Effect of γ-substitution on the thermoluminescence properties of terbium(III) acetylacetonate complexes with 1,10-phenanthroline

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The coordination compounds $[Tb(NO_3)_2acac(phen)_2]H_2O$ (where acac is acetylacetone or its derivatives substituted in the γ-position) were synthesized and studied by luminescence, IR, and UV spectroscopy. Thermoluminescence of the complexes containing acetylacetonate, 3-phenylthio-2,4-pentadionate, and 3-(*p*-methoxyphenylthio)-2,4-pentadionate was found. The structural and electronic aspects of the crystal thermoluminescence were discussed.

Key words: terbium(III), terbium acetylacetonate, 1,10-phenanthroline, γ-substitution, thermoluminescence.

Thermoluminescence (TL) of crystallophosphors and organic compounds is well studied.[1] It has been shown that TL of ionic crystals, glasses, and polymers is related to thermal release of electrons captured during irradiation from traps. A prolonged after-glow is due to recombination of charged particles, resulting in the formation of electron-excited molecules emitting photons.[2] Published data on the TL properties of complexes of rare-earth elements (REE) are virtually lacking, although the use of lanthanoid complexes in thermoluminescence dosimetry has several advantages over that of the known organic luminophores and crystallophosphor compounds (a high sensitivity, monochromaticity of TL, and the possibility to use them as low-temperature detectors of working elements and devices based on high-temperature superconductors operating in ionizing radiation fields).[3]

It has previously been found[4,5] that coordination compounds of Tb^{III} and Dy^{III} with acetylacetone and 1,10-phenanthroline exhibit intense TL and can accumulate the energy of UV and X-ray radiation. Explaining the TL effect, the authors of Refs. 4 and 5 concluded that the charge can be separated in different parts of a heteroligand complex. It was of interest to reveal the factors favoring the appearance of the TL properties in REE complexes. In this work, we studied the effect of γ-substituents of acetylacetone MeCOCHRCOMe (R = Me, Ph, S—Ph, S—Ph-*p*-OMe, S—Et) on the thermoluminescence properties of $[Tb(NO_3)_2acac(phen)_2]H_2O$ complexes.

Experimental

The complexes were synthesized by the known method.[4] C,H-Elemental analysis was carried out by burning a weighed sample in a quartz tube in an O_2 atmosphere in the presence of catalysts. The content of nitrogen was determined by the Dumas method, and the presence of sulfur was confirmed by qualitative analysis (the reaction with HNO_2). IR spectra were recorded on a Specord 751R spectrophotometer as Nujol suspensions in the 400—4000 cm^{-1} region.

Low-temperature spectra of luminescence and luminescence excitation were recorded on an installation assembled on the basis of an SDL-1 spectrometer and an MDR-23 monochromator; DRSh-250 and Tungsram-2500 lamps were used as excitation sources. X-ray luminescence and X-ray thermoluminescence were studied on a URS-01 apparatus (25 kV, 20 mA, a Ni anticathode) through a window of beryllium foil. The dose power on the sample was 1800 R min^{-1}. Samples for studying TL were prepared as pellets (diameter 3 mm, thickness 0.3 mm). A sample was placed in a vacuum cryostat for measurements in the 80—650 K temperature range. The heating rate during thermoscintillation was 0.3 K s^{-1}. The TL intensity was detected by an FEU-106 photoamplifier working in the photon counting mode. The spectral series of peaks was recorded simultaneously with detection of TL by the previously described procedure.[6] UV irradiation of samples was performed by non-filtered light from a DPT-250 mercury lamp.

The IR spectra of the complexes contain absorption bands of the NO_3 group (1480 cm^{-1}) and C=C double bonds (1508 cm^{-1}) and two bands at 850 and 863 cm^{-1}, which are characteristic of 1,10-phenanthroline. Absorption bands of the carbonyl groups of acetylacetonates with substituents in the γ-position lie in the 1550—1580 cm^{-1} region.

