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The Syntheses and Properties of the Benzothiazole or Benzimidazole Derivative Adducts of Tin(II, IV) and Antimony(III) Halides

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The benzothiazole, 2-amino-benzothiazole, benzimidazole-2-thiol, and benzothiazole-2-thiol adducts of tin(II, IV) chlorides, antimony(III) chloride, and antimony(III) bromide with the formulae of $M^{n+}L_mX_n^-$ (where L is the ligand and where X is Cl or Br) were synthesized. From their electronic and infrared spectra, it can be seen that the 2-amino-benzothiazole adducts are more stable than those of other ligands and that the metal–ligand bonds in the former remain even in the ethanolic solution.

Benzothiazole(BT), benzimidazole(BI), and their 2-derivatives (2-amino-benzothiazole (ABT), benzimidazole-2-thiol(BIT), and benzothiazole-2-thiol(BTT), for example) are interesting ligands, and many transition metal complexes have already been synthesized and investigated.[1-8] All of these studies, however, have been confined to the transition metal complexes; the tin(II, IV) and antimony(III) adducts have not yet been reported on. Since we expected that tin and antimony halides could also form adducts with such ligands, we attempted syntheses and thus obtained a series of adducts.

Experimental

Starting Materials. The ligands used were all Tokyo Kasei G. R. grade reagents. The tin(II) chloride, tin(IV) chloride, antimony(III) chloride, and antimony(III) bromide used were all G. R. or E. P. grade reagents of the Wako Chemical Co.; they were all used without any further purification.

The organic solvents used, such as isopropyl ether, acetone, and ethyl alcohol, were all of the E. P. grade and were used after distillation.

The Syntheses of the Adducts. *The synthesis of the Benzothiazole-2-thiol Adduct of Tin(IV) Chloride.* Anhydrous tin(IV) chloride and benzothiazole-2-thiol were dissolved in anhydrous ethyl alcohol in the mole ratio of 1 to 2. (The mole ratio of the starting materials varied between 1 : 2 to 2 : 1, but the same product was always obtained, though in different yields.) The solution was concentrated on a water bath to a syrupy liquid; then it was cooled and kept at room temperature several hours with stirring. The powder product thus obtained was washed well first with an isopropyl ether-acetone mixture, next by pure isopropyl ether, and finally by petroleum ether, washing being done several times with each material. The other adducts were synthesized in the same way. Some of them could be recrystallized by acetone, but the others could not. The products thus obtained were dried in a vacuum desiccator overnight.

Instruments. The magnetic moments were measured using a Gouy balance at room tempetature. The reflectance spectra were obtained with an Ito Model QU-3 spectrophotometer, using the reflectance attachment and a magnesium oxide standard. The electronic absorption spectra were obtained with a Hitachi EPS-2-type automatic recording spectrophotometer, using ethanolic-solution samples as well as nujol-mull samples. The infrared spectra were obtained by means of the nujol or hexachloro-1,3-butadiene mull procedure, using a Japan Spectroscopic Co. 403 G grating infrared spectrophotometer.

Results and Discussion

The analyses of the adducts and their expected chemical formulae are shown in Table 1. They are all diamagnetic at room temperature, and no abnormal valency of the central metal was expected. Therefore, the benzothiazole or benzimidazole derivatives in these adducts seem to be neutral, and the positive charge of the central metal ion is neutralized by halogen ions. The analytical data as well as the results of alkalimetric titration show that the 2-amino-benzothiazole adducts of tin(II, IV) chlorides contain two moles

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TABLE 1. COLORS, ANALYSES AND THE CHEMICAL FORMULAE OF THE ADDUCTS
(Figures are given in %)

