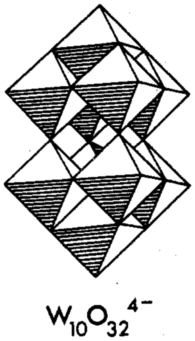

Figure 1. Polyhedral representation of the structure of $W_{10}O_{32}{}^{4-}$.

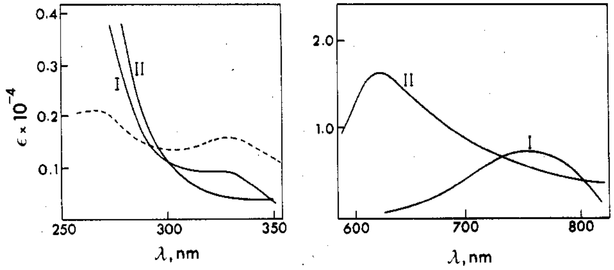

Figure 2. Absorption spectra of $W_{10}O_{32}{}^{4-}$ (broken line), $W_{10}O_{32}{}^{5-}$ (I), and $W_{10}O_{32}{}^{6-}$ (II) in PDC. The spectra of W_y, W_{yI}, and W_{yII} in aqueous solution correspond almost exactly with those shown here.

Solutions of tributylammonium decatungstate in acetonitrile or PDC are stable indefinitely according to their UV spectra. Cyclic voltammograms of the decatungstate in PDC (0.50 mM polyanion, 0.1 M $[(C_4H_9)_3NH]ClO_4$, sweep rate 1 V min^{-1}) showed two quasi-reversible reductions at −0.66 and −0.93 V (cathodic peak potentials) and with cathodic–anodic peak potential separations of 140 and 160 mV, respectively.[9] Controlled potential reductions at −0.8 and −1.0 V led respectively to the addition of one and two electrons per W_{10} species. The absorption spectra of the reduced products, presumably $[W_{10}O_{32}]^{5-}$ and $[W_{10}O_{32}]^{6-}$, are shown in Figure 2 and are virtually identical with those found for W_{yI} and W_{yII}. Complete restoration of the UV spectrum of $[W_{10}O_{32}]^{4-}$ was observed upon reoxidation. Since these measurements were made under nonhydrolytic conditions, they provide confirmatory evidence for the identification of $[W_{10}O_{32}]^{4-}$ with W_y.[10]

That the decatungstate structure is reducible in reversible one-electron steps to "heteropoly blue" species is consistent with the observation that only polyanions with one terminal oxo-oxygen per metal are reducible in this way.[11] There are, however, two unusual features of decatungstate: the 325-nm band and the high intensities of the intervalence bands in the spectra of the reduced anions. We suggest that both features are related to the presence of the near-linear (175°) W–O–W bridges that link both halves of the anion. The only other polytungstates with charge-transfer bands[12] as low as 325 nm are α- and β-$[P_2W_{18}O_{62}]^{6-}$ which also have dimeric structures[13] linked by almost linear (162°) W–O–W bridges. Furthermore the intervalence charge-transfer bands in reduced $P_2W_{18}O_{62}$ anions have relatively high extinction coefficients for a heteropoly blue (3600–6000 M^{-1} cm^{-1} per W(V)).[14] Launay[15] has pointed out that the intensities of intervalence transitions W^V–O–W^{VI} ↔ W^{VI}–O–W^V increase as the bond angle increases toward 180°. This principle is most dramatically illustrated with the spectra of $[W_6O_{19}]^{3-}$, ϵ_{max} = 280,[15] and $[W_{10}O_{32}]^{5-}$, ϵ_{max} = 7500, which correspond to intervalence transitions involving ~90 and ~180° bridges, respectively.

Acknowledgment. This work has been supported in part by National Science Foundation Grant No. CHE73-04793.

Registry No. W_y, 52261-16-2; W_{yI}, 64825-40-7; W_{yII}, 64825-39-4.

