Synthesis and characterisation of mixed ligand dinuclearmetal(II) complexes of anthranilic acid and pyridine-2-aldoxime

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ABSTRACT

Mn(II), Ni(II), Co(II), Cu(II), Zn(II) and Cd(II) complexes of anthranilic acid (L_1H) and pyridine-2-aldoxime (L_2H) were synthesized in an alkaline medium. The resulting complexes were characterized by CHN analysis, infrared and UV-Visible spectroscopies, molar conductance and magnetic susceptibility measurements. The CHN analyses showed the stoichiometries adopted by the mixed ligand complexes weredinulear$[M_2L_1L_2(OH)_2].xH_2O$ (M = Mn, Co, Cd), $[Ni_2(L_1)_2(OH)_2]$, $[Cu_2(L_2)_2Cl_2].C_2H_5OH$ and $[Zn_2L_1L_2(SO_4)(H_2O)_2]$. The infrared spectra establishedthe coordination ofL_1H as a bidentate anthranilate (L_1^-) through the carboxylate oxygen and amine nitrogen, and the deprotonated L_2H was bound to the metal ions through the pyridine and oxime nitrogen atoms. The reflectance spectra and magnetic moments of the metal complexes gave credence to their arrangement in a tetrahedral geometry. The conductance measurements revealed that the behavior of the complexes as non-electrolytes in DMF. Cd(II) complex showed promising inhibitory activity against Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa and Candida albicans.

Keywords: Mixed ligand, dinuclearcomplexes, anthranilic acid, pyridine-2-aldoxime, spectral properties

INTRODUCTION

Anthranilic acid, also known as vitamin L_1, is a chelating ligand. In an alkaline environment, the anthranilate ionis obtained by the deprotonation of anthranilic acid.Anthranilic acid has been used in the production of azo dyes, saccharin, perfumes, pharmaceuticals, corrosion inhibitors for metals, and mold inhibitors in soya sauce[1].Complexes of various transition metal ions with either anthranilic acid or substituted anthranilic acid have been reported in literature where they have shown unique characteristics in their color, IR bands, magnetism and biological activities[2,3]. Mixed ligand complexes of transition metals with anthranilic acid and other ligands have been reported[2].

Oxime-based ligands have played an important role in the continuing progress of coordination chemistry. In contrast to the great number of studies dealing with metal complexes of simple oximes and salicylaldoximes, relatively little is known about complexes of 2-pyridyloximes although this class of compound could offer unique features in terms of structural and physical properties.Pyridine-2-aldoxime is a bidentate ligand that binds through the nitrogen of the pyridine ring and the nitrogen of the oxime as a neutral bidentate ligand[4] or as an anionic bidentate ligand[5].

This present paper reports the synthesis, characterization and antimicrobial activity of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with mixed ligands anthranilic acid and 2-pyridinealdoxime.

MATERIAL AND METHODS

Materials and Methods

The chemicals and solvents obtained from Sigma Aldrich and BDH were of analytical grade and used without further purification. Melting points (uncorrected) were determined using the Gallenkamp melting point apparatus. CHN analysis was determined on Vario EL Cube analyser. FTIR spectra were recorded in the range 4000-400cm^{-1} on BrukerAlpha Drift spectrophotometer. The reflectance spectra of the solid complexes were obtained in the range40000–4000 cm^{-1}(2500–250 nm)on Cary 5000 Varian Spectrophotometer. Molar conductance values were determined on Jenway 4150 conductivity meter at concentrations of 10^{-3} M using DMF as solvent.Magnetic susceptibility measurements were taken on Sherwood magnetic susceptibility balance Mark 1.

Synthesis of metal(II) complexes of L_1H and L_2H

$[Mn_2(L_1)(L_2)(OH)_2].H_2O$: Anthranilic acid, L_1H (1.10 g, 8.02 mmol), pyridine-2-aldoxime, L_2H (0.98 g, 8.02 mmol) and potassium hydroxide (0.45 g, 8.02 mmol) were dissolved in 10 mL ethanol and stirred on a magnetic stirrer plate. An ethanol solution of $MnCl_2.4H_2O$ (1.44 g, 7.30 mmol) was added gradually and the mixture was further stirred for 3 h. The pale yellow precipitate formed was filtered, washed with diethyl ether and allowed to dry in air. The mass of the precipitate was 2.51 g (82%).A similar procedure was employed to obtain Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes.

