Synthesis and Characterization of Some Metal Complexes of [4-Methoxy-N-(pyrimidine-2-ylcarbamothioyl)benzamide]

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Abstract:
A new ligand [4-Methoxy -N-(pyrimidine-2-ylcarbamothioyl) benzamide] (MPB) was synthesized by reaction of (4-Methoxybenzoyl isothiocyanate)with (2-aminopyri-midine). The Ligand was characterized by elemental micro analysis (C,H,N,S),(FT-IR) (UV- Vis) and (1H,13CNMR)spectra. Some transition metals complexes of this ligand were prepared and characterized by (FT-IR, UV-Vis) spectra conductivity measurements magnetic susceptibility and atomic absorption. From the obtained results the molecular formula of all complexes was suggested to be [M(MPB)2Cl2] (M+=Cu, Mn, Co ,Ni ,Zn ,Cd and Hg),the proposed geometrical structure for all complexes was an octahedral.

Keywords: 2-Amino Pyrimidine, 4-Methoxy benzoyl isothiocyanate, complexes.

Introduction:
Nitrogen containing heterocycles act an important part in medicinal chemistry and also contribute to the society by helping as in different life processes[1]. Heterocyclic compounds are torrential in nature and are of great significance to life because their structural subunits exist in many natural products such as vitamins, hormones, antibiotics etc. A practical method for the synthesis of such compounds is of great interest in synthetic organic chemistry. Pyrimidine is a six-member heterocyclic compound that contains two nitrogen atoms at positions 1 and 3. The structure of the pyrimidine ring is similar to benzene and pyridine. The key role pyrimidines play in cellular processes has made them valuable leads for drug discovery. Pyrimidine derivatives are known to be biologically active compounds and substituted Pyrimidines have shown a wide range of biological activities like anti tubercular antibacterial, antioxidant, anti-inflammatory activity[2]. The chemistry of pyrimidines and their derivatives have been studied since past century due to their close pharmacological association with diverse pharmacological properties. Pyrimidine Scheme(1-a) was first isolated in 1899. Though pyrimidine itself does not exist in nature but substituted Pyrimidines moiety are found as part of more complex systems and are widely distributed. Pyrimidines[3].

These compounds are considered to be important not only because they are an integral part of the genetic material DNA and RNA as nucleotides and nucleosides but they also impart numerous biological activities such as bactericides, fungicides, viricides, insecticides and miticides. They have also found applications in agricultural and industrial chemicals.

Scheme 1. structures of pyrimidine and 2-Aminopyrimidine

2-Aminopyrimidine Scheme(1-b) is an interesting structural element present in several marketed drugs, and its derivatives possess divers biological activities, e.g. Antipsychotic, cardoprotective, and antimalarial [4]. Schiff bases derived from 2-aminopyrimidine have been used as antibacterial [5]. Antitumor agents[6]. In this work, a new ligand was prepared by the reaction of 2-Aminopyrimidine with N-2,4-Dihydroxy benzaldehyde. Also its complexes were prepared, (where M+=Cu, Pd, Zn, Co, Ni and M"= In,Ir)[7].

Materials and Methods:
Chemicals: The chemicals used in this work were all of reagent grade by BDH, Merck and Fluka.
**Materials:** (4-Methoxybenzoyl chloride), (2-amino pyrimidine), Manganese chloride tetra hydrate (MnCl₂·4H₂O), Cobalt chloride hexahydrate (CoCl₂·6H₂O), Nickel chloride hexahydrate (NiCl₂·6H₂O), Copper chloride hydrate (CuCl₂·2H₂O), Zinc chloride (ZnCl₂), Cadmium chloride hydrate (CdCl₂·H₂O) and Mercury chloride (HgCl₂).

**Preparation of ligand (MPB)**

The ligand was prepared by two steps (scheme-2)

**(A)- Preparation of the (4- Methoxybenzoyl isothiocyanate)**

Mixture of 4-Methoxy benzoyl chloride (3.51ml,26 mmol) and ammonium thiocyanate (2g, 26mmol) in 25 ml acetone was stirred under reflux for 3hrs then filtered, the filtrate was used for further reaction. [8]

**(B)- Preparation of [4-Methoxy -N-(pyrimidin-2-ylcarbamothioyl)benzamide] (MPB)**

A solution of (2.47g,26mmol) 2-Aminopyrimidine in 20 ml acetone was rapidly added to 4- methoxy benzoyl isothiocyanate and maintaining reflux. After refluxing for 6hrs the resulting solid was collected, washed with acetone, and recrystallized from ethanol, yield (79%), (m.p=170-172)°C, C% found (53.99 calc. (54.11), H% found(5.36) calc. (5.29),N %found(19.63) calc.(19.43),S% found (11.8) calc.(11.12).

