diorganotin derivatives must correspond to linear or nearly linear C–Sn–C moieties in the solids.

The dimethyl- and diphenyltin(IV) derivatives exhibit Mössbauer spectra at ambient temperatures, the former yielding quite a strong spectrum. While there are several monomeric molecular solids of known structure for which spectra can be recorded at these temperatures,[19] we interpret this observation in the light of the physical properties of these compounds in terms of a lattice composed of intermolecularly associated units extending in at least one dimension.[15]

The trimethyl- and triphenyltin(IV) derivatives, on the other hand, fail to produce resolvable spectra even after long counting times at ambient temperatures. We interpret this negative evidence as ruling out an intermolecularly associated extended lattice, and this conclusion is corroborated by the reduced melting points (Table I) and enhanced solubilties of these species in comparison with those of their diorganotin analogues (vide supra).

Structural Conclusions

The vibrational spectra of the dimethyltin(IV) derivatives in the $\nu(SnC_2)$ region obey the selection rules for a linear C–Sn–C system. The magnitude of the Mössbauer QS and ρ values specify a higher than four-coordinated situation at the tin atom, and the very large QS values corroborate a *trans*-diorganotin(IV) geometry seen for the dimethyl derivative in the infrared and Raman spectra. Structure F is thus eliminated, and the question of chelation vs. bridging is answered with respect to the ambient-temperature Mössbauer resonances observed for the dimethyl and diphenyl derivatives, which rule out structure G. Use of –O–P–O– bridges to link *trans*-diorganotin(IV) units as depicted in structure H is seen in solid tris[dimethyltin(IV)] bis(orthophosphate) octahydrate in which octahedral, *trans*-dimethyltin(IV) units are linked by PO_4 tetrahedra.[20] Our conclusion is consistent with the infusible, insoluble and nonvolatile nature of these solids.

The vibrational spectra in the $\nu(SnC_3)$ region of the trimethyltin(IV) derivative obey the selection rules for a planar SnC_3 system. The magnitude of the Mössbauer QS and ρ values specify a higher than four-coordinated situation at the tin atom. Structures A and B are thus eliminated because the former contains four-coordinated tin and the latter would not accommodate a planar R_3Sn unit. Thus the bridged form C would seem to be favored, but the trimethyl- and triphenyltin(IV) derivatives fail to show a Mössbauer spectrum at ambient temperatures. Considering the strong spectra developed by the diorganotin(IV) analogues, this negative evidence suggests that *n* in structure C is finite. A related compound, $(C_6H_5)_3SnO_2P(OC_6H_5)_2$, forms a cyclic hexamer in the solid,[1] rather than the helical polymer formed by $(CH_3)_3SnO_2P(C_6H_5)OH$.[10] The pentamer is the smallest structure capable of accommodating planar triorganotin(IV) units axially bridged by –O–P–O– linkages. The value of *n* in structure C must, therefore, be at least 5.

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Registry No. $(CH_3)_3SnOP(O)(C_6H_5)OC_6H_5$, 80243-52-3; $(n\text{-}C_4H_9)_3SnOP(O)(C_6H_5)OC_6H_5$, 80243-54-5; $(C_6H_5)_3SnOP(O)(C_6H_5)OC_6H_5$, 80243-56-7; $(CH_3)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-58-9; $(n\text{-}C_4H_9)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-60-3; $(n\text{-}C_8H_{17})_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-62-5; $(C_6H_5)_2Sn[OP(O)(C_6H_5)OC_6H_5]_2$, 80243-64-7; $C_6H_5P(O)(OC_6H_5)OH$, 2310-87-4; $(CH_3)_3SnCl$, 1066-45-1; $(n\text{-}C_4H_9)_3SnCl$, 1461-22-9; $(C_6H_5)_3SnCl$, 639-58-7; $(CH_3)_2SnCl_2$, 753-73-1; $(C_6H_5)_2SnCl_2$, 1135-99-5; $(n\text{-}C_4H_9)_2SnCl_2$, 683-18-1; $(n\text{-}C_8H_{17})_2SnCl_2$, 3542-36-7.

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(19) Bancroft, G. M.; Butler, K. D.; Sham, T. K. *J. Chem. Soc., Dalton Trans.* **1975**, 1483.

(20) Ashmore, J. P.; Chivers, T.; Kerr, K. A.; van Roode, J. H. G. *Inorg. Chem.* **1977**, *16*, 191.

Contribution from the Departments of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003,
and University of Oklahoma, Norman, Oklahoma 73019

Synthesis and Characterization of Novel Penta- and Hexacoordinated Sulfur-Containing Spirocyclic Tin(IV) Complexes

ARJUN C. SAU, ROBERT R. HOLMES,* KIERAN C. MOLLOY, and J. J. ZUCKERMAN

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Reactions of bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$ (**2**), with the bases dimethyl sulfoxide (Me_2SO), hexamethylphosphoramide (HMPA), and triphenylphosphine oxide (Ph_3PO) yield hexacoordinated spirocyclic neutral adducts. Hydroxide ion with **2** gives a hexacoordinated dianionic product. Various reactions of **2** with a variety of halide salts yield new spirocyclic pentacoordinated monoanionic compounds, $[XSn(TDT)_2]^-[R_4M]^+$ (M = N, P, As). Large cations tend to stabilize the complexes. Reversible color changes take place on heating the pentacoordinated derivatives. The substances are characterized by ^1H NMR and tin-119m Mössbauer spectroscopy. The isomer shift of the monohalo anions shows a decrease with halogen electronegativity consistent with electron withdrawal at the tin center. The quadrupole splitting (QS) values are in the range 1.06–1.44 mm s^{-1} for the pentacoordinated monoanions investigated. These low values, lower than many QS values for tetracoordinate tin(IV) compounds, are associated with rectangular-pyramidal geometries around tin, as found by X-ray diffraction studies on representative members.

Introduction

Comprehensive information is now available concerning the synthesis and stereochemical nonrigidity of pentacoordinated phosphorus compounds.[1-3] We have recently turned our attention to group 4A elements[4-10] to ascertain the extent to which structural principles for the pentacoordinated state are transferable from phosphorus chemistry. As with some five-

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* To whom correspondence should be addressed at the University of Massachusetts.

(1) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

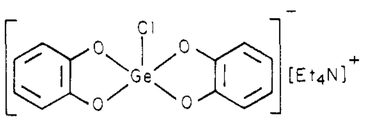
(2) Holmes, R. R. "Pentacoordinated Phosphorus—Structure and Spectroscopy"; American Chemical Society: Washington, D.C., 1980; ACS Monogr. Ser. No. 175.

(3) Holmes, R. R. "Pentacoordinated Phosphorus—Reaction Mechanism"; American Chemical Society: Washington, D.C., 1980; ACS Monogr. Ser. No. 176.

coordinated spirocyclic phosphorus compounds,[1,2] we have already learned that related compounds of silicon(IV),[11] germanium(IV),[5] and tin(IV)[6,9] exist as square pyramids.

