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Thermal studies on germanium(IV) complexes of *N*-alkylcyclohexyl dithiocarbamates[1]

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Abstract

Ge(IV) complexes of *N*-alkylcyclohexyl dithiocarbamates of the type $\mathrm{Ge[RCyhxdtc]}_n\mathrm{Cl}_{4-n}$ (Cyhx is cyclohexyl, R is Me, $n = 1$; R is Pr^i, $n = 1, 4$) have been synthesized and characterized by elemental and spectral studies (IR, UV-visible). The course of the thermal degradation of these complexes has been investigated using thermogravimetric (TG) and differential thermal analysis (DTA) techniques. The reaction order of the thermal decomposition was calculated from the TG curves using the Coats–Redfern, Piloyan–Novikova and Horowitz–Metzger methods. Heat of reactions of various steps of decomposition and calibration constants were calculated from the DTA curves.

Keywords: Germanium (IV) complexes; Dithiocarbamates; Thermal studies

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1. Introduction

The dithiocarbamates are a class of sulphur-donor ligands [1]. Interest in metal dithiocarbamate complexes derives from their diversified applications, including vulcanization accelerators, antioxidants and, in the biochemical field, correction of chronic alcoholism, insecticides, pesticides and fungicides [2].

Compounds of germanium with dithioligands are scarce although some organogermanium dithiocarbamates have been prepared [1]. The synthesis, IR and Raman spectra of $\mathrm{(Me)_3M(MeDtc)}$ complexes, where M is Si, Ge, Sn, have

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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also been reported [3]. Some trimethyl metal(IVB) esters of dithioacids have been prepared by treatment of secondary or tertiary amine salts of dithioacids with chloromethyl germane. Piperidinium dithioisobutyrate readily reacts with chlorotrimethyl germane to give a metalloidal dithioester in quantitative yield [4]. In continuation of our studies on metal dithiocarbamates [5–9], the present paper describes the thermal investigation of Ge(IV) complexes of *N*-alkylcyclohexyl dithiocarbamates. Kinetic parameters have also been calculated from the thermal degradation data.

2. Experimental

IR spectra were recorded on a PU 9706 Philips IR Spectrophotometer and the ν_{max} values expressed in cm^{-1}. Electronic spectra were recorded on a Shimadzu UV 260 spectrophotometer and absorptions expressed in nm. The thermal studies (TG and DTA) were recorded on a Rigaku-8150 thermal analyser attached to a NEC mini-computer for data processing. The heating rate was 10 K min^{-1} in a static air atmosphere. For DTA, a Pt crucible was used with α-alumina (99% pure) as the reference material. Sulphur was determined gravimetrically as $BaSO_4$ by Messenger's method [10]. Chlorine was determined gravimetrically as silver chloride and germanium was determined as GeO_2 [11].

3. Preparation and characterization of complexes

Sodium salts of dithiocarbamic acids were prepared as reported in the literature [12]. The complexes were prepared by the method reported by Zaidi et al. [13]. All the metal–dithiocarbamate complexes reported were prepared by the interaction of germanium tetrachloride with varying proportions of the ligands in ethanol–chloroform medium.

Elemental analysis data of the complexes are given in Table 1. Dithiocarbamates and their derivatives show high intensity absorptions in the UV region due to the

Table 1
Elemental analysis of the complexes

No.	Compound	Empiral formula	Analysis found (calc.)/%						Yield
			C	H	N	S	Ge	Cl	%
1.	$Ge[S_2CNMeCyhx]Cl_3$	$C_8H_{14}NS_2GeCl_3$	25.31	2.61	2.91	16.61	18.04	27.19	
			(26.22)	(3.82)	(3.82)	(17.4))	(19.94)	(28.68)	62.5
2.	$Ge[S_2CNPr^iCyhx]Cl_3$	$C_{10}H_{18}NS_2GeCl_4$	28.16	3.04	2.07	14.98	17.11	25.19	
			(30.45)	(4.50)	(3.55)	(16.24)	(18.52)	(26.60)	59.4
3.	$Ge[S_2CNPr^iCyhx]_4$	$C_{40}H_{72}N_4S_8Ge$	49.19	6.61	4.62	26.11	6.41	–	
			(51.22)	(7.68)	(5.97)	(27.32))	(7.79)	–	49.5

