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New Complexes of Pr(III),Sm(III),Gd(III),Ho(III),La(III) 1-(2'-Benzthyazolyl)-3-methyl-4-azo-(4''-nitrophenyl)-Pyrazolyn-5-one

Anca Emandi*,Mariana Balasoiu,Tudor Rosu***

*Faculty of Chemistry,Bucharest University,Dumbrava Rosie 23,sector 2, 70609 Bucharest,Romania
**Institute of Physical Chemistry of Romanian Academy,Splaiul Independentei 202, 77208 Bucharest, Romania.

ABSTRACT

1-(2'-Benzthyazolyl)-3-methyl-4-azo-(4''-nitrophenyl)-Pyrazolyn-5-one (HL) possesses a chelating behaviour.Its chelates with a number of trivalent lanthanide ions Pr(III), Sm(III),Gd(III), Ho(III),La(III) of the type $Na_3[Ln(L)_2(OH)_4]$ *have been isolated and characterized on the basis of their elemental analyses,IR and visible spectra,magnetic and molar conductance studies,thermal and X-ray analysis and molecular weight determinations.All chelates have a monomeric octa-coordinated structure and square antiprismatic* (C_2) *symmetry.*

KEYWORDS **Lanthanides complexes; Azodye; Pyrazolyn-5-one; UV-VIS; IR spectroscopy.**

RESUMO

1-(2'-Benztiazolil)-3-metil-4-azo-(4"-nitrofenil)-pirazolin-5-ona (HL) é um bom ligante. Forma complexos do tipo $Na_3/LnL_2(OH)_4/$ *com íons trivalentes de lantanídeos como Pr(III), Sm(III), Ho(III) e La(III). Estes complexos foram isolados e caracterizados usando análise elementar, determinação de peso molecular, espectroscópia no visível e infravermelho, condutância magnética e molar, raios-x e análise térmica. Todos os quelatos tem estrutura octa-coordenada e possuem simetria quadrado antiprismática* (C_2).

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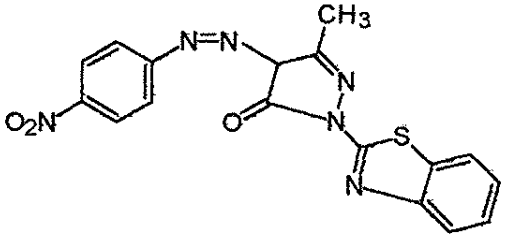
Introduction

A perusal of literature[1-4] reveals numerous ligands containing azo group –N=N–,the nitrogen of which coordinates to the metal ions.The arylazopyrazolones are commonly used in food coloring and in the production of magenta dyes in various color photographic processing[5-6].The effect of various types of Lewis bases in combination with 4(p)-nitrobenzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-5-one (NMPP) on the extraction of Eu(III) and Nd(III) has also been studied[7].

A method has been developed for the rapid determination of small amounts of Nd.,Ho,Er,Tm in a mixture of lanthanides with arylazopyrazolones derivatives[8-9].

The survey of the literature data revealed that hardly any data is available on the stereochemical properties of these complexes but a study of their spectral and magnetic behaviour[10-11]can poit out some of these properties.

In the present investigation,a number of five trivalent lanthanide ion complexes of 1-(2'-Benzthyazolil)-3-methyl-4-azo-(4'-nitrophenyl)-Pyrazolin-5-one structure (I) were prepared and characterized by a variety of spectral and analytical methods to clarify the structure as well as the nature of the bonding in these complexes in the solid state.



Structure (I)

This ligand is a good pigment for rubber,and we expect semiconductor properties for these complexes.

Experimental

Apparatus and Reagents

Elementary analyses were obtained with a CARLO ERBA EA 1108.Ln^{3+} concentrations were determined by gravimetric methods.

Magnetic moments were determined by Gouy's technique and diamagnetic corrections were calculated from Pascal's constans.

Conductivity measurements were carried out using a Wescan 212 conductivitity meter in N,N-dimethylformamide (DMF) 10^{-3}M at room temperature.

Molecular weights were determined in chloroform at 37°C with a Mechlorab Model 301A vapor pressure osmometer.The concentration of the solution were in the range of 10^{-3}-10^{-4}M.

