The stretching vibration of this band is shifted towards lower frequencies (about 10–25 cm^{-1}) for the studied diselenocarbamate compounds in comparison with the corresponding dithiocarbamate complexes.

The two bands around 820–875 cm^{-1} may be ascribed to the stretching vibration of $C\overset{\cdots}{-}Se$ bonds [3]. The observed red shift of diseleno complexes relative to dithio complexes is due to the difference between the mass of selenium and that of sulfur.

Electronic Spectra

The data obtained from the ultraviolet spectra of freshly prepared chloroform solutions of the prepared compounds are shown in Table III. The high intensity band (band I) at 34–37 kK is assigned to an intraligand $\pi \rightarrow \pi^*$ transition [11, 12]. The presence of the central atom and the basic character of the amine group affect the position of band I as in the case of bromo and iodo derivatives of the corresponding dithiocarbamate complexes [8, 9].

The position of band I in iodo derivatives is shifted to higher frequencies with a decrease in the molar absorption coefficient relative to tris(diselenocarbamate) complexes while it is shifted to lower

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TABLE I. Analytical and Physical Data.

Compound	Color	Yield %	M.P. ℃	C %		N %		H %		Se %		M %[a]		I %	
				C.	F.	C.	F.	C.	F.	C.	F.	C.	F.	C.	F.
I $As[Se_2CN(CH_3)C_6H_5]_3$	Pale Yellow	80	233–8 d[b]	31.89	31.56	4.65	4.52	2.65	2.78	52.49	52.09	8.30	8.00	–	–
II $Sb[Se_2CN(CH_3)C_6H_5]_3$	Dark Yellow	52	247–50 d	30.31	29.89	4.42	4.48	2.52	2.59	49.89	49.29	12.84	12.54	–	–
III $Bi[Se_2CN(CH_3)C_6H_5]_3$	Red Orange	32	189–94	27.77	27.97	4.05	3.72	2.31	2.36	45.70	45.40	20.15	19.85	–	–
IV $IBi[Se_2CN(CH_3)C_6H_5]_2$	Dark Red	61	256–8 d	21.62	21.59	3.15	3.08	1.80	1.80	35.56	35.30	23.53	23.43	14.29	14.09
V $IAs[Se_2CN(C_2H_5)_2]_2$	Yellow	90	170–2 d	17.49	17.76	4.08	4.15	2.91	3.04	46.06	45.56	10.93	10.73	18.51	18.21
VI $ISb[Se_2CN(C_2H_5)_2]_2$	Yellow	90	198–9 d	16.37	16.53	3.81	3.83	2.72	2.76	43.11	42.81	16.64	16.34	17.32	17.12
VII $IBi[Se_2CN(C_2H_5)_2]_2$	Red	90	190–1 d	14.63	14.89	3.41	3.91	2.43	2.63	38.53	38.12	25.48	25.08	15.48	15.18
VIII $ISb[Se_2CN(C_4H_9)_2]_2$	Yellow	80	192–3	25.56	25.16	3.31	2.89	4.26	4.23	37.39	37.09	14.43	14.13	15.02	14.78
IX $IBi[Se_2CN(C_4H_9)_2]_2$	Brick	50	190–1	23.17	21.38	3.00	2.82	3.86	3.66	33.90	33.40	22.42	22.12	13.62	13.32

[a] M = As, Sb, Bi. [b] d = decomposition.

TABLE II. Relevant I.r. Frequencies (cm^{-1}) of the Studied Diselenocarbamates and Their Assignments (KBr disks)[a].

