Complex Tin(II) Acetates

By J. D. Donaldson and J. F. Knifton

The preparations of alkali-metal, ammonium, and alkaline-earth triacetatostannates(II) are described and their solubilities in various solvents are reported. The crystal data on the complexes have been obtained from *X*-ray-diffraction photographs. Evidence is given for the existence of the species $Sn(CH_3{\cdot}CO_2)^+$, $Sn(CH_3{\cdot}CO_2)_2$, $Sn_3(CH_3{\cdot}CO_2)_7^-$, $Sn_2(CH_3{\cdot}CO_2)_5^-$, and $Sn(CH_3{\cdot}CO_2)_3^-$ in tin(II)–acetate solutions. The thermal decomposition of the salts has been studied in detail, and their stability to hydrolysis and oxidation reported. The stability of the pyramidal triacetatostannate (II) ion is discussed in terms of the outer electronic configuration of tin(II).

IN most solutions containing tin(II) and a suitable ligand, the predominant complex is the pyramidal three-co-ordinated species[1] based on sp^3 hybridisation of the tin(II) orbitals. There is generally little evidence for the existence of complexes with higher co-ordination involving the use of *d*-orbitals on the metal, but species of lower co-ordination are known. We have previously shown[2] that solutions containing tin(II) and formate are typical in this respect, there being no indication of the presence of ions with co-ordination greater than three. The species found[2] were, $SnHCO_2^+$, $Sn(HCO_2)_2$,

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[1] J. D. Donaldson, "A Review of the Chemistry of Tin(II) Compounds," International Tin Research Institute Publication No. 348, 1964.

[2] J. D. Donaldson and J. F. Knifton, *J. Chem. Soc.*, 1964, 6107.

$Sn_2(HCO_2)_5^-$, and $Sn(HCO_2)_3^-$. The formation of the polynuclear ion $Sn_2(HCO_2)_5^-$ shows the tendency for tin to maintain its stable, pyramidal, three-co-ordination even in solutions containing insufficient ligand to complex all of the tin as the triligand species. Similar polynuclear ions have been found in tin(II)–fluoride [3,4] and tin(II)–hydroxide [5,6] systems. The only solid derivatives obtained from tin(II)–formate solutions were derivatives of the triformatostannate(II) species, and the infrared spectra [7] of these materials were consistent with a pyramidal structure for the $Sn(HCO_2)_3^-$ ion. We now report similar results for the tin(II)–acetate system.

The preparation and properties of pure tin(II) acetate have been described,[8] but there are only two reports [8,9] of the preparation of solid derivatives of complex tin(II)–acetate ions, and there are no reports of detailed studies on the ions present in tin(II)–acetate solutions. During a study of the autoxidation rates of tin(II) acetate and of tin (II) monochloroacetate in solution, Baker and Tompkins [9] investigated the possibility of complex formation and isolated the complexes,$2NH_4Sn(CH_3{\cdot}CO_2)_3,C_6H_6$, $CaSn_2(CH_3{\cdot}CO_2)_6$, and $NH_4Sn(CH_2Cl{\cdot}CO_2)_3$. They reported that all three complexes were hydrolysed by water but gave clear solutions in the presence of an excess of acetate. There is also a report [8] of the precipitation of gelatinous hydrated complex tin(II) acetates by the addition of alkali hydroxide solutions to solutions of tin(II) acetate. The precipitates had the composition $MSn(CH_3{\cdot}CO_2)_3,2H_2O$ (M = Na, K, NH_4), but no further work on their nature and properties was carried out. We have obtained crystalline unsolvated alkali-metal, ammonium, and alkaline-earth triacetatostannate(II) complexes and have studied their properties, and the properties of tin(II)–acetate solutions.

EXPERIMENTAL

(1) *Preparation of the complexes*, $MSn(CH_3{\cdot}CO_2)_3$ (M = NH_4 or K). Pure tin(II) acetate,[8] (24 g. in 100 ml. of 60% w/w aqueous acetic acid) was heated under reflux, in an atmosphere of oxygen-free nitrogen, with an aqueous solution of potassium or ammonium acetate (0·1M in 50 ml. of water). The mixture was concentrated by vacuum rotary evaporation until no more solvent could be removed. The residue, a viscous yellow liquid, was set aside over phosphorus pentoxide in a vacuum desiccator for *ca.* 1—10 days. The white crystalline product was filtered off, washed with ether and benzene, dried *in vacuo* over phosphorus pentoxide, washed with acetone and ether, and dried *in vacuo* over potassium hydroxide. This method gave pure crystalline materials in good yields (50—80%) and was used in all subsequent work. The materials obtained by precipitation techniques were non-crystalline and less pure.

