Synthesis and Characterization of Complexes of Some Transition Metals With 2-amino-5- (4-hexyloxyphenyl)-1,3,4-thiadiazole.

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Abstract

New metal complexes of the ligand 2-amino-5-(4-hexyloxyphenyl)-1,3,4-thiadiazole with the metal ions Cr (III), Fe (III), Co (II), Ni (II) and Cu (II) were prepared in an alcohol-water medium.

The prepared complexes where characterized by FTIR Spectroscopy, electronic spectroscopy, magnetic susceptibility measurements and molar ratio method. From the spectral measurements, monomer structures for the complexes were proposed.

Introduction

Many enzymatic activities of thiadiazole are dependent upon their metal ion[1], besides their being good coordinating ligands because of presence of sulphur and nitrogen donor sites in them[2].

The aromatic thiadiazole nucleus is associated with a variety of pharmacological actions, such as fungicidal[3], and leishmenicides[4] activities. These activities are probably due to the presence of the –N=C–S group. In particular, the 1,3,4–thiadiazole derivatives showed these activities [5].

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

Experimental

All chemical used were of reagent grade (supplied by either Merck or fluka) and used as supplied. The FTIR spectra in the range (4000-200) cm^{-1} cut were recorded as cesium iodide disc on FTIR.8300 Shimadzu Spectrophotometer. The Uv-visible spectra were measured in ethanol using Shimadzu Uv-vis. 160 A-Ultra-violet Spectrophotometer in the range (200-1000) nm. Magnetic susceptibility measurement for complexes were obtained at room temperature using (Magnetic Susceptibility Balance) Jhonson Mattey catalytic systems division. Gallencamp M.F.B600.010 F melting point apparatus were used to measure the melting point of all the prepared compounds. Elemental microanalysis was carried out using CHNOS elemental analyzer model 5500 Carlo-Erba instruments (Italy).

Synthesis of 2-amino-5-(4-hexyloxybenzoic acid)- 1,3,4-thiadiazole (L).

A mixture of 4- hexyloxy benzoic acid (0.01 mol), thiosemicarbazide (0.01) mol, and phosphorus oxychloride (5 ml). The mixture was refluxed for five hours. After cooling, water was added (25 ml). The mixture was reflused for four hours and filtered. The solution was neutralized with potassium hydroxide .The precipitate was filtered and washed with distilled water and crystallized from (ethanol-water) to give this ligand.

The elemental analysis is shown below:

	%C	%H	%N
Calculated	60.73	8.06	17.69
Found	60.44	8.52	17.63

Preparation of complexes;

Addition of aqueous solution of the metals salt ($NiSO_4.6H_2O$, $CoCl_2.6H_2O$, $CuSO_4$, $CrCl_3.6H_2O$&$FeCl_3$) to an ethanol solution of (L) in 2:1 (ligand : metal) molar ratios. After string for half an hours, crystalline colored precipitates formed at room temperature, the rusting solids were filtered off, washed with distilled water dried and recrystallized from ethanol and dried at 50 °C.

Results and Discussion

Table (1) shows the decomposition point color and electronic absorption bands for ligand and complexes. The bands are classified into three distinct groups. The intermolecular transitions appear in the uv region, charge transfer from ligand to metal, and d-d transitions appear in the visible region[6]. These transitions are assigned in relevant to the structures of complexes, and also shown in Table (1).

The infrared data are shown in Table (2). The Table lists the stretching frequency (υ) for some of the characteristics groups exhibited by the ligand and complexes.

The formation of these complexes was confirmed by monitoring the changes both in location and intensity of the certain bands.

In the free ligand, the band at 1610 cm^{-1} is assigned to the stretching of C=N[7]. On complexation, this band is shifted to a lower frequency region. This shift is apparent in Cr(III), Fe(III), Co(II), and Ni(II) complexes.

This shift is probably due to the lowering of bond order of the carbon-nitrogen bond resulted from complexation of the metal to the ligand through nitrogen . However, in Cu(II) complex, this band is shifted to a higher frequency region. This shift could be attributed to the distortion that took place in the complex. The frequencies for the $\nu(N\text{-}H)_{asy.}$ and $\nu(N\text{-}H)_{sym.}$ in the complex has suffered from a shift (See Table 2) which indicates the coordination to the metal through this nitrogen atom . In Cr(II), Ni(II) and Cu(II), this band was not seen because it was covered by a broad band appeared in range the 3400-3550 cm^{-1} assigned to -OH stretching of water molecules. Stretching of metal nitrogen bonds of the complexes appeared in low frequency region[6] 378-459 cm^{-1} .

The molar ratio method was followed to detect the ratio of metal ion to ligand of complex. Ethanol was used as a solvent. The [M]/[L] ratio was found 1:2 to all complexes prepared. The values of magnetic moment in Table (3) supported the suggested structure.

Table (1): Electronic spectra for ligand and complexes in ethanol solvent.

