Monatshefte für Chemie 121, 377 – 383 (1990)

Monatshefte für Chemie
Chemical Monthly

Coordinating Ability of the Heterocycles 1,3-Dithia-2-arsa and Stiba-Cyclopentanes toward Sulfur Containing Ligands, Part I. Dialkyl-dithiocarbamate Complexes

Raymundo Cea-Olivares*, Jesús Wingartz, Elsa Ríos, and **Jesús Valdés-Martinez**

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior,
Ciudad Universitaria, México, 04510, D.F. Mexico

Summary. The heterocyclic compounds $ClMS_2(CH_2)_2$ (M = As, Sb) are tested by first time as source of starting materials in the synthesis of complexes. The preparation and characterization of heterocyclic dithiocarbamates $R_2NCS_2MS_2(CH_2)_2$, (M = As, Sb; R = *Me, Et, i-Pr*) is reported. Spectroscopic and analytical data suggest a bidentate behavior of the dithiocarbamate entity and the presence of a MS_4 core.

Keywords. Dithiocarbamates; Dithia-group cyclopentanes.

Die Koordinationsfähigkeit der Heterocyclen 1,3-Dithia-2-arsa- und -stiba-cyclopentan gegenüber Schwefel enthaltenden Liganden, I. Dialkyldithiocarbamat-Komplexe

Zusammenfassung. Die heterocyclischen Verbindungen $ClMS_2(CH_2)_2$ (M = As, Sb) werden erstmals als Quelle für Ausgangsmaterial zur Synthese von Komplexen herangezogen. Es wird über die Herstellung und Charakterisierung der heterocyclischen Dithiocarbamate $R_2NCS_2MS_2(CH_2)_2$ (M = As, Sb; R = *Me*, *Et*, *i-Pr*) berichtet. Spektroskopische und analytische Daten sprechen für ein bidentates Verhalten der Dithiocarbamat-Einheit und der Präsenz einer MS_4-Anordnung im Komplex.

Introduction

The coordination chemistry of systems where the metal is totally surrounded by sulfur atoms has been extensively studied. This field has grown from synthetic to reactivity studies, electron and molecular structure determinations, electrochemistry, etc. Complexes with different ligands as dithiocarbamates, dithiophosphinates, dithiocarboxilic acids, 1,1-dithiolates etc. have been obtained in order to correlate the structure of the complexes with their chemical properties [1]. The molecular structure of heavy metal complexes of group 15 with a MS_n core has a special interest in function of the presence or absence of a stereo active electron pair [2, 3], as long as a small change in the ligands produces an important variation in the geometry [4]. The MS_n core has also interesting bioinorganic implications in metalloenzymatic systems [5]. Main group dithiocarbamates often exhibit asymmetrical metal-sulfur bonds and in this aspect the crystallographic studies are very exciting [6, 7].

Arsenic (III) and Sb (III) dithiocarbamates are well known since the first detailed study made in 1939 [1, 8]. The studies are diverse, ranging from mass spectra to crystal structure determinations and all kind of spectroscopic studies. Almost all the synthesized complexes present a MS_6 core but also penta-coordinated cores exist as in $BrM(dtc)_2$ compounds [9]. Heterocyclic dithiocarbamates are known with transition and main group elements, but in these compounds the heterocyclic ring is formed through the nitrogen atom [10].

In order to obtain an MS_n core in As and Sb complexes, to prepare heterocyclic dithiocarbamates complexes where the heterocyclic ring is formed through the metal atom and to test the coordinating ability of the 1,3-dithia-2-arsa- or -2-stiba cyclopentanes, we intended the synthesis of complexes with sulfur chelating bidentade ligands. In this first case we report the synthesis of dithiocarbamate complexes $R_2dtcMS_2(CH_2)_2$ (*R* = *Me, Et, i-Pr*; *M* = As, Sb; *dtc* = dithiocarbamate) obtained through the reaction of $ClMS_2(CH_2)_2$ (*M* = As, Sb) with the sodium salts of dialkyl dithiocarbamates.

Experimental

All reagents were commercial and used as such. Melting points were determined with an Osyma instrument, molecular weight with a vacuum vapor pressure osmometer [11]. Infrared spectra were recorded in the region 4000–200 cm^{-1} on a Perkin-Elmer 283-B as KBr pellets or Nujol mulls in CsI, proton magnetic resonance on a Varian FT-80 instrument using $CDCl_3$ as solvent and *TMS* as internal reference, mass spectra determinations in a Hewlett-Packard MS/GC 598 by electron impact at 70 eV. C, H, As, and Sb elemental analyses were performed in commercial laboratories.

