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Complexation of thorium with pyridine monocarboxylate-N-oxides: Thermodynamic and computational studies

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Abstract

The feed wastes and waste water treatment plants are the major sources for the entry of N-oxides into the soils then to aquatic life. The complexation of actinides with potentially stable anthropogenic ligands facilitate the transportation and migration of the actinides from the source confinement. The present study describes the determination of thermodynamic parameters for the complexation of Th(IV) with the three isomeric pyridine monocarboxylates (PCNO) namely picolinic acid-N-oxide (PANO), nicotinic acid-N-oxide (NANO) and isonicotinic acid-N-oxide (IANO). The potentiometric and isothermal calorimetric titrations were carried out to determine the stability and enthalpy of the formations for all the Th(IV)-PCNO complexes. Th-PANO complexes are more stable than Th-NANO and Th-IANO complexes which can be attributed to chelate formation in the former complexes. Formation of all the Th-PCNO complexes are endothermic and are entropy driven. The geometries for all the predicted complexes are optimized the energies, bond distances and charges on individual atoms are obtained using TURBOMOLE software. The theoretical calculation corroborated the experimental determinations.

1. Introduction

The carboxylic acid derivatives of N-heterocyclic and N-oxide heterocyclic compounds have been used extensively as ligands in contemporary research [1]. The metal ion complexation with N-oxide moiety in both the solid and solution states are of great importance in organic chemistry and biochemistry for various applications in the fields of chemistry, synthetic chemistry, and industrial chemistry [2]. N-oxides also play a significant role in materials chemistry. Pyridine and quinoline N-oxides find their application in regioselective and enantioselective catalysis [3,4]. Many heteroaromatic N-oxides are identified as potential anticancer and antimalarial drugs or reductors of bacterial deposition [5–7] and as antitumor agents [8]. Further, N-oxides play an important role in the metabolism of drugs for the treatment of SARS (Severe Acute Respiratory Syndrome) [9] or HIV (Human Immunodeficiency Virus) [10]. The substituted pyridine N-oxides form an interesting group of compounds that find use as radiosensitizers in radiation therapy, catalysts [11–18].

Plant and animal tissues, microorganisms are the natural source of occurrence for N-oxides and play a key role in biological systems [19]. Through feed wastes or from wastewater treatment plants, N-oxides may contaminate the soils, sediments, and aquatic environments [20]. Thus, it is important to study the interaction of these N-oxide moieties with various metal ions present in aquatic environments which in turn will provide information on the fate of these contaminants in the aquatic environments. Monodentate pyridine N-oxides have the ability to form complexes yielding maximum coordination numbers for most metal ions [21]. The N-O moiety of pyridine N-oxides possesses a unique functionality which can act effectively as a push electron donor and as a pull electron acceptor group [22]. Further, certain functional groups on pyridine N-oxides, can serve as donor sites leading to the formation of chelate complexes. For example, 2-substituted pyridine N-oxides are capable of bidentate coordination with metals and have been extensively investigated as new sequestering agents for actinide(IV) ions by Raymond and his group [23,24].

Pyridine monocarboxylic acid-N-oxides (PCNOs as shown in Fig. 1) have an oxygen atom as donor instead of nitrogen as in the corresponding pyridine monocarboxylates. The flexible N-oxide functionalization of pyridine monocarboxylic acid-N-oxides enhances their capacities for coordination and/or hydrogen bonding resulting in different characteristics of metal pyridine monocarboxylate-N-oxide complexes as compared with the corresponding pyridine monocarboxylates complexes [25]. The transition metal ion and lanthanide ion complexes with pyridine...
monocarboxylate-N-oxides (PCNOS) in both solid and solution state are extensively studied to explore their applications in luminescence, catalysis and many other fields [26-39] but only a few studies on actinide complexes with pyridine monocarboxylates are available in literature [40-48]. Many studies have reported the solid state characterization of uranyl [49-53] and thorium [53-60] complexes with different aromatic-N-oxides but the studies on actinide complexes with pyridine monocarboxyllic acid-N-oxides, in particular, are very limited. Rickard et al investigated thorium tetrathionate complexes with pyridine N-oxide, lutidine N-oxide, collidine N-oxide, quinoline N-oxide, 2- and 4-picoline N-oxide in solid state [61]. Uranyl and thorium complexes of various pyridine and quinoline carboxylic acids were synthesized by Nimai to study their magnetic and spectral properties [62-64]. Stefan Let al. studied the complexion of uranyl with isonicotinic acid-N-oxide and report by Al Rifai on complexion of trivalent transuranium elements with ligand containing pyridine or quinoline ring, are the only available data in the literature on actinide complexes with these ligands in aqueous medium [65,66]. No study on Th(IV) complexion with the three isomeric pyridine monocarboxylic acid-N-oxides in aqueous phase is available in literature. To best of our knowledge, present work is the first report on thermodynamic investigations of thorium complexion of with these ligands in aqueous phase.

