# 1173. *Complex Tin*(II) *Formates.*

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The preparation and analysis of alkali-metal and ammonium derivatives of the triformatostannate(II) ion $Sn(HCO_2)_3^-$ are described. Their solubility in various solvents is reported. Their thermal decomposition has been studied in detail, the decomposition temperatures being in the range 188—194°, and the products tin(II) oxide, alkali-metal or ammonium formate, trioxymethylene, formaldehyde, and carbon dioxide. Hydrous tin(II) oxide (analytical composition $5SnO,2H_2O$) is obtained free from tin(IV) impurities by the controlled hydrolysis of the complexes. Unit cell dimensions, cell contents, and $X$-ray diffraction powder data of the triformatostannate(II) complexes are also reported. Evidence for the existence of the ions $Sn(HCO_2)^+$, $Sn_2(HCO_2)_5^-$, and $Sn(HCO_2)_3^-$ in tin(II) formate solutions is given.

THERE have been few reports of the preparation of solid derivatives of complex tin(II)–carboxylate ions. Baker and Tomkins[1] prepared three complex tin(II) acetates: $2NH_4Sn(CH_3 \cdot CO_2)_3C_6H_6$; $CaSn_2,(CH_3 \cdot CO_2)_6$; and $NH_4Sn(CH_2Cl \cdot CO_2)_3$, and there is a report[2] of the precipitation of complex tin(II) acetates by the addition of alkali solutions to a solution of tin(II) acetate. Complex tin(II) oxalates of composition $M_2Sn(C_2O_4)_2,H_2O$ (M = K or $NH_4$) have also been obtained.[3] The only reference to complex tin(II) formates is a report by Elöd and Kolbach[4] of the preparation of a series of compounds $M_2Sn(HCO_2)_4,5H_2O$ (M = Na,K, and $NH_4$) by dissolving tin(II) chloride (1M) in a solution of alkali-metal or ammonium formate (4M) in formic acid (35% w/w) and evaporating the solution. The first precipitate obtained was alkali-metal chloride but further concentration of the solution gave an impure complex tin(II) formate which was recrystallised from 35% formic acid. It is doubtful whether the method described by these authors could lead to a pure product. Elöd and Kolbach found that the complex formates had the normal properties of tin(II) compounds, that they hydrolysed in aqueous solution, and that their solutions in dilute formic acid were oxidised in air. The products of thermal decomposition of these materials were formic acid and formaldehyde.

We previously described[5] the preparation and properties of pure tin(II) formate and have now obtained the alkali-metal and ammonium triformatostannate(II) complexes and studied their properties.

## EXPERIMENTAL

*Preparation and Analyses.*—Two possible methods for preparing complex tin(II) formates were studied. The only solid materials obtained in a pure state were derivatives of the triformato-stannate(II) ion, $Sn(HCO_2)_3^-$.

*Preparation of the pure tin*(II) *complexes* $MSn(HCO_2)_3$ (M=$NH_4$,K,Rb, and Cs). Tin(II) formate (20 g.) was Soxhlet extracted, under an atmosphere of oxygen-free nitrogen, into a solution of alkali-metal or ammonium formate (100 g.) in 40% w/w aqueous formic acid (150 ml.). Between 60 and 90 ml. of solvent were distilled off, under nitrogen, and the solution was allowed to cool slowly. The white crystalline product was filtered off, washed with acetone and ether, and dried *in vacuo* over pellets of potassium hydroxide. This method gave the pure alkali-metal and ammonium triformatostannate(II) complexes in good yields (50—90%) and was used in subsequent work.

It was found that the concentration of formic acid could be altered without affecting the product. In the absence of a large excess of alkali-metal or ammonium formate, however, the product was

[1] E. M. Baker and F. C. Tomkins, *J.,* 1952, 4518.
[2] J. D. Donaldson, W. Moser, and W. B. Simpson, *J.,* 1764.
[3] S. Hausmann and J. Löwenthal, *Annalen,* 1854, **89**, 104.
[4] E. Elöd and F. Kolbach, *Z. anorg. Chem.,* 1927, **164**, 297.
[5] J. D. Donaldson and J. F. Knifton, *J.,* 1964, 4801.

tin(II) formate. The solid derivatives, sodium and lithium triformatostannate(II), could not be obtained by this method; the $Na^+$ and $Li^+$ ions are presumably too small to form a stable lattice with $Sn(HCO_2)_3^-$.

