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Coordination Ability of the Heterocycles 1,3-Dithia-2-arsa- and -stiba-cyclopentanes Towards Sulfur Containing Ligands, Part II. Diheterocyclic Dithiocarbamate Complexes. X-ray Structure of the 4-Morpholinecarbodithioate of 1,3-Dithia-2-arsa-cyclopentane**

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Summary. A series of diheterocyclic dithiocarbamate complexes of the type $RNCS_2MS_2C_2H_4$, where R = pyrrolidyl, 3-pyrrolyl, 4-morpholyl, 3-methlpiperidyl and M = As or Sb were obtained and characterized by IR, ^{1}H, and ^{13}C-NMR, mass spectroscopy and elemental analyses. The X-ray crystal structure determination of the 4-morpholinecarbodithioate of 1,3-dithia-2-arsa-cyclopentane shows a monodentate behaviour of the $RNCS_2$ entity.

Keywords. Arsenic, antimony complexes; Dithiocarbamate complexes; Dithiocarbamate X-Ray structure; Monodentate group 15 dithio complex.

Koordinationsvermögen von 1,3-Dithia-2-arsa- und -stiba-cyclopentanen gegenüber Schwefel-enthaltenden Liganden, 2. Mitt.: Diheterocyclische dithiocarbamat-Komplexe Röntgenstrukturanalyse des 4-Morpholinocarbodithioats von 1,3-Dithia-2-arsa-cyclopentan

Zusammenfassung. Es wurden eine Reihe von diheterocyclischen Dithiocarbamat-Komplexen des Typs $RNCS_2MS_2C_2H_4$ mit R = Pyrrolidyl, 3-Pyrrolyl, 4-Morpholyl, 3-Methylpiperidyl und M = As oder Sb hergestellt und mittels IR, ^{1}H- und ^{13}C-NMR, MS und Elementaranalysen charakterisiert. Die Röntgenstrukturanalyse des 4-Morpholinocarbodithioats von 1,3-Dithia-2-arsa-cyclopentan zeigt ein monodentates Verhalten der $RNCS_2$-Einheit.

** Dedicated to Dr. Lydia Rodríguez on the Occasion of her 60th Birthday.

Introduction

Compounds where the metal ion is totally surrounded by sulfur atoms are of special interest from several points of view, including biochemistry, inorganic synthesis, spectroscopy etc. [1]. Recently, in this journal we reported on the coordinating ability of the five membered heterocyclic rings $MS_2C_2H_4$ (M = As and Sb) towards some dialkyl-dithiocarbamates, and we were able to obtain compounds of the type $R_2NCS_2MS_2C_2H_4$ (Part I, Ref. [2]). Using the criteria of Ugo and Bonati [3] it was difficult to decide if both sulfur atoms or only one of the dithiocarbamate entity were involved in the coordination with the arsenic or antimony atom. It was not possible to find out if the As or Sb atom has a stereochemical active lone pair. The spectroscopic and crystallographic studies of the As and Sb dithiocarbamates of the type $M(S_2CNR_2)_3$, $XM(S_2CNR_2)_2$ or $X_2M(S_2CNR_2)$ (M = As, Sb; X = Cl, Br, I) indicate an aniso-bidentate behaviour of the ligand and a strong participation of the lone pair in the stereochemistry of the complexes [1], also the bis(diethyldithiocarbamate) of phenylarsenic [Ph-$AsS_2CN(Et)_2$] shows two different arsenic-sulfur distances [4].

The coordination behaviour of dithiocarbamates where the dialkyl groups are replaced by heterocycles has been extensively studied, including some Group 15 derivatives [1, 5, 6]. In these complexes the coordination is similar to that of the dialkyl derivatives. With 4-morpholyldithiocarbamate a symmetrically bidentate molecule is produced with Ru(III) [7], whereas an anisobidentate situation is present for Se(II) and Te(II) derivatives [8, 9] and a monodentate compound for the bis (4-morpholinethiocarbonyl)-trisulphide [10].

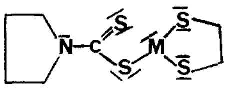
In this paper we report the synthesis and characterization of eight diheterocyclic carbodithioate complexes, $RNC(S)SMS_2C_2H_4$, (M = As, Sb), as well as the X-ray structure determination of the 4-morpholinecarbodithioate of 1,3,-dithia-2-arsacyclopentane. The present investigation was undertaken in order to determine a) if the dithiocarbamate entity shows a monodentate, anisobidentate or isobidentate behaviour toward the heterocycles $MS_2C_2H_4$ (M = As or Sb), b) if the group 15 element has a stereochemically active lone pair or not, which should help to resolve the questions raised in our recent paper about the structure of these types of complexes [2].

