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Synthesis and Characterization on some Metal Ions of 2-(6-Methoxynaphthalen-2-Yl)Propanoate Complexes

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Abstract

A total of five new metal complexes derivatives of 2-(6-methoxynaphthalen-2-yl) propanoate, HL with the metal ions (Cd(II), Zn(II), Sn(II), Ni(II) and Cu(II)) have been successfully prepared in alcoholic medium. The complexes were characterized quantitatively and qualitatively by using micro elemental analysis, FTIR spectroscopy, UV-Vis spectroscopy, 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: identification, spectral measurements, metal complexes.

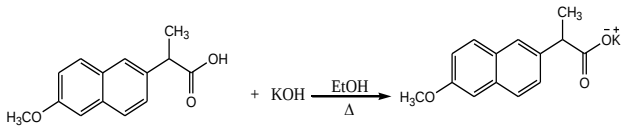
Introduction

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 [1-4]. Carboxylates complexes have attracted considerable attention due to their wide applications in many fields [5], such as biological activity and potential antineoplastic and antituberculosis agents [6], PVC stabilizers [7-11], PS photostabilizers [12] and anti-tumour drugs [13] as well as polymer catalysts [14]. Vast studies have been focused on carboxylates compounds and many of them have been characterized recently either by single crystal structure determination or by spectroscopy [15]. As a continuation of our series on the synthesis and characterization of carboxylates complexes [16-22], we report the diverse fields of synthesis of carboxylate complexes; we have synthesized new ligand 2-(6-methoxynaphthalen-2-yl) propanoate and its complexes with different metal ions.

Experimental

Synthesis of Potassium-2-(6-methoxynaphthalen-2-yl)propanoate

A mixture of 2-(6-methoxynaphthalen-2-yl) propanoic acid (0.1 mole) and (0.2 mole) of KOH (to make the medium alkaline) dissolved in (10 ml) ethanol and then refluxed for three hours to give Potassium-2-(6-methoxynaphthalen-2-yl) propanoate. The yellow precipitate which formed was filtered and recrystallized from ethanol to give the final product. The steps of the synthesis of Potassium-2-(6-methoxynaphthalen-2-yl) propanoate can be shown in the following Scheme (1).



Scheme (1): preparation reaction of the ligand.

Preparation of complexes [20]

Addition of ethanol solution of the suitable metal salt (Nickel (II) acetate tetrahydrate [$Ni(CH_3CO_2)_2.4H_2O$], Tin (II) chloride [$SnCl_2$], Copper (II) acetate [$Cu(CH_3CO_2)_2$], Cadmium (II) acetate dihydrate [$Cd(CH_3CO_2)_2.2H_2O$] and Zinc (II) acetate dihydrate [$Zn(CH_3CO_2)_2.2H_2O$] to an ethanol solution of potassium-2-(6-methoxynaphthalen-2-yl)propanoate in 2:1 (ligand : metal) molar ratios was carried out. After refluxe for half an hour, Crystalline colored precipitates formed at room temperature. The resulting solids were filtered off, wash, dried and recrystallized from ethanol and dried at 50 ^oC.

Results and Discussion

Infra-Red Spectroscopy

The synthetic route for the preparation of potassium-2-(6-methoxynaphthalen-2-yl) propanoate is outlined in chapter two. This ligand was prepared by the reaction of

one mole of 2-(6-methoxynaphthalen-2-yl) propanoic acid with two mole of potassium hydroxide (KOH). Table (1) shows the physical data for the ligand and the prepared complexes. The data of 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*	*M calc.%*	*M found%*
L	228-229	-	-
$Ni(L)_2$	76-78	10.17	10.28
$Cu(L)_2$	>205	9.31	9.72
$Zn(L)_2$	105-107	5.33	6.14
$Cd(L)_2$	178-180	21.16	21.45
$Sn(L)_2$	144-145	22.28	21.23

The reaction between this ligand with Ni (II), Cu(II), Zn(II), Cd(II) and Sn(II) gave different types of complexes. The FTIR spectrumof this ligand shows a characteristic stretching absorption bands at 3342 cm^{-1}, 1600 cm^{-1}, 1452 cm^{-1}, 1028 cm^{-1}, 1570 cm^{-1}, and 1309 cm^{-1} assigned to hydroxyl group, υ(COO) asym., υ(COO) sym., υ(OCH_3), υ(C=C) of the aromatic ring and υ(C-H) bending of ($–CH_3$) respectively. The (COO) stretching vibrations are important to predict the bonding mode of the ligand. The values of Δυ [Δυ = υ asym.(COO) - υ sym.(COO)] can be divided into 3 groups; (a) In compounds where Δυ(COO) > 350 cm^{-1}, the carboxylate group binds in a monodentate fashion. However, other very weak intra- and intermolecular interactions cannot be excluded. (b) When Δυ (COO) < 200 cm^{-1}, the carboxylate groups of these compounds can be considered to be bidentate. (c) In compounds where Δυ (COO) > 200 cm^{-1} and < 350 cm^{-1} an intermediate state between monodentate and bidentate (anisobidentate) occurs. It has also been suggested that the Δυ(COO) value in the chelating mode is less than the Δυ (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 (480-432) cm^{-1} [23]. The IR data of the ligand and complexes are shown in Table (2).