*Preparation of tin(II) formate complexes by Elöd and Kolbach's method.* Tin(II) chloride (1 mole) was extracted, in an atmosphere of oxygen-free nitrogen, into a solution of alkali-metal or ammonium formate (4 moles) in 35% w/w aqueous formic acid (200 ml.). The solution was concentrated in stages, under nitrogen, until about 30 ml. of solution remained; at each stage the solution was cooled slowly, and the product filtered off, washed with acetone and ether, and dried *in vacuo* (KOH). All the products were mixtures of alkali-metal or ammonium triformatostannate(II) complex and alkali-metal or ammonium chloride (analysis and $X$-ray powder data). Crystallisation of the products from 35% w/w aqueous formic acid did not remove all of the chloride impurity. The distinct hydrates of composition $M_2Sn(HCO_2)_4,5H_2O$ reported by Elöd and Kolbach were not obtained in this work.

The preparation was repeated using tin(II) sulphate instead of tin(II) chloride, but the products were mixtures of alkali-metal or ammonium triformatostannate(II) complex and alkali-metal or ammonium sulphate (analysis and $X$-ray powder data). These methods are, thus, not suitable for the preparation of pure complex tin(II) formates.

We have found that formate does not interfere with the determination of stannous tin and total tin by Donaldson and Moser's method,[5, 6] which was used in the present work. We determined the potassium content by flame photometry, and rubidium and cæsium gravimetrically as the tetraphenylborate.[7] The ammonium content was estimated by boiling a weighed quantity of the complex in an excess of sodium hydroxide solution. The ammonia evolved was collected in an excess of standard acid, and determined by back-titration of the excess of acid with standard alkali.

We determined formate by oxidising a known weight of sample in 2N-hydrochloric acid solution with lead tetra-acetate, and weighing the carbon dioxide liberated.

The average results of analyses on two samples of each of the four alkali-metal and ammonium triformatostannate(II) complexes are given in Table 1.

TABLE 1.

| Suggested compounds: | $KSn(HCO_2)_3$ | | | $RbSn(HCO_2)_3$ | | |
|---|---|---|---|---|---|---|
| | (1) | (2) | theo-retical | (1) | (2) | theo-retical |
| Sn(II) (%) | 40·6 | 40·6 | 40·7 | 34·0 | 34·0 | 35·0 |
| Total Sn (%) | 40·6 | 40·8 | 40·7 | 34·1 | 34·1 | 35·0 |
| Metal$^+$/$NH_4^+$ (%) | 14·6 | 14·5 | 13·3 | 26·1 | 25·8 | 25·2 |
| $HCO_2^-$ (%) | 45·6 | 46·4 | 46·0 | 40·0 | 40·0 | 39·8 |
| Suggested compounds: | $CsSn(HCO_2)_3$ | | | $NH_4Sn(HCO_2)_3$ | | |
| | (1) | (2) | theo-retical | (1) | (2) | theo-retical |
| Sn(II) (%) | 30·3 | 30·1 | 30·7 | 42·9 | 43·4 | 43·7 |
| Total Sn (%) | 30·2 | 30·2 | 30·7 | 43·0 | 43·3 | 43·7 |
| Metal$^+$/$NH_4^+$ (%) | 35·0 | 35·2 | 34·4 | 7·00 | 6·86 | 6·65 |
| $HCO_2^-$ (%) | 34·7 | 34·8 | 34·9 | 49·6 | 48·9 | 49·7 |

*Solubility of the Complexes.*—The solubility of the triformatostannate(II) complexes in 2N-formic acid, acetone, and ethanol, under a non-oxidising atmosphere, at various temperatures were measured by titrating[6] the tin(II) in solution. Because of the rapid decomposition of the complexes in water, their solubility in this solvent could not be estimated.