Compound	$\nu(C\overset{\cdots}{-}N)$	$\nu(C\overset{\cdots}{-}Se)$	Compound	$\nu(C\overset{\cdots}{-}N)$	$\nu(C\overset{\cdots}{-}Se)$
$As[Se_2CN(CH_3)C_6H_5]_3$	1483 vs	865 m	$IAs[Se_2CN(C_2H_5)_2]_2$	1500 vs	871 w
	1430 vs			1430 vs	821 m
			$ISb[Se_2CN(C_2H_5)_2]_2$	1495 vs	876 w
$Sb[Se_2CN(CH_3)C_6H_5]_3$	1483 w	870 m sh		1428 vs	820 m
	1430 vs	858 m			
			$IBi[Se_2CN(C_2H_5)_2]_2$	1490 vs	872 w
				1425 vs	821 m
$Bi[Se_2CN(CH_3)C_6H_5]_3$	1485 s	871 w			
	1430 s	860 w	$ISb[Se_2CN(C_4H_9)_2]_2$	1488 vs	871 w
				1425 vs	
$IBi[Se_2CN(CH_3)C_6H_5]_2$	1482 s	868 w	$IBi[Se_2CN(C_4H_9)_2]_2$	1510 vs	875 w
	1443 s			1434 s	

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

TABLE III. Electronic Spectra of the Studied Diselenocarbamate Complexes.[a]

Compound	Band I		Band III		Band IV	
	$\nu_{max}(kK)$	$\log\epsilon_{mol}$	$\nu_{max}(kK)$	$\log\epsilon_{mol}$	$\nu_{max}(kK)$	$\log\epsilon_{mol}$
$As[Se_2CN(CH_3)C_6H_5]_3$	34.8	4.62	–	–	41.8	4.53
$Sb[Se_2CN(CH_3)C_6H_5]_3$	35.0	4.48	–	–	41.7	4.36
$Bi[Se_2CN(CH_3)C_6H_5]_3$	35.0	4.84	–	–	39.8 sh[b]	4.65
$IBi[Se_2CN(CH_3)C_6H_5]_2$	35.5	4.54	–	–	41.7	4.40
$IAs[Se_2CN(C_2H_5)_2]_2$	36.2	4.62	–	–	41.6 sh	4.18
$ISb[Se_2CN(C_2H_5)_2]_2$	36.2	4.34	–	–	42.0	4.16
$IBi[Se_2CN(C_2H_5)_2]_2$	36.0	4.56	23.8	3.78	41.8	4.52
$ISb[Se_2CN(C_4H_9)_2]_2$	36.0	4.64	–	–	–	–
$IBi[Se_2CN(C_4H_9)_2]_2$	36.2	4.78	31.4	4.54	–	–

[a] In $CHCl_3$ solution. [b] sh = shoulder.

frequencies in comparison with the iododithiocarbamate complexes. The latter may be due to the greater electron affinity of the sulfur atom than the selenium one. The usual band II at 31–33 kK is absent and this may be evidence of the equivalent linking of the diselenocarbamate ligands [13], or there is an overlapping from band I. Band III appeared near the visible region in the spectra of the [N,N-(methyl)phenyl diselenocarbamate] complexes. This band is assigned to a charge transfer from the ligand to the metal [14] or to an $n \rightarrow \pi^*$ transition located on the sulfur or selenium atom [15, 16].

In the spectra of the studied compounds an extra band (Band IV) has been noticed in the region 40–42 kK with the exception of the [N,N-diisobutyl diselenocarbamate] complexes.

Proton Nuclear Magnetic Resonance Spectra

The p.m.r. spectra of the soluble complexes have been obtained in $CDCl_3$ and C_6D_6 solutions. The proton signals of the halogeno derivatives are generally shifted to lower fields as compared to those of the corresponding tris(diselenocarbamate) complexes with the exception of methylene proton signals of the halogeno derivatives. This can be justified assuming that the methylene protons of the halogeno derivatives are in the shielding cone of $C\overset{\cdots}{-}N$ bond [17, 18], since the bond order of the $C\overset{\cdots}{-}N$ bond increases, because of the –I inductive effect of the iodine atom more shielding is observed.

There is not great difference between the proton signals of diselenocarbamate and the corresponding dithiocarbamate complexes and only a small shift to lower frequencies can be noticed on going from dithiocarbamate to diselenocarbamate complexes. The ^1H signals of the complexes in deuterium benzene solutions showed a shift towards higher frequencies compared with those in $CDCl_3$ solutions. This is probably due to the formation of weak collision or van der Waals complexes between benzene (solvent) and diselenocarbamates (solutes) as has been shown in the p.m.r. spectra of the corresponding dithiocarbamate complexes [8, 9, 19].