The knowledge of the factors influencing the geometry of the pentacoordinated state[1,2] has an important bearing on the role of five-coordinated transition states postulated in applicable reaction mechanisms. For example, formation of pentacoordinated intermediates are postulated in the nucleophilic substitution reaction of tetracoordinated organotin compounds,[12-14] but sufficient information is not available concerning the stability and preferred geometry of the transition state.[15] Such knowledge would prove useful in understanding the mode of action of many organotin compounds used in industry and agriculture.[16,17]

Recently, we discovered that discrete pentacoordinated anionic complexes of germanium(IV) can be formed by the reactions of the spirocyclic derivatives bis(*o*-phenylenedioxy)germanium(IV) dihydrate, $Ge(C_6H_4O_2)_2{\cdot}2H_2O$, and bis(toluene-3,4-dithiolato)germanium(IV), $Ge(C_7H_6S_2)_2$, with halide ions.[5-7] The X-ray crystal structural analysis of **1**[5] and some closely related derivatives of germanium[18] shows the existence of a square-pyramidal geometry around germanium.

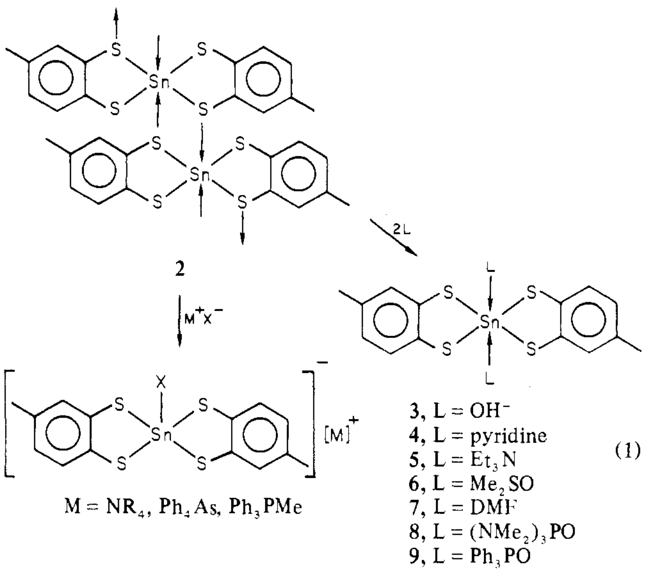


1

These findings for the germanium(IV) system prompted us to carry out a similar study for tin(IV) based on the spirocyclic tin compound bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$ (**2**). The reaction of **2** with various Lewis bases and the characterization of the products (by ^1H NMR and tin-119m Mössbauer spectroscopy) are reported here.

Results and Discussion

Reaction of $Sn(TDT)_2$ (2) with Donor Ligands and Formation of Hexacoordinated Tin(IV) Complexes. Bis(toluene-3,4-dithiolato)tin(IV), $Sn(TDT)_2$ (**2**), can be prepared easily by the reaction of $SnCl_4{\cdot}5H_2O$ with toluene-3,4-dithiol in water.[9] Previous workers carried out the preparation of **2** in a basic medium.[19,20] Compound **2** is an insoluble bright red amorphous solid having a high melting point. The solid state structure of **2**, albeit unknown with certainty, has been inferred by Mössbauer[19,21] and infrared[20,22] spectroscopic data to be polymeric via intermolecular sulfur-tin bridging. The data are consistent with the presence of hexacoordinated tin (eq 1).



2

M = NR_4, Ph_4As, Ph_3PMe

3, L = OH^-
4, L = pyridine
5, L = Et_3N (1)
6, L = Me_2SO
7, L = DMF
8, L = $(NMe_2)_3PO$
9, L = Ph_3PO

We found that addition of $Et_4N^+Br^-$ to an alkaline solution of $Sn(TDT)_2$ (**2**) results in the precipitation of a yellow crystalline solid which is characterized as the bis(tetraethylammonium) salt of the dianion (**3**) having the composition $[(OH)_2Sn(TDT)_2][Et_4N]_2$ (**10**) (Table I). The complex **10** can also be prepared by a direct reaction of **2** with tetraethylammonium hydroxide in water/acetone. Attempts to prepare the monohydroxy derivative $[(OH)Sn(TDT)_2][Et_4N]$ by varying the molar ratio of **2** and $Et_4N^+OH^-$ were not successful.

The intensity ratio of the various proton signals in the ^1H NMR spectrum (Table II) clearly confirms that **10** contains two $[Et_4N]^+$ cations. The observation of a broad band centered at 3400 cm^{-1} in the infrared spectrum of **10** supports the presence of O-H units in **10**.

The tin-119 Mössbauer isomer shift (IS) value of 1.05 mm s^{-1} (Table III) is consistent with a hexacoordinated tin(IV) atom surrounded by electronegative ligands.[23] Fitting the singlet spectrum as a doublet gave an unacceptably low value for the QS (0.48 mm s^{-1}). Only by study of a homologous series of cis- and trans-octahedral SnS_4O_2 dianions can the systematics of the QS variation with isomeric form be worked out, but the necessary data are not yet available[24] on this class of compounds (see the section on tin-119m Mössbauer data). The isolation of **10** in the solid state supports the earlier suggestion[20,25] of the formation of the dianion, $[(OH)_2Sn(TDT)_2]^{2-}$, when $Sn(TDT)_2$ (**2**) dissolves in alkali. In the absence of an X-ray study of **10**, the suggested structure is regarded as speculative.

Dissolution of **2** in pyridine, triethylamine, dimethylformamide, and dimethyl sulfoxide to form 1:2 hexacoordinated tin(IV) complexes (**4**–**6**) has been noted by earlier workers.[19,22] The dimethyl sulfoxide complex (**6**) of **2** was suggested to contain two molecules of dimethyl sulfoxide, but no analytical data were cited.[14] We can now confirm this composition from the analytical (Table I) and ^1H NMR data of **6** (Table II).

The reaction of **2** with 2 equiv of hexamethylphosphoramide (HMPA) affords the yellow crystalline solid adduct $[(HMPA)_2\,Sn(TDT)_2]$ (**8**), whose ^1H NMR spectrum in CH_2Cl_2 shows a doublet at δ 2.55 (Table II) due to the N-Me

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(4) Sau, A. C.; Carpino, L. A.; Holmes, R. R. *J. Organomet. Chem.* **1980**, *197*, 181.
(5) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7972.
(6) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1264.
(7) Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 4129.
(8) Sau, A. C.; Holmes, R. R. *J. Organomet. Chem.* **1981**, *217*, 157.
(9) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.
(10) Sullivan, S. A.; DePuy, C. H.; Damarauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.
(11) Harland, J. J.; Vollano, J. F.; Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5269.
(12) Britton, D.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2971.
(13) Gielen, M.; Sprecher, N. *Organomet. Chem. Rev.* **1966**, *1*, 455.
(14) Chan, S. C.; Wong, F. T. *Z. Anorg. Allg. Chem.* **1971**, *384*, 89.
(15) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251.
(16) Davies, A. G.; Smith, P. J. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 1.
(17) Zuckerman, J. J., Ed. "Organotin Compounds: New Chemistry and Applications"; American Chemical Society: Washington, D.C., 1976; Adv. Chem. Ser. 157, pp 134, 167, 177.
(18) Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 281.
(19) Epstein, L. M.; Straub, D. K. *Inorg. Chem.* **1965**, *4*, 1551.
(20) Poller, R. C. *Proc. Chem. Soc., London* **1963**, 312.
(21) Stöckler, H. A.; Sano, H.; Herber, R. H. *J. Chem. Phys.* **1967**, *47*, 1567.
(22) Poller, R. C.; Spillman, J. A. *J. Chem. Soc.* **1966**, 958.
(23) Zuckerman, J. J. *Adv. Organomet. Chem.* **1970**, *9*, 21.
(24) Herber, R. H.; Stöckler, H. A.; Reichle, W. T. *J. Chem. Phys.* **1965**, *42*, 2447.
(25) Abel, E. W.; Armitage, D. A. *Adv. Organomet. Chem.* **1967**, *5*, 37.