*Stability of the Complexes.*—All the triformatostannate(II) complexes were stable for several months when stored *in vacuo* (KOH), there being no change in analytical composition. On exposure to a moist atmosphere they were all found to be hygroscopic and subject to oxidation. The first sign of impurity was the formation of small yellow areas. This colour gradually deepened and spread throughout the sample, which completely lost its crystallinity. Analysis and $X$-ray powder data showed that the decomposition products consisted of mixtures of the original complex formate and tin(IV) oxide. The most stable complex in moist air was potassium triformatostannate(II), which showed no alteration in composition after 2 months. After a further 2 months,

[6] J. D. Donaldson and W. Moser, *Analyst*, 1959, **84**, 10.
[7] K. Sporek and A. F. Williams, *Analyst*, 1955, **80**, 347.

TABLE 2.

Solubility (g./l. of solution) of the alkali-metal and ammonium triformatostannate(II) complexes.

| Temp. | Acetone | | Ethanol | | | 2N-Formic acid | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 25° | 40° | 25° | 40° | 50° | 25° | 40° | 50° | 70° |
| $KSn(HCO_2)_3$ | 0·159 | 0·168 | ·0·307 | 0·702 | 0·753 | 42·70 | 45·19 | 45·82 | 51·58 |
| $RbSn(HCO_2)_3$ | 0·193 | 0·267 | 0·445 | 0·811 | 1·098 | 38·27 | 39·25 | 41·03 | 48·12 |
| $CsSn(HCO_2)_3$ | 0·262 | 0·345 | 0·947 | 2·120 | 3·597 | 57·50 | 62·90 | 66·95 | 89·15 |
| $NH_4Sn(HCO_2)_3$ | 0·428 | n.d. | 3·725 | 11·60 | 14·25 | 28·02 | 33·36 | 39·71 | 40·70 |

n.d. = not determined.

however, about 10% of the tin in the material had been oxidised. For the other triformatostannate(II) complexes, the time for the appearance of the first sign of impurity, and the amount of tin which had been oxidised after a given period was: Rb, 2 weeks, and 20% after 3 months, and $NH_4$ and Cs, 1 week, and 40—60% after 2 months.

The thermal stability of the alkali-metal and ammonium triformatostannate(II) complexes was studied by using a m. p. and a vacuum grid apparatus. The cæsium and ammonium complexes melt at 152—153° and 138—139°, respectively, and decompose at 188—194°; the rubidium and potassium complexes decompose without melting at 188—194°. In each case the main gaseous products of the decomposition were carbon dioxide and $CH_2O$ (infrared and chemical characteristics). A sublimate, trioxymethylene ($X$-ray and infrared characteristics), was also obtained, and the residue was a mixture of blue-black tin(II) oxide and alkali-metal formate (analysis and $X$-ray powder data). In the case of the ammonium triformatostannate(II) complex, the dissociation products of ammonium formate were detected, and the residue contained only blue-black tin(II) oxide.

*Hydrolysis of the Complexes.*—Alkali-metal and ammonium triformatostannate(II) complexes decomposed to blue-black tin(II) oxide when kept under water. This decomposition was rapid in boiling water and in alkaline solution. Under certain conditions, however, a white hydrolysis product was obtained. When a suspension of a complex (1 g.) in alkali-free deaerated distilled water (100 ml.) was shaken mechanically for $\frac{1}{2}$ hr., the product was a white powder that had an identical $X$-ray powder pattern to hydrous tin(II) oxide.[8] Three typical samples of the products of hydrolysis gave Sn(II) 82·8, 82·9, 82·8%, total Sn, 83·1, 83·2, 83·1% and $H_2O$, 5·1, 5·1, 5·1%. Hydrous tin(II) oxide, analytical composition $5SnO,2H_2O$, requires Sn(II) 83·7, $H_2O$ 5·1%.

