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COMPLEXES OF RARE EARTH ELEMENTS WITH 2-BUTYRYLCYCLOHEXANONE

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Abstract – Complexes of rare earth elements with 2-acetylcyclohexanone have been reported earlier. Complexes with 2-Butyrylcyclohexanone are prepared. These are characterised by u.v. and i.r. spectral data. Successive stability constant values are reported.

INTRODUCTION

COMPOUNDS of rare earth elements with straight chain β -diketones are well known[1-7]. The study is now extended to cyclic β -diketons. We have already reported complexes formed by 2-acetyl cyclohexanone [8] and another compound - Maltol[9]. Only the successive stability constant values of rare earth complexes with these ligands are reported. The present ligand has been chosen to see the effect obtained by extending the length of straight chain part of the β -diketone. The isolation and characterisation of the complexes formed by La, Pr, Nd, Sm, Gd and Y using i.r. and u.v. spectral data have been reported in this paper.

EXPERIMENTAL

2-Butyrylcyclohexanone

Preparation of anamine. The enamine is prepared by the method given by Stork *et al.*[10] from predistilled cyclohexanone and Morpholein in dry and thiophene free benzene. The boiling point recorded is $112^{\circ}/C/14 \text{ mm}$ (lit. value $110^{\circ}C/14 \text{ mm}$).

Preparation of diketone. The diketone is prepared from l-morpholinecyclohexene and butyryl chloride [11] in presence of dry trimethylamine (dried over KOH) in dry $CHCl_3$ medium. The homogeneous orange-red liquid is allowed to stand overnight and then hydrolysed by HCl. The separated $CHCl_3$ phase is thoroughly washed with water and the solvent is distilled under reduced pressure. The final compound is distilled under vacuum and the fraction between 133 and 135°28 mm is collected. The yield is 82 per cent.

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- 11. Organic Synthesis, Vol. III.

Tetramethylammonium hydroxide

The base is prepared by the action of freshly prepared Ag_2O on tetramethylammonium iodide. The mixture is shaken for 1 hr and rapidly filtered under suction. The filtrate is titrated with standard acid and the volume is adjusted for N/10 solution with calculated acetone-water mixture such that the final solution remains 3:1 w.r.t. acetone-water (v/v).

Rare earth perchlorate. Rare earth and yttrium oxides used are 99.9 per cent pure. Perchlorates are prepared as reported before [12].

Na-Perchlorate used is a molar solution of reagent grade sodium perchlorate in double distilled water.

Titration. The dissociation constant of the ligand and the stability constant values are determined by potentiometric method. Tetramethyl ammonium hydroxide has been used for titration. The pH values are measured at 30°C using a Cambridge Bench pH meter with a glass electrode supplied by the same company in conjunction with a saturated calomel electrode. The glass electrode is previously calibrated and checked with phthalate and borax buffers. The pH values recorded are mean of three different determinations.

Preparation of compounds. The rare earth nitrates are dissolved in rectified spirit and dilute ammonia is added drop by drop with vigorous stirring until slight precipitation or turbidity appears. It is filtered, evaporated to dryness and analysed and the results are given in Table 1.

U.V. spectral studies. The ultraviolet spectral study of rare earth complexes as well as of free ligand in methanol and in acetone have been taken in Spectromom 201 using the respective solvents as blank (Table 2).

I.R. spectral study of Praseodymium complexes have been recorded in Perkin-Elmer model 21 (Nujol mull). The bands are summarised in Table 3.

Compound		Calc.		Metal		Found		Metal
	С	Н	0	oxide	С	Н	0	oxide
$[La(L)_2(OH)(H_2O)]$	23.29	3.10	6.26	31.90	23.50	3.00	6.00	32.00
$[\Pr(L)_2(OH)(H_2O)]$	23.24	3.10	6.24	33.78	23.20	9.09	6.18	33.58
$[Nd(L)_2(OH)(H_2O)]$	23.30	3.26	6.21	32.42	23.52	3.08	6.25	32.38
$[\operatorname{Sm}(L)_2(\operatorname{OH})(\operatorname{H}_2\operatorname{O})]$	23.03	3.02	6.14	33.49	23.51	3.00	6.00	33.50
$[\operatorname{Eu}(L)_2(\operatorname{OH})(\operatorname{H}_2\operatorname{O})]$	22.94	3.06	6.11	33.65	22.91	3.02	6.00	33.70
$[\mathrm{Gd}(L)_2)(\mathrm{OH})(\mathrm{H}_2\mathrm{O})]$	22.52	3.06	6.15	34.69	22.55	3.00	6.09	34.59

