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New Nickel(II) Mixed Ligand Complexes of Dithiocarbamates with Schiff Base

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ABSTRACT

The synthesis, physico-chemical characterization and antimicrobial activity studies of new nickel(II) mixed ligand complexes of dithiocarbamates (dtc) with a Schiff base, ethylsalicylaldiminate (EtSal) are reported. The dithiocarbamate ligands are pyrrolidyl (Pyrrol), piperidyl (Pip), morpholyl (Morph), anilyl (Anil), p-chloroanilyl (p-Anil), p-toluidyl (p-Tol) and p-anisidyl (p-Anis). Elemental analyses correspond to 1:1:1 stoichiometry of the nickel(II) ion to the ligands. Infrared spectra reveal bidentate coordination of the ligand moieties to the nickel(II) ion through azomethine nitrogen, phenolic oxygen and both sulphur donor-atoms. Room temperature magnetic moments and solid reflectance spectra data of the complexes are consistent with diamagnetic, square planar geometry. Some of the complexes show moderate to high activity against some test microorganisms.

Keywords: mixed ligand complexes, characterization, dithiocarbamates, Schiff base, antimicrobial activity.

INTRODUCTION

There is currently a growing interest in mixed ligand complexes of dithiolates [1–4]. Dithiocarbamates, in particular, are versatile chelating agents with diverse applications in industry, agriculture and medicine [5, 6]. Although complexes of dithiocarbamates with monodentate and polydentate ligands have been prepared and characterized [7–13], mixed ligand complexes involving Schiff bases have received little attention [14]. Schiff bases and their metal complexes demonstrate diverse spectrum of biological and pharmaceutical activities [15–21]. In this article, we report the synthesis, characterization and antimicrobial activity of nickel(II) mixed ligand complexes of dithiocarbamates with the Schiff base, ethylsalicylaldimine.

EXPERIMENTAL SECTION

Materials

Analytical grade chemicals were obtained commercially from Sigma-Aldrich and British Drug Houses (BDH) Chemicals Limited. The reagents were used as supplied while the solvents were purified by standard methods [22]. The Schiff base, ethylsalicylaldimine, was prepared as the nickel(II) complex [23]. Carbon disulphide and the different amines were reacted together in ethanol to give the various dithiocarbamate ligands which were used without extracting from solution. Nutrient broth and Mueller Hinton agar were obtained respectively from Oxoid Limited, England and Lab M Limited, United Kingdom. The microorganisms used were supplied by the Department of Pharmaceutical Microbiology and Department of Botany and Microbiology, University of Ibadan, Nigeria.

Preparation of nickel(II) complexes, [Ni(EtSal)(R_2dtc)]

In a typical synthesis, 2.2 mmol bis(ethylsalicylaldiminato)nickel(II), Ni(EtSal)$_2$ was dissolved in 20 mL warm ethanol. To the stirring solution was added dropwise a stirred mixture of stoichiometric amounts (2.2 mmol) of the amine and carbon disulphide in 10 mL ethanol. After stirring the reaction mixture for a further 1 hour, the precipitates formed were collected by filtration under suction, washed with ethanol and dried *in vacuo* over silica gel.

Physical measurements

Microanalysis, infrared spectra and magnetic susceptibility measurements were performed at the Department of Chemistry, University of Zululand, KwaDelangezwa, South Africa. Elemental analyses were carried out on a Perkin Elmer 2400 Series II CHNSO Analyzer. Percentage nickel was determined by chelatometric titration. The melting points recorded were uncorrected. Infrared spectra were obtained on a Bruker FTIR Tensor 27 Spectrophotometer equipped with Silicon ATR, using pure samples of the compounds. Solid reflectance spectra were recorded on a Genesys 10 UV Scanning Spectrophotometer. Magnetic susceptibilities were measured at room temperature by Faraday method on a Sherwood Scientific Johnson Matthey Magnetic Susceptibility Balance calibrated with mercury tetrathiocyanatocobaltate(II), Hg[Co(SCN)$_4$]. The data were corrected for diamagnetism by use of Pascal's constants.

Antimicrobial test

Antimicrobial activity of the complexes was performed on the following bacteria and fungi: *Staphylococcus aureus, Bacillus subtilis, Escherichia coli*, *Pseudomonas aeruginosa*, *Proteus mirabilis, Klebsiella pneumoniae, Candida albicans, Candida glabrata, Candida tropicalis* and *Candida pseudotropicalis*. The media used, nutrient broth and Mueller Hinton agar, were prepared by dissolving the powders in deionized water according to manufacturers' instructions. The two media were sterilized in an autoclave at 121 ^{o}C for 15 minutes and then stored overnight in a refrigerator after cooling. Cultures of the bacteria and fungi in sterile nutrient broth were incubated for 24 hours at 37 ^{o}C and 27 ^{o}C, respectively. 0.1 mL of each of the overnight cultures in sterile test tubes with caps were made up to 10 mL with 9.9 mL of sterile deionized water to give 1:100 or 10^{-2} dilution of the microorganisms. Solutions of concentration 10 mg mL^{-1} of the compounds were made in dimethylsulphoxide (DMSO).

