

Synthesis, Characterisation and Biological Evaluation of Lanthanide(III) Complexes with 3-Acetylcoumarin-*o*-aminobenzoylhydrazone (ACAB)

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Lanthanide(III) complexes of the general formula $[\text{Ln}(\text{ACAB})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$ where $\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}, \text{Tb(III)}, \text{Dy(III)}$ and Y(III) , ACAB=3-acetylcoumarin-*o*-aminobenzoylhydrazone have been isolated and characterised based on elemental analyses, molar conductance, IR, ^1H - and ^{13}C -NMR, UV, TG/DTA and EPR spectral studies. The ligand behaves in bidentate fashion coordinating through hydrazide $>\text{C}=\text{O}$ and nitrogen of $>\text{C}=\text{N}$. A coordination number of ten is assigned to the complexes. Antibacterial and Antifungal studies indicate an enhancement of activity of the ligand on complexation.

Key words lanthanide metal complex; hydrazone complex; spectral study; antibacterial activity; antifungal activity

Coumarins generate strong interest stemming from their great physiological and biological activities¹⁾ which is further exemplified by their roles as anticoagulants (dicoumarols/warfarins), aflatoxins and psoralens,²⁾ the important drugs in use. Apart from the above, their role as caging agents in photoactivable “caged” analogues of biomolecules, cytidine diphosphate and glutamic acid,³⁾ and as probes for reactive oxygen species (ROS)⁴⁾ spurred further interest in these compounds. Earlier studies from our laboratory^{5,6)} on biological activity of coumarins and their complexes, showed significant enhancement of antibacterial and antifungal activity of the coumarin derivative on complexation. Keeping this in mind, and in continuation of our previous studies,^{5–7)} in the present contribution we report the synthesis and characterisation of Ln(III) complexes with a potentially quadridentate ligand, 3-acetylcoumarin-*o*-aminobenzoylhydrazone (ACAB) and effect of complexation on biological activity of this ligand.

Experimental

Materials Reagent grade chemicals were used without further purification. Methyl anthranilate was obtained from S.D. Fine Chemicals Ltd. and Hydrazine hydrate was from Rankem. 3-Acetylcoumarin and *o*-aminobenzoylhydrazone were synthesized according to literature method.^{8,9)}

Physical Measurements The metal contents of the complexes were determined by complexometric titrations against EDTA.¹⁰⁾ Carbon, Hydrogen and Nitrogen contents were determined by using a Carlo-Erba Strumentazione (Italy) CHN analyzer. Molar conductivities in DMSO ($10^{-3} \text{ mol l}^{-1}$) at room temperature (26 °C) were measured using an Elico conductivity bridge having platinum electrodes. Magnetic moments were determined by a Faraday balance. The IR spectra of ligand and its metal complexes were recorded on a Nicolet 170 SX FT-IR spectrometer in the range 400–4000 cm^{-1} using KBr discs. The EPR spectrum of the Gd(III) complex was recorded on a Varian E-4X band spectrophotometer. The 1D and 2D NMR spectra of the ligand were recorded in DMSO- d_6 on Bruker AMX 500 spectrometer operating at 500.13 MHz for ^1H and 127.77 MHz for ^{13}C using 5 mm $^1\text{H}/^{13}\text{C}$ dual probe. The ^1H - and ^{13}C -NMR spectra of La(III) complex were recorded in DMSO- d_6 on Bruker Avance 300 spectrometer operating at 300.13 MHz for ^1H and 75.47 MHz for ^{13}C using 5 mm $^1\text{H}/^{13}\text{C}$ dual probe. UV-Visible spectra were measured on a Hitachi 2001 spectrophotometer using dimethylsulfoxide (DMSO) as solvent. Thermogravimetry (TG) and Differential Thermal Analysis (DTA) measurements were made in N_2 atmosphere between 20 and 1000 °C using a Perkin-Elmer (Pyris Diamond) Analyzer. Lanthanide nitrates were prepared by dissolving the corresponding oxide (99.99%, Indian Rare Earth) in 50% HNO_3 , followed by the evaporation of the excess acid. The ligand (ACAB) was synthesized according to the scheme (Chart 1).

