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Tin(IV) Dithiocarbamates and Related Compounds

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Received July 31, 1968

Preparations and properties of the potentially eight-coordinate SnL_4, SnL_2Cl_2 (L = dimethyl-, diethyl-, and pentamethylen-dithiocarbamate), and $ClSn(O)[S_2CN(CH_2)_5].2H_2O$ are given. The possible structures are discussed on the basis of infrared, ^1H n.m.r., and other data.

Introduction

In preceding papers of ours[1,2,3] properties and possible structures for some tin(IV), and especially organotin(IV), complexes with dithiocarbamates and dithiophosphinates were reported. It was then decided to try and obtain compounds with a ratio of dithio ligand had been reported with 8-oxyquinolate[4] or SnL_4 compounds where L is a potentially bidentate ligand had beeen reported with 8-oxyquinolate[4] or tropolonate ion,[5] but not with bidentate ligands having soft donor atoms such as sulphur. Besides the presence of octacoordinated tin(IV) in these complexes was not agreed upon.[6] The only known example of octacoordinated tin(IV) was found in $Sn(NO_3)_4$ only quite recently,[7] although other are possible.[8]

Here compounds of general formula SnL_4 and SnL_2Cl_2 are reported, L being an *N,N*-disubstituted dithiocarbamate group; their properties are used to discuss their possible structures.

Results

Reaction of a water soluble tin(IV) salt, such as $SnCl_4.5H_2O$ or ammonium hexachlorostannate(IV), with a sodium salt of an *N,N*-disubstituted dithiocarbamate (LNa) afforded either yellow L_2SnCl_2 or orange-red SnL_4 as the main product when the molar ratio was *ca.* 1:2 or more than that, *e.g.* 1:3 or 1:4, respectively. The crude reaction products were generally contaminated by an yellow powder, insoluble in organic solvents and unaffected by a free flame, probably basic tin derivatives. The reaction products are not very stable even in the solid state, some insoluble white material being formed in a few weeks; their solutions are even more unstable, a precipitate being formed in a few hours.

The orange-red SnL_4 compounds (Table I) were obtained more neatly from SnL_2Cl_2 and LNa in acetone solution than according to the preceding route. The compound SnL_2Br_2 [3] was obtained by addition of bromine, dissolved in CH_2Cl_2, to the crude orange-

Table I. Compounds Obtained and Their Analytical Data

Compound and colour	m.p. °C	C [a]	H	N	Cl	MW
$Sn(S_2CNMe_2)_4$	>160	24.05	4.01	9.36	—	598.7
red-orange	(dec.)	23.95	4.03	9.48	—	450
$Sn(S_2CNEt_2)_4$	154-56	33.4	5.57	7.80	0.0	710.7
red-orange		33.77	5.43	7.82	0.0	623
$Sn[S_2CN(CH_2)_5]_4$	*ca.* 180	38.00	5.27	7.38	—	758.7
orange-red	(dec.)	37.43	5.29	7.24	—	560
$Sn[S_2CN(CH_2)_5]_4.2C_6H_6$	*ca.* 180	47.3	5.68	6.13	—	914.7
orange-red	(dec.)	46.86	5.65	6.00	—	683
$Zn[S_2Cn(CH_2)_5]_2$	229-30	37.4	5.2	7.27	—	385.4
white		37.38	5.13	7.21	—	365
$ClSn(O)[S_2CN(CH_2)_5].2H_2O$	330	19.9	3.87	3.87	13.28 [b]	347.2
pale yellow		20.66	3.60	4.04	13.59	—
$Cl_2Sn(S_2CNMe_2)_2$	244-6	16.76	2.79	6.51	16.54	429.7
pale yellow		16.73	2.78	6.44	16.20	503
$Cl_2Sn(S_2CNEt_2)_2$	200-201	24.7	4.12	5.77	14.63	485.7
pale yellow		24.66	4.10	5.62	14.69	523

[a] Calculated/found. [b] Oxygen.