References and Notes

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(7) M. Boyer, *J. Electroanal. Chem.*, **31**, 441 (1971).
(8) R. A. Prados and M. T. Pope, *Inorg. Chem.*, **15**, 2547 (1976).
(9) The voltammetric peak potentials were affected by the voltage sweep rate: at 2 V min^{-1}, −0.69, −0.97 V; at 3 V min^{-1}, 0.72, −1.01 V. The mean of the cathodic and anodic peak potentials remained constant at −0.59 and −0.85 V.
(10) Courtin and Lefebvre[5] have reported a molybdotungstate with UV and IR spectra very similar to those of W_y (but also to those reported for $W_{10}O_{32}{}^{4-}$). According to chemical analysis (C, H, N, Mo, W) of a tetramethylammonium salt, the formula of the molybdotungstate is $HMo_2W_{10}O_{39}{}^{5-}$, i.e., analogous to that given to W_y by Boyer. The analytical data are also in satisfactory agreement with the formula $(N(CH_3)_4)_4Mo_2W_8O_{32}$, except for Mo (found 6.22; calcd 7.76). Since Mo was determined polarographically and by difference, it is possible that a distinction between the 2:10 and 2:8 formulas cannot be made based on these analytical data.
(11) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).
(12) This statement excludes reduced anions and charge transfer involving the heteroatom. Oxygen-to-tungsten(VI) charge-transfer bands generally fall within the range 240–270 nm.
(13) H. D'Amour, *Acta Crystallogr., Sect. B*, **32**, 729 (1976); K. Y. Matsumoto and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 691 (1975).
(14) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9**, 667 (1970).
(15) J. P. Launay, private communication, 1977; J. M. Fruchart, G. Hervé, J. P. Launay, and R. Massart, *J. Inorg. Nucl. Chem.*, **38**, 1627 (1976); M. Dabbabi, M. Boyer, J. P. Launay, and Y. Jeannin, *J. Electroanal. Chem.*, **76**, 153 (1977). See also C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **12**, 1626 (1973), for discussion of $V^{IV} \rightarrow W^{VI}$ band intensities.
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Organotin(II)–Oxygen and –Sulfur Heterocycles through Protolysis of Tin(II) Dimethoxide

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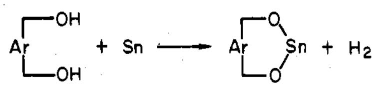
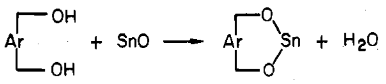
Protolysis by various tin substrates has been used to yield organotin(II)–oxygen derivatives, beginning with the action of tin metal with dihydric phenols at elevated temperatures to liberate hydrogen gas:[1]



(1)

Protolysis by blue-black tin(II) oxide releases water[2]



(2)

but long reaction times are required and the hydrous form of tin(II) oxide is a superior reagent since milder conditions can be used and the reaction is more general.[3] More recently, the high reactivity of the η^5-cyclopentadienyltin(II) linkage in stannocene has allowed the preparation of tin(II) oximes, hydroxylamines,[4] di- and triazoles,[4] thiolates,[5] β-keto–enolates,[6] alkyl- and arylcarboxylates,[7] and phenoxides[8] by protolysis

$$(\eta^5\text{-}C_5H_5)_2Sn + 2HOR \rightarrow Sn(OR)_2 + 2C_5H_6 \qquad (3)$$

but the method requires preliminary preparation of stannocene[4-9] which can be troublesome. Some time ago we investigated the general reactivity of the easily prepared tin(II) dimethoxide toward protic and other reagents.[10] We now report the convenient preparation of organotin(II) heterocycles from this starting material formed in situ from anhydrous tin(II) chloride without being isolated.

