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Synthesis, spectroscopic, thermal and quantum chemical studies on trivalent erbium NO chelating sulfamonomethoxine –cyclophosph(V)azane complex

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HIGHLIGHTS

- Novel cyclodiphosph(V)azane ligand and its Er(III) complex were synthesized and characterized.
- Analytical results have justified the $[Er_2(L)(H_2O)6Cl_6]2H_2O$ composition.
- Structure and spectra for the ligand and its Er(III) complex were computed at the B3LYP/6-31G(d).
- Two tautomers and geometrical isomers of the ligand were optimized at the *ab initio* level.
- Computed TD-DFT UV–VIS spectra show good agreement with measured electronic spectra.

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ABSTRACT

Novel hexachlorocyclophosph(V)azane of sulfamonomethoxine (L), was prepared and their coordinating behavior toward the lanthanide ion erbium (III) was studied. The structures of the isolated products were proposed based on elemental analyses, IR, UV–VIS, ^{1}H NMR, ^{31}P NMR, SEM, TEM, XRD, mass spectra, effective magnetic susceptibility measurements and thermogravimetric analysis (TGA). The coordination polyhedra of the eight donor atoms around the two erbium (III) ions are best described as distorted dodecahedral. Computational studies were carried out at the DFT-B3LYP/6-31G(d) level of theory on the structural and spectroscopic properties of L and its binuclear erbium (III) complex. Different tautomers of the ligand were optimized at the *ab initio* DFT level. Keto-form structure is about 30.5 kcal/mol more stable than the enol form (taking zpe correction into account). Simulated IR frequencies were scaled and compared with that experimentally measured. TD-DFT method was used to compute the UV–VIS spectra in gas phase and DMF.

1. Introduction

The complexes of d-block transition metals with various ligands have been studied extensively. However, in case of f-block lanthanide metal complexes, a limited study has so far been carried out. The complexes of lanthanide (III) metal ions with organic reagents are very important because of their application in many fields such as their use in visible–ultraviolet (VUV) lasers, luminescent chemosensors for medical diagnosis, Schift reagent for NMR spectroscopy, as scintillators, in industries and biological systems [1]. Cyclodiphosphazane derivatives are an important family of inorganic heterocyclic compounds containing a saturated four membered $[P—N]_2$ ring which gained considerable interest in synthesis and structural investigations [2,3]. This is due to the organic and inorganic properties of these compounds particularly the ability of the inorganic rigid P—N framework to combine with organic substituents. Moreover, the ability of these compounds to form transition metal complexes with remarkable chemical and biological properties is also of great interest [4]. The high reactivity of hexachlorocyclodiphospha(V)zane toward nucleophilic substitution provides possibility for chlorine atom(s) substitution by nucleophiles. Therefore, several cyclodiphospha(V)zanes containing active methylene, alcohols, thiophenes [5–7], aromatic and aliphatic

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amines [8] have already been synthesized and characterized. Cyclophosphamide and its derivatives were examples of phosphorus compounds which were one of the most effective anticancer agents with proven activity against a large variety of human cancers [9]. Hexachlorocyclodiphosph(V)azanes of sulfonamides and their complexes had been prepared [6,10–13]. In continuation to our interest to prepare hexachlorocyclodiphosph(V)azane of sulfa drugs [14], the present paper aims chiefly to prepare hexachlorocyclodiphosph(V)azane of sulfamonomethoxine, L and to explore its behavior toward erbium (III). To the best of our knowledge there is no reported quantum mechanical work on the title compound and its binuclear erbium (III) complex. It is one of our main objectives to perform a DFT calculations on these systems to evaluate its accuracy against the obtained experimental results.

2. Experimental

Melting points (°C, uncorrected) were determined in open capillaries on a Gallen Kemp melting point apparatus. Elemental analysis (C, H, N and S) was performed on Carlo Erba 1108 Elemental Analyzer. The chlorine content was determined by the Schöninger method, phosphorus content was determined by the vanadomolybdato-phosphoric acid spectrophotometric method and water molecules were determined by thermogravimetric analysis. Analysis of the erbium complex started with decomposition of the complex with concentrated nitric acid. The resultant solution was diluted with distilled water, filtered to remove the precipitated ligand. The solution was then neutralized with aqueous ammonia solution and the metal ions titrated with EDTA. The infrared spectra were recorded on a Shimadzu FT-IR spectrometer using KBr disks. Electronic spectra were recorded for solution of the ligand, L in DMF, and for the metal complexes as Nujel Mull on a Jasco UV–VIS spectrophotometer model V-550-UV–V1S. ^{1}H NMR spectra (in $CDCl_3$) were recorded on Bruker Ac-300 ultra-shield NMR spectrometer at 300 MHz, using TMS as internal standard. Electron impact Mass Spectra were recorded on a Shimadzu Gc–Ms-Qp 5000 instrument. ^{31}P NMR spectra were run, relative to external H_3PO_4 (85%), with a varian FT-80 spectrometer at 36.5 MHz. The mass spectrum of L was performed using a Shimadzu-Ge-Ms-Qp 100 EX mass spectrometer using the direct inlet system. The molar conductance measurements were carried out using a Sybron–Barnstead conductometer. Magnetic susceptibilities were measured at room temperature using the Faraday method with a Cahn–Ventron RM-2 balance standardized with $HgCo(NCS)_4$; diamagnetic corrections were estimated from Pascal's constants. Thermogravimetric analysis was performed under a nitrogen atmosphere using a Shimadzu TGA–50H with a flow rate of 20 ml min^{-1}.