Table I. Syntheses and Analytical Data of Spirocyclic Penta- and Hexacoordinated Sn(IV) Complexes Derived from $Sn(TDT)_2$ (2)[a]

				anal. found (calcd)			
no.	compd (mp, °C)	prep	recrystn solvent	% C	% H	% N	% halogen
6	$[(Me_2SO)_2Sn(TDT)_2]$ (185-215 dec)	2 + Me_2SO	Me_2SO	37.24 (36.98)	4.25 (4.13)		
8	$[(HMPA)_2Sn(TDT)_2]$ (183-184)	2 + 2HMPA	C_6H_6/hexane (1:1)	39.94 (39.74)	6.38 (6.16)	10.5 (10.7)	
9	$[(Ph_3PO)_2Sn(TDT)_2]$ (194-196)	2 + $4Ph_3P{=}O$	C_6H_6/hexane (2:1)	61.06 (61.04)	4.35 (4.30)		
10	$[(OH)_2Sn(TDT)_2][Et_4N]_2$ (221-222 dec)	2 + $2Et_4N^+OH^-$[c]	CH_3CN/C_6H_6 (1:1)	51.8 (49.92)	7.35 (7.54)	3.35 (3.88)	
11	$[FSn(TDT)_2][Me_4N]$[d] (222-223 dec)	2 + $Me_4N^+F^-\cdot 3H_2O$	CH_3CN[b]				
12	$[FSn(TDT)_2][Et_4N]$ (186-188)	2 + $Et_4N^+F^-\cdot 2H_2O$	CH_3CN/Et_2O[b] (1:3)	45.92 (45.83)	5.71 (5.56)	2.31 (2.43)	3.1 (3.3)
13	$[FSn(TDT)_2][Ph_4As]$ (244-245)	17 + $Et_4N^+F^-\cdot 2H_2O$ or $K^+F^-\cdot 2H_2O$	CH_3CN[b]	56.2 (55.0)	4.3 (3.89)		
14	$[ClSn(TDT)_2][Me_4N]$ (206-210)	2 + $Me_4N^+Cl^-$	CH_3CN	40.46 (40.27)	4.61 (4.47)	2.74 (2.61)	
15	$[ClSn(TDT)_2][Et_4N]$ (165-166)	2, 8, or 9 + $Et_4N^+Cl^-$	CH_3CN	44.47 (44.56)	5.42 (5.41)	2.05 (2.36)	
16	$[ClSn(TDT)_2][n\text{-}Bu_4N]$ (134-135)	2 + $n\text{-}Bu_4N^+Cl^-$	CH_3CN/C_6H_6[b] (1:4)	51.0 (51.1)	7.10 (6.86)	2.01 (1.99)	
17	$[ClSn(TDT)_2][Ph_4As]$ (185-186)	2 + $Ph_4AsCl\cdot xH_2O$	CH_3CN/C_6H_6 (1:3)	53.63 (53.9)	3.83 (3.81)		
18	$[BrSn(TDT)_2][Me_4N]$ (186-187)	2 + $Me_4N^+Br^-$	CH_3CN/C_6H_6 (10:1)	37.27 (37.2)	4.29 (4.16)	2.49 (2.41)	
19	$[BrSn(TDT)_2][Et_4N]$ (141-142)	2 + $Et_4N^+Br^-$	CH_3CN[b]	41.55 (41.45)	5.24 (5.06)	2.08 (2.19)	
20	$[BrSn(TDT)_2][Ph_3PMe]$ (153-154)	2 + $\{Ph_3P^+Me]Br^-$	CH_3CN[b]	50.62 (50.52)	4.02 (3.86)		
21	$[ISn(TDT)_2][Et_4N]$ (145-146)	2 + $Et_4N^+I^-$	CH_3COCH_3/hexane (5:1)	39.2 (38.6)	(5.1) (4.72)	2.1 (2.04)	

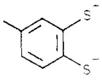
[a] TDT =  , HMPA = $(Me_2N)_3PO$, $Me_2SO = (CH_3)_2SO$. [b] Recrystallized at 0 °C. [c] An aqueous solution (10% w/v) of $Et_4N^+OH^-$ was used. [d] A good analysis was not obtained, hence this is a suggested formulation.

Table II. ^1H NMR Spectroscopic Data of the Spirocyclic Penta- and Hexacoordinated Complexes of Tin(IV)

		chem shifts (±0.05 ppm)				
		aromatic protons of TDT				
compd	solvent	group A[a]	group B[b]	Me group of TDT	$N\text{-}CH_2$ or $N\text{-}CH_3$	$N\text{-}C\text{-}CH_3$ or $N\text{-}C(CH_2)_2CH_3$
$[(Me_2SO)_2Sn(TDT)_2]$[c] (6)	$Me_2SO\text{-}d_6$	7.35 (m, 2 H)	6.75 (m, 1 H)	2.15 (s, 3 H)		
$[(HMPA)_2Sn(TDT)_2]$ (8)	CH_2Cl_2	7.42 (m, 2 H)	6.75 (m, 1 H)	2.21 (s, 3 H)	2.55 (d, 18 H), $^3J(P\text{-}H) = 10$ Hz	
$[(Ph_3PO)_2Sn(TDT)_2]$[d] (9)	CH_2Cl_2	7.3 (m, 2 H)	6.65 (m, 1 H)	2.20 (s, 3 H)		
$[(OH)_2Sn(TDT)_2][Et_4N]_2$[e] (10)	CD_3CN	7.15 (m, 2 H)	6.45 (m, 1 H)	2.15 (s, 3 H)	3.12 (q, 16 H)	1.13 (m, 24 H)
$[FSn(TDT)_2][Et_4N]$[f] (12)	CD_3CN	7.35 (m, 2 H)	6.7 (m, 1 H)	2.20 (s, 3 H)	3.05 (q, 8 H)	1.12 (m, 12 H)
$[FSn(TDT)_2][Ph_4As]$[g] (13)	CH_2Cl_2	7.35 (m, 2 H)	6.7 (m, 1 H)	2.20 (s, 3 H)		
$[ClSn(TDT)_2][Me_4N]$ (14)	CD_3CN	7.35 (m, 2 H)	6.75 (m, 1 H)	2.20 (s, 3 H)	3.00 (s, 12 H)	
$[ClSn(TDT)_2][Et_4N]$ (15)	CD_3CN	7.35 (m, 2 H)	6.75 (m, 1 H)	2.20 (s, 3 H)	3.10 (s, 8 H)	1.15 (m, 12 H)
$[ClSn(TDT)_2][n\text{-}Bu_4N]$ (16)	$CDCl_3$	7.35 (m, 2 H)	6.65 (m, 1 H)	2.15 (s, 3 H)	2.9 (q, 8 H)	0.6-1.65 (m, 28 H)
$[ClSn(TDT)_2][Ph_4As]$[g] (17)	CH_2Cl_2	7.35 (m, 2 H)	6.65 (m, 1 H)	2.15 (s, 3 H)		
$[BrSn(TDT)_2][Me_4N]$ (18)	CD_3CN	7.4 (m, 2 H)	6.8 (m, 1 H)	2.22 (s, 3 H)	3.05 (s, 12 H)	
$[BrSn(TDT)_2][Et_4N]$ (19)	CH_2Cl_2	7.35 (m, 2 H)	6.7 (m, 1 H)	2.20 (s, 3 H)	3.00 (q, 8 H)	1.10 (m, 12 H)
$[BrSn(TDT)_2][Ph_3PMe]$[h] (20)	CH_2Cl_2	7.4 (m, 2 H)	6.65 (m, 1 H)	2.18 (s, 3 H)		
$[ISn(TDT)_2][Et_4N]$ (21)	CH_2Cl_2	7.40 (m, 2 H)	6.75 (m, 1 H)	2.22 (s, 3 H)	3.00 (q, 8 H)	1.12 (m, 12 H)