Fig. 1. Scheme of Pyridine carboxylic acid N-oxides [From left to right: picolinic acid-N-oxide (PANO), nicotinic acid-N-oxide (NANO), isonicotinic acid-N-oxide (IANO)].

The objective of the present study includes, (i) bridging the gap in the chemical thermodynamic database for tetravalent actinides complexes with pyridine monocarboxylic acid-N-oxides in aqueous solution, (ii) to investigate the isomeric effect on complexion process with respect to position of carboxylate to N-oxide moiety, and (iii) comparison of literature data available with transition and lanthanide ion complexes of these ligands with thorium pyridine monocarboxylate complexes. Density functional theory based calculations have also been carried out to estimate the interaction energies, bond lengths, bond angles and charges on individual atoms in the complexes formed to support the experimental studies. The potentiometric and isothermal calorimetric titrations were carried out to determine the stability constants (log $\beta$) and complexation enthalpies ($\Delta H$) respectively for all the thorium pyridine monocarboxylic acid-N-oxides complexes formed during the course of reaction. These measurements in turn provided the data on in free energy ($\Delta G$) and entropy of formation ($\Delta S$).

2. Experimental

2.1. Reagents

All pyridine monocarboxylate-N-oxides (PANO of 97% purity and NANO and IANO of 99% purity) procured from Sigma Aldrich were used in the present studies. MilliQ (18 MOhm.cm) water was used for preparation of all the reagent solutions. Suprapure (70%) perchloric acid and high pure sodium hydroxide (>99.99% purity) pellets were used for the preparations of perchloric acid and sodium hydroxide working solutions respectively. Potassium hydrogen phthalate was used as primary standard to determine the strength of NaOH solution. The ligand solution for complexation titration were prepared by dissolving appropriate amounts in milliQ water and required amounts of standardized NaOH was added to make them half neutralized. The preparation and standardization of thorium perchlorate solution was done as in our previous work [45]. The concentrations of the ligand solutions were determined by the titration against standard NaOH solution.

2.2. Potentiometric titrations

All the potentiometric titrations were carried out on a Metrohm autotitrator (Model no: 916 DMS Titino) equipped with a Metrohm glass electrode. Prior to potentiometric titrations, the inner filling solution (saturated KCl) of glass electrode was replaced with 1.0 mol/dm$^3$ NaClO$_4$ to prevent the coagulation of frit by the formation of KClO$_4$. The electrode calibration was performed by carrying out a titration of strong acid (HClO$_4$) vs. strong base (NaOH) to determine the electrode parameters like standard electrode potential of the cell ($E_0$), slope of electrode, carbonate impurity in alkali using GLEE software [67]. The emf of the electrode was recorded as a function of the volume of the base and the emf vs. pH showed a linear plot in both the acidic and basic regions indicating a good performance of the electrode over complete pH range of usage. Titration of the metal ion solution with the standard alkali (~0.1 mol/dm$^3$ NaOH) was employed to determine the proton concentration in the metal ion solution by Gran’s method [68]. The complexation titrations were carried out by addition of half neutralized ligand solution to a fixed volume of thorium working solution. The electrode potential at each addition of ligand was measured after equilibration for 180 seconds, or until the drift in the potential had reached less than 0.2 mV/sec. The detailed concentrations of ligand and metal solutions were labeled in the speciation figure captions in the results and discussion section. All the titration were carried out at 298 K temperature and in 1.0 mol/dm$^3$ ionic strength adjusted by NaClO$_4$. The Hyperquad suit of programming [69] was used to determine the stability constants and the complexes formed during the course of metal-ligand titration to generate the speciation diagrams.

