

STRUCTURAL, THERMAL AND ELECTRICAL STUDIES OF COMPLEXES OF SILICON WITH SOME FIRST ROW TRANSITION ELEMENTS

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ABSTRACT

Mixed metal compounds of the main group element silicon and the first row transition elements iron, cobalt, copper and zinc have been prepared. The vibrational spectra, electronic spectra and some magnetic properties are reported for the compounds. The thermal behaviour of each compound has been studied using thermogravimetry. It is found that a mixed metal oxide is formed on decomposition for each compound. Electrical measurements are reported, including determinations of the conductivity and activation energy. For the zinc complex the room temperature conductivity is sufficiently high that device applications are a possibility.

INTRODUCTION

Thermal analyses, structural and electrical studies of some first row transition metal complexes with substituted pyrazines and pyridines have previously been reported [1–7]. Mixed metal complexes of the main group element silicon and the first row transition elements iron, cobalt, copper and zinc are discussed in this paper. Some spectral and magnetic properties along with electrical and thermal analysis studies of the complexes are reported.

EXPERIMENTAL

Preparation of compounds

Tris(2,4-pentanedionato)silicon chloride hydrochloride $[\text{Si}(\text{acac})_3]\text{ClHCl}$

20 g of silicon tetrachloride was 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 dropping funnel (containing 12 cm³ of 2,4-pentanedione in 30 cm³ of dry benzene) and reflux condenser, both fitted with calcium chloride drying tubes. The pentanedione–benzene solution was added dropwise 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 dessicator [8].

Iron–silicon compound

1.7 g of anhydrous iron(III) chloride was added to a solution of 4 g [Si(acac)₃]Cl · HCl in chloroform. The mixture was shaken gently until the evolution of hydrogen chloride was complete. The solution was filtered and ether was added to the filtrate. The mixture was allowed to stand at room temperature for 30 min. The yellow–green crystals which deposited were filtered and washed with dry ether [9].

Zinc–silicon compound

2.16 g of anhydrous zinc chloride was stirred in 30 cm³ of ethanoic acid to which 2.5 g ethanoic anhydride had been added. 5.5 g of [Si(acac)₃]Cl · HCl was added and the mixture allowed to stand for 30 min. A precipitate formed which was removed by filtration and then dissolved in the minimum of chloroform. The chloroform was heated with twice its volume of anhydrous ether and the mixture was allowed to stand for 15 min. A white crystalline solid formed which was isolated by filtration and washed with ether [10].

Copper–silicon compound

2.14 g of anhydrous copper(II) chloride was stirred in 30 cm³ ethanoic acid to which 2.5 g ethanoic anhydride had been added. 5.5 g of [Si(acac)₃]Cl · HCl was added and the mixture allowed to stand for 180 min. The precipitate which formed contained some unreacted copper(II) chloride. The copper(II) chloride was separated from the required complex by warming the solution and then filtering. The filtrate was allowed to cool and the precipitate formed was treated as for the zinc–silicon compound.

The method was also used for the preparation of the cobalt–silicon compound.

Elemental analysis

Silicon

The silicon content of the compounds was determined gravimetrically [11].

Carbon and hydrogen

The carbon and hydrogen analyses were obtained using a Carlo Erba elemental analyser.

Chloride

The chloride content of the compounds was determined gravimetrically [12].

Spectral and magnetic measurements

The electronic spectra were obtained using a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra.

The IR spectra were obtained using KBr discs, 4000–600 cm^{-1} and polyethylene discs, 600–200 cm^{-1} on a Perkin–Elmer IR spectrophotometer Model 598.

Measurements of magnetic moments were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant and corrections for diamagnetism were applied using Pascal's constants [13].

Thermal analysis

Thermal analysis data were obtained using a Stanton Redcroft Model STA 781 thermobalance. Thermogravimetry curves were obtained at a heating rate of $10^\circ\text{C min}^{-1}$ in static air. In all cases the 20–500 $^\circ\text{C}$ temperature range was studied.

