

PREPARATION AND THERMAL PROPERTIES OF TETRAHEDRAL CYANO COMPLEXES CONTAINING THE [Me₂PhS]⁺ CATION

K. Györyová

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF SCIENCES, P. J. ŠAFARIK
UNIVERSITY, MOYZESOVA 11, 041 54 KOŠICE, CSFR

The preparation of three new tetracyano complexes of the type [Me₂PhS]₂ [M(CN)₄] (*M* = Zn, Cd, Hg) is described in this paper. The prepared compounds were identified by elemental analysis and studied by using infrared spectroscopy and thermal analysis.

An original method for the synthesis of different cyano complex compounds containing a secondary iodonium [Ph₂I]⁺ cation and a tertiary trimethyl- or triphenylsulphonium cation, [Me₃S]⁺ or [Ph₃S]⁺, was recently developed in our Department, and some tens of different complex compounds with transition elements were prepared and characterized [1-3]. It seemed interesting to investigate the thermal decomposition of such cyano complex compounds with the tertiary sulphonium cation which contains both alkyl and aryl groups bonded to the sulphur atom. The results have been compared with those obtained earlier on analogous compounds containing either the tertiary alkylsulphonium [Me₃S]⁺ or arylsulphonium [Ph₃S]⁺ cation [3, 4].

Experimental

Preparation of samples

The complex cyano compounds [Me₂PhS]₂[Zn(CN)₄], [Me₂PhS]₂[Cd(CN)₄], and [Me₂PhS]₂[Hg(CN)₄] were synthesized via the reactions of the silver cyano complexes with dimethylphenylsulphonium iodide:

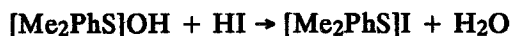
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The preparation method is analogous to that developed earlier [3]. $[\text{Me}_2\text{PhS}]\text{I}$ was prepared in a three-step synthesis. First, $[\text{Me}_2\text{PhS}]\text{ClO}_4$ was obtained by the method of Hinsbey [4]:



Dimethylphenylsulphonium iodide was prepared by using the following method:



Preparation of $[\text{Me}_2\text{PhS}]_2 [\text{M}(\text{CN})_4]$ ($M = \text{Zn}, \text{Cd}, \text{Hg}$)

We gradually added the calculated amount of a freshly prepared precipitate of $\text{Ag}_2[\text{M}(\text{CN})_4]$ to 5.32 g of $[\text{Me}_2\text{PhS}]\text{I}$ dissolved in 120 cm³ of water with constant stirring. The yellow precipitate of AgI formed was filtered off on an S-3 sintered glass filter. The filtrate was slowly evaporated on a water-bath. After cooling, small crystals of the complex cyano compounds $[\text{Me}_2\text{PhS}]_2[\text{M}(\text{CN})_4]$ appeared. The reaction yields were 60-75%. The compounds were very soluble in water, but less so in dimethylformamide and dimethylsulphoxide. They were insoluble in methanol, ethanol, ether, acetone and chloroform.

Methods used to characterize the samples

The prepared substances were identified by elementary analysis (CNH - Hewlett-Packard analyser) and by chemical analysis of the metals. The infrared spectra of the solid substances, gaseous products and intermediates of thermal decomposition were measured with a Specord instrument (Model 80, Jena, GDR) in the region 4000-200 cm⁻¹. The thermal properties of the substances were investigated in an argon atmosphere with a Derivatograph (MOM, Budapest, Hungary). The TG, DTG and DTA curves were recorded simultaneously. The following parameters were used: TG sensitivity 100 mg; heating rate 9 deg·min⁻¹; maximum temperature 900°. The samples were placed in platinum crucibles.

Results and discussion

1. The prepared compounds are stable in air and light. On the other hand, the silver cyano complexes are unstable and decompose in light. The synthesis of these compounds therefore requires strict observance of the reaction conditions given below.

