STABILITY CONSTANTS, STRUCTURE AND THERMOGRAVIMETRIC ANALYSIS OF La(III) COMPLEXES WITH SOME ARYLHYDRAZONES OF BENZOYLACETONE AND DIBENZOYLMETHANE

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ABSTRACT

The successive stability constants of La(III) with some arylhydrazones of benzylacetone (BAAH) and dibenzoylmethane (DBMAH) have been determined potentiometrically following the Bjerrum pH-metric titration. The stability constants of the metal chelates are correlated to the Hammett substituent constant (σ_x) and to the molecular structure. The structures of the complexes have been assigned on the basis of elemental analysis, IR, NMR spectroscopy and thermogravimetric analysis (TG). It is found that chelation occurs through the –NH and one carbonyl group of the β-diketone in addition to the OH^- group. The coordination number ranges from six to eight which is confirmed by thermogravimetric analysis. The structural formulae are suggested.

INTRODUCTION

Arylhydrazones of β-diketones are of great pharmaceutical importance as anti-diabetics [1], anti-malarial agents [2] and potential bactericides [3]. They are also used as dyes for artificial textiles and polyester fibres [4]. Yao [5] has studied the coupling of the diazonium ion with β-diketones (acetylacetone, benzoylacetone and dibenzoylmethane). He confirmed the formation of the hydrazo rather than the azo form using IR and NMR spectroscopy. Mitchell and Nonhebel [6,7] studied the IR and NMR spectra of some 2-arylhydrazones of 1,2,3-tricarbonyl compounds in an attempt to investigate the isolation, the interconversion of the tautomers and the influence of electronic and steric factors on the structure of the preferred tautomer.

Pichon et al. [8] investigated the structures and physical properties in solutions of compounds obtained from condensation of aryldiazonium salts with carbonions of β-diketones.

Recently, the electronic absorption spectra of some benzoylacetone arylhydrazone (BAAH) and dibenzoylmethane arylhydrazone (DBMAH)

derivatives in organic solvents were investigated. The structures of the arylhydrazones prepared were confirmed by IR and NMR spectroscopy [9].

The successive stability constants ($\log k_1$ and $\log k_2$) of the complexes of some benzoylacetonearylhydrazone (BAAH) **I** and dibenzoylmethanearyl-hydrazone (DBMAH) **II** derivatives with the La(III) ion have been determined by potentiometry and correlated with the σ_x (Hammett constant) of the ligand. The complexes formed have been investigated by conductimetric titration, IR, NMR spectroscopy, elemental and thermo-gravimetric analysis.

EXPERIMENTAL

Benzoylacetonearylhydrazone (BAAH) **I** and dibenzoylmethanearyl-hydrazone (DBMAH) **II** derivatives were prepared by the coupling of benzoylacetone (c.p.) or dibenzoylmethane (c.p.) (0.02 mol) dissolved in 50 ml ethanol, with substituted diazonium salt (0.02 mol) prepared in the usual manner [10], in the presence of sodium acetate as a weak base [5]. The resulting solutions were acidified with dilute (1 : 1) HCl. The products were filtered and recrystallized from ethanol to constant melting point. The purity of the resulting compounds was confirmed by elemental analysis.
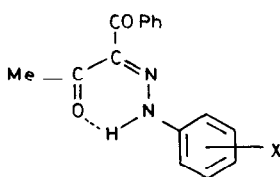
I
Benzoylacetonearylhydrazone
(BAAH) derivatives
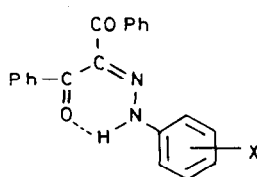
II
Dibenzoylmethanearylhydrazone
(DBMAH) derivatives

where X = H (a), p-Cl (b), p-CH$_3$, (c), p-OH (d), o-OH (e), m-NO$_2$ (f), p-OCH$_3$ (g), o-OCH$_3$ (h), o-COOH (i), p-SO$_2$NH$_2$ (j), o-AsO(OH)$_2$ (k), p-N(CH$_3$)$_2$ (l) and p-SO$_3$Na (m).

