

## Complexes of Rare-Earth Metals with Meconic Acid

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Two series of complexes of meconic acid ( $H_3Mec$ ) with rare-earths have been prepared by varying the preparative procedure. The compounds have the general formulae,  $[Ln(Mec)(H_2O)_2] \cdot 3 H_2O$  (where  $Ln = La, Ce, Pr, Nd, Sm, Ho$  and  $Y$ ) and  $[Ln(HMec)(H_2Mec)(H_2O)_2] \cdot 4 H_2O$  (where  $Ln = La, Pr, Nd$  and  $Sm$ ). The infrared spectral data indicate that the carboxylate groups are bound to the rare-earth metal in a bidentate fashion. Thermal studies indicate that two water molecules are coordinated in each case. The complexes are probably polymeric.

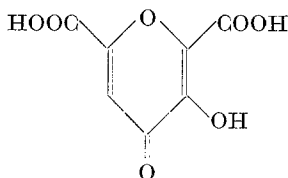
(Keywords: IR; Meconic acid; Rare earth complexes; Thermal studies)

### Komplexe von Seltenerd-Metallen mit Meconsäure

Es wurden zwei Reihen von Komplexen der Meconsäure ( $H_3Mec$ ) mit Seltenerd-Metallen mit den allgemeinen Formeln  $[Ln(Mec)(H_2O)_2] \cdot 3 H_2O$  ( $Ln = La, Ce, Pr, Nd, Sm, Ho, Y$ ) und  $[Ln(HMec)_2(H_2Mec)(H_2O)_2] \cdot 4 H_2O$  ( $Ln = La, Pr, Nd, Sm$ ) hergestellt. Die IR-Spektren zeigen, daß die Carboxylat-Gruppen in zweizähliger Weise mit den Metallionen koordinieren; thermische Untersuchungen ergeben, daß in beiden Reihen jeweils zwei Wassermoleküle zusätzlich koordiniert sind. Die Komplexe weisen wahrscheinlich eine Polymerstruktur auf.

### Introduction

Meconic acid ( $H_3Mec$ ) is a monohydroxy dicarboxylic acid which has a number of sites capable of bonding to a metal. But hardly any metal compounds of meconic acid are known. The present paper deals with the preparation of lanthanide compounds with meconic acid and their investigation by means of infrared spectral studies and thermal analysis. Both 1:1 and 1:2



complexes can be obtained by employing different synthetic procedures. The lanthanide complexes of kojic acid<sup>1,2</sup> and dipicolinic acid<sup>3</sup> which bear some resemblance to meconic acid have been reported earlier. The rare-earth diiodosalicylates<sup>4</sup> and dithiodiacetates<sup>5</sup> have also been synthesised and reported earlier from this laboratory together with a discussion of the nature of bonding of the carboxylate group to the metal.

## Experimental

### Materials

Meconic acid was recrystallised from ethanol. The rare-earth chlorides were prepared by treating the oxides with aqueous HCl.

### Preparation of the Complexes

*Method I:* Meconic acid (1.5 g) was dissolved in ethanol. An ethanolic solution of the rare-earth chloride (0.5 g oxide) was added to it dropwise with stirring. The complex precipitated immediately. Stirring was continued for 5-10 min and then the complex was filtered. It was washed with ethanol, dried first in air and then over phosphorus pentoxide under reduced pressure.