Tin(II) dimethoxide was first prepared by the reaction of anhydrous tin(II) chloride with sodium methoxide in methanol:[11]

$$\mathrm{SnCl_2 + 2NaOCH_3 \xrightarrow{CH_3OH} Sn(OCH_3)_2 + 2NaCl} \tag{4}$$

A more convenient method was developed by Morrison and Haendler through the action of triethylamine on tin(II) chloride in methanol:[12]

$$\mathrm{SnCl_2 + 2(C_2H_5)_3N + 2CH_3OH \xrightarrow{CH_3OH} Sn(OCH_3)_2 + 2(C_2H_5)_3N\cdot HCl} \tag{5}$$

The reactivity of tin(II) dimethoxide toward protic reagents has been demonstrated by its reaction with 8-hydroxyquinolinol[12] and thiophenol.[3] Despite its potential usefulness as a synthetic reagent in the preparation of tin(II) compounds, it has received little attention.

Experimental Section

Tin(II) chloride dihydrate was dehydrated by reaction with acetic anhydride. Methanol was dried by refluxing over magnesium metal and distilled just prior to use. Triethylamine was dried over barium oxide and distilled immediately before use. All other chemicals were of reagent grade quality and were used as received, except for 2,3-dihydroxypyridine, which was recrystallized from water.

Tin was analyzed as tin(IV) oxide through the action of nitric and sulfuric acids. Carbon and hydrogen analyses were performed by Instranal Laboratory, Inc., Rensselaer, N.Y.

Infrared spectra were recorded with a Beckman IR-12 spectrophotometer as Nujol mulls between potassium bromide plates. Tin-119m Mössbauer spectra were recorded on a cam-driven, constant-acceleration spectrometer previously described.[13]

All syntheses involving the use of tin(II) dimethoxide were performed under an atmosphere of nitrogen.

Tin(II) Dimethoxide. Anhydrous tin(II) chloride (2.00 g, 10.5 mmol) was dissolved in approximately 50 mL of methanol and triethylamine (2.14 g, 21.1 mmol) added dropwise. An exothermic reaction occurred as tin(II) dimethoxide precipitated as a white solid, which was filtered, washed with several portions of methanol followed by a wash with anhydrous diethyl ether, and stored under an inert atmosphere. The yield is nearly quantitative, mp 260–263 °C (sealed tube and uncorrected; lit. mp 242–243[14] and 300 °C[7]). Anal. Calcd for $C_2H_6O_2Sn$: Sn, 65.66. Found: Sn, 65.54. Tin(II) dimethoxide was used in all subsequent reactions without further purification, although purification could be effected by sublimation at 180 °C at 0.005 Torr.

Catechol with Tin(II) Dimethoxide. Tin(II) dimethoxide (1.00 g, 5.5 mmol) was added to a solution of catechol (0.61 g, 5.5 mmol) in methanol and the mixture stirred for 3 h. The white product was filtered and washed with methanol followed by diethyl ether. An infrared spectrum of the product identified it as *o*-phenylenedioxytin(II) by comparison with a spectrum of an authentic sample.[1-3]

Salicylic Acid with Tin(II) Dimethoxide. Tin(II) chloride (2.00 g, 10.5 mmol) was dissolved in methanol, triethylamine (2.14 g, 21.1 mmol) added, and the mixture stirred for ca. $^1/_2$ h. Salicylic acid (1.46 g, 10.6 mmol) dissolved in methanol was added and the mixture stirred for ca. 1 h. The infusible white product was filtered, washed with methanol, and then washed with diethyl ether. The infrared spectral bands listed are identical to those given by an authentic sample of *o*-oxybenzoyloxytin(II) prepared by published methods.[3] Prominent absorptions are found at 1600 (s), 1562 (s), 1522 (w, sh), 1495 (s), 1440 (s), 1403 (s), 1317 (m), 1255 (w, sh), 1235 (s), 1161 (m), 1143 (s), 1101 (m), 1039 (m), 958 (w), 885 (s), 830 (s), 806 (m), 775 (sh), 767 (s), 717 (s), 672 (s), 600 (m), 583 (m), 543 (w), 471 (w), and 435 (m) cm^{-1}.

