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Applied Chemistry

Elixir Appl. Chem. 76 (2014) 28493-28501

ISSN: 2229-712X

Synthesis, characterization and antibacterial studies of nickel (II) mixed ligand complexes of dithiocarbamate ligands with Schiff base

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ARTICLE INFO

Article history:

Received: 16 September 2014;

Received in revised form:

27 October 2014;

Accepted: 13 November 2014

Keywords

Nickel (II) mixed ligand complexes, Dithiocarbamate ligands, Schiff base.

ABSTRACT

Nickel (II) mixed chelates of Schiff base derived from salicylaldehyde and aniline with various dithiocarbamate ligands have been characterized by metal analysis, microbial activity, solubility, infrared and electronic spectral measurements. The compounds were generally insoluble in water and soluble in some solvents. The metal analysis gave values close to the expected percentage metal values confirming the coordination of the nickel metal in the complexes. The interpretation of the infrared spectra of the complexes showed that the two uninegative ligands coordinate to the metal ions in their complexes in a bidentate mode, the dithiocarbamate ligands binding through both sulphur atom and the Schiff base through the azomethine nitrogen and phenolic oxygen. The electronic spectra revealed that the nickel complexes are typical of square planar as evidenced by the presence of two d-d absorption bands. The synthesized compounds showed moderate to high antibacterial activity against the test bacteria and can be effective as antibiotics.

Introduction

Transition metal complexes with Schiff bases and dithiocarbamate ligands have expanded enormously and embraced wide and diversified subject comprising vast areas of bio-organic compounds. Many studies have been done on transition metal complexes of Schiff base and dithiocarbamate ligands due to the fact that both offer opportunities for inducing substrate chirality, tuning metal centred electron factor, enhancing the solubility and stability of either homogenous or heterogeneous catalyst as well as stabilizing (Amdio *et al*., 2009). Schiff base and dithiocarbamate ligands are able to coordinate many different metals and stabilize them in various oxidation states (Abd-Elzar, 2001). Transition metal complexes of S- and O-donor ligands (both the Schiff bases and dithiocarbamate ligands) have been found to have promising antibacterial, antifungal and anti-inflammatory activities and these activities are best explained using the chelation theory (that is, upon chelation the polarity of the metal ion is affected by the coordination of ligands). Transition metal complexes of N-donor ligands (Schiff bases) showed anti-*Candida* activities (Canpolat and Kaya, 2004). Transition metal complexes of Schiff base have become important due to their ability to serve as polymeric ultraviolet stabilizers, as luster dyes and molecular switches in logic or memory circuits, while dithiocarbamate metal complexes have been reportedly used as fungicides, insecticides, vulcanizers, floatation agents, high pressure lubricants and in catalysis (Amdio *et al*., 2009). The first row transition metal complexes such as cobalt (II) nickel (II) and copper (II) have been found to exhibit fungicidal, bactericidal and antiviral activity. The work attempts to extend the range of novel Schiff-base and dithiocarbamate mixed ligands and also to prepare their nickel(II) metal complexes.

Schiff bases

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde/ketone (Figure 1). The resultant compound, $R_1R_2C{=}NR_3$, is called a Schiff base (named after Hugo Schiff), where R_1 is an aryl group, R_2 is a hydrogen atom and R_3 is either an alkyl or aryl group. However, compounds where R_3 is an alkyl or aryl group and R_2 is an alkyl or aromatic group are also regarded as Schiff bases.

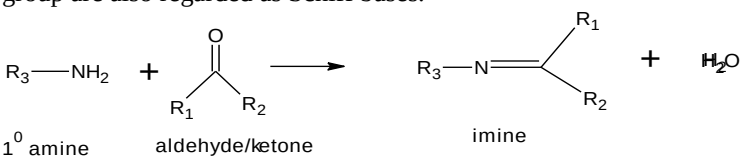

Figure 1. Condensation of primary amine and aldehyde or ketone to produce imines

Schiff bases that contain aryl substituent are substantially more stable and more readily synthesized, while those which contain alkyl substituent's are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable (Hine and Yeh, 1967), while those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehyde are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehyde (Fessenden and Fessenden, 1998).

Schiff bases are generally bidentate (1), tridentate (2), tetradentate (3) or polydentate (4) ligands capable of forming very stable complexes with transition metals. They can only act as coordinating ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six membered ring can be formed when reacting with a metal ion (Fig. 2).

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, *e.g*., biological, inorganic and analytical chemistry (Amdio *et*

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al., 2009). Applications of many new analytical devices require the presence of organic reagents as essential compounds of the measuring system.