[a] Protons adjacent to the sulfur atoms of the TDT ligand. [b] The unique aromatic proton of the TDT ligand. [c] The methyl protons of Me_2SO at δ 2.6. [d] The aromatic proton signals of $Ph_3P{=}O$ appear as a complex multiplet at δ 7.3-7.8. [e] The OH proton signals could not be located between δ 0 and 10. [f] The ^{19}F NMR data: singlet at −117.4 ppm. [g] The aromatic protons of Ph_4As^+ constitute a complex multiplet at δ 7.3-8.1. [h] The phenyl proton resonances of Ph_3P^+Me appear as a complex multiplet at δ 7.4-8.1. The PMe proton signal appears as a doublet at δ 2.62 ($^2J(P\text{-}CH_3) = 13$ Hz.

protons of the HMPA groups. This observation suggests that the HMPA ligands in **8** are present in an identical chemical environment in solution. Further support for this assignment comes from the appearance of a singlet at δ +25.3 in the ^{31}P NMR spectrum of **8**. The ^{31}P chemical shifts in the pentacoordinate tin(IV) complexes $R_3SnCl\cdot HMPA$ are found to be δ +25.6 (R = Ph) and 24.5 (R = Me) in $CDCl_3$.[4] These data indicate that there is a slight upfield shift (~1 ppm) of the ^{31}P signal on complexation of the HMPA ligand to tin (the ^{31}P chemical shift of HMPA in $CDCl_3$[26] = δ +26.5). The protons of the HMPA ligand are also found to be more shielded in $Ph_3SnCl\cdot HMPA$ than in the free ligand.

The X-ray crystal structural analysis of the complexes $R_3SnCl\cdot HMPA$ (R = Me[27] and Ph[28]) and $Me_nSnX_{4-n}\cdot$

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(26) Dennis, L. W., personal communication.

(27) Aslanov, L. A.; Attiya, V. M.; Ionov, V. M.; Permin, A. B.; Petrosyn, V. S. *J. Struct. Chem.* (*Engl. Transl.*) **1977**, *18*, 884.

Table III. Tin-119m Mössbauer Data on Penta- and Hexacoordinated Sn(IV) Complexes at 77 K

compd	IS[a]	QS[b]
[(HMPA)$_2$Sn(TDT)$_2$] (**8**)	0.91	2.00
[(Ph$_3$PO)$_2$Sn(TDT)$_2$] (**9**)	1.00	2.27
[FSn(TDT)$_2$][Et$_4$N] (**12**)	0.99	1.06
[ClSn(TDT)$_2$][Me$_4$N] (**14**)	1.14	1.44
[ClSn(TDT)$_2$][Et$_4$N] (**15**)	1.13	1.35
[ClSn(TDT)$_2$][Ph$_4$As] (**17**)	1.11	1.09
[BrSn(TDT)$_2$][Et$_4$N] (**19**)	1.17	1.08
[ISn(TDT)$_2$][Et$_4$N] (**21**)	1.19	1.11
[(OH)$_2$Sn(TDT)$_2$][Et$_4$N]$_2$ (**10**)	1.05	
Sn(TDT)$_2$	1.21[c,d]	1.52
	1.26[c,e]	1.37

[a] Isomer shift, ±0.03 mm s^{-1}. [b] Quadrupole splitting, ±0.06 mm s^{-1}. [c] Reference 19. [d] Reference 38. [e] Ambient temperature.

2HMPA[29] (n = 1, 2; X = Cl, Br) shows the coordination of the HMPA ligand to the tin through oxygen. For the latter class, the structures are found to be octahedral with a trans disposition of the HMPA ligands.[29] This same type of structure with a trans disposition of the HMPA ligands might prevail for **8**.

A 1:2 stoichiometric reaction of **2** and triphenylphosphine oxide, Ph$_3$P=O, in acetonitrile dissolves only half of the added **2**; complete dissolution of Sn(TDT)$_2$ occurs when 4 equiv of Ph$_3$P=O are added. The yellow crystalline product isolated from both the 1:2 and 1:4 stoichiometric reactions is found to be the bis adduct [(Ph$_3$PO)$_2$Sn(TDT)$_2$] (**9**) (Table I). Attempts to redissolve a sample of **9** in organic solvents (CH$_3$CN, C$_6$H$_6$, and CH$_2$Cl$_2$) by heating under reflux or stirring at room temperature result in the precipitation of **2**, indicating partial dissociation of **9**. The weight of the precipitate of **2** suggests decomposition of only half of the added **9**. The other half remains in solution along with 2 equiv of liberated Ph$_3$P=O. Precipitated **2** can be redissolved by the addition of 4 equiv of triphenylphosphine oxide. The lower stability of the triphenylphosphine oxide complex (**9**) compared to that of the HMPA complex (**8**) is consistent with the lower Lewis basicity of Ph$_3$P=O.

No reaction takes place between triphenylphosphine sulfide or triphenyl phosphate and **2** even when the reactants are heated under reflux in acetonitrile for several hours. The inability of Ph$_3$P=S and (PhO)$_3$P=O to form stable complexes with **2** again can be attributed to lowered basicity compared to that of HMPA.[30]

The Mössbauer QS values for both these complexes **8** and **9** (Table III) demand a trans ligand geometry at tin. Comparisons may be drawn with the variously substituted phosphine oxide complexes of the tin(IV) halides where *trans*-SnX$_4$B$_2$ geometry gives rise to QS values of ca. 1 mm s^{-1} and half that (barely resolvable) for cis.[23,31,32] Authenticated examples of *cis*-SnS$_4$O$_2$ geometries are, unfortunately, lacking.[12]

Reactions of Sn(TDT)$_2$ (2) with Halide Ions and Formation of Spirocyclic Pentacoordinated Tin(IV) Complexes. Reaction of **2** with the appropriate quaternary ammonium, phosphonium, or arsonium halide in a dipolar aprotic solvent gave 1:1 anionic complexes, [X-Sn(TDT)$_2$]$^-$[M]$^+$ (**11**–**21**, eq 1). Preparation of the fluoro complex **13** is achieved by the halogen-exchange reaction of **17** with Et$_4$NF·2H$_2$O (at room temperature) or KF·2H$_2$O (at 80 °C for 2 h) in acetonitrile (eq 2).

$$\underset{\mathbf{17}}{[\mathrm{ClSn(TDT)_2}][\mathrm{Ph_4As}]} \xrightarrow[\mathrm{KF\cdot 2H_2O}]{\mathrm{Et_4NF\cdot 2H_2O}} \underset{\mathbf{13}}{[\mathrm{FSn(TDT)_2}][\mathrm{Ph_4As}]} \quad (2)$$

These complexes (**11**–**21**, Table I) show a deepening of the color with decreasing electronegativity of the halide ion. Thus, in the series [XSn(TDT)$_2$]$^-$[Et$_4$N]$^+$ (X = F, Cl, Br, and I), the colors of the complexes **12**, **15**, **19**, and **21** are pale yellow, yellow, orange, and deep-orange respectively. Reversible deepening of color from yellow or orange to red was also noted on heating the complexes to higher temperature. They all melt with the formation of red liquid.

