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SYNTHESIS AND CHARACTERIZATION OF RARE EARTH COMPLEXES WITH BENZENE-1,3,5-TRICARBOXYLIC ACID

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ABSTRACT

Benzene-1,3,5-tricarboxylic acid (TMA) and its mononuclear rare earth complexes were synthesized and characterized by elemental analysis, TG-DTA, IR, fluorescence spectroscopy and X-ray powder diffraction analysis. It was shown that the three-coordinated rare earth ion is the central ion and located in the centre of a ligand basket forming the clathrate solid compound.

INTRODUCTION

Benzene-1,3,5-tricarboxylic acid is a tribasic aromatic carboxylic acid (H_3L). It has been used extensively as a catalytic agent for chemical reactions and as an additive agent for food[1,2]. Gao et al.[3-5] used it, for the first time, as a fluorescence ligand for the determination of terbium in aqueous solution and obtained

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satisfactory results. Compounds similar to TMA, such as benzene-1,2,4,5-tetracarboxylic acid[6] and benzene-1,4-dicarboxylic acid[7], are also excellent fluorescence ligands. However, except for the studies of the properties of the rare earth solid complexes of compounds similar to TMA,[8,9] to our knowledge, the synthesis and studies on the fluorescence properties of solid complexes of rare earth ions with TMA have not been reported yet. In this paper, solid complexes of rare earth ions with TMA, RE(L)$\cdot H_2O$, were prepared. The results show that the ligand can sensitize the fluorescence of Tb^{3+}, Eu^{3+} and Dy^{3+}. Other rare earth complexes emit only ligand fluorescence.

EXPERIMENTAL

Apparatus

Elemental analysis of C, H and N was carried out on a Perkin Elmer 2400 analyzer. The concentration of rare earth ions was determined by EDTA titration, using xylenol orange as indicator. IR spectra were recorded in the region 300~4000 cm^{-1} on an Alpha Centauri FT-IR instrument using KBr pellets. Fluorescence spectra were recorded with a Shimaduz RF-540 Spectrofluorimeter equipped with a xenon light source. A Shimaduz DT-40 analyzer was used for the TG-DTA analyses in the range from room temperature to 1000° C with a heating rate of $5^\circ C\cdot min^{-1}$ under N_2 atmosphere. The diffraction spectra were obtained with a D/MAX-C X-ray diffractometer with a scan rate of $3^\circ\cdot min^{-1}$ in the 2θ range of 0~60°.

Reagents

All reagents used in this paper were analytical reagent grade. The purity of rare earth oxides was more than 99.95%. The stock alcohol solutions of lanthanide ions ($0.1\ mol\cdot l^{-1}$) were prepared according earlier references.[3,4]

Synthesis of Ligand, TMA

The methods[10-12] used for the synthesis of aromatic carboxylic acids using methylbenzenes were modified because of the toxicity and volatility of methylbenzenes. The stirrer was replaced by short glass tube and solid potassium

Table I. The Results of Elemental Analyses for RE(L)·H_2O Complexes

Formula[a] and formula weight	Colour and appearance	%C		%H		%RE		Yield (%)	Melting point (℃)
		Found	Calc.	Found	Calc	Found	Calc.		
TMA $C_9H_8O_7$ 228.0	white powder	51.39	51.43	3.78	3.79			78	378-380
La(L)·H_2O 363.9	white powder	29.66	29.68	1.34	1.37	37.84	38.17	92.4	411.0
Ce(L)·H_2O 365.1	yellow powder	29.61	29.58	1.38	1.37	38.01	38.38	91.7	412.4
Pr(L)·H_2O 365.9	green powder	29.63	29.52	1.33	1.37	38.30	38.51	94.4	414.2
Nd(L)·H_2O 369.2	violet powder	29.43	29.25	1.33	1.35	38.79	39.06	90.7	414.9
Sm(L)·H_2O 375.4	white powder	28.81	28.77	1.35	1.33	40.23	40.06	96.0	416.3
Eu(L)·H_2O 377.0	white powder	28.44	28.65	1.29	1.33	40.12	40.31	98.3	418.4
Gd(L)·H_2O 382.3	white powder	28.03	28.25	1.37	1.31	41.09	41.38	95.2	420.2
Tb(L)·H_2O 383.9	white powder	28.27	28.13	1.34	1.30	41.12	41.39	93.0	421.7
Dy(L)·H_2O 387.5	white powder	27.92	27.87	1.35	1.29	41.74	41.94	94.1	423.1
Ho(L)·H_2O 389.9	white powder	27.82	27.69	1.26	1.28	42.01	42.30	89.4	425.4
Er(L)·H_2O 392.3	pink powder	27.64	27.53	1.26	1.28	42.37	42.64	94.2	426.9
Tm(L)·H_2O 393.9	white powder	27.61	27.42	1.29	1.27	42.67	42.88	91.7	429.7
Yb(L)·H_2O 398.0	white powder	27.01	27.14	1.27	1.26	43.12	43.47	92.4	431.1
Lu(L)·H_2O 400.0	white powder	27.19	27.00	1.31	1.25	43.63	43.75	93.1	432
Y(L)·H_2O 313.9	white powder	34.29	34.41	1.63	1.59	28.09	28.32	93.4	407.8

