

Spectral Studies of N-Benzoylglycine hydrazide, Acetone (N-benzoyl)glycyl hydrazone and their Ce(III) and Y(III) Complexes

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N-Benzoylglycine hydrazide (BzGH) and acetone (N-benzoyl) glycyl hydrazone (BzAGH) have been synthesized, characterized by IR, ^1H and ^{13}C NMR and mass spectral studies and their complexes of the types $\text{M}(\text{BzGH})_2\text{Cl}_3 \cdot n\text{H}_2\text{O}$ and $\text{M}(\text{BzAGH})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ where $\text{M} = \text{Ce}(\text{III})$ and $\text{Y}(\text{III})$ have been synthesized and characterized by analytical data, molar conductance, magnetic susceptibility, IR, ^1H and ^{13}C NMR spectral techniques. Infrared and ^1H NMR spectra suggest that both the ligands act as neutral bidentate species in their complexes.

INTRODUCTION

In continuation of our previous work^{1,2}, we describe here the spectral studies of N-benzoylglycine hydrazide, acetone (N-benzoyl)glycylhydrazone and their complexes with Ce(III) and Y(III) metal ions.

EXPERIMENTAL

Materials and Methods

Lanthanide trichlorides were obtained from Indian Rare Earths Ltd., Kerala. All the other chemicals used were of BDH analytical grade. The ligands, N-benzoylglycine hydrazide and acetone (N-benzoyl)glycyl hydrazone were prepared by reported methods^{3,4}. N-Benzoylglycine was purchased from Sigma Chemical Company, U.S.A.

BzGH: m.pt. 161° , lit. 161°C , Anal. Found: C, 55.62; H, 5.61; N, 21.60; N_2H_4 , 16.51%. Calcd. for $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2$: C, 55.95; H, 5.69; N, 21.76; N_2H_4 , 16.58%.

BzAGH: m.pt. 147° , lit. 147°C . Found: C, 62.0; H, 6.35; N, 18.20; N_2H_4 , 13.76%. Calcd. for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2$: C, 61.82; H, 6.43; N, 18.02; N_2H_4 , 13.73%.

Preparation and Analyses of the Complexes

The complexes were prepared by mixing together ethanolic/acetone solutions of the metal chloride and the corresponding ligand in 1 : 1 or 1 : 2 metal-ligand ratio. The reaction mixture was heated under reflux for **Ca** 2 hrs. Addition of **Ca** 10 ml of acetonitrile to the reaction mixture resulted in each case in the formation of a gummy solid which, after decanting the supernatant solution, was redissolved in ethanol and macerated with acetonitrile; successive repetitions of this process yielded

crystalline complexes which were filtered, washed with a mixture of acetonitrile and ethanol and dried in *vacuo*.

The metal ions were estimated volumetrically by EDTA titration⁵ after destroying the organic matter with aqua regia followed by treatment with sulfuric acid. Chloride was estimated gravimetrically as AgCl. Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. Nitrogen was microanalysed. The H₂O content was determined by the weight loss suffered on heating the complexes in the temperature range 100–180°C.

The C, H and N analyses were done on Perkin-Elmer 240C analyser. Molar conductance was measured at room temperature on a WTW conductivity meter. Room temperature magnetic susceptibility measurements were carried out on a Cahn-Faraday electrobalance using Hg[Co(NCS)₄] as the calibrant. Infrared spectra were recorded on a Parkin-Elmer 783 spectrophotometer while ¹H and ¹³C NMR spectra were recorded on a Jeol FX-90Q multinuclear NMR spectrometer. Mass spectra were recorded on Varian Mat CH-7 mass spectrometer.

RESULTS AND DISCUSSION

Characterisation of BzGH (I)

The IR spectrum of the ligand shows two sets of bands at 1760, 1560 & 1280 and 1650, 1520 & 1300 cm⁻¹. The former three may be assigned to amide I, II and III frequencies of the carbonyl group of the hydrazide moiety while the latter three to those of the benzamide carbonyl group⁶. The bands observed at 3495, 3390, 3300 cm⁻¹ are assignable to the ν (NH) of the primary and secondary amide groups. The ν (N-N) band appears at 1080 cm⁻¹.

