



ORIGINAL RESEARCH PAPER

Chemistry

SPECTRAL CHARACTERIZATION AND BONDING PARAMETERS EVALUATION OF HO (III)-BENZOTHAZOLE DERIVATIVE SYSTEM: EFFECT OF Ca^{2+} , Mg^{2+} AND Sr^{2+} CO-DOPING IN ALCOHOLIC AND MICELLAR MEDIA

KEY WORDS: Holmium(III); Benzothiazole Derivatives; UV-visible Spectroscopy; Co-doping; Judd-ofelt Parameters; Bonding Parameters; Covalency; Micellar Medium

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ABSTRACT

The coordination behaviour of Ho(III) with three thiazole-based ligands—2-amino benzothiazole (2AB), 2-chloro benzothiazole (2CB), and 2-hydroxy benzothiazole (2HB)—was investigated using UV-Visible absorption spectroscopy in ethanol (1:1) and Triton X-100 micellar media. Twenty-four Ho(III) systems, including co-doping with Ca^{2+} , Mg^{2+} and Sr^{2+} ions, were studied. Seven transitions were recorded and used to evaluate oscillator strengths, Judd-Ofelt parameters, symmetry and coordination ratios, and covalency parameters. The nephelauxetic ratio remained generally below unity, while positive bonding, Sinha covalency and angular-overlap parameters indicated covalent contributions to Ho-ligand bonding. Alkaline-earth co-doping generally increased the mean Sinha covalency percentage, demonstrating enhanced covalent character. Among the ligands, 2AB showed the strongest absorption and least symmetric coordination, whereas 2CB and 2HB exhibited weaker and similar spectra. The micellar medium maintained similar trends while reducing parameter variations.

INTRODUCTION

Coordination compounds of trivalent lanthanides have attracted considerable attention because their 4f-4f electronic transitions are shielded by the filled 5s and 5p subshells while remaining sensitive to ligand field, symmetry, and covalency. Consequently, absorption spectroscopy and quantitative intensity analysis provide useful tools for investigating lanthanide coordination and developing optical, laser, and sensor materials. Holmium (III) is particularly suitable for such studies because its $[\text{Xe}]4f^{10}6s^2$ configuration gives a $^5I_8$ ground state and numerous excited J-levels, producing well-resolved absorption bands in the visible region. Hypersensitive transitions, especially around 450 and 537 nm, respond strongly to changes in the coordination environment and can therefore provide information about ligand donor strength and metal-ligand interactions. Benzothiazole and its substituted derivatives are important N- and S-donor ligands for lanthanide coordination. In the present study, 2-amino benzothiazole (2AB), 2-chloro benzothiazole (2CB), and 2-hydroxy benzothiazole (2HB) were selected because substitution at the 2-position can modify electron density at the ring nitrogen and may introduce additional donor interactions. These structural differences are expected to influence the spectral properties and coordination behaviour of Ho (III).

UV-Visible absorption spectroscopy was employed to investigate these systems in ethanol (1:1) and Triton X-100 (TX-100) micellar media. The technique enables measurement of the positions and intensities of f-f transitions without requiring single crystals. Since these transitions are formally parity-forbidden, their weak intensities are particularly useful for monitoring changes in the coordination environment. The recorded spectra were quantitatively analysed using Judd-Ofelt theory. The intensity parameters T_2 , T_4 , and T_6 were determined from experimental and calculated oscillator strengths. Additional parameters, including the nephelauxetic ratio (β), bonding parameter ($b^1/2$), Sinha covalency percentage ($\delta\%$), and covalency angular-overlap parameter (η), were used to assess metal-ligand covalency and deviations from purely ionic bonding. Symmetry and coordination ratios further provided information about the coordination environment. Co-doping with Ca^{2+} , Mg^{2+} , and Sr^{2+} ions was used to perturb the local environment of Ho (III) without introducing competing d- or f-electron transitions. Changes in spectral and bonding

parameters can therefore indicate modifications in ligand interactions, ion pairing, ligand displacement, or coordination symmetry. The use of TX-100 micellar medium additionally provides a different microenvironment from ethanol, allowing medium-dependent effects to be examined.

Overall, the study systematically investigates twenty-four Ho(III) systems involving three benzothiazole ligands, two media, and alkaline-earth co-dopants. Oscillator strengths, Judd-Ofelt parameters, symmetry and coordination ratios, and covalency-related parameters are comparatively evaluated to establish the influence of ligand structure, co-doping, and medium on Ho(III) coordination and bonding behaviour.

Materials and Methods

Reagents

Holmium chloride of 99.9% purity (Indian Rare Earths Limited, India) was used as the source of Ho(III). The thiazole derivatives 2-amino benzothiazole (2AB), 2-chloro benzothiazole (2CB) and 2-hydroxy benzothiazole (2HB) were used as received. The non-ionic surfactant Triton X-100 was used to prepare the micellar medium at a stock concentration of 1.8×10^{-2} M (100 CMC). Ethanol:water (1:1, v/v) was used both as the solvent for the alcoholic:aqua system and for the preparation of the stock ligand and metal-ion solutions used in the micellar system.

Preparation of ligand and metal-ion solutions

Stock solutions of each ligand (2AB, 2CB, 2HB) were prepared at 0.2 M by dissolving the requisite amount in ethanol:water (1:1). A stock solution of Ho (III), 0.1 M, was prepared by dissolving the appropriate amount of holmium chloride in the same ethanol:water (1:1) medium.