[a] The empirical formula for all complexes is $REC_9H_5O_7$.

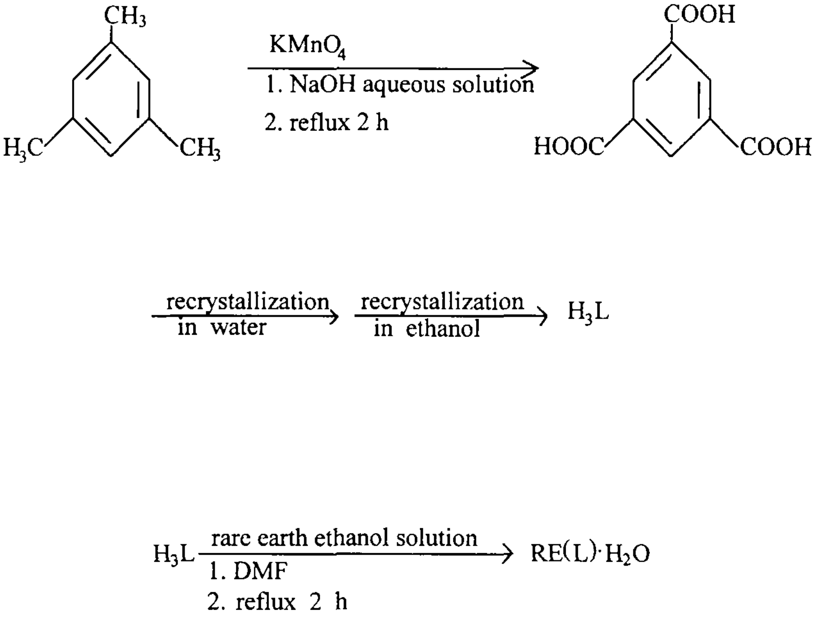

Fig. 1. Synthetic Scheme for TMA and RE(L)·H_2O

permanganate was substituted for its aqueous solution. The three-necked flask was sealed well except for the top of the condenser. The reported yield according to the published method[10-12] was 58.7% and it was improved to 78.0% by our modified method. TMA was recrystallized four times with alcohol and its purity, 98.6%, was checked by pH titration and elemental analysis. The elemental analysis agreed with the formula $C_6H_3(COOH)_3 \cdot H_2O$ and the results were listed in Table I.

Preparation of the Complexes

A 0.01 mol solution of TMA in 40 mL of DMF was placed into a 100 mL three-necked flask fitted with a condenser, dropping funnel and magnetic stirrer, and the DMF solution was heated to boiling. In the course of 1 h, 10 mL of a 0.1 molor solution of $TbCl_3$ in alcohol was added dropwise, and the reaction mixture was refluxed for 2 h. After the mixture had cooled to room temperature for 1 h, a precipitate was obtained. The precipitate was filtered, washed with alcohol, and dried over diphosphorus pentaoxide in a vacuum drier at room temperature for 4~5 d. The yield was 3.4 g (93.0%). Other rare earth solid complexes were synthesized by a similar method. The ligand and all complexes were characterized by elemental analyses, TG-DTA, IR, fluorescence spectroscopy and X-ray powder diffraction analysis. However, NMR spectral studies and conductance measurement could not be carried out due to the insolubility of the complexes in most of the common organic solvents as well as water.