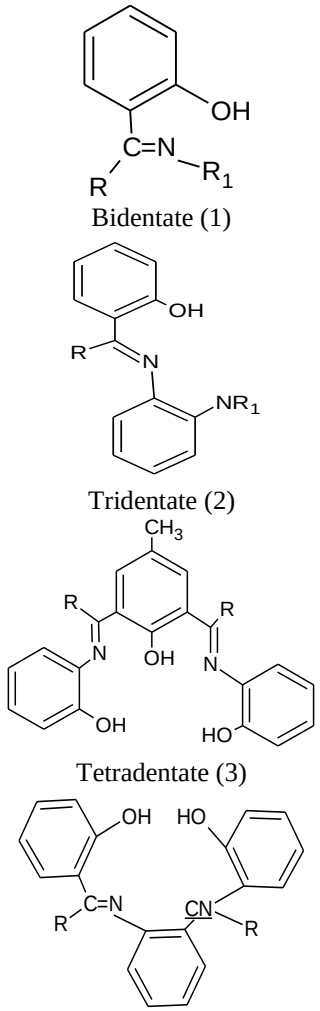

Figure 2. Some classes of Schiff base ligands

Schiff bases are used, *e.g*., in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhanced selectivity and sensitivity (Canpolat and Kaya, 2004). Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties (Amdio *et al*., 2009). Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which the azomethine bond is formed (determination of compounds with an amino or carbonyl group); using complex formation reactions (determination of amines, carbonyl compounds and metal ions); or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent (Metzler *et al*., 1980). Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions (Spinu *et al*., 2008). In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds.

The aim of this research is to prepare and investigate nickel (II) mixed chelates of Schiff bases with various dithiocarbamate ligands. The specific objectives of the study include the following:

❖Characterization of the synthesized metal (II) compounds by metal analysis, infrared and electronic spectral studies.

❖To study the *in vitro* antibacterial activities of nickel (II) mixed ligands complexes against three Gram-negative bacteria *(Escherichia coli, Pseudomonas aeruginosa and Salmonella typhi)* and two Gram-positive bacteria *(Staphylococcus aureus, and Bacillus subtilis*).

Materials and methods

Materials

All reagents and chemicals purchased from Aldrich-Sigma and British Drugs Houses (BDH) Chemicals Limited were of analytical/spectroscopic grade and used without further purification. However, the organic solvents were purified by standard methods. The microorganisms used for bioassay were obtained from the Department of Pharmaceutical Microbiology, University of Ibadan, Ibadan, Nigeria.

Reagents and solvents: The reagents and solvents used include ethanol, methanol, nitromethane, dioxan, zinc sulphate heptahydrate, nitric acid, distilled water, nickel(II) acetate tetrahydrate, ammonia, perchloric acid, salicylaldehyde, tetrahydrofuran, petroleum ether, chloroform, dimethylformamide, di-*n*-butylamine, *n*-ethylbutylamine, *n*-methylbutylamine, cyclo-hexylmethylamine, dibenzylamine,*p*-toluidine, ammonium chloride, sodium chloride, solochrome black, potassium nitrate, dichloromethane, dimethylsulphoxide, benzene, sodium methylphenyldithiocarbamate, sodium diethyldithiocarbamate, disodium dihydrogenethylenediaminetetraacetic acid.

Organisms: Microorganisms used for bioassay are *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Salmonella typhi*.

Preparation and standardization of reagents

Preparation of 0.01M Zinc Sulphate solution: This was done by dissolving 0.2875 g of $ZnSO_4.7H_2O$ in distilled water in a 100 ml standard flask. Complete dissolution of the zinc sulphate was ensured and the solution was made to the mark with distilled water.

Preparation of 0.01M EDTA solution 3.722 g of EDTA was weighed and transferred into a 1 litre volumetric flask. This was dissolved with distilled water and solution made to the mark with distilled water.

Preparation of ammonia/ammonium chloride buffer solution 17.801 g of NH_4CI was dissolved in 142 ml of concentrated ammonia in a 250 ml standard flask. Distilled water was added to, to make the solution up to the mark.

Standardization of EDTA solution: 10 ml of freshly prepared 0.01 M zinc sulphate ($ZnSO_4.7H_2O$) solution was pipetted into a conical flask, 1 ml of ammonia/ammonium (NH_3/NH_4CI) buffer and a speck of solochrome black indicator were added. The resultant purple solution was titrated against EDTA solution to a blue colour at end point. The concentration obtained for the standardized EDTA solution (0.0097 M) was used in all calculations involving the EDTA solution for the determination of percentage metal composition in the synthesized metal (II) complexes.

