



September 2007

Volume 2 Issue 3

Inorganic CHEMISTRY

Trade Science Inc.

An Indian Journal

Full Paper

ICAIJ, 2(3), 2007 [127-131]

Synthesis, Characterization And Antimicrobial Activity Of Co(II), Ni(II), Cd(II), Zn(II), Pd(II), Rh(III) And Ru(III) Complexes Of 2-(2-Naphthylthio)-Quinoline-3-Carboxaldehyde

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Received: 31st January, 2007 ; Accepted: 5th February, 2007

ABSTRACT

A new bidentate ligand, 2-(2-naphthylthio)-quinoline-3-carboxaldehyde(L) has been synthesized. Co(II), Ni(II), Cd(II), Zn(II), Pd(II), Rh(III) and Ru(III) complexes of the ligand have been prepared. The ligand is characterized by elemental analyses, infrared, UV, NMR and Mass spectral data and the metal chelates are characterized by elemental analyses, conductivity data, magnetic susceptibility measurements, infrared, ¹H-NMR and UV-Vis spectral data. On the basis of the above data it is inferred that the ligand behaves as a bidentate NS chelating agent. The ligand and the metal chelates were screened for their anti microbial activity against the gram positive bacteria *S.aureus* and gram negative bacteria *P.aeruginosa* and the fungi *C.albicans*, *A.flavus* and *A.niger*. The results show that the complexes are potent antimicrobial than the parent ligand and also indicate that the inhibition activity increases with increase of concentration. © 2007 Trade Science Inc. -INDIA

KEYWORDS

Chelating agent;
Antimicrobial activity;
2-Chloroquinoline-3-carboxaldehyde;
2-Naphthalenethiol;
Magnetic moment;
Quinoline.

INTRODUCTION

Quinoline derivatives represent the major class of heterocycles and a number of preparations have been known from the late 1980s. Quinoline derivatives are well known in medicinal chemistry, because of their wide occurrence in natural products^[1,2], drugs^[3,4], and also in polymer chemistry, electron-

ics and optoelectronics for their excellent mechanical properties^[5-7]. Diblock and triblock copolymers incorporating polyquinoline blocks have been found to undergo hierarchical self assembly into a variety of nano- and meso-structures with interesting electronic and photonic functions^[8,9]. On the other hand transition metal complexes containing N-N, N-S and N-O chelating agents has increased rapidly in the

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recent years due to their wide applicability in electronic, catalysis and particularly in biological fields. By considering the biological importance of metal complexes containing nitrogen and sulphur donor atoms we wish to report the synthesis of Co(II), Ni(II), Cd(II), Zn(II), Pd(II), Rh(III) and Ru(III) complexes of quinoline derivative derived by 2-chloro-3-quinolinecarboxaldehyde.

EXPERIMENTAL

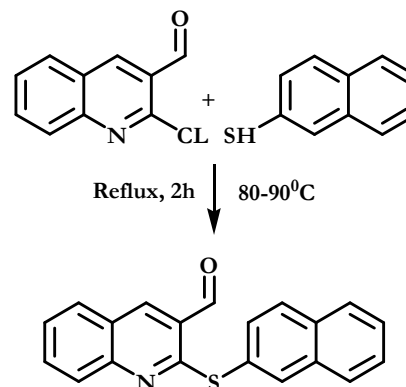
All necessary precautions were taken to exclude oxygen and moisture during the synthesis of compounds. Analytical reagent grade chemicals were used as received for all the experiments. Infrared spectra of the ligand and its metal complexes in KBr pellets were recorded in the spectral range 4000-250 cm^{-1} range with Shimadzu FTIR-8400S spectrometer. UV-Visible spectra were recorded on a Shimadzu double beam spectrophotometer. The C, H, N and S content analyses were determined by using Carlo-Erba 1106 model 240 Perkin Elmer analyzer at university of Mysore, Mysore. Magnetic susceptibilities were measured on a Guoy balance at room temperature using $\text{HgCo}(\text{NCS})_4$ as calibrant. $^1\text{H-NMR}$ spectra were recorded in DMSO-d_6 solution on a JEOL 300 MHz spectrometer and TMS was used as an internal reference. The molecular weight of the complexes was determined by Rast's method using biphenyl^[10]. The Mass spectra were recorded on a LC-MS spectrometer.

Antibacterial activity

Antibacterial activity of ligand and its complexes were studied against gram positive bacteria *S.aureus* and gram negative bacteria *P.aeruginosa* by employing paper disc method^[11]. The streptomycin (100mg) was used as a standard. For each concentration, the mean diameter (mm) of inhibition zone developed was calculated.

