TABLE V

STABLE STRUCTURES OF THE SESQUICHALCOGENIDES OF THE RARE
EARTH ELEMENTS Gd–Lu, Y, AND Sc[a]

	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sc
M_2S_3	A	A	A	D	D	D	D	E	E	F
M_2Se_3	A	B	B	F	F	F	F	F	?F?	F
	B									
	A									
M_2Te_3	B	C	F	F	F	F	F	?	?	G
	C									

[a] The elements are arranged in order of decreasing cation radius; A, defect Th_3P_4-type; B, orthorhombic phase; C, unknown; D, monoclinic phase; E, α-Al_2O_3-type; F, Sc_2S_3-type; G, Sc_2Te_3 structure.

the structure probably becomes unstable, because anion–anion contact, which provides a stable framework for a *cation-deficient* structure, no longer occurs. At small r_c/r_a the structure probably becomes unstable, because the small cation "rattles" in the close packed anion lattice. The individual range of r_c/r_a for stability of the tellurides (0.404–0.422) with the Sc_2S_3 structure is much narrower than that of the selenides (0.370–0.453). The average value of r_c/r_a, particularly for the tellurides, is also very close to 0.414., the value at which both anion–anion and cation–anion contact occurs.[23] Therefore, it appears that for the tellurides a double framework of these contacts is necessary for the stability of the structure. The selenides with the Sc_2S_3 structure tolerate considerable distortion before the structure becomes unstable. Reasons for this behavior are not immediately obvious, although clearly the hard sphere model can only be an approximation. That Sc_2S_3 is the only sulfide of this structure type is probably a consequence of the large increase in cation

(23) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd Ed., 1960, Chapter 13, pp. 520–530.

radius between Sc and Lu. The value of r_c/r_a for Sc_2S_3 (0.397) lies within the stability range for the selenides, but that for "Lu_2S_3" (0.461) lies outside it.

A logical extension of the above discussion is to consider whether the nonoccurrence of the Sc_2S_3 structure among other sesquichalcogenides (*i.e.*, other than those of the rare earth elements, yttrium, and scandium) can be understood solely in terms of the hard-sphere model. Elements of the first, second, and third transition series will not be considered in order to avoid complications due to crystal field effects. This eliminates from discussion all elements except Al, Ga, In, and Tl. Values of r_c/r_a for all but two sesquichalcogenides of these elements lie outside the stability limits for the Sc_2S_3 structure. The value of r_c/r_a for In_2S_3 (0.43) falls within the limits established for selenides; but since no limits could be definitely established for sulfides, the prediction may be ambiguous. The value of r_c/r_a for In_2Se_3 (0.40)[24] is definitely within the range for selenides, and the Sc_2S_3 structure would be predicted. However, the best characterized form of this compound occurs in a defect wurtzite structure.[26] This is not too surprising, since for r_c/r_a less than 0.414[23] structures with tetrahedral coordination in general are more stable than those with octahedral coordination. However, when one recalls that Sc_2Se_3 (0.370) forms the Sc_2S_3 structure, it is apparent that factors other than radius ratio alone are of considerable importance in determining the stability of selenides with this structure.

(24) The radius of In^{3+}, 0.79 Å., was obtained from the lattice parameter of In_2O_3[25] using the method of Templeton and Dauben.[19]

(25) N.B.S. Circular 539, Vol. V, U. S. Government Printing Office Washington, D. C., 1963, p. 26.

(26) S. A. Semiletov, *Kristallografiya*, **5**, 704 (1960).

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Some Phenyltin, -lead, and -antimony Dithiocarbamates

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The preparation and properties of 24 new dithiocarbamates containing phenyl groups bonded to either carbon, tin, lead, or antimony are described. Decomposition of trityl diorganodithiocarbamates gives the corresponding tetraorganothiuram disulfides. Tetraorganothiuram disulfides can be conveniently prepared by the reaction of triphenylantimony dichloride with the appropriate sodium diorganodithiocarbamate. Organometallic sulfides can be conveniently prepared by the reaction of ammonia with a carbon disulfide solution of the appropriate organometallic chloride or oxide.

Although the literature on the dithiocarbamates is quite extensive,[1] to our knowledge only one dithiocarbamate containing phenyl groups bonded to a group

IV-B element other than carbon has been reported.[2] In this paper are reported some dithiocarbamates containing phenyl groups bonded to either carbon, tin, lead, or antimony. The properties and analytical data are summarized in Table I.

(1) For a recent review see G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., Amsterdam and New York, 1962.

