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RESEARCH ARTICLE

SYNTHESIS, SPECTRAL AND ANTIMICROBIAL ACTIVITY OF MIXED LIGAND COMPLEXES OF Co(II), Ni(II), Cu(II) and Zn(II) WITH 4-AMINOANTIPYRINE AND TRIBUTYLPHOSPHINE

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ABSTRACT

Complexes of Co(II),Ni(II),Cu(II)and Zn(II) with mixed ligand of 4-aminoantipyrine (4-AAP) and tributylphosphine (PBu3) were prepared in aqueous ethanol with (1:2:2) (M:L:PBu3). The prepared complexes were characterized using flame atomic absorption, FT.IR and UV-Vis spectroscopic methods as well as magnetic susceptibility and conductivity measurements. In addition biological activity of the two ligands and their complexes against three selected type of bacteria were also examined. The general compositions of the complexes are found to be $[M(4\text{-}AAP)_2(PBu3)_2]\ Cl_2$ Where M= Co(II),Ni(II),Cu(II)and Zn(II). Some of the complexes exhibit good bacterial activities. From the obtained data the octahedral structures have suggested for all prepared complexes.

INTRODUCTION

Pyrazoles are in important heterocyclic compounds and pyrazoles are being used as psychopharmacological agents, pain relif agents and cholesterol lowering (Olivera *et al.,* 2002). Substituted pyrazoles have pronounced sedative action on central nervous system (Shetgiri *et al.,* 2006). Benzo-pyrazoles and other derivatives posses a variety of activities including anti-microbial, anti-tubercular and anti-inflammatory (Shukla *et al.,* 2013). Amino group in antipyrine as a site of chelation shows high lighting behavior with transition metal ions through covalent or coordinate (Abo-El-Ghar *et al.,* 2007). Tributylphosphine most commonly encountered as a ligand in transition metal complexes. (Taghreed *et al.,* 2013) In this paper we present the synthesis and study of Co(II),Ni(II), Cu(II), and Zn(II), complexes with 4-aminoantipyrine as a primary ligand and tributylphosphine as secondary ligand.

MATERIALS AND METHODS

Instrumentation

UV-Vis spectra were recorded on a (Shimadzu UV-160 A) Ultra Violet-Visble Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-8400 S) Fourier Transform Infrared. Spectrophotometer (4000-400) cm^{-1} with samples prepared as KBr discs. Atomic Absorption was obtained by using a (Shimadzu A.A-160A) Atomic Absorption / Flame Emission Spectrophotometer. Conductivities were measured for 10^{-3}M of complexes in DMSO at 25°C by using (Philips PW- Digital Conductimeter). Magnetic susceptibilities were performed by using (Brucker Magnet B.M.6) instrument at 25°C. In addition, melting points were obtained by using (Melting Point Apparatus).

Materials

The following chemicals were used as received from suppliers; Cobaltous chloride hexahydrate 98.8%, Nickel Chloride hexahydrate 99.9%, Copper Chloride dihydrate 98%,Zinc Chloride 98.8% (Merck), 4-Aminoantipyrine and Tributylphosphine (B.D.H).

Study of Biological Activity

Three selected types of bacteria were used in this study *Escherichia Coli (E.Coli)* as Gram Negative Bacteria, *Staphylococcus Aureus (Staph. Aurous)* as Gram Positive Bacteria and *Pseudomonas Aeruginosa (Ps. Aeruginosa)* in Neutrient Agar medium, using (DMSO) as a solvent and as a control, the concentration of the compounds in this solvent was

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10^{-3}M, using disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro- organism on agar plate. The plates were incubated for 24hrs at 37C°.

Preparation of Metal Complexes

A general method was used for the synthesis of the metal complexes. An aqueous solution of the metal salts containing 0.118g, 0.118g, 0.085g and 0.068g (1mmole) of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ respectively was added gradually with stirring to ethanolic solution (0.203g,2mmol) of 4-aminoantipyrine (4-AAP) and (0.5ml,2mmole) of tributylphosphine (PBu3) was added to the mixture in each case by using stichiometric amount (1:2:2) Metal: 4-AAP: PBu3 molar ratio. The mixture was refluxed with constant stirring for an hour. The v product formed was filtered off , and recrystillized from ethanol and dried at room temperature ,and analyzedemploying standard method.