		M	C	H	N	S	X
Benzothiazole adducts							
$Sn^{II}(C_7H_5NS)_2Cl_2$	Calcd	25.80	36.56	2.19	6.09	13.94	15.42
(white)	Found	25.12	36.37	2.41	6.00	13.92	14.93
$Sn^{IV}(C_7H_5NS)_2Cl_4$	Calcd	22.36	31.68	1.90	5.28	12.08	26.71
(pale brown)	Found	22.40	30.89	2.09	5.06	12.62	25.73
$Sb^{III}(C_7H_5NS)Cl_3$	Calcd	33.51	23.14	1.39	3.86	8.82	29.28
(pale brown)	Found	33.80	23.21	1.97	3.78	8.16	29.00
$Sb^{III}(C_7H_5NS)Br_3$	Calcd	24.51	16.93	1.01	2.82	6.46	48.27
(pale brown)	Found	24.45	17.01	1.47	2.75	6.50	47.80
2-Amino-benzothiazole adducts							
$Sn^{II}(C_7H_6N_2S)_2Cl_2 \cdot 2HCl$	Calcd	21.19	29.88	2.49	9.96	11.36	25.22
(white)	Found	22.22	30.05	2.59	9.83	11.61	24.00
$Sn^{IV}(C_7H_6N_2S)_2Cl_4 \cdot 2HCl$	Calcd	18.79	26.48	2.21	8.84	10.03	33.60
(white)	Found	19.23	27.01	2.31	8.83	10.30	33.00
$Sb^{III}(C_7H_6N_2S)Cl_3$	Calcd	32.18	22.22	1.60	7.41	8.47	28.11
(white)	Found	31.90	21.84	1.79	7.12	8.67	28.07
$Sb^{III}(C_7H_6N_2S)_2Br_3$	Calcd	18.40	25.41	1.83	8.47	9.69	36.22
(white)	Found	18.20	25.76	2.17	8.51	10.25	36.04
Benzimidazole-2-thiol adducts							
$Sn^{II}(C_7H_6N_2S)Cl_2$	Calcd	34.93	24.74	1.78	8.24	9.44	20.87
(white)	Found	35.00	24.01	1.86	7.84	9.42	20.06
$Sn^{IV}(C_7H_6N_2S)_2Cl_4$	Calcd	21.16	29.98	2.16	9.99	11.43	25.28
(yellow)	Found	21.90	29.20	2.14	9.36	11.70	24.40
$Sb^{III}(C_7H_6N_2S)Cl_3$	Calcd	32.18	22.22	1.60	7.41	8.47	28.11
(pale yelow)	Found	32.73	22.46	1.71	7.53	9.20	27.88
$Sb^{III}(C_7H_6N_2S)_2Br_3$	Calcd	18.40	25.41	1.83	8.47	9.69	36.22
(yellow)	Found	17.96	25.67	2.16	8.67	9.96	35.30
Benzothiazole-2-thiol adducts							
$Sn^{II}(C_7H_5NS_2)Cl_2$	Calcd	33.26	23.56	1.41	3.93	17.97	19.87
(yellow)	Found	34.02	23.31	1.79	3.75	18.52	19.30
$Sn^{IV}(C_7H_5NS_2)_2Cl_4$	Calcd	19.95	28.26	1.69	4.71	21.55	23.83
(yellow)	Found	20.60	27.50	1.66	4.57	21.97	22.88
$Sb^{III}(C_7H_5NS_2)Cl_3$	Calcd	30.80	21.27	1.28	3.53	16.21	26.90
(yellow)	Found	30.66	20.67	1.43	3.23	16.75	26.20
$Sb^{III}(C_7H_5NS_2)_2Br_3$	Calcd	17.49	24.16	1.45	4.05	18.43	34.44
(yellow)	Found	18.56	23.78	1.84	3.87	18.85	35.10

of hydrogen chloride per mole of the adduct. It is not the adsorbed one, since the content is always constant, but it is not yet known how these molecules are bound in the adducts.

In order to study why the colors of these adducts are sometimes more intense than those of the free ligands (white or light yellow), the absorption spectra of the nujol mulls of the solid adducts were examined. The wave numbers of the maxima of the spectra coincide approximately with those of the surface diffuse-reflectance spectra, although the latter were obtained only in the visible region; moreover, it was difficult to obtain precise data in both measurements because of the experimental difficulties. The results are shown in Table 2. The absorption maximum or a shoulder appears in about the 24—26 kK region in the cases of benzothiazole-2-thiol adducts and at about 28 kK in the cases of benzimidazole-2-thiol adducts. These peaks or shoulders disappear when the substances are dissolved in ethyl alcohol. The electronic absorption spectral data of the adducts and the ligands in ethanolic solutions shown in Table 3 show that the absorption maxima appear only in the ultraviolet region. All the metal complexes of the same ligand show nearly the same spectra; even the ABT adducts of Sn(II, IV) containing hydrogen chloride show almost the same spectra as the Sb(III) adducts which do not contain it. (Therefore, in Table 3 their average values are

TABLE 2. THE MAXIMUM WAVE NUMBER OF NUJOL MULL ABSORPTION SPECTRA OF ADDUCTS
(Figures are given in kK)

$\mathrm{Sn^{II}(BIT)Cl_2}$	28.3	28.9	31.1
$\mathrm{Sn^{IV}(BIT)_2Cl_4}$	27.0	33.0	34.3
$\mathrm{Sb^{III}(BIT)Cl_3}$	28.5	32.5	35.2
$\mathrm{Sb^{III}(BIT)_2Br_3}$	28.5	29.9	33.0
BIT		32.5	
$\mathrm{Sn^{II}(BTT)Cl_2}$	24.8	32.4 sh	34.9 sh
$\mathrm{Sn^{IV}(BTT)_2Cl_4}$	26.4 sh	30.1	
$\mathrm{Sb^{III}(BTT)Cl_3}$	26.7	31.0	
$\mathrm{Sb^{III}(BTT)_2Br_3}$	25.3	33.2	
BTT		30.5	35.7 sh

BTT: Benzothiazole-2-thiol.
BIT: Benzimidazole-2-thiol.

shown).

