

SYNTHESIS AND CHARACTERIZATION OF SOME METAL IONS WITH {[5-(4-CHLOROPHENYL)-1,3,4-OXADIAZOL-2-YL]THIO} ACETIC ACID

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Abstract

New metal complexes of the ligand {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid with the metal ions Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II) were prepared in alcoholic medium. The prepared complexes were characterized by FTIR Spectroscopy, electronic spectroscopy ^1H NMR, ^{13}C NMR, magnetic susceptibility and conductivity measurements. From the spectral measurements, monomer structures for the complexes were proposed. Square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.

Keywords: carboxylate, 1,3,4-oxadiazole, metal complexes, spectroscopy.

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]. 1,3,4-Oxadiazoles are a class of heterocycles which have attracted significant interest in medicinal chemistry and they have a wide range of pharmaceutical and biological activities including antimicrobial, anti-fungal, anti-inflammatory, and antihypertensive[4,5]. The widespread use of 1,3,4-oxadiazoles as a scaffold in medicinal chemistry establishes this moiety as an important bio-active class of heterocyclic.

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

Synthesis of {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid

A mixture of ethyl 4-chlorobenzoate (0.1 mole) and hydrazine hydrate (0.1 mole) was refluxed for two hours, ethanol (50 ml) was added and refluxed for (5) hours. The precipitate 4-chlorobenzohydrazide which separated on cooling was filtered and washed

with cold methanol. To a solution of 4-chlorobenzohydrazide (0.02 mole) in ethanol (100ml) at (0°C) were added carbon disulfide (0.04mol) and potassium hydroxide (0.02 mole) the mixture was refluxed for (7) hours .the solvent was evaporated and the residue dissolved in water and acidified with dilute hydrochloric acid. The precipitate was filtered and crystallized from (ethanol) to give 5-(4-chlorophenyl)-1,3,4-oxadiazole-2-thiol which react with one equivalent of chloroacetic acid in presence of KOH as a basic media to give {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid (Fig.(1)). The final product was recrystallized from methanol.

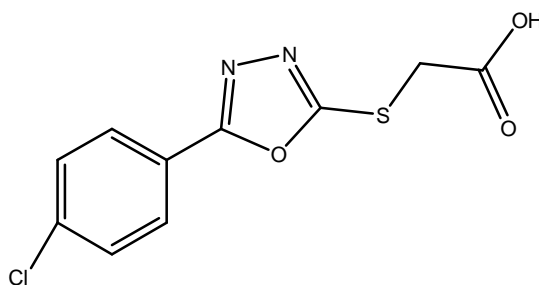


Fig.(1).

Preparation of Complexes

Addition of ethanol solution of the suitable metal salt (Nickel acetate tetrahydrate, Tin chloride, Copper acetate, Cadmium acetate dihydrate and Zinc acetate dihydrate) to an ethanol solution of {[5-(4-chlorophenyl)-1,3,4-

oxadiazol-2-yl]thio}acetic acid(HL) in 2:1 (ligand : metal) molar ratios was carried out. After reflux for half an hour, crystalline colored precipitates formed at room temperature. The rustling solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 °C. Table (1) shows the melting point of the prepared compounds

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 cut were recorded as CsI disc 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 ¹³C nuclear magnetic resonance spectra were recorded on a jeol 400 MHz spectrometer in dueteated DMSO, relative to the internal standard tetramethylsilane (TMS). Melting points were recorded on a hot stage Gallen Kamp melting point apparatus.

Result and Discussion

All chemicals and reagents were of reagent-grade quality. {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid was prepared by reaction one mole of 5-(4-chlorophenyl)-1,3,4-oxadiazole-2-thiol with one mole of chloroacetic acid in presence of KOH. The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent. Melting point and elemental analysis and 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.

