



SYNTHESIS AND METAL BINDING PROPERTIES of 1,3-N,N'-DIACYLHYDRAZONE-p-TERT-BUTYLCALIX[4]ARENES AND ANALOGUES DERIVED FROM β -CHLOROVINYL ALDEHYDES

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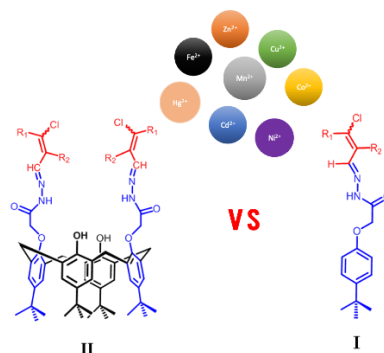
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This study aims to explore the role of preorganization of N-acylhydrazone moieties on p-tert-butylcalix[4]arenes platform for their conformational and binding properties. We investigate the metal binding properties of two series of acylhydrazone ligands derived from β -chlorovinyl-aldehydes: p-tert-butylphenoxyacylhydrazone (Ia-e) and p-tert-butylcalix[4]arene-1,3-N,N'-diacylhydrazone (IIa-e). Compound I features a single N-acylhydrazone moiety, while Compound II incorporates two receptors within a lower-rim 1,3-disubstituted calix[4]arene backbone. Utilizing UV-absorption spectrophotometry, we explore the interactions of these ligands with divalent transition and heavy metal cations (Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+}). Our analysis includes determining the binding properties, stoichiometries, and stability constants of the resulting solvent complexes. The results indicate that cone-structured lower-rim N,N'-diacylhydrazone-p-tert-butylcalix[4]arenes (IIa-e) exhibit superior complexation properties compared to their free analogues p-tert-butylphenoxyacylhydrazones (Ia-e). Furthermore, almost all tested N-acylhydrazone ligands demonstrate effective and selective binding to Cd^{2+} ions, suggesting potential applications in environmental biotechnology.



INTRODUCTION

Calixarenes, with their distinctive bowl-shaped structure and tunable functional groups, have emerged as intriguing scaffolds for the design of molecular receptors with diverse applications in supramolecular chemistry, materials science, sensing and biomedicine.^{1–6} Among the derivatives of calix[4]arene, hydrazone-derivatives ligands

have garnered significant attention for their versatile coordination properties^{7–10} and potential applications in complexation studies.^{11–16}

N-acylhydrazone Schiff base derivatives are well-known in the literature for their complexing properties towards transition metal ions, facilitated by the presence of NNO donor atoms that promote coordination with various cations, exhibiting different stereochemistries and nuclearity.^{17–22}

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However, to date, there has been limited exploration of N-acylhydrazones derived from β -chlorovinylaldehydes.

The synthesis of the reported N-acylhydrazone ligands described in this work typically involves the condensation reaction between β -chlorovinylaldehydes and p-tert-butylbenzohydrazide for the monomeric ligands (Ia-e), and p-tert-butylcalix[4]arene-hydrazine for the calixarene-based ligands (IIa-e), leading to the formation of molecular architectures that combine the structural rigidity of calix[4]arene with the coordination flexibility of acylhydrazones. Notably, these ligands possess pendant arms with functional groups capable of coordinating with metal ions, thereby offering opportunities for selective complexation with transition and heavy metal ions.

Transition and heavy metal ions, due to their variable oxidation states and diverse coordination geometries, represent pivotal targets for investigating the complexation behavior of calix[4]arene-based N-acylhydrazone ligands and their monomeric analogues. Of particular interest is the ability of these ligands to selectively bind metal ions, notably Cd^{2+} , given the environmental relevance of cadmium contamination and the potential for developing selective sensors or remediation strategies.

In this study, we aim to explore the complexation properties of calix[4]arene-based N-acylhydrazone ligands (IIa-e) derived from β -chlorovinylaldehydes, along with their monomeric counterparts derived from p-tert-butylbenzohydrazide (Ia-e), towards a range of transition and heavy metal ions. Employing UV-absorption spectrophotometry, we seek to elucidate the binding affinities and stoichiometries of the resulting metal-ligand

