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ORIGINAL PAPER

Complexation of a tripodal amine-catechol ligand tris((2,3-dihydroxybenzylamino)ethyl)amine towards Al(III), Ga(III), and In(III)

Suban K. Sahoo · B. K. Kanungo · Minati Baral

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Abstract The complexation of a tripodal amine-catechol ligand tris((2,3-dihydroxybenzylamino)ethyl)amine (TRENCAT, L) with group-13 metal ions, viz., Al(III), Ga(III), and In(III), were investigated by means of potentiometric titrations and spectrophotometric measurements in an aqueous medium of 0.1 M KCl at 25 ± 1 °C. The ligand shows the potential to form various monomeric complexes of the types MLH_3, MLH_2, MLH, and ML. At low pH, the ligand is coordinated through three more acidic *ortho*-catecholic O-atoms to give MLH_3 species. With the rise in pH, the species MLH_3 releases three protons in steps from the *meta*-catecholic O-atoms to form MLH_2, MLH, and ML. The order of stability Ga(III) > Al(III) > In(III) for the species MLH_3 and MLH_2 is changed into Al(III) > Ga(III) > In(III) for the species MLH and ML. The coordination modes, binding ability, selectivity, and the change in stability order were explained with the help of experimental evidence, molecular modeling calculations, and available literature.

S. K. Sahoo (✉) · B. K. Kanungo
Department of Chemistry, Sant Longowal Institute of Engineering and Technology (SLIET), Longowal, Punjab 148 106, India
e-mail: suban_sahoo@rediffmail.com

B. K. Kanungo
e-mail: b.kanungo@vsnl.com

S. K. Sahoo
Department of Applied Sciences, Seth Jai Prakash Mukund Lal Institute of Engineering and Technology (JMIT), Radaur, Haryana 135 133, India

M. Baral
Department of Chemistry, National Institute of Technology (NIT), Kurukshetra, Haryana 136 119, India

Keywords Tripodal amine-catechol ligand · Aluminum · Gallium · Indium · Formation constants

Introduction

There is burgeoning interest in the synthetic biomimetic siderophores (siderophores [1–3] are known as naturally occurring low-molecular-weight iron-chelating agents produced by micro-organisms in order to extract iron from the external environment and transport it into the organism) because of their (1) potential applications as clinical iron removal agents [4] and (2) use in design as structural probes and diagnostic tools [5]. Until now, more than 300 naturally occurring siderophores have been isolated and characterized [6]. Among these siderophores, the catechol-based enterobactin [7] (Fig. 1), which shows the highest iron chelating ability with log $K = 49$, is modeled extensively as biomimetic chelators with respect to its use in iron overload treatment [4]. These enterobactin analogs are also implemented as chelators for Al(III), Ga(III), and In(III) because of their common preference for the hard donor atoms, such as oxygen and similar coordination behaviors [8, 9].

Aluminum, a non-essential element, is involved in causing dialysis dementia in patients who are unable to eliminate aluminum because of renal dysfunction and also affects the central nervous system to cause different diseases, such as amyotropic lateral sclerosis [10–12]. The only approved drug currently available for the clinical treatment of aluminum intoxication is a natural siderophore desferrioxamine B (Fig. 1) [13], an O_6 donor, whose clinical use suffers from a few important drawbacks, such as high cost, lack of oral efficacy, and major side effects in the long term [14]. Therefore, attempts are required to

