Acetates and Acetato-complexes. Part 1. Preparation of Acetato-complexes and Conductimetric Studies in the Acetic Anhydride Solvent System

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Preparations using acetic anhydride as solvent are reported for $B_2O(O_2CMe)_4$, $AlCl(O_2CMe)_2$, $[TiO(O_2CMe)_2]$, $Ti(O_2CMe)_4{\cdot}2MeCO_2H$, and $M(O_2CMe)_4$ (M = Zr, Si, Ge, Sn, or Pb). Conductimetric titrations against potassium or tetramethylammonium acetate indicate the formation of $[B_2O(O_2CMe)_5]^-$, $[B_2O(O_2CMe)_6]^{2-}$, $[M_2(O_2CMe)_9]^-$, $[M(O_2CMe)_5]^-$, and $[M(O_2CMe)_6]^{2-}$ (M = Si, Ge, Sn, and Pb); the salts $Na[B_2O(O_2CMe)_5]$, and $K_2[M(O_2CMe)_6]$ (M = Si, Ge, Sn, or Pb), $K_2[Sn(O_2CMe)_6]{\cdot}(MeCO)_2O$, and $[NMe_4][Sn(O_2CMe)_5]$ have been isolated. Evidence for the nature of the solvent system is discussed.

THE properties of anhydrous acetates and particularly acetato-complexes remain little known, because they are usually very readily hydrolysed. In this series of papers we report preparative, spectroscopic, and structural studies of typical compounds, mainly of Group 4 elements. In this first paper we report the preparation and the behaviour as Lewis acids of a series of acetato-complexes in liquid anhydrous acetic anhydride.

With a good liquid range (—73 to 139 °C), fairly high dielectric constant (22.1 at 20 °C), and the ability to dissolve a wide range of inorganic and organic compounds, acetic anhydride is potentially a useful general solvent; however, its high reactivity means that most compounds are converted into acetates or acetato-complexes. The reported conductivity[1] of 2.38×10^{-8} S cm^{-1} (20 °C) has been attributed to autoionization, either as in (i) or (ii), but there must remain some doubt

$$(MeCO)_2O \rightleftharpoons MeCO^+ + MeCO_2^- \qquad (i)$$

$$2(MeCO)_2O \rightleftharpoons (MeCO)_3O^+ + MeCO_2^- \qquad (ii)$$

that the reported figure is the true value because of the enormous effect of trace amounts of moisture on the conductivity. Studies of reactions in acetic anhydride by Jander and Surawski[1,2] and by Paul and his co-workers[3] have been interpreted in the light of this ionization in terms of the solvent-system model.[4] This identifies the characteristic solvent reaction as being neutralization between an acid which produces the solvent cation (here acetyl, free or solvated) and a base which produces the characteristic anion (acetate). However, tracer experiments[5] show that exchange is slow between acetic anhydride and either sodium acetate or acetyl chloride. This suggests that the autoionization mechanism is likely to be unimportant in this solvent. Alternatively, the co-ordination model of Drago and Purcell[6] can be applied, placing the emphasis instead on solvent donation followed by solute ionization. A critical difference between the two theories lies in the behaviour of Lewis acids. Iron(III) chloride (for example) dissolves in acetic anhydride to give conducting solutions and these can be titrated with organic bases, *e.g.* pyridine, to a 1 : 1 end-point.[3a] The reactions involved on the solvent-system theory are (1) and (2),

$$FeCl_3 + (MeCO)_2O \longrightarrow MeCO^+ + [FeCl_3(O_2CMe)]^- \qquad (1)$$

$$(MeCO)_2O + B \longrightarrow (MeCOB)^+ + MeCO_2^- \qquad (2)$$

generation of $MeCO^+$ identifying $FeCl_3$ as an acid which is then neutralised as in (3). On the co-ordination

$$(MeCOB)^+ + [FeCl_3(O_2CMe)]^- + MeCO^+ + MeCO_2^- \longrightarrow 2(MeCO)_2O + B{:}FeCl_3 \qquad (3)$$

model, however, the solvent ionization and its reverse do not participate. Solution of $FeCl_3$ produces the reactions (4) and (5).