***o*-Mercaptobenzoic Acid with Tin(II) Dimethoxide.** Tin(II) chloride (2.00 g, 10.5 mmol) was dissolved in methanol, triethylamine (2.14 g, 21.1 mmol) added, and the mixture stirred for ca. $^1/_2$ h. *o*-Mercaptobenzoic acid (1.62 g, 10.5 mmol) dissolved in methanol was added and the mixture stirred for ca. 1 h. The light yellow product was filtered, washed with methanol, and then washed with diethyl ether. The yield of *o*-thiolatobenzoyloxytin(II), which decomposed at temperatures above 260 °C, was 68%. Anal. Calcd for $C_7H_4O_2SSn$: Sn, 43.82. Found: 43.32. Prominent absorptions in the infrared spectrum are found at 1584 (s), 1559 (s), 1492 (vs), 1432 (s), 1406 (s), 1255 (w), 1157 (m), 1122 (w), 1056 (m), 1032 (m), 876 (s), 800 (w), 743 (s), 730 (s), 707 (m), 643 (m), 580 (w), 490 (m), and 473 (m) cm^{-1}.

Mercaptoethanol with Tin(II) Dimethoxide. Tin(II) chloride (3.00 g, 15.8 mmol) was dissolved in methanol, triethylamine (3.21 g, 31.7 mmol) added, and the mixture stirred for ca. $^1/_2$ h. Mercaptoethanol (1.25 g, 16.0 mmol) was added and the mixture stirred an additional hour. The precipitate was filtered and washed with methanol followed by diethyl ether. The product, which decomposes without melting above 200 °C, was obtained in 99% yield. Anal. Calcd for C_2H_4OSSn: Sn, 60.93; C, 12.33; H, 2.07. Found: Sn, 59.81; C, 12.24; H, 2.10. Prominent absorptions in the infrared spectrum are found at 1411 (s), 1357 (m), 1288 (m), 1234 (w), 1063 (s), 1012 (s), 951 (m), 826 (s), 662 (m), 592 (w), 527 (s), and 441 (s) cm^{-1}.

3,4-Toluenedithiol with Tin(II) Dimethoxide. Tin(II) chloride (2.90 g, 15.3 mmol) was dissolved in methanol, triethylamine (3.10 g, 30.6 mmol) added, and the mixture stirred for ca. $^1/_2$ h. 3,4-Toluenedithiol (2.42 g, 15.3 mmol) was added and the mixture stirred for an additional hour. The product, 3,4-toluenedithiolatotin(II), was filtered under nitrogen, washed with methanol followed by diethyl ether, and stored under nitrogen. The yellow solid product was obtained in 85% yield and melted at 181–184 °C with decomposition. Anal. Calcd for $C_7H_6S_2Sn$: Sn, 43.49; C, 30.80; H, 2.22. Found: Sn, 43.65; C, 30.27; H, 2.94. Prominent absorptions in the infrared spectrum are found at 1590 (m), 1458 (s), 1372 (m), 1257 (m), 1155 (w), 1140 (w), 1111 (m), 1034 (m), 866 (m), 811 (s), 706 (w), 688 (m), 635 (m), 550 (m), 475 (w), and 441 (m) cm^{-1}.

Thioglycolic Acid with Tin(II) Dimethoxide. Tin(II) chloride (3.00 g, 15.8 mmol) was dissolved in methanol, triethylamine (3.21 g, 31.7 mmol) added, and the mixture stirred for ca. $^1/_2$ h. Thioglycolic acid (1.46 g, 15.8 mmol) was added and the mixture stirred for another hour. The precipitate was filtered and washed with methanol followed by diethyl ether. The light yellow product, which decomposed above 100 °C without melting, was obtained in 45% yield. Anal. Calcd for $C_2H_2O_2SSn$: Sn, 56.85; C, 11.51; H, 0.97. Found: Sn, 58.16; C, 11.58; H, 1.55. Prominent absorptions in the infrared spectrum are found at 1530 (s, br), 1376 (s), 1212 (m), 1022 (m), 934 (w), 889 (w), 781 (m), 722 (w), and 570 (m, br) cm^{-1}.

