Luminescence and energy transfer processes in europium and terbium complexes with 2-substituted cycloalkanones and 1,10-phenanthroline derivatives

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ABSTRACT

A series of solid lanthanide complexes with 2-substituted cycloalkanones (CA) of the composition Ln $(CA)_3$·Phn and Ln$(CA)_3$·Bpy (Ln = Eu, Tb, Gd) have been synthesized and investigated using luminescence spectroscopy. CA = 2-acetylcyclohexanone (AcCHex), 2-isobutyrylcyclohexanone, 2-acetylcyclopenta-none, 2-acetylbutyrolactone, 2-benzoylcyclohexanone, 2-acetyltetralone; Phn = 1,10-phenanthroline (Phen), 4,7-dimethyl-phenanthroline, 3,4,7,8-tetramethyl-phenanthroline, 5-phenyl-phenanthroline, 4,7-diphenyl-phenanthroline; Bpy = 2,2′-bipyridine. Tris and tetrakis compounds Ln$(CA)_3$·$2H_2O$ and LnNa$(CA)_4$ were also synthesized. The composition, structure and photophysical properties of the lanthanide cycloalkanonates having oligomethylene chain in the ligand are close to peculiarities of β-diketonates without tethered chain. But the presence of this chain can cause a decrease in the energy of the lowest triplet state of the ligand. The Stark structure of the Eu^{3+} electronic states in the europium CA adducts with heterocyclic diimines corresponds to the distorted tetragonal anti-prismatic coordination geometry of the luminescence center. The lifetimes of $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) states at 77 K are 0.55–0.85 ms. The luminescence efficiencies of the lanthanide CA adducts at 77 K are comparable with them for known β-diketonates. The back energy transfer from the $^5D_4$ (Tb^{3+}) state to the lowest triplets of the ligands is the main cause for the decrease in the $^5D_4$ lifetime and the Tb^{3+} luminescence efficiency at 295 K. In the Ln(AcCHex)$_3$·Phn complexes the energy absorbed by the two ligands is transferred to the lowest triplet state of Phn and then to Ln^{3+} ion. In other Ln$(CA)_3$·Phen compounds, the energy transfer to Ln^{3+} ion is carried out through the lowest triplet state of CA, which is located below the Phen triplet. The preliminary data on photochemical stability of the compounds were obtained.

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1. Introduction

Numerous investigations of lanthanide β-diketonates having a high quantum yield of the luminescence have been connected with the use of these compounds in analytical chemistry, devices of molecular electronics, physical and biological sensors, light transforming materials, etc [1–9]. In recent years an increasing attention has been given to the synthesis of novel β-diketonate complexes [10–19] and the design of new lanthanide materials with β-diketones [20–25].

In this paper, we synthesized and investigated new lanthanide complexes with 1,3-diketones tethered with oligomethylene chain: 2-substituted cycloalkanones (CA). It is important to study the effect of oligomethylene chain in β-diketonate ligands on

synthesis, luminescence properties, and photochemical stability of the lanthanide CA complexes. We are unaware of any papers on the investigation of solid lanthanide compounds with these alicyclic ligands. Solely, the stability constants of lanthanide complexes with 2-acetylcyclohexanone and 2-butyrylcyclohexanone in a solution have been examined [26,27]. The authors of these publications demonstrated that the cycloalkanones can be more suitable for the separation of rare-earth elements than β-dike-tones with straight chain. At the same time, 2-substituted cycloalkanonates of Ni(II), Cu(II), Cr(III), Fe(III) [28–30], Ir(III) [31] and oxovanadium(IV) [32] have been extensively studied. The iridium complex with 2-acetylcyclopentanone has been tested as component forming the light-emitting layer in electroluminescent device (OLED) [31]. It is stated that 2-acetylcycloalkanones can serve as an inhibitor in anti-corrosion compositions [30,33].

The processes of the keto–enol tautomerization of cyclo-alkanones and the kinetics of the racemization, which are crucial in the interpretation of complexation, have been studied in a series of

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papers [33–40]. The keto–enol equilibrium was reported to depend on solvent, temperature and concentration of the cycloalkanone. It is influenced by steric effects, the degree of coplanarity, ring size, conjugation relating to the β-diketone molecule. The extent of enolization is controlled appreciably by the strength of the intramolecular hydrogen bond. The authors of the paper [41] concluded that the acetyltetralone molecule in the enol form is endocyclic with the C–C double bond in the tetralone moiety. It has been shown [42,43] that 2-substituted cycloalkanones in a solution can undergo thermolysis and photolysis under the influence of atmospheric oxygen.

The present work reports the results of synthesis and spectroscopic study of the Eu, Tb and Gd complexes with six 2-substituted cycloalkanones and 1,10-phenanthroline derivatives and 2,2′-bipyridine. The data on the structure of Ln^{3+} luminescence center, luminescence efficiencies, lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, and energies of the lowest triplet states of the ligands were obtained. Energy transfer processes in the lanthanide CA complexes and the influence of a variation of both of the ligands on these processes are discussed. A problem of the chemical stability of the compounds synthesized is raised.