**Synthesis of the ligand complexes**

**Synthesis of the [Zn(MPB)₂Cl₂] complex**

A solution of (0.136 g, 1mmol ) ZnCl₂ in 10 ml ethanol was added to a solution of (0.576g,2mmol ) (MPB)in10 ml ethanol. The mixture was stirred under refluxed for 6 hrs at room temperature, the brown solid product was collected by filtration, washed with (1:1) mixture of water: ethanol, and dried in an oven at 50°C.

**Synthesis of [Cu (MPB)₂Cl₂], [Mn (MPB)₂Cl₂], [Co(MPB)₂Cl₂], [Ni(MPB)₂ Cl₂], [Cd(MPB)₂ Cl₂]and [Hg (MPB)₂Cl₂], complexes .**

A similar method to that mentioned for preparation of [Zn(MPB)₂Cl₂] complex was used to prepare the complexes of [Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+} and Hg^{2+}]ions with (MPB) ligand. Some physical properties of the prepared complexes are shown in Table(1).
Table 1. Some physical properties of the ligand (MPB) and its Complexes

| Molecular formula | Mwt gm/mol$^1$ | Color  | M.P Or dec. (°C) | M% Calculated (Found) | Molar Cond. Ohm$^2$cm$^2$mol$^{-1}$ in DMSO | $\mu_{\text{eff}}$ (B.M) |
|------------------|----------------|--------|------------------|------------------------|---------------------------------------------|-----------------------|
| (C$_3$H$_7$O$_2$N$_4$S) (MPB) | 288.32 | Orange | 170-172          | -                      | -                                           | -                     |
| [Mn (MPB)$_2$Cl$_2$] | 702.546 | Orange | 285-287          | 7.82 (7.64)            | 17.2                                       | 5.87                  |
| [Co(MPB)$_2$Cl$_2$] | 706.476 | Green  | 305(dec)         | 8.34 (8.19)            | 7.71                                       | 4.61                  |
| [Ni(MPB)$_2$Cl$_2$] | 706.256 | Green  | 280-282          | 8.31 (8.42)            | 14.2                                       | 3.01                  |
| [Cu(MPB)$_2$Cl$_2$] | 710.546 | Brown  | 310 (dec)        | 8.86 (8.64)            | 12.0                                       | 1.77                  |
| [Zn(MPB)$_2$Cl$_2$] | 710.916 | Orange | 288-290          | 8.91 (8.79)            | 13.4                                       | 0                     |
| [Cd(MPB)$_2$Cl$_2$] | 759.946 | Orange | 300 (dec)        | 14.79 (14.68)          | 18                                         | 0                     |
| [Hg(MPB)$_2$Cl$_2$] | 848.146 | Orange | 297 (dec)        | 23.63 (23.45)          | 8.5                                        | 0                     |

dec. = decomposition

Results and Discussion:

Ligand (MPB):
- The FT-IR spectrum of the free ligand (MPB), Figure(1) shows bands at(1681)cm$^{-1}$ and (1253)cm$^{-1}$ due to $\nu$(C=O)(amidic) and $\nu$(C=S) respectively. While another absorption band at (3379)cm$^{-1}$ could be explained as $\nu$ N-H [9,10]. Spectral data of the free ligand are listed in Table (2).

Figure 1. FT-IR Spectrum of the Ligand(MPB).

Table 2. The characteristic bands of FT-IR Spectra of ligand (MPB) and its metal complexes.

| Compound            | $\nu$ (N-H) | $\nu$ (C=O) Amide | $\nu$ (C=S) | $\nu$ (M-O) | $\nu$ (M-S) | $\nu$ (M-Cl) |
|---------------------|-------------|-------------------|-------------|-------------|-------------|--------------|
| Ligand(MPB)         | 3379 (s)    | 1681 (s)          | 1253 (s)    | -           | -           | -            |
| [Mn(MPB)$_2$Cl$_2$] | 3375 (s)    | 1649 (s)          | 1234 (s)    | 474(s)      | 329 (m)     | 250(m)       |
| [Co(MPB)$_2$Cl$_2$] | 3378 (m)    | 1647 (s)          | 1228 (m)    | 428 (s)     | 314 (w)     | 273(w)       |
| [Ni(MPB)$_2$Cl$_2$] | 3373 (m)    | 1658 (m)          | 1200 (s)    | 470 (s)     | 329(w)      | 229 (w)      |
| [Cu(MPB)$_2$Cl$_2$] | 3377 (m)    | 1612 (s)          | 1224 (m)    | 464 (m)     | 322 (w)     | 297 (w)      |
| [Zn(MPB)$_2$Cl$_2$] | 3375 (m)    | 1604 (m)          | 1234 (s)    | 432 (m)     | 306 (m)     | 260 (m)      |
| [Cd(MPB)$_2$Cl$_2$] | 3363 (s)    | 1662 (s)          | 1201 (s)    | 482 (s)     | 337 (m)     | 264 (w)      |
| [Hg(MPB)$_2$Cl$_2$] | 3380 (s)    | 1666 (s)          | 1226 (s)    | 449 (s)     | 327 (m)     | 262 (m)      |

$s$=strong $w$=weak $m$=medium $b$=broad UV-Vis spectra
The UV-Vis spectrum of the free ligand (MPB). Figure (2) exhibits a high intense absorption peak at (34722) cm\(^{-1}\) which may be attributed to electronic transition type \(\pi \rightarrow \pi^*\) [11] The data of electronic spectrum of the free ligand (MPB) is listed in Table (3).