Attempts of preparation of iodo bis[N,N-(methyl)-phenyl dithiocarbamate] of either arsenic or antimony led to a yellow–brown solid, m.p. 203–205 °C (d), soluble in chloroform and benzene. The i.r. and p.m.r. spectra of the product are similar to these of tris[N,N-(methyl)phenyl diselenocarbamates] with the only exception of the peak at 865 cm^{-1} in the i.r. spectra which became sharp and strong. The combination of these facts with the data of elemental analysis suggests that the yellow product (obtained from both arsenic and antimony compounds) is probably the selenuram diselenide of the N-methyl aniline. *Anal.* For the case of arsenic: C 34.28%, N 4.62%, H 2.76%. For the case of antimony: C 34.34%, N 4.67%, H 2.58%. Calculated for $C_{16}H_{16}N_2Se_4$: C 34.70%, N 5.07%, H 2.80%.

Their electronic spectra, obtained in chloroform solutions, show two bands at 41.5 kK (Band IV) and *ca.* 34.5 kK (Band I). The whole spectra seem to be shifted to lower frequencies towards the corresponding tris(diselenocarbamate) complexes. It is remarkable, however, that there is a difference inversely proportional in the band intensities of both products.

Experimental

Preparation

The known tris(dialkyl diselenocarbamate) complexes of As, Sb and Bi were prepared according to the published method [17]. The new tris[N,N-(methyl)phenyl diselenocarbamate] complexes of As, Sb and Bi were prepared as follows. To a solution of ≃10 mmol metal trichloride MCl_3 (M = As, Sb, Bi) in 100 ml carbon tetrachloride mixed with ≃30 mmol carbon diselenide, a solution of N-methyl aniline (≃60 mmol) in 50 ml CCl_4 was added dropwise in 30 minutes. The mixtures were continuously stirred for 2 hours at room temperature. The mixture was then filtered and the precipitate was washed with CH_3OH and recrystallized from a mixture of dimethylformamide and methanol. The obtained complexes are insoluble in common organic solvents and water (except compound III which is soluble in $CHCl_3$, CH_2Cl_2 and C_6H_6) but they are soluble in dimethylformamide and slightly soluble in $CHCl_3$ and CH_2Cl_2.

The iodobis(dialkyl diselenocarbamate) complexes of As, Sb, and Bi were prepared according to the published method [5]. Especially compounds IV through IX were prepared as follows. To a solution of the tris(dialkyl diselenocarbamate) complex (5 mmol) in 100 ml $CHCl_3$ or CH_2Cl_2, a solution of iodine (25 mmol) 4% w/v in $CHCl_3$, was added dropwise while stirring constantly for 3–5 hours. The mixture was then concentrated and after addition of ethanol the iodo complexes were precipitated and recrystallized from a mixture of CH_2Cl_2 and C_2H_5OH.

Compounds VI and VII are soluble in CH_2Cl_2 and C_6H_6 and all are soluble to slight soluble in CH_2Cl_2 and insoluble in CH_3OH, C_2H_5OH, petroleum ether, CCl_4, and water. The colour of the studied compounds turns from pale yellow to dark red on going from the arsenic to bismuth complexes and all are remarkably stable for selenium containing compounds.

Measurements

Infrared spectra were measured on a Perkin–Elmer 257 spectrophotometer using the KBr disc technique. Proton NMR spectra were recorded on a Varian A-60A (60 Mc/s) instrument, with TMS as an internal standard. Electronic spectra were obtained on a Zeiss PMQ II spectrophotometer with freshly prepared $CHCl_3$ solutions. Molecular weights were carried out by a Perkin–Elmer molecular weight apparatus Model 115 in $CHCl_3$ solutions. We could not take the molecular weights of all studied compounds, because of their lack of solubility in common solvents.

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