spectrum had not changed from its original appearance.[2]

The thermodynamic instability and low barrier to dissociation have important influences on the chemistry of I. If the interaction of unreactive solvent molecules with I provides sufficient perturbation to bring about slow dissociation, then the action of a strongly coordinating base would probably achieve similar results in a shorter time. This result is in fact what is observed. The generally accepted order of Lewis base strengths toward Al is $N > O > P$. Trimethylamine reacts rapidly with I to either partly or completely degrade I into its molecular components. Dimethyl ether behaves similarly followed by further chemical reaction affording CH_4. The relative carbonium character of CH_3 associated with $O(CH_3)_2$ and $N(CH_3)_3$ is in the expected order with respect to the relative ionic character of $^{\delta-}O\text{-}C^{\delta+}$ *vs.* $^{\delta-}N\text{-}C^{\delta+}$, 22 and 12%, respectively, as calculated by the Pauling method.[19] Trimethylphosphine serves principally as a solvent for the solution decomposition of I, similar in behavior to benzene. A charge refinement of the crystallographic data indicates that the hydride of I has a large residual negative charge of -0.45 e and the methide has -0.39 e residual charge.[3] These values imply that these moieties would made I a very good reducing agent. If the fact that I is thermodynamically unstable is superimposed on these values, one would conclude that I should be one of the strongest reducing agents known owing to the additional release of free energy in forming the more stable dissociation products.

It is interesting to compare the relative stabilities of $[(CH_3)_2AlH]_3$, $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$, $Al_3(CH_3)_6[N(CH_3)_2]_2H$, and $[(CH_3)_2AlN(CH_3)_2]_2$ toward nucleophilic attack. Dimethylaminodimethylaluminum, $[(CH_3)_2AlN(CH_3)_2]_2$, is a four-membered ring containing two nitrogen bridges and is unreactive toward $N(CH_3)_3$. As a rationale for this behavior, it is noted that hydride bridges and alkyl or aryl bridges are inherently "electron deficient"; *i.e.*, a closed-shell electron configuration cannot be simultaneously accomplished for all atoms in the molecule. Amine bridges, on the other hand, do not suffer from electron deficiency because the nitrogen atom has a lone pair of electrons which it may use to form a dative bond to aluminum. The result of such a bond is polarization of the electron cloud about nitrogen, not deficiency. Thus, in the series at hand, reaction by nucleophilic attack on the ring produces fissure of the ring until a certain amount of deficiency is lost; *i.e.*, the framework of $[(CH_3)_2AlH]_3$ contains 6 electrons spread over 6 bonds (1.0 electron/bond), I contains 12 electrons in 8 bonds (1.5 e/bond), $Al_3(CH_3)_6[N(CH_3)_2]_2H$ is proposed to contain 10 electrons for 6 bonds (1.67 e/bond), and $[(CH_3)_2AlN(CH_3)_2]_2$ 8 electrons and 4 bonds (2.0 e/bond). It would be interesting to compare molecular orbital calculations for each of these heterocyclic rings with the observed order of stability.

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Far-Infrared and Tin-119m Mössbauer Study of Complexes of Phosphorus- and Arsenic-Containing Ligands with Tin(IV) Halides

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Twenty-five complexes of the type SnX_4B_2, where X = Cl, Br, or I, B = R_3PO (R = C_2H_5, C_4H_9, C_6H_5), $(C_6H_5)_3AsO$, $(CH_3)_2SO$, $(C_6H_5)_3As$, R_3P (R = C_4H_9, C_6H_5, C_8H_{17}), or $C_6H_5(CH_3)_2P$, and B_2 = *o*-$[(C_6H_5)_2P]C_6H_4$, *o*-$(CH_3)_2N(C_6H_4)P(C_6H_5)_2$, or $[o\text{-}(CH_3)_2N(C_6H_4)]_2P(C_6H_5)$, fifteen of them previously unreported, have been synthesized and studied by ^{119m}Sn Mössbauer and far-infrared techniques. Cis and trans isomers have been distinguished by the number of $\nu(Sn\text{-}X)$ and $\delta(Sn\text{-}X)$ bands they exhibit; those assigned trans on this basis are found to exhibit Mössbauer quadrupole splittings of *ca.* 1 mm/sec. The point-charge model predicts that the QS for cis isomers should be half that for the trans, and the QS for these isomers is barely resolvable as expected. In one case, $SnCl_4 \cdot 2P(C_6H_5)_3$, the infrared and Mössbauer evidence leads to opposite stereochemical assignments. In general, the oxygen donor ligands give cis complexes while all the fifth-group donor ligands but triphenylarsine give the trans isomers except when bidentate. These differences are rationalized on steric arguments.

The quadrupole splitting (QS) parameter in ^{119m}Sn Mössbauer spectroscopy has, with the application of the results of point-charge calculations,[2] proved useful in distinguishing cis and trans isomers in octahedral organotin complexes. The extension of the point-charge model to other geometries[3,4] is proving useful as well, but the further application of QS data to the elucidation of molecular symmetries is limited by the apparently large number of cases of asymmetric tin(IV) compounds for which the QS is small compared with the relatively

[1] To whom all inquiries should be addressed.