The ¹H NMR spectrum of the BzGH exhibits bands at δ 9.15, 8.15 and 3.48 due to the imino protons of the hydrazide and benzamide moieties and the amino proton of the hydrazide moiety respectively while the aromatic protons show multiplets at δ 7.93 and 7.34.

¹³C NMR spectrum of the ligand shows 7 signals corresponding to 9 carbon atoms present in the molecule. All the ¹³C signals have been approximated applying the principle of substituent additivity⁷. The signals at 168.33 ppm and 166.48 ppm are due to the carbonyl carbons of the hydrazide and benzamide moieties respectively. The positions of the other carbons atoms are as follows: C₁, 131.21; C₂, 128.18; C₃, 127.31; C₄, 134.03; H₂C, 41.39 ppm.

In the mass spectrum (Fig. 1) of BzGH the base peak obtained at $m/e = 105$ corresponds to the fragment C₆H₅CO⁺. A weak intensity peak due to the molecular ion (M⁺) appears at $m/e = 193$. All the other peaks with appreciable intensity corresponding to the possible fragments⁸ are shown in Scheme I.

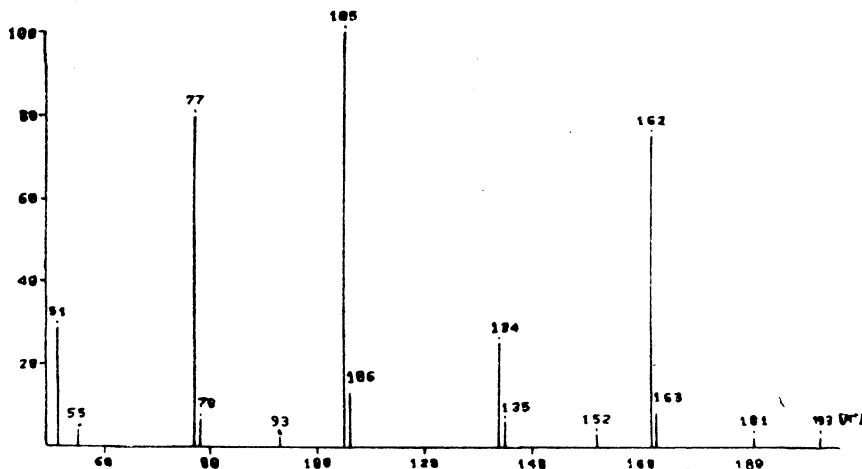
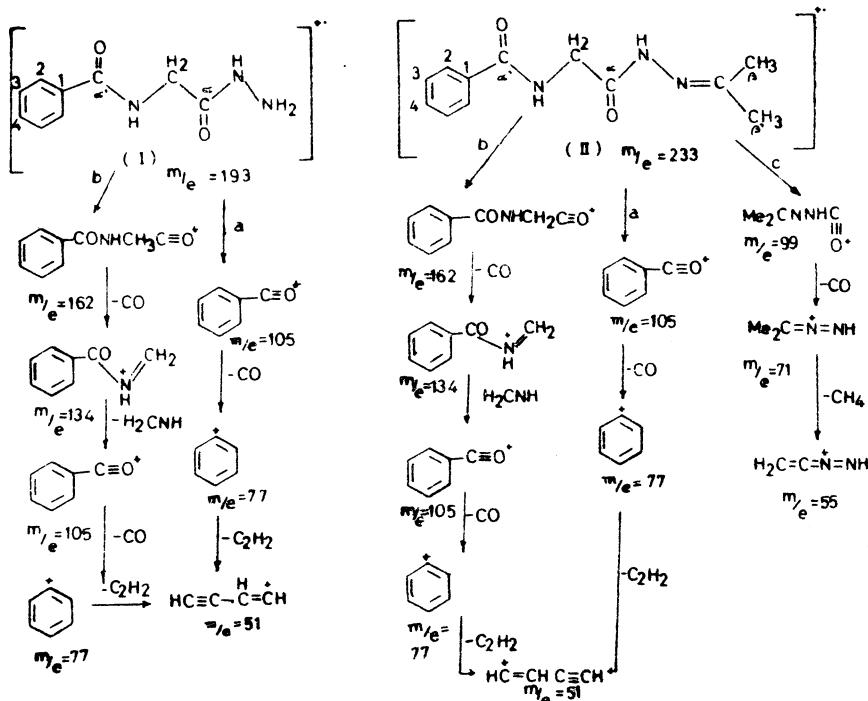


