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CHEMISTRY OF LANTHANONS – XXXI

LANTHANIDE CHELATES OF ETHYL BENZOYLACETATE AND 3-ALKYL ETHYLACETOACETATES

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Abstract – Lanthanide chelates of ethyl benzoylacetate (HEBA), 3-methyl ethylacetoacetate (HMEAA) and 3-ethyl ethylacetoacetate (HEEAA) have been prepared. The chelates have the compositions $[Ln(EBA)_2(OH)(H_2O)]$, $[Ln(MEAA)(OH)_2(H_2O)_2]$ and $[Ln(EEAA)(OH)_2(H_2O)_2]$ (where Ln stands for the lanthanide ions). U.V. and visible spectral studies of the ethyl benzoylacetate chelates are made. All the chelates have been characterised by i.r. spectra. pK_a values of 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate and the formation constants of their lanthanide chelates have been determined in acetone–water mixture (3 : 1 by volume) by pH-potentiometric method. In solution also, existence of 1 : 1 chelate as isolated has been inferred.

INTRODUCTION

In previous communications[1, 2], we have described the formation constants, preparation and characterisation of ethyl acetoacetate chelates. Studies on the lanthanide chelates with ethyl benzoylacetate and 3-alkyl-β-keto esters have not yet been reported. We have undertaken this investigation on the lanthanide chelates of ethyl benzoylacetate and 3-alkyl ethylacetoacetates to study the effect of substitution at the end and 3-position of ethylacetoacetate as a part of our previous work on the lanthanide chelates of β-keto esters. The present paper describes the preparation of lanthanide chelates of ethyl benzoylacetate, 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate and their characterisation by u.v., visible and i.r. spectra. The acid dissociation constants of 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate and the formation constants of their lanthanide chelates have been determined in acetone–water mixture (3 : 1 by volume) by pH-potentiometric method.

EXPERIMENTAL

Chemicals and reagents

The rare earth oxides used are specpure (supplied by Bhaba Atomic Research Centre, Trombay, India, and by Messrs. Johnson & Matthey). Yttrium oxide is 99·9 per cent pure (A. D. Mackay & Co.). The organic solvents employed are of reagent quality.

The preparation and standardisation of rare earth perchlorates have been described earlier[1].

Ethyl benzoylacetate is prepared by the method as described in the literature[3] and is identified by boiling point and i.r. spectra. The fraction boiling at 145–150°C/12 mm (lit. value, 145–150°C/12 mm) is used.

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1. N. K. Dutt and S. Rahut, *J. inorg. nucl. chem.* **31**, 3177 (1969).
2. Part XXVII of this series, N. K. Dutt and S. Rahut, *J. inorg. nucl. Chem.* **32**, 2905 (1970).
3. *Organic Synthesis* (Edited by N. Rabjohn), Vol. 4, p. 415, Wiley, New York (1962).

3-Methyl ethylacetoacetate and 3-ethyl ethylacetoacetate are B.D.H. samples and are distilled under reduced pressure prior to use. 3-methyl ethylacetatoacetate, b.p. 80–81°C/14 mm (lit. value, b.p. 80–80·5°C/14 mm) and 3-ethyl ethylacetoacetate, b.p. 95°C/16 mm (lit. value, 95°C/16 mm) are taken.

Titration

The procedure for the determination of acid dissociation constants of the ligands and the formation constants of lanthanide chelates have been described in an earlier issue [1].

Calculations

The formation constants are evaluated as described previously [1].

The results of the calculations of the formation constants of the lanthanide chelates of 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate along with the acid dissociation constants of the ligands are listed in Table 1.

