*ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 5, pp. 299–303. © Pleiades Publishing, Ltd., 2023.
Russian Text © The Author(s), 2023, published in Koordinatsionnaya Khimiya, 2023, Vol. 49, No. 5, pp. 303–307.*

Monovalent Thulium. Synthesis and Properties of TmI

A. A. Fagin[a], S. Yu. Bukhvalova[a, *], V. A. Kuropatov[a], and M. N. Bochkarev[a, **]
[a] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia*
**e-mail: sv-4.4.1991@iomc.ras.ru*
***e-mail: mboch@iomc.ras.ru*

Received September 2, 2022; revised October 12, 2022; accepted October 25, 2022

Abstract—The reaction of thulium shavings with iodine at 680°C gave a poorly separable product mixture A, consisting of thulium metal (65%), TmI_2 (14%), and TmI (21%). Monovalent thulium iodide could not be isolated in a pure state, but its presence among the products was confirmed, apart from magnetic measurements, by reactions with naphthalene and perylene, which proceed under mild conditions. The reaction of TmI with naphthalene, which takes place at −40°C, affords the trivalent thulium complex with naphthalene dianion, $[TmI(C_{10}H_8)(DME)_3]$. The multistep reaction with perylene starts with the formation of the divalent thulium radical anion complex, $[(TmI)^+(C_{20}H_{12})^{-\bullet}(DME)_3]$, and ends in the formation of trivalent thulium complex, $[(TmI)^{2+}(C_{20}H_{12})^{2-}(DME)_3]$. The presence of a radical anion intermediate in the reaction mixture in an early stage was confirmed by ESR spectroscopy.

Key words: monovalent thulium, thulium iodide, magnetic moment, reactivity, naphthalene, perylene, radical anion

DOI: 10.1134/S1070328423700525

INTRODUCTION

The synthesis and study of properties of compounds containing a monovalent metal is a challenge in lanthanide chemistry. Among Group III elements devoid of *f* electrons (Sc, Y, La), only for scandium, was a complex containing metal in 1+ oxidation state obtained. In particular, the triple-decker π-arene complex $[(t\text{-Bu})_2C_2P_3]Sc[(t\text{-Bu})_2C_3P_3]$-$Sc[(t\text{-BuC})_2C_2P_3]$ was synthesized as a mixture with the Sc^{2+} complex $[Sc(t\text{-BuC})_2C_2P_3)_2]$ by the co-condensation of scandium vapor with alkylphosphine *t*-BuC=P [1]. The valence state of scandium was confirmed by the effective magnetic moment (μ_{eff}) of the products (3.98 μ_B for Sc(I) and 1.7 μ_B for Sc(II)), ESR spectrum for the Sc(II) complex, and X-ray diffraction data for the Sc(I) complex [1, 2].

For the lanthanum monoiodide LaI, which was obtained by long-term heating of LaI_3 with lanthanum metal at 750°C [3], the metal oxidation state was not indicated in the publication; however, the metal-like properties of the compound attest to the formally trivalent state of the metal. Similar binary halides LnX_2, which possess metallic conductivity, have been obtained for most of lanthanides [4]. In the series of lanthanides, monovalent derivatives are known for Pr, Sm, Tb, Tm, and Yb, without strict proof of the valence state of the metal or chemical characteristics. The monovalent samarium chloride was reported to be formed upon gamma-irradiation of $SmCl_2$ in the KCl matrix [5]. This assumption was based on the fact that a band at 545 nm appeared in the absorption spectrum upon irradiation and simultaneously the bands corresponding to the divalent metal chloride decreased. The formation of monovalent ytterbium halides YbX was postulated for reactions of ytterbium metal with alkyl halides RX under specific conditions where ytterbium atoms as a molecular beam reacted with gaseous alkyl halides at 480°C [6]. The laser-excited fluorescence in the 5350–6450 Å range assigned to emission of YbX molecules was taken as evidence. The anionic boron–lanthanide clusters LnB_8^- (Pr, Tb, Tm, Yb) were obtained under the same conditions; the presence of these species in the flux of ions generated by laser-induced simultaneous evaporation of the metal and boron was detected by mass spectrometry [7]. Gadolinium, dysprosium, holmium, and thulium triiodides were tested in the search for mercury-free fluorescent materials for high-pressure discharge lamps [8, 9]. In the gas-discharge plasma at 3000–4000 K, all compounds generated emission in the 450–700 nm range; the emission spectrum was assigned to LnI. It was assumed that monovalent neodymium and dysprosium iodides LnI were formed as highly reactive intermediate species upon disproportionation of LnI_2 in tetrahydrofuran or dimethoxyethane (DME) [10].

