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Potentiometric, spectrophotometric, theoretical studies and binding properties of a novel tripodal polycatechol-amine ligand with lanthanide(III) ions

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Abstract

A new tripodal ligand *cis*,*cis*-1,3,5-tris[(2,3-dihydroxybenzylamino)aminomethyl] cyclohexane (TMACHCAT), bearing three catechol units attached to a tris-methylaminocyclohexane (TMACH) ring has been synthesized and characterized by elemental analyses, UV–VIS, IR and ^{1}H NMR spectral data. The lowest energy molecular geometry of TMACHCAT was obtained through empirical followed by quantum mechanical treatment. Theoretical UV–VIS, IR and ^{1}H NMR spectral data were calculated from the energy-minimized structure by applying semi-empirical ZINDO, PM3 and TNDO/2 method, respectively and compared with the experimental data. The complexation behaviour of the ligand with H^+, La(III), Gd(III) and Lu(III) in an aqueous medium of 0.1 M KCl at 25 ± 1 °C was studied by potentiometric and spectrophotometric methods. Six protonation constants were determined for the ligand and used as input data to evaluate the formation constants of the metal complexes. The formation of complexes between the partially protonated ligand and lanthanide ions of the types MLH_3, MLH_2, MLH, ML_2H_6 have been observed. The solution structures of the metal complexes were proposed through experimental evidences along with the calculated minimum strain energy through molecular mechanics calculation using CAChe's augmented MM3 force field.

Keywords: Tripodal polycatechol-amine ligand; Lanthanum; Gadolinium; Lutetium; Protonation constants; Formation constants; Molecular mechanics and semi-empirical method

1. Introduction

Lanthanide (III) coordination chemistry has recently received growing interest because of the numerous applications of lanthanide (III) complexes, such as relaxation agents in nuclear magnetic resonance imaging [1], luminescent probes in biology and medicine [2] or catalysts for the cleavage of RNA and DNA [3,4]. While dealing with such applications, the greatest interest is focused on the use of these complexes, gadolinium compounds in particular, as contrast agents in magnetic resonance imaging (MRI) [5], due to its effective magnetic moment and electronic relaxation time associated with the f^7 configuration. For this purpose, the most stringent requirement is high thermodynamic stability and possibly kinetic inertness, which can be achieved by complexation of suitable designed ligands. Much of this work has been based on the application of gadolinium complexes of poly(aminocarboxylate) ligands such as Gd-DTPA (DTPA = diethylenetriaminepentaacetic acid) [6] and Gd-DOTA (DOTA = 1,4,7,10-N,N',N'',N'''-tetraacetic acid) [7] and their derivatives [8]. Recently, efforts have been taken to synthesize multidentate tripodal ligands because of their intermediate chelation between open chain ligands and those based on macrocycles, where metal can be encapsulated by three arms of the suitably designed ligand [9–12]. Among such ligands,

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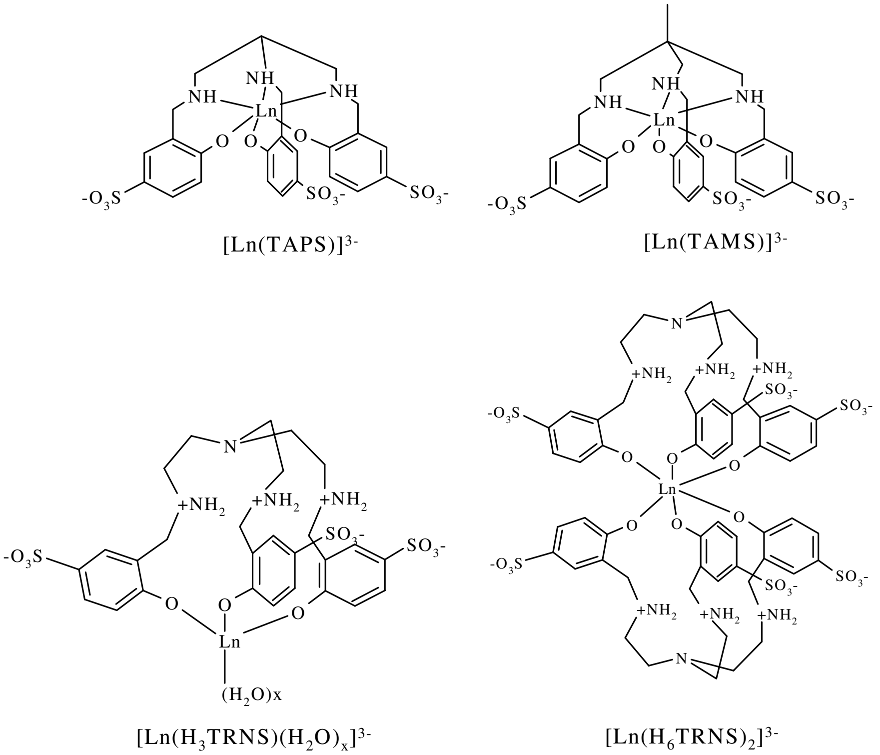
the natural occurring siderophore, enterobactin has a tripodal architecture with one catechol binding unit in each arm [13,14] shows the highest binding constants [15]. This led not only to model it through simple artificially synthetic molecules for the ultimate development of iron removal drugs for therapeutic use [16] and to mimic the various biological functions such as redox, spectroscopic, binding or assimilation [17] but also the study of the coordination chemistry of catechol-based ligands with 3d transition elements [18], trivalent group 13 metal ions [19], actinides [20] and trivalent lanthanides [21,22].

