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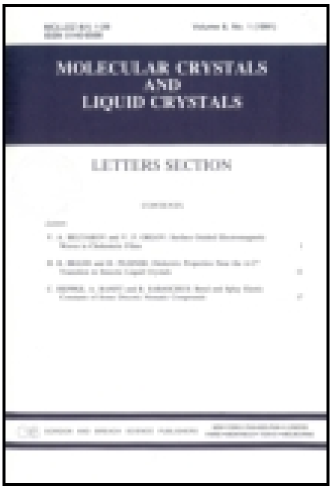

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Novel Ytterbium(III) β-Diketonate with Unsaturated Substituent as a Precursor of NIR-Emitting Materials

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Novel Ytterbium(III) *β*-Diketonate with Unsaturated Substituent as a Precursor of NIR-Emitting Materials

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Novel Yb(III) complex with unsaturated β-diketone methacrylacetophenone and its adduct with 1,10-phenanthroline were synthesized and characterized by a number of physicochemical methods (chemical and thermal analysis, infrared, electronic and luminescent spectroscopy). The results obtained indicate the possibility of using these compounds as precursors of NIR-emitting (near infrared) materials.

Keywords Ytterbium complex; unsaturated *β*-diketone; luminescence

1. Introduction

Luminescent lanthanide complexes with organic ligands belong to a special class of emitters with a high potential for different applications [1–3]. Recently much attention has been paid to near-infrared (NIR) emitting complexes due to their use in telecommunication, light conversion and bio-science [4–6]. Trivalent ytterbium ion has an extremely simple electronic structure with one unpaired electron and possesses a single emission line in the range of 0.98–1.03 μm. This allows using Yb(III) compounds for imaging tumor cells [4,5,7] and as efficient sensitizer in optical amplifiers [8,9].

β-Diketonates are one of the most intensively investigated lanthanide coordination compounds because of their excellent luminescent properties [1,10]. While the *β*-diketonates with saturated aliphatic and aromatic substituents are well studied, little is known about lanthanide complexes with unsaturated ligands. On the other hand, polymerization of monomeric complexes allows obtaining chemically homogeneous coordination polymers [10–14]. That's why the study of such class of compounds is of interest from both fundamental and applied points of view.

The aim of this work is to report about synthesis and characterization of novel Yb(III) complex with unsaturated *β*-diketone methacrylacetophenone (mphpd, 2-methyl-5-phenylpentene-1-dione-3,5) and its adduct with1,10-phenanthroline.

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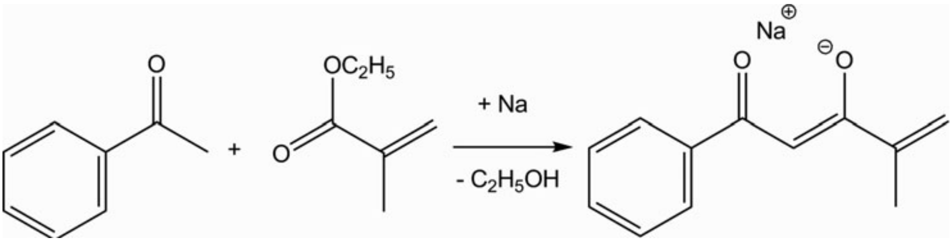

Scheme 1. Preparation of sodium salt of methacrylacetophenone.

2. Experimental

2.1 Materials

The sodium salt of methacrylacetophenone was prepared by means of Claisen condensation of acetophenone with ethyl methacrylate (Scheme 1).

The methods of preparation and purification of Na(mphpd) are described in [15]. Ytterbium chloride hexahydrate, 1,10-phenanthroline and reagents utilized for preparation of Na(mphpd) were of analytical quality and were used without further purification.

