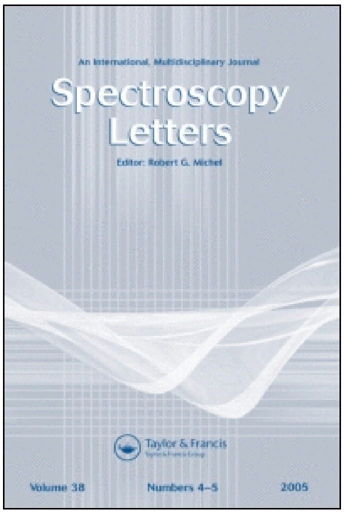

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Infrared Transmision and Photoacoustic Spectra (PAS) of Europium(III) Chelates with Schiff Bases. Part 1. Complex with H_2salen

Waldemar Nowicki[a]; Anna Sikorska[b]; Stanislaw Zachara[b]
[a] Department of Chemistry, University of Gdańsk, Sobieskiego, Poland [b] Laboratory of Acoustics and Spectroscopy, Institute of Experimental Physics, University of Gdańsk, Wita Stwosza, Poland

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Infrared Transmision and Photoacoustic Spectra (PAS) of Europium(III) Chelates with Schiff Bases. Part 1. Complex with H_2salen.

Key words: europium(III) complexes, Schiff bases complexes, IR spectra, photoacoustics spectra (PAS).

Waldemar Nowicki*, Anna Sikorska**, Stanisław Zachara**

**Department of Chemistry,*
University of Gdańsk,
80-952 Gdańsk, Sobieskiego 18, Poland
***Laboratory of Acoustics and Spectroscopy,*
Institute of Experimental Physics,
University of Gdańsk,
80-952 Gdańsk, Wita Stwosza 57, Poland

ABSTRACT

The results of application of infrared transmission and photoacoustics spectroscopic methods for characterization of europium(III) complex with Schiff base are presented in the spectral range of 400 - 3500 cm^{-1}. The analysis of the spectra enables the idetification of the frequencies corresponding to the vibrations of Eu-ligand bonds and the frequencies of the intraligand vibrations.

INTRODUCTION

Schiff bases easy form stable complexes with most of the metal ions of the Periodic Table. They play an important role in development of coordination chemistry. Catalytic properties, along with chemistry and conformation of the complexes, were extensively studied in some instances (1-4).

The reactivity and the redox potential of the core metal ion are very vulnerable to the nature of the chelating ring. The complexes of multidentate ligands possessing delocalised π-orbitals, for example Schiff bases and porphyrins, are of great interest because they are potential model molecules for some of the respiratory pigments and vitamin B_{12} coenzyme (5,6). It seems that indepth investigations of these complexes may be useful for studies of behaviour of biological macromolecules bearing metal ions.

The coordination chemistry of lanthanide and actinide cations with Schiff bases have been investigated and reviewed over the last few years. The development of the field of bioorganic chemistry provoked the interest in Schiff base complexes since it has been recognized that many of these complexes may serve as models for significant biological species. Simple di-, ter-, tetra-, and penta-dentate ligands have been used for metal complex formation and many lanthanide and actinide complexes have been characterised also by X-ray diffraction (7).

In the present work the infrared absorption spectra of both ligand and complex were applied for determination of molecular vibration frequencies in the range of 400 - 3500 cm^{-1}. The spectra were obtained using two methods: infrared spectroscopy (IR) and Fourier transformed infrared photoacoustic spectroscopy (FTIR PAS). The FTIR PAS is a rapidly developing and very promissing spectroscopic method. It offers some advantages over conventional transmission spectroscopy, especially for powdered samples. Contrary to the transmission mode, the PAS analysis does not require optical transparency of the sample and is relatively insusceptible to spurious effect of light scattering. Therefore PAS may be used for verification of the information obtain with classical method.

EXPERIMENTAL

N,N'-ethylenebis(salicylidenemine) - (H_2salen) and europium(III) complex were obtained as reported earlier (8).

IR spectra of ligand and europium(III) chelate on KBr tablets were recorded in the range 3500 ÷ 400 cm^{-1} by means of Perkin-Elmer 180 spectrophotometer. The IR spectra were measured at room temperature.

The Fourier transformed infrared photoacoustic (FTIR-PAS) spectra were carried out using an MTEC Model 200 Photoacoustic Detector. Powdered samples were placed into absorbance macrosampling head and spectra were recorded at room temperature.