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TABLE I

PHYSICAL PROPERTIES AND ^{119m}Sn MÖSSBAUER DATA

Complex SnX_4B_2					Mössbauer parameters,[a] mm/sec				% Sn	
No.	X	B	Color	Mp, °C	IS[b]	QS[c]	Γ(1)[d]	Γ(2)[d]	Calcd	Found
I*	Cl	$(C_2H_5)_3PO$	White	98–102	0.21	...	1.19	...	25.3	24.9
II*	Br		White	167–170	0.79	...	1.24	...	18.4	18.0
III	Cl	$(C_6H_5)_3PO$	White	>300[e]	0.31[f]	...[g]	1.57[h]	...[i]		
IV	Br		White	163–165	0.66[j]	...[k]	1.55	...		
V[l]	Cl	$(C_6H_5)_3AsO$	White	300[m]	0.75[n]	...[o]	1.37[p]	...[q]		
VI*	Br		Orange	75–79	0.97	...	0.86	...		
VII	Cl	$(CH_3)_2SO$	White	~280 dec[r]	0.42[s]	...	1.51[t]	...		
VIII	Br		White	~210 dec[u]	0.67[v]	...	1.40	...		
IX	Cl	$(C_6H_5)_3As$	White	158–162[w]	0.90	...	1.09	...		
X	Br		Orange	103–104[x]	1.06	...	1.73	...		
XI*	Cl	DP[y]	White	240–245	1.05	...	1.16	...	16.8	16.2
XII*[z]	Br		Yellow	*Ca.* 250 dec	1.21	...	1.14	...		
XIII*	I		Dark maroon	*Ca.* 250 dec	1.18	...	1.44	...	11.0	10.5
XIV*[aa]	Cl	PN[bb]	White	195–197	0.78	...	1.04	...		
XV*	Br		Cream	*Ca.* 160 dec	1.12	...	1.20	...	16.0	15.7
XVI*	I		Brown	*Ca.* 100 dec	0.84	...	1.46	...	12.7	12.6
XVII*[cc]	Cl	PDN[dd]	White	198	0.85	...				
XVIII*[ee]	Br		Pale yellow	200 dec	0.95	...	1.53			
XIX*[ff]	Br	$(C_4H_9)_3PO$	Yellow	78–80	0.51	...	1.61		13.6	13.5
XX	Cl	$(C_4H_9)_3P$	White	127–129[gg]	0.85[hh]	1.17[ii]	1.28	1.06		
XXI	Cl	$(C_6H_5)_3P$	White	128–130[jj]	0.56[kk]	...	1.47	...		
XXII	Cl	$C_6H_5(CH_3)_2P$	White	195–200[ll]	0.91[mm]	1.18[nn]	1.24	1.12	22.1	21.6
XXIII*	Br		Cream	192–200 dec	1.13	1.13	1.41	1.07	16.6	16.0
XXIV*	Cl	$(C_8H_{17})_3P$	Colorless	Oil	0.72	1.08	0.94	1.17	11.8	11.2
XXV*[oo]	Br		Yellow	Oil	0.94	0.89			10.0	9.2
Complex $[SnX_4B]_2$										
XXVI	Cl	$(C_6H_5)_3P$	White	114–116[pp]	1.14		1.27			

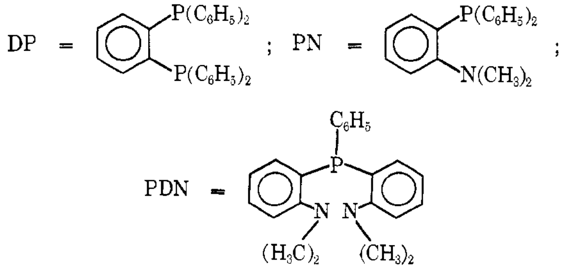
[a] Recorded at 77°K *vs.* a $Ba^{119m}SnO_3$ source (New England Nuclear Corp.). [b] ±0.06 mm/sec. [c] ±0.12 mm/sec. [d] Half-height width from best Lorenzian curve fit. [e] Reported as 323° in ref 32. [f] Reported as 0.27 in ref 32 and 0.35 in ref 19. [g] Reported as 0.51 in ref 32 and as 0.50 in ref 19. [h] Reported as 0.79 in ref 32. [i] Reported as 0.80 in ref 32. [j] Reported as 0.63 in ref 18. [k] Reported as 0.61 in ref 18. [l] *Anal.* Calcd: C, 39.93; H, 2.79. Found: C, 39.73; H, 3.40. [m] Reported as 148° in ref 3. [n] Reported as 0.437 in ref 32. [o] Reported as 0.70 in ref 32. [p] Reported as 0.80 in ref 32. [q] Reported as 0.72 in ref 32. [r] Reported as mp 284° in ref 32, as dec pt >270° in ref 14, as mp 287° in ref 13, and as dec pt 270–300° in ref 12. [s] Reported as 0.37 in ref 19, as 0.38 in ref 32, and as 0.44 in ref 32. [t] Reported as 1.11 in ref 32. [u] Reported as dec pt 198–204° in ref 13 and dec pt >215° in ref 14. [v] Reported as 0.66 in ref 19. [w] Reported as 160–162° in ref 12. [x] Reported as 104° in ref 12. [y] DP ≡ $[o\text{-}(C_6H_5)_2P]_2C_6H_4$. [z] *Anal.* Calcd: C, 40.1; H, 2.7. Found: C, 39.6; H, 2.8. [aa] *Anal.* Calcd: C, 42.5; H, 3.6. Found: C, 42.5; H, 3.6. [bb] PN ≡ $o\text{-}(CH_3)_2NC_6H_4P(C_6H_5)_2$. [cc] *Anal.* Calcd: C, 43.4; H, 4.1; N, 4.6. Found: C, 43.2; H, 4.0; N, 4.1. [dd] PDN = $[o\text{-}(CH_3)_2NC_6H_4]_2PC_6H_5$. [ee] *Anal.* Calcd: C, 33.6; H, 3.3; N, 3.6. Found: C, 33.2; H, 3.0; N, 3.1. [ff] *Anal.* Calcd: C, 32.95; H, 6.22. Found: C, 33.08; H, 6.43. [gg] Reported as 132–134° in ref 11 and 18. [hh] Reported as 0.87 in ref 19 and as 0.85 in ref 18. [ii] Reported as 1.0 in ref 19 and as 1.02 in ref 18. [jj] Reported as 132–134° in ref 12 and 18. [kk] Reported as 0.72 in ref 33 and as 0.75 in ref 18. [ll] Reported as 201–205° in ref 18. [mm] Reported as 0.85 in ref 18. [nn] Reported as 0.97 in ref 18. [oo] *Anal.* Calcd: C, 48.87; H, 8.71. Found: C, 48.60; H, 8.83. [pp] Reported as 115–116° in ref 11.