2. Substitution of the $[\text{Me}_2\text{PhS}]^+$ cation for an alkali metal cation in the cyano complexes results in a shift of the stretching vibration $\nu(\text{CN})$ towards lower wavenumbers. As concerns the complex cyano compounds containing the $[\text{Me}_2\text{PhS}]^+$ cation, the $\nu(\text{CN})$ values decrease with increasing atomic number of the central atom (Table 1). If the CN groups are bonded more strongly, the absorption band in the infrared spectrum appears at higher wavenumbers and vice versa [6]. Thus, the bond strength between the carbon and nitrogen atoms in the CN ligands is the highest for the compound containing zinc.

The elementary analyses and IR spectra are given in Table 2.

Table 1 Stretching vibrations $\nu(\text{CN})$ (cm^{-1}) in cyano complexes of the $[\text{M}(\text{CN})_4]^{2-}$ type for different cations

<i>M</i> :	Zn	Cd	Hg
K^+	2151	2146	2152
$[\text{Me}_2\text{PhS}]^+$	2140	2135	2125

3. The thermal decomposition of $[\text{Me}_2\text{PhS}]\text{ClO}_4$ (Fig. 1) starts with melting at 160° , with a sharp endothermic DTA peak, without change in the TG curve. Above 190° , the compound starts to decompose in an endothermic process, with a maximum of 220° in the DTA curve. One mole of Me_2S , one mole of PhCl and two moles of O_2 are liberated according to:



The thermal decomposition of $[\text{Me}_2\text{PhS}]_2[\text{Zn}(\text{CN})_4]$ (Fig. 2) starts at 260° with an endo process, in which one mole of Me_2S is lost.

The compound $[\text{Me}_2\text{PhS}]_2[\text{Cd}(\text{CN})_4]$ starts to melt at 140° (Fig. 3) and then decomposes in an endothermic process, in which one mole of Me_2S is lost from the molecule. At 360° , further decomposition follows in an exothermic process, which is connected with the liberation of two moles of MeCN .

Table 2 The elementary analysis and IR spectra

[Me ₂ PhS] ₂ [Zn(CN) ₄] white lustrous tiny crystals						
		C	H	N		Zn
Calc.:		53.88	4.93	12.57		14.67%
Found.:		53.47	4.56	12.25		14.08%
IR(KBr):	νC-H	3020;	νC=C	1450;	δC-H	1325;
		2925				
	νC-C	990;	γC-H	757;	νC≡N	2140 cm ⁻¹
				680		
[Me ₂ PhS] ₂ [Cd(CN) ₄] white tiny crystals						
		C	H	N		Cd
Calc.:		48.54	4.44	11.32		21.73%
Found.:		48.32	4.32	11.12		21.52%
IR(KBr):	νC-H	3025;	νC=C	1445;	δC-H	1325;
		2925		1420		
	νC-C	990;	γC-H	745;	νC≡N	2135 cm ⁻¹
				680		
[Me ₂ PhS] ₂ [Hg(CN) ₄] white tiny crystals						
		C	H	N		Hg
Calc.:		41.33	3.78	9.64		34.54%
Found.:		40.98	3.56	9.63		34.27%
IR(KBr):	νC-H	3020;	νC=C	1440;	δC-H	1325
		2925				
	νC-C	990;	γC-H	740;	νC≡N	2125 cm ⁻¹
				675		

[Me₂PhS]₂[Hg(CN)₄] in which (Fig. 4) decomposes in an endo process at 150°, in which one mole of Me₂S is lost. At 310°, there is a strong exothermic decomposition, with the loss of one mole each of MeCN and PhCN.

All the prepared sulphonium compound start to decompose through the loss of Me₂S in endothermic processes. At higher temperatures, [Me₂PhS]₂[Cd(CN)₄] loses two moles of MeCN, but [Me₂PhS]₂[Hg(CN)₄] loses not only the MeCN, but also one mole of PhCN.

The liberated gaseous components were checked via their IR spectra (in CH₂Cl₂).