*Studies of the Ions present in Tin(II)–Formate Solutions.*—*Potentiometric studies.* Potentiometric measurements were made on the tin–tin(II) ion couple to determine which ions exist in tin(II)–formate solutions. The cell used consisted of two half-cells $Sn/SnSO_4$, $2M-H_2SO_4$, containing equimolar quantities of tin(II) sulphate, connected by means of a agar-agar bridge. To prevent oxidation of the bivalent tin the half-cells were kept in a non-oxidising atmosphere throughout these experiments. The changes in voltage of the cell on addition of solutions of alkali-metal formate to one half-cell, and of distilled water to the other, were measured and plotted against the ratio of the concentration of tin(II) and formate in the solution. These measurements were carried out for cells containing concentrations of tin(II) sulphate of about 0·01M. The graphs showed four significant inflections at the tin : formate ratios of 1 : 1, 1 : 2, 2 : 5, and 1 : 3, corresponding to the tin(II)–formate species $Sn(HCO_2)^+$, $Sn(HCO_2)_2$, $Sn_2(HCO_2)_5^-$, and $Sn(HCO_2)_3^-$.

*Polarographic studies.* The polarographic studies were carried out with a Tinsley polarograph, a dropping mercury cathode (drop time 2—3 sec.), and a mercury pool anode. Various amounts of pure blue-black tin(II) oxide (0·1 to 0·9 g./l.) were dissolved in a freshly prepared standard solution of alkali metal or ammonium formate (0·04%) in 10% sulphuric acid, and a sample of the solution was placed in the cell. Oxygen-free nitrogen was then bubbled through the solution for 5 min., to prevent oxidation of the tin(II) present. A varying potential (from $+0·5$ to $-1·5$ v) was applied across the cell, and the corresponding changes in cell current were recorded automatically. The wave-height of the the tin species at about $-0·5$ v (against the mercury pool) was measured and plotted against the ratio of the concentrations of tin(II) and formate in the solutions. The graphs showed four significant breaks at the tin : formate ratios of 1 : 1, 1 : 2, 2 : 5, and 1 : 3, corresponding to the tin(II)–formate species $Sn(HCO_2)^+$, $Sn(HCO_2)_2$, $Sn(HCO_2)_5^-$, and $Sn_2(HCO_2)_3^-$.

[8] J. D. Donaldson, W. Moser, and W. B. Simpson, *J.*, 1961, 839.

*Ultraviolet Absorption Studies.*—The ultraviolet absorption of tin(II) formate solutions was measured to determine which ions exist in these solutions. There are three peaks in the u.v. spectrum, observed at 191, 229, and 243 mμ, which could be attributed to tin(II)–formate species. Various amounts of pure blue-black tin(II) oxide (0·015 to 0·30 g./l.) were dissolved in freshly prepared solutions of alkali-metal or ammonium formate (0·01 to 0·02%) in 10% sulphuric acid, and their u.v. absorbance was measured on a Perkin-Elmer 137 spectrophotometer in the region of the peaks at 191 and 243 mμ. A blank of alkali-metal or ammonium formate in 10% sulphuric

X-Ray-diffraction powder data for the alkali-metal and ammonium triformatostannate(II) complexes (s, m, w, etc., denote relative intensities).

Potassium triformatostannate(II)

