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Coordinating Ability of the Heterocycles 1,3-Dithia-2-Arsa- and Stiba-Cyclopentanes. Part III. Dithioacid and Dithiocarbamate Complexes Containing a Free Functional Group. Crystal Structure of 2-Pyrrolidonedithiocarbamate of 1,3-Dithia-Arsa-Cyclopentane

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ABSTRACT

Three 1,1-dithioacids containing an additional functional group, 2-pyrrolidone-1-carbodithioic acid, 2-hydroxycyclopentene-1-carbodithioic acid, and 2-pyrrolidone-1,3-bis(carbodithioic) acid, were reacted with the Group 15 heterocycles 2-chloro-1,3-dithia-2-arsa- and stiba-cyclopentanes ($ClMS_2C_2H_4$; M = As, Sb). The dithiocomplexes obtained were characterized by spectroscopic methods and elemental analyses. The X-ray structure determination of the 2-pyrrolidonedithiocarbamate of 1,3-dithia-arsa-cyclopentane shows a monodentate behavior of the dithiocarbamate entity and the absence of participation of the carbonyl oxygen in the coordination.

INTRODUCTION

Recently, we have studied the coordinating behavior of the five-member heterocycles 2-chloro-1,3-dithia-2-arsa- and stiba-cyclopentanes as a "metal source" toward some dialkyl and heterocyclic sodium dithiocarbamates. The X-ray structure of one such complex manifests a monodentate interaction, viz., dithiocarbamate-$MS_2C_2H_4$ (M = As, Sb) [1,2].

It is known that there are only a few examples of 1,1-dithio complexes in which the ligand has a free functional group not involved in coordination. This situation has important bioinorganic and pharmaceutical implications, with the presence of a latent functionality to bind a suitable carrier [3]. The evidence that some arsenic compounds are implicated in cancer chemotherapy [4] and the recent discovery of the first Sb(III) organometallic compounds possessing antitumor properties, $\Phi_2SbS_2PR_2$ (R = Φ, OΦ) [5], as well as the knowledge of arsenic implications in the epidemiology of human cancers, prompted us to synthesize com-

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plexes with the heterocycles Cl-$MS_2C_2H_4$ (M = As, Sb) and 1,1-dithioacids containing a free functional group.

We chose three carbonyl compounds, one of the dithiocarbamate type (2-pyrrolidone-1-carbodithioic acid), a 1,1-dithiocarboxylate (2-oxocyclopentane-1-carbodithioic acid), and a binuclear compound which contains both kinds of systems (2-pyrrolidone-1,3-bis(carbodithioic) acid), in an attempt to determine (a) if the interaction of these bifunctional ligands with the heterocycles $MS_2C_2H_4$ (M = As, Sb) involves only the 1,1-dithio entity or if the carbonyl group also participates in the coordination; (b) if the interaction is only through the 1,1-dithio group and to determine if the bonding situation is bidentate, monodentate, or anisobidentate; and (c) if the Group 15 element has a stereochemically active lone pair, as well as to enlarge our knowledge about the 1,1-dithio complexes with Group 15 elements with their important bioinorganic implications.

It is interesting to note that the first arsenic compounds with a dithiocarboxylate ligand were not made until 1980 [6]. Of the ligands chosen, only the binucleating ligand, 2-pyrrolidone-1,3-bis(carbodithioic) acid, has been tested in its coordination chemistry. Toward transition metal ions, it forms binuclear complexes, the spectroscopic and magnetic data of such complexes suggesting the participation of the carbonyl-oxygen in the coordination [7].

EXPERIMENTAL

All reagents were of commercial grade and used as such. Infrared spectra were recorded in the region 4000–200 cm^{-1} as KBr pellets using a Perkin-Elmer 283-B spectrometer. Proton and carbon-13 magnetic resonance spectra were recorded on a Varian VXR-300 or Geminis-200 MHz instrument using $CDCl_3$ or a mixture of $CDCl_3$/DMSO as solvents, and mass spectra determinations were performed on a Hewlett-Packard MS/GC 598 instrument by electron impact at 70 ev. Elemental analyses were performed in commercial laboratories.