Stock dye solutions (0.001 M) were prepared in absolute ethanol. A 0.01 M solution of La(ClO$_4$)$_3$ was prepared in water and standardized with EDTA [11] using Arsenazo I as indicator; then a 0.001 M solution was prepared by accurate dilution. Solutions of 0.107 M perchloric acid, 0.305 N NaOH and 1 M sodium perchlorate were also prepared.

Three mixtures were prepared as follows
(a) 5 ml 0.107 M HClO$_4$ + 4.5 ml 1 M NaClO$_4$ + 20 ml ethanol and the volume was made up to 50 ml with distilled water.
(b) 5 ml 0.107 M HClO$_4$ + 4.5 ml 1 M NaClO$_4$ + 20 ml 10^{-3} M ethanolic solution of the hydrazone and the volume was made up to 50 ml.

(c) 5 ml 0.107 M $HClO_4$ + 4.5 ml 1 M $NaClO_4$ + 20 ml 10^{-3} M ethanolic solution of the hydrazone + 4 ml 10^{-3} M $La(ClO_4)_3$ and the volume was made up to 50 ml.

The above three mixtures were titrated potentiometrically against 0.305 M NaOH using a pH meter (Schott Mainz Model CG 801 digital Ionalyzer) at $27 \pm 0.1°C$. The correction factor for converting the pH-meter reading in 40% (v/v) ethanol–water to pH values, amounts to 0.15 [12], and the pH versus volume of NaOH curves were plotted accordingly. The $\bar{n}_A$, $\bar{n}$ and pL values were calculated using the equations described by Irving and Rossotti [13]. The methods used for calculating the successive stability constants are interpolation at half $\bar{n}$ values, correction term, mid-point method and successive approximation [14].

Conductimetric titrations were performed using a PTI 18 digital conductivity meter at a frequency of 2 kHz. The solid complexes were prepared and characterized on the basis of microanalysis, thermogravimetric analysis, IR and NMR spectroscopy. The IR spectra of the ligands and lanthanum complexes were recorded as a kBr disc using a Pye Unicam SP 1000 infrared spectrophotometer, while their NMR spectra were scanned using a Varian EM-360, 60 MHz NMR spectrometer.

RESULTS AND DISCUSSIONS

The stability constants of lanthanum complexes (Table 1) with the arylhydrazones under investigation were determined potentiometrically using the method described by Sarin and Munshi [15]. The formation curves (of the La complexes) were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) against the free ligand exponent (pL). The successive stability constants were calculated using the methods mentioned before [14].

Plotting log β_1 versus pK_{NH} for the complexes of some BAAH and DBMAH derivatives with La shows good linear correlations ($r = 0.84$ and 0.87 for BAAH and DBMAH complexes respectively) (Fig. 1). Deviation from a slope of unity is mainly attributed to possible steric interactions, to π-electron back-donation from the metal ion to the ligand or to structural changes in the ligand which alter the strength of the metal-ion–donor-atom bonds within the ligand.

When log β_1 for La complexes with some BAAH and DMBAH derivatives was plotted against Hammett constant (σ), linear correlations were obtained (Fig. 1c). The statistically calculated slope values (a) are -1.16 and -2.035 for La complexes with BAAH and DBMAH respectively (Table 2). These linear correlations indicate that the complexation reactions of the BAAH and DBMAH dyes are susceptible to the influence of substituents on the arylhydrazone moieties. The negative sign of a indicates that complexa-

TABLE 1

Cumulative data of log β_1 and log β_2 for some BAAH–and DBMAH–lanthanum complexes

