CHAPTER V

SOLID RARE EARTHS COMPLEXES OF HYDROXAMIC ACIDS

ABSTRACT

The solid complexes of La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) with N-p-chlorophenyl-m-substituted benzohydroxamic acid (MBHA) have been prepared by precipitation. The optimum conditions of precipitation of these rare earths have been established. These solid complexes were characterised by elemental analyses and infrared spectra.

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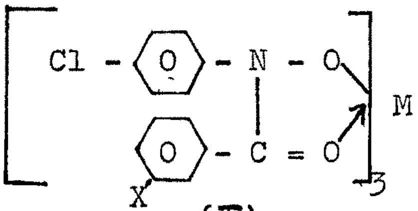
Hydroxamic acids have been widely used in the analysis of metal ions due to their powerful coordination as bidentate ligands (1-7). The formation constants of N-p-chlorophenyl-m-substituted benzohydroxamic acids, Chapter III, suggest that these ligands serve as functional groups in synthetic sequestering agents designated specifically for the trivalent lanthanides. In order to isolate and to know the stoichiometry of rare earths hydroxamate complexes the solid complexes were prepared. These complexes are characterised by m.p., elemental analysis and infrared spectra. The rare earth complexes of N-p-chlorophenyl-m-substituted hydroxamic acids are of the definite composition,(I) and can be used for the gravimetric estimations of the rare earths.



(I)

where X = H, CH_3, OCH_3 or F,

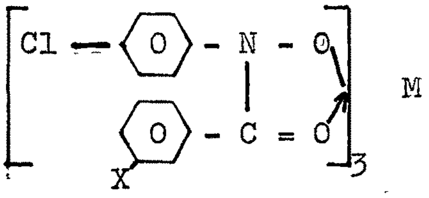
M = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} or Gd^{3+}.

EXPERIMENTAL

The details of the chemicals, reagents, apparatus and techniques are described in Chapters II, III and IV.

Preparation of solid complexes

In a litre beaker, a saturated solution of the metal ion and about 500 ml of distilled water were heated at 60° on water bath. About 20 ml of 0.01 M solution of the reagent in dioxan was added dropwise with constant stirring followed by 0.1 M ammonia solution until the precipitation was complete. The pH was adjusted for the precipitation of various rare earths by ammonium chloride (0.1 M). The granular complex thus obtained was digested for about 30 min, filtered through sintered glass crucible of porosity G4. The precipitate was washed thoroughly first with hot water and finally with 50% aqueous dioxan (10 x 10 ml). The solid complexes thus obtained were dried at 110°, and weighed directly as



where X = H, CH_3, OCH_3 or F

M = La, Pr, Nd, Sm, Eu, Gd.

The solid complexes formed are of definite composition.

RESULTS AND DISCUSSION

The pH of precipitation for solid complexes of La, Pr, Nd, Sm, Eu, and Gd with hydroxamic acid are given in Table 1. The physical properties of their solid complexes are given in Tables 2-5. These complexes are characterised by elemental analysis and infrared spectra.

Analysis

Weighed quantities of metal complexes were decomposed with a mixture of perchloric and nitric acid. The metal content was determined volumetrically (8).

The analyses values given in Tables 2-5 are in good agreement with the theoretical values.

Infrared spectra

The spectrum of N-p-chlorophenyl-m-substituted benzohydroxamic acid (Chapter II) showed peaks around 3150, 1625 and 900 cm^{-1} due to the vibrations of hydrogen bonded O-H, C-O and N-O. However, if hydroxyl oxygen is bonded to metal through a lone electron pair and still retains the hydrogen, the O-H stretching frequency would be altered and absorption peak(s) due to it shifted. From the spectra of

TABLE 1

pH OF PRECIPITATION OF RARE EARTHS WITH N-p-CHLOROPHENYL-m-SUBSTITUTED BENZOHYDROXAMIC ACID

Metal ions	pH of precipitation
La^{3+}	7.5 - 8.5
Pr^{3+}	8.6 - 9.2
Nd^{3+}	8.8 - 9.5
Sm^{3+}	9.6 -10.2
Eu^{3+}	9.5 -10.5
Gd^{3+}	10.3 -10.5