chromophore group NCS_2 [14]. Band I in the 240 nm region is most intense and it attributed to the intraligand π–π^* transition of the N==C==S group [15, 16]. Band II in the 300 nm region appears as a shoulder and is assigned to the π–π^* electronic transition located on the S atom [16]. In the case of complex $Ge[S_2CNPr^iCyhx]_4$, the co-planarity of the molecule is lost due to the four bulky groups. Consequently the π–π^* transition of the N---C---S group is absent and two bands at 206 and 307 nm are observed.

In the IR spectra, the 1430–1440 cm^{-1} region is assigned to the ν(C==N) vibration of the S_2C–NR_2 bond. The doublet in the region of 1000–1060 cm^{-1} is associated with ν(C==S) vibrations. The doublet separated by > 20 cm^{-1} is indicative of the monodentate nature of the ligand [17].

4. Thermal studies

4.1. Results and discussion

4.1.1 Trichloro (N-methylcyclohexyl dithiocarbamato) germanium(IV)

The TG curve for this complex (Fig. 1, curve a) shows that almost 50% mass loss occurs up to 673 K. The initial thermal decomposition step is over the range 400–673 K. At this temperature, the intermediate $Ge(SCN)_2Cl_2$ was formed (calculated Mass loss, 28.1%; found, 30%). The subsequent step at 956 K shows a mass loss; germanium oxide (GeO_2) is the end product (calculated mass loss 71.50%; observed, 73%).

The DTA curve (Fig. 2, curve a) shows an exothermic peak at T_{max} = 605.8 K, which is due to the formation of $Ge(SCN)_2Cl_2$. An endothermic peak at 872.6 K corresponds to complete decomposition of the complex [9].

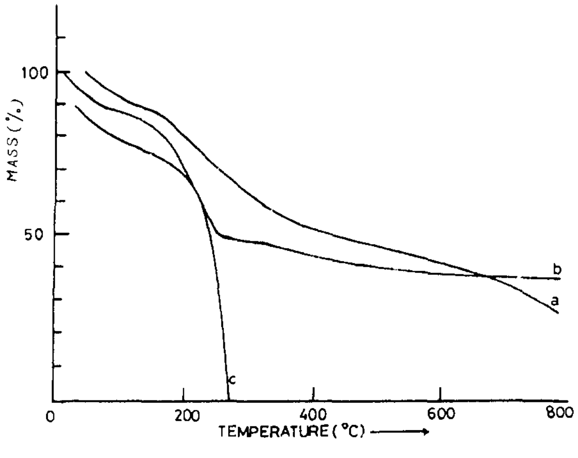

Fig. 1. TG curves: a, $Ge[S_2CNMeCyhx]Cl_3$; b, $Ge[S_2CNPr^iCyhx]Cl_3$; c, $Ge[S_2CNPr^iCyhx]_4$.

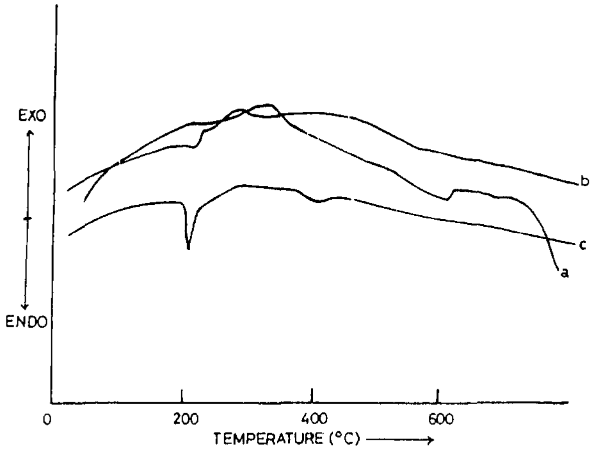

Fig. 2. DTA curves: a, Ge[S_2CNMeCyhx]Cl_3; b, Ge[S_2CNPr^{i}Cyhx]Cl_3; c, Ge[S_2CNPr^{i}Cyhx]$_4$.

