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Synthesis and characterization of TH (IV) Complex with tetrazoline Derivative

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Abstract
In this paper, octahedral geometry of the Thorium complex was reported. At first, ligand 1-phenyl tetrazoline-5-thione was prepared. Thereafter, complexation of the actinoid Th (IV) was completed by simple condensation method. The structure of the complex has been characterized on the basis of elemental analysis, conductivity measurements, magnetic and spectral data.

Keywords: terazoline, thione, thorium, ir spectra and electronic spectra

1. Introduction
Thorium is a less radioactive metallic in nature. Thorium is silvery and tarnishes black when it is exposed to air. High coordination numbers are the common for thorium complexes due to its large size [1]. Thorium complexes with organic ligands, such as oxalate, citrate, and EDTA, are much more stable [2]. In natural thorium-containing waters, organic thorium complexes usually occur in concentrations orders of magnitude higher than the inorganic complexes, even when the concentrations of inorganic ligands are much greater than those of organic ligands.
In the last few decades, the chemistry of 1, 2, 3, 4-tetrazoline and their fused heterocyclic derivatives has received considerable attention owing to their synthetic and effective biological importance [3]. For example, a large number of 1, 2, 3, 4-tetraazoline-containing ring system have been incorporated into a wide variety of therapeutically interesting drug candidates including anti-inflammatory, CNS stimulants sedatives, antianxiety, antimicrobial agents [4] and antimycotic activity such as fluconazole, intraconazole, voriconazole [4]. Also, there are known drugs containing the 1, 2, 3, 4-tetrazoline group. Moreover, sulphur-containing heterocycles represent an important group of sulphur compounds that are promising for use in practical applications. Among these heterocycles, the mercapto- and thione-substituted 1,2,3,4-tetrazoline ring systems have been well studied and so far a variety of biological activities have been reported for a large number of their derivatives, such as antibacterial [6], antifungal [7], antitubercular [8], antimycobacterial [9], anticancer [10], diuretic [11], and hypoglycemic [12] properties

Material and methods
The chemical used were of BDH, E-Merck of Anal-R grade.

Preparation of ligand
i. Preparation of 1-phenyl tetrazoline-5-thione
About 27 g of CS_2 and 45 ml (0.65 mol) of concentrated ammonia (sp.gr. 0.9) were placed in a round bottom 3 litre flask fitted with a mechanical stirrer and cooled in ice-salt bath. 0.3. ml of aniline was added with continuous stirring into a mixture from a dropping funnel, fitted in a round bottom flask at such a rate that the addition was completed in about 20 minutes.
The reaction mixture was allowed to stand for 30 minutes. During this time a heavy precipitate of ammonia phenyl dithiocarbamate formed, was separated out by filtration. The precipitate was dissolved in about 800 ml of water and transferred to 2.5 litre round bottom flask. 100 g of lead nitrate dissolved in 400 ml of hot water poured slowly in this flask with vigorous shaking. A black precipitate of lead sulphide was formed. The slurry was then steam distilled and the distillate was collected in a receiver containing 10 ml of N H_2SO_4 solution. About 1.5 litres of the distillate was collected. The oily layer of phenyl isothiocyanate was separated by means of separating funnel. The oil was dried over anhydrous $CaCl_2$ and distilled under reduced pressure. The yield of phenyl isothiocyanate boiling at 120-121 ^{0}C at 35 mm was about 25 g.
Now, 0.05 mole of the isothiocyanate was added to a 100 ml solution of sodium azide containing 4.9 g of the salt in a quick fitted round bottom flask. The mixture was refluxed for a period ranging 4-8 hours and then cooled. It was filtered from any suspended material and the filtrate was extracted twice with ether in order to remove any unreacted isothiocyanate. The aqueous layer was cooled in ice and acidified with conc. HCl to pH 3.0. The precipitated 1-phenyltetrazoline-5-thione was separated by filtration washed thoroughly with water and recrystallized from hot ethanolic solution.

i. Preparation of complexes of Th (IV) with 1-substituted tetrazoline-5-thione
0.1 g thorium chloride was taken and dissolved in hot dilute hydrochloric acid and was filtered. The pH was kept to 2-3. 1-phenyl tetrazoline-5-thione was dissolved in 10 ml of ethanol and filtered. The two filtrates are mixed when precipitate of the complex was immediately formed. The mixture was refluxed for 3-hours on water bath and filtered hob. The complex was crystallized in acetone. (M.P. = 189.5 ^{0}C).

Table 1: The data of elemental analysis of the newly synthesized complex are in following table.

	% Th	% C	% H	% N
Calculated	31.78	23.01	1.64	15.34
Found	31.05	23.00	1.55	15.20

Physicochemical Measurements

Magnetic Moments

Magnetic moments measurements were carried out at room temperature by Gouy's method. It was found that the synthesized complex was diamagnet in nature.

Conductivity measurements

The conductivity of the complexes was determined with the help of systronics Conductivity Metre Bridge in 10^{-3} M, DMF solution. The data of conductivity measurement of the complex showed its nonelectrolytic nature.

Infrared Spectra

Infrared spectra of the ligand and the metal complexes were recorded in KBr pellets on Perkin Elmer model-221 spectrophotometer, in the range 4000- 400 cm^{-1} by the courtesy of C. D. R. I., Lucknow. The infrared frequencies of the ligand have been influenced on complex formation with Th(IV) ion. The shifting of the ν_{NH} band of the ligand from 3060 cm^{-1} to 3090 cm^{-1} in the complex indicates [13] the absence of coordination through nitrogen atom of N-H group of the ligand. The band 2560 cm^{-1} in the spectrum of the ligand assigned to S-H mode of vibration. The absence of the band from the spectrum of the complex probably indicates [14] that the thione from the ligand has cooordinated to Th(IV) ion. Thus the coordination only through sulphur atom of the ligand is indicated. This is supported [15] by disappearance of $\nu_{C=S}$ band of ligand observed at 1240 cm^{-1} on the complexation with Th(IV). The disapperance of thioamide band-III (1050 cm^{-1}) and red shifting of the thioamide band-IV of the ligand by about 30 cm^{-1} also supports [16, 17] the coordination of the ligand through thio carbonyl sulphur atom. There is strong band at 1500 cm^{-1} in the spectrum of the ligand which is ost probably thioamide band-I having contributions from $\delta_{N-H}+\nu_{C=N}+\delta_{CH}$ modes of vibrations. This also supports [18] the fact that coordination of 1-phenyl tetrazoline-5-thione has not occurred through nitrogen atom of N-H group. There is a new band band in the infrared spectrum of the complex at 380 cm^{-1}. This may have contribution from ν_{Th-Cl} mode of vibtration [19]. The presence of a new but weak band at 325 cm^{-1} in the spectrum of this complex may be assigned [20] to ν_{Th-S} mode. Since, only ν_{Th-Cl} and ν_{Th-S} band are observed in the spectrum of the complex. On the basis of elemental analysis, magnetic measurement, conductivity measurement and spectral analysis, following octahedral structure of the complex has been proposed.

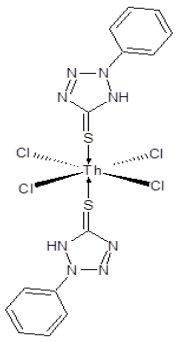

Fig 1

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