(2) E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, **3**, 905 (1964).
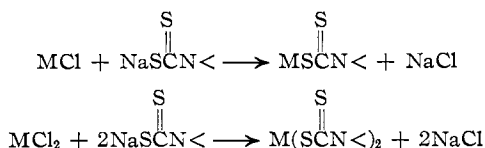
TABLE I

PHENYLTIN, -LEAD, AND -ANTIMONY DITHIOCARBAMATES

Compd. no.	M	% yield by method A[a]	% yield by method B[b]	M.p., °C	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Mol. wt.[e] Calcd.	Mol. wt.[e] Found	C-N str. freq.,[d] cm.$^{-1}$	λ_{max}, mμ	10^{-4} ϵ_{max}[e]
— **M—S—C(=S)—NHCH$_2$C$_6$H$_5$**															
1	(C$_6$H$_5$)$_3$C	59		138–140 dec.	76.22	76.03	5.41	5.49	3.29	3.30	425	324^f	1497	241 / 252 / 287	3.62 / 2.34 / 2.53
2[g]	(C$_6$H$_5$)$_3$Sn			124–126									1508	244 / 269	3.98 / 1.85
3	Cl(C$_6$H$_5$)$_2$Sn	83	74	139–140	48.94	49.14	3.67	3.88	2.84	2.65	490	490	1522	244 / 252 / 270 / 287	3.93 / 2.46 / 1.84 / 1.81
4	(C$_6$H$_5$)$_3$Pb	70	84	107–109	50.30	50.26	3.74	3.68	2.26	2.07	621	482^f	1495	243 / 275	7.69 / 4.16
M(S—C(=S)—NHCH$_2$C$_6$H$_5$)$_2$															
5	(C$_6$H$_5$)$_2$Sn	83	80	92–94	52.75	53.08	4.12	4.26	4.40	4.41	638	656	1497	245 / 274	4.31 / 3.75
6	(C$_6$H$_5$)$_2$Pb	70	94	102–103 dec.	46.32	46.19	3.58	3.73	3.86	3.85	725	396^f	1479	243 / 273	6.08 / 5.37
M—S—C(=S)—N(C$_6$H$_5$)$_2$															
7	(C$_6$H$_5$)$_3$Sn	81	70[h]	182–183	62.67	62.89	4.21	4.47	2.35	2.34	594	587	1490	241 / 266	4.75 / 3.71
8	Cl(C$_6$H$_5$)$_2$Sn	88		203–204	54.32	54.35	3.65	3.84	2.53	2.58	553	541	1486	243 / 278	3.09 / 4.50
9	(C$_6$H$_5$)$_3$Pb	90		163–165	54.52	54.50	3.70	3.76	2.05	2.04	683	749	1486	242 / 276	5.46 / 3.63
10	(C$_6$H$_5$)$_2$Sb	70	87[i]	186–188	57.72	57.97	3.84	3.81	2.69	2.57	520	547	1490	243 / 304	5.18 / 2.99
M[S—C(=S)—N(C$_6$H$_5$)$_2$]$_2$															
11	(C$_6$H$_5$)$_2$Sn	73		216–218	59.92	59.86	3.98	4.12	3.68	3.68	762	750	1486	242 / 272	5.20 / 5.10
12	(C$_6$H$_5$)$_2$Pb	63		166–168 dec.	53.68	53.85	3.56	3.85	3.30	3.31	850	495^f	1484	244 / 274	4.06 / 6.17
M—S—C(=S)—N(CH$_3$)$_2$															
13	(C$_6$H$_5$)$_3$Sn	96		136–137	53.65	53.84	4.46	4.62	2.98	2.81	470	457	1522	244 / 282	6.94 / 1.35
14	Cl(C$_6$H$_5$)$_2$Sn	85		139–141	42.04	42.09	3.73	3.88	3.26	3.37	428	436	1531	245 / 257 / 287	2.13 / 0.86 / 0.76
15	(C$_6$H$_5$)$_3$Pb	90		118–119	45.15	45.29	3.75	3.70	2.50	2.33	559	503	1499	246 / 276	2.43 / 0.11
16	(C$_6$H$_5$)$_2$Sb	70	90[i]	115–117	45.48	45.30	4.03	3.78	3.53	3.67	396	362	1508	244 / 274	5.01 / 3.85
M[S—C(=S)—N(CH$_3$)$_2$]$_2$															
17	(C$_6$H$_5$)$_2$Sn	74		203–205	42.12	42.22	4.28	4.28	5.46	5.49	513	518	1527	243 / 266 / 277	5.01 / 3.85 / 3.08
18	(C$_6$H$_5$)$_2$Pb	88		170 dec.	35.92	35.96	3.65	3.70	4.65	4.83	602	509^f	1508	245 / 258	6.63 / 6.30
M—S—C(=S)—N(C$_2$H$_5$)$_2$															
19	(C$_6$H$_5$)$_3$C	77		150	73.64	73.44	6.38	6.79	3.57	3.85	391	382	1486	242 / 285	2.00 / 1.56
20	(C$_6$H$_5$)$_3$Sn	91		133–134	55.45	55.30	5.02	5.11	2.81	2.83	498	475	1490	244 / 270	4.58 / 2.02