Table 1. *Analytical data*

Compound	% Metal		% Carbon		% Hydrogen	
	Found	Calc.	Found	Calc.	Found	Calc.
La( <i>Mec</i> ) · 5 H <sub>2</sub> O	32.82	32.62	19.65	19.72	2.72	2.58
Ce( <i>Mec</i> ) · 5 H <sub>2</sub> O	32.95	32.78	19.88	19.68	2.63	2.58
Pr( <i>Mec</i> ) · 5 H <sub>2</sub> O	32.75	32.93	19.84	19.63	2.38	2.57
Nd( <i>Mec</i> ) · 5 H <sub>2</sub> O	33.80	33.47	19.23	19.47	2.51	2.55
Sm( <i>Mec</i> ) · 5 H <sub>2</sub> O	34.38	34.38	19.42	19.21	2.71	2.52
Ho( <i>Mec</i> ) · 5 H <sub>2</sub> O	36.15	36.49	18.90	18.59	2.78	2.43
Y( <i>Mec</i> ) · 5 H <sub>2</sub> O	23.85	23.65	22.73	22.36	3.20	2.93
La( <i>HMe</i> )( <i>H<sub>2</sub>Mec</i> ) · 6 H <sub>2</sub> O	21.50	21.58	26.48	26.09	2.93	2.64
Pr( <i>HMe</i> )( <i>H<sub>2</sub>Mec</i> ) · 6 H <sub>2</sub> O	21.93	21.81	25.68	26.00	2.52	2.63
Nd( <i>HMe</i> )( <i>H<sub>2</sub>Mec</i> ) · 6 H <sub>2</sub> O	22.35	22.24	25.70	25.87	2.88	2.62
Sm( <i>HMe</i> )( <i>H<sub>2</sub>Mec</i> ) · 6 H <sub>2</sub> O	23.00	22.95	25.82	25.64	2.29	2.59

*Method II:* Meconic acid (1.5 g) was dissolved in ethanol and an ethanolic solution of ammonia was added dropwise with stirring till all the meconic acid was precipitated as the ammonium salt. The ammonium salt was filtered, washed with a little ethanol and then dissolved in water. To this an aqueous solution of the rare-earth chloride (0.5 g oxide) was added dropwise with stirring. The precipitated complex was filtered, washed with water and then with ethanol. The complex was air dried and kept over phosphorus pentoxide under reduced pressure.

*Method III:* The rare-earth chloride and meconic acid, dissolved in ethanol, were mixed in 1:3 mole ratio. The precipitate formed was dissolved by adding dilute HCl drop by drop with stirring. The solution was filtered and the sides of the beaker containing the filtrate were scratched with a glass rod for about 10 min. The solution was kept overnight, when the complex precipitated in a fine crystalline form. The complex was washed with warm alcohol and dried over phosphorus pentoxide under reduced pressure.

#### *Analytical and Physical Methods*

The metal content in the rare-earth meconates was estimated by igniting them to the corresponding oxides at 1000°C. Carbon and hydrogen were estimated by micro-analytical methods. The analytical data are given in Tab. 1. The infrared spectra and the differential thermograms were obtained as described in a previous paper<sup>5</sup>.

### Results and Discussion

The synthetic procedures I and II gave the same compounds as was shown by chemical analysis and infrared spectral data. These compounds have the composition  $Ln(Mec) \cdot 5H_2O$ , where  $Ln = La, Ce, Pr, Nd, Sm, Ho$  and  $Y$ . Method III yielded compounds having the composition,  $Ln(HMec)(H_2Mec) \cdot 6H_2O$ , where  $Ln = La, Pr, Nd$  and  $Sm$ . The compounds are non-hygroscopic and stable in air. They are insoluble in water and common organic solvents.

Meconic acid is usually obtained as a hydrate. It can be dehydrated by heating at 100°C for about an hour. The dehydrated sample was used for recording the infrared spectrum. Meconic acid shows two strong absorptions at 1,695  $cm^{-1}$  and at 1,730  $cm^{-1}$  which nearly overlap with each other, and another at 1,640  $cm^{-1}$ . These absorptions are due to the C=O stretching vibrations of the ketonic and the two carboxyl groups. Both 1:1 and 1:2 complexes show a broad band around 1,600  $cm^{-1}$  where probably the two antisymmetric  $\nu COO^-$  frequencies are overlapping. This band occurs at a frequency lower than that in the sodium salt (1,625  $cm^{-1}$ ). The symmetric  $\nu COO^-$  frequencies in the rare-earth meconates occur at ca. 1,430  $cm^{-1}$  and ca. 1,356  $cm^{-1}$  for the 1:1 complexes and at ca. 1,420  $cm^{-1}$  and ca. 1,360  $cm^{-1}$  for the 1:2 complexes. These bands are not much shifted when compared to the corresponding bands in the spectrum of the sodium salt (1,424  $cm^{-1}$  and 1,355  $cm^{-1}$ ). Thus, the positions of the asymmetric and symmetric  $\nu COO^-$  frequencies in the rare-earth meconates with reference to those in the sodium salt indicate that the bonding of the carboxylate groups to the metal is bidentate<sup>4,5</sup>. Judging from the structure of the ligand, it is unlikely that the two carboxylate groups are bonded to the same metal ion; the carboxylate groups bind probably to different metal ions forming polymeric chains. The insolubility of the complexes in common

