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Mössbauer Studies of Tin(IV) Complexes with Chelating Anionic Ligands

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*Mössbauer parameters are reported for tin(IV) complexes with anions of 3,5-diphenyl,4-methyl, 1-hydroxy-2-pyrazole N-oxide (I), 8-hydroxyquinoline N-oxide (II), 8-quinoline thiol (III), N,N'-*o*-phenylenebis(salicylaldimine) (IV) and N,N'-*o*-phenylenebis(pyrrolaldimine) (V). Correlations are made of isomer shifts reported for octahedral dihalotin(IV) complexes with fifteen chelating anionic ligands. The dihalotin complexes of (I) have larger isomer shifts than those with any other* $\overset{\frown}{O\ O^{-}}$ *ligand reported to date. The dichloro- and dibromotin complexes with (III) have the largest quadrupole splittings reported for octahedral dihalotin complexes. The diorganotin complexes with (I) are highly distorted. Data available to date indicate that six-membered chelate rings effect a lower electron density at the tin nucleus than do five-membered rings in neutral dihalotin(IV) complexes.* Sn^{119}*C–H coupling constants are reported for* $(CH_3)_2Sn(I)_2$. $(CH_3)_2Sn(III)_2$ *and* $(CH_3)Sn(2\text{-}SPyO)_2$ *in* $DCCl_3$.

Introduction

In a previous article [1] from this Laboratory correlations were made of the electron density at the tin nucleus effected by $^{-}\overset{\frown}{O\ N}$, $\overset{\frown}{O\ S^{-}}$, and $\overset{\frown}{S\ S^{-}}$ chelating ligands. Later some $\overset{\frown}{O\ O^{-}}$ type ligands were investigated [2]. It is of interest to extend this comparison to $\overset{\frown}{N\ S^{-}}$ and to other $\overset{\frown}{O\ O^{-}}$ type ligands, as well as to tetradentate $\begin{smallmatrix}\overset{\frown}{N\ N}\\ ^{-}O\ O^{-}\end{smallmatrix}$ and $\begin{smallmatrix}\overset{\frown}{N\ N}\\ ^{-}N\ N^{-}\end{smallmatrix}$ ligands. The Mössbauer parameters of diorganotin(IV) complexes with these ligands are expected to give some indication of the configurations of these complexes.

Experimental

Preparation and Purification of Compounds

The potassium salt of 3,5-diphenyl, 4-methyl, 1-hydroxy-2-pyrazole N-oxide was prepared by J. F. Hansen and made available through the courtesy of Professor J. P. Freeman. The complexes of this ligand were prepared by mixing methanol solutions of this salt in a 2:1 mol ratio with methanol solutions of R_2SnCl_2 or SnX_4 with stirring. The complexes, $R_2Sn(Ph_2pyzo_2)_2$ and $X_2Sn(Ph_2pyzo_2)_2$ precipitated immediately. They were washed with methanol and vacuum dried at 78 °C over P_4O_{10}. The dimethyl compound is pink, the diiodo yellow, and the others white.

8-Hydroxyquinoline N-oxide was obtained from Aldrich Chemical Co. The sodium salt, Na(8-OQuinO) was prepared with sodium hydroxide in ethanol and the filtrate poured into excess diethyl ether. The salt precipitated as an orange microcrystalline solid. The difluoro complex was prepared by reacting tin(IV) fluoride with 8-hydroxyquinoline N-oxide in a 1:2 mol ratio in absolute methanol. The other dihalo complexes were precipitated similarly, using the sodium salt of the ligand and stirring for twenty minutes. Each complex was washed several times with methanol and dried under vacuum at 56 °C for twelve hours. The diiodo compound is orange and the others yellow. The diphenyl compound was prepared similarly from Ph_2SnCl_2 and the sodium salt. Several attempts were made to prepare the dimethyl and di-n-butyl compounds, but none of the products gave a satisfactory infrared spectrum or a good analysis.

