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Search for Routes to Prepare Monovalent Thulium

A. A. Fagin[a], S. Yu. Bukhvalova[a], and M. N. Bochkarev[a, *]

[a] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia*

**e-mail: mboch@iomc.ras.ru*

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Abstract—The effective magnetic moments (μ_{eff}) of the prepared solid mixtures are used to determine the presence of monovalent thulium in the reaction products. Potassium does not react with thulium diiodide TmI_2 on heating to 680°C. Under the same conditions, the backward reaction of thulium with KI occurs easily to form metallic potassium and a mixture of thulium iodides TmI_x (x = 1, 2). For the product obtained after heating Tm and KI for 1 h, μ_{eff} corresponds to a mixture of 70% Tm (metal), 20% TmI_2, and 10% TmI. The reduction of TmI_2 to TmI occurs in the reaction with NdI_2. For a mixture of iodides obtained at 700°C, μ_{eff} (3.2 μ_B) corresponds to the following contents: 10% Tm (metal), 1% TmI_2, 44% TmI, 44% NdI_3, and 1% NdI_2. Iodide TmI cannot be isolated from the obtained mixtures. However, the presence of highly reactive species in the products is confirmed by the reaction of tetrahydrofuran (THF) with the product of the reaction of thulium with potassium iodide. The reaction occurs at room temperature and is accompanied by the release of hydrogen and formation of unidentified derivatives of cleaved THF. The initial substances (Tm, KI) and possible products (TmI_2, TmI_3, and metallic K), except for TmI, do not react with THF under the conditions used.

Keywords: monovalent thulium, thulium diiodide, neodymium diiodide, reduction, magnetic moment, stability, reactivity

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INTRODUCTION

The predominant majority of inorganic, organic, and coordination compounds of lanthanoides is known to contain the trivalent Ln^{3+} cation. The unstable tetravalent derivatives were synthesized for Ce, Pr, and Tb [1–5]. The complexes with the Ln^{2+} cation with the $4f^n s^0 d^0$ configuration were synthesized for Eu, Sm, Yb, Tm, Dy, and Nd [6–11]. Their stability decreases on going from Eu to Nd. The relatively stable compounds bearing divalent cations with the $4f^{n-1} s^0 d^1$ configuration containing an alkaline metal atom in the molecule were synthesized for Ce, Pr, Gd, Tb, Ho, Er, and Lu [12, 13], as well as for Nd and Dy [14]. The Nd and Dy compounds can exist in both the $4f^n d^0$ and $4f^{n-1} d^1$ configurations depending on the method used for the synthesis of the complex. Monovalent lanthanoides remain mysterious. Confirmed published data on the synthesis and properties of the compounds with the Ln^{1+} cation are nearly lacking. Monovalent samarium cations are assumed to be formed under the γ-irradiation at 77 K of samarium dichloride ($SmCl_2$) doped to a NaCl matrix [15]. The assumption is based on the appearance upon irradiation of a band at 545 nm in the absorption spectrum of the substance, which was assigned to the transition $4f^6 6s^1 \rightarrow 4f^5 6s^2$ on the Sm^+ cation, and a simultaneous decrease in the intensity of the bands of divalent samarium. The fluorescence laser excitation spectra detected in the reactions of metallic ytterbium with alkyl halides RX (X = F, Cl, Br, I) are assumed [16] to correspond to molecules of monovalent halides YbX. It is reported that the burning of triiodides LnI_3 (Ln = Dy, Ho, Tm) in an electric arc plasma results in the formation of lanthanoide monoiodides generating emission of various intensity in a range of 400–700 nm [17, 18]. The emission spectrum was assigned to LnI molecules. Although no progress is observed in the field of monovalent lanthanoides, this trend in the chemistry of subvalent derivatives of rare-earth metals remains attractive for researchers as an alluring and difficultly attainable purpose of fundamental studies. In addition to the above presented data, a possibility to solve the problem is favored by a similarity of the electronic configurations of Ln^+ ions of some lanthanoides to the configurations of stable di- and trivalent cations of other lanthanoides. In particular, the configurations of Sm^+ ($4f^7$) and Tm^+ ($4f^{14}$) correspond to the configurations of the stable Gd^{3+} and Yb^{2+} ions.