2.3. Isothermal titration calorimetry

The enthalpy of formation ($\Delta H$) for all the complexes formed during the course of reaction were determined by an isothermal titration calorimetry (Nanocalorimeter TAM-III, Thermometric AB, Sweden) in heat flow mode. The details on instrumentation, chemical and electrical calibration along with the methodology to determine the enthalpy of formation ($\Delta H$) for a reaction involving successive complexation steps (ML$_i$, i = 1–4) from the raw measurements (heat release vs. time for each addition of ligand solution to metal solution in a calorimetric cup) are given elsewhere [70]. All the experimental conditions, concentrations of metal and ligand solution employed in the calorimetric studies were same as in potentiometric studies.

3. Computational protocol

The structures of Th-PCNO complexes were optimized without imposing any symmetry restriction using B3LYP functional [71,72] with split valence plus polarization basis set def-SV(P) i.e O(7s4p1d)[3s2p1d],C(7s4p1d)[3s2p1d],N(7s4p1d)[3s2p1d],H(4s)[2s], and Th (14s13p10d8f1g)/[10s9p5d4f1g] with effective core potential (i.e. 60 core electrons) for Th as implemented in TurboMole package [73]. All the complexes studied here confirmed as the minimum energy structures on the potential energy surfaces from the real vibrational frequencies. The use of B3LYP/SVP level of
theory for geometry optimization and B3LYP functional using triple zeta valence plus polarization (TZVP) basis set (i.e. O (11s6p1d)[5s3p1d], C (11s6p1d)[5s3p1d], N (11s6p1d)[5s3p1d], H (5s1p)[3s1p], and Th (14s13p10d8f1g)[10s9p5d4f1g]) for energetics has been reported earlier for actinide-lanthaneide complexes as the thermodynamic parameters can be well predicted using B3LYP/TZVP level of theory [74–80]. The enthalpy of formation (ΔH°C) and Gibbs free energy (ΔG°C) of formation for the Th(IV)-PCNO complexes were obtained by frequency calculations including thermal corrections and zero-point energy with the B3LYP/TZVP/RECP level of theory in the gas phase (298.15 K, 0.1 MPa). The aqueous solvent effects in the energetic were incorporated using conductor like screening model (COSMO) approach [81,82]. The default COSMO radii were used for all elements. The dielectric constant, $\varepsilon$ of water was taken as 80. The gas phase optimized geometries were used for the single point energy calculation in COSMO phase [74–80,83–89].

4. Results and discussions

4.1. Potentiometry

The complexation of thorium with pyridine monocarboxylic acid-N-oxides (represented as L) involves the following reaction schemes

$$\text{L}^- + \text{H}^+ \rightarrow \text{LH}$$  \hspace{1cm} (1)

$$\text{Th}^{4+} n\text{LH} \rightarrow \text{ThL}_n + n\text{H}^+$$  \hspace{1cm} (2)

The Eq. (1) represents the protonation of ligand while the Eq. (2) represents the complexation of thorium with protonated ligand in which the complex formation is accompanied by the release of proton. Thus, the complexation of metal ion with acidic ligands like carboxylates and aminocarboxylates, is always accompanied by deprotonation of ligand, and hence necessitates the determination of thermodynamic parameters for ligand protonation. The protonation constants of all the three pyridine monocarboxylates under present experimental conditions were taken from our previous work [90] as inputs to analyze the potentiometric data of Th-PCNO complexation to determine the stability constants of all the complexes formed during the course of reaction. The potentiometric titration data was analyzed by using Hyperquad suit of programming [69]. The software involves the treatment of data by a non-linear least square fitting of experimental data with a modeled data in which the approximate species that can form during the complexation reaction along with their stability constants is given as input. When the species expected with the given stability constants are reasonably well predicted, the modeled data matches with experimental data indicating the validity of predicted species with corresponding stability constants. Different stoichiometry of Th-PCNO complexes including the polynuclear and ternary Th-PCNO-OH complexes are considered during the treatment of data by Hyperquad but consideration of only mononuclear binary Th-PCNO complexes resulted in the best fit of the data. The potentiometric data analysis by Hyperquad indicated the formation of $\text{ML}_j$ ($j = 1–4$) for Th-PANO complexes and $\text{ML}_j$ ($j = 1–3$) for Th-NANO and Th-IANO complexes. The variation in the percentage of formation of the different stoichiometric complexes with respect to total metal concentration and pH can be well represented as speciation diagrams (Fig. 2).
The speciation diagrams are very much helpful in predicting the concentrations of various complexes present under any experimental condition (pH, Ligand to Metal ratio). The stability constants along with the other thermodynamic parameters (ΔG, ΔH and ΔS) are given in Table 1.

