

ORIGINAL ARTICLES

In Situ Synthesis and Characterisation of 2-((2-(2,4-dinitrophenyl)-hydrazono)-methyl)phenol Metal Complexes and their Investigation as Antibacterial and Antifungal Agents

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ABSTRACT

In situ synthesis is usually used in industrial plants. As an approach new series of Cu(II), Cd(II), Fe(III), Ni(II), Co(II), Zn(II) and Mn(II) of the 2-((2-(2,4-dinitrophenyl)hydrazono)methyl)phenol, HL, have been synthesized and characterized by elemental analysis, IR, UV and ESR spectra, magnetic susceptibility and molar conductivity measurements. The spectral data and magnetic measurements of the complexes indicate that, the geometries are either square planar or octahedral. The results indicated also that the complexes show more reactivity than the ligand.

Key words: In Situ Synthesis, Metal Complexes, Schiff Base, Thermal Analysis, Biological Study.

Introduction

2-Hydroxy Schiff base ligands and their complexes derived from the reaction of derivatives of salicylaldehyde with amines have been extensively studied in great details for their various crystallographic, structural and magnetic features. (Yildiz, Kilic *et al.* 1998, Sunatsuki, Motoda *et al.* 2002) Schiff bases constitute an important class of ligands, which have very rich and extensive chemistry, reviewed recently by Vigato and Tamburini. (Vigato and Tamburini 2004) Metal complexes of Schiff bases have found diverse applications in addition to interesting structural chemistry. Chelation causes drastic change in the biological properties of the ligands and also the metal moiety. It has been reported that chelation is the cause and cure of many diseases including cancer. A number of Schiff base complexes (Arion, Reisner *et al.* 2003, Drabent, Bialoska *et al.* 2004) have been tested for antibacterial activities and they have been found antibacterial (Kabeer, Baseer *et al.* 2001, More, Bhalvankar *et al.* 2001), antifungal (Singh and Dash 1988, More, Bhalvankar *et al.* 2001), anticancer (Desai, Desai *et al.* 2001) and herbicidal (Samadhiya and Halve 2001) activities. We report in this article the in situ synthesis and characterization of the Cu(II), Cd(II), Fe(III), Ni(II), Co(II), Zn(II) and Mn(II) of the 2-((2-(2,4-dinitrophenyl)hydrazono)methyl)phenol. The coordination behavior of the Schiff base ligand towards metal ions was investigated via IR, UV, ESR as well as conductivity and magnetic moments measurements. The antibacterial and antifungal activities of the compounds showed that, metal complexes exhibited a greater inhibitory effect than the ligand.

Materials:

All the reagents employed for the preparation of the ligand and its complexes were of the best grade available and used without further purification.

Experimental:

The ligand and its metal complexes were analyzed for C, H, N, Cl and metal contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. Analytical and physical data of the ligand and its metal complexes are reported. IR spectra of the ligand and its metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400-4000 cm⁻¹ and in the 500-100 cm⁻¹ region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. Electronic spectra of the ligand and its complexes were obtained in Nujol mulls using a Shimadzu UV-240 UV-Vis recording spectrophotometer. Magnetic susceptibilities were measured at 25°C by the Gouy method using mercuric tetrathiocyanatocobaltate (II) as the magnetic susceptibility standard.

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Diamagnetic corrections were estimated from Pascal's constant. (Salama, Ahmed *et al.* 2006) The magnetic moments were calculated from the equation: $\mu_{\text{eff}} = 2.84\sqrt{\chi_M^{\text{corr}} \cdot T}$. Molar conductances were measured on a Tacussel type CD₆NG conductivity bridge using 10⁻³M DMF solutions. ESR measurements of solid complexes at room temperature were made using a Varian E-109 spectrophotometer, with DPPH as a standard material.

Synthesis of the ligand, HL:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.50 g, 4.09 mmol) was added drop wise to an ethanol solution (40 mL) of (2,4-dinitrophenyl)hydrazine (0.81 g, 4.09 mmol) and stir for 2 h. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P₄O₁₀ (0.87 g, 70 % yield). IR (KBr): $\nu(\text{OH})$ 3288(s), $\nu(\text{NH})$ 3190-3120, $\nu(\text{C}=\text{N})$ 1622 (s), $\nu_{\text{as}}(\text{NO})$ brood head 1277-1274(s), $\nu_{\text{s}}(\text{NO})$ 1110 m. Elemental analysis for C₁₃H₁₀N₄O₅ (302.24): calcd. C, 51.66; H, 3.33; N, 18.54; found C, 51.54; H, 3.40; N, 18.61.