Table I (*Continued*)

Compd. no.	M	% yield by method A[a]	% yield by method B[b]	M.p., °C	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Mol wt.[c] Calcd.	Mol wt.[c] Found	C–N str. freq.,[d] cm.$^{-1}$	λ_{max}, mμ	10^{-4} ϵ_{max}[e]
21	Cl(C$_6$H$_5$)$_2$Sn	88		143–145	44.72	44.78	4.38	4.47	3.07	3.29	456	437	1520	243	2.61
														259	1.12
														282	1.03
22	(C$_6$H$_5$)$_3$Pb	90		140–142	47.09	47.28	4.26	4.53	2.39	2.38	587	579	1490	243	5.13
														256	2.05
														277	2.17
23	(C$_6$H$_5$)$_2$Sb	85	60[i]	68–69	48.14	48.15	4.72	4.85	3.30	3.48	424	436	1493	244	2.58
														273	2.71

$$\begin{array}{c} \text{S} \\ \| \\ M\left[\text{S}-\text{C}-\text{N(C}_2\text{H}_5)_2\right]_2 \end{array}$$

Compd. no.	M	% yield by method A[a]	% yield by method B[b]	M.p., °C	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Mol wt.[c] Calcd.	Mol wt.[c] Found	C–N str. freq.,[d] cm.$^{-1}$	λ_{max}, mμ	10^{-4} ϵ_{max}[e]
24	(C$_6$H$_5$)$_2$Sn	83		152–154	46.41	46.89	5.27	5.49	4.92	5.23	569	560	1506	243	5.28
														258	4.15
														275	3.63
25	(C$_6$H$_5$)$_2$Pb	91		208–210 dec.	40.17	40.41	4.56	4.36	4.26	4.30	658	622	1486	244	5.61
														263	6.27

[a] Stoichiometric quantities of MCl or MCl$_2$ and the appropriate sodium dithiocarbamate were allowed to react in a suitable solvent for 2 hr. at room temperature. The reaction mixture was filtered to remove the NaCl, the solvent was removed from the filtrate *in vacuo* at room temperature, and the residue was recrystallized from acetonitrile except for no. 5 (benzene), 9 (benzene–acetonitrile), 14 (chloroform–acetonitrile), and 24 (chloroform–acetonitrile). The solvent used was chloroform except for no. 1 (acetonitrile), 4 (benzene), 6 (acetonitrile), 9 (benzene), and 12 (benzene). [b] A stoichiometric quantity of benzylamine dissolved in chloroform was allowed to react with a carbon disulfide solution of the organometallic oxide (hydroxide in the case of no. 4) for 2 hr. at room temperature. The reaction mixture was filtered, the solvent was removed from the filtrate *in vacuo* at room temperature, and the residue was recrystallized from the appropriate solvent (see footnote *a*). [c] Thermoelectric in benzene at 37° by the method of C. Tomlinson, *Mikrochim. Acta*, 3, 457 (1961). [d] Determined in KBr. [e] Determined in chloroform (concentration 0.004 mg./ml.). [f] The low value is probably due to decomposition of the compound. [g] See ref. 2. [h] Equimolar quantities of triphenyltin acetate and sodium diphenyldithiocarbamate were allowed to react in acetonitrile for 2 hr. at room temperature. [i] Equimolar quantities of diphenylantimony acetate and the appropriate sodium dithiocarbamate were allowed to react for 2 hr. at room temperature. Benzene–acetonitrile was used as solvent for no. 10; chloroform was used as solvent for no. 16 and 23.
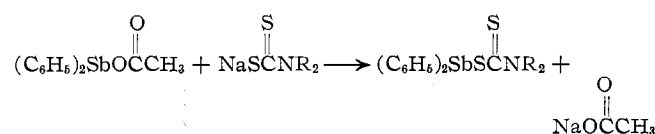
Each of the compounds in Table I was prepared by allowing a sodium dithiocarbamate to react with an organometallic chloride, organometallic dichloride, or trityl chloride (method A).

$$\begin{array}{cc} \text{S} & \text{S} \\ \| & \| \\ \text{MCl} + \text{NaSCN}< \longrightarrow \text{MSCN}< + \text{NaCl} \end{array}$$

$$\begin{array}{cc} \text{S} & \text{S} \\ \| & \| \\ \text{MCl}_2 + 2\text{NaSCN}< \longrightarrow \text{M(SCN}<)_2 + 2\text{NaCl} \end{array}$$