4.1.2. *Trichloro* (N-*isopropyl cyclohexyl dithiocarbamato*) *germanium*(*IV*)

The TG curve (Fig. 1, curve b) for this complex shows a gradual initial mass loss which accelerates around 454 K and terminates around 545 K. The curve shows almost 50% mass loss at this temperature. At 545 K, the intermediate Ge $(SCN)_2Cl_2$ is formed (calculated mass loss, 33.3%; found, 35%). A further mass loss is observed in the second step to 1073 K. GeO_2 is the final product after decomposition but the mass loss should be 73.59% (calculated) and actually it is found out to be 65% from the thermogram, which suggests incomplete conversion to oxide at 1073 K.

The DTA profile (Fig. 2 curve b) shows a shallow endothermic peak at 493 K, which is due to the initial decomposition of the complex. There is a small exothermic peak at 553 K which is due to further reaction of the intermediate.

4.1.3. *Tetrakis* (N-*isopropyl cyclohexyl dithiocarbamato*) *germanium*(*IV*)

The TG curve (Fig. 1, curve c) for this complex shows a completely different trend. The thermal decomposition commences with the increase in temperature. The compound is highly volatile and by 550 K, 100% of the complex is volatilized.

The DTA profile (Fig. 2, curve c) for this complex shows an endothermic peak at $T_{max} = 483$ K, which is due to melting of the complex. The second endothermic peak is at $T_{max} = 538.8$ K, which is due to the volatilization of the complex.

Thus from the TG trends it is revealed that the thermal stability of the complexes is in the order: Ge(S_2CNPr^{i}Cyhx)$_4$ < Ge(S_2CNMeCyhx)Cl_3 < Ge(S_2CNPr^{i}Cyhx)Cl_3.

From the TG curves, the reaction order (n) for the first thermal decomposition step has been determined by the methods of Coats and Redfern (Figs. 3 and 4) [18], Piloyan and Novikova (Figs. 5 and 6) [19] and Horowitz and Metzger (Figs. 7 and 8) [20].

The heat of reaction (ΔH) can be read directly in microvolts from the DTA curve, obtained from the computer attached to thermoanalyser; this can be converted to kJ

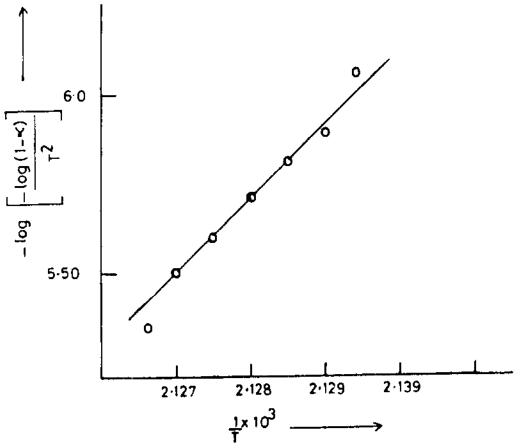

Fig. 3. Coats–Redfern plot for Ge[S$_2$CNMeCyhx]Cl$_3$.

