Surface complexation onto nanosized lanthanum fluoride

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The surface chemical modification of LaF_3 nanocrystals with 4-(2-pyridylazo)resorcinol and Xylenol orange was investigated. The study of the complexes of these ligands with lanthanum ions in aqueous solution and on the LaF_3 surface revealed significant differences in their properties. The surface complexes are characterized by the slower kinetics of the formation and higher stability.

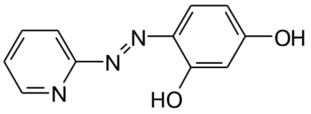
Key words: lanthanum fluoride, nanoparticles, complexes, surface modification.

The surface modification of ionic crystals is a promising field of modern chemistry.[1—10] Studies in this field are stimulated by the development of nanotechnology and investigations of the possible use of nanosized ionic compounds as adsorbents, sensors, components of electronic and optical devices, *etc*. The surface modification of such materials is necessary both for stabilization of the nanosized state and the surface protection from the exposure to environmental components; the latter can lead, in particular, to the hydrolysis and oxidation. The introduction of a modifying agent at the synthesis stage enables the control of the size and the shape of the resulting nanoparticles,[2—4] as well as of the charge and the degree of hydrophobicity of the surface, which is essential for the purification and isolation of the product.[2,5]

In the majority of studies, the surface modification of ionic crystals was performed with the use of organic compounds containing complex-forming functional groups. This is not surprising because the formation of the coordination bond between the molecule of the modifying agent and the metal ion in the crystal lattice is the most general method for the modification of such surfaces. In spite of the fact that there are several hundreds of publications only on the synthesis of quantum dots of the composition $A^{II,III}B^{V,VI}$ stabilized by various ligands, investigations on the interaction of organic ligands with the ionic crystal surface are virtually absent. However, the understanding of the characteristic features of the complexation is necessary for both the prediction of the characteristics of the grafted layer and the optimization of procedures for the modification.

The aim of the present study was to somewhat close this gap. We used LaF_3 as the model ionic compound. The latter is convenient because it is insoluble in water, and La^{3+} ions are prone to form complexes with a wide range of ligands. In addition, modified rare earth fluorides are of particular practical interest. These compounds can be used as optical materials, LaF_3 often serving as the matrix for luminescent components.[6,7] Rare earth fluorides are also promising for biological and medical applications (luminescent labels, visualization of living cells and tissues, contrast agents for NMR spectroscopy and NMR tomography[8,9]).

We used 4-(2-pyridylazo)resorcinol (**1**) and Xylenol orange (**2**), which are organic reagents widely employed for the analytical detection of rare earth elements,[11,12] as modifying agents. The choice of these reagents was dictated by the fact that these compounds, as well as their complexes, are intensely colored and, consequently, the complexation can be studied by absorption spectroscopy.



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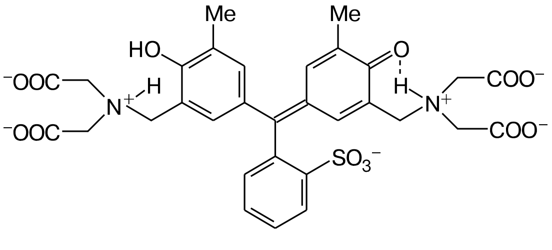

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Experimental

All reagents, including $La(CH_3COO)_3 \cdot 1.5H_2O$ ($LaAc_3$), NaF, 4-(2-pyridylazo)resorcinol, 3,3´-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonephthalein tetrasodium salt or Xylenol orange (**2**), 1-(2-pyridylazo)-2-naphthol (**3**), and

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ethylenediaminetetraacetic acid (EDTA) disodium salt, were at least of the reagent grade and were used as is. The acetate buffer solution was prepared by mixing AcOH and NaOH solutions. The borate buffer solution was prepared by dissolving sodium tetraborate in degassed water. The pH value was controlled with the use of HCl and NaOH solutions.

