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INFRARED AND MÖSSBAUER STUDIES OF SOME DIAMINE COMPLEXES WITH TRIMETHYLTIN HALIDES AND DIMETHYLTIN DIHALIDES

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Summary

To obtain more structural information on complexes formed between alkyltin halides and bidentate ligands, the solid-state IR and Mössbauer spectra of the 1,2-ethanediamine and 1,4-butanediamine complexes of trimethyltin halides and dimethyltin dihalides were examined. The structures of the trimethyltin halide complexes were found to be trigonal bipyramidal with coplanar methyl groups. The dimethyltin dihalide complexes were octahedral with the methyl groups in the *cis*-positions and the halides *trans* to each other. However, there were no differences in the structures of the chloro and bromo complexes of either type.

Introduction

There are many studies in the literature pertaining to the structures of alkyltin halides and their derivatives with monodentate ligands [1–4]. Most of the structural investigations, however, have been focused on studies of the monodentate ligand complexes of trimethyltin halides, R_3SnX, and dimethyltin dihalides, R_2SnX_2. The results show that the trimethyltin halide complexes, $R_3SnX \cdot L$, are trigonal bipyramidal (TBP) while those formed with dimethyltin dihalides are octahedral. Few studies have been reported with bidentate ligands, especially with trimethyltin halides.

Therefore, in order to gain more structural information on complexes formed between alkyltin halides and bidentate ligands, our laboratories have studied the complexes of trimethyltin halides and dimethyltin dihalides with two diamine ligands (1,2-ethanediamine and 1,4-butanediamine).

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Experimental

Reagents

1,2-Ethanediamine (en) obtained from the Fisher Chemical Co. and 1,4-butanediamine (db) obtained from Pfaltz and Bauer, Inc. were both purified by distillation over metallic sodium. 1,2-Ethanediamine was collected at 116°C; Lit., 116.5°C [5] and 1,4-butanediamine was collected at 158°C; Lit., 158–159°C [5].

The organotin halides were obtained from Alfa Products, Inc. and used without further purification. The melting points were within 1°C of the literature values. Trimethyltin chloride and bromide melted at 38 and 27°C, respectively; Lit. 37.5–39.5 and 26–27°C [1–4], while dimethyltin dichloride and dimethyltin dibromide had melting points of 108 and 75°C, respectively; Lit., 107–108 and 74–77°C [1–4].

The solvents used in the synthetic work were reagent grade and were used without further purification.

Preparation of complexes

The complexes were prepared by the reaction of the organotin halide with the diamine ligand (1/1 molar ratio) under a nitrogen atmosphere at room temperature. A typical reaction was as follows: A mixture of 10 mmol of en in 30 ml of anhydrous ethyl ether was added dropwise, with stirring, to a solution containing 10 mmol of dimethyltin dichloride in 30 ml of anhydrous ethyl ether. The reaction was stirred for an additional 1.5 h. The product was then collected by vacuum filtration under a nitrogen atmosphere and washed several times with cold ethyl ether. The yield for a typical reaction was between 80–90%.

Elemental analyses

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Spectra

The infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls between CsI plates with a Perkin–Elmer 457 grating infrared spectrophotometer.

The Mössbauer spectra were measured using a constant acceleration spectrometer with the samples mounted in a cryostat. The computer program has been previously described [6]. The source was a 1 mCi $\text{Ba}^{119m}\text{SnO}_3$, and all parameters were measured relative to the source. The velocity range was calibrated with a composite of BaSnO_3 and Sn foil at room temperature (splitting 2.52 mm s^{-1}).

Results and discussion

$(CH_3)_3SnX \cdot L$ complexes

Since the diamine ligands, en and db, possess two donor sites, they may act as a monodentate, bidentate or as a chelating ligand. Thus, several stereoisomers are possible for the trimethyltin halide complexes. The structures may be monomeric with either chelating or non-chelating diamine groups or dimeric in which the diamine behaves as a bridged ligand.