Synthesis of Ligand 3-Acetyl coumarin (18.81 g, 100 mmol) was added

to the solution of *o*-aminobenzoylhydrazide (15.1 g, 100 mmol) in methanol (130 ml) and stirred for 2–3 h, which yielded an orange crystalline product, which was filtered, washed with alcohol and air-dried. It was further recrystallised from methanol. (Yield 92%, mp 115–116 °C.)

Preparation of Complexes $\text{Ln}(\text{NO}_3)_3$ (1 mmol) dissolved in minimum quantity of methanol was added to a hot solution of ligand (1 mmol) in 30 ml methanol/ CHCl_3 (1 : 1, v/v) and refluxed for 1 h. The pH was then raised to 6.5 by adding methanolic solution of sodium acetate and was further refluxed for 4–5 h. The clear orange solution formed was concentrated to a small volume and the precipitate obtained was washed swiftly with cold distilled water and air-dried. (Yield 85%, mp > 250 °C.)

Results and Discussion

The reaction of ACAB with $\text{Ln}(\text{NO}_3)_3$ resulted in the formation of complexes of the composition $[\text{Ln}(\text{ACAB})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$, where $\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}, \text{Tb(III)}, \text{Dy(III)}$ and Y(III) (Table 1). The complexes are non-hygroscopic, readily soluble in common organic solvents such as ethanol, methanol, acetone, dichloromethane, DMF and DMSO. All complexes are extremely soluble in water. Molar conductivity measurements of the complexes are commensurate with 1 : 1 electrolytic behaviour.¹¹⁾

Magnetic Properties and EPR Spectra The La(III) and Y(III) complexes are diamagnetic as expected. The room temperature magnetic moments of the complexes do not show much deviation from Van Vleck values¹²⁾ indicating that there is no significant participation of the 4f electrons in bonding since they are well shielded by the $5s^2 5p^6$ octet. However in case of Sm(III) and Eu(III) complexes a slight variation from Van Vleck values was observed.¹³⁾ Due to the

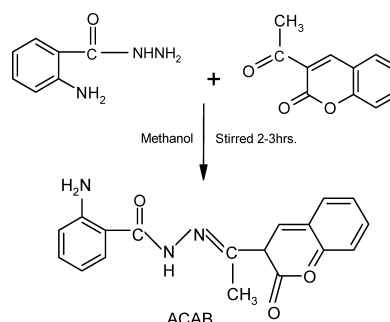


Chart 1

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Table 1. Analytical, Conductance and Magnetic Data of Ln(III) Complexes of ACAB

Code	Compound	Magnetic moment (BM)	Conductance ^{a)}	Elemental analysis (%) ^{b)}			
				M	C	H	N
C0	ACAB	—	—	—	67.31	4.77	13.17
C1	[La(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	dia	43.22	(—	67.28	4.98	13.08)
C2	[Pr(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	03.78	48.27	13.42	21.45	1.42	07.01
C3	[Nd(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	03.72	49.59	(13.60	21.15	1.76	06.85)
C4	[Sm(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	02.05	44.56	13.56	21.39	1.63	06.54
C5	[Eu(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	03.78	47.21	(13.70	21.28	1.75	06.84)
C6	[Gd(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	07.98	41.09	14.55	21.23	1.44	06.66
C7	[Tb(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	09.82	48.92	(14.05	21.04	1.75	06.82)
C8	[Dy(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	10.77	48.45	14.89	20.93	1.81	06.81
C9	[Y(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	dia	41.87	(15.12	20.77	1.73	06.73)
				14.91	21.21	1.69	06.78
				(15.26	20.75	1.72	06.72)
				15.08	20.55	1.73	06.59
				(15.55	20.67	1.72	06.70)
				08.69	21.92	1.89	07.04
				(09.15	22.24	1.85	07.20)

a) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, b) calculated values are in parentheses. dia=diamagnetic.

low J–J separation, the energy level between the ground state and the next higher level being only of the order of KT, the excited states are also populated leading to anomalous magnetic moments. This is known as the first order Zeeman effect.^{14,15)}

Gd (III) has an $^8s_{7/2}$ single ion ground state and a spin value $I=3/2$. The ground state is orbitally non-degenerate and well separated from the excited states. Compared to the other lanthanides, it does not show large anisotropic effects, thus giving rise to single ion magnetic properties.¹⁶⁾ The EPR spectra (both at RT and LNT) were broad having similar $\langle g \rangle$ value of 2.0, which is nearly equal to the free electron value (TCNE $\langle g \rangle=2.00277$). Similar line widths at both the temperatures indicate spin–lattice and spin–spin relaxation processes contribute equally to line width.

