Phthalanilinc Acid Complexes of Titanium (IV) and Zirconium (IV)

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Abstract

In this paper we report the synthesis of a number of titanium (IV) and zirconium (IV) complexes of the formulas $[Ti(LH_2)Cl_2]Cl_2$, $[Zr(LH_2)_2](NO_3)_4$, $[ZrO(LH_2)]Cl_2$, $[Ti(L)Cl_2]$, $[Zr(L)_2]$, $[Zr(OH)_2(L)]$, by the reaction of the phthalanilic acid ligand, furfuroylhydrazido-ortho-acetobenzoic acid (LH₂, scheme 1), with titanium tetrachloride, zirconium nitrate or zirconyl chloride. The ligand prepared by the reaction of furfuroylhydrazide with phthalic anhydride. Reactions of this ligand with the metal salts in both neutral and basic solutions gave cationic and neutral complexes, respectively. The prepared ligand and its complexes were characterized by elemental analysis, molar conductance and by infrared and ultraviolet spectra. In all complexes the ligand acts as neutral tetradentate in neutral medium and dibasic tetradentate in basic medium. Titanium complexes are hexacoordinated with octahedral structure, while zirconium complexes have different structures. Zirconium nitrate complexes of zirconyl chloride obtained from neutral and basic media are penta- and hexa-coordinated with the most common square pyramidal and octahedral structures, respectively.

Keywords: Phthalanilic acid, Furfuroylhydrazide, Titanium complexes, Zirconium complexes.

Introduction

The study of anilic acids interested many workers due to their importance in different industrial and biological fields [1-4]. Also, they have good coordination properties forming different types of complexes with many metal ions [5, 6]. Complexes with calcium, aluminum, titanium, zirconium and thorium ions are interesting from both industrial and theoretical points of view [7-10]. Complexes of such type of ligands with chromium (III) ion, which occurred in brewers, yeasts and other foods, are of great biological activity [11].

Titanium (IV) ion formed different types of complexes with large number of organic and inorganic ligands [12, 13]. These complexes have many industrial values [14]. The importance of zirconium (IV) complexes is due to their use in the field of analytical chemistry [15] and in separating zirconium and hafnium by solvent extraction [16], in addition to different structural geometries adopted by these complexes [17-20].

In this paper we report synthesis and characterization of a number of complexes formed by the reaction of titanium (IV) and zirconium (IV) salts with the anilic acid type of ligand, furfuroylhydrazido-orthoacetobenzoic acid (LH₂), formed by the reaction of phthalic anhydride and 2-furfuroylhydrazide (scheme 1).

Experimental

Materials and methods:

All chemical used throughout this work were of reagent grade from Fluka or B.D.H. and used as supplied without further purification. Furfuroylhydrazide was prepared according to the reported method [21].

Synthesis of the ligand, furfuroylhydrazido-orthoacetobenzoic acid (LH₂):

The ligand was prepared (scheme 1) by refluxing a mixture of phthalic anhydride (0.01 mol, 1.48 g) and furfuroylhydrazide (0.01 mol, 1.26 g) in ethanol for about 4h. The mixture was then cooled and the precipitate was filtered off, washed with cold ethanol, dried in vacuum and characterized.



Scheme I: The route for the synthesis of the ligand

Preparation of the complexes:

In all cases complexes were prepared using 1:2 metal to ligand ratio.

i- The neutral medium complexes were prepared by refluxing an ethanolic solution containing the proper amounts of the metal salts and the ligand (for TiCl₄, 0.005 mol, 0.95 g, for Zr (NO₃)₄, 0.005 mol, 1.7 g, for ZrOCl₂, 0.005 mol, 0.89 g and the ligand 0.01 mol, 2.74 g). The reaction was continued for about 40

minutes. The separated complexes were filtered off, washed with cold ethanol and dried.

ii-The basic medium complexes were prepared by treating an ethanolic solution containing the metal salt and the ligand (the same quantities were used as in the first procedure) with 1M KOH. The ethanolic solution of KOH was added slowly with continuous stirring until the p^{H} reached 8.5-9.0, where complete precipitation occurred. The precipitate was filtered

off, washed with ethanol, to remove any contamination with potassium salts or un-reacted excess materials and then dried under vacuum.

Analyses and physical measurement:

The ligand and its complexes were analyzed for carbon, hydrogen and nitrogen by using Carlo Erba Elemental Microanalyses. Molar conductances were measured for 10⁻³ M solution in acetonitrile with a LF-42 conductivity bridge. Infrared absorption spectra were recorded on Pye-Unicam SP-1100 Spectrophotometer as KBr discs in the 400-4000 cm⁻¹ range. UV-Spectra were recorded on Shimadzu TJV-160 Spectrophotometer for 10⁻³ M solution of the compounds in acetonitrite at room temperature using quartz cell.