Preparation of the Ho (III)-ligand systems

For the alcoholic: aqua system, 3.0 mL of ligand solution (0.2 M) was taken in a 5 mL volumetric flask and 1.0 mL of Ho(III) solution (0.1 M) was added and mixed, giving a metal:ligand ratio of 1:3; the UV-Visible spectrum of each resulting solution was then recorded. For the micellar system, the same 1:3 metal:ligand combination was prepared using 1.0 mL of Ho(III) solution (0.1 M) and 3.0 mL of ligand solution (0.2 M) in Triton X-100 medium in a 5 mL volumetric flask, and the absorbance spectrum was recorded in the same way.

Preparation of the codoped systems

Co-dopant stock solutions of Ca^{2+} , Mg^{2+} and Sr^{2+} were each prepared at 0.1 M. After the spectrum of the bare Ho (III)-ligand system had been recorded, 1.0 mL of the appropriate co-dopant solution was added to the sample, one co-dopant at a time, and the UV-Visible spectrum was re-recorded after each addition. This procedure was applied to each of the three ligand systems in both the alcoholic:aqua and micellar media, giving Ho(III)-ligand, Ho(III)-ligand- Ca^{2+} , Ho(III)-ligand- Mg^{2+} and Ho(III)-ligand- Sr^{2+} spectra for each of the three ligands in each of the two media—twenty-four systems in total.

UV-Visible spectral measurements and data analysis

Absorption spectra were recorded on a UV double-beam spectrophotometer (LABINDIA Analytical, UV 5704-SS, ECI) at GCRC. Peak positions and optical densities were obtained using UV-Win software v6.0.0 and Origin 9.0 for peak-picking and spectral export. The measured band positions and absorbances were processed using an Excel-based computation sheet to obtain, for each system, the experimental and calculated oscillator strengths, the Judd–Ofelt intensity parameters (T_2 , T_4 , T_6), the symmetry (T_4/T_6) and coordination (T_4/T_2) ratios, and the nephelauxetic, bonding, Sinha covalency and covalency angular-overlap parameters, following the relations summarised in Section 3.

Theoretical Basis and Calculation of Parameters

Oscillator strength

The intensity of each observed f-f transition was expressed as an experimental oscillator strength, P_{exp} , obtained from the integrated area of the corresponding absorption band. Oscillator strengths of the order of 10^{-6} are typical of parity-forbidden 4f-4f transitions and were computed and tabulated as $P \times 10^6$ for convenience, alongside the corresponding Judd–Ofelt calculated value, P_{cal} , for each transition.

Judd–Ofelt intensity parameters

Within Judd–Ofelt theory, the calculated oscillator strength of a transition between the ground level and an excited level is expressed as a linear combination of three phenomenological intensity parameters, T ($= 2, 4, 6$), each multiplying the squared reduced matrix element of the unit tensor operator $U^{(\lambda)}$ connecting the two levels. The set of T_2 , T_4 and T_6 values that best reproduces the observed oscillator strengths across the recorded transitions was obtained for each Ho(III) system by least-squares fitting of the experimental data, following the standard Judd–Ofelt formalism.

Symmetry and coordination parameters

The ratio T_4/T_6 is commonly used as an indicator of the local site symmetry around the lanthanide ion, while the ratio T_4/T_2 reflects the degree and nature of metal-ligand coordination; both ratios were computed directly from the fitted $T\lambda$ parameters for each system.

Nephelauxetic ratio (β)

Complexation of a free lanthanide ion is generally accompanied by a small red shift of its f-f absorption bands relative to the aqua-ion, arising from expansion of the 4f orbital radius and consequent lowering of the interelectronic repulsion parameters—the nephelauxetic effect. The nephelauxetic ratio was calculated for each transition as

$$\beta = \nu_c / \nu_f$$

where ν_c and ν_f are the wavenumbers of the corresponding f-f band in the complex and in the free (aqua) ion respectively.

Bonding parameter ($b^{1/2}$)

The bonding parameter was obtained from the mean nephelauxetic ratio, β , as

$$b^{1/2} = [(1 - \beta) / 2]^{1/2}$$

A positive value of $b^{1/2}$ indicates covalent character in the metal-ligand interaction, while a negative value indicates predominantly ionic character.

Sinha covalency parameter ($\delta\%$)

The percentage covalent character was estimated using Sinha's covalency parameter,

$$\delta\% = [(1 - \beta) / \beta] \times 100$$

Covalency angular-overlap parameter (η)

The covalency angular-overlap parameter, representing the extent of overlap between the metal and ligand orbitals, was calculated as

$$\eta = (1 - \beta^{1/2}) / \beta^{1/2}$$

Higher magnitudes of $b^{1/2}$, $\delta\%$ and η correspond to a greater degree of covalent character in the Ho(III)-ligand bond, while values close to zero or negative are associated with predominantly electrostatic (ionic) bonding.

RESULTS AND DISCUSSION

The UV-Visible spectra of Ho(III) alone and of its complexes with 2AB, 2CB and 2HB, before and after co-doping with Ca^{2+} , Mg^{2+} and Sr^{2+} ions, all display the characteristic manifold of $^5I_8$ -derived transitions of Ho(III) in the 300–700 nm region, with the bands near 417, 451, 537 and 641 nm consistently the most intense across every system examined (Fig. 1). Complexation with each of the three ligands preserves this overall band pattern while changing the relative intensities, confirming that the ligands coordinate without disrupting the fundamental 4f-4f transition scheme of the Ho (III) ion.

