Synthesis and Characterization of Mn(II), Co(II), Ni(II) and Cu(II) complexes with 4′-azachalcone and their adducts with 1,10-phenanthroline

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الخلاصـــة

يتضمن البحث تحضير معقدات ومركبـات إضـافة جديـدة ذوات الـصيغ العامـة $[M(L)_2Cl_2]$، $[M_2(L)_2Cl_4]$ وكذلك $[M(L)_2(phen)Cl_2]$ ، حيث L= 4′ - ازاجـالكون، phen = 10,1 – فينـانثرولين، M= Ni(II),Co(II),Mn(II) و Cu(II). تـم تـشخيص المعقدات ومركبات الإضافة وذلك بالتحليل العنصري الدقيق، قياسات التوصيلية الكهربائيـة وقياسات العزم المغناطيسي والأطياف الالكترونية وطيف الأشعة تحت الحمراء. ان قيم العزم المغناطيسي والطيف الالكتروني أعطت أدلة لوجود الأشكال الرباعية حول الايون الفلزي في المعقدات والثمانية السطوح في مركبات الإضافة.

ABSTRACT

New complexes of general formula $[M(L)_2Cl_2]$, $[M_2(L)_2Cl_4]$ and adducts $[M(L)_2(phen)Cl_2]$,where L=4′-azachalcone ,phen = 1,10-phenanthrolin, M=Mn(II),Co(II),Ni(II) and Cu(II) have been prepared. The complexes and adducts were characterized by elemental analysis, conductivity measurements, magnetic moment and spectral (IR and electronic) studies. Magnetic moment values and electronic spectral data provide evidence for the existance of tetrahedral environment around the metal ions in the complexes and octahedral geometry in the adducts.

Introduction:

The study of transition metal complexes has often focused on the synthesis of the complexes between a metal ion and ligands containing, nitrogen, oxygen, sulphur phosphorus as donors. Azachalcons are widely investigated because of their important roles that play in preparing of number of biologically active compounds [1,3].

The substituted picolinamide ligands N-(2-aminophenyl)- and N-(3-aminophenyl) pyridine-2-carboxamide have been shown to coordinate to the bivalent metal ions in different manners because they have six donating atom N_2O_4[4-6].

An x-ray determination for the complex $[Mn(Pdc)_2(H_2O)_2].2H_2O$ where Pdc = 3-pyridazine carboxylic acid by Ardiwinanta etal. is reported[7], they found that the structure is centrosymmetric octahedral molecules coordinated through N_2O_2 enviroments and are linked by hydrogen bonds on hydroxy groups of the carboxylic acid where as the coordination occur through N-atom of pyridine ring and oxygen of the carbonyl groups, involving the two lattice waters. The structure is differs from that of the corresponding 2-pyridine carboxylic acid complexes of the formula $[M(pic)_2(H_2O)_2].2H_2O$ (M =Co,Ni,Zn) only in the term of hydrogen bonding network [8,9] .

The preparation and study of cobalt (II) ,nickel (II),copper (II),zinc (II),palladium (II) and platinum (II) complexes with N-(2aminophenyl) quinoline 2′ - carboxamide, showing that these ligand to coordinate to the metal ions in several modes[10].

Acccording to the interesting results, we report the synthesis of some Mn(II),Co(II),Ni(II) and Cu(II) complexes with 4′-azachalcons ligand and their adducts with 1,10-phenanthroline and the details of the structure elucidation.

Experimental:

All chemicals used were of high purity. Analysis of complexes carried out using a CHN elemental analyzer model (Carlo Erba). Melting point and decomposition temperature were determined on a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra within the range 4000-200 cm^{-1} were recorded on a Perkin – Elmer 580 B spectrophotometer. The samples used were in the form of KBr or CsI discs. Electronic spectra were obtained with a shimadzu UV/Vis. recording UV 160 spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3} M of the complex in dimethyl sulfoxide (DMSO).The magnetic moments were carried out at 25°c on the solid by Faraday's method using Brucker BM6 instrument. The metal content was estimated spectrophotometrically using Shimadzu AA 670 spectrophotometer. Conductivity measurements have been

carried out with an electrical conductivity measing set Jenway using 10^{-3}M dimethyl sulfoxide solution at room temperature.

Preparation of the ligand (4′-azachalcones):

The ligand is prepared by treating 4-acetylpyridine (2g,0.017 mol) and benzaldehyde (1.8g,0.017 mol) in water (100 cm^3). The mixture was stirred at 15°C for 1h.,and (5 cm^3) of 10% NaOH solution was added to the above mixture. Stirring was continued for 3h., the precipitate was filtered off, washed with water and recrystallized from petroleum spirit (60-80°c),the m.p of the ligand is 87-88°c.