$$FeCl_3 + (MeCO)_2O \rightleftharpoons FeCl_3{:}O(OCMe)_2 \rightleftharpoons [FeCl_2{:}O(OCMe)_2]^+ + Cl^- \qquad (4)$$

$$FeCl_3 + Cl^- \rightleftharpoons [FeCl_4]^- \qquad (5)$$

To test the two theories, we examined the spectra of solutions of $FeCl_3$ (anhydrous, sublimed under vacuum at 150 °C) in acetic anhydride. The i.r. spectrum showed no absorption in the range 2 100—2 300 cm^{-1} in

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which $MeCO^+$ has a strong characteristic peak. The u.v. spectrum of a very dilute solution showed the characteristic absorption of $[FeCl_4]^-$ with a peak at 362 nm. Thus, equation (1) is excluded, and (5) and the co-ordination theory is confirmed.

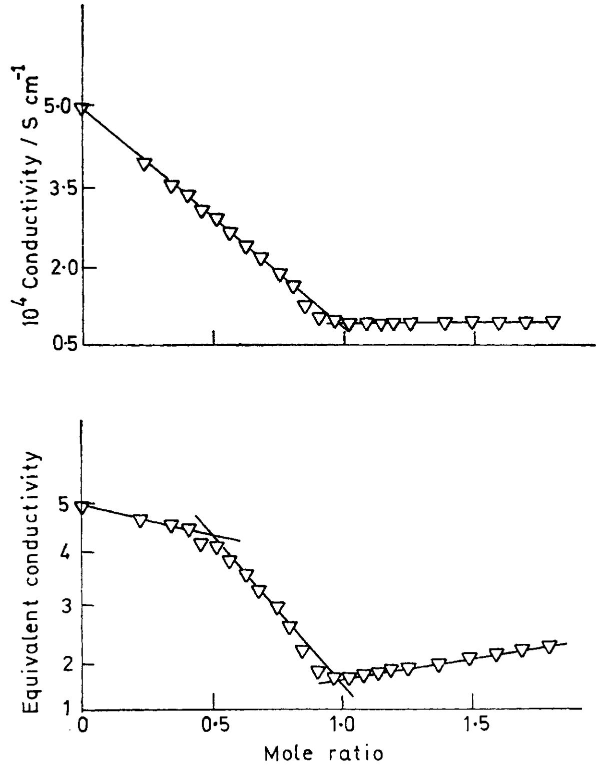

FIGURE 1 Conductimetric titration of $B_2O(O_2CMe)_4$ against $K[O_2CMe]$

TABLE 1

Summary of end-points found in conductimetric titrations between anhydrous acetates of some Group 3 and Group 4 elements and soluble univalent acetates in acetic anhydride

		End-points				
		Base : Acid				Precipitate
Acid	Base	0.5 : 1	1 : 1	2 : 1	θ_c/°C	formation
$B_2O(O_2CMe)_4$	$K[O_2CMe]$		Yes		0	None
$Si(O_2CMe)_4$	$K[O_2CMe]$	Yes	Yes	Yes	Room	White
$Ge(O_2CMe)_4$	$K[O_2CMe]$	Yes	Yes	Yes	0	White
	$[NMe_4][O_2CMe]$	Yes	Yes	Yes	0	Faint white
$Sn(O_2CMe)_4$	$K[O_2CMe]$	Yes	Yes	Yes	0	White
	$[NMe_4][O_2CMe]$	Yes	Yes	Yes	0	Faint white
$Pb(O_2CMe)_4$	$K[O_2CMe]$	Yes	Yes	Yes	0	None
	$[NMe_4][O_2CMe]$	Yes	Yes	Yes	0	Faint white

We used the high solvolytic power of acetic anhydride to prepare anhydrous acetates or related compounds of boron, aluminium, titanium, zirconium, germanium, tin, and lead. Most of these acetates can function as acetate acceptors, *i.e.* Lewis acids, and we performed conductimetric titrations between $B_2O(O_2CMe)_2$, $Si(O_2CMe)_4$, $Ge(O_2CMe)_4$, $Sn(O_2CMe)_4$, and $Pb(O_2CMe)_4$ and the bases potassium acetate and tetramethylammonium acetate in the solvent. The former are nominally acids according to the solvent-system theory, for example as in (6).