Again, the complexation of lanthanide ions in aqueous medium has been studied mostly with carboxylato- and phosphonato-oxygen donors because of their oxoplilicity [23]. Very less attention has been given to the phenolato-group as anionic oxygen donor for these metal ions [24,25]. The main reason why the coordination of lone phenol is hindered is the weak acidity of the hydroxy group (pK_a of phenol ~10) [24] and since the lanthanide aqueous ions are themselves weak Lewis acids, they generally cannot compete with the hydrogen ion for complexation of phenol in water and precipitate as hydroxides above pH 8. Thus, a ligand containing only amines and phenols could not be expected to be a particularly good ligand for aqueous lanthanide chelation as it should simply be too basic. Nevertheless, it has been reported that introduction of phenol groups into a well-preorganized structure allows the ligand to form strong lanthanide (III) complexes [25,26]. Coordination chemistry of different sulfonated water soluble tripodal amino-phenolate ligands tris-((2-hydroxy-5-sulfobenzylamino)ethyl)amine (TRNS), 1,1,1-tris-(((2-hydroxy-5-sulfobenzyl)amino)-methyl)ethane (TAMS), 1,2,3-tris-((2-hydroxy-5-sulfobenzyl)amino)propane (TAPS) have been investigated by Orvig et al. in solution where it was found that Ln(III) was encapsulated by podands possessing short and rigid tripods to give $[Ln(TAPS)]^{3-}$ and $[Ln(TAMS)]^{3-}$, while the more flexible TREN spacer in TRNS prevented regular wrapping of the chelating side arms around Ln(III), thus leading to monocapped $[Ln(H_3TRNS)(H_2O)_x]$ and bicapped $[Ln(H_3TRNS)_2]^{3-}$ podates (Fig. 1) [25,26]. Recently, Di Bernardo and others suggested that introduction of catechol group in tris((2,3-dihydroxybenzyl-amino)ethyl) amine (TRENCAT) as binding units instead of phenolate donor showed high complexing ability towards lanthanide metal ions at nearly physiological pH [27,28].

Based on these above facts we were interested to study the coordination behaviour of a new polycatechol-amine ligand by changing the spacer unit TREN into a cyclohexane based tripod tris-aminomethylcyclohexane (TMACH), which is expected (i) to increase the degree of freedom and flexibility of podants and (ii) to reduce the steric constraints within the tripod thus favouring regular wrapping of the binding side arms. Thus, in this communication, we present the synthesis and structural characterization of a multidentate tripodal ligand *cis*,*cis*-1,3,5-tris[(2,3-dihydroxybenzyl-



$[Ln(TAPS)]^{3-}$

$[Ln(TAMS)]^{3-}$

$[Ln(H_3TRNS)(H_2O)_x]^{3-}$

$[Ln(H_6TRNS)_2]^{3-}$

Fig. 1. Coordination modes of lanthanide metal ions with different tripodal aminophenolate ligands in solution.