$$2\mathrm{LnI}_2 \rightleftharpoons \overset{\overset{\bar{e}}{\curvearrowright}}{[\mathrm{LnI}_3]^-\ [\mathrm{LnI}]^+} \rightleftharpoons \mathrm{LnI}_3 + \mathrm{LnI}\ (\mathrm{Ln} = \mathrm{Nd, Dy})$$

The high reactivity of NdI and DyI accounts for easy reactions of NdI_2 and DyI_2 with reagents that are inert towards diiodides of other lanthanides, including thulium [4, 11]. This feature may serve as indirect evidence for the formation of monovalent thulium in the reactions considered below.

Previously, we found that reactions of thulium metal with potassium iodide and thulium diiodide TmI_2 with neodymium diiodide NdI_2 give mixtures of iodides that contain, according to the results of magnetic measurements, monovalent thulium iodide TmI with the $4f^{14}$ electron configuration of the metal [12]. In both reactions, the difficult-to-separate mixture of products contained other chemically reactive components, which hampered studying of the properties of target TmI. In this study, we report the development of a more convenient method for the preparation of TmI and study of its reactivity.

EXPERIMENTAL

The reactions were performed in evacuated sealed 2–3 mL Pyrex borosilicate glass tubes under conditions that excluded contact with air. Thulium shavings (22–40 mesh) and iodine (98.7%) were used. Iodine was purified prior to use by two vacuum sublimations. DME was dried over sodium benzophenone ketyl and withdrawn for the reaction by condensation in vacuum. The thulium content in the samples was determined by complexometric titration using xylenol orange as the indicator. The content of iodine was determined using argentometric titration (Volhard method).

IR spectra were measured on an FSM-1201 Fourier transform IR spectrometer in the 4000–450 cm^{-1} range. The samples were prepared as mineral oil suspensions. Elemental analysis was performed on an Elementar Vario ELcube Analyzer. ESR spectra were run on a Bruker ESR 200D-SCR spectrometer. The magnetic moments were measured at room temperature using a laboratory-made instrument based on the Faraday method and using comparison with known samples as described previously [13]. The error of measurements did not exceed 5%. The samples were heated in a Nabertherm tubular furnace. X-ray diffraction data were obtained on a SMART APEX diffractometer (graphite monochromator, $\mathrm{Mo}K_\alpha$ radiation, φ–ω scan mode, $\lambda = 0.71073$ Å).

Synthesis of TmI. Thulium shavings (200 mg, 1.2 mmol) were placed in a tube (50 × 10 mm) and heated to 700°C in a dynamic vacuum to remove adsorbed gases and water. After cooling, iodine (75 mg, 0.3 mmol) was added to the shavings, the tube was sealed, and the mixture was stirred by long-term shaking. The tube was mounted in a horizontal position and the mixture was uniformly distributed along the tube by shaking. One end of the tube was heated with a gas burner until the mixture ignited. Over a few seconds, the burning area propagated along the whole layer of the reaction mixture. The tube with a dark brown iodide ingot was placed into a furnace and heated for 1 h at 680°C. After cooling, the ingot was cooled in liquid nitrogen and broken by gently tapping the tube against a hard surface. Some of the obtained product mixture (A) was used to measure the magnetic moment. The μ_{eff} value of the sample was found to be 6.0 μ_{B}. Considering the stoichiometry of the starting reactants and composition of the product (thulium metal, $\mu_{\mathrm{eff}} = 7.5\ \mu_{\mathrm{B}}$; TmI_2, μ_{eff} 4.5 μ_{B}; and TmI, $\mu_{\mathrm{eff}} = 0.0\ \mu_{\mathrm{B}}$), the found that the magnetic moment corresponded to a mixture of 65% Tm(metal), 14% TmI_2, and 21% TmI. This meant a TmI yield of 73 mg (41%).

The reaction of TmI with naphthalene. A solution of naphthalene (34 mg, 0.268 mmol) in DME (7 mL) was added at –40°C to mixture A (300 mg) prepared as described in the previous experiment. During stirring, the solution acquired a bright green color. The solution was separated from the remaining thulium shavings, which were washed with DME once again. From the combined solutions, the solvent was removed by condensation in vacuum. The product formed as a dark green non-crystalline solid highly sensitive to air. The precipitate was washed with diethyl ether and dried in vacuum. This gave 190 mg of a green finely crystalline solid. Recrystallization of the product from DME afforded 112 mg of green crystals of $TmI_2(DME)_3$ (confirmed by X-ray diffraction data [14]) and 75 mg (40% based on the formed monovalent Tm) of $[TmI(C_{10}H_8)(DME)_3]$ (**I**) as a colorless non-crystalline powder. The magnetic moment was 7.1 μ_{B}.

