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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis, Characterization, and Thermal Analysis of $Re(C_{10}H_9N_2O_4)_3 \cdot nH_2O$ Complexes

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Synthesis, Characterization, and Thermal Analysis of Re(C₁₀H₉N₂O₄)₃ · nH₂O Complexes

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Six new complexes of $C_{10}H_{10}N_2O_4$ with light rare earth ions $RE(C_{10}H_9N_2O_4)_3 \cdot nH_2O$, (RE = La, Ce, Nd, Sm, Eu, Gd) have been synthesized in alcohol aqueous solution. The composition of the complexes is determined by elemental analysis, IR, UV, and X-ray powder diffraction. The thermal decomposition processes of the six complexes were studied by TG-DTG curves. It was found that the thermal decomposition processes of the complexes could be divided into three stages. The plot of apparent activation energies of the second thermal decomposition stage for the complexes versus the atomic number showed a grouping effect of the lanthanide elements.

Keywords rare earth, pyruvic acid-salicylhydrazone, synthesis, characterization, thermal analysis

INTRODUCTION

Aroylhydrazone as a ligand has attracted much attention for its excellent bioactivity, strong coordination ability and complicated coordination behavior.^[1–3] There are some reports about the complexes of aroylhydrazone with rare earth elements,^[4–11] and it was found that the coordination form has three kinds: keto-form, enolic form and the dehydrogenation coujugation form. The results of these reports also show the lanthanide (III) complexes can accelerate the cleavage of double-stranded DNA more efficiently than lanthanide ion alone. Recently, a new aroylhydrazone ligand C₁₀H₁₀N₂O₄ and its complexes with heavy rare earth element RE($C_{10}H_9N_2O_4$)₃ · 2H₂O have been synthesized by our research group.^[12] It was shown that the new kind of complexes have effective inhibitor against *Botrytis cirerea* Pers.ex Tris., *Alternaria alternata* Fries keissler and *Puccinia striiformis Westendorp*.

In this paper, six new complexes of $C_{10}H_{10}N_2O_4$ with light rare earth element $RE(C_{10}H_9N_2O_4)_3 \cdot 2H_2O$ have been synthesized and characterized. The coordination behavior, the thermal decomposition process and thermal stability were discussed and compared.

EXPERIMENTAL

Reagents

 $Re(NO_3)_3 \cdot nH_2O$ was prepared from RE_2O_3 (99.95%) and HNO_3 .^[13] Glycin and pyriuvic acid are biochemical reagents. Methyl salicylate, hydrazine hydrate, nonaqueous alcohol and sodium hydroxide are all of analytical purity standards.

Elemental analysis was performed on a P.E. 2400 elemental analyzer. IR spectra were recorded on a GXIV 5.0.1 Fourier IR spectrometer. The UV spectrum was obtained by a TU-1900 UV-VIS spectrophotometer. X-ray powder diffraction was operated on an X-ray powder diffraction. TG-DTG curve was measured by TG-209 gravitational thermal analyzer.

Synthesis of the Ligand and the Complexes

The ligand pyruvic acid-salicylhydrazone ($C_{10}H_{10}N_2O_4$) was prepared according to the report.^[14] Pyriuvic acid (1.42 mL) was added to the solution of salicyloyl hydrazide (3.09 g) in nonaqueous alcohol (30 mL). The mixture was stirred on a water bath (80°C) for 2 hours. The precipitate was filtered and recrystallized from alcohol and washed by ether. The white needle crystal was obtained with a yield of 60%.

 $RE(NO_3)_3 \cdot nH_2O$ was dissolved in nonaqueous alcohol, then a solution of glycin was added dropwise with stirring. The mixture was heated at 60°C for 1 hour, then the alcohol

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aqueous solution of the ligand was added dropwise with stirring and a large quantity of deposit appeared. The reaction was carried out at 80°C for 1 hour. The pH of reaction system was adjusted between 3-4. After filtering and washing with anhydrous ethanol and ether, the powdery complex was dried in a desiccator to weight stability.

RESULTS AND DISCUSSION

Composition and Solubility of the Complexes

The results of elemental analysis for all the complexes are listed in Table 1. From Table 1, it can be seen that the found values are in agreement with the calculated ones.

The complexes are insoluble in ether, sparingly soluble in water, methanol and alcohol, and easily soluble in DMF and DMSO.