The confirmation of the valence state of the metal is one of the most difficult tasks in the synthesis of monovalent lanthanoide derivatives. The spectral methods, X-ray diffraction (XRD) analysis of phases, or cocrystallization of the products with inorganic substances with the known lattice parameters [19, 20]

applied for this purpose are technically difficult and do not give unambiguous answers. XRD can give a reliable conclusion about the valence state of lanthanoide in the product. However, in this case, the necessary condition is the preparation of the substance as single crystals, which is technically difficult for very unstable monovalent lanthanoide derivatives. The measurement of effective magnetic moments (μ_{eff}) of the synthesized substances was used in this work to identify monovalent samarium and thulium ions. The method is technically simpler in practice than other methods. It is more substantial that, in the cases of samarium and especially thulium, the method makes it possible to reliably and rapidly determine the presence of Sm^+ and Tm^+ ions, since their expected magnetic moments for the configurations of Sm $4f^7$ (8.0 μ_B) and Tm $4f^{14}$ (0.0 μ_B) differ sharply from the moments of all other ions of the corresponding metal. It should be mentioned that the Sm^+ and Tm^+ ions can take the forms $4f^6s^1$ and $4f^{13}s^1$ in addition to the configurations presented above. In this case, magnetic measurements are less indicative, but the formation of such ions is less probable, which was shown in the present study. The third variant of existing Sm^+ and Tm^+ cations are metal-like inorganic phases, where electrons of the reduced metal are generalized to form a conduction band. Similar systems are known for trivalent lanthanoide halides LnX_2 [21, 22]. In these substances, the trivalent state of the metal is shown by the formula $(Ln^{3+})(e^-)(X^-)_2$. In this case, magnetic measurements would also be indicative as for other mixtures with a trivalent component. An advantage of using magnetometry for the identification of monovalent products is also an additivity of the magnetic susceptibility, which makes it possible to calculate (with an insignificant error) the monovalent metal content even in a mixture with other paramagnetic cations. Since the differences in the magnetic properties of Sm^+ and other samarium ions are substantially lower than those in the series of thulium ions, the present study is restricted by the search for synthetic methods of monoiodide TmI.

EXPERIMENTAL

The reactions were carried out in evacuated sealed ampules of Pyrex glass using Tm fillings (22–40 mesh) and KI (98%) (Aldrich). Diiodides TmI_2 and NdI_2 were synthesized from fillings of the corresponding metal and iodine using a previously developed method [9]. Since a metal excess is used in the reactions according to the conditions of diiodide synthesis, samples of TmI_2 contained 30 wt % Tm, which cannot be separated from the target TmI_2, unlike Nd. The magnetic moments were measured at room temperature on the previously designed instrument by comparing with the known samples as described earlier [23]. The procedure is based on Faraday's method. A sensitive unit is a float with a sample holder made of diamagnetic glass and immersed into a vessel filled with ethanol. The relative measurement error did not exceed 5%. GLC analysis was carried out on a Tsvet 800 chromatograph with a thermal conductivity detector. Mass spectrometry was carried out on a Trace GC Ultra/Polaris Q mass spectrometer coupled with a chromatograph. To obtain a preparative amount of products, the syntheses were carried out in 2–3-mL ampules. A Nabertherm tubular furnace was used for heating the samples.

Reaction of TmI_2 with potassium. Diiodide TmI_2 (7.5 mg, 0.017 mmol) and metallic potassium (3 mg, 0.075 mmol) were placed in a 0.5-mL ampule, the ampule was evacuated and sealed, and the sample was used to measure the magnetic moment. For thulium in the sample, μ_{eff} was found to be 5.6 μ_B. The sample was heated at 680°C for 2 h, and μ_{eff} was measured again after cooling to room temperature. The magnetic moment remained unchanged.

Reaction of Tm with potassium iodide. Thulium fillings (5.5 mg, 0.0296 mmol) and KI powder (2.4 mg, 0.014 mmol) were placed in an ampule as described in the previous experiment, and the ampule was sealed. The mixture was stirred by shaking, and μ_{eff} based on thulium involved in the reaction was determined (7.5 μ_B). The sample was heated at 680°C for 2 h, which was accompanied by a change in the color of the mixture to dark brown and the formation of droplets of sublimed potassium on the unoccupied walls of the ampule. The sample was placed in the instrument to measure the magnetic moment, and μ_{eff} was found to be 6.6 μ_B.