$[Co_2(L_1)L_2(OH)_2].½H_2O$:Complex was prepared using L_1H (1.10 g, 8.02 mmol), L_2H (0.98 g, 8.02 mmol), KOH (0.45 g, 8.02 mmol) and $CoCl_2.6H_2O$ (1.73 g, 7.27 mmol). Yield: 1.60 g.

$[Ni_2(L_1)_2(OH)_2]$:Complex was prepared using L_1H (1.10 g, 8.02 mmol), L_2H (0.98 g, 8.02 mmol), KOH (0.45 g, 8.02 mmol) and $NiCl_2.6H_2O$ (1.73 g, 7.28 mmol). Yield: 2.55 g.

$[Cu_2(L_2)_2Cl_2].C_2H_5OH$: Complex was prepared using L_1H (1.10 g, 8.02 mmol), L_2H (0.98 g, 8.02 mmol), KOH (0.45 g, 8.02 mmol) and $CuCl_2.2H_2O$ (1.24 g, 7.27 mmol). Yield: 2.27 g.

$[Zn_2(L_1)(L_2)(SO_4)(H_2O)_2]$:Complex was prepared using L_1H (1.10 g, 8.02 mmol), L_2H (0.98 g, 8.02 mmol), KOH (0.45 g, 8.02 mmol) and $ZnSO_4.7H_2O$ (2.1 g, 7.30 mmol). Yield: 2.45 g.

$[Cd_2(L_1)(L_2)(OH)_2]$:Complex was prepared using L_1H (1.10 g, 8.02 mmol), L_2H (0.98 g, 8.02 mmol), KOH (0.45 g, 8.02 mmol) and $CdCl_2.2½H_2O$ (1.67g, 7.31 mmol). Yield: 2.96 g.

Antibacterial Susceptibility Testing

The agar well diffusion method was used. Mueller Hinton Agar (20 mL) was prepared, autoclaved, allowed to cool to 20–30°C,poured into petri dishes. The microbial strains used were *Staphylococcus aureus* ATCC 29213, *Bacillus subtilis* ATCC 6633, *Escherichia coli* ATCC 35218,*Pseudomonas aeruginosa* ATCC 27853 and the clinical strains of*Candida albicans*and *Aspergillusniger*.The cultures were prepared according to standard procedure.0.1 mL broth cultures were pipetted into 9.9 mL sterile normal saline to make 10^{-2} dilutions from which inoculation was done onto agar plates by surface spread with the aid of sterile cotton swabs. A sterile cork borer (diameter8 mm) was used to create equidistant wells on the inoculated agar plates. The test compounds were prepared by dissolving 10 mg in 10 mL solvent(1 mL DMSO and 9 mL sterile distilled water). 0.2 mL (200 µg) of each compound was pipetted intothe wells.The agar plates were allowed to pre-diffuse before incubation. $DMSO/H_2O$ (1:9 mL) (which showed no activity against the microorganisms used) wasused as the negative control while Gentamycin (10 µg/mL) and Ketoconazole (10 µg/mL) were used as positive controls. The plates were then incubated at 25°C (24

h) and 37°C (48 h)for the bacterial and fungal strains respectively. The tests were carried out in duplicates.The diameters of inhibition zones were measured and the results have been recorded in Table 4.

RESULTS AND DISCUSSION

Chemistry

Mixed ligand Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of anthranilic acid (L_1H) and pyridine-2-aldoxime (L_2H) have been synthesized in an alkaline medium. Table 1 shows the physical and analytical data of these complexes.