![Figure 2. Electronic spectrum of ligand (MPB).](image)

| Compounds          | \(\lambda(\text{nm})\) | \(\upsilon(\text{cm}^{-1})\) | ABC | \(\epsilon_{\text{max}}\) molar\(^{-1}\text{cm}^{-1}\) | Transitions |
|--------------------|-------------------------|-------------------------------|-----|----------------------------------|-------------|
| (Ligand MPB)       | 288                     | 34722                         | 1.884 | 1884                             | \(\pi \rightarrow \pi^*\) |
| [Mn(MPB)\(_2\)Cl\(_2\)] | 784                     | 12755                         | 0.020 | 20                               | \(6\text{A}_{1g} \rightarrow \text{T}_2\text{g}(F)\) |
|                    | 866                     | 11547                         | 0.018 | 18                               | \(6\text{A}_{1g} \rightarrow \text{T}_1\text{g}(G)\) |
|                    | 276                     | 36231                         | 2.167 | 2167                             | \(\text{T}_1\text{g}(P) \rightarrow \text{T}_1\text{g}(P)\) |
| [Co (MPB)\(_2\)Cl\(_2\)] | 517                     | 19342                         | 0.018 | 18                               | \(4\text{A}_{2g} \rightarrow \text{T}_2\text{g}(F)\) |
|                    | 864                     | 11574                         | 0.015 | 15                               | \(4\text{A}_{2g} \rightarrow \text{T}_2\text{g}(F)\) |
|                    | 282                     | 45460                         | 2.416 | 2416                             | \(\text{C.T overlap with}\) |
|                    | 368                     | 27173                         | 0.272 | 272                              | \(3\text{A}_{2g}(F) \rightarrow \text{T}_2\text{g}(F)\) |
| [Ni(MPB)\(_2\)Cl\(_2\)] | 554                     | 18015                         | 0.020 | 20                               | \(3\text{A}_{2g}(F) \rightarrow \text{T}_1\text{g}(F)\) |
|                    | 890                     | 11235                         | 0.015 | 15                               | \(3\text{A}_{2g}(F) \rightarrow \text{T}_1\text{g}(F)\) |
| [Cu(MPB)\(_2\)Cl\(_2\)] | 273                     | 36630                         | 1.925 | 1925                             | \(3\text{A}_{2g}(F) \rightarrow \text{T}_2\text{g}(F)\) |
|                    | 864                     | 11574                         | 0.025 | 25                               | \(\text{C.T overlap with}\) |
| [Zn (MPB)\(_2\)Cl\(_2\)] | 291                     | 34364                         | 2.457 | 2457                             | \(\text{C.T overlap with}\) |
| [Cd (MPB)\(_2\)Cl\(_2\)] | 271                     | 36900                         | 1.481 | 1481                             | \(\text{C.T overlap with}\) |
| [Hg (MPB)\(_2\)Cl\(_2\)] | 274                     | 36496                         | 1.978 | 1978                             | \(\text{C.T overlap with}\) |

L.F = ligand field, C.T = charge transfer

The \(^1\)H-NMR spectrum of free ligand (MPB), Figure (3) was recorded in DMSO-d\(_6\) solvent showed the following signals: singlet peak at \(\delta(2.5)\) ppm or DMSO , singlet Peak at (3.79) ppm for (3H, OCH\(_3\)), multiplet peak at \(\delta(6.73-8.73)\) ppm for aromatic protons, singlet peak at \(\delta(9.90)\) ppm refers to (1H, NH sec. amine), signals peak at \(\delta(11.00)\) ppm, for (1H, NH sec. amide).
Figure 3. $^1$H-NMR spectrum of ligand (MPB).

$^{13}$CNMR spectrum of the free ligand (MPB) in DMSO-d$_6$. Fig.(4) showed for the following signals: singlet at δ(38.61-40.27) ppm for DMSO, signal at δ(55.22-55.49) ppm for (OCH$_3$), signal at δ(109.88-157.56) ppm for aromatic carbons, signal at δ(159.39) ppm for (C=Osec.amid), signal at δ(167.33) ppm for (C=S)[9,12]

Figure 4. $^{13}$C -NMR spectrum of ligand (MPB).

