

Electrical Conductivity and Solution Behaviour of an Eight-Coordinate Mixed-Ligand Thorium (IV) Complex in Aqueous and Organic Media.

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Abstract:

Electrical conductivity measurements provide valuable physicochemical information regarding the electrolytic behaviour, ionic dissociation, and solution stability of coordination compounds. In the present study, the electrical conductivity and solution behaviour of an eight-coordinate mixed-ligand thorium(IV) complex containing 2-hydroxy-5-sulfobenzoic acid (SSA) and 1,10-phenanthroline (phen) were investigated in aqueous and organic media to evaluate its electrolyte character and correlate the results with its previously established coordination structure. The thorium (IV) complex was synthesized following the procedure reported earlier by our research group, and its conductometric properties were evaluated at ambient temperature using a digital conductivity meter. Conductivity measurements were carried out in distilled water and ethanol, and the results were interpreted in conjunction with the physicochemical properties of these solvent systems to elucidate the influence of solvent polarity, dielectric constant, viscosity, and solvation on ionic mobility and solution behaviour. The comparatively low conductivity values obtained in both media indicate that the complex behaves as a non-electrolyte, suggesting that the nitrate ions remain coordinated within the inner coordination sphere without significant ionic dissociation. These findings are in agreement with the structural formulation previously established by elemental analysis, FTIR, UV–Visible spectroscopy, powder X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis. Comparison with related mixed-ligand coordination compounds reported in the literature further supports the proposed coordination environment and demonstrates that conductometry is a simple, rapid, and effective complementary technique for evaluating the solution behaviour and structural stability of mixed-ligand actinide complexes.

Keywords: Thorium (IV) complex; Conductometry; Electrical conductivity; Mixed-ligand complex; 2-Hydroxy-5-sulfobenzoic acid; 1,10-Phenanthroline; Non-electrolyte; Actinide coordination chemistry.

1. Introduction

Electrical conductivity measurements have long been recognized as an important physicochemical technique for investigating the solution behaviour of coordination compounds. Conductometric studies provide valuable information regarding ionic mobility, electrolyte dissociation, charge transport, and the nature of coordination species in solution. In coordination chemistry, molar conductivity measurements are routinely employed as a complementary analytical tool alongside spectroscopic and thermal techniques to distinguish between electrolytic and non-electrolytic complexes and to evaluate the position of counter ions within or outside the coordination sphere.^{1–4}

Thorium (IV), one of the most important tetravalent actinide ions, exhibits a large ionic radius, high charge density, and strong affinity towards oxygen- and nitrogen-donor ligands. These characteristics enable Th(IV) to form stable coordination compounds with coordination numbers ranging from eight to ten and a wide variety of structural geometries. Owing to their exceptional coordination versatility, thorium complexes continue to attract considerable attention in actinide chemistry, nuclear fuel processing, environmental remediation, separation science, and advanced functional materials.^{5–9}

Mixed-ligand coordination compounds have received increasing interest because the simultaneous coordination of two or more ligands frequently enhances structural rigidity, thermodynamic stability, and physicochemical properties. Among oxygen-donor ligands, 2-hydroxy-5-sulfobenzoic acid (SSA) is particularly attractive because of its ability to coordinate through phenolic and carboxylate oxygen atoms while simultaneously participating in hydrogen-bonding interactions. Likewise, 1,10-phenanthroline (phen) is a well-established aromatic bidentate nitrogen-donor ligand possessing excellent chelating ability, high complexation efficiency, and remarkable structural rigidity. The combination of SSA and 1,10-phenanthroline therefore provides a favourable ligand environment for the formation of stable mixed-ligand thorium(IV) complexes.^{10–14}

Characterization of thorium coordination compounds generally relies on elemental analysis together with complementary spectroscopic and physicochemical techniques such as Fourier-transform infrared (FTIR) spectroscopy, UV–Visible spectroscopy, nuclear magnetic resonance (NMR), powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermal analysis, and electrical conductivity measurements. While spectroscopic techniques establish the coordination mode of ligands and the geometry around the metal centre, conductometric investigations provide additional insight into the behaviour of the complex in solution by assessing ionic dissociation, electrolyte character, and structural stability under different solvent environments.^{1, 10, 15–17}

In our previous investigation, an eight-coordinate mixed-ligand thorium (IV) complex of 2-hydroxy-5-sulfobenzoic acid and 1,10-phenanthroline was successfully synthesized and comprehensively characterized using elemental analysis, FTIR spectroscopy, UV–Visible spectroscopy, PXRD, SEM, and thermogravimetric analysis. The characterization results confirmed the proposed coordination structure and suggested that the nitrate ions remain coordinated within the primary coordination sphere. Preliminary conductivity measurements further indicated that the complex exhibits non-electrolytic behaviour in solution.¹⁸ However, the conductometric characteristics of the complex have not previously been discussed in detail, nor have the observed conductivity values been interpreted in relation to solvent properties and the proposed coordination environment.

