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POLYNUCLEAR GERMANYLMERCURY COMPLEXES OF LANTHANIDES

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The complexes obtained by the reaction of $[(C_6F_5)_3Ge]_2Hg$ (I) with Pr, Nd, and Ho, which we characterized in our previous work [1, 2], are among the few known polynuclear lanthanide compounds. The formula proposed for these compounds is

$$\{[(C_6F_5)_3Ge]_3Hg\}^{-} \{Ln[Ge(C_6F_5)_3]_2\}^{+} \cdot DME$$

(DME is dimethoxyethane).

In a study of polynuclear derivatives of rare-earth metals, we attempted to synthesize pentafluorophenyl compounds with the Ge-Ln bond by the hydride method, which is one of the most convenient techniques for obtaining heteroorganic groups. In particular, this method was used to obtain compounds with the Sn-Pr and Sn-Nd bond containing nonfluorinated Me₃SiCH₂ groups [3].

However, in all the reactions of $(C_6F_5)_3$ GeH with R_3 Ln [Ln = Pr, Sm, Eu; R = t-BuO and $(Me_3Si)_2N$], instead of the expected products of the type $[(C_6H_5)_3Ge]_3$ Pr, we found fluoride ions and the formation of a multicomponent mixture which is difficult to resolve with di-

substituted perfluorophenyl rings $-GeC_6F_4Ge \leftarrow [4]$ (in addition to RH). These results indicated

that pentafluorophenyl derivatives with Ge-Ln groups, which likely are formed in the initial stages of these reactions, are unstable and rapidly dissociate into lanthanide cations and highly reactive $(C_5F_5)_3Ge^-$ anions, which participate in the nucleophilic replacement of fluorine in C_6F_5 substituents, which is characteristic for perfluoroaromatic compounds [5].

These results indicated doubt relative to the existence of the Ge-Ln σ bond in pentafluorophenyl organogermanium complexes of lanthanides obtained by transmetallation. A subsequent, more detailed study of the complexes indeed showed that the composition and structure of these complexes differ somewhat from the previously proposed composition and structure. These compounds contain not one but two mercury atoms per molecule and thus, lanthanide hept_kis[tris(pentafluorophenyl)germanyl]dimercurates have the general formula [(C_6F_5)_3Ge]_7Hg_2~ Ln 3DME [Ln = Pr(II), Nd(III), Ho(IV)].

We should note that the calculated content of C, H, F, and Ln for the initially proposed formula and the revised formula differ by 0.5-1.5%, i.e., within experimental error. The difference in mercury content (6.08 and 8.31%) is more significant. However, the chemical methods used to analyze for mercury, as later shown by special experiments, give an underestimation. The actual mercury content in the complexes was found by the x-ray fluorescence method. This composition of the complexes corresponds to the amount of mercury liberated in the transmetallation. One hour after the onset of the reaction of (I) with praseodymium filings in DME medium at 70°C, the mercury yield reaches 42.5% (of the total amount) and is subsequently without change upon heating of the mixture under these conditions for several hours.

Institute of Chemistry, Academy of Sciences of the USSR, Gorki. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.'11, pp. 2589-2594, November, 1981. Original article submitted April 1, 1981. We may assume that the reaction of (I) with lanthanides, as in reactions with thallium [6], involves reduction of germanylmercury on the lanthanide surface to yield metallic mercury and highly reactive $(C_6F_5)_3Ge^-$ in the initial steps. In this case, the metal surface acquires a positive charge. The germanium anions add to the starting germanylmercury molecules and give significantly less reactive mercury anions $[(C_6F_5)_3Ge]_4Hg^{2-}$ and $[(C_6F_5)_3Ge]_3Hg^{-}$. In subsequent steps, the action of mercury anions leads to the liberation of lanthanide cations as ionic complexes (II), (III), and (IV). The process is described by the overall equation

$$7_{i}(I) + 2Ln \xrightarrow{DME} 2 \{ [(C_{6}F_{5})_{3}Ge]_{7}Hg_{2} \}^{3} Ln^{3+} \cdot 3 DME + 3Hg$$

$$Ln = Pr, Nd, Ho.$$
(1)

The reaction time is 50 h at ~ 20 °C. The reaction rate increases significantly with increasing temperature.

