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TRIS-N(ETHYL, m-TOLYL)DITHIOCARBAMATO COMPLEXES OF ARSENIC(III), ANTIMONY(III) AND BISMUTH(III)

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ABSTRACT

Tris-*N*(ethyl, *m*-tolyl) dithiocarbamato complexes of arsenic(III), antimony(III) and bismuth(III) abbreviated as $As(S_2CNRR')_3$, $Sb(S_2CNRR')_3$ and $Bi(S_2CNRR')_3$, respectively, where $R = C_2H_5$ and $R' = m\text{-}C_6H_4CH_3$, have been synthesized. These complexes have been characterized on the basis of elemental analyses, molecular weight determinations, conductance measurements and infrared spectral studies. Thermal studies of these complexes have been carried out in nitrogen and air to determine their modes of decomposition. Kinetic parameters, such as apparent activation energy and order of reaction, have been determined by the graphical method of Coats and Redfern [1].

INTRODUCTION

The chemistry of arsenic dithio complexes has been investigated in much greater detail than any of its congeners [2—4]. The organo-arsenic dithiocarbamato complexes are used as fungicides and herbicides [5]. Few complexes of antimony(III) and bismuth(III) with dithiocarbamate ligands are known. The formation of water-insoluble $Sb(R_2dtc)_3$ complexes [6] has been utilized for the analysis of Sb(III) [7] and also finds use in bacteriocides [8]. The crystalline Bi(III) dithiocarbamates [8,10] have been found useful in the determination of Bi(III) [9]. A literature survey reveals that little work has been carried out on the thermal studies of metal dithiocarbamato complexes [11—13].

EXPERIMENTAL

Materials and methods

The ligand sodium *N*(ethyl, *m*-tolyl)dithiocarbamate has been synthesized by the general method described in the literature [14]. All the chemicals used were of analytical grade.

Preparation of complexes

All the reactions were carried out in aqueous medium. Tris-*N*(ethyl, *m*-tolyl)dithiocarbamato arsenic(III), antimony(III) and bismuth(III) have been synthesized by mixing an aqueous solution of salts of arsenic(III), antimony(III) and bismuth(III) with an aqueous solution of the ligand in 1 : 3 molar ratio. A white complex of arsenic, a cream-coloured complex of antimony and a canary yellow complex of bismuth were precipitated and washed with distilled water and dried over P_2O_5 under vacuum. Yield: 70—80%.

Analyses

The ligand was estimated by the method of Shankaranarayana and Patel [15]. Arsenic, antimony and bismuth were estimated by the standard gravimetric methods [16] after digestion of the complexes as reported by Erdey [17]. Nitrogen was estimated by the Kjeldahl method and sulphur as barium sulphate.

Physical measurements

Molecular weights were determined in benzene by a Gallenkamp (U.K.) Ebulliometer fitted with a thermistor. Conductance measurements were made in nitrobenzene at 30 ± 0.05° C with a Beckmann conductivity bridge Model No. RC-18A. Infrared spectra were recorded in the solid state (KBr pellets) in the region 4000—200 cm^{-1} with a Perkin-Elmer 621 grating spectrophotometer. Thermal studies (TG and DTG) were carried out on a Setaram G-70 thermobalance (France), sample size 20—30 mg, heating rate 7° C min^{-1} and flow rate of gas 10 ml min^{-1}. Atmospheres of both nitrogen and air (dynamic) were employed.