The present study therefore provides a comprehensive conductometric evaluation of the previously synthesized eight-coordinate mixed-ligand thorium (IV) complex. Experimental conductivity measurements obtained in distilled water and ethanol are analysed in conjunction with the physicochemical properties of these solvent systems and interpreted with reference to the proposed coordination structure. In addition, the conductometric behaviour of the complex is compared qualitatively with related mixed-ligand coordination compounds reported in the literature. The study demonstrates that conductometry is a simple, rapid, and reliable complementary technique for

assessing the electrolyte behaviour, solution stability, and structural integrity of mixed-ligand actinide complexes.

2. Experimental

2.1 Materials

Thorium nitrate pentahydrate $[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}]$, 2-hydroxy-5-sulfobenzoic acid (SSA), and 1,10-phenanthroline monohydrate (phen) of analytical reagent (AR) grade were obtained from commercial sources and used without further purification. Double-distilled water was used throughout the experimental work. Ethanol (AR grade) served as the organic solvent for conductometric measurements. All glassware employed during synthesis and conductivity measurements was thoroughly cleaned, rinsed repeatedly with double-distilled water, and dried before use to minimize contamination.

2.2 Synthesis of the Thorium (IV) Complex

The mixed-ligand thorium (IV) complex was synthesized according to the procedure reported previously by our research group.¹⁸ An aqueous solution of thorium nitrate pentahydrate was reacted with an aqueous solution of 2-hydroxy-5-sulfobenzoic acid under continuous magnetic stirring. Subsequently, an ethanolic solution of 1,10-phenanthroline was added dropwise while maintaining constant stirring. The reaction mixture was stirred until complete precipitation of the mixed-ligand thorium (IV) complex was achieved. The precipitate was filtered, washed repeatedly with distilled water followed by ethanol to remove excess ligand and soluble impurities, and finally dried over anhydrous calcium chloride in a vacuum desiccator.

The composition and structure of the synthesized complex were established previously by elemental analysis, Fourier-transform infrared (FTIR) spectroscopy, UV–Visible spectroscopy, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA), confirming the formation of an eight-coordinate mixed-ligand thorium(IV) complex.¹⁸

2.3 Conductometric Measurements

The electrical conductivity of the synthesized thorium (IV) complex was measured at ambient temperature using a Multiparameter LMMP30 conductivity meter. Conductivity measurements were performed for distilled water (blank), the thorium (IV) complex in distilled water, and the thorium(IV) complex in ethanol under identical experimental conditions. In addition to specific conductivity (κ), total dissolved solids (TDS), pH, and solubility characteristics of the samples were recorded. The experimental conductivity data were subsequently interpreted to assess the electrolyte behaviour of the complex and correlated with its proposed coordination structure using established conductometric principles reported for coordination compounds.^{1, 13, 16, 17}

2.4 Data Interpretation

The conductometric results obtained in the present investigation were interpreted in conjunction with the physicochemical properties of the solvent systems and compared qualitatively with previously reported mixed-ligand coordination compounds exhibiting similar conductometric behaviour.^{13, 16, 17} Particular emphasis was placed on correlating the observed conductivity with the proposed eight-coordinate structure established in our earlier investigation.¹⁸ The influence of solvent polarity, dielectric constant, viscosity, and ion-solvation characteristics on the electrical conductivity of the thorium(IV) complex is discussed to provide a comprehensive understanding of its solution behaviour and non-electrolytic nature.^{1, 2}

3.1 Electrical Conductivity and Conductometric Behaviour of the Thorium (IV) Complex

Electrical conductivity is one of the most informative physicochemical parameters for evaluating the electrolyte character and solution behaviour of coordination compounds. In coordination chemistry, low conductivity values generally indicate the formation of neutral coordination species in which the anionic ligands remain coordinated to the central metal ion, whereas comparatively higher conductivity values are characteristic of ionic complexes containing dissociable counter ions. Consequently, conductometric measurements have been widely employed as a simple and reliable complementary technique for assessing coordination environments and verifying the electrolytic or non-electrolytic nature of metal complexes.^{1-4, 13, 16, 17}

The experimentally determined specific conductivity (κ), total dissolved solids (TDS), pH, and solubility characteristics of the synthesized thorium (IV) complex are summarized in **Table 1**.