Sodium 8-thioquinolinate, C_9H_6NSNa, was prepared by the method of Shevchuk and Luksa [3] starting with 8-quinolinesulfonyl chloride obtained from Aldrich Chemical Co. The dihalo complexes were prepared and purified in a manner similar to those from the sodium salt of 8-hydroxyquinoline N-oxide. The diiodo compound is orange and the others yellow. The dimethyl, di-n-butyl and diphenyl complexes were prepared by reacting the diorgano tin dichlorides in a 1:2 mol ratio with the sodium salt of the ligand in absolute methanol. The dimethyl and dibutyl complexes were recrystallized from methanol and the diphenyl complex was washed several times with methanol. All were dried as above.

$Ph_2Sn(NCS)$(8-SQuin) and $Ph_2Sn(NCS)$(8-OQuinO) precipitated on stirring $Ph_2Sn(NCS)_2$ and the sodium salts of the ligands in a 1:1 ratio in methanol solution for several hours. The products were washed several times with small amounts of methanol and dried as above.

N,N'-*o*-phenylenebis(salicylaldimine), [(Hsal($_2$-phen] was prepared by mixing methanol solutions of *o*-phenylenediamine and salicylaldehyde in a 1:2 mol ratio and adding a drop of glacial acetic acid. The disodium salt was obtained by adding sodium methylate to a methanol solution of $\mathrm{(Hsal)_2phen}$. Diphenyl- and the dihalotin(IV) ($\mathrm{sal_2phen}$) complexes were prepared by mixing hot methanol solutions of diphenyltin dichloride or $\mathrm{SnX_4}$ and $\mathrm{Na_2(sal_2phen)}$ in a 1:1 ratio. Orange precipitates were obtained immediately for the halide complexes, whereas the yellow diphenyl complex precipitated after ten hours stirring. The di-n-butyl complex was obtained as an oily residue on evaporation of a methanol solution. It was extracted with benzene to remove sodium chloride, evaporated and dissolved in petroleum ether (30–60 °C) and cooled in dry-ice–acetone to give an orange precipitate which was dried at room temperature.

N,N'-*o*-phenylenebis(pyrrolaldimine) was prepared from pyrrole aldehyde and *o*-phenylenediamine and the disodium salt was prepared as above. Di-n-butyltin(IV)($\mathrm{pyrral_2phen}$) was prepared by mixing methanol solutions of the disodium salt and dibutyltin dichloride. The complex precipitated and was separated immediately and dissolved in methylene chloride to remove sodium chloride and the filtered solution was diluted with pentane and evaporated to dryness to yield the orange product. The diphenyl complex precipitated on adding a methanol solution of diphenyltin dichloride to a methanol solution of $\mathrm{(Hpyrral)_2}$-phen containing excess 2,4,6-trimethylpyridine. The precipitate was treated immediately as above and the complexes were dried at 78 °C.

Infrared spectra were obtained with Perkin-Elmer spectrometers, Models, 421, 521 and 457, in KBr disks.

Mössbauer spectra were obtained as previously described [4] with the source at room temperature. A palladium–tin source was used for compounds **21** and **22**; all other measurements were made with a barium stannate source. The isomer shifts in Table I, relative to barium stannate, are considered to be accurate to ±0.03 mm s^{-1} with a relative precision of 0.02 mm s^{-1}.

NMR spectra were obtained as previously described [1].

TABLE I. Characterization and Mössbauer Parameters (mm s^{-1}) at 80 K.