2.2 Methods

The ytterbium percentage was determined by combusting the complex in air, dissolving the resulting residue in nitric acid and titration of $Yb(NO_3)_3$ obtained with EDTA (ethylenediaminetetraacetic acid) solution using arsenazo indicator [16]. Thermal analysis was performed on a Q-1500D type derivatograph (F. Paulik, J. Paulik, L. Erdey system) in air at a heating rate of 5°C/min in the temperature range from 20 to 500°C. The infrared (IR) spectrum was recorded in a KBr pellet on a PerkinElmer Spectrum BX II FT–IR spectrophotometer in the range from 400 to 4000 cm^{-1}. The electronic absorption spectra were recorded in a dimethylformamide solution on a UV-VIS-IR Shimadzu UV-3600 spectrophotometer in the range from 200 to 1500 nm. The luminescence spectra of solid samples and solutions in chloroform were recorded on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorimeter (450 W Xe lamp) using OC 11 filter. Photoresistor InGaAs (DSS-IGA020L, Electro-Optical Systems, Inc, USA) cooled to liquid nitrogen temperature was used as a radiation detector for the IR region. The luminescence spectra were corrected in accordance with the distribution of the radiation sensitivity of the xenon lamp and a photomultiplier.

2.3 Synthesis

The complex was prepared by reaction between $YbCl_3$ and sodium salt or methacrylacetophenone (taken in molar ratio 1:3) in alkalescent (pH = 8 – 9) aqueous medium:

$$YbCl_3 + 3Na(mphpd) \rightarrow Yb(mphpd)_3 + 3NaCl,$$

where mphpd is a methacrylacetophenone ligand. The 100 ml of an aqueous solution of Na(mphpd) (1.5 mmol) was slowly added to a stirred solution of $YbCl_3$ (0.5 mmol in 100 ml water). The resulting precipitate was filtered off, washed with water several times and dried

Table 1. Band assignments of Yb(mphpd)$_3 \cdot 2H_2O$

Frequency (cm^{-1})	Band assignment
3400	ν(OH)
3059	ν(CH)
3028	
2969	$\nu(CH_3)$
1680	$\nu(C = C)$
1595	$\nu_{\mathrm{sym}}(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{O})$
1556	$\nu_{\mathrm{anti}}(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{C})$
761	$\delta(C_6H_5)$
702	

over anhydrous $CaCl_2$. The ytterbium percentage in $YbC_{36}H_{37}O_8$ (%): 22.45 (calculated), 22.27 (found).

3. Results and Discussion

Thermal analysis was performed in order to obtain information about hydration structure of the complex and its thermal behavior. The dehydratation of ytterbium complex with methacrylacetophenone occurs at 120°C and results in weight loss corresponding with the elimination of two coordinated water molecules. The weight loss at 220–300°C is due to the detachment of one mphpd molecule. The second molecule of the ligand detaches in the temperature region of 300–390°C. Further heating is accompanied with a number of exothermic effects at 450–500°C and leads to the complete decomposition of the complex.

To determine the coordination mode of ligand with Yb^{3+} ion the IR spectrum was recorded and band assignments of Yb(mphpd)$_3 \cdot 2H_2O$ are presented in Table 1. The $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{O}$ and $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{C}$ stretching bands of metal β-diketonates lie at 1500–1600 cm^{-1} region. These bands characterize the system of conjugate bonds in chelate ring as a single unit. The higher frequency band is attributed mainly to a $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{O}$ stretching and the lower one–to a $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{C}$ stretching respectively [10, 17]. Therefore, the shoulder at 1595 cm^{-1} is assigned to the $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{O}$ symmetrical stretching and the peak at 1556 cm^{-1} is assigned to the $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{C}$ antisymmetrical stretching. The frequency of $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{O}$ vibration is strongly shifted to lower

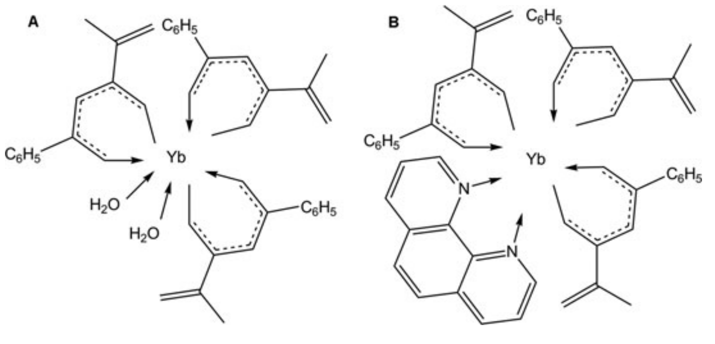

Figure 1. The schematic structures of Yb(mphpd)$_3 \cdot 2H_2O$ (A) and Yb(mphpd)$_3$ · Phen (B).