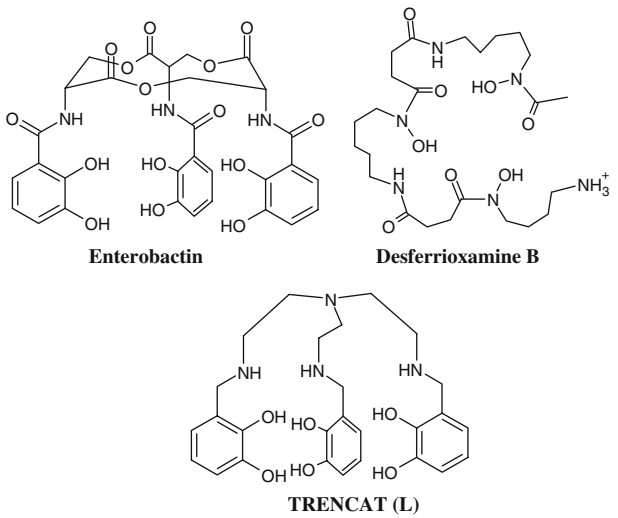

Fig. 1 Chemical structures of enterobactin, desferrioxamine B, and TRENCAT

replace desferrioxamine B by other simple synthetic molecules [15]. Again, there is also a search for new chelators for Ga(III) and In(III) with respect to the potential application of ^{67}Ga, ^{68}Ga, and ^{111}In complexes as diagnostic radiopharmaceuticals [16–20].

In the search for new ligands for the group-13 metal ions, the tripodal amine-catechol ligands, such as TRENCAT (Fig. 1), can be a best choice due to its structural analog to enterobactin. Previous studies of TRENCAT by Bismondo et al. [21] have revealed that the ligand is able to form a strong tris(catechol) complex with Th(IV) ion. Some recent studies of the tripodal amine-catechol ligands derived from cyclohexane-based triamine, such as *cis,cis*-1,3,5-tris [(2,3-dihydroxybenzylamino)aminomethyl]cyclohexane (TMACHCAT) and N^1,N^3,N^5-tris(2-(2,3-dihydroxybenzylamino)ethyl)cyclohexane-1,3,5-tricarboxamide (CYCOENCAT), have illuminated their potential to encapsulate metal ions, such as Al(III) and Ln(III) (Ln = La, Ga, and Lu), in the tris(catechol) compartment [22, 23]. Also, it was found that the more flexible ligand CYCOENCAT shows comparatively high selectivity towards Al(III) compared to desferrioxamine B [23].

Considering the above facts, the present work aims to study the selectivity and binding ability of tris((2,3-dihydroxybenzylamino)ethyl)amine (TRENCAT) to group-13 metal ions, viz., Al(III), Ga(III), and In(III). The complexation of TRENCAT with the above metal ions has been studied by potentiometric and spectrometric method in an aqueous medium of 0.1 N KCl and 25 ± 1 °C. The formation constants of the complexes formed in solution with Al(III), Ga(III), and In(III), their coordination modes, and selectivity of the ligand towards these metal ions have been presented. Further, some complementary information on the structure of the metal complexes formed in solution has been proposed through molecular modeling calculations.

Results and discussion

Metal complex formation

Potentiometric titrations of TRENCAT (L) with Al(III), Ga(III), and In(III) metal ions in 1:1 and 1:2 metal-ligand molar ratios were carried out in aqueous medium at $\mu = 0.1$ M KCl and 25 ± 1 °C. The titration curves for 1:1 metal-ligand molar ratio are shown in Fig. 2, where the symbols represent equilibrium points collected when no solid phase was present in the solution, while dotted lines represent points collected when turbidity or precipitation appeared in the solution. The deviation in the metal-ligand titration curves from the free ligand curve implies the formation of metal complexes. Also, the shape of the titration curves qualitatively infers that the ligand TRENCAT has considerable affinity for the metal ions. The equilibrium points collected before $a = 0$, where "*a*" is moles of base added/mole of ligand, are due to the neutralization of excess acid present in the solution. Formation of turbidity or precipitate occurred from $a = \sim 5.5$ implies that more than five protons may be displaced from TRENCAT possibly either (1) from the three *ortho*-catecholic hydroxyl groups and three from the protonated *sec*-amine groups whose protonation constants were evaluated or (2) six from the three catechols only (three of whose protonation constants are unknown).