IR Spectra The IR band assignments are given in Table 2. IR spectra of the complexes shows that ACAB behaves as a bidentate ligand, coordinating through hydrazide carbonyl and azomethine nitrogen, with the carbonyl of lactone and ring —NH_2 remaining free. The coordinating behavior of the ligand is shown in Fig. 1. (Lattice molecules have been omitted for clarity.)

In the free ligand, a sharp peak at 3646 cm^{-1} is due to the presence of a methanol molecule, which fulfils a space-filling role in the lattice. Single crystal study of the ligand indicates that it is involved in a series of intermolecular and intramolecular hydrogen bondings¹⁷⁾ and the relevant ones are shown in Fig. 2.

The hydrazide carbonyl is intramolecularly hydrogen bonded (Fig. 2) with hydrogen of —NH_2 and lattice held methanol. Similarly, the lactone carbonyl oxygen is intermolecularly hydrogen bonded with amide NH, H5C and CH_3 group. The νNH stretch is observed at 3260 cm^{-1} . The bands at 3437 and 3367 cm^{-1} were assigned to the $\nu(\text{asym})$ and $\nu(\text{sym})$ vibrations of the —NH_2 group respectively.¹⁸⁾ A band at 1584 cm^{-1} is assigned to the —NH deformation mode of the primary amine.¹⁹⁾ Intense bands observed at 1695 and

1649 cm^{-1} were assigned to the $\nu(\text{C=O})$ lactone²⁰⁾ and $\nu(\text{C=O})$ ²¹⁾ of the hydrazide group, respectively. A band at 1617 cm^{-1} was ascribed to the $\nu(\text{C=N})$ of the azomethine group.²⁰⁾ Because of the involvement of lactone carbonyl in hydrogen bonding with the CH_3 group, it is observed at a lower frequency.¹⁷⁾ The amide II band is observed at 1518 cm^{-1} whereas a band at 1248 cm^{-1} is assigned to the amide III band.¹⁷⁾

The presence of the $\nu(\text{C=O})$ or amide I band at a relatively low wave number (1649 cm^{-1}) suggests the involvement of the carbonyl oxygen in strong intramolecular hydrogen bonding with the NH_2 group²²⁾ as mentioned earlier.

On complexation, the $\nu(\text{C=O})$ of hydrazide is shifted to lower wave number ($1644\text{—}1646 \text{ cm}^{-1}$) as is the amide II band²¹⁾ which is also shifted to lower frequency ($1512\text{—}1516 \text{ cm}^{-1}$) whereas the amide III band (1248 cm^{-1}) undergoes a shift to higher frequency ($1256\text{—}1262 \text{ cm}^{-1}$).²³⁾ These changes in amide group vibrations indicate the coordination of the amide oxygen to the metal ion.^{24,21)}

Increase in lactone carbonyl frequency ($13\text{—}21 \text{ cm}^{-1}$) has been observed, which is attributed to the deconjugation of the carbonyl group due to coordination *via* azomethine nitrogen²⁵⁾ and breakdown of hydrogen bonding between lactone oxygen and hydrogen of methyl group.

Further, coordination of the azomethine nitrogen to the metal leads to reduction in electron density of the azomethine linkage, which results in a downward shift ($10\text{—}11 \text{ cm}^{-1}$) of $\nu(\text{C=N})$ band.^{26,27)} The complexes exhibit bands at 1488 (ν_4), 1285 (ν_1), $1029\text{—}1035$ (ν_2), $810\text{—}813$ (ν_6), $751\text{—}754$ (ν_3) and $693\text{—}695 \text{ cm}^{-1}$ (ν_3) corresponding to the coordinated nitrate molecules. The magnitudes of $\nu_4\text{—}\nu_1$ and $\nu_3\text{—}\nu_5$ lie in the range $207\text{—}208 \text{ cm}^{-1}$ and $50\text{—}58 \text{ cm}^{-1}$ respectively, which is characteristic of bidentate coordination of nitrate moiety.²⁸⁾

A broad band between $3370\text{—}3380 \text{ cm}^{-1}$ due to coordinated water molecules obscures the NH_2 stretching frequencies. However the non-involvement of the latter in coordina-