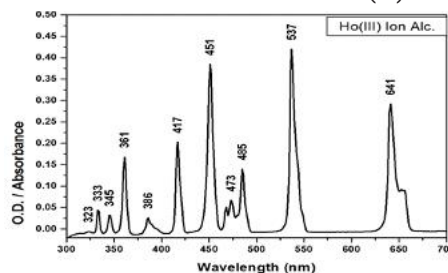


Fig. 1 — UV-Visible absorption spectrum of Ho (III) ion in alcoholic:aqua (1:1) medium.

Ho (III)-2AB system

The oscillator strengths of the seven transitions examined for the Ho(III)-2AB system in alcoholic:aqua medium are given in Table 1. The experimental oscillator strengths of the bare Ho(III)-2AB system range from 0.0595×10^{-6} ($^5I_8 \rightarrow ^5G_5$) to 1.97×10^{-6} ($^5I_8 \rightarrow ^3K_7$), with the $^5I_8 \rightarrow ^3K_7$ and $^5I_8 \rightarrow ^3K_8$ transitions the most intense. Co-doping with Ca^{2+} , Mg^{2+} and Sr^{2+} lowers the experimental oscillator strength of most transitions relative to the bare system, most noticeably for $^5I_8 \rightarrow ^3K_8$ and $^5I_8 \rightarrow ^5F_2$, while the calculated oscillator strengths fall by a comparable or larger margin, so that the r.m.s. deviation between observed and calculated values improves markedly on co-doping, from 12.6 for the bare system to 4.07 (Ca^{2+}), 4.2 (Mg^{2+}) and 1.62 (Sr^{2+}) (Table 1). This indicates that the Judd–Ofelt fit becomes more internally consistent once the alkaline-earth ion is present, consistent with a co-dopant-induced simplification or stabilisation of the coordination geometry around Ho(III).

The corresponding Judd–Ofelt parameters (Table 7) show T_2 values that remain negative throughout (-1.00 to -3.03×10^{-10}), while T_4 and T_6 both decrease on co-doping relative to the bare system (T_4 : $4.10 \rightarrow 1.51$ – 1.77×10^{-10} ; T_6 : $3.58 \rightarrow 1.22$ – 1.33×10^{-10}). The symmetry ratio T_4/T_6 nonetheless increases slightly from 1.15 in the bare system to 1.18–1.33 on co-

doping, and the coordination ratio T_4/T_2 becomes markedly more negative ($-4.10 \rightarrow -4.97$ to -6.30), which together suggest a change in the effective local symmetry of the Ho(III) site once Ca^{2+} , Mg^{2+} or Sr^{2+} is introduced.

Ho (III)-2CB system

For the Ho (III)-2CB system in alcoholic: aqua medium (Table 2), the bare-system oscillator strengths follow a broadly similar pattern to 2AB, with $^5I_8 \rightarrow ^3K_7$ and $^5I_8 \rightarrow ^3K_8$ again the strongest transitions. The Mg^{2+} -codoped system shows a markedly different profile from the Ca^{2+} and Sr^{2+} systems, with several transitions (notably $^5I_8 \rightarrow ^3H_6$ and $^5I_8 \rightarrow ^5F_2$) showing sharply elevated experimental and calculated oscillator strengths and a correspondingly large r.m.s. deviation of 44.4, compared with 1.38×10^{-5} , 4.80 and 2.29 for the bare, Ca^{2+} - and Sr^{2+} -codoped systems respectively. This is consistent with the Judd–Ofelt parameters in Table 8, where the Mg^{2+} system shows a T_2 of 6.4×10^{-10} and a T_4/T_2 ratio of 6.24, both well outside the range spanned by the bare, Ca^{2+} - and Sr^{2+} -codoped systems (T_2 : -0.50 to -1.8×10^{-10} ; T_4/T_2 : 1.16–1.18). Within the limits of the present dataset, this points to the Mg^{2+} -codoped Ho(III)-2CB system in alcoholic medium adopting a distinctly different local coordination environment from the corresponding Ca^{2+} and Sr^{2+} systems, rather than a simple monotonic co-dopant trend common to all three alkaline-earth ions.

Ho (III)-2HB system

The Ho(III)-2HB system in alcoholic:aqua medium (Table 3) shows generally lower oscillator strengths than 2AB or 2CB across most transitions, and the calculated values from the Judd–Ofelt fit systematically overestimate the experimental oscillator strengths for the $^5I_8 \rightarrow ^5G_4$ and $^5I_8 \rightarrow ^5G_5$ transitions, particularly in the Mg^{2+} -codoped system, where the r.m.s. deviation rises to 19.6 compared with 9.49, 5.08 and 3.05 for the bare, Sr^{2+} and (by comparison) Ca^{2+} systems respectively — though the Ca^{2+} deviation of 9.49 in this system is itself the largest among the bare, Ca^{2+} - and Sr^{2+} -codoped sets. The Judd–Ofelt parameters for 2HB (Table 9) are comparatively more stable across the four conditions than for 2AB or 2CB, with T_4/T_2 remaining within a narrow band (4.16 to 4.51) regardless of co-doping, suggesting that the hydroxy-substituted ligand imposes a more consistent coordination geometry on the Ho(III) centre than the amino- or chloro-substituted analogues.

Micellar (TX-100) medium — Oscillator strengths

The corresponding oscillator-strength data for the three ligand systems in TX-100 micellar medium are given in Tables 4–6; the comparative trends across ligands and co-dopants in this medium are discussed together with the alcoholic-medium results in Sections 4.6 and 4.7.

Judd–Ofelt intensity parameters

Table 7–Table 9 summarise the Judd–Ofelt intensity parameters, symmetry ratio and coordination ratio for the three ligand systems in alcoholic:water (1:1) medium; these are discussed alongside the oscillator-strength data in Sections 4.1–4.3.