The benzyldithiocarbamates were further prepared by adding benzylamine to a carbon disulfide solution of the appropriate organometallic oxide (hydroxide in the case of (C$_6$H$_5$)$_3$Pb) (method B).

$$\begin{array}{c} \text{S} \\ \| \\ \text{M}_2\text{O} + 2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + 2\text{CS}_2 \longrightarrow 2\text{MSCNHCH}_2\text{C}_6\text{H}_5 + \text{H}_2\text{O} \end{array}$$

$$\begin{array}{c} \text{S} \\ \| \\ \text{MO} + 2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + 2\text{CS}_2 \longrightarrow \text{M(SCNHCH}_2\text{C}_6\text{H}_5)_2 + \text{H}_2\text{O} \end{array}$$
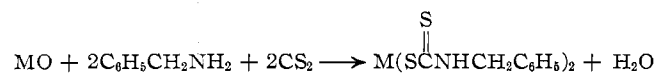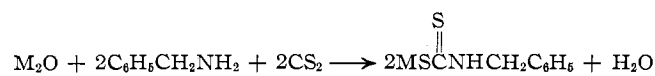
In addition, the diphenylantimony dithiocarbamates were conveniently prepared by allowing the appropriate sodium dithiocarbamate to react with diphenylantimony acetate.

$$\begin{array}{cc} \text{O} & \text{S} \\ \| & \| \\ (\text{C}_6\text{H}_5)_2\text{SbOCCH}_3 + \text{NaSCNR}_2 \longrightarrow \end{array}$$
$$\begin{array}{c} \text{S} \\ \| \\ (\text{C}_6\text{H}_5)_2\text{SbSCNR}_2 + \\ \\ \text{O} \\ \| \\ \text{NaOCCH}_3 \end{array}$$

This procedure is advantageous since the diphenyl-

antimony chloride required in method A is probably best prepared from the acetate.[3]

Strong absorption in the infrared spectra of dithiocarbamate derivatives has been assigned[4] to a "thioureide" band. This band lies between the C—N stretching frequencies in amines and the C=N frequency,[5] indicating partial double bond character in the C—N linkage.[6,7] As has been observed for dialkyldithiocarbamate complexes of metal carbonyls[8] and gold dithiocarbamates,[9] our compounds exhibit C—N stretching frequencies (1479–1531 cm.$^{-1}$) indicative of a partial double bond. In the case of the diphenyldithiocarbamates the C—N stretching frequencies are approximately the same for tin, lead, and antimony. In the other cases, the C—N stretching frequencies are approximately the same for carbon and lead but are somewhat higher for tin and antimony. The higher value for tin may be due to extra bonding between a filled p orbital on sulfur and an empty 5d orbital on tin.

(3) F. F. Blicke, V. O. Oakdale, and F. D. Smith, *J. Am. Chem. Soc.*, **53**, 1025 (1931).

(4) H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

(6) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, **177**, 1042 (1956).

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

(8) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

(9) H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, *J. Organometal. Chem.*, **2**, 236 (1964).

Bonding of the p–d type may be insignificant in the case of lead owing to the larger size of the 6d lead orbital which would make orbital overlap less effective.[10]

Another characteristic feature of a dithiocarbamate derivative is its ultraviolet absorption spectrum. For example, Janssen[11] has observed that methyl dithiocarbamates in a hydrocarbon solvent absorb at 241–247, 274–279, and 343–357 mμ. All of the compounds in Table I are seen to have an absorption in the region 241–245 mμ and to have at least one other absorption which is at about 275 mμ for most of the compounds.

Upon thermal decomposition, the benzyldithiocarbamates gave benzylisothiocyanate, and, in the case of tin and lead, the corresponding bis(triphenylmetal) sulfide or diphenylmetal sulfide trimer. The results are summarized in Table II.

results are summarized in Table III. The products are probably due to hydrolysis by the moisture of the air of an initially formed compound having a metal-nitrogen bond. This hypothesis is supported by the numerous reports of the hydrolytic instability of the Sn–N bond.[12–15] Furthermore, in an attempt to prepare N-diphenylaminotriphenyltin, Baum, Lehn, and Tamborski[16] obtained instead bis(triphenyltin) oxide, which probably resulted from hydrolysis of the expected product.