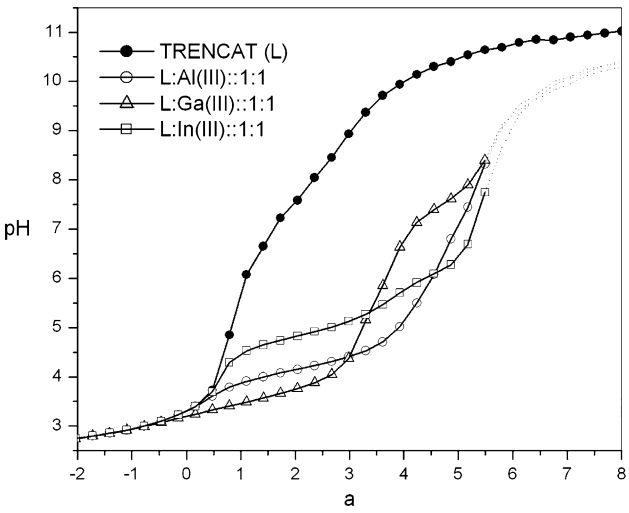

Fig. 2 Potentiometric titration curves of TRENCAT in the absence and presence of metal ions, viz., Al(III), Ga(III), and In(III), in a 1:1 ligand-metal molar ratio, where "*a*" is moles of base added per mole of ligand present

Keeping all the above preliminary observations, many sets of possible complexes were tested in the minimization program, and the best-fit model was obtained when formation of species of the types MLH_3, MLH_2, MLH, and ML were considered. No additional species were observed from the data of 1:2 metal-ligand molar ratio. The overall formation constants (log β) for the species were calculated using the Hyperquad 2000 program in which the previously determined log K values (11.23, 10.61, 9.75, 8.51, 7.58, and 6.32) of TRENCAT were used [21]. The first three log K values were assigned to the secondary amines, whereas the last three values to the hydroxyl groups of catechol units at *ortho*. Protonation constants for the hydroxyl groups of catechol units at *meta* could not be evaluated within the adopted experimental conditions (pH ~ 2.5–11.5) [21]. Therefore, the neutral TRENCAT is addressed as LH_3, and the fully protonated form is considered as LH_6^{+3}. The overall formation constants calculated for the various metal complex species are summarized in Table 1, and the equilibrium reactions are given in the Eqs. 1–4 (charges are omitted for clarity):

$$M + L + 3H \rightleftharpoons MLH_3,\ \log\beta_{113} = \frac{[MLH_3]}{[M][L][H]^3} \quad (1)$$

$$M + L + 2H \rightleftharpoons MLH_2,\ \log\beta_{112} = \frac{[MLH_2]}{[M][L][H]^2} \quad (2)$$

$$M + L + H \rightleftharpoons MLH,\ \log\beta_{111} = \frac{[MLH]}{[M][L][H]} \quad (3)$$

$$M + L \rightleftharpoons ML,\ \log\beta_{110} = \frac{[ML]}{[M][L]} \quad (4)$$

It is well known that the group-13 metal ions do not give any specific band in the electronic spectra. However, the coordination modes of the ligands can be explained from the shift in the intra-ligand transitions of the metal complexes with respect to free ligands and the supporting help of the potentiometric results. So, in order to supplement the potentiometric results, spectrometric titrations of TRENCAT were carried out in 1:1 metal-to-ligand ratio by keeping the ligand concentration $[L] = 4.02 \times 10^{-5}$ M and the metal ion concentration $[M(III)] = 4.02 \times 10^{-5}$ M with varying the pH between ~3.5 and ~8.0. After pH ~8.0, the solution became turbid. The experimental electronic spectra for TRENCAT-M(III) systems are shown in Fig. 3. The ligand peak was shifted towards higher wavelength with concomitant rise in the absorbance upon successive rise in pH, which indicates the formation of metal complexes. Similar variations in the electronic spectra of ligand TRENCAT with respect to the metal ions at different pHs indicate the identical modes of complexation. In analysis of the whole experimental electronic spectra using a non-linear least-square fitting program, pHAb gave best-fit models MLH_3, MLH_2, MLH, and ML, whose calculated formation constants are summarized in Table 1 along with the potentiometric results, which agree well with each other.