Antifungal activity

The antifungal studies of ligand and its complexes were tested on the fungal strains namely, *C. albicans*, *A.flavus* and *A.niger* in the growth media by using Batemann poisoned food technique^[12]. The average percentage inhibition was calculated by us-



2-(2-naphthylthio)-quinoline-3-carboxaldehyde(L)
SCHEME 1: Synthesis of 2-(2-naphthylthio)-quinoline-3-carboxaldehyde(L)

ing the reported method^[13].

Synthesis of ligand^[14]

Into a mixture of 2-chloro-3-quinolinecarboxaldehyde (0.958g, 5mmol), 2-naphthalenethiol (0.8g, 5mmol) and potassium carbonate (1.38g, 10mmol), anhydrous dimethylformamide (50ml) was added. The mixture was heated at 80-90°C for 2h with constant stirring and was then cooled to room temperature. The product obtained was filtered and dried (SCHEME 1).

Synthesis of cobalt(II) and nickel(II) complexes

An alcoholic solution of ligand (2mmol, 50ml) and Metal chloride (1mmol) was refluxed for 8 hours and its volume was reduced in a rotary evaporator until a precipitate appeared. After cooling, the solid was filtered off, purified with water, methanol and ether. The complexes were dried under reduced pressure at room temperature after purification.

Synthesis of cadmium(II) and zinc(II) complexes

The metal salt (10mmol) was added to a solution of ligand (10mmol) in dry ether (30ml) with continuous stirring and stirring was continued for 1h at 0°C and 18h at room temperature. The resulting solution was concentrated to give a white compound. The compound was recrystallized by using chloroform/hexane (1:1) mixture to give the desired complex.

Synthesis of Pd(II), Rh(III) and Ru(III) complexes

TABLE 1: Physical constants of ligand and its complexes

Compound	Yield %	Elemental analysis found(Calcd)						Molar conductivity mhos cm ² mol ⁻¹	Magnetic moment μ_{eff} , BM	Mol. Wt. found(Calcd)	
		C	H	N	M	S	Cl			A	B
Ligand (L)	85	76.35 (76.16)	4.32 (4.15)	4.63 (4.44)	--	9.85 (10.2)	--	--	--	310.59 (315.38)	317.25
[CoL ₂ Cl ₂]	79	64.36 (63.16)	3.54 (3.45)	3.73 (3.68)	7.92 (7.75)	8.02 (8.4)	9.46 (9.32)	26.05	4.92	755.65 (760.61)	758.48
[NiL ₂ Cl ₂]	79	62.40 (63.10)	3.30 (3.40)	3.80 (3.60)	7.90 (7.70)	7.97 (8.43)	9.40 (9.30)	26.70	3.34	755.10 (760.37)	755.91
[CdLCl ₂]	80	46.21 (48.17)	2.76 (2.63)	2.68 (2.81)	23.12 (22.54)	6.51 (6.43)	14.41 (14.2)	15.60	--	495.12 (498.71)	500.17
[ZnLCl ₂]	75	50.98 (53.18)	2.89 (2.90)	3.15 (3.10)	14.52 (14.48)	7.21 (7.10)	15.89 (15.7)	16.70	--	447.69 (451.70)	453.57
[PdLCl ₂]	81	48.75 (47.58)	2.65 (2.56)	2.84 (2.78)	21.60 (21.83)	6.51 (6.48)	14.39 (14.5)	27.30	--	487.92 (492.72)	490.27
[RhL ₂ Cl ₂]Cl	80	53.98 (57.20)	2.86 (3.12)	2.94 (3.33)	10.58 (12.25)	6.75 (7.63)	11.06 (12.7)	47.04	1.82	836.17 (840.07)	838.81
[RuL ₂ Cl ₂]Cl	75	56.01 (57.32)	3.05 (3.13)	3.24 (3.34)	11.58 (12.06)	7.03 (7.65)	12.12 (12.7)	46.05	1.85	834.52 (838.23)	840.62

A: Molecular weight determined by Rast's method, B: Molecular weight determined by mass spectrometer

The complexes were prepared by mixing an ethanolic solution of PdCl₂/RhCl₃·3H₂O/RuCl₃·3H₂O(2.5mmol) with ligand in hot ethanol in 1:1 metal-ligand ratio for Pd(II) and 1:2 for Rh(III) and Ru(III) complexes, respectively. The resultant solution was refluxed at 110°C for three hours. When the complex precipitated, it was filtered, washed several times with ethanol and dried under reduced pressure.