Table 2. IR Spectral Data of ACAB and Its Ln(III) Complexes

Compd	$\nu(\text{OH})$	$\nu(\text{NH})_2$	$\nu(\text{C}=\text{O})$ lactone	$\nu(\text{C}=\text{O})$ hydrazide	Amide II	Amide III	$\nu(\text{C}=\text{N})$	-NO ₃ modes				
								ν_4	ν_1	ν_2	ν_6	ν_3
ACAB	—	3437, 3367 s	1695 s	1649 m	1518 s	1248 s	1617 m	—	—	—	—	—
C1	3372 b	<i>a)</i>	1703 m	1644 m	1512 s	1256 m	1607 m	1488 m	1284 m	1029 m	812 w	694 w
C2	3372 b	<i>a)</i>	1711 m	1644 m	1512 s	1259 m	1608 m	1488 m	1285 m	1029 m	813 w	694 w
C3	3372 b	<i>a)</i>	1716 s	1644 m	1512 s	1258 m	1608 m	1488 m	1286 m	1035 m	810 w	693 m
C4	3378 b	<i>a)</i>	1711 s	1644 m	1516 s	1258 m	1608 m	1488 m	1285 m	1029 m	812 w	695 w
C5	3371 b	<i>a)</i>	1711 s	1645 m	1514 s	1258 m	1608 m	1488 m	1286 m	1029 m	813 w	695 w
C6	3378 b	<i>a)</i>	1711 s	1645 m	1516 s	1258 m	1609 m	1488 m	1286 m	1029 m	813 w	695 w
C7	3375 b	<i>a)</i>	1708 s	1646 m	1512 s	1262 m	1611 m	1486 m	1285 m	1030 m	815 w	694 w
C8	3375 b	<i>a)</i>	1711 s	1644 m	1515 s	1259 m	1608 m	1488 m	1286 m	1029 m	812 w	695 w
C9	3374 b	<i>a)</i>	1712 s	1645 m	1512 s	1258 m	1608 m	1488 m	1286 m	1029 m	812 w	695 w

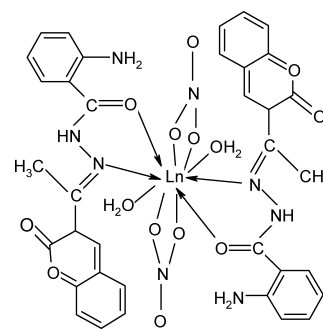
a) Obscured by $\nu(\text{OH})$ of coordinated water; b=broad, s=sharp, m=medium, w=weak.

Fig. 1

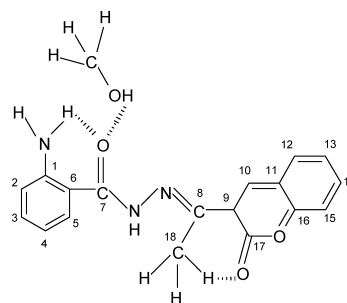


Fig. 2

tion is proved by ^1H -NMR studies. The presence of coordinated water molecules in all complexes was indicated by their characteristic rocking frequency of non ligand band between 812–826 cm^{-1} .²⁹⁾ The band due to ionic nitrate was observed at 1384 cm^{-1} . The presence of ionic nitrate is in confirmation with the conductivity measurements.

^1H -NMR Spectra The ^1H -NMR spectra of ACAB and its La(III) complex was recorded in DMSO- d_6 and the spectral assignments (Table 3) have been made based on comparisons with NMR assignments of 3-acetylcoumarin and methyl anthranilate^{30,31)} and 2D HETCOR (HMQC) (Fig. 3) NMR of ACAB.

A sharp singlet appearing in the upfield region at 2.31 ppm integrates for three protons of the methyl group (Fig. 2). The signal due to $-\text{NH}$ (D_2O exchangeable) appears at 10.59 ppm as a broad singlet and corresponds to one proton. A signal at 6.22 ppm is assignable to protons of the free $-\text{NH}_2$ (exchanges with D_2O) and accounts for two protons. The aromatic protons are observed in the range 6.59–8.23 ppm.

