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SYNTHESIS OF RARE EARTH COORDINATION COMPOUNDS OF SALICYLALDEHYDE-β-ALANINE SCHIFF BASE AND THEIR THERMAL BEHAVIOURS I.

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ABSTRACT

New rare earth coordination compounds of salicylaldehyde Schiff base with β-alanine were synthesized and characterized by using elemental analysis and thermogravimetry, and their compositions have the formula, $LnL_3 \cdot xH_2O$, where x=3, Ln=La, Sm; x=2.5, Ln=Gd; x=2, Ln=Nd; x=1.5, Ln=Ce, Pr, Eu; $L=OH-C_6H_4-CH=N-CH_2-CH_2-COO^-$. IR spectra, molar conductance and solubility for the coordination compounds have been made and their dehydration and decomposition behaviours were also studied by means of DTA-TG-DTG and IR techniques.

INTRODUCTION

Since the biological activities of some Schiff base-metal coordination compounds are found[1], studies on syntheses, properties and structure of these compounds have attracted considerable attention. Up to now, the metals in the investigated Schiff base-metal coordination compounds were focused on the first transition series, while the studies on the rare earth elements were rarely reported[2-4]. The investigations on the thermal behaviours of the Schiff base-rare earth coordination compounds were seemly much rarer. Recently it has been found that the rare earth elements also possess many biological and medicinal actions[5-6], and therefore systematic study for their syntheses, properties and structures will be of important significance.

EXPERIMENTAL

Materials

Salicylaldehyde(c.p) is purified by distillation before using it, and β-alanine is procured from E. Merck Co.. Salicylaldehyde-β-alanine Schiff base is prepared by mixing a hot solution of β-alanine in enthanol and salicylaldehyde in the molar ratio of 1:1 with stirring and refluxing. The mixing

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solution is concentrated, thus the Schiff base is precipitated and filtered and washed twice with distilled water and ethanol, respectively, and dried over P_2O_5 in a desiccator. Calculated values for $OH-C_6H_4-CH=N-CH_2-CH_2·COOH$: N, 7.25; H, 5.74; C, 62.15. Found values: N, 6.86; H, 5.87; C, 62.29. Hydrated lanthanide trichloroacetates are prepared as reported[7]. All other chemicals used in this work are of reagent grade.

Synthesis

The coordination compounds are prepared by mixing the respective hydrated rare earth trichloroacetates with the salicylaldehyde-β-alanine Schiff base in propanone in the molar ratio of 1:3 under gentle reflux. The resulting solid compounds are filtered, washed with propanone three times, and dried over P_2O_5 in a vacuum desiccator until constant weights are reached. The coordination compounds obtained are all brown yellow color.

Instrument and analysis

IR spectra are recorded in KBr pellet with a DS-701G spectrophotometer. Measurements of TG, DTG and DTA curves are carried out under the reported experimental conditions[8]. The rare earth elements are determined by igniting the coordination compounds to oxides at 1000°C. The crystallization water is estimated by thermogravimetry. The nitrogen element is measured by using Dumas method. The molar conductance data are measured with a DDS-11A diagometer.

RESULTS AND DISCUSSION

Composition analysis

The determined contents of rare earths, nitrogen and crystallization water in the Schiff base-rare earth coordination compounds are given in Table 1. From Table 1, we notice that the observed values are in good agreement with the values calculated by the assumed formulas.

Determinations of Properties

The above seven coordination compounds can dissolve in dimethylsulfoxide (DMSO) and dimethylformamide (DMF), but they are very slight soluble or essentially non-soluble in common solvents used in laboratory, such as, benzene, enthanol, ether, pyridine, acetone and water, and so on.

Molar conductance data of the coordination compounds in DMF solutions are listed in Table 2.

