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Analytical, Spectral And Structural Elucidation of The Complexes of Co(II), Ni(II), Cu(II) and Zn(II) With Furil-Bis-(2-Aminothiophenol)

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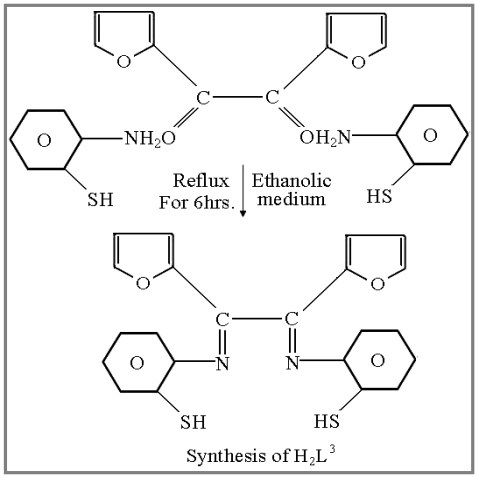
ABSTRACT

Binuclear complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Furil-bis-2-aminothiophenol (Schiff base) ligand have been synthesized and characterized on the basis of molar mass, elemental analysis, IR as well as electronic spectral studies, molar conductance and magnetic susceptibility measurement. On the basis of above physicochemical and spectrometric measurements it is proposed that the compounds act in a bi-dentate manner. Such complexes have varieties of useful pharmaceutical activities and many of them gained wide acceptance in clinical practices. The resulting complexes have been tested for their antifungal activity against various organisms. Complexes, excepting that of Zn(II), are colored. Electronic spectra and magnetic susceptibility study proposes octahedral geometry of the complexes.

Graphical Abstract



Synthesis of furil-bis-2-amminothiophenol.

Keywords: Binuclear complexes, Furil-bis-(2-aminothiophenol), Diketones, Octahedral).

INTRODUCTION

An overview of the research works, going on in the field of coordination chemistry, presented by Cambridge Structural Data (CSD) base shows that the Transition Metal Chemistry has become the pioneer chemistry today. There are enumerable compounds formed by transition metal having diversified role in several aspects of life. Several transition and inner-transition metal complexes having nitrogen and oxygen donor atoms play an important role in biological systems [**1-3**]. Some of the metal complexes were show carcinostatic and tuberculostatic activity [**4-5**]. There are several fascinating examples of transition metal complexes having catalytic, biological and pharmaceutical importance [**6-8**]. There has been a recent upsurge in the research activity of zinc due to its recently discovered zinc finger protein and zinc complexes with scorpionate ligands [**9**].

Present programme deals with synthesis, characterization and study of a series of binuclear complexes [**10-11**] of Co(II), Ni(II), Cu(II) and Zn(II) with furil-bis-(2-aminothiophenol) ligand having nitrogen and sulphur donors. The complexes have been synthesized by refluxing the ethanolic solutions of metal chloride with that of furil-bis-(2-aminothiophenol) with aqueous NaOH.

The principal objective of the present work is to prepare some binuclear complexes having nitrogen and oxygen donor atoms and their characterization by means of analytical, spectral and magnetic studies. Magnetic moment data and electronic spectral bands indicate an octahedral environment around each metal ion.

