PALLADIUM COMPLEXES OF DI-2-THIENYLKETOXIME

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ABSTRACT

The reaction between di-2-thienylketoxime and the palladium (II) ion has been studied. The compounds prepared were the complexes dichlorobis(di-2-thienylketoxime-N,N')palladium (II), biaquobis(di-2-thienylketoxime-N,N')palladium (II) half hydrate, and polymeric forms of the chelate bis(di-2-thienylketoxime)palladium (II).

INTRODUCTION

A recent investigation of complex formation between bivalent palladium and 2-thienyltrans-aldoxime has illustrated the utility of a thiophene derivative as an analytical reagent (1). The purpose of the present work was to investigate complex formation between bivalent palladium and di-2-thienylketoxime.

A survey of the literature reveals a surprising lack of information regarding thiophene derivatives in complex formation with the transition metals. Although thenyltrifluoro-acetone has been used for the separation of zirconium and hafnium (2) and the stability constants of metal complexes of 2-thiophenecarboxylic acid have been measured (3) no other thiophene derivatives seem to have been studied.

Oximes in general form stable complexes with metals, particularly with those of the transition triads of the Periodic Table, and are widely used for the detection and estimation of those metals. Examples are salicylaldoxime (4) and benzylmethylglyoxime (5).

EXPERIMENTAL

Di-2-thienylketoxime

A solution of 11.2 g of di-2-thienylketone (6), 11.2 g of hydroxylamine hydrochloride, and 44 g of potassium hydroxide in 500 ml of alcohol was refluxed for 2 hours. The reaction mixture was poured into 1000 ml of water and made acid to litmus by the addition of hydrochloric acid. The precipitate was filtered under suction and dissolved in alcohol. Water was added until the solution became turbid. On cooling, colorless needles separated which were filtered under suction and air-dried. There was obtained 10.3 g, 86% yield, of white needles, m.p. 134–136°. Anal. Calc. for $C_9H_7NOS_2$: C, 51.63; H, 3.37; N, 6.69. Found: C, 51.56; H, 3.46; N, 6.55.

Dichlorobis(di-2-thienylketoxime-N,N')palladium (II)-Compound I

To a 400-ml beaker was added 1.0 g of di-2-thienylketoxime, 50 ml of alcohol, and 4.2 ml of concentrated hydrochloric acid. A solution of 0.40 g of anhydrous palladium (II) chloride in 5 ml of concentrated hydrochloric acid was prepared in a 100-ml beaker by warming on a hot plate. To the palladium (II) chloride solution was added 50 ml of water and the pH was adjusted to zero by dropwise addition of a concentrated potassium hydroxide solution. The palladium (II) chloride solution and 100 ml of 1 N hydrochloric acid were added with stirring to the oxime solution. After standing the solution for 1 hour the yellow precipitate was filtered under suction and air dried. There was obtained 1.30 g, 93% yield, of yellow crystals, m.p. 212–214° with decomp. Anal. Calc. for PdC₁₈H₁₄Cl₂N₂O₂S₄: Pd, 17.85; N, 4.70; Cl, 11.87. Found: Pd, 17.85; N, 4.58; Cl, 11.83.

On dissolving a few milligrams of I in 10 ml of alcohol and adding alcoholic silver nitrate, a clear solution was obtained which on standing for 3 hours became opalescent.

Regeneration of Di-2-thienylketoxime from I

To a 250-ml separatory funnel was added 0.3 g of I, 50 ml of acetone, 50 ml of chloroform, and 50 ml of concentrated hydrochloric acid. On shaking the mixture for 3 minutes, the solid went into solution and the chloroform layer became colored a pale yellow. The chloroform layer was withdrawn, washed first with a solution of 50 ml of acetone and 50 ml of concentrated hydrochloric acid, then four times with 50-ml portions of water, dried over anhydrous sodium sulphate, and filtered. On evaporation of the chloroform there was obtained a colorless, crystalline residue amounting to 0.22 g, 100% yield, m.p. 133–136°. A mixture melting

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point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133–136°.

Biaquobis(di-2-thienylketoxime-N,N')palladium (II) Half Hydrate-Compound II

To a 250-ml separatory funnel was added 1.33 g of 1, 50 ml of benzene, 50 ml of acetone, and 50 ml of water. The mixture was shaken for 10 minutes, at the end of which time all the solid had gone into solution to give a dark red-brown benzene layer. The benzene layer was washed with seventeen 50-ml portions of water and allowed to stand overnight. The yellow crystalline precipitate was filtered under suction and dried *in vacuo* over anhydrous calcium sulphate. The residue amounted to 0.80 g, 63% yield, m.p. 185–188° with decomp. Anal. Calc. for PdC₁₈H₁₄N₂O₂S₄.2¹/₂ H₂O: Pd, 18.73; H₂O, 7.93. Found: Pd, 18.77; H₂O, 8.06.

The above procedure was repeated with 0.7221 g of I. The combined water washings were titrated with 0.102 N NaOH using phenolphthalein as indicator. Calc. for $PdC_{18}H_{14}Cl_2N_2O_2S_4$: HCl, 12.18. Found: HCl, 12.14.