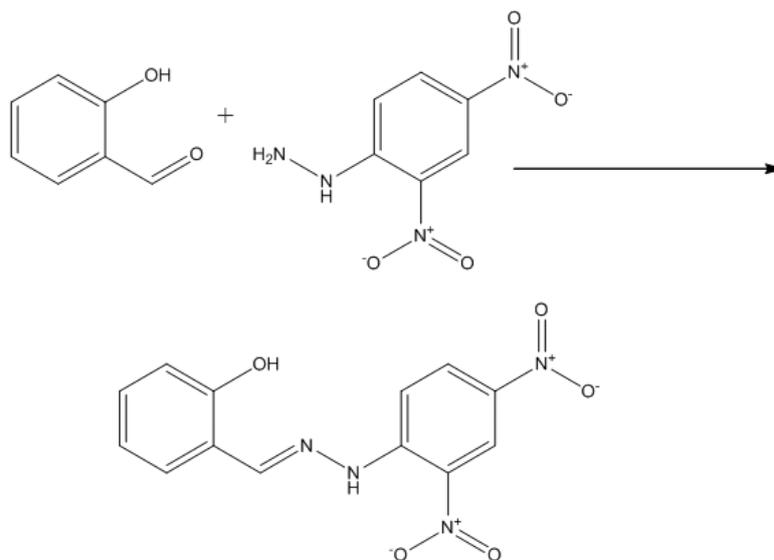


Fig. 1: Preparation of the ligand H₂L.

Metal complexes:

[LCuCl(H₂O)]3H₂O, complex 2:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.30 g, 2.46 mmol) was added drop wise with stirring to ethanol solution (50 mL) of (2,4-dinitrophenyl)hydrazine (0.49g, 2.46 mmol). After 15 min a methanol solution (50 mL) of CuCl₂·2H₂O (0.42 g, 2.46 mmol) was drop wise added with stirring and efflux for 3 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 40 mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P₄O₁₀ (0.95 g, 82% yield). Conductance Λ_m : 14 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ UV (Nujolmul (nm)): $\lambda = 549$ and 617 nm. Magnetic moments: 1.96 B.M. ESR: $g_{\parallel}2.23$, $g_{\perp}2.044$, $g_{//A}209$, G 5.46, $g_{\text{iso}}2.11$. IR (KBr): $\nu(\text{H}_2\text{O})$ 3460-3445(br), $\nu(\text{NH})$ 3192-3130, $\nu(\text{C}=\text{N})$ 1613(s), $\nu_{\text{as}}(\text{NO})$ brood head 1279-1275(s), $\nu_{\text{s}}(\text{NO})$ 1110 m, $\nu(\text{M}-\text{N})$ 445, $\nu(\text{M}-\text{O})$ 540, $\nu(\text{M}-\text{Cl})$ 365. TGA (found (Calc., temp.): 3 H₂O 11.34 (11.45, 81°C), 1 H₂O 3.95 (3.82, 124°C), 1 Cl atom 7.65 (7.51, 210 °C), CuO 16.97 (16.84, 520°C). Elemental analysis for C₁₃H₁₇ClCuN₄O₉ (472.29): calcd. C, 33.06; H, 3.63; Cl, 7.51; Cu, 13.45; N, 11.86; found C, 32.91; H, 3.70; Cl, 7.46; Cu, 13.33; N, 11.90.

[LFeCl₂(H₂O)₂]3H₂O, complex 3:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.50 g, 4.09 mmol) was added drop wise with stirring to ethanol solution (80 mL) of (2,4-dinitrophenyl)hydrazine (0.81 g, 4.09 mmol). After 15 min a methanol solution (90 mL) of FeCl₃·6H₂O (1.11 g, 4.09 mmol) was drop wise added with stirring and efflux for 2.5 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 60 mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P₄O₁₀ (1.61 g, 73 % yield). Conductance Λ_m : 12 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ UV (Nujolmul (nm)): $\lambda = 532$, 655 and 849. Magnetic moments: 5.92 B.M. IR (KBr): $\nu(\text{H}_2\text{O})$ 3465-3447(br), $\nu(\text{NH})$ 3190-3140, $\nu(\text{C}=\text{N})$ 1612 (s), $\nu_{\text{as}}(\text{NO})$ brood

head 1278-1275 (s), $\nu_s(\text{NO})$ 1111 m, $\nu(\text{M-N})$ 470, $\nu(\text{M-O})$ 535, $\nu(\text{M-Cl})$ 372. TGA (found (Calc., temp.): 3 H_2O 10.14 (10.03, 78 °C), 2 H_2O 6.52 (6.68, 128 °C), 2 Cl atom 13.24 (13.15, 214 °C), $\frac{1}{2}$ Fe_2O_3 16.97 (16.84, 605°C). Elemental analysis for $\text{C}_{13}\text{H}_{19}\text{Cl}_2\text{FeN}_4\text{O}_{10}$ (518.06): calcd. C, 30.14; H, 3.70; Cl, 13.69; Fe, 10.78; N, 10.81; found C, 30.02; H, 3.81; Cl, 13.57; Fe, 10.69; N, 10.97.