Infrared Spectra

The main IR data of the ligand and their complexes are presented in Table 2. The IR spectra of all the complexes are similar to each other. IR spectra of the ligand and the complexes are identified according to Nakamoto.^[15] The absorption peak at 1755 cm⁻¹ assigned to ν (COOH) in the free ligand has been replaced by two new peaks: $v_{as}(COO^{-})$ (1) $611-1614 \text{ cm}^{-1}$) and $\nu_{s}(\text{COO}^{-})$ (1368-1369 cm⁻¹) in all the complexes. The $\Delta v(v_{as} - v_s)$ values of all complexes are

more than 200 cm⁻¹, which indicate that COO⁻ is coordinated with the lanthanide ion in the form of one dentate. The amine I (ν C==O) is shift from 1700 to 1657–1662 cm⁻¹ after coordination, which indicates that the C=O was coordinated. The ν (N-H) of the free ligand at 3291 cm⁻¹ and its complexes at $3234-3246 \text{ cm}^{-1}$ show that active hydrogen of -NHN= group still exists in the complexes. These shifts indicate that the ligand is coordinated in keto-forms. Amine $II(\delta_{N-H})$ is at 1531 cm^{-1} in the free ligand and in its complexes at 1539-1541 cm⁻¹ show that hydrogen of -NH- group still exists after coordination. All complexes show a strong IR peak in 1657–1662 cm⁻¹ assigned to ν (C=N) vibration, whereas ν (C=N) appears at 1646 cm⁻¹ in free ligand, which indicates that the C=N (N atom) was coordinated. The bands at 820- 822 cm^{-1} and $582-587 \text{ cm}^{-1}$ indicate that water was coordinated.[16]

UV Spectra

UV spectra of the ligand and the complexes were obtained in DMF solution with DMF as a reference. The results are listed in Table 3. From Table 3, it can be seen that there is a strong band at 312.5 nm in the ligand, which is the π - π * transition of the salicyloyl group. The band blue shift to 284.2-288.5 nm in the complexes shows that the conjugation of the salicyloyl group has been weakened after coordination.

RE

16.67

17.05

17.47

18.05

18.23

18.75

	TABLE 1 Elementary analysis of the complexes						
Complexes	Found/%			Calculated/%			
	С	Н	Ν	RE	С	Н	Ν
$La(C_{10}H_9N_2O_4)_3 \cdot 2H_2O_4)_3$	42.88	3.470	10.03	7.06	42.96	3.732	10.02
$Ce(C_{10}H_9N_2O_4)_3 \cdot H_2O$	44.04	3.194	10.37	17.36	43.85	3.560	10.23
$Nd(C_{10}H_9N_2O_4)_3 \cdot H_2O$	43.95	3.213	10.11	17.84	43.63	3.537	10.18
$Sm(C_{10}H_9N_2O_4)_3 \cdot H_2O$	43.88	3.186	10.13	17.88	43.47	3.491	10.11
$Eu(C_{10}H_9N_2O_4)_3 \cdot H_2O$	43.56	3.242	10.12	17.97	43.23	3.510	10.08
$Gd(C_{10}H_9N_2O_4)_3 \cdot H_2O$	43.21	3.042	10.08	18.35	42.96	3.480	10.02

TABLE 2 Important IR bands of the complexes (cm^{-1})

Compound	v(COOH)	$\nu_{as}(COO^{-})$	$\nu_{s}(COO^{-})$	ν(C==0)	ν(C==N)	δ(N-H)	ν(N-H)	$\rho_{\text{O-H}}(\text{H}_2\text{O})$	$\omega_{\text{O-H}}(\text{H}_2\text{O})$
$C_{10}H_{10}N_2O_4$	1755	_		1700	1646	1531	3291	_	_
$La(C_{10}H_9N_2O_4)_3 \cdot 2H_2O_4)_3 \cdot 2H_2O_4$		1611	1369	1657	1573	1540	3234	821	582
$Ce(C_{10}H_9N_2O_4)_3\cdot H_2O$	_	1614	1369	1659	1572	1540	3236	821	582
$Nd(C_{10}H_9N_2O_4)_3\cdot H_2O$	_	1612	1368	1660	1571	1539	3236	821	582
$Sm(C_{10}H_9N_2O_4)_3 \cdot H_2O$		1613	1369	1662	1572	1539	3246	822	583
$Eu(C_{10}H_9N_2O_4)_3 \cdot H_2O$		1612	1369	1661	1573	1541	3238	822	587
$Gd(C_{10}H_9N_2O_4)_3\cdot H_2O$		1614	1368	1662	1571	1540	3242	820	585

TABLE 3
UV spectral data and luminescence properties for the ligand
and complexes

