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Ditolyldithiophosphates of Gadolinium(III): Synthesis and Spectroscopic Characterization.

Atiya Syed

Department of Chemistry, University of Jammu, Jammu, (India)

ABSTRACT

Ditolyldithiophosphate complexes of Gadolinium(III) corresponding to $[\{(ArO)_2PS_2\}_3Gd]$ (Ar = *o*-, *m*- and *p*-$CH_3C_6H_4$), have been synthesized by the reaction of Gadolinium chloride, $GdCl_3$, sodium ditolylphosphorodithioates, (*o*-, *m*-, *p*-$CH_3C_6H_4O)_2PS_2Na$, and sodium neopentylenephosphorodithioate, $OCH_2C(CH_3)_2CH_2OPS_2Na$, in 1:3 molar ratio in acetonitrile under anhydrous conditions. Characterization of these newly synthesized complexes has been by various physico-chemical techniques like elemental analyses, ESI-mass and IR spectral studies. An eight coordinated gadolinium atom has been established in the complexes leading to dodecahedral geometry.

Keywords: Gadolinium, Dithiophosphate, Phosphorus, Sulfur, MRI

I. INTRODUCTION

The arena of medicine and diagnosis has consistently welcomed novel compounds. Magnetic resonance imaging is one such technique that has proved to be an indispensable part of the biomedical field. On the other hand the coordination chemistry exhibited by the rare earth elements has been of interest since decades due to their extensive versatility[1]. Their complexes play important roles in biochemical[2], medical[3], and industrial[4-5] processes. The presence of seven unpaired electrons in Gadolinium (with electronic configuration as $[Xe]4f^75d^16s^2$) has made Gd(III) the metal ion of choice for several magnetic resonance applications, the most important one being the MRI contrast agents in medical diagnostics[6-7]. Efforts have been done to incorporate Gd(III) onto or into nanoparticles that will enhance their sensitivity by increasing their specificity, prolonging circulation time, and reducing their toxicity[8]. The dithiophosphate chemistry of gadolinium(III) has been investigated to some extent[9-10]. There is however scarcity of reports on lanthanides with such ligands and ditolyldithiophosphates[11-13]. Recently, ditolyldithiophosphates of lanthanum(III) and their adducts with nitrogen and phosphorus donor bases have been reported from my laboratory[14]. It was therefore thought worthwhile to synthesize and investigate the coordination chemistry of novel mixed ligand complexes of gadolinium(III) with sulfur donor ligands.

II. EXPERIMENTAL

Stringent precautions were taken to exclude moisture. Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk's techniques. *Ortho*-, *meta*- and *para*-hydroxytoluene (cresols) were distilled before use. Gadolinium trichloride hexahydrate (Himedia) was used as received. The solvents used (toluene, hexane and acetonitrile) were purified and dried by standard methods before use. The ligands (*o*-$CH_3C_6H_4O)_2PS_2Na$,(*m*-$CH_3C_6H_4O)_2PS_2Na$ and (*p*-$CH_3C_6H_4O)_2PS_2Na$ were prepared by literature

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method[15]. Elemental analyses of C, H, N and S were done on Vario EL III and CHNS-932 Leco elemental analyzer their results were found to be in good agreement (±0.3%) with the calculated values. The mass spectra were recorded on ESQUIRE3000_00037 spectrophotometer. IR spectra were recorded using KBr pellet in the range of 4000-200 cm^{-1} on a Perkin Elmer Spectrum 400-I FTIR spectrophotometer.

1. Synthesis of Tris-*O,O′*-*o*-ditolyldithiophosphatogadolinium(III) [{(*o*-$CH_3C_6H_4O)_2PS_2$}$_3$Gd($CH_3CN)_2$] (1)