RESULTS AND DISCUSSION

The solid complexes were prepared by reaction of alcoholic solution of the tow ligands with the aqueous solution of the metal ions in a (M: (4-AAP): (PBu3) of (1:2:2). The metal contents of these complexes were in good agreements with the calculated values (Table 1) includes the physical properties. The molar conductance of the complexes as (10^{-3} M) in DMSO indicating their electrolytic nature ratio (1:2) (Geary, 1971), the data were recorded in (Table 1).

The complexes are soluble in dimethyl form amide (DMF) dimethyl sulfoxide (DMSO), while insoluble in water and common solvents. The test for chloride ion with $AgNO_3$ solution was positive indicating that chloride ion is out side of coordination sphere. (Taghreed *et al.,* 2013)

The UV/Visible spectra

The UV-Vis spectra data for the free ligands and all metal complexes are listed in (Table 2). The UV-Vis spectrum of the ligand 4-AAP shows two peaks at 235 nm and 283 nm assigned to ($\pi - \pi^*$) and ($n - \pi^*$) electronic transitions respectively. The electronic spectrum of tributylphosphine display absorption peak at 297 nm due to ($\pi - \pi^*$) (Sonme and Sekerci, 2002; Suzuki *et al.,* 1999).

The UV/Visible spectra and Magnetic Measurements μeff (μB) of the Mixed Ligand Complexes

The electronic spectra of the Cu(II), Ni(II),Co(II) and Zn(II) mixed ligand complexes have been recorded as DMSO solutions in the wavelength range 200-1100 nm.

[Co (4-AAP)2(PBu3)2]Cl_2

The magnetic susceptibility measurement after diamagnetic corrections Table (1) yielded a magnetic moment of 4.52 BM which is close to that expected for an octahedral Co(II) complexes. The (U.V-Vis) Co(II) d^7 (Term ^4F) spectrum, Table (3) exhibits four peaks, The first high intense peak at (272 nm)due to ligand field. The peak at 355 nm assigned to charge transfer. Other two peaks at 562 nm and 680 nm were found to be caused by (d-d) electronic transition type $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ and $^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ respectively (Taghreed *et al.,* 2012).

[Ni (4-AAP)$_2$(PBu3)$_2$] Cl_2

The magnetic moment Table (1) of the Ni(II) d^8 (Term^{3}F) complex is 2.77B.M, indicating the octahedral configuration of this complex. The spectrum of Ni(II) complex appeared absorption peak at 246 nm was related to ligand field.

Table 1. Physical properties of the ligand and it's complexes

Compounds	M. wt	Color	M.P °C	Yield%	M%	Λm ($S.cm^2.mol^{-1}$) in DMSO(10^{-3}M)
[Co (4-AAP)2(PBu3)2]Cl_2 $C_{46}H_{80}Cl_2CoN_6O_2P_2$	941.0	brown	183	68	6.79 (5.83)	51.67
[Ni(4-AAP)2(PBu3)2]Cl_2 $C_{46}H_{80}Cl_2CoN_6O_2P_2$	940.7	green	171	71	6.56 (5.95)	68.55
[Cu(4-AAP)$_2$(PBu3)$_2$]Cl_2 $C_{46}H_{80}Cl_2CoN_6O_2P_2$	945.6	dark blue	194	67	7.32 (6.82)	72.41
[Zn(4-AAP)2(PBu3)2] Cl_2 $C_{46}H_{80}Cl_2CoN_6O_2P_2$	947.4	pal yellow	155	73	7.42 (6.88)	77.32

Λm=Molar Conductivity, M.P = melting point

Table 2. UV-Vis, magnetic susceptibility and conductance measurements data

Compounds	λ_{max} (nm)	Wave number (cm^{-1})	€$_{max}$ ($L.mol^{-1}.cm^{-1}$)	Remarks	μ_{eff} (B.M)
PBu_3	297	33670	6095	$\pi \rightarrow \pi^*$	
Ligand (4-AAP)	235	42553	1191	$\pi \rightarrow \pi^*$	
	238	35335	746	$n \rightarrow \pi^*$	
$[Co(4\text{-}AP)_2(PBu_3)_2]Cl_2$	245	40816	1530	L.F	4.52
	355	28169	226	C.T	
	562	17793	183	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ $^4T_{1g(F)} \rightarrow$	
	680	14705	91	$^4T_{2g(F)}$	
$[Ni(4\text{-}AP)_2(PBu_3)_2]Cl_2$	246	40650	1876	L.F	2.77
	371	26954	846	C.T	
	590	16949	198	$^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$	
	720	13888	102	$^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$	
	856	11682	92	$^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$	
$[Cu(4\text{-}AP)_2(PBu_3)_2]Cl_2$	273	36630	1361	L.F	1.73
	392	25510	845	C.T	
	632	15822	205	$^2E_g \rightarrow {}^2T_{2g}$	
$[Zn(4\text{-}AP)_2(PBu_3)_2]Cl_2$	291	34364	1103	C.T	Diama
	395	25316	741	C.T	

The peak at 371 nm due to charge transfer, then other three peaks at 590 nm, 720 nm and 856 nm were assigned to electronic transition type

$^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$, $^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ and $^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ respectively (Mohamed *et al.,* 2006).