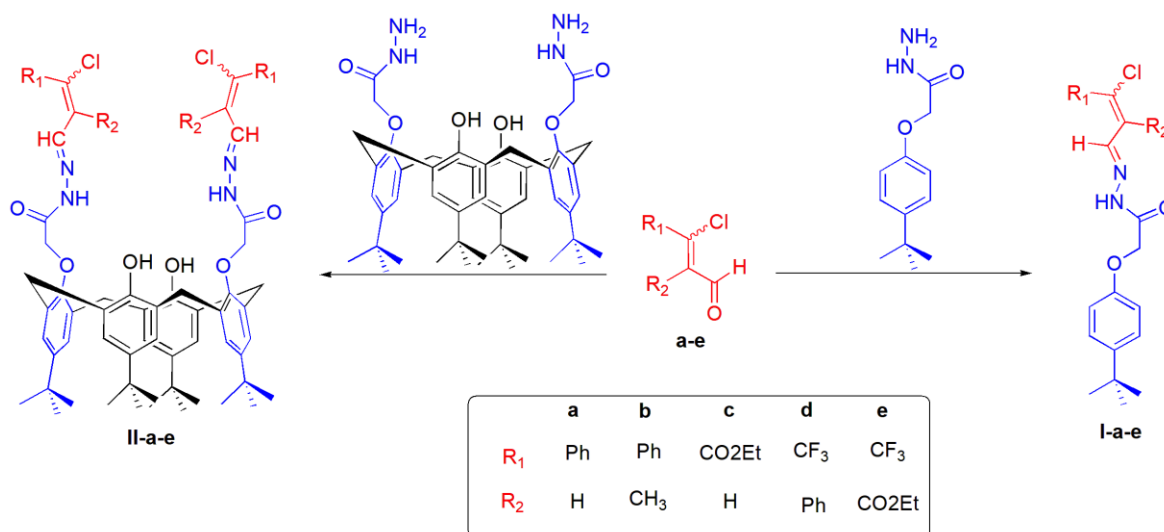
complexes. Furthermore, we aim to investigate the selectivity of these ligands towards Cd^{2+} ions and understand the underlying factors governing their preferential binding towards cadmium.

Through this comprehensive investigation, we endeavor to contribute to a deeper understanding of the complexation chemistry of N-acylhydrazones and calix[4]arene-based acylhydrazone analogues with transition and heavy metal ions, with a specific focus on selectivity towards Cd^{2+} . Insights gained from this study may pave the way for the development of novel molecular receptors for selective metal ion recognition and environmental remediation applications.

RESULTS AND DISCUSSION

Synthesis

As described in our previous work²³, the N-acylhydrazone (NAH) derivatives Ia-e were synthesized via the condensation reaction of p-tert-butylphenoxyhydrazide with β -chloro- α,β -unsaturated aldehydes a-e in refluxing chloroform for 1 hour, yielding NAHs Ia-e with yields ranging from 52% to 97%, as depicted in the scheme 1. NAHs Ia and Ic were isolated as single isomers, while NAHs Ib, Ic, and Id were obtained as a mixture of E and Z isomers, as confirmed by ¹H-NMR data. Comprehensive characterization was conducted using IR, (¹H, ¹³C, and ¹⁹F) NMR spectroscopy, and high-resolution mass spectrometry (HRMS). The E/Z ratios of isomers and cis/trans-amide percentages of conformers were determined through ¹H NMR analysis of crude product mixtures.



Scheme 1 – Synthetic routes of N,N'-diacylhydrazone-p-tert-butylcalix[4]arenes (IIa-e) and p-tert-butylphenoxyacylhydrazones (Ia-e).

Additionally, D-NMR experiments were performed to evaluate the energy activation barriers to rotation around the N–C(O) bond in these N-acylhydrazones Ia-e. Our findings revealed that the nature of the substituent R₂ significantly impacts the cis/trans equilibrium through electronic effects. Moreover, our results indicate that β -chloro- α,β -unsaturated aldehydes exhibit greater electron-withdrawing power than their corresponding aromatic derivatives.

Moreover, N,N'-diacylhydrazone-p-tert-butylcalix[4]arenes IIa-e, macrocyclic analogues of Ia-e, were synthesized by introducing N-acylhydrazone arms of α,β -unsaturated aldehydes onto the p-tert-butylcalix[4]arene scaffold²⁴. In all compounds, the proportions of Z and E isomers correspond to those of the starting aldehydes. Their structural analysis by NMR reveals the presence of three conformers: trans-amide/trans-amide, cis-amide/trans-amide, and cis-amide/cis-amide, resulting from di-substitution (rotation around the N-CO bond). The corresponding energy barrier of rotation was determined by dynamic NMR experiments. The calculated ΔG^\ddagger values are comparable to those of the free N-acylhydrazone arms Ia-e.

After an in-depth examination of the isomeric structures and conformations of N-acylhydrazones Ia-e and macrocyclic N,N'-diacylhydrazone-p-tert-butylcalix[4]arenes IIa-e in prior studies, this research shifts its focus to the binding capabilities of both Ia-e and IIa-e derivatives with transition and heavy metal cations. The study emphasizes the factors determining the efficiency and selectivity of these ligands. Specifically, we investigate the efficacy of donor sites, the isomeric and tautomeric

forms of acylhydrazone moieties, and the influence of the calix[4]arene platform on the probe properties. The affinity between transition and heavy metal ions and N-acylhydrazones is estimated from complexation data in MeOH using the methodology described in our previous works.