Electrical conductivity measurements

The experimental method used for electrical conductivity measurements was the same as that previously described [1–7]. Material, in powder form, was compressed to form discs of diameter 13 mm and thickness 0.8–1.5 mm, using a hydraulic press set to apply a force of 100 kN. Conducting silver paint electrodes of diameter 4.9 mm were applied concentrically to the flat faces of each disc after removal from the press. The d.c. characteristics of current I against voltage V were obtained at room temperature for each disc. The measurements of current were made using a Keithley 610C electrometer and corresponding voltages were obtained using a digital voltmeter. The voltmeter was connected so that the current passed did not contribute to that registered by the electrometer. Readings were obtained manually in the following order: increasing voltage, decreasing voltage in the same polarity, increasing voltage in the reverse polarity and decreasing voltage in reverse polarity. For the zinc–silicon compound, which was found to be the most conductive of the prepared compounds, the maximum applied voltage was 10 V and for the other compounds the peak applied

voltage was 2–3 times higher. The Joule heating rate was always < 2.3 mW during the measurements and, as the discs were mounted on a copper heat sink the internal rise in temperature was negligible.

The symmetry in the currents for the original and reversed polarities at any given magnitude of applied voltage was found to be within a few per cent, suggesting that the electrodes make ohmic contacts. This seems to be confirmed by a second disc of the same compound under an identical applied electric field where the current density was in agreement to within a factor of 1.5. The disc thicknesses were measured using a micrometer.

The temperature dependence of conductivity for a disc of each compound was investigated by measuring the current passed for a series of increasing and then decreasing disc temperatures with a constant voltage applied. The measurements were made with the disc in an electrically heated oven and the temperature range covered was from room temperature up to 349 K. The disc temperature was obtained by measuring the thermo e.m.f. of a previously calibrated copper–constantan thermocouple (formed from wires of 44 SWG) and with the hot junction mounted on the top surface of the disc. The applied voltage was 10 V for all compounds except the zinc–silicon compound where, because of its higher conductivity, 2 V was applied. During each measurement of disc current the oven heater current was temporarily switched off to prevent electrical pick-up signal into the disc circuit. The metal casing of the oven provided useful screening. For this reason the previously obtained room temperature data were also collected with the discs in the oven but without any heating.

RESULTS AND DISCUSSION

The compounds prepared have the stoichiometries $[\text{Si}(\text{acac})_3]\text{FeCl}_4$ and $[\text{Si}(\text{acac})_3]\text{MCl}_3$ where $\text{M} = \text{Co}, \text{Cu}$ and Zn . Table 1 shows the analytical results for the compounds to be in good agreement with the given formulae. The magnetic moments for the iron, cobalt and copper compounds are listed in Table 1. The bands in the electronic spectra of the iron, cobalt and copper compounds are listed in Table 2, together with the infrared spectra of the compounds. In the spectrum of the 2,4-pentadione a band is observed at 1705 cm^{-1} which we assigned to the stretching vibration of the carbonyl group. In the complexes this band was not present but they all exhibited a band at around 1542 cm^{-1} . This was due to the lowering of the frequency of the C–O stretching vibration as a result of the carbonyl groups now being bonded to the silicon. The silicon–oxygen bands and the metal–halogen bands are shown in Table 2.

The fact that the compounds were isolated as powders and not as single crystals meant that no complete structural determination could be made. However, from spectroscopic and magnetic data we can predict the environ-

Table 1

Analyses and magnetic measurements of the compounds

Compound	Colour	Calculated (%)			Found (%)			μ (B.M.)		
		Si	C	H	Cl	Si	C	H	Cl	
[Si(acac) ₃]Cl · HCl	White	7.06	45.34	5.58	17.84	6.24	44.36	5.36	16.93	DIA ^a
[Si(acac) ₃]FeCl ₄	Yellow	5.36	34.44	4.04	27.11	5.16	34.12	4.05	26.41	5.71
[Si(acac) ₃]CoCl ₃	Blue	5.72	36.71	4.31	21.67	5.31	36.38	4.01	21.07	4.51
[Si(acac) ₃]CuCl ₃	Yellow	5.67	36.37	4.27	21.47	4.88	35.42	4.86	20.91	1.72
[Si(acac) ₃]ZnCl ₃	White	5.64	36.23	4.25	21.39	5.12	35.63	4.08	21.22	DIA ^a

^a DIA, diamagnetic.