Table 1. Standardization of EDTA solution

Burette readings	1(ml)	2(ml)	3(ml)
Final reading	12.80	24.90	25.30
Initial reading	2.50	14.60	15.00
Actual reading	10.30	10.30	10.30

$$\text{Average titre value} = \frac{10.30 + 10.30 + 10.30}{30} = 10.30 \text{ ml}$$

Equation for the reaction

$ZnSO_4 + Na_2EDTA \longrightarrow Zn\ EDTA + Na_2SO_4$

Calculation

Volume of $ZnSO_4$ used = 10.0 ml
Molarity of $ZnSO_4$ = 0.01 M
Volume of EDTA used = 10.30 ml
Molarity of EDTA = unknown

$$\text{Molarity of EDTA} = \frac{M_{ZnSO4} \times V_{ZnSO4}}{V_{EDTA}} = \frac{0.1 \times 10.00}{10.30\ ml}$$

$$M_{EDTA} = 0.0097M$$

Preparation of complexes

Preparation of Ni(*p*-MePhSal)$_2$: 20.614 g (0.0685 mol) of $Ni(Sal)_2$ was dissolved in about 200 ml of ethanol and heated under reflux for a few minutes. 16.503 g (0.154 mol–25 % excess) of *p*-toluidine was also dissolved in 80 ml of ethanol and quantitatively transferred into the $Ni(Sal)_2$ mixture. The resulting solution was then heated under reflux for several hours until the complex was formed. The precipitate which separated on cooling was filtered by suction, washed with ethanol and dried over silica gel.

Equation of the reaction,

$$Ni(Sal)_2 + 2(p\text{-}MePh) \xrightarrow[Reflux]{EtOH} Ni(p\text{-}MePh)_2$$

$Ni(PhSal)_2$ was prepared by the same method using aniline as the amine.

Preparation of Ni(*p*-MePhSal)(MePhdtc): 1.533 g (0.0032 ml) of Ni(*p*-MePhSal)$_2$ was dissolved in 30 ml of ethanol. This was warmed and stirred until the Ni(*p*-MePhSal)$_2$ dissolved completely. 0.888 g of MePhdtcNa.4H_2O dissolved in 15 ml methanol was added dropwise to the warm stirring solution of Ni(*p*-MePhSal)$_2$. The resulting solution was stirred for about 1 hour and the precipitates formed was filtered under suction, washed with methanol and dried over silica gel.

Equation for the reaction,

Ni(*p*-MePhSal)$_2$ + MePhdtcNa ⟶ Ni(p-MePhSal)(MePhdtc) + *p*-MePhSal$^-$Na$^+$

This method was also used for the synthesis of Ni(p-MePhSal)(Et_2dtc), Ni(PhSal)(Et_2dtc) and Ni(PhSal)(MePhdtc).

Preparation of Ni(*p*-MePhSal)(*i*-Bu_2dtc): 1.533 g (0.0032 mol) of Ni(*p*-MePhSal)$_2$ was dissolved in 20 ml CH_2CI_2. It was warmed and stirred to effect dissolution. 0.56 ml (0.0032 mol) *i*-Bu_2NH mixed with 0.20 ml (0.0032 mol) of carbon disulphide in 10 ml of methanol were then added dropwise to the stirring Ni(p-MePhSal)$_2$ solution which was further stirred for about 1 hour. A light green precipitate was obtained which was filtered and washed with methanol and dried in a desiccator over silica gel.

Equation for the reaction,

Ni(*p*-MePhSal)$_2$ + *i*-Bu_2NH + CS_2 ⟶ Ni(p-MePhSal)(*i*-Bu_2dtc) + *p*-MePhSal$^-H^+$

This method was used for the preparation of the remaining complexes containing Ni(p-MePhSal) as well as those of Ni(PhSal).

Metal analysis

Percentage nickel composition in the complexes was determined by complexometric titration using EDTA solution, murexide indicator and ammonia/ammonium chloride buffer.

Preparation of sample solution: A known weight of metal complex (0.02-0.04 g) in a digestion bottle was on hot plate digested to dryness with drops of 1:1 nitric-perchloric acid mixture. After cooling, few drops of deionized water were added and the sample again heated to dryness. The residue, dissolved in about 5 ml of deionized water, was transferred into a 100 ml standard flask and made up to mark with deionized water.