Results and Discussion

The $[Tb(NO_3)_2acac(phen)_2]H_2O$ complex (**1**) possesses intense X-ray and photoluminescence, and, unlike the known β-diketonate complexes, Tb^{3+} can accumulate the energy of X-ray and UV irradiation at low

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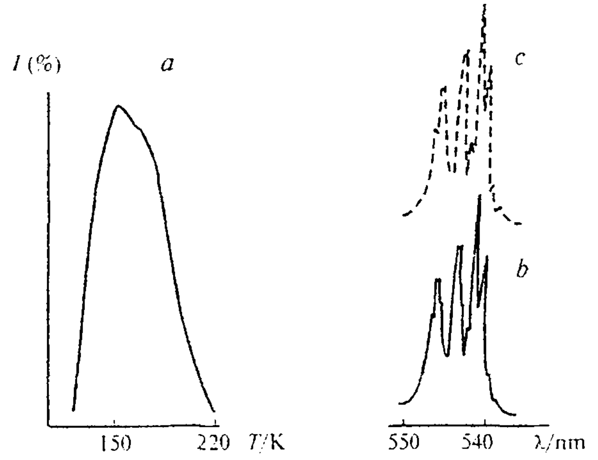

Fig. 1. TL glow curve (*a*) and spectra of luminescence (*b*) and thermostimulated luminescence (*c*) of $[Tb(NO_3)_2acac(phen)_2]H_2O$ (77 K).

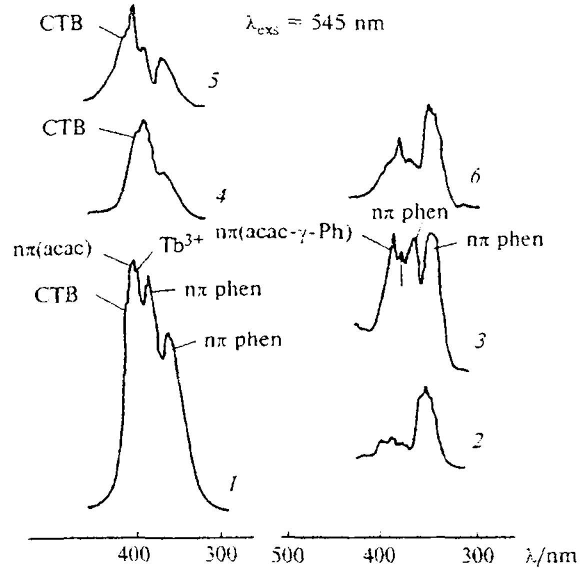

Fig. 2. Luminescence excitation spectra (λ_{exc} = 545 nm, 77 K) of $[Tb(NO_3)_2acac\text{-}\gamma\text{-}R(phen)_2]H_2O$, where R = H (*1*), Me (*2*), Ph (*3*), S—Ph (*4*), S—C_6H_4-*p*-OMe (*5*), and S—Et (*6*).

temperature (77 K).[4] When it is heated after preliminary X-ray and photoirradiation, the accumulated energy is liberated as a light beam: an intense green luminescence is observed at low temperatures (Fig. 1, *a*). The spectral composition of TL of complex **1** coincides with the X-ray and photoluminescence spectra and is due to the Stark transitions between the $^5D_4$—^7F_J levels of the Tb^{3+} ion (see Fig. 1, *b*). Analysis of the TL glow curves indicates the recombination mechanism of thermoluminescence.[4,5]

The bands in the luminescence excitation spectra (Fig. 2) were assigned on the basis of analysis of the spectra of compounds close in composition in which the nearest environment was successively changed. Along with the complexes under study, we examined the spectra of $Tb(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 2phen$, and $Tb(acac)_3 \cdot 2phen$. Excitation spectra of these compounds exhibit bands due to the intraconfiguration f—f-transitions of Tb^{3+} and transitions associated with the energy and electron transfer from the acac and phen ligands to Tb^{3+}. Analysis showed that the band in the 380—400 nm region is observed in the presence of the acetylacetonate group and its γ-derivatives and virtually coincides with the maximum of the f—f-transition of Tb^{3+} at 382 nm ($^5D_3 \leftarrow {}^7F_6$ transition). The shoulder at 390 nm, which was observed only for complexes **1**, **4**, and **5** with TL properties, was attributed to the charge transfer band (CTB). The bands at 370 and 346 nm correspond to transitions between the phen ligands. The complexes

Table 1. Elemental analysis data and relative intensity of luminescence (I_{lum}) of synthesized compounds

