

SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES OF 2-THIOACETIC ACID BENZOTHAZOLE LIGAND

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Abstract

New metal complexes of the ligand 2-thioacetic acid benzothiazole with the metal ions Fe(III), Rh(III), Pd(II), Pt(IV) and Au(III) were prepared in alcoholic medium. The prepared complexes were characterized by FTIR Spectroscopy, electronic spectroscopy, elemental analysis, ^1H NMR, ^{13}C NMR, magnetic susceptibility and conductivity measurements. Molar ratio and continuous variation studies in solution gave comparable result with those obtained from solid state study. From the spectral measurements, monomer structures for the complexes were proposed.

Keywords: thioacetic acid benzothiazole; metal complexes.

Introduction

Increasing physiological importance of oxygen donor organic compounds and active role played by coordination certain metal ions to them have interested use in synthesizing and studying structural aspects of metal complexes with some oxygen, sulphur and nitrogen donor ligands[1-3]. The aromatic benzothiazole nucleus is associated with a variety of antihistamine activity, pharmacological actions such as fungicidal and leishmanicides activities [4-7]. These activities are probably due to the presence of the $-\text{N}=\text{C}-\text{S}$ group. Substituted benzothiazole have been reported to display diverse applications as photostabilizer and metal complexing agents [8-10].

The wide range of application of the ligand and its metal complexes aroused our interest to prepare a new series of some metal complexes.

Experimental

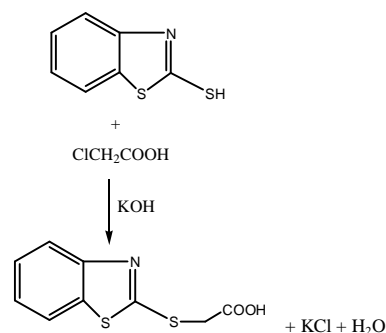
Chemicals:

All chemicals and reagents were of reagent-grade quality. The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent.

Synthesis of 2-thioacetic acid benzothiazole

A mixture of 2-mercapto benzothiazole (0.1 mole) and chloroacetic acid(0.1 mole) in presence of KOH as a basic media was refluxed for 3 hours to give 2-thioacetic benzothiazole (HL), then dilute HCl was

added to give a white yellow precipitate which was filtered and crystallized from ethanol to give the final product. The steps of the synthesis of 2-thioacetic acid benzothiazole are shown below:



Preparation of Complexes (C₁-C₅)

Ethanol solutions of the suitable metal salts [$\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot \text{XH}_2\text{O}$, $\text{PdCl}_2(\text{PhCN})_2$, $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot \text{H}_2\text{O}$] was added to an ethanolic solution of 2-thioacetic acid benzothiazole in 1:2 (metal : ligand) molar ratios and refluxed for half an hour, crystalline colored precipitates was formed at room temperature. The resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50°C for half hour. Table (1) shows the melting points of the prepared complexes.

Instrumentation

Elemental C, H, N and S analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000-200) cm^{-1} were recorded as CsI discs on FTIR.8300 Shimadzu spectrophotometer, UV-visible spectra were measured using Shimadzu UV-vis. 160 A-Ultra-violet spectrophotometer in the range (200-1000) nm. The magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility Balance of Bruke Magnet B.M.6, Atomic absorption measurements of the prepared complexes were obtained using Shimadzu 680cc-flame. The ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a jeol 400 MHz

spectrometer in DMSO, relative to the internal standard tetramethylsilane (TMS). Melting points were recorded on a hot stage Gallen Kamp melting point apparatus.

Results and Discussion

Melting points and elemental analysis of all the compounds studied are tabulated in Table (1). The data of CHNS and metal analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values.

Table (1)
Physical data for preparation ligand and the complexes.