The solution species distribution curves (Fig. 4) indicate that the complexation occurred from pH ~ 3. The first complex species MLH_3 is formed with the interaction of M with LH_3. Since in the present experimental conditions adopted here (pH < 11) it was only possible to determine the protonation constants of the secondary amino groups and the more acidic catecholic oxygen at *ortho*, the tri-deprotonated species LH_3 of the ligand TRENCAT should be considered where the three more acidic protons are released from the catecholic units. Accordingly, the complex $[MLH_3]^{+3}$ can be represented structurally by the monocapped geometry as shown in Fig. 5a where the three secondary amine nitrogen atoms remain in protonated form. Similar monocapped type coordination mode in tripodal ligands with different trivalent metal ions has been reported earlier by Orvig and coworkers both in solid and solution state [24–26].

As the pH increases subsequently, successive deprotonation from MLH_3 leads to the formation of three different complexes MLH_2, MLH, and ML prior to the appearance of solid phase during the titrations. The extrusion of protons from the complex MLH_3 may either take place from the NH_2^+ groups for which the protonation constant values have been evaluated or from *meta*-catecholic hydroxyl groups whose protonation constant values are unknown. These two probabilities lead to two distinct geometries for the complexes of metal ion, either nitrogen–oxygen encapsulated, i.e., tris(aminocatecholate) type, or oxygen–oxygen

Table 1 The overall formation constants (log β) of the metal complexes at 25 ± 1 °C and μ = 0.1 M KCl

	Al(III)		Ga(III)		In(III)	
	A	B	A	B	A	B
$[MLH_3]/[M][L][H]^3$	44.92 ± 0.09	45.11 ± 0.03	46.82 ± 0.06	46.75 ± 0.04	42.97 ± 0.09	43.11 ± 0.02
$[MLH_2]/[M][L][H]^2$	40.75 ± 0.06	40.82 ± 0.02	41.12 ± 0.07	41.32 ± 0.01	37.86 ± 0.05	38.03 ± 0.06
[MLH]/[M][L][H]	35.14 ± 0.04	35.21 ± 0.03	33.41 ± 0.02	33.45 ± 0.05	31.23 ± 0.04	31.31 ± 0.03
[ML]/[M][L]	27.89 ± 0.01	27.87 ± 0.09	26.13 ± 0.04	26.17 ± 0.04	25.56 ± 0.02	25.61 ± 0.01