It was found that the use of larger cations tended to stabilize the anionic complexes. For instance, the complexes [ClSn(TDT)$_2$]$^-$[NH$_4$]$^+$ and [ISn(TDT)$_2$]$^-$[NMe$_4$]$^+$ are formed by the reaction of **2** with H$_4$NCl and Me$_4$NI, respectively, in acetonitrile at 80 °C, but on cooling the reaction mixture to room temperature, partial redeposition of the starting materials was noted and the complexes could not be isolated in the solid state. Table I shows that the anionic chloro complex is formed in the solid state with Me$_4$N$^+$ ion and other larger cations (**14**–**17**) while the formation of the related solid iodo complex requires the Et$_4$N$^+$ cation (**21**). Related to the latter solid-state stabilization is the hydrolytic stability of the anionic complexes (**11**–**21**). We find that complexes containing the bulkier cations are more resistant to hydrolysis in the solid state and in acetone solution. Also, in the series [XSn(TDT)$_2$]$^-$[Et$_4$N]$^+$ (X = F, Cl, Br, and I), the fluoro derivative **12** is most resistant to hydrolysis in acetone solution.

^{1}H NMR Data. A notable feature in the ^{1}H NMR spectra of the complexes **12**, **14**–**16**, **18**, **19**, and **21** (Table II) is the observation of an upward shift of the ^{1}H signals associated with the tetralkylammonium cation compared to those found in the free tetraalkylammonium halides.[4] We noticed similar shielding of the tetraethylammonium protons in the spirocyclic pentacoordinate germanium(IV) complexes [XGe(catecholate)$_2$]$^-$[Et$_4$N]$^+$ [7] and attributed this to a possible ion-pair equilibrium allowing the tetraalkylammonium cation to experience partial shielding by the ring-current effect of the aromatic moiety of the toluene-3,4-dithiolato group.

Although the ^{1}H NMR data (Table II) are quite helpful in establishing the 1:1 stoichiometry of the anion–cation complexes, determination of the coordination number at tin must be supplemented by other data, particularly in view of the possibility of intermolecular tin–halogen and/or tin–sulfur bonding leading to the association of the anion. Several organotin halides are known to have associated structures arising from tin–halogen bonding.[17] Confirmation of the presence of a discrete pentacoordinated tin(IV) anion was obtained by a single-crystal X-ray analysis of both the chloro complex **14**[6,9] and the bromo complex **20**.[33] These results provide the first examples of a discrete square-pyramidal geometry for a tin compound. Earlier, K$_2$SnO$_3$ was found to contain square-pyramidal tin in an extended chain arrangement.[34] A partial X-ray analysis of **12**[35] suggests pentacoordinated tin here as well. On the basis of these results, the structure of the iodo

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(28) Gawienowski, J.; Day, R. O.; Sau, A. C.; Holmes, R. R., unpublished results.

(29) Aslanov, L. A.; Ionov, V. M.; Attiya, V. M.; Permin, A. B.; Petrosyn, V. S. *J. Organomet. Chem.* **1978**, *144*, 39.

(30) Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper & Row: New York, 1978.

(31) Ruddick, J. N. R. *Rev. Silicon, Germanium, Tin, Lead, Compd.* **1976**, *2*, 115.

(32) Harrison, P. G.; Lane, B. C.; Zuckerman, J. J. *Inorg. Chem.* **1972**, *11*, 1537.

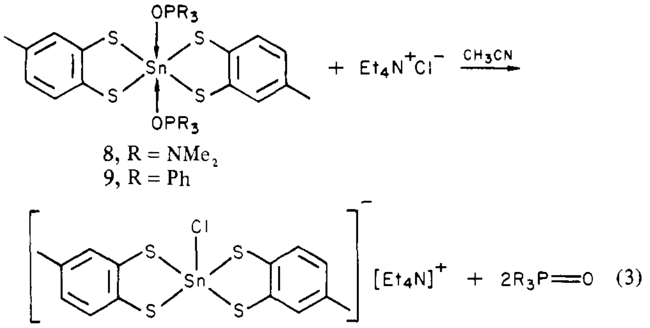
(33) Day, R. O.; Holmes, R. R., unpublished work.

(34) Gatehouse, B. M.; Lloyd, D. J. *J. Solid State Chem.* **1970**, *2*, 410.

(35) Day, R. O.; Holmes, R. R., unpublished work. Because of disorder, a complete X-ray analysis was not pursued.

complex **21** most likely contains pentacoordinated tin.

Formation of 15 from 8 or 9. The pentacoordinated chloro complex $[ClSn(TDT)_2]^-[Et_4N]^+$ (**15**) can also be prepared by the reaction of the hexacoordinated tin compounds **8** or **9** with 1 equiv of Et_4NCl in acetonitrile (eq 3). Formation of similar spirocyclic pentacoordinated germanium complexes by the reaction of the hexacoordinated germanium complex $[(HMPA)_2Ge(C_6H_4O_2)_2]$ with chloride and fluoride ions has been reported.[7] This reaction reflects the comparable stabilization effects of the spirocyclic penta- and hexacoordinate compounds of Sn(IV) and Ge(IV).



8, R = NMe₂
9, R = Ph

As shown in the present work, bis(toluene-3,4-dithiolato)tin(IV) (**2**) reacts with a wide variety of Lewis bases to form penta- or hexacoordinated complexes. In contrast, the corresponding germanium compound, $Ge(TDT)_2$, is unreactive toward any oxygen- or nitrogen-donor ligands, and among the halide ions only fluoride forms stable complexes, $[FGe(TDT)_2][M']$ (M' = Et_4N and Ph_3PMe).[7] This implies a lower Lewis acidity for $Ge(TDT)_2$ compared to that of $Sn(TDT)_2$ (**2**), which would be expected on the basis of the higher electronegativity of germanium.[36] The decomposition of the germanium complexes $[XGe(C_6H_4O_2)_2]^-[Et_4N]^+$(X = F, Cl, and Br) into their original components[7] and the stability of the tin complexes $[XSn(TDT)_2]^-[Et_4N]^+$ (X = F, Cl, Br, and I) in water under similar conditions are consistent with the greater sensitivity of the germanium–halogen bond toward water.

It is worth mentioning that hexacoordinated complexes are formed exclusively when $Sn(TDT)_2$ or $Ge(C_6H_4O_2)_2\cdot 2H_2O$[7] react with oxygen-donor ligands, whereas pentacoordinated species are formed under the influence of a halide ion. The selective stabilization of the pentacoordinated state by halide ions is not clearly understood, but formation of a dianion is apparently less favorable.

Tin-119m Mössbauer Data. The IS and QS data gathered in Table III fall into three groups; for the bis complexes of **2** with the phosphine oxide donors Ph_3PO and $(Me_2N)_3PO$, i.e., $Sn(TDT)_2B_2$, the monohalo anions $[Sn(TDT)_2X]^-[R_4E]^+$, and the dihydroxide dianion $[Sn(TDT)_2(OH)_2]^{2-}[Et_4N]^+_2$ (**10**). The IS values for all three groups lie in the same range, 0.99–1.19 mm s^{-1}, consistent wih a +4 oxidation state for tin. These values are somewhat lower than those recorded for the parent $Sn(TDT)_2$ (**2**), IS = 1.26 mm s^{-1},[21] although this material also contains higher than four coordinated tin (see eq 1). That the IS values are driven to lower velocities speaks to the greater donor power of the halide and oxygen ligands over the sulfur atoms which are also coordinated to the TDT moiety, ultimately engaging in a trifurcated interaction to produce a $CSSn_2$ center in the solid (**2**).