Preparation of the Ligands

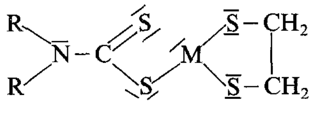
The dithiocarbamate sodium salts were obtained by treating the corresponding secondary alkyl amine R_2NH (*R* = *Me*, *Et*, *i-Pr*) with CS_2 and NaOH according to the common methods. The 2-chloro-1,3-ditha-2-arsa- and -stiba-cyclopentanes were prepared from the corresponding $AsCl_3$ or $SbCl_3$ and 1,2-ethanedithiol by the established methods [12, 13] and characterized by melting point, i.r., and ^1H n.m.r.

General Preparation of the Complexes

All the complexes were synthesized in N_2 atmosphere from reaction of an equimolecular solution of the corresponding dithiocarbamate sodium salt in absolute ethanol and a suspension of 2-chloro-1,3-dithia-2-arsa- or stiba-cyclopentanes also in absolute ethanol. The reaction mixture was stirred for 5 h after that the obtained solid was filtered and extracted with CH_2Cl_2, the CH_2Cl_2 was evaporated and the solid compound thus obtained was air dried. Yields were aproximatively 60%.

Results and Discussion

The solid compounds obtained correspond to the stoichiometry ligand: group 15 dithia-cyclopentane 1 : 1 as is suggested by their analytical data (Table 1). The compounds are air stable, soluble in common organic solvents as chloroform and benzene, but practically insoluble in water and hexane. They present sharp melting points (Table 1), and according to the molecular weight determinations they are monomeric dithiocarbamates of 1,3-dithia-2-arsa and stiba- cyclopentanes.



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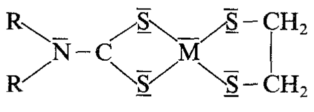

b

M = As, Sb
R = *Me, Et, i-Pr*

1	$Me_2dtc\mathrm{AsS}_2(\mathrm{CH}_2)_2$	**4**	$Me_2dtc\mathrm{SbS}_2(\mathrm{CH}_2)_2$
2	$Et_2dtc\mathrm{AsS}_2(\mathrm{CH}_2)_2$	**5**	$Et_2dtc\mathrm{SbS}_2(\mathrm{CH}_2)_2$
3	$i\text{-}Pr_2dtc\mathrm{AsS}_2(\mathrm{CH}_2)_2$	**6**	$i\text{-}Pr_2dtc\mathrm{SbS}_2(\mathrm{CH}_2)_2$

Table 1. Analytical data and melting points of the compounds $R_2dtcM\mathrm{S}_2(\mathrm{CH}_2)_2$

Compound	m.p. (°C)	%C found (calc.)	%H found (calc.)	%As found (calc.)	%Sb found (calc.)
1	84	21.21	3.57	25.99	
		(20.91)	(3.48)	(26.13)	
2	87	25.71	4.50	23.56	
		(26.67)	(4.44)	(23.81)	
3	135	30.12	5.10	22.04	
		(31.49)	(5.25)	(21.87)	
4	165	18.82	3.27		32.26
		(18.02)	(3.19)		(33.34)
5	150	23.53	3.83		32.22
		(23.27)	(3.88)		(33.52)
6	135	25.18	4.11		31.95
		(26.08)	(4.63)		(31.10)

Infrared Spectra

The main infrared bands of the complexes are given in Table 2. The i.r. spectra of the dithiocarbamate complexes have been extensively used as indicative for the coordination modes of the dithiocarbamate ligand. The i.r. spectra of the 1,3-dithia-2-arsa and stiba-cyclopentane derivatives have been studied thoroughly [14, 15]. Dithiocarbamate complexes show in the i.r. three regions of special interest [16, 17]: the "thioureide" band at 1450–1550 cm^{-1}, the region between 950 and 1050 cm^{-1} associated with the $\nu(\mathrm{C-S})$ and the far-i.r. region between 216–400 cm^{-1}, due to $M-\mathrm{S}$ bond stretching and ring deformation modes [18]. In our complexes the "thioureide" band appears in the expected position and suffers a displacement with the increase of the mass of the *R* group linked to the nitrogen of the dithiocarbamate entity. A small shift of the $\nu(\mathrm{C}\overset{-}{-}\mathrm{N})$ toward higher frequencies is observed in the Sb complexes with respect to the As complexes, these situations are common to the dithiocarbamate complexes previously described.