TABLE 2

PROPERTIES OF RARE EARTH COMPLEXES OF N-p-CHLOROPHENYLBENZOHYDROXAMIC ACID

Molecular Formula	Molecular weight	Elemental Analysis, %					IR Frequency(cm^{-1})	
		M	C	H	N	Cl	$\nu C=O$	$\nu N-O$
$La(C_{13}H_9NO_2Cl)_3$	878.92	15.85 (15.80)	53.41 (53.30)	3.15 (3.10)	4.80 (4.78)	12.08 (12.10)	1570	920
$Pr(C_{13}H_9NO_2Cl)_3$	880.93	16.05 (16.00)	53.15 (53.17)	3.09 (3.10)	4.74 (4.76)	12.06 (12.07)	1565	916
$Nd(C_{13}H_9NO_2Cl)_3$	884.25	16.40 (16.31)	52.92 (52.97)	3.00 (3.08)	4.75 (4.75)	12.05 (12.03)	1565	918
$Sm(C_{13}H_9NO_2Cl)_3$	890.42	16.85 (16.89)	52.53 (52.61)	3.15 (3.06)	4.70 (4.72)	11.96 (11.94)	1570	920
$Eu\ (C_{13}H_9NO_2Cl)_3$	891.97	17.15 (17.04)	52.46 (52.52)	3.03 (3.05)	4.69 (4.71)	11.93 (11.92)	1560	916
$Gd\ (C_{13}H_9NO_2Cl)_3$	897.27	17.50 (17.53)	52.15 (52.21)	3.00 (3.03)	4.65 (4.68)	11.84 (11.85)	1568	920

The theoretical values are given in parenthesis.

TABLE 3

PROPERTIES OF RARE EARTH COMPLEXES OF N-p-CHLOROPHENYL-m-METHYLBENZOHYDROXAMIC ACID

Molecular Formula	Molecular weight	Elemental Analysis, %					IR Frequency(cm^{-1})	
		M	C	H	N	Cl	ν C=O	ν N-O
La$(C_{14}H_{11}NO_2Cl)_3$	920.27	15.05	54.75	3.52	4.60	11.45	1560	910
		(15.09)	(54.81)	(3.61)	(4.56)	(11.55)		
Pr $(C_{14}H_{11}NO_2Cl)_3$	922.98	15.02	54.70	3.50	4.45	11.50	1566	992
		(15.26)	(54.66)	(3.60)	(4.56)	(11.52)		
Nd $(C_{14}H_{11}NO_2Cl)_3$	926.31	15.48	54.52	3.50	4.49	11.54	1555	908
		(15.57)	(54.46)	(3.59)	(4.54)	(11.48)		
Sm $(C_{14}H_{11}NO_2Cl)_3$	932.47	16.10	54.02	3.59	4.45	11.34	1550	910
		(16.13)	(54.10)	(3.57)	(4.51)	(11.41)		
Eu $(C_{14}H_{11}NO_2Cl)_3$	934.03	16.20	54.10	3.62	4.57	11.28	1560	910
		(16.27)	(54.01)	(3.56)	(4.50)	(11.38)		
Gd $(C_{14}H_{11}NO_2Cl)_3$	939.33	16.68	53.65	3.60	4.52	11.35	1564	910
		(16.74)	(53.70)	(3.54)	(4.40)	(11.32)		

The theoretical values are given in parenthesis.