The QS data of the bis(phosphine oxide) complexes, **8** and **9**, discussed above, can be easily interpreted in terms of a hexacoordinated octahedral geometry at tin which must be the trans isomer to generate the large (2.00–2.27 mm s^{-1}) QS values recorded. Point-charge calculations predict that the cis isomers should exhibit QS values half the trans,[23] and complexes of **2** with the bidentate ligands bipyridyl and *o*-phenanthroline give QS values of 0.92 and 1.26 mm s^{-1}, respectively.[19] Literature data[37,38] for the adducts of $(SCH_2CH_2S)_2Sn$, $[SCH_2CH(CH_3)S]_2Sn$, and $(SCH_2CH_2CH_2S)_2Sn$ with tertiary amines R_2SO, R_3NO, and bidentate ligands establish that QS values in the range 0.81–1.26 mm s^{-1} correspond to the cis isomers and those, in the range 1.62–1.95 mm s^{-1} to the trans. The QS values for **8** and **9** are thus the largest yet recorded for these systems and must, therefore, either correspond to the trans-O_h, D_{4h} isomers or to the less likely possibility of another geometry capable of producing such a large electric field gradient.

The lack of resolvable QS for the dihydroxide tin dianion (**10**) can be interpreted either in terms of a cis-O_h, D_{4h} geometry at tin (which we consider unlikely for this small ligand) or in terms of a geometry which is different from O_h but does not produce a large electric field gradient at the tin center (which seems equally unlikely) or by assuming that the systematics which govern the magnitudes of the QS values in these $[SnS_4O_2]^{2-}$ systems are different from those controlling the data for the neutral complexes. We prefer to await the development of a sufficient base of QS data upon which to decide the geometry of **10**.

The third category of QS values belongs to the monohalo anions, and here the IS values exhibit a monoatomic change, decreasing from the iodide (1.19), bromide (1.17), chloride (1.11–1.14, depending on the gegenion) to the fluoride (0.99 mm s^{-1}), in accord with the simplest notion of electron withdrawal from the tin atom. The QS data lie in the range 1.06–1.44 mm s^{-1}. Previously, values of the QS parameter for pentacoordinated tin compounds[23,39] fell in the range of about 3–4 mm s^{-1} and were associated with derivatives having a trigonal-bipyramidal geometry. The X-ray structures of **14**[6,9] and an analogue of **19**, i.e., $[BrSn(TDT)_2][Ph_3PMe]$ (**20**),[33] show rectangular-pyramidal geometries and are the first examples of this geometrical form for tin in a discrete complex. The respective QS values for **14** and **19** are 1.44 and 1.08 mm s^{-1}. Considering the range of QS values for the other monohalo anionic pentacoordinated species in Table III (1.06–1.44 mm s^{-1}), it is reasonable to associate rectangular-pyramidal geometries for these members. The much lower QS values for the rectangular pyramid compared to those for the trigonal bipyramid may serve as a useful diagnostic aid in assigning pentacoordinated geometries to tin(IV) anionic species. However, an explanation of these low QS values for pentacoordinated tin, lower than many QS values for tetracoordinate tin(IV) compounds,[39] must await further studies.

Experimental Section

^1H NMR spectra were recorded on a Varian Model A-60 NMR spectrometer at 60 MHz on 10% (w/v) solutions of the samples in appropriate solvents using tetramethylsilane as internal standard. ^{31}P NMR spectra were recorded on an NT-150 FT spectrometer (external standard, 85% H_3PO_4). ^{19}F NMR spectra were recorded on a Varian Model HR-300 spectrometer operated in CW mode at room temperature on samples in acetonitrile solution. C_6F_6 was used as the internal standard, and the observed ^{19}F chemical shifts were converted to the values relative to $CFCl_3$ as the reference. All of the NMR chemical shifts were expressed in parts per million and negative values are assigned to the shifts upfield from their reference. Infrared spectra were recorded as KBr pellets on a Beckman IR-12 spectrophotometer.

Tin-119m Mössbauer spectra were recorded at 77 K on a Ranger Engineering constant-acceleration spectrometer with $Ca^{119m}SnO_3$ as

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(36) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980.

(37) Poller, R. C.; Ruddick, J. N. R.; Spillman, J. A. *J. Chem. Soc. D* **1970**, 680.

(38) Poller, R. C.; Ruddick, J. N. R. *J. Chem. Soc., Dalton Trans.* **1972**, 555.

(39) Bancroft, G. M. "Mössbauer Spectroscopy"; Halsted Press, Wiley: New York, 1973.

both source and zero isomer shift reference standard. Velocity calibration was based upon β-tin and natural iron foils.

Syntheses. Bis(toluene-3,4-dithiolato)tin(IV) (**2**) was prepared by the reaction of $SnCl_4\cdot 5H_2O$ with toluene-3,4-dithiol in water.[9] The halogeno complexes **11–21** were prepared by the reaction of $Sn(TDT)_2$ (**2**) with the appropriate source of the halide ions. The details are given in Table I. The yields of the isolated products were 90–95%. Some typical procedures are described in detail.

Preparation of $[(Me_2SO)_2Sn(TDT)_2]$ (7). A suspension of bis(toluene-3,4-dithiolato)tin(IV) (**2**) (0.423 g, 1 mmol) in dimethyl sulfoxide (5 mL) was heated under reflux with vigorous stirring for 15 min. The yellow solution which resulted was filtered hot. On cooling the filtrate to room temperature, light yellow crystals of **7** deposited. When complex **7** was heated above 185 °C, loss of coordinated dimethyl sulfoxide molecules occurred to give $Sn(TDT)_2$ (**2**).

Preparation of $[(HMPA)_2Sn(TDT)_2]$ (8). Bis(toluene-3,4-dithiolato)tin(IV) (**2**) (0.853 g, 2 mmol) was added to a solution of hexamethylphosphoramide (0.717 g, 4 mmol) in acetonitrile (50 mL). The resulting heterogeneous reaction mixture was heated under reflux for $^1/_2$ h to obtain a light yellow solution. Filtration of the reaction mixture (to remove traces of suspended materials) followed by evaporation of solvent from the filtrate afforded a yellow crystalline residue which was dissolved in minimum volume of boiling acetonitrile. On cooling the solution to room temperature, pale yellow crystals of **8** deposited (yield 1.45 g, 92.3%).

Preparation of $[(Ph_3PO)_2Sn(TDT)_2]$ (9). Bis(toluene-3,4-dithiolato)tin(IV) (**2**) (0.423 g, 1 mmol) was added to a solution of triphenylphosphine oxide (1.12 g, 4 mmol) in benzene (100 mL). The resulting heterogeneous reaction mixture was heated under reflux with vigorous stirring for 1 h to obtain a clear yellow solution. Evaporation of solvent from the reaction mixture gave a yellow residue which was dissolved in a minimum volume of boiling acetonitrile, and the solution was filtered hot. On cooling the filtrate to room temperature, yellow crystals of **9** deposited. Several crops of crystals of **9** were isolated by further concentration of the mother liquor. The total yield of the isolated product (**9**) was 0.71 g (72.5%).