The X-ray powder diffraction study of the samples was performed at room temperature on a DRON-3M diffractometer (Co-Kα radiation, λ = 0.179021 nm) over the scanning range 2θ = 20—70°. The average crystallite size was determined according to the Scherrer equation

$$D = k\lambda/(\beta \cdot \cos\theta), \quad (1)$$

where k = 0.89 and β is the half-width at half-height of the reflection.

The micrographs of the samples were recorded with a LEO912 AB OMEGA transmission electron microscope. The specific surface (S_{sp}) was measured on an ASAP 2010 analyzer (Micromeritics) by the Brunauer—Emmett—Teller (BET) method using low-temperature nitrogen adsorption.

The absorption spectra of solutions were recorded on a Jenway 6310 spectrophotometer. The diffuse reflectance spectra of modified samples of LaF_3 were measured on a Spektrotron spectrocolorimeter. The Kubelka—Munk function was calculated from the measured intensities of reflections according to the equation:

$$F(R) = (1 - R)^2/2R,$$

where R is the diffuse reflection coefficient of the substance.

Synthesis of LaF_3 nanoparticles. A 0.51 M $LaAc_3$ solution (10 mL) and a 0.51 M NaF solution (30 mL) were added dropwise with continuous stirring to water (30 mL) at 20 °C, the addition of one drop of the $LaAc_3$ solution being followed by the addition of three drops of the NaF solution. When the addition of the reagents was completed, the reaction mixture was stirred for 30 min. The final product was isolated on a centrifuge at 8000 rpm for 15 min, washed several times with water, and dried in air.

Sorption measurements. In all experiments, the complexation was monitored based on the change in the concentration of the free ligand in solution at 20 °C. The concentration was determined from the calibration curve based on the absorption of compounds **1** and **2** at 410—415 and 430—440 nm, respectively. The La^{3+} complexes with **1** and **2** did not interfere with the determination because their absorption is observed at 510—515 (see Refs 13—15) and 570—576 nm,[11,16] respectively.

The amount of the adsorbed ligand was calculated from the difference between the introduced (n_0/mol) and remainder amounts (n_1/mol) of the free ligand in the solution. The degree of extraction was calculated from the equation

$$S(\%) = 100(n_0 - n_1)/n_0.$$

The surface density (ρ/molecule nm^{-2}) of the ligands was determined from the equation

$$\rho = (n_0 - n_1)N_A \cdot 10^{18}/(S_{sp}m),$$

where N_A is the Avogadro constant, S_{sp} is the specific surface area of the LaF_3 powder (m^2 g^{-1}), and m is the weight of the LaF_3 sample (g).

Adsorption kinetics. A borate buffer, pH 9.18 (2 mL), and a solution of **1** (2.5 mL, $6.7 \cdot 10^{-5}$ mol L^{-1}) were added to LaF_3 (0.01 g). Then the reaction mixture was vigorously stirred at 20 °C. At specified intervals of time, LaF_3 was precipitated on a centrifuge, and the absorption spectrum of the solution was recorded in the visible region. Then the solution and the precipitate were again stirred.

The adsorption kinetics of **2** was studied in the same way using an acetate buffer solution, pH 5.1 (3 mL), and a solution of **2** (0.75 mL, $9.3 \cdot 10^{-4}$ mol L^{-1}).

Results and Discussion

The synthesis of LaF_3 was performed using the double-drop method,[17,18] which enables the production of preparative amounts of nanoparticles having a narrow size distribution. According to the X-ray powder diffraction patterns, the resulting sample corresponded to the hexagonal structure of LaF_3 (JCPDS 32-0483, the space group P3—c1). Reflections belonging to other phases were absent in the X-ray diffraction pattern, which is indicative of the purity of the synthesized LaF_3 sample. The average crystallite size estimated from the Scherrer equation (1) was 16 nm.

According to the transmission electron microscopy data (Fig. 1), the resulting nanoparticles had a nearly hexagonal platelet shape with a diameter of 13—18 nm and a thickness of 2—4 nm. The specific surface S_{sp} of the powder was 120 m^2 g^{-1}.