(2) *Preparation of the complexes* $M[Sn(CH_3{\cdot}CO_2)_3]_2$ (M = Ca, Sr, or Ba). Pure tin(II) acetate (24 g. in 100 ml. of 60% w/w aqueous acetic acid) was heated under reflux, in an atmosphere of oxygen-free nitrogen, with an aqueous solution of the alkaline-earth acetate (0·1M in 50 ml. of water). 50—70% of the solvent was then distilled off under nitrogen, and the mixture filtered. The filtrate was allowed to cool slowly and the white crystalline product filtered off, washed with acetone and ether, and dried *in vacuo* over potassium hydroxide. Good yields (40—70%) of pure crystalline material were obtained. This method is similar to that used by Baker and Tompkins [9] to prepare the calcium triacetatostannate(II) complex, except that in the present work equimolar quantities of reagents were used: there appeared to be no advantage in adding an excess of alkaline-earth acetate since this led to contamination of the product.

Analyses.—Stannous and total tin were determined by Donaldson and Moser's method,[10] and potassium was determined gravimetrically as the tetraphenylborate.[11] The ammonium content was estimated by boiling a weighed quantity with an excess of sodium hydroxide solution; the ammonia evolved was collected in an excess of standard acid, and determined by back-titration. Alkaline-earth metal was estimated by dissolving a weighed quantity of the complex in 2N-hydrochloric acid (25 ml.), adjusting the pH to about 8 with 2N-sodium hydroxide solution, and filtering off the precipitated hydrous stannous oxide. The alkaline-earth content of the filtrate plus the washings was then estimated gravimetrically as the oxalate (Ca) or as the sulphate (Sr and Ba). Acetate was determined [12] by treating a known weight of complex with an excess of phosphoric acid, and distilling the liberated acetic acid into an excess of standard alkali solution. The analytical results (for two samples of each complex) are given in Table 1.

TABLE 1

Analytical results

	Found			Found		
	(i)	(ii)	Calc.	(i)	(ii)	Calc.
	$KSn(CH_3{\cdot}CO_2)_3$			$NH_4Sn(CH_3{\cdot}CO_2)_3$		
Sn(II) (%)	35·0	34·5	35·4	37·5	37·3	37·8
Total Sn (%)	34·9	34·5	35·4	37·4	37·3	37·8
Metal/NH_4 (%)	11·5	11·3	11·7	5·68	5·80	5·75
$CH_3{\cdot}CO_2$ (%)	52·4	51·9	52·9	55·8	55·7	56·4
	$Ca[Sn(CH_3{\cdot}CO_2)_3]_2$			$Sr[Sn(CH_3{\cdot}CO_2)_3]_2$		
Sn(II) (%)	37·5	37·4	37·6	35·0	34·9	34·9
Total Sn (%)	37·5	37·4	37·6	34·8	34·8	34·9
Metal (%)	6·36	6·30	6·35	12·4	12·5	12·9
$CH_3{\cdot}CO_2$ (%)	55·6	55·3	56·1	51·8	51·7	52·2
	$Ba[Sn(CH_3{\cdot}CO_2)_3]_2$					
Sn(II) (%)	32·6	32·6	32·6			
Total Sn (%)	32·4	32·5	32·6			
Metal (%)	18·8	18·3	18·9			
CH_3CO_2 (%)	48·0	48·3	48·6			

Solubilities.—The solubilities (Table 2) of all five complexes in 2N-acetic acid and of the alkaline-earth complexes in acetone and ethanol, under oxygen-free nitrogen, were

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[3] J. D. Donaldson and J. D. O'Donoghue, *J. Chem. Soc.*, 1964, 271.

[4] R. R. McDonald, A. C. Larson, and D. T. Cromar, *Acta Cryst.*, 1964, **17**, 1104.

[5] R. S. Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.

[6] J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 1961, 1996.

[7] J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, 1965, **21**, 1043.

[8] J. D. Donaldson, W. Moser, and W. B. Simpson, *J. Chem. Soc.*, 1964, 5942.