Titrimetric determination of metal content: 10 ml of the digested sample was pipette into a conical flask. A speck of murexide indicator was added and the pH of the solution was adjusted to about 10 by adding few drops of NH_3/NH_4Cl buffer. On addition of the buffer, the pink colour of the solution turned yellow. The resulting solution which was pale yellow was titrated against standardized EDTA solution to a pink colour at end point.

The percentage Ni^{2+} in (*P*-MePhSal)(i-Bu_2dtc) was determined using the fomular below

$$\%\ Ni^{2+} \text{ in the complex} = \frac{\text{Mass of } Ni^{2+} \text{ in the digested sample}}{\text{Weight of sample digested}} \times 100\ \%$$

This sample procedure was used for the determination of percentage Ni in the other Ni(II) complexes prepared. The results are shown in Table 4.

Estimation of percentage yield: The percentage yield of the complexes were determined from the formula,

$$\%\ \text{Yield} = \frac{\text{Experiment yield}}{\text{Theoretical yield}} \times 100\%$$

$$\text{Theoretical } Ni^{2+} = \frac{\text{Atomic mass of } Ni^{2+}}{\text{Molar mass of Ni(p-MePhSal)(i-Bu}_2\text{dtc)}} \times 100\ \%$$

Physical measurements

The physical properties of the synthesized compounds that were studied include solubility, infrared, and electronic analysis.

Solubility test: The solubility test of the complexes were determined in twelve common polar and non-polar solvents namely, methanol, ethanol, nitromethane, dioxan, distilled water, petroleum ether, benzene, dichloromethane, chloroform, DMF, THF, and DMSO. The results are shown in Table 4 and Table 5.

Infrared spectra: The infrared spectra of the synthesized complexes were recorded using the Perkin-Elmer Fourier Transform Infrared Spectrum BX Spectrophotometer equipped with KBr disc. A small portion of the sample was ground, mixed with ground KBr and pressed into a pellet. The spectra were run at the range 4000-400 cm^{-1}at the Multi-Disciplinary Central Research Laboratory, University of Ibadan, Ibadan. The results are shown in Table 6 and Table 7.

Electronic spectra: The electronic reflectance of all the complexes was recorded on a Spectro UV-VIS Double Beam PC Scanning Spectrophotometer-UVD-2960, LABOMED, INC., Department of Chemistry, University of Ibadan, Ibadan. The results are presented in Table 8 and 9.

Preparation of media and solutions of compounds: The antibacterial activity of all synthesized metal complexes has been investigated against strains of bacteria *Staphylococcus aureus* and *Bacillus subtilis* (Gram positive); *Escherichia coli*, *Pseudomonas aeruginosa* and *Salmonella typhi* (Gram negative), by the agar-well diffusion method. Gentamycin (10 µg/ml) was used as standard antibiotic. Serial dilutions of concentration of 200-6.25 mg/ml of the synthesized compounds were made in methanol.

24 hours broth culture of test bacteria diluted to obtain the McFarland standard was spread on the surface of Muller Hinton Agar (MHA) plates. Wells of 8 mm in diameter were created in medium with the help of a sterile metallic borer and nutrients agar medium were prepared by suspending 28 g in one litre (1000 ml) of distilled water, autoclave for 15 minutes and cooled down to 45℃. Then it was seeded with 0.2ml of the bacteria suspension.

Table 3. Physical properties and analytical data for nickel (II) phenylsalicyaldiminate- and *p*-methylphenysalicyaldiminate dithiocarbamates complexes

Compound	Colour	Formula Weight(g)	%Nickel Found	%Nickel Calculated	%Yield
Ni(PhSal)(Et_2dtc)	Dark green	403.19	14.65	14.56	78.31
Ni(PhSal)(Bz_2dtc)	Green	527.33	11.02	11.13	87.87
Ni(PhSal)(*i*-Bu_2dtc)	Green	459.30	12.80	12.78	76.80
Ni(PhSal)(*n*-Bu_2dtc)	Dark green	459.30	12.65	12.78	63.74
Ni(PhSal)(EtBudtc)	Dark green	431.24	13.50	13.61	85.95
Ni(PhSal)(MeBudtc)	Dark green	417.62	14.19	14.06	88.03
Ni(PhSal)(MePhdtc)	Green	437.21	13.34	13.43	95.16
Ni(PhSal)(*c*-HxMedtc)	Dark green	443.25	13.42	13.25	85.69
Ni(*p*-MePhSal)(Et_2dtc)	Green	417.22	14.11	14.07	65.39
Ni(*p*-MePhSal)(Bz_2dtc)	Green	541.36	10.85	10.84	81.18
Ni(*p*-MePhSal)(*i*-Bu_2dtc)	Light green	473.33	12.52	12.40	49.24
Ni(*p*-MePhSal)(*n*-Bu_2dtc)	Light green	473.33	12.43	12.40	35.38
Ni(*p*-MePhSal)(EtBudtc)	Light green	445.27	13.18	13.19	22.74
Ni(*p*-MePhSal)(MeBudtc)	Light green	431.65	13.38	13.60	16.65
Ni(*p*-MePhSal)(MePhdtc)	Green	451.24	13.15	13.01	88.57
Ni(*p*-MePhSal)(*c*-HxMedtc)	Light green	457.28	12.73	12.84	29.82