Symbol	Melting point $^{\circ}\text{C}$	Color	Found (Calcd.)%					Suggested formula
			C	H	N	S	M	
HL	177-179	Yellow	47.88 (48.00)	3.00 (3.11)	6.12 (6.22)	28.57 (28.44)	-	$\text{C}_9\text{H}_7\text{NO}_2\text{S}_2$
C1	200	Brown	36.34 (36.40)	2.22 (2.36)	4.55 (4.72)	21.66 (21.57)	9.22 (9.41)	$[\text{Fe}(\text{L})_2\text{ClH}_2\text{O}]2\text{H}_2\text{O}$
C2	198-200	Deep Orange	35.55 (35.74)	2.30 (2.31)	4.64 (4.63)	21.16 (21.18)	16.88 (17.02)	$[\text{Rh}(\text{L})_2]\text{Cl}\cdot\text{H}_2\text{O}$
C3	208-212	Brownish-red	28.06 (28.12)	1.90 (1.82)	3.55 (3.65)	16.60 (16.66)	25.23 (25.39)	$[\text{Pt}(\text{L})_2\text{Cl}_2]\cdot 3\text{H}_2\text{O}$
C4	195	Brown	37.22 (37.73)	2.20 (2.44)	4.75 (4.89)	22.29 (22.36)	18.77 (18.59)	$[\text{Pd}(\text{L})_2]\text{H}_2\text{O}$
C5	212	Pale Yellow	30.80 (30.92)	1.88 (2.00)	4.08 (4.00)	18.24 (18.32)	27.97 (28.20)	$[\text{Au}(\text{L})_2]\text{Cl}\cdot\text{H}_2\text{O}$

Infra-Red Spectroscopy

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3435, 1633, 1351, 1606, 1573 and 694 cm^{-1} assigned to hydroxyl, carbonyl $\nu(\text{COO})$ asym., $\nu(\text{COO})$ sym., C=N of the thiazole ring and the stretching of C-S group respectively. The COO stretching vibrations are important to predict the bonding mode of the ligand. The values of $\Delta\nu$ [$\Delta\nu = \nu$ asym.(COO)- ν sym.(COO)] can be divided into three groups; (a) In compounds where $\Delta\nu(\text{COO}) > 350 \text{ cm}^{-1}$

the carboxylate group binds in a monodentate fashion. However, other very weak intra- and intermolecular interactions cannot be excluded. (b) When $\Delta\nu(\text{COO}) < 200 \text{ cm}^{-1}$, the carboxylate groups of these compounds can be considered to be bidentate. (c) In compounds where $\Delta\nu(\text{COO}) > 200 \text{ cm}^{-1}$ and $< 350 \text{ cm}^{-1}$ an intermediate state between monodentate and bidentate (anisobidentate) occurs. It has also been suggested that the $\Delta\nu(\text{COO})$ value in

the chelating mode is less than the $\Delta\nu$ (COO) in a bridging mode.

The disappearance of the hydrogen from hydroxyl group on complexation indicate that the complexation is through the oxygen atom.

Stretching of metal-oxygen bands of the complexes appeared in low frequency region (497-472) cm^{-1} [11]. The IR data of the ligand and complexes are shown in Table (2).

Table (2)
Characteristic absorption bands of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole and its complexes.

Compound	$\nu(\text{O-H})$	$\nu(\text{COO})$ asym	$\nu(\text{COO})$ sym
HL	3435	1633	1351
C1	-	1588	1351
C2	-	1578	1346
C3	-	1592	1352
C4	-	1587	1354
C5	-	1599	1344