Effect of Ca^{2+} , Mg^{2+} and Sr^{2+} co-doping

Considered across all three ligand systems in alcoholic medium, co-doping with the alkaline-earth ions does not produce a single uniform effect on oscillator strength — in some systems (2AB) it lowers most transition intensities, while in others (2CB with Mg^{2+}) it substantially raises them. What is more consistent, and evident from the mean bonding parameters summarised in Table 11, is the effect on covalency: for every one of the six ligand-medium combinations examined, the mean Sinha covalency percentage (δ %) of at least one, and in most cases all three, co-doped systems exceeds that of the corresponding bare Ho(III)-ligand system.

For Ho(III)-2AB in alcoholic medium, for example, δ % rises from 0.112% (bare) to 0.201% (Ca^{2+}), 0.165% (Mg^{2+}) and 0.210% (Sr^{2+}); the same pattern, with Ca^{2+} and Sr^{2+} producing the largest increase, is seen for 2CB and 2HB in both media (Table 11). This indicates that, within the present dataset, the presence of Ca^{2+} , Mg^{2+} or Sr^{2+} ions in solution consistently increases the covalent contribution to the Ho(III)-benzothiazole interaction relative to the un-codoped system, even where the individual band-by-band oscillator-strength changes are less uniform. Among the three co-dopants, Sr^{2+} and Ca^{2+} tend to give the larger increase in δ % relative to Mg^{2+} , which may reflect the larger ionic radius of Sr^{2+} and Ca^{2+} relative to Mg^{2+} allowing a closer approach to, or more effective perturbation of, the Ho(III) coordination sphere.

Symmetry, coordination and covalency parameters

Across the twenty-four Ho(III) systems, the nephelauxetic ratio (β) remained close to unity (0.87–1.002), indicating relatively small spectral shifts in Ho(III)-benzothiazole complexes. The predominantly positive bonding parameter ($b_{\lambda/2}$) and Sinha covalency parameter (δ %) confirmed a measurable covalent contribution to Ho–ligand bonding. A few transitions showed slightly negative δ %, mainly due to small blue shifts, but these isolated values did not alter the overall covalent character. One anomalous data entry was identified for the bare Ho(III)-2AB system in TX-100 medium, where the $^5I_8 \rightarrow ^5F_2$ transition contained an inconsistent wavelength/wavenumber pair (4735 nm/2111.93 cm^{-1}). This produced unrealistic bonding parameters and was considered a decimal-placement error rather than a genuine spectral observation. Therefore, this value was excluded from the mean calculations, and the corresponding system was evaluated using six transitions instead of seven. *Spectral Characterization of Ho(III)–Benzothiazole System* $\lambda c = \text{wavelength of the corresponding band centre in the complex. Values are rounded to three decimal places for display; the full-precision values as computed are given in the corresponding tables of the source chapter (Tables 6.13–6.16). Values are means calculated by the present authors from theseven-transition dataset underlying Tables 6.13–6.36 of the source chapter. For the bare Ho(III)-2AB system in TX-100 medium, one transition ($^5I_8 \rightarrow ^5F_2$) was excluded from the mean owing to a wavelength/wavenumber recording artefact in the source data (see Section 4.5); $n = 6$ for that entry.$

Comparison of alcoholic:aqua and TX-100 micellar media

Comparing the alcoholic:aqua and TX-100 micellar results for the same ligand (Table 11) shows that the micellar medium generally narrows the spread of the mean bonding parameters relative to the alcoholic medium. For Ho(III)-2AB, the mean % for the bare system falls from 0.112% in alcoholic medium to 0.064% in TX-100 (excluding the flagged row), and the co-doped values in TX-100 (0.106%, 0.066% and 0.094% for Ca^{2+} , Mg^{2+} and Sr^{2+} respectively) are likewise more closely clustered than the corresponding alcoholic-medium values (0.201%, 0.165% and 0.210%). A similar narrowing is seen for 2CB and 2HB. This is consistent with the compartmentalised, more uniform microenvironment provided by the Triton X-100 micelle moderating the extent to which co-doping can perturb the local field around the Ho(III) centre, compared with the more open, fully solvated alcoholic:aqua system. The overall qualitative pattern established in alcoholic medium — that co-doping increases the mean covalency relative to the bare system — is nonetheless preserved in the micellar medium for every ligand examined, indicating that this is a robust feature of the present systems rather than an artefact of the alcoholic solvent alone.

Comparative spectral behaviour of the three ligands

The comparative UV-Visible spectra of Ho (III) complexes with 2-amino benzothiazole (2AB), 2-chloro benzothiazole (2CB), and 2-hydroxy benzothiazole (2HB) show that 2AB

exhibits the strongest absorption in both alcoholic and Triton X-100 media. The 2CB and 2HB spectra are comparatively weaker and closely overlap, with only minor differences in their fine spectral features. Numerical oscillator-strength data also confirm the highest absorption intensity for Ho(III)-2AB, followed by Ho(III)-2CB and Ho(III)-2HB. The stronger absorption of 2AB may be attributed to its electron-donating amino group, which produces a greater perturbation of the Ho(III) coordination environment. In contrast, the chloro and hydroxy substituents produce comparatively weaker effects. The TX-100 medium preserves the same overall spectral order while providing sharper absorption peaks. Overall, 2AB shows the strongest interaction with Ho(III) among the three benzothiazole derivatives studied.