The electronic spectra of all compounds were obtained by the diffuse-reflectance technique,dispersing the sample in MgO ,with a Specord M 400 Carl Zeiss Jena Spectrophotometer.

The IR spectra were run with a Perkin Elmer FT-IR spectrophotometer in the range of 4000-200 cm^{-1} in KBr pellets and in the range of 12000- 4000 cm^{-1} in solid state with a Cary 17D (NIR).

The gadolinium complex was studied by thermogravimetric(TG) and differential thermal analysis (DTA) in a static air atmosphere, with sample heating of 5^0/min using a MOM-Budapest OD 103 Paulik Evdey derivatograph.

The final residue was studied with X-rays using a HZG Diphractometer, with CoK_α radiations and Cu, Fe filter and TUR-M 62 generator, v=0.5^0/min,$6*10^4$imp/min.

All compounds and solvents were pure BDH grade chemicals.The ligand used was prepared according to a method described in the literature [12].

Preparation of lanyhanide complexes

Aqueous solution of lanthanide (III) chlorides (1.5×10^{-3}mole and 5 ml H_2O) were mixed with ethanolic suspensions of the ligand (3×10^{-3}mole in 10 ml ethanol) in a ratio M:L=1:2.After half an hour the pH of the reaction mixture was adjusted from 4.5 to 8 with aqueous $CH_3COONa.3H_2O$(3×10^{-3}mole) and the reaction mixture was refluxed for an hour.After an hour of reflux the pH of the reaction mixture was adjusted to 9 - 9.5 with aqueous solution 4% NaOH and was refluxed for half an hour.The product obtained on cooling was filtered off, washed succesivelly with ether and finnaly was recrystallized from an mixture of water : ethanol,1:2(v/v).

Results and Discussion

Elementary analysis shows a ratio lanthanide :ligand of 1:2.The molar condunctance values (200-240 Ω^{-1} cm^2 mol^{-1}) in DMF 10^{-3} M shows a 1/3 electrolyte behavior of the complexes.The analytical results shows a geneal formula $Na_3[Ln(C_{17}H_{11}N_6O_3S)_2(OH)_4]$ for the complexes .,where Ln=Pr(III),Sm(III),Gd(III),Ho(III)and La(III) (Table 1).

The thermal decomposition(Figure 1) is in good agremeent with literature data [14,15] and shows no coordinated water molecules,because in the range 120-190^{0}C there isn't a Loos through an endothermicprocess.In the third stage there are two exothermic effects 495^{0}C And 510^{0}C which represent NaOH elimination.In the third stage there are two exothermic effect at 560^{0}C corresponds to Gd_2O_3 formation.

The X-ray spectrum (Figure 2)is in good agreement with the presence of Gd_2O_3.

Magnetic moments .Allcoordination compounds under study except the La(III)-complex are paramagnetic while the latter is diamagnetic because of the presence of unpaired electrons in the 4f subshells,wich are shielded by 5s,5p and 5d orbitals .This makes it very difficult for the ligands to attack the inner 4f electron . Therefore ,the magnetic moments of the complexes should be affected to a lesser extent as compared to that of the metal salt itself.There is a slight variation in the experimental magnetic moment values (Table 1) which may be due to the thermal population of excited states whose degenerate levels have been split by the crystal field[16].

The molecular weight determinations show the complexes to be monomers .

The IR spectra of the bidentate azodye ligand and its complexes are quite informative .The IR spectra of the ligadd[16](Table 2) shows a band at 1642 cm^{-1} due to ν(C=O) group of the pyrazolone ring and a strong band at 1526 cm^{-1} due to [ν(N=N)+ν(C=N)] and a band at 1433 cm^{-1} assigned as ν_{as}(N=N).The positions of these bands are highly influenced by the nature of the substituent in the aryl ring.Their shifts to longer wavelengths are due to increasing overlap of the molecular orbitals of the N=N system.The strong band at 1343 cm^{-1}

Table 1. Analytical, molar conductance, magnetic moments data of the trivalent lanthanide ions complexes