RESULTS AND DISCUSSION

The complexes were microcrystalline coloured powder. They are stable at room temperature and soluble in DMSO and DMF. The elemental analyses agree well with a 1:1 metal-to-ligand stoichiometry for Cd(II), Zn(II) and Pd(II) and 1:2 for Co(II), Ni(II), Rh(III) and Ru(III) complexes(TABLE 1). The conductivity values measured in DMF at room temperature fell in the range 15.6-27.3 mhos cm² mol⁻¹, which indicates the non-electrolytic nature of all the complexes except Rh and Ru complexes, which show conductivity value of 47.04 and 46.05 respectively^[15].

Magnetic moments

The room temperature magnetic moment value (TABLE 1) support octahedral geometry for Co(II), Ni(II), Rh(III) and Ru(III), square planar for Zn(II) and Pd(II) and tetrahedral for Cd(II) complexes^[16-19].

Spectral study

The octahedral Co(II) complex exhibit three bands at 14372, 14836 and 16404cm⁻¹, pertaining to ⁴T_{1g}(F)→⁴T_{2g}(F)(v₁), ⁴T_{1g}(F)→⁴A_{2g}(F)(v₂) and ⁴T_{1g}(F)→⁴T_{1g}(P)(v₃) transitions, respectively. The absorption spectra of Ni(II) complex show two bands at 16250 cm⁻¹ and 23245 cm⁻¹ due to ³A_{2g(F)}→³T_{1g(F)}(v₂) and ³A_{2g(F)}→³T_{1g(P)}(v₃) transitions, respectively supporting the octahedral stereochemistry. The reflectance spectra of Zn(II) and Cd(II) complexes show no bands due to d-d transition. This phenomenon is natural as there is no possibility of transition due to non availability of empty d-orbital^[19]. By considering the spectral data, the tetrahedral geometry for Cd(II) complex and square planar geometry for Zn(II) complex have been proposed^[19-21]. The electronic bands observed at 16586, 21278 and 30272cm⁻¹ for Pd(II)complex ion are due to the transitions ¹A_{1g}→¹A_{2g}(v₁), ¹A_{1g}→¹B_{1g}(v₂) and ¹A_{1g}→¹E_{1g}(v₃) respectively in a square planar configuration. In the present investigation of Rh(III) complex, the observed electronic bands around 16600, 19400 and 22300 cm⁻¹ are due to the transitions ¹A_{1g}→³T_{1g}, ¹A_{1g}→¹T_{1g} and ¹A_{1g}→¹T_{2g}, respectively in an octahedral structure around Rh(III)ion^[19]. The UV-Visible spectra of Ru(III) complex exhibit octahedral absorption band at 24570 cm⁻¹ attributed to ¹A_{1g}→¹T_{1g} charge transfer transitions^[22].

IR spectra

The IR spectral data of ligand and its metal com-

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TABLE 2: Some important IR data of ligand and its complexes

Compound	IR spectral data, cm ⁻¹				
	$\nu(\text{C}=\text{N})$	$\nu(\text{CSC})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$
Ligand (L)	1650	760	--	--	--
[CoL ₂ Cl ₂]	1626	725	469	350	364
[NiL ₂ Cl ₂]	1626	730	453	390	285
[CdLCl ₂]	1620	730	436	368	355
[ZnLCl ₂]	1618	738	436	384	362
[PdLCl ₂]	1615	740	390	376	296
[RhL ₂ Cl ₂]Cl	1612	743	394	384	338
[RuL ₂ Cl ₂]Cl	1605	738	392	370	320

TABLE 3: Inhibition zone of bacterial growth(mm)

Compound	<i>P.aeruginosa</i>			<i>S.aureus</i>		
	0.1 %	0.2 %	0.3 %	0.1 %	0.2 %	0.3 %
Ligand (L)	1.5	1.8	3.6	1.7	2.1	3.0
[PdLCl ₂]	2.9	3.5	5.6	3.0	3.4	5.6
[ZnLCl ₂]	2.8	3.4	5.4	2.9	3.3	5.4
[CdLCl ₂]	2.4	2.8	5.0	2.7	3.1	4.5
[CoL ₂ Cl ₂]	2.1	2.5	4.6	2.4	2.7	3.8
[NiL ₂ Cl ₂]	2.0	2.3	4.4	2.2	2.6	3.7
[RhL ₂ Cl ₂]Cl	1.9	2.1	4.2	2.1	2.6	3.6
[RuL ₂ Cl ₂]Cl	1.8	2.0	4.2	2.0	2.5	3.6

plexes are presented in TABLE 2. The IR spectroscopy can provide valuable information as to whether or not a reaction has occurred. The infrared spectrum of the ligand exhibits the bands at 760 and 1710cm⁻¹ for $\nu(\text{CSC})$ and $\nu(\text{CHO})$ vibrations, respectively. The band at 1650cm⁻¹ is characteristic of $\nu(\text{C}=\text{N})$ vibrations^[23]. The lowering in this frequency, observed in complexes suggests the involvement of quinoline nitrogen atom in coordination. Also, the band due to $\nu(\text{CSC})$ suffers a negative shift by 20-35cm⁻¹ indicating the involvement of sulphur atom of ligand in bonding with metal ions. In addition the appearance of new bands in the range 390-468 and 350-390cm⁻¹ attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ vibrations, respectively, seen in the spectra of the metal complexes suggest that the complexes have been formed^[24-26]. On the basis of the above interpretation, it is concluded that the ligand behaves as a bidentate.