Table 1: Analytical Data for the metal complexes

Complexes	Colour	Mpt	C	H	N	%	Λ_m*
Formula, Mol wt		°C	Found (calculated)			Yield	
L_1H ($C_7H_7NO_2$), 137.14	Yellow	148-150	---	---	---	---	---
L_2H ($C_6H_6N_2O$), 122.13	Off-white	110-112	---	---	---	---	---
$[Mn_2(L_1)(L_2)(OH)_2].H_2O$	Off-white	>360	37.93	3.17	9.80	85	54.2
$Mn_2C_{13}H_{15}N_3O_7$,419.2			(37.25)	(3.61)	(10.03)		
$[Co_2(L_1)(L_2)(OH)_2].½H_2O$	Brown	>360	37.89	3.33	9.91	54	28.1
$C_{13}H_{14}Co_2N_3O_{5.5}$,418.1			(37.34)	(3.37)	(10.05)		
$[Ni_2(L_1)_2(OH)_2]$	Green	250^D	38.84	2.96	6.74	86	11.2
$Ni_2C_{14}H_{14}N_2O_6$, 423.7			(39.69)	(3.33)	(6.61)		
$[Cu_2(L_2)_2Cl_2].C_2H_5OH$	Yellow	>360	35.06	2.67	11.02	76	54.4
$Cu_2C_{14}H_{16}N_4O_3Cl_2$,486.3			(34.58)	(3.32)	(11.52)		
$[Zn_2(L_1)(L_2)(SO_4)(H_2O)_2]$	Green	>360	29.04	2.35	8.01	81	3.0
$Zn_2C_{13}H_{16}N_3O_{9.5}S$,529.1		(29.51)	(3.05)	(7.94)			
$[Cd_2(L_1)(L_2)(OH)_2]$	Off-white	>360	30.26	2.36	8.37	88	34.4
$Cd_2C_{13}H_{13}N_3O_5$,516.08			(30.25)	(2.54)	(8.14)		

Dec = Decomposition, $\wedge_m^*$ = molar conductance at 10^{-3} M in DMF (Ω^{-1} cm^2 mol^{-1})

The metal complexes were colored solids withyields of 54-88%. They had melting points above 360^{o}C while Ni(II) complex decomposed at 250^{o}C, and were soluble in DMSO, DMF and *N*-methylformamide. The stoichiometry of each metal(II) complex was established from the CHN elemental analysis, with the derived formulas$[Mn_2(L_1)(L_2)(OH)_2].H_2O$, $[Co_2(L_1)(L_2)(OH)_2].½H_2O$, $[Ni_2(L_1)_2(OH)_2]$, $[Cu_2(L_2)_2Cl_2].C_2H_5OH$, $[Zn_2(L_1)(L_2)(SO_4)(H_2O)_2]$ and $[Cd_2(L_1)(L_2)(OH)_2]$.

Infrared spectra

The important diagnostic bands of the free ligands and the synthesized complexes have been recorded in Table 2.

Table 2: Infrared spectra of the ligandsL_1H, L_2H and metal complexes in cm^{-1}

Compounds	L_1H	L_2H	[Mn]	[Co]	[Ni]	[Cu]	[Zn]	[Cd]
v(O–H)	---	---	3474*m*	3466*m*	3480*b*	3450*b*	3445*s*	3461*s*
v(O–H)	---	---	3167*m*	3139*m*	3129*b*	---	3133*s*	3131*s*
$v_{asy}(NH_2)$	3329*s*	---	3308*s*	3308*s*	3306*s*	---	3301*s*	3317*s*
$v_{sy}(NH_2)$	3245*s*	---	3234*s*	3224*s*	3207*s*	---	3216*s*	3216*s*
δ(O–H)	1601*s*	1655*s*	---	---	---	---	---	---
v(C=O)	1664*m*	---	---	---	---	---	---	---
$v_{asy}(COO^{-})$	---	---	1607*m*	1612*m*	1618*s*	---	1614*s*	1607*s*
$v_{sy}(COO^{-})$	---	---	1391	1410	1415	---	1410	1385
$v(C{=}N)_{pyr}$	---	1569	1549*s*	1540*s*	---	1555*s*	1543*s*	1542*s*
$v(C{=}N)_{ox}$	---	1520	1494*s*	1478*s*	---	1482*s*	1494*s*	1503*s*
v(C=C)	1461*s*	1471*s*	1451*s*	1459*s*	1459*s*	1460*s*	1458*s*	1450*s*
$v_{asy}(N–O)_{ox}$	---	1264*m*	1253*m*	1238*s*	---	1263*m*	1266*m*	1256*m*
$v_{sy}(N–O)_{ox}$	---	1049*m*	1058*m*	1050*s*	---	1077*m*	1054*m*	1059*m*
$v(M–N)_{NH2}$	---	---	555*w*	556*w*	567*w*	---	566*w*	549*w*
$v(M–N)_{pyr}$	---	---	536*w*	518*w*	---	522*w*	517*w*	521*w*
$v(M–N)_{ox}$	---	---	462*w*	450*w*	---	483*w*	482*w*	490*w*
$v(M–O)_{COO}$	---	---	412*w*	420*w*	425*w*	---	417*w*	406*w*