[9] E. M. Baker and F. C. Tompkins, *J. Chem. Soc.*, 1952, 4518

[10] J. D. Donaldson and W. Moser, *Analyst*, 1959, **84**, 10.

[11] K. Sporek and A. F. Williams, *Analyst*, 1955, **80**, 347.

[12] W. W. Scott, " Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 4th edn., 1925, vol. 11, p. 1547.

determined by titrating[10] the stannous tin in solution. Because of the rapid decomposition of the complexes in water, their solubility in this solvent could not be estimated.

TABLE 2

Solubility (g./l. of solution) of complex tin(II) acetates

Solvent	Acetone		Ethanol		
Temp.	25°	40°	25°	40°	50°
$Ca[Sn(CH_3{\cdot}CO_2)_3]_2$	0·523	0·677	0·746	3·02	4·08
$Sr[Sn(CH_3{\cdot}CO_2)_3]_2$	0·795	0·960	1·88	2·57	4·83
$Ba[Sn(CH_3{\cdot}CO_2)_3]_2$	0·354	0·433	1·39	1·76	2·07

Solvent	2N-Acetic acid			
Temp.	25°	40°	50°	70°
$NH_4Sn(CH_3{\cdot}CO_2)_3$	40·1	47·1	60·0	108
$KSn(CH_3{\cdot}CO_2)_3$	112	128	186	284
$Ca[Sn(CH_3{\cdot}CO_2)_3]_2$	43·8	54·7	71·2	112
$Sr[Sn(CH_3{\cdot}CO_2)_3]_2$	69·0	71·4	72·7	118
$Ba[Sn(CH_3{\cdot}CO_2)_3]_2$	95·7	261	378	637

Stability of the Complexes.—All five complexes were stable for several months when stored *in vacuo* over potassium hydroxide. On exposure to a moist atmosphere, the alkali-metal and ammonium triacetatostannates(II) were found to be hygroscopic, and were slowly oxidised to yellow non-crystalline compounds containing appreciable quantities of tin(IV).

Under similar conditions the metal(II) triacetatostannates(II) were moderately stable. The most stable complex in moist air was the calcium derivative, which showed no signs of yellowing or of alteration in composition after six months. For each complex the time for the appearance of the first sign of impurity (t_1) and the percentage of stannous tin that had been oxidised after a further time, t_2, are given in Table 3.

TABLE 3

Stability of the complex tin(II) acetates in moist air

$Sn(CH_3{\cdot}CO_2)_3^-$ deriv.	K	NH_4	Ca	Sr	Ba
t_1 (days)	21	7	—	60	30
t_2 (days)	30	42	>200	90	120
$Sn^{(II)}$ oxidised (%) ...	15	80	0	7	15

The thermal stability of the complexes was studied using a melting-point and a vacuum-grid apparatus. The calcium, strontium, and barium bistriacetatostannates(II) decomposed without melting in the ranges 288—295, 278—284, and 262—268°, respectively. The potassium and ammonium complexes melted at 160—161 and 132—133°, respectively, and decomposed slowly above 250°. In each case, the main gaseous products of the decomposition were acetone and carbon dioxide (infrared and chemical characteristics). Tin(II) acetate was also obtained as a sublimate (*X*-ray, infrared, and chemical characteristics) and the residue was a mixture of blue-black tin(II) oxide and the metal acetate (*X*-ray powder data). In the case of ammonium triacetatostannate(II), the decomposition products of ammonium acetate were also detected, and the residue contained only blue-black tin(II) oxide.

Hydrolysis of the Complexes.—All five complexes decomposed to blue-black tin(II) oxide when kept under water. The decomposition was rapid in boiling water and in alkaline solution. Under certain conditions, however, a white hydrolysis product was obtained. When a suspension of complex (1 g.) in alkali-free deaerated distilled water was shaken mechanically for $\frac{1}{2}$ hr., the product was a white powder. This had an *X*-ray-diffraction powder pattern identical with that of hydrous tin(II) oxide[13] but was not as pure as the material obtained by hydrolysis of tin(II) formate[2] under similar conditions.