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(1) F. Bonati, S. Cenini, and R. Ugo, *Istituto Lombardo (Rend. Sci.)*, *A99*, 825 (1965).

(2) F. Bonati, S. Cenini, and R. Ugo, *J. Organomet. Chem.*, *9*, 395 (1967).

(3) F. Bonati, and R. Ugo, *J. Organomet. Chem.*, *10*, 257 (1967).

(4) K. Ramaiah, and D. F. Martin, *Chem. Comm.*, 130 (1965); see however M. Frazer and Z. Goffer, *J. Chem. Soc.*, (*A*), 544 (1966).

(5) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, *86*, 5132 (1964).

(6) F. A. Cotton and G. Wilkinson, «Advanced Inorganic Chemistry», J. Wiley, London, p. 461 (1966).

(7) C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc.*, (*A*), 1949 (1967).

(8) S. J. Lippard, *Progr. Inorg. Chem.*, *8*, 114 (1967).

yellow reaction product obtained from aqueous tin(II) chloride and sodium diethyldithiocarbamate. This crude product and the related one from sodium dimethyldithiocarbamate, might be tin(II) dithiocarbamate, but their instability precluded their isolation in the pure state.

The products that form as by-products during the preparation of SnL_4 compounds are probably basic tin derivatives, as evidenced from the isolation from the mother liquor of $Sn[S_2CN(CH_2)_5]_4$ of a small quantity of $ClSn(O)[S_2CN(CH_2)_5] \cdot 2H_2O$.

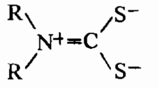
We then tried to obtain additional potentially eight-coordinate compounds between Pb^{IV} and dithiocarbamate or between Sn^{IV} and 8-oxyquinolate. However, reaction of excess 8-hydroxyquinoline with either tin tetrachloride or ammonium hexachlorostannate(IV) yielded only dichlorotin(IV) bis-oxyquinolate identical to the compound described by Frazer and Goffer.[4] The reaction between ammonium hexachloroplumbate(IV) and sodium diethyldithiocarbamate afforded mainly lead(II) diethyldithiocarbamate, identified by comparison with a known sample.[9]

Spectral and Other Data. The electronic spectra of the compounds prepared and those of reference zinc(II) compounds are given in the Table II. The two strong ultraviolet bands, found by us also in thallium(III) and arsenic(III) derivatives, as well as in many other organotin(IV) dithiocarbamates,[3] can be assigned to a $\pi \rightarrow \pi^*$ transition of the ligand; while no satisfactory explanation is possible now for the band at 438 mμ, which is also present in thallium(III) diethyldithiocarbamate. It can be remarked that the band at *ca.* 255 mμ is always stronger in tin(IV) dimethyl- than in diethyl-dithiocarbamates; the behaviour is quite similar to that observed on the corresponding zinc(II) derivatives. The different intensity of the band at *ca.* 255 mμ and of the shoulder at *ca.* 290 mμ in the tin(IV) derivatives of piperidinodithiocarbamate is in agreement with the presence of clathrated benzene in one of them.

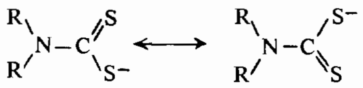
Table II. Electronic Spectra

Compound (solvent)	λ_{max}	ε
$Sn(S_2CNMe_2)_4$	260	61,500
(chloroform)	288 sh	*ca.* 38,000
	435 sh	*ca.* 1020
$Sn(S_2CNEt_2)_4$	254	51,000
(chloroform)	288 sh	*ca.* 20,000
	438 sh	*ca.* 775
(acetonitrile)	255	49,800
	295 sh	*ca.* 20,300
	435 sh	*ca.* 700
$Sn[S_2CN(CH_2)_5]_4$	257	36,500
(chloroform)	293 sh	*ca.* 11,900
$Sn[S_2CN(CH_2)_5]_4 \cdot 2C_6H_6$	255	53,000
(chloroform)	293 sh	*ca.* 18,600
$Cl_2Sn(S_2CNMe_2)_2$	253	41,200
(chloroform)	296 sh	*ca.* 3900
$Cl_2Sn(S_2CNEt_2)_2$	251	34,300
(chloroform)	294 sh	*ca.* 4500
$Zn(S_2CNMe_2)_2$	259	46,700
(chloroform)	280 sh	*ca.* 27,000
	315 sh	*ca.* 745
$Zn(S_2CNEt_2)_2$ [3]	263	38,000
(chloroform)	281	22,400
	312	1120

