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RESEARCH ARTICLE

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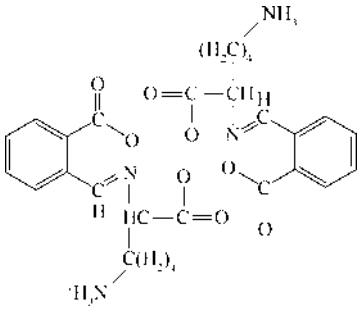
Synthesis and characterization of rare earth complexes with Phthalaldehyde-lysine Schiff base

Abstract Ten new rare earth complexes with Schiff base (HL) derived from phthalaldehyde with two –CHO groups and lysine, which has unsymmetrical α-and ε- $-NH_2$ groups, were synthesized and characterized by elemental analysis, TG-DTA analysis, UV–Vis, IR, and ^{1}H NMR spectra. They were confirmed to be as $LnL_2(NO_3)\cdot 4H_2O$ (Ln=La, Pr, Nd, Sm, Y) and $LnL_2(NO_3)\cdot 3H_2O$ (Ln=Gd, Tb, Dy, Er, Yb), respectively. Furthermore, their coordination mechanism, spectral properties and probable molecular structures were also discussed.

Keywords phthalaldehyde**,** lysine**,** rare earth metal, Schiff bases, complexation

Amino acid Schiff base containing O and N atoms is one of the important biological ligands, but the majority of the complexes with them studied are limited to transition elements. Some reported that rare earth complexes exhibit practical use in medicine, antiseptic, feedstuff, fertilizer [1], etc. and also show some interesting biological properties, such as less toxicity and anticancer activities [2, 3]. Lanthanide complexes with β-amino acid Schiff base synthesized in our group were shown to possess catalytic activity for polymerization [4]. Ten new rare earth complexes with Schiff base (HL) derived from phthalaldehyde possessing two –CHO groups and lysine, which has unsymmetrical α- and ε- $-NH_2$ groups [5, 6], were synthesized. Furthermore, their components, molecular structures (Scheme 1), coordination mechanism, and properties were also investigated. The force constants of rare earth ions with O or N atoms were determined in order to discuss the coordination bonds.



Scheme 1

1 Experimental

1.1 Materials and apparatus

Purity of $Ln_2O_3 \geqslant 99.9\%$. Lanthanide nitrates were prepared by dissolving Ln_2O_3 in nitric acid and removing the excess acid. Lysine: chromatographically pure, Shanghai Chemical Reagent Co.; ortho-phthalaldehyde and other reagents used were of A.R.

C, H, N content was measured on a Carlo-Erba analyzer, while Ln^{3+} was titrated by EDTA; The molar conductivities of complexes in DMF (10^{-3} M) were run on a DDS-12A conductometer at 293K; TG-DTA and UV-Vis spectra were taken on a PCT-1 thermal analyzer and Beckman DU-50 ultraviolet spectrograph, respectively; IR spectra and FIR spectra were run on a Shimadzu IR-470 spectrometer (4000–400 cm^{-1}) and PE-683 spectrometer (800–200 cm^{-1}) with KBr discs, respectively; ^{1}H NMR spectra of the Schiff base ligand and its complexes were recorded on a JEOL Fx-90Q NMR spectrometer.

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1.2 Synthesis of complexes

Lysine (2 mmol) was dissolved and refluxed in anhydrous ethanol, some insoluble yellow trace residue was filtered off, while a solution of methanol containing 2 mmol of ortho-phthalaldehyde was added dropwise at 40°C with stirring over 1 h and a deep red solution was obtained. Then, an ethanol solution containing 1 mmol rare earth nitrate was added dropwise into the solution, yellow or brown complex precipitates were isolated and filtered, washed by cold ethanol and dried in vacuo with P_2O_5. Reaction yield was about 60%–70%.