Table 4. Solubility data for nickel(II) phenylsalicyaldiminate-dithiocarbamates

Complexes	C_6H_6	CH_2Cl_2	$CHCl_3$	DMSO	DMF	Dioxan	THF	Acetone	CH_3NO_2	EtOH	MeOH	Pet ether	H_2O
Ni(PhSal)(Et_2dtc)	S	S	S	S	SH	S	SS	S	SS	SS	SS	SS	I
Ni(PhSal)(Bz_2dtc)	S	S	S	S	S	S	SS	S	SH	SS	SS	SS	I
Ni(PhSal)(i-Bu_2dtc)	S	S	S	S	S	S	SS	S	SS	SS	SS	SS	I
Ni(PhSal)(n-Bu_2dtc)	S	S	S	S	S	S	SS	S	SS	SS	SS	SS	I
Ni(PhSal)(EtBudtc)	S	S	S	S	S	S	SS	S	SH	SS	SS	SS	I
Ni(PhSal)(MeBudtc)	S	S	S	S	S	S	SS	SH	SS	SS	SS	SS	I
Ni(PhSal)(MePhdtc)	SS	S	S	S	S	S	SS	S	SS	SS	SS	SS	I
Ni(PhSal)(c-HxMedtc)	S	S	S	S	S	S	SS	SH	SS	SS	SS	SS	I

S = Soluble; SH = Soluble in hot solvent; SS = Slightly soluble; I = Insoluble

Table 5. Solubility data for nickel(II) *p*-methylphenylsalicyaldiminate-dithiocarbamates

Complexes	CH_3NO_2	DMSO	Dioxan	DMF	C_6H_6	THF	CH_2Cl_2	H_2O	EtOH	$CHCl_3$	Pet ether	MeOH
Ni(*p*-MePhSal)(Et_2dtc)	SS	SS	SH	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(Bz_2dtc)	SS	SS	SS	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(i-Bu_2dtc)	SS	SS	SH	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(n-Bu_2dtc)	SS	SS	SH	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(EtBudtc)	SS	SS	SH	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(MeBudtc)	SS	SS	SH	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(MePhdtc)	SS	SS	SH	SS	SH	SH	S	I	SS	S	SS	SS
Ni(*p*-MePhSal)(c-HxMedtc)	SS	SS	SH	SS	SS	SH	S	I	SS	S	SS	SS

S = Soluble; SH = Soluble in hot solvent; SS = Slightly soluble; I = Insoluble

Table 6. Characteristic infrared frequencies (cm^{-1}) of nickel(II) phenylsalicylaldiminate-dithiocarbamates complexes

Compound	C=N	C---N	C−O	C---S	Ni−O	Ni−N
Ni(PhSal)(Et_2dtc)	1604s	1533s	1230w	1003w	478m	546s
Ni(PhSal)(Bz_2dtc)	1613s	1488s	1228s	981w	429m	512m
Ni(PhSal)(i-Bu_2dtc)	1598s	1524s	1221m	1024m	451m	530s
Ni(PhSal)(n-Bu_2dtc)	1616s	1521s	1224m	972m	454m	534s
Ni(PhSal)(EtBudtc)	1610s	1506s	1236s	1012s	466m	512m
Ni(PhSal)(MeBudtc)	1604s	1522s	1216m	954w	466m	530m
Ni(PhSal)(MePhdtc)	1601s	1487s	1267s	1015s	448m	537s
Ni(PhSal)(c-HxMedtc)	1604s	1521s	1217m	1015s	451m	580s

s = strong; m = medium; w = weak

Table 7. Characteristic infrared frequencies (cm^{-1}) for nickel(II) *p*-methylphenylsalicylaldiminate- dithiocarbamates complexes