$$M(O_2CMe)_4 + (MeCO)_2O \longrightarrow MeCO^+ + [M(O_2CMe)_5]^- \quad (6)$$

Our results are summarized in Table 1 and typical conductimetric titration curves as shown in Figures 1—5. From the clear breaks in these curves it is clear that the equilibria (7) lie well to the right. However, solutions containing excess of $M(O_2CMe)_n$ are all poorly conducting, and this is further evidence that acid behaviour according to equation (6) and solvent ionization are unimportant. Clearly, the titrations can be well explained by equations similar to (7) without involvement of the solvent. Reaction (7) can also be carried out preparatively, and we isolated from their solutions in acetic anhydride, and characterized by analysis and physical measurements, samples of $K_2[Si(O_2CMe)_6]$, $K_2[Ge(O_2CMe)_6]$, $K_2[Sn(O_2CMe)_6]$, $K_2[Pb(O_2CMe)_6]$, and $[NMe_4][Sn(O_2CMe)_5]$. We also prepared in this way the already well characterized $Na[B_2O(O_2CMe)_5]$.

$$M(O_2CMe)_n + MeCO_2^- \rightleftharpoons [M(O_2CMe)_{n+1}]^- \quad (7)$$

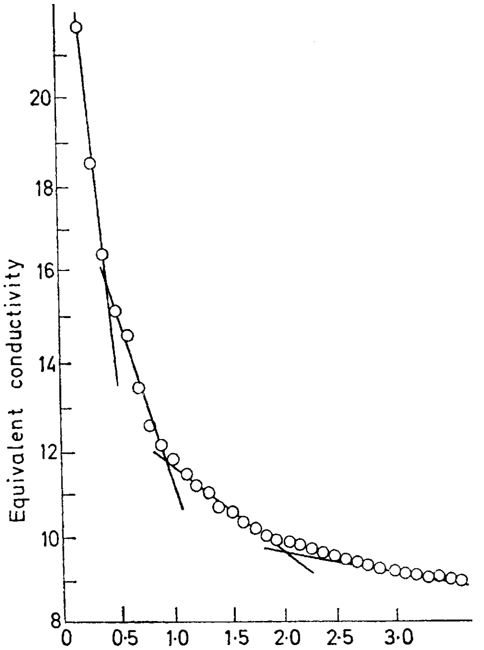

FIGURE 2 Conductimetric titration of $Si(O_2CMe)_4$ against $K[O_2CMe]$

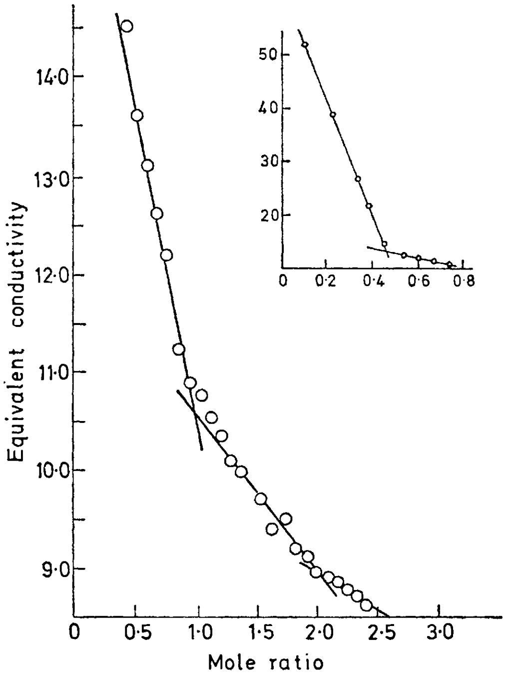

FIGURE 3 Conductimetric titration of $Ge(O_2CMe)_4$ against $K[O_2CMe]$. Inset, first end-point; main diagram, second and third end points. The two portions are shown with different scales for clarity

EXPERIMENTAL

Apparatus and Procedures.—Moisture was rigorously excluded at all stages. Materials were handled and solutions prepared in a Gallenkamp MA150 dry-box (P_4O_{10} desiccant), provided with filter-pump suction (protected by a silica gel–molecular sieve column). A beaker of K[OH] pellets was kept in the dry-box to absorb acid vapours. Most preparative reactions were performed on a conventional vacuum system, greased with Apiezon-N. Conductimetric titrations were made in a conductivity cell connected to a burette by Polythene tubing; both the cell and burette were protected by silica-gel guard tubes. The cell was small enough to be filled in the dry-box, and also to fit into a large Dewar vessel; the solutions could then be stirred magnetically (with a sealed stirrer; Rank Bros.,

