

An Unusual Thermal *trans* → *cis* Rearrangement

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Summary The thermal *trans*→*cis* rearrangement of dichlorobis(pentamethylenesulphide)platinum(II) is reported.

As part of the work on the co-ordinating ability of ligands containing donor atoms of Group VI^B we have studied the thermal behaviour of a series of dialkyl sulphide complexes of the form MX_2L_2 , where M = Pd or Pt, X = halogen, and L = a dialkyl sulphide. The platinum complexes with pentamethylene sulphide (PMS) have proved particularly interesting since for these compounds there is strong

evidence for thermal *trans*→*cis* isomerisation. Although several examples of thermal *cis*→*trans* isomerisation have been noted² very few observations of *trans*→*cis* rearrangements appear to have been reported.

The Figure shows d.t.a. traces for the $\text{PtX}_2(\text{PMS})_2$ complexes. Comparison of these traces with thermogravimetric data³ indicates that the large relatively broad endothermic peaks (D) correspond to the decomposition of the complexes to the metal halide. The decomposition peak in the d.t.a. traces is preceded by a very sharp endothermic peak (C) which corresponds to the m.p. of the complex. Comparison of the traces for the corresponding

trans- and *cis*-isomers show that the melting and decomposition curves are very similar. The results are summarised in the Table.

For the *trans*-isomers there is, in addition, an endothermic peak (A), T_{\max} 146 and 132° for the chloride and bromide, respectively. In both cases this is closely followed by a smaller exothermic peak (B). We conclude that the

additional endothermic peaks correspond to a solid-solid phase change, similar peaks having been observed with other dialkyl sulphide complexes. Such peaks have been shown to be reversible.³ The exothermic peak (B) can be associated with the isomerisation of the *trans*- to the *cis*-complex. Evidence for this type of rearrangement is obtained from the far i.r. spectra. Heating of the *trans*-isomers to just below their m.p.'s resulted in products of much paler colour whose far i.r. spectra were virtually identical with the corresponding *cis*-isomer, i.e. ν_{\max} (Pt-Cl) for *trans*-PtCl₂(PMS)₂ before heating was at 345 cm⁻¹; after heating it occurred at 326 and 312 cm⁻¹. ν_{\max} (Pt-Cl) for *cis*-PtCl₂(PMS)₂ is at 324 and 311 cm⁻¹.

The thermal *trans*→*cis* rearrangement was not observed for the analogous platinum dimethyl sulphide, diethyl

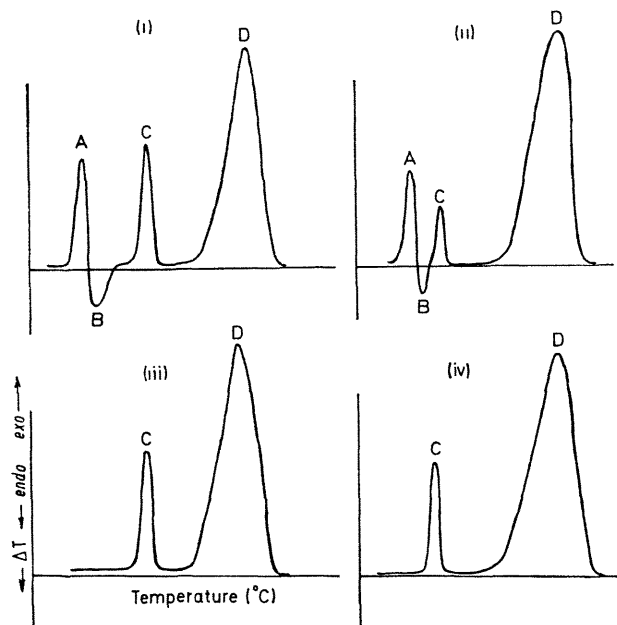


FIGURE. D.T.A. traces for various pentamethylene sulphide complexes of platinum; (i) *trans*-PtCl₂(PMS)₂; (ii) *trans*-PtBr₂(PMS)₂; (iii) *cis*-PtCl₂(PMS)₂; (iv) *cis*-PtBr₂(PMS)₂.

Maximum temperatures (T_{\max} , °) of d.t.a. peak (see Figure)

	A	B	C	D
<i>trans</i> -PtCl ₂ (PMS) ₂	146	152	179	288
<i>cis</i> -PtCl ₂ (PMS) ₂			180	294
<i>trans</i> -PtBr ₂ (PMS) ₂	132	142	153	304
<i>cis</i> -PtBr ₂ (PMS) ₂			152	305

Sample size approx. 20 mg diluted in alumina. Nominal heating rate 10° min⁻¹ in an atmosphere of nitrogen.

sulphide, and tetramethylene sulphide complexes and it is possible that the rearrangement of the platinum pentamethylene sulphide complexes is related to crystal structure effects. Preliminary studies using a differential scanning calorimeter to measure the heat change involved in the *trans*→*cis* isomerisation give a value of around 21 kJ mol⁻¹ for the *trans*→*cis*-PtCl₂(PMS)₂ reaction. This value is similar to that found for the *cis*→*trans* isomerisation of PtCl₂(C₅H₅N)₂.⁴

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¹ E. A. Allen, N. P. Johnson, D. T. Rosevear, and W. Wilkinson, *J. Chem. Soc. (A)*, 1970, 2137.

² M. I. Ivanova, *Zhur. neorg. Khim.*, 1957, **2**, 1317, 1324, 1775.

³ E. A. Allen and W. Wilkinson, to be published.

⁴ G. Beech, G. Marr, and S. J. Ashcroft, *J. Chem. Soc. (A)*, 1970, 2903.