Complexation Studies

p-tert-butylphenoxyacylhydrazones Ia-e

As shown in Fig. 1, the UV absorption spectra of ligands Ia-e in methanol before titration exhibit a structured intense band between 265 and 320 nm, attributable to the π - π^* transitions of the aromatic moieties and n- π^* transitions of the C=N and C=O groups. Additionally, a secondary smaller band between 222 and 224 nm is observed.

The experimental spectra obtained after the progressive addition of prepared metal solution to a ligand solution exhibit distinct spectral variations specific to each experiment.

For instance, the UV spectra of the titration of ligand I-e were recorded between 200 and 360 nm, with a maximum absorption observed at 285 nm in the ligand spectra. The complexation with metal cations is evidenced by a hypsochromic shift, with two isobestic points observed at 240 nm and 313 nm in the case of Cu²⁺ cation (Fig. 2), indicating the formation of a new and stable complex.

In the case of ligand Ia, upon addition of CoCl₂ solution, the spectra exhibited a decrease in absorbance intensity below 340 nm accompanied by a bathochromic displacement of 5 nm, and one isobestic point at 340 nm was observed (Fig. 3).

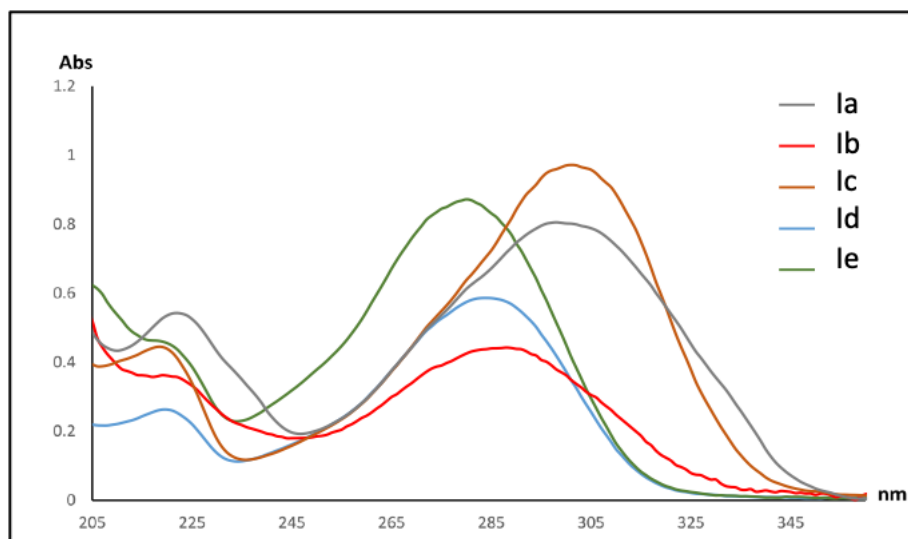


Fig. 1 – UV-Vis absorption spectra of ligands Ia-e in methanol; at 25°C, C_L ≈ 10⁻⁵M.

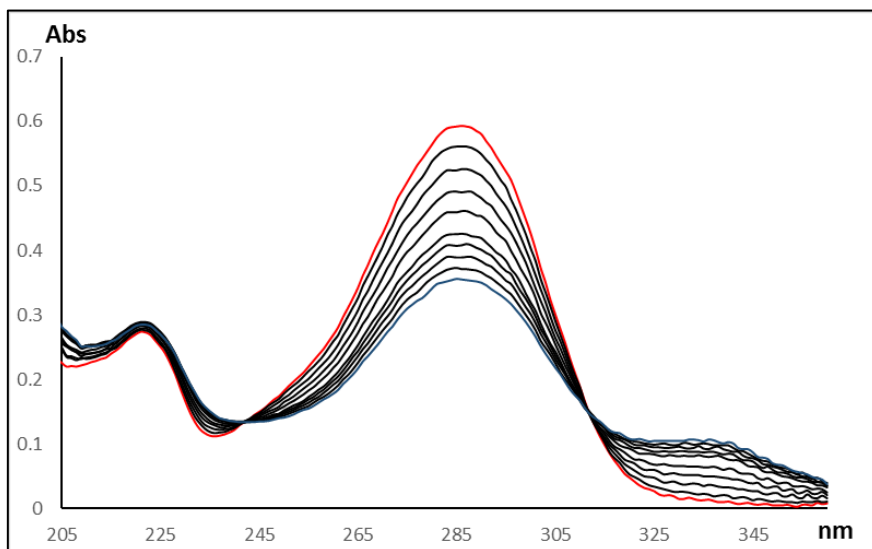


Fig. 2 – Changes in the UV-Vis absorption spectrum of ligand Ie upon addition of CuCl_2 in methanol; ($0 \leq R_{M/L} \leq 1.5$) at 25°C , $C_L = 10^{-5}\text{M}$, $C_{(\text{Et}_4\text{NCl})} = 0.01\text{ M}$.