Compound	Melting point °C	Found(Calcd.)%				
		C	H	N	S	M
HL	167-168	44.54(44.37)	2.44(2.61)	10.11(10.53)	11.12(11.85)	–
Ni(L) ₂	159-156	41.14(40.17)	2.12(2.02)	10.13(9.37)	11.01(10.72)	10.01(9.81)
Cu(L) ₂	154-155	39.32(39.84)	2.14(2.01)	9.22(9.29)	10.32(10.64)	11.10(10.54)
Zn(L) ₂	102-103	40.01(39.72)	2.14(2.00)	10.15(9.26)	11.92(10.60)	10.22(10.81)
Cd(L) ₂	121-123	35.17(36.86)	2.03(1.86)	9.26(8.60)	9.92(9.84)	17.24(17.25)
Sn(L) ₂	190-191	36.32(36.50)	1.14(1.48)	8.21(8.51)	9.98(9.75)	17.98(18.04)

Infra-Red Spectroscopy

The FTIR spectrum for HL, shows a characteristic stretching absorption bands at 3470 cm^{-1} , 1630 cm^{-1} , 1348 cm^{-1} , 1609 cm^{-1} , 1191 cm^{-1} and 1065 cm^{-1} assigned to hydroxyl group, $\nu(\text{COO})$ asym., $\nu(\text{COO})$ sym., C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching 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 3 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 the complexation is through the oxygen atom. Stretching of metal-oxygen bands of the complexes appeared in low frequency region [6] ($483\text{-}471\text{ cm}^{-1}$). The IR data of the ligand and complexes are shown in Table (2).

Table (2)

Characteristic absorption bands of {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid and its complexes.

Compound	$\nu(\text{O-H})$	$\nu(\text{COO})$ asym	$\nu(\text{COO})$ sym
HL	3470	1630	1348
Ni(L) ₂	-	1588	1344
Cu(L) ₂	-	1584	1343
Zn(L) ₂	-	1592	1346
Cd(L) ₂	-	1591	1344
Sn(L) ₂	-	1595	1342

Ultraviolet-Visible Spectroscopy

The ultraviolet visible electronic spectrum of the {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid in ethanol solvent was recorded in Table (3), a band at the wavelength (210 nm), this transition may be attributed to $\pi \rightarrow \pi^*$ electronic transition. And the other band appearing at 271 nm could be assigned to $n \rightarrow \pi^*$ electronic transition. The electronic spectra of {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid complexes show, as expected, different absorptions from that of

the free ligand. In complexes these bands was shifted to higher wavelength than the corresponding bands in the ligand (Table (3)).

The ligand field electronic transitions between the metal d orbital appear in Ni(II) and Cu(II) bands located in the visible region at 471 nm. for Ni(L)₂ assigned to the transition $^3T_{1g} \rightarrow ^3T_{1g(p)}$ and 687 nm. for Cu(L)₂ assigned to the transitions $^2E_g \rightarrow ^2T_{2g}$. The other complexes were diamagnetic as expected for d^{10} ions, so that no (d-d) transition can be expected in the visible region [7].

Table (3)

Electronic spectra for{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid and its complexes in ethanol solvent.

Compound	Color	Absorption Bands (nm)	Assigned Transition
HL	White	210	$\pi \rightarrow \pi^*$
		271	$n \rightarrow \pi^*$
Ni(L) ₂	Green	206	$\pi \rightarrow \pi^*$
		249	$n \rightarrow \pi^*$
		471	${}^3T_{1g} \rightarrow {}^3T_{1g(p)}$
Cu(L) ₂	Green	228	$\pi \rightarrow \pi^*$
		261	$n \rightarrow \pi^*$
		687	${}^2E_g \rightarrow {}^2T_{2g}$
Zn(L) ₂	White	230	$\pi \rightarrow \pi^*$
		257	$n \rightarrow \pi^*$
Cd(L) ₂	White	223	$\pi \rightarrow \pi^*$
		301	$n \rightarrow \pi^*$
Sn(L) ₂	White	224	$\pi \rightarrow \pi^*$
		277	$n \rightarrow \pi^*$

Magnetic susceptibility and conductivity measurements

The experimental magnetic moment for each metal complexes listed in Table (4). 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 Ni(II)

in any complex is approximately 3.11 B.M., this value refers to a high spin tetrahedral structure, while the value of Cu(II) is approximately 1.22 B.M. led to suggest the square planar structure[7] which can become in a good agreement with the data of electronic transitions. Other complexes have no magnetic moment because its diamagnetic. Molar conductivity measurement in DMF solvent at 25 °C showed that all the prepared complexes were non-electrolyte Table (4).

