

Synthesis and Characterization of Fe(II), Mn(II), Co(II), Hg(II) and Cr(III) Complexes of (Benzothiazol-2-ylsulfanyl)-Acetic Acid Ligand

Emad Yousif, Farah Muaiad and Hadeel Adil

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

Abstract

New metal complexes of the ligand (Benzothiazol-2-ylsulfanyl)-acetic acid with the metal ions Fe(II), Mn(II), Co(II), Hg(II) and Cr(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. From the spectral measurements, monomer structures for the complexes were proposed.

Keywords: Thioacetic acid; benzothiazole; metal complexes.

Introduction

The interest in this class of compounds ((Benzothiazol-2-ylsulfanyl)-acetic acid) are due to the presence of thioamide $\text{N}=\text{C}-\text{S}$ and oxygen donor organic moieties $\text{O}=\text{C}-\text{O}$, these moieties play an important role in chemotherapy by interaction these ligands with some metal ions, which is the field of biocoordination chemistry [1]. Metal complexes are suggested as a possible measure of drugs, since the action of many drugs is based on the ability of complex compound of metal ion to travers biomembrans. Metal chelats differ in their mode of action and activity in biological systems in accord with their structural considerations e.g, inert, highly stable metal chelats have a considerable activity against microorganisms, fungi and viruses [2].

Numerous amount of research into potentially pharmacologically active of thiazole and benzothiazole have been reported and many products which have emerged are antibiotic [3-5]. In addition thiazole and benzothiazole were reported to be of commercial interest, for e.g. thiazole use as accelerators in rubber vulcanization, antioxidant, photochromics and dyestuffs [6]. Another use of ligand and its complexes as photo stabilizers of poly vinyl chloride products which increased the utilization of this polymer in buildings, mainly in exterior applications, such as window profiles, cladding structure and sidings [7-9], so because of these applications of the ligand and its complexes, we have been extensively studied.

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 (Benzothiazol-2-ylsulfanyl)-acetic acid (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 (Benzothiazol-2-ylsulfanyl)-acetic acid are shown below:

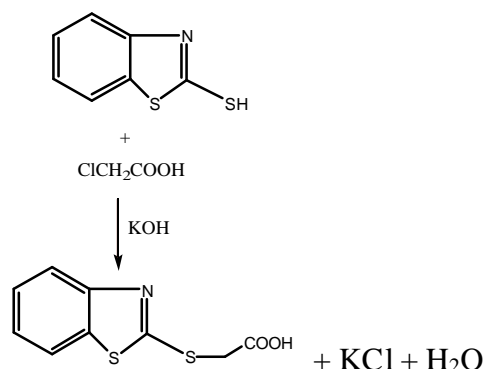


Fig.(1).

Preparation of Complexes (M1L-M5L)

Ethanolic solutions of the suitable metal salts [FeCl_2 , $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$] was added to an ethanolic

solution of (Benzothiazol-2-ylsulfanyl)-acetic acid 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, 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 prepared ligand and its complexes.

Symbol	Melting point °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)	-	$\text{C}_9\text{H}_7\text{NO}_2\text{S}_2$
M ₁ L	200-202	Orange	41.24 (41.37)	2.55 (2.68)	4.96 (5.36)	24.44 (24.56)	10.32 (10.69)	$[\text{Fe}(\text{L})_2] \text{H}_2\text{O}$
M ₂ L	245-247	Light Yellow	40.65 (41.44)	2.56 (2.68)	5.44 (5.37)	24.56 (24.60)	11.09 (10.54)	$[\text{Mn}(\text{L})_2] \text{H}_2\text{O}$
M ₃ L	100-101	red	41.46 (41.13)	1.90 (2.66)	3.55 (5.33)	16.60 (24.42)	25.23 (11.22)	$[\text{Co}(\text{L})_2] \text{H}_2\text{O}$
M ₄ L	240-242	Grey	32.22 (32.39)	2.20 (2.09)	4.32 (4.19)	20.11 (19.23)	30.41 (30.07)	$[\text{Hg}(\text{L})_2]\text{H}_2\text{O}$
M ₅ L	110-112	Green	36.80 (37.78)	2.84 (2.79)	4.58 (4.89)	22.23 (22.43)	8.98 (9.09)	$[\text{Cr}(\text{L})_2 \text{H}_2\text{O Cl}] \text{H}_2\text{O}$

Infra-Red Spectroscopy

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3435, 1633, 1351, 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 $\Delta\nu(\text{COO})$ 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 ($497\text{-}472 \text{ cm}^{-1}$) [10]. The IR data of the ligand and complexes are shown in Table (2).

Table (2)
Characteristic absorption bands of (Benzothiazol-2-ylsulfanyl)-acetic acid and complexes.

<i>Compound</i>	$\nu(\text{O-H})$	$\nu(\text{COO})$ <i>asym</i>	$\nu(\text{COO})$ <i>sym</i>
HL	3435	1633	1351
M1L	-	1583	1300
M2L	-	1550	1303
M3L	-	1600	1309
M4L	-	1602	1340
M5L	-	1608	1350

Ultraviolet-Visible Spectroscopy

The ultraviolet visible electronic spectrum of the (Benzothiazol-2-ylsulfanyl)-acetic acid 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). The solution spectrum of (**M1L**) complex shows two bands [11]. Electronic spectrum of (**M2L**) complex in DMF solution, showed three bands [12] at 19493 cm^{-1} (d-d) transition, 25773 cm^{-1} and 33003 cm^{-1} respectively indicating that Mn(II) complex is distorted tetrahedral. The solution spectrum of (**M3L**) complex showed two absorption bands of tetrahedral complex

[13]. The electronic spectrum of (**M4L**) shows single band, this complex was diamagnetic as expected for d^{10} ions, so that no d-d transition can be expected in the visible region [14]. The spectrum of the complex (**M5L**) gave three bands due to three spin allowed transition as shown in Table (3) which indicates an octahedral geometry [11,15,16] (Fig.(2)).