large natural line width of ^{119m}Sn.[5] Almost all early data were recorded using $^{119m}SnO_2$ sources which themselves give broad, unresolved-doublet spectra. Octahedral tin(IV) complexes of the type SnX_4B_2, where X = halogen and B is a ligand containing a fifth- or sixth-group atom bonded to tin, were found to give singlet resonances considered reasonably narrow for the SnO_2 source. With the introduction of $Ba^{119m}SnO_3$, whose γ-ray line width approaches the theoretical limit, it becomes possible to detect quadrupole splittings not before resolvable and to apply the principles governing the magnitude of the QS parameter to the solution of structural problems in tin(IV) tetrahalide complex chemistry.

We report in this paper a study of twenty-six such complexes with phosphorus- and arsenic-containing ligands, fifteen of them reported here for the first time. Results from far infrared spectroscopy are compared with those from the Mössbauer QS data.

Results

The complexes studied are listed in Table I with their physical properties, microanalytical data, and ^{119m}Sn Mössbauer parameters. The new compounds are starred. Infrared spectral assignments for the tin–oxygen and tin–halogen bands found between 600 and 33 cm^{-1} for the solid complexes mulled in Nujol and for complexes I and II in acetonitrile solution between 350 and 2000 cm^{-1} are listed in Table II.



Discussion

Infrared Spectra.—The vibrational modes expected for the cis and trans isomers of the O_h SnX_4B_2 structure from simple group theoretical considerations are listed in Table III with the infrared-active bands underlined. Thus the trans isomer (idealized point group symmetry D_{4h}) is expected to exhibit in the infrared region one ν(Sn–X), one ν(Sn–B), two δ(Sn–X), and one δ(Sn–B) modes, while for the cis isomer (idealized point group

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[5] J. J. Zuckerman, "Mössbauer Effect Methodology," Vol. III, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, p 15; *Advan. Organometal. Chem.*, **9**, 21 (1970).

TABLE II

FAR-INFRARED SPECTRAL ASSIGNMENTS[a]

Complex	ν(Sn–O)	ν(Sn–X)	δ(Sn–X)	Complex	ν(Sn–O)	ν(Sn–X)	δ(Sn–X)
I	429 sh	328 vs, br[b]	163 vs	XII		234 s	108 m
	419 m	310 sh, s	157 sh, s			220.5 vs	100 m
		291 s				208 sh	
		267.5 m		XIII		205 s	84 m
II	411 br	234 vs, br[c]	110 m, br			182.5 vs	78 sh, w
		204 s				167.5 sh, s	
III[d]	417 m, br	341 vs	179 s	XIV		325 vs	162 s
		324 vs	168 s			317 vs	149 m
		303 s				309 sh, s	
IV[d]	414.5 m	243 vs	113 m	XV		216 s	113 w
		222 vvs	102.5 m			203 m	
		205 vs	94 sh, vw	XVI		194 m, br	96 w
V	399	323.5 vs	182 m			139 s	
	393 m	315 vs	171.5 m	XVII[i]		324 vs, sh	166 s
		300 m	163.5 m			316 vs	160 s, sh
		285 s				302 vs	149 m
VI[e]	397 sh, m	229 sh, s	128 w	XVIII[i]		230 m	104 m
	386 m	220 vs	103 m			220 s, sh	
		196 s				211 vs	
VII[f]	482 vs	340 sh, vs	204 m			195 m, sh	
		320 vs	195 m	XIX	338 w, br	244 vs	108 m
		279 w	179 m			205 s	
		272 m	165 s			186 sh, m	
VIII[g]	472 s, br	236 s	157 w	XX[j]		312 m	172 s, sh
		226 s	139 w			292 s, sh	160 s
		204 sh	101 sh			284 s	
		183 m	107 m	XXI[k]		307 vs, sh	168 vs
IX[c,h]		334.5 vs	154 vs			301 vs	141 m
		317 sh	142.5 vs	XXII[l]		309 m	153.5 vs
		275 m	137 sh			283 vvs	134 s
X[f]		283 m	101 m	XXIII		193 vs, br	118 s
		257 vs		XXIV		312 w, sh	
		224.5 vs				293 vs	164.5 m
XI		323 vs	164 s	XXV		207.5 vs	122 w, sh
		311.5 vs	151 vs				113 m
		305 sh					