Thermodynamic parameters

The transition work-function values (Table 12, representative data for Ho(III)-2AB in alcoholic medium) closely track the observed band wavenumbers reported in Tables 1 and 10, decreasing systematically from about 23,900-23,930 cm⁻¹ for the ⁵I₈ → ³G₄ transition to about 15,460-15,480 cm⁻¹ for ⁵I₈ → ⁵F₅, with only small (typically under 30 cm⁻¹) differences between the bare and co-doped systems for any given transition. The associated thermodynamic efficiency of transition (TET), reported in the underlying dataset for each system, remains close to unity (0.992-0.996) throughout, indicating that the great majority of the absorbed energy for each transition is accounted for within the present thermodynamic treatment across all Ho(III)-ligand combinations and co-doping conditions examined, with no system showing an anomalous departure from this near-unity behaviour.

S.N.	Transition	Ho(III)-2AB		Ho(III)-2AB-Ca ²⁺		Ho(III)-2AB-Mg ²⁺		Ho(III)-2AB-Sr ²⁺	
		Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶
1	⁵ I ₈ → ³ H ₆	0.640	5.26	0.443	1.93	0.641	2.27	0.487	1.97
2	⁵ I ₈ → ³ K ₇	1.97	6.97	1.21	2.71	1.94	3.31	1.46	2.83
3	⁵ I ₈ → ⁵ G ₄	0.0857	1.64	0.176	0.587	0.316	0.630	0.233	0.572
4	⁵ I ₈ → ⁵ G ₅	0.0595	1.65	0.0800	0.587	0.161	0.612	0.098	0.564
5	⁵ I ₈ → ⁵ G ₆	0.226	2.98	0.354	1.06	0.503	1.10	0.37	1.02
6	⁵ I ₈ → ³ K ₈	1.60	8.44	0.772	3.02	0.732	3.27	0.716	2.96
7	⁵ I ₈ → ⁵ F ₂	0.869	9.08	0.291	3.27	0.439	3.62	0.319	3.23
8	r.m.s. (σ) deviation (±)	12.6	4.07	4.2	1.62				

Table 2 — Experimental (Pexp×10⁶) and calculated (Pcal×10⁶) oscillator strengths for various transitions of the Ho(III)-2CB system and co-doping of Ca²⁺, Mg²⁺ and Sr²⁺ ions in alcoholic:water (1:1) medium.

S.N.	Transition	Ho(III)-2CB		Ho(III)-2CB-Ca ²⁺		Ho(III)-2CB-Mg ²⁺		Ho(III)-2CB-Sr ²⁺	
		Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶
1	⁵ I ₈ → ³ H ₆	0.815	5.84	7.05	5.48	10.2	22.6	0.339	2.46
2	⁵ I ₈ → ³ K ₇	2.07	7.62	0.939	4.33	1.42	23.2	0.8	3.16
3	⁵ I ₈ → ⁵ G ₄	0.0689	1.79	0.0261	0.513	0.0148	5.30	0.0268	0.745
4	⁵ I ₈ → ⁵ G ₅	0.107	1.81	0.0681	0.316	0.0568	5.13	0.11	0.75
5	⁵ I ₈ → ⁵ G ₆	0.253	3.26	0.0448	0.570	0.0472	9.23	0.374	1.35
6	⁵ I ₈ → ³ K ₈	1.67	9.27	0.675	3.62	0.867	29.0	0.604	3.86
7	⁵ I ₈ → ⁵ F ₂	1.06	10.02	0.577	5.30	7.23	33.1	0.52	4.18
8	r.m.s. (σ) deviation (±)	1.38E-05	4.80	44.4	2.29				

Table 3 — Experimental (Pexp×10⁶) and calculated (Pcal×10⁶) oscillator strengths for various transitions of the Ho(III)-2HB system and co-doping of Ca²⁺, Mg²⁺ and Sr²⁺ ions in alcoholic:water (1:1) medium.

S.N.	Transition	Ho(III)-2HB		Ho(III)-2HB-Ca ²⁺		Ho(III)-2HB-Mg ²⁺		Ho(III)-2HB-Sr ²⁺	
		Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶	Pexp×10 ⁶	Pcal×10 ⁶
1	⁵ I ₈ → ³ H ₆	0.716	4.24	0.595	7.40	0.660	2.49	0.697	3.41
2	⁵ I ₈ → ³ K ₇	2.10	5.73	3.09	10.7	1.33	3.28	1.49	4.51
3	⁵ I ₈ → ⁵ G ₄	0.122	1.25	0.0375	3.03	0.117	0.668	0.125	1.02
4	⁵ I ₈ → ⁵ G ₅	0.0808	1.24	0.0104	3.20	0.614	0.650	0.618	1.02
5	⁵ I ₈ → ⁵ G ₆	0.251	2.23	3.11	5.77	0.212	1.17	0.286	1.84
6	⁵ I ₈ → ³ K ₈	1.17	6.45	6.00	15.1	0.470	3.51	1.11	5.29

CONCLUSION

UV-Visible absorption spectroscopy was used to investigate Ho(III) complexes with 2-amino benzothiazole (2AB), 2-chloro benzothiazole (2CB), and 2-hydroxy benzothiazole (2HB) in ethanol (1:1) and Triton X-100 media, before and after co-doping with Ca²⁺, Mg²⁺, and Sr²⁺ ions. Twenty-four systems were analysed for oscillator strengths, Judd–Ofelt intensity parameters, symmetry, coordination, and bonding characteristics. The nephelauxetic ratio remained generally below unity, while positive bonding, Sinha covalency, and angular-overlap parameters indicated significant covalent contributions to Ho(III)–benzothiazole bonding. Co-doping consistently increased the mean Sinha covalency percentage in all ligand–medium combinations, demonstrating enhanced covalent character.