Table 1. Log K_n values for the reaction of tervalent lanthanide ions with 3-methyl ethylacetoacetate ($pK_a = 12{\cdot}80$) and 3-ethyl ethylacetoacetate ($pK_a = 12{\cdot}80$) and 3-ethyl ethylacetoacetate ($pK_a = 13{\cdot}15$) at $T = 30°C$ and the ionic strength, $\mu = 0{\cdot}1$ M

Metal ion	3-Methyl ethylacetoacetate (log K_1)	3-Ethyl ethylacetoacetate (log K_1)
La^{3+}	7·07	7·58
Pr^{3+}	7·75	8·22
Nd^{3+}	7·84	8·43
Sm^{3+}	8·05	8·79
Eu^{3+}	8·22	9·04
Gd^{3+}	8·08	8·86
Dy^{3+}	8·36	9·10
Er^{3+}	8·62	9·17
Yb^{3+}	8·66	9·23
Y^{3+}	8·20	9·03

Apparatus

I.R. spectra of the chelates are recorded in Nujol mulls in Perkin-Elmer model 21 in the range 4000–700 cm^{-1}. U.V. and visible spectra are recorded using a Hilger Uvispek Spectrophotometer.

Preparation of ethyl benzoylacetate chelates

These are prepared by the same method as already described for the preparation of lanthanide chelates of ethylacetoacetate [2]. All the chelates are prepared within pH range 6·5–7. The chelates are purified by extraction with chloroform. Yields are always better than 90 per cent.

Preparation of chelates with 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate

The method of preparation is the same as adopted for ethylacetoacetate chelates [2]. Here the neutral metal nitrate is dissolved in acetone and the metal and the ligand are taken in the molar ratio of 1 : 5. In fact, even by using a large excess of the ligand only 1 : 1 chelate is obtained.

Analysis

Lanthanide metals are estimated as their oxides by direct combustion of the chelates; carbon and hydrogen by microanalysis. Analytical results are given in Table 2.

Table 2. Analytical results

			$[Ln(EBA)_2(OH)(H_2O)]$			$[Ln(MEAA)(OH)_2(H_2O)_2]$			$[Ln(EEAA)(OH)_2(H_2O)_2]$		
	Colour	M.P. (°C)	Metal oxide (%)	C (%)	H (%)	Metal oxide (%)	C (%)	H (%)	Metal oxide (%)	C (%)	H (%)
La	Cream	138	29·31	53·22	5·04	46·30	23·86	4·82	44·53	26·22	5·19
			(29·26)	(53·11)	(5·03)	(46·46)	(23·71)	(4·84)	(44·69)	(26·15)	(5·17)
Pr	Cream	168	30·89	53·01	5·02	48·87	23·72	4·80	47·01	26·08	5·16
			(30·75)	(53·18)	(5·05)	(49·06)	(23·79)	(4·83)	(47·14)	(26·14)	(5·13)
Nd	Light	164	29·94	52·69	4·99	47·05	23·56	4·76	45·28	25·87	5·11
	pink		(30·23)	(52·55)	(5·07)	(47·01)	(23·60)	(4·75)	(45·10)	(25·98)	(5·10)
Sm	Cream	155	30·68	52·07	4·93	47·93	23·12	4·68	46·15	25·44	5·03
			(30·42)	(52·01)	(4·98)	(47·32)	(23·05)	(4·62)	(46·31)	(25·48)	(5·08)
						48·22	23·01	4·65	46·43	25·33	5·01
						(48·31)	(23·04)	(4·64)	(46·40)	(25·31)	(5·03)
Gd	Cream	199	31·53	51·36	4·86	48·91	22·71	4·59	47·13	25·05	4·95
			(31·64)	(51·53)	(4·88)	(48·97)	(22·79)	(4·60)	(47·27)	(25·12)	(4·88)
Dy	Cream	198	32·18	50·81	4·81	49·60	22·38	4·53	47·81	24·65	4·88
			(32·11)	(50·72)	(4·77)	(49·74)	(22·47)	(4·51)	(48·48)	(24·57)	(4·91)
Er	Light	270	32·70	50·38	4·77	50·26	22·11	4·47	48·47	25·36	4·82
	pink		(32·82)	(50·49)	(4·79)	(50·62)	(22·02)	(4·45)	(48·36)	(24·40)	(4·85)
Yb	Cream	205	33·38	49·81	4·71	51·03	21·76	4·40	49·25	24·06	4·75
			(33·41)	(49·85)	(4·72)	(51·09)	(21·70)	(4·42)	(49·17)	(24·02)	(4·79)
Y	Cream	202	20·23	59·19	5·60	37·41	27·82	5·63	35·75	30·41	6·02
			(20·28)	(59·37)	(5·67)	(37·48)	(27·91)	(5·69)	(36·02)	(30·05)	(6·07)

Figures in the parentheses indicate theoretical values.