RESULTS AND DISCUSSION

In the preceding paper (8) we described synthesis, essential properties (elemental analyses, thermal properties) and emission spectra of three complexes of europium(III) and Schiff bases. The anion complex formed in the reaction of the Schiff base with europium(III) salt precipitates out as fine crystals in the presence of organic base (piperidine). The elemental analysis indicates that the obtained product is monomer $Eu(salen)_2 \cdot Hpip \cdot ½H_2O$ in which octacoordinated europium ion is bond with two molecules of Schiff base.

It is of interest to investigate the IR and PAS FTIR spectra of this complex. The IR and PAS spectroscopic data are listed in Table 1. The last column in the Table 1 gives the interpretation of some individual vibrations based on the data from literature and analyses of the spectra of Schiff base, piperidine and complex. The examples of IR and corresponding PAS spectra in the range 400 - 1800 cm^{-1} are presented on Figure 1. In general good confirmity of the two types of spectra can be seen. Almost all the frequencies occuring in IR spectra can be found in PAS spectra and the ratios of intensities of appropriate bands are similar to each other that agrees with the nature of absorption mechanism.

The broad band at 3420 cm^{-1} observed for the complex is associated with oscillations of OH group (11) and indicates incorporation of water molecule into the unoccupied spaces in the crystal lattice, and formation of hydrogene bonds.

Many bands corresponding to the vibrations of C-H bonds in aromatic ring (11), for example characteristic lines at frequencies of 3050 cm^{-1} and 3015 cm^{-1}, appear in the spectra of both the complex and the Schiff base.

The bands in the range of 3000 - 2800 cm^{-1} observed for the ligand and the complex should correspond to the stretching vibrations of CH and CH_2

Table 1. Vibration Frequencies in the range 400 - 3500 cm^{-1} determined from the IR and PAS spectra of H_2salen and Eu(salen)$_2$Hpip½H_2O, and their interpretation.