[a] 600–33 (±1) cm^{-1}. The band intensities are indicated as very strong (vs), strong (s), medium (m), weak (w), very weak (vw). A shoulder is indicated by (sh), and a broad peak as (br). These bands in the spectra of the complexes are not found in the spectra of the ligands they contain. [b] 329.5 (s), 320 (s), and 278 (m) in acetonitrile solution. [c] 236 (vs) and 205 (m) in acetonitrile solution. [d] The spectrum of triphenylphosphine oxide was assigned in ref 23. [e] Agrees with spectrum reported in ref 10 above 300 cm^{-1}. [f] Agrees with spectrum reported in ref 15. [g] Taken from ref 15. [h] The spectrum of triphenylarsine was assigned by K. M. Mackay, D. B. Sowerby, and W. C. Yong, *Spectrochim. Acta, Part A*, **24**, 611 (1968); J. H. S. Green, W. Kynaston, and G. A. Rodley, *ibid.*, **24**, 853 (1968); K. Shobatake, C. Postmus, J. R. Ferraro, and K. Nakamoto, *Appl. Spectrosc.*, **23**, 12 (1969). [i] The spectrum of PDN below 430 cm^{-1} is given by R. E. Christopher, I. R. Gordon, and L. M. Venanzi, *J. Chem. Soc. A*, 205 (1968). [j] Spectrum agrees with that reported in ref 18 between 400 and 200 cm^{-1}. [k] The spectrum of triphenylphosphine was assigned by J. Goubeau and G. Wenzel, *Z. Phys. Chem.* (*Frankfurt am Main*), **45**, 31 (1965); K. Shobatake, C. Postmus, J. R. Ferraro, and K. Nakamoto, *Appl. Spectrosc.*, **23**, 12 (1969); and ref 23. [l] Spectrum agrees with that reported in ref 18 between 400 and 200 cm^{-1}.

TABLE III

GROUP THEORETICAL PREDICTIONS FOR SnX_4B_2[a]

Geometry	Symmetry	ν(SnX)	ν(SnB)	Skeletal bending modes
Cis	C_{2v}	$\underline{2\ A_1} + \underline{B_1} + \underline{B_2}$	$\underline{A_1} + \underline{B_2}$	$\underline{3\ A_1} + 2\ A_2 + \underline{2\ B_1} + \underline{2\ B_2}$
Trans	D_{4h}	$A_{1g} + B_{1g} + \underline{E_u}$	$A_{1g} + \underline{A_{2u}}$	$B_{2g} + E_g + \underline{A_{2u}} + B_{2u} + \underline{2\ E_u}$

[a] The infrared-active species have been underlined.

symmetry C_{2v}) four ν(Sn–X), two ν(Sn–B), four δ(Sn–X), one δ(Sn–B), and two δ(X–Sn–B) modes are expected.[6] Accidental degeneracies are not precluded, nor is it certain that the symmetry-allowed bands will have appreciable intensities. Additional allowed bands will appear if restricted rotation of the ligands about the tin–ligand bonds lowers the symmetry, and additional splittings may occur because there is more than one molecule per unit cell or arise from other solid-state effects.

The infrared spectra of the complexes reported here contain two sets of bands which undergo marked change in frequency with change in halogen. Set 1: 330–280 (X = Cl) → 230–300 (X = Br) → 200–160 cm^{-1} (X = I). We assign these absorptions to ν(Sn–X).[7] Set 2: 180–150 (X = Cl) → 155–100 (X = Br) → ~80 cm^{-1} (X = I). We assign these absorptions to δ(Sn–X).

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(6) It is interesting to note that the descent of symmetry tables given by Cotton [F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963, p 285] is incorrect for the O_h to C_{2v} correlation as is the procedure suggested by other authors [see, *e.g.*, D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1967, p 353; E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 340] of descending in symmetry from O_h to C_{2v} by way of T_d which also gives incorrect results since the particular C_2 axis in cis-substituted octahedral geometries which is preserved between O_h and C_{2v} is not present in T_d. The correlations used here have been obtained by determining the symmetry elements of O_h which are preserved in C_{2v} and then determining the reduced form of an O_h representation in C_{2v} from the trace of the matrix for the O_h representation under the retained symmetry operations.

(7) R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, **7**, 1603 (1968), and references therein.

Complexes I–XIX show two to four bands in the infrared regions defined in set 1 for each halogen. The bands in the complexes do not appear in the free ligands nor in the complexes containing other halogens. The separation of these bands is *ca.* 40 cm^{-1}, but the half-height widths are *ca.* 15 cm^{-1}, and so the bands are not completely resolved. The bands in the ν(Sn–X) region of I and II were shown to persist in acetonitrile solution in which phase free rotation of the bulky triethylphosphine oxide ligands is assumed. Thus the observed splittings do not arise from solid-state effects. Compounds I–XIX also show two to three bands in the ranges listed in set 2. On the basis of these infrared data we assign cis stereochemistries to complexes I–XIX.

Only one infrared-active M–X stretch was observed in the related $UCl_4(R_3EO)_2$ complexes (R = C_2H_5, C_6H_5; E = P, As) which were assigned trans stereochemistries.[8] The observation of just one ν(M–X) suggests that our cis assignments for the corresponding tin complexes are correct and that the splittings seen in these latter cases do not arise from minor departures from D_{4h} symmetry nor from solid-state effects which would also be expected to appear in the uranium case.