$\begin{array}{l} b \times 10^{-4} \\ mol \cdot L^{-1} \end{array}$	$\begin{array}{c} UV\\ \lambda_1(nm) \end{array}$	Fluorescence $\lambda_2(nm)$
1.02	312.5	430.0
1.08	284.3	409.1
1.19	286.5	408.4
1.15	285.6	408.2
1.21	288.5	408.3
1.17	284.2	408.6
1.00	287.6	408.1
	$b \times 10^{-4} \\ mol \cdot L^{-1} \\ 1.02 \\ 1.08 \\ 1.19 \\ 1.15 \\ 1.21 \\ 1.17 \\ 1.00 \\ \end{cases}$	$\begin{array}{ccc} b\times 10^{-4} & UV \\ mol \cdot L^{-1} & \lambda_1(nm) \\ \hline 1.02 & 312.5 \\ 1.08 & 284.3 \\ 1.19 & 286.5 \\ 1.19 & 285.6 \\ 1.21 & 288.5 \\ 1.17 & 284.2 \\ 1.00 & 287.6 \\ \hline \end{array}$

The excitation wavelength of the excitation spectra is 360.0 nm; the excitation wavelength of the ligand is 430.0 nm; and, the excitation wavelength of the complexes is 408.1 - 409.4 nm; there is a small blue shift, which indicates that the ligand has been coordinated to the lanthanide ions, and the excitation of the ligand and the complexes belong to L*-L.^[17]

X-Ray Powder Diffraction

The results of the X-ray powder diffraction for the salt $(Nd(NO_3)_3 \cdot 4H_2O)$, ligand $(C_{10}H_{10}N_2O_4)$ and the complex are shown in Table 4, respectively. The X-ray powder diffraction data of the salt and the ligand are carried out according to Wu et al.^[13] From Table 4, it can be seen that X-ray power diffraction of the complexes is obviously different from the ligand and the salt, and the complex is not simple lap joint of the ligand and the salt either. It can be deduced that a new complex is formed.

Based on the above characterizations of all the complexes, the structure of the complexes may be as Figure 1.



FIG. 1. The structure of the $\text{RE}(\text{C}_{10}\text{H}_9\text{N}_2\text{O}_4)_3 \cdot \text{nH}_2\text{O}$ (n = 1, 2).

Thermal Analysis of the Complexes

The thermal decomposition stages along with the weight losses and the corresponding temperature ranges of the complexes under heating rate of $5^{\circ}C \cdot min^{-1}$ are listed in Table 5. For comparing, the decomposition process of ligand according to He et al.^[14] is also listed in Table 5. The thermal decomposition process of the complexes can be divided into three stage: The first-stage is connected with the loss of water from the complexes; the second stage is the lost of $3 N_2 + 6CO$; the third-stage is the further decarburization and dehydrogenation. The remainders are rare earth oxides. The mass loss of three stages is in accordance with the calculated value, showing that the analysis of thermal decomposition process is reasonable. Comparing the thermal decomposition process of ligand and complexes, it can be found that the ligand decomposes within 440-504-583 K and has no remainder. The decomposition temperature range of the complexes is in 513-613-1073 K, which is obviously larger than the ligand. It can be deduced that the stability of the complexes exceeds the ligand.

Data of X-ray for the ligand, salt and complexes									
Compound	X-ray powder diffraction data								
$Nd(NO_3) \cdot 4H_2O$	I/I ₀	100	80	80	20	20	8	6	
	d/nm	0.8870	0.5860	0.5460	0.3560	0.2860	0.2570	0.2020	
$C_{10}H_{10}N_2O_4$	I∕I₀	100	82	73	61	56	55	46	
	d/nm	0.3601	0.3386	0.3684	0.5611	0.6321	0.5764	0.6021	
$La(C_{10}H_9N_2O_4)_3\cdot 2H_2O$	I/I ₀	100	39	27	25	21	20	14	
	d/nm	1.4666	0.7840	0.4175	0.4130	1.2167	0.5212	0.7286	
$Ce(C_{10}H_9N_2O_4)_3\cdot H_2O$	I/I ₀	100	27	28	23	21	13	9	
	d/nm	0.7878	1.2134	0.4156	0.3414	0.5218	0.2877	0.2390	
$Nd(C_{10}H_9N_2O_4)_3\cdot H_2O$	I/I ₀	100	39	30	24	21	13	11	
	d/nm	0.7810	1.1652	0.4107	0.3401	0.5157	0.2859	0.6878	
$Sm(C_{10}H_9N_2O_4)_3\cdot H_2O$	$I/I_0 \ d/nm$	100 0.8008	49 1.1906	45 0.7811	34 0.4180	24 0.3435	22 0.5292	15 0.6986	

 TABLE 4

 Data of X-ray for the ligand, salt and complexe

TABLE 5 Thermal decomposition for the complexes ($\beta = 5$ K/min)