Studies of the Ions Present in Tin(II)*–Acetate Solutions.*—*Potentiometric studies.* Potentiometric measurements were made on the tin–tin(II) ion couple to determine which ions exist in tin(II)–acetate 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 an agar-agar bride. To prevent oxidation of the bivalent tin the half-cells were kept in a non-oxidising atmosphere. The changes in voltage of the cell on addition of solutions of alkali-metal acetate to one half-cell, and of distilled water to the other, were plotted against the ratio of the concentrations of tin(II) and acetate in the solution. The measurements were carried out for cells containing *ca.* 0·01M-tin(II) sulphate. The graphs showed five significant inflections at tin : acetate ratios of 1 : 1, 1 : 2, 3 : 7, 2 : 5, and 1 : 3, corresponding to the species $Sn(CH_3{\cdot}CO_2)^+$, $Sn(CH_3{\cdot}CO_2)_2$, $Sn_3(CH_3{\cdot}CO_2)_7^-$, $Sn_2(CH_3{\cdot}CO_2)_5^-$, and $Sn(CH_3{\cdot}CO_2)_3^-$.

Polarographic studies. These were carried out with a Tinsley polarograph, a dropping-mercury cathode (drop time 2—3 sec.), and a mercury-pool anode. Pure blue-black tin(II) oxide (0·08—0·8 g./l.) was dissolved in a freshly prepared standard solution of alkali-metal acetate (0·04—0·08%, w/w, 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 (+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 tin species at about −0·5v (against the mercury pool) was plotted against the ratio of the concentrations of tin(II) and acetate in the solutions. The graphs showed five significant breaks, at tin : acetate ratios of 1 : 1, 1 : 2, 3 : 7, 2 : 5, and 1 : 3, corresponding to the species $Sn(CH_3{\cdot}CO_2)^+$, $Sn(CH_3{\cdot}CO_2)_2$, $Sn_3(CH_3{\cdot}CO_2)_7^-$, $Sn_2(CH_3{\cdot}CO_2)_5^-$, and $Sn(CH_3{\cdot}CO_2)_3^-$.

Crystallography.—(*a*) Potassium triacetatostannate(II) consists of colourless, elongated rectangular crystals with cleavage (100) and extinction at 40° to the *c* axis. The crystals show low birefringence and positive elongation; $n = 1{\cdot}63$.

Crystal data: $KSn(CH_3{\cdot}CO_2)_3$, $M = 334{\cdot}9$. Monoclinic $a = 8{\cdot}55 \mp 0{\cdot}02$, $b = 17{\cdot}70 \mp 0{\cdot}04$, $c = 7{\cdot}31 \mp 0{\cdot}02$ Å, $\beta = 104°$, $U = 1140$ Å^3, $D_m = 1{\cdot}97$ (by displacement of organic solvents), $Z = 4$, $D_c = 1{\cdot}95$. Filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about *b*.

(*b*) Ammonium triacetatostannate(II) consists of colourless, elongated rectangular crystals with cleavage (100) and extinction at 40° to the *c* axis. The crystals show low birefringence and positive elongation; $n = 1{\cdot}60$.

Crystal data: $NH_4Sn(CH_3{\cdot}CO_2)_3$, $M = 313{\cdot}9$. Monoclinic, $a = 8{\cdot}61 \mp 0{\cdot}02$, $b = 17{\cdot}70 \mp 0{\cdot}04$, $c = 7{\cdot}52 \mp 0{\cdot}02$ Å, $\beta = 104°$, $U = 1181$ Å^3, $D_m = 1{\cdot}76$ (by displacement of organic solvents), $Z = 4$, $D_c = 1{\cdot}76$. Filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about *b*.

(*c*) Calcium bistriacetatostannate(II) consists of colourless, hexagonal plates with cleavage (010), parallel extinction, and low birefringence; $n = 1{\cdot}63$.

Crystal data: $Ca[Sn(CH_3{\cdot}CO_2)_3]_2$, $M = 631{\cdot}7$. Tetra-

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[13] J. D. Lonaldson and W. Moser, *J. Chem. Soc.*, 1961, 835.

gonal, $a = 8\cdot33 \mp 0\cdot02$, $c = 14\cdot40 \mp 0\cdot03$ Å, $U = 998\cdot8$ Å^3, $D_m = 2\cdot07$ (by displacement of organic solvents), $Z = 2$, $D_c = 2\cdot10$. Filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about a and c.

(*d*) Strontium bistriacetatostannate(II) consists of colourless, hexagonal plates with cleavage (010), parallel extinction, and low birefringence; $n = 1\cdot65$.