Upon decomposition, trityl diethyldithiocarbamate gave hexaphenylethane and tetraethylthiuram disulfide. Furthermore, attempts to prepare trityl diphenyldithiocarbamate and trityl dimethyldithiocarbamate by allowing trityl chloride to react with the appropriate sodium dithiocarbamate gave instead hexaphenylethane and the corresponding thiuram

TABLE II
DECOMPOSITION OF BENZYLDITHIOCARBAMATES[a]

Compound no.	Conditions	% benzylisothiocyanate[b]	Sulfide (%)	
1	Isopropyl alcohol, reflux, 5 hr.	63	$(C_6H_5)_3CSH$	(70)
3	Benzene, reflux, 1 hr.	84	$[(C_6H_5)_2SnS]_3$	(93)
4	Benzene, reflux, 1 hr.	88	$(C_6H_5)_3PbSPb(C_6H_5)_3$	(64)
5	Benzene, reflux, 1 hr.	89	$[(C_6H_5)_2SnS]_3$	(93)
6[c]	Diethyl ether, reflux, 0.5 hr.	53	$[(C_6H_5)_2PbS]_3$	(60)

[a] See ref. 2 for the decomposition of compound 2. [b] Based on the 1-benzyl-2-thiobiurea derivative (see ref. 2). [c] When the conditions were benzene, reflux, 1 hr., $(C_6H_5)_2PbS$ was isolated.

TABLE III
DECOMPOSITION OF DIPHENYLDITHIOCARBAMATES

Compound no.	Conditions	% diphenylamine	Oxide (%)	
7[d]	Neat, 250°, 3 hr.	95	$(C_6H_5)_3SnOSn(C_6H_5)_3$	(84)
8	Neat, 250°, 3 hr.	81	$Cl(C_6H_5)_2SnOSn(C_6H_5)_2Cl$	(63)
9[b]	Neat, 150°, 1 hr.; then 200°, 3 hr.	70	$(C_6H_5)_3PbOH$	(82)
10[c]	Neat, 250°, 3 hr.	70	$(C_6H_5)_2SbOSb(C_6H_5)_2$	(72)
11	Neat, 250°, 3 hr.	82	$(C_6H_5)_2SnO$	(96)
12	Neat, 200°, 3 hr.	63	$(C_6H_5)_2PbO$	(70)

[a] No appreciable decomposition occurred when the conditions were benzene, reflux, 3 hr. Identical results were obtained when the conditions were neat, 200°, 3 hr. [b] No appreciable decomposition occurred when the conditions were benzene, reflux, 3 hr. [c] No appreciable decomposition occurred when the conditions were neat, 200°, 3 hr.

$$3Cl(C_6H_5)_2SnS\overset{S}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}CH_2C_6H_5 \xrightarrow{\Delta} [(C_6H_5)_2SnS]_3 +$$
$$3C_6H_5CH_2NCS + 3HCl$$

$$2MS\overset{S}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}CH_2C_6H_5 \xrightarrow{\Delta} M_2S + 2C_6H_5CH_2NCS + H_2S$$
$$[\text{where } M = (C_6H_5)_3Pb]$$

$$3M(S\overset{SH}{\overset{\|}{C}}NCH_2C_6H_5)_2 \xrightarrow{\Delta} (MS)_3 + 6C_6H_5CH_2NCS + 3H_2S$$
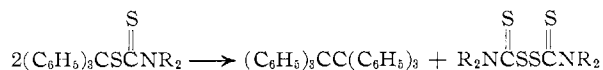$$[\text{where } M = (C_6H_5)_2Sn \text{ or } (C_6H_5)_2Pb]$$

The diphenyldithiocarbamates, upon thermal decomposition in air, gave diphenylamine and the corresponding bis(organometal) oxide (hydroxide in the case of $(C_6H_5)_3Pb$) or diphenylmetal oxide. The

disulfide. Evidently, the trityl ester was formed in these cases but decomposition occurred under the reaction conditions. Decomposition of these trityl esters represents a new method for the preparation of tetraorganothiuram disulfides.[17]

$$2(C_6H_5)_3CS\overset{S}{\overset{\|}{C}}NR_2 \longrightarrow (C_6H_5)_3CC(C_6H_5)_3 + R_2N\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}NR_2$$

It has been further found that tetraorganothiuram disulfides can be conveniently prepared by allowing a sodium diorganodithiocarbamate to react with triphenylantimony dichloride.

(10) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p. 219.
(11) M. J. Janssen, *Rec. trav. chim.*, **79**, 454 (1960).

