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Preparation and Characterization of Some Metal Complexes of the New Ligand : 2-[2-(5- Methyl benzothiazolyl)azo] -4- Methyl phenol (5-Me-BTAC).

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Abstract

This work reports the synthesis and characterization of some Co(111), Ni(11), Cu(11), Zn(11), Cd(11) and Hg(11) chelates of the new benzothia-zolylazo Ligand (5-Me-BTAC) . The compounds were Characterized by IR , electronic spectroscopy, magnetic susceptibility ,elemental analysis and molar conductance measurements .

The elemental analysis suggest the formula [ML2] x.nH2O where x=Cl , n=1 for M= Co(111) and x=o , n=o for the remaining metal ions

Electronic spectra and magnetic susceptibility data has supported the proposed octahedral geometry of Co(111) , Ni(11) and Cu(11) Complexes. Conductivity measurements refer to nonionic structure of these Complexes except of Co(111) .

Introduction

Thiazolylazo compounds are widely used in the dye-stuffes industry(1) and also more recently in the field of non-liner optic (2) . Both applications depend critically on the presence of intense absorption bands in the visible or near-Uv region . Thiazolylazo dyes have great important applications as a spectrophotometric reagents [3 – 5] . In complexometric titrations some of its compounds used as

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indicators (6) . The dyes give coloured chelating complexes especially with some transition metal ions (7). In this paper, new representative of this class of organic compounds (5-Me-BTAC) has been synthesized and some of their complexes were prepared and characterized .

Experimental

a-Physical measurements

All chemicals are of (BDH , Fluka or Aldrich) . Elemental analysis were carried out by perkin-Elmer 2400 elemental analyzer . Metal analysis were carried out by (Shimadzu-AA-160) Atomic Absorption /Flam emiss- ion Spectrophotometer . IR spectra were recorded on (pye Unicom SP3- 300) , in the 4000-200 Cm^{-1} range using CsI discs .Electronic spectra were recorded using (Shimadzu UV-160A) Spectrophotometer ethanol has been used as a solvent . Magnetic measurements data were recorded on Broker BM6 instrument . Electrical conductivity was measured by conductivity bride model 31A .

Mass spectrum was obtained using (QMG 511 Balzar General Mass Spectrometer) by direct insertion system .

_b-Synthesis

1)2-[2-(5- Methyl benzothiazolyl)azo] -4-methyl phenol (5-Me-BTAC)

2-Amino-5-methyl benzothiazole (3.28g , 20mmol) was dissolved in ($5cm^3$) of formic acid and ($10\ cm^3$) of concentrated sulfuric acid , then ($20\ cm^3$)of water was added.To this mixture a solution of (1.6g ,20mmol) of sodium nitrate in ($20cm^3$) of water was added dropwise at 0-5 C^o.

Separately 4-methyl phenol (2.16g ,20mmol) was dissolved in ($200cm^3$) alkaline ethanol and cooled to 0-5 C^0 . This solution was then added drop- wise to the above diazotized solution with vigorous stirring .

The mixture was stirred for an additional 2hrs. in an ice-bath and allowed to stand overnight . The precipitate formed was filtered off and first purified by the base-acid recrystallization method and further purified by recrystallization from ethanol-water . A dark redish brown solid which decomposes at 178 C^o , was obtained in a yield of about 45% . This ligand was identified by means of elemental analysis , Infrared , the data are reported in (tables 1 and 2) .

Mass spectrometer data support the proposed structure . The base peak has measured mass of (283) corresponding to the molecular formula of C15 H13 N3OS , the calculated formula weight is (283) . This formula is the ligand molecular formula . A fragment peak at (m / Z = 164) corres- ponding to the amino thiazole compound (8) .
Exact mass measurement of these peaks reveal the presence of the azo lig- and under consideration and the structural formula of this ligand is shown in fig. (1) . The ligand dissolved in methanol, ethanol, DMF, DMSO, chloroform,and some other organic solvents, but not in water.

2) Preparation of Complexes

The ligand (0.141g , 0.5mmol) was dissolved in hot ethanol (50cm^3) and added dropwise with vigorous stirring to (0.25 mmol) of metal chloride ,MCl_2 (M= Co, Ni, Cu, Zu, Cd and Hg) dissolved in (10 cm^3) hot distilled water . The reaction mixture was heated to 50C^o for (30 min) , left over night , then the complexes were precipitated , filtrated and washed by ethanol and dried over anhydrous calcium chloride (CaCl2) .

Results and Discussion

Physical properties of the prepared complexes are given in (table 1). On the basis of elemental analysis data , the molecular formula of their complexes is assigned to be : [ML2] , where M = Ni(11), Cu(11) , Zu (11) ,
Cd (11) and Hg(11) . Whereas the molecular formula of Co(111) complex is [ML2]Cl.H2O .