The infrared assignments for the previously unreported complexes I and II are similar to those proposed for the analogous trimethylphosphine oxide complexes,[9] and our results for complexes III–VI[10] and IX and X[11] agree with previously published infrared studies also, although no stereochemical assignments were made on the basis of these data. Complexes VII[12,13] and VIII[13] have been studied in the far-infrared[14] region and cis stereochemistries have been assigned.[15]

Complexes XXI–XXV exhibit only a single strong band in the ranges in set 1. While other very weak bands also appear in these regions probably arising from solid-state effects or from weak ligand modes, these complexes also show the two bands expected in the ranges in set 2 for trans stereochemistry, and on the basis of these data we assign them as the trans isomers. The related trimethylphosphine complexes of the fourth-group tetrahalides have been assigned trans stereochemistries on the basis of vibrational studies,[16] and preliminary X-ray crystallographic data support this assignment for $SiCl_4 \cdot 2(CH_3)_3P$.[17] Complexes XXI and XXII have recently been assigned as trans from infrared and Raman data.[18]

Complex XX, $SnCl_4 \cdot 2P(C_4H_9)_3$, presents a special problem. Bands at 312 (m), 292 (s, sh), and 284 (s) cm^{-1} are seen in the region of set 1 for X = Cl. The 312-cm^{-1} band is also seen in complexes XXII and XXIV but is very much weaker; it persists in acetonitrile solution, but the 284-cm^{-1} band becomes broad (half-height width 32 cm^{-1}) and two bands may be concealed within the wide envelope. The structure of this complex from the infrared data is thus uncertain. The electric dipole moment in dioxane solution has been reported as 2.4 D,[19] where homologous tin(IV) tetrahalide complexes known to be cis have dipole moments nearer to 10 D.[19,20] The sample we studied is most likely a mixture of the cis isomer, which would be expected to show two or three strong bands in the tin–halogen stretching region, and the trans isomer, which should show only one. The absence of a P–O stretching band near 1100 cm^{-1} rules out the presence of significant quantities of $SnCl_4(Bu_3PO)_2$ and excludes an explanation of the far-infrared spectrum of XX in terms of partial complex oxidation. On the basis of the infrared band intensities and the reported dipole moment, it appears that the trans isomer predominates.

No absorptions other than those found in the free ligands and the halostannanes are observed in the infrared spectra of complexes IX–XXV which contain fifth-group donor atoms bonded to tin. The modes associated with the bonds made between phosphorus, arsenic, and (for complexes XIV–XVIII) nitrogen and tin are apparently too weak to be assigned with any certainty.

The oxy ligands, on the other hand, do give rise to additional bands which can be ascribed to tin–oxygen modes. The alkyl derivatives, for example, show two groups of new bands in addition to the halogen-sensitive absorptions, the first at 482–470 cm^{-1} for DMSO and at 430–410 cm^{-1} for Et_3PO. The second is very close to ν(Sn–Cl) and is only seen in the bromo complexes where it appears in the spectrum of II at 314 and 305 cm^{-1}.

In the aryl derivatives the assignments are complicated by the large number of absorptions arising from the phenyl moieties which can be treated with reference to the Whiffen modes t, u, v, w, x, and y[21] after Brown, *et al.*[22] Whiffen's w band in free triphenylphosphine oxide and triphenylarsine oxide at ~400 cm^{-1} [23] does not involve motion of the P–O or As–O moiety and hence should not be affected greatly by coordination. In the triphenylarsine oxide complexes V and VI, it is even weaker than in the ligand. In the analogous phosphine oxide complexes III and IV, the bands at 417 and 414 cm^{-1} are, therefore, new bands probably associated with tin–oxygen modes, like the new bands near 390 cm^{-1} in the arsine oxide complexes. Wilkins, *et al.*, have assigned as the ν(Sn–O) mode the bands at ~320 and 380 cm^{-1} in $SnX_4 \cdot 2[(C_6H_5)_3EO]$ for E = P and As, respectively, and for X = F, Cl, Br, and I and have drawn conclusions concerning the relative donor power of the two fifth-group oxides from these frequencies. They considered the band at 420 cm^{-1} in the phosphine oxide complexes to correspond to the 403-cm^{-1} phenyl band in the free ligand.[10] We suggest instead that in the highly coupled E–O–Sn system, ν(E–O) will tend

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[20] Dioxane can give a solvation polarization of quite large magnitude. Since the atom polarization was not allowed for and may be large for a complex with balanced dipoles, there is sufficient uncertainty about the significance of the reported moment to rule out discussion of the relative contributions to the observed 2.4-D moment from the cis and trans forms.

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to be raised[24] and ν(Sn–O) lowered by a similar amount and that these effects of coupled vibrations may nullify or even reverse changes expected on the basis of bond force constant or reduced mass. Thus we consider the comparisons of donor strengths based upon the assigned positons of ν(Sn–O) in the phosphorus and arsenic complexes to be unjustified. In a later paper Wilkins, *et al.*, assigned Sn–O stretching frequencies at 400–470 cm^{-1} in the complexes $SnX_4[(CH_3)_3PO]_2$.[9]

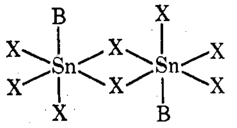
Rivest, *et al.*, assumed that triphenylphosphine and arsine complexes would take trans stereochemistries because of the bulky nature of these ligands. On this basis they assigned bands in the regions of our set 1 to tin–arsenic stretching modes.[11] Our set 2 bands were outside the region they studied. We consider it unlikely that the large-intensity bands observed can be associated with the very weak Sn–As modes.

