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Mössbauer and Infrared Spectra of Some Tin(II) Complexes

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Received October 25, 1968

Infrared and Mössbauer spectra have been obtained for eighteen complexes of divalent tin. Absorptions attributed to NH_2 stretching and deformation vibration in metal complexes indicate that the order of nitrogen-to-metal dative bond strengths is $N \rightarrow Cd > > N \rightarrow Sn^{II} > N \rightarrow Pb^{II}$. Carboxylate frequency shifts indicate that the OCO-Sn bond has a greater covalent character than the $OCO\text{-}Cu^{II}$ bonda. The large positive isomer shifts for stannous chloride and stannous bromide decrease on complex formation with organic ligands, the decreases being greater for the chloride, and the isomer shifts become smaller with increasing coordination number of tin. All complexes of tin(II) investigated show quadrupole splittings, the largest being observed for $Sn(oxine)_2$.

Introduction

Relatively few studies have been reported on properties of complexes of divalent tin; Sn^{II} is conspicuously absent from comparative studies of coordination compounds of divalent metals. X-ray diffraction measurements by Rundle and Olson[3] have shown threefold coordination for Sn^{II} with valence angles of about 90° in $SnCl_2$. SnS, orthorhombic SnSe, $SnCl_2 \cdot 2H_2O$ and $SnSO_4$. Stannous oxide has the PbO structure,[4] in which each tin atom is at the apex of a square pyramid with four oxygen atoms at the base.

Mössbauer spectra have been reported for a number of inorganic tin(II) compounds, particularly by Boyle, *et. al.*[5] and by Cordey-Hayes.[6] All these compounds shows the expected positive isomer shift relative to grey tin. The present Mössbauer and infrared studies were undertaken to determine the effect of the extent of coordination and the nature of the coordinating atoms on the magnitude of the isomer shifts and quadrupole splittings, and to compare the infrared spectra of a number of tin(II) complexes with those of other metal(II) complexes. In particular, Pb^{II} complexes were prepared and studied for comparisons.

Experimental Section

Preparation and Purification of Compounds. Anhydrous $SnCl_2$, reagent grade, was obtained from M and T Chemicals, Inc. and from Matheson, Coleman and Bell. $SnBr_2$ was prepared by refluxing mossy tin with constant boiling HBr until all the solid dissolved. The water and excess acid were removed by distillation and the solid product dried under vacuum at 110°.

p-Toluidine, obtained from Matheson, Coleman and Bell, was recrystallized from hot water and alcohol. Exact 2:1 mole ratios of this amine and the apropriate metal halide were agitated in a Wig-L-Bug. As completion of the reactions was ascertained by infrared spectra, no analyses were necessary. Reactions with $SnCl_2$, $SnBr_2$ and $ZnBr_2$ required one minute, and with $PbCl_2$ and $PbBr_2$ five minutes for completion.

Terpyridyl was obtained from G. F. Smith Company, o-phenanthroline from Aldrich Chemical Co., 8-aminoquinoline from Eastman Kodak α, α-dipyridyl from Matheson, Coleman and Bell. The 1:1 complexes of these ligands with stannous halides were prepared by adding an absolute ethanol solution of the anhydrous tin(II) halide to a similar solution of the appropriate ligand. The yellow or orange precipitate was washed with absolute ethanol, then with petroleum ether and dried under vacuum at room temperature.

Anal. *o*-phenanthroline complexes: Calcd. for $SnCl_2(C_{12}H_8N_2)$: C, 38.97; H, 2.18. Found: C, 39.18; H, 2.41. Calcd. for $SnBr_2(C_{12}H_8N_2)$: C, 31.41; H, 1.76. Found: C, 30.68; H, 1.98. 8-Aminoquinoline complex: Calcd. for $SnCl_2(C_9H_8N_2)$: C, 32.39; H, 2.42. Found: C, 32.39; H, 2.53. α, α-Dipyridyl complexes: Calcd. for $SnCl_2(C_{10}H_8N_2)$: C, 34.73; H, 2.33. Found: C, 34.85; H, 2.36. Calcd. for $SnBr_2(C_{10}H_8N_2)$: C, 27.63; H, 1.86. Found: C, 26.27; H, 2.11. Terpyridyl complex: Calcd. for $SnCl_2(C_{15}H_{11}N_3)$: C, 42.61; H, 2.62. Found: C, 42.45; H, 2.79.