Complex	Microanalysis Results				λ $\Omega^{-1}cm^2mol^{-1}$	μ_{eff} [BM]	Mol wt	Powder colour
	C %	H %	N %	Ln %				
$Na_3[La(C_{17}H_{11}N_6O_3S)_2(OH)_4]$	(39.46)* 40.01	(2.12) 3.00	(16.24) 16.25	(13.43) 13.50	240.01	(-) 0.25	1033.91	orange
$Na_3[Ho(C_{17}H_{11}N_6O_3S)_2(OH)_4]$	(33.30) 33.75	(1.79) 2.00	(13.71) 13.82	(13.46) 13.63	220.42	(4.89) 4.60	1224.86	brown -orange
$Na_3[Gd(C_{17}H_{11}N_6O_3S)_2(OH)_4]$	(38.77) 39.05	(2.09) 2.85	(15.96) 16.01	(14.94) 15.02	235.40	(7.94) 7.86	1052.25	brown -orange
$Na_3[Sm(C_{17}H_{11}N_6O_3S)_2(OH)_4]$	(39.02) 40.01	(2.10) 2.55	(16.07) 16.00	(14.38) 14.65	236.80	(5.91) 5.82	1045.35	brown -orange
$Na_3[Pr(C_{17}H_{11}N_6O_3S)_2(OH)_4]$	(39.38) 40.11	(2.12) 2.70	(16.21) 16.45	(13.60) 13.82	238.75	(2.83) 2.78	1035.91	brown -orange

* (Calculated) Experimental

Table 2. The IR (cm^{-1}) spectral data of the HL ligand and the $Na_3[Ln(L)_2(OH)_4]$ complexes (Ln = La^{III}, Pr^{III}, Sm^{III}, Gd^{III}, Ho^{III})

Assignements	Compounds					
	HL	$Na_3[La(L)_2(OH)_4]$	$Na_3[Pr(L)_2(OH)_4]$	$Na_3[Sm(L)_2(OH)_4]$	$Na_3[Gd(L)_2(OH)_4]$	$Na_3[Ho(L)_2(OH)_4]$
$\nu(C=O)$ of pyrazolon ring	1642	-	-	-	-	-
$\nu(C=N)+\nu(C=O)$ $\nu_{as}(C=O)$	1526 1433	1467	1468	1468	1470	1470
$\nu(OH)$ in hydroxo complexes	-	3445	3442	3444	3444	3445
$\delta(M\text{-}O\text{-}H)$	-	1183	1183	1183	1183	1183
$\nu(C=O)$ enolic coordinated	-	1320	1322	1322	1324	1324
O-H...N	3457	-	-	-	-	-
$\nu(M\text{-}O)$	-	470	472	475	475	475
$\nu(M\text{-}N)$	-	529	530	530	530	530

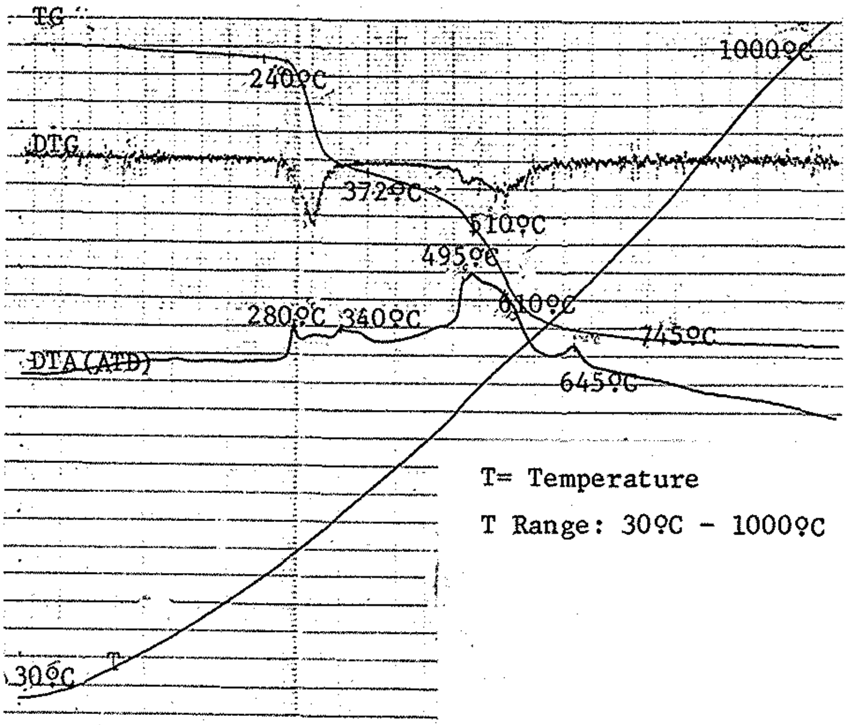


Figure 1.The differential thermogravimetric (DTG), thermogravimetric (TG) and differential thermal (ATD)analysis of the $K[Gd(L_2)(H_2O)_2]$ complex.