solvents may be due to this. The proton in the complexes of the type  $Ln(HMec)(H_2Mec) \cdot 6H_2O$  seems to be bonded to one of the carboxylate groups. This is indicated by the presence of a band around  $1,730\text{ cm}^{-1}$  attributable to the  $\nu C=O$  of the COOH group. This band is also present in the free ligand but absent in the complexes of the type  $Ln(Mec) \cdot 5H_2O$ .

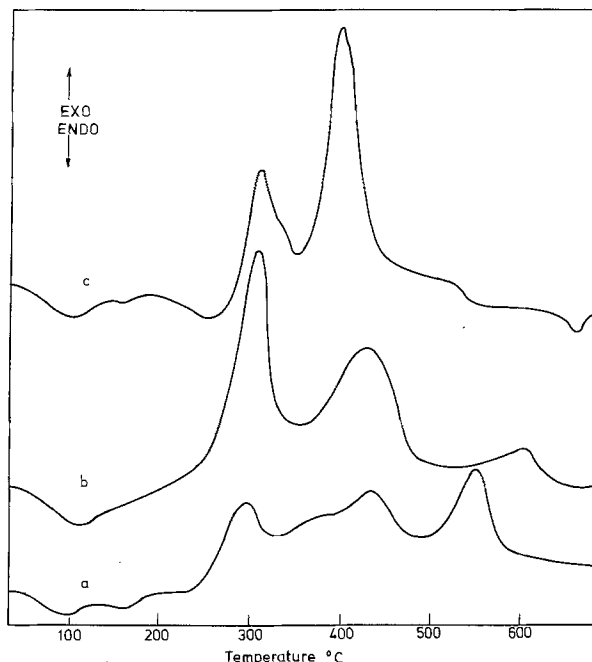


Fig. 1. DTA studies for complexes  $Ln(Mec) \cdot 5H_2O$ . a  $Ln = La$ ; b Nd; c Sm

The infrared spectra of both 1:1 and 1:2 chelates indicate the presence of lattice as well as coordinated water molecules. The bands due to the lattice and coordinated water molecules occur at about  $3,400\text{ cm}^{-1}$  and  $3,200\text{ cm}^{-1}$ , respectively.

The differential thermal analysis was carried out for the 1:1 chelates of La, Nd and Sm, and the 1:2 chelates of La, Pr and Nd. The differential thermograms are similar, except for minor changes, for the compounds of each set (Figs. 1 and 2). The 1:1 chelates show an endothermic peak around  $100^\circ\text{C}$  due to the removal of lattice held water molecules. Isothermal heating at  $110^\circ\text{C}$  for about 2-3 hours showed the removal of three molecules of water from the chelates (Tab. 2). Hence, three water molecules in the 1:1 chelates are only

lattice held and the other two are coordinated. Weight loss due to isothermal heating at 175 °C corresponded to the removal of one more water molecule (Tab.3). In the DTA traces there is no endotherm above 175 °C corresponding to the removal of the fifth molecule of water. Probably, the removal of the last molecule of water from the complex is not possible; there is only one ligand per metal ion, therefore