The treatment of LaF_3 with aqueous solutions of **1** or **2** led to the appearance of the intense color of the sample, which is indicative of adsorption of the ligand on the surface of LaF_3. The diffuse reflectance spectrum of **1**@LaF_3

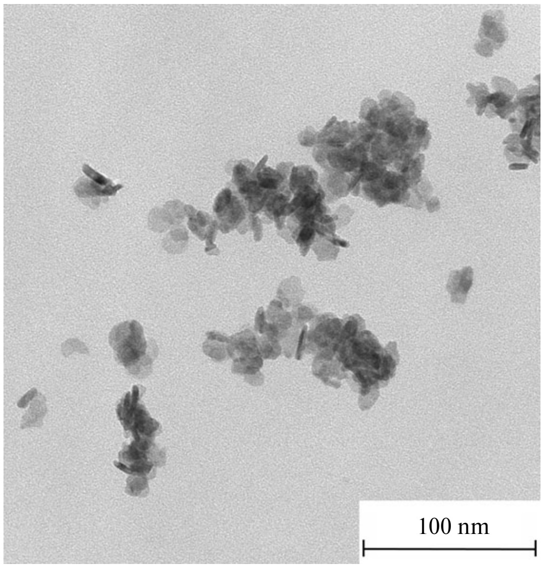

Fig. 1. Micrograph of the synthesized LaF_3 recorded by transmission electron microscopy.

(Fig. 2, *a*) shows three main components with maxima at 520, 470, and 405 nm. The first component coincides with the absorption band of the complex of ligand **1** with the La^{3+} ion in a homogeneous solution. Therefore, adsorption of a particular amount of the ligand on the surface is determined by the coordination binding to lanthanum ions in the crystal lattice to form a complex structurally identical to the complex in aqueous solution. In these complexes, 4-(2-pyridylazo)resorcinol (**1**) serves as a tridentate ligand. Evidently, only ions located at the edges and vertices of a nanocrystallite or at surface defect sites in the crystal structure can form analogous complexes on the surface. The band at $\lambda_{max} = 470$ nm may be assigned to a complex having a distorted structure,[13] in which **1** serves, for example, as a bidentate ligand. These complexes can be formed at the faces of a nanocrystallite. The band at $\lambda_{max} = 405$ nm corresponds to absorption of **1**. It could be suggested that the modifying agent is partially bound on the LaF_3 surface through the mechanism of physical adsorption. However, this suggestion is in contradiction with the results of the experiment with compound **3**, which is an analog of **1** containing the naphthol moiety instead of the benzene ring. In spite of the fact that this ligand forms stable complexes with rare earth ions in aqueous solution, it is not adsorbed on the surface of LaF_3 nanoparticles. The introduction of a bulky substituent can dramatically change the stability of the surface complexes, but it hardly can lead to the complete suppression of physical adsorption, if it occurs.