2,3-Dihydroxypyridine with Tin(II) Dimethoxide. Tin(II) chloride (3.00 g, 15.8 mmol) was dissolved in methanol, triethylamine (3.21 g, 31.7 mmol) added, and the mixture stirred for ca. $^1/_2$ h. 2,3-Dihydroxypyridine (1.74 g, 15.7 mmol) was added and the mixture stirred for another hour. The precipitate was filtered and washed with methanol followed by diethyl ether. The light brown product, 2,3-pyridinedioxytin(II), which decomposed above 200 °C without melting, was obtained in 95% yield. Anal. Calcd for $C_5H_3NO_2Sn$: Sn, 52.11. Found: Sn, 49.62. Prominent absorptions in the infrared spectrum are found at 1618 (s), 1595 (s), 1541 (s), 1450 (s), 1420 (m), 1352 (m), 1340 (m), 1277 (s), 1190 (m), 1180 (w, sh), 1108 (m), 1042 (m, sh), 1023 (s), 902 (s), 784 (s), 751 (m, sh), 735 (s), 606 (s), and 477 (m) cm^{-1}.

Ethanedithiol with Tin(II) Methoxide. Tin(II) chloride (3.00 g, 15.8 mmol) was dissolved in methanol, triethylamine (3.21 g, 31.7 mmol) added, and the mixture stirred for ca. $^1/_2$ h. Ethanedithiol (1.49 g, 15.8 mmol) was added and the mixture stirred for another hour. The light yellow solid ethanedithiolatotin(II) was filtered and washed with methanol followed by diethyl ether. The product, obtained in 99% yield, decomposed without melting above 180 °C. Anal. Calcd for $C_2H_4S_2Sn$: Sn, 56.29. Found: Sn, 57.35. Prominent absorptions in the infrared spectrum are found at 1420 (m), 1409 (s), 1280 (m), 1243 (s), 1111 (m), 922 (w), 820 (s), 722 (w), and 641 (w) cm^{-1}.

Results and Discussion

Tin(II) dimethoxide is a white solid which is only very slightly soluble in polar organic solvents. It can be purified by vacuum sublimation, but even in the vapor phase it is apparently associated as evidenced by the appearance of a large number of tin- and ditin-containing fragments in its mass

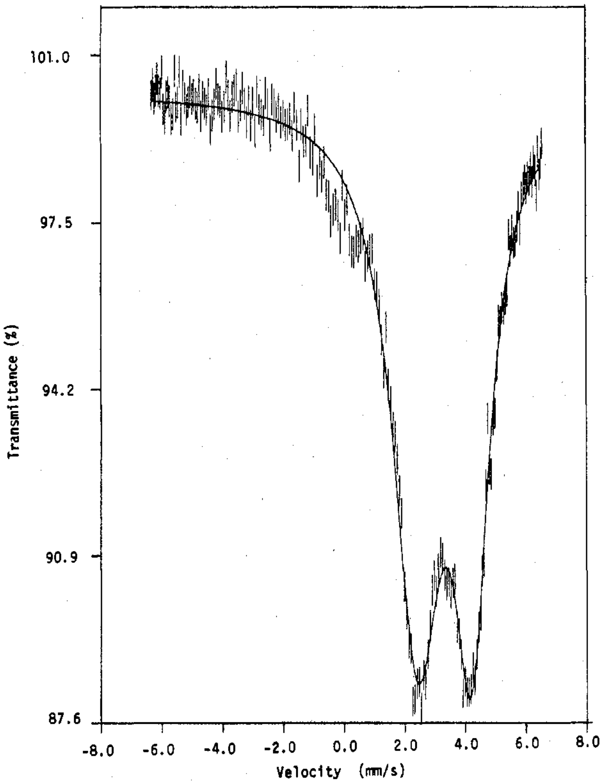
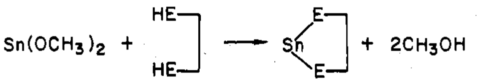