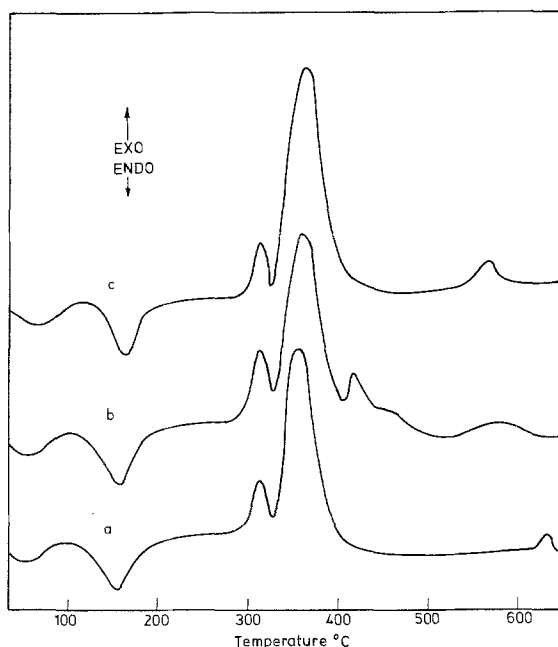


Fig. 2. DTA studies for complexes  $Ln(HMec)(H_2Mec) \cdot 6H_2O$ . *a*  $Ln = La$ ; *b* Pr; *c* Nd

the anhydrous compound would be coordinatively unsaturated. Strong exothermic peaks are observed around 300, 425 and 550 °C due to various stages of decomposition of the chelates.

The 1:2 chelates show an endothermic dehydration peak below 100 °C. Isothermal heating at 110 °C for 2-3 hours showed the removal of four molecules of water (Tab.2). This shows that two water molecules are coordinated and the rest four are lattice held. In these complexes, unlike in the 1:1 complexes, both the coordinated water molecules could be removed by heating the samples at 175 °C to get the anhydrous compounds (Tab. 3). The exothermic peaks above 300 °C are

Table 2. Weight loss during isothermal heating

Compound	%Wt. loss at		% Wt. loss expected for the removal of						No. of H <sub>2</sub> O molecules removed at	
	110 °C	175 °C	2 H <sub>2</sub> O	3 H <sub>2</sub> O	4 H <sub>2</sub> O	5 H <sub>2</sub> O	6 H <sub>2</sub> O	110 °C	175 °C	
Nd( <i>Mec</i> ) · 5 H <sub>2</sub> O	12.00	17.12	8.40	12.53	17.00	20.87	—	—	3	4
Sm( <i>Mec</i> ) · 5 H <sub>2</sub> O	12.05	16.66	8.30	12.36	16.47	20.60	—	—	3	4
La( <i>HMc</i> ) ( <i>H<sub>2</sub>Mec</i> ) · 6 H <sub>2</sub> O	10.80	17.45	—	8.40	11.19	14.00	16.80	16.80	4	6
Nd( <i>HMc</i> ) ( <i>H<sub>2</sub>Mec</i> ) · 6 H <sub>2</sub> O	10.90	17.02	—	8.33	11.11	13.90	16.66	16.66	4	6

due to the decomposition of the chelates. The praseodymium chelate shows two exothermic peaks at 425 °C and 465 °C which are not present for the other 1:2 chelates. These peaks may be due to conversions between the various forms of praseodymium oxide.

The complexes may thus be represented as  $[Ln(Mec)(H_2O)_2] \cdot 3 H_2O$  and  $[Ln(HMec)(H_2Mec)(H_2O)_2] \cdot 4 H_2O$  with the carboxylate groups of the ligand acting as bidentate and binding the lanthanide ions in a polymeric chain.

Table 3. *Analysis of compounds heated at 175 °C*

Compound	%Metal		% Carbon		% Hydrogen	
	Found	Calc.	Found	Calc.	Found	Calc.
Nd( <i>Mec</i> ) · H <sub>2</sub> O	39.94	40.12	23.00	23.40	1.02	0.84
Sm( <i>Mec</i> ) · H <sub>2</sub> O	40.55	41.10	22.72	23.01	1.10	0.82
La( <i>HMec</i> )( <i>H<sub>2</sub>Mec</i> )	25.63	25.93	30.93	31.34	1.25	0.93
Nd( <i>HMec</i> )( <i>H<sub>2</sub>Mec</i> )	25.56	25.69	31.18	31.06	1.29	0.92

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