An acetonitrile solution (~10 cm^3) of gadolinium trichloride hexahydrate (0.37 g, 1.00 mmol) was added to an acetonitrile solution (~20 cm^3) of sodium *O,O′*-*o*-ditolyldithiophosphate (1.0 g, 3.00 mmol) with constant stirring at room temperature for two hours followed by refluxing for three hours; white turbidity appeared due to the formation of sodium chloride. The contents were cooled and then sodium chloride was separated by filtration using alkoxy funnel fitted with G-4 disc. The product [{(*o*-$CH_3C_6H_4O)_2PS_2$}$_3$Gd] (**1**) was obtained as white solid from the filtrate after removal of excess of acetonitrile in *vacuo*. Yield: 89 %; *Anal*. Calc. for $C_{46}H_{48}O_6P_3S_6N_2Gd$: C, 47.32; H, 4.14; N, 2.40; S, 16.48, Found: C, 47.19; H, 4.01; N, 2.35; S, 16.32, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1108.1, s [*ν*(P)−O−C], 936.8, s [*ν*P−O−(C)], 682.1, s [*ν*P═S], 558.5, m [*ν*P−S], 338.7, w [*ν*Gd−S] cm^{-1}.

2. Synthesis of Tris-*O,O′*-*m*-ditolyldithiophosphatogadolinium(III) [{(*m*-$CH_3C_6H_4O)_2PS_2$}$_3$Gd($CH_3CN)_2$] (2)

The synthesis of complex **2** was carried out as described for complex **1**; 1.00 g of sodium *O,O′*-*m*-ditolyldithiophosphate (3.01 mmol) and 0.37 g of Gadolinium chloride (hexahydrated) (1.00 mmol) were used to give **2** as white solid. Yield: 87 %; *Anal*. Calc. $C_{46}H_{48}O_6P_3S_6N_2Gd$: C, 47.32; H, 4.14; N, 2.40; S, 16.48, Found: C, 47.11; H, 4.08; N, 2.29; S, 16.28, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1049.6, s [*ν*(P)−O−C], 940.4, s [*ν*P−O−(C)], 684.5, s [*ν*P═S], 562.8, m [*ν*P−S], 336.8, w [*ν*Gd−S] cm^{-1}; ESI-MS: m/z (%) = 1167.44 (6) [{(*m*-$CH_3C_6H_4O)_2PS_2$}$_3$Gd($CH_3CN)_2$], 344.45 (15) [Gd{$S_2P(OC_6H_4)$}]$^+$, 375.48 (42) [{(*m*-$CH_3C_6H_4O$)P(O)S_2}Gd]$^+$, 309.3 (86) [(*m*-$CH_3C_6H_4O)_2PS_2$]$^+$, 107.2 (98) [*m*-$CH_3C_6H_4O$]$^+$.

3. Synthesis of Tris-*O,O′*-*p*-ditolyldithiophosphatogadolinium(III) [{(*p*-$CH_3C_6H_4O)_2PS_2$}$_3$Gd($CH_3CN)_2$] (3)

The synthesis of complex **3** was carried out as described for complex **1**; 1.00 g of sodium *O,O′*-*p*-ditolyldithiophosphate (3.01 mmol) and 0.37 g of Gadolinium chloride (hexahydrated) (1.00 mmol) were used to give **3** as white solid. Yield: 91 %; *Anal*. Calc. $C_{46}H_{48}O_6P_3S_6N_2Gd$: C, 47.32; H, 4.14; N, 2.40; S, 16.48, Found: C, 47.15; H, 4.05; N, 2.31; S, 16.15, IR (cm^{-1}) = tolyl dithiophosphate moiety: 1201.1, s [*ν*(P)−O−C], 955.9, s [*ν*P−O−(C)], 681.1, s [*ν*P═S], 542.7, m [*ν*P−S], 335.3, w [*ν*Gd−S] cm^{-1}.

III. RESULTS AND DISCUSSION

Dithiophosphates of gadolinium(III) **(1-3)** were prepared as white solid in 87-91% yield by the reaction of gadolinium trichloride (hexahydrate), $GdCl_3.6H_2O$, with sodium salt of *O,O′*-di(*o*-, *m*-, and *p*-tolyl)dithiophosphates, $(ArO)_2PS_2Na$ [Ar = *o*-, *m*-, *p*-$CH_3C_6H_4$] **(1-3)**, in 1:3 molar ratio in acetonitrile under refluxing condition.

