

PHYSICAL METHODS
OF INVESTIGATION

The Role of Copper Ions in Tb(III) Luminescence Sensitization in Heterometallic Complexes with Podands

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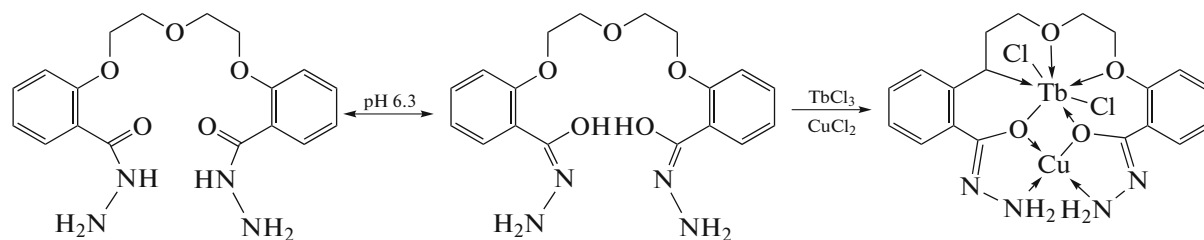
Abstract—It has been demonstrated that copper-induced terbium(III) luminescence sensitization in heterometallic complexes with hydrazine-containing podands is caused by the ligand ring closure and joint coordination of both metal ions to the carbonyl oxygen atoms as well as, mainly, by the reduction with the hydrazine substituents of Cu(II) to Cu(I), which is able to sensitize terbium luminescence.

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Copper(II) ions are known to be strong quenchers of lanthanide luminescence in solutions of their complexes with diverse organic reagents [1–4]. This is a serious hindrance to the determination of lanthanides in the presence of copper. The quenching effect of Cu(II), Ni(II), and Fe(II) ions on the Eu(III) luminescence in heterometallic complexes has been described in [5, 6].

As distinct from Cu(II), the Cu(I) ions exhibit intrinsic luminescence caused by the $1s^2...3p^63d^{10}$ electronic structure inherent in noble metal ions, namely, in silver(I) and gold(I). Formation of the $nd^9(n+1)s^2$ electronic configuration requires different

energy inputs $\Delta E(ds)$. The $\Delta E(ds)$ value (kJ mol^{-1}) for copper is the lowest one in the series Cu (34.4)–Ag (91.8)–Au (40.2) [7]. The Cu(I) luminescence in complexes with halide ions and pyridine derivatives has been reported [8]. In the $\text{Cu}(\text{dmp})\text{BH}_4$ complex with 2,9-dimethyl-1,10-phenanthroline (dmp) and borohydride (reducing agent), Cu(I) luminescence is observed in solution as well as in the solid state [9]. Efficient copper-induced Tb(III) luminescence sensitization has been observed for the first time in a solution of a heterometallic complex with a podand containing hydrazine substituents and oxygen atoms coordinated to the terbium and copper ions [10, 11]:



(L1)

Copper(II) ions form two five-membered rings with hydrazine substituents and hydroxyl oxygen atoms, thus closing the chain, which makes the ligand structure more rigid. Under these conditions, sensitized Tb(III) luminescence is observed, while the introduction of other d metals into the solution—

Zn(II), Cd(II), Pb(II), Ni(II), and Co(II)—does not induce luminescence. In addition, being coordinated to hydrazine substituents, Cu(II) ions are able to be reduced to Cu(I) and exhibit broadband luminescence with a maximum at 440 nm. The broad Cu(I) luminescence band overlaps the Tb(III) absorption band,

which is responsible for the possible energy transfer and sensitization of terbium 4*f* luminescence by the copper(I) ions in the heterometallic complex.