Preparation of Ligands and Cl-$MS_2C_2H_4$ (M = As, Sb)

2-pyrrolidone-1-carbodithioic acid (I) was prepared by a reported method [8], 2-hydroxycyclopentene-1-carbodithioic acid (II) by the same procedure as described by Takeshima for 2-oxocyclopentane-carbodithioic acid [9], and the binucleating ligand 2-pyrrolidone-1,3-bis(carbodithioic) acid (III) according to [8]. The heterocycles 2-chloro-1,3-dithia-2-arsa- and stiba-cyclopentane were prepared from $AsCl_3$ or $SbCl_3$, respectively, and 1,2-ethanedithiol by established methods [10,11]. All ligands and $ClMS_2C_2H_4$ were characterized by their IR, NMR, and MS spectra.

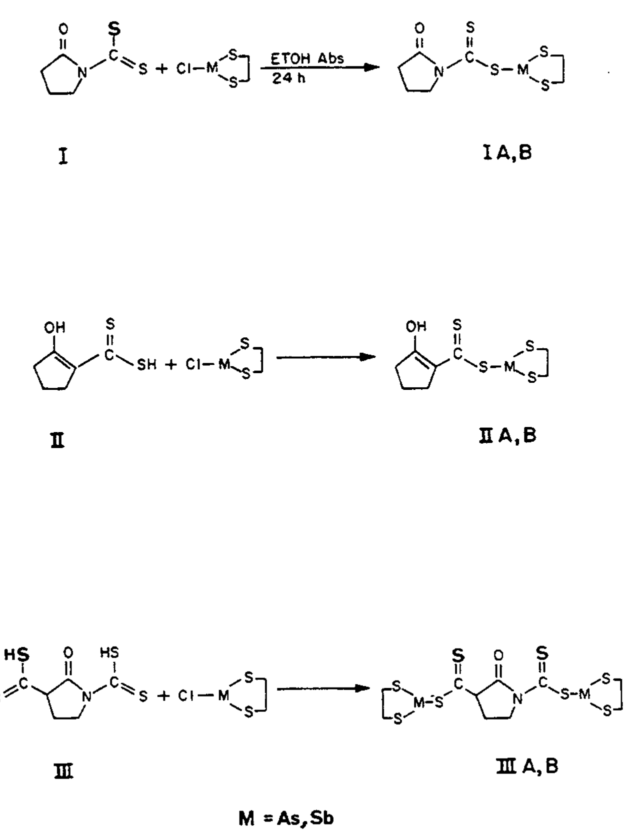

FIGURE 1

Preparation of Complexes

The syntheses of the six new compounds described herein were carried out by the same procedure (Figure 1). An equimolecular solution or suspension of ligand I or II, or a molecular ratio 1:2 for ligand III, was mixed in absolute ethanol with the corresponding dispersion of Cl-$MS_2C_2H_4$ (M = As, Sb), also in absolute ethanol. The reaction mixture was stirred during 24 hours at room temperature. The solids obtained were filtered off, washed with ethanol and water, and air dried.

X-Ray Diffraction Analysis

Crystals suitable for X-ray analysis of the 2-pyrrolidonedithiocarbamate of 1,3-dithia-arsa-cyclopentane (IA) were obtained in the following way: The compound was dissolved in CH_2Cl_2, and hexane was added giving rise to two phases; during 24 hours light-yellow crystals were formed. An octahedral-shaped crystal with a dimension of ca. 0.42 mm on edge was mounted on a glass fiber. All measurements were made on a Nicolet P3F *m* diffractometer with Ni-filtered CuK_α radiation. Cell constants were obtained from least-squares refinement, using the setting angles of 25 carefully centered reflections in the range $9.07 < 2\Theta < 27.96°$. The crystal belongs to the tetragonal system with unit cell dimensions, $a = b = 11.801(3)$, $c = 17.262(4)$ Å, and $V = 2404(1)$ Å^3. The space group, determined from systematic absences, is P_{-4n2}, $z = 8$, and fw = 327.32. The calculated density is 1.81 g cm^{-3}.

The intensity data were collected using the Θ:2Θ scan mode to a maximum value of $2\Theta = 100°$. Of 1612 reflections collected, 1383 were unique and 1341 considered observed according to $F > 3\sigma(F)$. The data were corrected for Lorentz and polarization effects. Empirical absorption corrections [μ CuK_α = 100.41 cm^{-1}] were applied.

The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically (hydrogen atoms were included in idealized positions with a temperature factor $U = 0.06$ Å^2). The weighting scheme corresponded to $w = [\sigma^2 (\mathrm{Fo}) + 0.003\ \mathrm{Fo}^2]^{-1}$, and the range of transmission factors used for the absorption corrections was max = 0.063 and min = 0.009. The final cycle of block-matrix least-squares refinement based on F for the observed reflections converged with unweighted and weighted agreement factors of $R = 0.059$ and $R_w = 0.057$. Neutral atom scattering factors were taken from Cromer and Weber [12], anomalous dispersion effects being included. All calculations were performed using the SHELXTL crystallographic software package [13].

