Thermoluminescent and magnetic properties of a heteroligand adduct of terbium(III) acetylacetonate containing a 1,10-phenanthrilonium ion in the outer sphere

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Thermoluminescent and magnetic properties of a heteroligand adduct of terbium, [PhenH][Tb$(NO_3)_2$(Acac)$_2$Phen], where Phen is 1,10-phenanthroline and Acac is acetylacetonate ion, have been studied using the luminescence, IR, and ESR spectroscopy techniques. It was found that the increase in the photoionization efficiency of the complex at 190—220 K is due to the strengthening of the outer-sphere interaction and by the transfer of electron from the complex anion to the outer-sphere cation.

Key words: terbium(III), terbium acetylacetonate; 1,10-phenanthroline; 1,10-phenanthrolonium; thermoluminescence, IR spectra, ESR spectra.

Aromatic amines such as 2,2′-dipyridyl(Dipy) and 1,10-phenanthroline(Phen) exhibit high σ-donating properties and, additionally, can interact with metals through their aromatic σ-orbitals. Therefore, they can form anion-radical adducts and charge-transfer complexes which are stable under normal conditions.[1,2] Earlier[3] it was found that thermoluminescence is typical of the complexes of rare-earth elements (REE) with outer-sphere cations [Dipy H]$^+$ and [Phen H]$^+$. The effects of the structure of organic outer-sphere cations on the luminescence spectra of crystalline europium chelates have been studied earlier.[4,5] According to literature data,[6] the perturbing action of the outer-sphere cation depends, to some extent, on external conditions, particularly, on temperature.

In this work, luminescence, and IR and ESR spectroscopic methods were used to study the thermoluminescent and magnetic properties of the heteroligand acido complex of Tb^{III} which consists of a complex anion, [Tb$(NO_3)_2$(Acac)$_2$Phen]$^-$, where Acac is the acetylacetonate ion, and the 1,10-phenatrolinium cation, PhenH, in the outer sphere.

Experimental

Synthesis and identification of the [PhenH][Tb$(NO_3)_2$(Acac)$_2$Phen] adduct have been described earlier.[3] The low-temperature luminescence and thermoluminescence (TL) spectra were registered on a SDL-1 spectrometer. The X-ray luminescence and X-ray thermoluminescence were studied using an URS-01 (25 kV, 20 mA, and Ni-anticathode) instrument through a beryllium-foil window. For UV irradiation, nonfiltered light of a DRT-250 mercury lamp was used. The IR spectra (for suspensions in vaseline oil) were recorded on Specord-75 and UR-20 spectrometers in the 400—4000 cm^{-1} range. The ESR spectra were measured in the X range of frequencies on an ESR-231 radiospectrometer in the 120—300 K temperature interval.

Results and Discussion

A detailed study of the chemical composition of the [PhenH][Tb$(NO_3)_2$(Acac)$_2$Phen] adduct indicates the presence of two 1,10-phenanthroline subunits, one of which (Phen) is a neutral molecule coordinated to Tb^{III}, while the other is an outer-sphere cation, [PhenH]$^+$. In the IR spectrum of this adduct there appear absorption bands that point to the intracomplex bidentante coordination of acetylacetone by the Tb^{III} ion (an intense peak at 1590 cm^{-1} assigned to a bound carbonyl group) as well as Phen (the split intense line δ(CH) deformational vibrations in the of 850 cm^{-1} region with peaks at 850 and 865 cm^{-1}).[3,7,8] The distinct IR absorption bands of medium intensity in the 3510—3540 cm^{-1} region attributed to ν(NH) valence deformation vibrations (see Refs. 7, 8) are typical only of the complexes with protonated diamine in the outer sphere. The presence of the outer-sphere Phen residue is also confirmed by the results of thermogravimetric and elemental analyses.