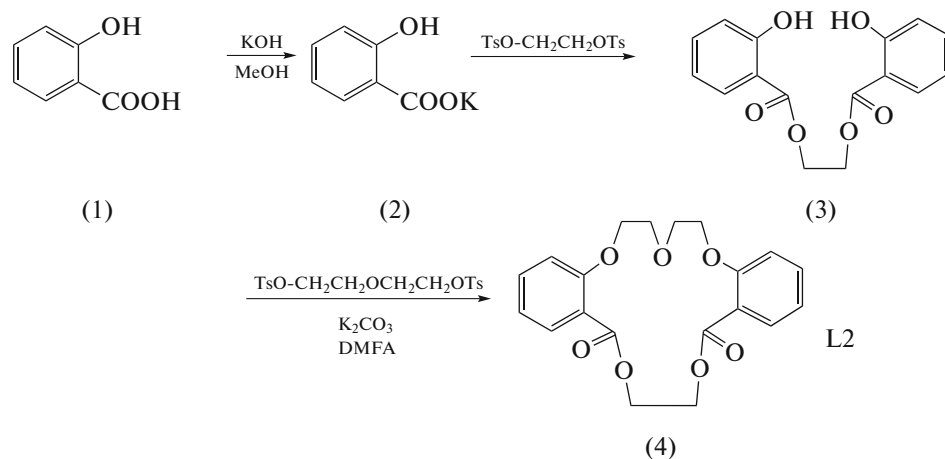
The aim of this study is to elucidate the cause of the Tb(III) luminescence sensitization effect of copper ions and assess the contributions of the ligand rigidity in going from the podand to the macroheterocycle and excitation energy transfer to the central ion when copper ions are reduced to Cu(I).

EXPERIMENTAL

The weak luminescence of Tb(III) ions in a solution of the complex with podand L1 (pH 3) revealed in [10, 11] sharply increases (up to 30 times) when a CuCl₂ solution is added but only in an acid medium (pH 6.1) optimal for the formation of both the CuL1 complex and the heterometallic complex CuTbL1.

Under these conditions, the Tb(III) ion is coordinated to all oxygen atoms of the podand and the Cu(II) ion is bound only to the enol oxygen atoms and the nitrogen atoms of the hydrazine NH₂ groups to give two five-membered rings [12]. The structure of the heterometallic complex is more rigid than that of the monometallic complex TbL1. A question arises whether the copper-induced Tb(III) luminescence will be observed if the ligand chain is closed with some moiety rather than with the copper ion. To answer this question, we synthesized ligand L2 in which the hydrazine moieties are replaced by an oxyethylene bridge closing a ring.

6,7,9,10,18,19-Hexahydro-16*H*,21*H*-dibenzo[*h,p*] [1, 4, 7, 11,14]pentaoxacycloheptadecane-16,21-dione (**4**) was synthesized by Scheme 1:



Scheme 1.

The reaction of salicylic acid (**1**) with KOH gave potassium salicylate (**2**). The latter was alkylated with ethylene glycol ditosylate (or 1,2-dibromoethane) in DMF in the presence of K₂CO₃ to give podand **3**, and its reaction with diethylene glycol ditosylate under the above conditions (Scheme 1) led to its macrocyclization to give the target macrocycle (**4**). Yield, 5.80 g (78%); mp = 152–153°C.

¹H NMR (CDCl₃, δ, ppm): 4.01 (s, 4H, ArOCH₂), 4.22 (s, 4H, OCH₂), 4.64 (s, 4H, COCH₂), 6.92–6.94 (d, 2H, ArH), 7.00 (s, 2H, ArH), 7.45 (t, 2H, ArH), 7.86–7.88 (d, 2H, ArH). Mass spectrum: *m/z* 372 (M⁺).

Acetonitrile solutions of ligands L1 and L2 (1 × 10⁻² mol/L) were prepared using exact weighed portions of solid compounds. They maximally absorb light in the range 260–370 nm. A stock ethanol solution of TbCl₃ (1 × 10⁻¹ mol/L) was prepared by dissolving terbium oxide (99.99%) in HCl; then, an acid excess was removed, and the solution was evaporated to dryness,

and the solid residue was dissolved in ethanol. An ethanol solution of copper chloride (1 × 10⁻² mol/L) was prepared from CuCl₂ · 2H₂O (pure for analysis grade). An acetonitrile solution of neocuproine (1 × 10⁻² mol/L) was prepared using an exact weighed portion of the compound. Working solutions were prepared by dilution of the stock solutions.

Solutions of the complexes were prepared by mixing solutions of the metal chlorides, the reagent, and an ammonium acetate buffer with pH 5.5–6.8 (pH_{opt} 6.2). The luminescence spectral characteristics of the solutions were measured within 30 min after preparation.

The excitation and luminescence spectra, as well as luminescence lifetimes, were recorded on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorimeter with a dual light source (continuous and pulsed xenon lamp 450 W). All measurements were carried out at room temperature (21–23°C). The triplet energies of the ligands (*E*_{T1}, cm⁻¹) were determined from the luminescence spectra of their Gd(III) complexes at 77 K.

