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Antibacterial Application of Novel Mixed-Ligand Dithiocarbamate Complexes of Nickel (II)

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Abstract: *Nine stable mixed ligand dithiocarbamate complexes of Nickel (II) ion were prepared. The complexes were characterized with electronic spectroscopy, infrared spectroscopy, conductance measurement, melting point and percentage metal analysis. Resulting analytical data gave credence to the assignment of a tentative square planar geometry to all the complexes. The complexes were proposed to have a general formulae of [Ni(Sal)(Rdtc)], where Sal = salicylaldehyde; R = dibenzylamine(Bz_2NH), methylphenylamine(MePhNH),pyrrolidineamine(pyrrolNH),piperidineamine(piperNH),morpholineamine(MorpNH), anilineamine(AnilNH), para-chloroanilineamine(p-ClAnilNH), toludineamine(TolNH) and anisidineamine(AnisNH); and dtc = dithiocarbamate anion. The metal complexes were screened against six different bacteria strain using Agar diffusion method. The antibacterial studies reveal that the metal complexes exhibit broad spectrum antibacterial activity against Escherichia coli, Staphylococcus aureus, Klebsiella oxytoca and Pseudomonas aureginosa with inhibitory range of 10.5.—20.0mm.*

Keywords*: Aromatic dithiocarbamate, Salicylaldehyde, Antibacterial studies and Nickel ion.*

I. Introduction

Dithiocarbamates are versatile compounds with wide range of chemistry. An extremely large number of dithiocarbamate complexes with transition and non transition metal ions have been reported (Dawood et al.2009; Daniel et al.2009 and Sarwar et al.2007). Compounds with dithiocarbamate moiety have attracted attention because of their potential biological activity (Leka et al. 2006). Their metal complexes present striking structural features and have diversified applications, such as high pressure lubricants, fungicides, pesticides, and accelerators used in vulcanization (Beer et al.2001).

There has been growing interest in the formation of mixed ligands chelates involving ligands containing different functional groups and transition metals of different oxidation states (Samus et al 2006 and Manov et al.2004). Coordination compounds with mixed ligands are of considerable importance in the field of metalloenzymes and are known to possess various biological activities (Rai et al.2005). Hence a large number of mixed ligand complexes with various transition metals are known (Mahapatra et al.1986 and Rai et al.2006).

As a continuation of our research on mixed ligand complexes of dithiocarbamate moiety with salicylaldehyde (Ekennia and Odola, 2013), we report herein, the synthesis, characterization and antibacterial application of nine mixed ligand complexes of aryl dithiocarbamate and salicylaldehyde moiety with the aim of producing lead compounds for the production of effective and more selective bactericides.

II. Experimentation

2.1 *Reagents*

Hydrated nickel(II) chloride, carbon disulfide, sodium hydroxide, dibenzylamine, methylphenylamine, pyrrolidineamine, piperidineamine, morpholineamine, anilineamine, para-chloroanilineamine, toludineamine and anisidineamine were bought from Aldrich and Sigma Co. and British Drug House and used as supplied.

2.2 *General Preparation of mixed ligand complexes*

The complexes were prepared according to literature (Ekennia and Odola, 2013). Equimolar concentration of the dithiocarbamate, metal ion and salicylaldehyde moiety was added to an ethanolic solution and refluxed for 3 hours. The resulting precipitate was filtered under vacuum, washed with diethylether and stored under silica gel in desiccator.