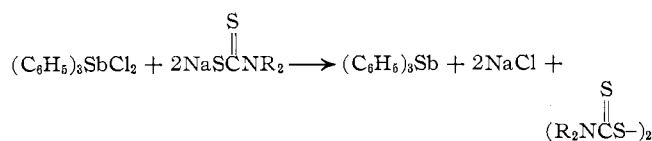(12) I. M. Thomas, *Can. J. Chem.*, **39**, 1386 (1961).
(13) K. Sisido and S. Kozima, *J. Org. Chem.*, **27**, 4051 (1962).
(14) K. Sisido and S. Kozima, *ibid.*, **29**, 907 (1964).
(15) D. Brady and B. R. Lerwill, *Chem. Ind.* (London), 1333 (1962).
(16) G. Baum, W. L. Lehn, and C. Tamborski, *J. Org. Chem.*, **29**, 1264 (1964).
(17) For a summary of previous methods see ref. 1, pp. 61, 62.

$$\underset{\text{S}}{\overset{\overset{\displaystyle \text{S}}{\|}}{(C_6H_5)_3SbCl_2}} + 2Na\overset{\|}{SC}NR_2 \longrightarrow (C_6H_5)_3Sb + 2NaCl +$$

$$\overset{\overset{\displaystyle \text{S}}{\|}}{(R_2NCS-)_2}$$

The results are summarized in Table IV.   In the case

TABLE IV

REACTION OF $Na\overset{\overset{\displaystyle \text{S}}{\|}}{SC}NR_2 \cdot nH_2O$ WITH $(C_6H_5)_3SbCl_2{}^a$

R	n	% $(C_6H_5)_3Sb$	% thiuram disulfide
$C_6H_5{}^b$	c	60	83
$CH_3{}^d$	2	60	93
$C_2H_5{}^d$	3	60	90

^{a} Mole ratio of triphenylantimony dichloride/sodium dithiocarbamate, 1:2; all reactions were carried out at room temperature for 2 hr. ^{b} Solvent was benzene–acetonitrile. ^{c} Not determined. ^{d} Solvent was chloroform.

of tetraphenylthiuram disulfide the present method is an improvement over that reported in the literature.[18] Reaction of triphenylantimony dichloride with sodium benzyldithiocarbamate (1:2 molar ratio) gave triphenylantimony sulfide (75%) and benzylisothiocyanate (91% based on the 1-benzyl-2-thiobiurea derivative).

During the course of this investigation, several known organotin, organoantimony, and organolead sulfides were required.   In a previous paper the reaction of a carbon disulfide solution of bis(triphenyltin) oxide or triphenyltin bromide with ammonia to give bis(triphenyltin) sulfide was described.[2]   This method has now been found to work equally well with diphenyltin dichloride, diphenyltin oxide, organoantimony oxides, diphenylantimony chloride, and organolead chlorides. The results are summarized in Table V.

TABLE V

PREPARATION OF ORGANOMETALLIC SULFIDES^a

Organometallic chloride or oxide	Sulfide (%)	
$(C_6H_5)_3PbCl$	$(C_6H_5)_3PbSPb(C_6H_5)_3$	$(90)^b$
$(C_6H_5)_2SbCl$	$(C_6H_5)_2SbSSb(C_6H_5)_2$	$(62)^b$
$(C_6H_5)_2SnCl_2$	$[(C_6H_5)_2SnS]_3$	$(87)^c$
$(C_6H_5)_2PbCl_2$	$[(C_6H_5)_2PbS]_3$	$(60)^d$
$(C_6H_5)_2SbOSb(C_6H_5)_2$	$(C_6H_5)_2SbSSb(C_6H_5)_2$	$(61)^b$
$(C_6H_5)_2SnO$	$[(C_6H_5)_2SnS]_3$	$(64)^d$
C_6H_5SbO	C_6H_5SbS	$(51)^e$

^{a} NH$_3$ was passed for 2–3 hr. into a CS$_2$ solution of the organometallic chloride or oxide.   The reaction mixture was filtered, the solvent was removed from the filtrate *in vacuo*, and the residue was recrystallized from a suitable solvent.   In every case the melting point agreed with the literature value. ^{b} Recrystallized from acetonitrile. ^{c} Washed with hexane. ^{d} Recrystallized from benzene–hexane. ^{e} Recrystallized from ethanol.

Experimental

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected.   The infrared absorption data were obtained with a Perkin-Elmer Model 21 double beam infrared spectrophotometer.   The ultraviolet absorption data were obtained with a Bausch and Lomb Spectronic 505.   Elemental analyses were performed by Dr. G. Weiler and Dr. F. Strauss, Microanalytical Laboratory, Oxford,

England.   The molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Sodium Benzyldithiocarbamate.—A solution of 107 g. (1.00 mole) of benzylamine in 250 ml. of anhydrous chloroform was added to 60 ml. of a 40% aqueous sodium hydroxide solution, and the reaction mixture was stirred for several minutes.   Carbon disulfide (500 ml.) was slowly added over 3 hr., and the solid which formed was collected on a filter, washed with petroleum ether (b.p. 30–60°) and acetonitrile, and vacuum-dried at 102° for 15 hr.   The yield was 164 g. (80%), m.p. 235° dec.