Ligand	log β_1				log β_2			
	A	B	C	Mean	A	B	D	Mean
La–BAAH complexes								
Ia	7.92	7.80	8.00	7.91	15.22	15.22	15.15	15.20
Ib	8.06	7.9	8.32	8.1	15.16	15.13	15.12	15.13
Ic	8.90	9.20	8.60	8.90	15.15	14.53	13.90	14.52
Id	8.60	8.70	8.52	8.60	15.50	15.51	15.00	15.34
Ie	4.75	4.73	4.77	4.75	9.00	8.97	8.95	8.97
If	7.79	7.80	7.79	7.79	14.64	14.3	13.96	14.35
Ig	9.33	9.05	9.63	9.33	17.43	17.49	17.56	17.49
Ih	9.12	9.09	9.15	9.12	17.20	16.79	16.20	16.73
Ii	11.65	11.95	11.34	11.65	20.15	19.16	18.9	19.55
Ij	7.80	7.74	7.86	7.80	14.23	14.13	14.04	14.13
Il	5.43	5.55	5.31	5.43	9.78	9.66	9.54	9.66
La–DBMAH complexes								
IIa	9.70	9.57	9.83	9.7	18.55	18.5	18.7	18.58
IIb	8.95	8.9	9.01	8.95	16.45	16.34	16.18	16.32
IIc	8.45	8.50	8.56	8.45	15.35	15.50	15.50	15.45
IId	10.80	10.75	10.85	10.8	18.45	19.02	19.6	19.03
IIe	10.00	10.05	10.01	10.00	18.00	18.55	19.00	18.51
IIg	9.60	9.65	9.56	9.60	17.68	17.7	17.68	17.68
IIi	9.51	9.53	9.50	9.51	18.88	18.90	18.90	18.19
IIk	12.78	–	12.79	12.78	17.08	–	17.0	17.04

A, interpolation at half $\bar{n}$ values method; B, correction-term method; C, successive approximation method; D, mid-point method.

tions are favoured by high electron densities at the coordination sites. These high electron densities could be brought about in two ways. Positive resonance interactions within the ligand would tend to increase the electron density at the chelation sites thereby increasing complex stability. Negative resonance interaction would show an opposite effect, normally resulting in a decrease in the complex stability.

The same argument could be applied for the relation of log β_2 versus σ for La complexes with BAAH and DBMAH derivatives.

It should be mentioned that for La complexes with DBMAH derivatives, the low correlation coffecients ($r = 0.54, 0.41$) may be attributed to the steric hindrance produced by the bulky ligand molecule which may lead to a decrease of the coplanarity.

The formation curves obtained for the La–BAAH and La–DBMAH derivatives reveal that the chelates have the stoichiometric ratios 1:1 and 1:2 (La^{3+}:L).

The conductimetric titration curves (Fig. 2) for the La–BAAH and La–DBMAH derivatives under investigation show two breaks at molar
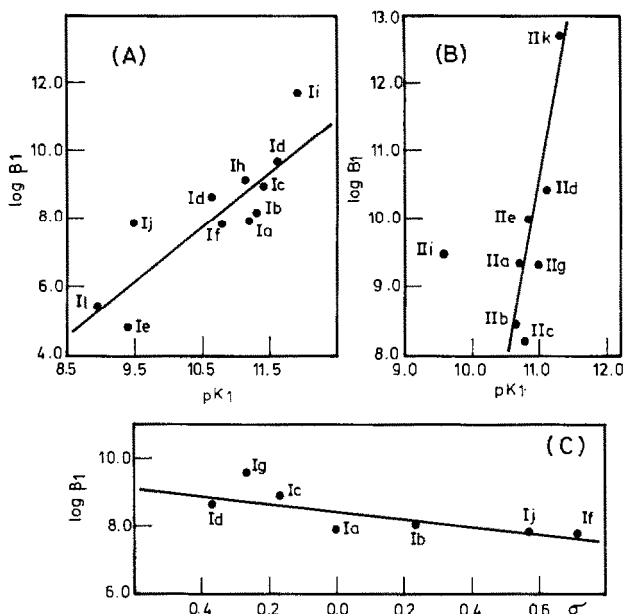
Fig. 1. (A) Log β_1 vs. pK_1 for lanthanum complexes of some BAAH derivatives, (B) log β_1 vs. pK_1 for lanthanum complexes with some DBMAH derivatives, (C) log β_f vs. σ for lanthanum complexes with Ia, Ib, Ic, Id, If, Ig and Ij.

