Luminescence properties of solid Eu, Sm, Tb and Dy compounds with the molybdoaluminate ion $Al(OH)_6Mo_6O_{18}^{3-}$

Alexander B. Yusov,* Alexander M. Fedosseev, Grigorii B. Andreev and Irina B. Shirokova

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation. Fax: +7 095 335 2005; e-mail ioussov@ipc.rssi.ru

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The structure and luminescence characteristics of new lanthanide complexes with the heteropoly anion $Al(OH)_6Mo_6O_{18}^{3-}$ were examined.

The crystalline lanthanide complexes with planar $IMo_6O_{24}^{5-}$ and $TeMo_6O_{24}^{6-}$ heteropoly anions (HPA) of the Anderson structure were synthesised and investigated by luminescence spectroscopy and X-ray diffraction analysis.[1,2] These HPA can form complexes with trivalent lanthanides in which the central ion has three or four oxygen atoms belonging to molybdate groups, which determine the luminescence properties of complexes. However, it is impossible to predict reliably the efficiencies of energy transfer to the central ion and luminescence quenching even if the structure of complexes is known.

The results of a luminescence study of lanthanides in new complexes with the polyanion $Al(OH)_6Mo_6O_{18}^{3-}$ are given below, which seem unexpected. This HPA[3] is structurally similar to $IMo_6O_{24}^{5-}$ and $TeMo_6O_{24}^{6-}$; however, $Al(OH)_6Mo_6O_{18}^{3-}$ was found a weaker ligand with respect to lanthanide ions than $IMo_6O_{24}^{5-}$ and $TeMo_6O_{24}^{6-}$. The energy transfer from HPA to the central ion in crystalline complexes remains rather effective. However, luminescence quenching *via* electron transfer, which was expected for terbium complexes, is practically absent.

The complexation of lanthanides with $(NH_4)_3[Al(OH)_6Mo_6O_{18}]\cdot nH_2O$ **1** in solution is rather weak. This is confirmed by spectrophotometric and luminescence† data. The absorption spectrum of a $Nd(NO_3)_3$ solution remained almost unchanged on the addition of compound **1** (0.03–0.04 mol dm^{-3}) to the solution. Additional information can be obtained with the use of a 5*f*-element, Am^{III}. The absorption spectra of Am^{III} in the presence of **1** are indicative of weak complexation with a stability constant of ~20 ($\mu = 0.1$, pH 3.9). The solutions of **1** containing europium(III) did not luminesce on exposure to light from a nitrogen laser because the absorption of the Eu^{III} ion at this wavelength is insignificantly low, and intermolecular energy transfer to Eu^{3+} from **1** does not take place. The complexation with the polymolybdate ion also does almost not take place.

Crystalline Eu, Tb, Sm and Dy compounds were separated from solutions. Single crystal X-ray data for a Sm compound suggested the composition $Sm[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$. According to powder X-ray diffraction data, all of the compounds are isostructural and have the composition $Ln[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$. The crystalline europium complex intensely luminesces on excitation by a nitrogen laser because of energy transfer from the ligand to the *f*-element ion. The compounds were prepared in solutions in both H_2O and D_2O.‡ During the preparation of solids from D_2O, crystal water from $(NH_4)_3Al(OH)_6Mo_6O_{18}\cdot nH_2O$ ($n \leq 10$) was introduced into the solution and the resulting solids contained about 3% H_2O (on a total water basis). The samples were sealed with supernatants in glass ampoules to prevent an additional introduction of H_2O.

Figure 1 shows the luminescence spectra of the europium(III) solid corresponding to emission transitions $^5D_0 \rightarrow {}^7F_i$, $i = 0, 1, 2,$ and the excitation spectra at 293 and 77 K. The low-intensity broad band at 270–370 nm and some narrow bands at 362, 375–385 and 394 nm are present in the excitation spectrum. The broad band arises due to light absorption by HPA followed by energy transfer from the ligand to Eu^{3+}, as it takes place in organic lanthanide complexes;[4] the narrow bands correspond to the absorption of the Eu^{3+} ion. The symmetry of the oxygen environment of europium(III) is responsible for the relative bands intensities and the Stark splitting[3] in emission spectra. At 77 K, a very weak band at 578.8 nm (transition $^5D_0 \rightarrow {}^7F_0$) and an additional peak at 583.0 nm are observed in the luminescence emission spectrum of the new europium complex. Usually, splitting of the transition $^5D_0 \rightarrow {}^7F_0$ indicates the existence of two (or more depending on the number of components) luminescence centres; however, according to X-ray data, all lanthanide atoms in the test complex are equivalent. We found that the peak at