IR (ν, cm^{-1}): 1460, 1377, 1290, 1285, 1250, 1240, 1150, 1112, 1084, 1071, 1019, 971, 856, 830, 791, 726, 577, 559.

For $C_{22}H_{38}O_6ITm$		
Anal. calcd., %	C, 38.05	H, 5.52
Found, %	C, 37.91	H, 5.57

Reaction of TmI with perylene. Perylene (61 mg, 0.24 mol) was added to mixture A (284 mg) obtained as in the previous experiment. Then DME (6 mL) was added at –60°C by vacuum condensation. The instantaneous formation of a dark blue solution was observed. Within 5 min, the solution color changed to green. The solution was decanted from metal shavings. The precipitate was washed with diethyl ether and dried in vacuum. This gave 140 mg of a green finely crystalline powder, which was subjected to fractional crystallization from DME to give dark green crystals of $TmI_2(DME)_3$ (28 mg) (identified by X-ray diffraction analysis [14]) and pale green finely crystalline powder of $[TmI(C_{20}H_{12})(DME)_3]$ (**II**) (110 mg, 52% in terms of the monovalent Tm formed). The magnetic moment was 7.0 μ_B.

IR (ν, cm^{-1}): 1945, 1849, 1593, 1462, 1379, 1259, 1209, 1094, 1016, 961, 869, 840, 783, 723, 663, 616, 480, 475.

UV-Vis (DME): λ_{max}, 515 nm.

For $C_{32}H_{42}O_6ITm$

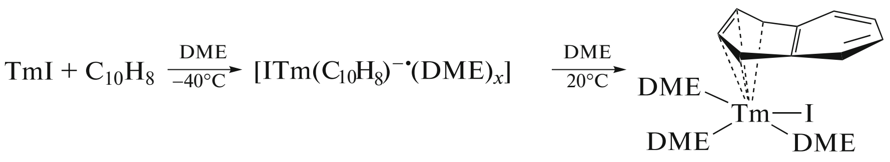
Anal. calcd., %	C, 46.96	H, 5.17
Found, %	C, 46.61	H, 5.11

For recording the ESR spectra of the products, the reaction was carried out directly in an analytical tube by adding DME to a mixture of perylene and thulium iodides at 170 K.

RESULTS AND DISCUSSION

While developing the synthesis of TmI by direct reaction of thulium with iodine, we found that a mixture of iodides with the highest content of the target product (21%) corresponding to the lowest magnetic moment of the mixture (6.0 μ_B) is formed when a twofold molar excess of the metal is used. The early stage of the synthesis (2–3 s) is accompanied by a bright flash and pronounced heat emission. Despite the high temperature developing in the reaction zone (above 1300°C), the reaction does not have enough time to proceed to completion. The product formed as a dark brown ingot had $\mu_{eff} = 6.9$ μ_B relative to contained thulium, which corresponds to a mixture of 77% of Tm metal, 21% of Tm^{2+}, and 2% of Tm^{1+}. The subsequent heating of the sample at a temperature of 680°C leads to a decrease in the magnetic moment, which reaches 6.0 μ_B after 1 h. Considering the ratio of thulium and iodine taken for the reaction, the found μ_{eff} may correspond to the composition of 65% Tm metal, 14% Tm^{2+}, and 21% Tm^{1+}. Further heating under the same conditions leads to increasing μ_{eff}.

In order to confirm the formation of monovalent iodide TmI in the reactions between thulium and iodine and to study its reactivity, reactions with naphthalene and perylene were carried out. Previously, it was shown that the by-product TmI_2, which is always present in product A as an inseparable impurity, does not react with naphthalene [15]. In the present study, we found that perylene, too, does not react with TmI_2 even on heating to 60°C in DME. Conversely, the addition of DME to a mixture of product A and naphthalene at –40°C results in immediate formation of a dark green solution. The dark green finely crystalline product remaining after removal of the solvent rapidly becomes lighter colored at room temperature to give, after several minutes, a mixture of green crystals of $TmI_2(DME)_3$ and a colorless compound, which was identified as $TmI(C_{10}H_8)(DME)_3$ (**I**) according to the elemental composition and IR spectrum. The product magnetic moment of 7.7 μ_B corresponds to trivalent thulium. The observed transformations are probably attributable to the oxidation of monovalent thulium with naphthalene in the initial stage to give an unstable green divalent thulium complex with the naphthalene radical anion $[(TmI)^+(C_{10}H_8)^{-\bullet}]$, which undergoes intramolecular electron transfer to be rapidly converted into the stable trivalent thulium complex with the naphthalene dianion, $[(TmI)^{2+}(C_{10}H_8)^{2-}(DME)_3]$ (Scheme 1). Attempts to record the ESR spectrum of the naphthalene radical anion in the intermediate $[(TmI)^+(C_{10}H_8)^{-\bullet}]$ or measure the magnetic moment were not a success because of its very low stability. Attempts to obtain the final stable product as crystals suitable for X-ray diffraction also failed; it can be assumed that the structure of this complex is similar to the structure of the dysprosium analogue $[DyI(C_{10}H_8)(DME)_2]$, which was obtained previously from dysprosium diiodide and naphthalene [16].



