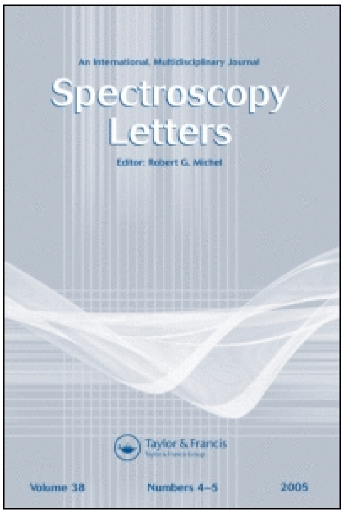

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Nowicki, Waldemar and Zachara, Stanisław(1992) 'Synthesis and Spectral Properties of the Europiumciiid Chelates with Schiff Bases', Spectroscopy Letters, 25: 4, 593 — 601
To link to this Article: DOI: 10.1080/00387019208021534
URL: http://dx.doi.org/10.1080/00387019208021534

SPECTROSCOPY LETTERS, 25(4), 593-601 (1992)

SYNTHESIS AND SPECTRAL PROPERTIES OF THE EUROPIUM(III) CHELATES WITH SCHIFF BASES.

Key words: europium(III) complexes, Schiff bases, emission spectra

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ABSTRACT

The complexes of Eu(III) and the Schiff bases were obtained and the structure, nature of chemical bonds, and symmetry of the compounds were eluciaded on the basis of spectroscopic and elemental analysis data. Two of the compounds were the monomers with 8-coordinated europium and one of them was a dimer with 6-coordinated europium.

INTRODUCTION

Since Tsumaki's discovery, complex of cobalt(II) and N,N'-ethylenebis(salicylimine) is able to bond molecular oxygene in a solution at room temperature [1], a number of complexes of different metals and Schiff bases were obtained and investigated. However, the research was focused mainly on compounds of Schiff bases and d-transition metals disregarding chemistry of complexes of lanthanides. The compounds of f-transition metals and Schiff bases are known for several years but no detailed description of their properties and structure is available, the investigations being frequently restricted due to its low solubility in organic solvents with a small dielectric constant. The complexes are moderately soluble in strongly coordinating polar organic solvents but a formation of solvent adducts occures, especially in the case of compounds type LnL_3 (where Ln is a lanthanide(III), and L is a Schiff base) being bridgeing ligands [2,3]. Moreover, such compounds are difficalt to obtain due to the oligomeric nature of lanthanide complexes, and the synthesis frequently leads to complexes of diverse molecular ratio (Ln:L) [2,4-9].

EXPERIMENTAL

Preparation of ligands and the complexes

1. N,N'-ethylenebis(salicylimine) - (H_2salen) and N,N'-(1,3-propylene)bis(salicylimine) -(H_2sal-1,3-pn).

The compounds were synthesed by reacting the salicylaldehyde (1 mole) with the diamine (2 moles) under reflux for 1 hour in chloroform. Next, the solution was evaporated and a precipitation was filtered off and dried on air. The resulting precipitates were recrystallized from a mixture of n-hexane and toluene (1:10) (H_2salen) or from methanol (H_2sal-1,3-pn). The products were dried *in vacuo* over P_2O_5. The products with melting points : 125-126°C - H_2salen, 48-50°C - H_2sal-1,3-pn were obtained.

2. N,N'-(1,2-phenylene)bis(salicylimine)-(H_2salphen)

H_2salphen was obtained by condensing 1,2-phenylenediamine and salicylaldehyde (1:2 mole ratio) under reflux for 2 hours in absolute methanol. After cooling the mixture the orange precipitate was released. The resulting precipitate was filtered off and recrystallized from methanol. The product was filtered, washed with a small amount of cold methanol and dried *in vacuo* over P_2O_5. The product with melting point 162-164°C was obtained.

3. Synthesis of the europium(III) complexes .

To a vigorously stirred solution of the appropriate Schiff Base (0.002 mol) and piperydyne (0.002 mol) in methanol (100 cm^3) the europium chloride (0.001 mol) in water (10 cm^3) was added dropwise. After 1 hour stirred the precipitate was filtered, washed with a cold methanol and dried *in vacuo* over P_2O_5.

Apparatus and measurements

Elemental analyses were performed with a Carlo--Erba elemental analyser MOD 1106.

Thermogravimetric and DTA curves were recorded on a Paulik-Paulik type OD 103 Derivatograph using Al_2O_3 as a reference.