2 Results and discussion

2.1 Composition and properties of the complexes

Table 1 summarizes the elemental analysis and molar conductivities of the complexes. The analytical data presented in Table 1 indicate that they were confirmed to be $LnL_2(NO_3)\cdot 4H_2O$ (Ln = La, Pr, Nd, Sm, Y) and $LnL_2(NO_3)\cdot 3H_2O$ (Ln = Gd, Tb, Dy, Er, Yb) respectively, L = $C_{14}H_{17}N_2O_4$; The stoichometry of L with metal to be 1:2. The complexes are insoluble in alcohol, chloromethene, acetone, and ether, but soluble in DMF and DMSO. Their molar conductivities in DMF imply that the complexes are nonelectrolytes [4], and the NO_3^- is coordinated.

2.2 TG-DTA analysis

TG-DTA were performed on the complexes of $LaL_2(NO_3)\cdot 4H_2O$ and $DyL_2(NO_3)\cdot 3H_2O$ respectively. A heat-absorbing broad peak appeared on the thermal-gravity curve of the complexes before 256°C and the TG-DTA curves of the complexes show that the dehydrations occurred before ca. 104°C, which corresponds to loss of three molecules of uncoordinated water 6.46% (6.53%) in $LaL_2(NO_3)\cdot 4H_2O$ and 6.33% (6.34%) in $DyL_2(NO_3)\cdot 3H_2O$, respectively. After heat liberation occurred at 471°C and 493°C with 79.23% (Anal. calcd. 80.31%) and 76.63% weight loss (Anal. calcd. 77.61%), respectively, the corresponding metal oxides were formed. According to the TG-DTA, the final decomposition temperature of $DyL_2(NO_3)\cdot 3H_2O$ is higher than that of $LaL_2(NO_3)\cdot 4H_2O$, which implies that the heavier lanthanide complexes are more thermostable than those of the lighter complexes, i.e., the thermal stability of the complexes increases with the lanthanide contraction; it is due to the different binding strengths between coordinated atoms.

2.3 UV-Vis spectra of the complexes

The UV spectra of the solution of the Schiff base condensed from phthalaldehyde and lysine, and its complexes of La, Nd, and Gd were measured in methanol (~10^{-5} mol·L^{-1}), respectively.

The electronic transition of the phenyl group of the Schiff base was influenced by the chromophoric group >C=N, its bands E_2, B are 207.0 nm and 239.5 nm, respectively, while the band at 329.0 nm can be assigned to the $\pi\rightarrow\pi^*$ transition of the >C=N group. After coordination, the bands of $NdL_2(NO_3)\cdot 4H_2O$ shifted to 205.0 nm, 238.5 nm, and 323.5 nm, while the bands of $GdL_2(NO_3)\cdot 3H_2O$ shifted to 205.0 nm, 238.0 nm, and 323.0 nm, respectively. Some blue shift was observed at 323.0 nm in the complexes as compared with the ligand. This is because the imine nitrogen atom is coordinated to the central metal, then the electron cloud density at $-NH_2$ group decreased and the transition energy lever increased, namely, the formation of complexes with Schiff base.

Vis spectra of $NdL_2(NO_3)\cdot 4H_2O$ (3) and $ErL_2(NO_3)\cdot 3H_2O$ (8), were measured in DMSO and some data are given in Table 2. The ε of the complex (3) at 583.0 nm, 523.0 nm and the complex (8) at 522.5 nm are much larger than corresponding aquo ions, which indicates that hypersensitive transition has occurred [7].