TABLE 1

ANALYTICAL DATA FOR $(CH_3)_3SnX\cdot L$ AND $(CH_3)_3SnX_2\cdot L$ COMPLEXES

Compound	M.p. (°C)	Found (calcd.) (%)		
		C	H	Sn
$(CH_3)_3SnCl\cdot en$ [a]	>158d	23.15 (23.16)	6.80 (6.61)	45.58 (45.76)
$(CH_3)_3SnBr\cdot en$	158–160	19.74 (19.74)	5.72 (5.59)	39.62 (39.14)
$(CH_3)_3SnCl\cdot db$	132–134	29.35 (29.20)	7.46 (7.30)	40.85 (41.40)
$(CH_3)_3SnBr\cdot db$	202–205	25.22 (25.30)	6.56 (6.30)	35.57 (35.80)
$(CH_3)_2SnCl_2\cdot en$	232–235	16.70 (17.08)	5.52 (4.98)	41.81 (42.35)
$(CH_3)_2SnBr_2\cdot en$	209–212	13.03 (13.00)	4.09 (3.79)	31.43 (32.25)
$(CH_3)_2SnCl_2\cdot db$	195–198	22.74 (23.38)	6.19 (5.84)	37.98 (38.64)
$(CH_3)_2SnBr_2\cdot db$	258–260	18.45 (18.14)	4.60 (4.53)	29.79 (29.97)

[a] Ref. 28.

The analytical data (Table 1) for the trimethyltin halide complexes indicated that they formed 1 : 1 complexes. Since trialkyltin halides have been shown to form pentacoordinated complexes [1–4], our analytical data eliminate the bridged structure (1 : 2 complexes) but not those of polymeric forms.

The major IR bands for the trimethyltin halide complexes are reported in Table 2. The observation of only the tin–carbon asymmetric vibration around 550 cm^{-1} in the IR spectra of the complexes supports a pentacoordinated structure with coplanar methyl groups. This is in agreement with the fact that triorganotin halides show a strong tendency to form 1 : 1 TBP complexes with axial ligands when reacted with monodentate ligands [7]. Further support for a non-chelated structure is the absence of bands around 445, 870 and 1160 cm^{-1} that is indicative of a chelated structure [8].

TABLE 2

MAJOR BANDS IN THE IR SPECTRA BETWEEN 2000–250 cm^{-1} FOR $(CH_3)_3SnX\cdot L$

X = Cl/L = en	X = Br/L = en	X = Cl/L = db	X = Br/L = db	Tentative assignments
1597m	1590m	1600m	1600m	NH_2 bend
1375m	1380m	1375m	1380s	CH_2 wag
1332m	1330w	1265s	1270w	CH_2 twist
1210m	1210w	1200w	1200w	CH_2 twist
1145s	1140m	1150m	1150m	NH_2 wag
1018s	1019s	1050m	1050s	CN stretch
1000m	1000s	–	–	NH_2 twist
793s	800s	790m	800s	NH_2 rock
680w	690s	–	640w	NH_2 rock
556s	560m	550m	550m	Sn–C asym. stretch
425m	420w	420w	420w	skeletal bend

TABLE 3

MÖSSBAUER PARAMETERS FOR $(CH_3)_3SnX \cdot L$ AND $(CH_3)_2SnX_2 \cdot L$ COMPLEXES AT LIQUID NITROGEN TEMPERATURE [a]

Compound	IS	QS	ρ	HW_+	HW_-
$(CH_3)_3SnCl \cdot en$	1.23 ± 0.01	3.12 ± 0.05	2.54 ± 0.05	0.54 ± 0.01	0.62 ± 0.01
$(CH_3)_3SnBr \cdot en$	1.23 ± 0.01	3.11 ± 0.01	2.53 ± 0.02	0.50 ± 0.01	0.49 ± 0.01
$(CH_3)_3SnCl \cdot db$	1.18 ± 0.01	2.93 ± 0.05	2.48 ± 0.05	0.53 ± 0.01	0.62 ± 0.01
$(CH_3)_3SnBr \cdot db$	1.26 ± 0.01	3.02 ± 0.05	2.40 ± 0.05	0.52 ± 0.01	0.50 ± 0.01
$(CH_3)_2SnCl_2 \cdot en$	0.90 ± 0.01	2.04 ± 0.04	2.27 ± 0.05	0.50 ± 0.03	0.80 ± 0.06
$(CH_3)_2SnBr_2 \cdot en$	0.99 ± 0.01	2.08 ± 0.04	2.10 ± 0.05	0.47 ± 0.03	0.45 ± 0.03
$(CH_3)_2SnCl_2 \cdot db$	0.87 ± 0.01	2.12 ± 0.03	2.44 ± 0.04	0.50 ± 0.02	0.65 ± 0.02
$(CH_3)_2SnBr_2 \cdot db$	0.94 ± 0.01	2.23 ± 0.04	2.37 ± 0.05	0.50 ± 0.03	0.55 ± 0.03

[a] All parameters are given in mm s^{-1} relative to $BaSnO_3$. HW is half width at half maximum.