The electronic spectrum bands suggest octahedral geometry around the Ni(II) ion

[Cu (4-AAP)$_2$(PBu3)$_2$] Cl$_2$

The magnetic moment Table (1) of the Cu(II) d9 (Term 2D), exhibits normal magnetic moments (1.73B.M.) which is in agreement with data reported by several research workers [5,13]. The spectrum of Cu(II) complex Table (2) gave absorption peak at 273 nm due to ligand field, the peak at 392 nm attributed to charge transfer. The peak at 632 nm was caused by electronic transition (Jebur *et al.,* 2013) $^2E_g \rightarrow {}^2T_{2g}$.

[Zn(4-AAP)$_2$(PBu3)$_2$] Cl$_2$

The spectrum of Zn(II) complex showed absorption peak at 291 nm due to ligand field, the Peak at 395 caused by charge transfer. The absence of absorption peaks in the visible region indicated no (d-d) electronic transition happened; this is a good result for octahedral complex (Lever and A.B, 1968).

Table 3. Infrared spectrum data (wave number ύ) cm^{-1} for the ((PBu3))

Compound	H-C-H Asymmetric & Symmetric Stretch	C–H bend	P-CH_2	C–H rock
(PBu3)	(2956-2872) vs	1462(m)	1413W	794,791

Table 4. Infrared spectra data (wave number ύ) cm^{-1} for the Compounds

Compounds	υ(NH_2)	υ(C=O)	υ(M-N)	υ(M-O)	υ(M-P)
Ligand (4-AAP)	3429 sh. 3323 sh.	1676 s.	-	-	-
[Co(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	3353 br. 3257 br.	1606 s.	542 w.	503 w.	445 w.
[Ni(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	3373 br. 3244 br.	1637 sho.	474 w.	457 w.	435 w.
[Cu(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	3377 br. 3191 br.	1596 s.	503 w.	459 w.	443 w.
[Zn(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	3365 br. 3259 br.	1612 sh.	576 w.	559 w.	406 w.

sh =sharp, sho=shoulder, s = strong, w =weak, br = broad

Table 5. Diameters (mm) of deactivation of bacteria for the 4-aminoantipyrine and it's complexes

Compounds	*Staphylococcus aurous*	*Escherichia coli*	*Pseudomonas aeruginosa*
Control DMSO	8	5	5
Ligand (PBu3)	16	12	15
Ligand(4-AAP)	25	17	10
[Co(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	31	15	15
[Ni(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	27	25	36
[Cu(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	13	32	20
[Zn(4-AAP)$_2$(PBu$_3$)$_2$]Cl$_2$	20	18	35

Fourier Transform Infrared (FTIR) Spectroscopy

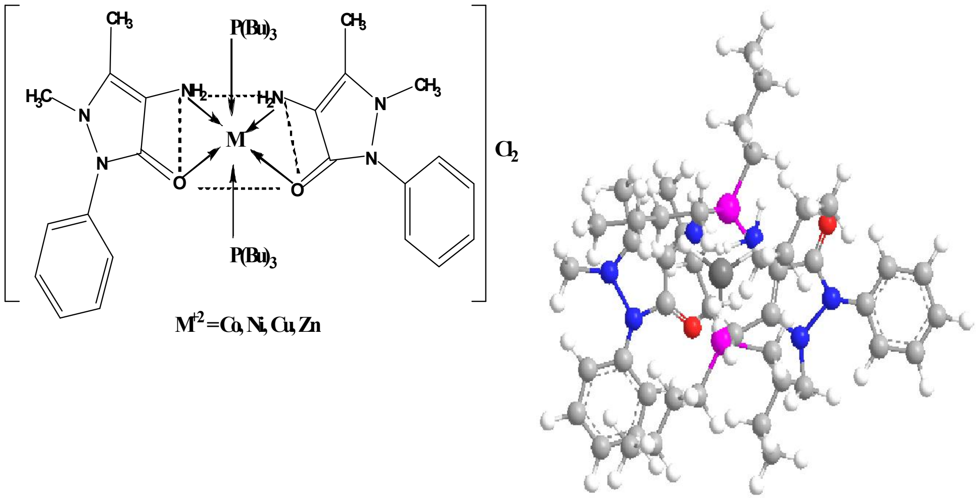
In order to study the binding mode of the ligands (4-aminoantipyrine) with the metal ions, a comparison was made for the FT.IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Tables 3 & 4). The IR spectrum of the ligand (4-AAP) exhibited bands at 3429 cm^{-1} and 3323 cm^{-1} were assigned to ν(NH_2) stretching frequency (Masoud *et al.,* 2003; Nakamot, 1996), on complexation a shifting with change in shape were observed from these bands, while increasing in intensity were noticed. The significant may be a result of coordination with metal ion. The bands at 1676 cm^{-1} in the ligand spectrum ascribed to ν(C=O), suffered a great change to lower frequency were also observed on complexation with metal ion (Nair *et al.,* 2005; Kirkan and Gup, 2008).