Table 1. Experimental conductivity and physicochemical parameters of the thorium (IV) complex.

S. No.	Chemical entity	Solubility	TDS (ppm)	pH	Specific conductivity, κ ($\mu\text{S cm}^{-1}$)	Interpretation
1	Distilled water	—	34.20	7.0	40.80	Blank
2	Thorium(IV) complex in distilled water	Soluble	12.20	7.0	24.40	Non-electrolyte
3	Thorium(IV) complex in ethanol	Sparingly soluble	3.27	7.0	6.62	Non-electrolyte

The specific conductivity of the thorium (IV) complex dissolved in distilled water ($24.40 \mu\text{S cm}^{-1}$) was considerably lower than that of the corresponding blank distilled water ($40.80 \mu\text{S cm}^{-1}$). When ethanol was employed as the solvent, the conductivity decreased further to $6.62 \mu\text{S cm}^{-1}$. The consistently low conductivity values indicate that the synthesized complex contributes only a limited concentration of mobile ionic species to the solution and therefore behaves predominantly as a non-electrolyte. Similar conductometric behaviour has been reported for several mixed-ligand coordination compounds

possessing coordinated anionic ligands and neutral molecular structures, where negligible ionic dissociation occurs under ambient conditions.^{13, 16, 17}

The lower conductivity observed after complex formation can be attributed to the strong coordination of the thorium(IV) ion by the oxygen-donor atoms of 2-hydroxy-5-sulfobenzoic acid and the nitrogen-donor atoms of 1,10-phenanthroline, resulting in a stable molecular coordination entity. Such coordination suppresses the release of free ions into solution and consequently reduces electrical conductivity. The present conductometric observations therefore support the formation of a neutral coordination complex in which the nitrate groups remain coordinated within the primary coordination sphere rather than existing as dissociated counter ions in solution. This interpretation is in excellent agreement with the structural formulation established previously through elemental analysis, FTIR spectroscopy, UV–Visible spectroscopy, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).¹⁸

In addition to electrical conductivity, the measured TDS values decreased progressively from 34.20 ppm for distilled water to 12.20 ppm for the aqueous solution of the thorium (IV) complex and further to 3.27 ppm in ethanol. Although TDS is not a direct measure of electrolyte behaviour, the observed trend is consistent with the reduced concentration of freely mobile dissolved ions following coordination of the thorium (IV) centre. Furthermore, the pH remained essentially neutral (≈ 7.0) for all measurements, indicating that the observed differences in conductivity primarily arise from coordination effects and solvent properties rather than significant changes in solution acidity.

Overall, the conductometric data clearly demonstrate that the synthesized thorium (IV) complex behaves as a stable non-electrolyte in both aqueous and ethanolic media. The low specific conductivity values are consistent with the proposed eight-coordinate molecular structure and provide independent support for the presence of coordinated nitrate groups within the inner coordination sphere of the thorium (IV) ion.¹⁸

3.2 Influence of Solvent Properties on Conductivity

The electrical conductivity of coordination compounds is governed not only by their molecular structure but also by the physicochemical properties of the surrounding solvent. Solvent characteristics such as dielectric constant, viscosity, polarity, and ion-solvation ability significantly influence ionic mobility and consequently affect the measured conductivity. Therefore, interpretation of conductometric data requires consideration of both the intrinsic properties of the coordination compound and the nature of the solvent medium.^{1, 2, 9, 20}

Although conductivity measurements in the present investigation were limited to distilled water and ethanol, the observed differences can be satisfactorily explained on the basis of their physicochemical properties. Water possesses a high dielectric constant and excellent ion-solvating ability, which facilitate the stabilization and mobility of charged species in solution. In contrast, ethanol exhibits a considerably lower dielectric constant and reduced polarity, thereby limiting charge separation and decreasing ionic mobility.^{1, 2, 9, 20} Consequently, the thorium(IV) complex exhibited higher specific conductivity in water than in ethanol.

To facilitate interpretation of the conductometric results, the relevant physicochemical properties of selected solvents commonly employed in coordination chemistry are summarized in Table 2.

Table 2. Physicochemical properties of selected solvents relevant to conductometric behaviour (literature values at approximately 25 °C).