Table (3)
Electronic spectra and Magnetic moment for metal complexes.

Comp. No.	Band cm^{-1}	Assignment	μ eff. B.M	Suggested Structure
M1L	17543 37037	${}^5E_g \rightarrow {}^5T_{2g}$ Ligand field	5.2	Tetrahedral
M2L	19493 25773 33003	${}^6A_{1g} \rightarrow {}^4T_{2g}$ L \rightarrow Mn(C.T) Ligand field	5.5	Tetrahedral
M3L	9345 15939	${}^4A_{2g}(F) \otimes {}^4T_{2g}(F)$ ${}^4A_{2g}(F) \otimes {}^4T_{1g}(F)$ ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	4.49	Tetrahedral
M4L	32573	Ligand field	diamagnetic	Tetrahedral
M5L	16920 23696 32467	${}^4A_{2g}(F) \otimes {}^4T_{2g}(F)$ ${}^4A_{2g}(F) \otimes {}^4T_{1g}(F)$ ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	3.8	Octahedral

Magnetic susceptibility 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 (M1L) is (5.2 B.M.) [11]. Magnetic moment for the (M2L) complex showed (5.5 B.M.) at room temperature, these value of magnetic moment reveals the presence of five unpaired electrons in Mn(II) complex [12]. The prepared (M3L) complex gave value (4.49B.M.) indicate that the Co(II) complex was paramagnetic and it is characteristic of high spin tetrahedral geometry [13]. The measured magnetic moment for (M4L) was diamagnetic [14]. The magnetic moment of (M5L) was found to be (3.8BM) which gave a good agreement for octahedral geometry [15, 16].

NMR Spectroscopy

The data of proton NMR of the (Benzothiazol-2-ylsulfanyl)-acetic acid 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 $-CH_2$ aliphatic group shifted to higher field also [14].

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

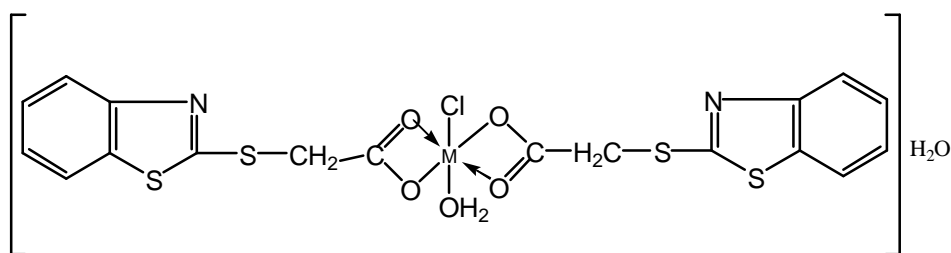
Symbol	-OH	-CH ₂ aliphatic	Aromatic
M1L	–	4.11	6.46-7.82
M2L	–	4.23	6.40-7.97
M3L	–	4.26	6.44-7.67
M4L	–	4.22	6.45-7.75
M5L	–	4.14	6.44-7.87
HL	12.22	4.19	7.35-8.12

The ¹³C NMR of the ligand and its complexes are presented in Table (5). The C=O resonance group of the complexes at (158.63-159.66) ppm were shifted downfield compared with the position in the free ligand

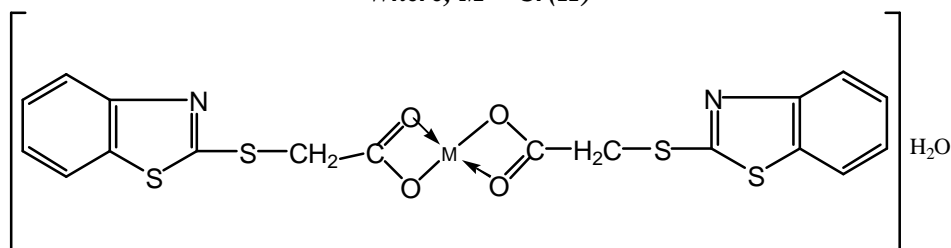
which appeared at 169.54 ppm. It is most likely that this shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion [14].

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

Symbol	C=O	aliphatic	Aromatic
M1L	159.66	28.34	121.34-115.64
M2L	158.63	28.46	121.23-114.33
M3L	158.63	29.43	121.58-114.43
M4L	159.56	28.53	121.16-115.18
M5L	158.65	29.47	121.14-114.17
HL	169.54	30.30	121.22-114.26



Where, $M = \text{Cr(II)}$



Where, $M = \text{Mn(II), Hg(II), Co(II) and Fe(II)}$

Fig.(2).

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الخلاصة

تم تحضير معقدات جديدة لليكاند (Benzothiazol-2-ylsulfanyl)-acetic acid مع الايونات الفلزية التالية : الكروم والمنغنيز والحديد والزنك والكوبلت وفي وسط كحولي. شخصت المعقدات المحضرة بتقنية الاطياف تحت الحمراء (FTIR) والامتصاصات الاليكترونية وقياسات الحساسية المغناطيسية. كما اعانت طريقة النسبة المولية في عملية التشخيص حيث تم اقتراح تركيب الوحدة الاساسية للمعقدات والتي اظهرت هندسة ثماني السطوح لمعقد الكروم، فيما كانت بقية المعقدات على شكل رباعي السطوح.