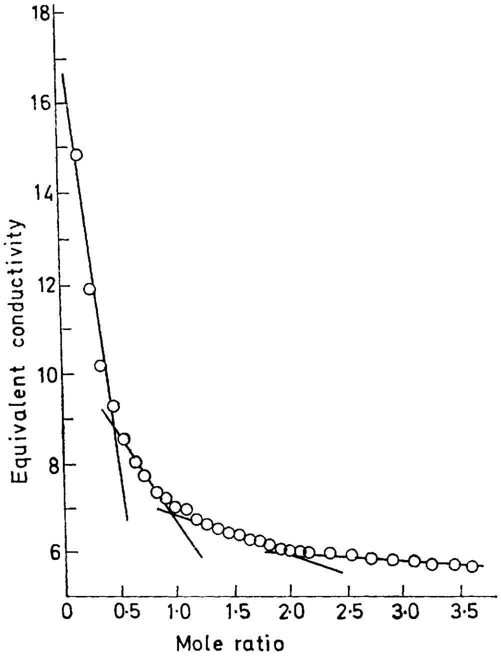

FIGURE 4 Conductimetric titration of $Sn(O_2CMe)_4$ against $K[O_2CMe]$

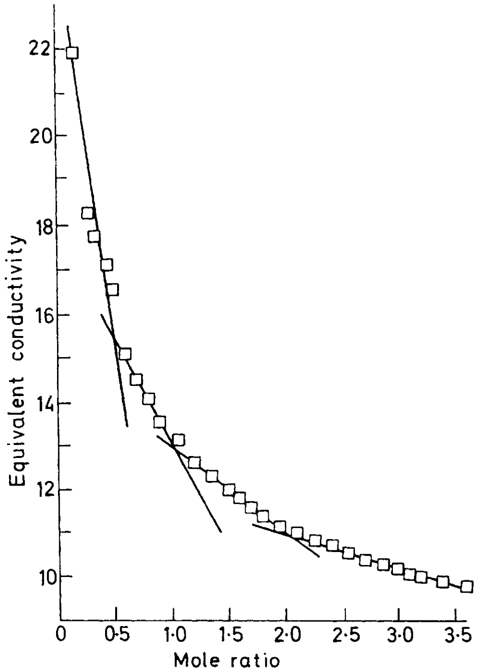

FIGURE 5 Conductimetric titration of $Pb(O_2CMe)_4$ against $K[O_2CMe]$

Bottisham). Most titrations were made at 0 °C, which was found to sharpen the end-points, presumably because it shifts the dissociation equilibrium (7) towards the complex ions.

The electrodes were platinum discs (diameter *ca.* 1 cm) placed 1 cm apart. The cell constant was determined from the conductivity of 0.02 mol dm^{-3} solutions of potassium chloride; it was plotted as a function of the volume in the cell and the appropriate value was used to calculate the equivalent conductivity of particular solutions. Plots of equivalent conductivity were preferable to those of conductivity because the change of dilution accompanying titration was substantial in some titrations involving acetates of low solubility (*cf.* Figure 1). Conductivities were measured with a Wayne–Kerr B2221 Universal Bridge.

Infrared spectra of solutions were recorded on a Perkin-Elmer model 457 spectrophotometer. The instrument was calibrated with a polystyrene film and found to be accurate to ± 1 cm^{-1}. Ultraviolet and visible spectra of solutions were recorded on a Unicam SP 800 spectrophotometer using silica cells.