The Table 1 shows that log β of complexes following the order Th-PANO > Th-IANO > Th-NANO. The higher log β values of the Th-PANO complexes can be attributed to the formation of six membered chelate ring involving the oxygen of N-oxide and that of carboxylate. The favorable position of N-oxide (at ortho position) to carboxylate group facilitates the chelate formation while the same cannot take place in Th-NANO and Th-IANO complexes due to higher separation of N-oxide with respect to carboxylate. Th-IANO forms stronger complexes than corresponding Th-NANO complexes as the carboxylate ligand in the former is in electron donating position (para) to N-oxide moiety for charge polarization where the same in NANO is at electron withdrawing position (meta) to N-oxide moiety. The actinides at higher oxidation state behave as hard acids and prefer binding with hard donors like fluorine, oxygen, etc., in which the major force of attraction is Coulombic in nature. Thus the actinides interactions (log KML) would follow a linear relation with the protonation constants (log Kp) of ligands. Such linear free energy relationship for the complexation of thorium with simple monocarboxylates is shown in Fig. 3. From the plot (Fig. 3), it could be observed that the Th-PANO complex is much above the line corresponding to Th(IV)-monocarboxylates indicating chelation in Th(IV)-PANO complexes. However, the log KML data for Th(IV)-IANO and Th(IV)-NANO was found to fall on linear free energy relationship for the complexation of thorium with simple monocarboxylates indicating similar binding through carboxylate group.

4.2. Isothermal titration calorimetry

Calorimetric titration of thorium solution with half neutralized ligand was carried out to determine the change in ΔH for the complexes formed. Each addition of ligand is associated with the change in total heat of the system (ΔHt) which includes both the heat of complexation (ΔHc) as well as heat of dilution (ΔHd). A separation of moles of each species present at all the points of titration (X

Table 1

| Complex                  | log β  | ΔG (kJ/mol) | ΔH (kJ/mol) | T ΔS [kJ/mol] | ΔS (J/K/mol) |
|--------------------------|--------|-------------|-------------|---------------|--------------|
| **Thorium PANO Complex**|        |             |             |               |              |
| ML                       | 4.44 ± 0.02 | −25.38 | 14.0 ± 0.6 | 39.40 | 132.14 |
| ML2                      | 3.29 ± 0.02 | −18.80 | 29.7 ± 2.0 | 48.48 | 162.62 |
| ML3                      | 2.77 ± 0.03 | −15.83 | 20.6 ± 1.3 | 36.48 | 122.36 |
| ML4                      | 1.62 ± 0.01 | −9.26  | 5.0 ± 0.3 | 14.22 | 47.69  |
| **Thorium NANO Complex** |        |             |             |               |              |
| ML                       | 2.83 ± 0.03 | −16.16 | 15.07 ± 1.1 | 31.23 | 104.73 |
| ML2                      | 1.85 ± 0.01 | −10.56 | 7.5 ± 0.4 | 18.02 | 60.44  |
| ML3                      | 1.69 ± 0.02 | −9.65  | 1.2 ± 0.2 | 10.83 | 36.32  |
| **Thorium IANO Complex** |        |             |             |               |              |
| ML                       | 2.90 ± 0.02 | −16.56 | 12.9 ± 0.7 | 29.45 | 98.76  |
| ML2                      | 2.12 ± 0.03 | −12.10 | 5.7 ± 0.6 | 17.74 | 59.51  |
| ML3                      | 1.80 ± 0.01 | −10.28 | 0.5 ± 0.1 | 10.75 | 36.04  |

* Standard uncertainties u are u(T) = 0.1 K, u(p) = 10 kPa, and the combined expanded uncertainties Uc are Uc(log β) and Uc(ΔH) for each set of data was given in the table. (level of confidence = 0.95)
constants of the complexes need to be given as inputs. The protonation constants and enthalpies of protonation of ligands from our previous work [90] and the stability constants determined in the present studies for all the complexes were used to obtain the concentrations of all the species formed during the course of reaction for all titration points. From these concentrations, the number of moles of species was calculated by using the equation

\[ \nu_i^X = \frac{[X]}{C_0} \]

where

- \( V_i \) Volume of solution after \( i \)th addition of ligand
- \([X] \) Concentration of the species 'X' at the \( i \)th point of titration

