

THERMAL AND ELECTRICAL STUDIES OF SILICON PHTHALOCYANINE DICHLORIDE AND TRIS(2,4-PENTANEDIONATO)SILICON CHLORIDE HYDROCHLORIDE

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ABSTRACT

Thermal analysis studies using thermogravimetry and differential thermal analysis have been carried out on the compounds tris(2,4-pentanedionato)silicon chloride hydrochloride and silicon phthalocyanine dichloride. The compound tris(2,4-pentanedionato)silicon chloride hydrochloride undergoes an endothermic reaction with loss of hydrogen chloride to give tris(2,4-pentanedionato)silicon chloride. The compounds tris(2,4-pentanedionato)silicon chloride and silicon phthalocyanine dichloride both undergo exothermic reactions with loss of the organic ligand and halogen to give silicon(IV) oxide. All of the materials exhibit a small departure from Ohm's law which is attributed to space charge effects. Under a field of 1×10^4 V m⁻¹, the conductivities are all in the range 7×10^{-8} – 1.5×10^{-7} Ω⁻¹ m⁻¹. The temperature dependence of conductivity is anomalous.

INTRODUCTION

Electronic devices are becoming steadily smaller; present-day computers are based on the silicon chip. Chemists frequently investigate silicon compounds to gauge their carrier mobilities. The skill in producing compounds having large mobilities is in choosing suitable combinations of ligands attached to one or more silicon atoms. In this work we report the thermal decomposition and electrical conductivity studies of silicon phthalocyanine dichloride [Si(C₃₂H₁₆N₈)Cl₂] and tris(2,4-pentanedionato)silicon chloride hydrochloride, [Si(C₅H₇O₂)₃]Cl · HCl. The thermal stability and electrical conductivity of tris(2,4-pentanedionato)silicon chloride, [Si(C₅H₇O₂)₃]Cl,

which is itself a thermal decomposition product of $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl} \cdot \text{HCl}$, is also reported.

EXPERIMENTAL

Preparation of compounds

$[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl} \cdot \text{HCl}$

20 g of silicon tetrachloride were dissolved in 50 cm³ of dry benzene. The solution, along with a PTFE-covered magnetic stirrer, was placed in a 250 cm³ two-necked flask equipped with a dropping funnel, containing 12 cm³ of 2,4-pentanedione in 30 cm³ of dry benzene, and a reflux condenser, both fitted with calcium chloride drying tubes. The pentanedione–benzene solution was added drop-wise from the dropping funnel to the silicon tetrachloride solution in benzene in the flask with constant stirring. The mixture was refluxed for 30 min. A white solid was deposited which was removed by filtration, washed with ether and dried over calcium chloride in a vacuum desiccator [1].

$[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl}$

The compound $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl} \cdot \text{HCl}$ was heated on a thermobalance at a fixed temperature of 112° C until a constant weight was obtained.

$[\text{Si}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2]$

The compound was supplied by the Aldrich Chemical Company.

Elemental analyses

- (1) The silicon content in the complex was obtained gravimetrically [2].
- (2) The carbon and hydrogen analyses were obtained using a Carlo Erba elemental analyser.
- (3) The chloride content of each complex was determined gravimetrically [3].

Thermal analysis

Using a Stanton–Redcroft Model STA 781 thermobalance, thermogravimetric and differential thermal analysis curves were obtained for each of the compounds over the temperature range 20–1000° C whilst their temperatures were raised in static air at a rate of 10° C min⁻¹.

Electrical measurements

Room temperature current–voltage characteristics and conductivity–temperature characteristics were obtained for the compounds in the form of

compressed pellets. These pellets were prepared as discs 13 mm in diameter and thicknesses in the range 1.1–1.5 mm and were provided with conducting silver paint electrodes applied concentrically on the flat faces of each disc. The method of preparation of the disc-shaped pellets and the method of obtaining the d.c. electrical measurements have been previously described [4].

RESULTS AND DISCUSSION

The experimental analysis data for each of the compounds are listed in Table 1. These analyses agree with the respective predicted values as calculated from the suggested stoichiometry for each compound.

The compound silicon phthalocyanine dichloride consists of bridging chlorine atoms between stacked silicon phthalocyanine ring systems [5], while the compound tris(2,4-pentanedionato)silicon chloride hydrochloride has the silicon atom in an octahedral environment of oxygen atoms [1].

