

SYNTHESIS AND CHARACTERIZATION OF THE HEAVY METALS; AU (III) ,Pd (II),Pt(IV) Rh(III) COMPLEXES OF S – PROPYNYL 2 –THIOBENZIMIDAZOLE

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Date of acceptance 11/2/2007

ABSTRACT:

Complexes of Au(III) ,Pd (II) , Pt (IV) and Rh(III) with S – propynyle -2-thiobenzimidazole (BENZA) have been prepared and characterized by IR and UV-Visible spectral methods in addition to magnetic and conductivity measurements and micro – elemental analysis (CHN).The probable structures of the new complexes have been suggested.

INTRODUCTION:

The aromatic benzimidazole (BNZ) nucleus form ,an important class of biologically active compounds with a variety of pharmacological actions. Benzimidazole and especially 3 –thio derivatives do belong mainly for their activity to the systemically active class of antibacterial agent (1) .Some derivatives ,however show a broad spectrum of activity to be as fungicides ,acaricides and nematocides as well (2).

BNZ compounds and their derivatives were used also in rubber industry to improve its efficiency and increase its durability (3,4).It was found that when it used with the α –olefine polymer it inhibited the degradation of the later ,when it exposed to the UV light (5).Therefore it is regarded as a stabilizer for the polymer. Its heavy salts with silver and lead were used in printing field ,and as stabilizers in photographic films(6,7) . They were used also in agriculture ,where they increase the growth activity activity (8).

BNZ compounds containing acetylenic moieties show awide range of biological activities of which are antimicrobial ,germicidal and disinfectant (9-11) .Moreover the interaction of the unsaturated compounds especially allylic have been

Studie with some transition metals (12). Impotents of metal complexes have been also established and some of them were found to possess biological activity.Some drugs have increased activity when administrated as metal complexes ,this attributed to the synergetic effect between the metal and the ligand (10,13).

EXPERMINTAL:

A : Chemicals and Appartus

All chemicals used were of high purity available from Fluka Company. Melting points were recorded uncorrected on Gallen Visual melting point apparatus. I.R.spectra were obtained using Pye–Unicam spectrophotometer in the range 4000 - 200 cm^{-1} ,U. V.-Vis. spectra were obtained using Pye–unicam 8700 series UV/Vis, spectrophotometer .Microanalytical data (CHN) were obtained using Perkin – Elmer 240 B elemental analyzer ,Magnetic susceptibility measurements were done using Bruker magnet BM6 .Conducativity measurements were obtained utilizing PW9527 Digital conductivity Philips apparatus.

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B:Methods of Preparation**1. Preparation of BNZA**

The BNZA was prepared according to the literature methods (14), starting from 2-hydroxy aniline. Crystals were obtained with a melting point 52°C.

2. Preparation of the BNZA**Metal Complexes****a. [Au₂(BNZA)Cl₄](AuCl₄)₂ (I)**

To a hot stirred solution of BNZA (2 mmole) in ethanol (50ml), (1.0mmole) of chloroauric acid dissolved in 30ml ethanol was added, the mixture was refluxed for one hour, then cooled to room temperature. Brown precipitate was filtered and washed two to three times with ethanol and dried under vacuum. It was identified and characterized by elemental analysis, I.R., UV-Vis, magnetic susceptibility and conductivity measurements. The results are shown in table(1)

b. [Pd(BNZA)Cl₂].C₂H₅OH(II)

0.208 mmole of dichloro bis(benzonitrile) palladium (II) (dissolved in 10ml ethanol), was added to 0.45mmole of BNZA (dissolved in 20ml of the same solvent). The mixture was stirred for 30min at room temperature and kept for one day at room temperature, an orange-brown precipitate was formed, which was separated by filtration and washed several times with little amount of ethanol, then dried under vacuum. The formation complex was studied by the same way as for complex(1) above.

c. [Pt (BNZA)₂ Cl₂]Cl₂.H₂O(III)

The platinum (IV) complex was prepared by the reaction of the potassium hexachloroplatinate (IV) with BENZA in (1:2) mole ratio, using (1:1) acetone /water mixture as a solvent, at room temperature. The product was washed with water and little acetone after filtration and drying under vacuum, it was identified by the same techniques described as above.

d. [Rh(BNZA)₂] Cl₃ . 2H₂O (IV)

The reaction of Rhodium trichloride hydrate (0.2635g, 1) mmole with BNZA (0.406 g, 2mmole) in a hot ethanol-water mixture yielded an orange precipitate, moderately soluble in ethanol, +water and sparingly soluble in benzene. It was characterized by the same techniques used for complexes (mentioned before).