Anal.   Calcd. for $C_8H_8NS_2Na$: N, 6.83.   Found: N, 6.55.

The infrared spectrum (KBr) showed C–N, 1499 cm.$^{-1}$; NH, 3226 cm.$^{-1}$; OH, 3333 cm.$^{-1}$ (compound may be a hydrate). The ultraviolet spectrum (H$_2$O) had λ_{max} 253 mμ (ϵ_{max} 2.56 × 10^4) and 285 mμ (ϵ_{max} 2.56 × 10^4).

Sodium Diphenyldithiocarbamate.—A solution of 85 g. (0.50 mole) of diphenylamine in 150 ml. of carbon disulfide was added over 1 hr. to a suspension of 19.5 g. (0.50 mole) of sodium amide in 200 ml. of anhydrous benzene.   The reaction mixture was stirred for 24 hr., and the solid which was present was collected on a filter and then stirred for 0.5 hr. with a solution containing 100 ml. of methanol and 300 ml. of diethyl ether.   The solid was collected on a filter, washed with a solution containing 125 ml. of methanol and 275 ml. of diethyl ether, and vacuum-dried overnight at 120°.   The yield was 82 g. (62%), m.p. 198–201° dec.

Anal.   Calcd. for $C_{13}H_{10}NS_2Na$: N, 5.24.   Found: N, 5.28.

The infrared spectrum (KBr) showed C–N, 1488 cm.$^{-1}$; OH, 3367 cm.$^{-1}$ (compound may be a hydrate).   The ultraviolet spectrum (H$_2$O) had λ_{max} 263 mμ (ϵ_{max} 2.74 × 10^4) and 294 mμ (ϵ_{max} 3.34 × 10^4).

Decomposition of Trityl Diethyldithiocarbamate.—Under a nitrogen atmosphere, 1.9 g. (0.0050 mole) of trityl diethyldithiocarbamate was heated at 150° for 4 hr.   The mixture was allowed to cool to room temperature, petroleum ether (b.p. 30–60°) was added, and the yellow solid was collected on a filter and washed with cold ethanol to give 0.5 g. (66%) of tetraethylthiuram disulfide, m.p. 69–72° (lit.[18] 72°), no depression on admixture with authentic tetraethylthiuram disulfide, infrared spectrum superimposable on that of authentic tetraethylthiuram disulfide.

The solvent was removed from the filtrate *in vacuo*, and the solid residue was washed with acetone to give 0.6 g. (52%) of hexaphenylethane, m.p. 140–144° (lit.[19] 145–147° dec.), no depression on admixture with authentic hexaphenylethane, infrared spectrum superimposable on that of authentic hexaphenylethane.

Reaction of Sodium Dimethyldithiocarbamate Dihydrate with Trityl Chloride.—Under a nitrogen atmosphere, a solution of 2.7 g. (0.010 mole) of trityl chloride in 50 ml. of carbon tetrachloride was added to a suspension of 1.8 g. (0.010 mole) of sodium dimethyldithiocarbamate dihydrate in 50 ml. of carbon tetrachloride.   The reaction mixture was stirred at room temperature for 2 hr. and then was filtered to give 0.5 g. of solid, which did not melt at 350° and gave a positive silver nitrate test.

The carbon tetrachloride was removed from the filtrate *in vacuo*, and the solid residue was stirred with petroleum ether (b.p. 30–60°).   The solid was collected on a filter and recrystallized from ethanol to give 1.0 g. (91%) of tetramethylthiuram disulfide, m.p. 152–154° (lit.[20] 156°), no depression on admixture with authentic tetramethylthiuram disulfide, infrared spectrum superimposable on that of authentic tetramethylthiuram disulfide.

The petroleum ether was removed from the filtrate *in vacuo*, and the solid residue was recrystallized from acetone to give 1.4 g. (60%) of hexaphenylethane, m.p. 145–146°, no depression on admixture with authentic hexaphenylethane, infrared spectrum superimposable on that of authentic hexaphenylethane.

Reaction of Sodium Diphenyldithiocarbamate with Triphenyl-

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(18) H. S. Fry and B. S. Farquhar, *Rec. trav. chim.*, **57**, 1223 (1938).

