METHYLENE DI SALICYLATES OF RARE-EARTHS

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ABSTRACT

Rare-earth methylene di salicylates of the general formula $M_2R_3 \cdot 8H_2O$, *where* $M = La, Ce, Pr, Nd, Sm, Gd, Ho, Yb$, *or* Y, *and* $R = MDSH_2^{2-}$, *have been prepared and characterized by chemical analyses, infrared and differential thermal analyses. The infrared data show that the bonding of the carboylate group to the metal is bidentate. The infrared and thermal studies reveal that the water present in the complexes is only lattice-held.*

Keywords: Rare-earths, Methylene di salicylic acid. Major discipline to which the article belongs: Inorganic Chemistry.

1. INTRODUCTION

Though 5, 5′-methylene di salicylic acid ($MDSH_4$) is an industrially important compound, no efforts have been made to study the nature of coordination of this ligand towards the metal ions. No solid complexes of $MDSH_4$ are known in the literature except that of aluminium [1]. In this ligand there are two active —OH and —COOH groups and hence this may be expected to act as a multidentate ligand. But the presence of an inactive CH_2-group is bound to give rise to pronounced steric effects. The present paper describes the preparation of its complexes with rare-earths metal ions and their characterization by analyses and DTA studies. The mode of coordination of the ligand has been deduced from the spectral data.

2. EXPERIMENTAL

Preparation of the Complexes: Hydrated rare-earth chlorides except that of cerium (III) were prepared by dissolving a weighed amount of the rare-earth oxide in AR hydrochloric acid and evaporating the solution on a steam-bath to dryness to remove the excess acid. Hydrated cerium (III) chloride was prepared by dissolving the cerium (III) hydroxide in AR hydrochloric acid and evaporating the solution to dryness. The resulting chlorides (0·3 gm of oxide) were dissolved in 50% ethylalcohol (20 ml). Calculated amounts (2 gm) of the recrystallised ligand (obtained by the courtesy of Grasser-Salicylates Limited, Sandy Craft, Chester, England) in alcohol (20 ml) were added to the above solutions, the mixture being kept stirred. The pH of the solutions was adjusted to about 6 by the addition of dilute ammonia drop-wise. Stirring was continued for another 15 minutes after the addition of ammonia. The precipitates obtained were filtered through sintered crucibles and washed well with water, alcohol and acetone respectively. The compounds were first air-dried and then over calcium chloride in a desiccator under reduced pressure. All the complexes are insoluble in water and also in common organic solvents. No cryoscpic or conductometric measurements could, therefore, be made.

Analyses: The metal content of the complexes was determined by direct ignition of a weighed amount of the chelate in a platinum crucible and weighing the residual oxide. Microanalytical results for carbon and hydrogen, for some representative compounds, were obtained from the Analytical Division, BARC, Bombay (INDIA). The results of the analyses are presented in Table I.

TABLE I

Analytical data

Compound	% Metal		% Carbon		% Hydrogen	
	Found	Calc.	Found	Calc.	Found	Calc.
$La_2(MDSH_2)_3 \cdot 8H_2O$	21·63	21·72	42·40	42·19	3·81	3·60
$Ce_2(MDSH_2)_3 \cdot 8H_2O$	22·01	21·84	42·31	42·12	3·81	3·59
$Pr_2(MDSH_2)_3 \cdot 8H_2O$	22·20	21·96	..	..	..	..
$Nd_2(MDSH_2)_3 \cdot 8H_2O$	22·56	22·32	..	..	..	..
$Sm_2(MDSH_2)_3 \cdot 8H_2O$	23·28	23·04	41·20	41·45	3·64	3·53
$Gd_2(MDSH_2)_3 \cdot 8H_2O$	24·01	23·86	40·75	41·01	3·55	3·49
$Ho_2(MDSH_2)_3 \cdot 8H_2O$	24·71	24·77	..	..	..	..
$Yb_2(MDSH_2)_3 \cdot 8H_2O$	25·74	25·68	39·85	40·06	3·45	3·41
$Y_2(MDSH_2)_3 \cdot 8H_2O$	15·21	15·09	46·12	45·76	4·02	3·90

Physical measurements: The infrared spectra of $MDSH_4$ and the complexes were recorded in Nujol mulls on a "CARL-ZEISS UR-10" spectrophotometer in the range 4000–400 cm^{-1}. Absorption bands of diagnostic value and their tentative assignments are given in Table II.