¹H NMR spectra

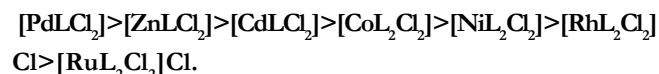
¹H NMR spectrum of the ligand in DMSO consists of several signals: a singlet at δ 9.6(s, H-C=O) and a multiplet at δ 7.4-8.6(m, Ar-H)^[27,28]. In the ¹H NMR spectra of complexes, these signals remain in the same position as in the free ligand which indicates the non-involvement of oxygen atom of alde-

hyde group.

Antibacterial activity

Antibacterial studies of ligand and its metal complexes are presented in TABLE 3.

The antibacterial screening data clearly illustrate that the metal complexes were more toxic than their parent ligand against the tested microorganisms under identical experimental conditions. The result of the inhibitory activity indicates that the inhibition of bacterial growth increase as the concentration of the complexes increases. The antimicrobial activity of Pd(II) and Zn(II) complexes were more than that of Cd(II), Co(II), Ni(II), Rh(III) and Ru(III) complexes. On comparing the inhibition zone values for the metal complexes, it seems that the antimicrobial activity may be due to the structure of the complexes and also the oxidation state of the metal ions. These results must be directly related to the greater biological activity exhibited by the square planar Pd(II), Zn(II) complexes compared to the tetrahedral Cd(II) and octahedral Co(II), Ni(II), Rh(III), Ru(III) complexes. The order of antibacterial activity of the metal complexes of ligand is as follows:



A possible explanation for the high toxicity of metal complexes can be explained as follows. The increase in the activity of metal complexes may be due to effect of metal ions on the normal cell process. The polarity of metal ion is considerably reduced on chelation which is mainly because of partial sharing of its positive charge with donor groups and possibly p-electron delocalization over the whole molecule. Such molecule increases the lipophilic character of the metal complexes which probably leads to break down of permeability barrier of the cells resulting in interference with normal cell process^[29]. Better activities of the metal complexes as compared to free ligands could also be understood in terms of chelation theory^[30], which explains that a decrease in polarizability of the metal could enhance the lipophilicity of the complexes.

Antifungal activity

The antifungal activity values of ligand and its

TABLE 4: Percentage inhibition of fungicidal growth

Compound	<i>C.albicans</i>			<i>A.niger</i>			<i>A.flavus</i>		
	0.1%	0.2%	0.3%	0.1%	0.2%	0.3%	0.1%	0.2%	0.3%
Ligand (L)	12.3	14.8	21.2	11.5	14.6	24.1	11.2	14.2	26.3
[PdLCl ₂]	14.5	23.0	31.6	14.9	17.6	28.6	14.8	17.7	29.5
[ZnLCl ₂]	14.2	21.1	30.3	14.6	17.3	28.4	14.6	17.5	29.2
[CdLCl ₂]	13.5	19.2	26.2	13.5	16.2	26.5	13.5	16.3	28.4
[CoL ₂ Cl ₂]	12.1	16.5	23.6	12.7	15.6	25.5	12.4	15.4	27.6
[NiL ₂ Cl ₂]	12.1	15.5	22.9	12.4	15.4	25.3	12.3	15.2	27.4
[RhL ₂ Cl ₂]Cl	12.0	14.8	22.5	12.3	15.3	25.2	12.1	15.1	27.3
[RuL ₂ Cl ₂]Cl	11.9	14.5	22.0	12.1	15.2	25.0	11.9	14.9	27.1

metal complexes are presented in TABLE 4. The antifungal screening data clearly shows that the complexes were more toxic than their parent ligand. The results of the inhibitory activity of the synthesized complexes on the organisms indicate that the inhibition of the fungal growth increases as the concentration of complexes increases.

ACKNOWLEDGMENT

We thank the Chairman, Department of Industrial Chemistry, Kuvempu University, Shankaraghatta-577 451, Karnataka, India for the provided laboratory facilities. One of the authors (B.Basavaraju) wishes to acknowledge financial support from Mr.G.M. Lingaraju, Secretary, GM Institute of Technology, Davangere-577 006, Karnataka, India.

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