In the infrared spectra (nujol mull) a band at *ca.* 1500 cm^{-1} is generally found in all the compounds here reported. This band is generally assigned to a CN stretching mode, where the CN bond order is intermediate between 1 and 2. The difference observed here between the derivatives of *N,N*-dimethyl- and *N,N*-diethyl-dithiocarbamate group is *ca.* +22 cm^{-1}, both with the SnL_4 and the SnL_2Cl_2 compounds. This difference, to be compared with the value (+26 cm^{-1}) observed in the analogous methyl and ethyl derivatives of thallium(III) and dimethylthallium(III),[2] is due to the stronger inductive effect of the N-bonded ethyl groups; these make possible a higher contribution of the canonical structure (II) over (I).



(I)



(II)

The pentamethylendithiocarbamate shows the same behaviour as the diethyldithiocarbamate since the inductive effect is not very different in the two cases. Conversely, electron withdrawing substituents on the metal atom, such as chloride groups, bring about a higher contribution of (I) over (II) and, therefore, a shift to higher wavenumber of the CN stretching mode. As the shift is indipendent from the nature of R, no other effect is likely to be operative. In particular the structure of SnL_4 compounds ought to be similar; that is either all of them are $SnL_3^+L^-$ or all of them are SnL_4, in the solid state. The same can be stated for SnL_2Cl_2 compounds, *mutatis mutandis.*

Comparison of the infrared spectra (4000-200 cm^{-1}) in nujol mull of Sn^{IV} and Zn^{II} diethyldithiocarbamate shows that additional strong bands are present in the tin compounds at 1408, 1262 and a weak one at 1002 cm^{-1}. No remarkable difference can be found on the other hand between the corresponding dimethyldithiocarbamates or pentamethylendithiocarbamates; in the latter case the spectrum is complicate enough to obscure any possible difference.

In the SnL_2Cl_2 compounds reported here the two tin-bonded chlorine atoms make the tin atom a fairly good acceptor. The structure is therefore likely to contain chelating dithiocarbamate groups and to be *cis*-octahedral, in agreement with the presence of a stronger and a weaker band at around 300 cm^{-1}, below the value found for the tin-sulphur vibration (*ca.* 380 cm^{-1}).

In the $Sn[S_2CN(CH_2)_5]_4 \cdot 2C_6H_6$ compound the evidence for the clathrated benzene molecule include the presence of an aromatic, weak CH stretching vibration and of two strong out of plane CH vibration at 672 and 693 cm^{-1}.

The n.m.r. data suggest that all the ethyl groups of $Sn(S_2CNEt_2)_4$ are equivalent in chloroform solution.

The molecular weight measurements, carried out in chloroform solution at 37°, afforded lower values than required for the SnL_4 compounds, and slightly higher than required for the SnL_2Cl_2 compounds. Normal values were found for the reference zinc(II) derivatives (Table I).

The electric conductance for solutions of SnL_4 compounds are given in Table III. While there is no difference in the behaviour of the methyl and ethyl derivative in acetonitrile solution, where both are 1:1 electrolytes, only the latter is an electrolyte in methylene chloride. The former does not dissolve in acetone, and the latter is not an electrolyte in this solvent.