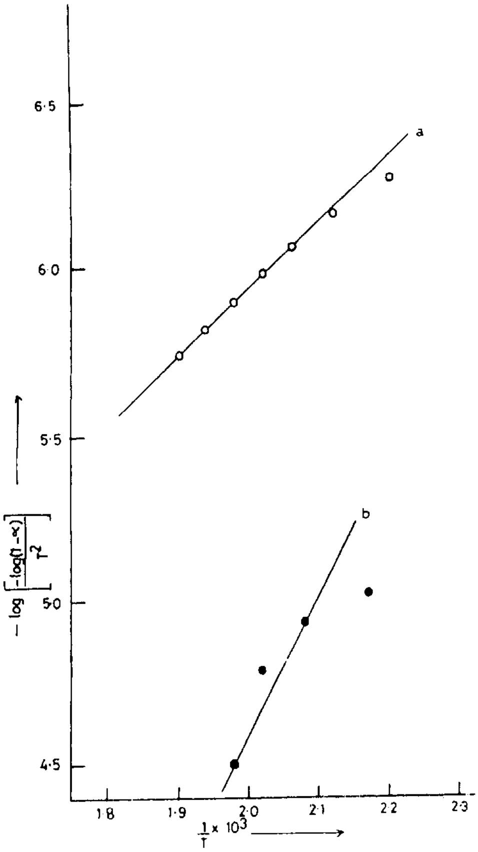

Fig. 4. Coats–Redfern plot for: a, Ge[S$_2$CNPr^{i}Cyhx]Cl$_3$; b, Ge[S$_2$CNPr^{i}Cyhx

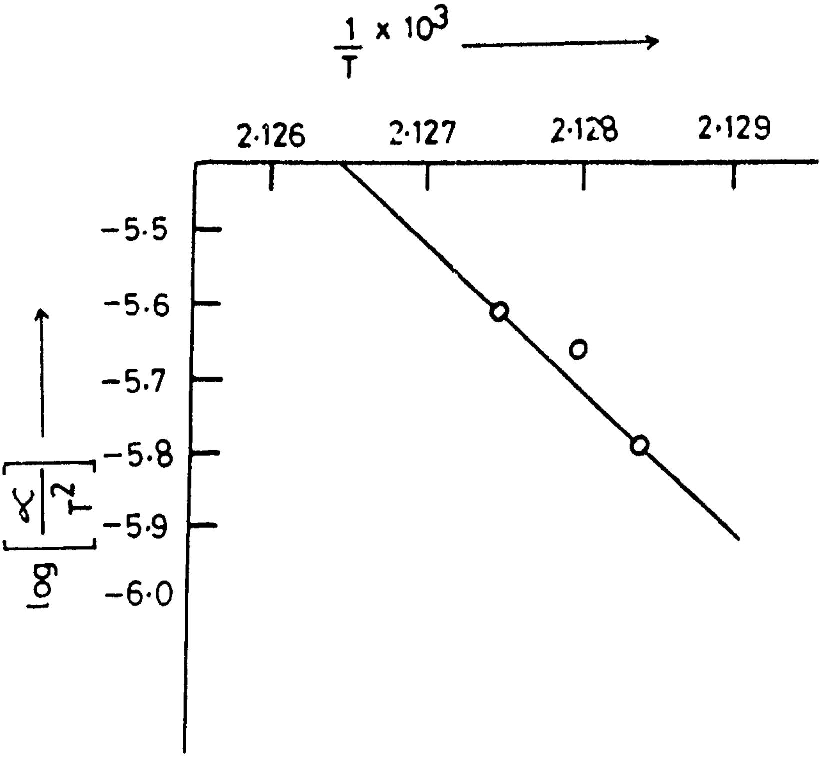

Fig. 5. Piloyan-Novkova plot for: $Ge[S_2CNMeCyhx]Cl_3$.

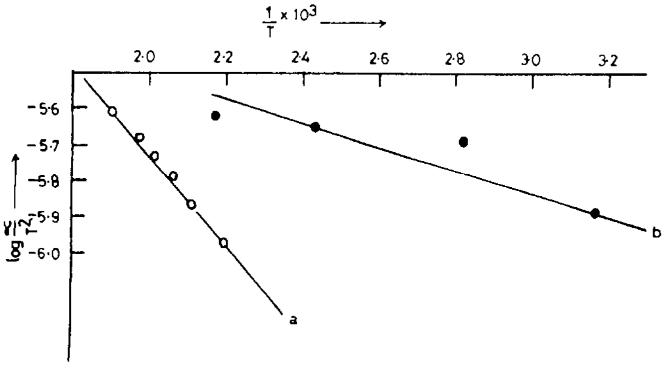

Fig. 6. Piloyan-Novikova plot for: a, $Ge[S_2CNPr^iCyhx]Cl_3$; b, $Ge[S_2CNPr^iCyhx]_4$.