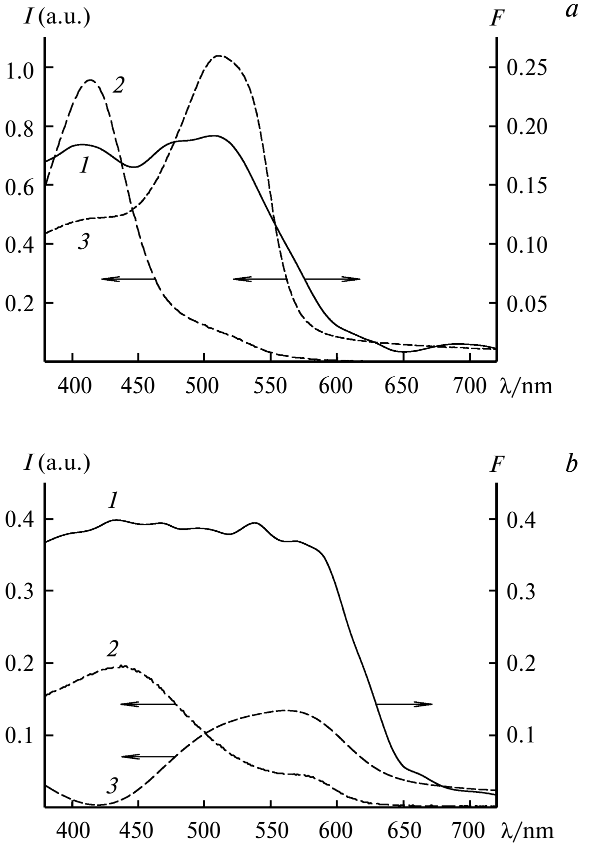

Fig. 2. Diffuse reflectance spectra of the modified samples: (*a*) $1@LaF_3$ (*1*) compared with the electronic spectra of solutions of **1** (*2*) and the molecular complex of **1** with La^{3+} (*3*); (*b*) $2@LaF_3$ (*1*) compared with the electronic spectra of solutions of **2** (*2*) and the molecular complex of **2** with La^{3+} (*3*).

Therefore, we suggest that an excess amount of **1** is retained on the particle surface due to lateral π—π interactions with the ligand molecules involved in the surface complexes (Fig. 3). The energy of these interactions is rather high because molecules **1**, which are not involved in the complexes, are not removed from the surface even after repeated washing. Moreover, if this hypothesis is true, analogous lateral interactions between the ligands involved in the surface complexes cannot be ruled out as well. In this case, adsorption of **1** on the LaF_3 surface should occur through the island mechanism.

A more complex situation is observed for compound **2**. The spectrum of $2@LaF_3$ (Fig. 2, *b*) shows at least five components, which can be assigned to surface complexes with different structures.

We also performed a comparative study of the complex formation of **1** and **2** with La^{3+} ions in a homogeneous solution and on the LaF_3 surface. As can be seen from Fig. 4, the rates of the formation of the complexes in these systems are substantially different. In a homogeneous solution, an equilibrium is established almost immediately, whereas the equilibrium for the $1+LaF_3$ and $2+LaF_3$ systems is established within 3 and 0.5 h, respectively.

Another difference concerns the thermodynamics of the process. In the homogeneous system, compound **1** was observed in the unbound state even in the presence of a large excess of La^{3+} ions, whereas compound **1** is fully bound in the heterogeneous system (at least the concentration of the free ligand was lower than the method detection limit used for the control). Hence, it can be con-

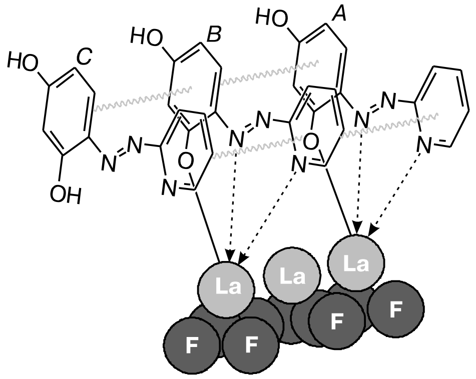

Fig. 3. Schematic representation of the lateral interactions between molecules **1** bound to the surface lanthanum ions on the LaF_3 surface (*A*—*B*) and the interactions of the coordinated ligand with free molecule **1** (*B*—*C*).