Table III. Conductivity Data at 22°

	$\Lambda_{0.001}$	Λ_0
$Sn(S_2CNMe_2)_4$ in:		
dichloromethane	3.8	10.2
acetonitrile	23	122.5
acetone	ins.	—
$Sn(S_2CNEt_2)_4$ in:		
dichloromethane	12.7	26.2
acetonitrile	*ca.* 5	140
acetone	2.8	10
$NaS_2CNEt_2 . 3H_2O$ in:		
acetonitrile	86	140

Discussion

The SnL_2Cl_2 compounds might be regarded as examples of pseudooctahedral tin(IV) derivatives; the values of the observed molecular weights, slightly higher than the calculated formula weights, reflect some trend toward association, either trough bridging groups or via a three coordinate sulphur; at the present time it is not possible to establish whether association extends to the solid state or not.

The SnL_4 compounds can be considered as derivatives of tin(IV) or as 1:1 adducts between tin(II) dithiocarbamate and *N,N,N',N'*-tetraalkyldithiouramedisulphide. The latter formulation can be discarded, as there is no difference between the ethyl groups in the n.m.r. spectrum of the compounds, against the requirement of this structure. An ionic structure is likely for these molecules in solution of solvents, such as acetonitrile, which make solvation easy. A similar trend toward a $SnL_3^+L^-$ type of structure is likely also in chlorinated solvents, in agreement with the conductivity data and the lower values of the molecular weights found in chloroform solution; ionic dissociation is evident from the Λ_0 value of the ethyl derivative. A fast exchange of L groups between the cation and the anion explains the presence of only one ethyl group in the n.m.r. spectrum in $CHCl_3$ solution; besides the two signals might be very near.

However, the presence of an ionic structure can be discarded in acetone solution for the ethyl derivative (the methyl derivative is insoluble). As ionization seems to take place only in certain solvents, and then can even be not complete, it is reasonable to assume that in the solid state the compounds are not ionic. The tin(IV) derivatives could have a coordination number of eight or less according to the number of potentially bidentate ligands which behave as such. Eight coordination is possible in principle, since the dithiocarbamate group is in the list of ligands which are able to form eight-coordinate complexes, *e.g.* with uranyl.[8] If one or more dithiocarbamate group were not chelating, it should be possible to observe some additional band in the infrared spectrum ;[3] and this band should be absent in the spectra of the ordinary, chelated dithiocarbamates, generally very similar.[9] There is no remarkable difference between the spectrum of the zinc(II) and tin(IV) dimethyldithiocarbamates, while additional bands were observed in the tin(IV) diethyldithiocarbamate; these bands were not present in zinc(II) or in other metal dithiocarbamates. This evidence is rather in favour of octacoordination for tin(IV) dimethyldithiocarbamate and against it for the ethyl derivative in the solid state. The difference between the two compounds is also evident in the conductivity of the dichloromethane solutions and in the solubility in acetone.

Other lines of evidence will be welcomed to check independently the conclusions suggested here: *e.g.* X-ray structure or Moessbauer spectra. In particular, structural data will be very useful to ascertain whether the four ligand around the tin atom are so arranged as to produce tetrahedral symmetry or another symmetry typical of eight-coordination. In the former case, then, the bond between the tin atom and the ligand could be explained as a three-center, two-electron bond, not involving necessarily d orbitals from the tin atom. In this case the molecular orbital will be formed from a tin sp^3 hybrid orbital and from a σ-type orbital from the ligand donor atoms, resulting in bonding, non-bonding, and antibonding combinations; only the bonding and non-bonding orbitals would be occupied by the four electrons from the ligand.

Experimental Section

The analytical and other data are given in table 1; the electronic spectra are reported in table 2; the conductance data are given in table 3. The infrared spectra reported here were recorded on Perkin-Elmer 457 or 621 instrument, employing nujol mulls on KBr or CsI discs, respectively. Molecular weight determinations were carried out on a Mechrolab Osmometer by Mrs. M. Bonfà. Chlorine was determined quantitatively by potentiometric titration after destroying the sample with hot alkaline hydrogen peroxide. The so-called Beilstein test for chlorine is often positive even when the halogen content is 0.0%, owing to the thiourea-like nature of the compounds.

