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Metal Halide Complexes with Trimethylstibine Sulfide

Takayuki SAITO, Junzo OTERA and Rokuro OKAWARA

Department of Applied Chemistry, Osaka University, Yamadakami, Suita, Osaka

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2 : 1 complexes of trimethylstibine sulfide (TMSS) with zinc(II), cadmium(II), mercury(II) and cobalt(II) halides were prepared. 1 : 1 complexes were also obtained with cadmium bromide and mercuric iodide. On the basis of infrared spectra, it was found that TMSS coordinates to the metal through the sulfur atom and that $Hg(TMSS)I_2$ has a sulfur-bridged structure. The electronic spectral parameters of the tetrahedral $Co(TMSS)_2X_2$ (X = Cl, Br and I) complexes are quite close to those of trimethyl-phosphine and -arsine sulfide complexes. These results indicate that for Co–S interactions, polarizability of the thioxo ligand is more important than polarity.

In previous papers, we reported the electronic character of the Sb–S bond in tertiary stibine sulfide[1] and the unique behavior of the bond towards organotin halides.[2]

Recently, various metal complexes with tertiary

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[1] J. Otera and R. Okawara, *J. Organometal. Chem.*, **16**, 335 (1969).

[2] M. Shindo, Y. Matsumura and R. Okawara, *ibid.*, **11**, 299 (1968): This Bulletin, **42**, 265 (1969).

phosphine[3–10] and arsine[11–14] sulfide were prepared and their properties were discussed in relation to the nature of the P–S or As–S bond. However, only a few investigations have been reported[2,8] on the metal complexes of tertiary stibine sulfide.

In the present paper, we describe the preparation and properties of the complexes of zinc(II), cadmium(II), mercury(II) and cobalt(II) halides with trimethylstibine sulfide (TMSS).

Experimental

Preparation of the Complexes. *Zinc and Cadmium Complexes.* These complexes were obtained by mixing the methanol solutions of the ligand and metal halides in stoichiometric ratios, followed by evaporation of the solvent. The complexes obtained were washed with methanol and dichloromethane. In the treatment of the ligand with cadmium bromide, the 1 : 1 complex was precipitated from the solution (yield 38%) and the 2 : 1 complex was obtained from the filtrate after evaporating the solvent under reduced pressure (yield 60%). When a large excess of the ligand was employed, only the 2 : 1 complex was obtained in a good yield.

$Hg(TMSS)_2Br_2$. On adding methanol solution of the ligand to mercuric bromide in methanol, yellow powder precipitated, which soon decomposed after separation from the solvent and could not be confirmed. From the filtrate the 2 : 1 complex was obtained. This complex decomposes slowly by heating and on exposure to light.

$Hg(TMSS)I_2$ and $Hg(TMSS)_2I_2$. To a suspension of mercuric iodide in methanol was added a slight excess of the ligand. The color of mercuric iodide gradually changed to pale yellow. Washing the obtained powder with dichloromethane gave the 1 : 1 complex. When a large excess of the ligand and mercuric iodide in chloroform were stirred until the color of mercuric iodide disappeared, white precipitates of the 2:1 complex were obtained.

$Co(TMSS)_2X_2$. The methanol solutions of trimethylstibine sulfide and cobalt halides were combined in 2:1 molar ratio. Evaporation of methanol under reduced pressure and washing the resulting precipitates with methanol and dichloromethane gave the corresponding complexes. The chloride complex, however was contaminated with a small amount of black precipitates which seemed to be CoS. The precipitates obtained by evaporating methanol were therefore quickly recrystallized from a large amount of dichloromethane-

Table 1. Analytical data and molar conductivities of trimethylstibine sulfide complexes

Compound	C% Found	C% Calcd	H% Found	H% Calcd	Λ_M cm²/ohm·mol
$Zn(TMSS)_2X_2$					
X=Cl	13.45	13.49	3.25	3.39	14.8[a]
Br	11.24	11.56	2.70	2.91	8.6[a]
I	10.37	10.04	2.55	2.53	16.5[a]
$Cd(TMSS)_2X_2$					
X=Cl	12.82	12.40	2.98	3.12	10.2[a]
Br	10.70	10.75	2.78	2.70	8.3[a]
I	8.83	9.43	2.25	2.37	b
$Hg(TMSS)_2X_2$					
X=Br	9.77	9.50	2.49	2.39	b
I	8.79	8.45	2.15	2.11	b
$Co(TMSS)_2X_2$					
X=Cl	13.58	13.66	3.54	3.44	<1[c]
Br	11.39	11.69	2.95	2.94	<1[c]
I	10.45	10.14	2.67	2.55	1.3[c]
$Cd(TMSS)Br_2$	7.55	7.64	2.01	1.92	22.2[d]
$Hg(TMSS)I_2$	5.78	5.51	1.50	1.30	b

a) 10^{-3} mol/*l* in acetonitrile. b) Not sufficiently soluble for measurement. c) 3×10^{-3} mol/*l* in dichloromethane. d) 10^{-4} mol/*l* in acetonitrile.