Ultraviolet-Visible Spectroscopy

The ultraviolet visible electronic spectrum of the 2-thioacetic acid benzothiazole (HL) in DMF solvent is recorded and shown in Table (3). Bands at the wavelengths (35461, 33222 and 30488 cm^{-1}) this transition may be attributed to $\pi \rightarrow \pi^*$ electronic transition. The electronic spectra of 2-thioacetic acid benzothiazole complexes showed, as expected, different absorptions from that of the free ligand, these bands were shifted to different wavelength than the corresponding bands in the ligand as shown in Table (3), which appeared in the wavelength range between 35714 to 26247 cm^{-1} . The solution spectrum of (C₁) complex shows three bands [12]. Electronic spectrum of the deep orange (C₂) complex in DMF solution, showed two shoulders at 23200 cm^{-1} and 26333 cm^{-1} . The octahedral geometry was excluded because the spectrum showed no band below 20000 cm^{-1} , this suggests a square planar geometry for C₂ [13]. The distinction between ligand field and charge transfer band can not be made sharply due to mixing of the ligand orbital with the metal orbital, therefore the ligand field bands can not be identified easily in the spectra of spin-paired square planar complexes, which agree with the available data for low spin d^6 ions, i.e., Co(III), Rh(III) and Ir(III). The solution spectrum of (C₃) complex showed three absorption bands, Table (3). The

spectrum was a typical of square planar Pd(II) complexes. The electronic spectrum of (C₄) shows three bands The spectrum of the complex (C₅) gave four absorption bands as shown in Table (3) which indicates a square planar geometry.

Magnetic susceptibility and conductivity measurements

The experimental magnetic moment for each metal complexes is listed in Table (3). Magnetic measurements are widely used in studying transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex. The magnetic moment for (C₁) is (6 B.M) with five unpaired electrons and an octahedral configuration. Conductivity measurements in DMF showed the complex is non-ionic. Magnetic moment for the (C₂) complex showed a higher (d-orbital) contribution, and conductivity measurement in DMF showed that the complex was conducting, Table (3), therefore the chlorine atom was not considered to be coordinated with metal ion and is located outer the coordination. The prepared (C₃) complex observed high magnetic value (2.55B.M) of the present platinum (IV) complex (d^6)

configuration agree with octahedral geometry around Pt(IV), this result indicates a higher orbital contribution around metal ion. The measured magnetic moment for (C₄) is (0.55B.M) showed that the complex to be with

low spin. Conductivity measurement in DMF showed that the complex was non-ionic. The complex of (C₅) was diamagnetic and conductivity measurement in DMF showed that the complex was conducting, Table (3).

Table (3)
Electronic spectra, Conductance (in DMF), and Magnetic moment for metal complexes.

Comp. No.	Band cm ⁻¹	Assignment	Molar cond. (μS.cm ⁻¹)	μ eff. B.M	Suggested Structure
C ₁	14750 18000 28555	⁶ A _{1g} → ⁴ T _{1g} ⁶ A _{1g} → ⁴ T _{2g} (L) → Fe(C.T)	24	6.00	Octahedral
C ₂	23200 26333	¹ A _{1g} → ¹ B _{1g} L → Rh(C.T)	150	2.55	Square planar
C ₃	18888 23656 30000	¹ A _{1g} → ³ T _{1g} ¹ A _{1g} → ¹ T _{2g} L → Pt(C.T)	22	2.55	Octahedral
C ₄	22121 24500 31100	¹ A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ E _g L → Pd(C.T)	15	0.55	Square planar
C ₅	16500 24012 30550 35600	¹ A _{1g} → ³ B _{1g} ¹ A _{1g} → ¹ B _{1g} ¹ A _{1g} → ¹ E _g L → Au(C.T)	165	0.77	Square planar

NMR Spectroscopy

The data of proton NMR of the 2-thioacetic acid benzothiazol and its complexes displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the complexes, Table (4). The observed changes are evidences of complexation had happened because the chemical shift of a compound is heavily depended on its electronic environment. The proton NMR spectra of the complexes confirmed the disappearance of OH signal at 12.22 ppm in

the free ligand. The δ 7.35-8.14 ppm resonance signal protons of the aromatic ring shifted to the higher field upon complexation, while the proton of the -CH₂ aliphatic group shifted to higher field also [14].