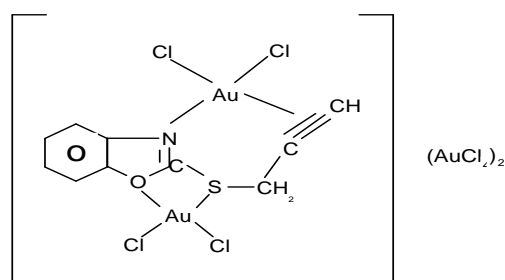
RESULTS AND DISCUSSION

Stable complexes were isolated in all cases. Based on the micro analytical data, the general formula of the complexes can be suggested as [M(BNZA)_xCl_y]Cl_z.X, where M= Pt and Pd ions x = 1,2, y = 1,2, z = 0,2 and X=H₂O or C₂H₅OH respectively. When M = Au or Rh ions; x = 1,2, y = 0,4, z = 0,3 and X = 2AuCl₄, 2H₂O respectively.

BNZA is a potential ligand which may coordinate through either the acetylenic or thioamide moieties or both. BNZA has the ability to form organometallic complexes by coordination through the acetylenic group with a number of metal ions (12), therefore it is expected that I.R. measurements are highly informative with respect to the complexation behavior with various metal ions. The characteristic frequencies of the free ligand and its metal complexes were readily assigned based on comparison with literature references (11, 15). The vibrational frequency corresponding to the $\nu_{C \equiv C}$ was clearly characterized and is of basic importance. The spectra of all complexes showed similar behavior where a red shift by $\sim 570 \text{ cm}^{-1}$ took place, which indicates a strong π -bonding between the metal and acetylenic group (16, 17). In addition the stretching frequency of the terminal C-H bond was noticed unchanged in the spectra of all complexes, Table (2), which further indicates a π -bonding (15).

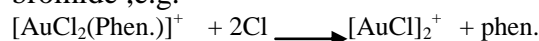
The spectrum of Au (III) complex shows the appearance of the band belonging to the $\nu \text{C} \equiv \text{C}$, with a change in the shape of the band of 1540 cm^{-1} , where it appeared at the same position, so a strong π – coordination can be suggested between gold atom the acetylenic bond. It can be also concluded that the sulfur atom coordinates with the gold ion because of the shift of the $\nu \text{C} - \text{S}$ to lower frequency by 15 cm^{-1} , and the shift of the thioamide band (II) to higher frequency in addition to the appearance of $\nu \text{Au} - \text{S}$ band at 410 cm^{-1} . The N – atom also coordinates with gold due to the appearance of a band at 510 cm^{-1} . The presence of two bands at 290 and 356 cm^{-1} indicate the coordination of chloride with gold, as seen in table (2).

When chloroauric acid was treated with BNZA, a brown product was formed, insoluble in dichloromethane and acetone, moderately soluble in DMSO. According to the results of elemental analysis, i.r., UV- Vis., and conductivity measurements the following formula may be assigned.



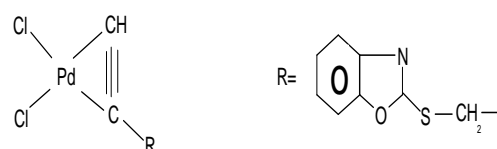
This formula reflects the following facts about the complex behavior (a) its appreciable conductance, (b) square geometry about gold, (c) noticeably low percentage of C, H and N and (d) the behavior of gold (III) as soft acid. The tendency of Au(III) to N and O donors in addition to acetylenic group as donors ligands leads to the conclusion that (a) not all the chlorides of AuCl_4^- are displaced by the ligand in most cases, (b) the coordination ligand, even when behaves as bidentate like 2,2- bipyridyl

(18), are readily replaced by chloride or bromide, e.g.