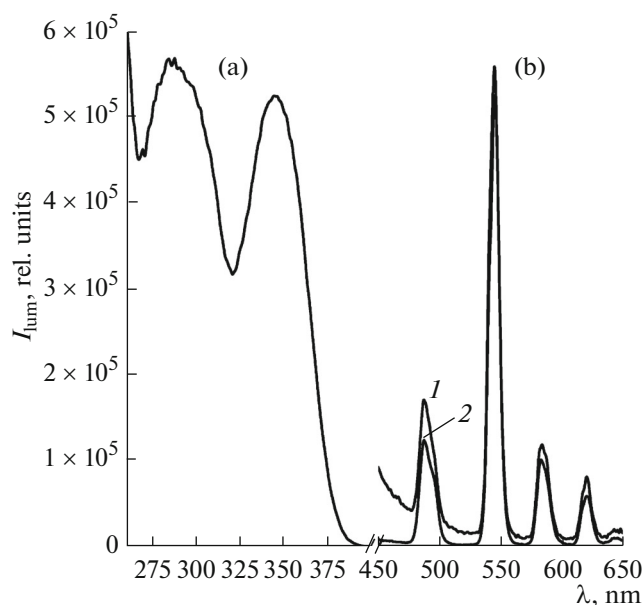


Fig. 1. (a) Excitation ($\lambda_{\text{lum}} = 545$ nm) and (b) luminescence (λ_{exc} : (1) 285 and (2) 345 nm) spectra of a solution of TbL2 ($c_{\text{TbL2}} = 1 \times 10^{-4}$ mol/L).

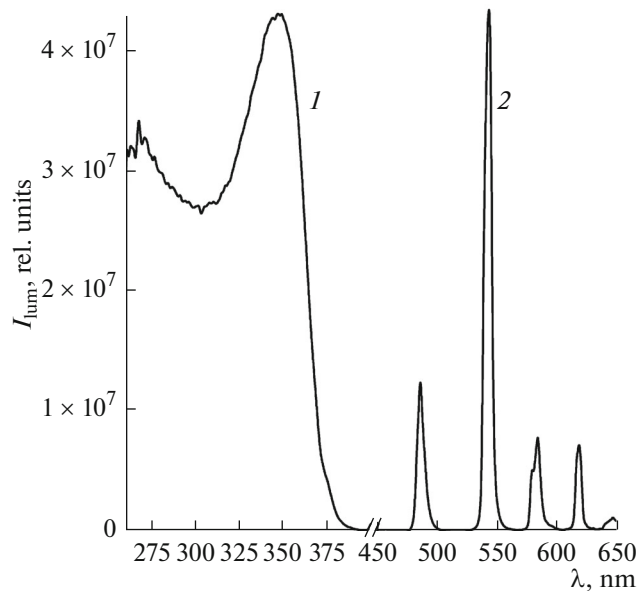


Fig. 2. (1) Excitation ($\lambda_{\text{lum}} = 545$ nm) and (2) luminescence ($\lambda_{\text{exc}} = 350$ nm) spectra of solid TbL2.

The terbium(III) luminescence spectra were recorded in the range 450–650 nm. The IR absorption spectra of samples as KBr pellets were recorded in the range 400–4000 cm^{-1} on a Shimadzu FTIR-8400S spectrophotometer. The X-ray powder diffraction patterns were recorded on a DRON diffractometer ($\text{CuK}\alpha$ radiation, nickel filter). The mass spectra were recorded on MX-1321 and VG 7070 instruments with an ionizing electron energy of 70 eV and an argon atom beam energy of 8 keV, respectively.

As an additional tool, MM+ calculations were used. Unfortunately, it is difficult to use more precise quantum-chemical calculations for lanthanide complexes. Molecular mechanics calculations, rough as they are, make it possible to evaluate the ligand strain energy caused by complexation, which is an essential factor determining the complex stability.

To evaluate the complex strain energy, the energies of the complexes (E_c) and the ligands in the complex conformation (E_l) were calculated. The strain energy is the energy difference $\Delta E = E_c - E_l$, which characterizes the change in the strain energy in the course of complexation. The E_c and E_l energies for each of the complexes were calculated by the molecular mechanics method (MMFF force field) with the HyperChem software.¹

RESULTS AND DISCUSSION

Since the Tb(III) complex with L2 is poorly soluble in water, the complexation reaction was carried out by

mixing an ethanol solution of TbCl_3 with an acetonitrile solution of L2, and acetonitrile was added to a volume of 10 mL. The component ratio in the complex was found to be Tb : L2 = 1 : 1.