Regeneration of Di-2-thienylketoxime from II

The procedure used for the regeneration of the ketoxime from I was followed with 0.15 g of II. There was obtained 0.11 g, 93% yield, of a crystalline residue, m.p. 133–136°. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133–136°.

Bis(di-2-thienylketoxime)palladium (II) High Polymer—Compound III

On heating II at 120° for 3 hours, there was obtained a yellow-brown residue, m.p. 187–190° with decomp. Anal. Calc. for PdC₁₈H₁₂N₂O₂S₄: Pd, 20.35; N, 5.36. Found: Pd, 20.38; N, 5.46.

Ultraviolet absorption measurements in chloroform gave for III λ_{max} 288 m μ ; $E_{1 \text{ cm}}^{1\%}$ 547.

On dissolving III in boiling benzene and allowing the solvent to evaporate at 50° a brown residue was obtained. This material in chloroform gave an ultraviolet absorption spectrum identical with that obtained with IV; $\lambda_{max} 284 \text{ m}\mu$; $E_{1 \text{ cm}}^{1\%} 507$.

A cyroscopic molecular weight of III in nitrobenzene gave a value of 533. The calculated value for the monomer of IV is 523. Evaporation of the nitrobenzene on a steam bath under an air current gave a dark brown solid residue of IV.

A dipole moment measurement of III in carbon tetrachloride solution gave $\mu = 1.86$ D.

Regeneration of Di-2-thienylketoxime from III

The procedure used for the regeneration of the ketoxime from I was followed with 0.15 g of III. There was obtained 0.12 g, 100% yield, of a crystalline residue, m.p. 133–136°. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133–136°.

Bis(di-2-thienylketoxime)palladium (II) Low Polymer-Compound IV

To a 1-liter beaker was added 1.1 g of di-2-thienylketoxime, 5 ml of a saturated solution of potassium hydroxide, and 1500 ml of water. The pH of the solution was adjusted to 6.9 by the addition of hydrochloric acid. A solution of 0.4 g of palladium (II) chloride was prepared in 5 ml of concentrated hydrochloric acid with warming and diluted to 75 ml with water. The pH of the palladium (II) chloride solution was adjusted to 6.2 by the addition of potassium hydroxide solution and the solution diluted to 100 ml. To the boiling ketoxime solution was added alternately 2.0 ml of the palladium (II) chloride solution and 0.70 ml of 0.1024 N sodium hydroxide with vigorous stirring. When all the palladium (II) chloride had been added and a total of 35.0 ml of the solution and air dried. The dried residue was dissolved in benzene and filtered from a small amount of palladium (II) oxide. After evaporation of the benzene the residue was suspended in alcohol overnight to remove any unreacted ketoxime. The suspended chelate was filtered under suction and air dried 0.75 g of IV, m.p. 175–185° with decomp. Anal. Calc. for PdC₁₈H₁₂N₂O₂S₄: Pd, 20.35; N, 5.36. Found: Pd, 20.39; N, 5.44.

Ultraviolet absorption measurements of IV in chloroform gave $\lambda_{\text{max}} 284 \text{ m}\mu$; $E_{1 \text{ cm}}^{1\%} 509$.

A dipole moment measurement of IV in carbon tetrachloride gave $\mu = 2.60$ D.

A cyroscopic molecular weight determination of IV in nitrobenzene gave a value of 519. The calculated value for the monomer is 523. A similar determination in benzene gave a value of 1290. On standing, the cold benzene solution deposited yellow-brown crystals of III, m.p. 185–190° with decomp. The value 1290 corresponds to an average degree of polymerization of 2.5 for IV.

Regeneration of Di-2-thienylketoxime from IV

The procedure used for the regeneration of the ketoxime from I was followed with 0.15 g of IV. There was obtained 0.07 g, 60% yield, of a crystalline residue, m.p. 133–136°. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression, mixture m.p. 133–136°.

DISCUSSION

In the present work di-2-thienylketoxime was found to form either a complex or a chelate with bivalent palladium, depending on the pH of the reaction medium. In 2 N

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hydrochloric acid a small amount of the complex (I) formed and the major part of the reagent was recovered. In 1 N acid solution an almost quantitative yield of the complex (I) was obtained, while in neutral or slightly basic solution there was a good yield of the chelate (IV). In moderately acid solution in the pH range 1 to 6, mixtures of I and IV formed.

The complex (I) is a pale yellow crystalline solid insoluble in water and slightly soluble in benzene and chloroform, while the chelate (IV) is a dark brown solid insoluble in water and very soluble in benzene and chloroform, giving dark red-brown solutions.

When the complex (I) was treated with a mixture of benzene and water, hydrogen chloride was eliminated quantitatively as was shown by titration of the water layer with standard base. On standing, the benzene layer deposited a yellow crystalline solid which at $120^{\circ} \text{ lost } 2\frac{1}{2}$ moles of water to give a light brown solid (III) insoluble in water and slightly soluble in benzene and chloroform.

