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DFT calculations, spectroscopic, thermal analysis and biological activity of Sm(III) and Tb(III) complexes with 2-aminobenzoic and 2-amino-5-chloro-benzoic acids

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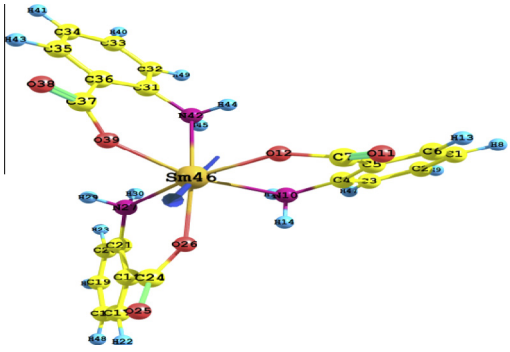
HIGHLIGHTS

- ($Sm[C_7H_6NO_2]_3$, $Tb[C_7H_6NO_2]_3$, $Sm[C_7H_5NO_2Cl]_3$ and $Tb[C_7H_5NO_2Cl]$,) complexes are prepared.
- Elemental, IR, UV, mass spectra and thermal analyses.
- An octahedral geometry has been assigned for the prepared $M(AA)_3$ complexes.
- Biological activities against gram positive, gram negative bacteria and fungi.
- Optimized geometry calculations at the B3LYP/6-311++G** level of theory.

GRAPHICAL ABSTRACT

The optimized geometry of the $Sm(AA)_3$ complex.



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ABSTRACT

The complexes of Sm(III) and Tb(III) with 2-aminobenzoic acid (*anthranilic acid*, AA) and 2-amino-5-chlorobenzoic acid (*5-chloroanthranilic acid,* AACl) were synthesized and characterized based on elemental analysis, IR and mass spectroscopy. The data are in accordance with 1:3 [Metal]:[Ligand] ratio. On the basis of the IR analysis, it was found that the metals were coordinated to bidentate anthranilic acid via the ionised oxygen of the carboxylate group and to the nitrogen of amino group. While in 5-chloroanthranilic acid, the metals were coordinated oxidatively to the bidentate carboxylate group without bonding to amino group; accordingly, a chlorine-affected coordination and reactivity-diversity was emphasized. Thermal analyses (TGA) and biological activity of the complexes were also investigated. Density Functional Theory (DFT) calculations at the B3LYP/6-311++G (d,p)_ level of theory have been carried out to investigate the equilibrium geometry of the ligand. The optimized geometry parameters of the complexes were evaluated using SDDALL basis set. Moreover, total energy, energy of HOMO and LUMO and Mullikan atomic charges were calculated. In addition, dipole moment and orientation have been performed and discussed.

Introduction

Anthranilic acid is biosynthesized from chorismic acid. It plays a vital part in the biosynthesis of tryptophan and its derivatives via

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the attachment of phosphoribosyl pyrophosphate to the amine group, as well as in several types of alkaloids [1]. Anthranilic acid is a versatile and low cost starting material in organic synthesis to generate the benzyne intermediate and to synthesize benzo-fused heterocycles [1]. Industrially, anthranilic acid is used as an intermediate for production of dyes, pigments, and saccharin. It and its esters are used in preparing perfumes to imitate jasmine and orange, pharmaceuticals and UV-absorber as well as corrosion inhibitors for metals and mold inhibitors in soya sauce.

In addition, anthranilic acid could be commonly used as fluorescent tag in detection of monosaccharides using liquid chromatography or capillary electrophoresis. It provides a monosaccharide labeling with a highly reproducible and accurate results [2]. Recently, a series of N-benzoyl anthranilic acid derivatives were prepared as inhibitors of penicillin binding proteins [3]. Other literatures [4,5] showed that substitution of the amino group in AA by different substituted aryl or heteroaryl moieties could markedly modulate the anti-inflammatory activity. The compound N-phenylanthranilic acid is used as a common intermediate in the synthesis of pharmaceutically important molecules such as antimalarials and antineoplatics [6].

Fluorescent rare earth complexes are of great interest owing to their broad applications in biochemistry, material chemistry, medicine and so forth. Rare earth complexes with carboxylic acids may be used as structural and functional probes of biological macromolecule systems [7]. It was found that the complex of a reactive ternary Tb(III) could be excited by 365 nm ultraviolet, and emitted green light attributed to the characteristic emission of Tb(III) ion [8].

Investigation of coordination compounds of samarium and terbium ions with organic ligands has been attracted significant attentions that focus on several potential applications of its luminescence [9–11]. Such as application in the lighting industry, ability to provide electroluminescent material for organic light emitting diodes (OLEDs) [12] and optical fibers for telecommunications, a capacity to yield functional complexes for biological assays and medical imaging purposes [13–15].