Materials.—To purify acetic anhydride, particularly from acetic acid (formed by hydrolysis), the procedure of Calcott *et al.*[7] was used. Immediately prior to use, the anhydride was redistilled from P_4O_{10}. The conductivity of a sample was found to be 1.17×10^{-7} S cm^{-1} (*cf.* 2.3×10^{-8}, ref. 1). Other solvents were dried with molecular sieves. Tetramethylammonium acetate was prepared by mixing equimolar quantities of tetramethylammonium chloride and thallium(I) acetate in $(MeCO)_2O$ and stirring at 30—40 °C under reflux for 1 h. After filtering off thallium(I) chloride and concentrating the solution to crystallizing point, tetramethylammonium acetate was filtered off, washed with dry diethyl ether, and stored *in vacuo* (Found: $[NMe_4]^+$, 55.2; $MeCO_2^-$, 44.2. $C_6H_{15}NO_2$ requires $[NMe_4]^+$, 55.6; $MeCO_2^-$, 44.4%).

Analyses.—Acetate was determined by dissolving samples in 3 mol dm^{-3} sulphuric acid, adding excess of 28% orthophosphoric acid, distilling into standard sodium hydroxide, and back titrating with standard H_2SO_4. Potassium was determined by atomic-absorption spectroscopy. Chloride was determined by Volhard's method. Boron (after hydrolysis to boric acid) was titrated with standard alkali in the presence of excess of mannitol, using phenolphthalein as indicator. Lead was precipitated as PbO_2, heated with KI solution, and then titrated with $K[IO_3]$.[8] Other elements were determined gravimetrically: aluminium with quinolin-8-ol, titanium with 5,7-dibromoquinolin-8-ol, silicon and tin as their dioxides, and germanium by the cinchonine method.[9] The tetramethylammonium cation was determined gravimetrically as its tetraphenylborate. Carbon, hydrogen, and nitrogen analyses were by Alfred Bernhardt.

RESULTS

Boron.—Although the formation of boron triacetate has been reported from the reaction of orthoboric acid with acetic anhydride, later work[10] has shown that the only product is μ-oxo-bis(diacetatoboron), $B_2O(O_2CMe)_4$. This was confirmed in the present work, m.p. 148 °C as ref. 10 (Found: B, 7.85; $MeCO_2^-$, 86.2. $C_8H_{12}B_2O_9$ requires B, 7.9; $MeCO_2^-$, 86.3%).

The conductimetric titration of potassium acetate with $B_2O(O_2CMe)_4$ (Figure 1) showed a clear break at a 1 : 1 mol ratio, corresponding to the formation of $K[B_2O(O_2CMe)_5]$. There was also a less definite break at 0.5 : 1, suggesting that $K_2[B_2O(O_2CMe)_6]$ may also exist. The sodium salt of $[B_2O(O_2CMe)_5]^-$ was prepared.[11]

Aluminium.—The reaction of aluminium trichloride with acetic anhydride has been reported[12] to yield aluminium triacetate, but we found that under a variety of conditions the product was invariably diacetatochloroaluminium (Found: Al, 14.95; Cl, 19.55; $MeCO_2^-$, 65.5. $C_4H_6AlClO_4$ requires Al, 14.95; Cl, 19.65; $MeCO_2^-$, 65.3%). Aluminium triacetate was prepared successfully by the method of Pande and Mehrotra[13] (Found: Al, 13.1; $MeCO_2^-$, 86.9. $C_6H_9AlO_6$ requires Al, 13.25; $MeCO_2^-$, 86.75%). An attempted conductimetric titration of $Al(O_2CMe)_3$ was unsuccessful because it was not sufficiently soluble in $(MeCO)_2O$.

Titanium.—The preparation of titanium tetra-acetate was attempted by refluxing for several hours a mixture of $(MeCO)_2O$ and titanium ethoxide (K and K Laboratories Inc.) in a 4 : 1 mol ratio. A white product separated on cooling and was filtered off and dried *in vacuo*; however, analysis showed this to be $[TiO(O_2CMe)_2]$ (Found: Ti, 25.7, 26.2; $MeCO_2^-$, 64.0, 64.1. $C_4H_6O_5Ti$ requires Ti, 25.8; $MeCO_2^-$, 64.3%). The literature[14] preparation of $Ti(O_2CMe)_4 \cdot 2MeCO_2H$ was repeated successfully, m.p. 320°, turning brown at 250 °C (Found: Ti, 12.2; $MeCO_2^-$, 87.2. $C_{10}H_{20}O_{12}Ti$ requires Ti, 11.9; $MeCO_2^-$, 87.7%). On heating the yellow crystalline solid to 30 °C *in vacuo* it turned white, but the i.r. spectrum still revealed the characteristic absorptions of free acetic acid.