The results of the thermogravimetry measurements are given in Figs. 1 and 2 and in Table 2. Thermal decomposition studies show that tris(2,4-pentanedionato)silicon chloride hydrochloride undergoes an endothermic reaction at 90 °C with loss of hydrogen chloride to form tris(2,4-pentanedionato)silicon chloride. This compound subsequently decomposes exothermically at 150 °C with loss of chloride and organic ligand to form SiO₂. Silicon phthalocyanine undergoes an exothermic reaction at 312 °C with loss of organic ligand to give SiO₂. The observed residual weights listed in Table 2 are in good agreement with those which have been calculated theoretically.

The room temperature current I versus voltage V characteristics were obtained under conditions of rising and falling voltage in both polarities. There is no evidence of blocking behaviour for either electrons or holes at the contacts as the replication of the current magnitude for a given voltage magnitude is within 15%. There is also no clear evidence for hysteresis in the characteristics and in this respect [Si(C₅H₇O₂)₃]Cl·HCl and [Si(C₅H₇O₂)₃]Cl differ from silicon–transition metal chloro-complexes based on the same organic ligand which have recently been reported [6]. All of the

TABLE 1
Analyses of the compounds

Compound	Theoretical (%)					Experimental (%)				
	Si	C	N	H	Cl	Si	C	N	H	Cl
[Si(C ₅ H ₇ O ₂) ₃]Cl·HCl	7.06	45.34	–	5.58	17.84	6.34	45.01	–	5.29	17.66
[Si(C ₅ H ₇ O ₂) ₃]Cl	7.78	49.93	–	5.86	9.82	7.70	49.12	–	5.76	9.03
Si(C ₃₂ H ₁₆ N ₈)Cl ₂	4.58	62.74	18.29	2.63	11.57	4.42	62.38	18.01	2.12	11.12

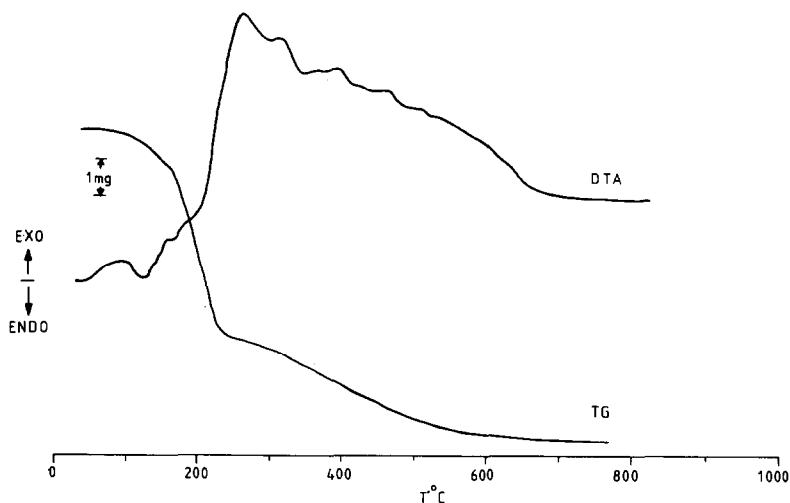


Fig. 1. TG/DTA curve for tris(2,4-pentanedianato)silicon chloride hydrochloride. Sample weight, 9.8 mg.

compounds in the present work exhibited a small departure from Ohm's law, the $I-V$ characteristics bending upward as the voltage is increased. This behaviour is exemplified in Fig. 3 for $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl} \cdot \text{HCl}$. When the same experimental data is replotted, Fig. 4, using logarithmic axes for both I and V , the points fit closely to a straight line showing that the relationship between I and V is $|I| \propto |V|^m$. The same relationship is also valid for $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)]\text{Cl}$, as shown in Fig. 4, and for $\text{Si}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2$, although the graph for the latter compound is not presented. The value of m found for