2.1. Synthesis of ligand (L)

Sulfamonomethoxine [N^1-4-amino-6-methoxypyrimidine-benzenesulfon-amide] (0.1 mol, 28.0 g) in 100 ml cold dry benzene was added in small portions to a well stirred cold solution of phosphorus pentachloride (0.l mol, 20.95 g) in 100 ml cold dry benzene during half an hour at ≈15 °C under dry conditions. After completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered while hot and the solid obtained was washed several times with dry benzene, diethyl ether and dried in vacuo to give the corresponding sulfamonomethoxine-hexachlorocyclodiphosph(V)azane (L) (Fig. 1).

L: White solid, Yield, 81%; m.p. 144 °C. Molar conductance (Λ_M): 0.052 Ω^{-1} cm^2 mol^{-1}. Anal. calcd. for $C_{22}H_{20}Cl_6N_8O_6P_2S_2$ (M.Wt. 831.24): C, 31.79; H, 2.43; Cl, 25.59; N, 13.48; P, 7.45; S, 7.71. Found: C, 31.78; H, 2.42; Cl, 25.58; N, 13.47; P, 7.45; S, 7.70.

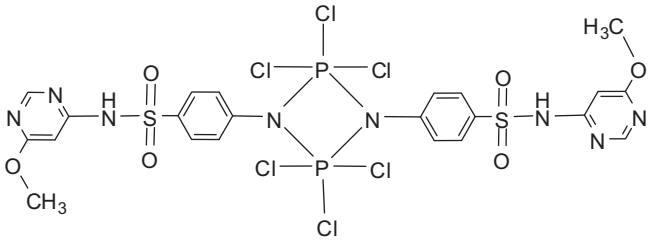

Fig. 1. Proposed structure of L ligand.

2.2. Synthesis of erbium complex

The erbium complex was prepared by adding drop wise hot aqueous (60 °C) solution (100 ml) of $ErCl_3{\cdot}6H_2O$ (0.76 g; 0.002 mol) to a solution of L (0.83 g; 0.001 mol) in tetrahydrofuran (THF) (20 ml) while stirring continuously. After complete addition of the $ErCl_3{\cdot}6H_2O$ solution, the reaction mixture was heated under reflux for about 15 h under dry conditions. The complex obtained was filtered, washed several times with water, ethanol, and THF and then dried in vacuo (Fig. 2).

[Er$_2$(L)(H$_2$O)$_6$Cl$_6$]2H$_2$O: Pale pinksolid, Yield, 73%; m.p. 206 °C: Molar conductance (Λ_M): 2.33 Ω^{-1} cm^2 mol^{-1}. Anal. calcd. for $C_{22}H_{36}Cl_{12}Er_2N_8O_{14}P_2S_2$ (M.Wt. 1522.60): C, 17.35; H, 2.38; Cl, 27.94; Er, 21.97; N, 7.36; P, 4.07; S, 4.21. Found: C, 17.35; H, 2.34; Cl, 27.90; Er, 21.95; N, 7.35; P, 4.08; S, 4.20.

3. Computational methods

All quantum chemical calculations were performed using the Gaussian09 suite of programs [15]. Geometry optimization of the ligand have been performed using the *ab initio* Density Functional Theory (DFT) at the B3LYP functional [16–18] in conjunction with the 6-31G(d) basis set in gas phase and DMF via the Polarizable Continuum Model (PCM) since the optical experimental characterization was done in DMF solvent. For each stationary point, we carried out a force constant harmonic frequency calculation at the same levels to characterize their nature as minima or transition states and to correct energies for zero-point energy and thermal contribution. The Frequencies are scaled by a factor of 0.98. The vibrational modes were animated using the ChemCraft program [19]. Natural charges were computed within full Natural Bond Orbital analysis, using NBO implemented in Gaussian 09 [15]. TD-DFT method was used to simulate the UV–VIS spectra of the ligand in both gas phase and DMF solving for ten exited states. Erbium binuclear complex was optimized at B3LYP with the universal Gaussian basis set (UGBS1P) [20] for the erbium atoms and 6-31G(d) for the rest of the molecule within the G09 package in the gas phase.

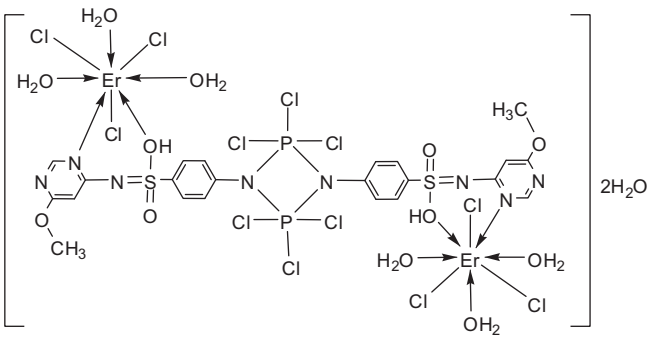

Fig. 2. Suggested structural formula of L erbium complex.