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### Double Acetates of Pb(IV) & Sn(IV) Acetates

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Received 11 September 1975; accepted 10 November 1975

Double acetates of composition  $M_2[M(OAc)_6]_x \cdot Ac_2O$  of Sn(IV) and Pb(IV) acetates and acetates of alkali metal, thallium and ammonium acetates have been isolated from acetic anhydride. Molar conductance, molecular weight and IR studies reveal two types of acetate coordination.

IN continuation of our studies on acetic anhydride as a polar solvent<sup>1-6</sup>, we report now the preparation and characterization of the double acetates of Pb(IV) and Sn(IV) acetates and their behaviour in acetic anhydride.

Tetra-acetates of lead and tin are fairly soluble in acetic anhydride and the resultant solutions are non-conducting. The solubility of the acetates and the conductance of the solution increase enormously if ammonium or thallous acetate or the acetates of alkali metals are added to the solutions. Conductometric titrations between the tetra-acetates of tin and lead and the alkali metal acetates in acetic anhydride show two breaks in the conductance—composition curves corresponding to the formation of the complexes of composition  $M(OAc)_5$  and  $M(OAc)_6$ . When solvent ether was added to these solutions, compounds of the composition  $M_2M(OAc)_6 \cdot xAc_2O$ , where  $x$  has a value between two and six, separated out. Stoichiometric compositions of these compounds have been determined by elemental analysis (Table 1). The solvent molecules are lost on heating the compounds to 150° under reduced pressure indicating that the solvent molecules are held loosely within the crystal lattice.

The compounds are stable in dry atmosphere but, when exposed to moisture, lead compounds become black in colour while the tin compounds become liquids. All the compounds have fairly high melting points. These are insoluble in benzene, carbon tetrachloride and chloroform but are soluble in nitromethane, nitrobenzene, acetonitrile and acetone. Molar conductance values of the millimolar solutions in nitrobenzene show them to be ionic in nature and the molecular weight determinations show them to be monomeric. Conductometric titrations of the compounds against hydrogen chloride in nitrobenzene show two breaks in the conductance-composition curves corresponding to the stepwise replacement of two acetates by chloride ions. Further addition of hydrogen chloride to the solution does not result in any significant change in the conductance suggesting that, in these complexes, two acetate groups are different from the four acetate groups and there is a complete analogy between  $SnCl_6^{2-}$  and  $Sn(OAc)_6^{2-}$  species in solution.

TABLE 1—MELTING POINTS, ANALYTICAL AND CONDUCTANCE DATA OF DOUBLE ACETATES OF TIN(IV) AND LEAD(IV)

Compound	m.p. (°C)	Metal (%)		$\Lambda_M$ (nitrobenzene) (ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> )
		Found	Calc.	
$Li_2[Sn(OAc)_6]6Ac_2O$	100*	10.60	10.80	33.5
$Na_2[Sn(OAc)_6]4Ac_2O$	136*	13.05	12.80	39.1
$K_2[Sn(OAc)_6]4Ac_2O$	Above 200	12.05	12.38	27.6
$(NH_4)_2[Sn(OAc)_6]4Ac_2O$	39	13.24	12.94	24.3
$Li_2[Pb(OAc)_6]6Ac_2O$	97	17.10	17.43	26.4
$Na_2[Pb(OAc)_6]4Ac_2O$	87*	20.04	20.39	29.8
$K_2[Pb(OAc)_6]4Ac_2O$	133	20.06	19.77	36.2
$(NH_4)_2[Pb(OAc)_6]4Ac_2O$	60	20.21	20.59	21.7

\*Melted with decomposition.

In the present compounds, there are two distinct types of acetate groups showing two types of asymmetric and symmetric carboxylate stretching frequencies. The absence of bands in the region 1590-1610 cm<sup>-1</sup> rules out the possibility of the existence of any bridging acetate group in these compounds<sup>7</sup>. This is in agreement with their non-polymeric nature as indicated by molecular weight studies. Two absorption bands at 1570 and 1350 cm<sup>-1</sup> assigned to  $\nu_{OCO_{as}}$  and  $\nu_{OCO_s}$  modes of the carboxylate group are observed which may be attributed to the unidentate nature of the acetate group<sup>8,9</sup>. The separation of the symmetric and asymmetric stretching mode of the carboxylate group is  $\sim 220$  cm<sup>-1</sup> suggesting that these acetate groups are covalently bonded to a good extent. The other symmetric and asymmetric carboxylate stretching modes are observed in the lower frequency region and the separation of the two modes is  $\sim 150$  cm<sup>-1</sup> (similar to that present in sodium acetate) which indicates a fair degree of ionic character.

The double acetates show an initial loss of alkali metal acetate during thermal decomposition and subsequently follow the same trend as proposed by Rao *et al.*<sup>10</sup>. There is no evidence to show the formation of oxycarbonate or lower acetates.

Thanks are due to Prof. C. C. Addison of the University of Nottingham for useful discussions.

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