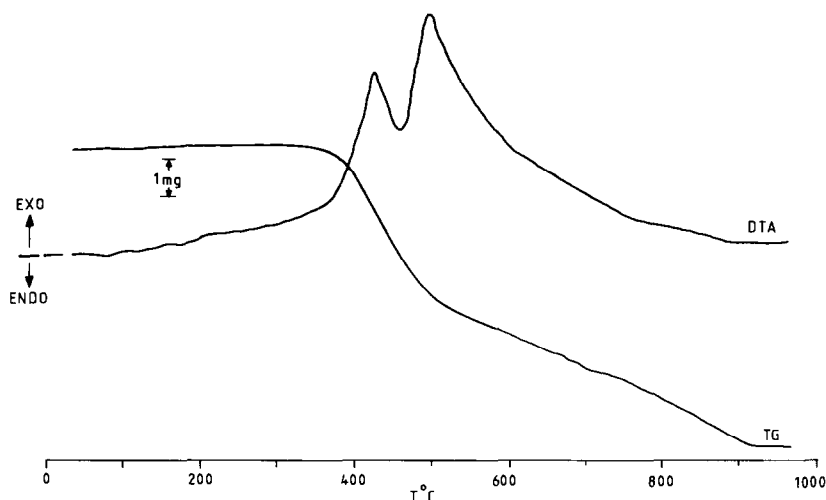


Fig. 2. TG/DTA curve for silicon phthalocyanine dichloride. Sample weight, 8.95 mg.

TABLE 2

Thermal decomposition data

Starting material	Decomposition temperature (° C)	% Mass ^a		Resulting compound
		Calc.	Obs.	
[Si(C ₅ H ₇ O ₂) ₃]Cl·HCl	90	90.80	90.81	[Si(C ₅ H ₇ O ₂) ₃]Cl
	150	16.13	16.83	SiO ₂
Si(C ₃₂ H ₁₆ N ₈)Cl ₂	312	9.83	8.93	SiO ₂

^a This is the mass of solid remaining, expressed in terms of percentage of the mass of the starting material.

each compound, determined from the gradient of the least-squares fitted line to its double-logarithmic plot of I against V , is given in Table 3. For [Si(C₅H₇O₂)₃]Cl and [Si(C₅H₇O₂)₃]Cl·HCl, the exponent m has the respective values of 1.13 and 1.18 and these are close to the result ($m = 1.2-1.6$) found for the silicon-transition metal chloro-complexes [6]. Si(C₃₂H₁₆N₈)Cl₂ has a room temperature $I-V$ characteristic specified by $m = 1.21$, which is close to that of the other two compounds. The fit of the current-voltage dependence to the expression $|I| \propto |V|^m$ with $m > 1$ suggests that the current is space-charge-limited although the model for this type of current limitation is more clearly formulated [7,8] to explain cases of $m > 2$ than it is for m only slightly larger than unity, as found in the present work. Another series of compounds which were measured under identical conditions and also yielded fits to the $|I| \propto |V|^m$ law, again with m only slightly larger than unity, has been reported from these laboratories [9]. An alternative expression to $|I| \propto |V|^m$, is $|I| = A|V| + B|V|^2$ in which A and B are constants for a given sample; this latter expression has a theoretical basis [10] but does not describe the results obtained for the compounds in the

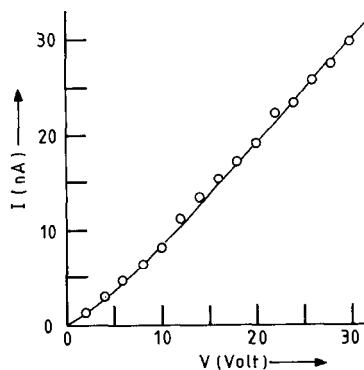


Fig. 3. Room temperature current I versus voltage V plot for a disc of [Si(C₅H₇O₂)₃]Cl·HCl of thickness 1.47 mm. The plot is based on the mean current at any given voltage V , with V rising and falling in both polarities. The slight curvature shows that Ohm's law is not valid.

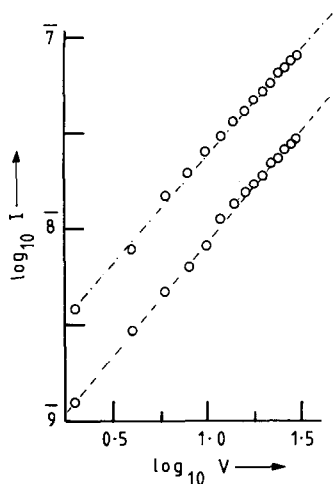


Fig. 4. Room temperature plots using double-logarithmic axes of the current I versus the voltage V for: lower line, $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]_3\text{Cl}\cdot\text{HCl}$ of thickness 1.47 mm; and upper line, $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]_3\text{Cl}$ of thickness 1.14 mm. The units of I and V are respectively amps and volts. The data points are based on mean currents as measured at each given voltage V , with V rising and falling in both polarities.

present or earlier investigations because plots of $|I/V|$ against $|V|$ are all highly non-linear.