Many Au(III) complexes with N, O and S donor chelate ligands were synthetic (19). Gold (III) forms complexes with soft ligand, e.g. S, Se, I and CN, which are more stable than those with O – or N – donor ligands and both O and S donor sites the S atom is always preferred by Au (III) center, also octahedral geometry could be obtained for soft ligands e.g. the tetragonally distorted octahedral trans $[\text{Au}_2(\text{diars})_2]^+ \text{I}^-$ (20). In the present case Au (III) coordinates to N, O, S and acetylenic group of BNZA and it seems that an equilibrium exists for the complexation reaction, this is evident by the presence of AuCl_4^- anion in the present structure, also only two chloride was displaced by BNZA.

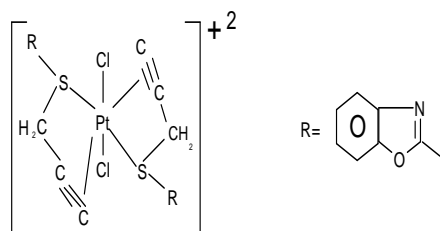
In the case of Pd(II) complex a shift of the stretching vibration of the triple bond took place by 390 cm^{-1} toward lower region, which refers to the strong coordination of the π – bond with the Pd (II) ion. This is more indicated by the presence of terminal CH bond stretching at 3300 cm^{-1} . A new strong band appeared at 340 cm^{-1} which indicates the formation of Pd – Cl bond. In addition another weak band was noticed at 235 cm^{-1} . Both are characterized as belonging to asymmetric and symmetric frequencies of two chloride atoms coordinating in a cis – position (15). No changes in the positions of thioamide bands were noticed. This may show that the ring atoms are not participating in coordination with the atom. In addition, a new band at 415 cm^{-1} was detected which belongs to Pd – bond. Therefore the following structural formula can be suggested:



The spectrum of Pt(IV) complex show

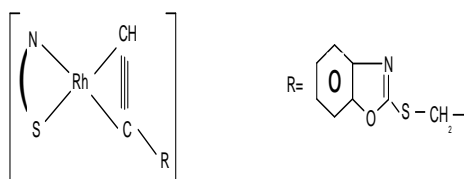
the $\nu \text{C} \equiv \text{C}$ to be shifted by 380 cm^{-1} toward lower frequency, which indicates the coordination of the metal through π -bond with the ligand. This is more indicated by the presence of the acetylenic νCH of 3300 cm^{-1} . Also the position of the C-S band absorption was shifted by 20 cm^{-1} and the appearance of Pt-S absorption band at 440 cm^{-1} . This indicates the coordination of Pt(IV) with the sulfur atom of BNZA.

This bonding behavior of Pt(IV) and S is expected, due to the softness of both atoms, the strong band appeared at 330 cm^{-1} which refers to the coordination of two chlorides at trans-position (15), Table (2). According to this, the following structural formula can be suggested:



The thioamide band (II) was shifted to higher frequency by 35 cm^{-1} in the spectrum of Rh (III) complex, which indicates the bonding of the N-atom of the SCN moiety with the metal ion. Also Rh-N bond stretching appeared at 503 cm^{-1} , and another one at 420 cm^{-1} which belongs to Rh-S bond.

The disappearance of the band belonging to $\nu \text{C} \equiv \text{C}$ and the appearance of a new one at 1680 cm^{-1} indicates the coordination of Rh with BNZA through π -system, which is further indicated by presence of νCH band at 3300 cm^{-1} , Table (2), therefore, the following structure can be suggested:

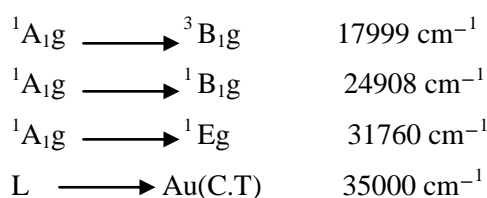


The broad bands at ~ 3400 - 3350 cm^{-1} and at 1610 cm^{-1} in the case of Pt (IV)

and Rh (III) complexes indicate the presence of water in the crystal lattice.