Zirconium.—A modification of the literature method[15] was used for the preparation of zirconium tetra-acetate in order to reduce the vigour of the reaction. Pure sublimed zirconium tetrachloride (2 g) was added to dry benzene (20 cm^3) in a stoppered flask (100 cm^3) in the dry-box. Glacial acetic acid (24.2 cm^3) was then added, dropwise with stirring; some heat was evolved, but there was no vigorous gas evolution. The flask was then removed from the dry-box and heated gently under reflux overnight. On evaporating the clear solution, white crystals were formed which were recrystallized from benzene, m.p. 160 °C (Found: Zr, 28.0. $C_8H_{12}O_8Zr$ requires Zr, 27.9%).

Silicon.—Among various reported methods for the preparation of silicon tetra-acetate, only that of Udovenko and Fialkov[16] gives good yields, m.p. 110 °C as ref. 17 (Found: Si, 10.4; $MeCO_2^-$, 89.35. $C_8H_{12}O_8Si$ requires Si, 10.6; $MeCO_2^-$, 89.4%).

Germanium.—The tetra-acetate was prepared by the

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reaction of germanium tetrachloride with thallium(I) acetate. A solution of germanium tetrachloride (10 g, 0.104 mol) in $(MeCO)_2O$ (20 cm^3) was added dropwise to a suspension of thallium(I) acetate (50 g, 0.19 mol) in $(MeCO)_2O$ (100 cm^3) in a three-necked flask (150 cm^3) equipped with a stirrer and a reflux condenser. The mixture was stirred at 80 °C for 15 min and then at room temperature for 45 min. After filtration, and evaporation to a volume of 10 cm^3, colourless needles of germanium tetra-acetate separated. These were filtered off, washed with dry diethyl ether, and dried *in vacuo*, m.p. 156 °C (Found: Ge, 24.1; $MeCO_2^-$, 75.4. $C_8H_{12}GeO_8$ requires Ge, 23.5; $MeCO_2^-$, 76.5%).

Tin.—Tin(IV) acetate was prepared [18] from thallium(I) acetate (16.8 g, 0.064 mol) and tin(IV) iodide (10 g, 0.013 mol) in $(MeCO)_2O$ (100 cm^3). The mixture was stirred at 80 °C for 90 min and at room temperature for 30 min. Filtration and concentration of the filtrate to 50 cm^3 gave white crystals; on further concentration pale yellow crystals were produced. Recrystallization from $(MeCO)_2O$ provided white crystals of tin(IV) acetate, m.p. 253 °C (Found: Sn, 33.9; $MeCO_2^-$, 67.1. $C_8H_{12}O_8Sn$ requires Sn, 33.4; $MeCO_2^-$, 66.6%).

Lead.—Lead tetra-acetate was prepared [19] by the reaction of red lead with acetic acid containing $(MeCO)_2O$, m.p. 180 °C (Found: Pb, 54.1; $MeCO_2^-$, 45.9. $C_8H_{12}O_8Pb$ requires Pb, 53.9; $MeCO_2^-$, 46.1%).

Conductimetric Titrations.—Titrations of potassium acetate or tetramethylammonium acetate (for Ge, Sn, or Pb) with the tetra-acetates of silicon, germanium, tin, and lead gave very similar results (Figures 2—5). All showed distinct breaks at mole ratios $[MeCO_2^- : M(O_2CMe)_4$ of 0.5 : 1, 1.0 : 1, and 2.0 : 1, corresponding to the formation of $[M_2(O_2CMe)_9]^-$, $[M(O_2CMe)_5]^-$, and $[M(O_2CMe)_6]^{2-}$. Slight white precipitates were seen at the end of all the titrations, except that of potassium acetate with lead tetra-acetate.

Complex Acetates.—The potassium complexes of silicon, germanium, tin, and lead acetates were prepared by dissolving potassium acetate (14 g, 0.1 mol) and the appropriate tetra-acetate (0.05 mol) in $(MeCO)_2O$ (10 cm^3). The mixtures were warmed at 50—60 °C for 30 min, and the white solids obtained on cooling were filtered off and washed with $(MeCO)_2O$ and diethyl ether. All the products were extremely moisture sensitive, liberating acetic acid very readily. The analyses (Table 2, 1—3) confirm the formation of *potassium hexa-acetatometallates*, $K_2[O_2CMe)_6]$, except for Sn^{IV} which gives an *acetic anhydride solvate*, $K_2[Sn(O_2CMe)_6]\cdot(MeCO)_2O$ which was desolvated *in vacuo*.