A potentiometry, *B* spectrophotometry

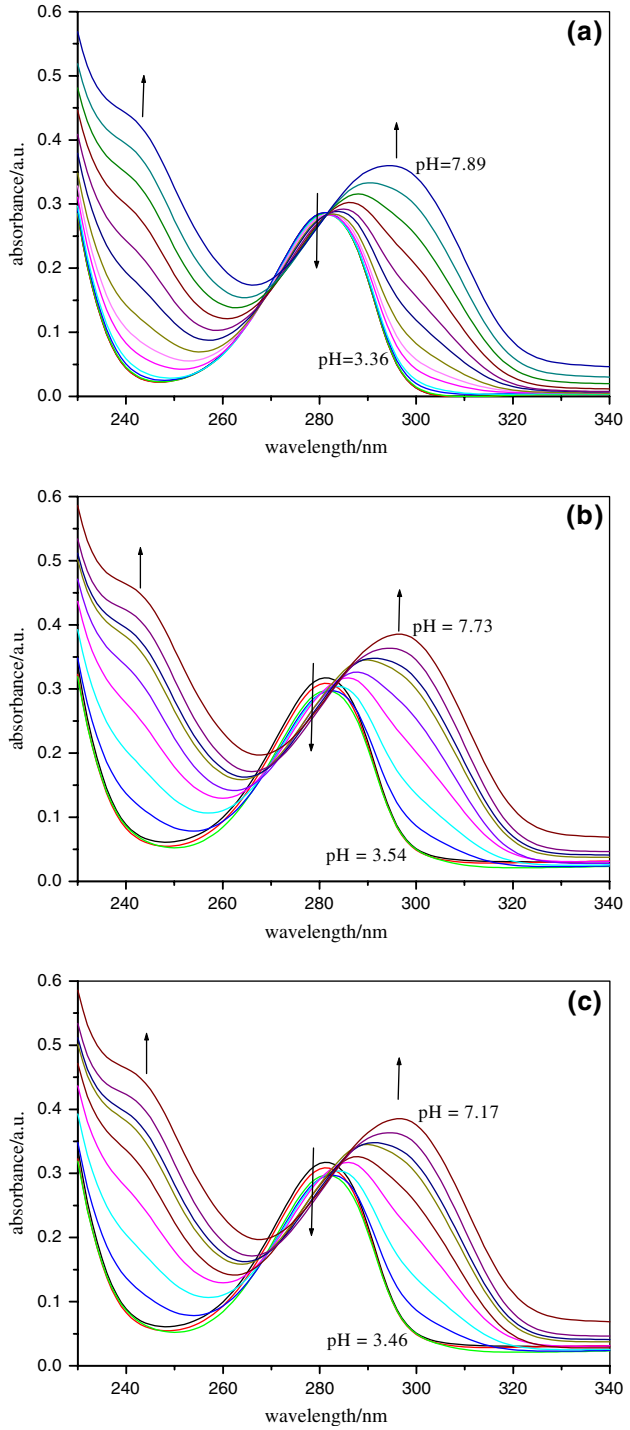

Fig. 3 Experimental electronic spectra of 1:1 metal-to-ligand ratio for the M(III)-TRENCAT systems at different pH, where M(III) = Al(III) (**a**), Ga(III) (**b**), and In(III) (**c**)

encapsulated, i.e., tris(catecholate). In the first case for the nitrogen–oxygen encapsulated, if the metal ion facilitates to enter into the nitrogen–oxygen cavity with the release of proton from the protonated secondary amine nitrogen atom upon coordination, it may get a repulsive force because of its higher charge-to-ionic radii in the presence of the other two

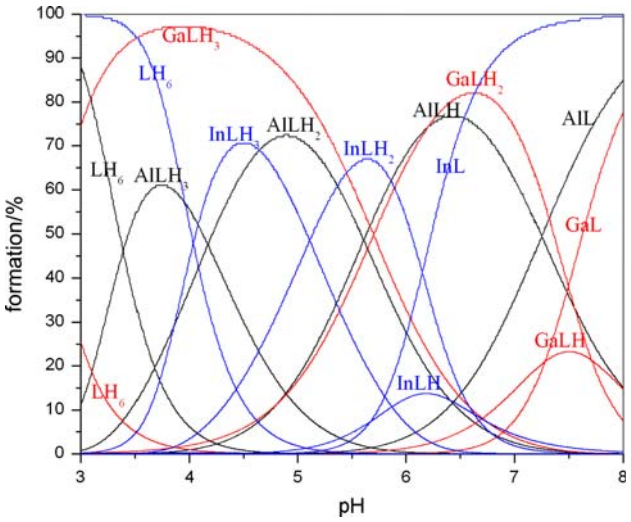

Fig. 4 Speciation diagram (% of formation vs. pH) calculated for 1:1 M(III)-TRENCAT systems, where M(III) = Al(III), Ga(III), and In(III)

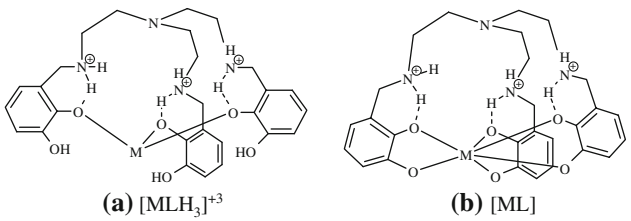

Fig. 5 Proposed modes of complexation of TRENCAT in the metal complex species **a** monocapped $[MLH_3]^{+3}$ and **b** encapsulated [ML]

protonated NH_2^+ groups, and secondly, on coordination, results in a six-membered chelate ring. However, in case of oxygen-oxygen encapsulated, the ligand coordinates through its less acidic catecholic oxygens as anionic donor to form five-membered chelate rings.