The [PhenH][Tb$(NO_3)_2$(Acac)$_2$Phen] adduct is characterized by intense photo- and X-ray luminescence. In contrast with the β-diketone complexes of Tb^{3+}, it contains diamine in the protonated form and can store ultraviolet and X-ray energies at low temperatures (80 K). When the preirradiated adduct is heated, the accumulated energy is released in the form of light: an intense

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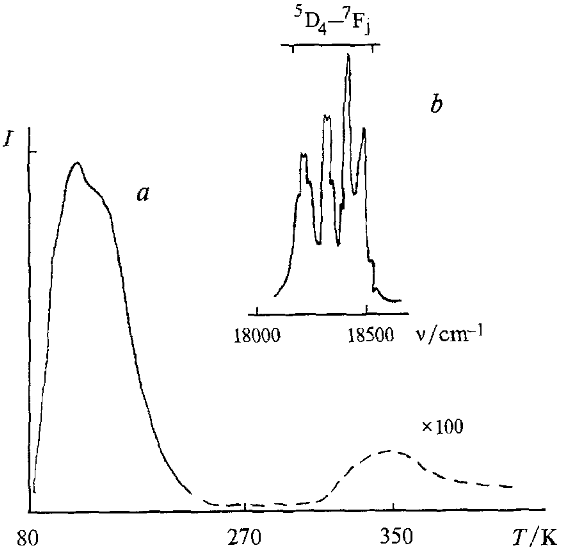

Fig. 1. (*a*) Temperature curve and (*b*) thermoluminescence spectrum of the (PhenH)[Tb(NO$_3$)$_2$(Acac)$_2$Phen] complex.

green glow at low temperatures (120—220 K) and weak luminescence at higher temperatures are observed (Fig. 1, *b*). The thermoluminescence spectrum of the complex studied coincides with its photo- and X-ray thermoluminescence spectra and results from Stark transitions $^5D_4$—^7F_j between the terbium ion levels (Fig. 1, *b*). Analysis of the thermoluminescence spectra indicates the recombinational mechanism of thermoluminescence.[3]

The ESR method presents additional information on specific features of the adduct state in the temperature range 77—300 K. The ESR spectrum of the polycrystalline powder (Fig. 2) is a superposition of two lines differing in the nature of the temperature dependence. From a comparison of the ESR spectra of the compound studied with the spectra of Tb_2O_3 and $Tb(NO_3)_3 \cdot 6H_2O$ and on the basis of published data,[9] the group of lines including the most intense signal with $g_{eff} = 2.54 \pm 0.03$, which increases with decreasing temperature, was assigned to the Tb^{4+} ion. The presence of Tb^{IV} in the powders is associated with the nonstoichiometry of the initial oxide Tb_4O_7, which contains Tb^{3+} and Tb^{4+} in equal amounts.[10] The ESR signal with $g_{eff} = 2.54 \pm 0.03$ (T = 293 K), as the most intense in the group, was ascribed to the transition between the spin sublevels of Tb^{4+} with $S_z = 1/2$ and $-1/2$. As the temperature decreases, the g_{eff} factor of this signal decreases from 2.54 at 293 K to 2.32 at 125 K, which apparently reflects the rearrangement of the crystal surroundings of Tb^{4+}.

The ESR signal with $g_{eff} = 2.13 \pm 0.03$ appears as a single inhomogeneously broadened line (see Fig. 2). Its intensity decreases with decreasing temperature. Such temperature dependence is typical of thermally excited triplet states of molecules.[11,12] It should be noted that a similar signal with g_{eff} = 2.1 to 2.2 is also observed in the ESR spectra of powders of $Phen \cdot H_2O$, $Tb(NO_3)_2Phen$, and $Tb(AA)_2(NO_3)Phen$. At the same time, this signal is not observed in the ESR spectra of terbium powders containing no Phen. Taking these facts into consideration, we assigned the ESR signal of [PhenH][Tb(NO$_3$)$_2$(Acac)$_2$Phen with g_{eff} = 2.13 to the low-energy triplet state of the coordinated Phen molecule thermally excited at room temperature. The populations of the triplet and singlet levels obey Boltzmann statistics and, therefore, the singlet-triplet splitting[12] can be evaluated from the temperature dependence of the ESR signal intensity. In our case it amounts to ~300 cm^{-1}.