TABLE II

Assignments to characteristic i.r. frequencies (cm^{-1})

$MDSH_4$	Na_2MDSH_2	$Pr_2(MDSH_2)_3 \cdot 8H_2O$*	Assignment
3450 m, b	3450 m, b	3450 w, b 3200 w, b	OH stretching
2625 w	..	..	
2540 w	..	..	OH stretching
2385 w	..	..	
1674 vs	..	..	C=O stretching
1622 s	1640 s	1640 s	C=C stretch
..	1585 vs	1560 s	COO^- assym. stretch
1500 s	1502 s	1500 s	C=C stretch
1456 vs	1455 s	1455 s	CH_2 scissors
1390 w	1395 s	1392 s	COO^- sym. stretch
1300 s	..	..	C—O stretch + OH deformation
1250 s	1255 s	1250 s	C—O stretch + OH deformation
900 s, br	..	..	OH out-of-plane, deformation
770 m	770 w	770 w	CH_2 rocking

Abbreviations: vs = very strong; s = strong; m = medium; w = weak; br = broad.

* The spectra of other chelates are very similar.

The DTA of two representative samples were recorded on an automatic instrument fitted with chromel-alumel thermocouple. All the samples were run at a heating rate of 2° C/min. Calcined alumina was used as the diluent and also as the reference material.

3. RESULTS AND DISCUSSION

Results of analyses conform to the general formula $M_2R_3 \cdot 8H_2O$ where M = La, Ce, Pr, Nd, Sm, Gd, Ho, Yb or Y; and R = $MDSH_2^{2-}$. All the compounds are stable in air, decompose in acidic media and are pink in colour.

There appears to be no data available in literature on the infrared spectra of methylene di salicylic acid. Hence an assignment of the infrared frequencies of the ligand has been made. This has been made with the help of the published data on the infrared spectra of salicylic acid and benzoic acid [2, 3]. The strong band appearing at about 1674 cm^{-1} can be assigned to C = O stretching frequency. The band at 1300 cm^{-1} can be due to C—O stretching vibration coupled with the in-plane bending vibration of the —OH group. All these bands are absent in the sodium salt as well as in the chelate spectra due to the removal of the hydrogen atom.

The bands due to symmetric and asymmetric COO^- stretching vibrations are present in both the sodium salt and the chelates. Compared to the sodium salt, both these frequencies are shifted to the lower frequency region in the rare-earth chelates. However, the symmetric COO^- stretching vibration shifts only a little (3 cm^{-1}), while the asymmetric COO^- stretching vibration shifts more (25 cm^{-1}). Hence the carboxylate group is acting as a bidentate ligand in the rare-earth chelates (4). The bidentate coordination of the carboxylate group to the metal results in a lowering of both the ν_{COO} frequencies due to the drainage of the electron density from the carboxyl group to the metal. At the same time the OCO angle is expected to decrease when the metal-oxygen bond becomes stronger. The valence-force-field equations for an XY_2 system [5] and the calculations for the triatomic model [6, 7] have shown that a decrease in the OCO angle results in a decrease in the frequency separation between the two ν_{COO} frequencies. These two factors act in the same direction for the asymmetric ν_{COO} frequency but are opposite for the symmetric ν_{COO} -frequency. Thus in a bidentate coordination of the carboxylate group, the asymmetric ν_{COO} frequency decreases and symmerric ν_{COO} frequency changes only a little compared to that of the sodium salt.

The strong band observed at 900 cm^{-1} in the ligand is assigned to the —OH out-of-plane deformation. As expected, this band is absent in both the sodium salt and the chelates due to the removal of the acidic protons. The band at 1250 cm^{-1} remains unshifted in both the sodium salt and chelate. This can be assigned to the C—O (Phenolic O) stretching vibration coupled with the —OH deformation.

DTA of praseodymium and holmium chelates have been carried out. Both showed very similar decomposition pattern. An endothermic peak observed at about 85° C is due to the removal of water. Hence the water present is only lattice-held water. The strong exotherm at about 300° C can be due to the decomposition of the chelate. The sharp exotherm at 480° C indicates the oxidation of the carbon formed.

The physical studies reveal that all the rare-earth metal ions are only hexa-coordinated.

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