The technique of agar-well diffusion was used for the study. The negative control was the solvent, DMSO. The positive controls for bacteria and fungi were discs of commercial antibiotics manufactured by Abtek Biologicals Limited and fluconazole dissolved in DMSO. The discs were carefully placed on the innoculated media with the aid of sterile forceps. The plates innoculated with bacteria were incubated at 37 ^{o}C for 24 hours, and those innoculated with fungi were incubated at 27 ^{o}C for 72 hours. Afterwards, the zones of inhibition of microbial growth that appeared around the wells of the compounds were examined and the diameters measured and recorded in millimeters (mm).

RESULTS AND DISCUSSION

Stoichiometry and physical characteristics

The nickel(II) mixed ligand complexes with their analytical data and physical characteristics are listed in Table 1. The compounds were obtained in reasonable yields of 53–91% except [Ni(EtSal)(*p*-Anisdtc)] which gave 44% yield. The melting points of the compounds fall within the range of 150–200 °C with the exception of [Ni(EtSal)(*p*-Anisdtc)] which melted at 128–130 °C. Elemental analyses gave satisfactory agreement between observed and calculated values for carbon, hydrogen, nitrogen and nickel compositions in the complexes. The results show that the compounds formed in ratio 1:1:1 of nickel to ethylsalicylaldiminate to dithiocarbamate, corresponding to the molecular formulae proposed for the nickel(II) mixed ligand complexes. The complexes exhibit shades of green colour and are generally insoluble in water, slightly soluble in ethanol, methanol and DMF, and soluble in acetone, dichloromethane, DMSO and THF.

Table 1. Physical properties and analytical data of the nickel(II) complexes

Compound (Colour)	Formula (Formula weight (g))	Melting point (^{o}C)	Yield (%)	Elemental analysis, % Found (% Calculated)			
				Carbon	Hydrogen	Nitrogen	Nickel
[Ni(EtSal)(Pyrroldtc)] (Pale green)	$C_{14}H_{18}N_2OS_2Ni$ (353.13)	170–172	90	47.58 (47.61)	5.44 (5.15)	7.92 (7.93)	16.57 (16.63)
[Ni(EtSal)(Pipdtc)] (Green)	$C_{15}H_{20}N_2OS_2Ni$ (367.16)	166–168	91	49.11 (49.07)	5.69 (5.50)	7.78 (7.63)	15.82 (15.99)
[Ni(EtSal)(Morphdtc)] (Green)	$C_{14}H_{18}N_2O_2S_2Ni$ (369.13)	184	88	45.01 (45.55)	5.19 (4.93)	7.69 (7.59)	16.07 (15.90)
[Ni(EtSal)(Anildtc)] (Green)	$C_{16}H_{16}N_2OS_2Ni$ (375.14)	173	70	50.64 (51.22)	5.70 (4.31)	7.91 (7.47)	15.82 (15.65)
[Ni(EtSal)(*p*-ClAnildtc)] (Dark green)	$C_{16}H_{15}ClN_2OS_2Ni$ (409.58)	162–164	59	45.58 (46.92)	4.57 (3.70)	7.82 (6.84)	14.39 (14.33)
[Ni(EtSal)(*p*-Toldtc)] (Green)	$C_{17}H_{18}N_2OS_2Ni$ (389.17)	168–170	53	51.51 (52.46)	5.63 (4.67)	7.91 (7.20)	15.07 (15.09)
[Ni(EtSal)(*p*-Anisdtc)] (Dark green)	$C_{17}H_{18}N_2O_2S_2Ni$ (405.17)	128–130	44	49.51 (50.39)	5.58 (4.49)	7.75 (6.92)	15.16 (14.49)

Infrared spectra

The significant infrared spectra bands of the mixed ligand complexes are presented in Table 2. In the infrared spectra of dithiocarbamate compounds, the region 1480–1550 cm^{-1} is primarily associated with the νN–CSS 'thioureide' band [24] which defines the carbon-nitrogen bond order between a single bond at 1250–1350 cm^{-1} and a double bond at 1640–1690 cm^{-1}. The

νC$\cdots$N thioureide band in the spectra of these mixed ligand nickel(II) complexes is observed at 1441–1509 cm^{-1}. The values noted for anilyldithiocarbamate and its derivatives are low and outside of range due to reduction in double bond character, and these have been explained to arise from the reluctance of the rigid aromatic rings to release electrons to the carbon-nitrogen bond in the N–CSS group [25]. The band corresponding to νC$\cdots$S is found in the range 942–1021 cm^{-1}, indicative of bidentate coordination of the dithiocarbamate moiety in the complexes through the two sulphur donor-atoms [26].