Table 2. Most important i.r. bands (cm^{-1})

Compound	ν(CN) (KBr)	ν(CS) (KBr)	Far i.r. (Nujol, CsI)
1	1 512 vs	975 s	342 s, 368 s
2	1 490 m	975 w, 1 005 w	255 w, 330 s, 360 vs, 368 m, 395 w
3	1 472 vs	1 028 s	333 m, 367 m
4	1 513 vs	964 s	270 sh, 280 m, 340 sh, 375 m
5	1 495 vs	980 m, 998 w	255 w, 295 s, 340 s, 373 m, 392 w
6	1 475 vs	1 023 s	290 m, 310 m, 335 w, 390 w

Table 3. Assignment of ^1H n.m.r. signals of the compounds $R_2dtcMS_2(CH_2)_2$ in CDCls (*TMS* int. reference, δ/ppm)

Compound	*R* signals	CH_2 (*cp*)
1	3.4 s (CH_3)	3.55 s
2	1.2 t (CH_3) 3.75 q (CH_2)	3.48 s
3	1.47 d (CH_3) 4.6 br (CH)	3.65 s
4	3.43 s (CH_3)	3.63 s
5	1.33 t (CH_3) 3.83 q (CH_2)	3.58 s
6	1.45 d (CH_3) 4.55 br (CH)	3.64 s

According with the criteria of Ugo and Bonati [16] the presence of only one strong C−S band in the region 950–1 050 is indicative of the bidentade behavior of the dithiocarbamate ligands and two bands indicate the monodentate mode. The methyl and the iso-propyl derivatives of arsenic and antimony here described show only one strong band at 950–1 050 cm^{-1} and it supports the bidentate character of the dithiocarbamate entity (Fig. 1 b). However for the ethyl derivatives the situation is not clear, and two bands exist. Since they are not strong there is no full evidence of the presence of a monodentate situation (Fig. 1 a). This ambiguity is present also in other compounds as in Me_3Sn (SSCNMe_2) [16]. In the present compounds, the far i.r. region is associated with the two types of *M*S bond: the bidetate mode of MS_2 of dithiocarbamate entity and the *M*S bonds of the five-membered heterocycle as well as with ring deformation modes.

Proton Magnetic Resonance

The proton magnetic resonance spectra of the 2-chloro, 1-3-dithia-2-arsa or -stiba-cyclopentanes (in $CDCl_3$) show only a singlet due to the methylene protons indicative for the equivalence of the two methylenes in solution. This equivalence has

Table 4. Mass spectral data for the main fragments (abundances of *m/z* and possible assignments; only monoisotopic data for Sb = 121

Assignment	Comp. **1**	Comp. **2**	Comp. **3**
M^+	287 (60)	315 (20)	343 (15)
$R_2dtc\mathrm{AsS_2}^+$	259 (10)	–	–
$R_2dtc\mathrm{As}^+$	195 (40)	223 (10)	251 (< 10)
$\mathrm{AsS_2(CH_2)_2}^+$	167 (100)	167 (50)	167 (25)
$\mathrm{AsS_2}^+$	139 (10)	139 (12)	139 < 10)
$\mathrm{R_2NCS_2}^+$	120 (35)	148 (35)	176 (100)
AsS^+	107 (55)	107 (100)	107 (35)
$i\text{-}Pr_2\mathrm{N}^+$	–	–	100 (10)
$R_2\mathrm{NCS}^+$	88 (99)	116 (20)	144 (< 10)
$R\mathrm{NCSH}^+$	74 (15)	88 (25)	102 (40)
$Et_2\mathrm{N}^+$	–	72 (18)	–
$\mathrm{S_2}^+$	64 (< 10)	64 (< 10)	64 (< 10)
$\mathrm{C_2H_4S}^+$, $\mathrm{SCNH_2}^+$	60 (< 10)	60 (< 38)	60 (12)
$\mathrm{C_2H_3S}^+$	59 (< 10)	59 (< 22)	59 (< 10)
$\mathrm{C_2H_2S}^+$	58 (< 10)	58 (< 15)	58 (< 20)
$\mathrm{C_2HS}^+$	57 (< 10)	57 (< 12)	–
CHS^+	45 (15)	45 (20)	–
$\mathrm{CS_2}^+$, $(Me_2\mathrm{N})^+$	44 (20) (Me_2N)	44 (20)	–
$i\text{-}Pr^+$	–	–	43 (15)