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methanol. The complexes decompose slowly in air in the solid state, and a little more rapidly in solution.

Sulfur-halogen Exchange Reaction. Trimethylstibine sulfide in methanol was added to an equimolar amount of mercuric chloride in the same solvent at room temperature. Black powder of mercuric sulfide was filtered off, and the filtrate gave trimethylantimony dichloride almost quantitatively. When trimethylstibine sulfide and mercuric bromide were mixed in hot methanol, a similar exchange reaction occurred, yielding trimethylantimony dibromide.

Analytical data of these complexes, together with their molar conductivities, are summarized in Table 1.

Physical Measurements. The infrared spectra in Nujol mulls were recorded with a Hitachi EPI-L grating spectrophotometer. Measurements of the electronic spectra were carried out by a Hitachi EPS-3 spectrophotometer. Molar conductivities were measured using a Yokogawa Universal Bridge (Bv-Z 13 C).

Results and Discussion

As shown in Table 1, trimethylstibine sulfide usually forms 2 : 1 complexes with the metal halides employed and also 1 : 1 complexes with cadmium bromide and mercuric iodide. No complex*1 can be obtained with mercuric chloride. However, sulfur-halogen exchange reaction (1) takes place, similar to that reported2) for some organotin halides.

$$(CH_3)_3SbS + HgCl_2 \longrightarrow (CH_3)_3SbCl_2 + HgS \quad (1)$$

The infrared frequency of the ν(Sb–S) band in all the complexes, as listed in Table 2, shifts to a lower frequency by 25—55 cm^{-1} from that of the free ligand, indicating coordination through the sulfur atom. These ν(Sb–S) frequencies are comparable with, or a little higher than those (357—381 cm^{-1}) in trimethylantimony halide thiocarboxylates.15) Thus, the Sb–S bond in the complexes seems to exist almost in the form of the semipolar structure, [I], although slight $d\pi$-$p\pi$ bonding might still remain in this bond.

TABLE 2. RELEVANT INFRARED FREQUENCIES (cm^{-1}) OF TRIMETHYLSTIBINE SULFIDE COMPLEXES (Nujol mulls)

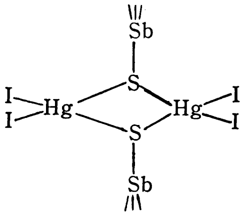
Compound	ν(Sb–S)	ν(M–S)	ν(M–X)
TMSS	433		
$Zn(TMSS)_2Cl_2$	403	280	300
$Zn(TMSS)_2Br_2$	403	278	210
$Zn(TMSS)_2I_2$	408	277	
$Cd(TMSS)_2Cl_2$	406	254	262
$Cd(TMSS)_2Br_2$	403	257	
$Cd(TMSS)_2I_2$	406,385	255	
$Hg(TMSS)_2Br_2$	397	250	
$Hg(TMSS)_2I_2$	406		
$Co(TMSS)_2Cl_2$	402	303,282	313
$Co(TMSS)_2Br_2$	399	295,280	236
$Co(TMSS)_2I_2$	404	305,280	
$Cd(TMSS)Br_2$	397	214	
$Hg(TMSS)I_2$	387,383		

$$[(CH_3)_3\overset{+}{Sb}-\overset{-}{S}]_2\cdot MX_2$$

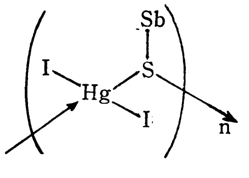
[I]

The molar conductivities (Table 1) suggest weak dissociation of the halide anion in the zinc and cadmium complexes in acetonitrile. However, both ν(M–S) and ν(M–Cl) (or ν(M–Br)) bands can be observed in some of their infrared spectra in Nujol mulls so that the complexes appear to have a non-ionic tetrahedral structure in the solid state.