Compound	Found/Calculated (%) C	H	N	I_{lum} (%)	TL
$[Tb(NO_3)_2acac(phen)_2]H_2O$ (**1**)	47.75 45.72	3.40 3.90	10.17 9.95	100	+
$[Tb(NO_3)_2acac\text{-}\gamma\text{-}Me(phen)_2]H_2O$ (**2**)	48.43 48.19	3.93 3.75	10.86 10.85	29	–
$[Tb(NO_3)_2acac\text{-}\gamma\text{-}Ph(phen)_2]H_2O$ (**3**)	49.89 50.17	3.62 3.58	10.13 10.03	47	–
$[Tb(NO_3)_2acac\text{-}\gamma\text{-}SPh(phen)_2]H_2O$ (**4**)	48.41 48.33	3.58 3.45	9.73 9.67	20	+
$[Tb(NO_3)_2acac\text{-}\gamma\text{-}SC_6H_4\text{-}p\text{-}OMe(phen)_2]H_2O$ (**5**)	48.51 48.05	3.68 3.56	8.93 9.34	28	+
$[Tb(NO_3)_2acac\text{-}\gamma\text{-}SEt(phen)_2]H_2O$ (**6**)	45.64 45.31	3.08 3.65	10.47 10.23	15	–

with TL are characterized by a relatively higher intensity of the band at 370 nm.

It follows from the data in Table 1 that complexes **4** and **5**, as the starting complex **1**, exhibit TL along with intense photoluminescence. Special studies are required to obtain direct data on the structure of traps in which electrons captured during ionization of the coordination compounds under study are localized; however, it can be assumed that TL is due to the specific features of the geometric and electronic structures of the adducts.

Compounds **1**—**6** are isostructural to the $[Dy(NO_3)_2acac(phen)_2]H_2O$ complex, which possesses TL properties and whose crystals are built of $Dy(NO_3)_2acac\text{-}(phen)_2$ molecules with H_2O connecting the Dy atoms by O—H...O bonds to form infinite chains along the *y* axis. The Dy atom is bidentately bound to five ligands (CN = 10): two phen, two NO_3 groups, and acac. The ligands are arranged around Dy as a "five-blade propeller."[7] In the *xz* planes arranged at the 1/4 and 3/4 levels along the *y* axis, monomeric molecules are packed in such a way that the hydrocarbon parts of the acetylacetone ligands are arranged between the phenanthroline ligands of the adjacent molecule. The specific features of packing of the π-conjugated systems provide a possibility of electron transfer *via* the chain: donor (acac) $\rightarrow$ reaction center (Ln^{3+}) $\rightarrow$ acceptor (phen). It is noteworthy that the $Tb(NO_3)_3(phen)_2$, $Tb(NO_3)_3acac$, $Tb(acac)_3phen$, and $Tb(acac)_3H_2O$ complexes, close in composition but different in structure, do not exhibit TL.

Despite the isostructural character of compounds **1**—**6**, complexes **2**, **3**, and **6** do not exhibit TL. The efficiency of TL depends on several factors, including the easiness of photoionization of the complex molecule. Analysis of the influence of the γ-substituent on the ionization potential of β-diketones shows that complex **1** possesses the most intense TL. According to the data of photoelectron spectroscopy, its structure has an important specific feature: a small energy gap between the partially filled $4f(Tb^{3+})$, O2p(acac), and N2p(phen) orbitals (close values of the ionization potentials of acac, phen, and Tb^{3+}).[8,9]

The data obtained show that introduction of a substituent into the γ-position of acac sharply decreases the light sum of the complexes. On the other hand, interpretation of the photoelectron spectra and quantum-chemical analysis of the electron effects of γ-substitution indicate their rather considerable (0.2—0.35 eV) effect on the displacement of the n^--, n^+-, and π^3-MO.[8,10] Similar effects were observed for the acac complexes of Al, Co, and others. For example, when H is substituted by SCH_2CH_3, two upper π^3 and n^- levels are shifted by 0.23 eV.[8,10] In any case, the shift of the n^--, n^+-, and π^3-orbitals during γ-substitution in acac results in an increase in the width of the energy gap between the $4f(Tb^{3+})$-, O2p(acac)-, and N2p(phen)-orbitals (Fig. 3). The important role of closeness of the ionization potentials of the ionized molecule is additionally assumed by the absence of TL in the complexes synthesized whose composition is similar, but acac is substituted by other β-diketone with a higher ionization potential.