RESULTS AND DISCUSSION

The syntheses of ligands I and III were carried out as previously described in the literature. However, the attempts to synthesize 2-oxocyclopentane-1-carbodithioic acid (II') led to the 2-hydroxy tautomer (II). The spectroscopic data of the tautomers are different: The 2-hydroxy tautomer shows a sharp band at 2480 cm^{-1} (SH) but does not show a band at 1700 cm^{-1} due to the νC=O vibration; instead, there is a strong band at 1540 cm^{-1} related to the enol presence. The ^{1}H NMR signals of both tautomers are

	H-1	H-3	H-4	H-5	SH	OH
II	—	2.79(q)	1.9(q)	2.73(q)	5.20(s)	14.1
II,[9]	2.7(m)	2.7(m)	1.9(m)	2.7(m)	5.24(s)	—

The intensity ratio of the signals around δ 1.9 and 2.7 corresponds to 1:2 in compound II and not to the possible situation 1:2.5 that would be required for the -oxo tautomer. Compound II presents the thiol proton signal at δ 5.2, but another signal appears at 14.9 due to an enolic proton in a chelated situation. Both signals exchange with D_2O. ^{13}C NMR also indicates the enolic tautomeric situation with signals at δ 17.8 (C-4), 32 (C-5), 35.5 (C-3), 120 (C-1), and 184.5 (C-2) and the dithioic carbon at 205. The melting point of II is 83–85° instead of the 90–91° reported for the 2-oxo compound. The mass spectrum exhibits the molecular ion m/z 160.

TABLE 1 Analytical Data and Melting Points

Compound Formula	C Found (Calcd)	H Found (Calcd)	As Found (Calcd)	Sb Found (Calcd)	Mp (°C)
IA	25.7	3.2	22.6	—	163–165
$C_7H_{10}AsNOS_4$	(25.7)	(3.1)	(23.0)	—	
IB	22.4	2.8	—	31.9	158–160
$C_7H_{10}SbNOS_2$	(22.5)	(2.7)	—	(32.6)	
IIA	29.4	3.4	22.9	—	119–121
$C_8H_{11}AsOS_4$	(29.5)	(3.4)	(23.0)	—	
IIB	25.2	3.05	—	33.1	111–113
$C_8H_{11}SbOS_4$	(25.8)	(2.95)	—	(32.7)	
IIIA	20.0	2.4	28.3	—	178 dec
$C_{10}H_{13}As_2NOS_8$	(21.1)	(2.3)	(26.36)	—	
IIIB	19.1	1.8	—	39.2	190 dec
$C_{10}H_{13}Sb_2NOS_8$	(18.1)	(2.0)	—	(36.75)	

The reaction between the three ligands and the Group 15 heterocycles $Cl\text{-}MS_2C_2H_4$ (M = As, Sb) gave the corresponding compounds IA, IB, IIA, IIB, IIIA, and IIIB as stable solids. The complexes arising from I and II ligands are partially soluble in solvents, such as $CHCl_3$, ethyl acetate, and DMSO, but insoluble in water and hexane. The IIIA and IIIB binuclear complexes are almost insoluble in all the common solvents. Table 1 presents elemental analysis data and melting points of the complexes herein described.

Infrared Spectra. All complexes reported here do not exhibit any band in the 2500 cm^{-1} region attributable to an -SH vibration; new bands appear in the region 400–216 cm^{-1} due to M–S bond vibrations and deformation modes of the -arsa or -stibadithiacyclopentane rings [14]. The I and III complexes present almost no shift of carbonyl vibration in relation to the corresponding position in the free ligands. The disappearance of the S–H band and the unaltered position of the C=O vibration suggest that the bonding in these derivatives occurs only through the sulfur atoms. For IIA and IIB, the free ligand enolic vibration at 1540 cm^{-1} exhibits a small shift appearing at 1520 cm^{-1}.

