

## Note

### THERMAL BEHAVIOUR OF THE THIURAMDISULPHIDE COMPLEX OF THORIUM(IV) NITRATE

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Thiuram sulphides are well-known rubber vulcanisation accelerators. A number of papers [1–3] have been published in recent years on the coordination compounds of thiurams with transition metals. Thorium(IV) complexes of sulphur-donor ligands are relatively very rare; to our knowledge, only one complex of thorium(IV) of dithiocarbamate has been reported [4]. In the present note, isolation, characterisation and thermal behaviour of the thorium(IV) complex of tetramethylthiuramdisulphide (TMTDS) is reported.

Elemental analyses of the white complex agree well with the formula  $\text{Th}(\text{NO}_3)_4 \cdot \text{C}_6\text{H}_{12}\text{N}_2\text{S}_4$ . The conductivity measurements in acetonitrile indicate the typical behaviour of a non-electrolyte. As expected [5], the complex is diamagnetic.

The assignments of infrared spectral bands were made by comparison with previously reported thiuram complexes [1,3]. The thiuram complexes show four important bands in the  $1500\text{--}800\text{ cm}^{-1}$  region [1]; (a) a strong band at about  $1500\text{ cm}^{-1}$ , called the “thiureide band”, (b) a band located at about  $1280\text{--}1240\text{ cm}^{-1}$  due to C–N vibration of the alkyl group, (c) a weak band at about  $1000\text{--}970\text{ cm}^{-1}$  which corresponds to the C=S stretching mode, and (d) a weak band at  $860\text{--}820\text{ cm}^{-1}$  due to the C–S stretching mode. In the complex  $\text{Th}(\text{NO}_3)_4 \cdot \text{C}_6\text{H}_{12}\text{N}_2\text{S}_4$ , bands are observed at  $1510$ ,  $1250$  and  $970\text{ cm}^{-1}$  which have been assigned to (a), (b) and (c), respectively. The corresponding bands in the free ligand are at  $1495$ ,  $1240$ , and  $960\text{ cm}^{-1}$ . The band observed at about  $860\text{ cm}^{-1}$  (due to C–S stretching) in the free ligand, does not appear in the complex. The presence of a bivalent nitrate group in the complex is indicated by the appearance of bands at  $1495$  ( $\nu_4$ ),  $1290$  ( $\nu_1$ ),  $1030$  ( $\nu_2$ ),  $810$  ( $\nu_6$ ) and  $730\text{ cm}^{-1}$  ( $\nu_3/\nu_5$ ) [6–8]. The Th–S stretching band is observed at  $350$  and  $340\text{ cm}^{-1}$  [4]. The overall infrared

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TABLE 1

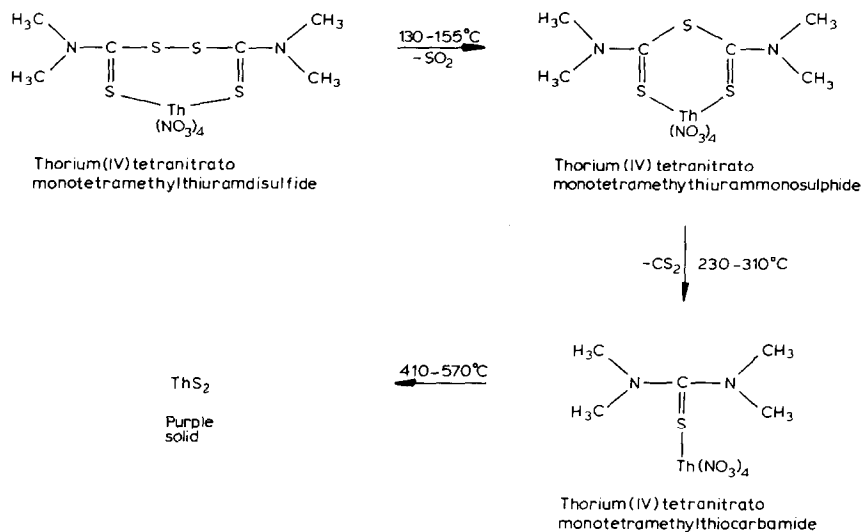
Thermal decomposition (TG) data for the  $\text{Th}(\text{NO}_3)_4 \cdot \text{TMTDS}$  complex

| Complex  | Decomp. temp. ( $^{\circ}\text{C}$ ) |       | Decomp. product  | Wt. loss (%) |        |
|--|--------------------------------------|-------|--|--------------|--------|
|  | Initial                              | Final |  | Found        | Calcd. |
| $\text{Th}(\text{NO}_3)_4 \cdot \text{C}_6\text{H}_{12}\text{N}_2\text{S}_4$ | 130                                  | 155   | $\text{Th}(\text{NO}_3)_4 \cdot \text{C}_6\text{H}_{12}\text{N}_2\text{S}_3$ | 5.32         | 4.44   |
|  | 230                                  | 310   | $\text{Th}(\text{NO}_3)_4 \cdot \text{C}_5\text{H}_{12}\text{N}_2\text{S}$   | 16.32        | 15.00  |
|  | 410                                  | 570   | $\text{ThS}_2$   | 60.10        | 58.88  |

spectral evidence suggests that TMTDS acts as a bidentate, S-S chelating agent forming a seven-membered ring with Th(IV). Hence, the coordination number of Th(IV) in this complex is likely to be ten.

The results of thermogravimetric analyses of the  $\text{Th}(\text{NO}_3)_4 \cdot \text{TMTDS}$  complex are summarised in Table 1.

The changes can be illustrated by



## EXPERIMENTAL

A mixture of  $\text{Th}(\text{NO}_3)_4$  solution (0.1 mmole in 50 ml acetone) and TMTDS solution (0.1 mmole in 150 ml acetone) was stirred for 12 h. A white precipitate separated out, which was filtered, washed several times with acetone and ether and dried in vacuo. The yield was ca. 60%. The complex  $\text{Th}(\text{NO}_3)_4 \cdot \text{C}_6\text{H}_{12}\text{N}_2\text{S}_4$  required Th, 32.22; C, 10.00; H, 1.66, N, 11.66 and S, 17.77%, and was found to contain Th, 32.69; C, 10.60; H, 1.70; N, 11.93 and S, 18.10%. The physical measurements were made as reported earlier [9].

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