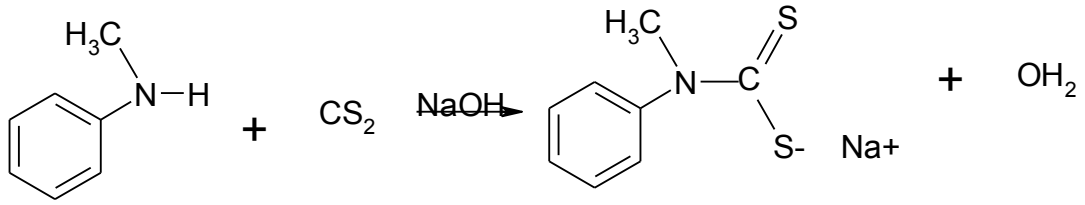

Fig 1.0: Synthesis of N-methyl-N-phenyl-dithiocarbamate

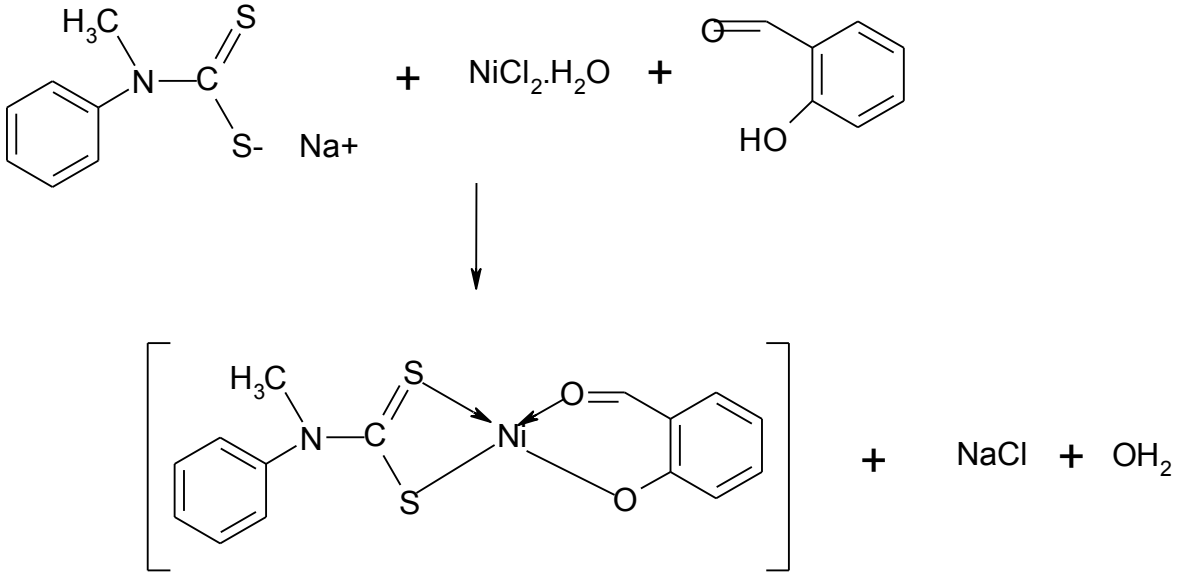

Fig 1.1: Diagrammatic presentation of mechanism of reaction of Ni(Sal)(MePhdtc)

2.3 ***Physical measurements***

The experimental percentage nickel content of the complexes was determined by chelatometric titration using murexide as an indicator. Electronic spectra were obtained using Genesys 10 UV Spectrophotometer. Infrared spectra were obtained using Buck 500 model spectrophotometer. Electrolytic conductivities of 1 X 10^{-3} M solution of the complexes in DMF were determined using Hanna conductivity meter model H19991300.

2.4 ***Antibacterial screening***

The in vitro evaluation of antibacterial activity was performed using the agar diffusion method. Three gram negative bacteria (*Klebsiella oxytoea, Pseudomonas aureginosa, Escherichia coli*) and three gram positive bacteria (*Bacillus cereus, Proteus mirabilis and Staphylococcus aureus*) were resuscitated from a nutrient slope and grown in nutrient broth at 37^{o}C for 24 hours. The surface of a petri dish was uniformly inoculated with 0.2 ml of 24-hour old test bacteria culture. Using a sterile cork borer, 7 mm wells were bored into the agar. Then 10 mg/ml solution of each test compounds in DMSO was added to the well bored. The plates were kept after inoculation at 37^{o}C for 24hours, after which the inhibitory zone (in mm) were taken as a measure of antibacterial activity.

III. Results And Discussion

3.1 [Ni(Sal)(Bz_2dtc)]

The compound was obtained as light green solid and re-crystalized in hot ethanolic solution. **Formulae mass**: 452.23g. **Yeild**: 61%. **M.P/D.T**.= *237^{o}C. **% Ni experimental (Calculated)** = 12.98(13.00). Λm= 13.00$\Omega^{-1}cm^2mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1653(vC=O), 1529(vC=N), 1229(vC-O),533(Ni-O) and 321(Ni-S). **Electronic spectra**(ε) λ max(kK): 16.02 (100), 24.80 (200), 25.78 (1 x 10^5) and 39.58 (1 x 10^5).