Preparation of complexes:

1- Complexes of the type $[M(L)_2Cl_2]$, M=Mn(II), Co(II), Ni(II) and Cu(II):

To an ethanolic solution (15cm^3) of $CoCl_2.6H_2O$ (0.24g, 0.001mol) was added to an ethanolic solution (15 cm^3) of 4′-azachalcone (0.45g, 0.002 mol). The reaction mixture was refluxed for 4h. then reduced to one thired of its volume.On cooling blue precipitate was obtained and recrystallized from ethanol.

An identical procedure was adopted for the synthesis of all other complexes.

2- Complexes of the type $[M_2(L)_2Cl_4]$

Treatment of dimethyl formamide solution (10 cm^3) of the complex $[Co(L)_2Cl_2]$ (0.58g,0.001mol) with an ethanolic solution (10 cm^3) of $CoCl_2.6H_2O$ (0.24g,0.001mol), the mixture was refluxed for 1h., resulting an immediate coloured precipitate was removed by filtration, washed with ethanol and diethylether and dried in vacuum.

Similar procedure was used to prepare the rest of the complexes.

3- Complexes of the type $[M(L)_2(phen)Cl_2]$

A mixture of $[M(L)_2Cl_2]$ (0.001 mol) and 1,10- phenanthroline hydrochloride (0.001 ml) was stirred at room temperature in methanol (20 cm^3) for 16h.The resultant suspended solid collected washed with diethyl ether and dried under vaccum.

Results and discussion:

The reaction of metal chloride with 4′-azachalcanes in ethanol yields complexes of the general formula $[M(L)_2Cl_2]$ as in equation(1). Further reaction of the prepared complexes with another mole of dichlorides of manganese,cobalt,nickel or copper gave stable bimetallic complexes as in equation(2).

$$MCl_2.XH_2O + 2L \xrightarrow{EtOH} [M(L)_2Cl_2] + XH_2O \quad \text{.....(1)}$$

$$[M(L)_2Cl_2] + MCl_2.XH_2O \xrightarrow{EtOH} [M_2(L)_2Cl_4] + XH_2O \quad \text{.....(2)}$$

The analytical and physical data for metal complexes are given in Table1. The values of molar conductance are in the range 10-25 Ω^{-1} mol^{-1} cm^2 for $[M(L)_2Cl_2]$, $(M_2(L)_2Cl_4)$ and adducts of the type $[M(L)_2(phen)Cl_2]$ in dimethyl sulfoxide solution which indicate that the complexes and adducts behaves as non-electrolytes [11].

The most important features of the IR spectra are listed in Table 2. The IR bands of the free ligand were included for comparison. The IR spectrum of the ligand exhibits two bands due to the heterocyclic ring vibration (C=C/C=N) stretching at 1615 and 1595 cm^{-1}, as well as the υ(C=O) band is observed at 1660 cm^{-1}. These bands were found at 1615, 1580 and 1630 cm^{-1} indicating that υ(C=N) and υ(C=O) bands were shared in coordination with metal ions through nitrogen atom of the pyridine ring for complexes (5-8) and oxygen atom[12] .Further support for this coordination was provided from the of new bands about 450-465 and 520-560 cm^{-1} which are tentivtey attributed to υ(M–N) and υ(M–O)[13]. Furthermore, the IR spectra of the adducts of the type $[M(L)_2(phen)Cl_2]$,show that the oxygen atoms of the ligands and nitrogen atoms of phenanthroline are shared in coordination (Table 2), further support for these coordination was obtained from the appearance of a new bands at 390-440 cm^{-1} and 525-540 cm^{-1} are assigned to υ(M – N) and υ(M – O)[13].respectively. Further the IR spectra of the complexes $[M(L)_2Cl_2]$ and $[M_2(L)_2Cl_4]$ showed another new band in the region of 330-280 cm^{-1} which may be due to the υ(M – Cl) frequency[14] .

U.V-visible and magnetic behavior of the complexes:

The ligand and complexes of the type $[M(L)_2Cl_2]$ and $[M_2(L)_2Cl_4]$ are solid stable crystalline materials. They are all strongly coloured, since these have highly intense absorptions in the UV-visible spectra in the region above 600 nm.

As consequence, d-d transitions of the central metal ions in the complexes are detectable only in the visible (>500nm.) (Table 2). summa- rizes the spectral data of the complexes in non-donor or weak donor solvents, such as DMSO.

The visible spectra of the complexes, in combination with room temperature magnetic susceptibility measurements, substantially confirm the assignment of four-coordinate tetrahedral structure for the complexes of the general formula $[M(L)_2Cl_2]$ and $[M_2(L)_2Cl_4]$.

