3.7 (m, 2 H, $-CH_2CH=$); 5.8 (t, 1 H, $-CH=$). IR (CCl_4), ν/cm^{-1}: 1690 (C=C). ^{13}C NMR, δ: 13.52 (Me); 22.37 (CH_2); 35.40 (CH_2S); 112.24 (=CH—); 107.2 (C(1)).

References

1. Yu. I. Puzin, G. V. Leplyanin, and S. R. Rafikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2073 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 1892 (Engl. Transl.)].
2. Yu. I. Puzin, G. V. Leplyanin, Yu. M. Shaul'skii, and G. A. Tolstikov, *Eur. Polym. J.*, 1988, **24**, 579.
3. Yu. I. Puzin, G. V. Leplyanin, R. R. Muslukhov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2138 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1988 (Engl. Transl.)].

Received February 23, 1994; in revised form July 18, 1994

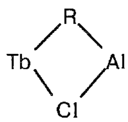
Chemiluminescence and photoluminescence of Tb^{III} in the $TbCl_3 \cdot 3Bu_3PO—Bu^i_3Al—C_5H_8$ catalytic system in toluene

S. P. Kuleshov, R. G. Bulgakov, and R. G. Akhmadeev*

Institute of Petrochemistry and Catalysis, Academy of Sciences of Republic Bashkortostan, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347) 231 2750

Luminescence of organolanthanide compounds has been reported only for ytterbium(III),[1] terbium(III),[2] europium(II,III),[3] and samarium(II,III)[3] cyclopentadienides.

The present communication reports the first example of photoluminescence (PL) and chemiluminescence (CL) of complex bridged alkyl derivatives of terbium of the general formula **1** obtained by the interaction of $TbCl_3 \cdot 3TBP$ (**2**), R_3Al (**3**), and piperylene (C_5H_8) (**4**) in toluene (TBP is tributyl phosphate; the **2** : **3** : **4** ratio is 1 : 15 : 5).[4] Systems analogous to **2**—**3**—**4** are well known as catalysts of the polymerization of dienes,[5] and PL methods combined with CL methods seem to be promising for studying these systems.



1

R = Bu^i

When oxygen (or air) is bubbled through solutions of compound **1** in toluene ([Tb] = $4.1 \cdot 10^{-2}$ mol L^{-1}, 298 K), chemilumiscence occurs ($I_{max} = 5 \cdot 10^7$ photons s^{-1} per mole Tb). The spectrum of this CL correlates well with the PL spectrum of a solution of compound **2** and with the PL spectrum of an oxidized solution of compound **1** (λ_{max} = 490, 445, and 585 nm, respectively).

The analysis of the spectra shows that in all of the cases the radiation is caused by f—f transitions of Tb^{III}, while emissions from the oxide and peroxide forms of Tb^{III} are responsible for the CL of compound **1** and the PL of the oxidized solution of compound **1**.

The formation of organoterbium peroxides during the oxidation of compound **1** is confirmed by the sharp increase in the intensity of the CL (with the same emitter, Tb) following the addition of water to a solution of **1** subjected to oxidation, *i.e.*, in the "aqueous CL-test" used by us previously.[3]

The comparison of the CL that appears during the air-induced oxidation of solutions of compound **1**, a solution of compound **3**, and a $NdCl_3 \cdot 3TBP$—**2**—**3** mixture allowed us to conclude that the excitation of the CL emitter, *viz.*, Tb^{III}, occurs both when the Tb—Alk bonds are oxidized and when energy is transferred to the Tb^{III} atom from the primary emitter, which is excited due to the oxidation of the Al—Alk bonds in the molecules of **1**.

References

1. H. R. Britain, J. M. Meadouws, and W. J. Evans, *Organometallics*, 1983, **2**, 1661.
2. A. C. Thomas and A. B. Ellis, *J. Chem. Soc., Chem. Commun.*, 1984, **19**, 1270.
3. R. G. Bulgakov, S. P. Kuleshov, V. N. Khandozhko, I. P. Beletskaya, G. A. Tolstikov, and V. P. Kazakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1937 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1735 (Engl. Transl.)].
4. USSR Pat. 1376531, 1986.
5. M. N. Bochkarev, G. S. Kalinina, L. N. Zakharov, and S. Ya. Khoroshev, *Organicheskie proizvodnye redkozemel'nykh elementov* [*Organic Derivatives of Rare-Earth Elements*], Nauka, Moscow, 1989 (in Russian).

Received May 16, 1994

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1682—1683, September, 1994.

1066-5285/94/4309-1593 $12.50