Aluminum(III) is the hardest metal ion and shows strong preference for hard donor atoms, such as negatively charged oxygen atoms [27], but its affinity towards the nitrogen atoms is very poor [28]. Hancock and co-workers [28] have estimated the formation constant of ammonia with the group-13 metal ions and found the log *K* trend for $M(NH_3)^{3+}$ formation as Al(III) $\ll$ Ga(III) $\sim$ In(III). Farkas and Csoka [29] demonstrated the aqueous coordination properties of Al(III) by using a ligand 2,3-dihydroxyphenylalanine-hydroxamic acid (DOPAHA) having three different bonding sites: catecholate, hydroxamate, and amine-type. They reported the formation of both catecholate and hydroxamate chelate, but the amine-type coordination mode did not occur with Al(III) [29]. Nevertheless, Orvig and coworker pointed out that in some tripodal aminophenolate ligands, introduction of phenol groups into a well-preorganized structure allows the phenolate groups to provide an anchoring effect for the

coordination of nitrogen atoms with Al(III) [30]. However, this effect is limited to the kind of tripods used. The derivative of a more flexible with larger cavity tripod like tris(((2-hydroxy-5-sulfobenzyl)amino)ethyl)amine (H_6TRNS) gave no stable complex in solution and forces precipitation as metal hydroxide [30]. On the basis of all the above observations, one can rationalize the preference of tris(catecholate) bonding to Al(III), and the possibility of nitrogen–oxygen encapsulation is less probable. Also, the formation of oxygen–oxygen encapsulation can be depicted from the bathochromic spectral shifting in absorbance spectra upon deprotonation from MLH_3 (Fig. 3). Since the catechol units are the only chromophores in TRENCAT, any change in λ_{max} is assignable to the further deprotonation and/or coordination of catecholic oxygens. Again, the tris(catecholate) type coordination modes for the ligand TRENCAT with Ga(III) and In(III) ions can also be proposed due to their similarity in the shifting of electronic spectra with respect to the Al(III)-TRENCAT system (Fig. 3). It is expected because the "hard" cation shows much preference towards negatively charged oxygen donors compared to the secondary amine nitrogen donors. Secondly, it is known that the complex stability is intimately related to the size of the metal ion and chelate ring, and stability generally increases as the chelate ring size changes from six to five. This stabilization is generally greater for larger metal ions [31, 32]. Moreover, tris(catechol) type complexation in tripodal amine-catechol ligands has been well documented with a number of trivalent metal ions [21–23]. Thus, for the ML species, oxygen–oxygen encapsulated structure as shown in Fig. 5b can be suggested.

Selectivity and binding abilities of the ligand

Table 1 indicates that when the first metal chelate MLH_3 is formed, Ga(III) shows much preference over the other two metal ions. The order of stability for MLH_3 species is found to be Ga(III) > Al(III) > In(III). Similar order has been reported earlier for many types of complexes [8], and it is expected because the larger ionic radius and lower "hardness" of In(III) lowers the stability of In(III) compared to Ga(III). Again, the hardest Al(III) shows better selectivity than In(III), but its considerably lower ionic radius results in lower stability than Ga(III). The ionic radius effect on stability has been well documented [33].

Again, from Table 1, it can be observed that the order of selectivity for the monocapped metal complex species MLH_3 is changed to Al(III) > Ga(III) > In(III) when the ligand is forced to form the encapsulated metal complex ML. The higher stability of Al(III) over Ga(III) towards the catechol type ligand is unusual, as Ga(III) usually forms stronger tris(catecholate) chelate than Al(III) and In(III) [31]. Since all the metal ions showed competitive coordination modes to form tris(catecholate) type complex instead of tris(aminocatecholate) type complex, the competitive coordination potential for Al(III) may be expected to be higher than the Ga(III) and In(III) due to their poor affinity towards *N*-donor atoms. Further, molecular mechanics calculations using the MM3 force field, carried out for the MLH_3 and ML complexes, indicate that a decrease in the change in strain energy $\left[\Delta U^{ML}_{MLH_3} = U_{ML} - U_{MLH_3}\right]$ calculated for $\Delta U^{AlL}_{AlLH_3}$ = 897.73 kJ/mol is much higher than the $\Delta U^{GaL}_{GaLH_3}$ = 827.73 kJ/mol and $\Delta U^{InL}_{InLH_3}$ = 732.40 kJ/mol. It is well established that if the steric strain in the complex is lower, then the complex formation reactions will be more favorable [34]. Accordingly, the order of stability for the ML species may also be due to the difference in steric energy during the complexation. The MM3-optimized model structure of AlL chelate (Fig. 6) predicted a distorted octahedral-type geometry and showed the presence of intramolecular hydrogen bonds between the amine protons and catecholic oxygens. Such intramolecular H-bonds are known to provide an extra stability for the formation of tripodal tris(catechol) type encapsulated complex, and this effect has been reported for the complexes of enterobactin and its analogs [1].