The thermal stabilities of these compounds decrease in the following sequence:



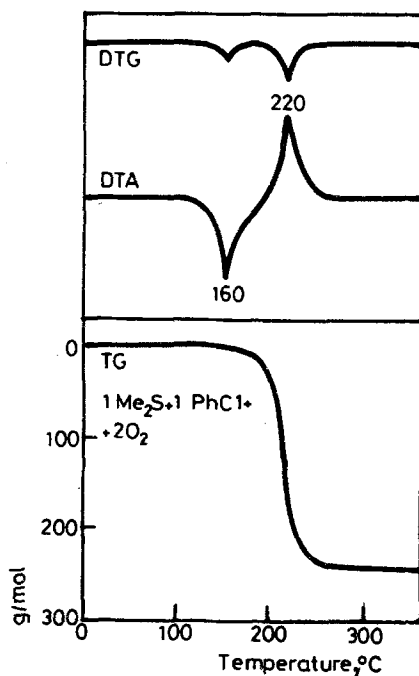
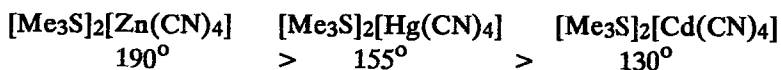


Fig. 1 Thermal decomposition of $[\text{Me}_2\text{PhS}]\text{ClO}_4$

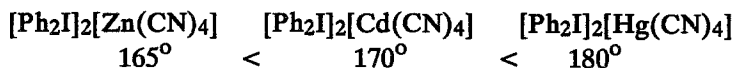
The cyano complexes with $[\text{Me}_2\text{PhS}]^+$ cation (besides the compound containing mercury) decompose at higher temperatures than the starting compound $[\text{Me}_2\text{PhS}]\text{ClO}_4$.

By comparison of the thermal decompositions of the cyano complexes containing zinc, cadmium and mercury with the $[\text{Me}_3\text{S}]^+$ cation, we could observe their decompositions at temperatures lower than in the case of the analogous compounds with cation of the $[\text{Me}_2\text{PhS}]^+$ type [3]:



In the first step they lose Me_2S and MeCN/NC . The solid products of their decomposition are $\text{Zn}(\text{CN})_2$, CdS and HgS [3].

The compounds containing the $[\text{Ph}_2\text{I}]^+$ cation lose PhI in an exothermic process in the first step of their decomposition, and only then liberate PhNC and PhCN . Their thermal stabilities [1] follow the sequence:



The thermal behaviour of the cyano complexes with the anion $[\text{M}(\text{CN})_4]^{2-}$ depends upon the cation.

The compounds containing the $[\text{Me}_3\text{S}]^+$ cation decompose at lower temperatures, i.e. they are less stable than the compounds containing the $[\text{Me}_2\text{PhS}]^+$ cation. When the phenyl group was introduced into the sulphur atom, the thermal stabilities of the cyano complexes increased, which is due to the electronic structures of the sulphonium cations. While the methyl groups are arranged tetrahedrally in the $[\text{Me}_3\text{S}]^+$ cation via only σ bond to the central atom, $p\pi - d\pi$ bonds arise between the π -electrons of the phenyl group and the d -orbitals of the sulphur in the compounds with the $[\text{Me}_2\text{PhS}]^+$ cation.

All compounds of this type with the $[\text{Ph}_2\text{I}]^+$ cation decompose exothermally in the first step with the loss of PhI , after which decomposition to PhNC starts. This may be explained in that, after the loss of the first PhI , the

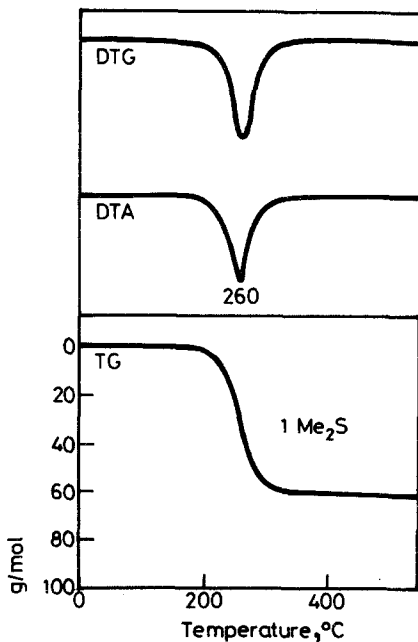


Fig. 2 Thermal decomposition of $[\text{Me}_2\text{PhS}]_2[\text{Zn}(\text{CN})_4]$

second phenyl group forms a σ bond $\text{Ph} - \text{NC} - \text{M}$. In the case of the $[\text{Me}_2\text{PhS}]^+$ cation, an exothermic process is observed for the compounds with the $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Hg}(\text{CN})_4]^{2-}$ anions only in the second step of the decomposition.