UV-vis Spectroscopy, conductivity and magnetic susceptibility measurements

Little information is available about the electronic spectra of the square planar gold complexes, and a reference to PdCl_4^{2-} ion is made because the later is a good example of the absorption behavior of the d^8 square planar environment. On comparison of the spectra of this ion and that of the new gold complex which was obtained from its ethanolic solution, a number of absorption bands have been assigned, which came in good accordance between the two spectra, and as follows (21):

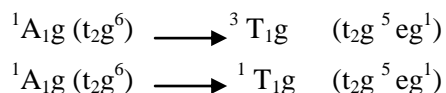


Therefore square planar geometry can be suggested for the Au (III) complex. Also the value of magnetic moment for the prepared complex was diamagnetic and the data of electrical conductivity measurements in DMSO solvent ($95 \mu\text{s} \cdot \text{cm}^{-1}$) agree with the suggested formula to be ionic.

The spectrum of the palladium complex shows absorption bands at 22988 cm^{-1} belonging to the $^1\text{A}_{1g} \longrightarrow ^1\text{B}_{1g}$ transition, which is equal to the $10 Dq$ and an other band at 27777 cm^{-1} which corresponds to the $^1\text{A}_{1g} \longrightarrow ^1\text{E}_g$ transition. Therefore square planar geometry can be assigned for the structure (22). This geometry is common for Pd (II) complexes, due to the effect of the large size of the ion on its ligand field strength, which is greater than the pairing energy (7, 23). The value of magnetic moment for the prepared complex was (0.75) B.M, which indicates the diamagnetic nature of the complex.

The electric conducted measurement in DMSO agreed with the suggested formula to be non-conducting Table, (3).

The electronic spectrums of the platinum (IV) shows two bands, the first weak one appeared as a shoulder at 21739 cm^{-1} , the second band appeared at 27322 cm^{-1} with higher intensity. These two bands can be assigned to the following transition in octahedral environment (21):



This coordination type is common for Pt (IV) complexes (21,22), study of conductivity behavior in DMSO shows the complex to be ionic $(105)\mu\text{cm}^{-1}$. The magnetic measurements data is 1.02 B.M shows which the complex to be diamagnetic.

The UV-Vis. spectrum of Rh(III) complex showed a main strong band at 34.200 cm^{-1} and two shoulders at 30.200 and 25.300 cm^{-1} . The tetrahedral geometry was excluded because no bands appeared below 20.000 cm^{-1} (21), therefore a spinpaired square planar configuration may be assigned to the complex in a monomeric state as suggested by the ready solubility in benzene, this geometry was converted to distorted octahedral due to the coordination of

two DMSO molecules as the complexes was dissolved in DMSO. Conductivity measurement in DMSO show the complex to be conducting, therefore the chloride is not considered to be coordinated with the metal and is located outside the coordination sphere.

The distinction between ligand field and charge transfer bands cannot be made sharply, due to mixing of the ligand orbital with the metal orbitals. Therefore, the ligand field bands cannot be easily identified in the spectra of spin-paired square planar complexes (22,23). Nevertheless and by referring to the available data for low spin d6 ions, i.e. Co^{+3} , Rh^{+3} and Ir^{+3} , published in the literature (22), the band at 25.300 cm^{-1} can be assigned to the transition $a_{1g} \longrightarrow b_{1g}$ which can be taken as the $10Dq$ value. The measured effective magnetic moment was (0.89) B.M. of diamagnetic behavior. The electric conductivity measurements show the complex to be conducting $(130)\mu\text{cm}^{-1}$, Table (3).