8-(2-Pyridylmethyleneamino)-quinoline (PMAQ) was prepared by the method of Lions and Martin,[7] using 8-aminoquinoline in ethanol and 2-pyridinealdehyde. The infrared spectrum of the product showed anomalous peaks at 3400 and 3370 cm^{-1} which did not disappear on recrystallization. These peaks were not present in the spectrum of the 1:1 complex of this ligand with zinc chloride, which was prepared in al-

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is A.E.C. document No. COO-38-401.

[2] Abstracted from a portion of the Ph. D. Thesis of Sister Mary Albertus Doskey, University of Notre Dame, 1967.

[3] R. E. Rundle and D. H. Olson, *Inorg. Chem.*, 3, 596 (1964).

[4] W. J. Moore and L. Pauling,. *J. Am. Chem. Soc.*, 63, 1392 (1941).

[5] A. J. F. Boyle, D. St. P. Bunbury and C. Edwards, *Proc. Phys. Soc.*, 79, 416 (1962).

[6] M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, 26, 915 (1964).

[7] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, 79, 2933 (1957).

cohol solution. $SnCl_2(PMAQ)$ could not be obtained as a pure product in this manner. It was prepared by adding, with stirring, a large excess of freshly distilled 2-pyridinealdehyde to a suspension of $SnCl_2$ (8-aminoquinoline) in absolute ethanol. The brick-red product was filtered, washed with anhydrous ether and dried under vacuum at room temperature. Its infrared spectrum was similar to that of the zinc chloride complex, with a weaker absorption in the 1620 cm^{-1} region.

Anal. Calcd. for $SnCl_2(C_{15}H_{11}N_3)$: C, 42.61; H, 2.62. Found: C, 41.87, H, 2.93. Calcd. for $ZnCl_2(C_{15}H_{11}N_3)$: C, 48.78; H, 3.00. Found: C, 48.61; H, 3.17.

Tin(II) complexes of anthranilic, picolinic, quinaldic and dipicolinic (2,5-pyridinedicarboxylic) acids were prepared in oxygen-free water under an atmosphere of nitrogen. The acid was dissolved in a stoichiometric amount of sodium hydroxide solution and the calculated quantity of $SnCl_2$ was added with constant stirring. The white or cream colored precipitate was washed with oxygen-free water and dried under vacuum at 110° for two hours. Lead(II) complexes with anthranilic and dipicolinic acids were prepared in a similar manner, using lead nitrate, without the precautions against oxidation.

Anal. Picolinate. Calcd. for $Sn(C_6H_4NO_2)_2$: C, 39.72; H, 2.22. Found: C, 39.64; H, 2.42. *Quinaldate.* Calcd. for $Sn(C_{10}H_6NO_2)_2$: C, 51.88; H, 3.26. Found: C, 51.17; H, 2.70. *Dipicolinates.* Calcd. for $Pb(C_7H_3NO_4)$: C, 29.63; H, 1.06. Found: C, 29.86; H, 1.28. Calcd. for $Pb(C_7H_3NO_4)$: C, 22.59; H, 0.81. Found: C, 22.41; H, 0.80. *Anthranilate.* Calcd. for $Sn(C_7H_6NO_2)_2$: C, 43.05; H, 3.10. Found: C, 42.27; H. 3.12. Calcd. for $Pb(C_7H_6NO_2)_2$: C, 35.06; H, 2.52. Found: C, 35.54; H, 2.65.

Bis(8-hydroxyquinolinato)tin(II), referred to as $Sn(oxine)_2$, was prepared as above, gentle heat being required to dissolve the ligand. The product was bright yellow. *Anal.* Calcd. for $Sn(C_9H_6NO)_2$: C, 53.12; H, 2.97. Found: C, 53.29; H, 3.07 .

SnCl(oxine) was prepared by the addition of an absolute ethanol solution of anhydrous stannous chloride to an ethanol solution of oxine. The yellow precipitate was washed with ethanol and dried under vacuum at room temperature. *Anal.* Cald. for $SnCl(C_9H_6NO)$: C, 36.34; H, 2.04. Found: C, 37.31; H, 2.17.