(**I**)

Scheme 1.

A possible alternative explanation to the easy reaction of naphthalene with product A is activation of the thulium surface with iodine. It is known that this technique is often used to activate not only main group metals [17–19], but also lanthanides [20, 21]. However, in this case, no metal activation with iodine takes place, as was shown in a separate experiment, which indicated that iodine-activated thulium does not react with naphthalene under the used conditions.

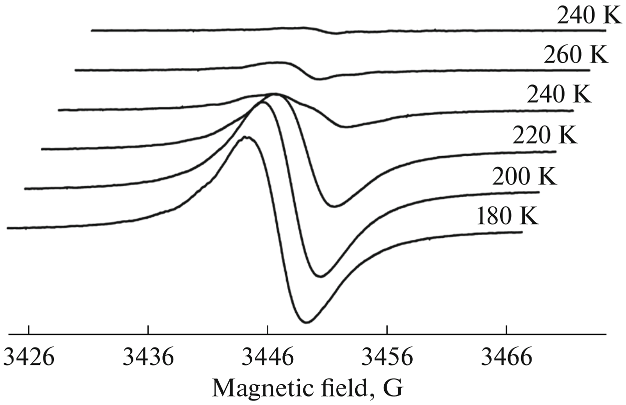
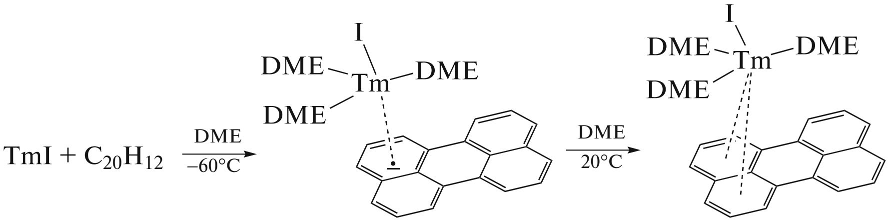


Fig. 1. Temperature dependence of the ESR spectrum of $[ITm^{2+}(C_{20}H_{12})^{-\bullet}(DME)_3]$ in DME in the temperature range of 180–260 K.

Like naphthalene, perylene readily reacts with TmI, but the products formed in this case are more stable, which makes it possible to record the ESR spectrum of the intermediate (Fig. 1). The change in the color of the reaction solution during the reaction, the appearance and rapid decay of the ESR spectrum of the perylene radical anion, and the composition of the final product attest to the multistage nature of the reaction (Scheme 2). Presumably, the first stage is perylene reduction with TmI to the radical anion, which gives a dark blue divalent thulium complex $[ITm^{2+}(C_{20}H_{12})^{-\bullet}(DME)_3]$.

The ESR spectrum of the solution shows one broadened signal (line width 4.9 G, $g = 2.0010$). As the temperature rises, the signal intensity rapidly decreases; at 260 K, the signal disappears. Simultaneously with the decrease in the signal intensity, the solution color changes to green, and the spectrum gradually becomes a superposition of two signals. The intensity of the secondary signal is much lower than the intensity of the primary one. The secondary spectrum is well resolved and its parameters are typical of free perylene radical anion [22]. The absence of anisotropic broadening and the *g*-factor of the former signal make it possible to assign it to the mononuclear product of perylene reduction with monovalent thulium iodide (intermediate). In the case, the unpaired electron should be mainly delocalized to the perylene radical anion, while the unresolved hyperfine structure of the spectrum may be due to the asymmetry of coordination of the thulium cation, resulting in decreasing symmetry of spin density delocalization over the perylene moiety. The formation of a minor amount of free perylene radical anion detected by ESR can be attributable to partial decomposition of the unstable radical anion intermediate at elevated temperature. In the second stage, the dark blue color of the solution and the initial ESR signal disappear. The solution becomes green due to TmI_2, which is contained in mixture A. Presumably, like in the reaction with naphthalene, these transformations proceed via intramolecular redox process giving a trivalent thulium compound with the perylene dianion **(II)**.