	St	age I	Sta	age II	Stage III	
Complexes	Temp range (K)	Weight loss (%)	Temp range (K)	Weight loss (%)	Temp range (K)	Weight loss (%)
C ₁₀ H ₁₀ N ₂ O ₄	$303 \sim 440$	19.38(19.80)	$440 \sim 504$	25.76(25.28)	$504 \sim 583$	20.85(19.80)
$La(C_{10}H_9N_2O_4)_3 \cdot 2H_2O_4$	$313 \sim 519$	4.21(4.29)	$519 \sim 613$	29.78(30.03)	$613 \sim 1073$	44.69(46.07)
$Ce(C_{10}H_9N_2O_4)_3 \cdot H_2O$	$313 \sim 521$	2.20(2.19)	$521 \sim 616$	28.86(30.66)	$616 \sim 1073$	46.89(47.08)
$Nd(C_{10}H_9N_2O_4)_3 \cdot H_2O$	$313 \sim 510$	2.15(2.17)	$510 \sim 615$	29.32(30.43)	$615 \sim 1073$	45.43(46.38)
$Sm(C_{10}H_9N_2O_4)_3 \cdot H_2O$	$313 \sim 515$	2.18(2.16)	$515 \sim 614$	28.43(30.29)	$614 \sim 1073$	47.63(46.15)
$Eu(C_{10}H_9N_2O_4)_3 \cdot H_2O$	$313 \sim 519$	2.19(2.16)	519~616	29.07(30.21)	$616 \sim 1073$	47.44(46.40)
$Gd(C_{10}H_9N_2O_4)_3 \cdot H_2O$	$313 \sim 514$	2.17(2.15)	$514 \!\sim\! 617$	31.23(30.04)	617~1073	46.03(46.13)

According to TG-DTG experiment data of the complexes, apparent activation energies of the second thermal decomposition stage were calculated by Kissinger's method.^[18]

The different heating rate (β) and corresponding peak temperature value (T_p) on DTG curve were substituted into Eq. (1):^[17]

$$\frac{d\ln(\beta/T_P^2)}{d(1/T_P)} = -\frac{E}{R}$$

Viz.

$$\ln(\beta/T_p^2) = \frac{E}{R}\frac{P}{T_P} + C \tag{1}$$

Apparent activation energies E were calculated by leastsquares method fitting in the computer. The decomposition peak temperature value T_p , slope (-ER), the linear correlation coefficient r and apparent activation energies E are listed in Table 6.

The plot of apparent activation energies of the second thermal decomposition stage for the six complexes versus atomic number of the corresponding rare earth element is shown in Figure 2. It can be seen from Figure 2 that the correlation between the apparent activation energies and the rare earth atomic number is monotonic increasing and divided into two curves, as if the front two groups of "quadripartite effect".^[19]

111	e second decompos	sing detrivate	chergy of con	npienes	
Complexes	$\beta/\mathrm{K}\cdot\mathrm{min}^{-1}$	T_P/K	E/R	r	$E/kJ \cdot mol^{-1}$
$La(C_{10}H_9N_2O_4)_3 \cdot 2H_2O_4)_3$	5.00	592.45	-10.515	-0.9995	87.43
	10.00	599.15			
	15.00	602.75			
$Ce(C_{10}H_9N_2O_4)_3 \cdot H_2O$	5.00	590.65	-13.592	-0.9910	113.0
	10.00	594.75			
	15.00	598.65			
$Nd(C_{10}H_9N_2O_4)_3 \cdot H_2O$	5.00	592.75	-16.911	-0.9848	140.6
	10.00	595.85			
	15.00	599.25			
$Sm(C_{10}H_9N_2O_4)_3 \cdot H_2O$	5.00	594.65	-20.291	-0.9999	168.7
	10.00	597.55			
	15.00	599.95			
$Eu(C_{10}H_9N_2O_4)_3 \cdot H_2O$	5.00	594.65	-27.786	-0.9916	231.1
	10.00	597.55			
	15.00	598.55			
$Gd(C_{10}H_9N_2O_4)_3 \cdot H_2O$	5.00	596.35	-32.860	-0.9332	273.2
	10.0	597.35			
	15.00	599.5			

TABLE 6 The second decomposing activate energy of complexes



FIG. 2. Apparent activate energy versus atomic number.

CONCLUSION

For the six new complexes $\text{RE}(\text{C}_{10}\text{H}_9\text{N}_2\text{O}_4)_3 \cdot \text{nH}_2\text{O}(\text{RE} =$ La, Ce, Nd, Sm Eu, Gd), three carboxyls in each complex are coordinated in the form of one dentate. The lanthanide ion is coordinated by three N atoms (C==N) and seven O atoms from one water and three tridentate ligands that coordinated via keto-form to form three stable five-membered rings. All the complexes exhibit excellent fluorescence properties at 408 nm. The thermal decomposition process of the complexes can be divided into three stages. The apparent activation energies increase along with rare earth atomic number increases, showing that the thermal stability of the complexes has the same enhancing tendency as rare earth atomic number increases. The correlation between the apparent activation energies and the rare earth atomic number shows a grouping effect of the lanthanide elements.

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