Preparation of Bis(tetraethylammonium) Bis(toluene-3,4-dithiolato)dihydroxostannate(IV), $[(OH)_2Sn(TDT)_2][Et_4N]_2$ (10). Bis(toluene-3,4-dithiolato)tin(IV) (**2**) (0.853 g, 2 mmol) was dissolved in an aqueous solution of potassium hydroxide (0.45 g dissolved in 50 mL water). A yellow solution containing traces of suspended material resulted. The solution was filtered, and to the filtrate was added tetraethylammonium bromide (0.84 g, 4 mmol). When the reaction mixture was stirred, a yellow crystalline precipitate formed. The precipitate was filtered under suction and air-dried. Recrystallization of the crude product from acetonitrile gave a pure sample of **2** in quantitative yield.

Complex **10** can also be prepared by adding 2 equiv of tetraethylammonium hydroxide (10% solution in water) to a suspension of $Sn(TDT)_2$ (**2**) in acetone. Stirring the reaction mixture for $^1/_2$ h, followed by dilution with water, gave the yellow crystalline precipitate (**10**) in quantitative yield.

Preparation of Tetraethylammonium Bis(toluene-3,4-dithiolato)fluorostannate(IV) (12). $Sn(TDT)_2$ (**2**) (0.423 g, 1 mmol) was added to a solution of tetraethylammonium fluoride dihydrate (0.185 g, 1 mmol) in acetonitrile (10 mL). The resulting heterogeneous mixture was stirred magnetically at room temperature for $^1/_2$ h. A yellow solution resulted containing traces of amorphous materials which were removed by filtration. Evaporation of the solvent from the filtrate afforded a yellow crystalline residue which was dissolved in a mixture of acetonitrile and diethyl ether (1:3). The solution was cooled at 0 °C for 2 days. Yellow crystals deposited. The crude crop of crystals was dissolved in a minimum volume of acetonitrile, and the solution was cooled at 0 °C for several days to obtain a pure sample of **12** (yield 0.45 g, 78.5%).

Preparation of Tetraphenylarsonium Bis(toluene-3,4-dithiolato)fluorostannate(IV) (13). Tetraethylammonium fluoride dihydrate (0.185 g, 1 mmol) was added to a solution of the chloro derivative **17** (0.841 g, 1 mmol) in acetonitrile (15 mL). The resulting mixture was stirred for 10 min to obtain a clear yellow solution. Evaporation of the solvent from the reaction mixture gave a yellow crystalline solid which was washed three times with water (10 mL) to remove the tetraethylammonium chloride byproduct. The water-insoluble, pale yellow solid was filtered under suction and air-dried. A pure sample of **13** was obtained by dissolving the crude product in a minimum volume of acetonitrile and cooling the solution to 0 °C for several days.

Preparation of Tetraphenylarsonium Bis(toluene-3,4-dithiolato)chlorostannate(IV) (17). $Sn(TDT)_2$ (**2**) (0.423 g, 1 mmol) was added to a solution of tetraphenylarsonium chloride (0.44 g, 1 mmol) in acetonitrile (25 mL). When the reaction mixture was stirred vigorously for 1 h at room temperature, a yellow solution was obtained. Filtration of the reaction mixture followed by evaporation of the solvent from the filtrate gave a yellow crystalline residue which was washed with water to remove traces of excess tetraphenylarsonium chloride. The water-insoluble yellow crystalline solid was air-dried and purified by recrystallization from a mixture of acetonitrile and benzene (1:3) at room temperature.

The details of the preparation of tetraethylammonium bis(toluene-3,4-dithiolato)chlorostannate(IV), $[ClSn(TDT)_2][Me_4N]$ (**14**) have been described earlier.[6,9] Other related chloro complexes (**15** and **16**) were prepared in an analogous manner.

Reaction of $[(HMPA)_2Sn(TDT)_2]$ (8) with Et_4NCl in Acetonitrile. Tetraethylammonium chloride (0.166 g, 1 mmol) was added to a solution of **8** (0.785 g, 1 mmol) in acetonitrile (40 mL) at room temperature. When the reaction mixture was stirred, the original pale yellow solution of **8** deepened to yellow. Stirring was continued for $^1/_2$ h. Evaporation of the solvent from the reaction mixture gave a yellow solid which was washed twice with hexane (5 mL). The hexane extracts were combined, and solvent was evaporated to obtain a viscous liquid which was identified by ^1H NMR spectroscopy to be hexamethylphosphoramide (0.35 g). The yellow residue was dissolved in a minimum volume of boiling acetonitrile. On cooling the solution to room temperature, yellow crystals (mp 185–186 °C) (0.56 g) of **18** deposited. The ^1H NMR spectrum of this compound was identical with that of an authenticated sample of **18**.

A similar reaction of $[(Ph_3PO)_2Sn(TDT)_2]$ (**9**) with 1 equiv of tetraethylammonium chloride in acetone at room temperature gave the chloro complex **15** and triphenylphosphine oxide. No reaction took place between $[(HMPA)_2Sn(TDT)_2]$ (**9**) and Et_4NBr in acetonitrile at room temperature.

Reaction of $[(HMPA)_2Sn(TDT)_2]$ (8) with 1 Equiv of $Et_4NF\cdot 2H_2O$ in Acetonitrile. Tetraethylammonium fluoride dihydrate (0.19 g, 1 mmol) was added to a solution of $[(HMPA)_2Sn(TDT)_2]$ (**8**) (0.785 g, 1 mmol) in acetonitrile (30 mL) at room temperature. When the reaction mixture was stirred, a color change (from pale yellow to green to yellow) of the solution was noticed and a yellow amorphous material (ca. 50 mg) precipitated. The formation of this material probably arises from a partial degradation of $Sn(TDT)_2$ (**2**) by fluoride ions. Filtration of the reaction mixture followed by evaporation of solvent from the filtrate gave a yellow solid which was washed twice with hexane (5 mL) to remove the liberated hexamethylphosphoramide (0.35 g). The yellow solid was recrystallized from acetonitrile at 0 °C to obtain the fluoro derivative $[FSn(TDT)_2][Et_4N]$ (**12**) (0.50 g).

Preparation of Tetramethylammonium Bis(toluene-3,4-dithiolato)bromostannate (IVe) (18). A suspension of $Sn(TDT)_2$ (**2**) (0.423 g, 1 mmol) and tetramethylammonium bromide (0.154 g, 1 mmol) in acetonitrile (20 mL) was stirred magnetically at room temperature for 1 h. A yellow solution was obtained. The solution was filtered to remove traces of suspended materials, and the filtrate was evaporated to dryness. The yellow residue was dissolved in minimum volume of acetonitrile, and then benzene was added dropwise to the solution until a turbidity appeared. On cooling the solution to room temperature, yellow crystals of **18** deposited.

The other bromo complexes, **19** and **20**, were prepared in a similar manner by the reaction of $Sn(TDT)_2$ (**2**) with Et_4NBr and $[Ph_3P^+Me]Br^-$, respectively.

Preparation of Tetraethylammonium Bis(toluene-3,4-dithiolato)iodostannate(IV). Tetraethylammonium iodide (0.514 g, 2 mmol) was added to a suspension of $Sn(TDT)_2$ (**2**) (0.846 g, 2 mmol) in acetone (50 mL) and the resulting mixture stirred for 1 h. A yellow solution was obtained containing some suspended material which was removed by filtration. Evaporation of the solvent from the filtrate gave an orange crystalline residue which was dissolved in a minimum volume of boiling acetone. To the clear solution in acetone was added dropwise hexane until a turbidity appeared. On cooling the solution to room temperature, orange crystals of **21** deposited.

