

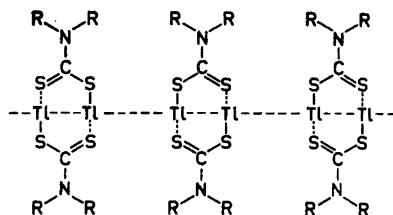
Thallium(I) N,N-Dialkyldithiocarbamates

STIG ÅKERSTRÖM

Research Department, AB Bofors, Nobelkrut, Bofors, Sweden, and Department of Organic Chemistry, Chemical Institute, University of Uppsala, Uppsala, Sweden

In many respects the thallium(I) compounds bear a certain resemblance to the metals of group I in the periodical table. In a previous paper¹ the author has discussed the gold(I) dialkyldithiocarbamates and the investigation is now extended to include the corresponding thallium(I) compounds. These as well as the gold(I) dialkyldithiocarbamates proved to be dimeric in benzene solution. The reaction between the latter salts and the corresponding thiuramdisulphide takes place at a moderate rate, yielding gold(III) compounds,² and the reaction has been shown to pass over the divalent oxidation stage.³

compounds to be chain polymers in the solid state. Recently Frasson *et al.*⁵ have shown the cyclopentadienils of monovalent thallium to have a chain structure. It seems reasonable to suppose that in the solid state the thallium(I) dialkyldithiocarbamates have a chain structure analogous to that of the gold salts:



The stability of the dimeric units in benzene solution is probably due to a strong coordination as indicated in the figure. The Tl—Tl distance in the dimeric units might be expected to be somewhat shorter than the distance between the thallium atoms of different units. The interaction between the thallium atoms of

Table 1. Data for the salts $\left[\begin{array}{c} R_2N-C-STl \\ || \\ S \end{array} \right]_n$. The molecular weight determinations are made cryoscopically in benzene.

R	m.p., °C	n	Tl calc.	Tl found
Methyl	130—131		62.97	62.86, 62.96
Ethyl	115—118	2	57.96	57.91, 57.84
Propyl	124.5—125.5	2	53.69	53.72, 53.79
Isopropyl	290 (decomp.)		53.69	53.77, 53.63
Butyl	73.5—76	2	50.00	50.10, 50.10
Isobutyl	167—168		50.00	50.82, 50.82, 50.85

The analogous reaction of the thallium (I) compounds gives thallium(III) compounds. As this reaction seems fairly suitable for studying the possible existence of the divalent oxidation stage of thallium, Vännegård and the author are in progress with such a study by ESR. The preliminary experiments have so far given negative results.

An X-ray crystallographic study of some gold(I) dialkyldithiocarbamates by Hesse⁴ gives evidence for some of these

different units is so far hypothetical but seems to be possible in the solid state.

1. Åkerström, S. *Arkiv Kemi* **14** (1959) 387.
2. Åkerström, S. *Ibid* **14** (1959) 403.
3. Vännegård, T. and Åkerström, S. *Nature* **184** (1959) 183.
4. Hesse, R. *To be published*.
5. Frasson, E. *et al. Nature* **199** (1963) 187.

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