Solving the Eq. (4) for all titration points gives the enthalpy of formation for all the complexes formed during the course of reaction. Graphically, the data can be shown as \( h_{vi} \) Vs. \( n_{avg} \)

The enthalpy of formation for the complexes could be obtained directly from these plots. Such plots for the complexation of thorium with the three pyridine monocarboxylate-N-oxides are shown in Fig. 4. The change in entropy of formation was calculated from the determined stability constants and change in enthalpy of formation of the complexes by following equations

\[ \Delta G = -2.303 \, RT \ln K \]  

(6)

\[ \Delta G = \Delta H - T \Delta S \]  

(7)

\[ \Delta S = (\Delta H - \Delta G) / T \]  

(8)

The \( \Delta H \) and \( \Delta S \) for all the Th(IV)-PCNO complexes are summarized in Table 1. From the table, it's clear that formation of all the Th(IV)-PCNO complexation are endothermic in nature and are mainly entropy driven. The hard acid–hard base interactions involved in actinide complexation by PCNOs constitute positive enthalpy reflecting the energy required for dehydration of both the metal ion and the ligands and a favorable entropy due to increase in disorder caused by the release of solvent molecules in both the primary as well as secondary solvation spheres, the bulk solvent and their reorganization around the resulting species. Furthermore, the similarity in enthalpy and entropy of formation between Th(IV)-NANO and Th(IV)-IANO complexation implies that the oxygen of N-oxide of NANO/IANO does not participate in the complexation process for coordination with Th(IV).

The trends in enthalpy of formation for complexes can be explained in terms of the perturbation of hydration sphere in the primary coordination sphere as well as in bulk structure of solvent. In general the stepwise enthalpy of formation follows a descending order as the charge neutralization becomes more prominent in the stepwise complexation process. Similar trends in enthalpy of formation were observed in case of Th(IV)-NANO and Th-IANO complexes but in case of Th(IV)-PCNO complexes, the enthalpy of formation follows a different trend \( \Delta H_{ML2} > \Delta H_{ML3} > \Delta H_{ML4} > \Delta H_{ML4} \). This anomaly in the enthalpy of formation could be explained on the basis of dehydration of both the metal ion and ligand molecules on complex formation. In general, ligand dehydration plays minor role in determining the enthalpy of formation as in case of simple monocarboxylates and neutral ligands like NANO and IANO for which the enthalpy of protonation are ~1.83 and 0.40 kJ/mol respectively [90], typical of carboxylic acids (\( \Delta H_p \approx 0–5 \) kJ/mol at 298 K). But, in case of ligands that do have relatively higher endothermic enthalpies of protonation, ligand deprotonation contributes more to the
enthalpy of formation of the complex with the metal ion. In our previous studies [90], it was reported that the protonation of PANO is an endothermic process ($\Delta H = 6.76 \text{kJ/mol}$) indicating an energy requirement for dehydration of deprotonated PANO in order to undergo complexation with Th(IV). Thus, the addition of more and more ligand requires higher energy for dehydration of ligand molecules, which results in higher enthalpies of formation as well as higher entropy of formation on stepwise complexation. Further, the drastic structural rearrangements of the ligand moieties around the metal ion also contribute to the abrupt increase of stepwise enthalpies of formation as in case of Th(IV) complexation by oxydiacetate complex for which $\Delta H$ for the formation of ML, ML$_2$ and ML$_3$ are 8.37, -11.46 and 35.90 kJ/mol respectively. Thus the anomalous trend in enthalpy of formation for Th(IV)-PANO complexes could be attributed to the cumulative effect of dehydration of both the metal and ligand ions and the structural rearrangement of ligand around the metal ion simultaneously [91].

The entropy of formation for a complex consists of three components namely translational, rotational, and conformational. The change in vibrational entropy can usually be neglected. Quantitative evaluation of the entropy effect in complexation is difficult as these three constituents terms of entropy of formation as in case of Th(IV) complexation by oxydiacetate complex for which $\Delta H$ for the formation of ML, ML$_2$ and ML$_3$ are 8.37, -11.46 and 35.90 kJ/mol respectively. Thus the anomalous trend in enthalpy of formation for Th(IV)-PANO complexes could be attributed to the cumulative effect of dehydration of both the metal and ligand ions and the structural rearrangement of ligand around the metal ion simultaneously [91].