Compound	% Carbon		% Hydrogen		M.p. (°C)	δ	ΔE_Q	Γ_1	Γ_2
	Calcd.	Found	Calcd.	Found					
1. $\mathrm{Me_2Sn(Ph_2pyzo_2)_2}$	60.09	60.90	4.71	5.01	232–235	0.93	2.50	0.97	0.90
2. $\mathrm{n\text{-}Bu_2Sn(Ph_2pyzo_2)_2}$	62.90	61.54	5.77	5.85	109–112	1.06	2.49	0.90	0.86
3. $\mathrm{Ph_2Sn(Ph_2pyzo_2)_2}$	64.30	63.38	4.73	4.34	242–244	0.88	2.19	1.0	0.94
4. $\mathrm{(Vin)_2Sn(Ph_2pyzo)_2}$	61.47	60.25	4.59	4.39	198–200	0.86	2.23	0.95	0.97
5. $\mathrm{Cl_2Sn(Ph_2pyzo_2)_2}$	53.33	54.22	3.61	3.80	260–263	0.42	–	1.26	
6. $\mathrm{Br_2Sn(Ph_2pyzo_2)_2}$	47.47	48.31	3.21	3.35	257–260	0.52	–	1.44	
7. $\mathrm{I_2Sn(Ph_2pyzo_2)_2}$	42.52	43.71	2.88	2.93	242–244	0.74	–	1.52	
8. $\mathrm{Ph_2Sn(8\text{-}OQuinO)_2}$	60.76	60.03	3.71	3.71	a	0.70	1.80	1.1	1.0
9. $\mathrm{F_2Sn(8\text{-}OQuinO)_2}$	45.33	44.99	2.54	3.09	a	−0.12	0.63	1.11	1.07
10. $\mathrm{Cl_2Sn(8\text{-}OQuinO)_2}$	42.40	41.72	2.37	2.85	a	0.22	0.65	1.00	1.00
11. $\mathrm{Br_2Sn(8\text{-}OQuinO)_2}$	36.10	34.52	2.02	2.17	a	0.37	0.62	1.05	1.09
12. $\mathrm{I_2Sn(8\text{-}OQuinO)_2}$	31.22	31.43	1.75	2.01	a	0.53	0.6	0.8	1.1
13. $\mathrm{Me_2Sn(8\text{-}SQuin)_2}$	51.20	50.96	3.93	4.43	218–219	1.31	2.63	1.02	1.01
14. $\mathrm{n\text{-}Bu_2Sn(8\text{-}SQuin)_2}$	56.4	55.9	5.42	5.43	212–215	1.45	2.80	0.96	0.99
15. $\mathrm{Ph_2Sn(8\text{-}SQuin)_2}$	60.73	59.82	3.73	3.50	209–212	0.90	1.21	1.2	1.1
16. $\mathrm{F_2Sn(8\text{-}SQuin)_2}$	45.31	45.03	2.53	2.75	a	0.48	1.01	1.36	1.16
17. $\mathrm{Cl_2Sn(8\text{-}SQuin)_2}$	42.39	41.78	2.37	2.56	a	0.82	1.41	0.99	1.01
18. $\mathrm{Br_2Sn(8\text{-}SQuin)_2}$	36.09	36.18	2.02	2.11	a	0.91	1.41	1.13	1.05
19. $\mathrm{I_2Sn(8\text{-}SQuin)_2}$	31.20	30.95	1.74	1.93	a	1.01	1.25	1.0	1.1
20. $\mathrm{Me_2Sn(2\text{-}SPyO)_2}$	b		b		198–199	1.34	3.08	0.98	0.98
21. $\mathrm{Ph_2Sn(NCS)(8\text{-}SQuin)}$	53.79	52.99	3.28	3.60	a	1.12	2.65	0.9	0.9
22. $\mathrm{Ph_2Sn(NCS)(8\text{-}OQuinO)}$	53.80	53.17	3.28	3.27	a	0.46	1.71	1.2	1.2
23. $\mathrm{n\text{-}Bu_2Sn(sal_2phen)}$	61.45	61.18	5.85	6.00	62–64	1.35	3.78	1.40	1.34
24. $\mathrm{Ph_2Sn(sal_2phen)}$	65.40	64.79	4.10	4.18	155–157	1.12	2.65	1.06	1.08
25. $\mathrm{Cl_2Sn(sal_2phen)}$	47.62	47.35	2.73	3.43	>290	0.27	0.6	1.16	0.96
26. $\mathrm{Br_2Sn(sal_2phen)}$	40.50	40.25	2.36	2.56	>290	0.35	–	1.74	
27. $\mathrm{I_2Sn(sal_2phen)}$	34.92	35.48	2.04	2.13	>290	0.45	–	1.52	
28. $\mathrm{n\text{-}Bu_2Sn(pyrral_2phen)}$	58.50	57.09	6.13	6.17	143–145	1.33	3.45	1.15	1.16
29. $\mathrm{Ph_2Sn(pyrral_2phen)}$	63.07	61.74	4.16	4.20	a	1.08	2.90	1.07	1.01

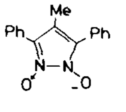
[a] Melting points not recorded. [b] C and H analyses checked within 1% of the calculated values.