Bis(salicylaldehyde)*o*-phenylenediimine, $(Hsal)_2phen$, was prepared from salicylaldehyde and *o*-phenylenediamine in a minimum volume of ethanol solution. The yellow-orange crystals were recrystallized from hot ethanol. To an ethanol solution of this ligand plus an equivalent amount of sodium hydroxide was added an ethanol solution of stannous chloride. The reddish orange precipitate which formed was washed with ethanol and dried under vacuum The desired product was separated from sodium chloride by dissolving in hot benzene ,.filtering, and reprecipitating by the addition of petroleum ether. The red product was washed with petroleum ether and dried under vacuum. *Anal.* Calcd. for $Sn(C_{20}H_{14}O_2)$: C, 55.45; H, 3.26. Found: C, 55.61; H, 3.37.

Ethylenediaminetetraacetatotin(II)monohydrate($Sn_2(EDTA).H_2O$) was prepared by a slight modification of the method of Langer.[8] $Na_2H_2(EDTA).2H_2O$ and $SnCl_2$ were mixed in aqueous solution in stoichiometric proportion under oxygen-free conditions. The white precipitated product was washed with ethanol, then with petroleum ether and dried under vacuum at room temperature. The resulting product was the monohydrate as indicated by carbon and hydrogen analyses and confirmed by thermogravimetric analysis. Langer reports his product as a dihydrate. *Anal.* Calcd. for $Sn_2(C_{10}H_{12}N_2O_8).H_2O$: C, 22.09; H, 2.60; H_2O, 3.31. Found: C, 22.13; H, 2.63; H_2O, 3.28.

Disodium ethylenediaminetetraacetatotin(II)dihydrate ($Na_2Sn(EDTA).2H_20$) was also prepared by the method of Langer,[8] adding an aqueous solution of stannous chloride to an equivalent mixture of sodium hydroxide and $Na_2H_2(EDTA).2H_2O$ in water under oxygen-free conditions. The product was crystallized from aqueous ethanol and dried under vacuum at room temperature. *Anal.* Calcd. for $Na_2Sn(C_{10}H_{12}N_2O_8).2H_2O$: C, 24.55; H, 3.30; H_2O, 7.37. Found: C, 24.61; H, 3.30; H_2O, 6.25.

Ethanediylidinetetrathiotetraacetic acid(H_4ETTA) was prepared by the method of Longo *et al.*[9], using glyoxal and mercaptoacetic acid. The tin and lead complexes, $Sn_2(ETTA)$ and $Pb_2(ETTA)$ were prepared in the same manner as the picolinato complexes. Repeated preparations of the tin complex yielded products with somewhat low carbon and hydrogen content, but the Mössbauer spectrum of the complex was clean. *Anal.* Calcd. for $Sn_2(C_{10}H_{10}O_8S_4)$: C, 19.25; H, 1.62. Found: C, 17.97; H, 1.50. Calcd. for $Pb_2(C_{10}H_{10}O_8S_4)$: C, 14.99; H, 1.26. Found: C, 15.22; H, 1.45.

Attempts to prepare the tin(II) complex of ethylenedithoidiacetic acid were unsuccessful. Several attempts, using varied conditions, were made to prepare solid tin(II) complexes of simple aliphatic aminoacids, such as glycine, without success.

Infrared Spectra. Spectra were obtained with a Perkin-Elmer Model 421 grating spectrometer in KBr disks and/or Nujol mulls.

Mössbauer Spectra. The instrumentation and calibration of spectrometer have been described previously.[10] A $Pd-Sn^{119m}$ source containing 12% tin by weight was used at room temperature. The absorbers were cooled to liquid nitrogen temperature. The counts per channel were plotted against channel number and the shift determined from the average midpoint of the widths of the absorption pattern in the region of the half width. For three compounds, $SnCl_2(p\text{-tol})_2$, $Sn_2(ETTA)$ and $Sn_2(EDTA).H_2O$, a Goldanski effect was observed. The data for these compounds were fitted, with the aid of a computer program,[10] including a least squares treatment, to the best envelope of Lorentzian type curves, using a Univac 1107 computer. The isomer shift and quadrupole splitting for each of these three compounds were obtained from the computer analysis.

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(8) H. G. Langer, *J. Inorg. Nucl. Chem.*, *26*, 767 (1964).

(9) F. R. Longo, A. Ventresca, J. E. Darch, J. McBride and R. F. Sauders, *Chemist-Analyst*, *54*, 101 (1965).