Among the ligands, 2AB exhibited the strongest absorption, whereas 2CB and 2HB showed weaker and closely overlapping spectra. The TX-100 medium maintained similar trends but reduced variations in bonding parameters. An identified data-entry error was excluded from summary calculations. Overall, the results provide useful spectral and bonding information for Ho(III)–benzothiazole systems.

Table 1 — Experimental (Pexp×10⁶) and calculated (Pcal×10⁶) oscillator strengths for various transitions of the Ho(III)-2AB system and co-doping of Ca²⁺, Mg²⁺ and Sr²⁺ ions in alcoholic:water (1:1) medium.

7	$^5I_8 \rightarrow ^5F_2$	0.685	7.04	0.190	15.4	0.537	3.91	0.541	5.74
8	r.m.s. (σ) deviation ($\pm$)	9.49		19.6		5.08		3.05	

Table 4 — Experimental ($P_{exp} \times 10^6$) and calculated ($P_{cal} \times 10^6$) oscillator strengths for various transitions of the Ho(III)-2AB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in TX-100 micellar medium.

S.N.	Transition	Ho(III)-2AB		Ho(III)-2AB- Ca^{2+}		Ho(III)-2AB- Mg^{2+}		Ho(III)-2AB- Sr^{2+}	
		$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
1	$^5I_8 \rightarrow ^3H_6$	0.331	2.08	0.395	2.65	0.498	1.70	0.510	3.26
2	$^5I_8 \rightarrow ^3K_7$	1.24	2.91	1.09	3.54	1.33	2.36	1.44	4.37
3	$^5I_8 \rightarrow ^5G_4$	0.0522	0.641	0.0181	0.820	0.102	0.401	0.0646	0.989
4	$^5I_8 \rightarrow ^5G_5$	0.0390	0.642	0.0424	0.827	0.482	0.372	0.391	0.992
5	$^5I_8 \rightarrow ^5G_6$	0.141	1.16	0.160	1.49	0.214	0.671	0.188	1.79
6	$^5I_8 \rightarrow ^3K_8$	0.745	3.30	0.908	4.23	0.801	2.13	1.04	5.11
7	$^5I_8 \rightarrow ^5F_2$	0.415	3.56	0.349	4.55	0.438	2.46	0.461	5.53
8	r.m.s. (σ) deviation ($\pm$)	4.67	6.23	3.07	2.99				

Table 5 — Experimental ($P_{exp} \times 10^6$) and calculated ($P_{cal} \times 10^6$) oscillator strengths for various transitions of the Ho (III)-2CB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in TX-100 micellar medium.

S.N.	Transition	Ho(III)-2CB		Ho(III)-2CB- Ca^{2+}		Ho(III)-2CB- Mg^{2+}		Ho(III)-2CB- Sr^{2+}	
		$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
1	$^5I_8 \rightarrow ^3H_6$	0.474	3.43	0.428	2.98	0.552	3.80	0.339	2.46
2	$^5I_8 \rightarrow ^3K_7$	0.951	4.41	1.03	3.89	1.23	4.95	0.80	3.16
3	$^5I_8 \rightarrow ^5G_4$	0.0379	1.11	0.0599	0.926	0.580	1.21	0.0268	0.745
4	$^5I_8 \rightarrow ^5G_5$	0.0427	1.13	0.0417	0.937	0.060	1.22	0.11	0.75
5	$^5I_8 \rightarrow ^5G_6$	0.244	2.04	0.171	1.69	0.183	2.21	0.0374	1.35
6	$^5I_8 \rightarrow ^3K_8$	1.25	5.70	0.912	4.78	1.37	6.21	0.604	3.86
7	$^5I_8 \rightarrow ^5F_2$	0.563	6.08	0.536	5.15	0.557	6.65	0.52	4.18
8	r.m.s. (σ) deviation ($\pm$)	8.36	7.07	9.15	2.29				

Table 6 — Experimental ($P_{exp} \times 10^6$) and calculated ($P_{cal} \times 10^6$) oscillator strengths for various transitions of the Ho(III)-2HB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in TX-100 micellar medium.

S.N.	Transition	Ho(III)-2HB		Ho(III)-2HB- Ca^{2+}		Ho(III)-2HB- Mg^{2+}		Ho(III)-2HB- Sr^{2+}	
		$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$	$P_{exp} \times 10^6$	$P_{cal} \times 10^6$
1	$^5I_8 \rightarrow ^3H_6$	0.583	2.95	0.481	2.18	0.419	3.05	0.866	2.89
2	$^5I_8 \rightarrow ^3K_7$	1.48	3.98	1.24	2.94	1.10	4.01	1.82	3.89
3	$^5I_8 \rightarrow ^5G_4$	0.576	0.858	0.91	0.593	0.553	0.949	0.125	0.739
4	$^5I_8 \rightarrow ^5G_5$	0.0495	0.850	0.469	0.577	0.581	0.959	0.102	0.707
5	$^5I_8 \rightarrow ^5G_6$	0.193	1.53	0.169	1.04	0.160	1.73	0.255	1.27
6	$^5I_8 \rightarrow ^3K_8$	0.853	4.45	0.398	3.10	0.943	4.90	0.515	3.9
7	$^5I_8 \rightarrow ^5F_2$	0.422	4.87	0.454	3.45	0.534	5.27	0.564	4.4
8	r.m.s. (σ) deviation ($\pm$)	6.54	4.54	7.24	2.28				

Table 7 — Judd-Ofelt intensity parameters T_{λ} ($\lambda = 2, 4, 6; \times 10^{-10}$), symmetry ratio (T_4/T_6) and coordination ratio (T_4/T_2) for the Ho(III)-2AB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:water (1:1) medium.