Assignment	Comp. **4**	Comp. **5**	Comp. **6**
M^+	333 (40)	361 (80)	389 (10)
$R_2dtc\mathrm{SbS_2}^+$	305 (< 10)	333 (< 10)	–
$R_2dtc\mathrm{Sb}^+$	241 (12)	269 (70)	297 (< 10)
$\mathrm{Sb(CH_2)_2}^+$	213 (12)	213 (42)	213 (< 10)
$\mathrm{SbS_2}^+$	185 (< 10)	185 (15)	185 (< 10)
SbS^+	153 (30)	153 (100)	153 (30)
Sb^+	121 (< 10)	121 (10)	121 (10)
$R_2\mathrm{NCS_2}^+$	120 (10)	148 (30)	176 (100)
$i\text{-}Pr_2\mathrm{N}^+$	–	–	100 (18)
$R_2\mathrm{NCS}^+$	88 (100)	116 (87)	144 (10)
RNCSH^+	74 (50)	88 (70)	102 (30)
$Et_2\mathrm{N}^+$	–	72 (25)	–
$\mathrm{S_2}^+$	64 (< 10)	64 (15)	64 (< 10)
$\mathrm{C_2H_4S_2}^+$, $\mathrm{SCNH_2}^+$	60 (15)	60 (80)	60 (13)
$\mathrm{C_2H_3S}^+$	59 (10)	59 (15)	59 (< 10)
$\mathrm{C_2H_2S}^+$	58 (10)	58 (10)	58 (15)
$\mathrm{C_2HS}^+$	57 (5)	57 (< 10)	57 (< 5)
CHS^+	45 (18)	45 (15)	45 < 5)
CS^+, $(Me_2\mathrm{N})^+$	44 (20) (Me_2N)	44 (30)	44 (< 10)
$i\text{-}Pr^+$	–	–	43 (12)

been ascribed to the labile character of the ring in solution giving effective planarity, or it may also be due to the effect of the large size of the As or Sb atom compared with the chloro atom, masking the stereo chemical effect on the methylene protons. However with the presence of a bulky substituent instead of chloro, (e.g. phenyl) the arsenic derivative exhibit a non-equivalence of the methylene protons and an AA'BB' pattern arises [19].

The ^{1}H n.m.r. spectra of these group 15 dithiocarbamates show the characteristic proton resonances in accordance with their proposed formulae (Table 3). All the complexes present singlets at about 3.5 ppm due to the methylenes of the five membered heterocyclic ring and this is again indicative for the equivalence of the methylene protons in solution.

Mass Spectra

Mass spectra of some transition and main group dialkyl-dithiocarbamates [20, 21], as well as the mass spectra of the 2-chloro-1,3-dithia-metalla-cyclopentanes of all the heavy elements of the group 15 have been described [22]. The mass spectra of the $R_2dtc\mathrm{MS}_2$ compounds (Table 4) exhibit clear parent molecular ions and in concordance with the molecular weight determinations indicate the monomeric state of these compounds. In the arsenic derivatives the abundance of the parent molecular ion decrease with the length of the alkyl chain linked to the nitrogen atom, but in the antimony complexes the change is unorderly. The decomposition pattern of all the compounds arises mainly from the formation and breaking of the As or Sb monodithiocarbamate ion, $(R_2\mathrm{NCS}_2M)^+$ and the As or Sb dithiacyclopentane ion, $[(M\mathrm{S}_2(\mathrm{CH}_2)_2)]^+$.

The low mass non-metal-containing fragments resulting from the breaking of the metal monodithiocarbamate ion are well established in the mass spectra of the sodium salts and metal complexes of dialkyl-dithiocarbamates [20]. Also the fragments resulting from the breaking of the $[M\mathrm{S}_2(\mathrm{CH}_2)_2]^+$ fragment: m/z 60, 59, 58, 57, and 45 are present in the mass spectra of the complexes as well as in the group 15 $\mathrm{Cl}M(\mathrm{CH}_2)_2$ (M = P, As, Sb, Bi) compounds [22] and in the mass spectra of the dithiolanes [23, 24]; they need no further discussion.

Acknowledgements

We thank Gabriela Carreón, Irma Camelo, Jorge Cárdenas, Rubén Gaviño, and Luis Velasco for their assistance.

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Received October 24, 1989. Accepted December 18, 1989