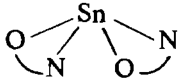
(10) M. A. Mullins and C. Curran, *Inorg. Chem.*, 6, 2017 (1967).

Table I. Infrared Absorption Maxima (cm^{-1}) in Bis(anthranilato)metal(II) Complexes.

Metal	Stretching		Bending		Wagging		Rocking		OCO Stretching	
	NH_2	ND_2	NH_2	ND_2	NH_2	ND_2	NH_2	ND_2	Antisym.	Sym.
Zinc	3302	2450	1590	1290	1049	822	650	484	1540	1405
	3135	2305		or 1237		or 799				
Cadmium	3295	2450	1585	1289	1020	790	656	482	1530	1396
	3140	2308		or 1243						
Tin	3338	2500	1607	1282	907	682	623	486	1560	1350
	3258	2360								
Lead	3345	2505	1605	1280	879	647	608	470	1530	1357
	3260	2360							1538	
Copper	3275	2435							1550	1375
	3132	2300								

Results and Discussion

Infrared Spectra. The absorptions of greatest interest in the spectra (4000-550 cm^{-1}) of the complexes studied are those associated with NH_2 and OCO vibrations. In the present investigation the former were identified by N-deuteration studies.

NH_2 Stretching Vibrations. The spectra of the biscomplexes of the anthranilate ion with the M^{2+} ions of Cu, Ni, Zn, Cd, Mg and Co all show similar absorption profiles in the 3-micron region.[11] This has been interperted as indicating similar, octahederal configuration for these solid complexes; the pink color of the cobalt complex supports this interpretation. The spectra of both the Sn^{II} and Pb^{II} complexes reveal a much smaller spacing between the two strong absorptions in the 3-micron region, Figure 1, suggesting a different type of coupling between the amino groups and a different configuration. The spatial requirements of the unshared electron pair suggest a square pyramidal arrangement of the metal and bonding atoms.  The lead complex absorbs at 3345 and 3260 cm^{-1}, significantly lower than any of the anthranilate salts, but higher than any other complex studied to date. The order of mean NH stretching frequencies, $Pb^{II} > Sn^{II} > Cd^{II}$, suggests and inverse order of N-M bond strengths.[12] The spectra of the complexes of *p*-toluidine with Pb^{II} and Sn^{II} in the 3-micron region are similar, and more complex than the spectrum of dibromobis (*p*-toluidine) zinc, Figure 1, again suggesting a difference in configuration. The high frequency peaks are in the order Pb > Sn > Zn.

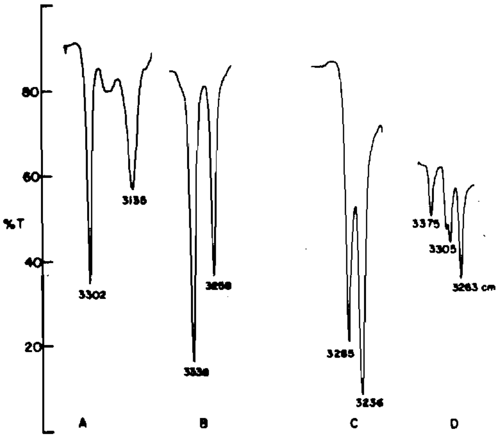


Figure 1. Absorption profiles in the 3-micron region (KBr disks). A, bis(anthranilato)zinc. B, bis(anthranilato)tin(II). C, dibromobis(*p*-toluidine)zinc. D, dichlorobis(*p*-toluidine)-tin(II.)

NH_2 Bending Vibrations. The spectra of the anthranilato complexes in the 1600 cm^{-1} region are complex; deuteration experiments suggest NH_2 scissors frequencies of 1605, 1607 and 1585 cm^{-1} for the Pb^{II}, Sn^{II}, and Cd^{II} complexes, indicating stronger N–M bonds in the latter.[13] The frequencies observed in the spectra of the bis-*p*-toluidine complexes of $SnCl_2$ 1580, $SnBr_2$ 1570, $PbCl_2$ 1580, and $PbBr_2$ 1579 cm^{-1}, are not significantly different from those for the corresponding complexes of other metal halides.[14]