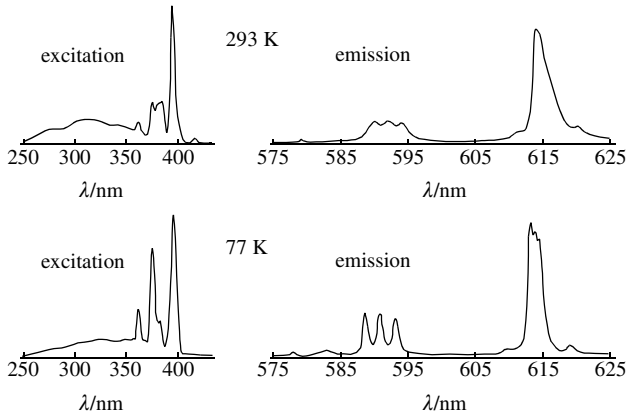

Figure 1 Excitation and emission luminescence spectra of crystalline $Eu[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$ at 293 and 77 K. The spectral resolution is 2.0 or 0.5 nm for the excitation and emission spectra, respectively.

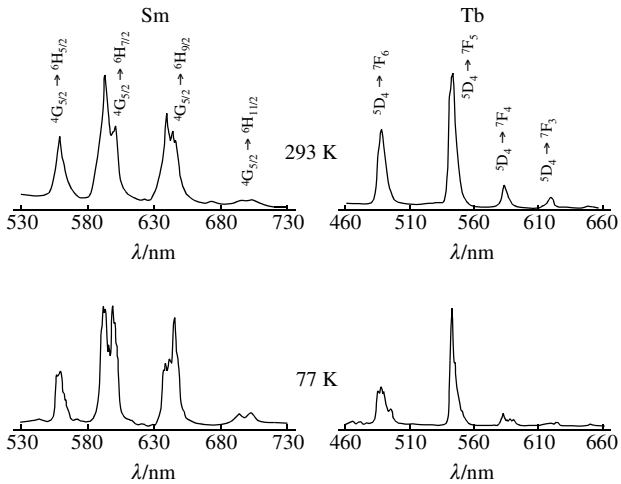

Figure 2 Luminescence spectra of crystalline $Ln[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$ (Ln = Sm or Tb) at 293 and 77 K. The spectral resolution is 0.5 or 0.8 nm for the spectra of Tb and Sm, respectively.

† The luminescence of lanthanide complexes with molybdoaluminate ions was excited by nitrogen laser (λ = 337.1 nm, pulse duration of 7–9 ns, power of 120 mW at a frequency of 1000 Hz). Uncorrected luminescence spectra were recorded using an MSD-1 monochromator. Luminescence lifetimes were measured using an S1-70 oscillograph. Excitation luminescence spectra were obtained on an SFL-2 spectrofluorimeter with a DKsSh-500 xenon lamp as light source. $(NH_4)_3[Al(OH)_6Mo_6O_{18}]\cdot nH_2O$ **1** was synthesised as described previously[3] and recrystallised from water.

‡ D_2O (Izotop, Russia) of 99.8% purity was used.

583.0 nm corresponds to the transition $^5D_1 \rightarrow {}^7F_3$. At ambient temperature, this transition is masked by the much more intense transition $^5D_0 \rightarrow {}^7F_1$. Other transitions from the $^5D_1$ level can be easily observed at 555, 535 and 525 nm even at ambient temperature. This interesting phenomenon has been observed earlier for europium molybdoiodate[1,2] and molybdotellurate.[1] The low-temperature luminescence spectrum of $K(NH_4)[Eu(IMo_6O_{24})(H_2O)_5]\cdot 4H_2O$ also exhibits a peak near 585 nm.[2] The lifetimes of the $^5D_1$-luminescence of europium molybdoiodate and europium molybdotellurate were measured.[1] The spectrum of $Eu[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$ is very similar to the spectrum of $K(NH_4)[Eu(IMo_6O_{24})(H_2O)_5]\cdot 4H_2O$, in which the coordination polyhedron of Eu^{III} is a tricapped trigonal prism.[2] The X-ray data showed that lanthanide ion in $Ln[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$ have the same polyhedron. The luminescence spectrum of europium molybdoaluminate corresponds to the lowest symmetry groups and agrees with structural data.

According to X-ray diffraction data, the difference in the europium(III) surroundings in molybdoiodate[2] and molybdoaluminate consists in the number of water molecules bonded to the lanthanide ion. In the former case, five oxygen atoms of H_2O and four oxygen atoms of molybdate groups enter the coordination sphere of europium, whereas in the latter complex there are seven and two atoms, respectively.

The luminescence method allowed us to evaluate rapidly the nature of compounds formed under changes in the synthesis conditions. An increase in the crystallisation temperature up to 90 °C remained the luminescence lifetime and spectra almost unchanged. The compound obtained from acid solutions luminesced very weakly under the supernatant. However, the luminescence intensity of the complex increased after drying, and the luminescence characteristics of dry compounds separated from neutral and acidic solutions were almost identical. The properties of complexes prepared from heavy water solutions differed only in the luminescence lifetime and intensity.