Infrared Spectra

The Infrared Spectroscopic data of (5-MeBTAC) and their complexes are summarized in (table 2) . These Spectra are complicated owing to
the extensive overlap of a number of bands arising due to ν (C = N) , ν (N = N) , ν (C = C) and other bands originate due to phenyl and thiazole rings appeared in the region below 1700 cm^{-1} , the shifts in the positions of the complex bands compared with those absorption bands due to free ligand suggest the probable modes of bonding in the complexes . Some
of these main shifts along with the conclusions are given below .

The spectrum of ligand shows a very broad and weak absorption band around 3300 cm $^{-1}$ due to ν(O - H). This suggests a strong intermolecular hydrogen bonding [9 ,10] . In the Spectra of Co(111), the band near 3350cm^{-1} indicates the presence of water molecule in this complex . But this band was disappeared in the Spectra of rest complexes . This band never been observed in the Spectra of all other complexes . on the other hand , two weak bands had been observed at 3040 and 2950 cm^{-1} in the ligands spectrum which are due to ν (C - H) aromatic and aliphatic respectively . These bands are stable in position in both ligand and metal complexes .

Ligand spectrum show another band at 1640 cm^{-1} , which is considered to be ν(C = N) of thiazole ring (11) , this band shifted to lower frequencies 1630-1610 cm^{-1} in the metal complexes spectra , this may refer to the linkage of metal ion with the nitrogen of thiazole ring .

Two absorption bands are observed at 1570 and 1490 cm^{-1} in the ligand spectrum , which are due to the azo group , while in complexes spectra

these bands are shifted to a lower frequencies 1540 and 1450 cm^{-1} . These shifts may suggest that the azo group is coordinated to the metal ion (12) .

A band at 835cm^{-1} has also been appeared in the ligand spectrum ,this band is due to ν(C –S) of heterocyclic ring (13) .The fixed position of this band in all metal complexes means that the sulfur atom of the thiazole ring does not participate in coordination .

Finally , some other new bands appeared in the 440-345 cm^{-1} region in the complexes spectra which haven't been present in the ligand spectrum , this may attributed to ν(M –O) and ν(M–N) bands (14,15) .

Thus, the above IR spectra data lead to suggest that the ligand behaves as a tridentate chelating agent coordinating through the positions of hydro- xy oxygen , nitrogen of azo group and thiazole ring nitrogen .

Electronic Spectra and Magnetic Properties

The data obtained from the measurements of electronic spectra and magnetic susceptibility are shown in (table 3) .

Cobalt (111) Complex

The electronic spectrum of this complex display two absorption band at 16100cm^{-1} and 20120cm^{-1} characteristic of octahedral stereochemistry (16) . They were assigned to the transitions:$^{1}A_{1}g \longrightarrow$

$^{1}T_{1}g$ and $^{1}A_{1}g \rightarrow {}^{1}T2g$. The Complex was found to be diamagnetic with low spin behavior.

This may also indicate that Co(11)is oxidized to Co(111)during complexation . The change of oxidation state agrees with earlier observation that shows the aqueous solution of Co(11) salts is spontaneously oxidized to Co(111) in the presence of strong ligand such as thiazolylazo compounds (17) .

Nickel (11) Complex

The electronic spectrum of Ni(11) Complex shows absorption bands at 23148cm^{-1} and 15674cm^{-1} corresponding to : $^{3}A_{2}g \rightarrow {}^{3}T_{1}g$ (F) and $^{3}A_{2}g \rightarrow {}^{3}T1g$ (p) respectively. These observations agreed with what had been found by (Manch and Fernetins)for v_2 and v_3 bands (18) .

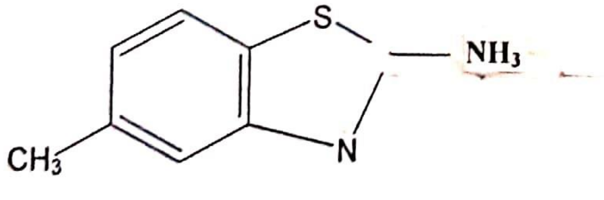
In this complex the v_1 absorption band is not observed because of the instrument range limitation.The calculated v1 value was in 9035 cm^{-1}, and were assigned to the first spin allowed $^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ (F) transition . This complex exhibits magnetic moment of 3 -16 B.M . Which can be a normal value for octahedral high-spin Ni (11) complex compared with what has been found in the literature (19) .

Copper (11) Complex

The visible absorption spectrum of this complex shows a broad band around 15748cm^{-1} , this may be reasonabl assigned to a distorted octahedral structure (20) . The value of magnetic moment for this complex is found to be 1.76 B.M ; this may suggest the presence of one unpaired electron in this Complex .

Zinc (11), Cadmium (11) and Mercury (11) Complexes

The electronic spectra of all these complexes do not show any d-d band . The magnetic susceptibility shows that all complexes have diamagnetic moment .



Conductivity Measurements

All complexes except of Co(111) complex show the conductivity measurement values ranging between 4.25-5.98 $S.mol^{-1}.cm^2$ (table 3) in methanol at room temperature , indicating nonionic structure of these complexes (21).But the low value of conductivity for the Co(111) complex (37.48 $S.mol^{-1}.cm^2$) indicating that the complex is (1:1) ionic structure .