Table 1 Analytical data of the coordination compounds

Coordination Compound[1]	Oxide of rare earth (%)		N(%)		Water of Crystallization (mol)	
	Obs.[2]	Calc.	Obs.	Calc.	Obs.[3]	Calc.
$LaL_3.3H_2O$	20.64	21.16	4.65	5.46	3.01	3.0
$CeL_3.1.5H_2O$	22.80	23.14	5.70	5.64	1.45	1.5
$PrL_3.1.5H_2O$	22.16	22.86	4.86	5.64	1.52	1.5
$NdL_3.2H_2O$	23.14	22.22	4.65	5.55	1.96	2.0
$SmL_3.3H_2O$	22.57	22.32	4.51	5.38	3.04	3.0
$EuL_3.1.5H_2O$	21.71	23.28	4.99	5.57	1.50	1.5
$GdL_3.2.5H_2O$	24.15	23.26	4.89	5.39	2.60	2.5

1. $L=OH-C_6H_4-CH=NCH_2-CH_2-COO^-$;
2. Average of two experiments ;
3. Average of three experiments

Table 2 Molar conductance data for the coordination compounds

Coordination Compound[1]	Concentration (Mol dm^{-3})	Conductivity(25°C) (μ℧/cm)[2]	Molar Conductance ($S.m^2.mol^{-1}$)
$LaL_3.3H_2O$	$5.716X10^{-4}$	2.20X10	$3.85X10^{-3}$
$CeL_3.1.5H_2O$	$1.0027X10^{-3}$	1.70X10	$1.70X10^{-3}$
$PrL_3.1.5H_2O$	$1.0044X10^{-3}$	1.80X10	$1.79X10^{-3}$
$NdL_3.2H_2O$	$9.972X10^{-4}$	3.70X10	$3.71X10^{-3}$
$SmL_3.3H_2O$	$9.143X10^{-4}$	1.51X10	$1.65X10^{-3}$
$EuL_3.1.5H_2O$	$1.032X10^{-3}$	1.25X10	$1.21X10^{-3}$
$GdL_3.2.5H_2O$	$1.0232X10^{-3}$	1.76X10	$1.72X10^{-3}$

1. $L=OH-C_6H_4-CH=NCH_2-CH_2-COO^-$;
2. Conductivity of DMF = 1.79 μ℧/cm.

From Table 2, we consider that the coordination compounds in DMF solutions occur in molecular state [9].

The IR spectra of the Schiff base and its rare earth coordination compounds are shown in Fig.1.

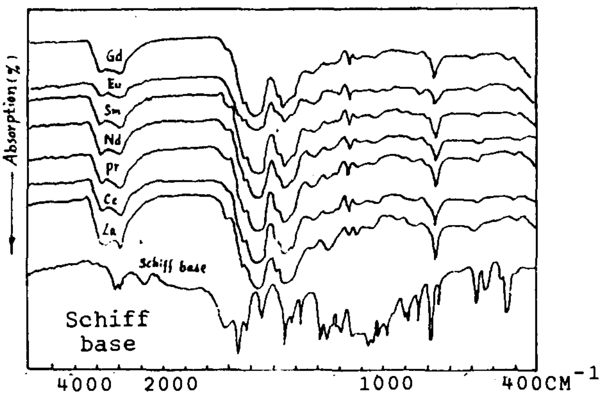

Fig. 1: IR spectra of the Schiff base and its rare earth coordination compound (spectra recorded in KBr pellets)

From Fig.1, we observe that the bands assigned to C=N(1630 cm^{-1}), COO^-_{sy} (1445-1450 cm^{-1}) and COO^-_{asy} (1560-1580 cm^{-1}) stretching vibrations in the Schiff base coordination compounds shift respectively to lower wavenumbers by 20 cm^{-1}, 90-95 cm^{-1} and 140-150 cm^{-1}, as compared with the Schiff base ($\nu_{C=N}$=1650cm^{-1} , $\nu_{COO^-_{sy}}$ =1540cm^{-1}, $\nu_{COO^-_{asy}}$ =1710cm^{-1}), the coordinatian sites are therefore considered to be the azomethine nitrogen and carboxylic oxygen. The bands at ~ 400cm^{-1} and ~ 600cm^{-1} may support the formation of RE-O bond[10]. In addition, the downward shifts of $\nu_{Ar-O}$and ν_{ArO-H} to lower wavenumbers in all the coordination compounds may be due to the formation of hydrogen bond between ArOH and water molecule. The bands of water molecule in the coordination compounds are in agrreement with the bands of ordinary solid wàter at ~ 3400 cm^{-1} [11], which again supports the presence of the hydrogen bond, this is the reason we conclude that the water molecules in the coordination compounds are not coordinated to the lanthanide ion. It is observed that all the compounds have lower inital decomposition temperatures, which is also in favour of the above hypothesis.