The strong bands due to asymmetric and symmetric vNH$_2$were observed in the spectrum of L_1Hat 3329and 3245 cm^{-1} respectively.In the metal complexes bothbands were shifted to lower frequencies in the ranges 3317–3301 $cm^{-1}$and 3224–3207 cm^{-1}. Thissuggested the coordination of L_1H through the amine nitrogen atom[6,7]. The strong band at 1664cm^{-1} was assigned to vC=Oof the anthranilic acid, L_1H[7,8], and was found absent in the spectra of the metal complexes. The metal complexes, except the Ni(II) complex, exhibited two strong bands in the ranges 1618–1607and 1415–1385cm^{-1} which are indicativeofasymmetric and symmetric vCOO⁻ respectively[14].This was corroborative ofthe deprotonation of carboxylic group and its binding through the oxygen asa carboxylate[6,9,10].The magnitude of separation between the carboxylate vibrational frequencies, $\Delta v_{(asy-sym)}(COO^{-})$in the range 202–222 cm^{-1} is indicative of a monodentate binding of the carboxylate to the metal ions[8,9]. The spectra of L_1H and L_2H displayed strong bands at 1601 and 1655 cm^{-1}, attributed to their respective O–H bending vibration. These bands were absent in the spectra of the metal complexes and showed the loss of carboxylic and oxime protons. Thebands due to v(C=N) were reduced from 1569 and 1520 cm^{-1} in L_2H to 1555–1540 $cm^{-1}$and 1503–1478 cm^{-1}in the metal complexes respectively. The lowering of these frequencies showed that both pyridine and oxime nitrogen atoms were involved in chelation to the metal ions[4]. The aromatic C=C stretching vibrations were found in the range 1471–1450 cm^{-1}in the ligands and metal complexes. The frequencies for the asymmetric and symmetric N–O stretches were seen at 1264 and 1049 cm^{-1} as medium bands in the spectrum of pyridine-2-aldoxime. These bands were present in the spectra of metal complexes, except in Ni(II) complex, and were found in the ranges 1266–1238 and 1077–1049cm^{-1}.Vibrational frequencies for the coordinated hydroxo species were found in the regions3480–3445 cm^{-1} and 3167–3130 cm^{-1} in the spectra of the metal complexes.[9,11]The sulphato vibrational frequencies were observed in the spectrum of Zn(II) complex at 985 cm^{-1} ($v_1(A_1)$, 1128 $cm^{-1}$$v_3(T_2)$ and 652 $cm^{-1}$$v_4(T_2)$. In the low frequency region of the spectra of the metal complexes, bands between 567 and 406 cm^{-1}were assigned to v(M–N) of the amine,v(M–N) of pyridine nitrogen, v(M–N) of oxime nitrogen and v(M–O) of carboxylate oxygen[3,6,12]. Bands around 270 cm^{-1} are indicative of M–Cl bond[13] which was beyond the range of the spectrometer used.

Electronic Spectra and Magnetic Moments. The reflectance spectra of the ligands and the mixed ligand complexes were recorded in Table 3.