3.2 [Ni(Sal)(MePhdtc)]

The compound was obtained as a dark green solid and recrystalized from hot ethanolic solution. **Formulae mass**: 362.11g. **Yeild**:97%. M.P/D.T:*200 ^{o}C. **%Ni(Cal):**16.21(16.32). Λm=17.00$\Omega^{-1}cm^2mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1624(vC=O), 1524(vC=N), 1201(vC-O),553(Ni-O) and 328(Ni-S). **Electronic spectra**(ε) λ max(kK): 16.15 (100), 23.70 (200), 43.79 (1 x 10^5) and 50.87 (1 x 10^5).

3.3 [**Ni(Sal)(Pyrroldtc)]**

The compound was obtained as a dark green solid and recrystalized from hot ethanolic solution. **Formulae mass:** 362.11g. **Yeild**: 97%. **M.P/D.T**:*200 ^{o}C. **%Ni(Cal):**16.21(16.32). Λm =17.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1624(vC=O), 1524(vC=N), 1201(vC-O),553(Ni-O) and 328(Ni-S). **Electronic spectra**(ε) λ max(kK): 16.15 (100), 23.70 (200), 43.79 (1 x 10^{5}) and 50.87 (1 x 10^{5}).

3.4 [**Ni(Sal)(Pipdtc)]**

The compound was obtained as a Light green solid and recrystalized from hot ethanolic solution. **Formulae mass**: 339.10g. **Yeild**:72%. **M.P/D.T**:*202 ^{o}C. **%Ni(Cal):**16.90(17.31). Λm=22.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1647(vC=O), 1529(vC=N), 1239(vC-O),532(Ni-O) and 321(Ni-S). **Electronic spectra**(ε) λ max(kK): 15.89 (100), 24.24 (200), 31.38 (1 x 10^{5}) and 42.54 (1 x 10^{5}).

3.5 [Ni(Sal)(Morphdtc)]

The compound was obtained as a lemon green solid and recrystalized from hot ethanolic solution. **Formulae mass**: 342.07g. **Yeild**:76%. **M.P/D.T**:*218^{o}C. **%Ni(Cal):**17.06(17.16). Λm=22.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1645(vC=O), 1529(vC=N), 1233(vC-O),548(Ni-O) and 334(Ni-S). **Electronic spectra**(ε) λ max(kK): 15.16 (100), 24.61 (200), 27.01 (1 x 10^{5}) and 41.38 (1 x 10^{5}).

3.6 [**Ni(Sal)(Anildtc)]**

The compound was obtained as a dark green solid and recrystalized from hot ethanolic solution. **Formulae mass**: 348.08g. **Yeild**:30%. **M.P/D.T**:*300 ^{o}C. **%Ni(Cal)**:16.76(16.87). Λm=27.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1625(vC=O), 1535(vC=N), 1249(vC-O),591(Ni-O) and 331(Ni-S). **Electronic spectra**(ε) λ max(kK): 16.99 (100), 25.81 (1 x 10^{5}) and 48.19 (1 x 10^{5}).

3.7 [Ni(Sal)(*p*ClAnildtc)]

The compound was obtained as a light green solid and recrystalized from hot ethanolic solution. **Formulae mass**: 382.52g. Yeild:33%. M.P/D.T:*300 ^{o}C. %Ni(Cal):15.48(15.35). Λm=10.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1653(vC=O), 1529(vC=N), 1252(vC-O),533(Ni-O) and 303(Ni-S). **Electronic spectra**(ε) λ max(kK): 17.47 (100), 24.24 (200), 36.55 (1 x 10^{5}) and 48.18(1 x 10^{5}).

3.8 [**Ni(Sal)(Toldtc)]**

The compound was obtained as a green solid and recrystalized from hot ethanolic solution. **Formulae mass**: 362.11g. **Yeild**: 20%. **M.P/D.T**:*278 ^{o}C. %Ni(Cal)**:**16.40(16.21). Λm=13.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1614(vC=O), 1506(vC=N), 1205(vC-O),522(Ni-O) and 329(Ni-S). **Electronic spectra**(ε) λ max(kK): 17.56 (100), 26.00 (1 x 10^{5}) and 41.76 (1 x 10^{5}).