Experimental Part

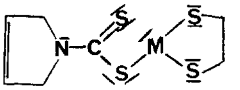
All reagents were commercial and used as such. Infrared spectra were recorded in the region 4000–200 cm^{-1} on a Perkin-Elmer 283-B instrument as KBr pellets, nuclear magnetic resonance spectra on a Varian VXR-300 or Geminis-200 MHz spectrometer using $CDCl_3$ or $DMSO$-d_6 as solvents. Mass spectra were recorded in a Hewlett-Packard MS-598 instrument by electronic impact, elemental analysis were performed in commercial laboratories.

Preparation of Ligands

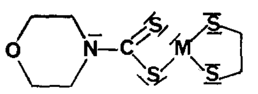
Dithiocarbamate sodium salts ($RdtcS_2Na$) were obtained starting from the corresponding heterocyclic amine (pyrrolidine, 3-pyrroline, morpholine, 3-methylpiperidine), CS_2 and NaOH by common methods [11]. The 2-chloro-1,3-dithia-2-arsa- and -stiba-cyclopentanes were prepared from $AsCl_3$ or $SbCl_3$ with 1,2-ethanedithiol by reported methods [12, 13].



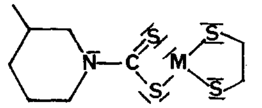
1 M = As
2 Sb



3 M = As
4 Sb



5 M = As
6 Sb



7 M = As
8 Sb

Preparation of the Complexes

The complexes **1–8** reported here were synthesized in the same way as described previously for the dialkyl homologs [2], yields ca. 60%.

X-ray Analysis of $O(CH_2)_4NC(S)SAsS_2C_2H_4$

Crystals suitable for X-ray analysis were obtained in the following way: The compound was dissolved in CH_2Cl_2, and hexane was added giving rise to two phases. In 24 h white crystals were grown. A colourless crystal of $C_7H_{12}NOS_4As$ with dimensions 0.22 x 0.32 x 0.20 mm was mounted on a glass fiber. All measurements were made on a Nicolet P3F m diffractometer with Ni-filtered Cu Kα radiation. Cell constants obtained from least-squares refinement using the setting angles of 25 carefully centered reflections in the range $12.93 \leqslant 2\Theta \leqslant 32.25$ gave a monoclinic cell with dimensions $a = 21.759(8)$, $b = 12.004(5)$, $c = 9.299(4)$ Å, $\beta = 93.50(3)°$, $V = 2424(2)$ Å^3. The space group was uniquely determined from systematic absences C2/c for $Z = 8$ and a formula weight of 329.34. The calculated density is 1.80 g cm^{-3}.

The data were collected using the $2\Theta:\Theta$ scan mode to a maximum value of $2\Theta = 100°$. Of 1376 reflections collected, 1247 were unique and 1140 considered observed $F > 3\sigma$ (F) The data were corrected for Lorentz and polarization effects. Empirical absorption correction [μ(MoKα) = 99.58 cm^{-1}] was applied.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically (hydrogen atoms were included in idealized positions with a temperature factor $U = 0.06$ Å^2). The final cycle of block-matrix least-squares refinement based on F for the observed reflections converged with unweighted and weighted agreement factors of $R = 0.065$, $R_w = 0.076$. Neutral atom scattering factors were taken from Cromer and Weber [14], anomalous dispersion effects were included. All calculations were performed using the SHELXTL crystallographic software package [15].

Results and Discussion

The reactions between the sodium dithiocarbamate, *Rdtc*Na, (R = pyrrolidyl, 3-pyrrolyl, 4-morpholyl and 3-methylpiperidyl) with Cl-$MS_2C_2H_4$ (M = As, Sb) yield the corresponding diheterocyclic complexes, $RNCS_2MS_2C_2H_4$. They are air-stable white solids, soluble in organic solvents such as chloroform, but practically insoluble in water or hexane. The solubility of the Sb derivative is less than that of the corresponding arsenic compounds. The analytical data (C, H, As or Sb) agree well within the experimental errors with value calculated for compounds $R\mathrm{NCS}_2M\mathrm{S}_2\mathrm{C}_2\mathrm{H}_4$.