TABLE 2

Cumulative results of pK_{NH}, log β_1 and log β_2 in relation to σ for some BAAH and DBMAH derivatives

	X	σ	I (BAAH)			II (DBMAH)		
			pK_{NH}	log β_1	log β_2	pK_{NH}	log β_1	log β_2
a	H	0.00	11.22	7.92	15.20	10.72	9.70	18.58
b	p-Cl	0.23	11.33	8.10	15.13	10.67	8.93	16.32
c	p-CH$_3$	-0.17	11.42	8.90	14.52	10.77	8.45	15.45
d	p-OH	-0.37	10.68	8.60	15.34	11.12	10.80	19.03
e	o-OH	–	9.41	4.75	8.97	10.85	10.00	18.51
f	m-NO$_2$	0.71	10.82	7.79	14.35	–	–	–
g	p-OCH$_3$	-0.27	11.61	9.33	17.49	11.02	9.60	17.68
h	o-OCH$_3$	–	11.15	9.12	16.73	–	–	–
i	o-COOH	–	11.88	11.65	19.55	9.60	9.51	18.19
j	p-SO$_2$NH$_2$	0.57	9.50	7.80	14.13	–	–	–
l	p-N(CH$_3$)$_2$	-0.83	8.95	5.43	9.66	–	–	–
k	o-AsO(OH)$_2$	–	–	–	–	11.30	12.78	17.04

Statistical results for the studied relations

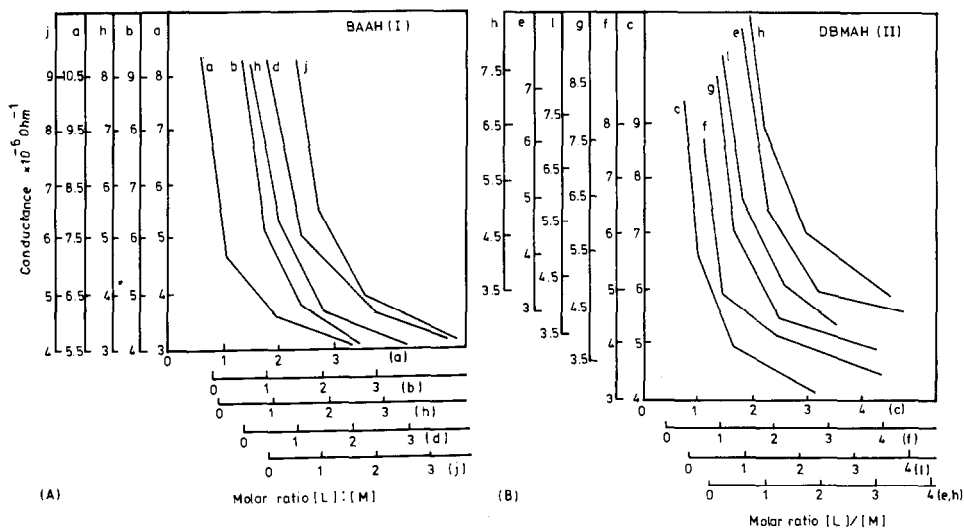| Relations	I (BAAH)				II (DBMAH)			
	a	b	r	s	a	b	r	s
log β_1 vs. pK_{NH}	1.59	-8.92	0.84	1.05	5.33	-48.25	0.87	0.76
log β_2 vs. pK_{NH}	2.70	-14.32	0.75	1.6	1.45	1.53	0.25	1.39
log β_1 vs. σ	-1.16	8.46	0.80	0.39	-2.03	9.26	0.54	0.86
log β_2 vs. σ	-1.67	15.33	0.62	0.96	-2.6	17.1	0.41	1.58

Fig. 2. (a) Conductimetric titration of a 10^{-3} M solution of La with 4×10^{-5} M solutions of Ia, Ib, Id, Ih and Ij, (b) conductimetric titration of a 10^{-3} M solution of Ld^{3+} with 50 ml of 4×10^{-5} M solutions of IIc, IIe, IIf, IIg, IIh and III.

ratios of 1 : 1 and 1 : 2 indicating the formation of two types of complexes with stoichiometric ratios 1 : 1 and 1 : 2 (La^{3+} : L), which is in accordance with the results obtained from pH-metric titrations. The titration curves indicate a gradual increase in the conductance values due to the displacement of protons from the ligands on complex formation.