THERMAL BEHAVIOUS

Typical thermal analysis curves of the coordination compounds are presented in Figs. 2-3.

Thermal analysis curves indicate that the decompositions of $LaL_3 \cdot 3H_2O$, $PrL_3 \cdot 1.5H_2O$, $NdL_3 \cdot 2H_2O$, $SmL_3 \cdot 3H_2O$, and GdL_3 $2.5H_2O$ take place in four stages in the range from room temperature to 650°C. In the first stage, the dehydration processes of the compounds are completed in a one step respectively, this can be proved by the following fact that the weight losses determined from TG curves of the above compounds are in good agreement with that calculated on the basis of losses of all the water of crystallization in their molecules. In the second step, the decomposition process of each anhydrous compound is thought to be mainly due to only one ligand broken at a N-C single bond, because a mass loss from TG curve is equivalent to the mass of " $OH-C_6H_4-CN$" compnent, they decompose at temperature range of 172-290°C, 128-319°C, 162-320° C, 172-315° C and 173-307°C respectively. In the third step, the rections involved are quite complex. According to the data of TG curves, the final products correspond to the formulas: $La_2O_2CO_3$(for LaL_3), $Pr_2O_2CO_3$(for PrL_3), $Nd_2O(CO_3)_2$ (for NdL_3), $Sm_2O(CO_3)_2$ (for SmL_3) and Gd_2O_3(for GdL_3) respectively in the fourth step.

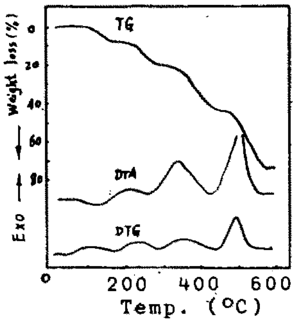

Fig. 2: Thermal analysis curves of $LaL_3.3HOH$

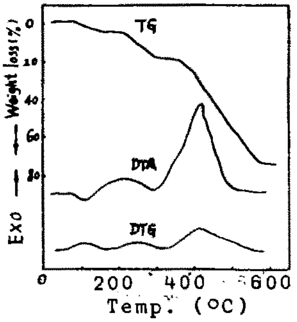

Fig. 3: Thermal analysis curves of CeL_3. 1.5HOH

Thermal determinations reveal that the decompositions of CeL_3 $1.5H_2O$ and $EuL_3 \cdot 1.5H_2O$ occur in three steps in the range from room temperature to 650°C. In the first step the coordination compounds lose all the crystallization water at temperature ranges of 56-146°C and 50-137°C respectively. In the second step, the decomposition of CeL_3 is the same as that of LaL_3, while the decomposition of EuL_3 seems to break two C-N single bonds in each coordination compound. The decompositions begin at 146°C (for CeL_3) and 137°C (for EuL_3), and finish at 300°C (for CeL_3) and 485°C (for EuL_3). The final products are CeO_2 (for CeL_3) and $Eu_2O_2CO_3$ (for EuL_3) in accordance with the data of TG curves of $CeL_3 \cdot 1.5H_2O$ and $EuL_3 \cdot 1.5H_2O$. The final products above mentioned (except CeO_2 and Gd_2O_3) are determined by IR and ν_{CO} and δ_{CO_3} characteristic peaks are observed which are considered to be the evidence of existences of oxycarbonates[12].

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