EBA = Ethyl benzoylacetate, MEAA = 3-methyl ethylacetoacetate and EEAA = 3-ethyl ethylacetoacetate anions.

RESULTS AND DISCUSSION

The chelates of ethyl benzoylacetate are readily soluble in common organic solvents and those of 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate are soluble in acetone *in situ* but once dried, turn practically insoluble. The chelates of 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate melt above 250°C and the colour of the chelates correspond to those of the respective lanthanide ions.

U.V. spectra

The spectra are recorded in ethanol. The wavelengths of the maxima of the absorption bands are listed in Table 3, along with the corresponding molar extinction coefficient values.

The u.v. spectrum of ethyl benzoylacetate has absorption maxima at 243 mμ and 285 mμ in ethanol. Both the bands at 243 and 285 mμ are composite bands. On chelation, molar extinction coefficient values increase fourfold with bathochromic shift of the 285 mμ band.

If the u.v. absorption spectra of ethyl benzoylacetate chelates are compared

Table 3. U.V. spectral data of the chelates

Compound	Ethanol λ_{max} (mμ)	ϵ_{max}
$C_6H_5COCH_2COOC_2H_5$	243	9650
	285	4800
$[La(EBA)_2(OH)(H_2O)]$	243	30,170
	290	16,030
$[Pr(EBA)_2(OH)(H_2O)]$	244	31,830
	291	15,380
$[Nd(EBA)_2(OH)(H_2O)]$	244	36,830
	291	18,690
$[Sm(EBA)_2(OH)(H_2O)]$	244	34,930
	291	19,070
$[Gd(EBA)_2(OH)(H_2O)]$	243	35,560
	290	18,840
$[Dy(EBA)_2(OH)(H_2O)]$	244	36,220
	290	16,830
$[Er(EBA)_2(OH)(H_2O)]$	243	35,300
	290	18,790
$[Yb(EBA)_2(OH)(H_2O)]$	243	34,890
	290	18,570
$[Y(EBA)_2(OH)(H_2O)]$	243	35,220
	290	18,680

EBA = Ethyl benzoylacetate anion.

with those of ethylacetoacetate chelates in the same solvent, ethanol, it is observed that the long wavelength band of the chelates increases in both wavelength and intensity in the order $[Ln(EAA)_2(OH)(H_2O)] < [Ln(EBA)_2(OH)(H_2O)]$. This order probably represents increasing participation of resonance structures

Table 4. Electronic absorption spectra of 0·1M aqueous $Pr(NO_3)_3$, $Nd(NO_3)_3$ and 0·1M $[Pr(EBA)_2(OH)(H_2O)]$ and $[Nd(EBA)_2(OH)(H_2O)]$ in chloroform

	Level	$Ln(NO_3)_3$ in water (Frequency, cm^{-1})	ϵ_{aquo}	$[Ln(EBA)_2(OH)(H_2O)]$ in chloroform (Frequency, cm^{-1})	$\epsilon_{complex}$	$\frac{\epsilon_{complex}}{\epsilon_{aquo}}$	$1-\beta$ ($\times 10^{-2}$)
Pr	$^3H_4 \longrightarrow$						
	$^1D_2$	16,980	1·85	16,920	1·95	1·05	0·35
	$^3P_0$	20,750	3·00	20·660	4·87	1·62	0·42
	$^3P_1$	21,320	4·22	21,230	5·97	1·42	0·41
	$^3P_2$	22,470	9·83	22,375	10·72	1·09	0·43
Nd	$^4I_{9/2} \longrightarrow$						
	$^4F_{5/2}$, $^2H_{9/2}$	12,470	6·36	12,420	8·20	1·29	0·40
	$^4F_{7/2}$, $^4S_{3/2}$	13,370	5·54	13,300	6,42	1·16	0·52
	$^4G_{5/2}$, $^2G_{7/2}$	17,270	6·06	17,120	17·28	2·85	0·87
	$^4G_{7/2}$	19,050	3·46	18,940	4·69	1·35	0·58
	$^2G_{9/2}$	19,460	1·61	19,380	2·72	1·691	0·40

involving phenyl group with the chelate rings. A similar progression toward longer wavelength and more intense absorption with increasing number of phenyl groups occurs with the longer wavelength band of the β-diketone chelates of lanthanons [4].