The solid complexes were prepared by reacting 1 : 1 and 1 : 2 stoichiometric proportions of La^{3+} and the ligands (Ia, Ib, Id, Ih, Ii, Ij, IIc, IId, IIe, IIf, IIg, IIh and III). The hot mixture was stirred and left for 30 min on a steambath; then dilute ammonium hydroxide solution was added dropwise with stirring. At pH values ranging from 8 to 9.50, the solid complexes were precipitated, collected and washed with cold ethanol. 1 : 2 complexes were obtained in all cases except for La^{3+} with Ii and III where 1 : 1 complexes were obtained (Table 3).

The TG results obtained using a DuPont 1090 thermal analyzer for La^{3+} complexes with Ia, Ib, Ih and III are in good agreement with the theoretical values.

The decreases observed in the temperature range 125–200°C for the thermograms of La^{3+} complexes with Ia, Ib, Ih and III corresponds to weight loss percentages 8.00, 2.00, 4.40 and 6.00%; hence the calculated number of water molecules is 3, 1, 2 and 2 respectively. Also, the temperature range in which the loss occurs indicates that these water molecules are coordinated to the central lanthanum ion.

The mode of bonding of the ligands to the La^{3+} was examined by recording the IR spectra of the complexes and comparing them with those of the ligands. Spectra of the lanthanum chelates of BAAH and DBMAH

TABLE 3

Elemental analysis of La complexes with some BAAH (I) and DBMAH (II) derivatives

Ligand (M:L)	Formula	C (%) Calc. (found)	H (%) Calc. (found)	N (%) Calc. (found)	La (%) Calc. (found)
Ia (1:2)	$La(C_{16}H_{14}N_2O_2)_2(H_2O)_2(OH)$	51.89 (51.10)	4.46 (4.40)	7.57 (7.60)	18.77 (18.20)
Ib (1:2)	$La(C_{16}H_{13}N_2O_2Cl)_2(H_2O)(OH)$	49.68 (50.50)	3.50 (3.95)	7.24 (7.30)	17.97 (18.10)
Id (1:2)	$La(C_{16}H_{14}N_2O_3)_2(OH)$	53.49 (54.20)	4.02 (4.40)	7.80 (7.30)	19.34 (19.00)
Ih (1:2)	$La(C_{17}H_{16}N_2O_3)_2(H_2O)_2(OH)$	51.98 (51.80)	4.58 (4.10)	7.13 (6.9)	17.70 (18.00)
Ii (1:1)	$La(C_{17}H_{14}N_2O_4)(H_2O)_3(OH)$	39.39 (39.56)	3.67 (4.00)	5.40 (5.21)	26.81 (27.10)
Ij (1:2)	$La(C_{16}H_{15}NO_4S)_2(OH)$	45.40 (46.10)	3.42 (3.60)	9.93 (9.70)	16.42 (15.90)
IIc (1:2)	$La(C_{22}H_{18}N_2O_2)_2(OH)$	63.01 (64.20)	4.17 (4.20)	6.67 (6.40)	16.57 (15.83)
IId (1:2)	$La(C_{21}H_{16}N_2O_3)_2(OH)$	59.86 (62.00)	3.68 (4.10)	6.65 (6.30)	16.49 (16.20)
IIe (1:2)	$La(C_{21}H_{16}N_2O_3)_2(H_2O)_2(OH)$	57.28 (57.50)	3.98 (4.20)	6.36 (6.10)	15.78 (15.30)
IIf (1:2)	$La(C_{21}H_{15}N_3O_4)_2(OH)$	56.00 (57.00)	3.22 (3.90)	9.33 (8.90)	15.43 (15.10)
IIg (1:2)	$La(C_{22}H_{18}N_2O_3)_2(H_2O)_2(OH)$	58.28 (57.50)	4.30 (4.00)	6.18 (5.90)	15.13 (14.90)
IIh (1:2)	$La(C_{22}H_{18}N_2O_3)_2(OH)$	60.70 (62.00)	4.02 (4.20)	6.43 (6.05)	15.96 (15.40)
IIl (1:1)	$La(C_{23}H_{21}N_3O_2)(H_2O)_2(OH)$	47.75 (47.60)	4.15 (4.20)	7.26 (7.10)	24.03 (22.9)