RESULTS AND DISCUSSION

Compositions of the Complexes

The complexes do not dissolve in the common solvents. No chloride ion was found in the complexes. The elemental analytical results shown in Table I are consistent with the formulas of the complexes. These compositions were also confirmed by TG-DTA analyses. Based on these data, the formulas RE(L)·H_2O, for all rare earth complexes were obtained. The synthetic scheme for the ligand and its complexes is shown in Fig. 1.

Infrared Spectra

Two strong bands at 930 cm^{-1} and 1685 cm^{-1}, respectively, as well as a broad band between 2500 cm^{-1} and 3200 cm^{-1} for the ligand show that three carboxyl groups exist in a form of associated hydrogen bonds. As the ligand coordinates with rare earth ions, the bands at 930 and 2500~3200 cm^{-1} disappear. The results indicate that the associated hydrogen bonds of the ligand disappear. The band of the ligand at 1685 cm^{-1} is shifted to lower frequency by 69.4 cm^{-1} and appears at 1616 cm^{-1} for the complexes. The variation of the frequency for this band between ligand and the complexes is very characteristic for the formation of a coordinate linkage of the oxygen atom of the hydroxyl group of the carboxyl group with the metal ion. Furthermore, a strong band at 430.4 cm^{-1} is assigned to (M—O) stretching, which proves that coordination occurs via the oxygen atoms of -COO^- groups.

Fluorescence Spectra

The continous variation method for aqueous solutions of the Tb(L)·H_2O were carried out. It was shown that the maximum fluorescence intensity appeared at pH

5.5 for the complex in solution. When a solution of the ligand was added to a solution of $TbCl_3$ (4.0×10^{-4} mol·L^{-1}) at pH 5.5, the fluorescence intensity increased in the beginning, and reached a maximum at the molar ratio of 1 to 1, which means the formation of the same complex of 1:1 molar ratio as that in the solid state. Excess of ligand solution led to a decrease in the fluorescence intensity due to the quenching of the excited state of the complex by collision with the excess ligand coexisting with the complex in solution. Similar results were obtained for complexes of the ligand with Eu^{3+} and Dy^{3+}, respectively.

The excitation and emission spectra for the solid rare earth complexes were obtained. All the emission bands of the complexes belong to the characteristic emission of Tb^{3+}, Eu^{3+} and Dy^{3+} ions and are sensitized fluorescence bands. However, the characteristic emission of Sm^{3+} does not appear. It is shown that the energy level of the triplet state of the ligand does not match that of the lowest excited singlet state and non-radiative deactivation occurs. Only sensitized ligand fluorescence was observed. All other rare earth complexes emit ligand fluorescence.

Results of XRD

The X-ray powder diffraction patterns of TMA and its rare earth solid complexes were recorded in the range of 0 ~ 60° and the results for TMA, Tb-TMA and Sm-TMA are shown in Fig. 2. The results indicate that the diffraction position (2θ) and relative intensity (I/I_0) for TMA are totally different from that of the rare earth complexes with TMA. That is to say, TMA and its rare earth solid complexes are different in structure. The diffraction positions (2θ) and relative intensities (I/I_0) not only for the RE-TMA solid complexes shown in Fig. 2, but also for those not in Fig. 2 are very similar as they are of the same structure.

Thermal Decomposition Mechanism

The thermal decomposition process of these rare earth solid complexes was investigated using TG and DTA techniques with Al_2O_3 as a reference, at a heating rate of 5° C·min^{-1} in a flowing nitrogen atmosphere. The analytical results further confirm the number of water molecules in the rare earth complexes. The results also indicate that the thermal decomposition processes of all these solid complexes are similar and consist of a dehydration process, a thermal melting process and a relatively acute exothermic decomposition process. All the complexes are stable below 109° C. One water molecule is