Table (1): Physical data for the metal complexes.

| Compounds | color | Reaction Solvent | Recrystal. Solvent | Melting Point $^{\circ}\text{C}$ | % yield | Microanalytical data Found(calc.) | | |
|---|-------------|---|------------------------------------|----------------------------------|---------|-----------------------------------|------------------|------------------|
| | | | | | | C% | H% | N% |
| [Au ₂ (BNZA)Cl ₄].2AuCl ₄ I | Brown | EtOH | EtOH | 119 _D | 35 | 10.80 (11.23) | 0.430 (0.655) | 1.08 (1.31) |
| [Pd(BNZA)Cl ₂].C ₂ H ₅ OH II | Light brown | EtOH | EtOH | 70 | 40 | 33.03 (34.99) | 3.010 (3.159) | 3.520 (3.402) |
| [Pt(BNZA) ₂ Cl ₂].Cl ₂ .H ₂ O III | Yellow | (CH ₃) ₂ CO/H ₂ O | (CH ₃) ₂ CO | 110 _D | 46 | 33.10 (32.78) | 2.10 (2.18) | 3.950 (3.825) |
| [Rh(BNZA) ₂ Cl ₃].2H ₂ O IV | Orange | EtOH/H ₂ O | EtOH | 87 | 32 | 46.10 (46.46) | 3.40 (2.71) | 5.37 (5.42) |

Table (2): selected I.R bands of S-propynyl -2 -thiobenzimidazole and its metal complexes

| Compounds | Thioamide(II) | Thioamide(IV) | $\nu_{\text{C}=\text{C}}$ | $\nu_{\text{C}=\text{CIII}}$ | $\nu_{\text{C}=\text{CIII}}$ | $\nu_{\text{M}-\text{N}}$ | $\nu_{\text{M}-\text{C}}$ | $\nu_{\text{M}-\text{S}}$ | $\nu_{\text{M}-\text{O}}$ | $\nu_{\text{M}-\text{Cl}}$ |
|-----------|---|---------------------------|---------------------------|------------------------------|------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|----------------------------|
| | $\nu_{\text{C}-\text{N}-\text{C}-\text{S}}$ | $\nu_{\text{C}-\text{S}}$ | | | | | | | | |
| BNZA | 1275 w | 770 s | 2100m | 3300w | 620w | - | - | - | - | - |
| I | 1295 m | 760 s | 1540 s | 3300 w | 620 w | 510 | 420w | 470w | - | 295 356 |
| II | 1275m | 770m | 1710s | 3300w | 620w | - | 415 | - | - | 340 325 |
| III | 1275m | 740m | 1720s | 3300 | 620 | - | 415 | 440 | - | 330 |
| IV | 1305m | 760m | 1680s | 3300 | 620 | 503 | 415 | 420 | - | - |

Table (3): Electronic spectral data of BNZA complexes and their probable assignments, and magnetic moments.

| Compands | Bands ,cm ⁻¹ | Assignment | μ_{eff} (B.M.) |
|----------|-------------------------|---------------------------------|------------------------------|
| I | 17999 | $^1A_{1g} \rightarrow ^3B_{1g}$ | 0.0 |
| | 24908 | $^1A_{1g} \rightarrow ^1B_{1g}$ | |
| | 31760 | $^1A_{1g} \rightarrow ^1E_g$ | |
| | 35000 | L \rightarrow A u(C.T) | |
| II | 22988 | $^1A_{1g} \rightarrow ^1B_{1g}$ | 0.75 |
| | 27777 | $^1A_{1g} \rightarrow ^1E_g$ | |
| II | 21739 | $^1A_{1g} \rightarrow ^3T_{1g}$ | 1.02 |
| | 27322 | $^1A_{1g} \rightarrow ^1T_{1g}$ | |
| IV | 34.350 | | 0.89 |
| | 30.200 & 25300 | | |

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**تحضير وتشخيص بعض معقدات العناصر الثقيلة
الذهب (III) البلاديوم (II) البلاتين (IV) والراديوم (III) مع الليكاند ثايوبروبانيل
2- ثايوبنزاميدازول**

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الخلاصة:

تم في هذا البحث تحضير معقدات الذهب (III) والبلاديوم (II) والبلاتين (IV) والراديوم (III) مع الليكاند ثايوبروبانيل 2- ثايوبنزاميدازول وتشخيصها بطرائق التحليل الدقيق للعناصر والطرق الطيفية ، الاشعة تحت الحمراء والاشعة فوق البنفسجية – المرئية بالاضافة الى القياسات الحساسية المغناطيسية والتوصيلية الكهربائية وتم اقتراح التراكيب المحتملة للمعقدات المحضرة الجديدة.