derivatives are compatible with the structure that would result if the chelated hydrogen of the ligand is replaced by lanthanum. Thus, the position of the free carbonyl bands of the ligand is marginally altered in the spectra of their La chelates. Instead of the free ligand bands at 1620 cm^{-1} (due to hydrogen-bonded carbonyl); the spectra of the La complexes exhibit another strong band at around 1580 cm^{-1} assignable [16] to C=O $\cdots$ M. In addition to these, metal–oxygen stretching and vibrational modes coupled with ring deformation $\nu_{(M-O)}$ and δ_{ring} were observed at about 650 cm^{-1}. Both BAAH–La^{3+} and DBMAH–La^{3+} complexes exhibit a broad band within the wavenumber range 3500–3400 cm^{-1} which is attributed to the stretching frequency of coordinated water molecules, while the bands observed in the ranges 1075–1110 cm^{-1} and 830–860 cm^{-1} were attributed to δ_{OH} and δ_{OH} of the bonded water molecule.

Substantial support for the results obtained from the IR spectra is gained by comparing the NMR spectra of some complexes with those of their

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ligands. The NMR spectra of the ligands Ia (H), Ib (*p*-Cl) and Ih (*o*-OCH₃) exhibit a singlet in the range 11–12.70 ppm. This band may be assigned to the ionizable proton of the NH group. As this band disappears after deuteration, this is evidence for the above assignment. The NMR spectra of their lanthanum complexes do not show this low field signal, thus confirming that the chelated hydrogen is replaced by the La(III) ion.

Thus the structure of the 1 : 1 and 1 : 2 (M : L) complexes of La(III) with Ii and IIi respectively may be formulated as follows

M–Ii (1 : 1)
M = La
III

M–IIi (1 : 2)
M = La
n = 1 or 3
V
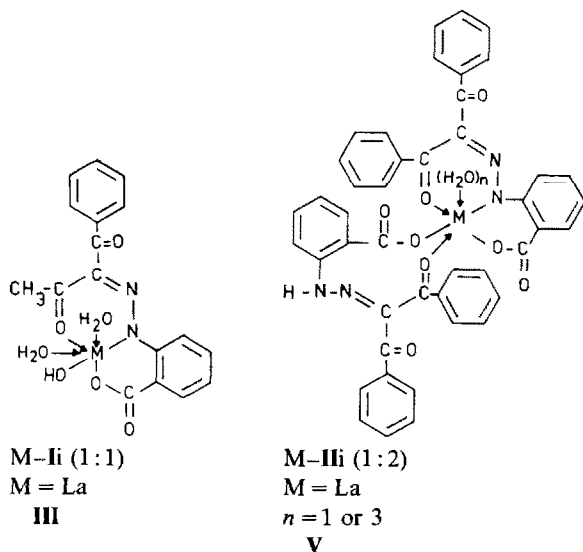
The structures of the 1 : 2 (M : L) complexes of La(III) with BAAH and DBMAH derivatives with x groups not involved in chelation may be formulated as follows

M–BAAH (1 : 2)
M = La
n = 1 or 3
IV

M–DBMAH (1 : 2)
M = La
n = 1 or 3
VI
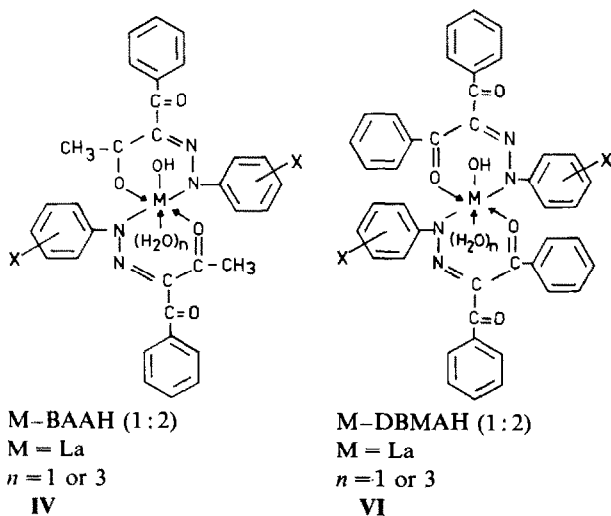
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