Fig. 1. Mass spectrum of BzGH

Characterisation of BzAGH (II)

The IR spectrum of BzAGH in acetonitrile solution exhibits intense absorption bands at 3310 and 3250 due to $\nu(\text{NH})$ while the bands at 1705 and 1665 cm^{-1} are assignable to the $\nu(\text{CO})$ of the hydrazone and benzamide moieties respectively. Of the four medium intensity bands at 1555,



Scheme I

1360, 1540 and 1315 cm^{-1} , the former two may be assigned to the amide II and III of the hydrazide moiety while the latter two to those of the benzamide moiety⁶.

The ^1H NMR spectrum shows bands at δ 10.00 and 8.81 which are due to the $-\text{NH}$ protons of the benzamide and hydrazide moieties respectively while the methyl protons are observed at δ 1.99 and 2.14. The aromatic ring protons appear as multiplets at δ 7.78 and 7.48.

In the ^{13}C NMR spectrum there are 10 signals corresponding to 12 carbon atoms in the molecule. The observed signals are as follows: C_α , 168.34; $\text{C}_{\alpha'}$, 166.93; NC, 149.80; C_1 , 131.32; C_2 , 128.34; C_3 , 127.31; C_4 , 133.80; CH_2 , 42.02 and CH_3 , 24.92 and 16.68 ppm.

The mass spectrum (Fig. 2) of BzAGH shows the base peak at $m/e = 105$ which corresponds to $\text{C}_6\text{H}_5\text{CO}^+$ fragment. The molecular ion peak appears with Ca 10% intensity at $m/e = 233$. The other peaks for the major fragments with appreciable intensity are shown in Scheme I.