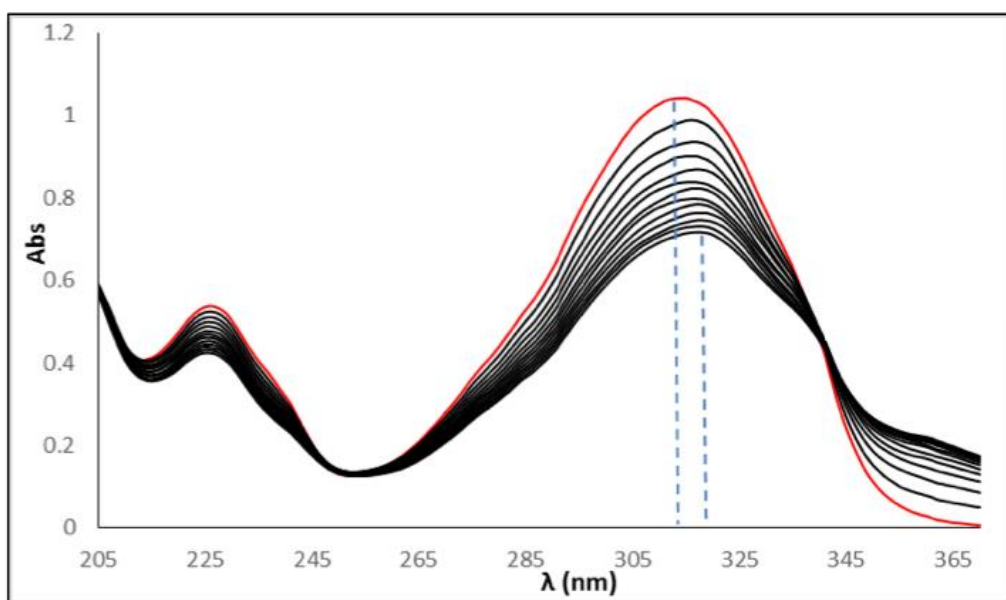


Fig. 3 – Changes in the UV-Vis absorption spectrum of ligand Ia upon addition of CoCl_2 in methanol; ($0 \leq R_{M/L} \leq 1.5$) at 25°C , $C_L = 10^{-5}\text{M}$, $C_{(\text{Et}_4\text{NCl})} = 0.01\text{ M}$.

The treatment of UV absorption spectra using letagrop^{25,26} enables us to determine the stoichiometries of various solvent complexes formed by ligands Ia-e with transition and some heavy metal cations in methanol at 25°C . Stability constants K_a were also calculated and are summarized in Table 1.

The complexes formed in solution by N-acylhydrazone ligands Ia-e with all studied cations are mononuclear species with a ligand-to-metal ratio of L:M = 1:1. This implies an interaction between one ligand molecule and one metal ion, which aligns with the number of coordinating atoms present in each ligand structure.

The stability constants K_a for the transition and heavy metal complexes, listed in Table 1, vary between $1.70 \times 10^3\text{ M}^{-1}$ and $2.82 \times 10^{11}\text{ M}^{-1}$, with particularly significant values observed for Cd^{2+} . Additionally, the calculation of the selectivity coefficient $S_{\text{Cd}^{2+}/\text{Mn}^{2+}}$ for ligand Ia demonstrates a significant value close to 10^8 . These results indicate an affinity of all ligands towards cadmium, except for ligand Ic, which unexpectedly exhibits relatively strong binding for Co^{2+} ($K_a = 3.02 \times 10^{10}\text{ M}^{-1}$). However, in general, the studied ligands show relatively less affinity for other cations such as Mn^{2+} , Zn^{2+} , Fe^{2+} , and Hg^{2+} .

Upon replacing hydrogen with a methyl group in ligand Ib compared to Ia, the stability constant values increase for all cations except for Fe²⁺ and Cd²⁺, with doubling observed for Mn²⁺ and Hg²⁺. However, the selectivity profile remains largely unchanged, with significant selectivity for cadmium as mentioned previously.

For analogues Ia and Ic, where the phenyl group (in Ia) is replaced by the ester group (in Ic), it is noted that the stability profile is affected. Ligand Ic exhibits selectivity for Co²⁺ primarily, along with Mn²⁺ and Fe²⁺, showing higher values of *K_a*. The selectivity observed for Co²⁺ by ligand Ic suggests

the contribution of the CO₂Et group in the coordination of the cation.