Table 2

Electronic and infrared spectra (cm^{-1})

Compound	Electronic spectra d-d transitions	Infrared spectra			
		$\nu_s(\text{C-H})$	$\nu_s(\text{C=O})$	$\nu(\text{Si-O})$	$\nu(\text{M-Cl})$
acac	—	2998 (w)	1705 (s)	—	—
$[\text{Si}(\text{acac})_3]\text{FeCl}_4$	18 800	3220 (w)	1542 (s)	468 (m)	282 (m)
$[\text{Si}(\text{acac})_3]\text{CoCl}_3$	8 000	3210 (w)	1543 (s)	464 (m)	292 (m)
	14 347				
	15 748				
$[\text{Si}(\text{acac})_3]\text{CuCl}_3$	9 803	3260 (w)	1540 (s)	465 (m)	290 (m)
$[\text{Si}(\text{acac})_3]\text{ZnCl}_3$	—	3240 (w)	1545 (s)	460 (m)	281 (m)

acac, acetylacetone; s, strong; m, medium; w, weak.

ment of the metal ions in the compounds. In the iron compound it is suggested that the structure consists of $[\text{Si}(\text{acac})_3]^+$ cations and $(\text{FeCl}_4)^-$ anions. The silicon atom is in an octahedral environment whilst the band at 282 cm^{-1} in the infrared spectrum due to the $\nu(\text{Fe-Cl})$ vibration is indicative of the iron atom in a tetrahedral environment [14]. The copper compound has stoichiometry $[\text{Si}(\text{acac})_3]\text{CuCl}_3$. Structural investigations of complexes of the type $[\text{cation}](\text{CuCl}_3)$ have shown the existence of discrete $\text{Cu}_2\text{Cl}_6^{2-}$ ions [15,16]. The dimers are stacked above each other so that each copper atom is bonded to a chlorine atom in the dimers above and below it to give an octahedral coordination for the copper atom. The band at 290 cm^{-1} corresponding to the $\nu(\text{Cu-Cl})$ vibration in the infrared spectrum of the $[\text{Si}(\text{acac})_3]\text{CuCl}_3$ compound shows that the copper atom is in an octahedral environment in the (CuCl_3^-) anion [17–19]. The compound has a band in its electronic spectrum at 9803 cm^{-1} and a magnetic moment of 1.72 B.M. The magnetic moment suggests negligible copper–copper interaction in the $\text{Cu}_2\text{Cl}_6^{2-}$ ions. The zinc compound has stoichiometry $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$. This suggests that the structure involves $[\text{Si}(\text{acac})_3]^+$ cations and $(\text{Zn}_2\text{Cl}_6)^{2-}$ dimeric anions [20]. In the anion the geometry about each zinc atom is tetrahedral which is consistent with the observation of the $\nu(\text{Zn-Cl})$ band at 281 cm^{-1} in the infrared spectrum [17]. The stoichiometry of the cobalt compound is $[\text{Si}(\text{acac})_3]\text{CoCl}_3$. No compounds of the type $[\text{cation}]\text{CoCl}_3$ appear to have been reported in the literature. The electronic spectrum and magnetic moment show that the cobalt atom is in a tetrahedral environment [21]. This suggestion is further supported by a band at 292 cm^{-1} in the infrared spectrum which is in the expected range for the $\nu(\text{Co-Cl})$ vibration for tetrahedral compounds [21]. It is postulated that $(\text{Co}_2\text{Cl}_6)^{2-}$ dimeric anions exist in this compound similar to those discussed for the zinc compound.

The TG curves for the compounds are shown in Fig. 1. Thermal decomposition data are listed in Table 3. The order of stability of the compounds

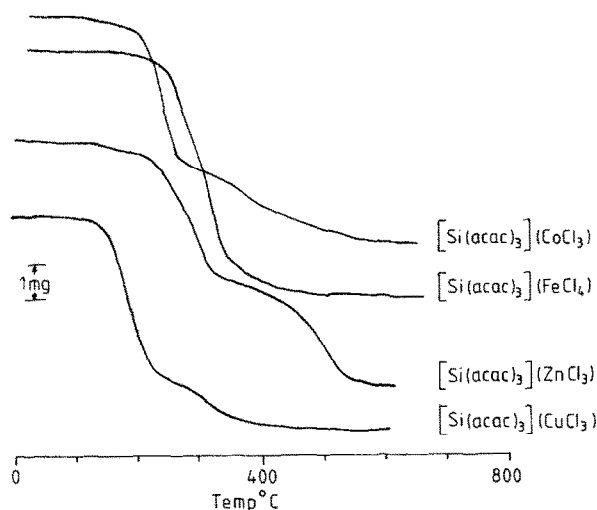


Fig. 1. Thermogravimetric curves for the metal complexes.

is: iron > zinc > cobalt > copper. The compounds all decompose to give mixed oxides.