A multiplet at 7.42 ppm is formed by the merger of a doublet and a triplet of H12 and H14. Three doublets at 7.88, 7.56 and 6.76 ppm are due to H5, H15 and H2. The triplets at 7.66, 7.21 and 6.59 ppm are ascribed to H13, H3 and H4. A sharp peak at 8.23 ppm is due to the H10 of the coumarin moiety.

A quartet and a singlet at 4.12 and 3.17 ppm are due to $-\text{OH}$ and $-\text{CH}_3$ protons of the lattice held methanol molecule. In this case, the coupling interaction between $-\text{CH}_3$ and $-\text{OH}$ was observed leading to splitting of the $-\text{CH}_3$ peak ($J=5.1$ Hz).¹⁷⁾

In the ^1H -NMR spectrum of La(III) complex, the $-\text{NH}_2$ signals remain almost unperturbed at 6.21 ppm indicating the non-involvement of this group in coordination. The signals due to $-\text{NH}$ and $-\text{CH}_3$ remain almost unchanged at 10.60 and 2.31 ppm. The aromatic protons do not show any shift com-

Table 3. ^1H - and ^{13}C -NMR Spectral Data (in δ ppm) of ACAB and Its La(III) Complex

Carbon	ACAB	La(III) complex	Proton	ACAB	La(III) complex
C1 ^{a)}	150.52	150.51	—	—	—
C2	115.25	115.24	H2	6.76 (d, $J=8.1$ Hz)	6.76 (d, $J=8.1$ Hz)
C3	133.28	133.29	H3	7.21 (t, $J=7.5$ Hz)	7.21 (t, $J=7.0$ Hz)
C4	116.86	116.86	H4	6.59 (t, $J=7.4$ Hz)	6.59 (t, $J=7.3$ Hz)
C5	133.08	133.10	H5	7.88 (d, $J=7.5$ Hz)	7.87 (d, $J=7.3$ Hz)
C6	115.76	115.76	—	—	—
C7	160.14	162.14	—	—	—
C8 ^{a)}	150.52	152.01	—	—	—
C9	119.66	119.81, 119.65	—	—	—
C10	142.39	142.40	H10	8.23 (s)	8.23 (s)
C11	117.14	117.16	—	—	—
C12	127.80	127.78	H12	7.42 (m)	7.42 (m)
C13	125.66	125.67	H13	7.66 (t, $J=7.7$ Hz)	7.66 (m)
C14	130.06	130.06	H14	7.42 (m)	7.42 (m)
C15	116.97	116.96	H15	7.56 (d, $J=7.7$ Hz)	7.56 (d, $J=7.6$ Hz)
C16 ^{b)}	154.30	154.28	—	—	—
C17 ^{b)}	154.30	154.37	—	—	—
C18	17.04	17.04	—CH ₃	2.31 (s)	2.31 (s)
C19*	49.46	49.46	—	—	—
—	—	—	—NH	10.59 (s, 2H)	10.60 (s)
—	—	—	—NH ₂	6.22 (s)	6.21 (s)

a) These signals appear as a single line. b) These signals appear as a single line. * CH₃ of lattice methanol.