Because $m \neq 1$, it follows that a unique conductivity cannot be defined, yet some guidance relating to the conductivity is useful for comparisons

TABLE 3

Electrical data for the compounds

Compound	m^a	σ^b ($\Omega^{-1} \text{ m}^{-1}$)	ΔE^c (eV)			Figures illustrating electrical behaviour
			Heat- ing	Cool- ing	Com- bined	
$[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]_3\text{Cl}\cdot\text{HCl}$	1.18	7.1×10^{-8}	1.22	2.02	1.61	3, 4, 5
$[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]_3\text{Cl}$	1.13	1.5×10^{-7}	1.95	2.30	2.01	4, 5
$\text{Si}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2$	1.21	6.7×10^{-8}	1.21	2.00	1.59	5

^a m is the exponent in the expression $I \propto V^m$ for the room temperature $I-V$ characteristic. The value of m quoted is the gradient of the least-squares fitted line to a plot of $\ln I$ versus $\ln V$ from combined data obtained in both polarities. Reproducibility of m for the two polarities is within ± 0.03 .

^b Conductivity, σ , at room temperature for a field E of $1 \times 10^4 \text{ V m}^{-1}$ (with E taken as applied voltage \div disc thickness).

^c ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where symbols have their conventional meanings. ΔE is obtained by least-squares fitting of a straight line to a plot of $\ln \sigma$ versus T^{-1} for the separate cases of temperature rising, temperature falling and combined heating/cooling.

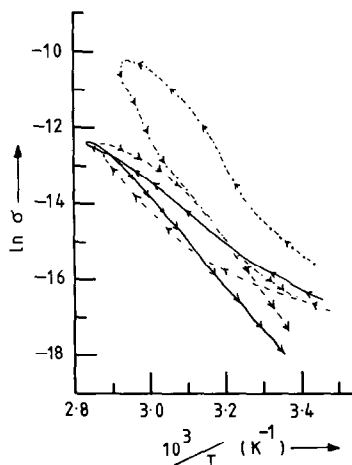


Fig. 5. Semi-logarithmic plot of conductivity σ (in units of $\Omega^{-1} \text{ m}^{-1}$) against reciprocal absolute temperature for: - - - - -, $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl}_2 \cdot \text{HCl}$; - · - · -, $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl}$; and ———, $\text{Si}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2$. In each case σ is taken as the ratio of the current density to the mean applied field under application of 10 V. The arrows show the direction of the temperature change.

between different materials. Accordingly, the conductivities have been determined for an applied field of $1 \times 10^4 \text{ V m}^{-1}$ and are listed in Table 3. This field is arbitrary but is chosen as being representative of the mid-range of fields covered in the electrical measurements for the compounds. The conductivities for the two compounds containing the pentanedionato group lie within the range found in earlier work [6] for silicon-transition metal chloro-complexes also containing this group.

The temperature dependence of conductivity σ is shown in Fig. 5 for each of the compounds as graphs of $\ln \sigma$ against $10^3 T^{-1}$ where T is the absolute temperature. For the purpose of obtaining the data in these graphs, the temperature was varied with a constant 10 V maintained across each disc. Linearity of these graphs would indicate that the relationship $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ describes the temperature dependence of conductivity with σ_0 and ΔE being constants for a given compound. However, as may be seen from the figure, the experimental data obtained for each compound can only be poorly represented by a straight line. It is believed significant that the shape of the curve in Fig. 5 for $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl} \cdot \text{HCl}$ is similar to those obtained for $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{MCl}_2$ complexes ($\text{M} =$ first row transition metal) in earlier work [6], and strengthens confidence that the observed shape is genuine rather than an artifact of the measurement technique. For $\text{Si}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2$ and $[\text{Si}(\text{C}_5\text{H}_7\text{O}_2)_3]\text{Cl}$, the graphs, of $\ln \sigma$ against T^{-1} are also non-linear, see Fig. 5. Values of ΔE as deduced from the gradients of the best-fitting (in a least-squares sense) lines in the plots of Fig. 5 are listed in Table 3 where separate results are quoted for the cases of rising tempera-

ture, falling temperature and combined data from the heating and cooling cycle. Evidently, in view of the described non-linearity of the plots, caution must be exercised in attaching meaning to the tabulated ΔE values. In obtaining the data on the temperature dependence of conductivity, none of the compounds were heated above 352 K and, from the thermogravimetric measurements, no decomposition would be expected at this temperature. Another possibility considered to explain the poor reproducibility of the temperature dependence of conductivity during heating and cooling is that water is evaporated during the heating phase; but this suggestion was rejected because the compounds were kept under desiccation for several days immediately before the measurements were made.

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