Medium to strong absorption in the 1455- 1650 cm^{-1} region often corresponds to aromatic ring vibrations. Finally the region extending from 1597 to 1662 cm^{-1} corresponds to stretching vibrations for C=C bonds. The new bands observed at (576-430) cm^{-1} are tentatively assigned to ν(M-N),ν(M-O) and ν(M-P) (Metal-Ligands) stretching bands (Thangadurai and Natarajan, 2002; Boghaei and Mohebi, 2001; Osowole, 2008).

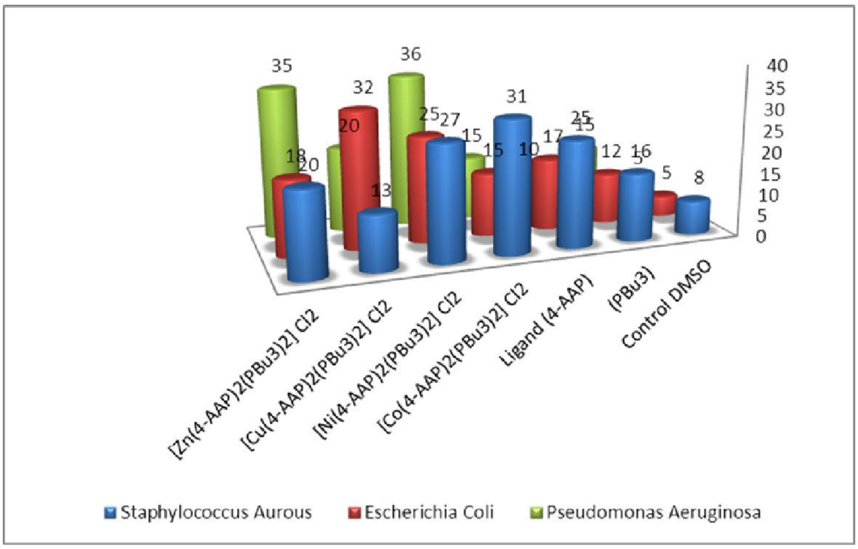
Primary ligand 4-aminoantipyrine act as bidentate ligands when coordinated to metal ion [21] while the secondary ligand (PBu3)binds the metal ion as mono dentate donors via phosphor atom.According to the results obtained and spectral analysis an octahedral structures have been suggested to these complexes. (Scheme 1)

Antibacterial Activities studies

The biological activities of the ligands and their complexes have also been tested against selected type of bacteria, (Table 5) show the deactivation capacity against the bacteria specimen of the prepared compounds under study.



Scheme 1. Proposed Structure of [M (4-AAP)2(PBu3)2] (3D space- filling conformation, left)



Scheme 1. Chart of biological effects of the studied compounds

The diameter of the susceptibility zones were measured in mm and the results are presented in Table (5) Scheme (1). Compounds were considered as active when the (IZ) was greater than 6 mm. Two ligands and their complexes individually were found to be biologically active showing various degrees of inhibitory effects on the growth of the tested bacterial species (Sönmez *et al.,* 2006). Mixed ligand metal shown weak to good activity when compared to the Control. Complexes have higher biological activities compared to the free ligands and inhibition diameter was varied according to the variation in the complex type and bacterial type. The increased inhibition activity of the metal complexes can be explained on the basis of Tweedy's chelation theory (Taghreed *et al.,* 2013; Tweedy, 1964; Taghreed *et al.,* 2014). In metal complexes, on chelation the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π-electrons over thewhole chelate ring. The ring of (4-AAP) moiety makes the complexes more lipophillic (Taghreed *et al.,* 2014).

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