Support for the scheme for the reaction of (I) with lanthanides may be found in the reaction of praseodymium with $[C_6F_5)_3Ge]_2BiEt$ [7], which occurs significantly more readily $(20^{\circ}C, 5 \text{ h})$ than with (I), but, as expected, in addition to metallic bismuth (85%), yields a complex mixture of products of the replacement of fluorine in C_6F_5 . In this case, $(C_6F_5)_3Ge^$ anions are also likely formed, but in light of the absence of (I) in the reaction system, these anions attack the pentafluorophenyl groups. On the other hand, running the reaction under the same conditions but in the presence of (I), which is capable of adding $(C_6F_5)_3Ge^$ anions, leads to the formation of complex (II). No side products of reactions involving fluoride ions were observed in this case.

In accord with the proposed deactivation of $(C_6F_5)_3Ge^-$ anions by the addition to the germanylmercury molecule, we found that the reaction of $(C_6F_5)_3GeH$ with R_3Pr in the presence of (I) discussed above gives a good yield of ionic complexes and is not complicated by side reactions

$$(t-\operatorname{BuO})_{3}\operatorname{Pr} + 3(\operatorname{C}_{6}\operatorname{F}_{5})_{3}\operatorname{GeH} + 2(\operatorname{I}) \xrightarrow{\operatorname{DME}} 3t-\operatorname{BuOH} + \{[(\operatorname{C}_{6}\operatorname{F}_{5})_{3}\operatorname{Ge}]_{7}\operatorname{Hg}_{2}\}^{3-}\operatorname{Pr}^{3+} \cdot 3_{\operatorname{DME}}$$
(2)

The germanylmercury complexes of Pr, Nd, and Ho are pale solids which melt with decomposition at 200-205°C. These compounds are highly soluble in DME, THF, and acetone, but are virtually insoluble in nonpolar aliphatic and aromatic hydrocarbons. The elemental analysis data are given for these compounds in Table 1.

In our opinion, the most likely structure for complexes (II), (III), and (IV) is as follows:

 $\begin{bmatrix} [(C_6F_5)_3Ge]_3Hg^- \\ [(C_6F_5)_3Ge]_4Hg^{2^-} \end{bmatrix} Ln^{3^+} \cdot 3 \text{DME}$

Support for this ionic structure is found in the rather high equivalent electrical conductivity of compound (II) in THF solution ($\lambda_{\infty} = 59.1 \text{ cm}^2/\Omega \cdot \text{mole}$) and the chemical properties of this compound discussed below. A detailed analysis of the IR spectra of (II), (III), and (IV) showed that the 860 cm⁻¹ band assigned initially to vibrations of the Ge-C bond in the C-Ge-Pr group [1] is due to the presence of coordinated DME in these compounds.

The reactions of the complexes with HCl and tris(pentafluorophenyl)bromogermanium occur at ~ 20 °C in several minutes. In the case of excess HCl, all the metal-metal bonds are destroyed

$$\{[(C_6F_5)_3Ge]_7Hg_2\}^{3-}Ln^{3+}\cdot 3DME + HCl (exc.) \xrightarrow{\text{THF}} 5(C_6F_5)_3GeH + 2(C_6F_5)_3GeCl + 2Hg + PrCl_3 + 3DME$$
(3)

The reactions of complex (II) with an equimolar amount of HCl and with 3 moles of HCl are given by Eqs. (4) and (5)

$$\{[(C_{6}F_{5})_{3}Ge]_{7}Hg_{2}\}^{3-}Pr^{3+}\cdot 3DME + HCl \xrightarrow{DME}_{20^{\circ}} (C_{6}F_{5})_{3}GeH + \{[(C_{6}F_{5})_{3}Ge]_{4}Hg\}^{2-}[PrCl]^{2+}\cdot 3DME + [(C_{6}F_{5})_{3}Ge]_{2}Hg$$
(4)

 $\{[(C_6F_5)_3Ge]_7Hg_2\}^{3-}Pr^{3+}\cdot 3DME + 3HCl \rightarrow 3(C_6F_5)_3GeH + PrCl_3+2 (I)$ (5)