RESULTS AND DISCUSSION

The elemental analyses (Table 1) indicate 1 : 3 metal to ligand stoichiometry for these complexes. All are soluble in most of the common organic solvents, particularly chloroform, acetone and benzene. The molar conductance of 10^{-3} M solutions of all these complexes in nitrobenzene are found to be in the range 0.30—0.35 ohm^{-1} cm^2 $mole^{-1}$, indicating that they are non-

TABLE 1

Analytical data of the complexes

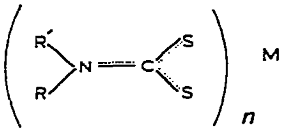
Complex *	Colour	Found (calc.) percentage of			M.W.	
		N	S	M	Found	Calc.
$As(S_2CNRR')_3$	White	5.8 (6.0)	27.1 (27.3)	10.1 (10.6)	695	704.92
$Sb(S_2CNRR')_3$	Cream	5.2 (5.9)	25.0 (25.5)	16.0 (16.1)	742	751.75
$Bi(S_2CNRR')_3$	Canary yellow	4.8 (5.0)	22.4 (22.9)	24.7 (24.9)	829	838.98

* $R = C_2H_5$ and $R' = m\text{-}C_6H_4CH_3$.

electrolytes. From the molecular weight determination of the complexes in benzene, it follows that the complexes are monomeric species. The antimony and bismuth complexes are stable indefinitely in air. $As(S_2CNRR')_3$ begins to decompose after a few days, but can be preserved in an air-tight sample tube for a long period. The ligand used is highly soluble in water and in common organic solvents, but its aqueous solution is not stable over long periods.

Infrared spectral studies

The ir spectra of the metal dithiocarbamates have been well established by Chatt et al. [18]. The spectra possess one medium intensity band at ~1000 cm^{-1}, indicating the presence of a four-membered ring system and supporting the bidentate nature of the dithiocarbamate ligand. The thioureide band (C=N) near 1500 cm^{-1} is a very important characteristic of the dithiocarbamates. The frequency of this band lies between the (C—N), 1250—1350 cm^{-1}, and (C=N), 1640—1690 cm^{-1}, which suggests that it possesses some double bond character. Therefore, the general formula



may be assigned to the compounds where R = ethyl, R' = *m*-tolyl, *n* is the oxidation state of the metal M and M is As, Sb or Bi.

The weak bands appearing in the arsenic, antimony and bismuth complexes at ca. 365, 360 and 360 cm^{-1} may be assigned to ν(As—S), ν(Sb—S) and ν(Bi—S), respectively.

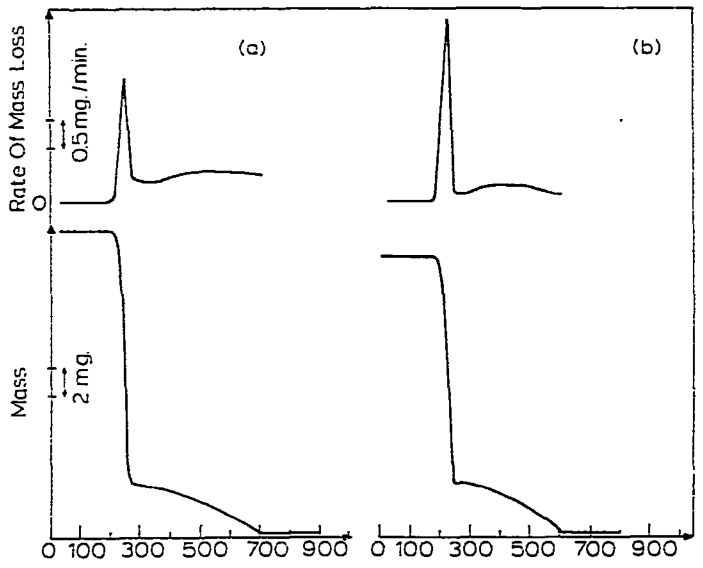


Fig. 1. TG and DTG curves of $As(S_2CNRR')_3$ in (a) nitrogen and (b) air.