TABLE 2

Analyses (%) of complex acetates,* $K_2[M(O_2CMe)_6]$

	M	K	M	$MeCO_2^-$
1	Si	16.4 (17.0)	5.4 (6.7)	77.6 (77.9)
2	Ge	14.9 (15.5)	13.5 (14.4)	70.6 (70.1)
3	Pb	11.4 (12.2)	33.1 (32.4)	54.6 (55.4)
4	Sn (solv.)	11.6 (12.0)	16.6 (18.2)	69.1 (68.9)
5	Sn	13.8 (14.2)	21.2 (21.5)	65.0 (64.3)

* Calculated values for $C_{12}H_{18}K_2MO_{12}$(1—3,5) are given in parentheses, and for $C_{16}H_{24}K_2O_{15}Sn$ (4) with $(MeCO)_2O$ contributing $2MeCO_2^-$.

The preparation of tetramethylammonium hexa-acetatostannate(IV) was attempted directly by warming a mixture of $[NMe_4]Cl$ (2.2 g, 0.023 mol), silver(I) acetate (10.01 g, 0.06 mol), tin(IV) iodide (6.26 g, 0.008 4 mol) in $(MeCO)_2O$ (60 cm^3) to 40—60 °C for 30 min [equation (8)]. After

$$2[NMe_4]Cl + SnI_4 + 6Ag(O_2CMe) \longrightarrow [NMe_4]_2[Sn(O_2CMe)_6] + 2AgCl + 4AgI \quad (8)$$

filtering off the yellow precipitate of mixed silver halides, and concentrating the solution, large transparent needle-shaped crystals were formed; these were carefully recrystallized from $(MeCO)_2O$, washed with the anhydride and then with diethyl ether, and stored *in vacuo*. However, analysis showed them to be *tetramethylammonium penta-acetatostannate*(IV), and presumably this is the least-soluble species in the system, m.p. 127 °C (Found: C, 32.5; H, 6.2; N, 3.1; Sn, 24.6. $C_{16}H_{30}NO_{12}Sn$ requires C, 34.4; H, 5.5; N, 2.9; Sn, 24.3. $C_{20}H_{42}N_2O_{12}Sn$ requires C, 38.7; H, 6.8; N, 4.5; Sn, 19.1%).

Spectroscopic investigation of the hexa-acetato-ions (see following paper) strongly suggested that the complex acetate ions of silicon and germanium were chemically similar, but that they differed from those of tin and lead. In order to confirm this, *X*-ray powder photographs were taken of each complex (as Nujol mulls, to avoid hydrolysis) with a Nonius–Guinier camera. This showed that $K_2[Si(O_2CMe)_6]$ and $K_2[Ge(O_2CMe)_6]$ were isomorphous (Table 3), but that the stannate and plumbate were not isomorphous with them or each other.

TABLE 3

d Values for potassium hexa-acetato-silicate and -germanate from films calibrated with monomethyl ammonium alum; $a_0 = 12.504$ Å

M = Si		M = Ge	
d	*I*	*d*	*I*
12.182	s	12.182	s
9.817	w	9.817	w
7.929	vw	7.893	w
7.075	vw	7.064	vw
6.627	vvw	6.651	vw
6.232	w	6.254	w
6.001	w	5.941	w
5.604	vw	5.622	vw
4.491	vvw	4.382	vw
4.178	vvw	3.992	w
3.948	m	3.931	m
3.767	w	3.751	w
3.616	vw	3.630	vw
3.336	s	3.463	s
3.171	vw	3.201	w
3.156	m	3.156	w
3.061	w	3.051	w
3.001	vw	3.001	vw
2.910	vvw	2.905	vvw
2.825	vvw	2.820	vvw

s = Strong, m = medium, w = weak, and v = very.

One of us (V. M. T.) thanks the S.R.C. for a studentship.

[6/635 *Received, 2nd April*, 1976]

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