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4.3. Theoretical calculations

Tianxiao Yang et al. reported the combined quantum mechanical and molecular dynamical simulations on thorium(IV) hydrates in aqueous solution and concluded that Th(H$_2$O)$_9$$^{4+}$ with $C_4V$ symmetry can form the most stable complex, the number of water molecules around the Th(IV) ion is 9 in the first shell [93]. Tsushima et al. proved that the energy difference between 9- and 10-coordination for Th(IV) is very small, about 1 kJ/mol [94]. From these data it can be concluded that the coordination number is either 9 or 10, and that equilibrium might exist between the 9- and 10-coordinated ions. The relative energies of U$^{4+}$ and Np$^{4+}$ ions with 8, 9 and 10 coordinated water indicate that the preferred coordination number for U$^{4+}$ is 9, while there might be an equilibrium between 8 and 9 coordination for Np$^{4+}$ [95]. Thus, in the present studies, Th(H$_2$O)$_9$$^{4+}$ is considered as the base moiety for Th(IV) aqua ion so that the studies can also be related to the other tetravalent actinides such as U(IV) and to a less extent to Np(IV).

The geometries for all the Th(IV)-PCNO complexes predicted under present investigations were optimized at density functional theory (DFT) level by using Turbomole programme. The optimized geometries for all the complexes of Th(IV)-PANO, Th(IV)-NANO and Th(IV)-IANO are shown in Figs. 5–7 respectively. The optimized geometries in Th(IV)-PANO complexes involve the chelate formation by Th(IV) through each oxygen atom of carboxylate and N-oxide moieties whereas the Th(IV)-NANO and Th(IV)-IANO...
complexes are formed by coordination of Th(IV) with carboxylate oxygen atoms. 

The metal ion-ligand complexation reaction (M:Ln) for all the three Th(IV)-PCNO complexes can be given as,

$$\frac{1}{2} \text{Th}(\text{H}_2\text{O})_9^{9+} + n\text{L} \rightarrow \frac{1}{2} \text{Th}(\text{H}_2\text{O})_x(L)_m^{x-} + (9 - x)\text{H}_2\text{O}$$

The strength of a metal ion complex with a particular ligand can be explained using binding energy or free energy. Hence, the gas phase binding energy is computed for the complexation reaction (9) using the following equation.

$$\Delta E = E_{\text{Th}(\text{H}_2\text{O})_9^{9+} + n\text{L}} - E_{\frac{1}{2} \text{Th}(\text{H}_2\text{O})_x(L)_m^{x-} + (9 - x)\text{H}_2\text{O}}$$

The thermal correction to the electronic energy (E_{el}), enthalpy (H) and free energy (G) of the optimized complexes has been performed following the earlier reported prescription [96,97]. The energetics (interaction energy (ΔE) and Gibbs free energy of formation(ΔG)) and the structural parameter (bond distances) for all the three Th(IV)-PCNO complexes are given in Table 2. The theoretically calculated interaction energies as well as Gibbs formation energies follow the order Th(IV)-PCNO > Th(IV)-IANO > Th(IV)-NANO among the three Th(IV)-PCNO complexes and ΔE/ΔG for a particular Th(IV)-PCNO complex follows the decreasing trend on stepwise complexation analogous to that observed in experimentally stability constants obtained by potentiometric titrations.

The shorter bond lengths of Th-O (of COO) in Th(IV)-PANO complexes than the other two complexes further supports the stronger interaction of Th(IV) with PANO than NANO and IANO.

In view of the predominantly Coulombic interaction between actinide and carboxylates, the detailed charge calculations on the individual atoms in each complex and its comparison with the charge on same atoms of the bare ligand would give insight into the charge polarization effects on complex formation of Th(IV) by pyridine monocarboxylate-N-oxides. This further helps in interpreting the trends in stability of all the three structurally isomeric pyridine monocarboxylate-N-oxides. The binding atoms (such as oxygen atoms of N-oxide and carboxylate group) and the atoms directly linked to binding atoms (nitrogen of N-oxide, carbon atoms of the carboxylate and the ring carbon attached to carboxylate group) in ligand are the most effected with respect to charge polarization on complexation with the metal ion. The charges on these key atoms of the complex are given in Table 3 while the charges on the identical atoms in bare ligands are given in Table 4.