[LCdCl(H₂O)]4H₂O, complex 4:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.32 g, 2.62 mmol) was added drop wise with stirring to ethanol solution (50 mL) of (2,4-dinitrophenyl)hydrazine (0.51 g, 2.62 mmol). After 15 min a methanol solution (50 mL) of CdCl_2 (0.48 g, 2.62 mmol) was drop wise added with stirring and efflux for 4 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 40mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P_4O_{10} (0.96 g, 68 % yield). Conductance Λ_m : $9 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR (KBr): $\nu(\text{H}_2\text{O})$ 3460-3435(br), $\nu(\text{NH})$ 3190-3135, $\nu(\text{C=N})$ 1613 (s), $\nu_{\text{as}}(\text{NO})$ brood head 1279-1272(s), $\nu_s(\text{NO})$ 1111 m, $\nu(\text{M-N})$ 455, $\nu(\text{M-O})$ 568, $\nu(\text{M-Cl})$ 382. TGA (found (Calc., temp.): 4 H_2O 13.28 (13.37, 75 °C), 1 H_2O 3.49 (3.34, 120 °C), 1 Cl atom 6.44 (6.58, 225 °C), CdO 23.67 (23.82, 520°C). Elemental analysis for $\text{C}_{13}\text{H}_{19}\text{CdClN}_4\text{O}_{10}$ (539.17): calcd. C, 28.96; H, 3.55; Cl, 6.58; N, 10.39; found C, 28.83; H, 3.67; Cl, 6.46; N, 10.51.

[LNiCl(H₂O)₃]H₂O, complex 5:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.43 g, 3.52 mmol) was added drop wise with stirring to ethanol solution (70 mL) of (2,4-dinitrophenyl)hydrazine (0.70 g, 3.52 mmol). After 15 min a methanol solution (80 mL) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.84 g, 3.52 mmol) was drop wise added with stirring and efflux for 3 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 35 mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P_4O_{10} (1.25 g, 76 % yield). Conductance Λ_m : $10 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. UV (Nujolmul (nm)): $\lambda = 690$ and 1010 nm. Magnetic moments: 3.17B.M. IR (KBr): $\nu(\text{H}_2\text{O})$ 3465-3427 (br), $\nu(\text{NH})$ 3185-3140, $\nu(\text{C=N})$ 1609 (s), $\nu_{\text{as}}(\text{NO})$ brood head 1279-1272 (s), $\nu_s(\text{NO})$ 1111 m, $\nu(\text{M-N})$ 440, $\nu(\text{M-O})$ 570, $\nu(\text{M-Cl})$ 387. TGA (found (Calc., temp.): 1 H_2O 3.67 (3.86, 84 °C), 3 H_2O 11.70 (11.57, 125 °C), 1 Cl atom 7.46 (7.58, 220 °C), NiO 16.11 (15.98, 515°C). Elemental analysis for $\text{C}_{13}\text{H}_{17}\text{ClN}_4\text{NiO}_9$ (467.44): calcd. C, 33.40; H, 3.67; Cl, 7.58; N, 11.99; Ni, 12.56; found C, 33.27; H, 3.81; Cl, 7.51; N, 12.09; Ni, 12.46.

[LCoCl(H₂O)₃].2H₂O, complex 6:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.37 g, 3.03 mmol) was added drop wise with stirring to ethanol solution (60 mL) of (2,4-dinitrophenyl)hydrazine (0.60 g, 3.03 mmol). After 15 min a methanol solution (70 mL) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.72 g, 3.03 mmol) was drop wise added with stirring and efflux for 5 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 40mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P_4O_{10} (0.99 g, 67 % yield). Conductance Λ_m : $15 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. UV (Nujolmul (nm)): $\lambda = 515$ and 1140 nm. Magnetic moments: 4.80 B.M. IR (KBr): $\nu(\text{H}_2\text{O})$ 3457-3435 (br), $\nu(\text{NH})$ 3185-3140, $\nu(\text{C=N})$ 1611 (s), $\nu_{\text{as}}(\text{NO})$ brood head 1278-1273 (s), $\nu_s(\text{NO})$ 1112 m, $\nu(\text{M-N})$ 457, $\nu(\text{M-O})$ 572, $\nu(\text{M-Cl})$ 390. TGA (found (Calc., temp.): 2 H_2O 7.54 (7.42, 79 °C), 3 H_2O 11.00 (11.13, 128 °C), 1 Cl atom 7.48 (7.30, 215 °C), $\frac{1}{2}$ Co_2O_3 17.19 (17.07, 595°C). Elemental analysis for $\text{C}_{13}\text{H}_{19}\text{ClCoN}_4\text{O}_{10}$ (485.70): calcd. C, 32.15; H, 3.94; Cl, 7.30; Co, 12.13; N, 11.54; found C, 32.04; H, 4.11; Cl, 7.19; Co, 12.02; N, 11.68.