H_2salen		Eu(salen)$_2$Hpip½H_2O		Type of vibrations
IR	PAS	IR	PAS	
430 m	430 s	438 w	440 m	δ(phenyl ring) (9,10), γ(C-N) (11)
472 m	475 s	459 m	465 s	
485 sh	485 sh	-	-	γ(C-N) (11)
-	-	508 w	508 m	ν(Eu-O), δ(chelate ring) (9,12)
-	-	555 m	560 m	ν(Eu-O) (9)
560 m	562 m	565 m	570 m	γ(C-C), δ(C-N) (12-14)
-	-	590 s	600 s	ν(Eu-O), δ(chelate ring) (12,13)
645 s	650 s	640 m	647 m	δ(phenyl ring) (12,13)
740 vs	747 m	730 vs	741 s	γ(C-H) (15)
750 vs	762 s	750 vs	762 s	γ(C-H)(phenyl ring) (12,13,16)
770 s	782 s	785 m	792 m	ν(C-N), γ(C-O) (14,17-19), γ(C-H) (12,13)
855 vs	867 s	850 m	857 m	$\rho(\text{CH}_2)$, γ(C-H), γ(C-N) (12,13,17,18)
900 m	900 sh	905 s	912 s	$\delta(\text{CH}_2)$, γ(C-H)(phenyl ring) (19)
945 m	940 m	940 m	945 m	γ(OH) (19)
980 s	980 s	980 m	982 m	$\nu(\text{C-N})_{\text{antisym.}}$ (11)
990 s	-	-	-	$\nu(\text{C-N})_{\text{sym.}}$ (11)
1020 vs	1024 s	1025 m	1032 m	δ(C-H) (12,13)
1040 vs	1045 s	1040 s	1050 m	ν(C-O), $\nu(\text{C-N})_{\text{sym.}}$ (11,15)
-	-	1090 m	1095 m	γ(C-C), $\nu(\text{CH}_2)_{\text{(piperidine)}}$, $\nu(\text{C-}\phi)$ (12-14)
1115 m	1120 m	1115 m	1125 m	δ(chelate ring) (12,13)
1150 vs	1152 s	1140 s	1145 s	ν(C-O)
1200 s	1202 s	1185 s	1195 s	ν(C-H) (12,13), ν(C-N) (16,20)
1220 s	1220 m	1210 w	1215 w	ν(C-O) (19), δ(C-H) (12,13)
1250 m	1250 m	1245 w	1248 m	ν(C-N) (11), ν(C-O) (16)
1280 vs	1282 s	1300 vs	1302 s	ν(C-O), $\nu(\text{C-}\phi)$ (10,17,18), $\delta(\text{CH}_2)$ (20)
1308 w	1317 w	1315 sh	1320 sh	$\delta(\text{CH}_2)$ (19), ν(C-O) (16)
-	-	1340 vs	1345 s	$\delta(\text{CH}_2)_{\text{(piperidine)}}$ (19), ν(C-O) (16)
1370 m	1370 s	1385 vs	1395 s	$\delta(\text{CH}_2)$ (19)
1420 s	1420 s	-	-	δ(O-H) (19), $\delta(\text{CH}_2)$
-	-	1435 vs	1445 s	ν(C-N)
1460 s	1460 s	1460 vs	1470 s	$\nu(\text{N=C-}\phi)$ (11), $\nu(\text{C-C})_{\text{(phenyl)}}$ (16), $\delta(\text{CH}_2)$
1500 vs	1498 s	1530 vs	1535 m	$\nu(\text{N=C-}\phi)$ (11), $\nu(\text{C-C})_{\text{(phenyl)}}$ (16)
1530 w	1530 w	1545 m	1545 m	$\nu(\text{C-C})_{\text{(phenyl)}}$ (16)
1580 vs	1580 s	1590 vs	1595 s	ν(C-N), ν(C-C)(phenyl) (16)
1610 s	1610 s	-	-	
1635 vs	1635 s	1620 vs	1627 s	ν(C-N), ν(C-O), $\nu(\text{C-C})_{\text{(phenyl)}}$ (16)
-	-	2400 w	-	
-	-	2500 w	-	
-	-	2835 s	-	
2860 m	2860 w	2850 s	2850 m	γ(CH) (12,13)
2900 m	2900 w	2890 s	2890 m	ν(CH) (12,13)
2920 m	2930 w	2920 s	2920 m	ν(CH) (12,13)
3010 m	3000 w	3015 s	3010 m	$\nu(\text{CH})_{\text{sym.}}$ (12,13,15)
3050 m	3050 w	3030 s	3030 m	$\nu(\text{CH})_{\text{antisym.}}$ (12,13,15)
-	-	3420 m	-	ν(OH)