The Mössbauer parameters are given in Table 3. The ratios of the quadrupole splitting to the isomer shift in the Mössbauer spectra, ρ, for five-coordinated complexes have been observed in the range 2.3–2.5 mm s^{-1} [9,10]. Thus, the observed ρ values of 2.40–2.54 is further evidence that the complexes studied in this work have a coordination number greater than four and fall within the range of known five-coordinated complexes. Furthermore, the observed quadrupole splitting (QS) of 2.93–3.12 mm s^{-1} is in the range of 2.76–3.86 mm s^{-1} found for other TBP complexes with axial ligands [11,12].

Therefore, IR and Mössbauer results show that the structures of the trimethyltin halide complexes are TBP with the methyl groups in the equatorial plane, which is consistent with earlier studies of other halide complexes.

$(CH_3)_2SnX_2 \cdot L$ complexes

Although several stereoisomers are possible for the dimethyltin dihalide complexes, the analytical data (Table 1) indicate that 1 : 1 complexes were formed. This suggests either a bridge or chelated structure for these complexes. This is in agreement with earlier studies showing that dialkyltin dihalides form hexacoordinated complexes with either mono- or bidentate ligands [13–15].

The tin–carbon asymmetric and symmetric stretching vibrations have been assigned in $(CH_3)_2SnCl_2$ as occurring between 542–575 and 481–507 cm^{-1}, respectively [16–19]. Thus, the observation of both of these vibrations (Table 4) in our complexes suggests a non-linear arrangement of the tin–carbon moiety. Also, the observations of absorptions around 1160, 875 and 445 cm^{-1} together with the negative shift of the CN asymmetric and symmetric vibrations around 1090–1070 to around 1080–1030 cm^{-1} indicate a chelated complex with a *cis* arrangement of the methyl groups [8,20] or a distorted *trans* arrangement of the methyl groups.

The lowering of the tin–chlorine stretching vibration upon complexation to below 250 cm^{-1} is well documented for tri- and dialkyltin complexes [7,21,22]. This has been attributed to bond lengthening owing to ligand–ligand repulsion forces and/or a decreased effectiveness of $(p \rightarrow d)\pi$ bonding [17]. Thus, the observation of the tin–chlorine stretching frequency at 332 cm^{-1} by Nelson [23] in complexes of the type $Cl_2Sn(acac)_2$ suggested strong $(p \rightarrow d)\pi$ bonding between the tin and chlorine atoms, indicating that the two chloro groups are *cis* to one another because this configuration is most favorable for $(p \rightarrow d)\pi$ bonding between the tin and

TABLE 4

MAJOR BANDS IN THE IR SPECTRA BETWEEN 2000–250 cm^{-1} FOR $(CH_3)_2SnX_2 \cdot L$

X = Cl/L = en	X = Br/L = en	X = Cl/L = db	X = Br/L = db	Tentative assignments
1600m	1585m	1610m	1605m	NH_2 bend
1575m	1560m	1595m	1590m	NH_2 bend
–	–	1405m	1405m	CH_2 wag
1335m	1350m	1345m	1345m	CH_2 wag
1295m	1315m	1280m	1285m	CH_2 twist
1195m	1200m	1200m	1200s	CH_2 twist
–	1180m	–	1180s	CH_2 twist
1160m	1175w	1180s	1175m	ring mode
1120s	–	1120s	1110s	not assigned
1040s	1035s	1035s	1040s	CN stretch
1020w	1008s	1025s	1035s	CN stretch
980w	975w	975w	970w	NH_2 twist
875w	880w	870s	870s	ring mode
815s	815s	–	–	NH_2 rock
795s	760s	765s	765s	NH_2 rock
725m	725m	725w	725s	CH_2 rock
580m	570s	570s	570s	NH_2 rock
550m	550s	550s	550s	Sn–C asym. stretch
530m	520m	520m	520m	Sn–C sym. stretch
450br	440br	440br	450br	ring bend

chlorine atoms. Examination of the IR spectra of the complexes synthesised in this work shows that this band at 332 cm^{-1} is missing, indicating that the chloro and bromo groups in our complexes are *trans* to one another. Thus, the IR data suggest that the structures of the complexes are octahedral with *cis*-methyl groups and *trans*-chloro groups.