Crystal data: $Sr[Sn(CH_3\cdot CO_2)_3]_2$, $M = 679\cdot3$. Tetragonal, $a = 8\cdot44 \mp 0\cdot02$, $c = 14\cdot66 \mp 0\cdot03$ Å, $U = 1044$ Å^3, $D_m = 2\cdot14$ (by displacement of organic solvents), $Z = 2$, $D_c = 2\cdot16$. Filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about a and c.

(*e*) Barium bistriacetatostannate(II) consists of colourless, rhombic plates with cleavage (001), extinction at 6°30′ to the a axis and low birefringence; $n = 1\cdot66$.

TABLE 4

X-Ray-diffraction powder data for the metal(I) and metal(II) triacetatostannate(II) complexes (a, m, w, etc., denote relative intensities)

d (Å)	Index of refl.	*d* (Calc.)	*d* (Å)	*d* (Å)
Potassium triacetatostannate(II)				
8·56s	100	8·55	2·49m	
7·31vs	001	7·31	2·44ms	
6·88s	011	6·79	2·40w	
6·28s	120	6·24	2·34m	
5·83w	030	5·90	2·28m	
5·45w	021	5·63	2·24m	
5·09s	101	5·02	2·20m	
4·78s	111	4·82	2·15ms	
4·21ms	210	4·18	2·13w	
	$\bar{2}01$			
3·90vw	220	3·88	2·08m	
3·58ms	012	3·58	2·04w	
3·48vs	230	3·48	2·01w	
3·25m	150	3·27	1·964m	
3·21m	$\bar{2}02$	3·20	1·931ms	
3·18m	051	3·18		
2·99m	$\bar{2}22$	3·00		
2·92m	231	2·92		
2·89m	$\bar{3}11$	2·88		
2·80m	160	2·80		
2·76m	$\bar{3}21$	2·77		
	132	2·75		
2·72m	320	2·73		
	250			
2·62w	$\bar{3}31$	2·62		
2·53m	070	2·53		
Ammonium triacetatostannate(II)				
8·85ms	020	8·85	2·43m	
7·53s	001	7·52	2·36w	
6·85s	011	6·95	2·28mw	
6·20s	120	6·23	2·20vw	
5·84w	030	5·90	2·17w	
5·54ms	021	5·75	2·12w	
5·11m	101	5·11	2·08vw	
4·50w	121	4·44	2·05w	
4·31mw	200	4·31	2·00vw	
3·84m	041	3·84	1·897vw	
3·66s	$\bar{1}41$	3·65	1·833w	
3·57ms	050	3·54	1·789w	
3·32ms	211	3·33	1·764vw	
3·19vw	$\bar{2}12$	3·19	1·649vw	
	$\bar{1}32$			
3·12w	240	3·11	1·633vw	
3·01w	122	3·01	1·556vvw	
2·93vw	$\bar{3}01$	2·93	1·521vw	
2·84vw	310	2·83	1·510vw	
2·69w	$\bar{1}61$	2·69	1·493vw	
2·59w	025	2·59		
	330			
	$\bar{1}03$			
2·53vw	070	2·53		
2·50vw	003	2·51		
Calcium ditriacetatostannate(II)				
8·53vvs	100	8·33	1·963s	1·455vw
7·18m	002	7·20	1·942w	1·443vw
5·50vs	102	5·45	1·896vw	1·426vw
4·15s	200	4·16	1·862vw	1·392w
3·73vvs	210	3·73	1·832m	1·369vw
3·66vvs	004	3·61	1·804m	1·346vw
	202		1·763vvw	1·316vvw
3·32m	212	3·31	1·702vvw	1·298vw
2·97s	220	2·95	1·675w	1·279vvw
2·75w	300	2·78	1·654w	1·262vw
2·72w	204	2·72	1·631w	1·238vvw
2·64m	310	2·64	1·622vw	1·228vvw
2·59m	302	2·59	1·571w	1·202vw
	214		1·542m	1·187vvw
2·40m	006	2·40	1·518vw	1·178vvw
2·30vs	106	2·30	1·489vvw	1·156vw
2·23m	116	2·22	1·476vvw	1·143vvw
2·08m	206	2·08		1·113vw
	400			
2·02m	410	2·02		
	216			
Strontium ditriacetatostannate(II)				
8·55vs	100	8·44	1·982vs	1·317w
7·34w	002	7·33	1·897m	1·301w
5·56vs	102	5·51	1·837ms	1·266w
4·22s	200	4·22	1·789vw	1·255vw
3·79vvs	210	3·77	1·686m	1·245w
3·69vvs	004	3·67	1·659m	1·207w
3·36m	104	3·36	1·649m	1·194w
	212	3·35	1·595m	1·172vw
3·00s	220	2·98	1·566m	1·159m
2·77m	204	2·77	1·541w	1·121w
2·65ms	310	2·67	1·496w	1·108vw
	214	2·63	1·470m	1·086vw
2·44s	006	2·44	1·449m	1·075vw
2·34s	320	2·34	1·409vw	1·047w
2·32vs	224	2·32	1·397w	1·037vw
2·25s	116	2·26	1·387vw	1·027vw
2·11s	400	2·11	1·365w	1·015vw
	206			
2·05s	410	2·05		
	216			
Barium ditriacetatostannate(II)				
9·91vs	002	9·93	2·39s	1·447vvw
7·48w	100	7·48	2·28m	1·417vw
7·11m	101	7·15	2·21w	1·405vw
6·79w	$10\bar{1}$	6·90	2·15w	1·381vw
6·44m	003	6·56	2·11vw	1·369vw
6·11w	102	6·13	2·05w	1·344vw
5·80s	$10\bar{2}$	5·86	1·973w	1·303vvw
5·05M	111	5·04	1·931w	1·284vvw
4·24m	$11\bar{3}$	4·24	1·891s	1·265vvw
	104		1·844s	1·242vw
4·03m	113	4·07	1·815vw	1·219vvw
	005		1·783vw	1·195vw
3·72s	200	3·72	1·737vw	1·191vw
3·63s	105	3·60	1·693w	1·124vvw
3·53m	114	3·54	1·641w	
3·42m	$10\bar{5}$	3·45	1·585vvw	
3·31m	120	3·31	1·555vvw	
3·22m	$20\bar{3}$	3·21	1·530vw	
3·10m	122	3·10	1·502vvw	
2·82w	$12\bar{4}$	2·82	1·476vvw	
2·67w	$20\bar{5}$	2·69		
2·51w	301	2·51		