Reaction (5) features decomposition of the ionic species and formation of undissociated

and the second se	Yield, %	Product color	Found Calculated			%	
Complex			C	H	F	Hg	Ln
$[(C_qF_5)_3Ge]_7Hg_2Pr\cdot 3DME$ (II)	86,5	Pale green	<u>34,24</u> 34,33	<u>1,02</u> 0,63	40,76 41,31	8,80 8,31	$\frac{3,27}{2,92}$
$\label{eq:GeF_3} [\ (C_6F_5)\ _3Ge\]_7Hg_2Nd\ \ 3DME\ (III)$	83,3	Pale blue	$\frac{34,82}{34,30}$	$\frac{0,81}{0,63}$	$\frac{40,89}{40,28}$		<u>3,22</u> 2,99
$[(C_6F_5)_3Ge]_7Hg_2Ho\cdot 3DME (IV)$	81,7	Bright brown	<u>33,68</u> 34,15	$\begin{array}{r} 0,99\\ \hline 0,62 \end{array}$	$\frac{41,29}{41,56}$	<u>8,87</u> 8,26	<u>3,38</u> 3,39
$[(C_6F_5)_3Ge]_4HgPrCl \cdot 3DME (V)$	78,8	Pale green	$\frac{33,22}{34,29}$	<u>1,55</u> 1,03		$\begin{array}{r} \underline{6,93}\\ \hline 6,82 \end{array}$	$\frac{4,82}{4,80}$
[(C_6F_5) ₃ Ge] ₄ HgPrBr 3DME (VI)	86,7	Pale green	$\frac{33,53}{33,78}$	<u>1,83</u> 1,01	$\left \begin{array}{c} 38,02\\ \hline 38,16 \end{array} \right $		$\frac{4,30}{4,72}$

TABLE 1.	Polynuclear	Germanyl	lmercury	Complexes	of	Lanthanides
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products. In the case of insufficient HCl, not all the ionic species are decomposed and reaction (4) leads to the formation of complex (V) with the mercury anion $[(C_6F_5)_3Ge]_4Hg^2-$ and $[PrCl]^{2+}$ species which function as cations. The retention of the anion with tetracoordinated mercury in this reaction indicates that $[(C_6H_5)_3Ge]_4Hg^2-$ is the more stable, towards HCl, of the pair of original polynuclear germanylmercury anions $[(C_6F_5)_3Ge]_3Hg^2-$ and $[(C_6F_5)_3Ge]_4Hg^2-$. This finding is in accord with the greater stability of inorganic complexes with tetracoordinated mercury HgX_4^2- relative to HgX_3- [8].

The analogous complex (VI) with the doubly charged mercury anion and the [PrBr]²⁺ cation was isolated in the reaction of complex (II) with tris(pentafluorophenyl)bromogermanium

$$[[(C_6F_5)_3Ge]_7Hg_2]^{3-}Pr^{3+} \cdot 3DME + (C_6F_5)_3GeBr \xrightarrow{DME}_{20^{\circ}} (C_6F_5)_3GeGe(C_6F_5)_3 + (I) + \{[(C_6F_5)_3Ge]_4Hg\}^{2-}[PrBr]^{2+} \cdot 3DME + (VI) \}$$

$$(6)$$

The reaction of (V) and (VI) with 2 moles of HCl leads to the decomposition of the ionic species and the formation, as in reaction (5), of an insoluble praseodymium salt, a hydride $(C_6F_5)_3GeH$, and $[(C_6F_5)_3Ge]_2Hg$

$$\{[(C_6F_5)_3Ge]_4Hg\}^2 - [PrX]^{2+} \cdot 3DME + 2HCl \xrightarrow{DME}_{20^\circ} 2(C_6F_5)_3GeH + (I) + PrCl_2X$$
(7)

Complexes (V) and (VI) are similar in their properties to (II), (III), and (IV). Elemental analysis of these derivatives is given in Table 1.