Figure 2 shows the luminescence spectra of samarium and terbium molybdoaluminate complexes. These spectra exhibit bands corresponding to transitions from the levels $^4G_{5/2}$ and $^5D_4$, respectively. The luminescence spectrum of dysprosium molybdoaluminate exhibits two most intense poorly defined bands at about 479 and 572 nm; these bands correspond to the transitions $^4F_{9/2} \rightarrow {}^6H_{15/2,13/2}$. At 77 K, the first band is split into two components with maximums at 479.3 and 484.1 nm.

It should be noted that the bright luminescence of terbium(III) in the new solid is unexpected. Although Tb^{III} is usually a brightly luminescent ion, it does not luminesce in isopolymolybdate solutions.[6] The reason of this phenomenon is that terbium luminescence can be quenched by electron transfer from the terbium ion to its coordination sphere, if it contains Mo^{VI}, W^{VI} or other ions possessing electron-acceptor properties. The quenching is a thermally activated process and hence strongly depends on temperature. In spite of the presence of Mo^{VI} in the coordination sphere of Tb^{III} in the molybdoaluminate complex, the temperature quenching of its luminescence is rather weak and terbium luminesces in the temperature range from 77 to 350 K. Electron transfer proceeds through a system of chemical bonds. Therefore, the reason for the weak quenching of terbium luminescence by charge transfer (CT) through the state Tb^{IV}–Mo^{V} can consist in that oxygen atoms from molybdate groups in the coordination environment of the Tb^{3+} ion occupy only two places of nine. Previously, we found that an increase in the number of bonds (from 4 to 8) between the curium ion and ligands in polytungstate complexes leads to an increase in Cm^{3+} luminescence quenching by CT *via* the state Cm^{IV}–W^{V}.[7]

The luminescence lifetimes of all compounds prepared from solutions in water (τ_{H_2O}) and heavy water (τ_{D_2O}) are given in Table 1.

Water and D_2O molecules, as well as other molecular groups in the environments of *f*-element ions, quench luminescence by an inductive-resonance mechanism.[8] Using the equation[9]

$$(k_H - k_D)n = 1/\tau_{H_2O} - 1/\tau_{D_2O}, \quad (1)$$

Table 1 Luminescence lifetimes τ (μs) of solid $Ln[Al(OH)_6Mo_6O_{18}]\cdot 11H_2O$ (Ln = Eu, Tb and Sm) and hydration numbers *n* of lanthanide ions in the complexes.

Lanthanide	τ_{H_2O}, 295 K	τ_{D_2O}, 295 K	τ_{H_2O}, 77 K	*n*
Eu	110±10	1150±50	110±10	7.7
Tb	310±10	1300±100	390±15	8.7
Sm	3.5±0.8	55±5	3.5±0.8	5.6[a], 8.6[b]
Dy	4–6[c]	≥ 30[c]	4–6[c]	—

[a] τ calculated by equation (1). [b] τ calculated by the simplified equation $k_D n = 1/\tau_{D_2O}$ on the assumption that, in the case of Sm, only the rate of luminescence quenching by D_2O molecules determines the value of τ_{D_2O} and other quenching pathways are neglected. [c]Luminescence decay is not exponential.

the hydration numbers of lanthanide ions can be calculated (k_H and k_D are the rate constants of quenching of *f*-element ion luminescence by a molecule of H_2O or D_2O that enters the first coordination sphere of the *f*-element ion, respectively). To determine k_H and k_D, we used the hydration numbers *n* of 8.3, 8.0 and 8.0 for Sm^{III}, Eu^{III} and Tb^{III} aqua-ions,[10] respectively, and published data[5] on the luminescence lifetimes of Ln^{3+}_{aq} ions in H_2O and D_2O solutions. From the Eu, Tb and Sm luminescence data, the mean value is $n = 7.65 \pm 1.44$. From X-ray data for any lanthanide ion, $n = 7$. Possible errors were discussed in ref. 9. The inaccuracy of the luminescent method is noticeably larger than ±0.5 given by Horrocks *et al.*[5] However, we suppose that this is due to a great value of *n*. Relative standard deviation in the determination of *n* is about 20%.

Thus, the lanthanide complexes with the molybdoaluminate ion are formed in solution only at high ligand concentrations. The complexes can be easily separated as solids. Only two molybdenum atoms are bonded to Eu, Sm, Dy or Tb ions through oxygen atoms, and seven coordination places are occupied by water molecules. Effective energy transfer from the ligand to the central ion takes place in the solid molybdoaluminate complexes, and the characteristic luminescence of lanthanide ions arises on the UV excitation of the complexes. The bright $^5D_1$-luminescence of Eu^{III} is of interest. The luminescence of Tb^{III} in a complex with $Al(OH)_6Mo_6O_{18}^{3-}$ is surprisingly intense, although the strong quenching by charge transfer to Mo^{VI} could be expected.

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