The room temperature current I versus voltage V characteristics for the two compounds exhibiting the highest conductivities, i.e. $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$ and $[\text{Si}(\text{acac})_3]\text{CoCl}_3$, each exhibit hysteresis. This is shown in Fig. 2 for $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$ where, for the polarity of voltage first applied, the current during growth of the voltage exceeds that for the same voltage during its removal. When the polarity is reversed the hysteresis is much less prominent. Identical behaviour has been observed in other compounds [6] which have been investigated using the same electrical method and was attributed to a combination of conduction and polarisation currents. Hysteresis effects for $[\text{Si}(\text{acac})_3]\text{CoCl}_3$ are qualitatively similar to those for $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$. For $[\text{Si}(\text{acac})_3]\text{FeCl}_4$ and $[\text{Si}(\text{acac})_3]\text{CuCl}_3$ no hysteresis in the I versus V plots is observed.

Table 3

Thermogravimetric data for the metal complexes

Initial Compound	Temperature at which decomposition begins (°C)	Temperature at which decomposition is complete (°C)	Final residue
$[\text{Si}(\text{acac})_3]\text{FeCl}_4$	190	605	SiO_2 ; Fe_2O_3
$[\text{Si}(\text{acac})_3]\text{CoCl}_3$	81	628	SiO_2 ; Co_3O_4
$[\text{Si}(\text{acac})_3]\text{CuCl}_3$	51	502	SiO_2 ; CuO
$[\text{Si}(\text{acac})_3]\text{ZnCl}_3$	101	540	SiO_2 ; ZnO

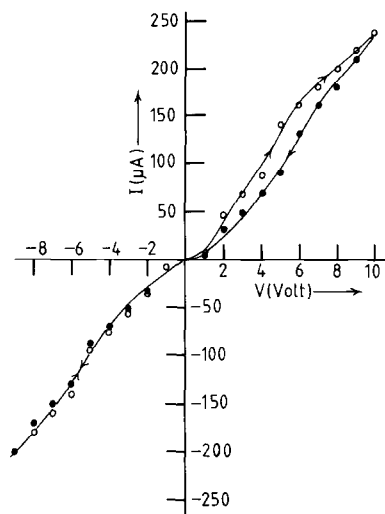


Fig. 2. Current I versus voltage V for a $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$ disc of thickness 1.47 mm at room temperature. $\circ$, $|V|$ increasing; $\bullet$, $|V|$ decreasing. The first application of voltage corresponds to the first quadrant of the graph. In the third quadrant no attempt is made to distinguish between the curves for increasing and decreasing voltages.

Plots of $\ln |\bar{I}|$ versus $\ln |V|$, where $|\bar{I}|$ is the magnitude of the current at a given voltage averaged over ascending and descending voltage data in both polarities, fit to a straight line for each compound, showing that the expression $|\bar{I}| \propto |V|^m$ describes the characteristics. The gradient m of each line was determined by least-squares fitting and these values, which all lie in the range $1.2 < m < 1.6$ are shown in Table 4. Since the I versus V characteristics for each compound do not differ by more than a few per cent in the two polarities applied, i.e. no significant rectifying properties were observed for the discs having the silver paint electrodes, the departure of m from unity is attributed to bulk properties of the compound rather than to a barrier at the contact. Almost certainly, space-charge-limited conduction is involved although the explanation is not so clearly defined for $1 < m < 2$ (as found for the compounds described here) as it is for $m > 2$ [22-24]. Since $m \neq 1$, a unique electrical conductivity cannot be defined. However, since some guidance relating to conductivity is useful for relating the electrical properties to those of other materials, the conductivity for each compound has been evaluated at a mean field (applied voltage/electrode separation) of 10^4 V m^{-1} and the results are shown in Table 4. The selected field is arbitrary but is typical of the range covered and the reported conductivities are based on the assumption of current being always perpendicular in direction to the electrodes. For $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$, which is the most conductive of the compounds, the conductivity determined in this way (viz. $3.2 \times 10^{-3} \Omega^{-1} \text{ m}^{-1}$) is much higher than has been found previously for metal

Table 4

Electrical properties of the compounds

Compound	m^a	Conductivity at room temperature ^b ($\Omega^{-1} \text{ m}^{-1}$)	ΔE^c (eV)
[Si(acac) ₃]FeCl ₄	1.2	5.5×10^{-8}	1.40 ± 0.15
[Si(acac) ₃]CoCl ₃	1.2	3.3×10^{-5}	— ^d
[Si(acac) ₃]CuCl ₃	1.2	7.3×10^{-8}	1.84 ± 0.18
[Si(acac) ₃]ZnCl ₃	1.6	3.2×10^{-3}	— ^d