Sodium dimethyldithiocarbamate and pentamethylendithiocarbamate were prepared according to the literature,[10] while sodium diethyldithiocarbamate was a commercial product. Zinc(II) pentamethylendithiocarbamate was prepared from the sodium and aqueous zinc sulphate; it was crystallized from ethyl acetate.

Tin(IV) Tetrakis(N,N-*dimethyldithiocarbamate*). To an acetone solution (150 ml) of dichlorotin(IV) bis-(dimethyldithiocarbamate) (1.19 g) sodium dimethyldithiocarbamate with 2.5 H_2O (1.83 g) in acetone

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(9) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, *B29*, 75 (1956).

(10) G. D. Thorn, and R. A. Ludwig, «The Dithiocarbamates and Related Compounds», Elsevier, Amsterdam (1962).

(150 ml) was added slowly with stirring. An orange precipitate was formed, filtered and dried in vacuum desiccator (2.6 g). The analytical sample was purified by dissolving a crude sample in methylene chloride and allowing the solution to evaporate under *ca.* 20 Torr. Both the crude and the crystallized sample exhibit the same infrared spectrum and no definite m.p. The compound is sparingly soluble in chloroform, and insoluble in acetone, ether, tetrahydrofuran, methanol, ethyl acetate and hydrocarbons. Infrared spectrum: 1532 s, 1495 s, 1465 s; 1415 sh, 1373 s; 1248 s; 1135 s, asymm., br.; 1048 w; 979 s; 575 w, 565 sh; 446 w, 438 sh; 384 w, 370 sh.

Tin(IV) Tetrakis(pentamethylendithiocarbamate). Aqueous (150 ml) sodium pentamethylendithiocarbamate pentahydrate (4.0 g) was dropped slowly with stirring to aqueous ammonium hexachlorostannate(IV) (7.96 g); the orange precipitate was collected by filtration and dried in a vacuum desiccator (5.78 g). No precipitate was obtained from the mother liquor on adding additional dithiocarbamate; a brown precipitate was obtained on addition of copper(II) acetate. The orange precipitate was extracted with benzene (200 + 200 + 100 ml), leaving a white residue (0.58 g), insoluble in common organic solvents and not flammable. The orange extract was concentrated under vacuum to 100 ml; the chlorine-free precipitate was filtered (3.84 g). The compound was purified again similarly using benzene as a solvent, to yield the analytical sample as red-orange crystals, dried in a vacuum desiccator, dec. *ca.* 180°. The sample was freed from the clathrated benzene molecules by heating at 64°/0.1 mm till constant weight (*ca.* 1 day): the weight loss was in agreement with the loss of two benzene molecules per tin atom.

The benzene containing compound is soluble in chloroform and in methylene chloride, less soluble in benzene, and insoluble in ether, petroleum ether and ethanol. Heating 3 hours at 170° decomposed the compound noticeably.

Infrared spectrum: 1505 s, 1468 s, 1457 s, 1448 s, 1423 s; 1377 m, 1361 m, 1350 m, 1280 m, 1262 m, 1240 s, 1226 s; 1160 w; 1132 s, 1112 s; 1070 w; 1023 m, 1000 s, 972 s, 948 w; 888 m; 858 m; 806 w; 622 vw; 604 w; 547 w; 506 m; 455 w; 405 w; 356 m; 335 m, sh; 270 w. The infrared spectrum of the benzene containing compound shows additional bands at 3090 vw, 3060 vw; 3040 w; 1470 s; 1437 s; 1034 m; 693 s, 672 s (recorded only down to 400 cm^{-1}).

Oxochlorotin(IV) Pentamethylendithiocarbamate, Bihydrate. The orange benzene extract from which tin(IV) tetrakis(pentamethylendithiocarbamate) was obtained gave on standing the pale yellow compound (99 mg). The compound is sparingly soluble in chloroform and insoluble in benzene and in acetone.