The Mn(II) complexes (1 and 5) show maximum absorption at 22450, 24500 cm^{-1} and a charge transfer bands at 36000-32000 cm^{-1} indicating that Mn(II) complexes are of tetrahedral geometry. In

tetrahedral fields the transition are still spin-forbidden but no longer parity forbidden[15]. The magnetic moments were found to be 5.9 and 5.66 B.M corresponding to high-spin (sp^3) tetrahedral environment.

The electronic spectra of Co(II) complexes (2 and 6) shows a bands observed in the visible region (15350-13888)cm^{-1} and are generally considered to correspond to a transition from singlet level of $^4A_2(F) \longrightarrow {}^4T_1(p)$.

The position, shape, and intensity of these bands are very similar to those found for bis (dipivalolylmethanido) cobalt (II), suggesting to be four coordinate tetrahedral geometry[16]. The μ_{eff} vales for the complexes of 4.30 and 4.49 B.M are substantially in line with expectation for high – spin Co(II) in tetrahedral geometry.

For the Ni(II) complexes (3 and 7), the observed bands at (13400-14150 cm^{-1}) are due to a transition from $^3T_1(F) \longrightarrow {}^3T_1(p)$ in tetrahedral geometry. The magnetic moment values of the complexes are 3.93 and 3.89 B.M at room temperature. This suggest the presence of two unpaired electrons which reveals the spin nature of the complexes. A corrgindly the complexes have tetrahedral stereochemistry[17].

The electronic spectra of Cu(II) (4 and 8) showed bands at (13300-15797 cm^{-1}) which correspond to the transition $^2B_1g \longrightarrow {}^2A_2g$ and other transition at 28000 cm^{-1} correspond to the change transfer, the magnetic moment value of the complexes are 1.92 and 1.79 B.M which predicate the presence of one upaird electron as expected for tetrahedral geometry[18].

The electronic spectra of the isolated adducts 9-12 with 1,10 – phenanthroline recorded in DMSO are listed in Table 2.

The Mn(II) complex 9 show four bands at 19350-29120 cm^{-1} ,due to the $^6A_1g \longrightarrow {}^4T_1g(^4G)$, $^6A_1g \longrightarrow {}^4A_1g(^4G)$, $^6A_1g \longrightarrow {}^4Eg\ (^4D)$ and $^6A_1g \longrightarrow {}^4T_1g(^4p)$ transitions respectively. These values suggest octahedral geometry for the Mn(II) complexes. The Co(II) complex (10) show the presence of two bands in the region (17605) and(21239) cm^{-1} are assigned to $^4A_2g \longrightarrow {}^4T_1g(F)(\upsilon_3)$ and $^4A_2g \longrightarrow {}^4T_1g(p)(\upsilon_2)$ transitions respectively . This shows that the positions of the electronic spectral bands have changed from tetrahedral to octahedral environment[18].The Ni(II) complex 11 show the presence of three bands in the region (11230-25773) cm^{-1} which are assigned to $^3A_2g \rightarrow {}^3T_1g(p)(\upsilon_3)$, $^3A_2g \longrightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g \longrightarrow {}^3T_2g(F)(\upsilon_1)$ transition respectively. This show that the structure are octahedral. Three shoulder bands appear at (14302,16660 and 27770) in Cu(II) complex 12 (Table 2) which may be assigned to $^2B_1g \longrightarrow {}^2A_1g$, $^2B_1g \longrightarrow {}^2B_2g$ and, $^2B_1g \longrightarrow {}^2Eg$ transition, respectively. This shows that the Cu(II) complexes have distorted octahedral geometry[19].

Table 2: Electronic and infrared spectral bands of the complexes and adducts

No.	λmax (cm^{-1})	υ(C = O)	υ(C = N)	υ(M–O)	υ(M – N)	υ(M – Cl)
1	22450,24480,32000	1620_m	1595_m	520_m	----	290_w
2	13888,14600	1630_m	1590_m	560_m	----	310_w
3	13900,14150	1625_s	1598_m	515_m	----	280_w
4	13300,15400,28000	1615_s	1594_m	515_m	----	320_w,290_w
5	22900,24500,36000	1620_m	1580_m	530_m	450_m	330_w
6	15335,14400	1610_s	1585_m	525_m	465_m	300_w
7	13400,14000	1625_s	1580_m	515_m	460_m	320_w
8	13600,15797	1620_m	1580_m	520_m	455_m	328_S,295
9	1350,23460,27245,29120	1625_m	1580_m	540_m	450_m	300_S
10	17605,21239	1615_s	1580_m	530_s	430_m	310_w
11	11230,17577,25773	1620_m	1580_m	525_m	390_m	330_w
12	14302,16660,27770	1610_s	1585_m	535_m	440_m	320_w

s= strong, m = medium, w = weak

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