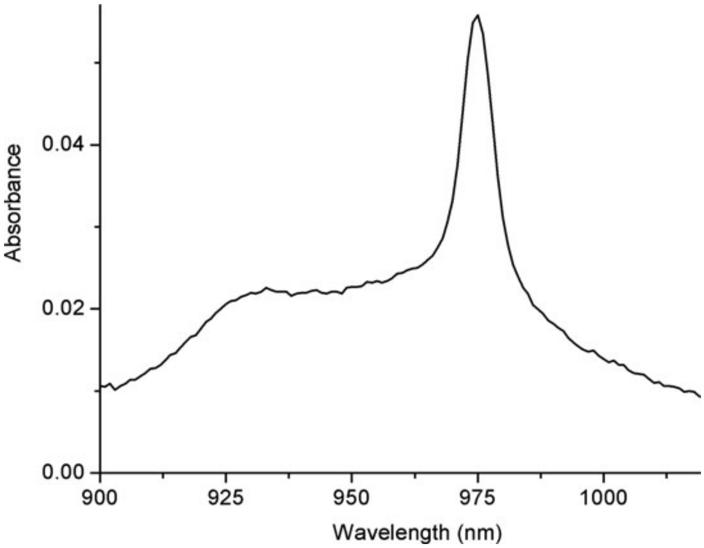

Figure 2. The absorption spectrum of $Yb(mphpd)_3 \cdot 2H_2O$ in DMFA.

wavenumbers compared to that of free ligand's carbonyl group. Band's shape and its position in spectrum indicate mphpd acting as bidentate ligand to coordinate to Yb^{3+} ion. The peak at 1680 cm^{-1} can be assigned to the double C=C bond stretching vibrations [18]. The broad absorption in the 3400 cm^{-1} region is due to O—H stretching in coordinated water molecules [19].

IR spectrum coupled with chemical and thermal analyses indicates the formation of the complex with formula $Yb(mphpd)_3 \cdot 2H_2O$ (Fig. 1A). Three methacrylacetophenone ligands coordinate in a bidentate mode to Yb^{3+} ion and the coordination sphere is supplemented with two water molecules.

The absorption spectrum of $Yb(mphpd)_3 \cdot 2H_2O$ presents two main bands. The band attributed to the ligand absorption lies in the near-ultraviolet region. The second band (Fig. 2) extended in the NIR region from 900 to 1015 nm is due to f-f transition from ground $^2F_{7/2}$ to exited $^2F_{5/2}$ states of the Yb^{3+} ion. The absorption maximum (Table 2) is shifted to higher wavelengths for about 2 nm compared to ytterbium aquo-ion (i.e. nephelauxetic effect) due to the partially covalence of the coordination bonds [20–22].

One of the most important parameters to characterize the emission processes in the lanthanide luminescent complexes is a radiative lifetime (τ_R) which is the lifetime of an excited state in the absence of nonradiative transitions [1]. According to [23] in the case

Table 2. Absorption maxima of $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition

Compound	λ_{max} (nm)
$YbCl_3$[a]	973
$Yb(mphpd)_3 \cdot 2H_2O$	975
$Yb(mphpd)_3 \cdot Phen$	976

[a] Ref. [21].

of trivalent ytterbium ion τ_R can be estimated from the absorption spectrum using the equation:

$$\frac{1}{\tau_R} = 2303 \times \frac{8\pi c n^2 \tilde{\nu}^2 \left(2J' + 1\right)}{N_A \left(2J + 1\right)} \int \varepsilon\left(\nu\right) d\nu,$$

where c is the speed of light in vacuum (in cm s^{-1}), N_A is Avogadro's constant, n is the refractive index of the medium, J′ and J are the total angular momentum quantum numbers for the ground and excited state respectively, $\tilde{\nu}$ is the average energy of the transition (in cm^{-1}) and $\varepsilon(\nu)$ is the absorption spectrum of the transition (in M^{-1} cm^{-1} vs. wavenumber). It was found that for $Yb(mphpd)_3 \cdot 2H_2O$ $\tau_R = 1.33$ ms (with $n = 1.4305$ and $\tilde{\nu} = 10435$ cm^{-1}). This result is in a good agreement with values of τ_R calculated for ytterbium complexes with diethylenetriamine pentaacetic (1.21 ms) [23] and dipicolinic (1.31 ms) [24] acids.