Reaction of TmI_2 with NdI_2. An ampule for measuring the magnetic moment was filled with TmI_2 (5.0 mg, 0.012 mmol) and NdI_2 (4.7 mg, 0.012 mmol), the mixture was thoroughly stirred by shaking, and the magnetic moment based on the averaged atomic mass of Tm and Nd was measured (4.6 μ_B). After sample heating at 400°C for 30 min, the magnetic moment remained unchanged. As the temperature rises to 650°C, the magnetic moment is decreased. The sample was heated at 680°C for 30 min, and μ_{eff} = 3.1 μ_B for the formed dark gray finely crystalline powder. The further heating resulted in an increase in μ_{eff}.

Reaction of Tm and Nd with iodine. Thulium fillings (225 mg, 1.33 mmol), neodymium fillings (192 mg, 1.33 mmol), and I_2 (676 mg, 2.66 mmol) were placed in an ampule. The ampule was sealed, and the mixture was thoroughly stirred by shaking. The sample was heated to ~700°C (the mixture ignited for a short time). At the end of the reaction, the sample was heated in a furnace at 680°C for 2 h and cooled to room temperature, and μ_{eff} was measured based on the averaged atomic mass of Tm and Nd involved in the reaction (4.4 μ_B).

Reaction of Tm and La with iodine. A sample containing thulium fillings (9.1 mg), lanthanum fillings (14.4 mg), and I_2 (7.0 mg) was prepared in the same way as in the reaction of TmI_2 with NdI_2, and μ_{eff} based on Tm involved in the reaction was determined for the mixture at room temperature (7.6 μ_B). The sample was heated to mixture ignition (~700°C). After the end of the exothermal phase, the mixture was heated at 680°C for 2 h and then cooled, and μ_{eff} based on Tm involved in the reaction (5.5 μ_B) was determined again.

RESULTS AND DISCUSSION

Since the reduction potential of potassium (−2.9 V) is higher than that of thulium (−2.3 V), it was expected that the direct reaction of TmI_2 with potassium would result in the formation of the target TmI. However, the experiment showed that the heating of a mixture of these substances to 700°C did not lead to the reduction of thulium. The result is consistent with the published data [24], which showed that on prolonged heating at 800°C potassium vapors reduced TmI_3 only to TmI_2. The established inertness of potassium toward TmI_2 allowed us to expect that a backward reaction is possible in spite of the ratio of the electrode potentials: potassium reduction to KI by metallic thulium with the formation of TmI. The assumption was experimentally confirmed: the heating of KI with a twofold excess of thulium at 680°C for 2 h led to the formation of metallic potassium and a mixture of thulium iodides TmI_x with μ_{eff} = 6.6 μ_B, which is substantially lower than that for the starting thulium (7.6 μ_B). The elongation of the heating time did not result in the further decrease in μ_{eff} of the products and formation of an additional amount of potassium, which is evidently due to the complete exhaustion of KI involved in the reaction. The obtained value of the magnetic moment with allowance for the stoichiometry of the starting reagents corresponds to a mixture of 70% Tm (metal), 20% TmI_2, and 10% TmI.

$$Tm + KI \xrightarrow{680°C,\ 1\ h} TmI_2 + TmI + K.$$

An attempt to extract individual TmI from the formed mixture of products was unsuccessful. The addition of dimethoxyethane (DME) to the mixture resulted in the formation of a green solution from which diiodide $TmI_2(DME)_3$ was isolated after solvent removal. A green solution of thulium diiodide is also formed upon the extraction of the mixture with THF, but the dissolution is accompanied, in this case, by the release of hydrogen bubbles. Hydrogen was identified by GLC, and the mass spectrometric analysis of the solution showed products of THF destruction. Similar transformations were observed earlier for the dissolution of diiodides NdI_2 and DyI_2 in THF and were explained by the reaction of the solvent with extremely reactive monovalent iodides NdI and DyI formed due to the disproportionation of the diiodides [25]. Since no disproportionation and subsequent THF destruction occur with diiodides of other lanthanoides, including TmI_2, the reaction with the solvent of the products of the reaction of thulium with KI confirms that the mixture contains highly reactive monovalent iodide TmI.