The complexes of arylamines with metal halides[15] do not show the regular decrease in NH_2 scissors frequency with increasing N–M bond strength that is characteristic of the complexes of aminoacid esters.[13]

NH_2 Wagging Vibrations. The spectra of aniline complexes with various metals[15] reveal strong absorptions associated with NH_2 wagging vibrations, the frequency increasing with increasing N–M bond strength. N-deuteration of the anthranilato complexes indicate NH_2 wagging frequencies of 1049, 1020, 907, and 879 cm^{-1} for Zn, Cd, Sn^{II}, and Pb^{II} respectively. The spectra of the tin^{II} and $lead^{II}$ complexes with *p*-toluidine are complicated by coupling between the NH_2 wagging and C–H out-of-plane bending vibrations, as evidenced by the doublet character of the former and the complexity of the absorption in the 800 cm^{-1} region. The order of frequencies is the expected one: Zn > Cd > Sn > Pb.

NH_2 Rocking Vibrations. The absorptions in the spectra of the bisanthranilato complexes assigned to the NH_2 rocking vibration occur at 656, 623, and 608 cm^{-1} for Cd, Sn, and Pb respectively, indicating again the weakest N–M bond[16] in the lead complex.

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(11) A. G. Hill and C. Curran, *J. Phys. Chem.*, *64*, 1519 (1960).

(12) G. F. Svatos, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, 77, 6159 (1955).

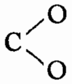
(13) M. P. Springer and C. Curran, *Inorg. Chem.*, *2*, 1270 (1963).

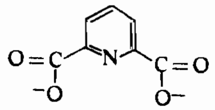
(14) F. R. Klebacher, Ph. D. dissertation, University of Notre Dame (1963).

(15) M. A. J. Jungbauer and C. Curran, *Spectrochim. Acta*, *21*, 641 (1965).

(16) L. Sacconi and A. Sabitini, *Nature*, *186*, 549 (1960).

The rocking frequencies for the *p*-toluidine complexes were not determined.

OCO Stretching Vibrations. In complexes containing the carboxylate group, the  $\mathrm{C}\begin{smallmatrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$ antisymmetric stretching vibration frequency increases with increasing covalent character of the O-M linkage. The absorptions attributed to this vibration occur at 1530 and 1538 cm^{-1} for the lead(II) complex and at 1560 cm^{-1} for the tin(II) complex with the anthranilate ion, lower and higher than the corresponding frequencies for the complexes reported previously,[10] (with the exception of 1564 cm^{-1} reported for the magnesium complex) indicating a large ionic character for the O–Pb bond an a relatively large covalent character for the O-Sn bond. The complexes of Sn^{2+} with the picolinate and the quinaldate ions absorb at 1640 and 1650 cm^{-1}, compared with the value of 1638 cm^{-1} for $Cu(pic)_2$ and 1608 cm^{-1} for sodium quinaldate. Resonance consideration suggest that the dipicolinate ion,



is probably planar and that coplanarity is preserved in its 1:1 complexes with M^{2+} ions. The disodium salt absorbs at 1615 cm^{-1}. In the spectra of the metal complexes multiple absorbtions occur in the regions of the antisymmetric and symmetric OCO frequencies suggesting a coupling between the two OCO vibrators. The spectrum of dipicolinatotin(II) in the disk is further complicated by an apparent reaction with potassium bromide. In Nujol this complex absorbs at 1660 and 1645 cm^{-1}, compared to 1605 and 1529 cm^{-1} for the lead complex.

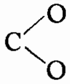
The symmetric  $\mathrm{C}\begin{smallmatrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$ stretching vibration frequency decreases with increasing covalent character of the O–M linkage. Absorptions attributed to this vibration occur at 1350 and 1330 cm^{-1} for the tin(II) complexes with the anthranilate and picolinate ion respectively, compared to 1375 and 1342 cm^{-1} for the corresponding copper(II) complexes. These data suggest a large covalent character for the O-Sn bond, probably greater than for the O–Cu bond.

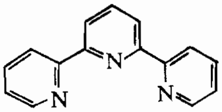
Table II. Isomer Shifts (δ) Relative to a Palladium-Tin Alloy Source, Quadrupole Splittings (ΔE_Q) and Percent Absorption for Tin(II) Complexes at 80°K.