Infrared spectrum: 3400 m, very broad; 1640 w, broad; 1500 s; 1461 s, 1448 s; 1380 w, broad; 1282 w, 1265 w, 1245 s; 1138 w, 1111 w; 1022 w, 1004 w; 979 w, 951 w; 888 w; 858 w; *ca.* 670 m, very broad (recorded only down to 400 cm^{-1}).

*Tin(IV) Tetrakis(*N,N*-diethyldithiocarbamate).* (a) To dichlorotin(IV) diethyldithiocarbamate (1.0 g) in acetone (250 ml) sodium diethyldithiocarbamate trihydrate (0.9 g) in acetone (50 ml) was added dropwise, with constant stirring. The orange precipitate formed was filtered off (1.01 g), m.p. 156°.

(b) An aqueous solution (650 ml) of sodium diethyldithiocarbamate trihydrate (13.8 g) was added to an aqueous solution (500 ml) of ammonium hexachlorostannate(IV) (6.5 g), dropwise, under constant stirring. Near the end and then after the addition was complete the colour of the precipitate was orange, while the pH was *ca.* 6. The filtered, chlorine-free precipitate was pumped 9 hours in a desiccator over $CaCl_2$ till constant weight (8.02 g). The analytical sample was crystallized from acetone; orange prisms, m.p. 156°, undepressed m.p. when mixed with the compound prepared under (a). The compound is soluble in CH_2Cl_2 and $CHCl_3$, sparingly soluble in ether, acetone, and benzene, very sparingly soluble in methanol. Although the compound is moderately soluble in tetrahydrofuran and dioxane, the solutions become colourless nearly at once. ^1H n.m.r. data were recorded in $CDCl_3$ solution, against tetramethylsilane as internal standard: triplet at 8.64 and quartet at 6.17 τ, $J(CH_3–CH_2)$ *ca.* 7 cps.

The aqueous mother liquor did not yield any precipitate by addition of additional sodium dithiocarbamate or of cupric acetate.

Infrared spectrum: 1510 s; 1471 s; 1461 s, br, sh, 1449 sh, m, 1439 w, sh, 1429 w, sh; 1408 s; 1378 m; 1358 sh, 1352 m; 1298 m, 1276 s, 1262 s, 1201 s; 1148 m, 1132 m; 1098 w, 1092 w, 1079 w, 1073 w, 1062 w; 1008 w, 989 m; 917 m, 912 m, sh; 843 vw, 830 m; 770 vw, br; 568 m; 520 w; 420 w; 398 w, 378 m; 321 w; 241 vw.

*Dichlorotin(IV) Bis(*N,N*-dimethyldithiocarbamate).* (a) An aqueous solution of sodium dimethyldithiocarbamate with 2.5 H_2O (8.46 g) was added dropwise and with constant stirring to an aqueous solution of tin tetrachloride pentahydrate (15.8 g). The precipitate was filtered, dried in a vacuum desiccator over $CaCl_2$ and then extracted with methylene chloride (70 ml). The extract was evaporated to dryness under reduced pressure and the residue (5.77 g) was taken up with chloroform (550 ml). Addition of CCl_4 (150 ml) gave the product (0.411 g) as a pale yellow precipitate, m.p. 246°. Repeated concentration of the mother liquor together with further addition of carbon tetrachloride yielded additional product (4 g), m.p. 243°. The compound is moderately soluble in chloroform, acetone, methylene chloride, insoluble in methanol, acetonitrile, ether and hydrocarbons. The compound was formed even when the molar ratio of the reagents was 1.0.

(b) The compound was obtained as a precipitate when concentrated solutions of $SnCl_4$ and of $Sn(S_2CNMe_2)_4$ in CH_2Cl_2 were mixed.

Infrared spectrum: 1548 s; 1460 s; 1412 s, 1402 s, 1378 s; 1242 s; 1160 s, broad and asymm.; 1048 m; 970 s, 966 sh; 760 w, br, 733 w, br; 568 m; 435 m; 382 m; 316 s; 275 m.

Acknowledgments. Financial support by Consiglio Nazionale delle Ricerche is gratefully acknowledged.