Solvent	Dielectric constant (ϵ)	Dynamic viscosity (mPa s)	Relative polarity	Expected influence on ionic mobility
Water	78.4	0.89	1.000	Highest
Methanol	32.6	0.54	0.762	High
Ethanol	24.3	1.07	0.654	Moderate–Low
DMF	36.7	0.80	0.386	Moderate
DMSO	46.7	1.99	0.444	Moderate

The solvent-property data presented in Table 2 provide a useful basis for interpreting the observed conductometric behaviour and predicting the expected response of the complex in other solvent systems. Methanol, owing to its lower viscosity and higher polarity than ethanol, would be expected to facilitate greater ionic mobility. Likewise, polar aprotic solvents such as DMF and DMSO possess relatively high dielectric constants but differ in viscosity and specific solvation characteristics, both of which influence ion transport and electrical conductivity. These observations demonstrate that the conductivity of coordination compounds depends not only on the structure of the complex itself but also on the physicochemical properties of the solvent environment.^{1, 2, 9, 20}

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Among the solvents listed, water possesses the highest dielectric constant ($\epsilon = 78.4$), enabling efficient stabilization of ionic species through extensive solvation. This property accounts for the relatively higher conductivity observed for the thorium (IV) complex in aqueous medium. Ethanol, with a dielectric constant of 24.3 and comparatively lower polarity, provides less favourable conditions for ion solvation, resulting in reduced electrical conductivity.^{1, 2, 9}

The solvent-property data presented in Table 2 also provide a theoretical framework for predicting the behaviour of the synthesized thorium (IV) complex in other commonly employed solvents. Methanol,

owing to its lower viscosity and higher polarity than ethanol, would be expected to permit somewhat greater ionic mobility and consequently higher conductivity. Polar aprotic solvents such as DMF and DMSO possess relatively high dielectric constants but differ considerably in viscosity and donor characteristics, factors that influence ion-solvent interactions and charge transport. Therefore, the conductivity behaviour of coordination compounds is determined by a combination of solvent dielectric properties, viscosity, molecular interactions, and the structural characteristics of the dissolved complex rather than by any single parameter alone.^{1,2,9}

The comparatively lower conductivity of the thorium (IV) complex in ethanol is therefore consistent with both its limited solubility and the reduced ion-solvating ability of the solvent. These observations support the conclusion that the measured conductivity primarily reflects solvent-dependent ionic mobility while preserving the molecular integrity of the neutral coordination complex in solution.

3.3 Correlation with the Proposed Coordination Structure:

Conductometric measurements provide valuable complementary evidence for the structural assignment of coordination compounds established through spectroscopic and thermal techniques. In general, coordination complexes that retain their molecular integrity in solution exhibit relatively low electrical conductivity, whereas ionic complexes containing outer-sphere counterions undergo partial or complete dissociation, resulting in considerably higher conductivity. Consequently, conductometric studies are frequently employed to distinguish neutral coordination species from ionic complexes and to assess the stability of coordination compounds in solution.^{1,13,16,17}

In our previous investigation, the mixed-ligand thorium (IV) complex was comprehensively characterized by elemental analysis, Fourier-transform infrared (FTIR) spectroscopy, UV–Visible spectroscopy, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The combined experimental evidence confirmed the formation of an eight-coordinate thorium (IV) complex in which 2-hydroxy-5-sulfobenzoic acid coordinates through oxygen donor atoms, while 1,10-phenanthroline acts as a bidentate nitrogen-donor ligand. Thermogravimetric analysis further demonstrated that the nitrate groups remain coordinated within the primary coordination sphere of the thorium (IV) ion rather than existing as dissociated counter ions.¹⁸

The conductometric results obtained in the present study provide independent support for this structural formulation. The low specific conductivity values measured in both distilled water and ethanol indicate that the coordination entity remains essentially intact in solution with negligible ionic dissociation. Had the nitrate ions existed as free counter ions outside the coordination sphere, substantially higher conductivity values would normally be expected because of the increased concentration of mobile ionic species. The observed conductometric behaviour therefore supports the presence of coordinated nitrate ligands and confirms the non-electrolytic character of the synthesized complex.^{13,16,17}

The difference in conductivity observed between aqueous and ethanolic media is attributed primarily to the physicochemical properties of the solvents rather than to structural changes in the coordination compound. Although water promotes greater ionic mobility because of its higher dielectric constant and superior ion-solvating ability, the conductivity values remain sufficiently low to indicate that the

molecular structure of the complex is preserved in solution. Similarly, the markedly lower conductivity observed in ethanol reflects the combined effects of reduced solvent polarity, lower ion-solvation efficiency, and limited solubility of the complex rather than any alteration in its coordination environment.^{1, 2, 9}

The conductometric findings are therefore entirely consistent with the previously proposed formulation of the thorium(IV) complex, $[\text{Th}(\text{SSA})(\text{phen})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, and provide additional physicochemical evidence supporting its assignment as a stable, neutral, eight-coordinate mixed-ligand coordination compound.¹⁸