Infrared (IR) spectra of the compounds in hexachlorobutadiene and Nujol mulls were recorded in

TABLE 1

Analytical data of europium(III) complexes.

Compounds	Analyses, calcd.(found) [%] C	H	N
$Eu(salen)_2Hpip \cdot {}^1/_2H_2O$	57.00(57.29)	5.30(5.35)	8.98(9.00)
$Eu(sal\text{-}1,3pn)_2Hpip \cdot 2H_2O$	56.11(55.78)	5.80(5.69)	8.39(8.17)
$Eu_2(salphen)_3 \cdot 2H_2O$	56.17(56.54)	3.61(3.47)	6.55(6.44)

the 4000 - 600 cm^{-1} range using a Specord IR 71 spectrometer; the spectra of the compounds in KBr tablets were recorded in the 520 - 40 cm^{-1} range using a Perkin-Elmer 180 spectrometer.

Emission spectra measurements were performed at 77 K. For this purpose the examined sample, placed in a quartz ampoule, was immersed directly in liquid nitrogen located in a quartz Dewar. The sample was excited by means of a HBO-50 mercury lamp and a filter transparent for the 365 nm mercury line. The emission spectra were obtained with a PGS-2 spectrograph, in which the photographic plate has been replaced by a photomultiplier tube of the type FEU-51 similar to that described in [10].

Results and Discussion

Two new complexes of europium and Schiff bases, $Eu(salen)_2Hpip \cdot {}^1/_2H_2O$ and $Eu(sal\text{-}1,3\text{-}pn)_2Hpip \cdot 2H_2O$, and a new synthesis of $Eu_2(salphen)_3 \cdot 2H_2O$ were described in the present paper. The elemental composition of this complexes were determined on the basis of elemental analysis. The results of elementar analyses are listed in Table 1. Despite the same synthesis condition, the obtained compounds were of different stoichiometry, probably due to different complexating power of the ligands. On the basis of the results of elemental analysis as well as from the thermogravimetric and IR spectrographic data it has been stated that the obtained complexes of europium(III) were hydrated. Thermogravimetric curves obtained as an aid to gain information on thermal decomposition of the compounds give evidence for hydration, in agreement with the analytical figures (Table 1.). For example, it has been found that $Eu(sal\text{-}1,3\text{-}pn)_2Hpip \cdot 2H_2O$ loose at about 150°C two water molecules (mass decrement: found 4.5%, calc 4.32%) and one molecule of piperidyne at about 200°C (mass decrement: found 9.5%, calc. 10.32%).

The investigated complexes were found stable up to about 350°C. At higher temperatures decomposition of the complexes (at 480°C for $Eu(sal\text{-}1,3\text{-}pn)_2Hpip2H_2O$ and 530°C for $Eu_2salphen)_3 \cdot 2H_2O$) was observed.

All obtained compounds show strong, orange-red luminescence at the temperature of liquid nitrogen when exposed to UV radiation. The narrow-band luminescence spectra resembled those of europium β-diketone chelates and indicated that the emission arose entirely from the $^5D_0$ level of trivalent europium ion. Emission spectra of $^5D_0 \longrightarrow {}^7F_{0,1,2}$ transitions, are illustrated in Fig.1. In the spectra shown in Fig.1., the axis of ordinates separates spectral regions, in which the spectral lines were recorded at different sensitivities of the detection equipment. This results from the large differences in intensities of the set of lines falling within the spectral range of the $^5D_0 \longrightarrow {}^7F_2$ transition (6100 -