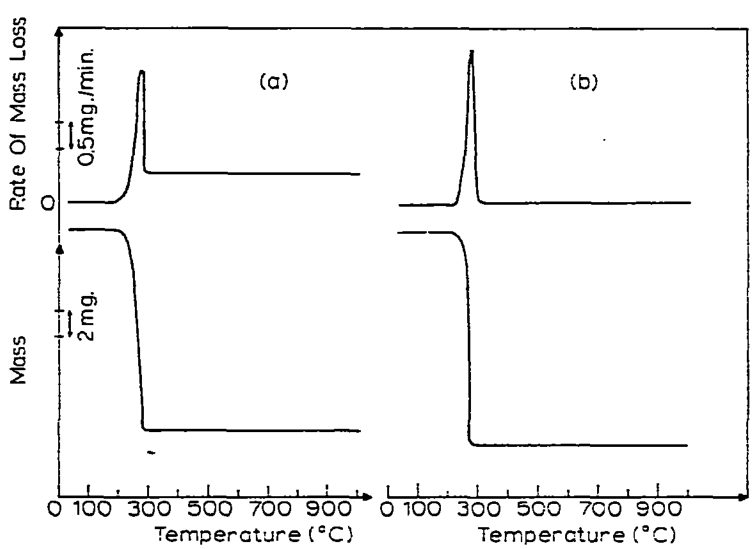


Fig. 2. TG and DTG curves of $Sb(S_2CNRR')_3$ in (a) nitrogen and (b) air.

Thermal analysis

The TG and DTG curves of $As(S_2CNRR')_3$, $Sb(S_2CNRR')_3$ and $Bi(S_2CNRR')_3$ in nitrogen and air are given in Figs. 1—3. The complexes show two-stage weight loss in their TG/DTG curves in a nitrogen atmosphere. In the case of the antimony and bismuth complexes, the first weight loss corresponds to the formation of their respective thiocyanates, while in the case of the arsenic complex, it corresponds to the formation of its sul-

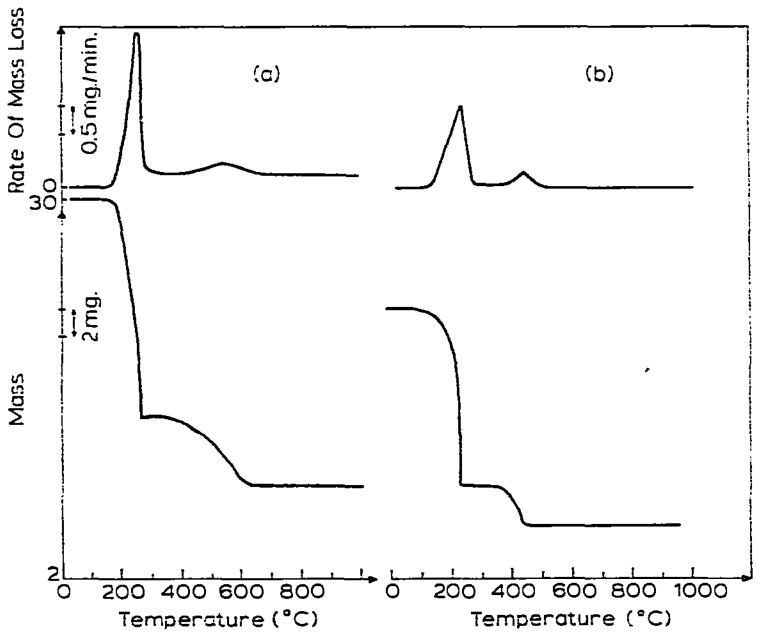


Fig. 3. TG and DTG curves of $Sb(S_2CNRR')_3$ in (a) nitrogen and (b) air.

