



Synthesis, spectroscopic studies, thermal analyses, biological activity of tridentate coordinated transition metal complexes of bi(pyridyl-2-ylmethyl)amine]ligand



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ABSTRACT

A new tridentate acyclic pincer ligand, [bi(pyridin-2-methyl)amine] (bpma, HL), was synthesized and reacted to form complexes with copper(II), nickel(II), iron(II), cobalt(II) and zinc(II) ions. Both the ligand and its complexes were characterized using elemental analysis, molar conductance, infrared, ¹H-NMR-spectroscopy, mass and thermal analyses. According to the spectroscopic data, all of the complexes share the same coordination environment around the metal atoms, consisting two nitrogen-pyridine entities, one nitrogen-methylamine entity, one/two water molecules and/or one/two chloride or bromide ions. Complexes also showed molar conductivity according to the presence of two halide anions outer the coordination sphere except Co(II) and Zn(II) complexes are non electrolytes. Analysis indicates that the metal ions have trigonal bipyramidal structure. Cu(II), Ni(II), Fe(II), Co(II), and Zn(II) metal complexes were screened for their antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus* (G+) and *Escherichia coli*, and *Pseudomonas aeruginosa* (G-) bacteria. They showed remarkable antimicrobial activity.

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1. Introduction

Catalytic activity of transition metal complexes that are coordinatively unsaturated may play an important role in catalytic processes [1]. Such compounds also find applications in degrading environmental pollutants as they act as biomimetic catalysts [2]. Que et al. reported the catalytic activity of a terapyridyl iron complex, the Fe(II)[N,N-bis-(2-pyridylmethyl)-N-di(2-pyridyl)methylamine] which is able to catalyze alkane oxidation with hydrogen peroxide [3]. Thus, the synthesis of new complexes is highly desirable. The synthesis of new receptors with pendant arms that have aromatic or aliphatic units is a fascinating area of research because of the importance of these receptors both in basic and applied chemistry. A subject of special interest is the design of homo- or hetero-binuclear complexes for biomedical applications that require covalent attachment of the macrocycle system to a recognition site [4–9].

Special interest has been devoted to the design of new catalysts

of late transition metal complexes consisting of tridentate nitrogen-based ligands as non-metallocene olefin polymerization catalysts [10–16]. These catalysts enhance both the activity and micro-structure of the resultant polymers as a pincer type ligand being thus capable of coordinate in a tridentate manner. The facility to modify and tune the properties of these ligands and their complexes has been reflected in their applications in different areas of chemistry, particularly in catalysis [17].

Reduction of the diisopropylarylbis(methylimino)pyridine iron dibromide, iPrPDI₂FeBr₂ (iPrPDI = 2,6-(2,6-(CHMe₂)₂C₆H₃N=CCH₃)₂C₅H₃N)(1-Br₂), yielded the corresponding bis (dinitrogen) compound, iPrPDI₂Fe(N₂)₂(1-(N₂)₂), which proved to be a thermally stable, highly active pre-catalyst for hydrogenation and hydrosilation of olefins [18]. The stability and catalytic activity of the complex has been attributed to the ligand's capacity to accept up to three electrons [19] from the metal center through conjugated π-acidic nitrogen atoms to mitigate the one electron redox changes intrinsic to iron [9].

Pyridine-containing macrocycles are interesting because of their versatility. They can be used as building blocks that lead to more complicated structures, including systems with more than one cavity, cages with three dimensional, and ligands having

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additional functional groups attached to the macrocyclic skeleton [20–26]. Some macrocycles involving *N*-methyl-pyridine, *N*-methyl-indole, or *N*-methyl-imidazole have been synthesized and their coordination ability towards divalent and trivalent metal anions was studied [27–30]. The preparation of new receptors with pendant arms that have aromatic or aliphatic units is an interesting area of research because of the importance of these receptors in basic and applied chemistry. One of the most interesting subjects is the design of homo- or hetero-binuclear complexes for biomedical applications that require covalent attachment of the macrocycle system to a recognition site [31–35]. Cytotoxic studies of transition metal ion concentrations have also been carried out using macrocyclic ligands with pendant arms [36,37]. Lanthanide (III) ions have also been employed as effective template agents [38,39] in the synthesis of large macrocycles with pyridine head units.

In this work, bi(pyridin-2-methyl)amine ligand and its Cu(II), Ni(II), Fe(II), Co(II), and Zn(II) metal complexes were prepared. The ligand and its new transition metal complexes were characterized by elemental analysis, IR, MS, ¹H NMR spectroscopy. Thermal stability and biological activity were investigated for selected compounds.

2. Experimental section

2.1. Materials and instruments

The metal salts CuCl₂·2H₂O (Sigma), CoCl₂·6H₂O and NiCl₂·6H₂O (BDH); ZnBr₂·4H₂O (Ubichem), and FeCl₂·2H₂O (Sigma) were used as purchased. All of the complexes synthesized melted above 300 °C. The solvents were reagent grade.

Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Egypt, using CHNS-932 (LECO) Vario Elemental Analyzer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)₄] was used as a calibrant. Molar conductivities of 10⁻³ M solutions of the solid complexes in DMF were measured on the using Jenway 4010 conductivity meter. IR spectra were obtained on an FT-IR Perkin-Elmer 1740 spectrophotometer (KBr pellets), covering the range between 400 and 4000 cm⁻¹. ¹H NMR spectra was recorded on a Bruker ARX-300 spectrometer (CDCl₃ solutions, tetramethylsilane was used as standard). The mass spectrum of the Ni(II) complex was recorded by EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument at the Microanalytical Center, Cairo University. Thermogravimetric analyses (TG/DTG) were carried out in the temperature range from 25 to 800 °C in a steam of nitrogen atmosphere using Shimadzu TG 50H thermal analysis. The experimental conditions were: platinum crucible, nitrogen atmosphere with a 30 ml/min flow rate and a heating rate 10 °C/min.

2.2. Microbiological investigations

For these investigations the filter paper disc method was applied according to Gupta et al. [40]. The investigated isolates of bacteria were seeded in tubes with nutrient broth (NB). The seeded NB (1 cm³) was homogenized in the tubes with 9 cm³ of melted (45 °C) nutrient agar (NA). The homogeneous suspensions were poured into Petri dishes. The discs of filter paper (diameter 4 mm) were ranged on the cool medium. After cooling on the formed solid medium, 2 × 10⁻⁵ dm³ of the investigated compounds were applied using a micropipette.

After incubation for 24 h in a thermostat at 25–27 °C, the inhibition (sterile) zone diameters were measured and expressed in mm. An inhibition zone diameter over 7 mm indicates that the

tested compound is active against the bacteria under investigation. The antibacterial activities of the investigated complexes were tested against four types of bacteria. The organisms used in the present investigations included two Gram positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*). Metal complexes were tested, as well as the standard. The concentration of each solution was 2.0 × 10⁻³ mol dm³.

2.3. Synthesis of [bi(pyridin-2-methyl)amine] (bpma)

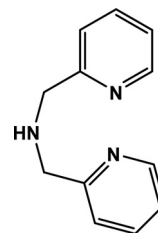
2-pyridinecarboxaldehyde (13.90 ml, 145 mol) dissolved in 40 ml ethanol was added dropwise to a solution of 2-(amino-methyl)pyridine (15.0 ml, 146 mol) in 150 ml ethanol. The mixture was left stirring for 15 min. Sodium borohydride (14.0 g, 0.370 mol) was added and the reaction was refluxed for 50 min. 15 ml of conc. HCl dissolved in 10 ml ethanol was added dropwise to the mixture while cooling in an ice bath. The mixture was left for 30 min in the ice bath and remained in the refrigerator overnight. A white precipitate was isolated by filtration. Sodium hydroxide (24 g, 0.6 mol) dissolved in 60 ml water was added to a dissolved product (180 ml of water), a two-phase system was formed with the product on top. Diethyl ether was added to extract the product. After removal of diethyl ether, the product was dissolved in 250 ml ethanol and filtered [41]. The filtered solution was cooled in an ice bath and 65 ml of conc. HCl was added, a white precipitate was formed then dried *in vacuo*. The resulting white crystals (Scheme 1) were isolated and subjected to elemental and spectroscopic analysis (24.8 g, 125 mol, 86% yield). FT-IR: ν(NH), ν(C=N) and δ(C=N) are 3170, 1589 and 620 cm⁻¹, respectively. ¹H NMR showed signals at δ = 8.76–7.52 (m, 8H, pyridine-H), 4.38 (s, 1H, NH) and 3.72 (br, 4H, CH₂) which can be assigned to the aromatic, N–H and methylene protons, respectively. Anal. calcd for C₁₂H₁₃N₃: C, 72.36; H, 6.53; N, 21.11, Found: C, 72.12; H, 6.83; N, 20.95.

2.4. Synthesis of [(C₁₂H₁₃N₃)Cu(H₂O)₂]Cl₂·H₂O

The complex was synthesized using CuCl₂·2H₂O (432 mg, 2.53 mmol). Blue precipitate was obtained. Yield: 0.73 g (78%). FT-IR: ν(H₂O), ν(NH), ν(C=N), δ(C=N), ν(M–O) and ν(M–N) are 3420, 3070, 1606, 650, 510 and 420 cm⁻¹, respectively. Anal. calcd for [(C₁₂H₁₃N₃)Cu(H₂O)₂]Cl₂·H₂O: C, 37.14; H, 4.90; N, 10.83. Found: C, 38.19; H, 3.82; N, 11.59.

2.5. Synthesis of [(C₁₂H₁₃N₃)Ni(H₂O)Cl]Cl·H₂O

By using NiCl₂·6H₂O (601.5 mg, 2.53 mmol). Blue precipitate was obtained, washed with ethanol and dried overnight under vacuum. Yield: 0.85 g (77%). FT-IR: ν(H₂O), ν(NH), ν(C=N), δ(C=N), ν(M–O) and ν(M–N) are 3420, 3242, 1606, 642, 554 and 430 cm⁻¹, respectively. Anal. calcd for [(C₁₂H₁₃N₃)Ni(H₂O)Cl]Cl·H₂O: C, 39.46; H, 4.65; N, 11.51. Found: C, 40.32; H, 3.41; N, 12.18.



Scheme 1. Structure of bi(pyridin-2-ylmethyl)amine ligand.

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