

Mercury (II) and Silver (I) Complexes of 3-Phenyl-2-thiohydantoin

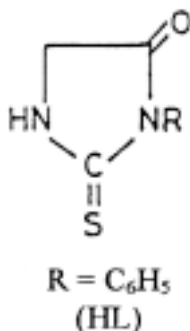
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ABSTRACT. Some metal complexes of 3-phenyl-2-thiohydantoin with Hg (II) and Ag (I) in neutral and basic media have been prepared. The isolated complexes were identified on the basis of analytical data, infrared, UV-visible and ¹H NMR spectra as well as mass spectra and molar conductivity measurements, and their structural evaluation was carried out. It was found that the ligand acts as monobasic or neutral monodentate S-coordinative agent towards the metal ions.

Introduction

Heterocyclic thiones have considerable coordination potential and their metal complexes have been used as analytical reagents^[1], in several industrial processes^[2-4], as metal corrosion inhibitors^[5], and as biologically active molecules^[6,7]. Most of the currently marketed antiarthritic drugs are gold (I) complexes containing S-donor ligands resembling heterocyclic thiones. Thiohydantoin and related compounds are used as analytical reagents for the determination of trace amounts of various metals^[8-10]. They have been used as anticonvulsant agents^[11] and some of them have been recommended for the treatment of tuberculosis and other infectious diseases. 3-Phenyl-2-thiohydantoin (HL) have been screened against selected bacteria and some of them were found to possess moderate to fairly good antibacterial activity^[12]. In many cases, coordination of these compounds to transition metal ions enhances their biological activity. Cobalt (II), nickel (II) and copper (II) complexes of some 2-thiohydantoin have been studied^[13,14]. Dioxouranium (VI) complexes of 5-substituted and 3-phenyl-2-thiohydantoin have been also reported^[15]. In view of these findings and owing to the scarcity of literature on the complexation of 3-

phenyl-2-thiohydantoin (3-phenyl-2-thioxo-4-imidazolidinone) and its derivative with metals, we describe here the synthesis and characterization of Hg (II) and Ag (I) complexes with 3-phenyl-2-thiohydantoin (HL).



Experimental

All the solvents and chemicals (Merck or B.D.H.) were used without further purification.

Preparation of 3-phenyl-2-thiohydantoin

A mixture of glycine (0.1 mol), phenylisothiocyanate (0.1 mol), and potassium hydroxide (10 g) was dissolved in glacial acetic acid (20 ml) and refluxed for ca. 2 hours. The reaction mixture was poured into cold water, solid was filtered off, washed with water and recrystallized from acetic acid. This method was described elsewhere^[14,15].

Preparation of the metal complexes

A hot solution of the metal salt (0.01 mol) (HgCl₂ or AgNO₃) in the minimum amount of water was added dropwise with continuous stirring to a solution of 3-phenyl-2-thiohydantoin (0.01 mol) in absolute ethanol or in an ethanolic solution of an equivalent amount of sodium acetate (0.10 mol). Sodium acetate was added to alkalyfy the solution. The resulting reaction mixture was gently refluxed for 30 min in a water bath. The reaction mixture was then left at room temperature for 3 hours. When the metal complexes precipitated, they were filtered, washed with little water and ethanol followed by ether and dried over P₄O₁₀.

Apparatus and physical measurements

Visible and ultraviolet spectra were determined in DMF with a Perkin-Elmer Lambda 4B UV-Visible spectrophotometer. The mass spectra were registered

on a Varian MAT 711 double focusing spectrometer equipped with a direct inlet system and operating at 70 eV electron beam energy. Infrared Spectra were measured with KBr discs on a model 408 Shimadzu spectrophotometer. Conductivity measurements in DMF were made at room temperature using a conductivity bridge Beckman model A18. Proton magnetic resonance in deuterated dimethylsulfoxide was taken on a Varian E.M. 390 NMR spectrophotometer. Chemical shifts are reported in δ ppm downfield from internal tetramethylsilane.

Results and Discussion

All the metal chelates are stable towards air and moisture. The reaction of silver (I) nitrate or mercury (II) chloride with 3-phenyl-2-thiohydantoin (HL) resulted in powder or microcrystalline complexes, insoluble in most common organic solvents but soluble in dimethylformamide and dimethylsulfoxide. Unfortunately, because of their insolubility in suitable solvents, growth of a good crystal for single crystal X-ray structural analysis could not be obtained. The recorded mass spectrum of the free ligand (3-phenyl-2-thiohydantoin) displays prominent molecular ion peak at $m/z = 192$ indicating the purity of the prepared free ligand. This spectrum shows a series of peaks corresponding to relatively low mass fragments which confirmed the free ligand structure. The mass spectrum of silver (I) complex displays a molecular ion peak at $m/z = 380$ which can be taken as an evidence for the formation of 1:1 metal:ligand stoichiometry for this chelate $[\text{HL-Ag}] \text{NO}_3 \cdot \text{H}_2\text{O}$ which was also confirmed by analytical results. The stoichiometric formula $[\text{HL-Hg}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ is suggested to Hg (II) complex prepared in ethanol while $[\text{L-Hg-Cl}] \cdot \text{H}_2\text{O}$ and $\text{Na}[\text{L-Ag-NO}_3] \cdot \text{H}_2\text{O}$ formulas are suggested for those isolated from the alkaline media. Analytical data are shown in Table 1. Molar conductance suggests the electrolytic nature for these chelates in DMF except complex 3 as shown in Table 1.