Table 2. Infrared spectra data of the nickel(II) complexes

Compound	ν(C=N)	ν(C$\cdots$N)	ν(C□O)	ν(C$\cdots$S)	ν(Ni□N)	ν(Ni□O)	ν(Ni□S)
[Ni(EtSal)(Pyrroldtc)]	1605m	1503vs	1212vs	942s	595s	465s	380vs
[Ni(EtSal)(Pipdtc)]	1609s	1509vs	1214vs	971s	596s	466vs	382vs
[Ni(EtSal)(Morphdtc)]	1608m	1488vs	1224vs	1010vs	595s	466vs	380vs
[Ni(EtSal)(Anildtc)]	1605vs	1441vs	1211vs	1020s	595vs	466vs	403vs
[Ni(EtSal)(*p*-ClAnildtc)]	1606vs	1442vs	1211vs	1019s	595vs	465vs	403vs
[Ni(EtSal)(*p*-Toldtc)]	1605vs	1442vs	1211vs	1019s	595vs	465vs	403vs
[Ni(EtSal)(*p*-Anisdtc)]	1606vs	1442vs	1211vs	1021s	595vs	465vs	403vs

vs = very strong; s = strong; m = medium

The ethylsalicylaldiminate moiety shows two bands in the regions 1605–1609 cm^{-1} and 1211–1224 cm^{-1} which are assigned to νC=N and νC–O, respectively. The positions of the two bands indicate a bidentate coordination of the ligand to nickel(II) ion through the azomethine nitrogen [14] and phenolic oxygen [14, 27–29]. All the mixed ligand complexes show absorption bands due to νNi–S, νNi–O and νNi–N vibrational modes at 380–403 cm^{-1}, 465–466 cm^{-1} and 595–596 cm^{-1}, respectively.

Table 3. Solid reflectance spectra data and magnetic moments of the nickel(II) complexes

Compound	Band maxima, λ_{max} (kK)	Assignment	μ_{eff} (BM)
[Ni(EtSal)(Pyrroldtc)]	15.92	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	21.14	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	23.75	Charge transfer	
	29.94, 36.90, 40.49	Intraligand transition	
[Ni(EtSal)(Pipdtc)]	15.70	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	20.24	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	23.75	Charge transfer	
	30.30, 36.90, 40.98	Intraligand transition	
[Ni(EtSal)(Morphdtc)]	15.39	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	20.04	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	24.10	Charge transfer	
	30.68, 36.90, 40.98	Intraligand transition	
[Ni(EtSal)(Anildtc)]	15.87	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	19.92	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	23.75	Charge transfer	
	30.40, 36.90, 40.98	Intraligand transition	
[Ni(EtSal)(*p*-ClAnildtc)]	15.87	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	20.24	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	23.75	Charge transfer	
	30.30, 36.90, 40.98	Intraligand transition	
[Ni(EtSal)(*p*-Toldtc)]	15.92	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	20.53	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	23.59	Charge transfer	
	30.49, 37.31, 40.98	Intraligand transition	
[Ni(EtSal)(*p*-Anisdtc)]	15.75	$^1A_{1g} \rightarrow {}^1A_{2g} (b_{2g} \rightarrow b_{1g})$	Dia
	20.16	$^1A_{1g} \rightarrow {}^1B_{1g} (a_{1g} \rightarrow b_{1g})$	
	24.10	Charge transfer	
	30.77, 37.31, 40.98	Intraligand transition	

kK = kiloKayser (1 kK = 1000 cm^{-1})

Electronic spectra and magnetic moments

The principal features of the solid reflectance spectra of the nickel(II) mixed ligand complexes are presented in Table 3. The spectra exhibit two intraligand $\pi \rightarrow \pi^*$ electronic transition bands for the dithiocarbamate moiety, one in the N⎓C⎓S chromophore (40.49–40.98 kK) and the other in the S⎓C⎓S group (29.94–30.77 kK) [30–32]. The band at 36.90–37.31 kK is assigned to $\pi \rightarrow \pi^*$ transition in the ethylsalicylaldiminate moiety. Bands due to charge transfer in the complexes are observed in the range 23.59–24.10 kK of the spectra. All the complexes show two d-d absorption bands in the regions 15.39–15.92 kK and 19.92–21.14 kK of their spectra. These bands are characteristic of four-coordinate configuration [7] and are therefore assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$) and $^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$) electronic transitions, respectively. The magnetic moments confirm that the nickel(II) mixed ligand complexes are diamagnetic with square planar geometry.