Regarding fluorinated ligands Id and Ie, where a trifluoromethyl group is incorporated in position β, both exhibit selectivity towards cadmium, with similar stability constant values. However, some variations in the stability profile are observed. In the case of compound Ie, the second selectivity is for Ni²⁺, while for compound Id, it is for Zn²⁺.

The results suggest that the nitrogen atoms and carbonyl oxygen from the N-acylhydrazone moiety, as well as the aldehydic moiety and/or solvent molecules, participate in chelation to M²⁺ ions.²⁷⁻³⁰

Table 1

Stability constants *K_a* (L:M = 1:1) of metal ions complexes with p-tert butylphenoxyacylhydrazones **Ia-e**, in MeOH at 25°C

Ligand	K_a (M⁻¹) for L:M=1:1							
	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Hg ²⁺
Ia	1.70 × 10 ³	7.59 × 10 ⁵	1.74 × 10 ⁵	1.58 × 10 ⁵	2.04 × 10 ⁵	9.12 × 10 ³	2.82 × 10 ¹¹	4.90 × 10 ⁴
Ib	1.91 × 10 ⁶	3.55 × 10 ⁴	2.40 × 10 ⁶	3.09 × 10 ⁵	7.59 × 10 ⁶	1.10 × 10 ⁵	1.07 × 10 ¹¹	9.77 × 10 ⁹
Ic	2.82 × 10 ⁹	3.16 × 10 ⁹	3.02 × 10 ¹⁰	1.91 × 10 ⁶	3.09 × 10 ⁵	4.27 × 10 ⁶	3.02 × 10 ⁶	1.51 × 10 ⁵
Id	4.27 × 10 ⁶	8.91 × 10 ⁵	1.74 × 10 ⁵	7.94 × 10 ⁷	2.57 × 10 ⁴	2.51 × 10 ³	1.74 × 10 ¹⁰	5.75 × 10 ⁶
Ie	4.79 × 10 ⁵	3.98 × 10 ³	3.89 × 10 ⁴	3.16 × 10 ⁵	1.58 × 10 ⁵	1.55 × 10 ⁸	3.39 × 10 ⁹	6.17 × 10 ⁵

p-tert-butylcalix[4]arene-1,3-N,N'-diacylhydrazones **IIa-e**

In order to investigate the complexation properties of multiple N-acylhydrazone units together, four distinct p-tert-butylcalix[4]arene-1,3-N,N'-diacylhydrazones (**IIa-d**) were studied.

The UV spectra of **IIa-d** ligands were recorded in methanol between 220 and 360 nm. They are almost similar and characterized by only one maximum of absorption appearing around 300 nm for **IIc** and **IId**, and at 284 nm and 270 nm for **IIa** and **IIb**, respectively (Fig. 4).

Titration of compounds **IIa-d** by metal cation solutions results in different spectral variations from one ligand to another and upon changing the metal cation. For instance, upon addition of CuCl₂ to **IIb** (Fig. 5), the absorbance recorded between 220 and 360 nm increases with a hypsochromic shift of 7 nm. Conversely, when replacing the previous ligand with **IIc**, a hypsochromic displacement of 20 nm is observed with three isosbestic points at 312 nm, 270 nm, and 214 nm (Fig. 6). These observations indicate a new and stable complexation of **IIc** with Cu²⁺ ion.

The spectral changes are analyzed using the program Letagrop,^{25,26} allowing for the determination of the stability constants of the various solvent complex species along with their stoichiometry. The obtained results are compiled in Table 2.

Table 2 illustrates the formation of binuclear species with all studied ligands and metal cations, indicating the potential of these ligands to shape binuclear complexes due to the presence of two arms of N-acylhydrazones supported on the calix[4]arene backbone.

The calculated stability constants suggest a particular affinity of ligands **IIa**, **IIb**, and **IIc** for Cd²⁺ (*S*_{Cd²⁺/Ni²⁺} = 10⁶ to *S*_{Cd²⁺/Cu²⁺} = 10¹⁰). Except for ligand **IId**, high selectivity for Mn²⁺ and Fe²⁺ is observed (*S*_{Fe²⁺/Ni²⁺} = 10⁵). Given the high binding ability of the investigated compounds, it is anticipated that both pairs of N-acylhydrazone moieties and the calixarene scaffold participate in the coordination of metallic ions.

In contrast to the complexation results, compound **IIb** forms the least stable M₂L complexes with most of the studied cations (Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, and Hg²⁺). However, it forms the most stable complex with cadmium compared to all studied systems, revealing high selectivity of up to 10¹⁰.

Comparing analogs **IIa** and **IIb**, unlike the case of free arms where the values are improved with the compound having the methyl group, stability constant values are improved in the case of the compound with α-vinyl hydrogen (**IIa**), except for cadmium stability constant increases in the case of ligand **IIb**.