The 1 : 1 complex, $Cd(TMSS)Br_2$, is less soluble than the corresponding 2 : 1 complex, $Cd(TMSS)_2Br_2$. The molar conductivity (22.2 cm^2/ohm·mol) seems to be too small to assume the ionic structure, $[Cd(TMSS)Br]^+Br^-$. The associated structure may be presumed in the solid state for the tetrahedral arrangement around the cadmium atom, but the present data are not sufficient to give a more detailed structure. The 1 : 1 complex, $Hg(TMSS)I_2$, shows the marked lower shift of the ν(Sb–S) frequency as compared with the 2 : 1 complex, $Hg(TMSS)_2I_2$. This is interpreted as suggesting that the sulfur-bridged structure [II] or [III] is more probable than the halogen-bridged structure. The latter structure is suggested for the 1 : 1 complex of mercuric bromide with tris(dimethylamino)phosphine sulfide on the basis of the infrared spectrum.10)



(II)



(III)

From the low molar conductivities as given in Table 1, ionic formulations are ruled out for the cobalt complexes in dichloromethane. In accordance with these results, the electronic spectra of the complexes (Table 3) give two structured bands characteristic of tetrahedral coordination (ν_3, $^4A_2$–$^4T_1$(P) and ν_2, $^4A_2$–$^4T_1$(F)). As presented in Table 4, the ligand field splitting energies, Δ, and the β values calculated from the above data fall in quite

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[*1] It has been reported5,7) that with mercuric chloride, trimethyl- and triphenyl-phosphine sulfide give 2 : 1 and 1 : 1 complexes, respectively.

15) J. Otera and R. Okawara, *J. Organometal. Chem.*, **17**, 353 (1969).

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Table 3. Electronic spectral date for the cobalt complexes[a] (cm^{-1})

Compound	ν_3	ν_2
$\mathrm{Co(TMSS)_2Cl_2}$	15870(475)[b]	6760(95)
	14710(519)	5950(30)
	13420(400)	5200(122)
$\mathrm{Co(TMSS)_2Br_2}$	15150(492)	6560(95)
	14080(539)	5860(47)
	13160(522)	5000(125)
$\mathrm{Co(TMSS)_2I_2}$	14490(570)	6250(126)
	13510(733)	5530(37)
	12500(701)	4830(126)

a) 2—3×10^{-3} mol/l in dichloromethane

b) Molar extinction coefficients given in parentheses.

Table 4. Electronic spectral parameters of the cobalt complexes

Compound	ν_3[c] (cm^{-1})	ν_2[c] (cm^{-1})	Δ[d] (cm^{-1})	β[e]	References
$\mathrm{Co(TMSS)_2Cl_2}$	14740	5890	3400	0.72	f
$\mathrm{Co(TMPS)_2Cl_2}$[a]	14990	5810	3340	0.74	g
$\mathrm{Co(TMAS)_2Cl_2}$[b]	14920	5900	3390	0.73	h
$\mathrm{Co(TMSS)_2Br_2}$	14110	5710	3300	0.69	f
$\mathrm{Co(TMPS)_2Br_2}$	14540	5700	3280	0.72	g
$\mathrm{Co(TMAS)_2Br_2}$	14580	5750	3310	0.72	h
$\mathrm{Co(TMSS)_2I_2}$	13440	5540	3200	0.65	f
$\mathrm{Co(TMPS)_2I_2}$	13710	5650	3260	0.66	g
$\mathrm{Co(TMAS)_2I_2}$	13760	5770	3340	0.66	h

a) TMPS; trimethylphosphine sulfide.

b) TMAS; trimethylarsine sulfide.

c) Evaluated from the center of gravity of the intensities.

d) Calculated according to Ref. 16; Values are ±100 cm^{-1}.

e) β=B(complex)/967 (free ion).

f) This work.

g) See Ref. 9.

h) See Ref. 13.

close values to those obtained for trimethyl-phosphine and -arsine sulfide complexes. In the series of these three ligands, the basicity of the sulfur atom is likely to increase from phosphorus to antimony, because the size difference between the central atom and the sulfur atom becomes larger and the extent of $d\pi$-$p\pi$ bonding should decrease in this order. The close similarity of the electronic spectral parameters of the cobalt complexes indicates that the interaction of the cobalt atom with ligand is not affected by polarity of the ligand. It is apparent from the low β values that a considerably large covalency is implied in the Co–S bond. Thus, polarizability (or covalent-bonding character) of the ligand seems to have a primary effect on Co–S interactions. This is consistent with the results reported for the relations between the trimethylphosphine and -arsine sulfide complexes.[9]

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