MATERIALS AND METHODS

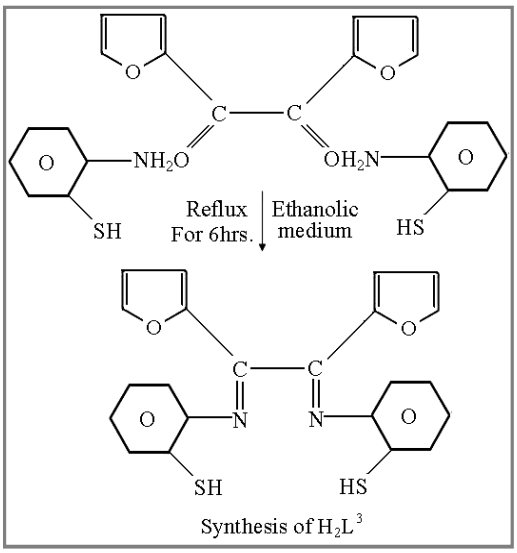
Chemicals namely furil-bis-(2-aminothiophenol) (Fluka) and all solvents used in this study were obtained from Merck and used as supplied without further purification. Chlorides of transition metal were also used as supplied. For the estimation of metals, the complexes were first decomposed to bring them in their proper ionic solution and then they were quantitatively analyzed. Cobalt was estimated from its ionic solution by oxidizing it with few drops of conc. HNO_3 after heating and cooling. Now the oxide of cobalt was converted into nitrate. On expelling HNO_3 by heating, it was treated with excess of conc. H_2SO_4 to convert it into sulphate. Finally it was heated between 450-500°C and weighed as $CoSO_4$.

From the ionic solution of nickel chloride, nickel was precipitated as bis-DMG nickel(II) in ammonical medium. The precipitate was heated at 110-120°C and weighed as nickel compound. Copper was estimated by repeated evaporation of the weighed amount of its complex with HNO_3 and $HClO_4$ in a Pyrex beaker until a clear solution was obtained. The solution was further boiled with HCl and the volume was reduced to 10-15 mL. Now the resulting solution was diluted with water and Cu was determined iodiometrically. On the other hand zinc was estimated by EDTA titration in an alkaline medium having pH 10.

Elemental analysis of C, H, N and S was carried out micro-analytically at CDRI Lucknow. The electronic absorption spectra of the complexes were recorded with Hitachi-300 spectrophotometer at CDRI Lucknow. Infrared spectra were also recorded at CDRI Lucknow on Perkin Elmer 577 spectrophotometer using KBr disc in the range of 4000-40 cm^{-1}. Magnetic susceptibility of all the complexes were measured by Guoy's method using $Hg[Co(NCS)_4]$ as calibrant. Electrical conductivity of the solution of complexes was measured by conductivity meter Systronics model 300 at room temperature in DMF using N/10 and N/100 KCl solution. Pure DMF and conductivity water were used as solvent.

Synthesis of ligand: The ligand furil-bis-(2-aminithiophenol) was synthesized by refluxing an ethanolic solution of furil (1 mL ~ 0.01 mol.) with an ethanolic solution of 2-aminothiophenol (0.02 mol.) for ~ 6 h. The resulting solution was concentrated and the precipitate was separated by filtration,

washed with ethanol and then air-dried. Following is the chemical reaction taking place during synthesis of furil-bis- (2-aminithiophenol) (Scheme 1).



Scheme 1. Synthesis of furil-bis-2-amminothiophenol.

Synthesis of complexes: Following is the general method used to synthesize the binuclear complexes of Co, Ni, Cu and Zn with furil-bis-(2-aminothiophenol). An ethanolic chloride solution of cobalt, nickel, copper and zinc were added separately to the ethanolic solution of furil-bis-(2-amino thiophenol) in a molar ratio (2:2 = M:L) or (1:1=M:L) followed by the addition of an aqueous solution of NaOH (0.02 mol.) to the resulting mixture. Now all the mixtures were refluxed separately for about 4 h. The formed precipitates were collected by filtration, washed several times with ethanol and water and finally dried in oven at 110°C (Table 1 and 2).