For IIa and IIc analogs, the stability constant values are close, except in the case of Cd^{2+} , where the value increases from $1.91 \times 10^{13} \text{ M}^{-2}$ for the compound having an ester at the β position (IIc) to $8.32 \times 10^{16} \text{ M}^{-2}$ for the analog having a phenyl group at the same position (IIa). In this case, an analogy with the obtained results for monomer acyclic analogs Ia and Ic.

The number of binding sites in these ligands, provided by oxygen and nitrogen atoms, allows transition and heavy metal cations to be complexed. It is suggested that coordinated cations are located

between phenolic oxygen, amide oxygen, and imino nitrogen. Published studies also support these sites as coordinated to these cations.³¹

The open conic structure of calixarene derivatives and the soft base characters of binding sites could explain the formation of binuclear complexes of transition and heavy metal cations, which have a soft acid character. Comparing the stability profile of acyclic monomer and calixarenic analogs was challenging. However, most of these ligands show significantly enhanced affinities towards Cd^{2+} .

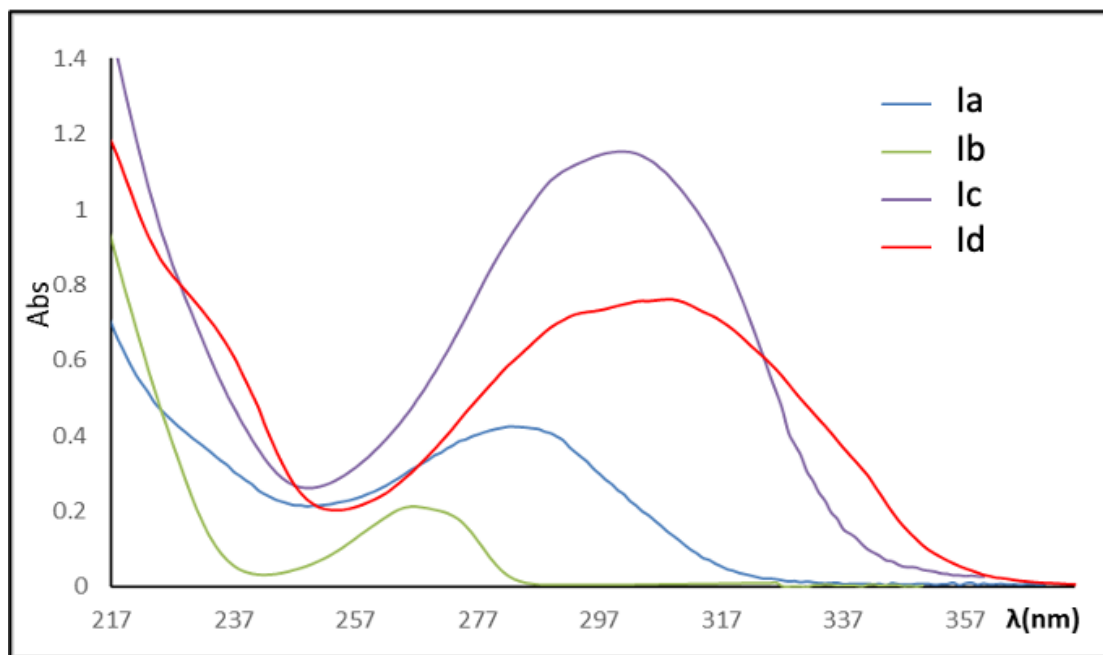


Fig. 4 – UV-Vis absorption spectra of ligands IIa-d in methanol; at 25°C , $10^{-4} \leq C \leq 10^{-5} \text{ M}$, $C_{(\text{E}4\text{NCl})} = 0.01 \text{ M}$.