Complexes	C=N	C N	C-O	C S	Ni-O	Ni-N
Ni(*p*-MePhSal)(Et_2dtc)	1610s	1521m	1224s	987s	491m	580s
Ni(*p*-MePhSal)(Bz_2dtc)	1613s	1488w	1224s	975m	478m	570m
Ni(*p*-MePhSal)(i-Bu_2dtc)	1596m	1533s	1196w	978m	475m	573m
Ni(*p*-MePhSal)(n-Bu_2dtc)	1616s	1538s	1224s	981s	488s	580s
Ni(*p*-MePhSal)(EtBudtc)	1616s	1530m	1198w	978m	484s	580s
Ni(*p*-MePhSal)(MeBudtc)	1598w	1498w	1201m	981m	475m	576m
Ni(*p*-MePhSal)(MePhdtc)	1601m	1521m	1221s	975m	488s	570m
Ni(*p*-MePhSal)(c-HxMedtc)	1625s	1527s	1223s	981s	478s	573m

s = strong; m = medium; w = weak

Table 8. Electronic spectra data for nickel(II) phenylsalicylaldiminate dithiocarbamates complexes

Compounds	Bands (cm^{-1})	Assignment	Tentative geometry
Ni(PhSal)(Et_2dtc)	47,393	I.T	Square planar
	42,553	I.T	
	30,488	I.T	
	23,095	C.T	
	22,321	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	16,129	$^1A_{1g} \rightarrow {}^1A_{2g}$	
Ni(PhSal)(Bz_2dtc)	47,393	I.T	Square planar
	42,553	I.T	
	36,900	I.T	
	29,155	C.T	
	21,132	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	16,138	$^1A_{1g} \rightarrow {}^1A_{2g}$	
Ni(PhSal)(i-Bu_2dtc)	50,251	I.T	Square planar
	46,729	I.T	
	42,553	I.T	
	30,488	I.T	
	24,120	I.T	
	21,127	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	15,848	$^1A_{1g} \rightarrow {}^1A_{2g}$	
Ni(PhSal)(n-Bu_2dtc)	49,505	I.T	Square planar
	42,553	I.T	
	30,488	I.T	
	24,326	C.T	
	20,941	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	15,974	$^1A_{1g} \rightarrow {}^1A_{2g}$	
Ni(PhSal)(EtBudtc)	50,251	I.T	Square planar
	47,393	I.T	
	40,486	I.T	
	30,769	I.T	
	23,310	C.T	
	20,790	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	15,773	$^1A_{1g} \rightarrow {}^1A_{2g}$	
Ni(PhSal)(MeBudtc)	50,251	I.T	Square planar
	42,017	I.T	
	36,496	I.T	
	20,524	$^1A_{1g} \rightarrow {}^1B_{1g}$	
	16,000	$^1A_{1g} \rightarrow {}^1A_{2g}$	

Ni(PhSal)(MePhdtc)	48,780 42,017 37,313 28,653 23,202 15,974	I.T I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(PhSal)(c-HxMedtc)	50,251 45,377 41,494 36,748 21,153 16,082	I.T I.T I.T I.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar

I.T = Intraligand transition; C.T = Charge transfer

Table 9. Electronic spectra data for nickel(II) *p*-methylphenylsalicyaldiminates dithiocarbamates complexes

Compounds	Bands (cm^{-1})	Assignment	Tentative geometry
Ni(*p*-MePhSal)(Et_2dtc)	46,083 43,141 35,971 19,608 16,515	I.T I.T I.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(Bz_2dtc)	47,416 43,746 31,056 24,114 20,488 15,753	I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(i-Bu_2dtc)	45,456 43,103 34,483 24,114 19,463 14,728	I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(n-Bu_2dtc)	50,226 46,729 43,917 24,237 17,422 16,000	I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(EtBudtc)	50,251 47,393 44,843 36,697 24,450 19,346 16,439	I.T I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(MeBudtc)	49,505 47,393 44,248 37,202 24,546 19,736 16,909	I.T I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(MePhdtc)	46,729 44,248 23,288 19,885 15,649	I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar
Ni(*p*-MePhSal)(c-HxMedtc)	51,020 48,077 46,729 24,331 19,920 17,458	I.T I.T I.T C.T $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar

Table 10. Antibacterial Activity of Ni(II) phenylsalicyaldiminates-dithiocarbamates