Visible spectra

Table 4 shows the absorption spectra of $[Pr(EBA)_2(OH)(H_2O)]$ and $[Nd(EBA)_2(OH)(H_2O)]$ in chloroform solution and of hydrated praseodymium and neodymium ions. The spectra show little effect on band positions and band intensifications except for the hypersensitive transition ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ in the neodymium chelate. Here the molar extinction coefficient value increases from $\epsilon = 6{\cdot}06$ in the salt to $\epsilon = 17{\cdot}28$ in the chelate. As in the case of the ethylacetoace-

Table 5. The i.r. spectra of the ethyl benzoylacetate chelates of praseodymium, samarium, gadolinium and erbium and those of the 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate chelates of praseodymium and erbium in the range of 4000–700 cm^{-1}

Ethyl benzoyl acetate	$[Pr(EBA)_2{}^{(OH)}_{(H_2O)}]$	$[Sm(EBA)_2{}^{(OH)}_{(H_2O)}]$	$[Gd(EBA)_2{}^{(OH)}_{(H_2O)}]$	$[Er(EBA)_2{}^{(OH)}_{(H_2O)}]$
3450 (m)	3340 (b)			
2950 (m)				
1740 (S)	1645 (s)	1645 (s)	1645 (s)	1645 (s)
1690 (s)	1625 (s)	1625 (s)	1625 (s)	1625 (s)
1618 (s)	1587 (s)	1585 (s)	1585 (s)	1585 (s)
1598 (m)	1545 (m)	1545 (m)	1543 (m)	1543 (m)
1576 (m)	1522 (m)	1520 (m)	1520 (m)	1518 (m)
	1268 (s)	1265 (s)	1265 (s)	1265 (s)
1442 (s)	1186 (s)	1185 (s)	1185 (s)	1185 (s)
1406 (s)	1113 (m)	1112 (m)	1110 (m)	1110 (m)
1380 (w)	1100 (m)	1100 (m)	1100 (m)	1100 (m)
1360 (m)	1070 (w)	1070 (w)	1068 (w)	1068 (w)
1320 (s)	1043 (m)	1042 (m)	1040 (m)	1040 (m)
1263 (s)	1030 (m)	1030 (m)	1030 (m)	1030 (m)
1196 (s)	1005 (w)	1002 (w)	1000 (w)	1000 (w)
1144 (s)	975 (w)	975 (w)	975 (w)	975 (w)
1095 (w)	920 (m)	920 (m)	920 (m)	920 (m)
1076 (m)	843 (w)	842 (w)	840 (w)	840 (w)
1035 (s)	805 (w)	805 (w)	805 (w)	805 (w)
1020 (s)	780 (s)	780 (s)	780 (s)	778 (s)
1000 (s)	702 (s)	702 (s)	700 (s)	700 (s)
940 (m)				
926 (m)				
900 (w)				
842 (w)				
806 (m)				
775 (s)				
756 (s)				
720 (m)				
686 (s)				

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4. R. G. Charles and R. C. Ohlmann, *J. inorg. nucl. Chem.* **27**, 255 (1965).

Table 5. (*Contd.*)