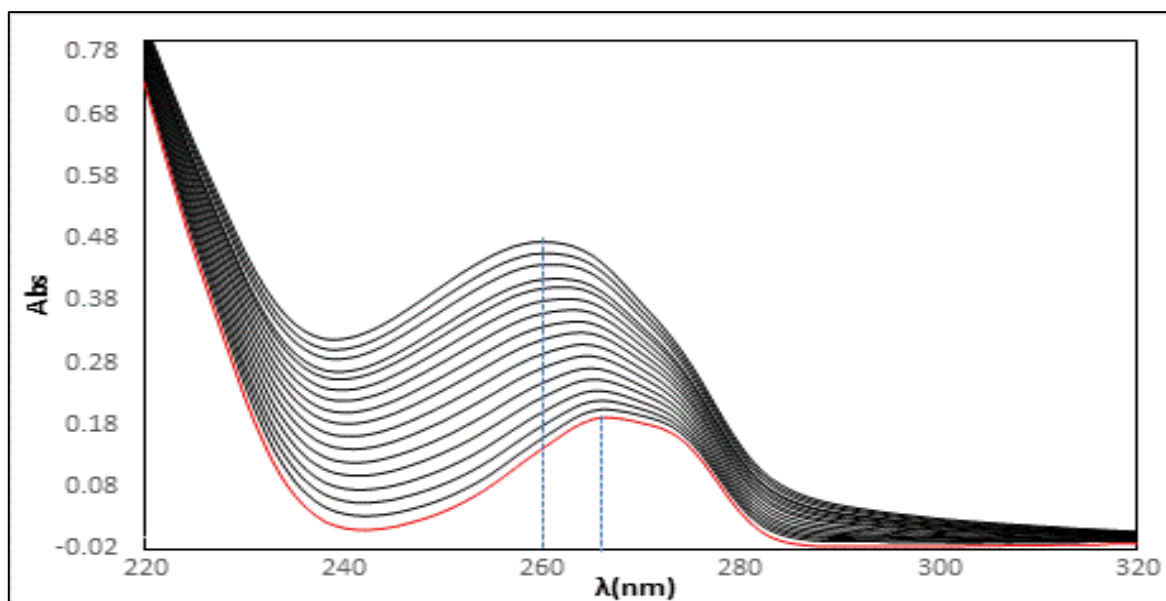


Fig. 5 – Changes in the UV-Vis absorption spectrum of ligand IIb upon addition of CuCl_2 in methanol; ($0 \leq R_{ML} \leq 3$) at 25°C , $C_L = 10^{-5} \text{ M}$, $C_{(\text{E}4\text{NCl})} = 0.01 \text{ M}$.

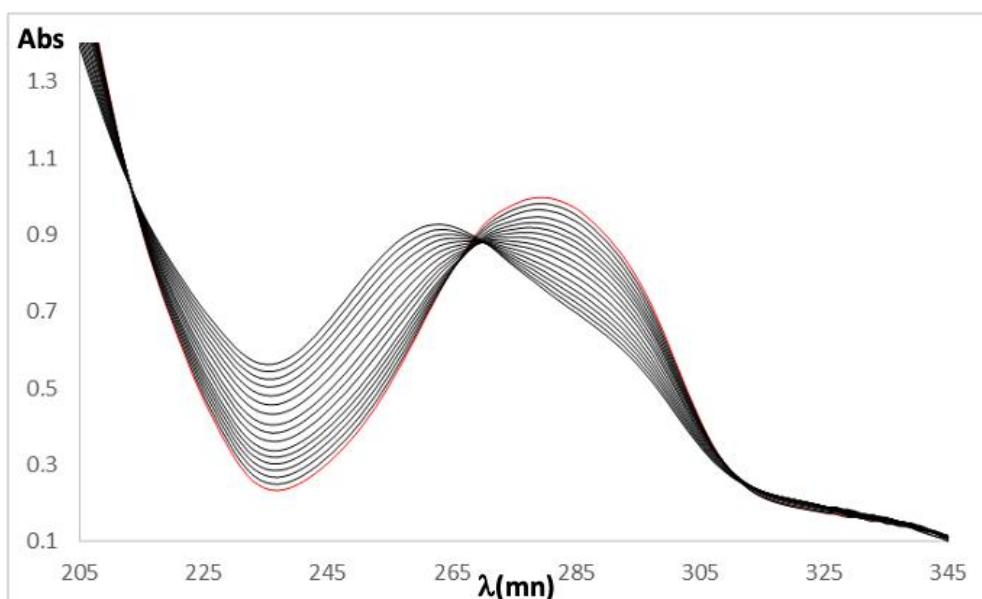


Fig. 6 – Changes in the UV-Vis absorption spectrum of ligand IIc upon addition of CuCl₂ in methanol; ($0 \leq R_{M/L} \leq 2.3$) at 25°C, $C_L = 2.710^{-5} \text{M}$, $C_{(\text{Et}_4\text{NCl})} = 0.01 \text{M}$.

It is evident from Tables 1 and 2 that the stability of the formed complexes increases and stoichiometry is doubled when the two arms were introduced onto the calix[4]arene. Thus, the integration of the N-acylhydrazone moieties into the calix[4]arene

backbone increases the extraction efficiency of the ligand. Indeed, the formation of binuclear complexes in the case of ligands IIa-d testifies to the participation of N-acylhydrazone groups located on the low rim of p-tert-butyl-calix[4]arene in the coordination process.