Table (4)
¹H NMR spectral data (δ, ppm) of the ligand and its complexes.

Symbol	-OH	-CH ₂ aliphatic	Aromatic
C ₁	-	4.14	6.43-7.85
C ₂	-	4.24	6.43-7.97
C ₃	-	4.21	6.44-7.65
C ₄	-	4.26	6.45-7.78
C ₅	-	4.16	6.46-7.87
HL	12.22	4.19	7.35-8.12

The ¹³C NMR of the ligand and its complexes are presented in Table (5). The C=O resonance group of the complexes at (158.53-159.66) ppm where shifted downfield

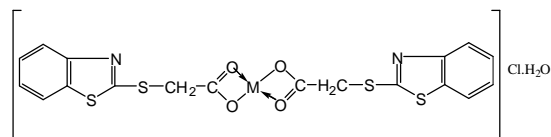
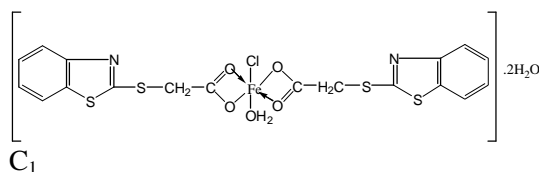
compared with the position in the free ligand which appeared at 169.54 ppm. It is most likely that this shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion [14].

Table (5)
¹³C NMR spectral data (δ, ppm) of the ligand and its complexes.

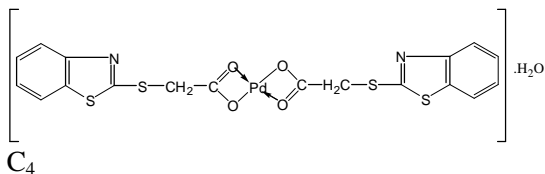
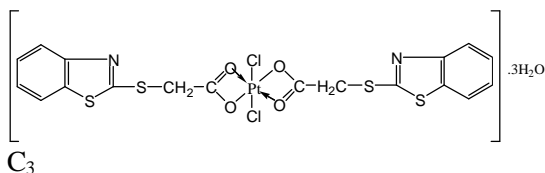
Symbol	C=O	aliphatic	Aromatic
C ₁	159.66	28.34	121.34-115.65
C ₂	158.65	28.46	121.22-114.23
C ₃	158.73	29.43	121.07-114.43
C ₄	159.43	28.53	121.15-115.17
C ₅	158.53	29.47	121.13-114.06
HL	169.54	30.30	121.22-114.26

Study of complex formation in solution

Complexes of (L) with metal ions were studied in solution using ethanol as a solvent, in order to determine [M:L] mole ratio in the complex follow Molar ratio method[15]. A series of solutions were prepared having a constant concentration (10⁻³M) of the metal ion and the [M:L] mole ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M:L]. The results of complexes in ethanol, suggest that the metal to ligand ratio was [1:2] for all complexes which were similar to that obtained from solid state study. On the basis of the preceding discussion, the structure of the complexes (C₁-C₅) may be suggested as follows:



Where, M = Rh and Au



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الخلاصة

حضرت المعقدات الجديدة للليكاند 2-ثايواسيتك اسد بينزوثايوزول مع الأيونات الفلزية التالية : الحديد (III) والروثينيوم (III) والبلاديوم (II) والبلاتين (IV) والذهب (III) في وسط كحولي مائي.

شخصت المعقدات بتقنية الاطياف تحت الحمراء بتحويلات فورير (FTIR) والامتصاصات الأليكترونية وتحليل العناصر والرنين المغناطيسي والتوصيلية الكهربائية والحساسية المغناطيسية ،تم قياس النسب المولية والمتغيرة في المحلول فأعطت نتائج مطابقة مع تلك التي تم الحصول عليها في الحالة الصلبة. حيث تم اقتراح هندسة الوحدة الأساسية للمعقدات.