(II)

Scheme 2.

The proposed transformation scheme is, to a large extent, arbitrary, because all stages are fast even at low temperature and, hence, other intermediates can also be present in the reaction mixture. However, this does not affect the general transformation route, and the reaction, as well as the reaction with naphthalene, confirms the presence of highly reactive monovalent iodide TmI in the initial mixture A.

ACKNOWLEDGMENTS

This study was performed using the equipment of the center for collective use Analytical Center of the Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, supported by the grant “Provision of the Development of the Material and Technical Infrastructure of Centers for Collective Use” (unique identifier RF–2296.61321X0017, contract number 075-15-2021-670).

FUNDING

This study was supported by the joint grant of the Russian Science Foundation and the Government of the Nizhny Novgorod Region (project no. 22-23-20149).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Arnold, P.L., Cloke, F.G.N., and Nixon, J.F., *Chem. Commun.*, 1998, p. 797.
2. Arnold, P.L., Cloke, F.G.N., Hitchcock, P.B., and Nixon, J.F., *J. Am. Chem. Soc.*, 1996, vol. 118, no. 32, p. 7630.
3. Martin, J.D. and Corbett, J.D., *Angew. Chem., Int. Ed. Engl.*, 1995, vol. 34, no. 2, p. 233.
4. Bochkarev, M.N., *Coord. Chem. Rev.*, 2004, vol. 248, p. 835.
5. Fong, F.K., Cape, J.A., and Wong, E.Y., *Phys. Rev.*, 1966, vol. 151, p. 299.
6. Dirscherl, R. and Lee, H.U., *J. Chem. Phys.*, 1980, vol. 73, p. 3831.
7. Li, W.-L., Chen, T.-T., Chen, W.-J., et al., *Nature Commun.*, 2021, vol. 12, p. 6467.
8. Käning, M., Hitzschke, L., Schalk, B., et al., *J. Phys. D: Appl. Phys.*, 2011, vol. 44, no. 22, p. 224005.
9. Käning, M., Schalk, B., and Schneidenbach, H., *J. Phys. D: Appl. Phys.*, 2007, vol. 40, p. 3815.
10. Bochkarev, M.N., Fagin, A.A., and Khoroshenkov, G.V., *Russ. Chem. Bull. Int. Ed.*, 2002, vol. 51, p. 1909.
11. Khoroshenkov, G.V., Fagin, A.A., Bochkarev, M.N., et al., *Russ. Chem. Bull.*, 2003, vol. 52, p. 1715.
12. Fagin, A.A., Bukhvalova, S.Yu., and Bochkarev, M.N., *Russ. J. Coord. Chem.*, 2022, vol. 48, p. 741. https://doi.org/10.1134/S1070328422110045
13. Bochkarev, M.N. and Protchenko, A.P., *Prib. Tekh. Eksp.*, 1990, no. 1, 1, p. 194.
14. Bochkarev, M.N., Fedushkin, I.L., Fagin, A.A., et al., *Angew. Chem., Int. Ed. Engl.*, 1997, vol. 36, nos. 1–2, p. 133.
15. Bochkarev, M.N., Fedushkin, I.L., Fagin, A.A., et al., *Chem. Commun.*, 1997, p. 1783.
16. Evans, W.J., Allen, N.T., and Ziller, J.W., *J. Am. Chem. Soc.*, 2000, vol. 122, p. 11749.
17. Levason, W., Matthews, M.L., Reid, G., et al., *Dalton Trans.*, 2004, p. 51.
18. Taylor, W.V., Xie, Z.-L., Cool, N.I., et al., *Inorg. Chem.*, 2018, vol. 57, no. 16, p. 10364.
19. Brown, M.D., Levason, W., Reid, G., et al., *Dalton Trans.*, 2006, p. 5648.
20. Mashima, K., Nakayama, Y., Nakamura, A., et al., *J. Organomet. Chem.*, 1994, vol. 473, p. 85.
21. Münzfeld, L., Schoo, C., Bestgen, S., et al., *Nature Commun.*, 2019, vol. 10, p. 3135.
22. Segal, B.G., Kaplan, M., and Fraenkel, G.K., *J. Chem. Phys.*, 1965, vol. 43, p. 4191.

Translated by Z. Svitanko