[LZnCl(H₂O)].5H₂O, complex 7:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.50 g, 4.09 mmol) was added drop wise with stirring to ethanol solution (80 mL) of (2,4-dinitrophenyl)hydrazine (0.81 g, 4.09 mmol). After 15 min a methanol solution (65 mL) of ZnCl_2 (0.56 g, 4.09 mmol) was drop wise added with stirring and efflux for 6 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 50mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P_4O_{10} (1.27 g, 61 % yield). Conductance Λ_m : $8\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. IR (KBr): $\nu(\text{H}_2\text{O})$ 3462-3425 (br), $\nu(\text{NH})$ 3180-3135, $\nu(\text{C=N})$ 1609(s), $\nu_{\text{as}}(\text{NO})$ brood head 1279-1272(s), $\nu_s(\text{NO})$ 1110 m, $\nu(\text{M-N})$ 480, $\nu(\text{M-O})$ 547, $\nu(\text{M-Cl})$ 378. TGA (found (Calc., temp.): 5 H_2O 17.74 (17.66, 82 °C), 1 H_2O 3.39 (3.53, 125 °C), 1 Cl atom 7.08 (6.95, 215 °C), ZnO 15.83 (15.95, 510°C). Elemental analysis for $\text{C}_{13}\text{H}_{21}\text{ClN}_4\text{O}_{11}\text{Zn}$ (510.16): calcd. C, 30.61; H, 4.15; Cl, 6.95; N, 10.98; Zn, 12.82; found C, 30.47; H, 4.26; Cl, 6.86; N, 11.11; Zn, 12.69.

[LMnCl(H₂O)₃]4H₂O, complex 8:

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (0.30 g, 2.46 mmol) was added drop wise with stirring to ethanol solution (50 mL) of (2,4-dinitrophenyl)hydrazine (0.49 g, 2.46 mmol). After 15 min a methanol solution (50 mL) of MnCl₂.4H₂O (0.49 g, 2.46 mmol) was drop wise added with stirring and efflux for 4 h. A few drops of trimethyl amine were added to allow precipitation then the volume of the solvent was reduced to 45 mL. The precipitate was then filtered off, washed with methanol and dried in a vacuum desiccator over P₄O₁₀ (0.93 g, 73 % yield). Conductance Λ_m : 10 Ω cm²mol⁻¹. UV/vis (Nujolmul (nm)): λ = 558. Magnetic moments: 4.97 B.M. IR (KBr): ν (H₂O) 3465-3430 (br), ν (NH) 3185-3135, ν (C=N) 1608 (s), ν_{as} (NO) brood head 1278-1272 (s), ν_s (NO) 1110 m, ν (M-N) 458, ν (M-O) 575, ν (M-Cl) 398. TGA (found (Calc., temp.): 4 H₂O 14.05 (13.92, 87°C), 3 H₂O 10.28 (10.44, 121°C), 1 Cl atom 7.00 (6.85, 225°C), ½ Mn₂O₃ 15.30 (15.25, 600°C). Elemental analysis for C₁₃H₂₃ClMnN₄O₁₂ (517.73): calcd. C, 30.16; H, 4.48; Cl, 6.85; Mn, 10.61; N, 10.82; found C, 30.2; H, 4.57; Cl, 6.80; Mn, 10.54; N, 10.99.

In-vitro Antibacterial and Antifungal Activities:

The investigation of the biological activities of the newly synthesized Schiff base ligands, there metal complexes and their corresponding metal salts were carried out in the Botany Department Lab. of microbiology, Faculty of Science, El-Menoufia University. The antibacterial and antifungal activities were investigated by disc diffusion method. The antibacterial activities were done using *Escherichia coli* and *Aspergillusniger* at 2000 ppm concentrations in DMSO. DMSO poured disc was used as negative control. The bacteria were subcultured in nutrient agar medium which was prepared using (g.L⁻¹ distilled water) NaCl (5 g), peptone (5 g), beef extract (3 g), agar (20 g). The fungus was subcultured in Dox's medium which was prepared using (g.L⁻¹ distilled water) yeast extract (1g), sucrose (30 g), NaNO₃, agar (20 g), KCl (0.5 g), KH₂PO₄ (1 g), MgSO₄.7H₂O (0.5 g) and trace of FeCl₃.6H₂O. These mediums were then sterilized by autoclaving at 120 °C for 15 min. After cooling to 45 °C the medium was poured into 90 mm diameter Petri dishes and incubated at 37 °C or 28 °C, respectively. After few hours, Petri dishes were stored at 4 °C. Microorganisms were spread over each dish by using sterile bent Loop rod. The test is carried out by placing filter paper disks with a known concentration of the compounds on the surface of agar plates inoculated with a test organism. Standard antibacterial drug (tetracycline), antifungal drug (Amphotericin B) and solution of metal salts were also screened under similar conditions for comparison. The Petri dishes were incubated for 48 h. at 37 or 28°C, respectively. The zone of inhibition was measured in millimeters carefully. All determinations were made in duplicated manner for each of the compounds. An average of the two independent readings for each compound was record.