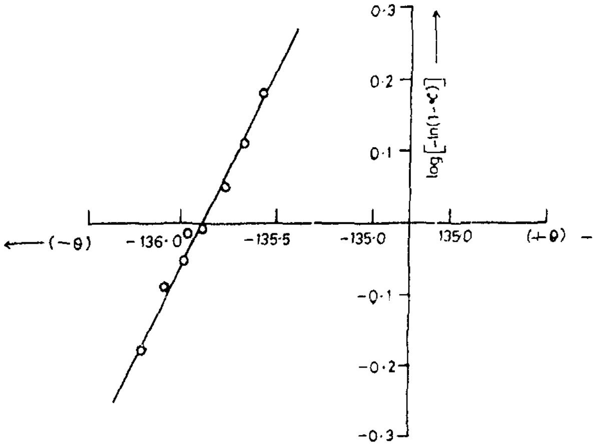

Fig. 7. Horowitz–Metzger plot for Ge[S$_2$CNMeCyhx]Cl$_3$.

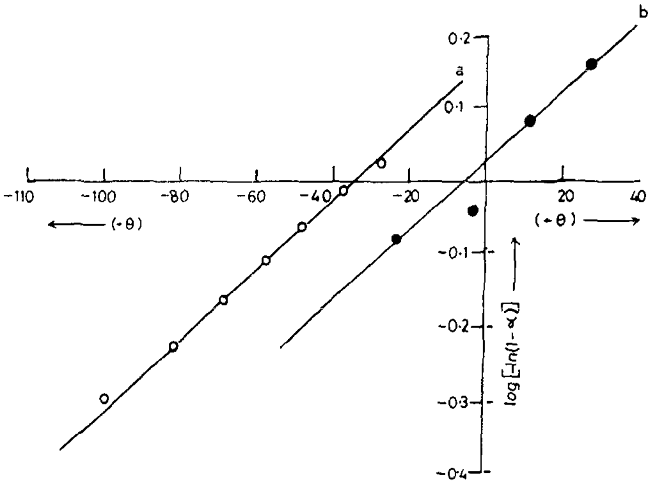

Fig. 8. Horowitz–Metzger plot for: a, Ge[S$_2$CNPr^{i}Cyhx]Cl$_3$; b, Ge[S$_2$CNPr^{i}Cyhx]$_4$.

mol^{-1} using the expression

$$\Delta H(\text{kJ mol}^{-1}) = \Delta H\ (\mu\text{V}) \times 60 \times \text{mol.wt.} \times 10^{-6}/1000$$

The temperature-dependent calibration constant was obtained from the Currel equation [21]

$$K = -1.3 \times 10^{-4} \times \text{peak temperature} + 0.2200$$

The kinetic parameters are summarized in Table 2.

Table 2
Kinetic parameters of the complexes for the first step of thermal decomposition

No.	Compound	Calibration constant $K/(\mathrm{kJ\ cm^{-2}})$	Equations	Order of reaction n	Heat of reaction $\Delta H/(\mathrm{kJ\ mol^{-1}})$
1.	$\mathrm{Ge[S_2CNMeCyhx]Cl_3}$	0.1412	Coats–Redfern	1	$\Delta H_1 = 20.049 \times 10^{-2}$
			Piloyan–Novikova	1	$\Delta H_2 = 10.3178 \times 10^{-2}$
			Horowitz–Metzger	1	
2.	$\mathrm{Ge[S_2CNPr^iCyhx]Cl_3}$	0.1481	Coats–Redfern	1	
			Piloyan–Novikova	1	Not recorded
			Horowitz–Metzger	1	
3.	$\mathrm{Ge[S_2CNPr^iCyhx]_4}$	0.1572	Coats–Redfern	1	
			Piloyan–Novikova	1	$\Delta H = 11.24526 \times 10^{-2}$
			Horowitz–Metzger	1	

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