3-Methyl ethyl-aceto-acetate	3-ethyl ethyl-aceto-acetate	[Pr(MEAA)$^{(OH)_2}_{(H_2O)_2}$]	[Pr(EEAA)$^{(OH)_2}_{(H_2O)_2}$]	[Er(MEAA)$^{(OH)_2}_{(H_2O)_2}$]	[Er(EEAA)$^{(OH)_2}_{(H_2O)_2}$]
3550 (b)	3550 (b)	3320 (b)	3320 (b)	3300 (b)	3310 (b)
3010 (s)	3000 (s)				
1745 (s)	1745 (s)	1635 (mb)	1635 (mb)	1635 (mb)	1635 (mb)
1720 (s)	1722 (s)	1610 (mb)	1610 (mb)	1610 (mb)	1610 (mb)
1650 (m)	1650 (m)	1540 (mb)	1540 (mb)	1535 (mb)	1540 (mb)
1620 (m)	1625 (m)	1510 (s)	1510 (s)	1508 (s)	1508 (s)
1455 (s)	1465 (s)	1410 (m)	1410 (m)	1405 (m)	1408 (m)
1360 (s)	1360 (s)	1350 (m)	1350 (m)	1347 (m)	1350 (m)
1325 (w)	1325 (w)	1250 (m)	1250 (m)	1248 (m)	1248 (m)
1265 (w)	1275 (w)	1165 (w)	1165 (w)	1160 (w)	1165 (w)
1245 (m)	1250 (m)	1050 (m)	1052 (m)	1050 (m)	1055 (m)
1025 (s)	1200 (s)	1020 (w)	1020 (w)	1017 (w)	1020 (w)
1152 (s)	1150 (s)	850 (s)	850 (s)	845 (s)	855 (s)
1095 (m)	1110 (m)	680 (m)	680 (m)	675 (m)	685 (m)
1075 (m)	1090 (m)	610 (m)	610 (m)	606 (m)	610 (m)
1050 (m)	1050 (m)				
1020 (s)	1020 (s)				
950 (w)	960 (w)				
860 (s)	860 (s)				
800 (w)	800 (w)				

s = strong; m = medium; b = broad; w = weak.

tate chelate[2], the nephelauxetic parameter values have also been calculated for the ethyl benzoylacetate chelates. The values obtained show the same trend as observed in the ethylacetoacetate chelates.

I.R. spectra

From the studies on the i.r. spectra of β-ketoesters[5, 6], the high frequency band has been assigned to the carbonyl stretching vibration of the ester and the lower frequency band to the ketone function. Table 5 gives the i.r. absorption spectral bands of ethyl benzoylacetate, 3-methyl ethylacetoacetate, 3-ethyl ethylacetoacetate and their lanthanide chelates.

Ethyl benzoylacetate chelates

The ethyl benzoylacetate chelates seem to have double chelate carbonyl bands, corresponding to the ester carbonyl and ketonic carbonyl of the ligands. The 1645 cm^{-1} band of the ethyl benzoylacetate chelates has been assigned to the ester carbonyl chelated to the lanthanide(III) ion and the lower frequency band at 1625 cm^{-1} must correspond to the chelated ketonic carbonyl group. The frequencies of both of these bands are therefore strongly shifted (*ca.* 100 cm^{-1}) to

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5. R. S. Rasmussen and R. R. Brittain, *J. Am. chem. Soc.* 77, 1073 (1949).
6. N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Peterson, *J. Am. chem. Soc.* **74**, 4070 (1952).

lower frequencies by coordination with the lanthanide(III) ion. Another band at 1545 cm^{-1} is assigned to a C=C stretching vibration. The 920 and 3340 cm^{-1} bands correspond to $C–C_6H_5$ and OH stretching frequencies respectively.

3-Methyl ethylacetoacetate and 3-ethyl ethylacetoacetate chelates

An evidence for the formation of metal oxygen bond with the ketonic carbonyl group of the ester may be found in the absence of the enol band (3550 cm^{-1}). The bands at 1635 cm^{-1} and 1610 cm^{-1} due to the ester carbonyl and ketonic carbonyl group frequencies of the ester are rather broad. A very intense broad band around 3320 cm^{-1} in all the chelates is assigned to OH stretching frequency.

Formation constant

For lanthanide chelates of 3-methyl ethylacetoacetate and 3-ethyl ethylacetoacetate only log K_1 values could be determined since the $\bar{n}$ values did not exceed 0·5–0·6 at pH 6·0 above which appreciable hydrolysis of the metal ions occur[7]. The formation constant values increase with the increase in atomic number with a break at gadolinium.

7. R. S. Tobias and A. B. Garrett, *J. Am. chem. Soc.* **80**, 3532 (1958).