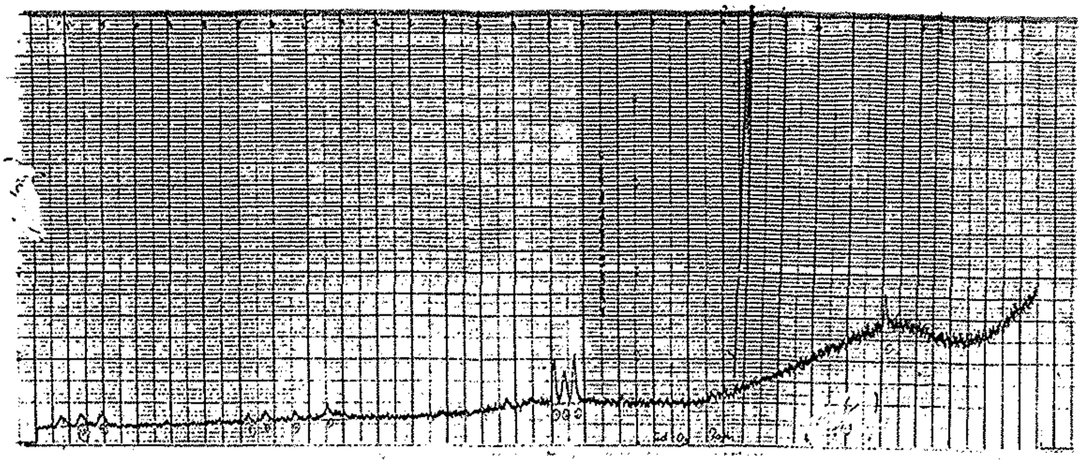
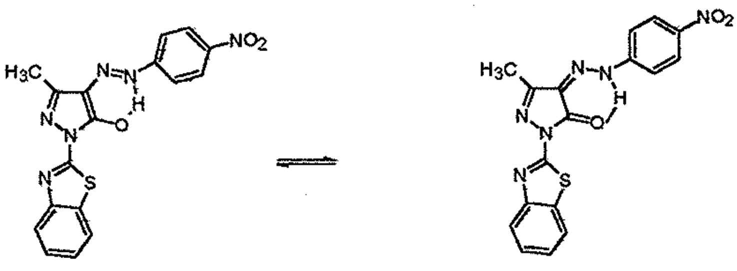


Figure 2.The X-ray spectrum of the $K[Gd(L_2)(H_2O)_2]$ complex.

can be attributed to the stretching ν of the (C-OH) group .The broad strong band at 3457 cm^{-1} is explained by the presence of an associate NH and OH hydrogen bond . It is clear from these data that the ligand certanly exists as azoenol –hydrazoketo tautomeric structures:



Azoenol form Hidrazoketo form

The IR spectra (Table 2) of the complexes exhibit a band at 3445cm^{-1} assignable to the OH stretching and a band at 1183 cm^{-1}assignable to the M-O-H bending in hydroxocomplexes of lanthanide ions and these data are in good agreement with the literature values[17].

The weak band at 1320cm^{-1}may be assigned to the enolic ν(C-O) coordinated to the metal ions[18].In all the metal complexes there are no bands corresponding to coordinated water molecules.In the metal chelates the band at 3457cm^{-1} due to intramolecular O-H……N[18] disappears showing the deprotonation of enolic hydroxyl group.The sharp band at 1526cm^{-1} in the azo dye due to [ν(N=N) and ν(C=N)] shifts to 1467cm^{-1} upon complexation indicating the bonding of one of the azo nitrogen atoms to the metal atoms[19,20].

The conclusive evidence of bonding is confirmed by the occurrence[21] of ν(M-O) and ν(M-N) bands at about 470cm^{-1} and 529cm^{-1},respectively.

Hence the azo dye behaves as monovalent and bidentate ligand bonded through the potential donor (N –O) atoms in azoenolic form.