TABLE II. Isomer Shifts (mm s^{-1}) for X_2SnL_2 and X_2SnL Type Compounds.

		Type	Cl_2	Br_2	I_2	Ref.
A.	$X_2Sn(sal)_2$	$^{-}\overset{6}{\widehat{\mathrm{O\ O}}}$	0.23	0.28	0.41	(12)
B.	$X_2Sn(8\text{-}OQuinO)_2$	$^{-}\overset{6}{\widehat{\mathrm{O\ O}}}$	0.23	0.38	0.53	
C.	$X_2Sn(acac)_2$	$^{-}\overset{6}{\widehat{\mathrm{O\ O}}}$	0.25			(13) (14)
			0.30	0.45		(15)
D.	$X_2Sn(kojate)_2$	$^{-}\overset{5}{\widehat{\mathrm{O\ O}}}$	0.30	0.45	0.65	(2)
E.	$X_2Sn(tropolonate)_2$	$^{-}\overset{5}{\widehat{\mathrm{O\ O}}}$	0.30	0.42	0.61	(2)
F.	$X_2Sn(Ph_2pyzo_2)_2$	$^{-}\overset{5}{\widehat{\mathrm{O\ O}}}$	0.42	0.52	0.74	
G.	$X_2Sn(pic)_2$	$^{-}\overset{5}{\widehat{\mathrm{O\ N}}}$	0.31	0.44	0.64	(16)
H.	$X_2Sn(ox)_2$	$^{-}\overset{5}{\widehat{\mathrm{O\ N}}}$	0.34	0.44	0.61	(12)
I.	$X_2Sn(sal_2phen)$	$^{-}\overset{6}{\widehat{\mathrm{O\ N}}}$	0.27	0.35	0.45	
J.	$X_2Sn(2\text{-}SPyO)_2$	$\overset{5}{\widehat{\mathrm{O\ S}}}^{-}$	0.59	0.69	0.90	(11)
K.	$X_2Sn(phthalocyanine)$	$^{-}\overset{6}{\widehat{\mathrm{N\ N}}}$	0.28	0.34	0.45	(17)
L.	$X_2Sn(8\text{-}SQuin)_2$	$^{-}\overset{5}{\widehat{\mathrm{S\ N}}}$	0.82	0.91	1.01	
M.	$X_2Sn(2\text{-}SPy)_2$	$^{-}\overset{4}{\widehat{\mathrm{S\ N}}}$	0.81		1.04	(7)
N.	$X_2Sn(S_2CNEt_2)_2$	$^{-}\overset{4}{\widehat{\mathrm{S\ S}}}$	0.78	0.90	1.05	(1)
			0.74	0.95	1.12	(18)
O.	$X_2Sn(S_2PEt_2)_2$	$^{-}\overset{4}{\widehat{\mathrm{S\ S}}}$	0.78	0.93	1.07	(19)

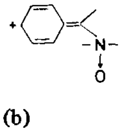
Results and Discussion

Mössbauer parameters are listed in Table I. The isomer shifts obtained for the dihalotin$(Ph_2pyzo_2)_2$ complexes are significantly larger than those reported for other corresponding $X_2Sn(\overset{O}{\underset{O}{\subset}})_2$ complexes (see Table II), indicating that the



(a)

ligand effects the largest electron density at the tin nucleus. This may result from



(b)