2. Experimental

2.1. Synthesis of the lanthanide CA complexes

A series of europium, terbium and gadolinium complexes with 2-substituted cycloalkanones (CA) of the composition $Ln(CA)_3\cdot Phn$ and $Ln(CA)_3\cdot Bpy$ have been synthesized and investigated. Ln = Eu, Tb, Gd; CA = 2-acetylcyclohexanone (AcCHex), 2-isobutyrylcyclo-hexanone (iButCHex), 2-acetylcyclopentanone (AcCPent), 2-ace-tylbutyrolactone (AcButLact), 2-benzoylcyclohexanone (BenzCHex), 2-acetyltetralone (AcTetr); Phn = 1,10-phenanthroline (Phen), 4,7-dimethyl-phenanthroline (DMPhen), 3,4,7,8-tetra-methyl-phenanthroline (TMPhen), 5-phenyl-phenanthroline (PhPhen), 4,7-diphenyl-phenanthroline (DPhPhen); Bpy = 2,2′-bipyridine. The tris and tetrakis compounds $Ln(CA)_3\cdot 2H_2O$ and $LnNa(CA)_4$ have been also prepared. A list of the compounds under investigation is given in Table 1. The Tb^{3+} and Gd^{3+} compounds synthesized are marked off by an asterisk. The structures of

molecules of 2-substituted cycloalkanones and a list of auxiliary ligands for each of CA adducts are presented in Fig. 1.

All of the reagents used for syntheses were purchased from Sigma–Aldrich and were analytical grade. To synthesize the $Ln(CA)_3\cdot 2H_2O$ compounds, at first, a water–ethanol (1:1) solution of $LnCl_3\cdot 6H_2O$ was added to an ethanol solution of CA. Then, the 3-N NaOH water solution was dropwise added to the prepared mixture of the lanthanide chloride and CA at heating in a water bath (at 60–70 °C) for approximately one hour. A molar ratio of the reagents CA: lanthanide chloride: NaOH was equal to 3:1:3. In the case of the $LnNa(CA)_4$ synthesis, the 3-N NaOH water solution was added to an acetone solution of CA. Then, a water solution of $LnCl_3\cdot 6H_2O$ was dropwise added to the alkalinized CA solution at heating in a water bath (at ~60 °C) for approximately one hour or sometimes without heating. A molar ratio of CA: lanthanide chloride: NaOH was equal to 4:1:4.

In the preparation of the $Ln(CA)_3\cdot Phn$ and $Ln(CA)_3\cdot Bpy$ adducts the 3-N NaOH water solution and an ethanol solution of Phn or Bpy were added to an ethanol solution of CA. Then, a water–ethanol (1:1) solution of $LnCl_3\cdot 6H_2O$ was drop by drop added to the previous mixture at heating in a water bath (at 60–70 °C) or sometimes without heating. A molar ratio of the reagents CA: Phn (Bpy): lanthanide chloride: NaOH was equal to 3:1:1:3. The compound $Eu(AcCHex)_3\cdot Phen$ was also synthesized by other method involving the preparation of an ethanol solution of a mixture of CA, Phen and $EuCl_3\cdot 6H_2O$ in a molar ratio of 3:1:1 and adjusting the pH value of reaction mixture to 6 with a liquid ammonia. It should be pointed out that the heating of the reaction mixture results in a decrease in the keto/enol ratio of cycloalkanone [37] that promotes a binding of CA with the Ln^{3+} ion. At the same time, the probability of decomposition of cycloalkanonate anion increases.

In all cases, a precipitated powder (or oily product obtained sometimes for $Ln(CA)_3\cdot 2H_2O$) was filtered. An extracted product was washed with water, acetone or isopropyl alcohol and dried under room conditions or in a vacuum exsiccator. The final products are homogeneous powdery substances. IR spectra given in Figs. S1 and S2 (Supplementary data) indicate the presence of coordinated CA and Phen ligands and the absence of water molecules in adducts. Results of the elemental analysis for the nitrogen content in $Eu(AcCHex)_3\cdot Phen$ (**1**) (Calc.: 3.74, Found: 3.65 %) and Tb

Table 1

Lanthanide 2-substituted cycloalkanonates synthesized, energy of the lowest triplet state of the ligand E_T and the value $\Delta = E_T - E(^5D_4\ Tb^{3+})$[a] (in brackets).

No.	Eu	Tb	Gd	E_T CA (Δ) (cm⁻¹)	E_T Phn, Bpy (Δ) (cm⁻¹)
	$Eu(AcCHex)_3\cdot 2H_2O$		*	21740 (1140)	
	$EuNa(AcCHex)_4$	*			
1	$Eu(AcCHex)_3\cdot Phen$	*	*		20920 (320)
2	$Eu(AcCHex)_3\cdot DMPhen$	*	*		20660 (60)
3	$Eu(AcCHex)_3\cdot PhPhen$	*	*		20160 (−440)
4	$Eu(AcCHex)_3\cdot DPhPhen$				
5	$Eu(AcCHex)_3\cdot Bpy$	*	*	21500 (900)	22080 (1480)
	$Eu(iButCHex)_3\cdot 2H_2O$		*	21050 (450)	
6	$Eu(iButCHex)_3\cdot Phen$	*	*	21000 (400)	21300 (700)
7	$Eu(iButCHex)_3\cdot DMPhen$				
8	$Eu(iButCHex)_3\cdot TMPhen$				
9	$Eu(iButCHex)_3\cdot DPhPhen$				
10	$Eu(iButCHex)_3\cdot Bpy$				
	$EuNa(AcCPent)_4$		*	21100 (500)	
11	$Eu(AcCPent)_3\cdot Phen$	*	*		21300 (700)
12	$Eu(AcCPent)_3\cdot TMPhen$				
	$Eu(AcButLact)_3\cdot 2H_2O$		*	20700 (100)	
13	$Eu(AcButLact)_3\cdot Phen$	*	*		21280 (680)
	$Eu(BenzCHex)_3\cdot 2H_2O$		*	20250 (−350)	
14	$Eu(BenzCHex)_3\cdot Phen$	*	*		20930 (330)
	$EuNa(AcTetr)_4$		*	18950 (−1650)	
15	$Eu(AcTetr)_3\cdot Phen$	*	*	19050 (−1550)	

[a] $E(^5D_4\ Tb^{3+}) = 20600\ cm^{-1}$.