Comparing the charges on these individual atoms in the complex and on bare ligands, the following observations can be made: 1) In case of Th(IV)-PANO complexes, during complexation, the charge on nitrogen is reduced while that on the oxygen is enhanced in N-oxide group and the charge on one (bonding to Th(IV)) of the oxygen atoms is enhanced whereas the charge on the other oxygen atom of carboxylate group was decreased as compared to that in bare ligand. 2) In case of Th(IV)-NANO/IANO complexes, the charge on nitrogen of N-oxide is more than that on the bare ligand while the charge on oxygen of N-oxide in complex is lower than on bare ligand. The charges on both the oxygen atoms of the carboxylate group are lower in complex than that on bare ligand. This trend in charges on nitrogen and oxygen atoms of N-oxide and oxygen atoms of carboxylate group is opposite to the trend observed in Th(IV)-PANO complexes. The charge on carbon atoms is more in complex form than in bare ligand for all the three Th(IV)-PCNO complexes. In case of Th(IV)-PANO complexes, PANO
binds Th(IV) by chelation through the oxygen atom of N-oxide moiety and the oxygen atom of carboxylate. Thus the coulombic interaction with these two atoms would be more resulting in higher charge polarization at these two atoms during complex formation. Large difference in charge on oxygen atoms of carboxylate also further supports the monodentate nature of carboxylate in complexation process and hence chelate formation in case of PANO binding by Th(IV). In case of Th(IV)-NANO/IANO complexes, the metal ion binds the ligand through both the oxygen atoms of the carboxylate group which is evident from the similar charge on both the oxygen atoms on complex formation also. Both the oxygen of N-oxide and carboxylate functional attached to base pyridine ring in the PCNOs are electron withdrawing groups and can pull the electron density towards them from the base pyridine ring. Further, the electron withdrawing effects in pyridine ring are more pronounced at ortho and para positions which are more favorable positions for charge polarization than meta position. Thus the charge polarization effects would be more prominent in PANO

![Optimized geometries for Thorium IANO complexes: a) ML, b) ML2, and ML3. (colour variation: blue – Thorium atom, violet – nitrogen atom, grey – carbon atom, red – oxygen atom, white – hydrogen atom).](image)

**Table 2**
The calculated interaction energy (ΔE), Gibbs free energy of formation (ΔG) (in kJ/mol) and bond lengths (in 10⁻¹⁰ m) between Thorium and the binding atoms of the ligands for all experimentally predicted Th(IV)-PCNO complexes. O (N-O), O (COO) and O (H₂O) represents the oxygen atoms of N-oxide, carboxylate of ligand molecule and water in Th(IV) aqua ion respectively.

| Complex  | ΔE   | ΔG   | d₆₅-Ο(N-O) | d₆₅-Ο(COO) | d₆₅-Ο(H₂O) |
|----------|------|------|------------|------------|------------|
| **Thorium PANO Complexation** |      |      |            |            |            |
| ML       | −189.82 | −211.46 | 2.301       | 2.218      | 2.550, 2.556, 2.567, 2.576, 2.584, 2.619, 2.631 |
| ML₂      | −145.66 | −183.17 | 2.399, 2.441 | 2.282, 2.285 | 2.572, 2.572, 2.574, 2.580, 2.613 |
| ML₃      | −130.30 | −181.92 | 2.400, 2.448, 2.489 | 2.273, 2.309, 2.360 | 2.464, 2.624, 4.367 |
| ML₄      | −60.81  | −95.19  | 2.459, 2.465, 2.486, 2.499 | 2.356, 2.367, 2.414, 2.450 | 2.65 |
| **Thorium NANO Complexation** |      |      |            |            |            |
| ML       | −99.91  | −88.37  | 2.356, 2.360 |            | 2.548, 2.569, 2.573, 2.608, 2.622, 2.623, 2.645, 2.660 |
| ML₂      | −91.79  | −88.32  | 2.483, 2.490, 2.492, 2.516 |            | 2.548, 2.561, 2.563, 2.592, 2.618, 2.620, 2.798 |
| ML₃      | −88.97  | −67.28  | 2.479, 2.513, 2.533, 2.535, 2.540, 2.564 |            | 2.566, 2.575, 2.624, 2.632, 2.649, 4.055 |
| ML₄      | −108.07 | −105.10 | 2.461, 2.476 |            | 2.546, 2.567, 2.570, 2.587, 2.611, 2.619, 2.645, 2.677 |
| ML₅      | −105.26 | −92.97  | 2.440, 2.486 |            | 2.503, 2.530, 2.553, 2.580, 2.583, 2.602, 4.164 |
| ML₆      | −61.99  | −42.26  | 2.454, 2.512, 2.506, 2.546, 2.534, 2.601 |            | 2.594, 2.606, 2.607, 2.637, 2.700, 4.009 |