Thus on the basis of our infrared data and supporting evidence we conclude that complexes I–XIX are cis and XXI–XXV are trans and that complex XX exists as an equilibrium mixture of the two isomers both in solution and in the solid state with the trans form predominating.

Mössbauer Data.—Our discussion of these SnX_4B_2 complexes is predicated on the assumption that the basic symmetries about tin are D_{4h} (trans octahedral) or C_{2v} (cis octahedral). No quadrupole splittings are observed for complexes containing potentially bidentate ligands (XI–XVII) or for complex XXVI where the simplest formula is SnX_4B. A monomeric structure can be ruled out for XXVI since this should give rise to large, resolvable QS.[3,4] Two other alternative structures for XXVI are

$[SnX_2\cdot 4B]^{2+}[SnX_6]^{2-}$

A



B

The complex $Cl_3SnOC_2H_5\cdot C_2H_5OH$ has been assigned the dimeric structure B on the basis of its vapor pressure[25] and dipole moment[26] in benzene, solid-state infrared spectrum,[25] and lack of resolvable QS.[27] Oxygen bridging in the solid state has been confirmed for the analogous methoxy–methanol compound[28] and the similar $[Cl_3SnO_2PCl_2\cdot OPCl_3]_2$ by X-ray crystallography.[29] Complex XXVI, which has been shown to be dimeric in concentrated solution in methylene dichloride by osmometry,[11] must have the chlorine-bridged structure B. The lack of resolvable QS for XXVI excludes five-coordination at tin and confirms a dimeric or oligomeric structure in the solid. The basic SnX_5B structure at each tin nucleus would on the basis of point-charge calculations[3,4] produce a QS equal to that given by a *cis*-SnX_4B_2 arrangement, which in our series of complexes is hardly resolvable.

We are unaware of tin complexes with structure A. Of the complexes like ours where X-ray crystallographic structural determinations have been carried out, *i.e.*, for $SnCl_4\cdot 2OSeCl_2$,[30] $SnCl_4\cdot 2OPCl_3$,[31] and $SnCl_4\cdot 2OS(CH_3)_2$,[32] it has been shown that the compounds are monomeric with pseudooctahedral structures about tin. Furthermore, several of our complexes have isomer shift and ν(Sn–Cl) values outside the range assignable to the $SnCl_6{}^{2-}$ unit.

It appears generally that the complexes assigned as trans on the basis of the infrared evidence exhibit a QS *ca.* 1 mm/sec in magnitude, while no resolvable QS is observed for those assigned as cis. Point-charge calculations suggest that the splitting in trans geometries should be twice that in the cis.[2–4] Splittings of 0.5 mm/sec would be at the limit of resolution, and the reporting of QS values for some of the complexes I–XIX would depend upon the assumptions employed in the computer decomposition of the somewhat broadened singlet resonances. For example, our curve-fitting program can be made to yield QS values of 0.45 and 0.60 mm/sec for the bidentate complexes XVII and XVIII, respectively, which are most likely cis. Curran, *et al.*,[19] likewise reported very small splittings for our complexes III and IV (0.50 and 0.61 mm/sec, respectively), using a narrow-line Pd–Sn γ-ray source, as did Sams, *et al.*, for complexes III and V (0.51 and 0.70 mm/sec, respectively), using a $BaSnO_3$ source,[33] presumably due mainly to different assumptions implicit in their curve-fitting programs for these somewhat broadened singlets. The resolvable QS for XX, on the other hand, was reported by Curran, *et al.*, as 1.0 mm/sec,[19] in good agreement with our value and that of Carty, *et al.*,[18] who reported 1.02 mm/sec against $BaSnO_3$. The dipole moments measured in dioxane by Curran, *et al.*,[19] are consistent with the cis assignments for III (9.5 D) and IV (10.1 D) and with a cis–trans equilibrium for XX (2.4 D) (*vide supra*). Complex XX was assigned as trans in ref 18 where dipole moment data were not considered after ascribing the extra infrared bands observed to solid-state distortions since their intensity is lower than that found in known cis complexes. For the same reason we assign an equilibrium with trans predominating. We reject the solid-state distortion argument since similar patterns are not observed for XXII or XXIV.

The isomer shift values for complexes III, IV, VII, VIII, and XX listed in Table I are in excellent agreement with the adjusted values, based on the SnO_2 *vs.* Pd–Sn conversion factor given by Curran, *et al.*,[19] for his data on these systems, as well as with the data of Sams, *et al.*,[33] for complexes III, V, and VII, with the data of Carty, *et al.*,[18] for XX–XXII using a $BaSnO_3$ source, and with the data of Vucelic[34] for VII and XXI using an SnO_2 source. As is generally observed, complexation drives tin IS values downward.[5] It is found here to be lower for the oxygen donors (I–VIII, XIX) than for the group V donors (IX–XVIII, XX–XXVI).

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No major differences between the cis and trans complexes are seen, but it may be noted that the IS values for the seven cis complexes of $SnCl_4$ and $SnBr_4$ with nitrogen and phosphorus donor atoms (XI, XII, XIV, XV, XVII, XVIII) lie, on the average, higher than those for the five trans cases (XXI–XXV). These differences are especially marked for the $SnCl_4$ complexes where direct comparisons are available, but it would be hazardous to use such small effects to diagnose geometry.