The criteria of Bonati and Ugo [15] have been extensively used as indicative of the coordination modes of 1,1-carbodithia complexes; the presence of only one strong C-S band in the region 950–1050 cm^{-1} has been suggested as indicative of bidentate behavior, and the two bands indicate the monodentate situation; however, these criteria have also been impugned [16]. The IA, IB, and IIA complexes show two strong bands in this region, but IIB exhibits only one. The situation for IIIA and IIIB is not as complex as would be expected for the two types of ligand centers in such compounds, with only one band appearing. As in other cases, the Ugo and Bonati criteria are not conclusive about the iso-, aniso-bidentate, or monodentate metal-sulfur bonding.

NMR Spectral Studies of the Complexes. Due to the low solubility of some of the compounds, it was possible to obtain ^{1}H NMR spectra only for IA, IIA, and IIB complexes. The sharp singlet observed for the -SH proton in the spectra of I and II ligands is found to be absent in the corresponding metal derivatives, indicating the removal of an -SH proton and the formation of an As- or Sb–sulfur bond. Complex IA shows the 2-pyrrolidone ring signals centered at δ 2.25(q), 2.85(t), and 4.35(t). The IIA and IIB proton NMR have enolic hydroxyl signals at δ 12.68 and 12.59, respectively. Exchanging with D_2O, the signals of the 2-hydroxycyclopentene ring correspond to the expected [IIA: δ 1.12(q), 1.94(t), 2.05(t); IIB: 1.85(q), 2.64(t), 2.28(t)]. The methylene protons of the arsa- or stiba-cyclopentane rings for the three complexes show an AA′BB′ pattern, centered at δ 3.68(IA), 2.81(IIA), and 3.62(IIB) [17].

It was only possible to obtain ^{13}C NMR spectra for IA and IIA due also to solubility limitations. The spectra are different, the first one corresponding to the presence of a carbonyl group and the second one manifesting the enolic situation in the complex: [IA: δ 17, 33, 43, 52.5, 173, and 202.5: IIA: 17.5, 31, 43, 121, 182, and 214]. The signals at δ 43 have been assigned to the carbons of the arsa-cyclopentane ring. The 173(IA) peak corresponds to the carbon of the C=O, and the signals at 182 and 121 for IIA could be assigned to the sp^2 C–2 and C–1. The carbons of the CS_2 entities appear at δ 202.5 and 214, respectively.

Mass Spectra. Mass spectra of some 1,1-dithiocarboxylate metal complexes, as well as mass spectra of Group 15 2-chloro-1,3-dithiahetero-cyclopentanes [1,18], have been described. Mass spectra of the four complexes IA, IB, IIA, and IIB present a fragmentation pattern with clear parent ions in accordance with the calculated molecular weights and indicative of the monomeric state of these compounds. However, IIIA and IIIB complexes show a typical thermal decomposition pattern and the absence of molecular ions. The fragmentation patterns of IA, IB, IIA, and IIB complexes arise from the formation and breaking of [As- or Sb-(R-dithiocarboxylate) and [As- or Sb-$MS_2C_2H_4$]$^+$ ions, in a situation similar to that found by us in $R_2dtcMS_2C_2H_4$ (M = As, Sb) complexes [1,2]. The IIIA and IIIB complexes present characteristic fragments corresponding to the binuclear ions [$C_2H_4S_2M$-S-$MS_2C_2H_4$]$^+$ (M = As, Sb) as well as polynuclear entities Sb_2Sn^+ (n = 2–5) in a situation similar to that found in antimony tris-dithiocarbamates [19].

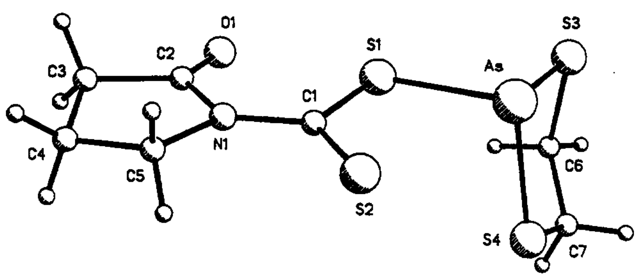

FIGURE 2 Structure of 2-pyrrolidonedithiocarbamate of 1,3-dithia-arsa-cyclopentane.