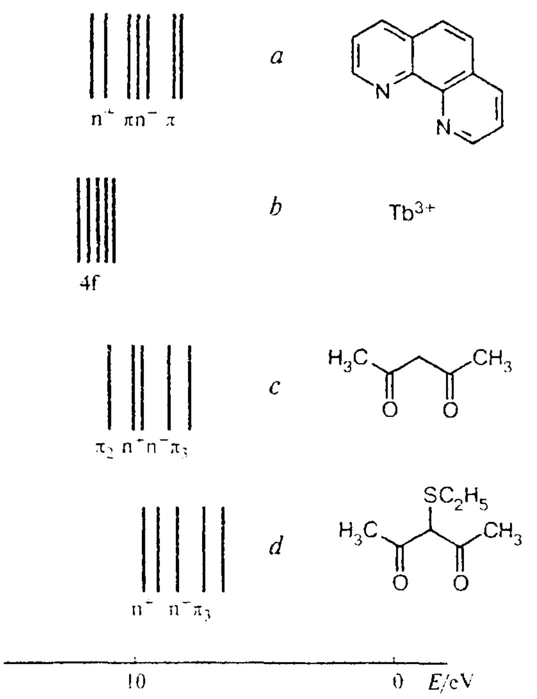

Fig. 3. Energy diagrams of valent MO: 1,10-phenanthroline (*a*); $TbCl_3$ (*b*); acetylacetonate (*c*); and 3-methylthio-2,4-propanedionate (*d*).

We have previously found[5] by ESR the specific features of the electron state of complex **1** in the 77—300 K temperature region. The ESR signal with g_{eff} = 2.13 was attributed to the radical anion state of the coordinated phen molecule. It is most likely that this signal is related to few molecules localized near defects of the crystal lattice rather than all molecules of the coordination compound. The disappearance of the signal with g_{eff} = 2.13 in the dark upon temperature decrease (190 K) indicates reversible thermal electron transfer to the phen radical anion to form the phen dianion. An increase in the electron density on the phen dianion should favor the efficiency of photoionization of the complex at low temperature.

Thus, close energies of the orbitals of Tb^{3+}, the electron-rich acac group, and electron-deficient phen, as well as the specific features of the structural packing, favor, most likely, an increase in the efficiency of photoionization of complexes **1**, **4**, and **5**. Electron transfer from one $Tb(NO_3)_2acac(phen)_2$ molecule through the bridge of the H_2O molecule (O—H...O hydrogen bonds bind the Tb atoms along the *y* axis to form infinite chains) to the trap formed by another

$Tb(NO_3)_2acac(phen)_2$ molecule, which is due to some defect of the crystal lattice, also seems highly probable.

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References

1. P. Prinsgeim, *Fluorestsentsiya i fosforestsentsiya* [*Fluorescence and Phosphorescence*], Izd-vo Inostr. Lit., Moscow, 1951, 638 pp. (Russ. Transl.).
2. D. Starick, W. Lange, and G. Herzog, *J. Therm. Anal.*, 1988, **33**, 889.
3. A. M. Gurvich, *Vvedenie v fizicheskuyu khimiyu kristallofosforov* [*Introduction into Physical Chemistry of Crystallophosphorus Compounds*], Vysshaya Shkola, Moscow, 1982, 376 pp. (in Russian).
4. I. N. Botova, A. G. Mirochnik, and V. E. Karasev, *Koord. Khim.*, 1992, **18**, 659 [*J. Coord. Chem.*, 1992, **18** (Engl. Transl.)].
5. I. N. Botova, A. G. Mirochnik, V. G. Kuryavyi, V. E. Karasev, and A. M. Ziatdinov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1038 [*Russ. Chem. Bull.*, 1994, **43**, 973 (Engl. Transl.)].
6. S. M. Erukhimovich, V. S. Startsev, Kh. S. Bagdasarov, A. M. Kevorkov, T. A. Melkonyan, and B. V. Shul'gin, *Zh. Prikl. Spektr.*, 1988, **48**, 496 [*J. Appl. Spectrosc.*, 1988, **48** (Engl. Transl.)].
7. V. E. Karasev, A. G. Mirochnik, and A. V. Gerasimenko, *Tez. dokl. Natsional'noi kristallokhimicheskoi konferentsii* [*Abstr. National Conf. on Crystal Chemistry*], Chernogolovka, 1998 (in Russian).
8. V. I. Vovna, *Koord. Khim.*, 1995, **21**, 435 [*J. Coord. Chem.*, 1995, **21** (Engl. Transl.)].
9. E. P. F. Lee, A. W. Potts, and J. E. Bloor, *Proc. R. Soc. London*, 1982, **381**, 373.
10. A. I. Cherednichenko, Ph. D. (Chem.) Thesis, Research Physicotechnical Institute at the Far-Eastern State Vladivostok University, Vladivostok, 1990, 182 pp. (in Russian).

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