3.9 [**Ni(Sal)(Anisdtc)]**

The compound was obtained as a green solid and recrystalized from hot ethanolic solution. **Formulae mass:** 362.11g. **Yeild**:97%. **M.P/D.T:***200 ^{o}C. **%Ni(Cal):**16.21(16.32). Λm=17.00$\Omega^{-1}cm^{2}mol^{-1}$. **Selected IR peaks**, v(cm^{-1}):1651(vC=O), 1529(vC=N), 1245(vC-O),533(Ni-O) and 308(Ni-S). **Electronic spectra**(ε) λ max(kK): 18.27 (100), 24.53 (200), 25.75(1 x 10^{5}) and 41.50 (1 x 10^{5}).

M.P/D.T = melting point/decomposition temperature, 1kK=1000cm^{-1}.

IV. Antibacterial screening

The complexes showed good activity against *Echerichia coli, Pseudomonas aureginosa, Klebsiella oxytosa* and *Staphylococcus aureus*. They were not active against *P.mirabillis* and *Bacillus cereus* except for Ni(Sal)(*p*ClAnildtc) and Ni(Sal)(Anildtc) that had moderate activity.

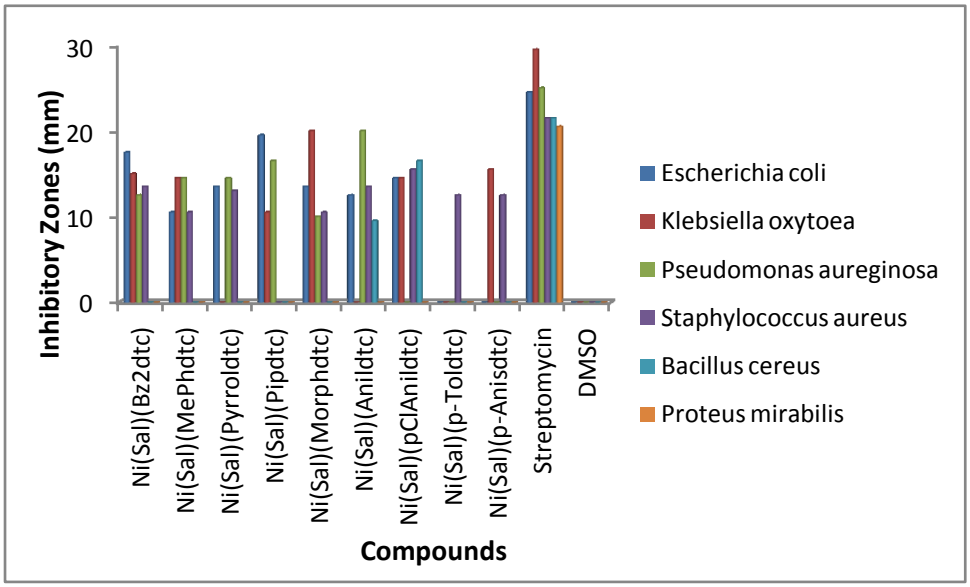

Fig 1.2: Histogram representation of the antibacterial screening of the mixed ligand complexes.

V. Conclusion

The assignment of a four coordinate geometry was corroborated by electronic sprectral measurements and percentage nickel content. The appearance of Ni-O and Ni-S bands in the infrared spectra gave proof to the coordination of the ligands to the nickel ion. The test compounds exhibited broad spectrum antibacterial activity against *Escherichia coli, Pseudomonas aureginosa, Klebsiella oxytosa* and *Staphylococcus aureus*. They were not active against *Bacillis cereus* and *Proteus mirabilis* except for Ni(Sal)(p-Clanildtc) and Ni(Sal)(anildtc) complexes. The resistance of the pathogens towards the test compounds can be attributed to the existence of cell wall in gram positive bacteria which reduces the permeability of the test compounds, while the activity of Ni(Sal)(p-Clanildtc) and Ni(Sal)(anildtc) complexes against them can be attributed to their greater lipophilicity. The high to moderate activities showed by all the complexes proved their usefulness as potential broad spectrum antibacterial agents.

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