The luminescence spectrum of TbL2 (Fig. 1) shows the bands corresponding to the transitions from the Tb(III) emitting level 5D_4 to the sublevels of the ground level 7F_j (where $j = 6, 5, 4, 3, 2$). Splitting of the

Table 1. X-ray powder diffraction data for ligand L2 and its Tb(III) complex

L2		TbL2		L2		TbL2	
$d, \text{\AA}$	$I/I_0, \%$	$d, \text{\AA}$	$I/I_0, \%$	$d, \text{\AA}$	$I/I_0, \%$	$d, \text{\AA}$	$I/I_0, \%$
13.200	100	12.900	20	3.000	8	3.133	15
8.320	25	10.600	100	2.789	15	3.929	16
6.490	72	7.740	20	2.551	3	2.922	16
5.880	24	6.310	20	2.391	10	2.614	15
5.510	20	5.880	20	2.258	12	2.760	100
4.970	14	4.910	20	2.226	18	2.448	10
4.610	5	4.650	90	2.184	7	2.343	5
4.218	6	4.258	30	2.079	12		
3.960	10	3.950	42	2.025	7		
3.822	7	3.637	25	1.891	3		
3.608	21	3.551	15	1.774	2		
3.366	8	3.540	30	1.648	5		
3.245	6	3.125	80	1.556	3		

¹ Here, an available trial version of HyperChem 7.01 was used.

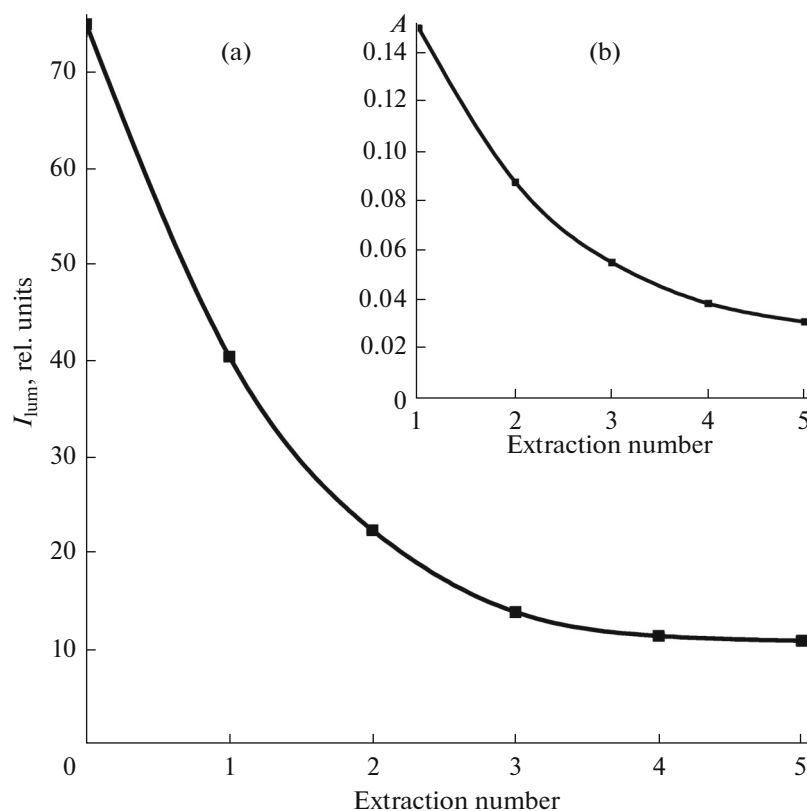


Fig. 3. (1) Luminescence intensity of the TbCuL1 complex before and after extraction of Cu(I) ions with neocuproine (a) and (2) the change in the absorbance of Cu(I) neocuproinate solutions ($c_{Tb, Cu, L1} = 1 \times 10^{-4}$ mol/L) (b).

bands at 490, 588, and 620 nm is poorly pronounced. The luminescence of the solid TbL2 complex is stronger about half an order of magnitude stronger than in solution, but the band pattern persists (Fig. 2). The X-ray powder diffraction data in Table 2 confirm the formation of the TbL2 complex.