Antimicrobial activity

The microbial growth inhibitory activity of the nickel(II) complexes was measured *in vitro* against *Staphylococcus aureus* and *Bacillus subtilis* (Gram positive bacteria), *Escherichia coli*, *Pseudomonas aeruginosa*, *Proteus mirabilis* and *Klebsiella pneumoniae* (Gram negative bacteria), and *Candida albicans*, *Candida glabrata*, *Candida tropicalis* and *Candida pseudotropicalis* (fungi). The results for the complexes and controls are given in Table 4. All the complexes are active against *Proteus mirabilis* and are non-active against *Staphylococcus aureus*, *Candida glabrata* and *Candida tropicalis*. They are either active or inactive against the other microorganisms. Generally, the complexes show moderate to high effectiveness [33] in instances of microorganisms against which they are active.

Table 4. Antimicrobial activity data of the compounds (10 mg mL^{-1}) and controls

	Growth inhibition zone in millimeters (mm)									
	Bacteria									
	(Gram positive)		(Gram negative)				(Fungi)			
Compound	*S. aur*	*B. subt*	*E. coli*	*P. mirab*	*P. aerug*	*K. pneu*	*C. alb*	*C. glab*	*C. trop*	*C. psdt*
[Ni(EtSal)(Pyrroldtc)]	-	14	-	20	-	-	15	-	-	10
[Ni(EtSal)(Pipdtc)]	-	-	-	18	-	-	12	-	-	-
[Ni(EtSal)(Morphdtc)]	-	-	-	18	-	-	-	-	-	-
[Ni(EtSal)(Anildtc)]	-	13	-	18	-	27	19	-	-	-
[Ni(EtSal)(*p*-ClAnildtc)]	-	18	12	18	14	15	11	-	-	17
[Ni(EtSal)(*p*-Toldtc)]	-	-	12	22	12	15	-	-	-	15
[Ni(EtSal)(*p*-Anisdtc)]	14	12	10	15	10	10	-	-	-	15
CHL 30	19	14								
CXC 5	-	-								
ERY 5	-	-								
COT 25	15	-	-	-	-	10				
GEN 10	14	13	20	-	09	-				
AUG 30	-	-	-	-	-	-				
AMX 25	-	-	-	-	-	-				
TET 10/30	10	-	10	-	-					
NIT 300			-	-		20				
NAL 30			14	-	15	20				
OFL 30			35	-	31	27				
FLU 30							-	-	-	-
DMSO	-	-	-	-	-	-	-	-	-	-

Resistance (-); Staphylococcus aureus (S. aur); Bacillus subtilis (B. subt); Escherichia coli (E. coli); Proteus mirabilis (P. mirab); Pseudomonas aeruginosa (P. aerug); Klebsiella pneumoniae (K. pneu); Candida albicans (C. alb); Candida glabrata (C. glab); Candida tropicalis (C. trop); Candida pseudotropicalis (C. psdt); Chloramphenicol 30 µg (CHL 30); Cloxacillin 5 µg (CXC 5); Erythromycin 5 µg (ERY 5); Cotrimoxazole 25 µg (COT 25); Gentamycin 10 µg (GEN 10); Augmentin 30 µg (AUG 30); Amoxycillin 25 µg (AMX 25); Tetracydin 10 µg for Gram positive bacteria and 30 µg for Gram negative bacteria (TET 10/30); Notrofurantoin 300 µg (NIT 300); Nalidixic acid 30 µg (NAL 30); Ofloxacin 30 µg (OFL 30); Fluconazole 30 µg (FLU 30); Dimethylsulphoxide (DMSO)

CONCLUSION

Nickel(II) mixed ligand complexes of dithiocarbamates with ethylsalicylaldiminate have been synthesized and characterized. The two ligand moieties display a bidentate coordination mode in the complexes. Solid reflectance spectra and magnetic data indicate that the nickel(II) complexes are diamagnetic and square planar in geometry (Figure 1).

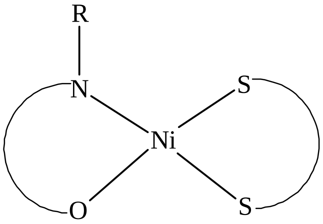

Figure 1. Structure of the nickel(II) complexes (R = C_2H_5)

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