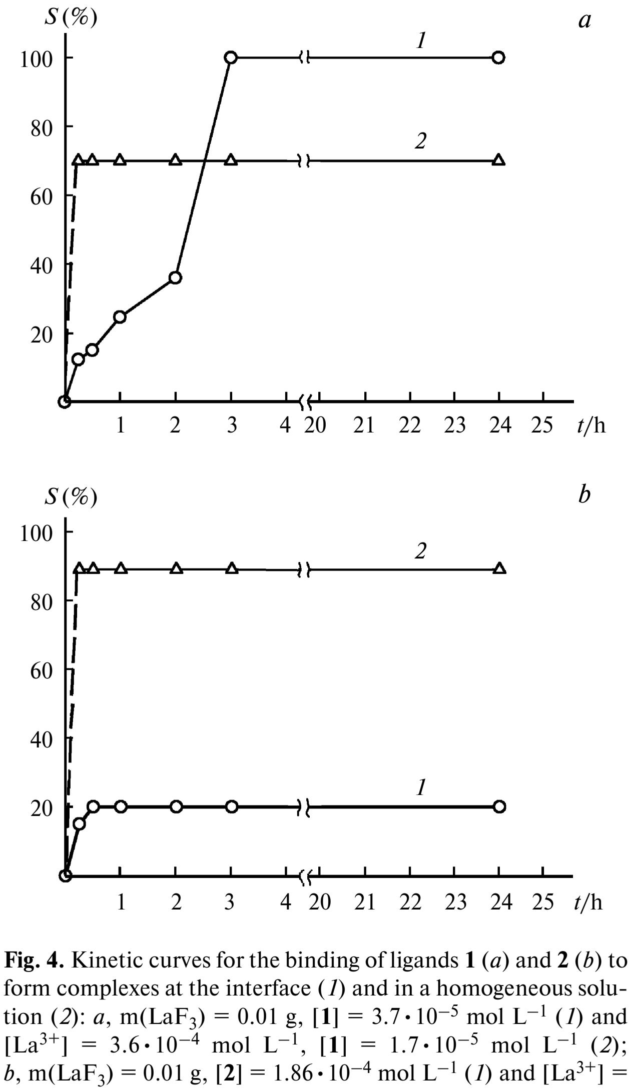

Fig. 4. Kinetic curves for the binding of ligands **1** (*a*) and **2** (*b*) to form complexes at the interface (*1*) and in a homogeneous solution (*2*): *a*, $m(LaF_3) = 0.01$ g, $[\mathbf{1}] = 3.7 \cdot 10^{-5}$ mol L^{-1} (*1*) and $[La^{3+}] = 3.6 \cdot 10^{-4}$ mol L^{-1}, $[\mathbf{1}] = 1.7 \cdot 10^{-5}$ mol L^{-1} (*2*); *b*, $m(LaF_3) = 0.01$ g, $[\mathbf{2}] = 1.86 \cdot 10^{-4}$ mol L^{-1} (*1*) and $[La^{3+}] = 3.6 \cdot 10^{-4}$ mol L^{-1}, $[\mathbf{2}] = 9.3 \cdot 10^{-5}$ mol L^{-1} (*2*).

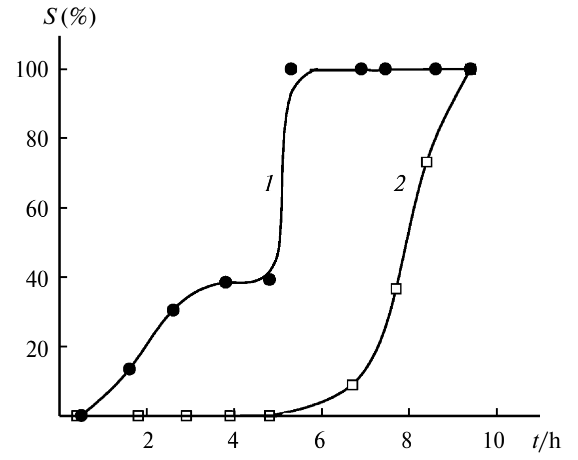

Fig. 5. Influence of the pH on the stability of the surface (*1*) and molecular (*2*) complexes **1**—La^{3+}.

cluded that the surface complexes **1**—La^{3+} are more stable than their molecular analogs.

This conclusion is confirmed by the data on the hydrolytic stability of the molecular and surface complexes (Fig. 5). The concentration of the complexes of **1** with La^{3+} ions in aqueous solution monotonically decreases with increasing acidity of the solution from pH = 9; at pH < 4, their concentration is negligible. The surface complexes **1**—La^{3+} are more stable. Their gradual decomposition begins only at pH ≈ 5, and a substantial amount of the coordinated ligand is present on the LaF_3 particle surface even at pH = 2. The pH profile is indicative of the presence of surface complexes having different stability. At pH ≈ 5, less stable complexes decompose and the sharp desorption of **1** occurs. At pH < 3, the gradual decomposition of the other, more stable, complexes takes place.

For the system **2**@LaF_3, it was found that the change in the acidity of the solution from 1 *M* HCl to pH = 12 does not lead to the removal of the ligand from the nanocrystallite surface. Attempts to displace the bound ligand with the use of EDTA also failed, although the analogous ligand exchange occurs in aqueous solution and is used, in particular, in the complexometric titration.