Table (2)
Characteristic absorption bands of potassium-2-(6-methoxynaphthalen 2-yl) propanoate and its complexes.

Compound	*υ (COO) asymetrical cm^{-1}*	*υ (COO) symetrical cm^{-1}*	*Δυ = [υ asym.(COO) – υ sym.(COO)]*	*υ (M-O) cm^{-1}*
L	1600	1452	148	-
$Ni(L)_2$	1568	1409	159	435
$Cu(L)_2$	1587	1404	183	474
$Zn(L)_2$	1600	1454	146	476
$Cd(L)_2$	1545	1392	153	432
$Sn(L)_2$	1606	1460	146	480

Magnetic Susceptibility and Conductivity Measurements

The experimental magnetic moment for each metal complexe is listed in Table (3). Magnetic measurements are widely used in studying transition metal complexes [20]. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbitals in the outer shell of this elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex. The resultant magnetic moment of an ion is due to both orbital and spin motions. The magnetic moment is given by the following equation:

$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$ B.M

μ = Magnetic moment.
S = Spin quantum number.
L = Orbital quantum number.
B.M = 9.27×10^{-24} J.T $^{-1}$

Although detailed determination of the electronic structure requires consideration of the orbital moment, for most complexes of the first transition series the spin-only moment is sufficient, as any orbital contribution is small.

$\mu_s = \sqrt{4S(S+1)}$ B.M.

Or

$\mu_s = \sqrt{n(n+2)}$ B.M.

$S = n\ (1/2)$
n = Number of unpaired electrons.

The value of magnetic susceptibility of the prepared complexes at (25 ºC) temperature was calculated using the following equation:

$\mu_{eff} = 2.83 \sqrt{X_A . T}$ B.M

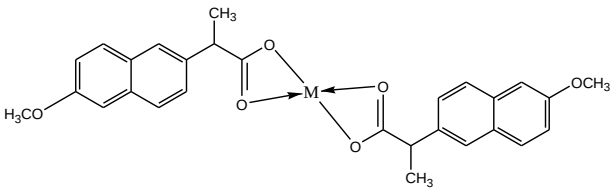
Where :
$X_A = X_m + D$
$X_m = X_g$. Mwt.
Mwt = Molecular weight of complex.
X_g = Mass susceptibility.
D = Pascal`s constant.
X_m = Molar susceptibility which was corrected from diamagnetic.
μ_{eff} = Effective magnetic moment.
T = Temperature in Kelvin (ºC +273).

The magnetic moment for Ni(II) complex was approximately 2.91 B.M., this value refers to a high spin tetrahedral structure. While the value of Cu(II) complex is approximately 1.53 led to suggest the square planar structure [21-23]. Molar conductivity measurement in DMF solvent at 25 ºC showed that all the complexes were non-electrolyt as shown in Table (3).

Table (3)
Magnetic Moment, Conductivity measurements for potassium-2-(6-methoxynaphthalen-2 yl) propanoate and its complexes in DMF solvent.

Symbol	*Name*	*Conductivity $ohm^{-1}cm^2mol^{-1}$*	*Magnetic Moment (B.M)*	*Suggested Structure*
L	Potassium-2-(6-methoxynaphthalen-2-yl)propanoate	-	-	-
Ni(L)$_2$	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] nickel(II)	13	2.91	Tetrahedral
Cu(L)$_2$	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] copper(II)	15	1.53	Square Planner
Zn(L)$_2$	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] zinc(II)	11	0.00	Tetrahedral
Cd(L)$_2$	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] cadmium(II)	10	0.00	Tetrahedral
Sn(L)$_2$	Bis[2-(6-methoxynaphthalen-2-yl)propanoate] tin(II)	14	0.00	Tetrahedral

On the basis of the preceding discussion, the structures of the complexes may be suggested as follows:



Where M = Sn(II), Cd(II), Ni(II), Zn(II) and Cu(II)

Acknowledgement

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الخلاصة

تـــم تحضـــير معقـــدات جديـــدة لليكانـــد 2-(6-methoxynaphthalen-2-yl) propanoate مع الايونات الفلزية التالية: الكروم والحديد والكوبلت والنحاس والنيكل وفي وسط كحولي مائي. شخصت المعقدات المحضرة بتقنية الاطياف تحت الحمراء المعززة بتحويلات فورير (FTIR) والامتصاصات الإليكترونية والتوصيلية الكهربائية والحساسية المغناطيسية. على اساس ذلك تم اقتراح هندسة الوحدة الأساسية للمعقدات .