phide. The intermediates after the first weight loss have been confirmed on the basis of their elemental analyses. The second weight loss in the case of antimony and bismuth leads to the formation of their respective sulphides, while in the case of the arsenic complex, it is due to the volatilization of its sulphide. The thermal stability of these complexes and their decomposition ranges are given in Table 2. In air, arsenic and bismuth complexes show a two-stage weight loss in their TG curves while the antimony complex gives a single-stage weight loss in its TG curve. The first weight loss in the case of the arsenic and antimony complexes corresponds to the formation of their respective sulphides, while in case of the bismuth complex, it is the sulphate which remains at the end of this step. Further, in the case of the arsenic complex, the second weight loss is merely due to volatilization of the sulphide, whereas the bismuth complex forms the oxide. These intermediates and end products have been confirmed on the basis of their elemental analyses. The thermal stability and decomposition range of the complexes are given in Table 2. The calculation of apparent activation energy and order of reaction have been performed for the first-stage decomposition reaction for all the complexes in a nitrogen atmosphere only, employing the graphical method of Coats and Redfern. The plot of $-\log\{[-\log(1-\alpha)]/T^2\}$ against $1/T \times 10^3$ for $n = 1$ (where n = apparent order of reaction) results in a straight line (Fig. 4) with slope $= -E/2.303RT$. The apparent activation energy and order of reaction for the solid state decomposition reactions, viz.

$As(S_2CNRR')_3 \rightarrow As_2S_3$

$Sb(S_2CNRR')_3 \rightarrow Sb(SCN)_3$

and

$Bi(S_2CNRR')_3 \rightarrow Bi(SCN)_3$

are given in Table 2.

TABLE 2

Temperature range of thermal decomposition and kinetic parameters

Complex *	1st decomp. wt. loss (°C)	2nd decomp. wt. loss (°C)	Activation energy for 1st decomp. reaction (kcal mole^{-1})	Order of reaction for 1st decomp. reaction
$As(S_2CNRR')_3$ in N_2	200—265	275—700	47.16	1
$Sb(S_2CNRR')_3$ in N_2	200—290	300—490	24.34	1
$Bi(S_2CNRR')_3$ in N_2	160—280	300—640	13.51	1
$As(S_2CNRR')_3$ in air	180—250	280—650		
$Sb(S_2CNRR')_3$ in air	220—275			
$Bi(S_2CNRR')_3$ in air	120—285	400—500		

* $R = C_2H_5$ and $R' = m\text{-}C_6H_4CH_3$.

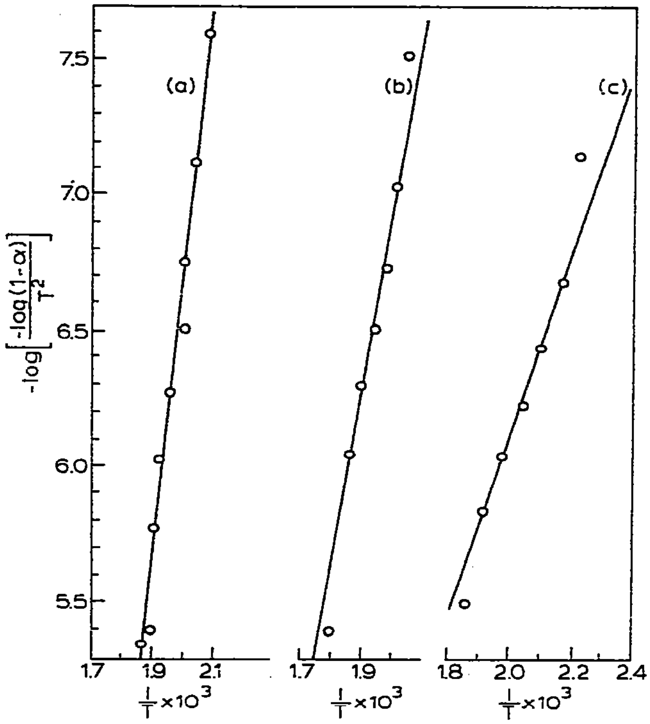


Fig. 4. Coats and Redfern's linearization curves of (a) $As(S_2CNNR')_3$ (b) $Sb(S_2CNRR')_3$ and (c) $Bi(S_2CNRR')_3$.

CONCLUSION

The above results are suggestive of bidentate coordination of the ligand through

sulphur [19—21]. The bismuth complex is thermally less stable than the arsenic and antimony complexes. Arsenic sulphide is more volatile than the antimony and bismuth sulphides. The first-stage decomposition reactions in all cases in a nitrogen atmosphere follow first-order kinetics.

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