Complexes of the ligand (MPB)
The solid complexes are soluble in some common solvents such as dimethyl form amide, dimethyl sulphoxide and relatively thermally stable. The molar conductivity values of all complexes in DMSO solvent in $10^{-3}$M at 25°C(Table-1) indicated non-electrolyte. The atomic absorption measurements for all complexes gave approximated values when compared with theoretical values, Table(1) includes the physical properties for the ligand and its complexes.

FT-IR Spectra of complexes
These spectra exhibited marked differences between bands, Figure(5), belonging to the stretching vibration of $\nu$(C=O amido)in the range between (1666-1604) cm$^{-1}$ shifted to lower frequencies by (77-15) cm$^{-1}$ suggesting the possibility of the coordination of ligand through the oxygen atom at the carbonyl group [14], while the band caused by $\nu$(C=S) appeared between (1234-1200) cm$^{-1}$ shifted to lower frequencies by (75-19) cm$^{-1}$ which indicates the coordination of ligand through the sulfur atom at the thion group to the central ion [13-15]. The stretching vibration band $\nu$(N-H) either shows no change or very little in their frequencies (3380-3363) cm$^{-1}$ indicating to non coordination between the metal ion on the metal ligand. Metal-oxygen and metal-sulfur bonds were confirmed by the presence of the stretching tremor of $\nu$(M-O), $\nu$(M-S) and $\nu$(M-Cl) around (482-424) cm$^{-1}$, (337-306) cm$^{-1}$ and (229-297) cm$^{-1}$ respectively. The spectra of complexes [14].Table (2) describe the important bands and assignment for free ligand (MPB) and its complexes.
Magnetic moment

The values of measured magnetic susceptibility and effective magnetic moment (µeff) for the Mn (II), Co(II), Ni (II) and Cu(II) complexes are shown in Table(1). Mn(II), Co(II), Ni (II) and Cu (II) complexes exhibit µeff (5.87, 4.61, 3.01, 1.77 ) B.M respectively, which reflect normal values for high spin octahedral complexes.[16]

Electronic spectra for complexes
- [Mn(MPB)₂Cl₂] d⁵

The Orange complex of Mn (II), Figure (6), shows band at (36363)cm⁻¹ due to (L.F) and other bands at (12755)cm⁻¹ and (11547)cm⁻¹ which are attributed to (d-d) the electronic transition type ⁴A₁g → ⁴T₂g(G) and ⁴A₁g → ⁴T₁g(G) respectively, suggesting an octahedral geometry around Mn (II) ion [17].
- [Co(MPB)₂Cl₂] d⁷

The spectrum of the Green complex gave four bands at (36231)cm⁻¹ (25510)cm⁻¹ (19342)cm⁻¹ and (11574)cm⁻¹ attributed to (L.F), ⁴T₁g(F), ⁴T₁g(G), ⁴A₂g(F) and ⁴T₁g(F) respectively and the each inter electronic repulsion parameter (B' ) was found to be (675)cm⁻¹, from the relation β=B' / B⁰, was found to be equal (0.695); these parameter are accepted to Co(II) octahedral complex[18].
- [Ni(MPB)₂Cl₂] d⁸

The spectrum of Green complex of Ni(II) has exhibited four (L.F), ³A₂g → ³T₁g(F), ⁴A₂g → ⁴T₁g(F), and ³A₂g → ⁴T₂g(F), which refer to electronic transition bands at (35460) cm⁻¹, (27173)cm⁻¹, (18050)cm⁻¹, and (11235)cm⁻¹ respectively. The (B') value is found to be (767.8) cm⁻¹,while β was equal to(0.73). These are the characteristics for octahedral complexes of Ni(II)[19].
- [Cu (MPB)₂Cl₂] d⁹

The spectrum of Brown complex of Cu(II) shows two bands at (36630) cm⁻¹ and (11574)cm⁻¹, which refers to (L.F), ⁴Eg → ⁴T₂g(F), electronic transition respectively which was in good agreement for distorted octahedral complex for Cu(II) ion[20].
The complexes of [Zn(MPB)2Cl2] , [Cd(MPB)2Cl2] and [Hg(MPB)2Cl2] The spectrum of these complexes displayed one peak at range(271-291)nm (36900-34364)cm⁻¹ which attributed to £-F [21], with their assignments are summarized in Table(3). Suggested structures for complexes on the basis of molar conductivity , magnetic moment ,spectroscopic studies (FT-IR, UV-Vis and atomic absorption) and ¹H,¹³CNMR for ligand (MPB) only the ligand (MPB) behaves as bidentate on coordination with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions via oxygen atom of (C=O) amido group and sulfur atom of (C=S) group, suggesting octahedral geometry around metal ions for all the prepared complexes.

M = Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II)

Figure 7. The proposed chemical structure formula of the complexes

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