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COMPLEXES OF RARE-EARTH ELEMENT CHLORIDES WITH 1,10-PHENANTHROLINE

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ABSTRACT

The preparation, the thermal stability and the x-ray diffraction measurements of the complexes of the rare-earth element (r.e.e.) chlorides with 1,10-phenanthroline have been reported.

INTRODUCTION

The complexes formed by 1,10 -phenanthroline and 2,2' bipyridyl with the nitrates and the sulfates of the lanthanides are known (1, 2, 3) but no information is available on the r.e.e chloride complexes formed with 1,10-phenanthroline (phen), except that reported by Russian workers (1, 2, 3) on the non formation of such complexes with r.e.e chlorides. The present paper deals with such complexes. The r.e.e chlorides react with phen. to give the anhydrous complexes $MCl_3.2$ phen, where M stands for Lanthanum, Europium, Gadolinium and Ytterbium.

EXPERIMENTAL

Bis (phenanthroline) Lanthanum trichloride.

1.54 g of phen., dissolved in 5 ml of alcohol, was added to 1 g of $LaCl_3.6\ H_2O$ in 20 ml of alcohol. After about 5 minutes, a white microcrystalline precipitate began to separate and the solution was kept for 2 - 3 hrs. for complete precipitation. The product was filtered off by suction, washed with alcohol and dried in an oven at 80 - 90°C.

Bis (phenanthroline) Europium chloride.

2.3 g of Eu_2O_3 was evaporated to near dryness with ~ 1 ml of 12 M HCl few times, and then the resulting chloride was dissolved in 10 ml of 80 - 90 % alcohol. To this alcoholic solution, was added 4.7 g of phen. dissolved in 5 ml of alcohol. Soon after mixing and a little bit of stirring a slightly pinkish white solid compound $EuCl_3$. 2 phen., was obtained. The product was filtered off, washed with alcohol and dried in an oven at 80 - 90°C.

Bis (phenanthroline) Gadolinium chloride.

It was prepared in a similar way as $LaCl_3$. 2 phen, starting with 1 g of gadolinium trichloride and stoichiometric amount of phen.

Bis (phenanthroline) Ytterbium chloride.

It was prepared in a similar way as $EuCl_3$, 2 phen, starting with Yb_2O_3.

Chloride and phen. analysis.

The chloride was determined potentiometrically using Ag electrode after the dissolution of the sample in dilute HNO_3.

Phen. was analysed acidimetrically after dissolving the sample in an excess HNO_3. By titrating it with soda, the first equivalent point gave the amount of excess acid and the second equivalent point corresponded to the neutralization of orthophenanthronilic acid.

Thermogravimetric analysis.

The thermal properties of these complexes were studied using a Mettler recording thermoanalyzer of precision $\pm$ 0.05 mg. It continuously records the changes in weight and simultaneously enthalpic effects of a substance in relation to temperatures up to 1600 °C. The results are fed to a 12 channel recorder, which simultaneously draws the temperature curve, general TGA diagram (1 scale div = 1 mg), the expanded TGA diagram (1 scale div = 0.1 mg) and DTA curve. The standard used was Al_2O_3, which, like the test specimen, was put in a platinum crucible ; 100 mg of material was used. The heating was at the rate of 10 deg/min., and was continued until decomposition was complete, leaving the metal oxide M_2O_3 as the final product. The

metal content in the complexes was calculated from the above known weight of M_2O_3.

X-ray measurements.

X-ray diffraction measurements were made using a wide range goniometer Model PW/1050/25 in conjunction with philips Model PWV-1310 x-ray unit. The diffractrometric spectra were all taken with Cu K radiation filtered through nickel foil.

RESULTS AND DISCUSSION

The analyses of the chloride, the phen. and the metal are summarized in Table I.

TABLE I. Analytical Results of the Complexes.

compound	# of mols./mol. of complex		% metal	
	phen.	chloride	found	calculated
$LaCl_3$.2 phen.	1.95	2.94	23.06	22.94
$EuCl_3$.2 phen.	1.86	2.85	24.48	24.57
$GdCl_3$.2 phen.	1.97	2.89	25.05	25.17
$YbCl_3$.2 phen.	1.95	3.02	27.28	27.05

The thermogravimetric and differential heating curves for complexes of the r.e.e chlorides with 1,10 phen. are shown in Fig. 1. For the sake of clarity only one DTA curve is shown in Fig. 1, as the other DTA curves are similar except the shift in peak positions. These complexes do not contain water of crystallisation, as the thermogravimetric analyses confirmed. However, these complexes are little bit hygroscopic, they absorb moisture from atmosphere varying from 1 to 5 %. Thermogravimetric examination of these complexes shows that the decomposition starts at around 200°C, but up to (350 - 400°C) phenanthroline is released very slowly and latter more rapidly, as shown by the steep slope of the differential curve and the more rapid loss in weight. At 400°C and above, the endothermic effects due to the liberation of phen. and the instantaneous exothermic effects due to the reaction of the phen. with chloride complexes follow one another closely and their interpretation is not possible. On subsequent heating the change in weight on the thermogravimetric curves correspond to the decomposition of