The treatment of LaF_3 with a large excess of the modifying agent afforded samples with the surface density of the agent up to 1 molecule nm^{-2} for **1** and 0.2 molecule nm^{-2} for **2**, which is close to the multilayer surface coating.

The present study revealed certain features of the complexation of ionic compounds on the nanocrystal surface. A series of complexes with different structures and of different stability are formed on the surface due to the binding of the ligand to metal ions at the vertices, edges, and faces of nanocrystals. The rate of the complex formation on the surface is much lower than the rate of this process in a homogeneous system. We have observed[19] a similar effect upon binding of amino acids to the surface of ZnS nanoparticles. Apparently, this process has a general character and is associated with the water structuring at interfaces and the slow breaking of the hydration shell of nanoparticles. The surface complexes are more stable than their homogeneous analogs. This may be associated, first, with the more strong binding of organic ligands to the ions involved in the crystal lattice, second, with lateral interactions between the ligand molecules on the surface, and, third, the shielding effect of the ligand surface layer, which hinders the access to the metal—ligand bond.

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References

1. L. Wang, M. Zhang, X. Wang, W. Liu, *Mater. Res. Bull.*, 2008, **43**, 2220.

2. A. Safronikhin, T. Shcherba, H. Ehrlich, G. Lisichkin, *Appl. Surf. Sci.*, 2009, **255**, 7990.
3. A. V. Safronikhin, H. V. Erlikh, G. V. Lisichkin, *Zh. Obshch. Khim.*, 2011, **81**, 177 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2011, **81**, 277].
4. X. Yang, X. Dong, J. Wang, G. Liu, *J. Alloys Compd.*, 2009, **487**, 298.
5. H. Bala, W. Fu, Y. Guo, J. Zhao, Y. Jiang, X. Ding, K. Yu, M. Li, Z. Wang, *Colloid Surf. A: Physicochem. Eng. Aspect*, 2006, **274**, 71.
6. B. Kokuoz, C. Kucera, J. R. DiMaio, J. Ballato, *Opt. Mater.*, 2009, **31**, 1327.
7. J. W. Stouwdam, F. C. J. M. van Veggel, *Langmuir*, 2004, **20**, 11763.
8. N. Huntzschel, F. Zhang, F. Eckert, A. Pich, M. A. Winnik, *Langmuir*, 2007, **23**, 10793.
9. F. Evanics, P. R. Diamente, F. C. J. M. van Veggel, G. J. Stanisz, R. S. Prosser, *Chem. Mater.*, 2006, **18**, 2499.
10. A. Safronikhin, H. Ehrlich, T. Shcherba, N. Kuzmina, G. Lisichkin, *Colloid Surf. A: Physicochem. Eng. Aspect*, 2011, **377**, 367.
11. L. Sommer, H. Novotna, *Talanta*, 1967, **14**, 457.
12. A. K. Mukherji, *Microchem. J.*, 1966, **11**, 243.
13. Y. Shi, E. M. Eyring, R. van Eldik, *J. Chem. Soc.*, *Dalton Trans.*, 1998, **21**, 3565.
14. K. N. Munshi, A. K. Dey, *Microchim. Acta*, 1968, **56**, 1059.
15. C. Li, J. Yang, H. Lian, J. Lin, *Chem. Mater.*, 2008, **20**, 4317.
16. J. Wang, S. Bo, L. Song, J. Hu, X. Liu, Z. Zhen, *Nanotechnology*, 2007, **18**, 465606.
17. M. P. Zhilenko, K. V. Lupandina, H. V. Erlikh, G. V. Lisichkin, *Izv. Akad. Nauk, Ser. Khim.*, 2010, 1277 [*Russ. Chem. Bull.*, *Int. Ed.*, 2010, **59**, 1307].
18. M. P. Zhilenko, H. V. Erlikh, G. V. Lisichkin, *Ross. Nanotekh.*, 2009, **4**, 33 [*Nanotechnol. Russ.*, 2009, **4**, 302].
19. H. Ehrlich, T. Shcherba, M. Zhilenko, G. Lisichkin, *Mater. Lett.*, 2011, **65**, 107.

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