Table 1. Analytical data

Table 2. Complexes of rare earths with 2-Butyrylcyclohexanone pK = 12.56(Fig. 1) $[\mu = 0.1M]$

Metal	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta$	ΔF (kcal/mole)
La	8.52	7.33		.=	<u>.</u>
Pr	9.20	8.53	8.02	25.75	35.35
Nd	9.43	8.53	8.59	26.55	36-44
Sm	9.69	8.79	8.44	26.92	36.96
Eu	9.92	8.92	8-09	26.93	36-99
Gd	9.42	8.78	8.45	26-65	36.59
Dv	9.88	9.02	8.63	27.53	37.79
Er	10.72	8.95	9.03	26.70	36.65
Yb	10.81	9.76	9.61	30.18	41.43
Y	9.13	8.02			

12. B. Block and G. McIntyre, J. Am. chem. Soc. 75, 5667 (1953).

730	Sharp
768	Medium
820	Sharp
845	Medium
900	Small
960	Medium
990	Medium
1056	Sharp
1080	Medium
1130	Medium
1160	Sharp
1200	Sharp
1220	Medium
1255	Medium
1280	Broad
1320	Sharp
1340	Medium
1400	Small
1460	Sharp
1570	Sharp
1600	Sharp
2820-2990	Broad
3250-3400	Broad

Table 3

DISCUSSION

Theoretical

For determining the dissociation constants of rare earth complexes, a prior knowledge of acid dissociation constant of the ligand is essential.

Average number of ligand bound per metal ion, \bar{n} is represented as

$$\bar{n} = \frac{1}{C_M} \left\{ C_A - \frac{K}{\mathrm{H}^+} \left(C_A + \mathrm{E} + \mathrm{OH} - \mathrm{H}^+ - C_B \right) \left(1 + \frac{\mathrm{H}^+}{K} \right) \right\}$$

where C_M = concentration of metal ion

 $C_A =$ concentration of ligand

 $C_B =$ concentration of base

K = dissociation constant of the ligand,

the successive formation constants, k_1 , k_2 , k_3 are determined with the help of the following equations due to Block and McIntyre[12].

$$k_{1} = (L_{3}^{*}M_{23}^{'*} - L_{3}^{'*}M_{23}^{*})/(M_{13}^{*}M_{23}^{'*} - M_{13}^{'*} \cdot M_{23}^{'*})$$

$$k_{2} = (L_{1}^{*}L_{3}^{*} - L_{1}^{*}L_{3}^{'*})/(L_{2}^{*}L_{3}^{'*} - L_{2}^{'*}L_{3}^{*})$$

$$k_{3} = (L_{1}^{*}L_{2}^{'*} - L_{1}^{'*}L_{2}^{*})/(L_{1}^{'*}L_{3}^{*} - L_{1}^{*}L_{3}^{'*})$$

where

$$J_n = (n - \bar{n}) [A]^n$$

$$J'_{n} = (n - \bar{n}) ([A]')^{n}$$
$$J^{*}_{n} = (n - \bar{n}^{*}) ([A]^{*})^{n}$$
$$L'_{n} = \bar{n}J'_{n} - \bar{n}^{'}J_{n}$$
$$L^{*}_{n} = \bar{n}J^{*}_{n} - \bar{n}^{*}J_{n}$$
$$L'_{n}^{*} = \bar{n}^{'}J^{*}_{n} - \bar{n}^{*}J'_{n}$$

n = actual number of ligands bound to a given metallic ion

 \bar{n} = average number of ligands bound per metallic ion in a given solution

M = general symbol for a metallic ion

A = general symbol for a 2 ligand

[] = molar concentration of species indicated in the brackets

$$M'_{np} = J_n J'_p - J'_n J_p$$
$$M^*_{np} = J_n J^*_p - J^*_n J_p$$
$$M'^*_{np} = J'_n J^*_p - J^*_n J'_p.$$