Conclusions

For complexes I–XX and XXII–XXV both far-infrared evidence and Mössbauer evidence suggest the same geometry. Dipole moment data[19] for III, IV, and XX are also consistent. The cis structure of $SnCl_4 \cdot 2DMSO$ (VII) is known from X-ray crystallography.[32] Thus, for this series at least, the infrared techniques clearly distinguish the geometry while Mössbauer quadrupole splittings are easily resolvable for the trans isomers but not for the cis.

In one case, $SnCl_4 \cdot 2P(C_6H_5)_3$ (XXI), conflicting geometries are assigned from the far-infrared and Mössbauer data. The infrared spectrum of XXI contains a band in the ν(Sn–Cl) region [301 (vs), 307 (vs, sh) cm^{-1}] with two bands in the δ(Sn–Cl) region [168 (vs), 141 (m) cm^{-1}]. Direct comparison is possible with the bidentate analog, complex XI, where three bands are seen in the ν(Sn–Cl) region [323 (vs), 311.5 (vs), and 305 (sh) cm^{-1}] and two in the δ(Sn–Cl) region [164 (s) and 151 (vs) cm^{-1}]. The infrared spectra of XXI and XI are sufficiently different to assign a trans geometry to the former, but the reasonably narrow singlet Mössbauer resonance observed[35] throws the infrared assignment into doubt. In an attempt to prepare the $SnBr_4$ analog of XXI, we observed oxidation of the ligand to form complex IV. The microanalytical and Mössbauer data for the material previously reported as $SnBr_4 \cdot 2P(C_6H_5)_3$[19] correspond more closely to IV. The complex $SnBr_4 \cdot 2P(C_4H_9)_3$ likewise undergoes air oxidation. The sample we prepared exhibited Mössbauer data characteristic of the expected trans complex [IS = 1.09, QS = 1.08 mm/sec], but the material rapidly converted to XIX on handling. The infrared spectrum of XXI is substantially different from that of III, thus ruling out oxidation of the ligand during examination of the complex.

Neglecting XXI which is uncertain, it appears that all the oxygen donor ligands give cis complexes while all the fifth-group donor ligands but triphenylarsine give trans complexes except when bidentate. Both steric and bonding considerations argue for this result.[36] The more pointed oxygen donor ligands can apparently occupy cis positions without giving rise to larger repulsions between X and the ligand than between X and X in the SnX_4B_2 octahedra. The phosphine ligands, on the other hand, are more sterically crowding since the donor atom in these cases itself holds the organic substituents, and these systems adopt trans configurations to minimize the X–ligand repulsions. The larger arsenic atom apparently allows its organic substituents to be sufficiently remote from the X atoms to favor the cis configuration again. It should be noted that, on the basis of these arguments since the chloro complex XX exists as an equilibrium mixture, the more crowded bromo complex should be predominantly trans as suggested by the Mössbauer QS evidence collected on a freshly prepared sample before oxidation to XIX took place. By the same token, if the smaller $C_6H_5(CH_3)_2P$ ligand gives rise to a trans complex, XXII, then the more sterically demanding triphenylphosphine ligand should produce a trans complex as well XXI as suggested by the infrared but not by the Mössbauer evidence. Recent reports suggest that the QS decreases as alkyl groups attached to coordinated phosphorus are replaced by aryl groups in isostructural complexes as in the series $(C_2H_5)_3P$ (0.95 mm/sec), $(C_2H_5)_2C_6H_5P$ (0.99 mm/sec), $C_2H_5(C_6H_5)_2P$ (0.46 mm/sec[18]), and $(C_6H_5)_3P$ (QS too small to resolve), and this may rationalize the differences between the infrared and the Mössbauer evidence in the case of XXI. For this compound the infrared evidence is particularly conclusive since direct comparison with the chelating *o*-$(C_6H_5)_2PC_6H_4P(C_6H_5)_2$ ligand in XI is possible.

Why is cis stereochemistry favored over trans and adopted where sterically allowed? Creation of the large electric dipole in the cis geometry requires energy, but the bonding of the trans form must involve predominantly the same orbital on the central atom, and it appears that this factor controls the stereochemistry of the complexes we have studied.

It is interesting, finally, to compare the analogous $UX_4 \cdot 2OPR_3$ complexes (X = Cl, Br; R = C_2H_5, C_6H_5) which are trans.[8] Both systems are labile, and hence kinetic factors are unlikely to produce the observed differences. Crystal packing should be the same for both series, and solubilities are similar. But hexacoordinated uranium(IV) should be larger than Sn(IV), and hence steric effects should be less severe, allowing the formation of the cis isomers in the uranium series. Clearly, the relative importance of the bonding considerations discussed above is reversed in this related series of complexes.

A paper by Cunningham, Frazer, and Donaldson[37] reporting vibrational and Mössbauer data for our complexes IX, X, XX, XXI, and XXVI appeared as this article was being submitted. The QS values are in excellent agreement, but the IS data differ outside experimental error for XXI, from our data and the data of ref 17, and for XXVI. These authors observed the ligand oxidation to give XIX and assigned a dimeric octahedral structure to XXVI in the solid state. They found only a single ν(Sn–X) band in each of the other complexes, however, and concluded that all are trans on this basis, ascribing the absence of a resolvable QS in IX, X, and XXI to the nonpolar group V–tin bonds in the phenyl-substituted derivatives.