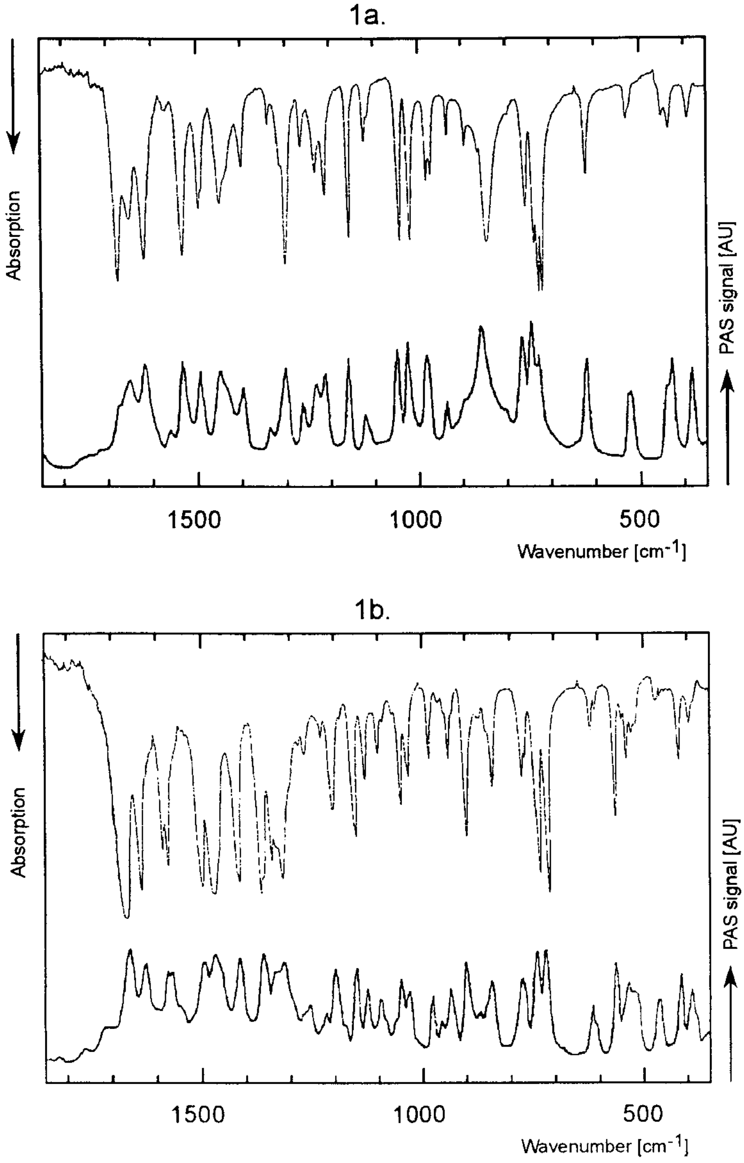

Figure 1. The IR and PAS spectra of Hsalen (1a.) and Eu(salen)$_2$·Hpip·½H_2O (1b.).

groups (21). It must be kept in mind that, after complex formation, the structure of Schiff base become more rigid and the rotation around the C-C bond in ethylenediamine is no longer possible. The aldehyde aromatic rings in the complex should be coplanar (21).

The strong band at about 1600 cm^{-1} assigned to the C-C stretching vibrations in the aromatic ring appears both in the spectrum of the complex and in the spectrum of the unbounded ligand.

The surprisingly numerous resolved bands about $1635 \div 1500$ cm^{-1} is an interesting feature of IR spectrum of the complex. It is generally accepted that bands in this region are due to C-O and C-C stretching vibrations, and to C-H out-of-plane bending vibrations. Thus it is fairly certain that the first absorption band at 1610 cm^{-1}, which is always very strong and is found only in the ligand, can be assigned to the C-O stretching vibration in the hydrogen-bonded ring systems (21).

According to Das Sarma et al. (20,22), the C-N frequencies of the complex are only slightly changed compared to the unbounded Schiff base. The band $\nu(C=N)$, appearing in the ligand at about 1500 cm^{-1}, is shifted to about 1530 cm^{-1} (1498 to 1535 cm^{-1} in PAS spectra). The band at 1635 cm^{-1} (Schiff base), which may be assigned to the stretching vibrations of C-O and C-N bonds, is also shifted to 1620 cm^{-1} (IR) or 1627 cm^{-1} (PAS) in the complex.

The bands due to various vibrations of C-H bond (for example: 1460, 1370, 900 cm^{-1}) are much more intense in complex than in the Schiff base. This is probably owing to increase in molecular density of this atom system after association with piperidine. The band at 1435 cm^{-1}, absent in the Schiff base, appears in the spectrum of the complex; this frequency corresponds to the vibration of C-N bond in piperidine.

The bands at 1280 and 1150 cm showing in the spectrum of the unbounded ligand may be assigned to stretching vibrations of CO-H bond. These bands in the complex, moved by 20 and 10 cm^{-1} respectively, are due to the vibrations of CO-Eu bond. The bands corresponding to the vibrations of Eu-O in the complex can also be observed in the investigated spectral region that, in turn, is over to the deforming vibrations in the ligands. These are low energy vibrations below 600 cm^{-1}.

Europium in the complex is bonded by two oxygen and two nitrogen atoms of the Schiff base ligands. The ligand molecules are perpendicular, so the N and O atoms in the coordination sphere occupy the apices of two interlacing tetrahedrons. The octahedral symmetry is significantly disturbed in the result of formation of the molecular crystals of $Eu(salen)_2Hpip \cdot ½H_2O$. The symmetry of the molecule will manifest itself in degeneration of energy levels in europium ion. The analysis of transitions from $^5D_0$ to the ground ^7F state in the emission spectra (8) enables us to determine the splittings of $^5D_0$, $^7F_1$, and $^7F_2$ levels and distinguish pure electronic from vibronic transitions. From the number of components of the spectra and from the energy diagrams (23) constructed on the basis of obtained data it may be inferred that for a compound the degeneracy of the $^7F_{1,2}$ levels is completly removed; three and five components in the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions appear in these regions respectively. The analysis shows that the chelate belongs to group of low symmetry. The ligand field is of symmetry of one of the point groups C_1, C_{1h}, C_2, C_{2v}.

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