Results and Discussion

The analytical and physical data, spectral data are compatible with the suggested structures. The complexes are colored, stable in air and insoluble in H₂O, ethanol and non-polar solvents such as benzene. However, they dissolve in polar solvents such as DMF and DMSO. All the complexes are non-electrolytes.

Infrared spectra:

IR spectra of the complexes were recorded to confirm their structures. The assignments of the characteristic vibrational frequencies of the complexes were made by comparison with the vibrational frequencies of the free ligand. The ligand behaved as monobasic bidentate ligand coordinating through the imine nitrogen and the phenolic oxygen. In all complexes the signals of the imine groups was shifted to lower wave number accompanied by a decrease in its intensity, indicating it is involved in complex formation (Cescon and Day 1962, Naresh Kumar and Ramesh 2005, Balasubramanian, Parameswari *et al.* 2006, Yin and Chen 2006)but the signals due to nitro and amino groups almost retained its original position indicating they are not involved in complex formation.(Gakias, Rix *et al.* 2006)In all complexes the band due to hydroxyl group disappeared indicating the deprotonation of the ligand prior to coordination throughphenolic oxygen.(Mohamed, Omar *et al.* 2005, Shauib, Elassar *et al.* 2006). The new signals in the 480-440 and 575-535 cm⁻¹ ranges may assigned to ν (M-N) and ν (M-O) respectively. (Cescon and Day 1962, Fernandez-G., Tepal-Sanchez *et al.* 2006, Majumder, Rosair *et al.* 2006)The spectra of all complexes showed weak intensity ν (M-Cl) bands in the 398-365 cm⁻¹ range indicating terminal Chloro ligands(Ferrari, Fara *et al.* 1991).

Molar conductivity:

The molar-conductance of all metal complexes are in the $8\text{-}15 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ range, indicating their non-electrolytic nature. (Golcu, Tumer *et al.* 2005).

Electronic spectra:

Cu(II) complex showed two bands at 549 and 617 nm, which can be assigned to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively indicating that the copper(II) have tetragonal distorted octahedral geometry. (Mohamed and El-Wahab 2005, Mohamed, Omar *et al.* 2005) The magnetic moment is 1.96 B.M., which falls within the range normally observed for octahedral copper complexes. (Mohamed, Omar *et al.* 2005) Three peaks observed at 849, 655 and 532 nm in the spectra of iron complex are due to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$, ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions, respectively, suggesting its octahedral nature. (Mohamed, Omar *et al.* 2005) The magnetic moment of the iron complex is 5.92 BM which is closer to the spin only value indicating an octahedral structure for the complex. Complex 5 shows d-d transitions at 1010 and 690 nm assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) spin allowed electronic transitions, which are characteristic of Ni^{2+} in an octahedral configuration. (Mohamed, Omar *et al.* 2005, Mohameda and El-Wahab 2005, Kumar and John 2006) The electronic spectra of cobalt(II) complex has spectral typical of an octahedral system showing two bands at 515 and 1140 nm which can be assigned to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, respectively, in an octahedral geometry. (Sengupta, Pandey *et al.* Lu, Zhang *et al.* 2005, Sarkar, Ray *et al.* 2006) The magnetic moments values (μ_{eff}) found to be 4.80 B. M., which lie in the range reported for high spin ($S = 3/2$) octahedral cobalt(II) complexes. (Zhao, Niel *et al.* 2004, Alam, Nethaji *et al.* 2005) The Mn(II) complexes show broad bands near 558 nm, that is attributed to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ transition in octahedral structures. (A.B.P. Lever, Mostafa, Bekheit *et al.* 2000) The magnetic moment value of 4.97 B.M. indicates a high-spin $3d^5$ system. (A.B.P. Lever)

ESR:

The X-band ESR spectra of the complex provide further insight into the environment around the metal centers. The ESR spectrum of the solid copper(II) complex at room temperature showed the g values: $g_{\parallel} = 2.23$ and $g_{\perp} = 2.044$. These complex showed an axial shape with $g_{\parallel} > g_{\perp}$, characteristic of complexes with ${}^2B_1(d_{x^2-y^2})$ ground state. The average g values were calculated according to the equation $g_{\text{av}} = 1/3[g_{\parallel} + 2g_{\perp}]$ (2.11). The complex exhibits $g_{\parallel} < 2.3$, suggesting covalent characters of the copper-ligand bonding in this complex. The parameter $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ shows the possibility of exchange interaction in the Cu(II) complex. The G values for the copper complex ($G > 4$) indicate that there is no direct copper-copper interaction in the solid state. (Shauib, Elassar *et al.* 2006) The $g_{\parallel}/A_{\parallel}$ is taken as an indication for the stereochemistry of the copper(II) complexes. Addison (Labisbal, Rodriguez *et al.* 2006) has suggested that this ratio may be an empirical indication of the tetrahedral distortion of the square planar geometry. The values lower than 135cm^{-1} are observed for square planar structures and those higher than 150cm^{-1} for tetragonal distorted complexes. The value of $g_{\parallel}/A_{\parallel}$ for the copper complex lies above 150cm^{-1} indicating tetragonal distorted complex.