| $d$ (Å) | Index of ref. | Calc. $d$ spacings |
|---|---|---|
| 8·84m | 002 | 8·82 |
| 6·48vs | 011 | 6·48 |
| 6·14mw | 100 | 6·10 |
| 5·79m | 101 | 5·77 |
| 5·46m | 012 | 5·46 |
| 4·53m | 110 | 4·59 |
| 4·40m | 004 | 4·42 |
| 4·23vs | 103 | 4·23 |
| 4·04s | 112 | 4·07 |
| 3·65mw | 113 | 3·62 |
| 3·56mw | 104 | 3·58 |
| 3·48ms | 020 | 3·48 |
| 3·22m | 022 | 3·23 |
| 3·14ms | 015 | 3·15 |
| 3·05vs | 200 | 3·05 |
| 2·94ms | 006 | 2·94 |
| 2·82ms | 115 | 2·80 |
| 2·72ms | 016 | 2·71 |
| 2·66ms | 106 | 2·65 |
| 2·52mw | 213 | 2·52 |
| 2·46w | 025 | 2·48 |
| 2·38ms | 017 | 2·37 |
| 2·30ms | 205 | 2·31 |
| 2·25s | 026 | 2·25 |
| 2·21ms | 117 | 2·21 |
| 2·18ms | 215 | 2·19 |
| 2·13m | 223 | 2·14 |
| 2·08vw | 108 | 2·08 |
| 2·04w | 224 | 2·04 |
| 1·997vw | | |
| 1·966ms | | |
| 1·931ms | | |
| 1·894ms | | |
| 1·871m | | |
| 1·836m | | |
| 1·807mw | | |
| 1·793mw | | |
| 1·742vw | | |
| 1·714ms | | |
| 1·684vw | | |
| 1·666m | | |
| 1·658m | | |
| 1·646m | | |
| 1·628mw | | |
| 1·600mw | | |
| 1·582vw | | |
| 1·563m | | |
| 1·542mw | | |
| 1·506mw | | |
| 1·478m | | |
| 1·415vw | | |
| 1·398vw | | |
| 1·356w | | |
| 1·331w | | |
| 1·319w | | |
| 1·307vw | | |
| 1·298w | | |
| 1·281w | | |
| 1·263vw | | |
| 1·245w | | |
| 1·222w | | |
| 1·206vw | | |
| 1·173w | | |
| 1·158vw | | |
| 1·149vw | | |
| 1·124vw | | |
| 1·112vw | | |
| 1·102vvw | | |
| 1·084vvw | | |
| 1·074vvw | | |
| 1·064vw | | |
| 1·038vvw | | |
| 1·023vvw | | |
| 1·012vw | | |
| 1·006vw | | |

Rubidium triformatostannate(II)

| $d$ (Å) | Index of ref. | Calc. $d$ spacings |
|---|---|---|
| 6·66vs | 011 | 6·65 |
| 6·36mw | 100 | 6·34 |
| 5·56m | 012 | 5·57 |
| 4·69w | 110 | 4·74 |
| 4·42w | 004 | 4·41 |
| 4·29vs | 103 | 4·31 |
| 4·19ms | 112 | 4·18 |
| 3·75m | 014 | 3·76 |
| 3·64w | 104 | 3·62 |
| 3·59m | 020 | 3·59 |
| 3·50vw | 021 | 3·50 |
| 3·29m | 022 | 3·32 |
| 3·17s | 200 | 3·17 |
| 3·12m | 201 | 3·12 |
| 3·08m | 105 | 3·08 |
| 3·05w | 023 | 3·06 |
| 3·01w | 202 | 2·98 |
| 2·96vw | 122 | 2·95 |
| 2·93vw | 006 | 2·94 |
| 2·86m | 211 | 2·86 |
| 2·81m | 203 | 2·82 |
| 2·71m | 016 | 2·72 |
| 2·56w | 124 | 2·55 |
| 2·49vw | 116 | 2·50 |
| 2·45w | 214 | 2·43 |
| 2·39w | 017 | 2·38 |
| 2·36m | 205 | 2·36 |
| 2·31w | 032 | 2·31 |
| 2·28m | 026 | 2·28 |
| 2·22m | 033 | 2·22 |
| 2·16vw | 206 | 2·16 |
| 2·11w | 018 | 2·11 |
| 2·05vw | 302 | 2·05 |
| 2·02m | 311 | 2·02 |
| 1·994w | | |
| 1·970w | | |
| 1·947mw | | |
| 1·877w | | |
| 1·864w | | |
| 1·850w | | |
| 1·818w | | |
| 1·777w | | |
| 1·737vw | | |
| 1·706vw | | |
| 1·673w | | |
| 1·655w | | |
| 1·589w | | |
| 1·561vw | | |
| 1·525w | | |
| 1·504w | | |
| 1·476vw | | |
| 1·457vw | | |
| 1·439vw | | |
| 1·423vw | | |
| 1·417vw | | |
| 1·393vw | | |
| 1·363vw | | |
| 1·353vw | | |
| 1·336vw | | |
| 1·324vw | | |
| 1·287vw | | |
| 1·263vw | | |
| 1·244vw | | |
| 1·225vw | | |
| 1·210vw | | |
| 1·193vw | | |
| 1·159vvw | | |
| 1·138vvw | | |
| 1·121vw | | |
| 1·101vvw | | |
| 1·079vw | | |