	Concentration (mg/ml)	*S. typhi*	*E. Coli*	*B. subtilis*	*S. aureus*	*P. aeruginosa*
Ni(PhSal)(Et_2dtc)	200	20	22	18	-	16
	100	18	18	16	-	14
	50	16	16	14	-	12
	25	14	14	12	-	10
	12.5	12	12	16	-	-
	6.25	10	10	-	-	-
Ni(PhSal)(Bz_2dtc)	200	20	-	14	20	20
	100	18	-	12	18	18
	50	16	-	-	16	16
	25	14	-	-	12	12
	12.5	12	-	-	10	10
	6.25	10	-	-	-	-
Ni(PhSal)(i-Bu_2dtc)	200	18	16	18	16	16
	100	14	14	16	14	14
	50	12	12	14	12	12
	25	10	10	12	10	10
	12.5	-	-	10	-	-
	6.25	-	-	-	-	-
Ni(PhSal)(n-Bu_2dtc)	200	20	22	18	20	20
	100	18	18	16	16	18
	50	16	12	14	14	16
	25	14	-	12	-	14
	12.5	12	-	10	-	-
	6.25	10	-	-	-	-
Ni(PhSal)(EtBudtc)	200	24	14	20	14	20
	100	18	12	16	12	16
	50	14	10	14	10	10
	25	12	-	12	-	-
	12.5	10	-	10	-	-
	6.25	-	-	-	-	-
Ni(PhSal)(MeBudtc)	200	20	-	12	26	20
	100	18	-	10	24	18
	50	14	-	-	20	16
	25	12	-	-	18	14
	12.5	-	-	-	14	12
	6.25	-	-	-	12	10
Ni(PhSal)(MePhdtc)	200	20	20	20	26	16
	100	16	18	18	20	14
	50	-	14	14	14	-
	25	-	12	12	12	-
	12.5	-	-	10	-	-
	6.25	-	-	-	-	-
Ni(PhSal)(c-HxMedtc)	200	18	20	28	14	16
	100	14	18	24	12	14
	50	-	12	14	-	-
	25	-	-	10	-	-
	12.5	-	-	-	-	-
Control	6.25	-	-	-	-	20
		28	26	28	28	20

– = no activity; control = Conc.of standard drug (Gentamycin 10µg/ml)

The plate was prepared by pouring 40 ml of seeded nutrient agar and about two or three drops of each of the 200-6.25 mg/ml solutions of the synthesized compounds was consistently injected into the wells and allowed to diffuse into the agar media for a minimum of 30-1 hour. Experimental plates were then incubated for 18-24 hours and zones of inhibition of bacterial growth (millimeter) was measured and compared with standard antibiotic Gentamycin.

Results And Discussion

Physical and analytical measurements: Some physical properties of the synthesized compounds and data observed are presented in Table 4.1 for Ni(PhSal) and Ni(*p*-MePhSal) series respectively.

Colour: All the synthesized complexes show different shades of green colour (Table 3)

Percentage yield: The yields of five of the synthesized compounds (Table 3) are below 50 % while others are above and as high as 95.16 % for nickel(II) *p*-methylphenylsalicyaldiminate-dithiocarbamates (Table 3). The lowest yield of 16.65 % was found for Ni(p-MePhSal)(MeBudtc).

Percentage metal: The experimental percentage Nickel found for the complexes (Table 3) was in close agreement with the calculated values with a difference of about ± 0.2.

Solubility: According to Table 4, nickel(II) phenylsalicyaldiminate-dithiocarbamates dissolved readily in chloroform, dichloromethane, DMSO, DMF, benzene and dioxan, but showed varied degree of solubility in all other solvents.

According to Table 5, nickel(II) *p*-methylsalicyaldiminate-dithiocarbamates dissolved readily in chloroform and dichloromethane, but showed varied solubility in all other solvents. Generally, all the complexes were insoluble in water, a behavior that is indicative of covalent and non-electrolytic character.

Infrared spectra: Metal complexes of salicylaldiminate ligands show four major bands in their spectra which are due to νC=N, νC−O, νM−N and νM−O vibrations. These bands and C⋯N and C⋯S present in dithiocarbamate ligands are characteristics of infrared spectra of the synthesized nickel(II) mixed ligand complexes. However, in the spectra of the compounds synthesized and reported, the νO−H and νN−H vibrational frequencies appear at 3522-3313 cm^{-1} and 3399-3129 cm^{-1} respectively, while the several weak bands in the range 2850-3100 cm^{-1} are assigned to aliphatic and aromatic C−H stretching.

In addition to the bands due to vibrations in the dithiocarbamate moiety, the spectra of the nickel (II) mixed complexes also show two principal infrared absorption bands which are attributed to the coordination of phenylsalicylaldiminate ligand to the complexes. The bands which appear at 1596-1625 cm^{-1} confirm the coordination of the Schiff base and are assigned to νC=N vibration, while the other bands in the range 1196-1267 cm^{-1} are attributed to C−O stretching frequency (Table 6 and 7). The position of the two bands indicate a bidentate coordination of the phenylsalicyaldiminate moiety to nickel(II) ion through the azomethine nitrogen and phenolic oxygen (Zidan, 2001).