The calculated pM (pM = −log $[M^{n+}]$) corroborates well with the stability order obtained for MLH_3 and ML complexes. The metal ion competes with the protons during complexation in solution, and the proton competition mainly depends on the pH and pK_a of the ligand. Therefore, the pM is a better value of the relative complexation efficiency of the ligand under given conditions of pH, M^{n+},

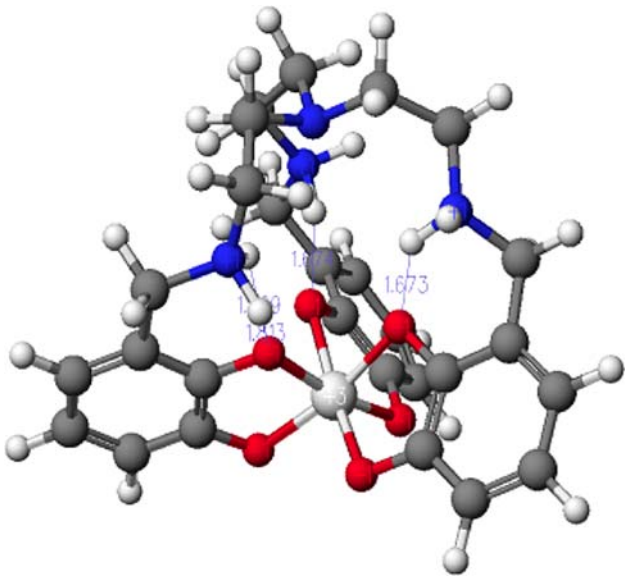

Fig. 6 MM3-optimized model structure for the [Al(III)L] complex (calculated H-bond lengths NH…O were between 1.673 and 1.817 Å)

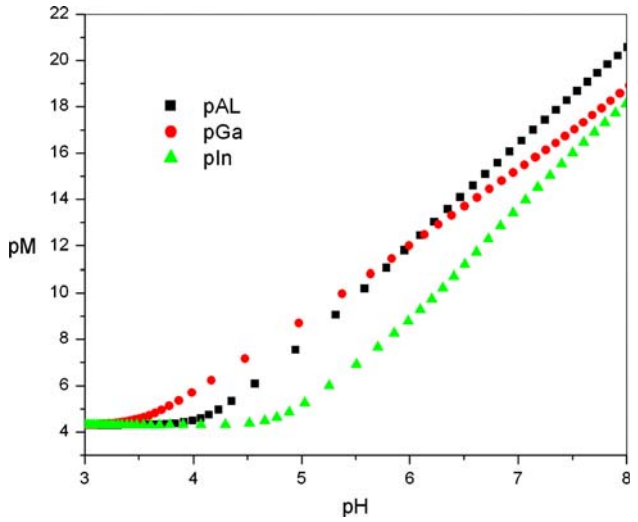

Fig. 7 Plot of pM ($pM = -\log [M^{n+}]$) vs. pH. pM was calculated for $[L] = 5 \times 10^{-4}$ M, $[M^{n+}] = 5 \times 10^{-5}$ M ($M^{n+} = Al^{3+}$, Ga^{3+}, and In^{3+}) using the protonation constants of ligand TRENCAT, and the complexation constants β_{11n}

and L concentrations. The pM ($M^{3+} = Al^{3+}$, Ga^{3+} and In^{3+}) values were calculated at different pH = 3–8, $[L]_{total} = 5 \times 10^{-4}$ M and $[M^{3+}]_{total} = 5 \times 10^{-5}$ M. From the plots of pM as a function of the pH (Fig. 7), it can be pointed out that the selectivity of ligand for the metal ions is maintained over the pH range 3.0–8.0. At low pH, the ligand binds Ga(III) more selectively than Al(III) and In(III). As the pH increases from 6.0, the pM values indicate that the ligand binds Al(III) more selectively than Ga(III) followed by In(III).