Table 3: Electronic spectra of the ligandsL$_1$H, L$_2$H and metal complexes in cm^{-1} (nm)

Compounds	$\pi\to\pi^*$	$n\to\pi^*$	$n\to\pi^*$	$d\to d$		μ_{eff}(BM)
L$_1$H	38084 (263)	28850 (347)	28384 (352)	----		----
L$_2$H	38518 (260)	29900 (334)	28950 (345)	----		----
[Mn]	38417 (260)	30730 (325)	27270 (367)	16700 (599)		5.9
[Co]	38334 (261)	31417 (318)	26284 (380)	20027 (499)	14950 (670)	4.8
[Ni]	39117 (256)	31651 (316)	26450 (378)	15850 (630)	9471 (1056)	3.1
[Cu]	38000 (263)	33334 (300)	26734 (374)	20930 (478)	14150 (707)	2.2
[Zn]	38117 (262)	31250 (320)	26500 (377)	----		0
[Cd]	38500 (260)	31370 (319)	----	----		0.7

The bands of low intensity in the spectra of L$_1$H and L$_2$H at 260-263 nm were assigned to $\pi\to\pi^*$ transition within the aromatic rings. This band was not affected in the spectra of metal(II) complexes and was found in the range 256-263 nm. The more intense absorptions in the ranges 334-347 nm and 345-352 nm were ascribed to $n\to\pi^*$ transition from the nitrogen lone pairs to the aromatic rings[15]. These bands were respectively shifted hypsochromically (300-325 nm) and bathochromically (367-380 nm) in the spectra of the complexes due to the participation of the lone pairs in binding to the metal ions. The metal complexes showed other absorption bands in the visible region. Mn(II) complex displayeda weak absorption band at 599 nm which wasattributed to$^6A_1\to{}^4T_1(G)$ transition in a tetrahedral field[16].The magnetic moment of 5.9 BM showed that the Mn(II) complex is paramagnetic and has a high spin tetrahedral geometry[16].Co(II) complex displayed two bands at 499 and 670 nm and these were assigned to $^4A_2(F)\to{}^4T_1(P)$ (ν_3) and $^4A_2(F)\to{}^4T_1(F)$ (ν_2) of a tetrahedral geometry respectively. The lowest energy band due to $^4A_2(F)\to{}^4T_2(F)$ (ν_1)transition was not observed. The magnetic moment of 4.8 BM is within the range 4.4-4.8 BM expected for high spin d^7 tetrahedral complexes[17].Ni(II) complex exhibited absorption bands at 630 and 1056 nm which were assigned to the

$^3T_1(F) \rightarrow ^3A_2(F)$ (v_2) and $^3T_1(F) \rightarrow ^3T_2(F)$ (v_1)transitions in a tetrahedral geometry respectively. $^3T_1(F) \rightarrow ^3T_1(P)$ (v_3) transition was not observed.The magnetic moment of 3.1 B.M was within the range 2.9-3.9 BM expected for high spin d^8 tetrahedral Ni(II) complexes.Tetrahedral Cu(II) complexes are expected to exhibit one broad band above 1000 nm ($^2E \rightarrow T_1$)[18]. The broad bands at 478 and 707 nm which have been described as tetragonally distorted transitions in a pseudo tetrahedral geometry were obtained for this yellow Cu(II) complex[19, 20].Magnetic momentsof tetrahedral copper complexes are found in the higher end of therange 1.9-2.2 BM. The magnetic moment of 2.2 BM for this Cu(II) complex supported the assigned pseudo tetrahedral geometry[17].The reflectance spectra of Zn(II) and Cd(II) complexes exhibited no $d \rightarrow d$absorption bands, as expected, due to their d^{10} configuration.Zn(II) complex was diamagnetic while the Cd(II) showed a magnetic moment of 0.7 BM[21].

Molar Conductance

The molar conductance of themetal complexeswas determined in DMF. The obtained values were in the range 3.2–54.2 Ω^{-1} cm^2 mol^{-1},indicating their behavior as non-electrolytes in DMF and the covalent binding of anions present within the coordination sphere of the complexes[22]. Values in the range 94.0– 05.0 Ω^{-1} cm^2 mol^{-1} are indicative of 1:1 electrolyte[23].

Antimicrobial Screening

The antimicrobial assay results are recorded in Table 4.