In a study of the synthetic scope of transmetallation as a method for obtaining polynuclear organometallic lanthanide derivatives, we investigated the reactions of a number of trinuclear compounds of mercury and cadmium with metallic praseodymium in solution in DME. The derivatives of mercury with hydrocarbon groups $(Et_3Ge)_2Hg$, $(Ph_3Ge)_2Hg$, and $[(Me_3SiCH_2)_3-Sn]_2Hg$ and pentafluorophenyl derivatives $[(C_6F_5)_3Si]_2Hg$ and $[(C_6F_5)_3Ge]_2Cd$ are inert relative to metallic praseodymium below 100°C. On the other hand, $[(C_6F_5)_3Sn]_2Hg$ reacts with Pr, Nd, and Lu at $\sim 20°C$ in only a few minutes [9], which leads to the formation of products analogous in their physical and chemical properties to germanium complexes (II)-(IV). Their structure is presently under study.

Thus, we may conclude that the reactivity of compounds $(R_3M)_2M'$ (R = Et, Ph, C₆F₅, and Me₃SiCH₂, M = Si, Ge, and Sn, M' = Cd and Hg) in transmetallation with lanthanides decreases in the series $[(C_6F_5)_3Sn]_2Hg > [(C_6F_5)_3Ge]_2Hg \gg [(C_6F_5)_3Si]_2Hg ~ (Et_3Ge)_2Hg ~ (Ph_3Ge)_2Hg ~ (Ph_3$

likely are formed with DME under the conditions of the reactions studied.

Gladyshev et al. [11] showed that silylmercury complexes of lithium and potassium (Me₂PhSi)₄HgM₂ readily react in toluene solution with excess metallic mercury and give free lithium or potassium and (Me₂PhSi)₂Hg. In contrast to this complex, (II) does not react under comparable conditions with excess mercury in DME. In this case, the significant difference in the solvation energies between the lanthanide complexes and the proposed product of reverse transmetallation (I) apparently plays the predominant role. Starting compound (II) exists as strongly solvated complexes, while (I) is a relatively weak complexing agent. Thus, the reverse reaction (1) is thermodynamically unfavorable in the major solvents. On the other hand, the use of nonpolar solvents such as hexane or benzene is not possible as a consequence of the low solubility of complexes (II), (III), and (IV) in such solvents.

EXPERIMENTAL

All the reactions were carried out in evacuated sealed ampuls. Special attention was given to eliminate traces of moisture from the walls of the instruments used, solvents, and starting reagents. The melting points were determined in evacuated sealed capillaries. The gas-liquid chromatographic analysis was carried out on a Tsvet-129 chromatograph equipped with flow meters on a 50×0.4 -cm column packed with 7% OV-17 on Chromaton N-AW-DMCS and a 300×0.3 -cm column packed with 5% SE-30 on Inerton AW with helium as the carrier gas. The IR spectra were taken on a UR-20 spectrometer. Samples of the solid compounds were prepared in vacuum as suspensions in Vaseline oil. The melting points and decomposition temperatures are given without correction.

<u>Complex of Praseodymium Heptakis[tris(pentafluorophenyl)germanyl]dimercurate with Di-</u> methoxyethane (II). a) A solution of 1.0 g (0.742 mmole) (I) in 6 ml DME was added to praseodymium (0.8 g, 5.7 g-atom) and shaken for 2 h at 70°C. The pale green solution formed was separated from excess praseodymium and the mercury liberated by centrifugation and decantation. The precipitate contained 0.063 g (42%) mercury (of the total amount). DME was removed from the solution by condensation in vacuum. The residue was washed repeatedly and dried in vacuum to yield 0.88 g (86.5%) complex (II) with mp 200-205 (dec.). Complexes (III) and (IV) were synthesized analogously.

b) A solution of 0.42 g (0.303 mmole) $[(C_6F_5)_3Ge]_2BiEt$ and 2.4 g (1.78 mmole) (I) in 15 ml DME was added to praseodymium filings (0.4 g, 2.85 g-atom). The mixture was periodically shaken over 5 h at $\sim 20^{\circ}C$. The solution was separated from metals by centrifugation and decantation. The metal mixture contained 0.05 g (70%) bismuth and 0.08 g (22.5%) mercury (of the total amount). DME was removed from the solution by condensation in vacuum. The residue was washed with toluene and dried in vacuum to yield 0.9 g (263.6%) (II). We should note that in the reaction (I) is consumed in parallel reaction (1), which accounts for the high yield of (II). Hence, a fivefold excess of (I) must be introduced in the reaction of the germanylbismuth compound with praseodymium.