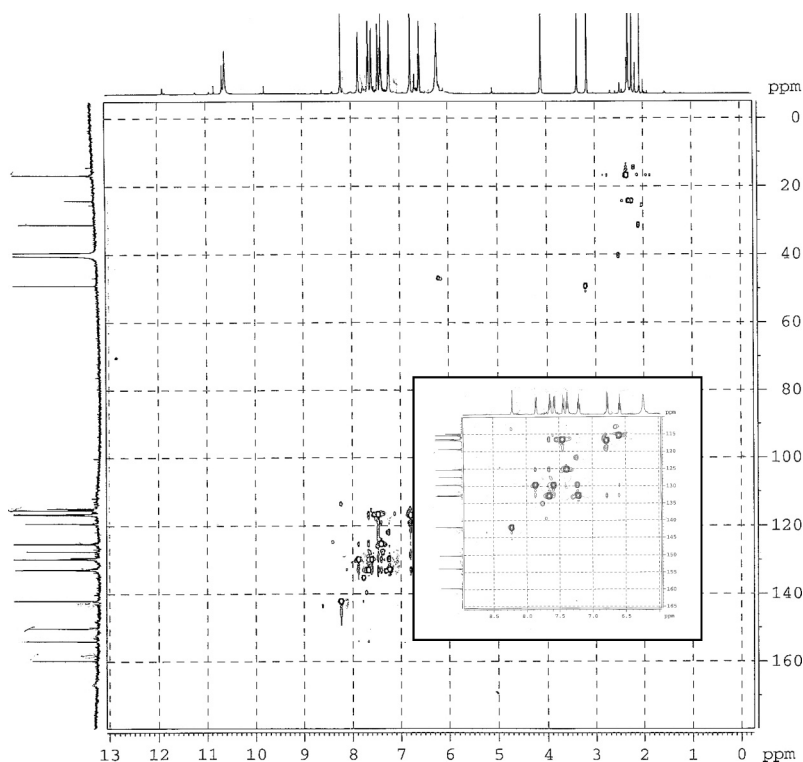


Fig. 3. 2D HETCOR NMR Spectrum of ACAB

pared to the ligand and are observed at 6.59–8.23 ppm, indicating that the lactone oxygen and the $-\text{NH}_2$ moiety are not involved in coordination.

^{13}C -NMR Spectra The ^{13}C -NMR spectra of ACAB and its La(III) complex was carried out in $\text{DMSO}-d_6$ and the assignments are shown in Table 3. In spectra of ACAB, the carbon of lactone carbonyl is observed at 154.70 ppm. A peak at 17.04 ppm is due to carbon of the $-\text{CH}_3$ group. The methyl carbon (Fig. 2) of the lattice held methanol appears at 49 ppm. In the spectra of the La(III) complex, the signals are

observed at the same position as in ligand. However, the C7 signal of hydrazide $\text{C}=\text{O}$ group is shifted to 162.14 ppm from 160.14 ppm confirming the coordination of carbonyl to metal ion. An intense peak at 150.51 ppm assigned to C1 and C8 in ACAB undergoes a splitting into two signals appearing at 150.51 and 152.01 ppm on complexation, indicating the coordination of $\text{C}=\text{N}$ to the metal ion. The C16 and C17 signal appears as a single line at 154.30 ppm in the ligand. In the complex, it splits into two lines with a new signal appearing at 154.28 ppm which was earlier merged with the lactone

Table 4. UV-Visible Data of ACAB and Some Ln(III) Complexes

Complex	Assignments	$\lambda_{\max}$ of ion (cm ⁻¹)	$\lambda_{\max}$ of complex (cm ⁻¹)	β	Other parameters
[Nd(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	⁴ I _{9/2} — ⁴ F _{3/2}	11515	11415	0.9913	$\delta=0.46414$
	— ² H _{9/2}	12475	12450	0.9979	$b^{1/2}=0.04806$
	— ⁴ F _{7/2}	13347	13498	1.0113	$\eta=0.068128$
	— ² P _{1/2}	20292	20145	0.9927	
	— ⁴ G _{11/2}	21720	21367	0.9837	
[Dy(ACAB) ₂ (NO ₃) ₂ (H ₂ O) ₂]·NO ₃ ·H ₂ O	⁶ H _{15/2} — ⁶ F _{5/2}	12376	12300	0.99385	$\delta=0.301908$
	— ⁴ I _{15/2}	22123	22069	0.99755	$b^{1/2}=0.03879$
	— ⁴ G _{11/2}	23324	23314	0.99957	$\eta=0.05494$

>C=O, indicating complexation of $\nu(C=N)$ to the metal.

Electronic Spectra The UV-Visible spectrum of the ligand exhibits bands at 299 and 332 nm assigned to the $n-\pi^*$ transitions. The spectra of the complexes were similar with a slight shift of spectral bands to lower energy compared to the respective aquo ions.³²⁾ The nephelauxetic parameter (β),³³⁾ bonding parameter ($b^{1/2}$)³⁴⁾ and Sinha's covalency parameter (δ)³⁵⁾ and angular covalency (η) for the Dy(III) and Nd(III) complexes are presented in Table 4. The Sinha's parameter (δ) suggests the degree of covalency and is obtained by the equation, $\delta=(1-\beta_{av})/\beta_{av} \cdot 100$ where β_{av} is the average value of the ratio of $\nu_{complex}/\nu_{aquo}$. The magnitude of the bonding parameters ($b^{1/2}$) suggests the degree of involvement of 4f orbitals in metal-ligand bonding and is related to nephelauxetic ratio (β) by the equation, $b^{1/2}=[(1-\beta_{av})/2]^{1/2}$. Angular covalency (η)= $(1-\beta_{av})^{1/2}/\beta_{av}^{1/2}$. The intensity of the f-f transitions presents an interesting observation. The intensity of the normal f-f transitions does not show much change. However the hypersensitive transitions (environment sensitive transitions) are found to show large changes in intensity. According to Karraker,³⁶⁾ the shape and intensity of these transitions indicate the geometry of the complex. In the present complexes, nephelauxetic ratio (β) being less than one and positive values of $b^{1/2}$ and δ indicate slight covalent bonding between metal and ligand.