Table 1 Elemental analysis and molar conductivity of complexes

Complex	Ln%	C%	H%	N%	Λ S • cm^2 • mol^{-1}
$LaL_2(NO_3)$ • $4H_2O$ (1)	16.83(16.78)	40.32(40.63)	4.80(5.07)	8.93(8.46)	43
$PrL_2(NO_3)$ • $4H_2O$ (2)	16.91(16.99)	40.60(40.54)	4.97(5.06)	8.74(8.44)	47
$NdL_2(NO_3)$ • $4H_2O$ (3)	17.16(17.32)	40.01(40.38)	4.53(5.04)	8.64(8.40)	45
$SmL_2(NO_3)$ • $4H_2O$ (4)	17.89(17.90)	40.18(40.04)	4.46(5.00)	8.76(8.34)	45
$GdL_2(NO_3)$ • $3H_2O$ (5)	18.71(18.99)	40.57(40.62)	4.72(4.87)	8.72(8.46)	61
$TbL_2(NO_3)$ • $3H_2O$ (6)	18.87(19.16)	40.59(40.53)	4.13(4.86)	8.56(8.44)	62
$DyL_2(NO_3)$ • $3H_2O$ (7)	19.14(19.51)	40.34(40.36)	4.44(4.83)	8.91(8.40)	60
$ErL_2(NO_3)$ • $3H_2O$ (8)	20.18(19.96)	40.06(40.14)	4.18(4.81)	8.48(8.36)	56
$YbL_2(NO_3)$ • $3H_2O$ (9)	20.14(20.51)	39.11(39.86)	4.78(4.77)	8.61(8.30)	62
$YL_2(NO_3)$ • $4H_2O$ (10)	11.65(11.43)	42.97(43.25)	4.98(5.40)	9.14(9.00)	42

* Data in parentheses are calculated results.

Table 2 UV absorption peaks of $NdL_2(NO_3)\cdot 4H_2O$ and $ErL_2(NO_3)\cdot 3H_2O$

	Transition	Complex			Ln^{3+}(aq)			$P_{complex}$ ($\times 10^6$)	P_{free} ($\times 10^6$)	$P_{complex}/P_{free}$	$b^{1/2}$	δ
		λ_{max}	A	ε	λ_{max}	A	ε					
$Nd^{3+}_{(aq)}$ and (3)	$^4I_{9/2}\rightarrow{}^4G_{7/2}$, $^4G_{9/2}$	523.0	0.726	39.89	524.0	0.045	2.473			*		
	$^4I_{9/2}\rightarrow{}^4G_{5/2}$,$^2G_{7/2}$	583.0	0.568	32.21	581.0	0.140	7.69	3.70	0.360	10.30	0.0412	0.3412
	$^4I_{9/2}\rightarrow{}^4F_{3/2}$, $^4S_{2/2}$	746.0	0.166	9.12	748.0	0.113	6.209	0.949	0.393	2.42		
$Er^{3+}_{(aq)}$ and (8)	$^4I_{15/2}\rightarrow{}^4F_{5/2}$, $^4F_{7/2}$	484.5	3.689	263.4	487.0	0.018	1.295	3.67	0.229	16.03		
	$^4I_{15/2}\rightarrow{}^4S_{3/2}$,, $^2H_{11/2}$	522.5	1.902	135.0	520.0	0.058	4.172	–	–	–	0.0490	0.4823

The oscillator strength P[A1] can be used for describing the absorption intensity of the bands [8].

$$P = 4.31\times 10^{-9}\left[\frac{9\eta}{\left(\eta^2+2\right)^2}\right]\int \varepsilon_i(\tilde{\nu})\,\mathrm{d}\tilde{\nu} \quad (1)$$

Experimental oscillator strengths were obtained by the area under the absorption curve after appropriate correction for the base line when $\eta = 1.478$ in DMSO solvent. From the value of $P_{complex}/P_{free}$, we know that the oscillator strength of a complex is larger than that of the free ion, indicating the formation of complex with Schiff base.

