Letters to the Editor

Bright blue photoluminescence of Eu^{II} in the complex $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i{}_2Al)_2O$

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Photoluminescence (PL) of Eu^{II} has been first detected in the fluorite matrix.[1] Later[2—4] it was observed (298 K) in matrices of compounds containing a wide scope of metals (Na, K, Rb, Cs, Ba, Sr, Al, and others) doped (0.05—5%) with Eu^{II} salts. The PL of Eu^{II} in frozen (77 K) aqueous solutions of HCl and $HClO_4$,[5] the Eu^{II} complexes with organic ligands (298 K),[6] Cp_2Eu (77 K),[7] and $NaEu(BH_4)_4 \cdot 4DME$ (77 and 298 K)[8] is known. In this case, the Eu^{II} ions are generated by the reduction of the Eu^{III} compounds in chemical and photo- and electrochemical reactions. The PL spectra of the Eu^{II} ion in these compounds have a diffuse maximum at $\lambda = 400$—490 nm. The ability of Eu^{II} to emit blue PL is widely used[9,10] in the production of luminescent lamps, X-ray dosimeters, bleaching agents for paper, *etc*. Therefore, the synthesis of new Eu^{II} compounds luminescing at room temperature is an urgent task. In the present work, a new Eu^{II} complex with bright PL at room temperature was synthesized by the method undescribed earlier.

The Eu^{II} complex was synthesized in an argon atmosphere (298 K) by the treatment of a suspension of $EuCl_3 \cdot 6H_2O$ (**1**) (0.54 mmol) in toluene with $Bu^i{}_3Al$ (**2**) (10.8 mmol). After Eu^{III} was completely reduced to Eu^{II} (~60 min), which was monitored by the cessation of an increase in the PL intensity of Eu^{II} ($\lambda_{max} = 485$ nm), the solid phase was separated from the solution by centrifuging, washed with toluene (3×20 mL), and dried *in vacuo* (10 Torr). The powdered light yellow (characteristic color of the Eu^{II} salts) product was analyzed by a known procedure[11] to the content of Eu and Al (complexonometically), Cl^- (according to Volhard), H_2O (according to Fischer), Al—C

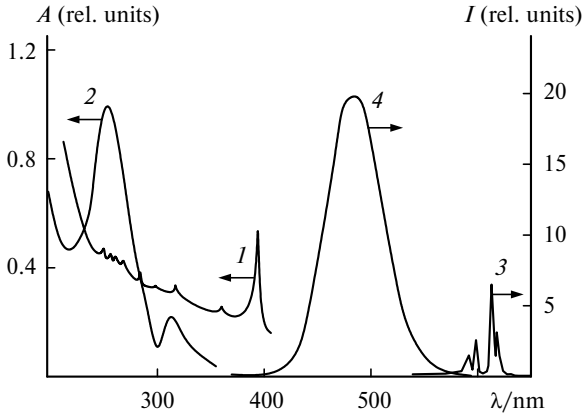

Fig. 1. Absorption (*1*, *2*) and PL (*3*, *4*) spectra of the Eu^{III} and Eu^{II} compounds at 298 K: *1*, solution of $EuCl_3 \cdot 6H_2O$ in 0.65 *M* HCl, [Eu] = $2 \cdot 10^{-1}$ mol L^{-1}; *2*, solution of $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i{}_2Al)_2O$ in 0.65 *M* HCl, [Eu] = 10^{-3} mol L^{-1}; *3*, $EuCl_3 \cdot 6H_2O$, $\lambda_{exc} = 365$ nm; *4*, $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i{}_2Al)_2O$, $\lambda_{exc} = 280$ nm.

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bonds (from the volume of Bu^iH evolved upon hydrolysis of 0.1 *M* HCl), and C, H, and O (elemental analysis). The composition of the powder corresponds to the molecular formula $EuCl_2 \cdot 0.5H_2O \cdot 0.05(Bu^i{}_2Al)_2O$ (**3**). The yield of compound **3** was 100%.

Unlike $EuCl_3 \cdot 6H_2O$, the absorption spectrum of a solution of complex **3** in 0.65 *M* HCl (Fig. 1) contains (instead of narrow bands of Eu^{III}) new diffuse and more intense bands at λ = 250 and 325 nm characteristic[5] of Eu^{II}. Even at room temperature complex **3** exhibits the bright blue PL distinctly observed by the unaided eye. The PL intensity of compound **3** is much higher than that of the red PL of a powder of compound **1** (see Fig. 1) caused by the emission of Eu^{III}*. The PL spectrum of complex **3** has a diffuse band at λ = 485 nm, *i.e.*, in the region characteristic of PL of the Eu^{II} ion. It is important that the PL intensity of complex **3** remains unchanged on its storing under argon for a very long time (~1.5 years).

References

1. K. Przibram, *Nature*, 1935, **135**, 100.
2. F. D. S. Butement, *Trans. Faraday Soc.*, 1948, **309**, 617.
3. K. Przibram, *Acta Physica Austriaca*, 1949, **3**, 126.
4. M. Peng, Z. Pei, G. Hong, and Q. Su, *Chem. Phys. Lett.*, 2003, **371**, 1.
5. R. G. Bulgakov, V. P. Kazakov, and V. N. Korobeinikov, *Optika i spektroskopiya* [*Optics and Spectroscopy*], 1973, **35**, 850 (in Russian).
6. G.-Y. Adachi, K. Tomokiyo, K. Sorita, and J. Shiokawa, *J. Chem. Soc., Chem. Commun.*, 1980, 914.
7. R. G. Bulgakov, S. P. Kuleshov, V. N. Khandozhka, I. P. Beletskaya, G. A. Tolstikov, and V. P. Kazakov, *Dokl. Akad. Nauk SSSR*, 1989, **304**, 114 [*Dokl. Chem.*, 1989, **304** (Engl. Transl.)].
8. R. G. Bulgakov, B. A. Tishin, S. P. Kuleshov, V. D. Makhaev, A. P. Borisov, V. P. Kazakov, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 491 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38** (Engl. Transl.)].
9. W.-M. Li, T. Hanninen, M. Leskela, J. Saari, and A. Hase, *J. Alloys Compounds*, 2001, **323**, 236.
10. H. A. Hoppe, H. Lutz, P. Morys, W. Schnick, and A. Seilmeier, *J. Phys. Chem. Solids*, 2000, **61**, 2001.
11. R. G. Bulgakov, S. P. Kuleshov, A. N. Zuzlov, I. R. Mullagaleev, L. M. Khalilov, and U. M. Dzhemilev, *J. Organomet. Chem.*, 2001, **636**, 56.

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