Figure 1. Tin-119m Mössbauer spectrum of *o*-oxybenzoyloxytin(II) at 77 K vs. Ba^{119m}SnO$_3$.

spectrum at *m*/*e* values in excess of its calculated molecular weight.[14] Even the very soluble tin(II) di-*n*-butoxide is a dimer in methylene chloride. Tin(II) dimethoxide may be stored under an inert atmosphere for short times, but a resonance in the tin(IV) region of its ^{119m}Sn Mössbauer spectrum gradually increases with time.

Tin(II) dimethoxide is comparatively easy to prepare from tin(II) chloride relative to dicyclopentadienyltin(II) and can be reacted conveniently in situ without being isolated. It is highly reactive toward protic reagents, the reactions occurring rapidly and usually in high yield, factors that make it superior to the blue-black[2] or hydrous[3] tin(II) oxides, which require longer reaction times and often result in low yields.[3] A problem frequently encountered in preparing tin(II) compounds is their intractability. The attempted purification by vacuum sublimation of *o*-thiolatobenzoyltin(II), prepared from *o*-mercaptobenzoic acid and blue-black tin(II) oxide, for example, results only in decomposition. The products obtained by reaction with tin(II) dimethoxide, on the other hand, are often pure as isolated:



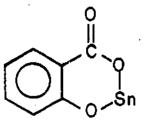
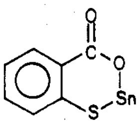
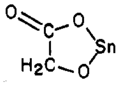
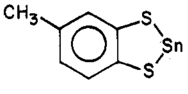
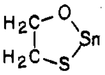
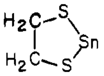
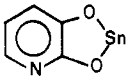
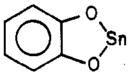
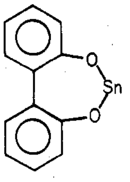
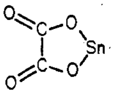
(6)

However, this is not the case in all the reactions attempted, such as that of 2,3-dihydroxypyridine.

The heterocycles reported here can be prepared by two methods. The first involves isolating the tin(II) dimethoxide before reaction with the protic reagents. In the second, tin(II) dimethoxide is prepared as in eq 5 and the protic agent added in situ. The yields of the heterocycles containing only OH and SH groups are nearly quantitative but the compounds containing carboxylic acid groups give lower yields. For these derivatives the two-step method is preferable.

Differentiating between open-chain polymeric and cyclic monomeric forms of bifunctional compounds is a problem in organotin chemistry.[15] For example, blue-black tin(II) oxide reacts with dihydric phenols[2] and salicylic acid[3] to give heterocycles containing tin(II) atoms that sublime in vacuo, presumably entering the gas phase as monomers. However, the product of the reaction of ethylene glycol with hydrous tin(II) oxide is believed to be a polymer with the structure [-OCH$_2$CH$_2$O-Sn-]$_n$.[3]