Thermal Analysis The TG/DTA curve of a representative La(III) complex suggests the following stages of decomposition. The first step of decomposition in the temperature range between 24—100 °C indicates the loss of a lattice held water molecule. The observed value is in accordance with calculated one (Obs: 1.32%, Calc: 1.77%). The next weight loss occurs between 197—263 °C, which corresponds to the loss of two coordinated water molecules is indicated by an exothermic peak on the DTA curve. (Obs: 4.47%; Calc: 4.84%). The subsequent weight loss in the temperature range 263—290 °C corresponds to the loss of an ionic nitrate molecule (Obs: 10.94%; Calc: 10.54%). Further weight losses in the region 290—723 °C correspond to the loss of two coordinated nitrates and two coordinated ligand molecules. Finally it decomposes to the most stable oxide La₂O₃. The weight of the residue is in good agreement with the metal contents obtained by analytical measurements.

Biological Evaluation The biological activity of the ligand and complexes (Table 5) was screened simultaneously with metal salts, and the standards, against the fungi *Aspergillus niger* (AN) and *Penicillium notatum* (PN) and the bacteria *Pseudomonas aeruginosa* (PA) and *Bacillus cirrofla-*

Table 5. Inhibitory Activity of ACAB and Its Ln(III) Complexes

Compound	Fungi		Bacteria	
	AN	PN	PA (gram-ve)	BC (gram+ve)
ACAB	+	+	+	+
C1	+	+	—	++
C2	+	+	—	++
C3	+	++	—	++
C4	+	+	—	++
C5	+	+	—	+
C6	++	+	—	++
C7	++	+	—	++
C8	++	+	—	++
C9	++	+	—	++
Grisofulvin	+++	+++	—	—
Norfloracin	—	—	+++	+++
Control	—	—	—	—

Key to interpretation: —=no activity; +=less active; ++=moderately active; +++=highly active.

gellosus (BC) by the cup-plate method.³⁷⁾ The concentration used for testing was 1 mg/ml of DMSO. Grisofulvin and Norfloxacin were used as standards against fungi and bacteria respectively. DMSO was used as the control. The cultures of the fungi and the bacteria consisted of peptone (0.6%), yeast extract (0.3%), beef extract (0.13%) and nutrient agar. The nutrient agar further consisted of definite volumes of peptone (0.5%), yeast extract (0.15%), beef extract (0.15%), NaCl (0.35%), dipotassium phosphate (0.36%) and potassium dihydrogen phosphate (0.13%).

Wells were made by scooping out the nutrient agar with a sterile cork borer. The solutions of the test compounds (0.1 ml) were added to the wells using sterile pipettes. The plates were further incubated for 37 °C for 48 h. The antimicrobial activity was estimated on the basis of size of inhibition zone formed around the wells in the plates.

The ligand ACAB was less active against both the fungi and bacteria. In case of AN, the Gd(III), Tb(III), Dy(III) and Y(III) complexes showed enhanced activity compared to the ligand whereas the remaining complexes showed equal activity. In case of PN, Nd(III) complex showed enhanced activity compared to ligand. The complexes were inactive against PA compared to ligand. This inactivity stems from the higher lipid content in the cell membrane of PA compared to BC which prevents easy diffusion of complex into the cell. The complexes exhibited moderate activities against BC compared to the ligand and Eu(III) complex which were less ac-

tive. The coumarin ring has been found to have a toxic effect on microorganisms.³⁸⁾ On comparison with the ligand the complexes were found to have increased activities which is attributed to the synergistic effect that increases the lipophilicity of the complex.³⁹⁾ The increased lipophilicities of complexes permit easy penetration into lipid membranes of organisms and facilitates blockage of metal binding sites in enzymes.

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