Thermal Analysis of Metal Complexes:

The thermo-gravimetric analysis (TG) was measured in the temperature $20\text{-}800^\circ\text{C}$ range. The results were in good agreement with the proposed structures, figure 2. All complexes showed the same pattern of losing lattice water in then coordinated water followed by the removal of chlorine atom/s then the organic constituents of the complexes start to decompose, finally leaving the metal oxides.

Antibacterial and Antifungal Screening:

The results of biological activity tested for the ligand and its complexes are given in figures 3, 4. Diameter of inhibition zone (mm) including the disc diameter was measured for each treatment. The overall results indicated that Ni(II) and Zn(II) complexes exhibited the maximum antibacterial and antifungal activities. The results indicate that the complexes show more activity than the ligands. This would suggest that the chelation could facilitate the ability of a complex to cross a cell membrane and can be explained by Tweedy's chelation theory. (N., I.J. *et al.* 1998) Chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron delocalization over the whole chelate ring. Such chelation could also enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane. (M., D. *et al.* 2007).

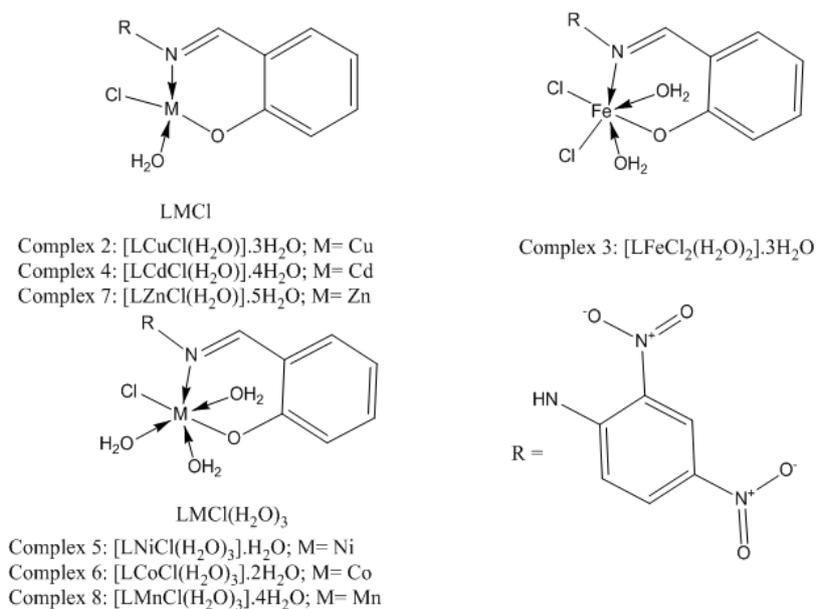


Fig. 2: The proposed structures of metal complexes of the ligand H₂L.

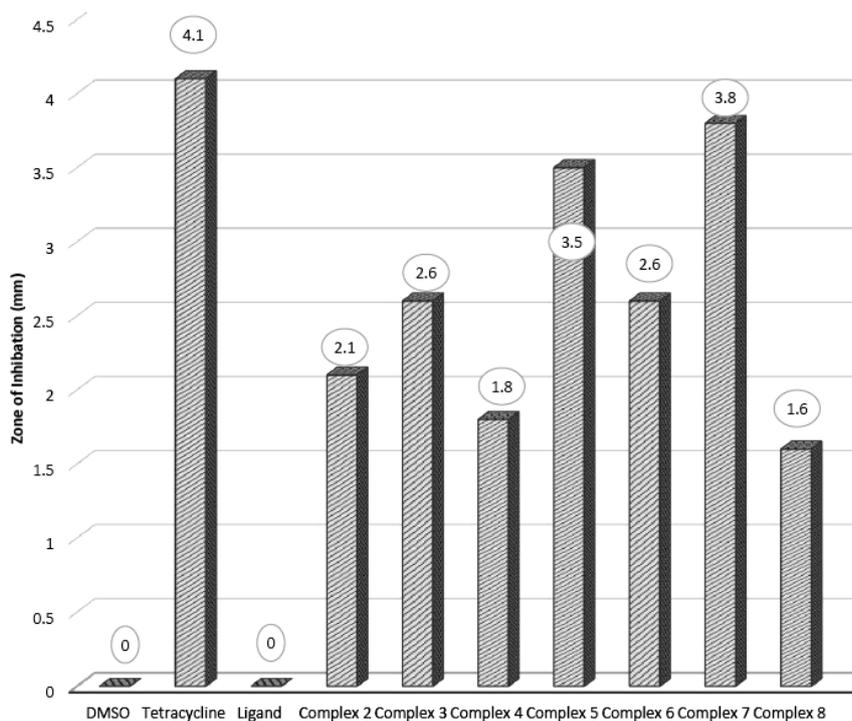


Fig. 3: Antibacterial activity of the ligand and its metal complexes against gram-negative bacterium (*E. coli*).