3.4 Comparison with Reported Mixed-Ligand Coordination Compounds:

To place the present conductometric investigation in a broader context, the behaviour of the synthesized thorium (IV) complex was compared qualitatively with representative mixed-ligand coordination compounds reported in the literature. Conductometric investigations have consistently demonstrated that neutral mixed-ligand coordination compounds exhibit comparatively low electrical conductivity owing to the absence of freely dissociable counter ions, whereas ionic coordination compounds display significantly higher conductivity because of increased ionic mobility in solution.^{13, 16, 17} The use of conductance measurements as a criterion for distinguishing electrolytic from non-electrolytic coordination compounds has long been established in coordination chemistry, particularly in non-aqueous solvent systems.¹⁹

The conductometric behaviour of the present thorium (IV) complex is in good agreement with reports describing mixed-ligand Schiff base, heterocyclic, and phenanthroline-containing coordination compounds. Although the metal ions, ligand systems, solvent media, concentrations, and experimental conditions differ among these investigations, the reported complexes consistently exhibit low conductivity values characteristic of non-electrolytic behaviour, indicating that the coordinated anionic ligands remain within the primary coordination sphere of the metal ion rather than existing as dissociable counter ions in solution.^{10–17, 19}

Table 3. Qualitative comparison of the conductometric behaviour of the present thorium (IV) complex with representative literature reports.

Complex	Solvent/Medium	Conductometric behaviour	Reference
Thorium(IV)-SSA-phen complex (present work)	Distilled water	Non-electrolyte	Present work
Thorium(IV)-SSA-phen complex (present work)	Ethanol	Non-electrolyte	Present work
Mixed-ligand transition-metal complexes	DMF	Non-electrolyte	10–12
Mixed-ligand thorium(IV)/Schiff base complexes	DMF	Non-electrolyte	13

Mixed-ligand coordination compounds	heterocyclic	DMSO/DMF	Non-electrolyte	16
Mixed-ligand complexes	transition-metal	DMSO	Non-electrolyte	17

Although direct quantitative comparison is not possible because of differences in solvent systems, concentrations, temperatures, and experimental methodologies, the qualitative agreement among these studies demonstrates that low electrical conductivity is a characteristic feature of neutral mixed-ligand coordination compounds. The present thorium (IV) complex exhibits conductometric behaviour consistent with this established trend, thereby providing additional support for its proposed molecular formulation and confirming the absence of significant ionic dissociation in solution.^{13, 16, 17}

When considered together with the spectroscopic and thermal characterization reported previously, the conductometric investigation further strengthens the proposed formulation of the complex as $[\text{Th}(\text{SSA})(\text{phen})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, in which both nitrate ions remain coordinated within the inner coordination sphere of the thorium(IV) ion.¹⁸ Accordingly, conductometry serves as a simple, rapid, and effective complementary technique for evaluating the solution behaviour of mixed-ligand actinide complexes and for supporting structural assignments obtained from conventional spectroscopic and thermal methods.

4. Conclusion:

A systematic conductometric investigation of the previously synthesised eight-coordinate mixed-ligand thorium (IV) complex containing 2-hydroxy-5-sulfobenzoic acid and 1,10-phenanthroline has been carried out in aqueous and ethanolic media. The experimentally determined specific conductivity values demonstrated that the complex exhibits predominantly non-electrolytic behaviour under the investigated conditions. The comparatively low conductivity observed in both solvents indicates negligible ionic dissociation and supports the formation of a neutral coordination species in solution.

The conductivity measured in distilled water was higher than that in ethanol, which is attributed to the superior dielectric constant, polarity, and ion-solvating ability of water. The solvent-dependent variation in conductivity therefore reflects differences in solvent properties rather than changes in the coordination environment of the thorium (IV) complex. The observed conductometric behaviour is consistent with the expected influence of solvent polarity and ionic mobility on electrical conductivity.

The conductometric results correlate well with the structural formulation established previously by elemental analysis, FTIR spectroscopy, UV–Visible spectroscopy, powder X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis, confirming that the nitrate ions remain coordinated within the primary coordination sphere of the thorium (IV) ion. The present investigation therefore provides additional physicochemical evidence supporting the proposed formulation $[\text{Th}(\text{SSA})(\text{phen})(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ and its assignment as a stable eight-coordinate mixed-ligand thorium(IV) complex.¹⁸

Overall, the study demonstrates that conductometric measurements constitute a simple, rapid, and reliable complementary technique for evaluating the solution behaviour of mixed-ligand actinide complexes. The present work further highlights the usefulness of electrical conductivity measurements, in conjunction with spectroscopic and thermal characterization, for confirming the non-electrolytic nature and solution stability of coordination compounds.

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