X-Ray-diffraction powder data for the alkali-metal and ammonium triformatostannate(II) complexes—*continued.* (s, m, w, etc., denote relative intensities.)

Cæsium triformatostannate(II)

| $d$ (Å) | Index of ref. | Calc. $d$ spacings |
|---|---|---|
| 6·75s | 011 | 6·82 |
| 5·64s | 012 | 5·65 |
| 4·68s | 111 | 4·77 |
| 4·41vs | { 103 | 4·42 |
|  | 004 | 4·41 |
| 4·19vs | 112 | 4·27 |
| 3·81s | { 014 | 3·79 |
|  | 113 | 3·79 |
| 3·69w | 020 | 3·69 |
| 3·61w | 921 | 3·61 |
| 3·40w | 022 | 3·40 |
| 3·34w | 200 | 3·34 |
| 3·29w | 114 | 3·30 |
| 3·25m | 120 | 3·23 |
| 3·19m | 015 | 3·18 |
| 3·12vs | 105 | 3·12 |
| 3·03w | 122 | 3·03 |
| 2·96mw | 006 | 2·94 |
| 2·91s | 203 | 2·90 |
| 2·81m | 024 | 2·83 |
| 2·75m | 016 | 2·73 |
| 2·66w | 204 | 2·66 |
| 2·63mw | 124 | 2·61 |
| 2·53s | 116 | 2·53 |
| 2·44m | 031 | 2·44 |
| 2·40m | 017 | 2·39 |
| 2·37m | 032 | 2·37 |
| 2·31m | 130 | 2·31 |
| 2·27m | 033 | 2·27 |
| 2·22s | 301 | 2·21 |
| 2·19w | { 206 | 2·20 |
|  | 126 | 2·18 |
| 2·15w | 133 | 2·15 |
| 2·13w | 310 | 2·13 |
| 2·08m | 027 | 2·08 |
| 2·02m | 035 | 2·02 |
| 1·928s | | |
| 1·843m | | |
| 1·769mw | | |
| 1·743w | | |
| 1·730mw | | |
| 1·697mw | | |
| 1·668m | | |
| 1·631w | | |
| 1·617w | | |
| 1·588mw | | |
| 1·569mw | | |
| 1·544m | | |
| 1·530vw | | |
| 1·476vw | | |
| 1·456w | | |
| 1·446w | | |
| 1·436w | | |
| 1·421w | | |
| 1·407vw | | |
| 1·388mw | | |
| 1·372w | | |
| 1·351m | | |
| 1·316w | | |
| 1·301w | | |
| 1·267mw | | |
| 1·242w | | |
| 1·233w | | |
| 1·138w | | |
| 1·133w | | |
| 1·119vw | | |
| 1·108vw | | |
| 1·086vw | | |
| 1·073vw | | |
| 1·051vw | | |
| 1·018vw | | |
| 1·001vw | | |

Ammonium triformatostannate(II)