resonance. The quadrupole splitting for $Bu_2Sn(Ph_2pyzo_2)_2$, 2.49 mm s^{-1}, compares with values of 3.70 and 3.68 mm s^{-1} for $Bu_2Sn(kojate)_2$ and $Bu_2Sn(tropolonate)_2$ [2], indicating a large deviation from 180° for the C–Sn–C bond angle in the first compound. The relatively small tin s-character for the C–Sn bonds in this compound is evidenced by the isomer shift of 1.06 mm s^{-1} compared to 1.38 mm s^{-1} for $Bu_2Sn(kojate)_2$. The former value is the smallest reported for a $Bu_2Sn(\overset{O}{\underset{O}{\subset}})_2$ compound. This small tin s-character is also evidenced by the Sn^{119}–CH coupling constant, 72.4 cps, obtained for $Me_2Sn(Ph_2pyzo)_2$ in $DCCl_3$, compared to 99.3 cps for $Me_2Sn(acac)_2$ [5] and 83.3 cps for $Me_2Sn(kojate)_2$ [6]. The isomer shift and quadrupole splitting values for $Ph_2Sn(Ph_2pyzo_2)_2$, 0.85 and 2.19 mm s^{-1} and for $Vin_2Sn(Ph_2pyzo_2)_2$, 0.86 and 2.23 mm s^{-1}, indicate distorted *cis* configurations. These values compare with 0.75 and 1.93 mm s^{-1} for $Ph_2Sn(tropolonate)_2$ [2]. The large half width, 1.52 mm s^{-1} of the Mössbauer absorption for $I_2Sn(Ph_2pyzo_2)_2$ suggests an unresolved quadrupole splitting.

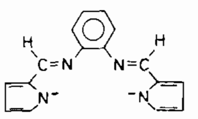
The isomer shift and quadrupole splitting values, 0.70 and 1.80 mm s^{-1} respectively for $Ph_2Sn(8\text{-}OQuinO)_2$ indicate a *cis* arrangement of C–Sn bonds in this compound. The isomer shifts for the four $X_2Sn(8\text{-}OQuinO)_2$ compounds show a linear variation with Mulliken–Jaffe electronegativity values for the halogens.

The Mössbauer parameters for the diorganotin-(8] SQuin)$_2$ compounds are difficult to analyze in that neither Mössbauer nor crystal structure data have been reported for similar compounds with five-membered rings. The relative values of the isomer shifts, 1.45 and 0.90 mm s^{-1}, and quadrupole splittings, 2.80 and 1.29 mm s^{-1} for the dibutyl and diphenyl compounds respectively, indicate a much smaller C–Sn–C bond angle in the latter compound. This is in contrast to the four-membered ring compounds $R_2Sn(2\text{-}SPy)_2$, which have isomer shift values of 1.51, 1.35 and 1.30 mm s^{-1} and quadrupole splitting values of 2.87, 2.56 and 2.31 mm s^{-1} for the dibutyl, dimethyl and diphenyl compounds respectively [7], indicating similar configurations for all these compounds.

Sn^{119}–CH coupling constants of 78.5 cps and 83.0 cps were obtained for $Me_2Sn(8\text{-}SQuin)_2$ and $Me_2Sn(2\text{-}SPyO)_2$. In the event of equal C–Sn–C bond angles, the coupling constant is expected to be smaller for the former compound because of the smaller difference in tin s-character in the C–SnN than in the C–SnO bonds. The coupling constant for $Me_2Sn(8\text{-}SQuin)_2$ does indicate a larger C–Sn–C bond angle than in $Me_2Sn(Ph_2pyzo_2)_2$ (J Sn^{119}–CH = 72.4 cps).

The quadrupole splittings obtained for $Cl_2Sn(8\text{-}SQuin)_2$ and $Br_2Sn(8\text{-}SQuin)_2$, 1.41 mm s^{-1} are the largest reported to date for six-coordinate X_2SnL_2 compounds. The infrared spectrum of the dichloro compound has a broad absorption at 285 cm^{-1} attributed to a Sn–Cl stretching vibration. Two peaks at 525 and 512 cm^{-1} in the spectrum of $F_2Sn(8\text{-}SQuin)_2$, attributed to F–Sn–F stretching vibrations, suggest *cis* Sn–F bonds in this compound. The quadrupole splittings for the four-membered ring compound $Cl_2Sn(2\text{-}SPy)_2$ is 0.60 mm s^{-1} [7] and the crystal structure of this compound [8] reveals *cis* Sn–Cl bonds.