S.N.	Parameter	Ho(III)-2AB	Ca^{2+}	Mg^{2+}	Sr^{2+}
1	$T_2 \times 10^{10}$	-1.00	-3.03	-0.281	-0.27
2	$T_4 \times 10^{10}$	4.10	1.51	1.77	1.53
3	$T_6 \times 10^{10}$	3.58	1.27	1.33	1.22
4	T_4/T_6	1.14629	1.184547	1.3343182	1.255567
5	T_4/T_2	-4.09621	-4.97294	-6.295489	-5.64932

Table 8 — Judd-Ofelt intensity parameters T_{λ} ($\lambda = 2, 4, 6; \times 10^{-10}$), symmetry ratio (T_4/T_6) and coordination ratio (T_4/T_2) for the Ho(III)-2CB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:water (1:1) medium.

S.N.	Parameter	Ho(III)-2CB	Ca^{2+}	Mg^{2+}	Sr^{2+}
1	$T_2 \times 10^{10}$	-1.1	-1.8	-6.4	-0.50
2	$T_4 \times 10^{10}$	4.56	4.28	17.62	1.92
3	$T_6 \times 10^{10}$	3.92	0.687	11.13	1.63
4	T_4/T_6	1.161915	6.238317	1.5833887	1.18125
5	T_4/T_2	-3.96527	-2.3815	-2.754082	-3.83589

Table 9 — Judd-Ofelt intensity parameters T_{λ} ($\lambda = 2, 4, 6; \times 10^{-10}$), symmetry ratio (T_4/T_6) and coordination ratio (T_4/T_2) for the Ho(III)-2HB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:water (1:1) medium.

S.N.	Parameter	Ho(III)-2HB	Ca^{2+}	Mg^{2+}	Sr^{2+}
1	$T_2 \times 10^{10}$	-0.734	-1.31	-0.446	-0.64
2	$T_4 \times 10^{10}$	3.31	5.79	1.95	2.67
3	$T_6 \times 10^{10}$	2.69	6.97	1.41	2.22
4	T_4/T_6	1.231267	0.831566	1.3809073	1.199536

5	T4/T2	-4.51043	-4.42296	-4.375526	-4.16208
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Fig. 2 — Comparative UV-Visible absorption spectra of the Ho (III)-2AB system with co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:aqua (1:1) medium.

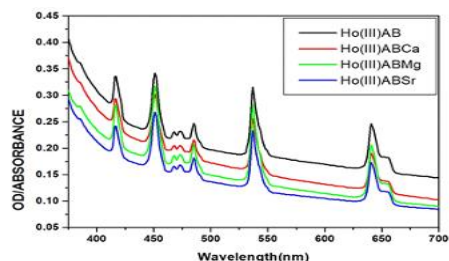


Fig. 3 — Comparative UV-Visible absorption spectra of the Ho(III)-2CB system with co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:aqua (1:1) medium.

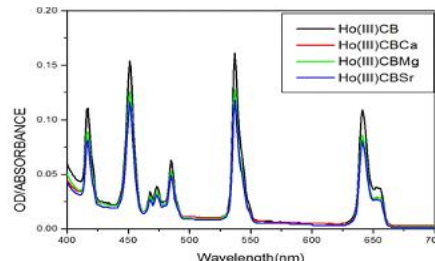


Table 10 — Computed values of bonding parameters — nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha covalency ($\delta\%$) and covalency angular-overlap (η) — for the Ho(III)-2AB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:water (1:1) medium.

S.N.	Transition	λ c(nm)	Ho(III)-2AB				+ Ca^{2+}				+ Mg^{2+}				+ Sr^{2+}			
			β	$b^{1/2}$	$\delta\%$	η	β	$b^{1/2}$	$\delta\%$	η	β	$b^{1/2}$	$\delta\%$	η	β	$b^{1/2}$	$\delta\%$	η
1	$^5\text{I}_8 \rightarrow ^3\text{H}_6$	416	1.002	0.035	-0.240	0.001	1.002	0.031	-0.192	0.001	1.001	0.027	-0.144	0.001	1.001	0.025	-0.120	0.001
2	$^5\text{I}_8 \rightarrow ^3\text{K}_7$	452	0.998	0.033	0.222	0.001	0.997	0.041	0.333	0.002	0.998	0.033	0.222	0.001	0.997	0.038	0.288	0.001
3	$^5\text{I}_8 \rightarrow ^5\text{G}_4$	468	0.998	0.033	0.214	0.001	0.997	0.039	0.300	0.001	0.997	0.037	0.278	0.001	0.997	0.040	0.321	0.002
4	$^5\text{I}_8 \rightarrow ^5\text{G}_5$	474	0.998	0.032	0.211	0.001	0.997	0.040	0.317	0.002	0.998	0.032	0.211	0.001	0.997	0.040	0.317	0.002
5	$^5\text{I}_8 \rightarrow ^5\text{G}_6$	486	0.998	0.032	0.206	0.001	0.997	0.039	0.309	0.002	0.998	0.035	0.247	0.001	0.997	0.037	0.268	0.001
6	$^5\text{I}_8 \rightarrow ^3\text{K}_8$	537.5	0.999	0.022	0.093	0.000	0.998	0.030	0.186	0.001	0.998	0.030	0.186	0.001	0.998	0.035	0.242	0.001
7	$^5\text{I}_8 \rightarrow ^5\text{F}_2$	641.5	0.999	0.020	0.078	0.000	0.998	0.028	0.156	0.001	0.998	0.028	0.156	0.001	0.998	0.028	0.156	0.001

Table 11 — Mean bonding parameters (β , $b^{1/2}$ mean, $\delta\%$, η), averaged over the seven recorded transitions, for all Ho (III)-ligand systems in both media before and after co-doping with Ca^{2+} , Mg^{2+} and Sr^{2+} ions.