Results and Discussion

The ligand was characterized by elemental analysis. The analysis gave reasonable agreement between theoretical and practical data (Table 1), and also, by analyzing its infrared absorption spectrum. The spectrum showed good agreement with the characteristic bands of its functional groups. The bands located at 1280, 1430, 1480,1580, 1650, 1680, 1700 and 3200 cm⁻¹ are due to the stretching vibrations of: C-O-C (furan ring), symmetrical OCO (carboxylate), C-N, C=C (phenyl ring), C=O (hydrazide), C=O (phthalanilic), asymmetrical OCO (carboxylate) and N-H, respectively [22-26].

The resulting complexes showed different stoichiometry in spite of using 1:2 metal to ligand ratio in all the preparations. This observation suggests that the formation of the complexes depends on their geometries and not on the ratio of the ligand used. All the complexes have yellow colour, formed in good yields (~ 85%) and are stable in air at room temperature but decomposed without melting above 250 °C. They formed in neutral and basic media as shown in equations (1-6).

$TiCl_4 + LH_2 \longrightarrow [Ti (LH_2) Cl_2]Cl_2(1)$
$TiCl_4 + LH_2 + 2KOH \longrightarrow [Ti (L)Cl_2] + 2KC1 + 2H_2O \dots (2)$
$Zr (NO_3)_4 + 2LH_2 \longrightarrow [Zr (LH_2)_2](NO_3)_4(3)$
$ZrOCl_2.8H_2O + LH_2 \longrightarrow [ZrO (LH_2)]Cl_2 + 8H_2O \dots (4)$
$Zr (NO_3)_4 + 2LH_2 + 4KOH \longrightarrow [Zr (L)_2] + 4KNO_3 + 4H_2O \dots (5)$
$ZrOCl_2.8H_2O + LH_2 + 2KOH \longrightarrow [Zr (OH)_2(L)] + 2KC1 + 10H_2O (6)$

Table (1): Analytical and molar conductance (cm².ohm⁻¹mol⁻¹ in acetonitrile) data

Compound	$\Lambda_{\rm M}$ cm ² . Ohm ⁻¹ . mol ⁻¹	Found (calc.) %		
		С	Н	Ν
LH ₂	-	56.89(56.93)	3.22(3.65)	10.44(10.22)
[Ti(LH ₂)Cl ₂]Cl ₂	210	33.89(33.62)	2.32(2.16)	6.21 (6.03)
[Zr(LH ₂) ₂](NO ₃) ₄	405	35.46(35.17)	2.41 (2.25)	12.38(12.63)
[ZrO(LH ₂)]Cl ₂	225	34.72(34.51)	2.36(2.21)	6.43 (6.19)
[Ti(L)Cl ₂]	22	39.80(39.90)	2.30(2.05)	7.29(7.16)
$[Zr(L)_2]$	16	49.42(49.13)	2.73 (2.52)	8.61 (8.82)
$[Zr(OH)_2(L)]$	24	39.55 (39.29)	2.68 (2.52)	7.25 (7.05)

The above formulas of the complexes are in good agreement with the obtained analytical and molar conductance data (Table 1). Their electrical molar conductance in acetonitrile [21] indicates 1:2 and 1:4 electrolytic nature for neutral medium complexes and non-electrolytic nature for basic solution complexes.

The coordination of the ligand to the metal ions was deduced by careful comparison of its infrared absorption spectrum with the spectra of its complexes. The main characteristic functional bands in the spectrum of the free ligand (as indicated above) are affected in the spectra of complexes according to their involvement in coordination. For complexes formed in neutral medium, the NH stretching mode which due to both symmetrical NH-groups, split into two bands, one with lower value by about 100-110 cm⁻¹ indicating coordination through one of the nitrogen atoms. Due to geometrical reasons, the coordination should be through the nitrogen atom adjacent to hydrazide carbonyl group (Fig. 1) [27]. The asymmetrical OCO band was observed at a lower value by about 40 cm⁻¹, while the symmetrical OCO band remains almost unaffected upon complexation. This behavior indicates coordination through the carboxylate oxygen without deprotonation. Negative shift of about 20-25 cm⁻¹ was observed in the hydrazide carbonyl group suggesting coordination of carbonyl oxygen of the hydrazide part [22]. The band due to the carbonyl group of phthalanilic part was nearly unaffected upon complexation and so suggesting no involvement of this group in coordination. This type of coordination was supported by the splitting of C-N bands, one with higher value of about 15 cm⁻¹ [28]. In addition the furan ring (C-O-C) stretching vibration was observed at a lower frequency value by about 30-35 cm⁻¹ indicating coordination through the furan ring oxygen atom [29]. For complexes formed in a basic medium the drastic decrease of carboxylate asymmetrical stretching band to about 1530 cm⁻¹ suggested the coordination of carboxylic group through deprotonation [30]. The disappearance of the band due to the hydrazide carbonyl group suggested coordination via deprotonation of the enolic group, as observed in similar systems [31]. The third and fourth coordination sites were occupied, as mentioned for neutral medium complexes through both nitrogen atom adjacent to hydrazide carbonyl and the furan ring oxygen atom (Fig. 2) as confirmed by the shift of their stretching bands to lower values by about 100 and 35 cm⁻ respectively.