At physiological pH = 7.4, the ligand TRENCAT (pAl = 18.12, pGa = 16.61, and pIn = 15.53) showed a higher affinity only in the presence of Al(III) ion compared to the corresponding transferrin [35] (pAl = 14.50, pGa = 20.90, and pIn = 18.70) and the well-known chelating agent EDTA [30] (pAl = 16.30, pGa = 21.00, and pIn = 23.10), but showed slightly lower affinity than desferrioxamine B (pAl = 19.10) [36]. The chelates with high kinetic and/or thermodynamic stability with respect to the hydrolysis are usually tested for medicinal purpose and demetalation by the serum protein transferrin [37]. Moreover, Santos and coworkers [38] suggested that sequestering ligands with free amines as in desferrioxamine B may improve their usefulness as a drug, where the amine groups are used as a point of attachment to a polymeric solid matrix, which enhanced the properties of removing "hard" ions from water solutions. Such free amines are also present in the ligand TRENCAT and in their complexes depicted in solution. Therefore, *the tripodal amine-catechol ligand TRENCAT can be a useful chelator for Al(III).*

Experimental

Materials and measurements

The compound tris((2,3-dihydroxybenzylamino)ethyl) amine (TRENCAT) was synthesized according to Ref. [21]. AL(III), Ga(III), and In(III) nitrates were obtained from Sigma–Aldrich and used directly. All other chemicals: potassium hydroxide, hydrochloric acid, and potassium chloride were obtained from Merck.

All solutions for the different titrations were prepared prior to the experiments in double-distilled deoxygenated water. KOH solution of 0.1 M was prepared and standardized against potassium hydrogen phthalate. HCl solution (0.1 M) was prepared and standardized against standard KOH. Solutions of 0.01 M ligand and 0.01 M metal ions were also prepared in deoxygenated water. The formation constants of the metal complexes were determined by potentiometric and spectrophotometric titrations at 25 ± 1 °C maintained from a double-wall glass-jacketed titration cell connected to a constant-temperature circulatory bath. For all titrations, the observed pH was measured as $-\log [H^+]$ using a ThermoOrion $720A^+$ pH-meter equipped with a combined glass electrode. The electrode was calibrated to read pH according to the classical method [39]. A standard hydrochloric acid solution was titrated with a standard KOH solution, and the calculated hydrogen ion concentrations ($pKw = 13.77 \pm 0.05$) were used to convert the pH-meter reading to hydrogen ion concentration. Final concentration of ligand (1×10^{-3} M) and metal (1×10^{-3} M and 5×10^{-4} M) were maintained for the different titrations. Following titrations with metal-to-ligand molar ratios: $c_M/c_L = 0{:}1$; $c_M/c_L = 1{:}1$, 1:2 ($M = Al^{+3}$, Ga^{+3}, and In^{+3}) were carried out. The ionic strength was maintained at 0.1 M by adding an appropriate amount of 1 M KCl. A non-linear least-square computer program Hyperquad 2000 has been used to calculate the formation constants of the metal complexes [40].

In the spectrophotometric studies, a dilute solution of ligand (4.02×10^{-5} M) and metal ion (4.02×10^{-5} M) was acidified with 0.1 N HCl at an ionic strength of 0.1 M KCl and 25 ± 1 °C, and then titrated with 0.1 N KOH. After each adjustment of pH, an aliquot was taken, and spectra were recorded. The formation constants were calculated by global fitting of the whole spectral data using a non-linear least-square fitting program, pHAb [41].

Molecular modeling calculations

Molecular modeling calculations were performed by using the computer program CAChe (Computer-Aided Chemistry) Version 6.1.1 software from the Oxford Molecular Group [42]. The probable structures of the metal

complexes formed in solution were drawn using CAChe Editor, and then the geometry was optimized through molecular mechanics calculation by applying MM3 force field and adopting the eigenvector following (EF) method. For all the metal ions, six coordinated structures for each complex species were drawn by adding the appropriate number of water molecules.

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