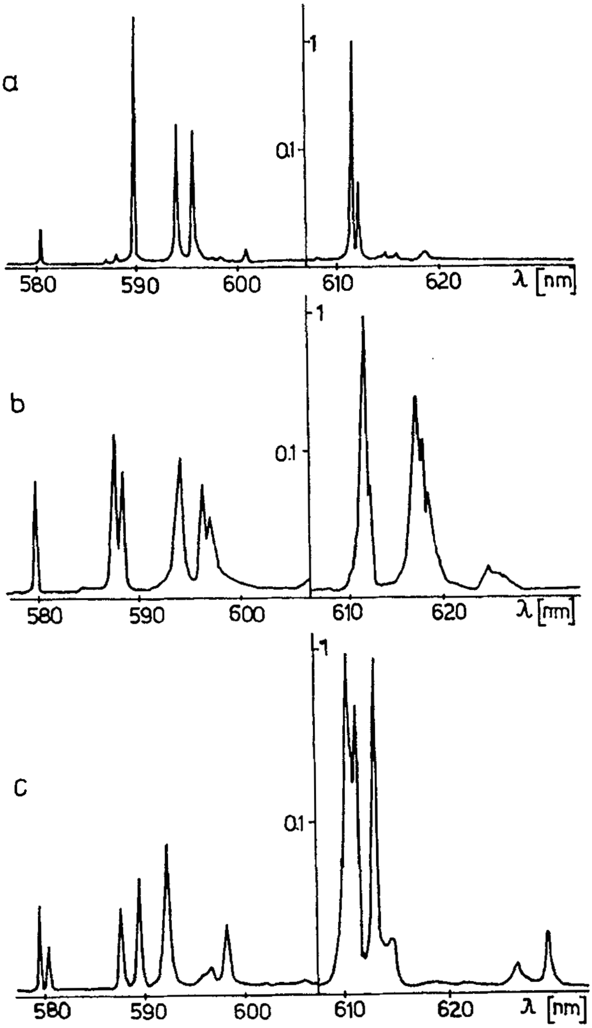

Fig. 1. Emission spectra in the region of $^5D_0 \longrightarrow {}^7F_{0,1,2}$ transitions for the following chelates of europium(III):

a) Eu(salen)$_2$Hpip$\cdot {}^1/_2$H$_2$O,

b) Eu(sal-1,3-pn)$_2$Hpip$\cdot$2H$_2$O,

c) Eu$_2$(salphen)$_3\cdot$2H$_2$O.

- 6300 Å) as compared with the intensities of other lines. For all the three complexes no emmision in the $^5D_1 \longrightarrow {}^7F_{0,1,2}$ regions could be observed above the noise level characteristic of the instrumentation.

The spectra of two complexes (Fig.1.a,1.b) exhibit a single line at about 580 nm. These lines are due to $^5D_0 \longrightarrow {}^7F_0$ transition. Since this spectroscopic states are not degenerated, a single line is consisted with the assumption that europium ion containing species is responsible for the observed spectrum. The third complex (Fig.1.c) exhibits spectrum of two different species, possibly with different crystal structures by only 15 cm^{-1} in energy of the $^5D_0 \longrightarrow {}^7F_0$ transition.

The analysis of the $^5D_0 \longrightarrow {}^7F_1$ (585 - 600 nm) and $^5D_0 \longrightarrow {}^7F_2$ (610 - 630 nm) multiplets enables one to determine the spliting of $^7F_1$ and $^7F_2$ levels. The maximum spliting of these levels may be 3- or 5-fold, respectively. The low symmetry (monoclinic or triclinic systems) of the close sorroundings of europium ion entirely excludes degeneration of these levels. The multiplets observed in the spectrum ranges of these transitions may be caused by two effects: (a) vibronic transitions, and (b) existing of several structures in the close sorroundings of europium ion.

Because the spectrum bands of the low-symmetric complex $Eu(salen)_2Hpip \cdot {}^1/_2H_2O$ (Fig. 1.a) are sharp and their number is in agreement with the assumption of no degeneration of spectroscopic stages, it could be stated that the complex existed in one crystalline form. In the case of $Eu_2(salphen)_3 \cdot 2H_2O$ complex (Fig 1.c) the spectral bands were also sharp , but its number, in the appriopriate transition ranges, was greater than one could expect according to the theory.

This may indicate formation of a complex containing two europium ions subjected to slightly different crystal fields. The number of spectral bands show that the symmetry of the fields is also low. Spectral lines of $Eu(sal\text{-}1,3\text{-}pn)_2Hpip \cdot 2H_2O$ complex were broad and its number was greater than permissible. It may indicate formation of oligomeric complex (of systematic but slightly disturbed structure).

The elemental analysis data as well as analysis of the spectra show that two compounds, $Eu(salen)_2Hpip \cdot {}^1/_2H_2O$ and $Eu(sal\text{-}1,3pn)_2Hpip \cdot 2H_2O$, were monomers of eight-coordinated structure of the three-walent europium ion, and $Eu_2(salphen)_3 \cdot 2H_2O$ was a dimer of six-coordinated structure of Eu^{3+} ion.

Acnowledgment

This work was supportyd in part by a research grant of KBN of Poland

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Date Received: 12/20/91
Date Accepted: 01/21/92