Attempted Preparation of Tetramethylammonium Bis(toluene-3,4-dithiolato)iodostannate(IV). A mixture of $Sn(TDT)_2$ (**2**) (0.423 g, 1 mmol) and tetramethylammonium iodide (0.201 g, 1 mmol) in acetonitrile (30 mL) was heated under reflux until a clear yellow solution formed. On cooling the reaction mixture to room temperature, partial redeposition of **2** and Me_4NI occurred, indicating the instability of $[ISn(TDT)_2][Me_4N]$ in the solid state.

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Registry No. **2**, 13241-47-9; **6**, 80657-94-9; **8**, 80631-25-0; **9**, 80631-22-7; **10**, 80631-24-9; **11**, 80631-21-6; **12**, 76566-55-7; **13**, 80631-20-5; **14**, 76566-57-9; **15**, 80631-19-2; **16**, 80631-18-1; **17**, 80641-90-3; **18**, 80641-89-0; **19**, 76581-59-4; **20**, 80658-37-3; **21**, 76581-57-2.

Contribution from the Laboratoire de Chimie de l'Ecole Normale Supérieure, associé au CNRS, 75231 Paris Cédex 05, France,
Laboratoire de Spectrochimie des éléments de Transition, ERA No. 672, Université de Paris-Sud, 91405 Orsay, France,
and Laboratoire d'Electrochimie Organique et Analytique, Département de Recherches Fondamentales,
Centre d'Etudes Nucléaires de Grenoble, 85X, 38041 Grenoble Cédex, France

An Intermediate-Spin Iron(III) Porphyrin Complex with a Vinylidene Group Inserted into an Fe–N Bond: Paramagnetic Susceptibility, EPR, and Mössbauer Properties

DANIEL MANSUY,* IRÈNE MORGENSTERN-BADARAU, MARC LANGE, and PIERRE GANS

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The $Fe(TPP)[C{=}C(p\text{-}ClC_6H_4)_2](Cl)$ complex **2a** exhibits a magnetic moment of 3.9 μ_B which is constant between 300 and 40 K. The EPR spectrum of a solid sample at 4 K displays a typical rhombic pattern with g values of 4.64, 3.55, and 2.01. Mössbauer studies reveal an isomeric shift ($\simeq$0.3 mm/s) typical of an iron(III) complex and a large quadrupole splitting (2.88 mm/s) which is not temperature dependent between 300 and 1.6 K. The visible and EPR spectra and magnetic moment of complex **2a** either in the solid state or in solution are very similar. This complex thus appears as the first example of a Fe(III) porphyrin in a pure intermediate spin state in both conditions. The peculiar coordination state of its iron atom, caused by the insertion of the vinylidene group into a Fe–N(pyrrolic) bond, which yields a highly distorted geometry, should be at the origin of its very stable intermediate spin state in solution and in the solid state.

Introduction

A one-electron oxidation of iron porphyrin–vinylidene carbene complexes, $Fe^{II}(porphyrin)(C{=}CAr_2)$,[1] by $CuCl_2$ leads to very stable compounds of general formula $Fe(porphyrin)(C{=}CAr_2)(Cl)$.[2] These complexes exhibit electronic spectra[2] very similar to those of compounds I of catalase or horseradish peroxidase (HRP), which are formed by reaction of these hemoproteins in their native ferric state with two-electron oxidants such as H_2O_2 or alkyl hydroperoxides.[3]

Very recently, an X-ray structure analysis[4] of one of these complexes, $Fe(TTP)[C{=}C(p\text{-}ClC_6H_4)_2](Cl)$[5] (**2b**) has been made; it shows that the vinylidene group is actually inserted between the iron and one nitrogen atom of a pyrrole ring. This complex involves an unusual, highly distorted five-coordinate geometry, with an iron(III) ion only bound to three pyrrolic nitrogens, to a vinylic carbon, and a chlorine atom in trans position[4] (Figure 1).

Its peculiar electronic spectrum with a broad and weak Soret peak and a single band around 670 nm in the visible region is unexpected for an iron(III) porphyrin and is presumably due to the important distortion of the porphyrin ring. Because of the similarity of this spectrum with that of catalase compound I (CAT I), an analogous structure with an oxygen atom inserted into a Fe–N bond has been proposed for CAT I.[4]

So far, only very few data are available concerning the electronic structure and the spin state of the iron in complexes **2**. They include the magnetic moment of complex **2a** in C_6H_6 at room temperature, determined by the Evans method, and the EPR g values of complex **2a** in toluene at 77 K.[2] From these preliminary results, it was not possible to establish the actual spin state of the iron of complexes **2** in solution. Moreover, no data were available concerning the spin state of complexes **2** in the solid state. This paper describes a detailed study of the EPR spectra of complex **2a**, either in solution or in the solid state at 300 and 4 K, and of the Mössbauer spectra and magnetic moment of complex **2a** in the solid state between 300 and 4 K. The data from these studies establish a "pure" intermediate $S = {}^3/_2$ spin state for complex **2a** in the solid state and are in favor of the same spin state for complex **2a** in solution.

Experimental Section

Synthesis of Complexes 2. A 1.1-equiv sample of $CuCl_2$ in 10 mL of dry CH_3CN is added progressively to a solution of complex **1**[1] (100 mg) in CH_2Cl_2 (200 mL) (0.11 equiv/30 min). After the last addition, the solution is stirred for 1 h and then washed with water. The organic layer is dried over $MgSO_4$ and filtered and its volume reduced to about 10 mL. Upon column chromatography on silica gel, unreacted complex **1** is first eluted with C_6H_6 and complex **2** with acetone/C_6H_6 30/70. Complex **2** is then dissolved in the minimum amount of hot acetone, and an equivalent volume of pentane is added. Black shiny crystals of complex **2** (40% yield) are obtained from this solution kept several days at −20 °C.

Elemental analyses were obtained after powdering and lyophilization of the samples. Anal. Calcd for $C_{58}H_{36}N_4FeCl_3$ (**2a**): C, 73.22; H, 3.78; N, 5.89; Cl, 11.20. Found: C, 73.10; H, 3.96; N, 5.83; Cl, 12.00. λ (ϵ) in C_6H_6: 424 (54) and 669 (7.8 n^{-1} cm^{-1}) nm. Calcd for

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* To whom correspondence should be addressed at the Laboratoire de Chimie de l'Ecole Normale Supérieure.

(1) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3214.

(2) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6437.

(3) (a) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187. (b) Yonetani, T. *Adv. Enzymol.* **1970**, *33*, 309. Yamasaki, I. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 33.

(4) (a) Chevrier, B.; Weiss, R.; Lange, M.; Mansuy, D.; Chottard, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2899. (b) During the submission of this paper a ^1H NMR study of complex **2a**, concluding to the same bridged structure, has appeared: Latos-Grazynski, L.; Cheng, Ru-Jen; La Mar, G. N.; Balch, A. L. *Ibid.* **1981**, *103*, 4270. The authors also mention preliminary data on an independent X-ray structure determination of complex **2b**.

(5) Abbreviations: TPP and TTP are respectively the dianions of *meso*-tetraphenylporphyrin and *meso*-tetra-*p*-tolylporphyrin.