Table I. ^{119m}Sn Mössbauer Data at 77 K in mm/s vs. Ba^{119m}SnO$_3$

Compd	IS	QS	Γ_1	Γ_2	Ref
Sn(OCH$_3$)$_2$	2.82 ± 0.06	1.99 ± 0.12	1.64	1.34	
	3.02	1.97			4
	2.80	2.02			13
	3.31 ± 0.06	1.80 ± 0.12	1.98	1.45	
	3.31 ± 0.06	1.99 ± 0.12	1.48	1.28	
	3.43 ± 0.06	1.85 ± 0.12	1.96	1.16	
	3.36 ± 0.06	1.63 ± 0.12	1.19	1.20	
	3.08 ± 0.06^a	1.69 ± 0.12^a	1.32	1.08	
	3.08 ± 0.06	1.58 ± 0.12	2.39	1.37	
	3.21 ± 0.06^a	1.90 ± 0.12^a	0.92	0.83	
	3.19 ± 0.06	1.87 ± 0.12	1.26	1.26	
	2.89 ± 0.06	2.13 ± 0.12	1.38	1.09	
	2.95 ± 0.06^a	1.53 ± 0.12^a			14
	2.95 ± 0.06	1.76 ± 0.12			14
	3.13 ± 0.06	1.98 ± 0.12			14
	3.47 ± 0.06	1.59 ± 0.12			19

[a] Recorded at ambient temperature.

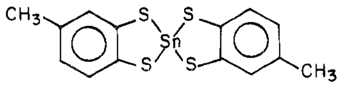
Heterocycles containing tin(II)–oxygen bonds are notable for their high degree of thermal and hydrolytic stability, presumably arising from the associated lattices consisting of intermolecularly coordinated tin atoms.[1-3,16] The carbonyl stretching vibrations of *o*-oxybenzoyloxytin(II), *o*-thiolatobenzoyloxytin(II), and the tin(II) heterocycle derived from thioglycolic acid are all shifted to lower frequencies (to ca. 1560 cm^{-1}), similar to those observed for intermolecularly coordinated acetoxy groups in tin(IV) compounds,[17,18] evidence that suggests carbonyl oxygen–tin interaction.

Table I lists the ^{119m}Sn Mössbauer data for the tin(II) compounds prepared, along with previously published data on related heterocyclic tin(II) compounds. All compounds exhibit isomer shift values greater than that of β-tin, evidence generally taken as confirmation of the presence of tin(II).[19,20] A typical Mössbauer spectrum is illustrated in Figure 1, for *o*-oxybenzoyloxytin(II).

o-Phenylenedioxytin(II),[16] tin(II) oxalate,[15] and the tin(II) derivatives derived from mercaptoethanol and ethanedithiol exhibit Mössbauer resonances at room temperature, evidence generally considered to indicate strong polymeric lattices which contribute to large recoil-free fractions.[19] The recent observation of ambient-temperature tin-119m Mössbauer spectra for certain molecular solids[21] does not affect our conclusion which is based upon close analogies with other associated tin(II) solids whose structures are known.[22]

Ample evidence is available in the literature of tin structures[22] to support the idea of bridging oxygen and sulfur groups at ψ-trigonal-bipyramidal or φ-square-pyramidal tin(II) atoms to give association polymers in the solid state. The original molecules can, as in the case of the infusible *o*-phenylenedioxytin(II),[1] preserve their integrity in the crystal, sublime as the monomer, and be recovered unchanged from strongly donating solvents. The physical properties of the infusible derivatives containing carboxylic acid groups prepared here, in which the infrared ν(C=O) shifts to lower frequencies, argue likewise for a strongly associated solid through carbonyl oxygen atom bridging. Associated structures through oxygen atom bridging have also been proposed for the tin(II) dialkoxides[12,14] and diphenoxide,[8] with a double bridge proposed for tin(II) dimethoxide.[14] The products from mercaptoethanol and ethanedithiol, like the analogous material from ethylene glycol,[3] are presumably open-chain polymers with the backbone structure $[-ECH_2CH_2E'-Sn-]_n$ in which E = O, E′ = S and E = E′ = O,[3] S. The thioglycolate derivative, on the other hand, is more likely an associated solid made up of heterocyclic units linked together by carbonyl oxygen atom bridges. The related tin(II) oxalate apparently uses only one of its carbonyl oxygen atoms to bridge, the other remaining free.[15]