The luminescence of NIR emitting lanthanide ions is efficiently quenched by O–H vibrations in coordinated water molecules [4]. In order to overcome this hindrance synthesis of 1,10-phenanthroline adduct of the studied complex was performed. The adduct was prepared by reaction between $YbCl_3$, sodium salt or methacrylacetophenone and 1,10-phenanthroline (taken in molar ratio 1:3:1) in alkalescent (pH = 8–9) aqueous-alcoholic medium:

$$YbCl_3 + 3Na(mphpd) + Phen \rightarrow Yb(mphpd)_3 \cdot Phen + 3NaCl,$$

where Phen stands for 1,10-phenanthroline.

The absorption spectrum of $Yb(mphpd)_3 \cdot Phen$ (figure not shown) is similar to that of $Yb(mphpd)_3 \cdot 2H_2O$. The absorption maximum is insignificantly (~1 nm) shifted to higher wavelengths indicating the substitution of water molecules in the coordination sphere of Yb^{3+} ion without considerable changes of coordination polyhedron (Fig. 1B).

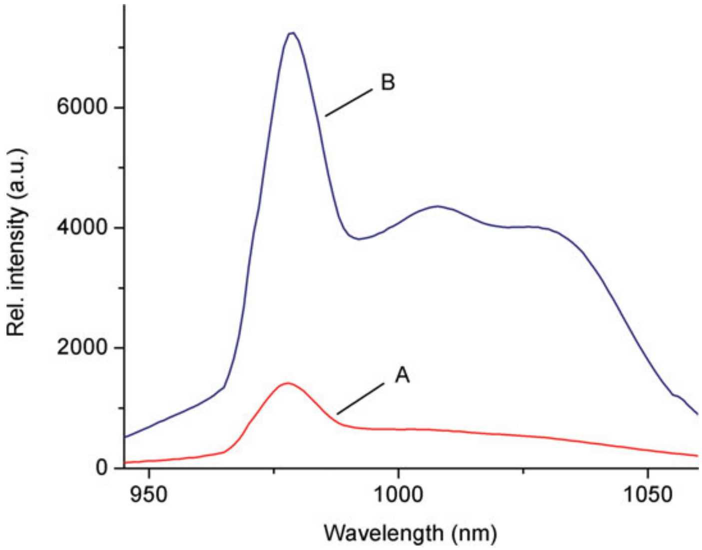

Figure 3. The emission spectra of $Yb(mphpd)_3 \cdot 2H_2O$ (A) and $Yb(mphpd)_3 \cdot Phen$ (B) in $CHCl_3$ under excitation at 410 nm.

Table 3. Quantum efficiency of studied complex and its adduct with 1,10-phenanthroline

	$Yb(mphpd)_3 \cdot 2H_2O$		$Yb(mphpd)_3 \cdot Phen$	
	Solid	$CHCl_3$ solution	Solid	$CHCl_3$ solution
Quantum efficiency (%)	0.022	0.013	0.032	0.015

Under excitation at 410 nm the complex and its adduct both exhibit NIR luminescence corresponding to $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (Fig. 3). The luminescence intensity and its quantum efficiency are higher for adduct (Table 3) due to the absence of water molecules in the inner sphere of Yb^{3+} ion.

4. Conclusions

To summarize, the results obtained indicates the possibility of using ytterbium complex with methacrylacetophenone and its adduct with 1,10-phenanthroline as a precursor of NIR-emitting materials. These materials may be obtained by polymerization of the complexes studied with common monomers which results in formation of chemically homogeneous coordination polymers with enhanced optical properties.