(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
followed by IANO than NANO. Thus the charge reduction on oxygen atoms of carboxylate would be more in NANO (from −0.770 in NANO to −0.704 in Th(IV)-NANO complex) than in IANO (from −0.775 in IANO to −0.719 in Th(IV)-IANO complex). Among Th(IV)-NANO and Th(IV)-IANO complexes, the reduction of charge on oxygen atoms of carboxylate in NANO is more than IANO reflecting higher coulombic interaction of IANO than NANO with Th(IV). Hence the Th(IV)-IANO complexes are more stable than Th(IV)-NANO complexes, which matches with the experimental observation (Table 1).

5. Conclusions

The thermodynamic parameters for the complexation of thorium with three structurally isomeric pyridine monocarboxylate-N-oxide were studied by experiment and theory. It was found that formation of all the complexes are endothermic and entropy driven. The chelate nature of Th(IV)-PANO is the responsible for higher stability of these complexes over the other two isomers. The variations in thermodynamic parameters are interpreted in terms of perturbation in hydration spheres of metal and ligand ions. Further, the theoretical calculation to determine the charges on individual atoms further enhanced the knowledge in interpreting the trends within and among the Th(IV)-PCNO complexes in terms of electrostatic interactions. The linear free energy relationship of log b of the complex with pKa of ligand also showed the chelate and carboxylate kind of binding in Th(IV)-PANO and Th(IV)-NANO/IANO complexes respectively. Overall, the mutual position of the two functional groups, the N-oxide and carboxylate, has a key role on the thermodynamics of complexation process.

Table 3

| Ligand  | q(N-O) | q(COO) | q(C-COO) |
|---------|--------|--------|----------|
| PANO    | −0.571 | 0.098  | −0.780, −0.740 |
| NANO    | −0.614 | 0.082  | −0.772, −0.770 |
| IANO    | −0.605 | 0.085  | −0.775, −0.775 |

Table 4

The charges on key atoms of all experimentally predicted Th(IV)-PCNO complexes. O (N-O), O (COO), N (N-O), O (COO) and O (C-COO) represents the oxygen atoms of N-oxide, carboxylate, nitrogen of N-oxide and carbon atoms of carboxylate and the carbon directly attached to carboxylate carbon of ligand molecule respectively.

| Complex | q(Th) | q(N-O) | q(COO) | q(C-COO) | q(O(OCO)) | q(N(CO)) | q(C(COO)) | q(C(C-COO)) |
|---------|-------|--------|--------|----------|----------|----------|----------|-------------|
| Th(IV)-PANO Complexation | 2.230 | −0.617 | 0.072  | −0.794, −0.575 | 0.764 | 0.087 |
| ML      | 2.133 | −0.588 | 0.081, 0.084 | −0.790, −0.599 | 0.759, 0.759 | 0.066, 0.061 |
| ML2     | 2.240 | −0.565 | 0.083, 0.087 | −0.774, −0.655 | 0.767, 0.764, 0.760 | 0.074, 0.061, 0.060 |
| ML3     | 1.979 | −0.534 | 0.086, 0.092, 0.093, 0.094 | −0.729, −0.655 | 0.763, 0.764, 0.754, 0.762 | 0.063, 0.065, 0.063, 0.058 |
| Th(IV)-NANO Complexation | 2.124 | −0.542 | 0.105  | −0.704, −0.708 | 0.793 | −0.193 |
| ML      | 1.875 | −0.560 | 0.101, 0.101 | −0.691, −0.683 | 0.778, 0.778 | −0.176, 0.174 |
| ML2     | 1.793 | −0.560 | 0.097, 0.098, 0.098 | −0.705, −0.663 | 0.783, 0.79, 0.778 | −0.168, 0.165, 0.168 |
| Th(IV)-IANO Complexation | 2.103 | −0.460 | 0.148  | −0.729, −0.719 | 0.772 | −0.204 |
| ML      | 2.027 | −0.507 | 0.130, 0.129 | −0.718, 0.693 | 0.767, 0.763 | −0.184, 0.184 |
| ML2     | 1.784 | −0.527 | 0.121, 0.120, 0.122 | −0.694, 0.693 | 0.775, 0.767, 0.774 | −0.174, 0.171, 0.179 |

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