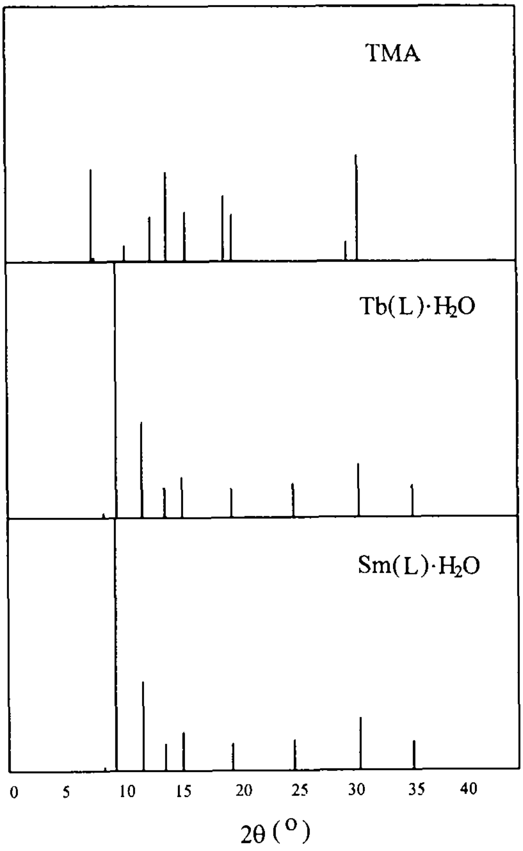

Fig. 2. X-ray Diffraction Patterns of TMA and Its Tb(III) and Sm(III) Complexes

removed in the temperature range of 109~123° C in a single step. The observed weight loss is found to be in the range of 4.5~6.0% for the rare earth complexes as against the calculated weight loss in the range 4.7~6.1% from La(L)·H_2O to Y(L)·H_2O. The DTA curves of the complexes show an endothermal peak between 411~432° C, but there is no weight loss in the TG curves. Thus, the endothermal peaks indicate the melting processes of the complexes. Up to 617.4° C, weight loss in the TG curve as well as an exothermal peak are observed, which correspond to the decomposition of the complexes. The final,

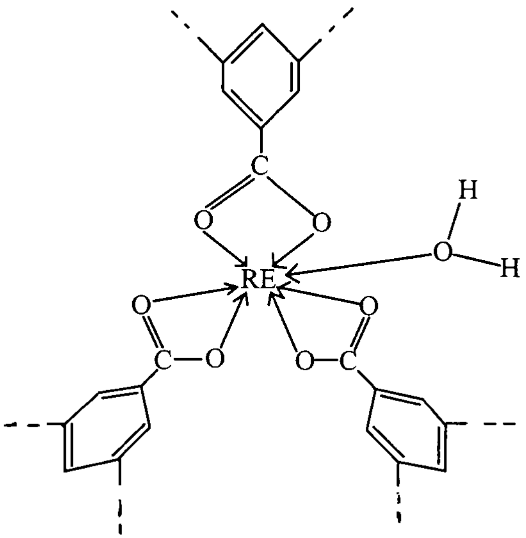

Fig. 3. Suggested Structure of the Complexes

thermally stable residues above 989° C are the rare earth oxides (Found: 37.9~51.3%, calc.: 38.2~52.1%).

Suggested Structure of the Complexes

The results of X-ray powder diffraction analyses indicate that all the rare earth complexes with TMA have the same structure. The coordination number 7 can be calculated from the formula, RE(L)·H_2O, the ligand forming three four-membered rings. This structure should not be stable according to the general principles of coordination chemistry, however, the title complexes are very stable, not only in aqueous solution but also in the solid state and their compositions do not vary in different environments. These facts indicate that the title complexes have a structure different from common complexes. Based on the experimental results, a stereoscopic net complex structure is suggested. That is to say, a polymeric formulation structure is formed by each lanthanide coordinated to carboxylate groups from different benzene-1,3,5-tricarboxylic acids. Every rare earth ion is surrounded by different TMA molecules and every TMA molecule is surrounded by different rare earth ions. This kind of structure is advantageous for the energy transfer from the excited ligand to the central metal ion. Thus, the strong fluorescence sensitized by the excited ligand was obtained for the Tb^{3+}, Eu^{3+} and Dy^{3+} complexes, respectively. The suggested structure of the complexes is shown in Fig. 3.

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