References

[1] Binnemans, K. (2009). *Chem. Rev.*, *109*, 4283.

[2] Bünzli, J.-C. G. (2010). *Chem. Rev.*, *110*, 2729.

[3] Kalyania, N. T., & Dhobleb, S. J. (2012). *Renew. Sust. Energ. Rev.*, *16*, 2696.

[4] Comby, S., & Bünzli, J.-C. G. (2007). *In: Handbook on the Physics and Chemistry of Rare Earths*, Gschneidner, K. A., Jr., Bünzli, J.-C.G., & Pecharsky, V. K. (Eds.), 37, Chapter 235, Elsevier Science B.V.: Amsterdam, 217.

[5] Eliseeva, S. V., & Bünzli, J.-C.G. (2010). *Chem. Soc. Rev.*, *39*, 189.

[6] Bünzli, J.-C. G, & Eliseeva, S. V. (2010). *J. Rare Earth*, *28*, 824.

[7] Jiang, F. L., Poon, C. T., Wong, W. K., Koon, H. K., Mak, N. K., Choi, C. Y., Kwong, D. W. J., & Liu, Y. (2008). *Chem. Bio. Chem.*, *9*, 1034.

[8] Song, L., Liu, X., Zhen, Zh., Chen, C., & Zhang, D. (2007). *J. Mater. Chem.*, *17*, 4586.

[9] Chen, C., Zhang, D., Li, T., Zhang, D., Song, L., & Zhen, Zh. (2009). *Appl. Phys. Lett.*, *94*, 041119.

[10] Binnemans, K. (2005). *In: Handbook on the Physics and Chemistry of Rare Earths*, Gschneidner, K. A., Jr., Bünzli, J.-C. G., & Pecharsky, V. K. (Eds.), 35, Chapter 225, Elsevier Science B.V.: Amsterdam, 107.

[11] Wang, L.-H., Wang, W., Zhang, W.-G., Kang, E.-T., & Huang, W. (2000). *Chem. Mater.*, *12*, 2212.

[12] Dzhardimalieva, G. I., Pomogailo, A. D., & Volpert, V. A. (2002). *J. Inorg. Organomet. Polym.*, *12*, 1.

[13] Ivanovici, S., Peterlik, H., Feldgitscher, C., Puchberger, M., & Kickelbick, G. (2008). *Macromolecules*, *41*, 1131.

[14] Hamza, F., & Kickelbick, G. (2009). *Macromolecules*, *42*, 7762.

[15] Uflyand, I. Ye., Ilchenko, I. A., Starikov, A. G., Sheikner, V. N., & Pomogailo, A. D. (1990). *Izv. Akad. Nauk SSSR. Ser. Khim.*, *451* (in Russian).

[16] Fritz, J. S., Oliver, R. T., & Pietrzyk, D. J. (1958). *Anal. Chem.*, *30*, 1111.

[17] Nehoroshkov, V. P., Kamalov, G. L., Zheltvay, I. I., Ososkov, A. K., & Berestetskaya, E. D. (1984). *Koord. Khim.*, *10*, 459 (in Russian).

[18] Larkin, P. (2011). *Infrared and Raman Spectroscopy; Principles and Spectral Interpretation*, Elsevier: Amsterdam.

[19] Nakamoto, K. (2009). *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Sixth Edition, Part B*, Wiley: Hoboken, New Jersey.

[20] Yatsimirskii, K. B., & Davidenko, N. K. (1979). *Coord. Chem. Rev.*, *27*, 223.

[21] Poluektov, N. S. *et al.* (1989). *Spectrophotometric and Luminescence Methods for Determination of Lanthanides*, Naukova Dumka: Kiev (in Russian).

[22] Sastri, V. S. *et al.* (2003). *Modern Aspects of Rare Earths and their Complexes*, Elsevier Science B.V.: Amsterdam.

[23] Werts, M. H. V., Jukes, R. T. F., & Verhoeven, J. W. (2002). *Phys. Chem. Chem. Phys.*, *4*, 1542.

[24] Aebischer, A., Gumy, F., & Bünzli, J.-C. G. (2009). *Phys. Chem. Chem. Phys.*, *11*, 1346.