The spectroscopic data of the complexes are very similar to those of the dialkyl compounds described previously. Therefore we will present only a brief description. The IR spectra of all the compounds show a band in the range 1420–1442 cm^{-1} indicative of the considerable double-bond in the carbon-nitrogen bond [6]; the absorptions between 950–1050 cm^{-1} are due to the ν(C–S) vibrations (Table 1). The presence of several more or less strong bands in the region 950–1050 cm^{-1} is not conclusive regarding monodentate or bidentate coordination. Proton magnetic resonance spectra of the complexes show only singlets at 3.5–3.6 ppm due to the methylene protons of the group 15 five members heterocyclic system and are indicative of the solution equivalence of the protons. The ^{13}C resonance of the methylene carbon atoms appear at ca. 39 ppm, the carbon atoms of the carbodithioic entity at ca. 190 ppm.

Table 1. Selected IR bands (cm^{-1})

Compound	ν (CN)	ν (CS)	Far IR
1	1438 vs	998 m, 990 w, 950 m	360 s, 342 m
2	1425 vs	996 vs	378 m, 360 s, 338 m
3	1428 vs	988 s, 1020 s	380 m, 362 s, 332 s, 288 w
4	1432 vs	1040 m, 960 m, 950 s	365 m, 330 m
5	1440 vs	990 m	330 m, 292 m
6	1430 vs	992 m	345 m, 330 s, 285 s
7	1428 s	1022 s, 1010 m, 982 s	350 w, 335 s, 280 s
8	1430 s	10040 w, 970 w, 950 s	335 s 280 m

Table 2. Mass spectral data (main fragments, only monoisotopic data for Sb = 121)

Assignment	**1**	**2**	**3**	**4**
M^+	313(35)	311(18)	329(33)	341(24)
$Rdtc\mathrm{As}^+$	221(30)	219(5)	237(18)	249(21)
$\mathrm{AsS}_2\mathrm{C}_2\mathrm{H}_4^+$	167(62)	167(43)	167(95)	167(53)
Assignment	**5**	**6**	**7**	**8**
M^+	359(12)	357(22)	374(M-1) (19)	387(5)
$Rdtc\mathrm{Sb}^+$	267(38)	265(17)	283(40)	295(3)
$\mathrm{SbS}_2\mathrm{C}_2\mathrm{H}_4$	213(17)	213(25)	213(38)	213(62)

The mass spectra of the complexes (Table 2), exhibit parent ions in accordance with the molecular weight and are indicative of the monomeric state of the compounds. One prominent feature of the mass spectra is the absence of characteristic peaks corresponding to polynuclear compounds of general formula M_nS_m ($n = 1$–4, $m = 0$–4) common in tris-dithiocarbamato complexes [16]. The fragmentation process is similar to that of the dialkyl compounds described previolusly [2], arising from the formation and breaking of the ion $(RNCS_2M)^+$ and the five membered ring $(MS_2C_2H_4)^+$. The fragmentation process of metal dithiocarbamates [16] and $MS_2C_2H_4$ entity [17] is well established.

Description of the Structure

The crystals consist of separate molecules as shown in Fig. 1. Tables 3 and 4 show the positional parameters and the bond distances and angles. The most important features of the molecular structure is the monodentate character of the dithiocarbamate ligand with the As–S(1) long distance (2.943 Å). To the author's knowledge this is the first example reported in the literature of a structural determination of a monodentate arsenic dithiocarbamate.

The dithiocarbamate group shows a short and a long C–S bond, with lengths corresponding within experimental error to double and single bonds, respectively. The As^{III}–S bonds in molecular compounds are reported to be as short as 2.228(5) and as long as 2.330(6) Å [18]. For the anisobidentate arsenic dithiocarbamates the values are between 2.26 and 2.354 Å for the short bond and between 2.274 and 2.819 Å for the long ones [19]. In our case the As–S bond of the dithiocarbamate is 2.290(3) Å. The C(7)–N(4) length, 1.313(11) Å, is significantly shorter than the sum of the respective covalent single bond radii, 1.47 Å, as the nitrogen is involved in π bonding to the carbon (cf. Br_2As (Et_4dtc) [19]). The two angles S(2)–As–S(3) and S(2)–As–S(4) are different, 101.2(1) and 92.3(1)°, respectively; this values and the intra-five member ring angle S(3)–As–S(4) of 93.3(1)° suggest some tendency towards orthogonality as compared with the idealized tetrahedral configuration in a situation similar with the one found in tris(phenylthio)arsine [18], but very