TABLE 1. Analytical and conductance data for the metal complexes.

No.	Complex	C% found (calcd)	H% found (calcd)	N% found (calcd)	S% found (calcd)	Λ $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
1	$[\text{HL-Ag}] \text{NO}_3 \cdot \text{H}_2\text{O}$	28.82 (28.42)	2.94 (2.63)	11.42 (11.05)	8.21 (8.42)	110.5
2	$[\text{HL-Hg}] \text{Cl}_2 \cdot \text{H}_2\text{O}$	22.61 (22.42)	2.18 (2.07)	8.91 (8.72)	6.42 (6.64)	160.2
3	$[\text{L-Hg-Cl}] \cdot \text{H}_2\text{O}$	24.52 (24.26)	2.21 (2.02)	9.61 (9.43)	7.25 (7.18)	–
4	$\text{Na} [\text{L-Ag-NO}_3] \cdot \text{H}_2\text{O}$	26.94 (26.87)	2.19 (2.23)	10.32 (10.45)	7.84 (7.96)	115.9

Infrared spectra

The appearance of a broad absorption band centered around 3500 cm^{-1} in the infrared spectra of all the resultant metal chelates indicates the presence of water molecules in these complexes. Since it is known that free water absorbs at 3520 and 3445 cm^{-1} while coordinated water absorbs around 3095 cm^{-1} ^[16], one can suggest that water molecules in the complexes prepared exist as molecules of crystallization. The infrared spectra of the complexes prepared in basic ethanol sodium acetate solution do not show any $\nu\text{N-H}$ stretching band nor a band due to $\nu\text{C} = \text{S}$ with simultaneous appearance of new bands at 1594 cm^{-1} and at $696\text{-}698\text{ cm}^{-1}$ assignable to $\nu\text{C} = \text{N}$ and $\nu\text{C} - \text{S}$ respectively. This indicates the deprotonation of the proton of the N-H group to form the thiol form of the ligand. In this case the free ligand is coordinated to the central metal ion as monoanion through thiol sulphur atom as monodentate ligand. This may be due to the fact that the basicity of the medium facilitates the deprotonation of the N-H moiety of the ligand. The infrared spectra of the complexes isolated from ethanol are identical to the spectrum of the free ligand with some difference in the position of the $\nu\text{C} = \text{S}$ bands which are shifted to lower frequencies (10 cm^{-1}). This indicates that the ligand reacts in the neutral thione form as a neutral monodentate ligand through the thiocarbonyl group. The spectra of complexes indicate $\nu\text{C} = \text{O}$ bands at the $1766\text{-}1765\text{ cm}^{-1}$ at nearly the same position as shown in spectrum of the free ligand. This result indicates that the $\text{C} = \text{O}$ group is not involved in the complex formation.

¹H NMR Spectra

The proton magnetic resonance spectrum of the free ligand (3-phenyl-2-thiohydantoin) displayed multiplet at 7.5 ppm and a broad singlet at 12.5 ppm corresponding to resonance resulting from the protons of the aromatic ring of phenyl group at position 3 and the proton of the N-H group respectively. The absence of a peak due to the N-H group in the ¹H NMR spectra of the metal complexes is considered as additional indication of the deprotonation of this group. This supports the above-mentioned infrared spectral data for the complexes isolated from the basic media.

Based on the foregoing discussion of this study, the free ligand (3-phenyl-2-thiohydantoin) behaves as a neutral or uninegative S-monodentate coordinative agent towards silver (I) and mercury (II) ions. Determination of the exact geometries for the metal complexes under study requires single crystal X-ray analysis.

Electronic Spectra

The complexes were found to be diamagnetic as expected for a d^{10} system. The electronic spectrum of 3-phenyl-2-thiohydantoin free ligand in DMF dis-

plays a sharp band at 270 nm. This band may be assigned to intraligand L-L* . The electronic spectra of Hg (II) complexes in DMF exhibit an intense band at 270 nm and two broad bands at 475-480 nm and 500-505 nm, while those of the Ag (I) complexes in DMF exhibit a sharp band at 265-270 nm and one broad band around 430-435 nm. The higher energy bands at 270 nm and 265-270 nm may be attributed to L-L* transition, while the other bands at the lower energy positions may be assigned to L-M transitions.

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متراكبات الزئبق الثنائي والفضة الأحادية مع

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المستخلص . تم تحضير متراكبات الزئبق الثنائي والفضة الأحادية مع ٣-فنيل-٢-ثيوهيديتوين في الوسط المتعادل وفي الوسط القاعدي وتم فصلها . وقد أجريت لهذه المتراكبات القياسات الفيزيوكيميائية للتعرف عليها ودراستها والتوصل إلى معرفة تركيبها الكيميائي . ومن هذه القياسات التحليل الدقيق للعناصر ، وقياسات أطيف الأشعة تحت الحمراء و المرئية وفوق البنفسجية ، وأطيف الكتلة ، والرنين النووي المغنطيسي ، بالإضافة إلى قياسات التوصيل الكهربائي المولاري . وقد دلت النتائج أن الليجند في هذه المتراكبات يتناسق مع أيون الفلز كليجند متعادل أو أحادي القاعدية وحيد الترابط من خلال ذرة الكبريت .