The synthetic reaction during the synthesis of metal complexes can be represented as

$$2M(Ac)_2 + 2H_2L + 2NaOH \rightarrow [(M)_2L_2(H_2O)_4] + 4HAc$$

[M = Co(II), Ni(II), Cu(II) and Zn(II)]

Table-1. Color, yield, decomposition temperature, analytical and molar conductance data of the complexes of furil-bis-(2-aminothiophenol)

Compound	Colour	Yield (Gram)	Decomp. (0^c)	Analytical Data (Cal./Found %)				Cal.(Found) %	Λ_M
				C	H	N	S	Metal	$ohm^{-1} cm^2 mol^{-1}$
$[(Co)_2(L^3)_2(H_2O)_4]$	Dark Brown	76	332	65.34/64.98	3.96/3.92	6.93/6.88	15.84/15.76	11.87(11.79)	8
$[(Ni)_2(L^3)_2(H_2O)_4]$	Yellow	70	342	65.34/64.98	3.96/3.92	6.93/6.88	15.84/15.76	11.88(11.78)	10
$[(Cu)_2(L^3)_2(H_2O)_4]$	Brown	71	328	65.34/64.98	3.96/3.92	6.93/6.88	15.84/15.76	12.66(12.59)	15
$[(Zn)_2(L^3)_2(H_2O)_4]$	Yellow	69	358	65.34/64.98	3.96/3.92	6.93/6.88	15.84/15.76	13.00(12.97)	16

Table 2. Important IR spectral data of the complexes of furil-bis-(2-aminothiophenol) (cm^{-1})

Compound	$\upsilon(H_2O)$	υ(C=N)	Rocking $\upsilon(H_2O)$	Wagging $\upsilon(H_2O)$	υ(M-N)	υ(M-S)
$[(Co)_2(L^3)_2(H_2O)_4]$	3412	1595	891	755	377	496
$[(Ni)_2(L^3)_2(H_2O)_4]$	3416	1592	869	756	383	489
$[(Cu)_2(L^3)_2(H_2O)_4]$	3442	1591	879	763	375	491
$[(Zn)_2(L^3)_2(H_2O)_4]$	3455	1581	856	742	376	497

RESULTS AND DISCUSSION

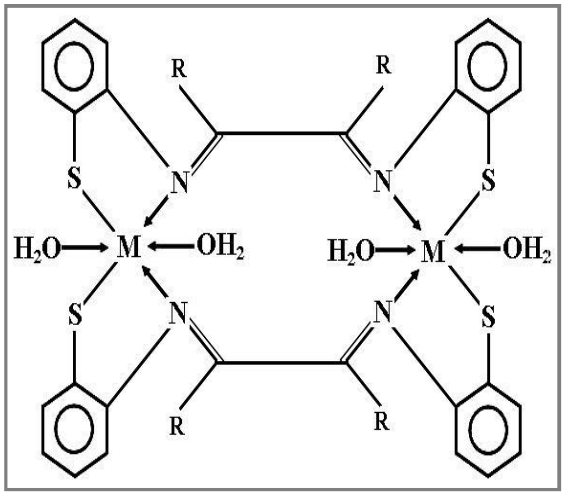
The complexes obtained from furil-bis-(2-aminothiophenol) were powers, stable in air at room temperature. Insolubility of these complexes in common organic solvents such as acetone, methanol and chloroform and their decomposition temperature support the binuclear structure of these complexes. The molar conductance of the complexes in DMSO was in the range of (16-8) ohm^{-1} cm^2 mol^{-1}. On the basis of above data these complexes can be considered as non-electrolyte [12].

IR-spectral studies: The characteristic IR spectral bands of the complexes when compared with that of the free ligand provide ample evidences for the mode of binding of the ligand to the metal ion. In the IR spectrum of furil-bis-(2-aminothiophenol) ligand, a sharp band observed at 1595 cm^{-1} was assigned to the υ(C=N) mode of the azomethine group which was shifted to lower wave numbers in all the complexes, suggesting the coordination of the azomethine nitrogen to the metal ion centres [13]. This is further substantiated by the presence of the new band at 375-383 cm^{-1} assignable to υ(M-N). The characteristic thiophenolic υ(S-H) mode was observed at 2475 cm^{-1}. A band at 1293 cm^{-1} due to υ(C-S) thiophenolic was also observed in the spectrum of ligand [14]. The disappearance of thiophenolic υ(S-H) bond in the complexes under study suggests the coordination by thiophenolic sulphur after deprotonation to the metal ion. This is further supported by the shifting of υ(C-S) thiophenolic to lower wave numbers in all the metal complexes [15]. The IR spectra of the complexes also show a band in the 3412-3455 cm^{-1} region, indicating the presence of coordinated water in these complexes. The presence of coordinated water was further confirmed by the appearance of a non-ligand band in the 856-891 cm^{-1} and 742-763 cm^{-1} regions, assignable to the rocking and wagging modes of water, respectively [16].