| $d$ (Å) | Index of ref. | Calc. $d$ spacings |
|---|---|---|
| 9·05ms | 002 | 8·99 |
| 6·56vs | 011 | 6·52 |
| 5·91ms | 101 | 5·90 |
| 5·53vw | 012 | 5·53 |
| 5·18vw | 102 | 5·13 |
| 4·52ms | 111 | 4·51 |
| 4·32s | 103 | 4·32 |
| 4·14vs | 112 | 4·14 |
| 3·66w | 113 | 3·68 |
| 3·50ms | 020 | 3·50 |
| 3·22s | 114 | 3·23 |
| 3·12vs | 200 | 3·12 |
| 3·01vs | 121 | 3·01 |
| 2·94w | 202 | 2·95 |
| 2·81ms | 211 | 2·82 |
| 2·76w | 024 | 2·76 |
| 2·72ms | 123 | 2·72 |
| 2·52w | 116 | 2·52 |
| 2·42vs | 017 | 2·43 |
| 2·32s | { 031 | 2·31 |
|  | 125 | 2·33 |
| 2·28s | 026 | 2·28 |
| 2·24ms | 215 | 2·24 |
| 2·16w | 206 | 2·16 |
| 2·12w | 132 | 2·12 |
| 2·07w | { 034 | 2·07 |
|  | 027 | 2·07 |
| 2·03m | 302 | 2·03 |
| 1·969s | | |
| 1·939m | | |
| 1·911ms | | |
| 1·872w | | |
| 1·849m | | |
| 1·832m | | |
| 1·796w | | |
| 1·752vw | | |
| 1·727m | | |
| 1·708m | | |
| 1·677m | | |
| 1·654vvw | | |
| 1·631w | | |
| 1·618w | | |
| 1·598vw | | |
| 1·587vw | | |
| 1·574vw | | |
| 1·558vw | | |
| 1·542vw | | |
| 1·519w | | |
| 1·500w | | |
| 1·478w | | |
| 1·462vw | | |
| 1·447w | | |
| 1·434vw | | |
| 1·421 | | |
| 1·397vw | | |
| 1·384w | | |
| 1·359w | | |
| 1·342w | | |
| 1·316vw | | |
| 1·311vw | | |
| 1·304vw | | |
| 1·296w | | |
| 1·290w | | |
| 1·287w | | |
| 1·275vvw | | |
| 1·263vw | | |
| 1·250vw | | |
| 1·233vw | | |
| 1·223vvw | | |
| 1·212vw | | |
| 1·204vvw | | |
| 1·194vvw | | |
| 1·182vvw | | |
| 1·176vvw | | |
| 1·161vvw | | |
| 1·152vvw | | |
| 1·144vvw | | |
| 1·133vw | | |
| 1·121w | | |
| 1·111vw | | |
| 1·097vw | | |
| 1·094vw | | |
| 1·085vw | | |
| 1·078vw | | |
| 1·060vvw | | |

acid was used. The observed changes in absorbance of both peaks were plotted against the ratio of the concentrations of the tin(II) and formate in the solutions. The graphs showed four significant inflections at the tin : formate ratios of 1 : 1, 1 : 2, 2 : 5, and 1 : 3, corresponding to the tin(II)–formate species $Sn(HCO_2)^+$, $Sn(HCO_2)_2$, $Sn_2(HCO_2)_5^-$, and $Sn(HCO_2)_3^-$.

*Crystallography.*—(*a*) Potassium triformatostannate(II) consists of colourless, elongated rectangular crystals with cleavage parallel to the elongation. The crystals show low birefringence and positive elongation; $n = 1.65$.

Crystal data: $KSn(HCO_2)_3$. $M = 292.7$. Orthorhombic $a = 6.10 \pm 0.02$, $b = 6.96 \pm 0.02$, $c = 17.67 \pm 0.03$ Å, $U = 750.1$ Å$^3$, $D_m = 2.60$ g./c.c. (by displacement of organic solvents), $Z = 4$, $D_c = 2.59$ g./c.c. Filtered Cu–$K_\alpha$ radiation, single crystal rotation and Weissenberg photographs about $a$ and $b$.

(*b*) Rubidium triformatostannate(II) consists of colourless, elongated rectangular crystals with cleavage parallel to the elongation. The crystals show low birefringence and positive elongation; $n = 1.74$.

Crystal data: $RbSn(HCO_2)_3$. $M = 334.2$. Orthorhombic $a = 6.34 \pm 0.02$, $b = 7.18 \pm 0.02$, $c = 17.67 \pm 0.03$ Å, $U = 804.2$ Å$^3$, $D_m = 2.80$ g./c.c. (by displacement of organic solvents), $Z = 4$, $D_c = 2.80$ g./c.c. Filtered Cu–$K_\alpha$ radiation, single crystal rotation and Weissenberg photographs about $a$ and $b$.