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$$3(ArO)_2PS_2Na + GdCl_3 \xrightarrow[\text{Reflux ~3h}]{\text{Acetonitrile}} [\{(ArO)_2PS_2\}_3Gd(CH_3CH)_2]$$
$$\text{-3NaCl}$$

[Ar = *o*-, *m*- or *p*-$CH_3C_6H_4$ **(1-3)**]

Scheme 1: Synthesis of tris-*O,O'*-di(*o*-, *m*-, *p*-tolyl)dithiophosphates of gadolinium(III) (1-3).

The solvent appears to occupy the vacant coordination sites of gadolinium(III) atom. These complexes were obtained after separation from NaCl. These complexes are soluble in tetrahydrofuran, chloroform, DMSO and insoluble in solvents like *n*-hexane and carbon tetrachloride. These complexes appear to be slightly moisture sensitive.

1. IR Spectra

Two strong intensity bands were observed in the IR spectra of these complexes in the region 1201.1-1049.6 cm^{-1} and 955.9-936.8 cm^{-1}, have been ascribed to the ν(P)−O−C and νP−O−(C) vibrations, respectively. The observation of two closely spaced bands arising from $\nu(PS_2)$ vibrations bands for $\nu P-S_{(asym)}$ and $\nu P-S_{(sym)}$ in the region 681.1-632.1 cm^{-1} and 542.7-558.5 cm^{-1} is characteristic of bidentate chelating dithiophosphates units. The presence of a band in the region 338.7-335.3 cm^{-1}, attributed to νGd−S, is indicative of the formation of gadolinium-sulfur bond. This is supported by the literature survey[9-10].

2. Mass Spectra

The mass spectra of $[\{(m\text{-}CH_3C_6H_4O)_2PS_2\}_3Gd(CH_3CN)_2]$ has been carried out and has shown the molecular ion peak $[M^+]$ at 1167.44 (m/z). The fragmented species produced after the consecutive removal of different groups also indicate their formation in the mass spectra. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes while the rest of the diagnostic peaks were found to be consistent with the possible fragmentation pattern.

IV. CONCLUSIONS

The elemental analysis and ESI-mass and IR spectroscopic analyses data of the new synthesized complexes of ditolyldithiophosphates of gadolinium(III) revealed a probable structure for these complexes. It is interesting to note that appearance of new bands was observed in the IR spectra of these complexes in comparison to the parent dithiophosphate ligands. The ESI-mass analyses in agreement with elemental analyses data confirmed the monomeric nature and eight folded coordination pattern around the gadolinium(III) *tris-O,O'*-di(*o*-, *m*-, *p*-tolyl)dithiophosphate. The $\Delta\nu$ value for the $\nu P-S_{(asym)}$ and $\nu P-S_{(sym)}$ bands for both the moieties in comparison to the parent dithiophosphate ligands also indicate the formation of these complexes. Octacoordinate geometry may be proposed around the gadolinium(III) atom (Figure 1).

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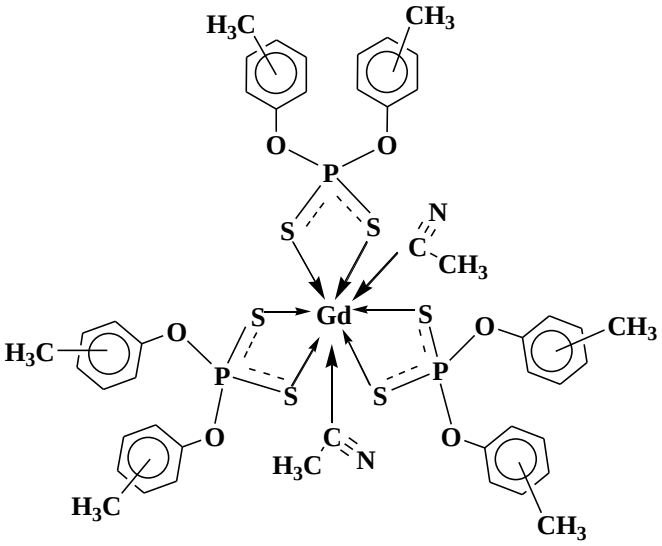

Figure 1: Proposed eight coordinate structure of tris-*O,O'*-di(*o*-, *m*-, *p*- tolyl)dithiophosphates) of gadolinium(III) (1-3).

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