Table 2

Stability constants K_a (L:M = 1:2) of metal ions complexes with p-tert-butylcalix[4]arene-1,3-N,N'-diacylhydrazones II, in MeOH at 25°C

Ligand	K_a (M^{-2}) for L:M = 1:2							
	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
IIa	9.77×10^{11}	2.24×10^{11}	8.32×10^{10}	1.35×10^{11}	1.10×10^{12}	1.10×10^{11}	8.32×10^{16}	1.26×10^{10}
IIb	1.23×10^8	7.41×10^8	4.17×10^8	1.10×10^8	6.17×10^{11}	2.29×10^9	1.74×10^{18}	2.45×10^8
IIc	3.02×10^{11}	1.74×10^{13}	1.78×10^{11}	4.57×10^9	2.88×10^{10}	2.14×10^{11}	1.91×10^{13}	3.39×10^{10}
II d	1.07×10^{15}	3.55×10^{15}	1.48×10^{11}	1.20×10^{10}	1.78×10^{10}	6.61×10^{12}	1.20×10^{12}	2.88×10^{13}

EXPERIMENTAL

Instrument and Materials

p-tert-butylcalix[4]arene-1,3-N,N'-diacylhydrazones and their monomers analogues derivatives were synthesized according to published procedures.^{23,24}

Methanol (Riedel-deHaën for HPLC) was used without further purification. The supporting electrolyte used in the stability constant determinations was NET_4Cl (Fluka). The metal salts chosen were chlorides MCl_2 (Fluka, purum). The

spectra were recorded on a Perkin Elmer Lambda 11 using quartz cuvettes (Hellma).

Stability constant measurements

The stability constants β_{xy} being the concentration ratios $[\text{M}_x\text{L}_y^{x-ny}]/[\text{M}^{n+}]^x[\text{L}]^y$ and corresponding to the general equilibrium: $y\text{L} + x\text{M}^{2+} \rightleftharpoons \text{M}_x\text{L}_y^{x-2+}$ (where M^{2+} = metal cation, L = ligand) were determined in methanol by UV-absorption spectrophotometry at 25 °C. The ionic strength has been maintained at 0.01 M using NET_4Cl . The spectra of ligand solutions of concentrations ranging between 10^{-5} and 10^{-4} M

and increasing concentration of metal ion were recorded between 200 nm and 360 nm.

Generally, the metal to ligand ratio R at the end of the titration did not exceed 3 and the equilibria were quasi-instantaneous for all the systems. Addition of the metal ion salts to the ligand induced in the spectra changes large enough to allow the analysis of the resulting data using the program "Letagrop".^{25,26}

LETAGROP programme, a widely adopted computational tool in speciation and complexation studies, was used to refine initial stoichiometric models and calculate formation constants by least-squares fitting of UV-Vis spectral data.

Best values for the formation constants β_{xy} of the various complex species and their molar absorptivity coefficients for various wavelengths, are deduced from the best fit between the experimental and calculated UV spectra.

The best fit is reflected by the lowest value of U (the sum of U values for all lambda given) corresponding to the square sum of a differences between experimental and calculated absorbances ($U = \sum(A_{cal} - A_{exp})^2$). The β_{xy} values correspond to the arithmetic means of at least three independent experiments.

Selectivity

The selectivity of a ligand toward different metal ions was evaluated by calculating the selectivity coefficient (S), which reflects the ligand's preference for binding one metal ion (M_1) over another (M_2) in solution. It is defined as the ratio of the corresponding stability constants (association constants, K_a) of the metal-ligand complexes: $S(M_1/M_2) = K_a(M_1) / K_a(M_2)$.

A higher S value indicates stronger binding of the ligand to M_1 relative to M_2 . For example, an $S_{Cu^{2+}/Zn^{2+}} = X$, means that the ligand binds Cu^{2+} ions X times more strongly than Zn^{2+} ions under the same conditions.

CONCLUSION

A series of cone-structured lower-rim N,N'-diacylhydrazone-p-tert-butylcalix[4]arenes (IIa-d) and their relative free arms p-tert-butylphenoxyacylhydrazones (Ia-e) were synthesized to assess their complexation abilities towards transition and heavy metal cations.

The obtained data have highlighted that all examined N-acylhydrazones exhibit excellent affinity towards transition and heavy metal cations.

Notably, the incorporation of acylhydrazone moieties into the calix[4]arene backbone significantly enhances the complexation efficiency. While p-tert-butylphenoxyacylhydrazones (Ia-e) form 1:1 (ligand:metal) complexes, N,N'-diacylhydrazone-p-tert-butylcalix[4]arenes (IIa-d) ligands form di-cationic systems. They coordinate via acylhydrazone-NNO and phenol-calixarene O atoms to the metal center, exhibiting higher association constants compared to those of free arms p-tert-butylphenoxyacylhydrazones (Ia-e).

These findings suggest that the size of the calixarene macro ring plays a pivotal role in the complexation phenomenon. The results presented herein contribute to the understanding of the structural factors influencing complexation behavior.

Overall, the results presented in this study introduce N-acylhydrazone of β -chloroaldehyde scaffold as a valuable addition to the library of chelating molecules, demonstrating significant sensitivity and selectivity towards transition and heavy metal ions.

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