It has been observed in the Mössbauer spectra of octahedral R_2SnX_4 complexes that the QS values for the *trans*-isomer is approximately twice that of the *cis*-isomer [24]. Octahedral complexes with *trans*-R groups have QS values of around 4 mm s^{-1} while *cis*-complexes have QS values of around 2 mm s^{-1}. Thus, the Mössbauer spectra for the diamine complexes of $(CH_3)_2SnX_2$ indicate hexacoordinated structures with a *cis*-arrangement of the methyl groups because the QS values range from 2.04–2.33 mm s^{-1}. The Mössbauer spectra support the proposal that the methyl groups are in a *cis*-arrangement as suggested from the IR data. However, this gives no information as to the arrangement of the halogen atoms.

The positions of the halogens can be determined by performing point-charge model calculations [25] on the two isomers in which the methyl groups are in the *cis*-position. Since the values of the partial quadruple splittings (pqs), $[1/2\ L]^{oct}$ for en and db are not known, they were calculated using the relationship, $[L]^{tba}/[L]^{oct} = 0.904$ as proposed by Bancroft et al. [26]. The values for $[1/2\ L]^{tba}$ were calculated using the Mössbauer data of the TBP complexes (Table 3). The calculated value for $[1/2\ en]^{tba}$ was -0.14 and -0.21 mm s^{-1} for $[1/2\ db]^{tba}$. These values were calculated using values [26] of $[X]^{tba} = [Cl]^{tba} = [Br]^{tba} = 0$ and $[CH_3]^{tba} = -1.13$ mm s^{-1} and the expression: $V_{ZZ} = 2[X]^{tba} + 2[1/2\ L]^{tba} + 2[1/2\ L]^{tba} - 3[CH_3]^{tba}$. Then, the values for $[1/2\ en]^{oct}$ and $[1/2\ db]^{oct}$ are -0.15 and -0.23 mm s^{-1} respectively.

Using these pqs values, the calculated QS for the octahedral configuration in which the halogens are in the *cis*-position was -1.18 mm s^{-1} for the en complexes and -1.26 mm s^{-1} for the db complexes. For the configuration where the halogens are *trans* to each other, the calculated QS values were 2.21 mm s^{-1} for the en complexes and 2.52 mm s^{-1} for the db complexes. The equations used for these calculations were $V_{ZZ} = [CH_3]^{oct} + [L]^{oct} - 2[X]^{oct}$ for the structure in which the halogens are in the *cis*-positions and $V_{ZZ} = 4[X]^{oct} - 2[CH_3]^{oct} - 2[L]^{oct}$ for the structure where the halogens are *trans* to each other. The value used for $[CH_3]^{oct}$ was -1.03 mm s^{-1} and for $[X]^{oct} = [Cl]^{oct} = [Br]^{oct} = 0.0$ [25].

The experimental QS values in Table 3 of the en complexes were 2.04 and 2.08 mm s^{-1}, while those of the db complexes were 2.12 and 2.23 mm s^{-1}. The results of the point-charge model calculations suggest that the halogens are in the *trans*-position because the experimental QS values are in the same order of magnitude as the calculated values. Therefore, the Mössbauer data are consistent with the dimethyltin dihalide complexes being octahedral complexes with the methyl groups in the *cis*-position and the halogen atoms in the *trans*-position.

Sham and Brancroft [27] used the QS values to predict the carbon–tin–carbon angle in diorganotin(IV) derivatives with octahedral geometries. The calculated angles are as follows for the compounds examined here: $(CH_3)_2SnCl_2 \cdot$ en, 90°; $(CH_3)_2SnBr_2 \cdot$ en, 92°; $(CH_3)_2SnCl_2 \cdot$ db, 97°; and $(CH_3)_2SnBr_2 \cdot$ db, 103°.

The analytical, IR, and Mössbauer data indicate that the dimethyltin dichloro and dibromo complexes have octahedral structures with *cis*-methyl groups and *trans*-halogen atoms.

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