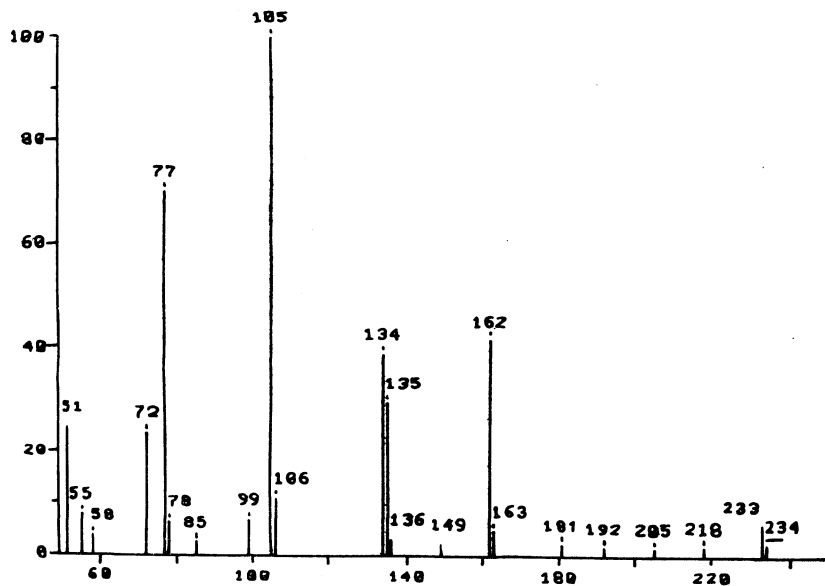


Fig. 2. Mass spectrum of BzAGH

Characterisation of the Complexes

The analytical data of the complexes (Table I) indicate a 1 : 2 and 1 : 1 metal to ligand stoichiometry corresponding to the general formulae $\text{M}(\text{BzGH})_2\text{Cl}_3 \cdot n\text{H}_2\text{O}$ and $\text{M}(\text{BzAGH})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ [$\text{M} = \text{Ce}(\text{III})$ and $\text{Y}(\text{III})$]. The complexes are soluble in water, methanol, ethanol, pyridine, dimethylformamide and dimethylsulfoxide. The electrical conductance measurements of 0.001 M methanolic solutions (147.3–158.4 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)

show their 2 : 1 electrolytic nature⁹. Thermal studies of the complexes in the temperature range 80–180°C indicate the loss of three water molecules in all cases except Ce(BzGH)₂Cl₃·nH₂O where four molecules are lost.

The room temperature magnetic moments of the Ce(III) complexes were determined and presented in Table 1. The magnetic moments show little deviation from Van Vleck values¹⁰ indicating very little participation of 4f-electrons in bond formation in these complexes.

The bonding sites of the ligand involved in coordination with the metal ion have been determined by a careful comparison of the IR spectrum of the ligand with the spectra of the complexes. The nujol mull spectral data of the complexes are given in Table 2. The bathochromic shifts of the amide I and II bands and the hypsochromic shift of the amide III band observed in the complexes are consistent with the coordination of the hydrazide >C = O group¹¹. The coordination of the amino nitrogen/azomethine nitrogen is suggested on the basis of the observed hypsochromic shift in the ν(N–N) mode¹². The positions of the amide I, II and III bands arising from the benzamide moiety remain almost unchanged in the spectra of all the complexes relative to those of the parent ligands indicating non-involvement of the benzamide carbonyl group in coordination¹¹.

The ¹H NMR spectra of BzGH, BzAGH and the Y(III) complexes were recorded in DMSO-d₆/CDCl₃ solutions and the spectral data along with the assignments are given in Table 3. The spectra of the Y(III) complexes show a down-field shift of the hydrazido imino proton, suggesting coordination of the carbonyl oxygen and amino nitrogen/azomethine nitrogen¹³. Coordination of the amino nitrogen in Y(BzGH)₂Cl₃·3H₂O is further suggested on the basis of the down-field shift of the amino proton. However, the signal position of the benzamide imino proton remains unaltered in all the complexes suggesting its non-coordination with the metal ion.

The 22.49 MHz proton-noise decoupled ¹³C NMR spectra of BzGH, BzAGH and the Y(III) complexes were recorded in DMSO-d₆ solutions. The spectral data along with the assignments are given in Table 4. The effect of coordination is to strongly influence the carbon shifts in the metal complexes particularly those of the hydrazide carbonyl and the azomethine groups which directly interact with the metals. The signal due to the carbonyl carbon of the hydrazide moiety undergoes a significant down-field shift in the spectrum of the complexes which clearly suggests the coordination of the hydrazide carbonyl group with the metal ions¹⁴. The signal due to the carbonyl carbon of the benzamide moiety precisely appears at the same position in the spectra of the parent ligands as well as the complexes suggesting non-coordination of the group.

Thus, the ¹H and ¹³C NMR spectral data support the inference drawn earlier on the basis of the infrared spectra about the non-involvement of

TABLE I
ANALYTICAL DATA AND GENERAL BEHAVIOUR OF Ce(III) AND Y(III) COMPLEXES

Complex	Colour	m.pt. (°C)	Found (Calcd.) %			N ₂ H ₄	μ_{eff} (B.M.)	Molar conductance ohm ⁻¹ cm ² mol ⁻¹
			N	M	Cl			
Ce(BzGH) ₂ Cl ₃ ·4H ₂ O	light red	216 ^a	11.90 (11.93)	19.70 (19.89)	15.30 (15.12)	—	2.61	148.1
Y(BzGH) ₂ Cl ₃ ·3H ₂ O	colourless	>300	12.83 (12.86)	13.52 (13.60)	15.82 (16.30)	9.85 (9.79)	diamag.	145.3
Ce(BzAGH)Cl ₃ ·3H ₂ O	cream	228 ^a	7.85 (7.87)	26.30 (26.30)	20.02 (19.96)	—	2.14	158.4
Y(BzAGH)Cl ₃ ·3H ₂ O	colourless	174 ^a	8.70 (8.71)	18.51 (18.43)	22.13 (22.08)	6.64 (6.63)	diamag.	147.3