In the UV-VIS region of the ligand the following bands appear : (nm) 387(-N=N-),225(C=N),270(aromathic ring) and 280(C=O) of the pyrazolone ring[12].In the complexes these bands are shifted as following :(nm) 365(-N=N-),325(C=N),265(aromathic ring) and the at 280 nm disappears because the π-bonding of (C=O) of the pyrazolone ring is quenched[19].

The electronic spectra of the lanthanide complexes are the same as in aqueous solution of the lanthanides cation Ln^{3+} because the **f-f** transition are not influenced by the neighbours[22].In our lanthanides complexes all the bands are shifted compared with Ln^{3+}(aqueous).The bands between 16000-20000cm^{-1} are very sensitive to the coordination number.Inthis region we discovered bands in good agreement with the octacoordinated Ln^{3+}.

[$PrL_2(H_2O)_2$]. We found the following transitions:

16900 cm^{-1} for $^3H_4 \rightarrow {}^1D_2$ (in Pr^{3+}(aq) 16980 cm^{-1})
20200 cm^{-1} for $^3H_4 \rightarrow {}^3P_0$ (in Pr^{3+}(aq) 20700 cm^{-1})
. 20850 cm^{-1} for $^3H_4 \rightarrow {}^1I_6$ (in Pr^{3+}(aq) 21500 cm^{-1}).This transition is sensitive to the number of neighbours and it is in a good agreement with the octa-coordination of Pr^{3+}.The band at the 33300cm^{-1} corresponds to the transition $4f^n \rightarrow 4f^{n-1}d$ [23,24](Figure 3).

[$SmL_2(H_2O)_2$]. We found the following bands :

17450 cm^{-1} for $^6H_{7/2} \rightarrow {}^4G_{5/2}$ (in Sm^{3+}(aq) 17880 cm^{-1})
18340 cm^{-1} for $^6H_{7/2} \rightarrow {}^4F_{3/2}$ (in Sm^{3+}(aq) 18880cm^{-1})
. 20400 cm^{-1} for $^6H_{7/2} \rightarrow {}^4G_{7/2}$ (inSm^{3+}(aq) 19950cm^{-1}) (Figure 4).

The hyper sensitive transition to $^6F_{1/2}$ appears in NIR range at:

5995 cm^{-1} for $^6H_{7/2} \rightarrow {}^6F_{1/2}$ (in Sm^{3+}(aq) 6200cm^{-1})
6305 cm^{-1} for $^6H_{7/2} \rightarrow {}^6H_{15/2}$ (in Sm^{3+}(aq) 6460cm^{-1})
. 6468cm^{-1} shoulder for $^6H_{7/2} \rightarrow {}^6F_{3/2}$ (inSm^{3+}(aq) 6640cm^{-1})