In the cases of BT, BIT, and BTT complexes, each free ligand also shows the same spectra as the respective metal adduct. However, in the case of ABT complexes the absorption peaks of the free ligand is somewhat different from those of the metal adducts.

Duff has reported[8] that, in the cases of nickel, copper, and cobalt complexes of benzothiazole and all its derivatives except 2-amino-benzothiazole, the ligand bonds to the central metal ion by means of the nitrogen hetero-atom of the ring just like pyridine in its complexes and not by means of the sulfur atom of the thiol or the thion group on the 2-carbon, while the 2-amino-benzothiazole shows a different behavior toward metal ions and the amino nitrogen atom seems to act as a donor atom. Probably this is also true in these tin and antimony adducts, since the spectral data indicate that 2-amino-benzothiazole adducts are more stable than the others and that their metal–ligand bonds are kept even in an ethanolic solution. On the other hand, in the cases of benzothizaole, benzimidazole-2-thiol, and benzothiazole-2-thiol adducts, the spectra show that the adducts are perfectly dissociated in the solution. However, the existence of metal-ligand bonds in the solid adducts of these ligands is quite probable (*cf.* the specific colors of the solid products and the characteristic bands in the near-ultraviolet region in the nujol mull of reflectance spectra). Among the bands of the solid adducts observed, the band at 30.5 kK of benzothiazole-2-thiol and that at 32.5 kK of benzimidazole-2-thiol are probably due to the transition of conjugated p_π electrons of the thiazole or imidazole ring. When the ligand coordinates to the metal ion by means of the hetero-atom of the ring, the electronic structure of the conjugated ring π-system changes and there should be a shift of the band. The phenomenon was observed in the cases of several BIT or BTT adducts.

The main peaks of the infrared spectra (1700—400 cm^{-1}) of the ligands and the tin(IV) chloride adducts are shown in Table 4. The general fea-

TABLE 3. THE MAXIMUM WAVE NUMBERS AND THE ABSORPTION COEFFICIENTS OF THE ELECTRONIC SPECTRA OF SOME METAL ADDUCTS (in ethanolic solution)
Figures are given in kK for wave numbers and log ε (calculated for the concentration of ligand) for intensities (in parentheses)

Benzothiazole						
ligand	34.1 (3.35)	35.3 (3.41)	36.2 sh (3.35)	38.4 (3.83)	40.0 (3.92)	46.0 (4.42)
adducts	34.1 (3.38)	35.3 (3.37)	36.2 sh (3.35)	38.4 (3.78)	40.0 (3.86)	46.0 (4.47)
2-Amino-bezothiazole						
ligand	34.1 (3.38)	35.1 (3.52)		38.2 (4.08)		45.1 (4.53)
adducts	35.2 (3.79)	36.0 (3.77)		39.2 (3.95)		46.3 (4.35)
Benzimidazole-2-thiol						
ligand	32.8 (4.40)	33.6 (4.32)			40.5 (4.13)	45.9 (4.22)
adducts	32.8 (4.41)	33.6 (4.32)			40.5 (4.15)	45.9 (4.27)
Benzothiazole-2-thiol						
ligand	30.8 (4.42)			38.8 (3.73)	41.6 (4.12)	43.5 (4.11)
adducts	30.8 (4.46)			38.8 (3.75)	41.6 (4.12)	43.5 (4.14)

Table 4. Infrared wave numbers of the ligands and their adducts in 1700—400 cm^{-1} region (cm^{-1})