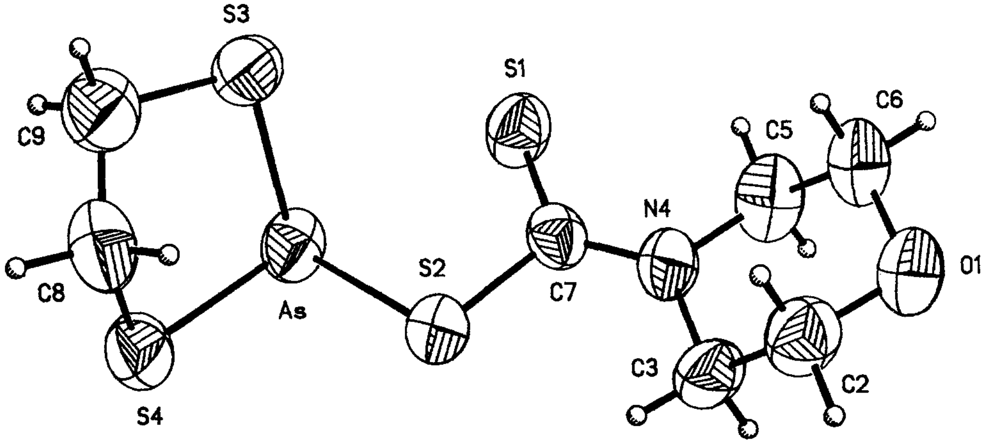


Fig. 1. Structure of the 4-morpholinecarbodithioate of 1,3-dithia-2-arsa-cyclopentane

Table 3. Atom coordinates ($\cdot 10^4$) and temperature factors ($Å^2 \cdot 10^3$)

Atom	*x*	*y*	*z*	*U**
As	1544(1)	2843(1)	97(1)	63(1)
S(1)	2193(1)	1886(2)	2679(3)	68(1)
S(2)	892(1)	2385(2)	1847(3)	63(1)
S(3)	1966(1)	4396(2)	992(3)	67(1)
S(4)	793(1)	3769(2)	−1209(3)	77(1)
O(1)	877(3)	944(5)	7057(7)	69(2)
C(2)	497(4)	1512(9)	5975(10)	68(4)
C(3)	614(4)	1120(8)	4512(10)	66(4)
N(4)	1256(3)	1309(6)	4238(8)	60(3)
C(5)	1663(5)	790(9)	5348(11)	72(4)
C(6)	1501(5)	1173(8)	6767(10)	66(4)
C(7)	1456(4)	1800(7)	3095(9)	52(3)
C(8)	854(5)	5078(8)	−241(11)	76(4)
C(9)	1512(5)	5422(1)	−14(11)	77(4)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised *U* tensor

Table 4. Bond lenghts (Å) and angles (deg.) with standard deviations in parentheses

As–S(2)	2.290(3)	As–S(3)	2.218(3)
As–S(4)	2.268(3)	S(1)–C(7)	1.674(9)
S(2)–C(7)	1.781(9)	S(3)–C(9)	1.804(11)
S(4)–C(8)	1.812(10)	O(1)–C(2)	1.434(11)
O(1)–C(6)	1.428(12)	C(2)–C(3)	1.477(14)
C(3)–N(4)	1.451(12)	N(4)–C(5)	1.458(12)
N(4)–C(7)	1.313(11)	C(5)–C(6)	1.461(14)
C(8)–C(9)	1.492(15)		
S(2)–As–S(3)	101.2(1)	S(2)–As–S(4)	92.3(1)
S(3)–As–S(4)	93.3(1)	As–S(2)–C(7)	97.2(3)
As–S(3)–C(9)	100.3(4)	As–S(4)–C(8)	97.5(3)
C(2)–O(1)–C(6)	106.9(7)	O(1)–C(2)–C(3)	111.8(8)
C(2)–C(3)–N(4)	109.6(7)	C(3)–N(4)–C(5)	111.0(7)
C(3)–N(4)–C(7)	125.7(7)	C(5)–N(4)–C(7)	123.2(8)
N(4)–C(5)–C(6)	109.6(8)	O(1)–C(6)–C(5)	113.2(8)
S(1)–C(7)–S(2)	117.2(5)	S(1)–C(7)–N(4)	125.8(7)
S(2)–C(7)–N(4)	117.0(7)	S(4)–C(8)–C(9)	110.6(8)
S(3)–C(9)–C(8)	112.0(8)		

different from the NS_3 environment in tris(phenylthio)amine with an average S–N–S angle of 119.5° [20].

Regarding the 1,3-dithia-2-arsa or -stibacyclopentane rings, only the crystal structure of the 2-chloro-stiba derivative, $ClSbS_2C_2H_4$, is known, showing the presence of a non-planar ring [21]. The arsenic five membered ring of the compound here described is also non planar, the As–S(3) and As–S(4) bonds are significantly different, 2.218(3) and 2.268(3) Å, whereas in $ClSbS_2C_2H_4$ the corresponding As–S bonds are equal. The other part of the molecule, the 4-morpholyl ring has a chair conformation and bond lengths and angles corresponding to the normal values within experimental error [7].

Acknowledgments

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