Description of the Structure

A representation of a crystal of IA is shown in Figure 2. Tables 2–4 provide the positional parameters, bond distances, and angles. The most important features of the molecular structure are the monodentate character of the dithiocarbamate li-

TABLE 2 Atom Coordinates (×10^4) and Temperature Factors (A^2 × 10^3) for the 2-Pyrrolydonedithiocarbamate of 1,3-Dithia-Arsa-Cyclopentane (IA)

Atom	*x*.	*y*	*z*	*U**
As	5117(1)	8194(1)	8274(1)	102(1)
S(1)	3572(2)	7018(2)	8311(1)	86(1)
S(2)	2984(2)	9361(2)	8794(2)	111(1)
S(3)	6264(3)	6705(3)	8036(2)	141(1)
S(4)	5557(2)	8188(2)	9532(1)	114(1)
C(1)	2598(8)	8040(6)	8609(4)	87(3)
N(1)	1486(5)	7728(5)	8659(4)	84(2)
C(2)	1026(8)	6660(8)	8503(6)	100(3)
O(1)	1592(5)	5846(5)	8349(4)	110(2)
C(3)	−224(9)	6738(10)	8562(10)	133(5)
C(4)	−452(10)	7853(9)	8926(7)	114(4)
C(5)	575(8)	8520(8)	8846(7)	107(4)
C(6)	6345(12)	6167(13)	9004(9)	157(6)
C(7)	6460(13)	7050(14)	9610(9)	193(9)

*Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U* tensor.

TABLE 3 Bond Lengths (Å) for the 2-Pyrrolydonedithiocarbamate of 1,3-Dithia-Arsa-Cyclopentane (IA)

As-S(1)	2.293(2)	As-S(3)	2.255(4)
As-S(4)	2.233(3)	S(1)-C(1)	1.744(8)
S(2)-C(1)	1.655(8)	S(3)-C(6)	1.790(16)
S(4)-C(7)	1.719(17)	C(1)-N(1)	1.366(11)
N(1)-C(2)	1.399(11)	N(1)-C(5)	1.460(12)
C(2)-O(1)	1.199(11)	C(2)-C(3)	1.483(14)
C(3)-C(4)	1.482(16)	C(4)-C(5)	1.451(15)
C(6)-C(7)	1.483(22)		

TABLE 4 Bond Angles (°) for the 2-Pyrrolidonedithiocarbamate of 1,3-Dithia-Arsa-Cyclopentane (IA)

S(1)-As-S(3)	90.6(1)	S(1)-As-S(4)	99.0(1)
S(3)-As-S(4)	92.0(1)	As-S(1)-C(1)	96.5(3)
As-S(3)-C(6)	98.0(5)	As-S(4)-C(7)	102.9(5)
S(1)-C(1)-S(2)	121.8(5)	S(1)-C(1)-N(1)	117.8(6)
S(2)-C(1)-N(1)	120.4(6)	C(1)-N(1)-C(2)	127.1(7)
C(1)-N(1)-C(5)	123.3(7)	C(2)-N(1)-C(5)	109.5(7)
N(1)-C(2)-O(1)	123.3(8)	N(1)-C(2)-C(3)	108.4(8)
O(1)-C(2)-C(3)	128.3(9)	C(2)-C(3)-C(4)	105.4(9)
C(3)-C(4)-C(5)	106.8(9)	N(1)-C(5)-C(4)	106.8(8)
S(3)-C(6)-C(7)	114.5(11)	S(4)-C(7)-C(6)	115.9(11)

gand and the absence of participation of the carbonyl oxygen in the coordination. The dithiocarbamate group in the molecule herein described presents a short and a long C–S bond, with lengths corresponding to double and single bonds, respectively. In As(III) molecular compounds, the As–S bonds are as short as 2.228(5) and as long as 2.330(6) Å [20]. For 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 [21]. In our case, the As–S bond of the dithiocarbamate is 2.293(2) Å and the nonbond distance As–S(2) is 3.007 Å. The C(1)–N(1) length, 1.366(11) Å, is 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. The angles S(1)-As-S(3) and S(1)-As-S(4) are different, 90.6(1) and 99.0(1)°, respectively. These values and the S(3)-As-S(4) value of 92.6(1)° suggest an orthogonality around the As similar to that found in tris(phenylthio)arsine [20] with S-As-S angles of 96.38(3)° but very different from the environment in the corresponding tris(phenylthio)amine with a S-N-S angle of 119.5° [22]. In relation to the 1,3-dithia-2-arsacyclopentane ring, the entity is nonplanar, as is also the situation in $ClSbS_2C_2H_4$ [23]. The As-S(3) and As-S(4) bond lengths, 2.255(4) and 2.33(3) Å, are significantly different, whereas, in $ClSbS_2C_2H_4$, the corresponding bond lengths are equal. The 2-pyrrolidyl ring has bond lengths and angles which are normal values within experimental error, showing a typical C=O bond distance of 1.199(11) Å.

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