For the complexes formed with zirconyl chloride in neutral medium (Fig. 3), the Zr=O stretching band was observed at 965 cm⁻¹ [32], while this band was absent in the spectrum of the complex formed in basic solution (Fig. 3) as a result of the formation of the $Zr(OH)_2$ moiety[33]. In the spectra of all complexes, new bands (not observed in the free ligand spectrum) were observed at

450 and 480 cm⁻¹ and assigned to M-O and M-N stretching modes respectively [34]. The coordination of the chloride ions in titanium complexes could not be observed from the infrared spectra since M-C1 band is located below the limits of the IR spectrophotometer. However, chloride ions coordination was deduced from conductance data given in Table 1.

Two characteristic UV-absorption bands were observed in the free ligand spectrum. The high intensity band appeared at about 310 nm is attributed to $\pi \rightarrow \pi^*$ transition of furan and benzenoid moieties. The second band of lower intensity located around 360 nm is assigned to $\pi \rightarrow \pi^*$ transition of azomethine and carbonyl group. In the UV spectra of the complexes both bands showed a red shift due to coordination with the metal ions. These observations further support the suggested coordination drawn from the IR spectra [35].

From the above discussion it is concluded that the ligand is tetradentate in neutral medium forming cationic complexes. On the other hand, in basic solution, the ligand acts as dibasic tetradentate formed neutral complexes. Thus. titanium (IV) formed hexacoordinated complexes (in both media) having octahedral structure. Zirconium nitrate formed octacoordinated complexes (in both media) most likely being square antiprism (as this geometry is the most common for such coordination number). Furthermore, zirconyl chloride formed in neutral medium pentacoodinated complex with square pyramidal being the most likely structure, while in basic medium hexacoordinated complex having an octahedral structure was observed. The structural models for all the complexes are given in Figures (1-3).



Fig. 1







Fig. 3

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الملخص

تضمن هذا البحث تحضير عدد من معقدات التيتانيوم والزركونيوم مع الليكاند من نوع حامض الفثالاتيليك، فورفورايل هيدرازيدو -أورثو -أسيتو حامض بنزويك (LH2، المخطط رقم 1)، وذلك بتفاعل رباعي نترات الزركونيوم وكلوريد الزركونيل مع الليكاند المذكور. تم الحصول على الليكاند من تفاعل هيدرازيد الفورفوريل مع أنهدريد الفثالاتيليك. وحضرت المعقدات في كل من الوسطين المتعادل والقاعدي، إذ نتج عن الوسط المتعادل معقدات أيونية موجبة ذات الصيغ، [Ti(LH2)Cl2]Cl و X(OO)[2(Cl(LH2)] و ZrO(LH2)] و ZrO(LH2)] ، في حين أعطى الوسط القاعدي معقدات متعادلة لها الصيغ، [Ti(L)Cl2] و Zr(LH2)[Cl). وتم تشخيص الليكاند ومعقداته بالتحليل الدقيق للعناصر وقياسات التوصيل الكهربائي وأطياف الأشعة تحت الحمراء وفوق البنفسجية.

وقد دلت التحاليل على أن الليكاند يسلك بشكل رباعي السن متعادل في الوسط المتعادل ورباعي السن ثنائي القاعدة في الوسط القاعدي. واتضح أن أيون التيتانيوم في هذه المعقدات يتخذ النتاسق السداسي ذو بنية ثماني السطوح، ويأخذ أيون الزركونيوم النتاسق الثماني ذو بنية معكوس الموشور المربع، الأكثر احتمالاً. من ناحية اخرى، اتضح أن لمعقد كلوريد الزركونيل الناتج عن الوسط المتعادل النتاسق الخماسي ذو بنية الهرم المربع الأكثر شيوعاً. في حين أظهر معقد كلوريد الزركونيل الناتج عن الوسط القاعدي التناسق السداسي ذو بنية المائعة.