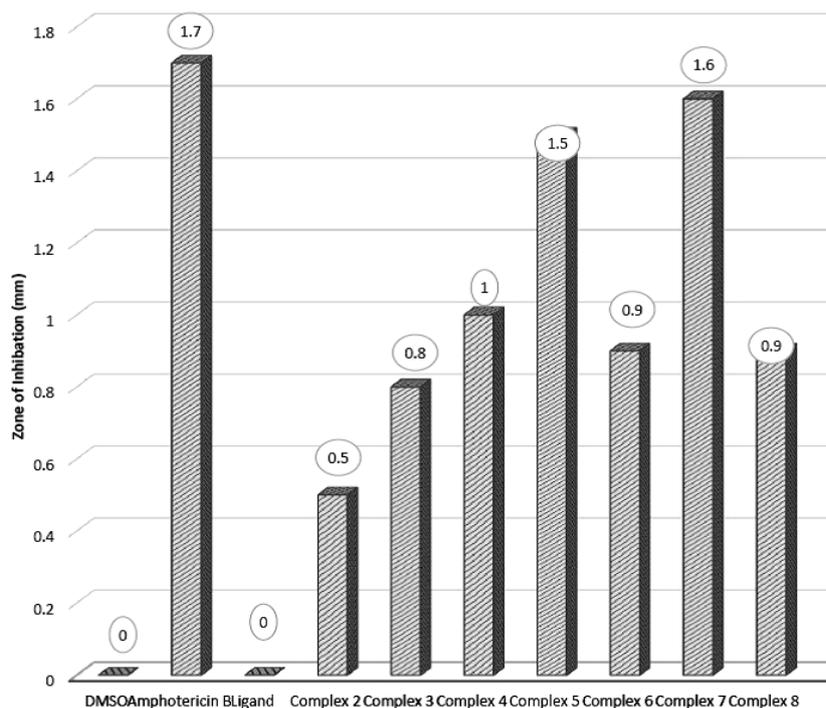


Fig. 4: Antifungal activity of the ligand and its metal complexes against Fungus (*Aspergillus niger*).

Conclusion:

The ligand was synthesized to compare its spectrum analysis to that of its metal complexes for their characterization. The spectral data and magnetic measurements of the complexes indicate that, the ligand behaved as monobasic bidentate ligand and the geometries are either square planar or octahedral. The ligand and its metal complexes have been synthesized and identified by elemental analyses, molar conductivities, and spectral (UV, IR) and magnetic moment measurements techniques. Conductance measurements suggest the non-electrolytic nature for all the metal complexes. The overall results indicated that Ni(II) and Zn(II) complexes exhibited the maximum antibacterial and antifungal activities. The results indicate that the complexes show more activity than the ligand.

References

- Cotton, F.A., G. Wilkinson, 1998. *Advanced Inorganic Chemistry*, John Wiley and Sons, New York.
- Offiong, E.O., S. Martelli, I.L. Farm., 1994. 49: 513.
- Collee, J.G., J.P. Duguid, A.G. Farser, B.D. Marmion (editors), 1989. "Practical Medical Microbiology" New York, Churchill Livingstone.
- Nakamoto, K., 1970. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed., John Wiley and Sons Inc.
- Lever, A.B.P., 1968. *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam.
- Lever, A.B.P., I.E.S. Elsevier Science Publisher, B.V. Amsterdam, 1984. Oxford, New York, Tokyo.
- Alam, M.A., M. Nethaji and M. Ray, 2005. *Inorg. Chem.*, 44: 1302.
- Arion, V.B., E. Reisner, M. Fremuth, M.A. Jokupec, B.K. Keppler, V.Y. Kukushkin and A.J.L. Pombeiro, 2003. *Inorg. Chem.*, 42(19): 6024-6031.
- Balasubramanian, K.P., K. Parameswari, V. Chinnusamy, R. Prabhakaran and K. Natarajan, 2006. *Spectrochim. Acta Part A*, 65: 678-683.
- Cescon, L.A. and A.R. Day, 1962. *J. Org. Chem.*, 27: 581.
- Desai, S.B., P.B. Desai and K.R. Desai, 2001. *Heterocycl. Commun.*, 7(1): 83-90.
- Drabent, K., A. Bialoska and Z. Ciunik, 2004. *Inorg. Chem. Commun.*, 7(2): 224-227.
- Fernandez, G., J.M.P. Tepal-Sanchez and S. Hernandez-Ortega, 2006. *J. Mol. Struct.*, 787: 1-7.
- Ferrari, M.B., G.G. Fara, M. Lafranchi, C. Pelizzi and M. Tarasconi, 1991. *Inorg. Chem. Acta*, 181: 253.
- Gakias, S., C. Rix, A. Fowless and M. Hobday, 2006. *Inorg. Chim. Acta*, 359: 2291-2295.
- Golcu, A., M. Tumer, H. Demirelli and R.A. Wheatley, 2005. *Inorg. Chim. Acta*, 358: 1785.
- Kabeer, A.S., M.A. Baseer and N.A. Mote, 2001. *Asian. J. Chem.*, 13(2): 496-500.
- Kumar, K.G. and K.S. John, 2006. *React. Funct. Polym.*, 66: 1427-1433.