Table (4)
Magnetic Moment, Conductivity measurements in DMF solvent.

Symbol	Name	Conductivity $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$	Magnetic Moment (B.M)	Suggested Structure
<i>HL</i>	<i>{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid</i>	-	-	-
<i>Ni(L)₂</i>	<i>Bis{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid} nickel(II)</i>	14	3.11	<i>Tetrahedral</i>
<i>Cu (L)₂</i>	<i>Bis{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid} copper(II)</i>	10	1.22	<i>Square Planner</i>
<i>Zn(L)₂</i>	<i>Bis{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid} zinc(II)</i>	11	0.00	<i>Tetrahedral</i>
<i>Cd(H)₂</i>	<i>Bis{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid} cadmium(II)</i>	9	0.00	<i>Tetrahedral</i>
<i>Sn(H)₂</i>	<i>Bis{[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid} tin(II)</i>	11	0.00	<i>Tetrahedral</i>

Nuclear magnetic resonance

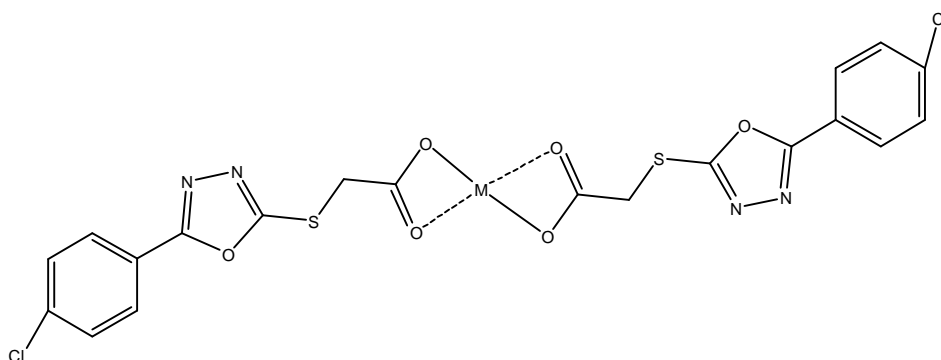
The data of proton NMR of {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid and its complexes displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the complexes. The observed

changes are evidences of complexation had happened because the chemical shift of a compound is heavily depended on its electronic environment. The spectra also exhibit a singlet -OH peaks at 9.61 ppm due to hydroxyl group. The hydroxyl resonances is absent in the spectra of the complexes indicating deprotonation and coordination of metal ions to

the oxygen. The δ 7.69-7.81 ppm resonance signal protons of the aromatic ring shifted to the higher field upon complexation, while the downfield shift of the protons in the $-\text{CH}_2$ aliphatic group shifted from δ 3.78 (in the free ligand) to 3.31-3.36 (in the metal complexes). However, we have been able to detect all proton and carbon signals separately. The ^{13}C NMR of the ligand and its complexes were recorded in DMSO. The C=O resonance group of the complexes at (168.70-170.11) ppm were shifted to higher field compared with the position in the free ligand which appeared at 169.33 ppm. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion.

Study of complex formation in solution

Complexes of (HL) with metal ions were studied in solution using ethanol as a solvent, in order to determine [M/L] ratio in the complex follow Molar ratio method [9]. A series of solutions were prepared having a constant concentration (10^{-3} M) of the metal ion and (L). The [M/L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M/L]. The results of complexes formation in solution. 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 observed spectral evidence, the following structures square planar geometry for the copper complex. The other complexes were proposed to be tetrahedral (Fig.(2)).



Where $M = \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{Cd(II)}$ and Sn(II)

Fig.(2).

Conclusion

The ligand {[5-(4-chlorophenyl)-1,3,4-oxadiazol-2-yl]thio}acetic acid was successfully synthesized. The ligand was treated to different metal ions salts to afford the corresponding complexes. It concluded that the ligand coordinated through carboxylate to the metal atom leading to the formation of four member ring chelate. Square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.

Acknowledgments

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