BT	Sn^{IV}(BT)$_2$Cl$_4$	ABT	Sn^{IV}(ABT)$_2$Cl$_4$·2HCl	BIT	Sn^{IV}(BIT)$_2$Cl$_4$	BTT	Sn^{IV}(BTT)$_2$Cl$_4$	Tentative assignments
1691 m	1670 w	1641 s						
1590 m			1629 s	1612 w	1610 w			ν(C=C)
1552 m	1560 w	1586 w	1562 m			1595 w	1593 w	
		1523 s		1508 s	1494 s	1495 s	1485 s	(II)* ν(N-C=S)
1458 s	1462 m		1467 s					
1450 s	1454 m	1444 s		1461 s	1446 m	1451 m	1459 m	aromatic
1424 m	1408 m	1370 w	1365 w	1382 w	1410 m	1420 m	1412 m	
				1355 s	1348 m			C_6H_5-NH
1313 s		1316 m 1307 m				1319 m		
1290 s	1294 w		1302 w			1280 m	1303 m	
1262 s	1271 m	1281 w	1255 m	1270 w			1261 w	(III)* δNH and others
1195 m	1193 m	1247 w	1242 w	1256 m	1250 m	1242 m		
1154 m	1153 w	1152 w	1153 m	1180 s	1169 w	1153 m	1153 m	(I)* ν(C=S) and others
1121 s	1079 m		1087 br		1075 m	1076 s	1080 s	1,2-disubst C_6H_6
1067 s	1066 m	1064 w				1034 m	1037 w	
1010 s	1022 m	1014 w	1011 w	1012 m	1011 w	1011 m	1025 w	
794 s	787 m						786 m	
757 s	761 s		752 s			753 s	753 s	δ(C-H)
729 s	727 m 707 m	741 s 720 s	741 s 710 m	741 s	748 s			
668 s	670 w	682 m	694 w	658 s	665 s	668 s	692 m	
			663 m	597 s	597 m	603 s	597 s	
		624 m	646 s			568 m	574 s	
582 w	580 m	564 m	582 s				564 s	
531 m	537 s					524 m	517 w	
505 w	510 m	501 m	490 s	470 s	460 m	502 w	498 m	
423 s	425 s	483 s	479 s	430 s	432 m	425 m	433 m	
		430 s	425 m	418 s	418 w			

* I, II, III, mean first, second and third thioamide-bands respectively.
s: strong, br: broad, m: medium, w: weak, sh: shoulder, BT: benzothiazole, ABT: 2-amino-benzothiazole, BTT: bezimidazole-2-thiol, BTT: benzothiazole-2-thiol.

TABLE 5. FAR-INFRARED SPECTRA OF ADDUCTS (400—200 cm^{-1})
Refer Table 4 for the abbreviations

Metal salt	Ligands				Tentative assignment
	BT	ABT	BIT	BTT	
$\mathrm{Sn^{II}Cl_2}$	284 m	271 s	258 m	285 s	ν(Sn-Cl)
	247 s	237 s	243 s	245 w	(Sn-L)*
$\mathrm{Sn^{IV}Cl_4}$	320 s	313 s	302 s	323 s 310 s	ν(Sn-Cl)
	287 m 263 m	290 s	289 s 280 s	293 s	(Sn-L)*
$\mathrm{Sb^{III}Cl_3}$	313 s 293 s	304 s	329 s	320 s	ν(Sb-Cl)
	280 s	271 s	295 s	272 s	(Sb-L)*
$\mathrm{Sb^{III}Br_3}$	210 s	212 m	213 s	212 m	ν(Sb-Br)
	302 m 245 s	302 s 253 m	311 w 260 m 248 s	301 m 277 s	(Sb-L)*

* Probably the mixture of ν(M-N) and other ring vibrations.

tures of the spectra of the adducts resemble those of the respective free ligand. As these peaks seem to be mainly caused by the ligands, their tentative assignments are obtained with reference to those of the benzothiazole or benzimidazole derivatives.[9–12]

In the cases of 2-amino-benzothiazole adducts, the bands of the free ligand at 1641, 1523, and 1444 cm^{-1} shift to 1629—1638, 1562—1568, and 1467—1470 cm^{-1} respectively. These bands all correspond to the stretching modes of particular bonds or to conjugated modes of the thiazole ring. Therefore, the shifts seem to be due to the bonding of of the metal, which causes the change in the bonding states in the ring system, such as the prohibition of the tautomeric transition of the ring system. The adducts of the other ligands show only far smaller shifts of the corresponding bands.

The metal-halogen and the metal-ligand stretching bands appear in the 400—200 cm^{-1} region. The metal-halogen stretching bands (Sn(II)-Cl,[13] Sn(IV)-Cl,[14–16] Sb(III)-Cl,[17] and Sb(III)-Br,[17]) have already been reported; they appear as an almost pure group vibration, and do not mix with other modes. Consequently, the bands have been assigned according to the references mentioned above.

On the other hand, the metal-ligand group frequencies are not clear. Only a very few references have yet been published for the pure group-stretching vibration between tin or antimony and nitrogen or sulfur. Duff[8] shows that the metal-nitrogen stretching mode of benzothiazole complexes is apt to mix with some ring-vibrations, as in the cases of pyridine complexes. Therefore, the bands in this region, which appear only in the spectra of the adducts and are not identified as metal-halogen stretching bands, may be assigned tentatively to the metal-ligand vibrations. The results are summarized in Table 5.

Thus, the exact structures of the adducts are not yet clear; the ligand may bond not only by means of –N but, in some cases, also by means of –S, forming a multi-layer polymer structure, as in the cases of some benzothiazole complexes reported by Duff,[8] although all the metal-ligand bonds are certainly not very strong.

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