The nephelauxetic ratio β [A1] values can be obtained from Eq. (2):

$$\beta = \frac{\overline{\nu}_{compl}}{\overline{\nu}_{Nd_{aq}^{3+}}}, \qquad \beta = \frac{\overline{\nu}_{compl}}{\overline{\nu}_{Er_{aq}^{3+}}}, \quad (2)$$

According to nephelauxetic ratio β values 0.9966 and 0.9952 at $^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$ and $^4I_{15/2}\rightarrow{}^4S_{3/2}$, $^2H_{11/2}$ transitions, respectively, the bonding parameter $b^{1/2}$ and δ were calculated and tabulated. It is obvious that the value β increased or $b^{1/2}$ decreased with the decrease of the covalent degree of the coordinating bond [8]. As we know from the above $b^{1/2}$ value, the covalent degree of the coordinating bonds between the complex and ligand is weaker for the attending 4f bonding orbital, which agrees with the corresponding results of FIR.

2.4 IR spectra of the complexes

All IR spectra of the complexes are quite similar to one another, implying that the structures of all complexes are presumed to be also similar. IR spectra of the ligand derived from phthalaldehyde and lysine and its complexes with La, Nd, Gd, Dy, Y in the 4000–400 cm^{-1} range are listed in Table 3.

Free lysine presents as an inner salt $H_3N^+(CH_2)_4OH(NH_2)COO^-$, its spectra show $-NH_3^+$ and $-COO^-$ characteristic absorption peaks. The differences between antisymmetric vibration frequencies and symmetric vibration frequencies in the above complexes, $\Delta\upsilon$ are: 198 cm^{-1}, 197 cm^{-1}, 198 cm^{-1}, 210 cm^{-1}, and 205 cm^{-1}, respectively, implying that likely the $-COO^-$ group in the lysine coordinated to lanthanide ions as monodentate, while $-NH_3^+$ characteristic peak still retained in the complex.

From the IR spectra of *o*-phthalaldehyde, two weak frequencies observed at 2850 cm^{-1} and 2751 cm^{-1} are assigned to the υ_{CH} characteristic absorption. It is due to the Fermi resonance effect arising from the double-frequency between υ_{CH} and δ_{CH} and 1670 cm^{-1} is attributed to the absorption of $\upsilon_{C=O}$ band. From the IR spectra of the ethanol solution of *o*-phthalaldehyde and lysine, $-NH_3^+$ and $\upsilon_{C=N}$ at 1640 cm^{-1} could be observed. They are characteristic bands apparently

Table 3 IR absorption peaks of complexes (cm^{-1})

Complex	$\nu_{NH_3^+}$		COO^-		$\nu_{>C=N}$	$\nu_{NO_3^-}$				ν_{OH^-}
	υ_{as}	υ_s	υ_{as}	υ_s						
HL*	**	2530	1530	1400	1640					3 100–3 500
$LaL_2(NO_3)\cdot 4H_2O$	3080	2540	1605	1413	1650	1520	1030	1310	820	3410
$NdL_2(NO_3)\cdot 4H_2O$	3080	2560	1605	1411	1648	1521	1033	1305	816	3410
$GdL_2(NO_3)\cdot 3H_2O$	3085	2561	1609	1407	1647	1516	1034	1315	825	3405
$DyL_2(NO_3)\cdot 3H_2O$	3085	2510	1607	1411	1650	1454	1031	1297	813	3408
$YL_2(NO_3)\cdot 4H_2O$	3080	2535	1615	1410	1645	1510	1034	1306	825	3400

*HL-The solution of the ligand derived from phthalaldehyde and lysine; **An overlapping ν_{OH^-} broad peak

Table 4 Far-infrared spectra (cm^{-1}) and bond force constants *f* (N/cm) of the complexes

The complex	Ln-O				Ln-N					
	υ	*f*	υ	*f*	υ	*f*	υ	*f*	υ	*f*
$NdL_2(NO_3) \cdot 4H_2O$	410	1.427	475	1.921	215	0.3476	230	0.3977	250	0.4699
$YbL_2(NO_3) \cdot 3H_2O$	410	1.453	475	1.950	210	0.3366	235	0.4215	250	0.4770
$YL_2(NO_3) \cdot 4H_2O$	410	1.345	480	1.840	220	0.3450	230	0.3771	250	0.4455

due to the formation of Schiff base in solution. Owing to its high solubility, the solid Schiff base could not be isolated easily. The $\upsilon_{C=N}$ shifted from 1640 cm^{-1} to 1645–1650 cm^{-1}, while υ_{CH} and $\upsilon_{C=O}$ of *o*-phthalaldehyde disappeared in the IR spectra of the complex, indicating the formation of Ln-N coordination band in the complex.