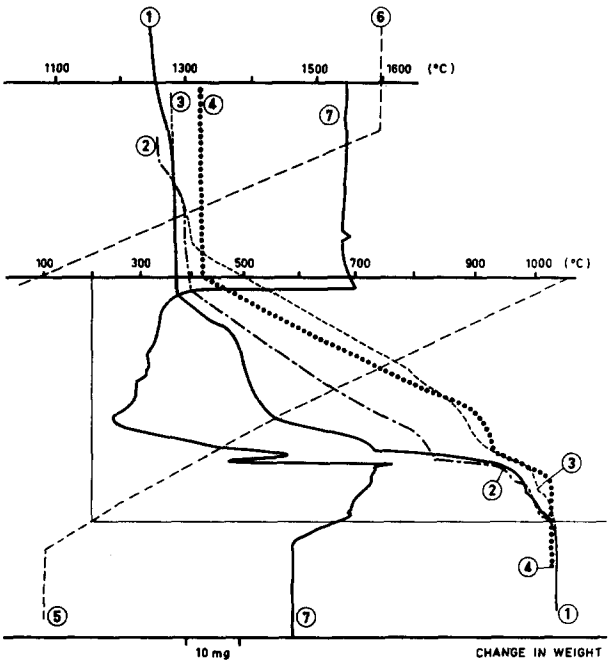

Fig.1_THERMOGRAVIMETRIC CURVES

1)_La Cl_3-2 phen ; 2)_Eu Cl_3-2 phen ;
3)_Gd Cl_3-2 phen ; 4)_Yb Cl_3-2 phen
5) and 6) Température curves
7)_DTA curve for Eu Cl_3-2 phen

the chlorides to oxy-chlorides except in the case of $YbCl_3$.2 phen. The further decomposition leads to the formation of the r.e.e oxides (M_2O_3) ; this agrees with the published results (4, 5). However, within the sensitivity region used on our DTA, this effect is not reflected on the form of the differential curve. In general, the thermal decomposition of these complexes agrees rather well with that of complexes of r.e.e. nitrates with 1,10 phenanthroline (6). The thermogravimetric results showing the loss in weight during oxychloride formation and the total loss in weight during the formation of M_2O_3 are summarised in Table II.

The interplanar spacing d and the observed relative intensities for each of these complexes are tabulated in table III. The x-ray spectrum of orthophenanthroline obtained in this way agreed well with the data on ASTM powder diffraction file (7).

TABLE II. Thermogravimetric Results.

compound	Total loss in wt. in mg. observed	calculated	temperature in °C at which these compounds were obtained
LaOCl	71.0	71.7	1000
La_2O_3	76.3	76.4	1600
EuOCl	77.5	78.1	700
Eu_2O_3	83.4	83.3	1470 - 1600
GdOCl	67.0	66.4	1170
Gd_2O_3	70.9	70.8	1300
Yb_2O_3	64.6	64.9	1350

With only 15 lines or so, all at very low angles, it is very difficult to draw conclusion regarding the crystal symetry and consequently the lattice parameters. We obtained many powder patterns also on these complexes butnone of them show more than 15 - 20 lines all at very low angles. Under these circumstances nothing definite can be said regarding the crystal structure.

TABLE III. Diffraction Data.

$LaCl_3$.2 phen.		$EuCl_3$.2 phen.		$GdCl_3$.2 phen.		$YbCl_3$.2 phen.	
d(A°)	I(obs)	d(A°)	I(obs)	d(A°)	I(obs)	d(A°)	I(obs)
8.67	100	12.48	21	8.88	100	8.57	35
7.93	58	8.93	68	7.83	55	7.82	100
6.53	100	8.04	12	7.35	58	7.08	36
5.90	47	6.51	100	6.51	63	5.74	27
4.87	39	5.81	28	5.68	64	5.50	28
4.62	49	4.58	29	5.58	69	5.10	29
4.46	29	4.39	50	5.01	70	4.86	28
4.21	29	4.27	20	4.81	63	4.32	80
3.98	45	4.05	20	4.30	73	3.40	47
3.71	26	3.80	20	4.22	73	3.34	42
3.30	50	3.62	18	4.04	71	3.24	35
3.14	41	3.56	19	3.94	73	2.98	32
2.81	30	3.51	30	3.76	64	2.73	33
2.66	28	3.45	18	3.28	80		
		2.98	21	3.22	74		
		2.50	15	3.02	69		

Altough we studied these complexes with La, Eu, Gd and Yb only, there is no reason not to believe that the remaining of the lanthanide elements will behave alike.

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