No.	Symbol	Dec. Point °C	Color	Absorption Bands (nm)	Assigned Transition
1	L	170	yellow	230	$\pi \rightarrow \pi^*$
				275	$\pi \rightarrow \pi^*$
				295	$\pi \rightarrow \pi^*$
2	Cu(II)	101	Green	210	$\pi \rightarrow \pi^*$
				250	$\pi \rightarrow \pi^*$
				304	Charge Transfer
				455	$^2Eg \rightarrow {}^2T_2g$
3	Co(II)	160	Sky blue	205	$\pi \rightarrow \pi^*$
				226	$\pi \rightarrow \pi^*$
				250	$\pi \rightarrow \pi^*$
				307	Charge Transfer
				430	$^4T_1g^{(F)} \rightarrow {}^4t_1g^{(p)}$
				760	$^4T_1g \rightarrow {}^4A_2g$
4	Ni(II)	311	Pale green	245	$\pi \rightarrow \pi^*$
				281	$\pi \rightarrow \pi^*$
				311	Charge Transfer
				380	$^3A_2g \rightarrow {}^3t_1g^{(p)}$
				510	$^3A_2g \rightarrow {}^3t_1g^{(F)}$
5	Cr(III)	142	Gray	210	$\pi \rightarrow \pi^*$
				250	$\pi \rightarrow \pi^*$
				304	Charge Transfer
				470	$^4A_2g \rightarrow {}^4t_1g$
				595	$^4A_2g \rightarrow {}^4t_1g$
				690	$^4A_2g^{(F)} \rightarrow {}^4t_1g^{(p)}$
6	Fe(III)	210	Blue greenish	215	$\pi \rightarrow \pi^*$
				282	$\pi \rightarrow \pi^*$
				315	Charge Transfer
				415	$^5T_2g \rightarrow {}^5Eg$

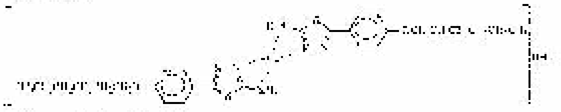
Table (2): The absorption bands in infrared for ligand and its complexes.

No.	Symbol	ν(C=N)	ν(N-H) asy.	ν(N-H) sym.	ν(O-H)	ν(M-N)
1	L	1610(s)	3290(s)	3200(s)	-	-
2	Cu(II)	1606 (s)	-	-	3510(B)	455(m)
3	Co(II)	1607(s)	3531(s)	3404(s)	-	459(s)
4	Ni(II)	1605 (s)	-	-	3435 (B)	437(s)
5	Cr(III)	1612(s)	-	-	3440(B)	457(s)
6	Fe(III)	1607(s)	3300 (s)	3230(s)	-	378(s)

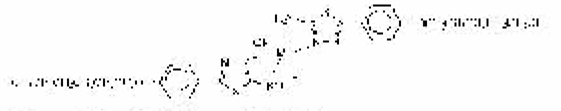
Table (3): Magnetic moment and suggested suggested structure for the complexes.

No.	Symbol	Suggested Formula Structure	Name	Magnetic Moment (B.M.)	Suggested Structure
1	L	$C_{14}H_{19}N_3SO$	2-amino-5-(4-hexyloxyphenyl) -1,3,4-thiadiazole.	-	-
2	Cu(II)	$[Cu(C_{14}H_{19}N_3SO)_2].H_2O$	Aqua bis(2-amino-5-(4-hexyloxyphenyl) -1,3,4-thiadiazole) Copper(II)	0.72	Square Planner
3	Co(II)	$[Co(C_{14}H_{19}N_3SO)_2Cl_2]$	Dichloro bis(2-amino-5-(4-hexyloxyphenyl) -1,3,4-thiadiazole) Cobalt(II)	5.14	Octahedral
4	Ni(II)	$[Ni(C_{14}H_{19}N_3SO)_2].H_2O$	Aqua bis(2-amino-5-(4-hexyloxyphenyl) -1,3,4-thiadiazole) Nickel(II)	3.44	Octahedral
5	Cr(III)	$[Cr(C_{14}H_{19}N_3SO)_2].2H_2O$	Aqua bis(2-amino-5-(4-hexyloxyphenyl) -1,3,4-thiadiazole) Chromium(III)	3.15	Octahedral
6	Fe(III)	$[Fe(C_{14}H_{19}N_3SO)_2Cl_2]$	Dichloro bis (2-amino-5-(4-hexyloxyphenyl) -1,3,4-thiadiazole) Iron(III)	4.52	Octahedral

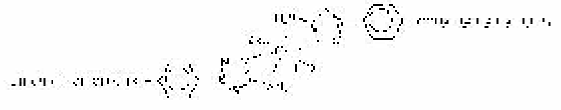
On the basis of the preceding discussion, the structure of the complexes may be suggested as follows:



Where M= Cu(II)



Where M = Co(II) and Fe(III)



Where M= Cr(III)

الخلاصة

تم تحضير معقدات جديدة لليكاند 2-أمينو-5-(4-هكسيلوكسي فنيل) -1,3,4- ثايودايازول مع الأيونات الفلزية التالية : الكروم والحديد الثلاثي والكوبلت والنيكل والنحاس الثنائية في وسط كحول مثيلي .

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