- Labisbal, E., L. Rodriguez, A. Sousa-Pedrares, M. Alonso, A. Vizoso, J. Romero, J.A. Garcia-Vazquez and A. Sousa, 2006. *J. Organomet. Chem.*, 691: 1321-1332.
- Lu, Z., D. Zhang, S. Gao and D. Zhu, 2005. *Inorg. Chem. Commun.*, 8: 746.
- M., T., E.D., T.F. and B.A., 2007. "Synthesis, characterization and properties of some divalent metal(II) complexes: Their electrochemical, catalytic, thermal and antimicrobial activity studies." *Spectrochimica Acta*, A67(3-4): 916.
- Majumder, A., G.M. Rosair, A. Mallick, N. Chattopadhyay and S. Mitra, 2006. *Polyhedron*, 25: 1753-1762.
- Mohamed, G.G. and Z.H.A. El-Wahab, 2005. *Spectrochim. Acta*, Part A61.
- Mohamed, G.G., M.M. Omar and A.M.M. Hindy, 2005. *Spectrochim. Acta*, Part A62: 1140-1150.
- Mohamed, G.G., M.M. Omar and A.M.M. Hindy, 2005. *Spectrochim. Acta*, Part A62.
- Mohameda, G.G. and Z.H.A. El-Wahab, 2005. *Spectrochim. Acta*, Part A61: 1059-1068.
- More, P.G., R.B. Bhalvankar and S.C. Patter, 2001. *J. Ind. Chem. Soc.*, 78(9): 474-475.
- Mostafa, S.I., M.M. Bekheit and M.M. El-Agez, 2000. *Synth. React. Inorg. Met. Org. Chem.*, 30: 2029.
- N., F., G.I.J. and S. R.V., 1998. "Sulfur bonded palladium(ii) and platinum(ii) complexes of biologically potent thioamides." *Phosphorus, Sulfur Silicon Relat. Elem.*, 132: 1-8.
- Naresh Kumar, K. and R. Ramesh, 2005. *Polyhedron*, 24: 1885-1892.
- Salama, T.M., A.H. Ahmed and Z.M. El-Bahy, 2006. *Microporous and Mesoporous Materials*, 89: 251-259.
- Samadhiya, S. and A. Halve, 2001. *Orient J. Chem.*, 17(1): 119-122.
- Sarkar, B., M.S. Ray, M.G.B. Drew, A. Figuerola, C. Diaz and A. Ghosh, 2006. *Polyhedron*, 25: 3084-3094.
- Sengupta, S.K., O.P. Pandey, B.K. Srivastava, V.K. Sharma, 1998. 349 *Trans. Met. Chem.*
- Shauib, N.M., A.Z.A. Elassar and A. El-Dissouky, 2006. *Spectrochim. Acta Part A63* 714.
- Shauib, N.M., A.A. Elassar and A. El-Dissouky, 2006. *Spectrochim. Acta*, Part A63: 714-722.
- Singh, W.M. and B.C. Dash, 1988. *Pesticides*, 22(11): 33-37.
- Sunatsuki, Y., Y. Motoda and N. Matsumoto, 2002. *Coord. Chem. Rev.*, 226: 199.
- Vigato, P.A. and S. Tamburini, 2004. *Coord. Chem. Rev.*, 248: 1717.
- Yildiz, M., Z. Kilic and T. Hokelek, 1998. *J. Mol. Struct.*, 441: 1.
- Yin, H.D. and S.W. Chen, 2006. *Inorg. Chim. Acta*, 359: 3330-3338.
- Zhao, L., V. Niel, L.K. Thompson, Z. Xu, V.A. Milway, R.G. Harvey, D.O. Miller, C. Wilson, M. Leech, J.A.K. Howard and S.L. Heath, 2004. *Dalton Trans*, 1446.