Experimental Section

Mössbauer data were collected using our cam-drive, constant-acceleration spectrometer at 77°K *vs.* $Ba^{119m}SnO_3$ (New England Nuclear Corp.). Our curve-fitting procedure has been described previously.[38] Infrared data were recorded on a Beckman IR-11 spectrometer. Analysis for tin was accomplished by ashing and treatment of the residue with HF. A summary of the physical, Mössbauer, and microanalytical data is presented in Table I.

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[35] No QS was resolved when this complex was measured against an SnO_2 source as reported in ref 34.

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The complexes were prepared according to standard procedures. In general the ligand (0.002 mol for ligands except DP, PN, and PDN which were used in 0.001-mol quantities) was added dropwise in dry benzene or methylene chloride (*ca.* 10 ml) to a solution of the tin tetrahalide (0.001 mol) in the same solvent (*ca.* 10 ml). In most cases the complex separated immediately or soon after mixing. Complex I separated as an oil which crystallized slowly beneath petroleum ether (bp 40–60°). Complex X could not be prepared in methylene chloride since rapid exchange took place in this solvent to precipitate complex IX. Complexes XXIV and XXV are freely miscible in petroleum ether and could not be recrystallized. The DMSO complexes VII and VIII were prepared by the general method of Cotton, *et al.*[39]

The complexes are usually white powders or microcrystalline solids (from $SnCl_4$) or colored crystalline solids (from $SnBr_4$ and SnI_4) and were characterized by melting point and published infrared spectra if known. New compounds, which are starred in Table I, were characterized by melting point and infrared spectral comparisons with similar, published complexes. Microanalytical data for C, H, and Sn were recorded only for key examples of these parallel series and are listed in Table I.

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Eight-Coordination. I. Dodecahedral Vanadium(IV) Complexes with Sulfur-Chelating Ligands

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Dithiocarboxylates (L = C_6H_5–CSS^- = dtb^-, *p*-CH_3–C_6H_4–CSS^- = dtt^-, CH_3–CSS^- = dta^-, C_6H_5–CH_2–CSS^- = $dtpa^-$) react with both VO^{2+} ion and V(III) to give stable VL_4 complexes. Magnetic measurements, infrared spectra, and molecular weight measurements in solution are consistent with eight-coordinated V(IV). Epr and preliminary X-ray results demonstrate an approximate D_{2d} geometry for the VS_8 chromophores. Electronic spectra are discussed.

Introduction

Increasing interest is being shown in the chemistry of complexes involving second-row donor atoms, especially sulfur. A main stimulus is the rationalization of the increasing number of unusual steric and electronic properties of these complexes, on the basis of specific differences in polarizability, covalency, π-bonding ability, etc., between second- and first-row donor atoms.

Related to these studies are recent preparations and characterizations of some V(IV) complexes with sulfur-chelating ligands. Direct reaction of VO^{2+} ion with $R_2NCS_2^-$ in water gives "normal" $VO(R_2NCS_2)_2$ complexes[1,2] for which the usual C_{4v} symmetry has been suggested. Eight-coordinate $V(R_2NCS_2)_4$ complexes are obtained[3–6] from insertion reactions of CS_2 and $V(NR_2)_4$ in dry cyclohexane, under dry, oxygen-free conditions. Apart from some "noninnocent" 1,2-dithiolenes[7,8] and $S_2P(OEt)_2^-$ (which produces V(III)),[9] the behavior toward VO^{2+} of no other system of this type has been characterized, in contrast to the hundreds of VO^{2+} complexes with N, O, or Cl donor ligands which have been studied in detail.[10]

In this paper an extension of the coordination chemistry of dithiocarboxylates to V(IV) is described. The main result is the cleavage of the oxo–vanadium bond by R–CSS^- ions with the consequent formation of $V(R\text{–}CSS)_4$ species for which an eight-coordinate, dodecahedral structure is established. A preliminary interpretation of the electronic structure is also given.

Experimental Section

VCl_3, $VOSO_4 \cdot 2H_2O$, $VOCl_2 \cdot nH_2O$, VCl_4.—These compounds were obtained commercially and were used as received.

Ligands.—Acids and sodium salts were prepared following known procedures: C_6H_5–CSSH(dtbH),[11] *p*-CH_3–C_6H_4–CSSH (dttH),[12] CH_3–CSSH (dtaH),[13] C_6H_5–CH_2–CSSH (dtpaH).[14]

Complexes.—The vanadium(IV) complexes with the above dithiocarboxylates may be obtained very easily as impure products. Addition of an aqueous solution of vanadyl chloride or sulfate to aqueous solutions of the sodium salts of the ligands causes immediate precipitation of dark yellow, gummy masses. Little, if any, difference may be noted among the behavior of the different ligands. Powders were obtained, on washing and drying these products, which gave chemical analyses roughly in agreement with a stoichiometry $V(RCSS)_4$.

Powders with approximately the same elemental analyses and melting points can be obtained by adding the ligands, as free acids, dissolved in the minimum amount of ether, to an alcoholic solution of vanadyl sulfate or chloride.

Replacement of vanadyl salts by vanadium trichloride leads to similar products in both water and alcohol.

In spite of their simplicity, the two methods described are not suitable since attempts to purify the crude products by recrystallization from inert solvents, chromatography, etc., were unsuccessful. Decomposition occurred in all cases. To avoid this difficulty, a procedure had to be found which gave pure reaction products directly, for reliable and reproducible chemical and physical measurements. The following methods were the most successful.

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