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antimony Dichloride.—A solution of 2.1 g. (0.0050 mole) of triphenylantimony dichloride in 50 ml. of benzene was added to a suspension of 2.7 g. (0.010 mole) of sodium diphenyldithiocarbamate in 50 ml. of acetonitrile. The reaction mixture was stirred at room temperature for 2 hr. and then was filtered to give a solid which was stirred with hot benzene. The hot mixture was filtered to give a solid, which did not melt at 350° and gave a positive silver nitrate test.

Upon cooling, the benzene filtrate yielded needles which were collected on a filter to give 2.0 g. (83%) of tetraphenylthiuram disulfide, m.p. 217° dec. (lit.[18] 217.6° dec.).

Anal. Calcd. for $C_{26}H_{20}N_2S_4$: C, 63.91; H, 4.09; N, 5.74. Found: C, 63.51; H, 3.87; N, 5.59.

The infrared spectrum had C–N, 1493 cm.$^{-1}$. The ultraviolet spectrum (chloroform) had λ_{max} 243 mμ (ϵ_{max} 1.16 × 10^4) and 280 mμ (ϵ_{max} 3.17 × 10^4).

The solvent from the original benzene–acetonitrile filtrate was removed *in vacuo*, and the solid residue was recrystallized from methanol to give 1.0 g. (60%) of triphenylantimony, m.p. 47–50°, no depression on admixture with authentic triphenylantimony, infrared spectrum superimposable on that of authentic triphenylantimony.

Color and Nonintegral Valence in Niobium and Tantalum Subhalides

BY M. B. ROBIN AND N. A. KUEBLER

The electronic spectra of the Ta and Nb subhalide ions, $M_6X_{12}^{2+}$, have been interpreted using a molecular orbital scheme involving both metal–metal and metal–ligand interactions. The only reasonable analysis follows from assuming that the Nb complexes are built upon an Nb_6 framework having octahedral symmetry, whereas the corresponding Ta complexes are tetragonally elongated. This conclusion follows from the fact that certain degenerate transitions in the Nb series are split in the Ta series as would be expected for a descent in symmetry. Two-electron oxidation of the Ta complexes yields ions having a tetragonally flattened geometry, as judged by the criterion just mentioned.

A spate of recent crystallographic work on the Re^{3+} halides indicates that a great many of the structures are built upon a common unit, the trinuclear species $Re_3X_{12}^{3-}$.[1] As yet unpublished work by Schäfer on Nb and Ta halides demonstrates that in a good many cases one again has a common polynuclear building block, the stoichiometry here being M_6X_{12}.[2] As is also the situation with the Re compounds, halide ions are shared between the M_6X_{12} units in the crystal, the number shared being determined by the over-all stoichiometry of the substance. This paper is concerned with the relationship between the color and the molecular and electronic structure of the $M_6X_{12}^{2+}$ building block ions.

The $M_6X_{12}^{2+}$ ions, where M = Nb or Ta and X = Cl, Br, or I, are of special interest because they provide compact units of known geometry which exhibit not only metal–metal bonding and nonintegral valence, but offer for study a stable "monomeric" unit which may be taken as one of a large class of X_6Y_{12} polynuclear complexes having M_6 octahedral metal frameworks in common. As of the moment, this class includes the $M_6X_{12}^{2+}$ ions mentioned above, Mo_6Cl_{12},[3] $Rh_6(CO)_{16}$,[4] Pt_6Cl_{12},[5] and the nontransition metal complex $Bi_6(OH)_{12}^{+6}$.[6]

That the $M_6X_{12}^{2+}$ ions of Nb and Ta exhibit strong metal–metal bonding is evident not only from overlap considerations, but also from the metal–metal distances, which are observed to be approximately those of the pure metal. As for the nonintegral valence phenomenon, consider that the twelve halogens contribute a −12 formal charge to the complex, and that the net charge of +2 then leads to the six metal atoms contributing a +14 formal charge. Thus the average formal valence of the metal atoms is $+2^1/_3$. This phenomenon of average nonintegral valence has been studied previously[7] in Prussian blue, $KFe_2(CN)_6$, where it was shown that the two iron ions of average valence $+2^1/_2$ in fact have the integral valences +2 and +3. The integral valence results from the fact that a nonintegral valence situation can be expected only for ions in equivalent or near equivalent environments, and in the Prussian blue crystal the two iron ions are in distinctly different sites. By analogy with Prussian blue, if we are to know the correct valences of the metal ions in the $M_6X_{12}^{2+}$ complex we must first investigate the equivalence of the geometries of the local ligand fields. If the metal atoms are all in equivalent ligand fields within the complex, then the formal valence at each metal must be taken as $+2^1/_3$, whereas nonequivalent ligand fields at the metals will tend to trap the integral valences. A most likely configuration for the latter would result from a tetragonal distortion of the M_6 octahedron yielding four ions of +2 and two of +3 formal valence.

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