	δ mm/sec	ΔE_Q mm/sec	% abs.
1. $SnCl_2$	2.53	——	8
2. $SnBr_2$	2.35	——	4
3. $SnCl_2$(dipyridyl)	2.01	1.05	6
4. $SnCl_2$(*o*-phenanthroline)	2.09	1.03	5
5. $SnBr_2$(*o*-phenanthroline)	2.09	0.83	3
6. $SnCl_2$(*p*-toluidine)$_2$	1.95	1.22	8
7. $SnBr_2$(*p*-toluidine)$_2$	2.03	0.94	5
8. $SnCl_2$(8-aminoquinoline,	1.93	1.30	9
9. $SnCl_2$(terpyridyl)	1.65	1.12	5
10. $SnCl_2$(PMAQ)	1.81	1.10	5
11. SnCl(oxine)	1.58	1.70	5
12. Sn(oxine)$_2$	1.38	2.01	6
13. Sn(sal$_2$phen)	1.53	1.34	3
14. Sn(anthranilate)$_2$	1.68	1.77	10
15. Sn(picolinate)$_2$	1.58	1.81	8
16. Sn(quinaldate)$_2$	1.52	1.78	5
17. Sn(dipicolinate)	1.69	1.63	10
18. Sn_2(EDTA) . H_2O	1.92	1.57	7
19. Na_2Sn(EDTA) . $2H_2O$	2.11	1.25	10
20. Sn_2(ETTA)	1.80	1.83	7

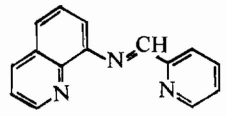
PMAQ-8-(2-pyridylmethyleneamino)quinoline (Hsal)$_2$phen-bis-(salicylaldehyde)*o*-phenylenediimine H_4ETTA-ethanediylidenetetraacetic acid.

Mössbauer Spectra. The isomer shifts and quadrupole splittings obtained are liste in Table II. They are considered to be accurate to ±0.07 mm/sec. with a relative precision of ±0.05 mm/sec. Leis and Flinn[17] report quadrupole splittings of 0.66 and 0.50 mm/sec. for $SnCl_2$ and $SnBr_2$ using a Mg_2Sn source, but no splitting was observed with the Pd–Sn source. The large positive isomer shifts for $SnCl_2$ and $SnBr_2$ indicate appreciable s character for the unshared outer tin electrons. Complex formation brings about a decrease in isomer shifts. This suggests a shielding of the unshared pair of electrons of the dative bonds and/or a change in hybridization resulting in decreased s character for the unshared pair. The decrease is greater for $SnCl_2$ complexes. This suggests a greater increase in polarity of the Sn-Br than of the Sn-Cl bond on complex formation, resulting in a decreased shielding of the unshared pair by the electrons of the Sn-Br bond. The reason for the smaller quadrupole splittings of the $SnBr_2$ complexes is not evident at this time.

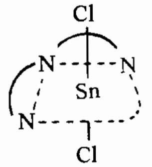
Complex formation between the two tridentate ligands, terpyridyl and PMAQ, is expected to result in pentacoordinated tin. As resonance favors coplanar nitrogen atoms, a distorted trigonal bipyramid arrangement of the three nitrogen and two chlorine atoms about tin is likely.



Terpyridyl



PMAQ



#9 and 10

The pentacoordinated complexes show the expected smaller isomer shifts — associated with the greater shielding of the unshared pair by the three dative bonds — than the tetracoordinated complexes of $SnCl_2$. Terpyridyl is expected to be a better electron donor than PMAQ, and the smaller isomer shift observed for the terpyridyl complex is consistent with this expectation. (An attempt was made to obtain a Mössbauer spectrum of the terpyridyl complex at room temperature, but absorption was negligible).

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(17) J. K. Leis and P. A. Flinn, *J. Chem. Phys.*, *48*, 882 (1968).

No significant change in quadrupole splitting is observed on formation of the third N–S dative bond. Attempts to prepare six-coordinated tin(II) complexes with neutral ligands such as bis(8-quinolinaldehyde) *o*-phenylenedimine have been unsuccessful.