Thulium diiodide was reduced to monovalent iodide in the reaction with neodymium diiodide under comparable conditions. A change in the magnetic moment of a mixture of equimolar amounts of TmI_2 and NdI_2 (4.6 μ_B) was found to start on heating to 300°C, but the reaction was very slow. The process accelerated substantially with temperature increasing. At 680°C μ_{eff} of the mixture decreased to 3.1 μ_B within 45 min. Taking into account the values of μ_{eff} of the substances involved in the reaction (TmI_2 4.5, NdI_2 2.8), metal-containing impurities (Tm 7.5, Nd 3.3), and triiodides (TmI_3 7.5, NdI_3 3.3), as well as possible products (TmI 0 with the configuration $4f^{14}$ or 4.8 with the configuration $4f^{13}s^1$, NdI_3 3.3), we can propose the only possible explanation of the obtained low value of μ_{eff}: the formation of monovalent thulium with the even electronic configuration $4f^{14}$. The presence of seven paramagnetic components in a poorly separable mixture does not allow one to calculate the exact content of TmI. An approximate estimate shows that more than 80% of diiodide TmI_2 involved in the reaction are reduced to monovalent iodide TmI.

$$TmI_2 + NdI_2 \xrightarrow{680°C,\ 45\ min} TmI + NdI_3.$$

The direct reaction of thulium, neodymium, and iodine in a ratio of 1 : 1 : 2 gives an analogous result. In this case, the initial stage proceeds in the same way as in the synthesis of diiodides with the ignition of the mixture. To cease the process, the sample was additionally heated at 680°C for 2 h.

$$Tm + Nd + 2I_2 \xrightarrow{680°C,\ 2\ h} TmI_2 + NdI_3.$$

For the initial mixture, μ_{eff} (5.7 μ_B) corresponded to the sum of magnetic moments of thulium and neodymium involved in the reaction. The magnetic moment of the mixture of iodides formed upon heating (4.4 μ_B) considerably exceeds μ_{eff} of the mixture of products from the above presented reaction of diiodides TmI_2 and NdI_2. An approximate estimate shows that only 10–15% Tm involved in the reaction are oxidized to monoiodide TmI.

An analogous result was obtained when neodymium was replaced by diamagnetic lanthanum in the above presented reaction. In this case, a decrease in the number of paramagnetic components in the formed mixture of products makes it possible to calculate the relative content of TmI with a high accuracy. A metal excess was used in the reaction to diminish the formation of TmI_2 and TmI_3. After burning and heating of a mixture of Tm, La, and I_2 in a ratio of 2 : 4 : 1

for 2 h, μ_{eff} of the mixture decreased from 7.6 to 5.5 μ_B, which possibly corresponds to contents of 20, 35, and 45% for Tm^+, Tm^{2+}, and Tm^{3+}, respectively. It should be mentioned that the elongation of the heating time for the reaction mixtures increased the magnetic moment in all cases, which is likely due to the reaction of the formed active TmI with the reactor glass leading to metal oxidation.

To conclude, a comparison of the magnetic moments of mixtures of metallic thulium with potassium iodide, thulium diiodide with neodymium diiodide, metallic thulium and neodymium with iodine, and metallic thulium and lanthanum with iodine and the magnetic moments of the same mixtures after heating at 680–700°C showed that μ_{eff} decreased in all cases. The effect observed is explained by the reactions resulting in the formation of diamagnetic thulium monoiodide TmI with the $4f^{14}$ electronic configuration of the metal along with other products. Thulium monoiodide is the first compound containing monovalent lanthanoide. We failed to isolate the formed TmI in the individual state. However, the calculations of the magnetic moments of the reaction products taking into account the additivity of the magnetic susceptibility of the paramagnetic substances and stoichiometry of the reagents involved in the reaction allow us to convincingly conclude that the target monoiodide TmI is present in the products. In addition, an indirect confirmation of the result is the destruction of THF on contact with a mixture of products formed on heating Tm with KI.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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