On prolonged standing in air, a resonance in the tin(IV) region appears in the Mössbauer spectra of the compounds studied here. However, one compound, 3,4-toluenedithiolatotin(II), is apparently much less stable than the others. When exposed to the atmosphere, a freshly prepared sample changes color from yellow to red within 1 day. No color change occurs when the compound is stored under nitrogen. The red color is characteristic of the spiro tin(IV) compound,[23] and 3,4-toluenedithiol is used in the colorimetric determination of tin.[24]



The red tin(IV) spirane is an associated polymer in the solid state. No other related tin(IV) dithiolato compounds, or the pyridine or dimethylformamide adduct of the spirane, exhibit the red color.[23]

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Registry No. Sn(OMe)$_2$, 37182-97-1; *o*-phenylenedioxytin(II), 1767-80-2; *o*-oxybenzoyloxytin(II), 28637-75-4; *o*-thiolatobenzoyloxytin(II), 64957-59-1; thiolatoethyleneoxytin(II), 64957-60-4; 3,4-toluenedithiolatotin(II), 42549-83-7; thioglycolatotin(II), 64957-61-5; 2,3-pyridinedioxytin(II), 64957-62-6; ethanedithiolatotin(II), 6570-39-4; SnCl$_2$, 7772-99-8; CH$_3$OH, 67-56-1; catechol, 120-80-9; salicylic acid, 69-72-7; *o*-mercaptobenzoic acid, 147-93-3; mercaptoethanol, 60-24-2; 3,4-toluenedithiol, 496-74-2; thioglycolic acid, 7283-42-3; 2,3-dihydroxypyridine, 16867-04-2; ethanedithiol, 107-21-1; ^{119}Sn, 14314-35-3.

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Kinetics and Mechanism of the Reduction of Bromate Ion by Hexachloroiridate(III)

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The bromate ion oxidation of metal ions has been studied with the reducing agents Ce(III),[1,2] Mn(II),[1,2] Np(V),[1-3] VO^{2+},[4,5] V^{3+},[6] V^{2+},[6] Fe^{2+},[7] Fe(CN)$_6^{4-}$,[8] Fe(bpy)(CN)$_4^{2-}$,[9] Fe(bpy)$_2$(CN)$_2$,[9] Fe(bpy)$_3^{2+}$,[9] Ru(CN)$_6^{4-}$,[10] Hg^0 (from disproportionation of Hg$_2^{2+}$),[11] and U^{4+}.[12] These reactions exhibit a remarkable variety of mechanistic behavior. The reactions with Ce(III), Mn(II), and Np(V) exhibit induction periods and autocatalysis, with rate laws independent of the metal ion, caused by the bromous acid reduction of bromate to give the reactive oxidant BrO$_2$.[1-3] The VO^{2+} reaction exhibits simple mixed-second-order kinetics but involves a disproportionation of bromous acid in competition with its reduction by VO^{2+}.[4] The reductions by V^{3+} and V^{2+} proceed in two consecutive steps with apparently complex mechanisms and were not studied completely.[6] The Fe^{2+} reduction follows simple mixed-second-order kinetics with a complex hydrogen ion dependence indicating the involvement of a binuclear steady-state intermediate.[7] The reactions with Fe(CN)$_6^{4-}$, Fe(bpy)(CN)$_4^{2-}$, Fe(bpy)$_2$(CN)$_2$, and Ru(CN)$_6^{4-}$ have both a direct path and an autocatalytic path caused by the Br$^-$–BrO$_3^-$ reaction.[9] The Fe(bpy)$_3^{2+}$ reaction is also partially autocatalytic and involves reactions with both monomeric and dimeric Br(V) species.[9] The reactions with Hg^0 and U^{4+} follow simple kinetics, first-order in each reactant and possibly involve the transfer of two electrons.[11,12] We report here on the bromate oxidation of IrCl$_6^{3-}$, which also exhibits simple kinetics with no indication of complexities in the mechanism.