Table 4: Diameters of inhibition zones (mm) by the ligandsand metal complexes

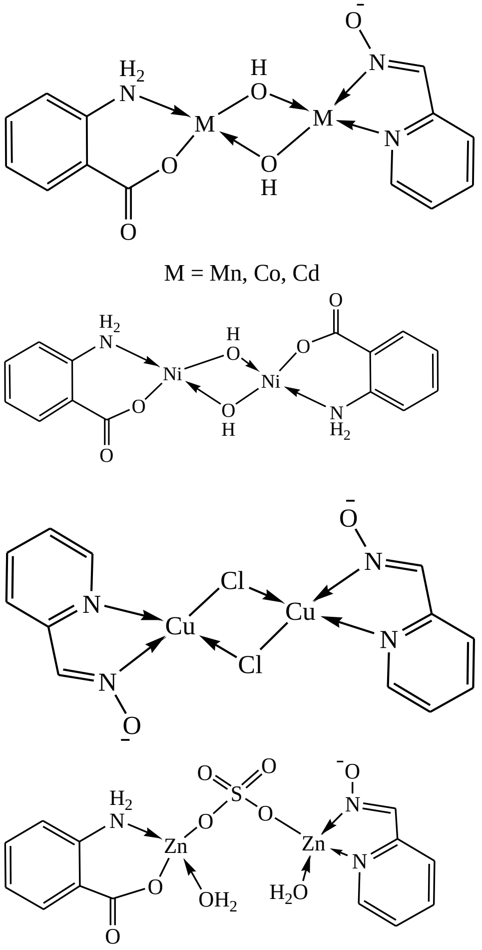
Compounds	*S. aureus*	*B. subtilis*	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. niger*
L_1H	13	11	12	13	8	8
L_2H	13	15	19	23	8	8
[Mn]	8	8	10	8	8	8
[Co]	8	8	8	8	8	8
[Ni]	8	8	8	8	8	8
[Cu]	12	8	8	8	13	8
[Zn]	8	8	8	8	8	8
[Cd]	26	18	16	17	30	8
GENT	15	8	17	19	8	8
KTZ	8	8	8	8	19	20

GENT = Gentamycin, KTZ = Ketokonazole

Cd(II) complex showed promising antimicrobial activity against most of the tested strains with inhibition zone of 16–30 mm. The exception was *Aspergillus niger* which was generally resistant to all the compounds. Cu(II) complex was also active against *S. aureus*and *C. albicans*., showing the inhibition zones of 12 and 13 mm respectively. The parent ligands demonstrated better inhibitory activity (11–23 mm) than the metal complexes except the Cd(II) complex. The standard drug, gentamicin showed inhibitory zone of 15–19 mm but was inactive against the *B. subtilis*.

CONCLUSION

The reaction of the anthranilic acid (L_1H), pyridine-2-aldoxime (L_2H) with metal(II) salts in an alkaline ethanol solution yielded metal complexes of different stoichiometries: $[M_2L_1L_2(OH)_2].xH_2O$ (M = Mn, Co, Cd), $[Ni_2(L_1)_2(OH)_2]$, $[Cu_2(L_2)_2Cl_2].C_2H_5OH$ and $[Zn_2L_1L_2(SO_4)(H_2O)_2]$. Theformulas were established on the basis of elemental CHN analysis and the proposed structures are shown in Figure 1.



M = Mn, Co, Cd

Figure 1: Proposed structures of mixed ligand metal(II) complexes

The infrared spectra showed that the strongly alkaline reaction medium facilitated the abstraction of the carboxylic acid and aldoxime protons, rendering them as monoanionic ligands. The mixed metal complexes were formed by the chelation of L_1H through the amine nitrogen and carboxylate oxygen, and L_2H through the pyridine and aldoxime nitrogen atoms to each metal ion. Binding by the hydroxo species were observed in the Mn(II), Co(II), Ni(II) and Cd(II) complexes which resulted into dinuclearhydroxo-bridged compounds. The chloride and sulphato species acted as ligands in Cu(II) and Zn(II) complexes respectively, which were also observed to be dinuclear chloride- and sulphato-bridged complexes. The reflectance spectra and the magnetic moments of the metal complexes were indicative of tetrahedral geometries based on $d \rightarrow d$ transitions observed in each metal complex. The antimicrobial activity assessment of the parent ligands and the synthesized metal complexes (200 µg/well) revealed that Cd(II) complex showed a promising antimicrobial activity against the strains tested and Cu(II) had moderate activity against *S. aureus*and *C. albicans*.

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