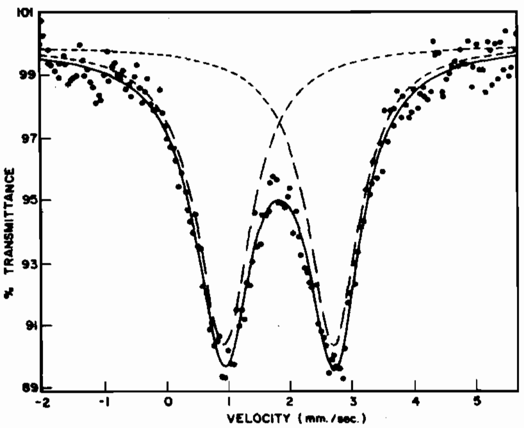
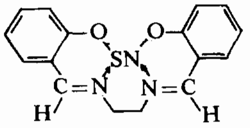


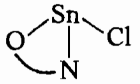
Figure 2. Mössbauer Spectrum of bis(anthranilato)tin(II).

All the complexes of tin(II) with anionic ligands show larger quadrupole splittings than do the stannous halide complexes with neutral ligands. A comparison of Sn(oxine)$_2$ # 12, probably pyramidal, with bis(salicylaldehydato) o-phenylenediiminetin(II), # 13, a likely planar ligand, reveals a smaller ismer shift for the oxinate.



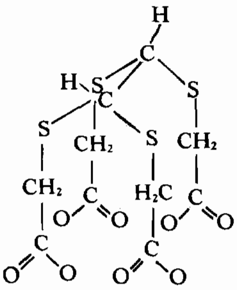
13

This suggests a greater electron release by the oxygen atom of the oxinate group, which is not directly conjugated with the quinoline nitrogen atom. An additional factor working in the same direction is the more basic character of the ring nitrogen atom. The much smaller quadrupole splitting for # 13, 1.34 mm/sec, than for the oxinate, 2.01 mm/sec., suggests a decrease in electric field gradient on flattening the pyramidal structure.

As there is no evidence for halogen bridging to give a higher coordination number than 3 in tin(II) complexes, the tin atom in SnCl(oxine), # 11, is probably three coordinate  This compound has a larger isomer shift, 1.58 mm/sec., than Sn(oxine)$_2$, 1.38 mm/sec., as expected for the decreased shielding of the unshared pair. The bonding of tin to three different elements in the 1:1 complex results in a larger quadrupole splitting, 1.70 mm/sec. than the values for most three-coordinate stannous compounds. This splitting, however, is less than that for the four-coordinate Sn (oxine)$_2$.

All the remaining complexes contain two or more carboxylate groups. They show greater splittings than do the complexes of stannous halides with neutral ligands, but smaller than the 2:1 oxine. The complexes of Sn^{2+} with the picolinate, # 15, and quinaldate, # 16, anions show smaller isomer shifts than the anthranilate, # 14, suggesting that the amino nitrogen is a poorer donor than the ring nitrogen atom, and the expected smaller shifts and larger splittings than three-coordinate tin in dipicolinatotin(II), # 17.

In Sn$_2$(EDTA)..H$_2$O, # 18, each tin atom is probably bonded to one nitrogen atom and two carboxylate groups; this compound shows the relatively large isomer shift and small quadrupole splitting characteristic of three-coordinate tin. The large isomer shift obtained for Na$_2$Sn(EDTA) . 2H$_2$O, 2.11 mm/sec., is surprising. It suggests a tin ion bound to four carboxylate groups, with no nitrogen-to-tin bonds an unexpected arrangement. The relatively small quadrupole splitting, 1.25 mm/sec., indicates less asymmetry for this complex than for the others containing the COO$^-$ group. The S$_2$C–CS$_2$ skeleton of ETTA in the eclipsed form has a tent-like structure:



The formation of the Sn$_2$(ETTA) complex very probably results in five-membered rings in which two sulfur atoms on a side (rather than on an end) of the tent are bonded to one tin atom. In such a complex a possible configuration is one having a short tin-to-tin distance. A bond between the tin atoms, however, is ruled out by Mössbauer spectrum; only divalent tin is present. This suggests that the two pairs of methylene groups are far apart. The large isomer shift, 1.80 mm/sec., compared to that for the bispicolinate, 1.58 mm/sec., is surprising, as sulfur is expected to effect a greater electron release than nitrogen and therefore to exert a greater shielding effect on the unshared outer tin electrons. The quadrupole splitting for Sn$_2$(ETTA) is slightly larger than that for complexes of tin with the pyridine and quinoline carboxylic acids.