Reaction of Complex (II) with HCl. a) With excess HCl. A solution of 1.1 g (0.228 mmole) (II) and 122.7 ml (5.48 mmole) dry HCl in 10 ml THF was maintained overnight at $\sim 20^{\circ}$ C. To complete the reaction, the mixture was heated for 2 h up to 70°C. The organic layer was decanted from the precipitate formed which contained 0.06 g (65.5%) metallic mercury and 0.05 g (89%) PrCl₃. Gas-liquid chromatographic analysis of the organic layer showed the presence of 0.62 g (94.5%) (C₆F₅)₃GeH, 0.02 g (72.2%) (C₆F₅)₃GeCl, and 0.06 g (97.5%) DME. The reactions of complexes (III) and (IV) with excess HCl were performed analogously.

b) In 1:3 ratio. A solution in 0.51 g (0.106 mmole) (II) and 7.1 ml (0.317 mmole) gaseous HCl in 3 ml DME was maintained for 30 min at $\sim 20^{\circ}$ C. The solvent was removed by condensation in vacuum. The residue of fractional sublimation yielded 0.18 g (99%) (C₆F₅)₃GeH (identified by gas—liquid chromatography) and 0.26 g (91.5%) (I) with mp 229-231°C. A mixed melting point with an authentic sample [12] was undepressed. The unsublimated residue contained 0.023 g (88%) PrCl₃.

c) In 1:1 ratio. A solution of 1.0 g (0.208 mmole) (II) and 4.6 ml (0.205 mmole) gaseous HCl in 8 ml DME was maintained for 1 h at \sim 20°C. DME was removed from the solution. The residue was washed several times with toluene and dried in vacuum to yield 0.48 g (79%) complex (V). This product melts with decomposition above 205°C. Removal of the solvent from the toluene extract and sublimation of the residue yielded 0.26 g (93%) (I) with mp 228-230°C

(mixed sample) and 0.12 g (100%) (C_6F_5)₃GeH.

Complex of Bromopraseodymium Tetrakis[tris(pentafluorophenyl)germanyl]mercurate with Dimethoxyethane (VI). A solution of 0.18 g (0.275 mmole) $(C_6F_5)_3$ GeBr in 5 ml DME was added to a solution of 1.34 g (0.278 mmole) (II). A precipitate of $(C_6F_5)_3$ GeGe(C_6F_5)_3 began to appear in 1-2 min. The solution was decanted from the precipitate, which was washed with DME and dried in vacuum to yield 0.3 g (94.5%) of the digermanium compound with mp 312-318°C. A mixed melting point with an authentic sample [12] was undepressed. DME was removed from the solution by condensation. The residue was washed repeatedly with toluene and dried in vacuum to yield 0.72 g (86.5%) (VI) with mp 200-205°C (dec.). After removal of the solvent from the toluene extract, the residue was sublimated in vacuum to yield 0.36 g (95.5%) (I) with mp 228-230°C (mixed sample).

Reaction of the Complex of Chloropraseodymium Tetrakis[tris(pentafluorophenyl)germanyl]mercurate with Dimethoxyethane (V). A sample of 11 ml (0.491 mmole) gaseous HCl was added to a solution of 0.73 g (0.248 mmole) (V) in 5 ml DME. The mixture was maintained for 30 min at $\sim 20^{\circ}$ C. After removal of DME from the residue by fractional sublimation in vacuum, we obtained 0.21 g (74%) (C₆F₅)₃GeH and 0.33 g (98.5%) (I) with mp 228-230°C (mixed sample). The unsublimated residue contained 0.012 g (98.5%) PrCl₃.

The reaction of complex (VI) with 2 moles HCl was carried out analogously.

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CONCLUSIONS

The transmetallation of $[(C_6F_5)_3Ge]_2$ Hg with metallic praseodymium, neodymium, and holmium yielded complexes $[(C_6F_5)_3Ge]_2$ Hg_Ln·3DME (DME is dimethoxyethane), for which the ionic structure $\{[(C_6F_5)_3Ge]_2$ Hg_ $\}^3$ -Ln³⁺·3DME was proposed on the basis of electrical conductivity and chemical properties.

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