For cases under consideration, the \bar{n} equations are: $\bar{n} = J_1k_1 + J_2k_1k_2 + J_3k_1k_2k_3$, $\bar{n}' = J'_1k_1 + J'_2k_1k_2 + J'_3k_1k_2k_3$ and $\bar{n}^* = J_1^*k_1 + J_2^*k_1k_2 + J_3^*k_1k_2k_3$ for N = 3.

The pK value of acetyl cyclohexanone as reported earlier is 12.18. The lengthening of straight chain part raises the pK value slightly and found to be 12.56. The overall stability constant values show greater departure as is evident from Table 4.

While studying the effect of substitution of higher homologues in the straight chain diketones, Dutt and Bandyopadhyaya[1] have shown that the substituted groups affect the stability of the complexes and the ligands can be arranged in the order of increasing stability of complexes as acetylacetone < propionylacetone. Similar trend is also seen in our case. Thus the log k_1 values for a particular metal gradually increase in the order of

$2 \operatorname{Acetylcyclohexanone} < 2 \operatorname{Butyrylcyclohexanone}.$

The log K_2 and log K_3 are not seen to maintain this trend. This is most probably because of the fact that the formation of *tris* complex is not strictly always stepwise. However the overall stability constant values (β) is seen in all cases to maintain this trend.

The tervalent rare earth ions form a unique series for a study of the influence of the size of the central ion on the properties of the coordination compounds. If the metal ligand bond is considered to be purely electrostatic in nature, the strength of the bond should linearly increase with increasing ionic potential Z^2/r where Z^2 is the charge and r is the radius of the ion. A measure of this bond strength is ΔH for the reaction $M + A \rightleftharpoons MA$. Because of the experimental difficulties in the determination of ΔH , ΔF for the same reaction is often used as an alternative. $\Delta F = -RT \ln K$ where K is the equilibrium constant for the reaction. The values of F are given in Table 4.

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The stability constant values report three ligands bound to each metal atom in all cases except with La and Y. That lanthanum and yttrium do not give *tris* complex is most probably due to their lesser solubility in 3:1 acetone-water medium. This case is also evidenced in 2-acetylcyclohexanone series.

Using different methods and different proportions of metal: ligand, always the same bis complex [Ln(2-but cyclo)₂(OH)(H₂O)] is obtained probably due to lesser solubility of the bis series than the tris one. In solution study however the solutions being very dilute $(2 \times 10^{-3}M)$, none of the species is precipitated and formation goes up to the tris stage in solution.

The ligand seems to be completely ionised in methanol solution. The peaks do not shift either by addition of one drop of concentrated sulphuric acid or molar sodium hydroxide. Three main peaks are obtained at 232, 273 and at 315 m μ . Three types of bonds are expected for β diketones and their complexes, which exist largely in enol form in solution, viz., $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. Both the bands at 275 and 315 m μ seems to be composite bands and the intensity of lower frequency band may be taken as directly proportional to the enol content of the system as in benzoylacetone[13]. Thus the 310 m μ band may be assigned to be the $n \rightarrow \sigma^*$ band. The enol form of acetylacetone absorbs at 270 m μ due to conjugated double bond. That of 2-butyrylcyclohexanone appears at 273 m μ . The $\pi \rightarrow \pi^*$ band of benzoylacetone has been reported to be at 210 m μ . This band appears at 230 m μ in the case of 2-butyrylcyclohexanone.

The i.r. bands of $[Pr(2-butyrylcyclohexanone)_2(OH)(H_2O)]$ are shown in Table 3. The very broad but distinctive band at 3350 cm⁻¹ seems to be due to O-H stretching. Enolic stretching appears at 1600. Perturbed carbonyl band may be ascribed to that appeared at 1570 cm⁻¹.

13. R. A. Mortan, Ali Hassan and T. C. Colloway, J. chem. Soc. 883 (1934).