Anthranilic acid offers two possible coordination sites, one carboxylic and one amino group. The coordination of metal ions toward the ligand is discussed very controversial in the literature. For example, a bidentate binding mode via the two oxygen atoms of the carboxylic group was postulated for Tb(III) anthranilate complexes in solid state [16,17]. Other authors suggested that the coordination of the metal ion takes place via a chelate formation through the nitrogen atom of the amino group and one oxygen atom of the carboxylic group [18,19].

Large discrepancies have been published for the interaction of anthranilic acid with trivalent lanthanides [20]. By employing an alternative synthetic route, a range of lanthanoid anthranilates were synthesized and characterized. The results reveal a diverse range of structural classes exhibited by lanthanoid anthranilates [21]. This prompted us to confirm the pattern of coordination in these complexes using for the first time a dual experimental and theoretical insight. Sm(III) and Tb(III) anthranilate and 5-chloroanthranilate solid complexes were synthesized then spectroscopically characterized and subjected to extensive theoretical calculations. The DFT calculations for the model systems correlate well with experimentally determined metrical parameters. Moreover, the thermal stability of the reported metal complexes as well as their biological activities has been studied.

Experimental

Materials and reagents

All chemicals and reagents were of reagent grade quality and were used as received without further purification. Anthranilic acid, (2-amino benzoic acid, AA) and chloroanthranilic acid (2-amino-5-chloro benzoic acid, AACl) were provided from Fluka. Terbium chloride hexahydrate, $TbCl_3{\cdot}6H_2O$ was obtained by treating Tb_4O_7 (99.9%, Chempur) with concentrated HCl and the surplus HCl was removed by evaporation. The residue was dissolved with deionized water and evaporated for three times results finally to the crystals of hexahydrate terbium chloride. Samarium chloride hexahydrate, $SmCl_3{\cdot}6H_2O$ (99.9%) was provided from Sigma–Aldrich. Bi-distilled water is usually used in all preparations.

Instrumentation

Elemental microanalyses of the separated solid chelates for C, H, N were performed in the Microanalytical Center at Cairo University. The analyses were repeated twice to check the accuracy of the data. Infrared spectra were recorded on a Perkin–Elmer FTIR type 1650 spectrophotometer in the region 4000–400 cm^{-1} as KBr discs. The absorption spectra were recorded with a double beam Perkin–Elmer Lambda 25 UV–Visible spectrophotometer. The pH was measured using pHs-JAN-WAY 3330 research pH meter at 25 °C. The thermal analysis (TG and DTA) were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10 °C min^{-1} using Shimadzu TG-60H and DTA-60H thermal analyzers.

Synthesis of metal complexes

As an example, the anthranilate complex with Tb^{3+} ions was simply prepared by adding (126 mg) sodium bicarbonate of pure grade (Aldrich) to a hot water–ethanol solution (30 mL, 10:20 v/v) of an equimolar amount of AA (206 mg). The mixture was stirred for 15 min at 70 °C. After that, ethanolic solution (10 mL) of $TbCl_3{\cdot}6H_2O$ (186.69 mg, 0.5 mmol) was added drop wisely under continuous stirring. The resulting mixture was kept under stirring for 4 h at 60 °C forming a white precipitate. The precipitate was separated by filtration and washed with bidistilled water to separate sodium chloride from the solid formed complex which is insoluble in water. The complex dissolves readily in DMF, DMSO and in hot absolute ethanol. The complex was recrystallized from ethanol to give 231 mg of pure compound (Yield 81.6%). The same procedure was performed to synthesize the samarium anthranilate complex (Yield 80.3%) and in the synthesis of both samarium and terbium chloroanthranilate complexes giving yields of 85.7% and 84.8%, respectively.

Biological activity

The in vitro antimicrobial activity of the free ligand and their complexes were tested against the bacteria: *Staphylococcus aureus* (gram +ve) and Escherichia coli (gram −ve) in Mueller Hinton-Agar medium and fungi: *Aspergillus flavus* and *Aspergillus niger* in YPD-agar medium. The standard disc-agar diffusion method [22] was followed to determine the antibacterial and antifungal activity of the synthesized compounds. The tested compounds were dissolved in DMF (which has no inhibition activity), to get concentrations of 100 mg/mL. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume (0.1 mL) from the specific concentration of dissolved tested compounds and carefully placed on incubated agar surface. After incubation for 48 h at 37 °C, inhibition of the organisms which evidenced by clear zone surround each disk was measured and used to calculate the mean of inhibition zones [21,23].