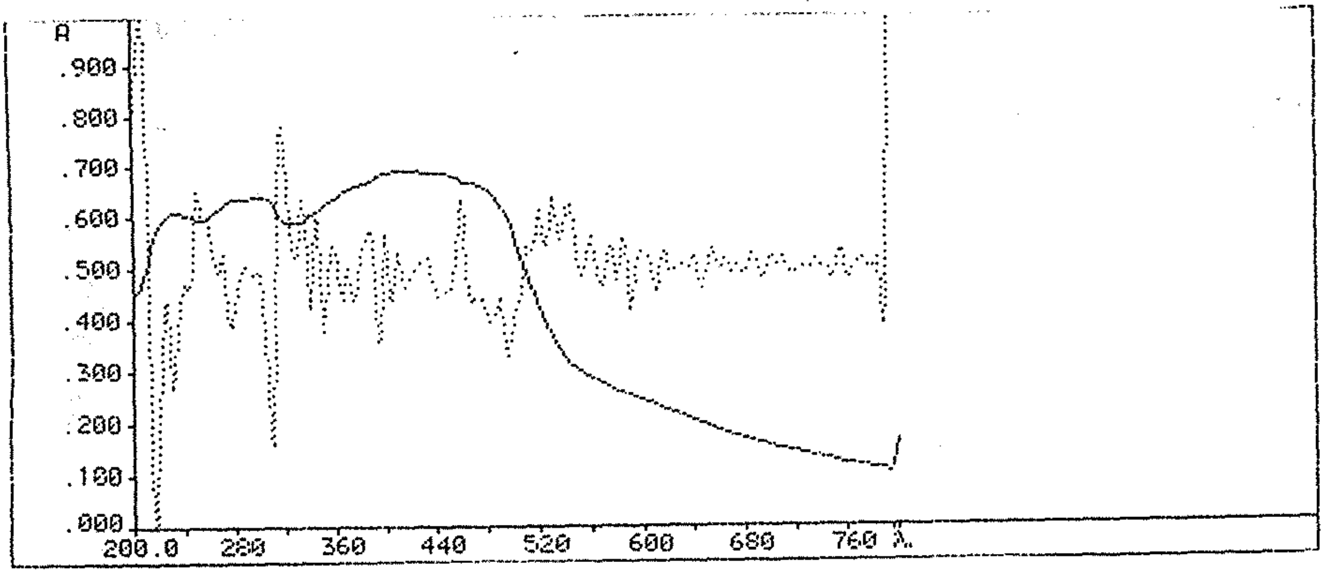


Figure 3. The UV-VIS (nm) spectrum of the $K[Pr(L_2)(H_2O)_2]$ complex

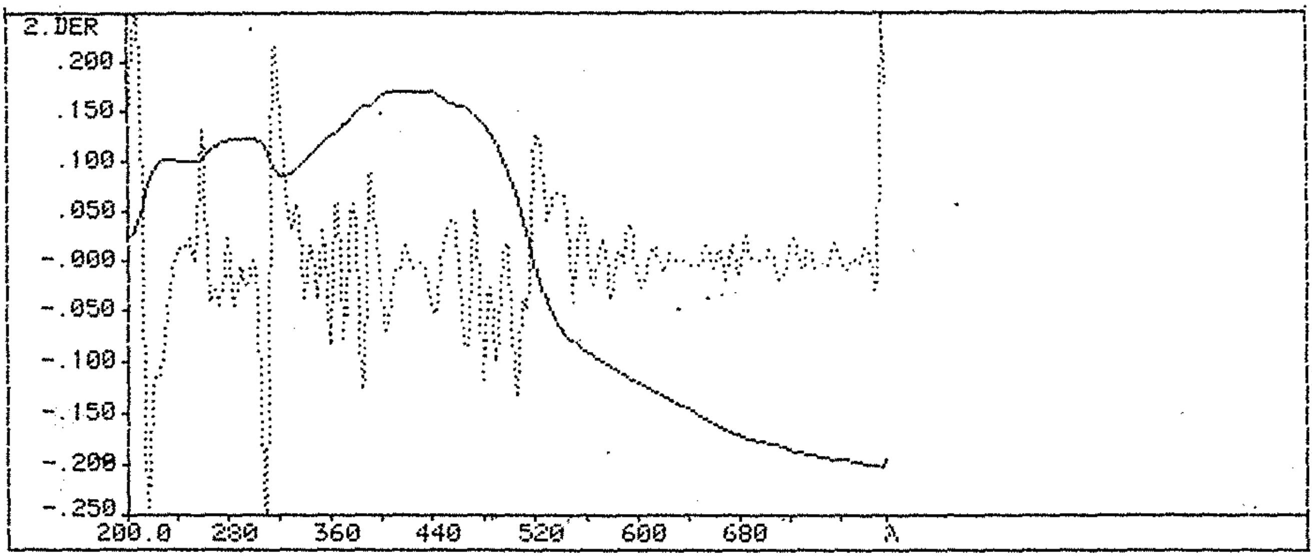


Figure 4. The UV-VIS (nm) spectrum of the $K[Sm(L_2)(H_2O)_2]$ complex

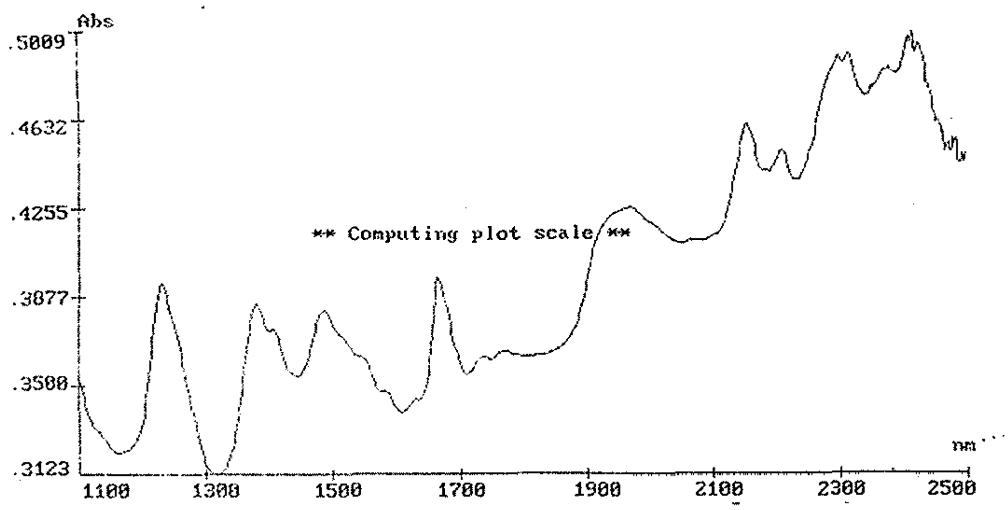


Figure 5. The NIR spectrum of the $K[Sm(L_2)(H_2O)_2]$ complex

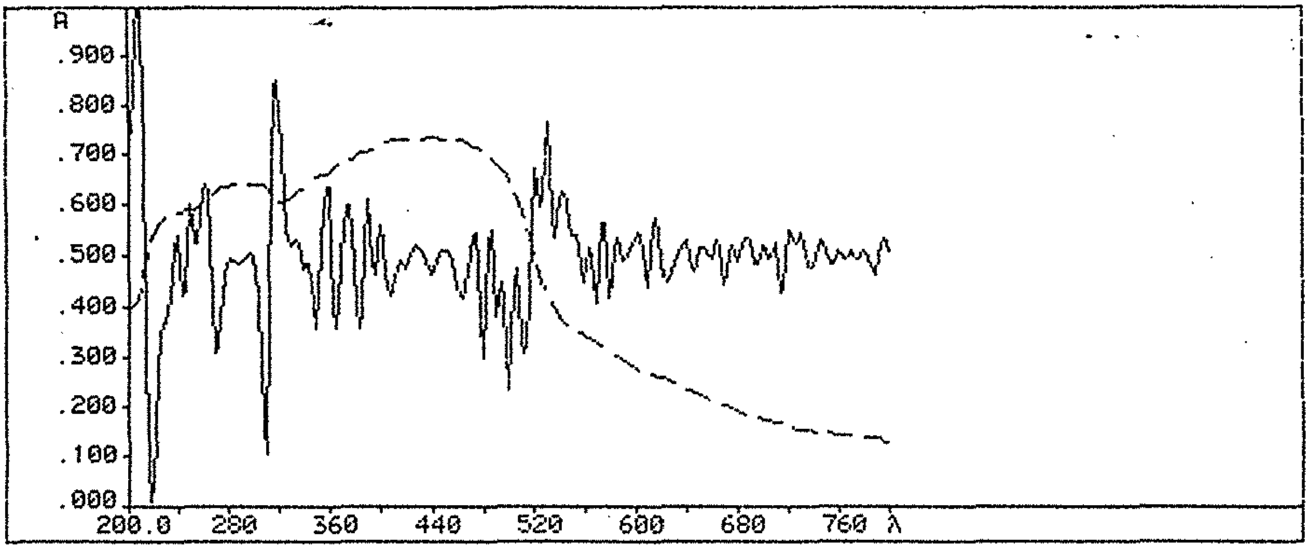


Figure 6. The UV-VIS (nm) spectrum of the $K[Gd(L_2)(H_2O)_2]$ complex

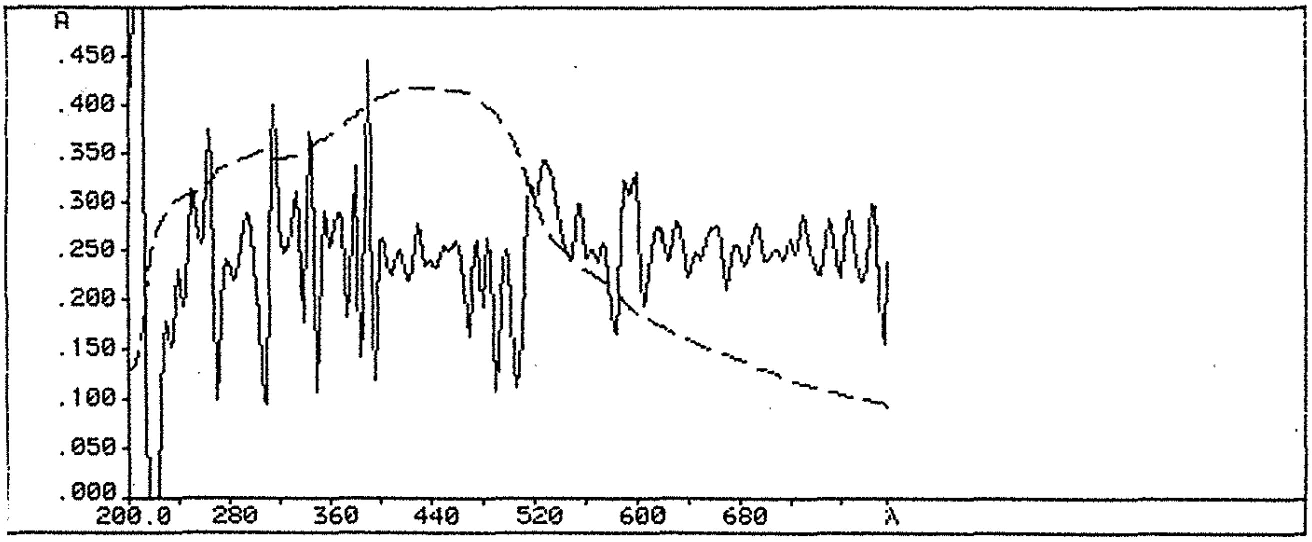


Figure 7. The UV-VIS (nm) spectrum of the $K[Ho(L_2)(H_2O)_2]$ complex

[$GdL_2(H_2O)_2$]. The bands between 32000-33000 cm $^{-1}$ were assigned by Sidall and Stewart[24].We found three bands in this range assigned to the following transitions:

31250 cm^{-1} for $^8S_{7/2}\rightarrow{}^6P_{7/2}$
32258cm^{-1} for $^8S_{7/2}\rightarrow{}^6P_{5/2}$
32894cm^{-1} for. $^8S_{7/2}\rightarrow{}^6P_{3/2}$

The transitions to ^6I ($^6I_{7/2}$, $^6I_{9/2}$, $^6I_{17/2}$, $^6I_{11/2}$, $^6I_{13/2}$,$^6I_{15/2}$) appear in the range : 36000-37000 cm^{-1}.In our spectrum there is one very intense ligand band at 36340 cm^{-1},assignedto$^8S_{7/2}\rightarrow{}^6I_{9/2}$.The band at 45454 cm^{-1} was assigned to the transition $^8S_{7/2}\rightarrow{}^6D(^6D_{9/2,1/2,7/2,3/2,5/2})$.(Figure 6)

[$HoL_2(H_2O)_2$]. In the spectrum of this compound the bands were assigned as follows:

11111cm^{-1}	$^4I_{15/2}$	$\rightarrow{}^5I_5$
16260cm^{-1}		$\rightarrow{}^5F_5$
17094cm^{-1}		$\rightarrow{}^5S_2$
18018cm^{-1}		$\rightarrow{}^5F_4$
19607cm^{-1}		$\rightarrow{}^5F_3$
20000cm^{-1}		$\rightarrow{}^5F_2$
21052cm^{-1}		$\rightarrow{}^3K_8$
23255cm^{-1}		$\rightarrow{}^5G_6$
25000cm^{-1}		$\rightarrow{}^5G_4$
25974cm^{-1}		$\rightarrow{}^3K_7$
28169cm^{-1}		$\rightarrow{}^3G_6$
28985cm^{-1}		$\rightarrow{}^3D_3$
35714cm^{-1}		$\rightarrow(^3H_4,{}^5D_4,{}^1G_4)$.[23]

The $^5G_6$ and $^3G_6$ (23255 and 28169 cm^{-1}) are the hypersensitive transitions.
All the band correspond to coordination number eight and a square antiprismatic (C_2) geometry[23,24].(Figure 7)

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