Electronic spectra and magnetic moment studies: The electronic spectra of the free ligand, furil-bis-(2-aminothiophenol), and its Co(II) complexes were recorded in DMSO at room temperature. Electronic absorption [17] spectral data of the ligand shows the $\pi\rightarrow\pi^*$ transitions related to benzene ring in the range 43000-44000 cm^{-1} and imine $n\rightarrow\pi^*$ transitions in the range 30500-31000 cm^{-1}. The $[(Co)_2L_2(H_2O)_4]$ complex exhibits one band in the range 9850-10000 and another band in the range of 23800-23900 cm^{-1}. The bands are assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\upsilon_1)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\upsilon_3)$ respectively. The magnetic moment of the complex, $[(Co)_2L_2(H_2O)_4]$, at room temperature was observed in the range of 4.20-4.60 B.M. per Co atom. On the basis of the position of the bands and the magnetic moment [18] value the geometry of $[(Co)_2L_2(H_2O)_4]$ complex is presumably octahedral.

The Ni(II) complex, $[(Ni)_2L_2(H_2O)_4]$, reported herein was found to have room temperature magnetic moment value in the range of 3.75-3.80 B.M. corresponding to two unpaired electrons. Electronic spectra of the aforesaid complex display three absorption bands in the range 11250-11570, 16200-16350, and 28115-26240 cm^{-1}. These bands can be assigned to three spin allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively. The position of these bands indicates that the complex has an octahedral geometry around Ni(II) ions.

The electronic spectra of Cu(II) complex, $[(Cu)_2L_2(H_2O)_4]$, shows a single broad band in the region 20000-20300 cm^{-1} attributable to $^2T_{2g}\rightarrow{}^2E_g$ transition indicative of distorted octahedral geometry around Cu(II) ions. A low energy band at 10341 cm^{-1} and the magnetic moment of 1.78 B.M. per Cu(II) ion support the octahedral geometry the copper complex. Zn(II) complex, $[(Zn)_2L_2(H_2O)_4]$, shows zero magnetic moment suggesting the diamagnetic nature of the complex. The electronic spectra of Zn(II) complex shows a single broad band in the region 23000-25000 cm^{-1} attributable to charge transfer transition. The electronic spectroscopy does not permit the establishment of a clear cut stereochemistry for Zn(II) complex. But taking into consideration of similarity with light congeners, Zn(II) complex has been proposed to have octahedral geometry. Hence, the proposed structure of transition metal complexes $[(M)_2L_2(H_2O)_4]$ having octahedral geometry is shown as :



$[(M)_2\mathbf{L}_3(H_2O_4)]$, [M = Co(II), Ni(II), Cu(II) or Zn(II) and R = CH_3, C_6H_5,C_4H_3O]

Scheme 2: The proposed structure of the complexes.

APPLICATION

The chemistry of 2-aminothiophenol has wide applications in biomimetic catalytic reactions. It is used in oxidative reactions with π–deficient compounds. In addition to industrial applications it has wide medicinal applications also viz. it functions as antifungal, antibacterial, anticancer and antiviral agent.

CONCLUSION

Present programme reveals that complexes of Co(II), Ni(II), Cu(II) and Zn(II) with furil-bis-(2-amminothiophenol) assume an octahedral geometry by virtue of their magnetic moment values but Zn(II) complex, diamagnetic in nature having zero magnetic moment value, is proposed to have octahedral geometry due to its similarity with light congeners.

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