TABLE 2
IR SPECTRA DATA OF BzGH, BzAGH AND THEIR COMPLEXES

Complex	Benzamido moiety			Hydrazido moiety			$\nu(\text{N-N})$
	Amide I	Amide II	Amide III	Amide I	Amide II	Amide III	
	BzGH ^a	1645	1520	1300	1760	1560	
Ce(BzGH) ₂ Cl ₃ ·4H ₂ O	1645	1520	1300	1665	1535	1300	1135
Y(BzGH) ₂ Cl ₃ ·3H ₂ O	1645	1520	1300	1670	1535	1295	1140
BzAGH ^a	1665	1540	1315	1705	1555	1360	980
Ce(BzAGH)Cl ₃ ·3H ₂ O	1665	1540	1310	1640	1530	1390	1005
Y(BzAGH)Cl ₃ ·3H ₂ O	1665	1540	1310	1640	1530	1395	1010

^aSpectra recorded in acetonitrile solution.

TABLE 3
¹H NMR SPECTRAL DATA* OF BzGH, BzAGH AND THEIR Y(III) COMPLEXES

Protons	BzGH (DMSO-d ₆)	Y(BzGH) ₂ Cl ₃ ·3H ₂ O (DMSO-d ₆)	BzAGH (CDCl ₃)	Y(BzAGH)Cl ₃ ·3H ₂ O (DMSO-d ₆)
—NH benzamide	8.15	8.19	10.00	9.76
—NH hydrazide	9.15	10.03	8.81	9.10
—NH ₂ hydrazide	3.48	5.19	—	—
—CH ₂	3.90	4.05	4.14, 4.52	4.48, 3.91
H ₃ C—	—	—	2.14, 1.99	2.12
Aromatic	7.93, 7.94	7.95, 7.52	7.78, 7.48	8.00, 7.48

*Signals are measured in δ w.r.t. TMS.

TABLE 4
 22.49 MHz PROTON-NOISE DECOUPLED ¹³C NMR SPECTRAL DATA* OF BzGH, BzAGH AND THEIR Y(III) COMPLEXES

Carbon atoms	BzGH	Y(BzGH) ₂ Cl ₃ ·3H ₂ O	BzAGH	Y(BzAGH)Cl ₃ ·3H ₂ O
C _α	168.33	171.99	168.34	172.77
C _{α'}	166.48	166.64	166.93	166.97
—H ₂ C—	41.39	41.34	42.02	41.34
—NCH—	—	—	149.80	—
H ₃ C—	—	—	24.92, 16.68	25.25, 18.26
C ₁	131.21	131.60	131.32	131.81
C ₂	128.18	128.40	128.34	128.62
C ₃	127.31	127.58	127.31	127.80
C ₄	134.03	133.76	133.80	133.82

*Signals are measured in ppm w.r.t. DMSO-d₆ (39.50 ppm).

the benzamide carbonyl group and the coordination of the hydrazide carbonyl oxygen and the amino nitrogen/azomethine nitrogen with the metal ions.

Based on the elemental analyses and the various physico-chemical studies the empirical formulae $[M(\text{BzGH})_2\text{Cl}(\text{H}_2\text{O})_n]\text{Cl}_2$ and $[M(\text{BzAGH})\text{Cl}(\text{H}_2\text{O})_3]\text{Cl}_2$ have been proposed for the BzGH and BzAGH complexes respectively involving a neutral bidentate functional ligand.

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