(*c*) Cæsium triformatostannate(II) consists of colourless, elongated rectangular crystals with cleavage parallel to the elongation. The crystals show low birefringence and positive elongation; $n > 1.74$.

Crystal data: $CsSn(HCO_2)_3$. $M = 386.6$. Orthorhombic $a = 6.68 \pm 0.02$, $b = 7.38 \pm 0.02$, $c = 17.67 \pm 0.03$ Å, $U = 871.2$ Å$^3$, $D_m = 2.95$ g./c.c. (by displacement of organic solvents), $Z = 4$, $D_c = 2.95$ g./c.c. Filtered Cu–$K_\alpha$ radiation, single crystal rotation and Weissenberg photographs about $a$ and $b$.

(*d*) Ammonium triformatostannate(II) consists of colourless, elongated rectangular crystals with cleavage parallel to the elongation. The crystals show low birefringence and positive elongation; $n = 1.63$.

Crystal data: $NH_4Sn(HCO_2)_3$. $M = 271.7$. Orthorhombic $a = 6.24 \pm 0.02$, $b = 7.01 \pm 0.02$, $c = 17.97 \pm 0.03$ Å, $U = 786.1$ Å$^3$, $D_m = 2.28$ g./c.c (by displacement of organic solvents), $Z = 4$, $D_c = 2.30$ g./c.c. Filtered Cu–$K_\alpha$ radiation single crystal rotation and Weissenberg photographs about $a$ and $b$.

Each crystal had the same systematic absences of reflection, *viz.*, $0k0$ absent for $k$ odd, $00l$ absent for $l$ odd. The space group is therefore $P22_12_1$. The $X$-ray-diffraction single-crystal and powder data suggest that the four alkali metal triformatostannates(II) are isostructural.

The annexed Table contains the $X$-ray diffraction powder data of all four complexes, obtained by using an 11·64 cm. camera with Cu–$K_\alpha$ radiation. The $d$ spacings longer than 2·00 Å have been indexed.

## DISCUSSION

In most solutions containing tin(II) and a donor species the stable and predominant complex is the three-co-ordinated species [9] based on $sp^3$ hybridisation of the tin(II) orbitals; there is generally little evidence for the existence of complexes of higher co-ordination. In this respect the tin(II)–formate system is typical. Potentiometric, polarographic, and spectroscopic studies on tin(II)–formate solutions provide evidence for the existence of a number of species [$SnHCO_2^+$, $Sn(HCO_2)_2$, $Sn_2(HCO_2)_5^-$, and $Sn(HCO_2)_3^-$], but the solid phases obtained from solution are all derivatives of the triformatostannate(II) ion. There was no evidence for the existence of a four-co-ordinated complex, $Sn(HCO_2)_4^{2-}$, in solution and no solid derivative of this ion was obtained. An infrared study [10] of the solid complex tin(II) formates showed that the formate ion was a unidentate ligand towards tin(II) and that the spectra were consistent with the presence of a pyramidal $Sn(CHO_2)_3^-$ ion in these materials.

An indication of the donor strength of the formate ion towards tin(II) is obtained from the thermal decomposition of the complex formates. Oxygen-containing tin(II) compounds can

[9] J. D. Donaldson, "A Review of the Chemistry of Tin(II) Compounds," Publication No. 348 of the International Tin Research Inst. London, 1964.
[10] J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, to be published.

decompose thermally to give either tin(II) oxide or tin(IV) oxide. The product obtained depends upon the donor strength of the anionic part of the compound towards the tin. With weak donors the product is tin(IV) oxide,[11,12] but with strong donors, such as formate in the complex formates and in tin(II) formate,[5] the product is tin(II) oxide.

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[11] J. D. Donaldson and W. Moser, *J.*, 1961, 835.
[12] J. D. Donaldson and W. Moser, *J.*, 1960, 4000.