In alcoholic silver nitrate solution I gave no immediate precipitate, but on standing, the solution became turbid and silver chloride began to precipitate. This indicates that the chlorine atoms are bound covalently to the palladium. Analysis of I showed that two molecules of the ketoxime and two atoms of chlorine are associated with each palladium atom. Palladium therefore has a coordination number of four. This is to be expected since the existence of palladium (II) compounds with a coordination number greater than four has never been convincingly demonstrated (7). Although there is no experimental evidence to indicate whether coordination is with the nitrogen of the oxime group rather than with the sulphur of the thiophene ring, nevertheless the coordinating ability of the oxime group and the very strong donor properties of the oxime nitrogen are very well known (8). Further, one would expect the donor ability of the sulphur to be decreased because of resonance with the unsaturated ring.

Magnetic susceptibility measurements showed I and II to be diamagnetic. The complex (I) therefore is considered to be planar rather than tetrahedral. This is in accord with the fact that no tetrahedral structure for palladium (II) complexes has yet been identified positively, unless, of course, it is sterically impossible for the compound to assume a planar configuration. Also coordination theory predicts a planar configuration for ions such as bivalent palladium which have one d-orbital available for bond formation. In such a situation dsp^2 hybridization occurs and a square planar structure results.

The postulated hydrogen bonding for I eliminates the possibility of cis-trans isomerism. Such bonding would give rise to a more stable structure, since it has been long observed that an increase in the number of rings within a particular complex structure results in greater stability (9). Such a postulated bonding has precedent in the literature. For example, Brady and Meurs (10) proposed such bonding in their study of the nickel derivatives of biacetyl dioxime. That the complex (I) exists in the trans form is borne out by the facile elimination of hydrogen chloride. The ease of such elimination indicates that the hydrogen and chlorine atoms are adjacent to each other, whereas a cis configuration would place them on opposite sides of the molecule. Further molecular models reveal that a cis configuration would be more strained than a trans configuration. Infrared spectra of I indicate hydrogen bonding. Such spectra reveal no hydroxyl band present in the region 3400–3700 cm⁻¹, but do show a very broad band at 3100 cm⁻¹. Thus, the hydroxyl group band has been shifted considerably to a lower frequency. Such a shift is considered evidence for strong intramolecular bonding.

The structure shown for the hydrate (II) is based on the analysis and the course of the reaction used in its preparation. Thus, on shaking I in a mixture of benzene and water

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the benzene layer becomes colored a dark red-brown and hydrogen chloride is produced in the water layer. The color of the benzene layer indicates that a chelate has formed. On standing, the color disappears and a yellow crystalline precipitate forms. This is interpreted as being due to a displacement of the palladium–sulphur bond in the chelate with formation of a complex in which water molecules are coordinately bonded to palladium. Molecular models reveal that the two water molecules must be trans since a cis configuration would impart a large strain. The remaining one-half water molecule is considered to be involved in crystal formation.

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The structure assigned to III is based on the analysis and on molecular weight determinations of III and IV. Thus IV in freezing benzene gave a molecular weight corresponding to that of a low polymer of IV, the average degree of polymerization being 2.5. On standing, the cold benzene solution deposited a yellow-brown solid with the same melting point as III. Thus IV is converted to III from cold benzene solution. This indicates that III is a polymer of IV. No direct molecular weight determination of III could be carried out in benzene owing to its insolubility in this solvent. On suspending III in boiling benzene and allowing the solvent to evaporate at 50° IV was obtained. Thus in hot benzene III is reconverted to IV. In freezing nitrobenzene III gave a molecular weight corresponding to that of a monomer of IV. On evaporation of the nitrobenzene a dark brown residue of IV was obtained. Substance III is thus converted to a low polymer of IV from warm nitrobenzene.

The analyses of III and IV showed these substances to be isomeric. That III and IV are not simply dimorphic is borne out by an examination of their ultraviolet absorption spectra in chloroform solution. Small, but definite, differences in their spectra were found.

The possibility of III and IV being cis-trans isomers was eliminated by dipole moment measurements in carbon tetrachloride solution. The moments of III and IV were 1.8 and 2.6 D respectively. If IV were a cis isomer the dipole moment would be expected to be much higher. Also a cis configuration for IV would mean that the two negatively charged oxygens of the nitrone groups would be adjacent to one another. It is highly unlikely that such a separation of like charges would take place since the resulting compound would be highly unstable.

The assignment of the chelate structure to IV is based on the analysis and on its solubility in benzene or chloroform to give highly colored solutions. Molecular weight determination in benzene indicates that IV is a low polymer of the structure shown. Similar determination in nitrobenzene reveals IV as the monomer in this solvent. That the structure contains two nitrone groups is inferred by reference to the studies made by Pfeiffer (11) on the nickel dimethylglyoxime chelate. In this case the author showed that a covalent linkage exists between nitrogen and the metal rather than between oxygen and the metal.

Finally, that the ketoxime reagent undergoes no change in structure is shown by the fact that it could be readily regenerated in high yield from each of I, II, III, and IV by treatment with strong hydrochloric acid solution.

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