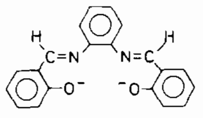
The isomer shift and quadrupole splitting values reported for $Me_2Sn(sal_2en)$ are 1.13 and 3.46 mm s^{-1} and for $Ph_2Sn(sal_2en)$ 0.88 and 2.84 mm s^{-1} [9]. The crystal structure of the former compound [10] reveals a nearly coplanar arrangement of the two nitrogen and two oxygen atoms and a C–Sn–C bond angle of 161°, the methyl groups bending slightly toward the O- - -O side. The $Sn{<}^{O}_{O}$ angle is 128° and the $Sn{<}^{N}_{N}$ angle is 73°. Resonance effects are expected to result in a similar coplanarity of oxygen and nitrogen atoms bound to tin in the $R_2Sn(IV)$ complexes with the dianion of N,N'-*o*-phenylenebis(salicylaldimine)



(c)

The isomer shift and quadrupole splitting values (Table I) for $Bu_2Sn(sal_2phen)$ are 1.35 and 3.78 mm s^{-1} and for $Ph_2Sn(sal_2phen)$, 1.02 and 3.25 mm s^{-1}. The latter values suggest a larger C–Sn–C bond angle in $Ph_2Sn(sal_2phen)$ than in $Ph_2Sn(sal_2en)$. $Cl_2Sn(sal_2phen)$ has a quadrupole splitting value of 0.6 mm s^{-1} and the large half width of the absorption for the dibromo compound, 1.74 mm s^{-1}, suggests an unresolved quadrupole splitting.

The dianion of N,N'-*o*-phenylenebis(pyrrolaldimine)



(d)

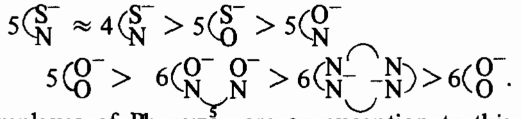
is also expected to be resonance stabilized in a nearly coplanar arrangement of nitrogen atoms in its complexes with tin(IV). The Mössbauer parameters of the dibutyltin and diphenyltin complexes with this ligand, Table I, indicate a *trans* arrangement of C–Sn–C bonds. Unfortunately the diorganotin complexes with phthalocyanine and porphyrins are not available for comparison with the "open ring" complexes.

The two isothiocyanate complexes reported in Table I have NCS absorptions at 2040 and 2055 cm^{-1} respectively, suggesting that there is no NCS bridging which would lead to the formation of six coordinate dimers or polymers.

The Mössbauer parameters for $Ph_2Sn(NCS)(8\text{-}SQuin)$, **21**, are nearly equal to those for $Ph_2Sn(NCS)(2\text{-}SPyO)$ [11]. The very different values obtained for $Ph_2Sn(NCS)(8\text{-}OQuinO)$, **22**, suggest a different configuration for the latter compound with perhaps one phenyl group occupying an axial position (less tin s-character) in a distorted trigonal pyramid.

A comparison of the isomer shifts for some neutral dihalo six-coordinate complexes is given in Table II. For $X_2Sn(\langle^{O}_{O}\rangle)_2$ complexes it is evident that five-membered rings effect a greater electron density at the tin nucleus than do six-membered rings, and the limited data suggest that this is also true for $Sn\langle^{O}_{N}\rangle$ rings. Fortunately there are a number of potential complexes which will provide a further test of this conclusion, and some are under investigation by one of us (F.P.M.). More data are needed for complexes with β-diketones in which the two oxygen atoms are equivalent.

It is interesting that the six-membered $Sn\langle^{N}_{N}\rangle$ rings in dihalotin(IV) phthalocyanine (K) effect the same electron density at tin as do the six-membered $Sn\langle^{O}_{N}\rangle$ rings in $X_2Sn(sal_2phen)$ (I). It is also interesting that the 8-mercaptoquinoline complexes (L) have about the same isomer shifts as the four-membered ring complexes with 2-mercaptopyridine (M). The order of effectiveness of chelating ligands in promoting a large electron density at the tin nucleus appears to be



Complexes of Ph_2pyzO_2 are an exception to this order. $\left(\begin{smallmatrix}S^-\\S\end{smallmatrix}\right.$ ligands are expected to be most effective, but in the two sets of four-membered ring complexes reported to date the ligands are anisobidentate with one of the two Sn–S distances significantly larger than for a true covalent bond.

It is recognized that the nature of the donor atom, for example whether it is a C=O oxygen or N → O oxygen, should affect the electron release to tin. Mössbauer isomer shifts appear to be the most sensitive measurement for detecting differences in polarity of ligand–tin bonds in chelate rings.

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