Uncoordinated NO_3^- (D_{3h}) peaks disappeared in the IR spectra of the complexes, its $\Delta\upsilon = |\upsilon_1 - \upsilon_4| \approx 200$ cm^{-1} showing that the NO_3^- ion is in the form of bidentate coordination.

The band at ~3400 cm^{-1} may be assigned to υ (O—H) stretching one, which means that there are some water molecules in the complex, while the characteristic peaks of coordinated water appeared at 600 cm^{-1} and 870 cm^{-1} in the lighter rare earth and Y complexes, respectively.

2.5 Far-infrared spectra

Nd, Yb, and Y complexes were chosen for the FIR analysis, and the results are listed in Table 4. The force constants (*K*) of Ln-O and Ln-N were calculated according to the equation of $\upsilon = \frac{1}{2\pi C}\sqrt{\frac{K}{\mu}}$, derived from Hooke's law, where the υ is wave number (cm^{-1}), while μ and *C* are reduced mass and velocity of light, respectively. Table 4 shows that the force constants of the heavier rare earth complexes are greater than those of lighter rare earths, but both Ln-O and Ln-N bonds are weak, which represents that the bond of rare earth ion between coordinated atoms is static attraction.

2.6 ^{1}H-NMR spectra

The ^{1}H-NMR spectra for La(III) complex were measured in the deuterated DMSO solvent using TMS as an internal standard at 28°C. From the standard spectrum of the *o*-phthalaldehyde, it is known that δ_H = 10.51 ppm is assigned to the proton of the —CHO group, while δ_H for the azomethine groups (—CH=N—) in the complex appeared at 8.10 ppm. This highfield shift is due to the fact that electronegativity of the O atom is higher than that of the N atom, the electronegativity of the neighboring atom decreases with the increase of the surrounding electron cloud density of the hydrogen nucleus and the shielding effect. which results in a highfield shift for δ_H. From the ^{1}H-NMR standard spectrum of lysine, we know that the electron cloud density of H atom at α–CH group is decreased after coordination with lanthanide ion on α-N atom of imine. It will increase the deshielding effect and result in δ_H of α-CH downfield shift to 4.36 ppm from 3.29 ppm. In the range of δ=8.10 ppm to 17 ppm, the absorption peaks of the —CHO and free –COOH groups were not observed, implying the absence of any protons of —CHO and free —COOH groups. The ratio of integral areas of H atom signals for ArH, —CH=N—, —CH and $-CH_2$ groups is 4:1:1:8, which is in line with the theoretical predication of the proton ratio in the ligand. It confirms the presence of the corresponding Schiff base groups in the complex.

According to the interesting expectation, whether it will be able to synthesize unsymmetrical Schiff base derived from *o*-phthalaldehyde and lysine directly, the above results are obvious that only a single Schiff base could be obtained in such experimental conditions due to space hindrance of ortho-position —CHO groups and large volume of lysine. We presume that in the present case, the single Schiff base derived from one of the —CHO groups and α-NH_2 group in lysine was synthesized and coordinated with the lanthanide ion to form a five-ring compound. The other —CHO group was oxidized to carboxylic acid due to its instability and space hindrance. According to the results obtained, it is believed that the coordination numbers of the lighter lanthanides and yttrium complexes are nine due to one water molecule being contained, but the coordination numbers of heavier lanthanide are eight under the condition of that there are six donated atoms from two ligands and two from bidentate nitrate group. Certainly, it remains to be proven.

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