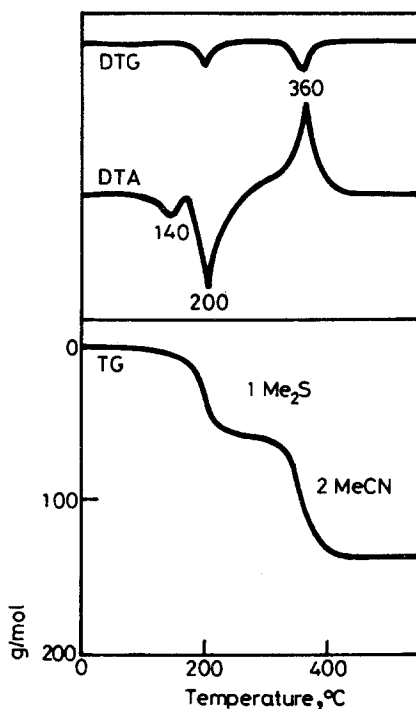


Fig. 3 Thermal decomposition of $[\text{Me}_2\text{PhS}]_2[\text{Cd}(\text{CN})_4]$

Conclusions

1. The values of $\nu_{\text{C}\equiv\text{H}}$ for the prepared series of compounds decrease in the following sequence: $\text{Zn} \rightarrow \text{Cd} \rightarrow \text{Hg}$. This value is always lower than the analogous tetracyano complexes containing an alkali metal.

2. The compounds with the $[\text{Me}_2\text{PhS}]^+$ cation start to decompose with the loss of Me_2S , and the anion decomposes only later. The thermal stability is lower with a higher atomic number of the central atom present in the coordination compound.

3. The compounds with $[\text{Me}_2\text{PhS}]^+$ decompose at temperatures higher than those for the compounds containing the $[\text{Me}_3\text{S}]^+$ cation. This is con-

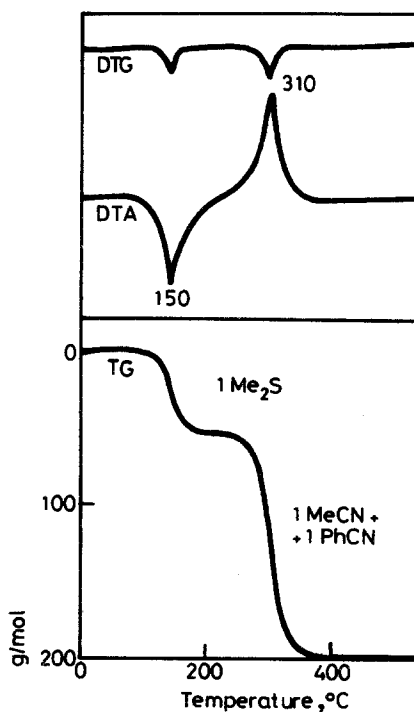


Fig. 4 Thermal decomposition of $[\text{Me}_2\text{PhS}]_2[\text{Hg}(\text{CN})_4]$

nected with the different electronic structures of the different sulphonium cations.

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Zusammenfassung — Es wird die Darstellung von drei neuen Tetracyanokomplexen des Types $[\text{Me}_2\text{PhS}]_2[\text{M}(\text{CN})_4]$ mit $M = \text{Zn}$, Cd bzw. Hg beschrieben. Die hergestellten Verbindungen

dungen wurden durch Elementaranalyse identifiziert und mittels IR-Spektroskopie und Thermoanalyse untersucht.