Ligand	Medium	System	β (mean)	$b^{1/2}$ (mean)	$\delta\%$ (mean)	η (mean)
2AB	Alc: Water (1:1)	Ho(III)-L	0.9989	0.0295	0.1121	0.000903
2AB	Alc: Water (1:1)	+ Ca^{2+}	0.9980	0.0354	0.2013	0.001280
2AB	Alc: Water (1:1)	+ Mg^{2+}	0.9984	0.0319	0.1653	0.001032
2AB	Alc: Water (1:1)	+ Sr^{2+}	0.9979	0.0345	0.2104	0.001223
2CB	Alc: Water (1:1)	Ho(III)-L	0.9995	0.0143	0.0499	0.000249
2CB	Alc: Water (1:1)	+ Ca^{2+}	0.9987	0.0253	0.1335	0.000667
2CB	Alc: Water (1:1)	+ Mg^{2+}	0.9978	0.0326	0.2189	0.001094
2CB	Alc: Water (1:1)	+ Sr^{2+}	0.9983	0.0280	0.1701	0.000850
2HB	Alc: Water (1:1)	Ho(III)-L	0.9992	0.0196	0.0786	0.000393
2HB	Alc: Water (1:1)	+ Ca^{2+}	0.9991	0.0283	0.0864	0.000831
2HB	Alc: Water (1:1)	+ Mg^{2+}	0.9987	0.0250	0.1291	0.000645
2HB	Alc: Water (1:1)	+ Sr^{2+}	0.9987	0.0254	0.1322	0.000661
2AB	TX-100	Ho(III)-L	0.9994	0.0256	0.0640	0.000677
2AB	TX-100	+ Ca^{2+}	0.9989	0.0310	0.1061	0.000989
2AB	TX-100	+ Mg^{2+}	0.9993	0.0268	0.0658	0.000757
2AB	TX-100	+ Sr^{2+}	0.9991	0.0227	0.0938	0.000622
2CB	TX-100	Ho(III)-L	0.9992	0.0187	0.0823	0.000411
2CB	TX-100	+ Ca^{2+}	0.9982	0.0297	0.1784	0.000892
2CB	TX-100	+ Mg^{2+}	0.9987	0.0252	0.1280	0.000640
2CB	TX-100	+ Sr^{2+}	0.9986	0.0239	0.1365	0.000682
2HB	TX-100	Ho(III)-L	0.9997	0.0188	0.0262	0.000448
2HB	TX-100	+ Ca^{2+}	0.9986	0.0259	0.1441	0.000720
2HB	TX-100	+ Mg^{2+}	0.9986	0.0259	0.1393	0.000696
2HB	TX-100	+ Sr^{2+}	0.9987	0.0244	0.1273	0.000636

Table 12 — Observed transition work-function values, Aobs (cm^{-1}), for the Ho(III)-2AB system and co-doping of Ca^{2+} , Mg^{2+} and Sr^{2+} ions in alcoholic:water (1:1) medium (representative dataset).

S.N.	Transition	Ho(III)-2AB	+ Ca^{2+}	+ Mg^{2+}	+ Sr^{2+}
1	$^5\text{I}_8 \rightarrow ^3\text{H}_6$	23930.92	23916.60	23907.84	23900.01
2	$^5\text{I}_8 \rightarrow ^3\text{K}_7$	22024.82	21996.70	22024.70	22007.92
3	$^5\text{I}_8 \rightarrow ^5\text{G}_4$	21244.82	21232.00	21240.97	21229.56
4	$^5\text{I}_8 \rightarrow ^5\text{G}_5$	20971.59	20951.59	20979.08	20953.13
5	$^5\text{I}_8 \rightarrow ^5\text{G}_6$	20460.73	20442.98	20458.31	20451.78
6	$^5\text{I}_8 \rightarrow ^3\text{K}_8$	18504.00	18481.24	18480.83	18470.31
7	$^5\text{I}_8 \rightarrow ^5\text{F}_2$	15483.23	15462.84	15465.94	15463.52

Fig. 4 — Comparative UV-Visible absorption spectra of Ho(III), Ho(III)-2AB, Ho(III)-2CB and Ho(III)-2HB systems in TX-100 micellar medium.

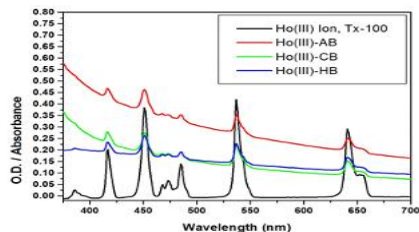
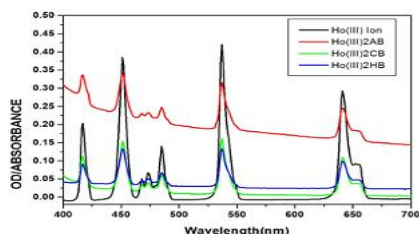


Fig. 5 — Comparative UV-Visible absorption spectra of Ho(III), Ho(III)-2AB, Ho(III)-2CB and Ho (III)-2HB systems in alcoholic:aqua (1:1) medium.



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