Strong absorption bands in the region 1487-1538 cm^{-1} are attributed to the vibration of the C⋯N, thioureide bond in the dithiocarbamates moiety which indicated a partial double bond character in the C- N band due to the mesomeric drift of electrons from the dithiocarbamate moiety towards the metal centre, thus increasing the contribution of the thioureide form.

The bands observed in the region 954-1024 cm^{-1} indicates the presence of C-S bond, supporting the uninegative bidentate coordination of the dithiocarbamate anion to the metal. The bands which appear at 429-491 cm^{-1} and 512-580 cm^{-1} are attributed to νNi−O, and νNi−N modes, providing evidence of Schiff base coordination to the nickel(II) ion and the formation of the nickel(II) mixed chelates.

Electronic spectra: The complexes showed absorptions in the region 14,728-22,321 cm^{-1} which were attributed to d-d transitions (Table 8 and 9). The bands were assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ for the lowest bands and $^1A_{1g} \rightarrow {}^1B_{1g}$ for the higher ones and are typical of square planar nickel (II) complexes. For some of the complexes, strong intense bands were observed in the region 23,095-24,546 cm^{-1} which correspond to charge transfer processes of the type metal-ligand typical of square planar nickel(II) (Kaul and Pandeya, 1979).

Antibacterial Analysis: Metal complexes of dithiocarbamates and Schiff bases are capable of inhibiting bacterial growth and activity by interfering with the metabolic processes in the bacteria. According to Table 10, the complexes were generally active against all the test bacteria used except for Ni(PhSal)(Et_2dtc) which was inactive against *S. aureus*, and Ni(PhSal)(Bz_2dtc), Ni(PhSal)(MeBudtc) which was inactive against *E. coli*. Ni(PhSal)(c-HxMedtc) gave the widest inhibition zone of 28 mm against *B. subtilis*.

The minimum inhibitory concentration of 6.25 mg/ml was observed for Ni(PhSal)(Et_2dtc), Ni(PhSal)(Bz_2dtc), Ni(PhSal)(n-Bu_2dtc) against *S. typhi* and Ni(PhSal)(MeBudtc) against *S. aureus* and *P. aeruginosa* as being the most potent of all the compounds. At 12.5 mg/ml, the minimum inhibitory concentration was also observed for Ni(PhSal)(Et_2dtc), Ni(PhSal)(i-Bu_2dtc), Ni(PhSal)(n-Bu_2dtc) Ni(PhSal)(EtBudtc) and Ni(PhSal)(MePhdtc) against *B. subtilis*. Generally, significant antibacterial activities were observed for all the compounds as compared to a standard drug (Gentamycin) while they were independent of the solvent used (i.e., methanol).

Conclusions

The synthesized nickel(II) mixed ligand complexes of phenylsalicylaldiminate and *p*-methylphenylsalicylaldiminate with various dithiocarbamate ligands have been prepared and characterized by physical techniques as well as by their anti-bacterial properties. The nickel(II) complexes are mostly shades of green colour, and are generally insoluble in water indicating covalent and non-electrolyte character.

Infrared spectra of the metal(II) complexes show that the two uninegative ligands coordinate to the metal ions in their complexes in a bidentate mode, the dithiocarbamate ligands binding through both sulphur atoms of the –NCSS group and the phenysalicylaldiminate and *p*-methylphenylsalicyaldiminate ligand through the azomethine nitrogen and phenolic oxygen. Electronic spectra data of the complexes indicate that the nickel(II) complexes are diamagnetic and square planar. The synthesized compounds show moderate to high antibacterial activity against the test bacteria and can be effective as antibiotics. The proposed structure for the synthesized metal (II) complexes is shown in Figure 3 below.

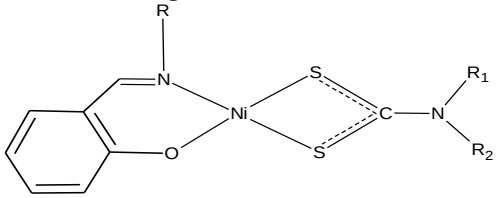

Figure 3. Suggested structure for nickel(II) phenyl and *p*-methylphenyl- salicylaldiminate-dithiocarbamate complexes (R = Phenyl or *p*-methylphenyl; R_1 or R_2 = alkyl or aryl)

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