Crystal data: $Ba[Sn(CH_3\cdot CO_2)_3]_2$, $M = 729\cdot0$. Triclinic, $a = 7\cdot48 \mp 0\cdot02$, $b = 7\cdot48 \mp 0\cdot02$, $c = 19\cdot90 \pm 0\cdot04$ Å, $\alpha = 88°$, $\beta = 88°$, $\gamma = 90°$, $U = 1109$ Å^3, $D_m = 2\cdot21$ (by displacement of organic solvents), $Z = 2$, $D_c = 2\cdot18$. Filtered Cu-K_α radiation, single-crystal rotation and Weissenberg photographs about a and b.

Table 4 contains the *X*-ray-diffraction powder data, obtained by using an **11·64**-cm. camera with Cu-K_α radiation: The *d*-spacings longer than 2·50 Å have been indexed for the potassium, ammonium, and barium complexes, and the spacings longer than 2·00 Å for the calcium and strontium complexes.

DISCUSSION

In view of the small energy separation [14] between the *s*- and *p*-orbitals of tin(II), all the *p*-orbitals should, if possible, act as acceptor orbitals towards a suitable ligand. Complexes based on sp^3 hybrids should thus be very stable. The inclusion of appreciable *d*-character in the tin(II)–ligand bonds depends upon the *s*–*d* as well as the *s*–*p* separation and would appear to be less likely. These views are confirmed by this study on the tin(II)–acetate system. There is considerable evidence for the stability of the triacetatostannate(II) ion, but no evidence for the existence of complexes of higher co-ordination. The fact that there is evidence for polynuclear complexes of the type $Sn_n(CH_3\cdot CO_2)_{2n+1}$ ($n = 2$ or 3) suggests that the stable three-co-ordination is maintained even in the presence of insufficient ligand to complex all of the metal as the triacetatostannate(II) ion. Moreover, the only solid derivatives obtained from tin(II)–acetate solutions are derivatives of the triacetatostannate(II) species. An infrared study [7] of the solid complex tin(II) acetates showed that the acetate ion is a monodentate ligand towards tin(II), and the spectra were consistent with the pyramidal structure expected for the $Sn(CH_3\cdot CO_2)_3^-$ ion.

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