According to these results the structural formula of prepared complexes in this work may be proposed in figure (2) shown below .

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Table(1) I.R. absorption bands of the ligand and its Complexes In cm^{-1} unites.

Compound	V(O - H)	V(C = N)	V (N = N)	V(C –S)	V(M –O)	V(M–N)
LH	3300 wbr	1640 m	1570 m 1490 m	840 m	—	—
$[CoL_2]Cl.H_2o$	3350 wbr	1625 m	1540 m 1460 w	840 m	440	330 w
$[NiL_2]$	—	1620msh	1555 w 1450 w	835 m	435	340 w
$[CuL_2]$	—	1630msh	1540 w 1465 m	840 m	425	345 w
$[ZnL_2]$	—	1625 m	1550 w 1480 m	835 m	430	320 w
$[CdL_2]$	—	1620msh	1560 m 1460 w	840 m	415	335 w
$[HgL_2]$	—	1610 m	1545 w 1475 w	840 m	430	340 w

LH = ligand , W = weak , m = medium , sh = shoulder , br = broad .

Table(2) Electronic Spectra, Conductivity and Magnetic moment data of Metal Complexes .

Complex	Absorption Band cm^{-1}	Transition	Conductivity $S.mol^{-1}cm^{2}$	μeff (B.M)
$[CoL_2]Cl.H_2o$	16100 20120	$^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$	37.48	dia
$[NiL_2]$	9035 15674 23148	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{2g}(p)$	5.98	3.16
$[CuL_2]$	15748	$^2B_2S \rightarrow {}^3A_{2g}$	5.81	1.76
$[ZnL_2]$	—	—	5.17	dia
$[CdL_2]$	—	—	4.85	dia
$[HgL_2]$	—	—	4.25	dia

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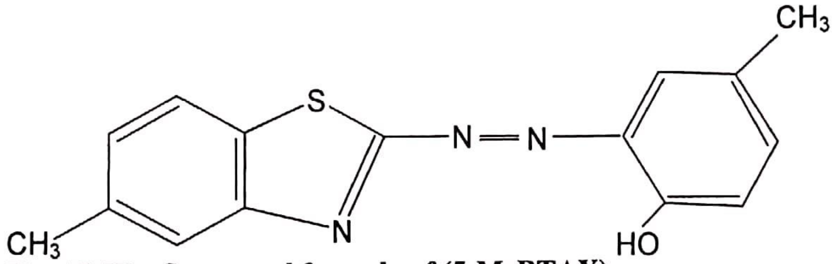

Fig .(1) The Structural formula of (5-MeBTAX)

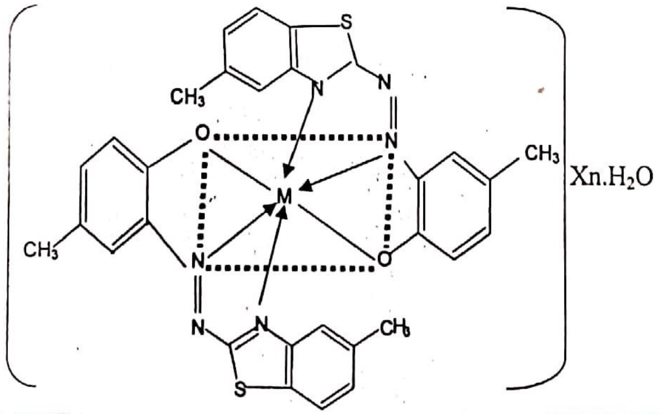

Fig. (2)M = Ni^{+1} , Cu^{+2}, Zn^{+2}, Cd^{+2} , Hg^{+2}, x = 0 , n = 0
M = Co^{+3} x = cl , n = 1

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تحضير ودراسة بعض المعقدات مع الليكاند الجديد -2]-2 (5-Methyl benzothiazolyl)azo]-4- Methyl phenol (5-Me-BTAC).

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الخلاصة

يتضمن هذا البحث تحضير وتشخيص بعض المعقدات المخلبية الجديدة لكل من الفلزات Hg (II), Cd((II),Zn(II)),Cu((II)),Ni(II),Co(III) المشتقة من الليكاند benzothiazolylazo (5-Me-BTAC) . وقد تم تشخيص المركبات باستخدام مطيافية الأشعة تحت الحمراء وفوق البنفسجية – المرئية وكذلك قياس الحساسية المغناطيسية وتحليل العناصروقياس الموصلية المولارية .

واستنادا الىالتحليل الدقيق للعناصر تم أقتراح الصيغة التركيبية للمركب ، $[ML_2]X.nH_2O$. حيث Co(III)=M عندما 1=n,Cl =x,0=n,0=x للأيونات المتبقية. وأن القياسات الطيفية والحساسية المغناطيسية تدعم الصيغة المقترحة لمعقد ثماني السطوح لكل من معقدات العناصر Cu(II),Ni(II),Co(III). كما ان قياس الموصلية الكهربائية للمركبات المحضرة أثبتت بأنها أيونية بأستثناء معقدات الكوبلت III .