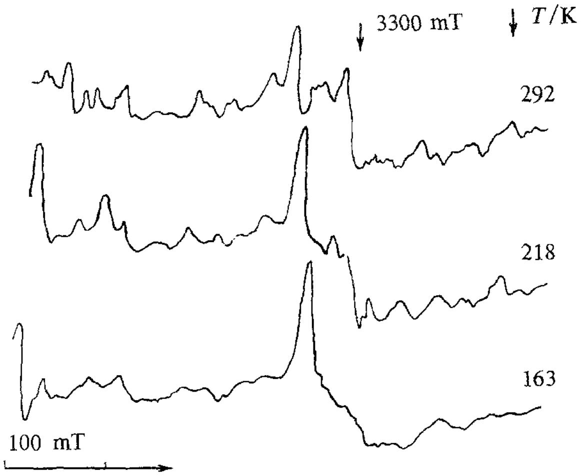

Fig. 2. ESR spectra of the (PhenH)[Tb(NO$_3$)$_2$(Acac)$_2$Phen] complex (powder) at different temperatures.

The temperature dependence of the intensity of the ESR signals (Fig. 3) implies the existence of a critical point (T = 190 K) within the temperature range corresponding to the luminescence of the energy stored at

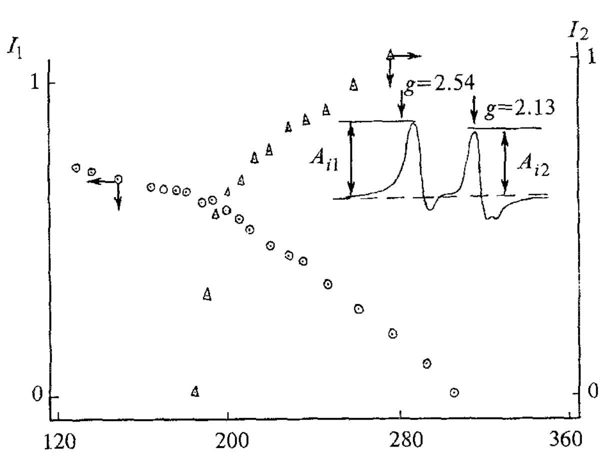

Fig. 3. Temperature dependences of parameters $I_1 = 1 - A_{i1}/A_1$ and $I_2 = A_{i2}/A_2$ (A_1 and A_2 are the intensities of peaks in the ESR spectra of the (PhenH)[Tb(NO$_3$)$_2$(Acac)$_2$Phen] powder (293 K) at g_{eff} = 2.54 and g_{eff} = 2.13, respectively).

low temperatures (Fig. 1). The curve for the ESR signal of Tb^{4+} also shows an inflection at 190 K. All temperature variations of the ESR spectra are reversible. It can be assumed that the observed temperature effect is derived from the specific outer-sphere interaction between the $[PhenH]^+$ cation and the complex anion $[Tb(A)]^-$ in the critical temperature range.

Earlier[13], the transfer of an electron from adduct-forming agents [Phen and triphenylphosphinoxide (TPPO)] to a metallocycle was established for heteroligand compounds of europium. The binding energy of the skeleton electrons in the free forms of Phen and TPPO is significantly lower than in the molecules coordinated to the metal. Therefore, one can suggest that, in the adduct studied, the outer-sphere cation $[PhenH]^+$ is photoionized more readily than the Phen molecule coordinated with Tb^{III}.

In the complex under study, the outer-sphere interaction of the $[PhenH]^+$ cation with the complex anion $[Tb(A)]^-$ occurs through donor-acceptor N—H...A hydrogen bonds. The strengthening of this interaction at 190—220 K must be accompanied by the transfer of an additional electron from the complex anion to the outer-sphere cation. Analysis of the temperature changes in the IR spectra showed that the temperature decrease causes an increase in the integral intensity of the NH valence vibration band in the $[PhenH]^+$ cation. The maximum of the low-frequency peak of the two-component band is shifted to low frequencies, which indicates[6] the strengthening of the H-bond between the outer-sphere cation and the complex anion. In its turn, the increase in the negative charge in the σ electron system $[PhenH]^+$ must sharply increase its basity[1,2] and, correspondingly, the efficiency of photoionization at low temperatures.

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