^a m , the exponent in the expression $I \propto V^m$ for the room temperature data.^b Conductivities at a mean field (applied voltage/electrode spacing) of $1 \times 10^4 \text{ Vm}^{-1}$.^c ΔE is the energy term appearing in the expression $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, where k is Boltzmann's constant, T is the absolute temperature and σ_0 is a constant for a given material.^d ΔE not determined because the conductivity was found to be independent of temperature for small increases above room temperature.

complexes with pyrazines and pyridines [1–7]. This is with the exception of certain complexes of quinoxaline [2] where the conductivity is of comparable value. The measured conductivities of [Si(acac)₃]CuCl₃ and [Si(acac)₃]FeCl₄ are lower by nearly five orders of magnitude than for [Si(acac)₃]ZnCl₃. This may mean that the relatively high conductivity of the latter compound is due to the inclusion of unintended donor or acceptor impurities.

Figure 3 shows the temperature dependence of conductivity (σ) for [Si(acac)₃]FeCl₄ as a $\ln \sigma$ versus T^{-1} plot where T is the absolute temperature. For data fitting to a straight line the relationship between σ and T is $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where ΔE is an activation energy which may be found from the gradient. The points fit roughly to a linear graph (Fig. 3), and similar behaviour was found for [Si(acac)₃]CuCl₃. To increase the objectivity in fitting the best straight lines in the $\ln \sigma$ versus T^{-1} plots for both [Si(acac)₃]FeCl₄ and [Si(acac)₃]CuCl₃, a least-squares linear regression program was used. The coefficients of determination in fitting the lines are 0.894 and 0.890 respectively. The corresponding values of ΔE are 1.40 ± 0.15 eV for [Si(acac)₃]FeCl₄ and 1.84 ± 0.18 eV for [Si(acac)₃]CuCl₃. A possible interpretation for ΔE , assuming that the language of band structure is appropriate, is that it represents the energy gap between valence and conduction bands [25,26]. It is also possible that ΔE is the energy barrier to release of a free carrier from donor or acceptor centres [25,26]. The former interpretation for our measured values of ΔE in [Si(acac)₃]FeCl₄ and [Si(acac)₃]CuCl₃ is more probable because they are of similar value, as would be expected for activation across the valence band to conduction band gap in similar compounds, and also because the determined values of ΔE would be surprisingly large for donor or acceptor ionisation energies.

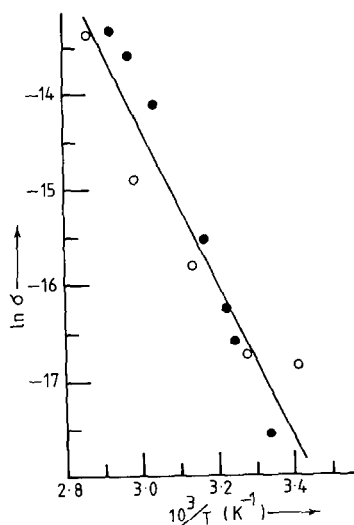


Fig. 3. Plot of $\ln \sigma$ versus $10^3/T$ for a disc of $[\text{Si}(\text{acac})_3]\text{FeCl}_4$ of thickness 1.17 mm and under a constant applied voltage of 10 V. The conductivity σ is in units of $\Omega^{-1} \text{ m}^{-1}$ and the line is fitted using a least-squares program. ○, T increasing; ●, T decreasing.

The preparations of $[\text{Si}(\text{acac})_3]\text{FeCl}_4$ and $[\text{Si}(\text{acac})_3]\text{CuCl}_3$ are similar in all of the electrical properties studied (Table 4) and this suggests that the conductivities are intrinsically controlled rather than influenced by impurities. The fact that the environment of the metal atom in the two compounds is different appears to be unimportant for electrical characteristics.

The conductivities of $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$ and $[\text{Si}(\text{acac})_3]\text{CoCl}_3$ were little affected by rises in temperature above room temperature. The two compounds were the most conductive of the complexes prepared, so the most likely explanation is that their room temperature conductivities result from activation of carriers from donor or acceptor levels which are already fully ionised at room temperature.

In summary, the evidence suggests that the observed conductivities in $[\text{Si}(\text{acac})_3]\text{FeCl}_4$ and $[\text{Si}(\text{acac})_3]\text{CuCl}_3$ are due to intrinsically generated carriers, whilst those observed for $[\text{Si}(\text{acac})_3]\text{ZnCl}_3$ and $[\text{Si}(\text{acac})_3]\text{CoCl}_3$ are due to carriers released from impurity centres.

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