TABLE 4

PROPERTIES OF RARE EARTH COMPLEXES OF N-p-CHLOROPHENYL-m-METHOXYBENZOHYDROXAMIC ACID

Molecular Formula	Molecular weight	Elemental Analysis, %					IR Frequency(cm^{-1})	
		M	C	H	N	Cl	νC=O	νN-O
La $(C_{14}H_{11}NO_3Cl)_3$	968.90	14.28	52.12	3.56	4.31	10.91	1550	880
		(14.34)	(52.06)	(3.43)	(4.34)	(10.97)		
Pr $(C_{14}H_{11}NO_3Cl)_3$	970.91	14.55	51.91	3.45	4.30	10.91	1555	870
		(14.51)	(51.96)	(3.43)	(4.33)	(10.95)		
Nd $(C_{14}H_{11}NO_3Cl)_3$	974.24	14.84	51.75	3.38	4.30	10.82	1558	875
		(14.81)	(51.78)	(3.41)	(4.31)	(10.92)		
Sm $(C_{14}H_{11}NO_3Cl)_3$	980.40	15.31	51.40	3.31	4.22	10.87	1555	880
		(15.34)	(51.45)	(3.40)	(4.29)	(10.85)		
Eu $(C_{14}H_{11}NO_3Cl)_3$	981.96	15.41	51.41	3.32	4.32	10.86	1555	880
		(15.47)	(51.37)	(3.38)	(4.27)	(10.83)		
Gd $(C_{14}H_{11}NO_3Cl)_3$	987.26	15.96	51.05	3.30	4.20	10.67	1550	885
		(15.93)	(51.10)	(3.36)	(4.26)	(10.77)		

The theoretical values are given in parenthesis.

TABLE 5

PROPERTIES OF RARE EARTH COMPLEXES OF N-p-CHLOROPHENYL-m-FLUOROBENZOHYDROXAMIC ACID

Molecular Formula	Molecular weight	Elemental Analysis, %						IR Frequency (cm^{-1})	
		M	C	H	N	Cl	F	νC=O	νN-O
La $(C_{13}H_8NO_2ClF)_3$	932.88	14.81	50.15	2.66	4.57	11.32	6.05	1555	960
		(14.89)	(50.21)	(2.60)	(4.50)	(11.40)	(6.11)		
Pr $(C_{13}H_8NO_2ClF)_3$	934.89	15.01	50.06	2.51	4.47	11.33	6.02	1558	950
		(15.07)	(50.11)	(2.58)	(4.50)	(11.38)	(6.10)		
Nd $(C_{13}H_8NO_2ClF)_3$	938.22	15.31	49.89	2.54	4.42	11.29	6.01	1555	960
		(15.37)	(49.94)	(2.57)	(4.48)	(11.34)	(6.07)		
Sm $(C_{13}H_8NO_2ClF)_3$	944.38	15.86	49.66	2.51	4.40	11.24	5.97	1550	955
		(15.93)	(49.60)	(2.56)	(4.46)	(11.26)	(6.03)		
Eu $(C_{13}H_8NO_2ClF)_3$	945.94	16.01	49.42	2.53	4.39	11.21	5.95	1550	955
		(16.06)	(49.52)	(2.56)	(4.44)	(11.24)	(6.02)		
Gd $(C_{13}H_8NO_2ClF)_3$	951.24	16.47	49.11	2.51	4.37	11.15	5.90	1556	953
		(16.53)	(49.24)	(2.54)	(4.42)	(11.20)	(6.00)		

The theoretical values are given in parenthesis.

metal complexes (Tables 2-5) as KBr pellets, evidence was not obtained for the absorption peak ascribed to such a group in the region of 4000 - 700 cm^{-1}. Therefore, it may be concluded that the O-H stretching frequency disappears in metal chelates because, in the formation of chelates, the hydrogen ion is lost and the oxygen atom is coordinated with the metal ion.

The absorption peak due to the carbonyl stretching vibration in the spectra of rare earth hydroxamates is located at around 1550 cm^{-1} due to the bonding of the carbonyl oxygen to the metal as $- C = O \quad M$.

The peak due to the N - O stretching vibration at 900 cm^{-1} in hydroxamic acid is almost unaffected in the metal complexes except for its intensity which is increased.

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