Comparison of the IR spectra of L2 and TbL2 shows that there is a sharp decrease in the intensity of the C=O ($\nu = 1693$ cm^{-1}) and aromatic C–C groups ($\nu = 1604$ cm^{-1}) bands. In the spectrum of the complex, the –O–CH₂–CH₂–O– band (doublet, $\nu = 1303$ and 1249 cm^{-1}) and the bands of the ring C–H groups and C=O ($\nu = 748$ cm^{-1}) become weaker. The absorption band at ($\nu = 550$ cm^{-1}) in the spectrum of TbL2 can be assigned to Tb–O bond vibrations.

The heterometallic complex with podand L1 has two coordination sites formed by the Tb(III) and Cu(II) ions, which are both coordinated to the carbonyl oxygen atoms [10], whereas there is no such compound in the case of L2. The cyclic ligand forms a complex with the Tb(III) ion, while the effect of the copper ions can only be outer-sphere as a result of diffusion.

Comparison of the luminescence intensities of Tb(III) complexes (Table 2) demonstrates that the closure of podand L1 with the Cu(II) ion to form a

heterocycle results in a 115-fold rise of the luminescence of TbCuL1 as compared with TbL1, which is due to both the more rigid ligand structure and Tb(III) luminescence sensitization by reduced Cu(I) ions. The closure of the podand with an ethylene bridge (L2) leads to a 49-fold rise of the luminescence of TbL2 as compared with TbL1 caused by the formation of a more rigid ligand structure.

The reduction of Cu(II) to Cu(I) by the hydrazine substituents in the TbCuL1 complex has been proven by the fourfold Cu(I) extraction with a neocuproine solution (Fig. 3). As copper ions are removed from the heterometallic complex, the Tb(III) luminescence is reduced.

The introduction of a CuCl₂ solution into a solution of TbL2 reduces the Tb(III) luminescence by a factor of 4.2 (Table 2). In this case, the Cu(II) ions quench the TbL2 luminescence, as is observed in solutions of complexes with other ligands as well. Reduction of Cu(II) to Cu(I) by introducing hydrazine hydrate into the solution leads only to a further decrease (by a more than one order of magnitude) in Tb(III) luminescence intensity. This behavior can be explained by that the hydrazine-reduced Cu(I) ions in the heterometallic complex TbCuL1 exhibit intrinsic luminescence and, owing to joint coordination to the

Table 2. Luminescence intensity of solutions of the Tb(III) complexes with ligands L1 and L2 in the absence and presence of Cu(II) ions ($c_{\text{Tb, Cu}} = 1 \times 10^{-4}$ mol/L (ethanol), $c_{\text{L1, L2}} = 1 \times 10^{-4}$ mol/L (acetonitrile), $c_{\text{hydrazine hydrate}} = 1 \times 10^{-4}$ mol/L (ethanol))

No.	Solution composition	I_{lum} , rel. units	Intensity ratio	$\Delta E = E_c - E_l$, kcal/mol
1	TbL1	4 (I_0)	$I/I_0 = 115$	-183.1
2	TbCuL1	460 (I)		-215.2
3	TbL2	196 (I_1)	$I_1/I_2 = 4.2$	-103.2
4	TbL2 + CuCl ₂ (1 : 1)	47 (I_2)	$I_1/I_3 = 11.5$	-
5	TbL2 + CuCl ₂ + hydrazine hydrate (1 : 1 : 1)	17 (I_3)		-

The I_{lum} values are reduced to the common recording conditions.

oxygen atoms, sensitize the Tb(III) luminescence. As distinct from this pattern, the Cu(I) ions reduced by hydrazine hydrate quench the TbL2 luminescence more strongly than Cu(II), presumably because of the more efficient excitation energy transfer to Cu(I) than to Cu(II).

For the TbL1, TbCuL1, and TbL2 complexes, the complex strain energy was evaluated. In all cases, $\Delta E < 0$. The TbCuL1 complex is the most favorable one. It is impossible to model a TbL2 complex with copper since the closed ligand can form a complex only with Tb(III).

Despite the fact that molecular mechanics models provide rough estimates of the complexation energies and that quantum-chemical methods should be used to evaluate the strain energy, our results are consistent with the experimental data.

Thus, we believe that the role of copper(I) in the TbCuL1 complex consists of fixing the macroheterocycles, which results in the higher stability of the Tb complex; at the same time, and this is more important, the Cu(I) ions is located at a definite distance ($R \sim 3.6 \text{ \AA}$) from the Tb(III) ion optimal for its sensitization. The copper(I) ion located in the outer sphere of this complex has no such an effect; rather, it results in luminescence quenching.

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